

A STUDY OF THE ELECTRONIC CHARACTERISTICS AND PHOTOELECTROCHEMICAL
ACTIVITY OF EXTRINSIC CERAMIC STRONTIUM TITANATE
AND TITANIUM DIOXIDE

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The dissertation "A Study of the Electronic Characteristics and Photoelectrochemical Activity of Extrinsic Ceramic Strontium Titanate and Titanium Dioxide" by Bruce Odekirk has been examined and approved by the following Examination Committee:

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DEDICATION

This work is dedicated to the cause of solar energy and to all who support it, and in particular to my family, without whose love and support this would not have been possible.

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ABSTRACT

A Study of the Electronic Characteristics and Photoelectrochemical Activity of Extrinsic Ceramic Strontium Titanate and Titanium Dioxide

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A study of the characteristics of extrinsic, ceramic SrTiO_3 and TiO_2 is presented. These materials have been known to assist in the photoelectrochemical dissociation of water without undergoing decomposition, but their wide intrinsic bandgaps (3.0–3.2 eV) make them unsuitable for efficient solar energy conversion. Consequently, a wide variety of samples were studied in the highly extrinsic state, produced both by the introduction of impurities and by strong reduction.

Electrical conductivity (throughout the range $10 \leq T \leq 500$ K), thermopower, and photoconductivity were all measured, and compared to photoelectrochemical (PEC) cell performance. Single crystal samples of strongly reduced TiO_2 were similarly examined for comparison with the ceramic materials.

It was found that oxygen vacancies produced upon high temperature reduction of undoped SrTiO_3 form O_V -impurity bands, with activation

energies in the range 0.03-0.075 eV (for $n = 10^{17} - 10^{13} \text{ cm}^{-3}$). Impurity band formation was also found in La-doped SrTiO_3 for $[\text{La}] \geq 0.2\%$, and the spectral response confirmed expectations from dark conductivity measurements that the conduction and impurity bands are fully merged with a substantial band tail when $[\text{La}] = 1.0\%$. This resulted in the diminution of the optical bandgap from $\approx 3.2 \text{ eV}$ to $\approx 2.8 \text{ eV}$, and with that, significantly enhanced photoanode performance was obtained.

The behavior of σ with reduction for La:SrTiO_3 confirmed that the defect structure at room temperature consists of controlled atomic imperfection under oxidizing conditions, which gives way to a controlled valency mechanism upon reduction. This transition produces a semiconducting material.

High temperature reduction of undoped TiO_2 was found to produce a large number of donor defects, with room temperature conduction-band electron densities in the range $n = 10^{17} - 10^{19} \text{ cm}^{-3}$. Ta-doped TiO_2 ceramics demonstrated activated transport in the temperature range 100-300 K, with minimum activation energies of 0.01-0.04 eV, which increased with $[\text{Ta}]$.

The activation energy was found to increase with P_{O_2} for single crystal TiO_2 , but not for undoped ceramics, indicating that the extended defect concentration plays a strong role in determining the rate of thermal quenching of defect-related charge carriers. Impurity

dominated conduction in the P_{O_2} range studied (10^{-8} - 10^{-18} atm) was found only for the highest doping level ($[Ta] = 1.0\%$), with activation energies of 0.04-0.06 eV. Consequently, Ta-doping was not found to substantially alter the photoresponse or the PEC cell performance of TiO_2 ceramics.

CHAPTER ONE

INTRODUCTION

1.1 Photoelectrochemical Cells

The large cost and diminishing supplies of fossil fuels have spurred a great deal of research over the past several decades concerning sources of cheap and/or renewable energy. Since all forms of energy are ultimately derived from the sun, methods of putting sunlight into direct use (as with photovoltaics) or of storing solar energy for remote site use has drawn attention. A great deal of progress has been made in the art of photovoltaics (1-2), wherein sunlight is captured by a semiconducting material (usually silicon) and converted into electrical energy. This energy can then either be used immediately or collected in a storage device such as a battery. An alternative method of collecting solar energy is to convert it into chemical energy, whence it can be easily stored. This is done naturally in photosynthesis. To do this artificially would require the selection of a two level chemical reaction reasonably well matched to the solar spectrum.

The solar spectrum peaks at a wavelength of about 460 nm, corresponding to an energy of 2.70 eV, and drops to zero at a wavelength of about 300 nm (4.13 eV). Figure 1.1 shows the spectral distribution of sunlight at air mass one. The bulk of the solar energy is found in the range 1.13-4.13 eV (1100 to 300 nm), and any

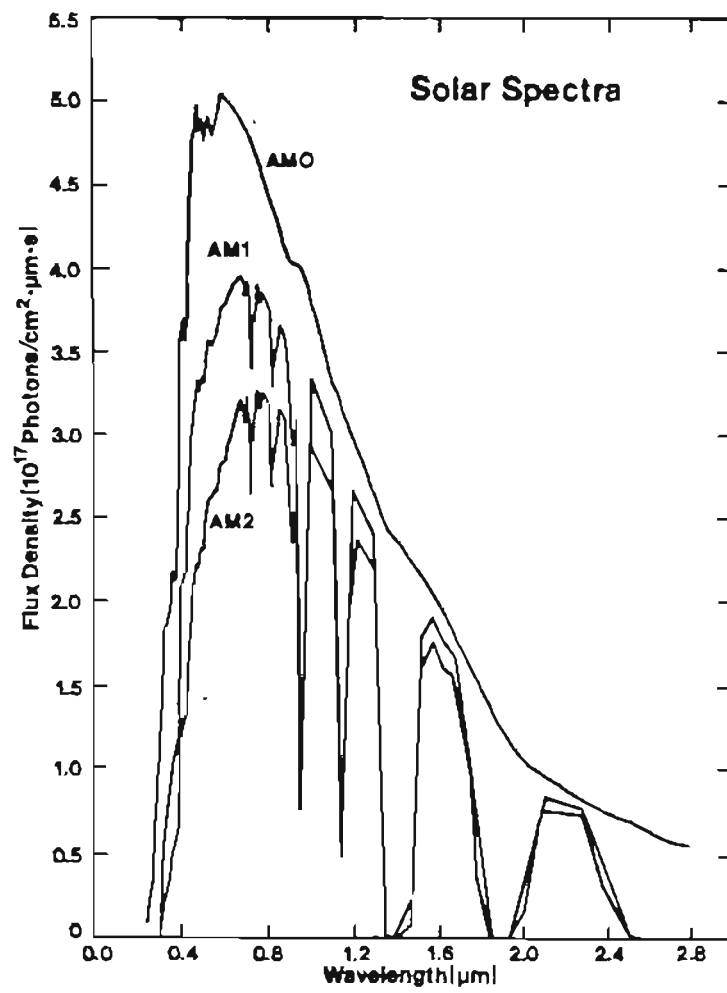
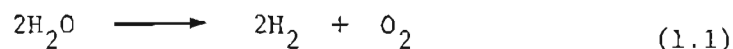


Figure 1.1. Spectral distribution curve of solar irradiation at AM0, AM1, and AM2.

chemical reaction chosen to capture that energy efficiently must have an oxidation/reduction potential overlapping that range. In addition, the chemical reaction products must be suitable for use as a storable, portable fuel with a minimum energy cost of retrieval.

As it turns out, the photodissociation of water is ideally suited for this. The theoretical oxidation/reduction potential of the reaction:



is 1.23 eV, but oxygen electrode overpotential considerations (3) actually place the energy minimum at about 1.60 eV. This overpotential is caused by barriers to charge transfer at the semiconductor/electrolyte interface.

The reaction embodied in Eqn. 1.1 can be utilized in a photoelectrochemical cell (PEC). Most commonly, this is a liquid-semiconductor junction device wherein sunlight is absorbed by a photoactive semiconducting electrode. Figure 1.2 is a schematic energy diagram of just such a device utilizing an n-type semiconducting photoanode and a metallic cathode. In this device absorption of sunlight of energy greater than the semiconductor bandgap energy, E_g , would produce hole-electron pairs available for conduction. Equilibration of the Fermi level throughout the cell results in the formation of a space charge region within the semiconductor (4-6); pairs created in this region can then be separated to produce

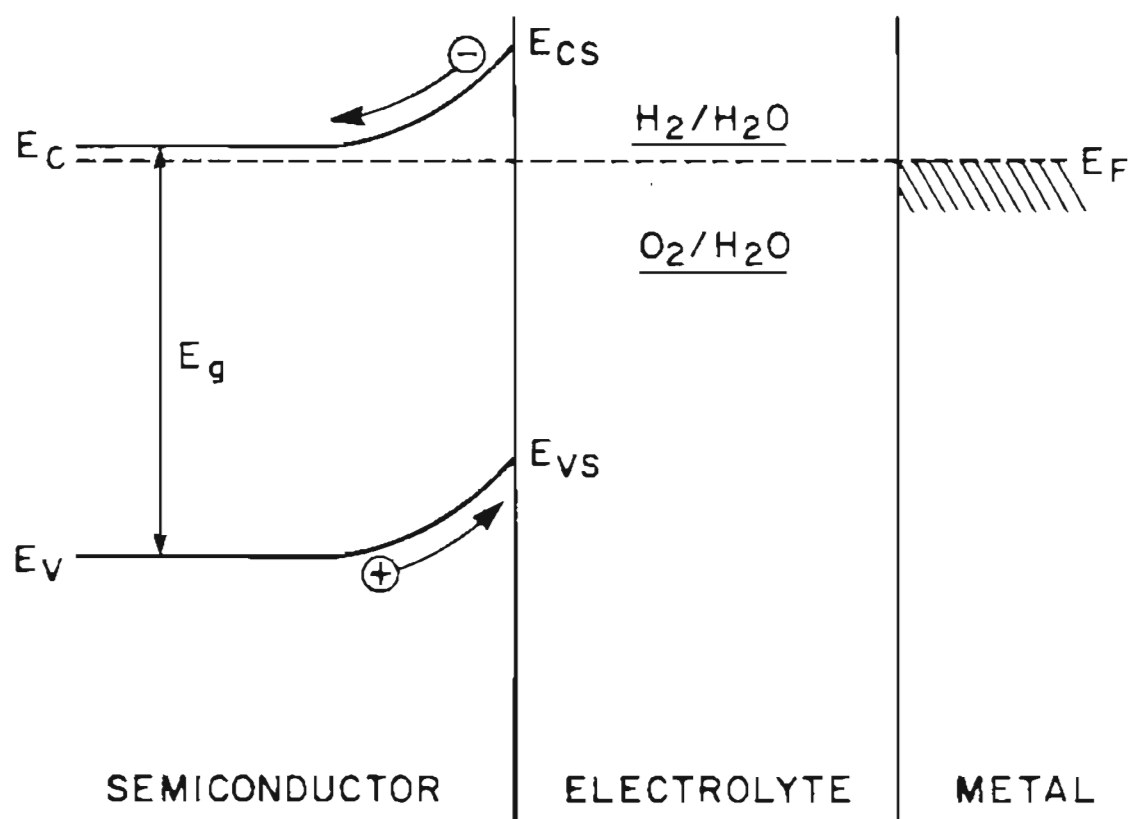


Figure 1.2. Energy band structure of photoelectrochemical cell.

current through the cell.

This current can be supported by the electrolyte in either of two ways. One is by the chemical reaction of Eqn. 1.1, in which holes arriving at the photoanode react with water molecules or OH^- ions (depending on the pH) to form oxygen molecules, and electrons arriving at the cathode react with H_2O or H^+ ions to form hydrogen molecules. The other is by a reversible reaction in which the same chemical species reduced at the cathode is oxidized at the anode. The former case is referred to as a photoelectrochemical reaction. The latter, in which no net chemical change occurs, is simply a photovoltaic process. A number of excellent reviews (7-15) have been written on the early development of these devices and some of the techniques now being considered.

Hydrogen has a number of characteristics that make it an ideal potential fuel source. One of these is its very high energy density; at 28.2 kcal/gm, it is nearly two and a half times that of methane (12.1 kcal/gm). Another is the abundant supply of the starting material, water, and the renewable nature of the burning cycle. The latter property also relates to another attractive feature of hydrogen fuel: it burns cleanly.

The storage, handling and delivery of hydrogen gas is a problem that has been studied for a number of years and requires only economic incentives to be overcome. Water electrolysis has been a primary source of H_2 for some time (16) and the thermodynamics of Eqn. 1.1 have been well studied (17-18). What remains is to develop

a way to cheapen the energy cost of extraction of hydrogen from water, and it is to this end that the study of a device such as that shown in Fig. 1.2 is aimed.

1.2 PEC System Requirements

A great deal of theoretical (19-30) and experimental (31-39) work has been done on the problem of charge transfer reactions at solid/electrolyte interfaces, and Göpel (40) has written an excellent review concerned solely with semiconductor surfaces. Consequently, a thorough review of this subject will not be attempted here. Rather, the results obtained most pertinent to the development of efficient semiconducting photoanode materials will be presented.

Figure 1.3 shows the potential energy as a function of position as measured from the semiconductor surface at a SC/electrolyte junction. Included for future reference are the bell-shaped curves corresponding to the density of states for the oxidation and reduction reactions of interest. The semiconductor pictured is an idealization of a wide bandgap n-type material such as those being studied here. A good general discussion of the various regions formed, particularly those within the electrolyte, can be found in any of the standard texts on electrochemistry (41). It should be here noted that the various regions normally demarcated within the electrolyte (inner Helmholtz plane, outer Helmholtz plane, Guoy-Chapman layer, etc.) have for simplicity been grouped into two regions: the interface region and the Helmholtz layer. A justification for this can be found in the article by Reiss (42).

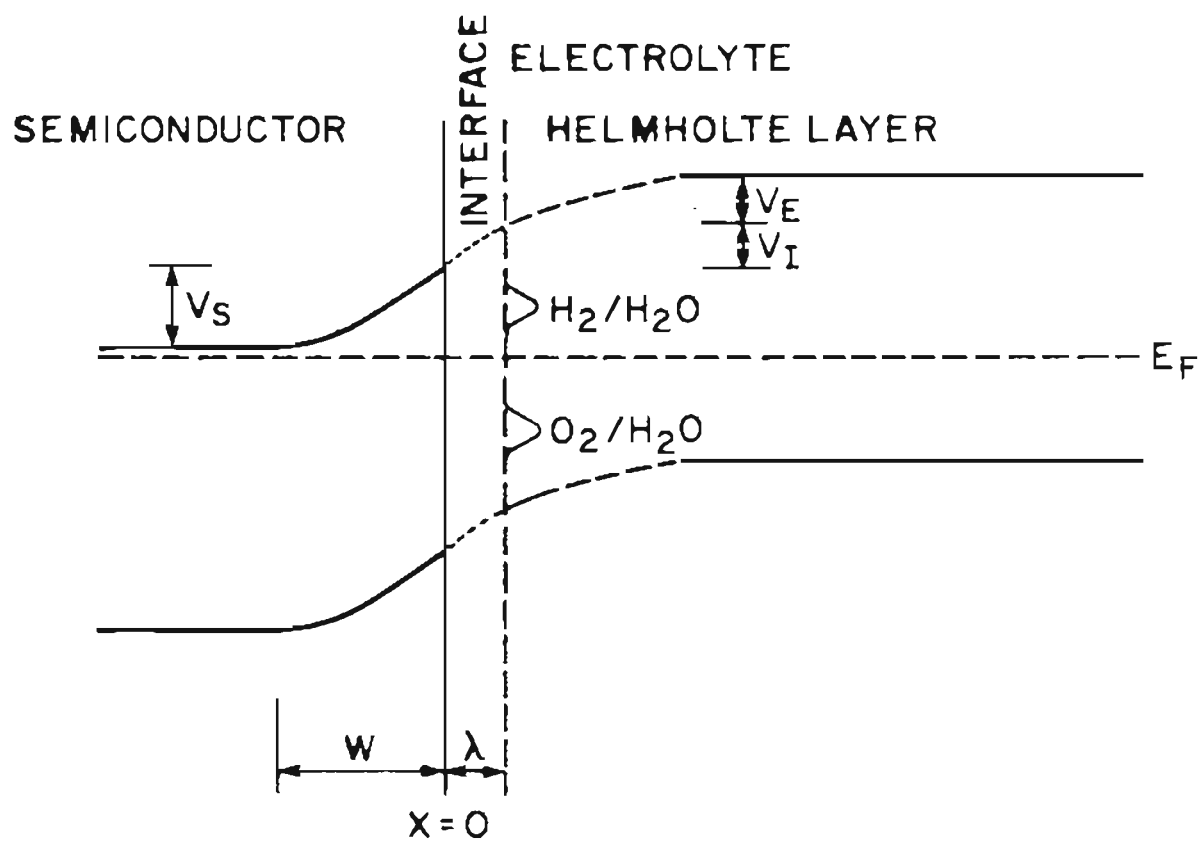


Figure 1,3. Relative energy level diagram across semiconductor/electrolyte interface.

For photoelectrolysis to occur, we must have the following:

i) photoabsorption of photons of energy $h\nu \geq E_g$; ii) efficient separation of hole/electron pairs; iii) electronic conduction through the semiconductor bulk; iv) charge transfer between anode and electrolyte (photooxidation); and v) charge transfer between cathode and electrolyte (photoreduction). These processes can most easily be discussed as a sequence of independent steps, thus allowing a coherent presentation of the assumptions made in modeling such a system and emphasizing the requirements of a practical device.

The first requirement restricts the choice of materials. As mentioned in section 1.1, matching the energy requirements of Eqn. 1.1 to the energy available in sunlight (Fig. 1.1) in a unipolar PEC would require a semiconductor with a bandgap in the range 1.60 - 4.00 eV. We here distinguish between a unipolar and a bipolar PEC in the sense that a unipolar cell is composed of one photoactive electrode and a reversible metallic counter electrode, whereas a bipolar cell would have both a photoanode and a photocathode. In the case of a bipolar cell, the overall energy requirement is that:

$$h\nu_a + h\nu_c \geq 1.60 \text{ eV} \quad (1.2)$$

where the subscripts a and c refer to light absorption at the anode and cathode. This leads to the bandgap requirements of the n- and p-type semiconducting materials to be used in a bipolar cell:

$$E_{g,a} + E_{g,c} \geq 1.60 \text{ eV} \quad (1.3)$$

The individual bandgaps can then clearly be less than 1.60 eV, leading to a greater variety of usable materials. However, the chemical efficiency of the cell is then reduced, as hydrogen production becomes a two-photon process. This investigation will be confined to materials suitable for use in a one compartment unipolar cell. Information concerning bipolar cells can be found in the literature (3,7,9-10,12-13,15,43-44).

1.2.1 Recombination, Charge Transport, and Pair Separation

The second requirement for photolysis is that provisions be made for the efficient separation of hole/electron pairs created by light absorption. In addition, non-radiative recombination must be avoided. There are a variety of possible mechanisms for non-radiative recombination (45-48). Most important for the considerations here are Auger recombination, defect or impurity recombination, and surface recombination. A band to band Auger process is one involving three charge carriers in which collisions between two like carriers provides the energy required to allow one of them to bridge the energy gap. In n-type material, this process would begin with a collision between two conduction band electrons, the result of which would leave one of the electrons depleted of sufficient energy and momentum to allow recombination with a hole in the valence band without photoemission. The hot electron can then de-excite itself with the sequential emission of any number of phonons. This process is clearly dependent on carrier concentration,

and the resultant minority carrier lifetime can be expressed in the following way (47):

$$1/\tau_a = A n p + B n^2 \quad (1.4a)$$

In extrinsic semiconductors Auger recombination can also occur through traps. Theoretical analyses by Haug for this type of process in direct gap semiconductors (49) and indirect gap semiconductors (50) show that the minority carrier lifetime in either case will be related to the majority carrier concentration in the following manner:

$$1/\tau_a = T N_t n_o \quad (1.4b)$$

where N_t is the density of available trap sites and the Auger coefficient T is on the order of $10^{-26} \text{ cm}^6 \text{ s}^{-1}$.

From Eqns. 1.4 it is expected that Auger events will become more numerous as the electron concentration is increased. However, as the impurity concentration increases beyond $\approx 10^{19} \text{ cm}^{-3}$, impurity related recombination can predominate. Precipitation of impurities can form which act in the same way as localized defects (such as grain boundaries in microcrystalline materials). These defects can produce a localized continuum of energy states within the bulk bandgap. Electrons and holes coming within a diffusion length of these defects can recombine non-radiatively (51).

Another impurity related process is recombination via trapping, called Hall-Shockley-Read (HSR) recombination (52-53). In this case, essentially discrete impurity levels can alternately trap electrons and holes where they then recombine. Efficient HSR traps are generally related to mid-gap impurity states. The capture of charge carriers by the trap need not be radiative, and in general won't be; however, the requirements imposed on impurities to allow them to act as HSR traps considerably lessens their importance in this investigation. Before leaving the topic of defect related recombination, it should be mentioned that a mathematically elegant and simplified technique for handling recombination at dislocation edges has been developed by McKelvey (54). This technique, called the conservation of flux method, employs standard optical methods of calculating transmission coefficients of beams at interfaces (55-58).

Surface recombination is a more important consideration for photoelectrolysis. A surface represents a very strong perturbation in the lattice structure. Inherent flaws (such as dangling bonds) can combine with surface impurities (such as ambient absorbants) to produce surface state densities on the order of $N_s(E) \approx 10^{15} \text{ cm}^{-2} \text{ eV}^{-1}$ (59-61). These surface states can form a continuous localized distribution of energy levels across the bandgap, leading to non-radiative recombination. More typically, minority carriers can be trapped at discrete surface levels within the bandgap. This can either hinder or enhance photolysis and will be discussed further in section 1.2.2.

The semiconductor and the electrolyte will in general have different electrochemical potentials. This difference will force an alignment of the Fermi energy across the interface region, and this will bring with it an associated potential energy drop. Because of its much lower conductivity, the semiconductor will absorb this potential drop in forming a space-charge region with a characteristic barrier width, W (4-6,42). Charge separation is accomplished when light is absorbed within this space-charge region (leading to the requirement that $W > 1/\alpha$, where α is the absorption coefficient of the semiconductor) and when the degree of band bending (V_s in Fig. 1.3) is sufficient. If the carrier diffusion length (L_d) is significantly greater than W , recombination and scattering losses can be avoided and quantum efficiencies can be quite high. This has been shown to be the case for TiO_2 , where Ghosh and Maruska (62) have found that $L_d/W \approx 10-100$ and $\eta \approx 1.0$.

The third requirement for photolysis relates to the electrical conductivity of the semiconducting material as well as to the problem of recombination. Recombination has been discussed above, and the empirical parameters of interest are the carrier diffusion lengths, mobilities and concentrations. Clearly it would be desirable to maximize the conductivity of a given material without adversely affecting the photoresponse, and that goal will be one of the primary objectives of this investigation.

Depletion-layer photoeffects have been discussed by Gärtner (63), and digital simulations of charge transport phenomena in photoelectrodes have been carried out by Laser and Bard (64-66). A similar

analysis of the effects of charge injection into the electrolyte has been done by Feldberg (67). The conservation of flux method discussed above has also been successfully applied to the problem of charge transport within the semiconductor bulk (68-71), and the transport and kinetics of minority carriers in photoelectrodes has been discussed by Albery et. al. (72).

1.2.2 Charge Transfer

Having achieved photoabsorption within the space-charge region (or at least within a diffusion length thereof), having effected efficient charge separation, and having provided for low resistance electronic conduction throughout the cell components, we still do not necessarily arrive at photoelectrolysis. The last obstacle is the actual charge transfer processes at the respective electrode/electrolyte interfaces. Electrode overpotentials exist even for isoenergetic charge transfer processes due to such factors as configurational entropy changes, hence even small differences between the energy levels involved in the charge transfer process can produce large differences in overall efficiency.

Figure 1.3 illustrates the problem involved in operating a PEC under the constraint of direct charge transfer. The energy levels for the oxidation/reduction reactions within the electrolyte will be thermally distributed about the most probable solvation state energy, with exponential tails above and below that value (6). For high quantum efficiencies, we require that charge transfer be roughly isoenergetic. Hence the system Fermi level must lie closer

to the vacuum level than the majority of the $\text{H}_2\text{O}/\text{H}_2$ states. Similarly, for direct isoenergetic charge transfer, the distribution of $\text{O}_2/\text{H}_2\text{O}$ states must overlap the valence band edge at the semiconductor surface. Clearly both of these requirements can not be met by a semiconductor with a bandgap greater than ≈ 1.50 eV without significant bandbending within the semiconductor space-charge region. This in turn would require the application of large biasing potentials which reduces the net energy conversion efficiency of the PEC.

Fortunately mechanisms for indirect charge transfer exist (73) which turn out to be quite efficient. Indirect charge transfer refers to the situation where charge transfer occurs despite a large misalignment of the energy levels involved, such that direct transfer by hot electrons or hot holes is not possible. For example, in Fig. 1.3, charge transfer between the $\text{O}_2/\text{H}_2\text{O}$ levels in the electrolyte and the valence band of the semiconductor could only happen by indirect processes. One means of indirect charge transfer is through the action of excited states within the electrolyte. This does not appear to be a significant contributor to photolysis. A second mechanism is through electron tunneling through the semiconductor space-charge region, but as this requires the overlap of electrolytic states with the semiconductor bulk band states, it can only be a factor for those few materials for which this fortuitous condition holds.

A third mechanism of indirect isoenergetic charge transfer is through the action of semiconductor surface states. Holes arriving at the surface of an (n-type) semiconductor can easily be thermalized

to low-lying surface states. If the density of such states is great enough and the energy spread sufficient, the hole can eventually reach a level where isoenergetic (or nearly so) charge transfer with the electrolyte can occur.

In general, it can not be expected that E_{VS} (the valence band edge at the semiconductor surface) will overlap the density of states of the desired oxidation reaction. While it is true that the exact mechanism of charge transfer across the interface region has not been conclusively established, the high quantum efficiencies ($\eta \approx 1.0$ is not uncommon) of a broad range of materials tested in the past have led to the consensus that mediation by surface states is a significant factor. One reason for this viewpoint is the broad range of potential sources of these states. As mentioned previously, intrinsic surface states can be expected to arise from the termination of translational symmetry. Extrinsic surface states can also develop from at least three sources: impurities, defects (such as deviations from stoichiometry), and adsorbants.

In the case of oxide semiconductors, H^+ and OH^- ions adsorbed on the surface are expected to result in surface states with energy levels closer to the oxidation/reduction levels than the band edges (74). These can sometimes form a continuum of states across a portion of the bandgap, facilitating thermal activation.

The phenomena of current doubling (73,75) deserves mention here, as it relates to the affects of excited states within the electrolyte in assisting charge transfer. A current doubling reagent R

will donate an electron to a photogenerated hole, forming R^+ . R^+ can then inject an electron into the conduction band, forming R^{2+} . The quantum efficiency for this process can then have a maximum value of two. This process will not be of concern in photolysis.

An analysis of the current-voltage characteristics of PEC's including the derivation of expressions for the quantum yield and maximum electrode efficiencies has been carried out by Ahlgren (76).

The primary motivation behind the study of PEC's is economic. Consequently the primary goal is the optimization of the energy conversion efficiency of the cell. The quantum efficiency discussed in connection with charge transfer processes relates only to the ratio of cell current to light absorbed; i.e.,

$$\eta = \frac{\text{\# electrons through circuit}}{\text{\# photons absorbed}} \quad (1.5a)$$

The energy conversion efficiency (EFF) is the ratio of the net energy produced by the cell to the input energy:

$$\begin{aligned} \text{EFF} &= \frac{\text{Energy stored as } H_2 - \text{Power Supply Energy}}{\text{Incident Solar Energy}} \\ &= \frac{(1.47 - V_b) I_{ss}}{P_{in}} \end{aligned} \quad (1.5b)$$

where 1.47 is the heat of combustion of H_2 in eV, V_b is the applied

biasing potential, I_{ss} is the PEC short circuit photocurrent density, and P_{in} is the average solar irradiation. Maruska and Ghosh (9) showed that the maximum overall efficiency (EFF_{max}) for a material of bandgap $E_g = 2.20$ eV under AM1 solar illumination is 16%. This compares favorably with silicon photovoltaics, particularly since only a quarter the surface area is required (9).

Looking at Eqn. 1.5, it is clear that the only adjustable parameters are V_b and I_{ss} . The short circuit photocurrent is determined by the factors already discussed: the semiconductor bandgap, the quantum efficiency, and losses through recombination and photovoltaic processes. Since EFF is maximized when V_b is zero, a measurable parameter related to the biasing requirements of a given material would be quite useful. Such a parameter exists and is called the flat band potential (V_{fb}), being the electrode potential at which the semiconductor bands are flat. V_{fb} is also useful in gauging the efficiency of charge separation in the space-charge region, since it is related directly to the band bending within the semiconductor, V_s , by the relation:

$$V_s = E_F - V_{fb} \quad (1.6)$$

The flat band potential is also a function of the electrolyte as can be seen from the following (10):

$$V_{fb}(NHE) = (\chi + \Delta E_F + V_H) - 4.5 = (\phi_{SC} + V_H) - 4.5 \quad (1.7)$$

where χ is the electron affinity of the semiconductor, ϕ_{SC} is the work function, ΔE_F is the difference between the Fermi level and the conduction band edge, V_H is the potential drop across the Helmholtz layer ($V_E + V_I$ in Fig. 1.3), and 4.5 is the scale factor relating the terms on the right of Eqn. 1.7 to the reference electrode, in this case the normal H^+/H_2 redox potential. The latter factor is required since V_{fb} can only be measured relative to a reference electrode.

Equation 1.7 suggests that V_{fb} can be predicted from a knowledge of electron affinities. Butler and Ginley (77) have proposed a theoretical model whereby χ is calculated from the electronegativities of the constituent elements of the material in question. They found that flatband potentials for metal oxides can be predicted to within ≈ 0.2 V in this manner if specific adsorption of OH^- and H^+ ions can be properly accounted for. The variation of V_{fb} with electrolyte pH is expected to be -0.059 V per pH unit, due to the change in V_H with specific adsorption.

Under short circuit conditions, V_{fb} represents the maximum Fermi level possible for the system (11). Hence if V_{fb} for a material lies below the H^+/H_2 potential (as is the case for the material shown in Fig. 1.3), H_2 can not be evolved at the cathode. Current flow will then be accomplished by the decomposition of O_2 at the cathode and the cell will be operating in the photovoltaic mode. The application of an external bias will then be required to raise the Fermi level above the H^+/H_2 redox potential.

Knowledge of V_{fb} is consequently of fundamental importance, and a variety of techniques have been developed for its measurement. The most basic of such methods utilizes cell capacitance measurements as a function of applied potential. The Mott-Schottky relationship for a PEC is given by (9,28,78-79):

$$1/C_{sc}^2 = (2/q\epsilon\epsilon_o n_o)(V - V_{fb} - kT/q) \quad (1.8)$$

where ϵ is the semiconductor dielectric constant, n_o is the carrier concentration, and V is the applied voltage. The cell capacitance will consist of three capacitors in series: the semiconductor space-charge region (C_{sc}), the Helmholtz layer including the interface region, and the solution diffuse double layer (Guoy layer). Normally C_{sc} is much smaller than the other components of the total capacitance. When this is true, a plot of $1/C^2$ versus V will yield a straight line from which n_o and V_{fb} can be obtained. Elliott et. al. (80) describe this method in detail with an application to tin oxide. The effects of non-ideal contacts at the semiconductor surface on capacitance measurements have been thoroughly analyzed by Goodman (81).

Another method for determining V_{fb} for both polycrystalline and single crystal materials relying on differential stress measurements has been developed by Handley and Bard (82). This is based on the relationship between the differential surface stress, the surface charge density and the deformation on an electrode as given

below:

$$\partial\sigma_s/\partial E = -q - \partial q/\partial\theta \quad (1.9)$$

where $(\partial\sigma_s/\partial E)$ is the differential surface stress, q the surface charge density, and θ the ratio of the surface area before and after deformation. The surface charge density will dominate the terms on the right of Eqn. 1.9, and both terms will go to zero at the flat band potential. At potentials negative of V_{fb} , Eqn. 1.9 will be positive (since the space charge region will have an excess of electrons) and at potentials positive of V_{fb} , it will be negative. Hence a plot of the differential stress versus potential will give V_{fb} at the intercept. Using this technique, Handley and Bard measured V_{fb} for single crystal GaP and SrTiO₃, and polycrystalline TiO₂. Their values were in excellent agreement with previously reported values, and they found that V_{fb} changed with pH for the oxides at the rate of about -59 mV/pH unit.

A third technique for determining V_{fb} utilizes the photoresponse of the material (83). This is based on the measurement of the photocurrent as a function of applied bias, wherein the intercept of the I_{ph}^2 versus V plot yields V_{fb} . Wilson and Park (84) employed this technique in a specific study of the pH dependence of V_{fb} for n-TiO₂ in a variety of electrolytes; they found the pH shift to be -53 mV/pH.

An alternative method is by rectified alternating photocurrent voltammetry (RAPV). This is an AC phase-sensitive detection tech-

nique based on the same principle as that mentioned in the paragraph above. McCann and Pezy (85) have demonstrated the simplicity of this AC technique over the DC photocurrent method, and found good agreement with capacitance measurements for a wide variety of materials.

In summary, the system requirements of a PEC can be expressed by the following energy balance equation:

$$E_g + V_a = V_s + (E_C - E_F) + \Delta G/nF + \eta_a + \eta_c + iR + V_H \quad (1.10)$$

where V_a is any applied bias, E_C is the conduction band edge, $\Delta G/nF$ is the free energy change per electron for the chemical reaction, η refers to the electrode overpotentials, iR is the Ohmic losses, and V_H is the Helmholtz layer potential drop. The free energy change is 1.23 eV, and $E_C - E_F$ is typically around 0.1 eV. The Ohmic losses and V_H are generally close to 0.05 eV (9), hence the bandgap requirement for a cell with no external biasing reduces to:

$$\begin{aligned} E_g &= V_s + 0.1 + 1.23 + \eta_a + \eta_c \\ &\quad + 0.05 + 0.05 \\ &= V_s + \eta_a + \eta_c + 1.43 \text{ eV} \end{aligned} \quad (1.11)$$

For n-type semiconductors, the use of a platinum cathode can reduce η_c to essentially zero (9). Then the bandgap requirements depend on the degree of band bending, which in turn is related to

the flatband potential, and the anodic overpotential. The overpotential is typically on the order of 0.2 - 0.4 eV, hence the optimum bandgap for photoelectrolysis is often quoted at $E_g \approx 2.20$ eV (9). This value allows sufficient band bending to promote pair separation. However, a material with this bandgap would still have to exhibit the proper alignment of energy levels with the redox potentials in the electrolyte to avoid biasing requirements.

1.3 Semiconducting Photoelectrodes

In 1972 Fujishima and Honda (86) first reported on the successful photodissociation of water using n-TiO₂ as the semiconducting photoanode. Since that time a wide variety of materials and combinations of materials have been tested in the hope of finding the right combination to yield a satisfactory energy conversion efficiency. Some of the more exotic attempts have been reported in a number of books (87-89), and the list of articles in print is far too lengthy to acknowledge here.

However, the problems involved in developing appropriate semiconducting photoelectrode materials can be simply stated. To maximize solar absorption in the usable energy range, a material bandgap of $\approx 1.70 - 2.50$ eV would be desirable. Nevertheless a great deal of work has been centered around materials with bandgaps greater than this. The reason relates to the most serious problem one encounters in developing photoelectrode materials, instability. Materials with bandgaps less than about 2.50 eV (which will in this context be

called small bandgap materials) tend to either decompose under illumination in electrolytic solutions or require significant biasing. In the decomposition of photoanodes, the holes migrating to the semiconductor surface react with surface bonds instead of solution ions, freeing surface atoms from the semiconductor. The physics of this problem will be discussed in the next section.

On the other hand, wide bandgap materials ($E_g \geq 2.50$ eV) tend to be stable to decomposition under the same circumstances. For these materials the energy conversion efficiency is going to be small regardless of how well suited otherwise they are for the task at hand, and any biasing requirements will virtually rule them out as potential devices. Nonetheless, the study of wide bandgap photoelectrodes is of intrinsic worth both for gaining knowledge concerning PEC device physics and for studying materials modification techniques for the optimization of the overall performance of a given material. This thesis will be concerned with the latter aspect.

1.3.1 Small Bandgap Materials

In Appendix 1 can be found a list of a large number of materials that have been considered as potential photoelectrodes. Clearly it would be most desirable to find a small bandgap material ($E_g \leq 2.50$ eV) suitable for photolysis, and many attempts have been made. A few of these attempts will be mentioned below to highlight the difficulties to be overcome in selecting suitable materials.

Tomkiewicz and Woodall (90) found that p-GaP ($E_g \approx 1.70$ eV) produced H_2 in .5M H_2SO_4 with an energy conversion efficiency of 0.1% at a biasing potential of 1.3 V. They also found this material to be stable in low pH solutions. The low efficiency was attributed to a very poor minority carrier diffusion length, leading to inordinately high biasing requirements.

Madou et. al. (91) have measured flatband potentials for both n and p-type single crystal GaP using capacitance methods. They found a frequency dependence in the measured capacitance and attributed it to dipole relaxation in the space-charge region of the semiconductor. Their value of $V_{fb} = 0.86$ V (SCE) in pH = 2.1 electrolyte for n-GaP predicts the need for large biasing, since the H^+/H_2 level in the same solution is about -0.55 V (SCE).

A number of people have reported on the characteristics of CdX (X = S, Se, Te) (92-95). Heller et. al. (92) found $E_g(CdS) = 2.42$ eV and $E_g(CdSe) = 1.71$ eV, and that subbandgap surface states on single crystal samples reduced the overall power conversion efficiency. These surface states were found to be related to structural imperfections and were removed by chemical etching. Power conversion efficiencies of 1.3 and 7.2% were measured for n-CdS and n-CdSe, respectively, when operated in photovoltaic mode. They did not report on photoelectrolytic activity; hence the full impact of the surface states found can not be fully evaluated.

A number of materials with $E_g \leq 2.50$ eV have been tested as photoelectrodes (see Appendix 1). Of these, the following have been

found to corrode in aqueous electrolytes: FeTiO_3 , Fe_2TiO_4 , Cu_2O , CuO , Si , InP , GaAs , and CdSe . The following have been found to be stable: Fe_2TiO_5 , Fe_2O_3 , p-GaP , CdFe_2O_4 , $\text{PbFe}_{12}\text{O}_{19}$, $\text{Pb}_4\text{Ti}_3\text{WO}_{13}$, $\text{Hg}_2\text{Ta}_2\text{O}_7$, $\text{Hg}_2\text{Nb}_2\text{O}_7$, and In_2O_3 . However, all of the latter materials display a flatband potential considerably higher than that of the appropriate redox potential of the electrolyte. Consequently substantial biasing is required to assist photolysis.

Iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) is a material deserving of special mention. The bandgap of n-type $\alpha\text{-Fe}_2\text{O}_3$ is around 2.20 eV, making it ideally matched to the solar spectrum. The flatband potential in $\text{pH} = 13.6$ electrolyte is -0.67 V, and photoanodes made from this material are known to be stable in solutions of $\text{pH} \geq 6.0$ (96). Quinn et. al. (96) found that single crystal Fe_2O_3 photoanodes displayed a rather poor collection efficiency and attributed this to a large photon absorption depth (i.e., a small absorption coefficient, α) such that $1/\alpha$ is greater than the carrier diffusion length and the depletion layer width. The application of a biasing potential will increase the depletion layer width and hence the collection efficiency.

Polycrystalline samples of iron oxide in various configurations have since been examined as potential photoanodes (97-102) and a V_{fb} value of -0.73 V in $\text{pH} = 13.8$ electrolyte has been reported (99). Doping with from 0.1 to 1.0 at. % TiO_2 has resulted in a value of $V_{\text{fb}} = -1.00$ V ($\text{pH} = 13.6$) (99). In a study of the affects of various redox reagents in the PEC behavior of iron oxide, Iwanski et. al. (101) found that a significant affect exists due to the action of surface

states in mediating a backreaction between photogenerated holes with conduction band electrons. This is assumed to partially account for the low collection efficiency. Kennedy et. al. (102) found that group IVA elements act as donor impurities and increase the conductivity of polycrystalline Fe_2O_3 ; however, as the increase in majority carrier concentration decreases the depletion region width, the problem of the relatively long photon penetration depth becomes more pronounced.

Kennedy and Frese (100) measured the absorption coefficient for iron oxide spectrophotometrically, and indirectly through photocurrent measurements. In the former case they arrived at a typical value of $\alpha \approx 2 \times 10^5 \text{ cm}^{-1}$. Photocurrent measurements, on the other hand, yielded values an order of magnitude smaller. It was felt that this could be accounted for by a charge transfer process in direct competition with those producing photocurrents, possibly metal to metal. At any rate, the low absorption coefficients and poor diffusion lengths ($2 - 4 \times 10^{-7} \text{ cm}$) of $\alpha\text{-Fe}_2\text{O}_3$ provide more serious obstacles to be overcome in producing useful photoanodes from this material.

To summarize, the problems presented by small bandgap materials have been twofold. Firstly, a great number of them are not stable. Those that are stable have thus far all displayed the second problem of requiring excessive biasing to facilitate charge transfer with the electrolyte. On the other hand, wide bandgap materials have shown a greater tendency to be stable to corrosion, while at the same

time displaying flatband potentials better suited to the desired reaction. It is for this reason that those materials have received the amount of attention they have.

1.3.2 Wide Bandgap Materials

The first material demonstrated to assist in the photodissociation of water without undergoing decomposition was TiO_2 (86), and the first material demonstrated to do the same without the need of an externally applied biasing potential was SrTiO_3 (103). The bandgaps of these materials are about 3.00 and 3.20 eV, respectively. Since that time a number of workers have investigated the PEC behavior of metal oxide semiconductors (78, 104-108). In general, oxide semiconductors tend to have intermediate to wide bandgaps ($2.20 \leq E_g \leq 3.70$ eV) and negative flatband potentials (in pH = 13.0 electrolyte, with the expected variation of V_{fb} with pH of -59 mV/pH). Hence biasing requirements tend to be minimal. The flatband potential for SrTiO_3 in pH = 13.0 solution is around -1.15 V, and since it is known that this material will allow photolysis to occur without biasing, then $V_{fb} < -1.10$ V is a reasonable value to look for in a material. (The H^+/H_2 level at pH = 13 is -1.19 V.)

Kung et. al. (105) studied a large number of oxide semiconductor photoanodes and found a roughly linear relationship between bandgap and V_{fb} with a slope of $\Delta E_g / \Delta V_{fb} = -1.5$. They also found a similarly linear relationship between V_{fb} and the heats of formation per metal

atoms per bond. For example, McCann and Bockris (106) found that $n\text{-In}_2\text{O}_3$ functioned as a stable photoanode in high pH electrolyte (1M NaOH), but required a biasing potential of about 0.3 V. The band-gap of In_2O_3 was determined to be about 2.3-2.5 eV with V_{fb} about -0.72 V, compared to $E_g(\text{SrTiO}_3) \approx 3.20$ eV and $V_{fb}(\text{SrTiO}_3) \approx -1.15$ V.

In most of these materials and particularly in oxide semiconductors, photogenerated holes are associated with valence bands based on p-orbitals. Tributsch (109) discovered that holes photogenerated in materials with d-orbital valence bands react differently. Specifically, he found that such holes do not constitute broken crystal bonds and hence do not lead directly to anodic photodecomposition of the electrode. Unfortunately, he found that MoS_2 ($E_g = 1.75$ eV) and MoSe_2 ($E_g = 1.40$ eV) were both susceptible to corrosion through the interaction of minority carriers with OH^- ions.

Another slightly different approach taken is the study of the characteristics of materials consisting of cationic valence and conduction bands. Blasse et. al. (110) have made a study of Bi^{3+} and transition metal compounds in the hopes of finding photoactive materials for which this is true. They concluded that the material Bi_2WO_6 does indeed have cationic valence and conduction bands but that it is not suitable for photoelectrolysis due to very poor carrier mobilities. They also found that the Bi^{3+} ions in the family of compounds $\text{Bi}_2\text{M}_{n-1}\text{R}_n\text{O}_{3n+3}$ do introduce an extra valence band, but distortions prevent the formation of broad bands. They did find photocurrents produced by NiNb_2O_6 , however the wide band gap ($E_g =$

3.60 eV) does not make it suitable for photolysis. In general, they demonstrated that it is possible to create oxides with cationic valence bands; however, problems with large bandgaps and small polaron formation (leading to low mobilities) do not make this very promising.

In summary, it is important to note that the ideal material for photolysis will combine the best attributes of small and wide bandgap materials. As a single material of moderate bandgap that is both stable to corrosion and displays a flatband potential of less than -1.10 V (pH = 13) has not yet been discovered, several ingenious attempts have been made to combine those materials already studied in such a way as to accentuate the positive attributes of each and to eliminate the negative. This will be the topic of the next section.

1.3.3 Hybrid Materials

There are basically two alternative goals involved in the study of mixed systems. One of these is the sensitization of a wide bandgap stable material with something responsive to sub-bandgap light which can in turn exchange charge with the host material, thus facilitating photolysis. The most popular method for doing this to date has been through dye sensitization (111-112), wherein a suitable dye is coated over a known stable, wide-bandgap photoelectrode.

Alonso et. al. (112) found that Rhodamine B and Ru (II) complex dyes can sensitize ZnO photoelectrodes to wavelengths of 600 nm

(2.07 eV), compared to the bandgap of ZnO of 3.20 eV. The dye has a distribution of energy levels situated within the semiconductor bandgap with excited state levels near the conduction band edge. Hence sub-bandgap light can be absorbed by the dye, promoting it to an excited state wherefrom it can donate an electron to the semiconductor conduction band, relaxing to an ionized state.

The second methodology employs either thin films, mixed (colloidal) films, or alloys. The objective is a juxtaposition of small bandgap unstable materials with stable wide bandgap materials in such a way as to derive the best benefits of each. With this in mind, Kohl et. al. (113) applied thin films of TiO_2 via CVD to single crystal samples of n-Si, p-Si, n-GaAs, p-GaAs, n-GaP, n-InP and n-CdS, all of which have bandgaps between 1.11 and 2.42 eV and all of which are known to corrode under illumination in aqueous solution. They found that crack-free coatings on n-type samples produced electrodes that did not corrode; however, the holes photogenerated in the bulk material were unable to penetrate the TiO_2 barrier. Hence the electrodes behaved simply as TiO_2 electrodes. The problem seems to be largely related to the mismatch of the conduction band edges at the bulk/film interface.

An attempt to circumvent this band edge mismatch by Liou et. al. (114) met with some success. They prepared $\text{Fe}_2\text{O}_3/\text{TiO}_2$ heterojunction electrodes by CVD application of TiO_2 onto Fe_2O_3 substrates. They calculated the band edge mismatches to be 0.38 eV at the conduction band and 0.42 eV at the valence band. They theorized that

if the TiO_2 film were made thin enough ($\approx 1000 \text{ \AA}$), the depletion region of the sample might extend through the TiO_2 film into the substrate. This will then allow photogenerated pairs to be separated, bringing the holes from the substrate to the film barrier. The application of a small anodic bias will then allow the holes to overcome the valence band energy barrier. They found that this does occur; however, the necessity of an external bias remains a problem.

Somewhat more imaginative tactics are being employed by a group at MIT headed by Mavroides (115), where both the application of mixed films and characteristics of alloys are being investigated. Figure 1.4a demonstrates the former. In this case a substrate of CdSe ($E_g = 1.71 \text{ eV}$) is overlaid with a thin film of thickness about $500 \text{ \AA}$ of small CdSe grains ($\approx 50 \text{ \AA}$ in size) imbedded in a matrix of SrTiO_3 . When immersed in an aqueous electrolyte, the CdSe grains exposed at the surface are dissolved until only a continuous coating of SrTiO_3 remains. Figure 1.4b is an energy diagram of the resulting material. As it turns out, the conduction band edges of CdSe and SrTiO_3 are well matched, allowing photogenerated electrons to flow through the material without much trouble. The valence band edge of CdSe lies near the midgap of SrTiO_3 , where significant surface states are thought to exist. These mediate the hole transfer through the coating to the electrolyte. This is a relatively new technique and many questions related to the overall efficiency of this type of photoelectrode raised in the article by Mavroides remain to be answered.

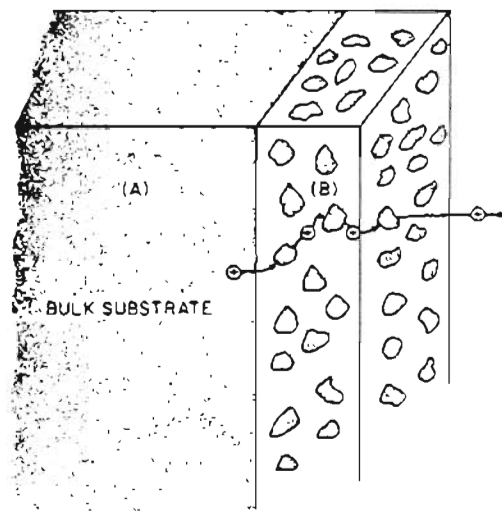


Figure 1.4a. Schematic of CdSe-SrTiO₃ composite electrode. (Reference 115).

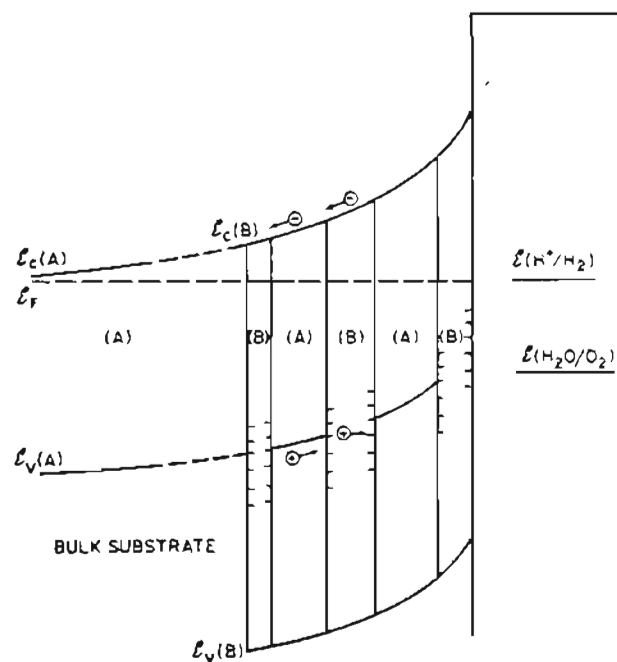


Figure 1.4b. Energy band diagram of CdSe-SrTiO₃ electrode. (Reference 115).

Alloying either TiO_2 or SrTiO_3 with other materials to produce a solid solution with reduced bandgap has also been examined (115). Mavroides et. al. (115) found that the solution $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$ produced a photoresponse out to energies of 1.80 eV, and that the mixture $0.8 \text{ SrTiO}_3 : 0.2 \text{ LaFeO}_3$ extended the response tail to ≈ 2.50 eV, although the responsivities below 3.00 eV were not appreciable. This approach is similar to that taken by the work reported herein.

1.4 PEC Stabilization Requirements

The problem of corrosion of photoelectrodes has received considerable attention in the hopes of discovering methods of stabilizing otherwise attractive materials. As mentioned above, those materials known to have bandgaps well matched to the solar spectrum and V_{fb} negative of the H^+/H_2 redox level are susceptible to photodecomposition. This is particularly true of binary compound semiconductors with pronounced ionic character (116). The physics of this problem is of considerable interest to materials researchers and will be briefly presented in energy diagram form in the next section. Following that will be an overview of some of the stabilization methods that have been tried.

1.4.1 Decomposition Levels

Williams (116) has discussed the process of photodecomposition of ZnSe in a qualitative fashion. ZnSe ($E_g = 2.70$ eV) is stable in the dark but undergoes rapid decomposition under illumination. Analysis of the solution in which ZnSe electrodes have been immersed

has shown that Zn^{2+} ions are lost in the corrosion process. As a Zn^{2+} ion goes into solution, the negative charge left behind becomes associated with valence band Se^{2-} ions. In the dark, these electrons remain bound and electrostatic charge balance prevents further dissolution. Under illumination, however, the electrons can be excited from the Se^{2-} levels into the conduction band thus allowing current to flow. As a result, no barriers to decomposition form and the material quickly corrodes. This process is qualitatively similar to the photodecomposition mechanisms of other unstable materials.

Energy diagrams relating the thermodynamic potentials for photodecomposition to semiconductor band edges and electrolyte redox levels have recently been developed (117). Figures 1.5 and 1.6 (after Gerischer, ref. 117) graphically demonstrates the relationship between semiconductor flatband potentials and decomposition levels. Figure 1.5 depicts the four possible situations: electrodes that are stable, unstable, stable to anodic corrosion, and stable to cathodic corrosion.

Disregarding the interaction of charge carriers with solution species, a semiconductor will be stable to decomposition if the decomposition energy level of interest lies outside the semiconductor bandgap. Hence the susceptibility to decomposition for a given material can be predicted beforehand by examining the appropriate energy levels. An example for several materials is given in Fig. 1.6. Here it can be seen that Cu_2O , GaP and GaAs would be susceptible to

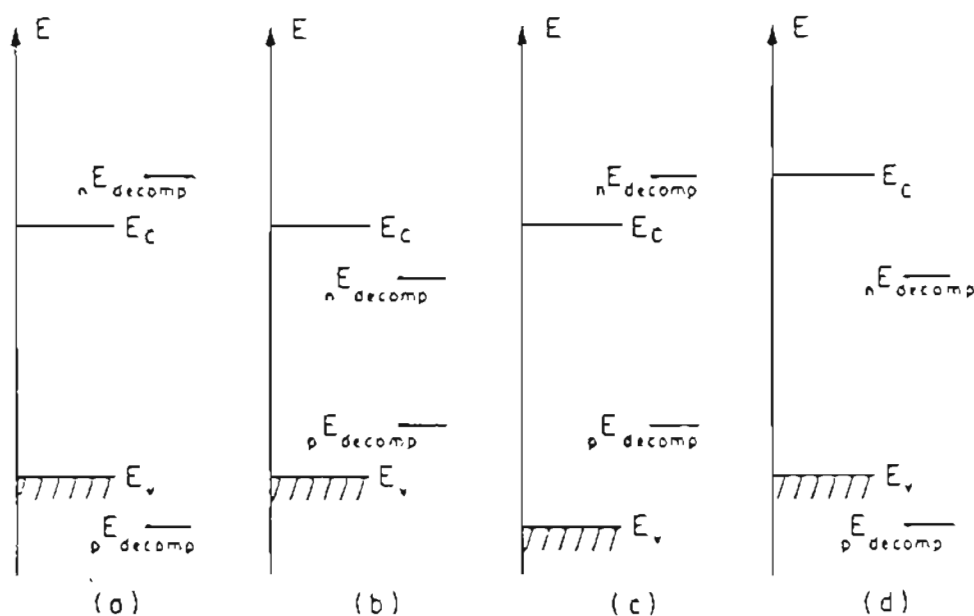


Figure 1.5. Energy correlations between band edges and decomposition Fermi levels, characterizing susceptibility to photodecomposition. (a) Stable, (b) unstable, (c) susceptible to anodic photodecomposition, (d) susceptible to cathodic photodecomposition. (Ref. 117).

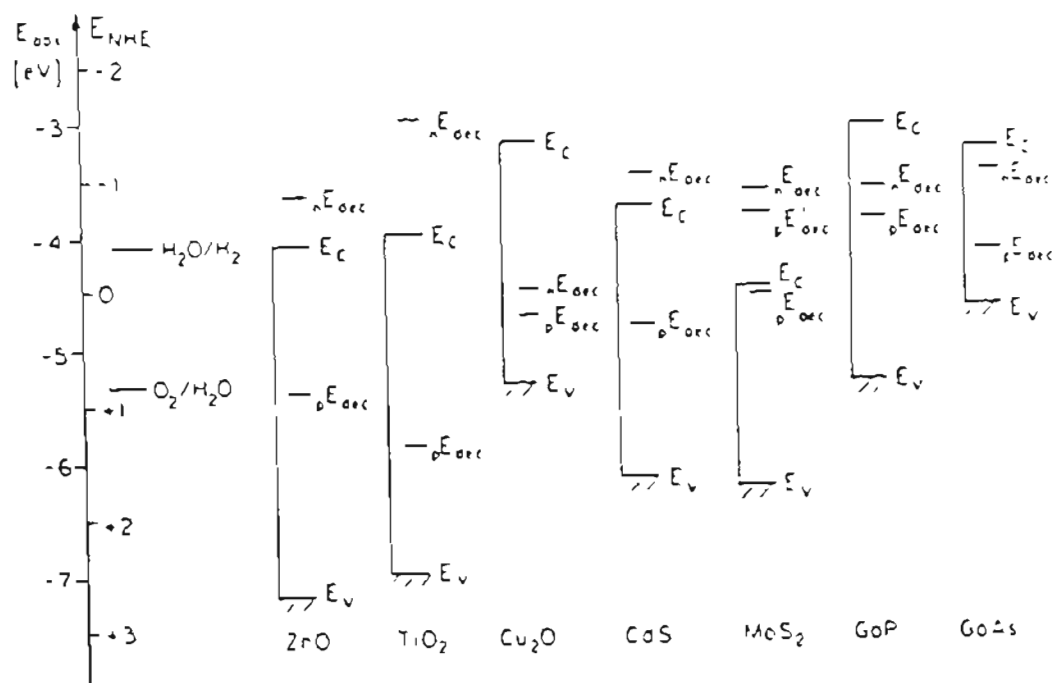


Figure 1.6. Position of band edges and decomposition Fermi levels of various semiconductors and of water in absolute (E_{abs}) and electrochemical energy scale (E_{NHE}). (1)

both cathodic and anodic photodecomposition.

Whether or not a given material will actually decompose in an electrolyte depends not only on the relative position of appropriate decomposition level to the band edge, but also on the position of solution redox levels. If there exists a solvent decomposition level lying deeper in the semiconductor bandgap than the semiconductor decomposition level, then corrosion may be avoided since the interaction with the solution would be thermodynamically favored. This forms the basis of some of the early attempts at stabilizing semiconductor photoelectrodes and will be discussed below.

1.4.2 Methods of Stabilizing Materials

There have thus far been two primary techniques employed to stabilize semiconductor photoelectrodes susceptible to corrosion. The first of these is by the introduction of electroactive species into the PEC that effectively compete with the corrosion reaction. Wrighton et. al. (118) have reported on the successful stabilization of photoanodes made from CdS, CdSe, CdTe, Gap, GaAs, InP and Si by the introduction of X^{2-}/X_n^{2-} species into the electrolyte. The first six materials were all found to be inert when $X = \text{Te}$, with some of them being stabilized by $X = \text{S}$ and Se . Silicon was found to be stabilized by ferrocene reagents in solutions of ferrocene.

As alluded to above, this technique works if the electroactive species has a redox potential deeper in the semiconductor bandgap than the semiconductor decomposition level of interest or if the reaction rate for the charge transfer process with the redox agent

is significantly greater than that for the decomposition reaction. The problem with this type of stabilization is that the initial charge transfer reaction is from the semiconductor to the stabilizing agent. Photodissociation of water can then be accomplished only if the reagent becomes covalently bonded to the semiconductor surface in the course of the reaction and then exchanges charge with hydroxyl ions in the electrolyte. This is referred to as derivatization with the reagent (118) and has been discussed above in connection with dye sensitization as a means of extending the spectral response of a material. More typically, stabilization with a reagent results in enhanced photovoltaic activity at the expense of photoelectrochemical activity.

A stabilization technique aimed at retaining photoelectrochemical activity is corrosion suppression by the application of a chemically inert coating (see also section 1.3.3). Frese et. al. (119) tested the effects of metal coatings on GaAs and found that films on the order of a monolayer were quite effective in stabilizing the material. They concluded that holes generated at the valence band edge would enter the metal as hot holes and would have very long mean free paths. Hence films on the order of a monolayer would be completely transparent to holes. An advantage to this technique is that metal coatings (such as platinum) could also act as a catalyst for the desired reaction.

Fan et. al. (120) combined these two techniques to improve the ability of n-Si to function in the presence of Fe^{2+} . They found

that a thin metal film underneath a polypyrrole film substantially improved the stability of n-Si in aqueous electrolyte containing $\text{Fe}^{2+}/\text{Fe}^{3+}$ couples.

The technique of coating potential photoelectrode materials is particularly attractive in that it can stabilize the material against corrosion, aid in extending the spectral response, and act as a catalyst for the chemical reaction of interest.

CHAPTER TWO

REVIEW OF RELATED WORK

2.1 Strontium Titanate

2.1.1 Physical Structure and Energy Bands

Strontium titanate is of the perovskite structure and at room temperature belongs to the simple cubic space group O_h^1 (Pm3m). The unit cell and Brillouin zone for this structure are shown in Figure 2.1, using the notation of Bouckaert, Smoluchowski and Wigner (BSW). The irreducible representations of the groups of the wave vector for this space group were first published by BSW (121), and the corresponding lattice harmonics by Altmann and Cracknell (122). A phase change occurs for SrTiO_3 at around 110 K wherein the crystal structure assumes a tetragonal form (123). Another possible phase transition has been identified at around 65 K and has been associated with a structure of orthorhombic or lower symmetry (124). The nature of these phase transitions will be discussed in the next section.

A number of energy band models have been proposed for SrTiO_3 over the years and a collection of energy versus wave vector diagrams thus produced can be found in Appendix II. A room temperature intrinsic gap $E_{g,i} = 3.22$ eV is indicated by the fundamental absorption edge, as deduced by Cardona (125) from normal incidence reflectance. Cardona deduced real and imaginary parts of the dielectric constant over the range 3-20 eV from Kramers-Kronig reflectance

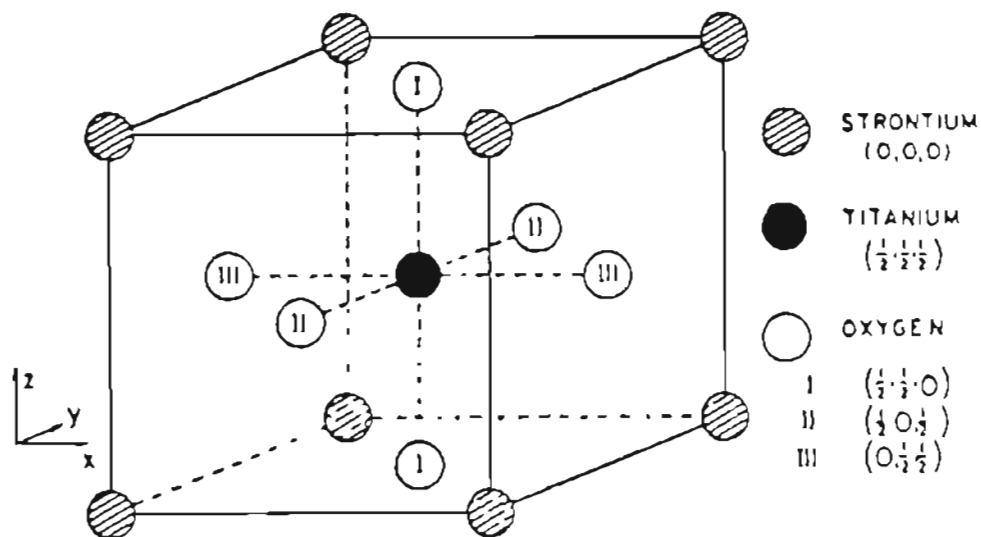


Figure 2.1a. Unit cell of Strontium Titanate.

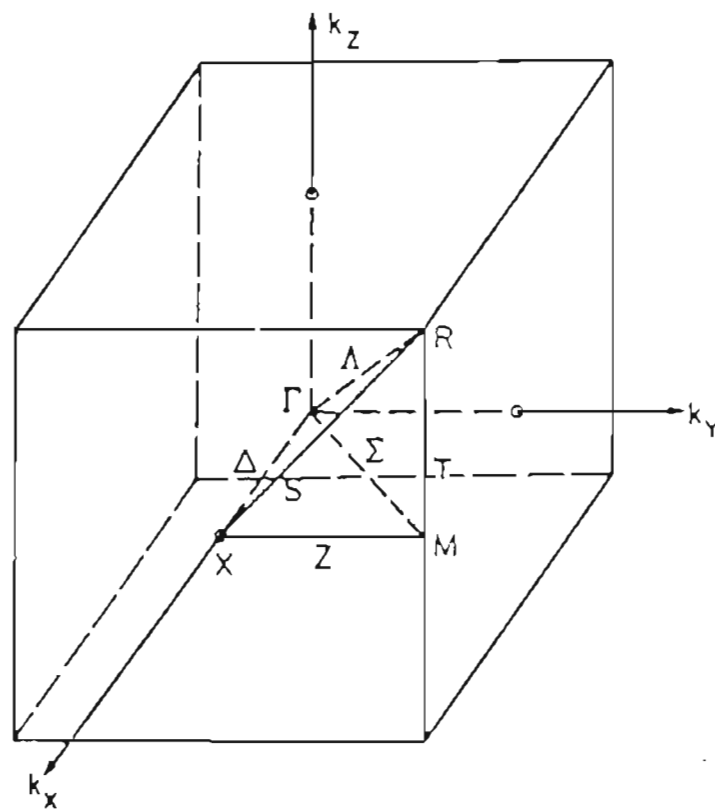


Figure 2.1b. Brillouin zone of Strontium Titanate. Notation of BSW.

analysis. The consequences of this can be compared with band models.

Kahn and Leyendecker (126) first proposed an LCAO band model (hereafter designated the KL model) which led to filled valence bands formed from oxygen 2p orbitals and empty conduction bands derived from titanium 3d orbitals. In cubic SrTiO_3 they indicated that there are six lowest-conduction-band ellipsoids lying along [100] directions of k-space with minima near the Brillouin zone boundary. The longitudinal effective mass was found to be 20-50 m_0 and the transverse mass about 1 m_0 . They deduced an overall conduction band width of about 4 eV, a valence band width of about the same magnitude, and a bandgap of about 3 eV. The Ti-4s and Sr-5s levels were found to lie 9 and 15 eV (respectively) above the Ti-3d bands.

In the KL model, the lowest conduction band is flat along the cubic axis and the inclusion of Ti-Ti overlap depresses the band at the edge of the Brillouin zone by about 0.02-0.05 eV. Spin-orbit interaction further splits the lowest conduction band by about 0.03 eV, hence conduction above 77 K is expected to be multiple band. The lowest conduction band width is on the order of 0.6 eV and the highest valence band width about 0.2 eV. They also pointed out that if the ionicity of SrTiO_3 were complete, the bandgap would be expected to be about 15 eV, while an ionicity of 85% yields an energy gap of 3.25 eV.

Simanek and Sroubek (127) pointed out that the KL model incorrectly neglected the change in the ionization potentials of the

oxygen and titanium ions with the degree of ionicity selected to fit the bandgap; however, this change turns out to be compensated by the effect of the polarizability of the oxygen ion (also neglected in the KL model). Hence the LCAO KL model has had good success at withstanding comparison with experiments despite these oversights. For example, Frederikse et al. (128) measured the magnetoresistance of semiconducting SrTiO_3 at 4.2 K and found that the lowest conduction band can be approximated by 3 or 6 spheroids along the [100] axes in k-space. They also found the transverse effective mass to be $m_t = 1.9 m_0$ and the longitudinal effective mass to be $m_l = 7.6 m_0$.

Nevertheless, there have been some discrepancies. In studying the electron tunneling characteristics of In- SrTiO_3 :Nb Schottky barriers, Sroubek (129) found that the density-of-states effective mass had a value of $m_d = 1.3 m_0$. For ellipsoidal energy surfaces, the density-of-states mass is related to m_t and m_l in the following manner (130):

$$m_d = (3)^{2/3} (m_t^2 m_l)^{1/3} \quad (2.1)$$

Hence using the mass anisotropy ratio of $m_l/m_t = 4.0$ measured by Frederikse (128) and equation 2.1, Sroubek found that his measurements indicated that $m_t = 0.4 m_0$ and $m_l = 1.6 m_0$. In support of the KL model, however, he did find that the overall width of the d bands was about 3.4 eV.

Tufte and Stelzer (131) measured the piezoresistive properties of reduced SrTiO_3 in single crystal form in the temperature range 4.2 to 296 K. They deduced from these measurements that the conduction band edge consists of two types of energy minima, separated by several hundredths of an eV, with the minimum at $k = 0$ being the lowest in energy. They also found that the piezoresistive effect becomes very anisotropic below about 110 K, and attributed it to stress induced alignment of the tetragonal domains brought about by the cubic-to-tetragonal phase transition. The placement of the conduction band minimum at the zone center is the most serious discrepancy with the KL model.

Soules et al. (132) subsequently proposed an energy band model for SrTiO_3 using a nonrelativistic self-consistent-field (SCF) procedure based upon the LCAO formalism. They found for the 2p valence band a width of about 5.9 eV and for the 3d conduction band a width of about 6 eV. They also found that the conduction band structure was in good agreement with the KL model despite the differences in overall widths, with the minimum along the $\{100\}$ direction, a flat lowest conduction band of width about 0.2 eV, and a flat upper valence band of width about 1.0 eV. However, their LCAO Hartree-Fock calculation yielded a transverse effective mass of $m_t = 0.4 m_0$ and a bandgap of 12.1 eV. It is also to be noted that the conduction band minimum at the zone boundary was found to be very close in energy to the degenerate levels at the zone center. Clearly the bandgap discrepancy is excessive in this model.

Mattheiss (133) has applied the nonrelativistic APW method fitted to the Slater and Koster LCAO interpolation scheme to calculate the energy bands of SrTiO_3 . The LCAO parameters were adjusted to fit the optical-bandgap and cyclotron-mass data. The major differences with the KL model were that the conduction bands were found to consist of warped bands at the zone center, and that the fundamental p-d bandgap was found to be direct. The valence band width was ~ 5.4 eV, the conduction band width ~ 9.5 eV, and the bandgap ~ 6.2 eV. He attributed the overestimate in the bandgap to a combination of self-consistency and exchange effects.

Wolfram (134) examined the lowest conduction bands of several perovskites, which are principally associated with the $(\text{pd}\pi)$ interaction. He found that the planar character of the $(\text{pd}\pi)$ interaction causes the three equivalent t_{2g} conduction bands to depend strongly on only two of the components of the wave vector. This two dimensional character accounts for the characteristic structure in the density of states and the optical properties of SrTiO_3 . In particular, the effective density of states would be expected to increase linearly with temperature rather than as $T^{3/2}$, and electronic impurity states will tend to be trapped in the energy gap. The latter is due to logarithmic singularities in the real part of the single-particle Green's function at the conduction band edge. This effect will have a strong influence on the surface characteristics and will be discussed further in section 2.1.4.

Ellialtioglu and Wolfram (135) subsequently developed simple

analytic functions of dimensionless variables from which the density of states, including all of the 14 primary conduction and valence bands of perovskites, can be derived. They found good agreement with energy band calculations; however, this model also predicts an energy gap a factor of two greater than is actually encountered.

Gyemant and Kelly (136) devised a scheme for obtaining densities of states for bulk SrTiO_3 from non-orthogonal basis functions and recursion techniques. This method yielded density of states curves quantitatively similar to those found from orthogonal orbitals; unfortunately, the overestimation of the bandgap remained.

It seems likely that both the valence and conduction bands have shallow extrema at the zone center and at high symmetry points towards the zone boundary for very similar energies. These conduction band characteristics mean that the density of thermally accessible conduction band states will be large for SrTiO_3 down to quite low temperatures. The electron mobility $\mu_n = \sigma/en$ must be viewed as an average over the various classes of mobile electron. For each of these classes, the scattering opportunities that limit mobility are affected by the E-k relations of this relatively flat-band system, by the large permittivity, and by impurity and electronic disorder. The latter points will be discussed further below. A thorough analysis of the energy band structure models of SrTiO_3 with the application of an interpretive technique applying parameters found in a newly proposed solid state table of the elements has been presented by Harrison (137).

2.1.2 Lattice Dynamics and Raman Spectra

The elastic constants of SrTiO_3 were first measured by Poindexter and Giardini (138), and Cowley (123) made an early experimental and theoretical study of the lattice dynamics and phase transitions. In a structure of M atoms per unit cell there will be $3M$ normal modes of vibration; hence SrTiO_3 will exhibit 3 acoustic modes (one longitudinal and two transverse) and 12 optic modes (139). Cowley found that the temperature dependence of the transverse optic mode of lowest frequency follows that of the dielectric constant, as predicted by Cochran (140). He also suggested that the accidental degeneracy of the lowest frequency TO branch with the LA branch at 110 K accounts for the cubic-to-tetragonal phase transition. An important point in Cochran's theory of ferroelectricity (140-141) is that one of the transverse optical branches tends to zero for small values of k . This was verified for SrTiO_3 by Cowley using neutron spectrometry.

Cohen et al. (143) studied the optical absorption spectrum in the region 0.05-0.3 eV and observed multiphonon creation processes. In particular, they found that two phonon processes in the region of the Brillouin zone extending from X along Δ support the model of Cowley. Achar et al. (144) performed lattice dynamic calculations of harmonic and first-order anharmonic properties at the zone center using a shell model and found that the harmonic part of the model was equivalent to Cowley's model. The anharmonic part was found to yield a consistent description of third-order elastic and electro-

striction constants when compared to experimental data extrapolated to absolute zero.

The cubic-to-tetragonal phase transition that occurs at 110 K has received considerable attention. Thomas and Müller (145) developed a theoretical model of structural phase transitions in perovskite-type ABO_3 crystals involving rotations of BO_6 octahedra. They obtained the frequencies associated with the "soft" normal modes (which become zero at the transition temperature, T_a) both above and below T_a . In writing the Hamiltonian for rotations about the BO_6 octahedra to fourth order, they found that the energy can be expressed in the following form:

$$\begin{aligned}
 E = E_o(T) &+ \frac{1}{2}a(T)(\phi_x^2 + \phi_y^2 + \phi_z^2) \\
 &+ \frac{1}{4}b(T)(\phi_x^4 + \phi_y^4 + \phi_z^4) \\
 &+ \frac{1}{2}c(T)(\phi_x^2\phi_y^2 + \phi_y^2\phi_z^2 + \phi_z^2\phi_x^2)
 \end{aligned} \tag{2.2}$$

where ϕ refers to the internal energy. For perovskites they found that if $0 < b < c$, then the energy has a minimum corresponding to rotation about a tetragonal axis. If $b > c$ and $b > -2c$, then the energy has a minimum corresponding to rotation about a trigonal axis. Outside of these ranges, there exists no energy minimum. Hence the nature of the phase transition depends on the relative magnitudes of the temperature dependent coefficients b and c .

Several studies of the soft TO phonon mode responsible for the 110 K phase transition have been made. Fleury et al. (146) inter-

preted the Raman spectrum below 110 K as evidence that the soft phonon mode is at the corner of the cubic Brillouin zone. Specifically, they proposed a model wherein the triply degenerate phonon F_{2u} (Γ_{25}) at the R point of the Brillouin zone approaches zero frequency (softens) and that as T falls below T_a the point R becomes a reciprocal lattice point and the unit cell becomes twice as large as in the cubic phase. This results in the doubling of the number of zone-center excitations which harden as the temperature is further lowered. That the phase transition around 110 K is caused by the condensation of the triply degenerate Γ_{25} optical mode at the [111] zone boundary is now generally accepted (147).

Unoki and Sakudo (148) identified the space group of the tetragonal phase as D_{4h}^{18} using electron-spin-resonance techniques and found no evidence of any further reductions in symmetry down to 4.2 K. However, in a subsequent study of the dielectric properties of monodomain samples (124) they identified an anisotropy within the plane perpendicular to the c axis occurring at around 65 K which suggested orthorhombic or lower symmetry.

The space group D_{4h}^{18} is a nonsymmorphic space group with a body-centered tetragonal Bravais lattice. In general, a space group element can be expressed as the sum of two terms:

$$G_{sp} = G_{point} + G_{trans} \quad (2.3)$$

where G_{point} is a point group element without translations and G_{trans}

is a translation of the unit element of the point group. If there exists an element within the space group such that its components G_{pt} and G_{tr} are not themselves members of the space group then the space group is called nonsymmorphic. In general it is difficult to obtain the character tables for the irreducible representations of a nonsymmorphic space group (149). Mattheiss (150) has undertaken an LCAO analysis of the effects of the 110 K phase transition on the conduction bands of $SrTiO_3$. To circumvent the problems encountered at the zone boundaries of nonsymmorphic groups, he concerned himself only with the band structure for wave vectors within the Brillouin zone near $\vec{k} = 0$, using the irreducible representations for the point group D_{4h} tabulated by Koster (151).

As a result of his calculations, Mattheiss found that the Γ_{25} conduction band minimum is split by about 90 meV (at 4.2 K) into a lower doubly degenerate Γ_5+ state and an upper nondegenerate Γ_4+ state. The lower degenerate state is further split by spin-orbit coupling by about 25 meV. The result is a warped single-valley conduction band at low carrier densities and a two-band model for electron densities $n > 10^{19} \text{ cm}^{-3}$. This splitting is similar to the splitting caused by the ferroelectric transition in $BaTiO_3$.

Photoluminescence studies have been used to probe the phonon spectrum and the phase transitions. Sihvonen (152) examined the photoluminescence spectrum between 400-1300 nm as a function of temperature and 365 nm irradiation. He found associated peaks in intensity at 35 K and 95 K which he related to a ferroelectric-

paraelectric transition and the cubic-tetragonal transition, respectively. He also found a maximum in the photocurrent at 105 K and a minimum at 35 K, along with extensive trapping effects. His absorption measurements showed that the optical bandgap rose from 3.15 eV at 300 K to 3.29 eV at 77 K and that a single trapping level existed at about 1.58 eV below the conduction band. He also found evidence for a distribution of traps and recombination centers extending from about 0.2-1.5 eV below the conduction band. The ferroelectric transition alluded to above is anomalous in SrTiO_3 and will be discussed more fully in section 2.1.3.

Grabner (153) measured the photoluminescence spectra at 77 K for undoped, 0.05% Sm-doped and 0.005% Cr-doped SrTiO_3 . He found good agreement with reported phonon lattice spectra with the additional identification of several zone boundary phonons. Comparison of the excitation spectra of the three materials indicated that there exists a tightly bound center facilitating energy transfer from Sm or Cr dopants that appears to be an intrinsic defect or an exciton. They were able to conclude that if the center was indeed produced by exciton formation, that the exciton would have to be a Frenkel-like exciton wherein the electron and hole are tightly bound and are screened by the optical (rather than the static) dielectric constant.

Finally, Kozyreva (154) calculated the frequencies of plasma oscillations related to the interaction of LO phonons and longitudinal oscillations of free charge carriers. From this he concluded

that the changes in the reflection spectra of conducting samples of SrTiO_3 are a result of plasmon-phonon resonance.

The Raman spectrum of SrTiO_3 has drawn a considerable amount of attention over the years (155-159). The selection rules for the cubic perovskite structure require that the Raman spectrum be entirely second order while in that phase. This has been confirmed by a number of investigators (155-157,159). First order Raman scattering is allowed in the tetragonal phase and has been observed (156,158-159). Nilsen and Skinner (157) found that the second order Raman active modes have wave vectors at or near the Brillouin zone boundary and tend to be transverse polarized. They compared the Raman spectra of pure and doped samples and found that the two undergo different phase transitions as the temperature is reduced. Although they were not able to identify any first-order Raman scattering in the tetragonal phase, they were nevertheless able to conclude that at lower temperatures the crystal structure does take on reduced symmetry.

Taylor and Murray (158) reported on the Raman spectrum of tetragonal SrTiO_3 and the effect of impurities. They did find first-order peaks but they also found that most of them were difficult to distinguish from the multi-phonon background. They also found that impurities can lead to the breaking of the selection rules with the intrusion of two infrared active modes and a ferroelectric soft mode.

More recently Balachandran and Eror (159) have done a thorough analysis of the Raman spectra of polycrystalline SrTiO_3 as a function

of temperature. In agreement with Nilsen and Skinner, they found that the bands in the second-order spectrum are associated with wave vectors near the Brillouin zone boundary. They also found five first-order bands below 120 K and an impurity induced band at 46 cm^{-1} (at 100 K) corresponding to the ferroelectric T_{1u} soft mode. The energies of phonon branches at the zone boundary deduced from the Raman spectrum were in good agreement with those obtained from neutron inelastic scattering experiments.

2.1.3 Optical and Dielectric Properties

The first single crystals of SrTiO_3 were felt to be potentially useful for their optical properties, hence a number of early studies were done on the optical characteristics. In the first of these, Levin et al. (160) measured the transmittance and absorption and found the activation energy to be 3.1 eV. Gandy (161) later measured the optical transmission of heat treated samples in the photon energy range 0.1 - 3.4 eV. He found that vacuum heating induced absorption maxima at 0.9 and 2.9 eV, which could be subsequently removed by heating in oxygen. Prolonged heating in oxygen produced no observable change in absorption. He also examined the optical absorption induced in Fe and Co-doped samples by heat treatment in oxygen and attributed it to a controlled change in the valence state of these impurities. Vacuum heating removed the optical absorption in these doped materials.

Casella (162) studied the optical properties under applied stress and electric fields and derived selection rules for polarized optical

transitions in the region of the absorption edge. Barbosa et al. (163) studied the transmission in the nonsaturated (Urbach's) region from room temperature up to 853 K and noticed a strong change in reflectivity with temperature.

Cohen and Blunt (164) studied the absorption coefficient, reflectivity and electroreflectance in the temperature range 4.2-300 K in the region of the absorption edge. Urbach's rule (165-168) states that the low-energy tail of the direct absorption edge of polar materials decreases exponentially in the following manner:

$$\alpha = \alpha_0 \exp[-\sigma(E_g - E)/kT] \quad (2.4)$$

Cohen and Blunt found from their measurements that the above coefficients took on the following values: $\alpha_0 = 1.3 \times 10^4 \text{ cm}^{-1}$, $\sigma = 1.0$, and $E_g = 3.37 \text{ eV}$. However, they were not able to establish from their observed data whether the fundamental transition in SrTiO_3 is direct or indirect.

Capizzi and Frova (169) studied the absorption below the fundamental edge at low temperature in an attempt to identify the nature of the transitions. They concluded from the oscillatory behavior near 77 K that the transition centered around 3.27 eV is indirect ($\Gamma_{15} \rightarrow X_3$) and involved a 51-meV LO phonon. They also found no evidence of excitons, and identified what they considered to be the first direct transition ($X_{51} \rightarrow X_{31}$) at $\approx 3.46 \text{ eV}$. The absorption at low temperature deviates from Urbach tail behavior, allowing observation of the indirect structure. At higher temperatures,

broadening effects masked this structure. They also concluded that the upper valence band width is about 0.19 eV and the the lowest conduction band width is of comparable size. This result implies a longitudinal effective mass of $m_1 \sim 10 m_0$ and is consistent with the KL band model.

Blazey (170) has studied the optical absorption edge around the 110 K phase transition and found a bandgap shift of 22 meV attributed to fluctuations at the second-order phase transition. He also found a quadratic temperature dependence for the bandgap energy between 200 - 300 K of the following form:

$$E_g = E_0 - \alpha T^2 \quad (2.5)$$

where $E_0 = 3.281$ eV and $\alpha = 1.26 \times 10^{-6}$ eV K².

The dielectric properties of SrTiO₃ are of particular interest for two reasons. The first of these is that the high static dielectric constant makes the material useful in device applications such as boundary layer capacitors. The second is the ambiguous ferroelectric properties of the material. The Curie temperature calculates to ~ 45 K but measures to ~ 35 K (171) and is not accompanied by any discontinuity in the dielectric coefficient. Barker and Tinkham (172) obtained the real and imaginary parts of the dielectric constant for the region $2.5\text{--}3000\text{ cm}^{-1}$ from reflectivity measurements. They found a rapid rise in ϵ_0 with decreasing temperature (from ~ 330 at 300 K to ~ 1200 at 93 K), which is characteristic of ferroelectrics. It

was felt that this rise is due to the softening of the lowest TO mode. Barker (173) subsequently made a more detailed study of the temperature dependence of the TO and LO mode frequencies using infrared reflectivity measurements. He once again found that the lowest TO mode shifts in a manner consistent with Cochran's theory of ferroelectricity (140-141) and that all the other optic modes remain stable to at least 1 or 2%.

Spitzer et al. (174) also measured the room temperature reflectivity in a range overlapping that of Barker (70 to 5000 cm^{-1}). Kramers-Kronig and classical dispersion theory analysis were used to obtain the real and imaginary parts of the dielectric constant; all of the infrared-active modes allowed by the crystal symmetry were found, and the soft TO mode responsible for the phase transition was identified at 87.7 cm^{-1} . The large static dielectric constant was attributed to this mode, which is associated with TiO_6 octahedra vibrations.

Sakudo and Unoki (124) studied the low temperature behavior of the dielectric constant and found that at around 65 K there develops dielectric anisotropy in the plane perpendicular to the c axis. This implies that the crystal structure takes on orthorhombic or lower symmetry; however, they were not able to identify the mechanism responsible for this behavior.

2.1.4 Surface Properties

The potential significance of electronic surface states in assisting charge transfer between wide bandgap semiconductors and ionic

species within the electrolyte in the photodissociation of water has been discussed in chapter one. There it was pointed out that the high quantum efficiencies measured in SrTiO_3 and TiO_2 (approaching 100 %) can best be accounted for by such states. Consequently the electronic properties of the SrTiO_3 surface are of great interest and the observations of a number of studies will be summarized below.

A theoretical model for the surface states associated with d-band perovskites with applications to SrTiO_3 has been developed over the years in a series of articles by Wolfram et al. (175-180). They have demonstrated that surface states derived from the lower conduction band produce a square-root singularity peak in the density of surface states at energies within the bandgap and that these states are highly localized and exhibit nearly pure d-state character. These states are assumed by Wolfram et al. to account for the catalytic properties of the perovskites (176-178).

Using LCAO methods combined with a generalized-Seitz-ionic model, they calculated both bulk and surface energy bands (177). It was found that the surface bands move deeper into the bandgap as the surface perturbations to the Hamiltonian increase. This effect is of particular significance for ceramic materials. It was also found that changes in the potential at the surface can be of the order of several eV, indicating the possible formation of significant midgap states. A subsequent analysis of MO_6 (where M is a transition metal ion) cluster surface states using an empirical molecular-orbital model was developed and it was noted that chemisorption

and catalysis on very small particles may be described by a cluster model.

Ellialtioglu and Wolfram (180) improved on the calculations by using a Green's function method with the LCAO model previously developed. They obtained approximately self-consistent solutions for the local density of states which showed that the bandgap surface states aren't quite as deep in the bandgap as had been thought. They found that a surface oxygen vacancy concentration of about 3 or 4% would be sufficient to compensate intra-atomic Coulomb repulsion and stabilize the surface states in the bandgap. Hence bandgap surface states would be less likely to occur on oxidized samples.

It should be recalled that the band structure calculations applied to the predominant $pd\pi$ interaction by Wolfram (134) indicated that the two-dimensional character of the conduction band will tend to trap impurity-related states in the bandgap. This characteristic is particularly noteworthy when considering the distribution of energy states at the SrTiO_3 surface.

Experimental investigations of the SrTiO_3 surface have since confirmed many of the characteristics predicted by the models mentioned above. Powell and Spicer (181) deduced from UVPS analysis that midgap surface states on the (001) face, if existent, would have a density less than 10^{13} cm^{-2} . On the other hand, Henrich et al. (182) (also using UVPS techniques) found for vacuum-fractured surfaces a surface state density $\sim 5 \times 10^{13} \text{ cm}^{-2}$ at an energy some

1.7 eV above the valence band edge (E_V). These results are not necessarily inconsistent, since the existence of bandgap surface states is critically dependent on sample treatment due to the tendency of oxygen vacancies to stabilize surface states in the bandgap. In fact, the surface states found by Henrich et al. were attributed to extrinsic states composed of $Ti^{3+}-O_V$ complexes since they were found to diminish with increasing O_2 exposure. States were also found near $E_V + 2.2$ eV and were associated with step sites on the fracture plane.

Using a variety of analytical techniques (LEED, AES, EELS, UVPS), Lo and Somorjai (183) also reported midgap surface states on $SrTiO_3$, near $E_V + 1.6$ eV. They attributed these to Ti^{3+} ions. Using a vibrating capacitance probe for surface photovoltage measurements, Mavroides and Kolesar (184) found a strong dependence of the $SrTiO_3$ work function on the incident light frequency - caused presumably by filling and emptying of surface states within the gap.

Henrich et al. (185-186) have also reported on the effects of O_2 adsorption on disordered surfaces of crystalline $SrTiO_3$. They found no significant bonding effects of adsorbed H_2O on annealed samples but did for argon-ion-bombarded samples. No evidence was found for OH on the surface. They did find that low O_2 exposure produced an adsorbed phase with a sticking coefficient of 0.2 - 1 which depopulated the surface states. Tomkiewicz (187) has shown that orbital overlap of oxygen adsorbants can result in a broad surface band of width ~ 3 eV.

The significance of this section is to emphasize that midgap surface states do appear in a number of guises on SrTiO_3 surfaces, and that the effectiveness of SrTiO_3 as a photoanode material depends critically on the role such states can play. Thus the condition of the crystal surface, how this was formed, and the defect chemistry of the underlying lattice, all influence the photoactivity. It is thus suggested that a (controllably) disordered surface may well be superior to an ordered one for photoelectrochemical purposes, provided this can be created reproducibly, and that it is stable. The suitability of microcrystalline ceramic SrTiO_3 as a photoanode material thus merits careful examination: on the one hand since this can be much less costly than the single crystals used for much of the previous work, and also because this could well be more effective than the same mass of monocrystal in providing useful surface states.

2.1.5 Electronic Transport

The electronic characteristics of SrTiO_3 are of interest not only for purposes of device applications, but also as an aid in testing the validity of the various energy structure models that have been presented.

The first complete study of electronic transport in single crystal SrTiO_3 was performed by Frederikse et al. (188), who studied both reduced and doped samples in the temperature range 4.2 - 300 K. In the oxidized state, nominally pure SrTiO_3 is an insulator, transparent through the visible range. Reduction in this study was accomp-

lished by heating at temperatures above 1100 K in vacuum (with $P \approx 5 \times 10^{-7}$ mm Hg) for long periods. Doped samples had been purchased with an impurity content of 0.05 and 0.005 wt. % Nb, and conductivity, Hall and Seebeck coefficients were measured as a function of temperature. They found that reduction resulted in very shallow donors, and that there existed a small concentration of compensating centers which strongly influenced the temperature dependence of the Hall coefficient (R_H) and the resistivity (ρ) for lightly reduced samples. They were not able to determine the exact nature of these compensating centers, but their presence became less prominent as the donor concentration exceeded $\sim 10^{18} \text{ cm}^{-3}$. For example, samples doped with 0.005 wt. % Nb ($3-4 \times 10^{17} \text{ cm}^{-3}$) displayed a resistivity at room temperature of $\approx 10^{10} \Omega \text{ cm}$. On the other hand, samples doped with 0.05 wt. % Nb ($n \approx 5 \times 10^{18} \text{ cm}^{-3}$) showed a resistivity value of $\rho(300 \text{ K}) = 0.20 \text{ Ohm-cm}$.

Frederikse et al. also found the Hall mobility to be fairly insensitive to reduction and dopant species down to 100 K; but that at lower temperatures, μ_H diverged widely from sample to sample. The mobility was found to be $\sim 6 \text{ cm}^2/\text{V-sec}$ at 300 K, rising at 100 K to about $150 \text{ cm}^2/\text{V-sec}$. They found that in the temperature range 100 - 300 K, $\mu_H \propto T^{-x}$, with x between 2.7 and 3.2. They proposed a tentative explanation for this behavior wherein acoustical lattice scattering dominated, leading to the dependence: $\mu_H \propto (m^*)^{-5/2}$, with the effective mass (m^*) having a $T^{1/2}$ dependence. The effective mass was deduced from thermopower measurements, wherein it was

found that m_{av}^* (300 K) $\approx 16 m_0$ and m_{av}^* (78 K) $\approx 7 m_0$.

A further study of the Hall mobility in reduced and doped $SrTiO_3$ by Frederikse and Hosler (189) in the temperature range 1 - 1000 K indicated that the primary scattering mechanism above 300 K is by the highest two LO modes, and that below 10 K, ionized impurity scattering predominates. They were not able to identify the scattering mechanism in the intermediate temperature range. They performed measurements on nominally undoped single crystal samples reduced to provide carrier concentrations in the range 3×10^{17} to $5 \times 10^{20} \text{ cm}^{-3}$, and on samples doped with both Nb (0.01 - 1.0 wt. %) and La (0.025 and 0.1 wt. %). A table of their results can be found in Appendix III. They found the Hall coefficient to be roughly independent of temperature and μ_H to be independent of doping level above 200 K, indicating intrinsic scattering mechanisms.

The magnetic susceptibility of insulating and semiconducting $SrTiO_3$ was measured by Frederikse and Candela (190) at 300, 78, and 4.2 K. They found that insulating $SrTiO_3$ has a magnetic moment which is partly diamagnetic and partly (Van Vleck) paramagnetic. Free carriers contribute to the paramagnetic moment and at concentrations $\geq 6 \times 10^{20} \text{ cm}^{-3}$, pure Pauli paramagnetism is observed. From this they deduced a conduction band effective mass of $5 m_0$.

Baer (191) studied free carrier optical absorption in the range 0.4 - 5 μm at 300 and 77 K. He found that absorption varies as $\lambda^{2.5}$, which is supportive of predominantly LO mode scattering.

Tufte and Chapman (192) extended the Hall mobility measurements to the range 1.6 - 550 K for reduced and Nb-doped samples ($10^{17} \leq n \leq 2.5 \times 10^{19} \text{ cm}^{-3}$). They found that Nb donor centers are hydrogenic and remain fully ionized down to 1.6 K, and that oxygen vacancies form doubly charged donor centers. In heavily doped samples, overlap and screening effects place both of the O_V energy levels in the conduction band. Their results suggested that at intermediate doping, one of these levels lies below the conduction band in the energy gap, and that for lightly doped samples, both of the levels are in the energy gap. This results in a large degree of deionization with decreasing temperature. They also found that the Hall mobility at low temperature in Nb-doped samples is about four times greater than in reduced samples; however, μ_H at low temperature was two orders of magnitude smaller than that predicted by ionized impurity scattering theory. They attributed this to a high concentration of compensating defects. This is reasonable in light of the findings by Frederikse et al. (188) of a concentration of compensating centers of about $5 \times 10^{17} \text{ cm}^{-3}$. The high temperature results were consistent with scattering from a polar optical mode with a characteristic temperature of 600 K, and the Hall mobility was found to obey the following relationship:

$$\mu_H(T > 100 \text{ K}) = 2.9 \times 10^7 T^{-2.7} \text{ cm}^2/\text{V-sec} \quad (2.6)$$

Lee, Yahia, and Brebner (193) subsequently studied the electronic

transport properties (resistivity, Hall mobility and Hall coefficient) of lightly reduced single crystal SrTiO_3 ($n < 10^{17} \text{ cm}^{-3}$) in the temperature range 2 - 300 K. They found the low temperature mobility to be much smaller than that found previously for crystals with higher carrier concentrations. For example, at 4.2 K they found the mobility to be in the range 5 - 700 $\text{cm}^2/\text{V-sec}$ for $n = 10^{13}$ to $4 \times 10^{16} \text{ cm}^{-3}$, whereas previous work (188-191) indicated that $\mu_H(T = 4.2 \text{ K})$ falls in the range 10^3 to $2 \times 10^4 \text{ cm}^2/\text{v-sec}$ for $n = 10^{17}$ to $5 \times 10^{20} \text{ cm}^{-3}$. They also found that the mobility at low temperature increases with carrier concentration, implying that ionized impurity scattering is not predominant. This is consistent with the carrier concentrations involved. Optical absorption measurements indicated that the mobility at room temperature was fixed by LO mode scattering.

Perhaps the most interesting property discovered by Lee et al. was the behavior of the resistivity as a function of temperature. They found that for carrier concentrations around 10^{16} cm^{-3} , ρ goes through a maximum and a minima at different temperatures depending upon the degree of reduction. They attributed this to the possible formation of oxygen-vacancy-related impurity bands, which merge with the conduction band at donor concentrations above 10^{17} cm^{-3} . This is consistent with the finding of Tufte and Chapman that the energy levels related to O_V lie in the energy gap for small doping levels. It was estimated that the impurity band thus formed is separated from the conduction band by about 0.04 - 0.08 eV. Conduction at low temperature was felt to be exclusively within the impurity band.

Parker and Yahia (194) performed AC Hall measurements on reduced samples of single crystal SrTiO_3 in the temperature range 190 - 500 K. They found that the Hall mobility in this temperature range increases with carrier concentration and that the temperature dependence of μ_H is of the form:

$$\mu_H = \mu_0 \exp(\Theta/T) \quad (2.7)$$

where $\Theta = 700$ K and μ_0 ranged from 0.42 to 1.42 $\text{cm}^2/\text{V-sec}$ depending on the degree of reduction, and increasing with reduction.

Superconductivity in SrTiO_3 has also been well studied (195-198). The dependence of the superconducting transition temperature on carrier concentration in reduced undoped SrTiO_3 indicates a maximum of $T_c \approx 0.5$ K for $n \approx 10^{20} \text{ cm}^{-3}$ (195). Superconductivity occurs in SrTiO_3 over the greatest range of carrier concentrations (8.5×10^{18} to $3 \times 10^{20} \text{ cm}^{-3}$) and at the lowest concentrations found (195). Addition of a few percent of BaTiO_3 reduces the minimum carrier concentration for superconductivity by another order of magnitude (198). Ambler et al. (196) measured magnetization curves from 0.15 K to T_c , and heat capacity down to 0.3 K; these curves can be found in Appendix III. From their results they concluded that SrTiO_3 is a type II superconductor.

Binnig et al. (197) studied two-band superconductivity in Nb-doped and reduced SrTiO_3 . From tunneling measurements, they found a distinctive double-gap structure upon increasing the carrier

concentration beyond a certain point ($\approx 10^{19} - 10^{20} \text{ cm}^{-3}$). This was attributed to the filling of the two lowest conduction bands as n rose through this concentration range. Their observance of two-band superconductivity in bands separated by about 32 meV is supportive of the energy band calculation of Mattheiss (133), which predicted two lowest conduction bands at the zone center separated by approximately 20 meV.

2.1.6 Impurity-Related Effects

Some of the earliest studies of impurity-related effects in SrTiO_3 had as their purpose the characterization of intrinsic properties. The first generally accepted experimental verifications of the 110 K cubic-to-tetragonal phase transition were accomplished by EPR studies of manganese (199) and gadolinium (200) ions in SrTiO_3 . In studying the EPR spectrum of Gd^{3+} impurities, Rimai and DeMars (200) were able to verify that such a transition does occur, that it occurs at $110 \pm 2.5 \text{ K}$, and that the transition is brought about by a cooperative phenomenon in the host crystal. In this study, they also examined the temperature dependence of the birefringence pattern to insure that the transition was not a property of the neighborhood of the impurity alone; the result indicated that a phase change was indeed occurring.

Weber and Schaufele (201) studied the fluorescence and vibronic spectrum of Eu^{3+} impurities in SrTiO_3 in order to obtain information about the lattice vibrations and to study the TO soft mode responsible for the 110 K phase transition. They were able to confirm that this

transition occurs at 110 K by the observance of additional fluorescence lines. However, the lack of additional crystal-field splittings in the spectral lines indicated that the noncubic distortions were small.

Iron centers in SrTiO_3 have been of interest for a variety of reasons. These in particular include the study of the nature of charge compensation in this material (202-204), photochromic behavior induced by the addition of transition metal impurities (205-208), electrocoloration (209), thermochromism (210), and the identification of energy levels within the bandgap (211). Kirkpatrick et al. (202) found from EPR spectra of Fe-doped samples that Fe^{3+} centers are charge compensated at nearest-neighbor oxygen sites. Mössbauer studies (203) have confirmed that iron enters the SrTiO_3 lattice substitutionally at the Ti^{4+} site and is charge compensated by oxygen vacancy formation. Vacuum firing tends to convert Fe^{3+} ions into Fe^{2+} through the creation of more oxygen vacancies.

Faughnan and Kiss (204) examined photoinduced reversible charge-transfer processes in SrTiO_3 doped simultaneously with Fe and Mo and found broad visible absorption bands induced by the dopants. They found that iron originally enters the lattice in the Fe^{3+} state, and molybdenum in the Mo^{6+} state; neither of these exhibit optical absorption. Upon irradiation with blue light, charge transfer takes place through either the conduction or valence band, and the ions become Fe^{4+} and Mo^{5+} . These ions both absorb in the visible. They also found that when Mo is absent, an unknown center acts as an

electron trap; this was felt to be related to oxygen vacancies.

Faughnan et al. in further studies of the photochromic properties of SrTiO_3 (205-207) have identified photochromism in samples doped with Ni/Mo, Ni, Fe, and Co. They found that all of the transition metals studied enter the lattice substitutionally on Ti^{4+} sites, and that charge compensation occurs either by double doping of donors and acceptors or by oxygen vacancy formation. Single doping with these impurities produces some visible absorption through the smearing out of the band edge, with a greater degree of extension of the absorption edge in the cases of Co, Dr, and Mn.

Irradiation with light in the range 390 - 430 nm results in the appearance of several broad visible absorption bands induced by charge-transfer processes such as mentioned above. For Ni/Mo doped samples, it was found that Mo acts just as in the Fe/Mo case, with Ni entering in the Ni^{2+} state and being oxidized to Ni^{3+} . The Ni^{3+} band peaks at $\lambda \approx 490$ nm, with a half-width of about 0.8 eV. In the case of single Ni doping, photochromism is aided by active traps shallower than the Mo^{6+} set, identified as Ni in axial sites. Four absorption bands have been found to occur in Ni-doped samples. Two of these, D_1 and D_2 (where $\lambda(D_1) = 480$ nm and $\lambda(D_2) = 575$ nm), are sharp bands introduced by reduction, and a third (B, $\lambda(B) = 490$ nm) is a broad band introduced by oxidation. The fourth band (E, $\lambda(E) = 700$ nm) is smaller in intensity and has not been identified. Through EPR spectra analysis, these bands have been associated with the following centers: B arises from the Ni^{3+} center, and the D bands

arise from $\text{Ni}^{3+}\text{-V}_\text{O}(2\text{e})$ centers (i.e., Ni^{3+} ions next to an oxygen vacancy field with two electrons)(212).

Fe doping was found to result in photochromic behavior only at low temperatures (≈ 77 K), indicating that shallow electron traps are available but that thermal decay times at room temperature are short (less than one second). The nature of these traps are unknown. The absorption bands thus found at 425 and 585 nm (of half-widths 0.83 and 0.50 eV, respectively) are consistent with the switching of Fe^{3+} to Fe^{4+} cubic centers. Faughnen (207) postulated that at higher iron concentrations, some Fe^{2+} might be present, which would allow the process $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ to occur. Bhide and Bhasin (203) have observed $\text{Fe}^{2+}\text{-V}_\text{O}$ sites by Mössbauer spectroscopy; in addition, Müller et al. (208) identified photochromic Fe^{5+} from paramagnetic resonance measurements.

Cobalt was found to introduce amphoteric photochromic centers wherein Co^{3+} ions absorb ultraviolet light, release an electron, and form Co^{4+} . The electron is then trapped by another Co^{3+} ion, creating a Co^{2+} site. The optical bands thus produced are centered around 500 nm and about 780 nm, and a variety of other complex Co bands can be introduced by heat treatment. Chromium has been found to introduce a strong absorption band centered at 500 nm, while vanadium shows only a slight photochromic effect. Manganese is stable in SrTiO_3 in the Mn^{4+} form and hence does not exhibit photochromism. Optical density curves of photochromic transition-metal-doped SrTiO_3 are reproduced in Appendix VI.

The application of Smakula's equation (213) yields an estimate of the oscillator strengths for these transition-metal-ions in SrTiO_3 :

$$N f = 0.87 \times 10^{17} [n/(n^2 + 2)^2] k_{\max} W \quad (2.8)$$

where N is the number density of absorbing impurity centers, f is the oscillator strength, n is the index of refraction (2.4 for SrTiO_3), $k_{\max}$ is the peak absorption coefficient of the absorption band in cm^{-1} , and W is the half-width of the absorption band in eV. From optical absorption, EPR data, and equation 2.8, the following values were obtained (207): $f_{\text{Fe}^{4+}} \approx 0.4$, $f_{\text{Ni}^{3+}} \approx 0.25$, and $f_{\text{Mo}^{5+}} \approx 0.1$. Faughnan pointed out that oscillator strengths of this magnitude would be consistent with a charge transfer process consisting of a transition from a nearest-neighbor oxygen to the impurity ion.

Blanc and Staebler (209) studied electrocoloration effects in transition-metal-doped SrTiO_3 in the temperature range 370 - 600 K. They were able to account for this phenomena quantitatively by a model wherein doubly positive oxygen vacancies drift across high field regions and cause the oxidation and reduction of stationary transition-metal ions. They demonstrated that at room temperature, conduction in insulating SrTiO_3 is largely ionic, with oxygen vacancy formation on the order of $N_V \approx 10^{18} \text{ cm}^{-3}$. The photochromic centers and visible photochromic bands created by electric fields are the same as those induced by irradiation and have been discussed above. What is of interest about the electrocoloration effect is that the vacancy

mobility can be calculated, and was found by Blanc and Staebler to be $\mu_V(T = 573 \text{ K}) \approx 5.5 \times 10^{-7} \text{ cm}^2/\text{V sec}$ and $\mu_V(T = 473 \text{ K}) \approx 1.5 \times 10^{-8} \text{ cm}^2/\text{V sec}$.

Wild et al. (210) observed thermochromic behavior in pure and transition-metal-doped SrTiO_3 that (unlike photochromism) was stable at room temperature. The effect is dependent on doping level, annealing temperature, and the rapidity of the quench, and it can be removed by cooling slowly to room temperature from any temperature above 1100 K. The annealing atmosphere can be reducing, oxidizing, or inert. They found that heavily doped SrTiO_3 has a bandgap in the range 2.7 - 2.9 eV and a broad absorption band centered at 2.1 - 2.2 eV, attributed to the presence of Fe^{4+} in the lattice.

Morin and Oliver (211) combined ESR and optical absorption measurements reported in the literature (and referred to above) with their own measurements of thermally stimulated current, electrical conductivity, and thermoelectric effect in an attempt to locate the energy levels associated with iron and aluminum in the bandgap of SrTiO_3 . They arrived at the following assignments: oxygen-ion-vacancy donor at $(E_C - 0.085)\text{eV}$; Al^{3+} acceptor at $(E_C - 0.18)\text{eV}$; Fe^{5+} acceptor at $(E_C - 0.75)\text{eV}$; Fe^{4+} acceptor at $(E_C - 1.06)\text{eV}$; and Fe^{3+} -vacancy acceptor at $(E_V + 1.35)\text{eV}$. In addition, they identified unknown acceptors at $(E_V + 0.50)\text{eV}$ and $(E_V + 0.65)\text{eV}$, and an unknown donor at $(E_C - 0.35)\text{eV}$.

A number of studies of chromium levels in SrTiO_3 have also been done (214-218). Stokowski and Schawlow (214-215) identified a

sharp-line fluorescence and absorption centered at 793.5 nm attributed to the ${}^2E \leftrightarrow 4A_2$ (R line) transition of the Cr^{3+} ion. This line was found to exhibit very large shifts with temperature and applied electric fields, which were felt to be due to interactions with the soft TO phonon branch. Zeeman effect measurements (216) supported these observations. Ghosh et al. (217) concluded from thermoluminescence, thermally stimulated capacitance, photoluminescence, and photoconductivity measurements that the dominant excitation mechanism of Cr^{3+} in SrTiO_3 is a charge-transfer process.

Ensign and Stokowski (219) have probed hole centers in SrTiO_3 with EPR and optical absorption measurements and have found two principal centers: an Al-O^- center formed by hole sharing among the oxygens surrounding Al^{3+} , and a similar center with a hole more deeply trapped by a charge defect of unknown origin (called X-O^-).

In studying the effects of defects formed by hydrogen reduction of undoped SrTiO_3 , Hastings et al. (220) found that the critical temperature for the cubic-to-tetragonal phase transition, T_c , decreases linearly with increasing carrier concentration. They were not able to correlate this precisely with the number of defects formed by reduction. However, it has been shown that the defect concentration is comparable to and increases with the carrier concentration (221). They did find a linear relationship between the defect concentration of Ti^{3+} on Sr^{2+} sites and the order parameter for the phase transition. The existence of this type of defect has been shown by ESR measurements (222-223).

Tom Feng (224) has recently reported on a detailed study of anomalous photoelectronic processes in nominally pure SrTiO_3 . He found a sharp narrow peak near the fundamental absorption edge in both photoconductivity and photoluminescence excitation spectra, although it was not observable in absorption spectra. The temperature dependence of its half-width was similar to that of F center absorption bands in alkali halides. He concluded from the results of the experiments performed that this peak is due to a discrete transition from the ground state of a highly localized sensitizing center to an excited state in the conduction band, from which auto-ionization frees an electron which is then available for conduction. Anomalous-peak as well as band-to-band radiation can be used to excite electronic transitions within a Cr^{3+} impurity ion responsible for infrared emission.

Feng found that below about 60 K, SrTiO_3 is in a state of high photosensitivity, with a photoconductive gain at 10 K of about 8×10^5 . Above 60 K, thermal quenching of the photocurrent occurs with an activation energy of 0.35 eV. These and other results suggested the presence of the highly localized sensitizing center alluded to above, and that it has a large capture cross section for holes but a small one for electrons. It was pointed out that the activation energy corresponds to the thermal depth of the hole in the sensitizing center from the top of the valence band. Optical quenching measurements, on the other hand, indicated a depth of 0.64 eV from the valence band; the difference between the values

of the location of the sensitizing level obtained by thermal and optical quenching was attributed to Franck-Condon effects. The absorption constant associated with this unknown center was found to be less than about 10 cm^{-1} .

2.1.7 Defect Structure

The defect structure of SrTiO_3 has received considerable attention over the years, due in large part to the relative ease of control over the material stoichiometry. Early work on undoped single crystal samples led to a straight-forward interpretation of the defect structure of that form. From oxygen self-diffusion and oxidation measurements, Paladino et al. (225-226) concluded that oxygen vacancies were the primary defect species over the temperature range 1100 - 1800 K. In agreement with this, Walters and Grace (227) found that conductivity and thermopower measurements in the range 875 - 1575 K for reduced single crystal SrTiO_3 fit the predictions based on an oxygen vacancy defect model. More recent work on ceramic SrTiO_3 further substantiated these findings. Balachandran and Eror (228) found that electrical conductivity measurements in ceramic SrTiO_3 , for the temperature range 1075 - 1325 K, and with oxygen partial pressure (P_{O_2}) in the range 10^{-22} to 1 atm., produced a Kroger-Vink diagram (229) consistent with the oxygen vacancy defect model.

It has also been shown by standard electronic and optical measurements (230) that oxygen vacancies formed at high temperatures can be quenched in by rapid cooling of a single crystal. Electron trans-

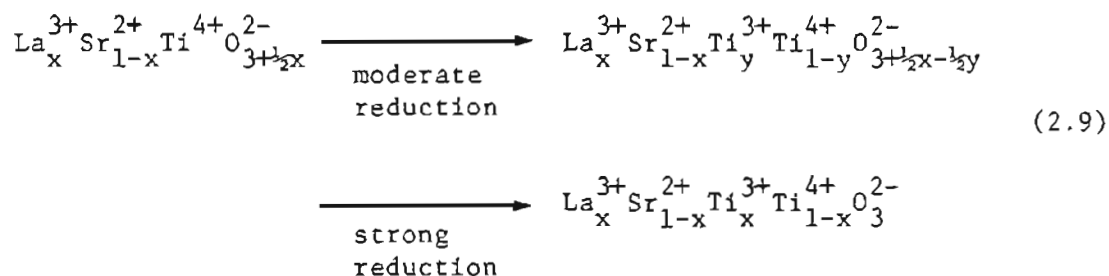
port measurements below room temperature for such reduced and quenched crystals (188-192,230) imply that isolated oxygen vacancy double donors may have one ionization energy of some 0.08 eV (192), and low temperature carrier freeze-out is prominent in a lightly reduced crystal. However, carrier freeze-out can be deferred to liquid helium temperatures for a strongly reduced crystal (192) - suggestive of impurity banding (193).

Franco and Regi (231) claimed from electron diffraction patterns and electron micrographs displaying superlattice fringes that anion vacancy ordering occurs when an anion deficiency of about 16 % is obtained ($\text{SrTiO}_{2.5}$). They claimed to have seen sixfold superlattices parallel to (111); however, Tofield (232) subsequently reproduced their experiments and found first that he could only obtain an anion deficiency of about 7 % ($\text{SrTiO}_{2.81}$), and secondly that for this material no defect ordering was observable.

Nominally undoped SrTiO_3 may contain potentially active impurity atoms in concentrations up to 0.005 %, as Morin and Oliver (211) demonstrated by mass spectroscopic analysis. However, the material can be doped sufficiently to permit control by a single dopant species. The SrTiO_3 for the present work was prepared by a liquid mix technique (233) that permitted chemical control of all ingredients to 0.001 %.

For SrTiO_3 doped with lanthanum, the defect structure at high temperature is fundamentally different from the oxygen vacancy model noted above for the undoped case. When the oxygen pressure is large

during high temperature equilibration, and when the cation ratio, Sr/Ti, is unity, the lanthanum dopant is accompanied by excess oxygen uptake (234). This is likely to be accommodated by the formation of SrO layers interleaved with perovskite layers (234-236). This would result in La compensation by Sr vacancies - called self-compensation or controlled atomic imperfection (229). High temperature reduction would cause a loss of the excess oxygen, and a change in the La compensation mechanism to the controlled-valency form (237), wherein Ti atoms undergo a valency change: $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$. The overall reaction can be written:



The model of Eq. (2.9) predicts that (for a given temperature), σ will vary with oxygen pressure for high P_{O_2} , but will not for strong reduction. Balachandran and Eror (228,234,238-239) found the model of Eq. (2.9) to agree very well with experiment for the temperature range 1075 - 1325 K. Gravimetric analysis showed a close correlation between the measured weight change after reduction and the value predicted by the model of Eq. (2.9), as demonstrated in Figure 2.2 (234). This inter-layer ordering would be difficult to detect by conventional x-ray powder diffraction techniques, since

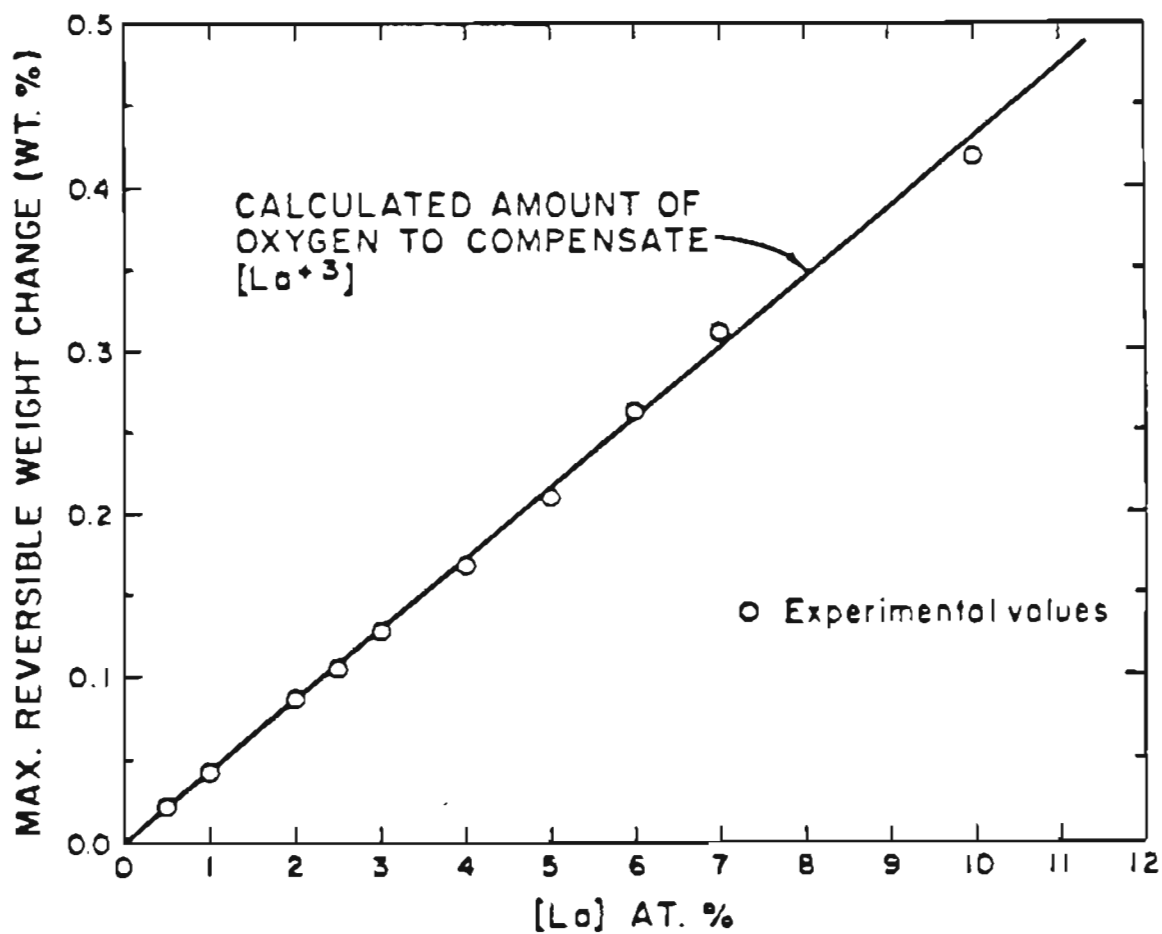
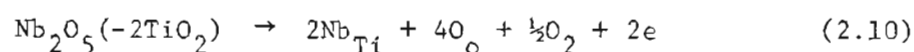


Figure 2.2. Maximum reversible weight change observed for $SrTiO_3$ as a function of La dopant concentration after reduction at 1323 K. Straight line is calculated from expectations of Eq. (2.9). (From reference 234).

only one SrO layer for every ten SrTiO₃ layers would be needed to compensate a La concentration of 20 at.%. The solid solubility limit of La in SrTiO₃ is about 35 at.%, as can be seen by examining the change in the lattice parameter with increasing lanthanum concentration (Figure 2.3) (234).

Chan et al. (240) have recently reported on the defect chemistry of polycrystalline SrTiO₃ as a function of reduction state, impurity content, and Sr/Ti ratio. They found that excess TiO₂ plays a significant role on the response to a reducing atmosphere, and that the doubly ionized oxygen vacancy is the primary defect in all cases. They also found little or no defect association. In their study, they used Nb as the donor dopant, and found a drastic change in conductivity for a given reduction state as the ratio Sr/Ti was changed. This is due to the mechanism of niobium accommodation in SrTiO₃, as given below for Sr/Ti = 1.0:



Since Nb replaces Ti, and since no defect association occurs, free electrons are initially present and conductivity is independent of P_{O_2} . For Sr/Ti ratios less than 1.0, the V_{O}'' content increases and the donor-type behavior of the Nb impurities is lost. Hence the defect chemistry of Nb-doped SrTiO₃ is fundamentally different from that of La-doped SrTiO₃.

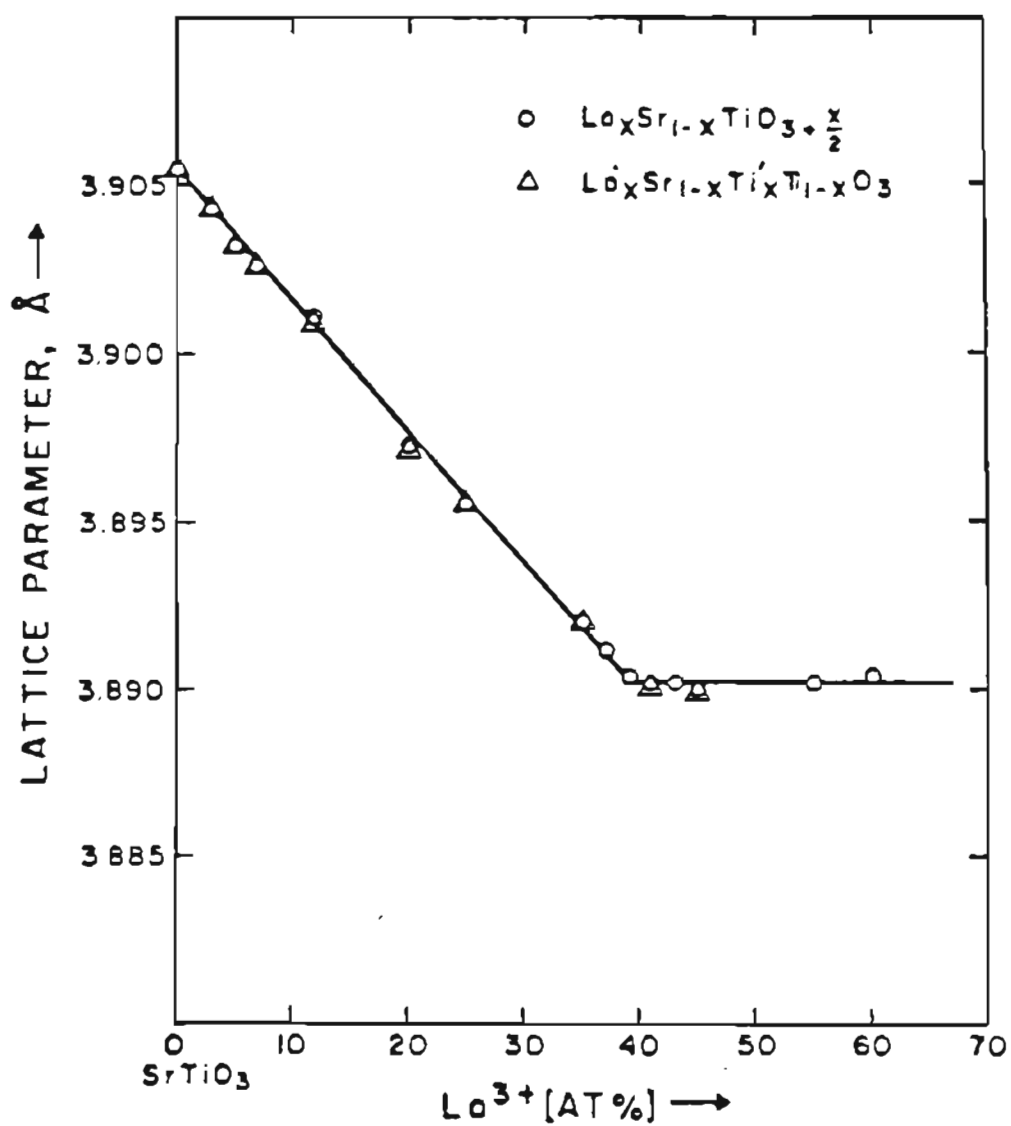


Figure 2.3. Lattice parameters of solid solutions in La-doped SrTiO_3 . (From reference 234).

Balachandran and Eror (241) examined the electrical conductivity of undoped SrTiO_3 with nonideal cationic ratios in the temperature range 1123 - 1323 K and the P_{O_2} range 10^0 to 10^{-22} atm. They found that the effects of nonideality in Sr/Ti were minimal for nominally undoped samples, and concluded that defects related to the deviation from ideal cationic ratio are associated into neutral vacancy pairs ($V_{\text{Sr}}'' V_{\text{O}}''$). They also found that the bandgap changed very little with changes in Sr/Ti. In a similar study of acceptor-doped SrTiO_3 (242), they found that impurity-related oxygen vacancies are filled at higher oxygen pressures, resulting in a stoichiometric excess of oxygen.

Balachandran and Eror (243) also studied the donor dopant Ta in SrTiO_3 , which replaces Ti (as does Nb) and contributes a free electron to the conduction band. They found that the defect structure at high temperature in this case is completely analogous to that found with La doping, with a stoichiometric excess of oxygen at high P_{O_2} . That this was not found for Nb by Chan et al. (240) could be due to the fact that tantalum exists only in the Ta^{5+} state, whereas niobium can enter as Nb^{5+} , Nb^{4+} , or Nb^{3+} . Hence the effect on the conductivity as well as the defect structure can be significantly different for the two impurities.

2.1.8 Single Crystal Photoanodes

Strontium titanate was the first semiconductor photoanode material demonstrated to assist the photoelectrolysis of water without decomposing and without requiring the application of an external

bias. In one of the first reports on this material, Wrighton et al. (103) demonstrated that the current efficiencies for SrTiO_3 were superior to SnO_2 and comparable to TiO_2 . Using a 200 Watt Hg arc lamp and the 351, 364 nm doublet from an argon ion laser, they showed that the photocurrent peaks at 330 nm and that the response varies linearly with light intensity. They also found quantum efficiencies of $\eta = 1.0 \pm 0.20$, for $\lambda < 330$ nm and applied potentials of $V_b \geq 1.5$ V. H_2 and O_2 were found to be produced in the correct stoichiometric ratios and in appropriate proportion to the electron flow.

The samples tested by Wrighton et al. were made n-type semiconducting by H_2 reduction for four hours at 1323 - 1373 K, and operated in a one compartment PEC with a Pt wire counter electrode. They found that optimum performance is obtained in strongly basic solution, with less O_2 being formed in lower pH electrolytes; this was attributed to the formation of H_2O_2 in the latter environment. The onset of photocurrent was found to occur at -1.2 V (vs. SCE) in 9.5 M NaOH solution, and sustained photoinduced conversion of H_2O to H_2 and O_2 at $V_b = 0$ was obtained.

The photoresponse edge was found to be $\lambda \approx 380$ nm, corresponding to an optical bandgap of about 3.26 eV. The average photocurrent density found in 9.1 M NaOH with no biasing was $J_{\text{ph}} \approx 1.5 \text{ mA/cm}^2$. Figure 2.4 shows the photocurrent versus biasing potential obtained by Wrighton et al., from which it can be seen that the maximum photocurrent is obtained at about $V_b = 2.0$ V, and that the response at zero bias is about 10 % of the peak response. The peak average

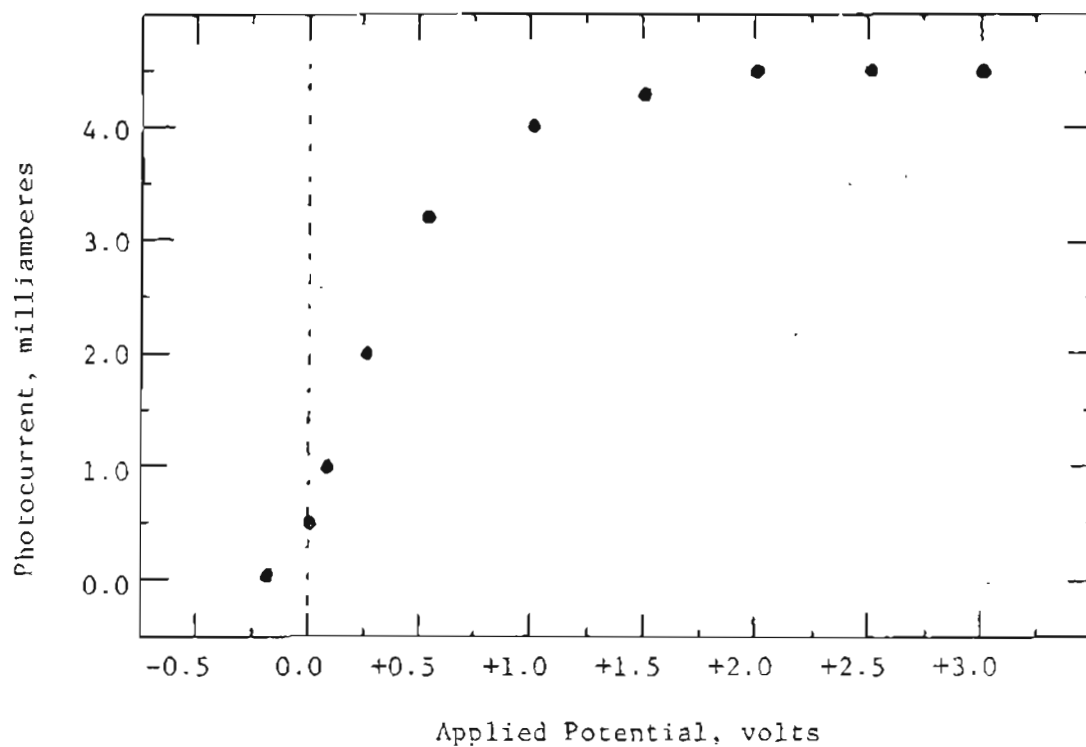


Figure 2.4. Photocurrent vs. applied potential (+ lead to SrTiO_3) for H_2 reduced single crystal SrTiO_3 (5 mm by 5 mm) in 9.5 M NaOH . Light source is a 200 Watt Hg arc lamp. (From reference 103).

photocurrent density indicated in Fig. 2.4 is about 16 mA/cm^2 . It is useful to define the optical energy conversion efficiency, η , as in chapter one:

$$\eta = \frac{(\text{energy stored as } \text{H}_2) - (\text{energy from battery})}{(\text{energy in from light})} \quad (2.11)$$

Using this definition, Wrighton et al. found η_{max} occurring at a biasing potential between 0.25 and 0.40 V and having a value of 0.20 for 330 nm light. This is an order of magnitude greater than what had been measured for TiO_2 .

Mavroides et al. (244) published results of experiments with H_2 reduced single crystal SrTiO_3 photoanodes concurrently with Wrighton's group. In this case, reduction was done at 1173 K for 3 hours, leading to anodes of somewhat higher resistivity ($\rho \approx 15 \text{ } \Omega\text{-cm}$). Photoanodes were made from disks of 5 - 15 mm diameter, and tests were done in a single compartment cell with a platinized-Pt cathode. Provisions were made for gas collection, as well as for N_2 or Ar flushing to remove dissolved oxygen. Differential space-charge capacitance and surface photovoltage measurements were done to determine the flatband potential as a function of pH, and it was found that the maximum band bending (and hence highest efficiency) was obtained at $\text{pH} \geq 13$. They also found that V_{fb} for SrTiO_3 exceeds that of TiO_2 by about 0.2 V under the same conditions. An added benefit of using high pH electrolytes is that the solubilities of both O_2 and H_2 are

reduced, allowing gas evolution even without O_2 purging. The gases thus formed were collected and analyzed and found to correspond to the desired reaction, both in composition and quantity. Analysis for dissolved Sr or Ti within the solution by atomic absorption spectroscopy was negative.

Mavroides et al. found that the external quantum efficiency for zero applied bias reaches a maximum of 10 % in the region $h\nu = 3.7$ to 3.9 eV. This was an order of magnitude greater than that found for TiO_2 . The efficiencies were found to increase dramatically with biasing potential, reaching a maximum of about 80 % for $h\nu = 3.8$ eV and $V_b > 1.0$ V. Defining the power efficiency as:

$$\eta_p = \frac{(1.23)I}{(P_{opt} + V_b I)} \quad (2.12)$$

they found a maximum (for $h\nu = 3.8$ eV) of 25 %, obtained at $V_b = 0.7$ V. This is comparable to the energy conversion efficiencies measured by Wrighton et al. (103).

At the same time that Mavroides et al. and Wrighton et al. were engaged in the work described above, a group in Japan (Watanabe, Fujishima, and Honda) was embarked on a similar study of $SrTiO_3$ photoanodes (245). They used single crystal samples reduced in vacuum ($P \approx 1$ mT) at 873 K for several hours. This treatment would be expected to yield samples of higher resistivity than those discussed above and, indeed, the resistivity was found to be around $10^3 \Omega\text{-cm}$.

Photoanodes thus prepared had a surface area of 2.5 cm^2 , with the (001) face presented to the electrolyte. The counter electrode was a platinized platinum plate of surface area 10 cm^2 , and the PEC was a two-compartment cell connected by an Agar salt bridge. The light source was a 500 Watt xenon lamp. Flatband potentials were measured via the capacitance measurement technique, and were found to be about 0.30 V less than those of TiO_2 . Gases formed were collected and measured, and the amount of charge passing through the cell was counted. Figure 2.5 demonstrates the nearly exact correlation between the measured dependence of evolved O_2 on charge passing through the circuit with the theoretical curve based on a current efficiency of 100 % for photoelectrolysis. They found an energy conversion efficiency of 20 % (for $V_b = 0$) occurring at $\lambda = 350 \text{ nm}$ (3.54 eV), which fell by a factor of $\frac{1}{2}$ in a one-compartment cell. They also concluded that SrTiO_3 photoanodes were stable.

Kung et al. (105) studied the photoanode characteristics of a variety of oxide semiconductors in the hopes of finding predictable patterns. Interpretation of their results was based on the assumption that the type of interface formed by the semiconductor and the electrolyte was one in which the semiconductor is highly polarizable and forms bulk compounds with the electrolyte. They studied single crystal samples of SrTiO_3 reduced in H_2 at 1373 K, for which the resistivities were less than $10 \Omega\text{-cm}$. As in the studies mentioned above, contact was made by attaching a wire to indium evaporated onto the back side of the photoanode. Stability of SrTiO_3 electrodes

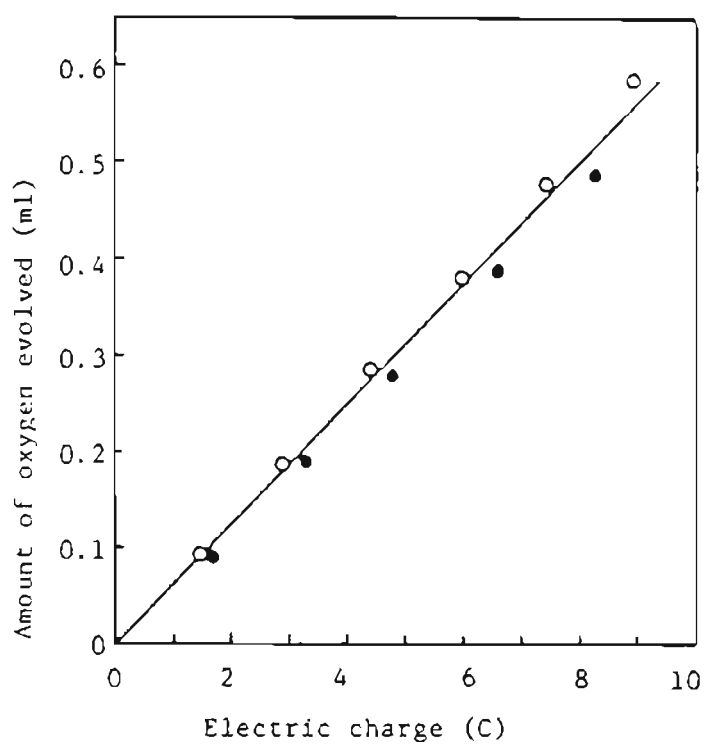


Figure 2.5. Dependence of the amount of oxygen evolved at the SrTiO_3 electrode surface on the amount of the electric charge passed through the external circuit. Solid line represents theoretical relationship for 100 % photolysis. Open and full circles represent two independent measurements. (From reference 245).

was demonstrated by each of the following six tests: (1) absence of large hysteresis in I-V profiling; (2) observation of gas evolution; (3) absence of anodic dark current at voltages less than the thermodynamic voltage for O_2 evolution; (4) reproducibility of the data; (5) absence of noticeable changes when examined with an optical microscope; and (6) absence of significant weight changes after testing.

Kung et al. determined V_{fb} for the group of oxides studied (TiO_2 , $SrTiO_3$, $BaTiO_3$, Fe_2O_3 , CdO , $CdFe_2O_4$, WO_3 , $PbFe_{12}O_{19}$, $Pb_2Ti_{1.5}W_{0.5}O_{6.5}$, $Hg_2Ta_2O_7$, and $Hg_2Nb_2O_7$) by extrapolating the I-V curve to zero current. They found a correlation between the bandgap and V_{fb} , as shown in Figure 2.6, which they attributed to the nature of the semiconductor/electrolyte interface. They also found a similar linear relationship between V_{fb} and the heat of formation of the oxide per metal atom per metal/oxygen bond, which they interpreted as suggesting that the semiconductor/electrolyte barrier height is determined by the heat of formation of the semiconductor (metal)/electrolyte (oxygen) bond.

Bocarsly et al. (246) studied the effects of high intensity laser illumination on single crystal $SrTiO_3$ and TiO_2 photoanodes. Excitation intensities of up to 380 W/cm^2 were obtained from an Ar ion laser tuned to the 351, 364 nm lines. They found no detectable change in surface composition of $SrTiO_3$ after high intensity irradiation, wherein photocurrent densities of up to 5 A/cm^2 were produced. They did find a slight decrease in quantum efficiency with light

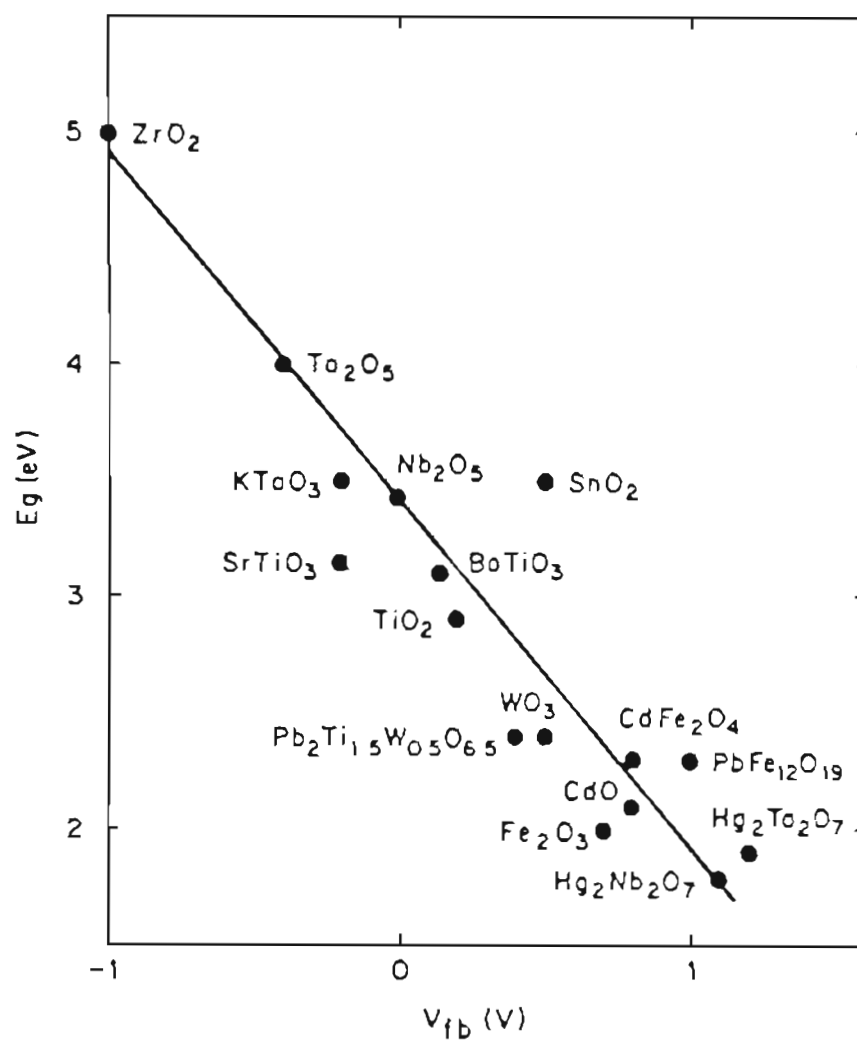


Figure 2.6. Relationship between band gaps and flatband potentials of the oxide electrodes. V_{fb} was measured against a hydrogen electrode in pH 13.3 solution. (From reference 105).

intensity, but current-voltage characteristics were unaffected. They further found that SrTiO_3 could sustain the conversion of 380 W/cm^2 (of wavelengths less than 330 nm) to chemical energy at an efficiency of about 8 %, yielding an energy conversion rate of about 30 W/cm^2 . It was evident from their work that the cell rate limiting step is controlled by illumination intensity.

Mavroides and Kolesar (184) performed surface photovoltage experiments on single crystal SrTiO_3 photoanodes, in which they measured the wavelength response of the photovoltage developed between the SrTiO_3 surface and a vibrating Au reference electrode, both in vacuum and in a water vapor ambient, in order to obtain information about surface states. They found a strong dependence of the work function of SrTiO_3 on incident light frequency, and were able to determine that there exists a fast transition that tends to decrease the work function and a separate slow transition that tends to increase the work function. These were attributed to the emptying and filling of sub-bandgap surface states. It was found that peaks obtained in these H_2 reduced samples were diminished when exposed to water vapor. This is evidence for oxygen-vacancy-related sub-bandgap surface states.

Vandermolen et al. (247) also found evidence for surface states in the study of single crystal SrTiO_3 photoanodes. In their study, SrTiO_3 samples were heated between 1173 - 1273 K in H_2 for several hours. The dark current was then measured in solutions of $\text{Fe}(\text{CN})_6^{3-}$, Fe^{3+} , and IrCl_6^{2-} as a function of applied voltage, concentration of

oxidizing agent, and pH. They found that direct electron transfer could not account for the observations made. From the saturation currents measured in the high current density region, it was estimated that the SrTiO_3 surface state density is on the order of 10^{10} cm^{-2} .

Butler et al. (248) studied the sub-bandgap photoresponse of TiO_2 and SrTiO_3 single crystal photoanodes, and found it to be linear with light intensity and to occur only for $h\nu \geq 2.2 \text{ eV}$. It was also found to depend on the square root of the applied potential and to be independent of temperature and electrolyte composition. They pointed out that the dependence of the photocurrent density on the square root of V_b is suggestive of a bulk excitation process involving impurity and defect-related sub-bandgap states. This can be seen by analyzing Butler's (83) expression for the photocurrent density at the semiconductor/electrolyte interface:

$$J_{\text{ph}} = e\phi_0 \left(1 - \frac{e^{-\alpha W}}{1 + \alpha L} \right) \quad (2.13)$$

For sub-bandgap radiation, α is small, and $\alpha W \ll 1$; expanding the exponential in Eqn. (2.13) then leads to the following:

$$J_{\text{ph}} \approx e\phi_0 \alpha W \quad (2.14)$$

Then, since Butler (83) notes that

$$W = W_0 (V - V_{\text{fb}})^{1/2} \quad , \quad (2.15)$$

for a bulk process occurring uniformly throughout the depletion region, the square of the photocurrent should depend linearly on applied potential; this was found to be the case. Since the process was found to be temperature independent, it was concluded that it was most likely a two-step optical process involving midgap states. The variation of the quantum efficiency with wavelength was found to follow the theoretical curve predicted by this model.

Reichman and Byvik (249) studied the effect of temperature changes on the photovoltage response of single crystal SrTiO_3 , and found that the energy conversion efficiency is maximized at 353 K. They also found that the onset potential for photocurrent increases with temperature, as does the saturation photocurrent. The onset potential is related to V_{fb} , and it was shown that the change with temperature is due to thermal effects on the potential across the Helmholtz layer (see Eqn. 1.7).

Two compartment cells using p-type semiconductor photocathodes along with single crystal SrTiO_3 anodes have also been tested. Ohashi et al. (44) found energy conversion efficiencies of 0.18 % for $\text{SrTiO}_3:\text{CdTe}$ bipolar cells, and 0.67 % for $\text{SrTiO}_3:\text{GaP}$ cells.

Schwerzel et al. (250) have been able to demonstrate the occurrence of photocorrosion in single crystal SrTiO_3 under photo-Kolbe reaction conditions in acidic electrolyte containing both sulfuric acid and acetic acid. No corrosion was in evidence in aqueous sulfuric acid alone. Since SrTiO_3 photoanodes work most efficiently in strongly basic solutions, this potential problem need never arise.

Pertinent results previously reported concerning the PEC characteristics of SrTiO_3 can be found tabulated in Appendix IV.

Prior to this investigation, it does not appear that the photoanode characteristics of either polycrystalline or doped SrTiO_3 have been reported; it has been one of the primary objectives of this work to remedy that situation.

2.2 Titanium Dioxide

The physical and electronic characteristics of TiO_2 have been well studied over the years, and a number of excellent review articles have been written (251-255). Consequently, no attempt will be made to duplicate those efforts, and the following will serve only as a brief summary of features most relevant to photoelectrochemistry. This investigation will only be concerned with the rutile phase of TiO_2 , which crystallizes in a tetragonal structure with lattice parameters: $a = 4.59 \text{ \AA}$ and $c = 2.96 \text{ \AA}$ ($a/c = 1.55$). Its density is 4.26 gm/cm^3 , and the melting point is 2120 K .

2.2.1 Electronic Band Structure

Daude et al. (256) performed the first theoretical energy band calculations for TiO_2 , using a combined tight-binding and pseudopotential method. They found for the upper valence band ($\text{O}^{2-} 2p$ bands) a width of about 16 eV , with a maximum at the zone center (Γ_3). The lowest conduction band was also found to be broad (about 4 eV , derived from $\text{Ti } 3d$ bands), with a minimum at Γ_1 . The transition $\Gamma_3 \rightarrow \Gamma_1$ is forbidden to first order. The first allowed direct transition is $X_1 \rightarrow X_1$, with many possibilities of indirect allowed

transitions. The $X_1 \rightarrow X_1$ transition is predicted to have an energy of 3.45 eV. The lowest allowed transitions are found to be indirect (2.91 eV, $X_1 \rightarrow \Gamma_1$, and 3.05 eV, $X_2 \rightarrow \Gamma_1$). Good agreement was obtained with experimental values.

Fischer (257) deduced a complete molecular-orbital energy level diagram from X-ray emission and absorption band spectra. With this method he was able to logically account for all of the occupied and vacant orbitals within about 25 eV of the Fermi level, and good agreement was found with published electroreflectance data.

Knotek and Houston (258) probed the valence and conduction band density of states structures and the surface structure of TiO_2 using Auger electron and characteristic loss spectroscopies (AES, CLS). The most significant result found for purposes of photoelectrochemical applications was that the TiO_2 surface demonstrated a valence structure indicating some surface reduction.

Vos and Krusemeyer (259) performed reflectance and electroreflectance measurements on single crystal TiO_2 to determine the optical spectra, and Vos (260) subsequently fitted the results to electronic energy levels. They found the fundamental edge to be an indirect transition of 3.037 eV, due to the gap $\Gamma_3 \rightarrow M_{1,2}$, which involved the emission of an M_9^+ phonon. They found the lowest direct gap to be at 3.57 eV. Effective polaron masses of about $6 m_0$ were calculated at the fundamental edge.

Mathieu et al. (261) investigated the effect of uniaxial stress along high symmetry directions, and confirmed the direct forbidden

edge corresponding to a $\Gamma_{3\nu} \rightarrow \Gamma_{1c}$ transition, and also identified a subsidiary valence band maximum along the Δ direction. Pascual et al. (262) subsequently used polarization-dependent absorption and wavelength-modulated absorption to examine the fine structure in the intrinsic absorption edge in the temperature range 1.6 to 300 K. They confirmed an indirect allowed transition ($\Sigma_{4\nu} \rightarrow \Gamma_{1c}$) characterized by a small doublet (3.061 - 3.065 eV at 1.6 K) as the fundamental transition for light polarized parallel to the c-axis. The same indirect transition plus a forbidden direct transition ($\Gamma_{3\nu} \rightarrow \Gamma_{1c}$) appears at 3.031 eV at 1.6 K for light polarized perpendicular to the c-axis.

A thorough study of the lattice dynamics of TiO_2 has been reported by Traylor et al. (263). They measured the phonon dispersion curves by coherent inelastic scattering of thermal neutrons along principal symmetry directions. They found that a shell model with tensor forces for all interactions except the second-neighbor oxygen-oxygen interaction gave acceptable qualitative agreement with the data.

2.2.2 Electronic Transport

A number of studies have been performed on the electrical properties of TiO_2 . In one of the earliest, Cronmeyer (264) found that comparison between the high temperature conductivity, the optical absorption threshold, and the photoconductivity maximum indicated a bandgap of about 3.05 eV. He found that hydrogen reduction at 1073 K produced semiconducting samples with an optical absorption

maximum at 0.73 eV. An optical activation energy of 0.68 eV was derived from the conductivity data; this correlates well with the predicted ionization energy of the first electron from an oxygen vacancy of 0.74 eV. The room temperature mobility in slightly reduced single crystals was found to be about $1 \text{ cm}^2/\text{V-sec}$. Crone-meyer further found that a comparison of electron concentrations calculated from weight loss in strongly reduced samples with those derived from Hall coefficient data indicated that for samples in which $n \sim 10^{20} \text{ cm}^{-3}$, all defect sites contribute to conduction at room temperature.

Breckenridge and Hosler (265) performed resistivity and Hall measurements on both ceramic and single crystal semiconducting TiO_2 in the temperature range 83-773 K, from which the variations of mobility and charge carrier concentration with temperature were determined. They found that lattice scattering predominates at high temperature, and ionized impurity scattering at low temperature. Low mobility values indicated an anomalously large effective mass (between 30 and $100 m_0$), with $m_c \sim 2m_a$. Their results indicated that the donor centers may be oxygen ion vacancies at which one or two electrons are trapped as Ti^{3+} ions. They suggested that free oxygen vacancies produced upon reduction form a narrow impurity band (with concentrations on the order of 10^{17} cm^{-3}) which accounts for the high effective masses. $\text{O}_V\text{-Ti}^{3+}$ complexes then form energy levels about 3.05 eV above the valence band and about 0.2 eV below the impurity band. The ionization energy between the neutral and ionized $\text{O}_V\text{-Ti}^{3+}$ com-

plexes is about 0.01 eV. Their model is depicted in Figure 2.7.

Earle (266) performed electrical conductivity measurements as a function of oxygen pressure on rutile ceramic TiO_2 and found two different regions in the resultant Kroger-Vink diagram (229). For oxygen pressures above 30 mm Hg (4 atm), the slope of $\log(\sigma)$ versus $\log(P_{\text{O}_2})$ showed a value of $-1/4.3$. The slope at lower pressures (down to ~ 0.1 atm) varied from $-1/2$ at low temperatures to $-1/3$ at high temperatures. This is consistent with a defect structure consisting of interstitial Ti at high pressures; the change in the slope at lower pressures was attributed to background impurities. The variation of σ with T indicated an activation energy of about 1.7 eV.

Conductivity, Hall effect and thermopower measurements performed at low temperatures on slightly reduced single crystals of TiO_2 by Frederikse et al. (267) indicated the existence of two conduction mechanisms. One of these is a free electron model in a narrow 3d-band of titanium, occurring at temperatures above 5 K. The other is conduction by self-trapped electrons or polarons in a polaron band, seen at temperatures below 5 K. The ionization energy of the polaron was found to increase from 0.01 to 0.07 eV with increasing temperature.

Yahia (268) used a combination of thermogravimetric and electrical conductivity data to determine the mobility of TiO_2 in the temperature range 1123-1323 K. He made the assumption that the primary defect structure consisted of oxygen vacancies to calculate

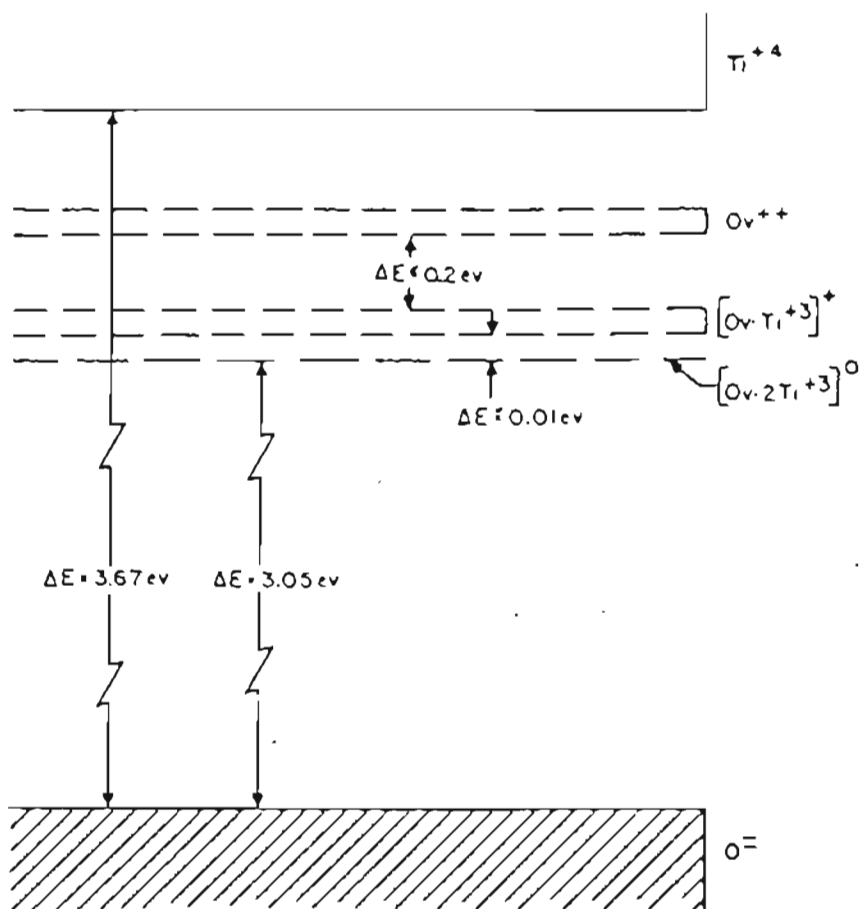


Figure 2.7. Thermal equilibrium energy-level diagram of semiconducting rutile. (From reference 265).

mobilities on the order of $10^{-5} \text{ cm}^2/\text{V-sec}$ in this temperature range. The mobility was found to increase with temperature in the range of study, and this was accounted for by attributing conduction to a diffusion mechanism (i.e. activated mobility) due to self-trapping.

Becker and Hosler (269) performed Hall coefficient and electrical conductivity measurements on n-TiO₂ in the range 2-600 K, and found evidence for multiple-band conduction at temperatures above 40 K. The primary evidence for this was a pronounced temperature dependence of the ratio of the two Hall coefficients for this anisotropic material. They found this effect to be intrinsic, and the energy separation between the lowest and next lowest conduction bands to be about 0.05 eV.

Itakura et al. (270) studied the electronic characteristics of Nb and Ta-doped TiO₂ (ceramic and single crystal) and arrived at a number of conclusions. They found that for doping levels up to 4 mole-percent, the specimens were n-type non-degenerate semiconductors with a density-of-states effective mass of about $20 m_0$. They also found that lattice scattering plays a dominant role at room temperature, and that $\mu_H(300 \text{ K}) \approx 0.4 \text{ cm}^2/\text{V-sec}$ for lower doping levels and falls to $10^{-2} \text{ cm}^2/\text{V-sec}$ with increasing doping. The Hall mobility was also found to increase with decreasing temperature for light doping, and to decrease with temperature for doping greater than 0.1 mole-percent. The activation energy of the donor centers due to the doping was found to be about 0.02 eV, compared to an activation energy for reduced, undoped TiO₂ of about 0.01 eV.

Iguchi et al. (271) reported on the resistivity of reduced TiO_2 in the important temperature range of 300–1100 K. Three distinct ranges were identified. In the first (started by room temperature), activated transport was clearly identified with an activation energy of about 0.028 eV. The second range occurred at intermediate temperatures and corresponds also to activated transport, but with activation energies that vary from 0.031 to 0.061 eV, according to the degree of reduction. The third range occurs at the high temperature end, and shows a resistivity minimum. They tentatively ascribed the behavior in the second range as being due to the action of oxygen vacancies.

2.2.3 Surface Properties

The surface properties of TiO_2 are of fundamental interest due to their significance in mediating charge transfer between photoanodes and electrolyte species in a PEC, just as discussed for SrTiO_3 . Since the qualitative features of this process have been presented elsewhere, the following will consist merely of a brief presentation of experimental findings.

Henrich et al. (272) studied TiO_2 single crystal surfaces bombarded by Ar ions. A combination of UV photoemission, EEL, AES, and LEED studies indicated the formation of three distinct phases dependent upon the extrinsic surface-defect concentration. Phase I contains isolated surface states 0.7 eV below the conduction band, phase II is associated with the creation of Ti^{3+} pairs, and phase III consists of a surface layer of ordered Ti_2O_3 .

Chung et al. (273) performed LEED and electron spectroscopy studies of clean single crystal TiO_2 surfaces, and found that both the (110) and (100) surfaces are stable, but that the latter gives rise to three distinct surface structures, in which the O/Ti ratio decreases from about 1.7 to about 1.3. Surface sensitive transitions were found at 8.2, 5.2 and 2.4 eV. Ar or oxygen ion bombarded surfaces showed a strong transition at 1.6 eV, and it was found that Ar^+ bombarded surfaces showed a decrease in the work function and the surface band bending of almost 1 eV. The latter effect was presumed due to the loss of oxygen from the surface. The ability to appreciably alter the surface band bending by treatment is of particular significance to photolysis, as a large space-charge voltage is needed to facilitate electron-hole pair separation and delivery of photo-generated holes to the surface.

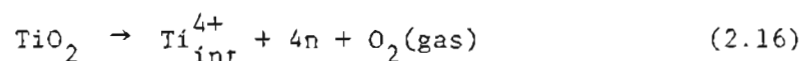
Sayers and Armstrong (274) studied the changes in surface composition of single crystal TiO_2 photoanodes due to PEC operation, by using XPS. Reduction of the electrode in hydrogen resulted in an oxygen deficient surface; it was found that photoelectrolysis at current densities of $10\text{--}15 \text{ mA/cm}^2$ for periods up to 8 hours appeared to return the electrode surface to nearly stoichiometric form.

Tomkiewicz (187) studied the surface states on chemically modified TiO_2 and found a broad Gaussian distribution with a maximum near the bottom of the conduction band. The width was found to vary linearly with surface coverage. A model was proposed based on the formation of a surface state band through overlap of the orbitals of randomly distributed surface adsorbants.

2.2.4 Defect Structure

The nature of the defect structure in reduced TiO_2 has been a matter of controversy for a number of years. Early high temperature conductivity and weight loss measurements as a function of oxygen pressure yielded results indicative of oxygen vacancy formation (275-276) as well as of titanium interstitials (266,277-278). Also, ESR experiments by Frederikse (252) were interpreted as indicative of Ti interstitials.

One standard method for interpreting the defect structure in an oxide is to examine the slope of the plot of $\log(\sigma)$ versus $\log(P_{\text{O}_2})$, called a Kroger-Vink diagram (229). The formation of a titanium interstitial will proceed in the following manner:



From chemical equilibrium theory, Eqn.(2.16) is seen to yield the following relationship between oxygen pressure and charge concentration:

$$P(\text{O}_2)^{-1} = K(T)\{\text{Ti}_{\text{int}}^{4+}\}n^4 \quad (2.17)$$

Since we have: $4\{\text{Ti}_{\text{int}}^{4+}\} = n$, Eqn.(2.17) reduces to:

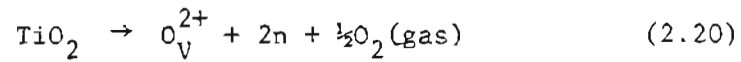
$$P(\text{O}_2)^{-1} = \frac{1}{4}K(T)n^5 \quad (2.18)$$

This in turn leads to:

$$\sigma = ne\mu(T) = K'(T)P(O_2)^{-1/5} \quad (2.19)$$

Hence a Kroger-Vink diagram indicative of Ti_{int} as the primary defect structure should exhibit a slope of $-1/5$.

For oxygen vacancies, on the other hand, defect formation occurs by the following reaction:



which leads to:

$$P(O_2)^{-1/2} = K(T)\{O_V^{2+}\}n^2 \quad (2.21)$$

But since: $2\{O_V^{2+}\} = n$, then:

$$P(O_2)^{-1/2} = \frac{1}{2}K(T)n^3 \quad (2.22)$$

or:

$$\sigma = K'(T)P(O_2)^{-1/6} \quad (2.23)$$

Hence the Kroger-Vink slope corresponding to oxygen vacancy formation in TiO_2 should be equal to $-1/6$.

Greener et al. (279) found that conductivity measurements in the temperature range 873-1673 K for both mono- and polycrystalline rutile (for P_{O_2} between 5×10^{-3} and 1 atm.) produced a Kroger-Vink slope of $-1/4$ above 1473 K. This was attributed to singly-ionized oxygen vacancy defects with an activation energy of 1.8 eV. At temperatures below 1173 K, σ was found to be independent of P_{O_2} in this pressure range and was felt to be impurity controlled. At intermediate T, these two mechanisms were felt to act in parallel.

Prior to the work of Greener et al., Yahia (280) studied the $\sigma(P_{O_2})$ relationship for pure and Al-doped TiO_2 single crystals in the pressure range 1.3×10^{-5} to 1.3×10^2 atm at elevated temperature (~ 1000 K). The Kroger-Vink slope for undoped TiO_2 at pressures greater than 1.3 atm was found to be $-1/6$, and for pressures less than 1.3 atm, $-1/5$. This is consistent with the view that at high pressures, the primary defect structure consists of anion vacancies, whereas at low pressures, titanium interstitials predominate. Yahia showed further that for Al-doping, both models can give rise to the same pressure dependence.

Blumenthal et al. (281) extended the high temperature (1273-1773 K) conductivity measurements of single crystal TiO_2 to much lower oxygen pressures (1 to 10^{-15} atm). The slopes found from their data tended towards $-1/5$ at high temperatures and broke into two regions at lower temperatures. At the low pressure side of these regions, the slope ranged from $-1/4.2$ to $-1/4.8$ as T increased. At the high P_{O_2} side, these slopes ranged from $-1/5.6$ to $-1/4.8$. Clearly,

these results are not unambiguous. Nevertheless, Blumenthal et al. interpreted this as demonstrating the existence of titanium interstitials which become both triply and quadruply ionized!

The conflicting and ambiguous results of gravimetric and conductivity measurements up to that time led Ghosh et al. (282) to examine the defect structure of rutile using a wide variety of other tools. Photoconductivity, photoluminescence excitation spectra, thermoluminescence, thermally stimulated current, electroreflectance spectra, kinetic response of photoconductivity, and optical and thermal bleaching of traps were used to identify a large number of defect energy levels. They felt that a consistent interpretation of the data, combined with a knowledge of expected crystal field splittings, pointed to the existence of Ti^{3+} interstitial ions as the primary defect. Figure 2.8 shows the various defect levels tentatively assigned by these measurements. It must be noted that the assignments of these levels are tentative, and that they did also identify levels felt to be associated with oxygen vacancies. The questions introduced in the interpretation of these measurements did not allow for an end to the controversy over the TiO_2 defect structure.

More recent work has been done on this problem using the more traditional thermogravimetric and conductivity methods. Marucco et al. (283) performed these measurements on both ceramic and single crystal TiO_2 in the temperature range 1073-1473 K and in the oxygen pressure range 10^{-22} to 1 atm. They also found two distinct regions at lower temperatures, with the break point moving to lower activities of oxygen as the temperature is decreased. In the high pressure

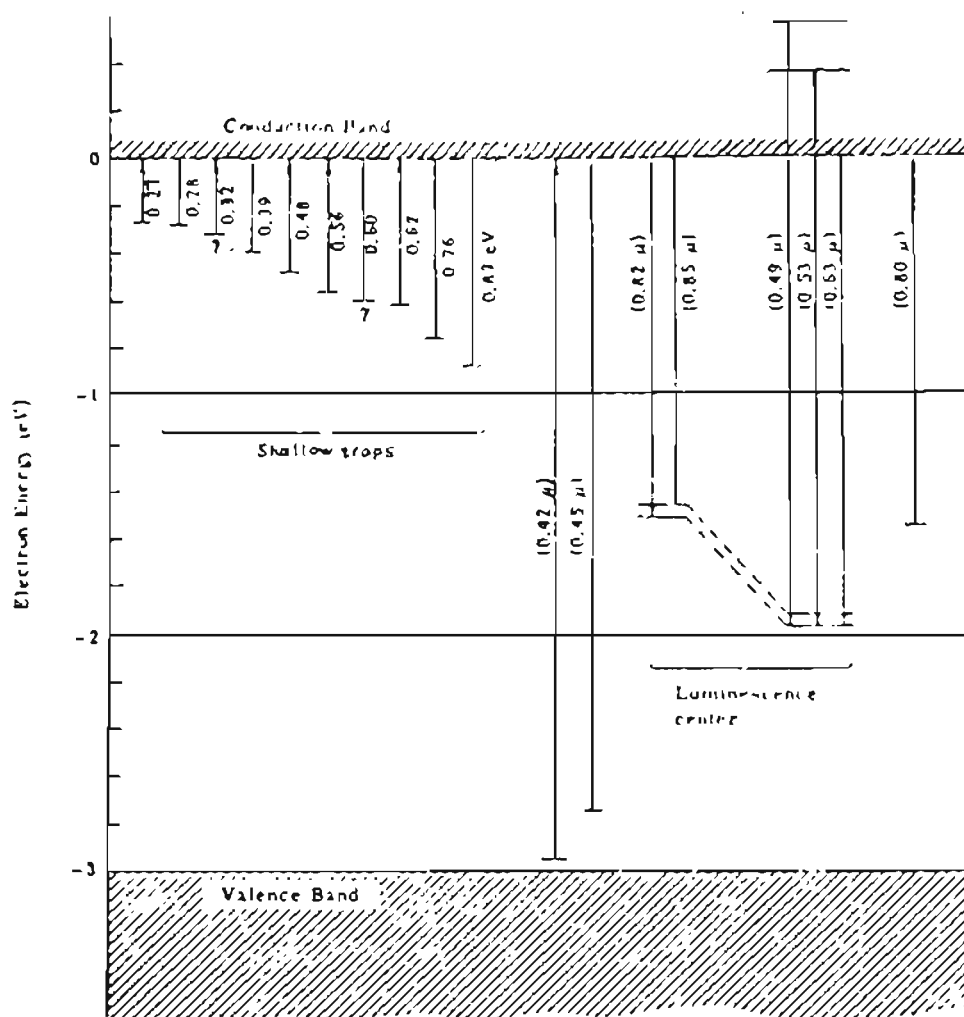


Figure 2.8. Sketch of the proposed energy-level diagram of defect states in TiO_2 . The luminescence center is tentatively identified as a Ti(III) ion. (From reference 282).

side of the Kroger-Vink curve for a given temperature, the slope was found to be $-1/4$. The slope on the low pressure side was found to change from $-1/6$ at lower temperatures to $-1/5$ at 1473 K. They concluded from this that oxygen vacancies are prominent at lower temperatures; whereas at higher temperatures, interstitial titanium predominates. They further concluded that the region of slope $-1/4$ was not simply a region wherein accidental acceptor impurities dominated (as had been sometimes previously assumed), but that this behavior was due to singly ionized oxygen vacancies. This conclusion was forced upon them by both the supporting weight loss measurements and the fact that identical results were obtained from samples of widely different background. They were further able to conclude that conduction was of the classical band type and not by a hopping process.

Balachandran and Eror (284) analyzed conductivity measurements performed on ceramic TiO_2 samples in the temperature range 1123-1323 K and the P_{O_2} range 10^{-19} -1 atm and found a slope of $-1/6$ for pressures less than 10^{-15} atm. For $P_{\text{O}_2} > 10^{-15}$ atm, the slope was found to be $-1/4$. They also observed p-type conduction for $P_{\text{O}_2} > 0.01$ atm at the lower temperatures. They did not see any regions of slope $-1/5$. From this they concluded that doubly ionized oxygen vacancies are the primary defects at elevated temperatures in the P_{O_2} range 10^{-19} - 10^{-15} atm. They attributed the $-1/4$ th slope to accidental acceptor impurities rather than to singly ionized oxygen vacancies. They found from Arrhenius plots of σ_{min} that the bandgap was ≈ 3.07 eV.

To date, the most careful studies of the defect structure of TiO_2 at elevated temperature seem to indicate that oxygen vacancies are the primary defect under strong reducing conditions. It will be one of the goals in this study to correlate this information with the electronic characteristics at room temperature.

Several studies have also been done on the defect structure and mechanism of charge compensation in doped TiO_2 . Eror and Smyth (285) and Baumard and Tani (286) have done independent studies on Nb-doped samples. In the former study, Nb doping levels of up to 16 at. % were studied over the P_{O_2} range $1-10^{-15}$ atm, and it was found that the monoclinic phase TiNb_2O_7 exsolved under oxidizing conditions for Nb^{5+} concentrations greater than 8 at. %. The exsolved phase transformed into Nb^{4+} doped TiO_2 upon reduction. Charge compensation under oxidizing conditions therefore is accomplished by the incorporation of excess oxygen, which can comfortably fit interstitially in the open rutile lattice. Hence the defect structure transforms from lattice to electronic (controlled valency) defects in going from oxidizing to reducing conditions, just as found for La:SrTiO_3 . The results of Baumard and Tani (286) agree with those of Eror and Smyth.

Tani and Baumard (287) have also studied the effects of another donor impurity, tantalum, as well as the acceptor chromium. They found that charge compensation for Ta is identical to that for Nb, with lattice point defects for high P_{O_2} (i.e., oxygen overstoichiometry) and controlled valency for low P_{O_2} . It was found that Cr

may be incorporated as Cr^{3+} under reducing conditions, but that no conclusions could be reliably drawn as to the valence state under oxidizing conditions.

The electrical properties of $\text{Cr}:\text{TiO}_2$ have also been studied by Inoue and Iguchi (288). These measurements were performed on single crystal samples prepared by heating undoped crystals on Cr_2O_3 pellets at 1573 K in air. Resistivity and dielectric constant measurements were then done in the temperature range 201–333 K. The dielectric constant and the DC resistivity were both found to increase uniformly with doping. They found that the impurity levels due to the Cr ions were exhausted below about 150 K, and that the room temperature resistivity was roughly inversely proportional to the concentration of carriers introduced by the Cr impurities. The subsequent increase in the resistivity with doping at 273 K was thus ascribed to the formation of CS planes in the crystals.

Andersson et al. (289) studied charge compensation in Fe-doped TiO_2 . EPR spectra indicate that iron substitutes as Fe^{3+} , and it was their conclusion that charge compensation occurs by Ti^{4+} interstitials. They also found a strong absorption line associated with iron precipitates. In general, the defect structure and charge compensation mechanisms in acceptor doped TiO_2 are much less clearly understood than in the case of donor doped and undoped TiO_2 .

2.2.5 TiO_2 Photoanodes

As previously mentioned, TiO_2 was the first material shown to promote the photoelectrochemical dissociation of water without decomposing (86). In a study previous to that, Boddy (290) demonstrated that oxygen evolution on single crystal TiO_2 that had been reduced in H_2 occurred by electron tunneling from oxide ions in the crystal surface, and that this was the rate determining step.

Since that time, the photoanode characteristics of TiO_2 have drawn a lot of attention. A number of studies on semiconducting (reduced) single crystal (291-295) and polycrystalline samples have appeared. In the latter class, there have been studies of undoped photoanodes produced by oxidation of titanium foil (296-298) as well as by CVD growth over Ti substrates (299). As has been previously mentioned, it is found that the flatband potential of TiO_2 ($V_{fb} \approx -0.80 \text{ V(SCE)}$ at $\text{pH}=13$) does not allow hydrolysis until a biasing voltage of about 0.25 V is applied. When operating in the photovoltaic mode, external quantum efficiencies for current production for single crystal specimens have been reported as high as 80-85% (292). Nozik (293) reported energy conversion efficiencies in homogenous cells of between 1.0 and 4.1%, rising to around 10% in cells with a pH gradient. He also reported photocurrent densities in the neighborhood of 5 mA/cm^2 .

In studying oxidized Ti foil, Houlihan et al. (297) reported energy conversion efficiencies of at least 0.8%. They also found a slight decrease in the optical bandgap from the intrinsic value of

3.02 eV, which they attributed to the formation of mixed phases of the titanium-oxygen system (Magneli phases) in the semiconductor film. Typical photocurrent densities reported for polycrystalline TiO_2 have been around 0.1 mA/cm^2 .

Laser and Bard (300) did a study on the photovoltaic response of CVD thin film n- TiO_2 anodes operated with an oxygen cathode, and found that under short-circuit conditions, quantum efficiencies of 26% and power efficiencies of 1-2% were obtained. Open-circuit cell voltages of 0.89 V were reported. They also reported continuous operation with no apparent deterioration in performance after 6 hours.

Stability of photoanodes is an important point, and the reputed longevity of TiO_2 has been a topic of several studies (246,301-304). The general conclusion has been that TiO_2 is stable under high pH conditions, but that in certain acidic solutions significant aging can occur (301). It has also been shown that corrosion in solutions of H_2SO_4 can be suppressed with the addition of 1M cobaltous ion without interfering with water decomposition (302,304). This behavior was attributed to the formation of high energy intermediates that successfully compete with the corrosion process. These intermediates are formed by single-electron transfer reactions, and they then go on to split water independently of the electrode.

Illumination intensity effects on TiO_2 anode performance have been reported (305-306), and it was found that a saturation current independent of pH was proportional to light intensity. Desplat (305) found that single crystal TiO_2 in a two-compartment cell (pH gradient

of ≈ 12) demonstrated a quantum efficiency of about 60% and produced current densities of about 0.7 mA/cm^2 with no biasing.

The study of surface states and TiO_2 /electrolyte interface characteristics is also well advanced. Sub-bandgap photoresponse of n-TiO_2 has been identified and found to be sensitive to dissolved oxygen in the solution (307). Independent investigations have subsequently indicated that this effect is of a photothermal nature (249,308). The significance of band bending and the need for the location of surface states within the bandgap have been pointed out (309), and subsequent confirmation of the predictions made have been done. Tomkiewicz (310-312) has made a number of contributions to this. From Mott-Schottky plots, he measured V_{fb} over a wide range of pH and found the expected variation of 60 mV/pH (310). Non-linearities in these plots due to surface states were pointed out, with their corresponding number, energy, and energy distribution. He also demonstrated that chemical modification of the surface can result in a broad Gaussian distribution of surface states with a maximum near the bottom of the conduction band, which act as recombination centers for minority carriers (312).

Non-linearities found in the Mott-Schottky plots of single crystal TiO_2 were studied in greater detail by Schoonman et al. (313). They presented modified Mott-Schottky equations to account for surface roughness and nonuniform donor distributions which gave a good account for the experimental curves.

The influence of pH on the quantum efficiency of TiO_2 photoanodes has been reported and interpreted as the result of surface OH^- groups and physisorbed OH^- ions, which act as intermediates in hole trapping and charge transfer mechanisms at the interface (315). In that work, a maximum density of surface centers for charge transfer was calculated to be about 10^{14} cm^{-2} .

Siripala and Tomkiewicz (316) have undertaken the direct observation of surface states at the TiO_2 /electrolyte interface by using relaxation spectrum analysis, and found a surface state density of about $1.8 \times 10^{13} \text{ cm}^{-2}$ located at 2.2 eV above the valence band.

Lo et al. (317) have performed more standard surface analysis (LEED, ELS, AES, UPS) of TiO_2 surfaces of varied stoichiometry. They found evidence for the existence of Ti^{3+} species on clean oxygen deficient surfaces, and found that this causes distinct differences in chemisorption characteristics. In particular, it was found that water adsorbs associatively on stoichiometric surfaces, but that it tends to dissociate into surface hydroxyl groups on Ti^{3+} rich surfaces. Exposure to greater-than-bandgap light regenerates Ti^{3+} from Ti^{4+} .

The study of extrinsic TiO_2 photoanodes is also fairly advanced (318-331). These include the effects of hydrogen content (318) and reduction (320-321). It was found that V_{fb} is not greatly affected by reduction (320) and that the optical bandgap remains similarly unaffected (320-321). A small sub-bandgap photoresponse was seen centered at 2.2 eV (321), and was ascribed to Magneli phases formed

at the interface as discussed above. Mixed oxides of the form $\text{TiO}_2\text{-M}_x\text{O}_y$ for $M = \text{Al, Sr, Ga, Eu}$ and B have also been studied (319), with no modification in the bandgap being seen.

A great deal of interest has been stimulated by a reported extension of the spectral response by some 3d transition metal dopants, particularly Cr ; consequently a number of such studies have been done (322,325,327-331). Co was reported to extend the spectral response to about 550 nm (2.25 eV), attributed to the formation of a d-band by the interaction of interstitial Ti or Co ion (327). The intrinsic drop in the photoresponse at about 420 nm is still seen, with the extended response about a factor of 10 less than the intrinsic response. Natural mineral TiO_2 high in iron exhibited behavior similar to synthetic Fe -doped samples; neither showed any significant decrease in the optical bandgap (328).

Campet et al. (329) demonstrated an extension of the spectral response to 550 nm by Cr doping; however, photosensitization was found to be impressive only for large biasing. Matsumoto et al. (330) found this extension not only for Cr but also for V and Cu , and concluded that this effect is due to the formation of an impurity band near the π^* conduction band of TiO_2 . Claverie et al. (331) found the same result for samples doped with a combination of Nb and Ni ($\text{TiO}_2\text{:2\% NbO}_2\text{:1\% NiO}$). The effect of the Nb^{4+} in this case is to stabilize Ni^{2+} in the lattice without the reduction to Ni metal, as occurs when doping with Ni^{2+} by itself is attempted.

It has also been found that quantum efficiencies and I/V characteristics of TiO_2 can be enhanced by Be-doping (323). Houlihan and Hamilton (324) have also reported improved response by doping with Al, Y, and B, with energy conversion efficiencies of 1% for Al and Y-doped polycrystalline samples and 1.1% for B doping. The doping levels used were 100 PPM for Al and Y, and 500 PPM for boron. Salvador performed a further study on Al-doped polycrystalline TiO_2 (326) and concluded that the main role of Al is in the formation and stabilization of Ti^{3+} donor centers during reduction.

CHAPTER THREE

OBJECTIVES

3.1 Strontium Titanate

The usefulness of single crystal SrTiO_3 as a photoanode material has been demonstrated and reviewed in Chapter Two. However, despite the fact that the flatband potential and stability of this material make it extremely attractive for this application, no systematic analysis of the photoelectrochemical (PEC) characteristics as a function of material modification has been done. Consequently, the primary objective of this investigation has been to obtain such an analysis for thermodynamically defined ceramic samples of the family La:SrTiO_3 , with La doping concentrations of 0, 0.1, 0.2, 0.3, 0.5, and 1.0 at. %. This study was intended to include an evaluation of the effects of reduction on sample performance.

The choice of lanthanum as the dopant species was based on its unambiguous nature. It is well known that La^{3+} enters the SrTiO_3 perovskite lattice substitutionally for Sr^{2+} (189). Furthermore, the defect structure of La-doped SrTiO_3 at high temperature is well defined (228,234-239), and displays interesting oxygen pressure-dependent characteristics (Eqn. 2.9) that add another dimension to material processing and control. The ranges of La-doping and reduction ($10^{-20} \leq P_{\text{O}_2} \leq 10^{-12}$ atm) selected for study were meant to provide a complete picture of this system.

Ceramic samples have been provided by U. Balachandran after preparation by the liquid mix technique (LMT)(233), wherein dilution of cationic dopant species in weak organic acids to 500 PPM permits chemical control to 0.001%. These materials are identical to those used in identifying the high temperature defect structure (238-239), allowing accurate comparison of the results obtained here with those found in the high temperature regime.

Fundamental to the goals of this characterization is the measurement of electrical conductivity as a function of doping concentration and reduction for low to moderate temperatures (10-500 K). Reasonable conductivities cannot be obtained in these low mobility materials without the generation of large carrier densities. This, coupled with the interpretive complications of grain boundary scattering in polycrystalline materials, makes Hall effect measurements an ineffective tool. Consequently, thermoelectric power measurements were recognized from the outset as necessary for some samples, to provide qualitative correlations between doping, reduction, and free carrier concentration, and to thus complement the conductivity data.

Electrical conductivity measurements can serve two primary objectives. The first of these is the characterization of the electronic properties of this family of materials in the temperature range of interest. The second is a determination of the defect structure at low temperatures. For this, it was anticipated that the dependence of σ on oxygen activity might be exploited in the standard way, to produce Kroger-Vink diagrams (229) for comparison

with the known high temperature behavior.

Evaluation of the photoanode performance of such quenched samples was envisaged as being carried out in a homogenous PEC under AM2 solar simulated illumination. Initially, photoanodes should be tested in solutions of varying pH, after which testing can be done under the most favorable conditions. Aging effects were to be sought, not only by continuous monitoring of photocurrents, but also by remeasurement of σ after PEC testing. Samples should also be subjected to a second reduction after PEC testing in cases where σ has been found to change appreciably, the goal being to examine the possibility of sample oxidation in the course of photoelectrolysis.

The photoconductivity of these materials was also planned for investigation, with particular emphasis placed on the determination of their spectral response. From this, the effects of doping and reduction on the optical bandgap should be determinable. In conjunction with conductivity measurements, conclusions could then be drawn regarding the processing steps to be taken to optimize the photoanode characteristics of La:SrTiO_3 , and these conclusions checked against PEC performance.

3.2 Titanium Dioxide

TiO_2 , both doped and undoped, and in both mono- and polycrystalline form, has been much more thoroughly reported on in the published literature than SrTiO_3 . Consequently, it plays a smaller role in this investigation.

Ceramic samples of $\text{Ta}_x\text{Ti}_{1-x}\text{O}_2$ for x between 0 and 0.01 were to be prepared by the LMT, and characterized electronically as a function of doping and reduction ($10^{-20} \leq P_{\text{O}_2} \leq 10^{-8}$ atm) in the temperature range 10-500 K. The variation of σ with P_{O_2} was planned for examination, in an attempt to identify the defect structure at these low temperatures, and for comparison with the various results and defect models noted in Sections 2.2.2 and 2.2.4.

Photoanodes were also to be made from these samples, and performance tested in a homogenous PEC (1M NaOH) under AM2 solar simulated illumination. Photoconductivity measurements would then analyze the spectral response of these samples, with the particular goal of determining the effects of Ta-doping and reduction on the optical bandgap.

Single crystal samples cut from a nominally undoped boule purchased from the Nakazumi Crystal Corporation would then be reduced, quenched, and subjected to the same measurements indicated above, for comparison between the ceramic and single crystal form.

Additionally, acceptor doped (Fe, Al, Cr) samples prepared also by LMT should be used for photoconductivity measurements, to look for changes in the spectral response due to addition of these 3d transition metal impurities.

CHAPTER FOUR

EXPERIMENTAL PROCEDURES

4.1 Sample Preparation

The samples used in this investigation were prepared by U. Balachandran of the Materials Science department, Oregon Graduate Center, using a liquid mix technique (LMT) (233,332). In this technique, the dopant cations are complexed in weak organic acids with dilution to 1 PPM. The individual solutions are then gravimetrically analyzed for dopant concentrations to a precision of better than 10 PPM, allowing for precise control of all the cation concentrations in the final product. The resultant oxides thus exhibit as high a purity as the starting materials, yielding thermodynamically defined ceramics with chemical control to 0.001%.

The powders thus produced were pressed under a load of 40,000 PSI into discs of about 1 cm diameter and about 0.1 cm thickness, and sintered in air at 1625 K for 12 hours. The densities of the SrTiO_3 samples were found to be $\approx 4.85 \text{ gm/cm}^3$, and of the TiO_2 samples, $\approx 4.05 \text{ gm/cm}^3$. These densities correspond to about 95% of the X-ray densities for single crystals. Sintered discs were then equilibrated at a chosen P_{O_2} (from a flowing CO_2/CO or H_2/CO_2 gas mixture) for a period of from 8 to 18 hours at 1323 K, and quenched in the ambient gas. These processing steps were also performed by U. Balachandran (332).

Visual surface analysis was done using a JEOL JSM-35 scanning electron microscope to determine grain sizes. To prevent surface charging of these semiconductors, samples intended for SEM analysis were coated with a Au-Pd film using a Technics Hummer II sputtering system. Initially, examination was done on as-received samples. To insure that the grain sizes thus recorded were not merely the powder dimensions, samples were then pretreated by etching and polishing and reexamined.

Polishing was done on a Raytech-Shaw Faceter in three stages. The first stage involved polishing with CarbiMet 180 grit grinding paper and water, and served the purpose of grinding through the surface layers to get at the bulk material. In the next stage, CarbiMet 600 grit paper was used with water to even off the new surface. The final polish used a Texmet polishing cloth (Buehler Ltd, No. 40-7602) with water and Al-Ox 0.3 μm paste (Lapstar), followed by a microcloth polishing cloth (Buehler Ltd, No 40-7212) and 0.3 μm Dia-Ox polishing paste (Lapstar). Visual inspection under a Bausch and Lomb optical microscope (7X to 60X) revealed a smooth surface with an apparent porosity similar to that of the starting material. Etching was done in hot ($\sim 150^\circ\text{C}$) concentrated H_2SO_4 for 10-50 minutes.

4.2 Low Temperature Electrical Conductivity Measurements

Ceramic discs were cut into square or rectangular shapes with edge lengths of about 5 mm, using either an airbrasive (S.S. White Industrial airbrasive unit model F) unit, a high speed diamond saw with micrometer control, or a low speed diamond saw (South Bay Tech-

nology Model 650), also with micrometer control. In all cases, the samples were mounted to cutting blocks with black apiezon wax. After cutting, samples were cleaned by rinsing in trichloroethylene in an ultrasonic bath, followed sequentially by a distilled water rinse, an ethanol rinse, and another distilled water rinse.

In considering methods of performing conductivity measurements on semiconducting materials, it was felt that the nonuniform shapes and dimensions likely to be encountered in these ceramics indicated that the standard four point van der Pauw technique was the most suitable (333-338). In this method, four contacts are made to the circumference of the sample of interest; the only restrictions on the shape of the sample are that it be flat and that it be singly connected (i.e., it should not have isolated holes).

In the case of square or rectangular samples, contact is most conveniently made to each of the four corners. Theoretical analysis (333-334) of the field and current lines thus produced leads to the following relationship between the conductivity and measurable quantities:

$$\sigma = \frac{2 \ln 2 (V_A + V_B)}{\pi t f_{AB} I} \quad (4.1)$$

The parameter t is the sample thickness in cm, I is the current in amperes, and f_{AB} is a dimensionless geometrical correction factor related to the ratio of the voltages, V_A and V_B . These voltages are measured by passing a known current through two adjacent contacts and

measuring V_A across the opposite two contacts, then rotating the sense of current flow by 90° and measuring V_B in the same manner.

Figure 4.1 illustrates the electronic contact arrangement used for the low temperature (10-300 K) conductivity measurements. A switch box was used to direct current from a Keithley 225 constant current supply through contacts 7 and 1 for the measurement of V_A , and through contacts 3 and 1 for the measurement of V_B . Voltage measurements were made using a Keithley 172A, 177, 191, or 616 digital multimeter of input impedance $> 10^{10} \Omega$, with V_A recorded across contacts 5 and 3, and V_B across contacts 5 and 7. For an isotropic, square sample, $V_A/V_B = 1$, and $f_{AB} = 1$. The factor f_{AB} corrects for deviations from squareness and for material anisotropies. In all cases, voltage measurements were performed for both directions of current flow through the contacts in order to average out non-zero instrumentation base levels (as were frequently encountered at low temperatures). Hence four data recordings were made for each conductivity value presented.

The problem of producing ohmic contacts of low resistance to semiconductors is nontrivial (339-340), and a number of techniques have been proposed that are of particular relevance to ceramic oxides (341-346). Landis (343) found that indium amalgam could be rubbed on to BaTiO_3 , producing ohmic contacts with a resistance of $R_c \approx 24 \Omega$. Ultrasonic soldering of In yielded approximately the same results. Carnes and Goodman (344) found that the low work function materials such as In ($\Delta\phi \approx 0.5\text{V}$) and Mg ($\Delta\phi \approx 0.48\text{V}$) formed low resistance con-

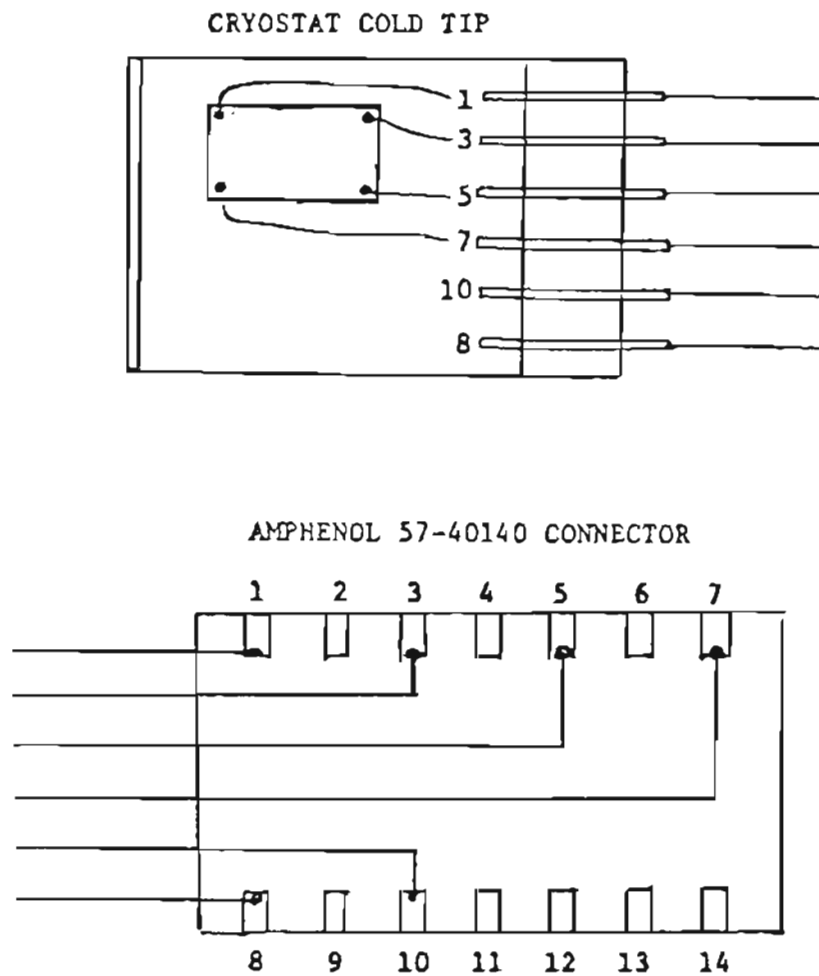


Figure 4.1. Wiring arrangement for Air Products Displex and cryotips for electrical conductivity measurements.

tacts to single crystal SrTiO_3 (4) refers to the effective work function of the metal with respect to the SrTiO_3 conduction band). Subsequently, Fleming and O'Bryan (345) found that ultrasonic soldering of In:Ga alloys produced the lowest apparent resistivities in BaTiO_3 ceramics, and that rubbed-on In:Ga yielded contacts that appeared to be ohmic over a 10^4 range of applied field strength, with similarly low apparent R_c values. They did find a slight increase in the measured resistance of the BaTiO_3 sample with rubbed-on In:Ga contacts after allowing these to sit one day, indicating the possibility of contact aging. Fleming and O'Bryan also found that the In and In-alloy contacted samples demonstrated negligible contact resistances ($\rho_c < 0.1 \Omega\text{-cm}^2$).

Consequently, it was felt that the most appropriate method of applying low resistance, ohmic contacts to these ceramic oxide semiconductors would be by rubbing or low temperature soldering of an $\text{In}_{0.995}\text{Ga}_{0.005}$ alloy.

Samples with contacts thus applied were then mounted to alumina ceramic sample holders, using a small drop of GE 7031 varnish under one corner of each sample. Fine tinned copper wire leads were then attached to the In:Ga contact pads by means of DuPont conducting Ag paste. The contacts were tested for ohmic behavior by measuring the apparent conductivity of each sample over four to five orders of magnitude of field strength, using the van der Pauw technique discussed above. Contacts were also tested for aging by remeasuring the conductance of a given sample periodically over a period of up to two years.

Low temperature (10-300 K) conductivity measurements were carried out in an Air Products Displex He-gas refrigerator. The sample environment was evacuated to a pressure of ≈ 1 mTorr (1.3×10^{-6} atm) with a liquid nitrogen cold-trapped Sargent-Welch roughing pump followed by an absorption pump. The system pressure was monitored with a Granville-Phillips series 275 Pirani vacuum gauge. The temperature of the sample was monitored with an Air Products Digital Temperature Indicator/Controller, which uses a Au(0.7% Ni) vs. Chromel thermocouple for temperature detection, and a Minco 46.6 Ω thermofoil strip heater. The thermocouple junction was soldered with In to the displex sample mounting base, directly behind the sample holder. This system provides temperature control to 0.05 K. Equilibrium was assured at each reading by allowing the voltage response of the sample to stabilize before recording data.

4.3 Moderate Temperature Electrical Conductivity Measurements

Measurement of σ in the temperature range 300-500 K was also carried out by the van der Pauw technique, with the same provisions for current reversal and voltage measurements, and using the Keithley instrumentation described above. The samples were provided with In:Ga contacts to each corner just as before, and electrical contact was then accomplished by phosphor-bronze pressure clips. The sample holder was machined from Macor machinable ceramic, and measurements were carried out in a Lindberg tube furnace. Pt wires were attached to the phosphor-bronze clips and provided with ceramic feed-through insulation. The temperature was monitored with a Chromel-Alumel

thermocouple, glued to the sample holder opposite the sample mounting area. Digital temperature readout was provided by an Omega Model 199 Digital Temperature Indicator. These measurements were carried out in an atmosphere of flowing N_2 gas to reduce the possibility of oxidation.

4.4 Thermoelectric Power Measurements

Thermoelectric power (Seebeck coefficient) measurements were made in the 150–300 K temperature range. Samples were prepared for this purpose by cutting into rectangular rod shapes of dimensions typically about $1 \times 1 \times 7 \text{ mm}^3$, and cleaning in the fashion already discussed. One end of such a sample maintained thermal contact (via GE 7031 varnish) with the cold tip of an Air Products N_2 Cryotip (Joule-Thomson) refrigerator. The temperature of the other end was controlled by thermal contact to a 100Ω resistor; this permitted establishment of a temperature differential of from 1 to 20 K across the sample. The cold end temperature was controlled by varying the nitrogen pressure in the Cryotip, and the hot end temperature was controlled by varying the voltage across the resistor with a DC power supply. Thermal contact between the heater resistor and the sample was accomplished by gluing (with GE 7031 varnish) to each end of a copper wire. Figure 4.2 demonstrates the experimental arrangement.

Of great concern in performing thermopower measurements is that temperature and voltage measurements recorded be well correlated. Consequently, two different sample mounting arrangements were used, in conjunction with two different methods of measuring ΔV . For the

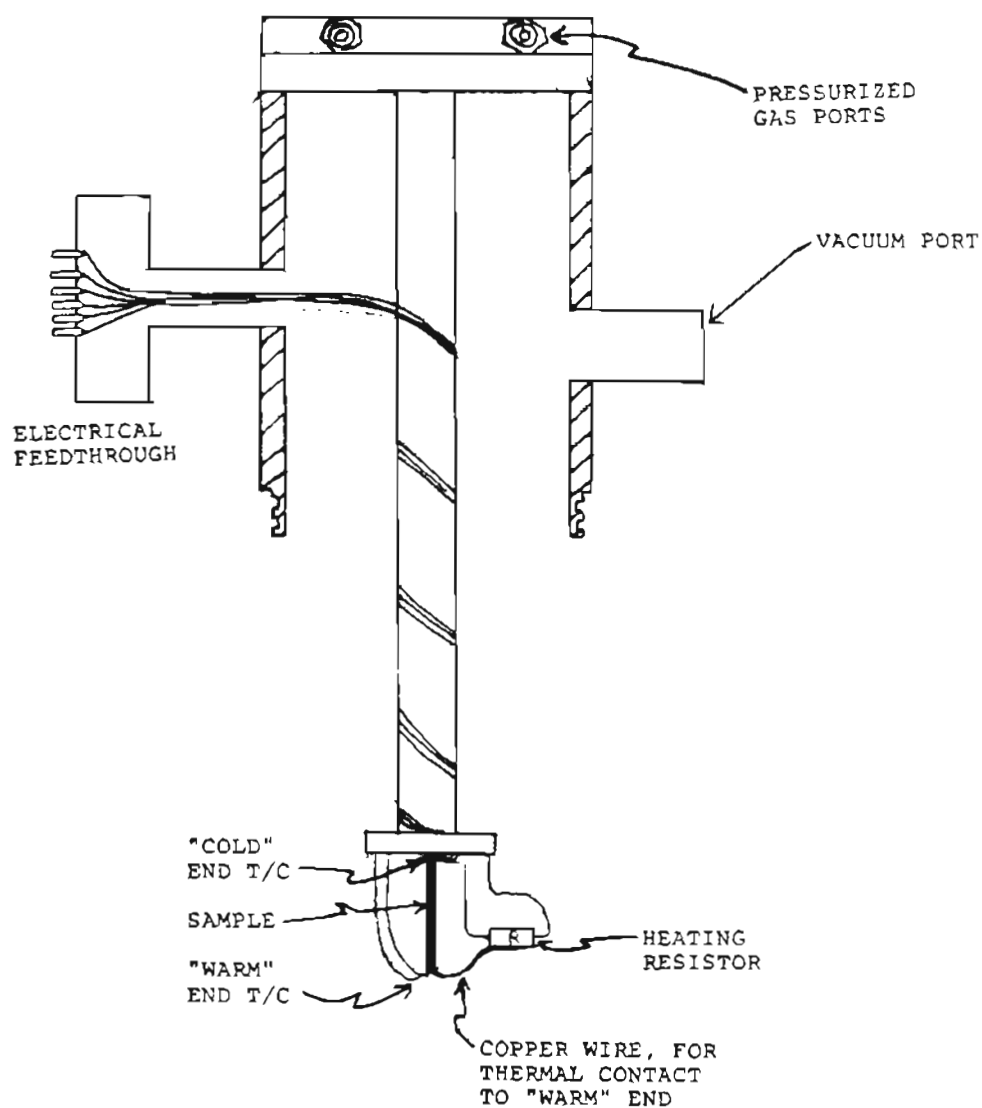


Figure 4.2. Use of a 'cryotip' Joule-Thomson cooler for measurements of the Seebeck effect (thermoelectric power) of a bulk semiconductor sample in the temperature range 100-300 K.

measurement of thermovoltages, it is always preferable to use the same metal thermocouple wires from the opposite ends of the sample. The problem encountered in this is that it is generally much easier to establish thermal contact than it is to establish good, ohmic electrical contact. Hence whenever it was found possible to establish electrical contact with one side of the thermocouple wires to the In-rubbed ends of the sample, these wires were used as the voltage probes. In such a situation, no ambiguity arose as to whether or not the measured ΔV corresponded to the measured ΔT . When electrical contact could not be established in this way, tinned copper wires were In-soldered onto In:Ga pads at each end of the sample, adjacent to the thermocouple probes. In this arrangement, great care was taken to insure a direct correspondence between the two measurements, and samples were frequently remounted when deviations were seen.

Temperatures were recorded using Cu:Constantan thermocouples, and when these doubled as voltage probes, the Cu wires were used. As mentioned, two methods were employed in sample mounting, and the differences dealt with the manner in which the thermocouples contacted the sample. In one, the thermocouple junctions were either glued with GE 7031 varnish to each end face of the sample, or were bent so as to provide mechanical spring-force attachment to the end faces. Bending was used when it was found that good electrical contact between the Cu thermocouple wire and the sample could be obtained. The second method employed drilling holes near each end of the sample using the airbrasive unit, lining the holes with In:Ga alloy, and

putting the thermocouple junctions into the holes. Figure 4.3 is a photograph of a sample mounted in this fashion. In this method, the Cu thermocouple wire was always used to measure ΔV . The results obtained from these two different methods of thermocouple attachment were indistinguishable.

The actual measurement process was accomplished by attaching the voltage outputs from the two thermocouple cold junction compensators (Omega CJ), along with the ΔV output, to the input of a Digitec 10-point scanner. The scanner output was sent to a Keithley 177 micro-volt DMM, from which all measurements were recorded. Stability of ΔT and ΔV was checked before recording each data set. It was found that the temperatures T_h and T_c ($\Delta T = T_h - T_c$) could be held fairly constant for several minutes, allowing the measurement of ΔV with reasonable confidence. The sample chamber was maintained at a pressure of 1 mTorr (1.3×10^{-6} atm) with an oil diffusion pump and liquid N_2 -trapped Sargent-Welch roughing pump.

4.5 Photoconductivity Measurements

Photoconductivity measurements were planned as a means of determining the spectral response of the materials under study. Initially, direct photoconductivity measurements were attempted in the temperature range 10-300 K by mounting samples in the Air Products He-refrigerator for phase-sensitive detection of changes in the voltage response of the sample as a function of illumination. Sample preparation and mounting procedures were identical to those described in Section 4.2. Figure 4.4 depicts the experimental arrangement involved. A Keithley

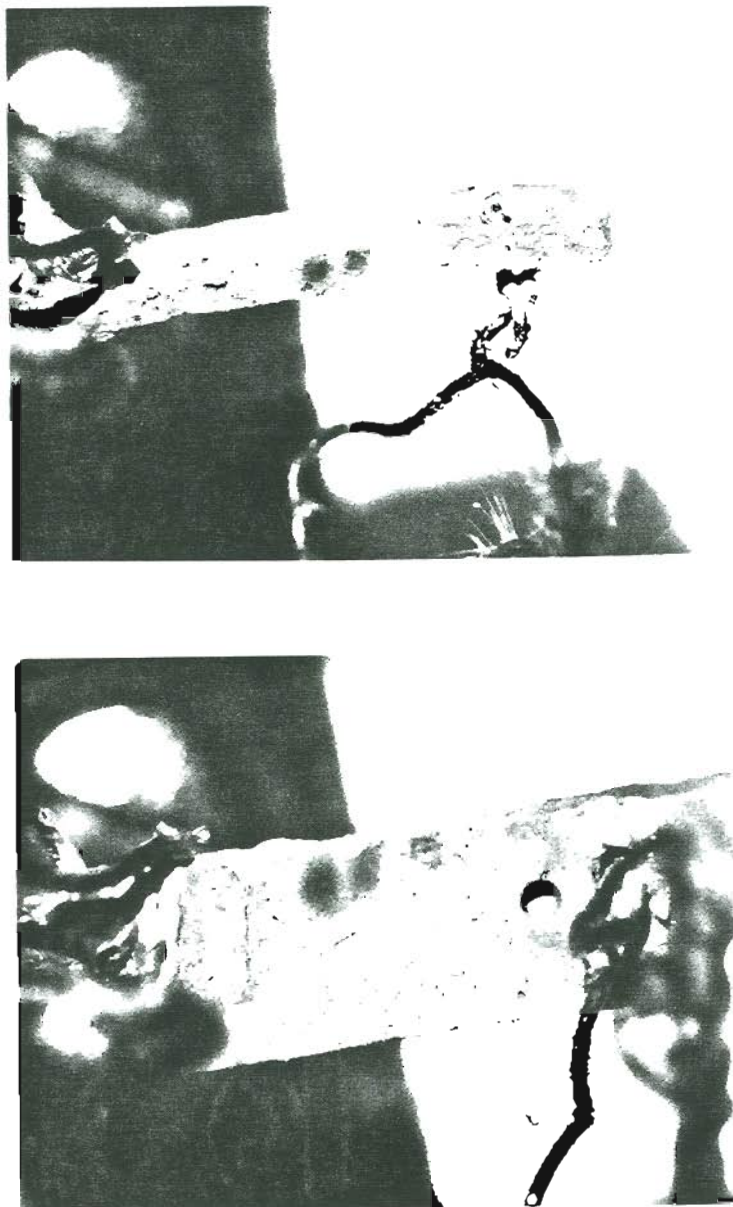


Figure 4.3. Photograph of thermoelectric power mounting procedure for ceramic samples with airblown holes near each end, side and top views.

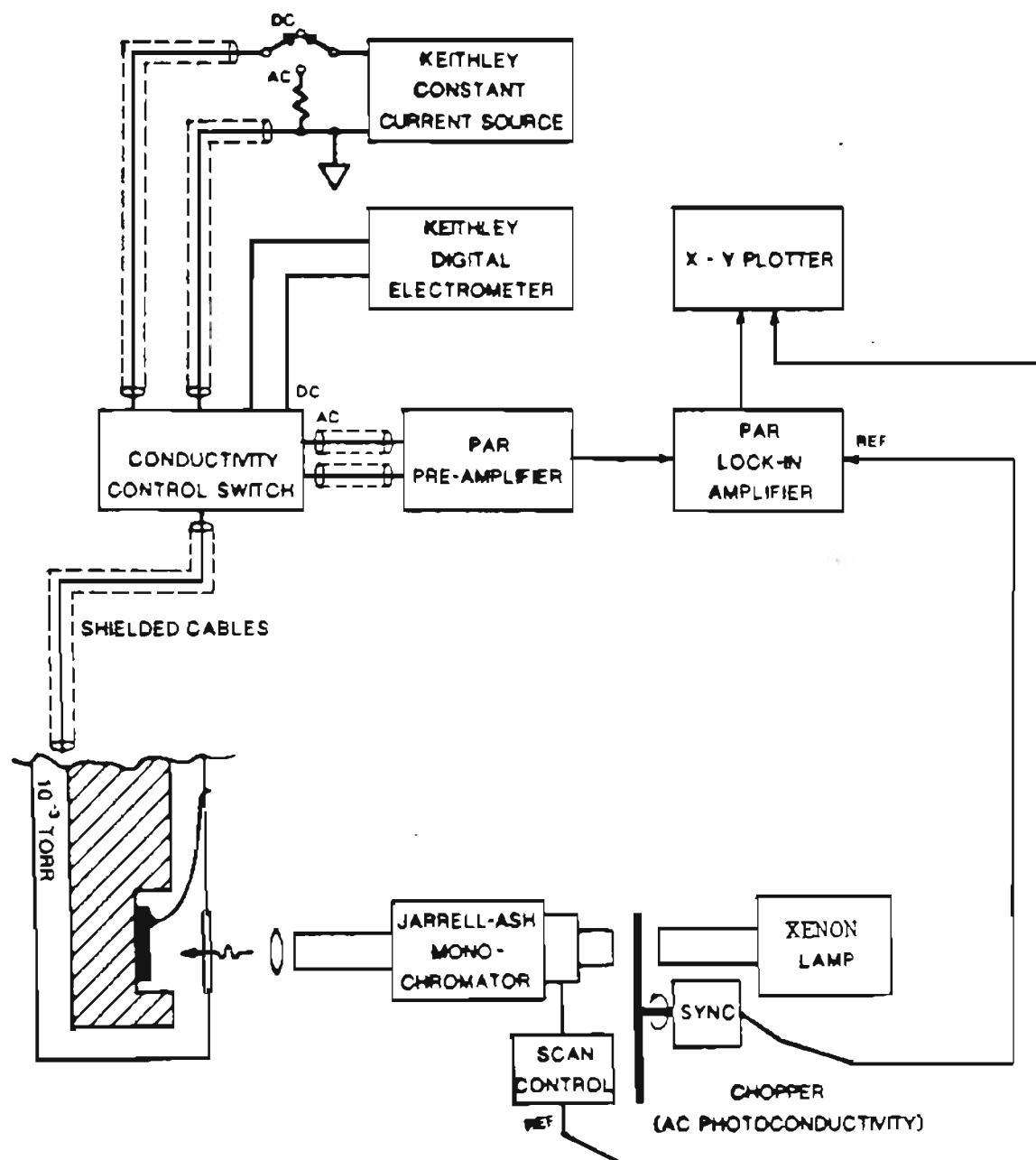


Figure 4.4. Experimental arrangement for direct measurement of photoconductivity in the temperature range 10-300 K.

constant current source was used to provide currents on the order of $1\ \mu\text{A}$ to the sample, and voltages were monitored by a Keithley 616 digital electrometer. A 75 Watt Oriel Xenon arc lamp with an attached focusing lens was used for illumination. The light was chopped with a 270 Hz chopper wheel, and the chopping frequency was fed into the reference signal input of a PAR 5101 Lock-In amplifier. The chopped light was focused onto the entry slit of a Jarrell-Ash Mark X variable slit monochromator, equipped with a direct drive motor with spectral scan speed control. The output of the monochromator was focused by means of a CaF_2 lens through a quartz window mounted on the dispex vacuum shroud, onto the sample face. Focusing was adjusted to provide a spot size covering 80-90% of each sample tested.

The sample voltage was fed into a PAR 113 pre-amplifier with bandpass filtering set between 100 and 500 Hz. The pre-amplifier output was sent into the signal input of the Lock-In amplifier, and the phase relationship between the reference and signal inputs was adjusted to maximize the signal. The output of the Lock-In was then used to drive the ordinate scale of a Hewlett-Packard 7035B X-Y recorder, and spectral response curves were derived from the X-Y recorder traces, using the signal from the monochromator spectral drive to control the abscissa scale.

Unfortunately, for reasons to be discussed in Section 5.6, it was very difficult to pick out the photoresponse of these samples from the background noise at temperatures above 30 K. Since the spectral response at room temperature is the primary quantity of

interest in PEC work, an alternative means of measurement had to be devised. This was accomplished by utilizing the unique PEC characteristics of these materials.

The method ultimately used to characterize the room temperature spectral response of these materials employed phase sensitive detection of AC photocurrents, produced in a homogenous PEC by focusing chopped light onto photoanodes made from the material under study. Much of the hardware employed in the technique discussed above was retained, as can be seen in the schematic shown in Figure 4.5. A homogenous PEC of high pH (4M NaOH) was constructed using a Pt helical coil cathode. Photoanodes were made using L-shaped glass tubes, but otherwise as described in the next section, and a 100 Ω precision resistor was connected in series between the two electrodes.

Illumination from a 75 Watt Xenon lamp was chopped by a Rofin variable speed chopper and focused through a monochromator onto the sample, just as described above. The PEC vessel was a Vycor (Corning 7913, 97% quartz) 1 liter beaker with an external transmittance of better than 90% in the spectral range of interest (250-600 nm) (347). The photocurrent output at the chopping frequency (50-800 Hz) was detected with the PAR 113/5101 preamplifier/Lock-In detector combination; coaxial cable was used for contacts to both PEC electrodes to obviate extraneous pickup. It was found that the spectral response curves were unaffected by changes in the chopping frequency.

For some samples, spectral response curves were obtained with the PEC operating under external bias. In those cases, the voltage source

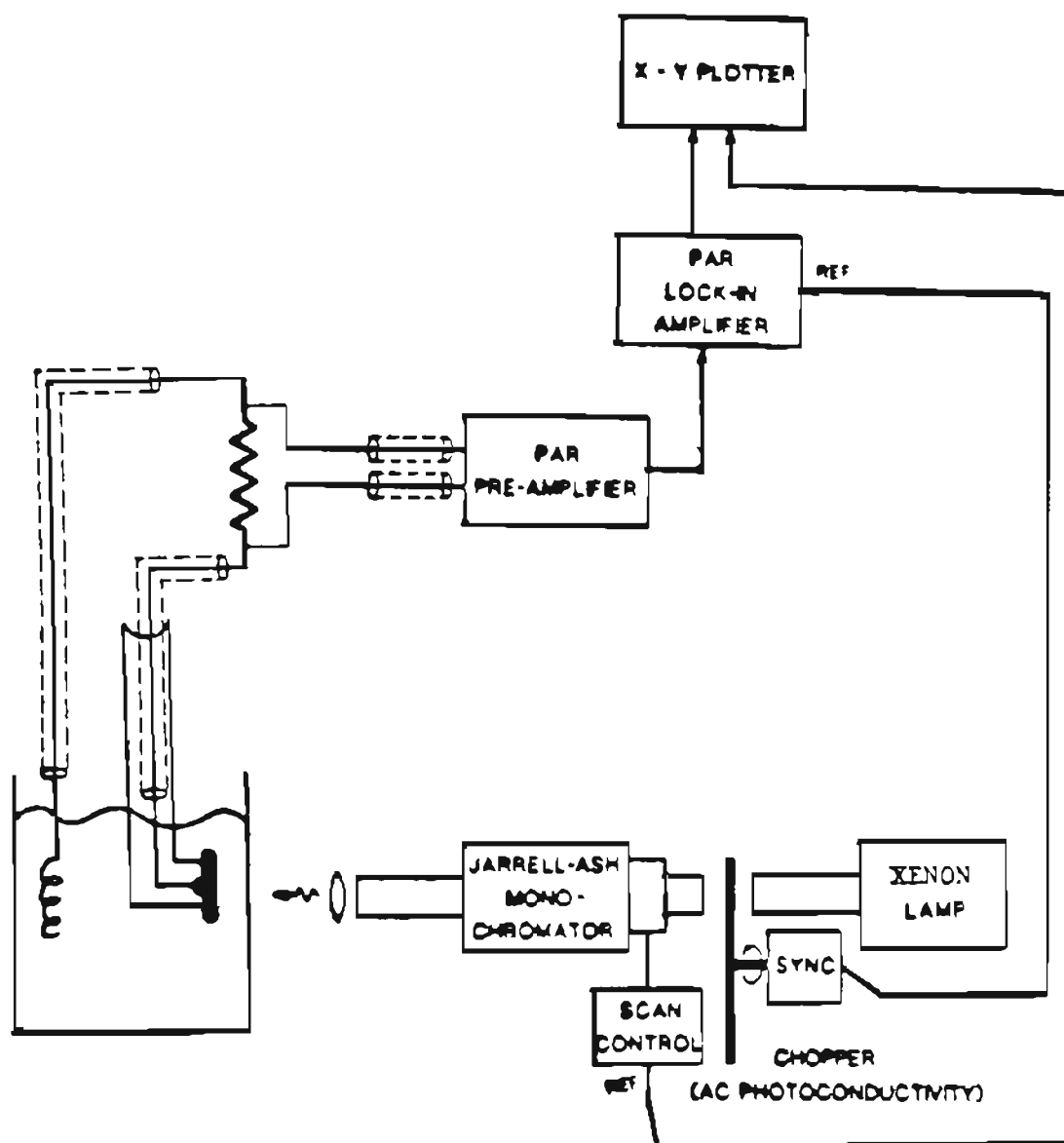


Figure 4.5. Experimental arrangement for measurement of photo-response of material using a homogenous PEC.

was a Kepco power supply connected in series between the photoanode and the precision resistor, with the positive side towards the semiconductor. The actual spectral response curves were drawn on an X-Y plotter as discussed above.

4.6 PEC Measurements

Photoanodes were prepared from ceramic discs of diameter about 1 cm and thickness about 0.1 cm, reduced (at 1323 K), and from a monocrystal TiO_2 sample of surface area $\approx 0.9 \text{ cm}^2$ and thickness $\approx 0.2 \text{ cm}$, reduced in $P_{\text{O}_2} = 10^{-20} \text{ atm}$ at 1323 K. Ohmic contact was provided by rubbing the back surface of each prospective photoanode with $\text{In}_{0.995}\text{Ga}_{0.005}$ alloy. Indium solder was then used to attach a tinned copper wire to this back surface, which was then coated with DuPont conducting silver paste. In the course of this investigation, it has been found that contacts so prepared are ohmic, of low resistance, and exhibit no detectable aging effects at room temperature for periods of up to two years (Section 5.3).

The photoanodes were then sealed with epoxy resin (Armstrong Industrial Epoxy, kit A-2/W) to the lower open end of a U-shaped glass tube, so that only the untreated front face was exposed to the electrolyte; the rear contact wire being protected inside the U-tube.

For the cathode of the PEC, a Pt wire helix (of surface area $\approx 0.3 \text{ cm}^2$) or Pt foil (of area $\approx 6 \text{ cm}^2$) was used. Samples were tested in electrolytes ranging in pH from 2 to 14; with acid solutions made from reagent grade HCl and deionized water, and basic solutions from reagent grade NaOH and deionized water. Electrolyte pH was measured

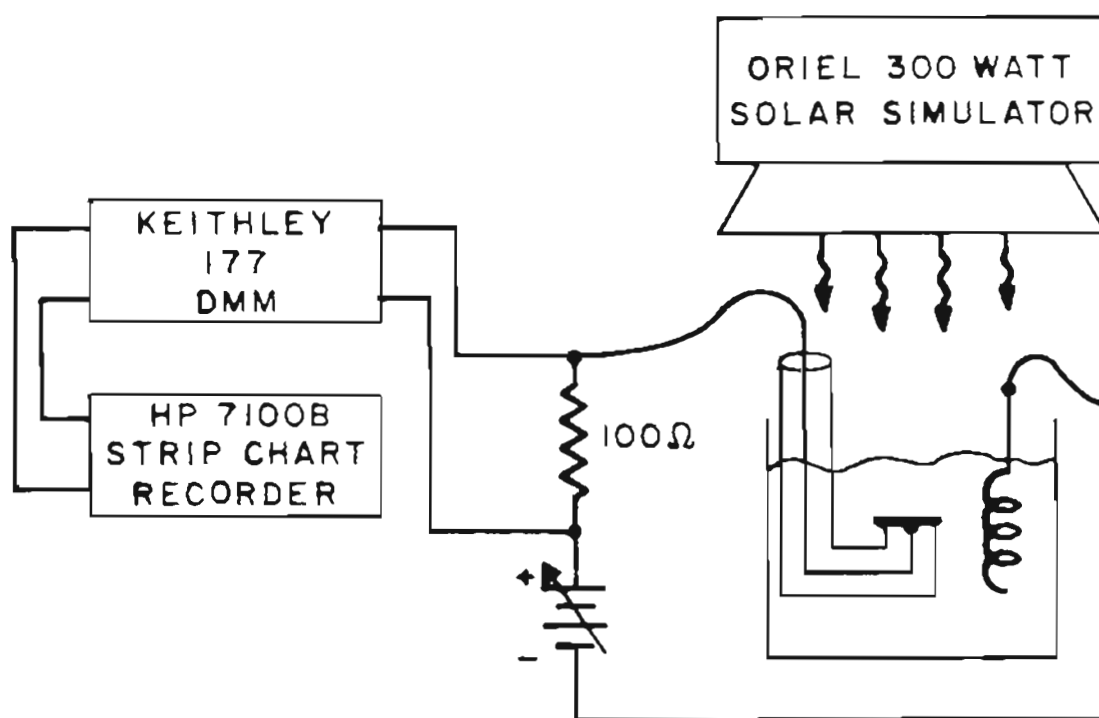


Figure 4.6. Photoelectrochemical cell arrangement used in measuring photoanode performance.

with a VWR digital pH meter.

Figure 4.6 demonstrates the PEC experimental arrangement. Irradiation for PEC cell operation was provided by an Oriel 300 Watt solar simulator filtered to AM2. The photocurrent was monitored from the voltage across a $100\ \Omega$ precision resistor, and continuously plotted with a Hewlett-Packard 7100B strip chart recorder. This voltage was simultaneously monitored with a Keithley 177 microvolt DMM. External bias, when applied, came from a Hewlett-Packard 6248A DC power supply.

CHAPTER FIVE

EXPERIMENTAL RESULTS AND DISCUSSION

5.1 SEM Analysis of Ceramic SrTiO_3 and TiO_2

SEM analysis was undertaken on ceramic samples of both SrTiO_3 and TiO_2 in order to determine the average grain size. Initial examinations were done on these materials in the condition that they were received.

Figures 5.1 and 5.2 show the typical general surface structure seen on as-received SrTiO_3 samples. These pictures were taken of an undoped sample reduced in $P_{\text{O}_2} = 10^{-6}$ atm at 1323 K. Reduction and doping did not result in any observable changes in structure under SEM analysis. Figures 5.3-5.4 present the same SrTiO_3 surface under high magnification (7800X and 11,000X, respectively). The apparent grain sizes in these pictures are in the range 0.1-0.5 μm .

These small grain sizes are consistent with the high melting point of SrTiO_3 ($T_m \approx 2400$ K). TiO_2 ($T_m \approx 2120$ K) has a melting point considerably lower than that of SrTiO_3 , and would thus be expected to produce larger grain sizes. Figures 5.5-5.7 bear out this expectation. This larger grain size produces a somewhat smoother and more uniform surface structure on TiO_2 , as can be seen by comparing Figures 5.1 and 5.5, and noting that the magnification of Fig. 5.5 (1000X) is only half that used in producing Fig. 5.1.

These SEM pictures of TiO_2 -based materials were taken of a sample doped with 4 at.% tantalum and reduced in $P_{\text{O}_2} = 10^{-16}$ atm.

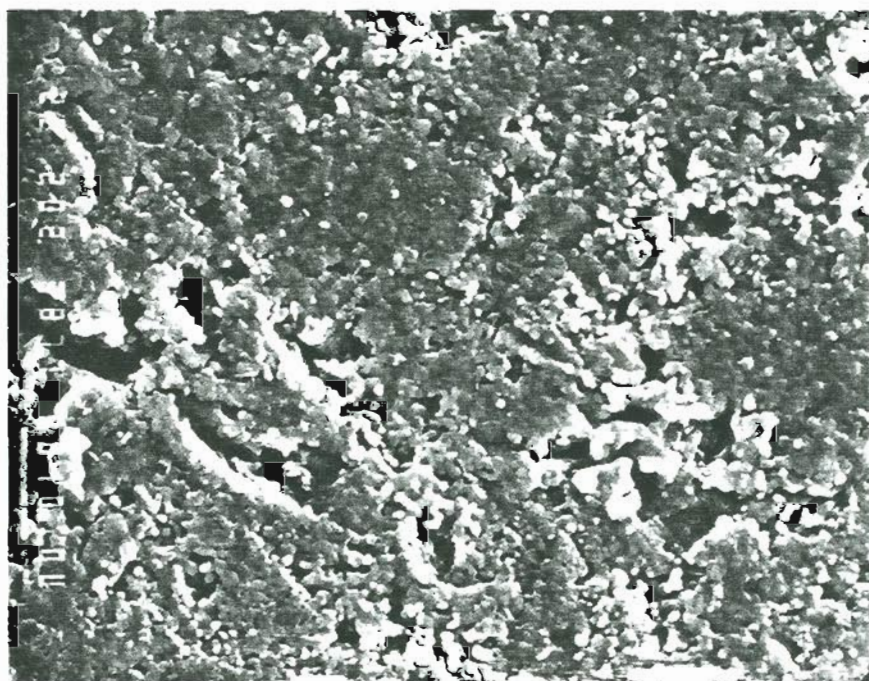


Figure 5.1. SEM picture of untreated SrTiO_3 surface (sample reduced in $P(\text{O}_2) = 10^{-6}$ atm; magnification = 2000X).



Figure 5.2. SEM picture of untreated SrTiO_3 surface (sample reduced in $\text{P}(\text{O}_2) = 10^{-19}$ atm; magnification = 3600X).

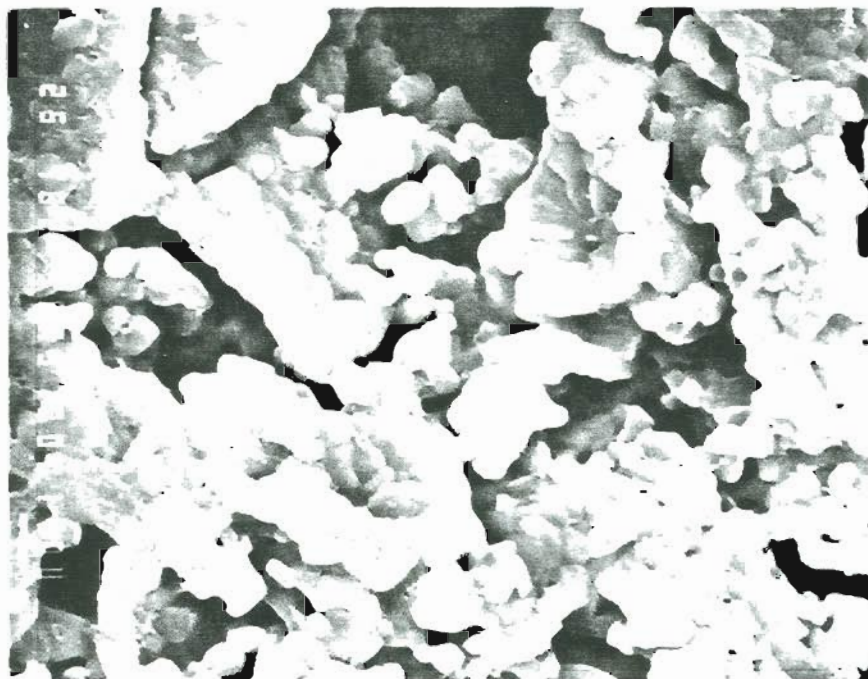


Figure 5.3. SEM picture of untreated SrTiO₃ surface shown in Fig. 5.1.1, with magnification = 7800X.

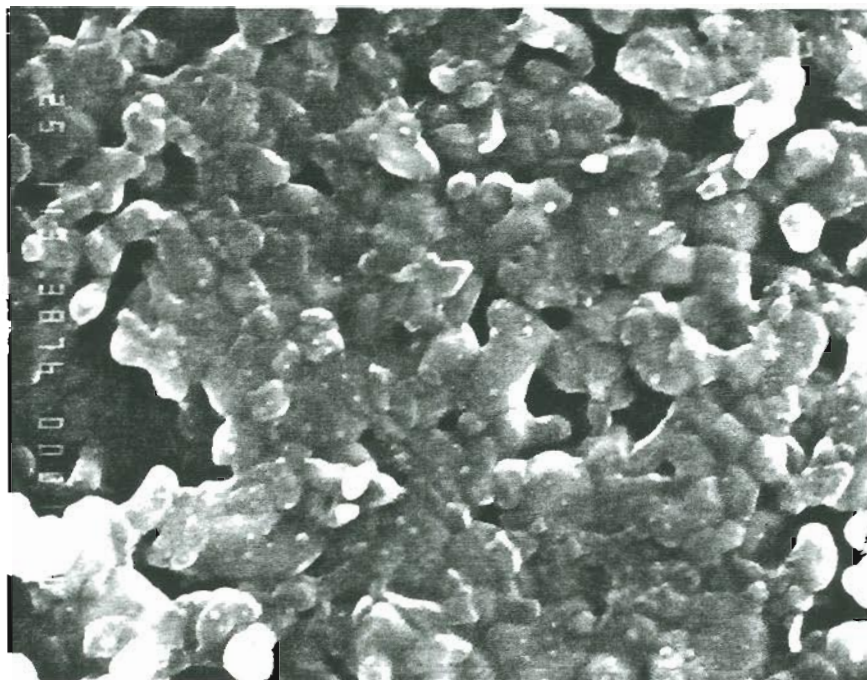


Figure 5.4. SEM picture of untreated SrTiO₃ surface shown in Fig. 5.1.1 and 5.1.3, with magnification = 11,000X.

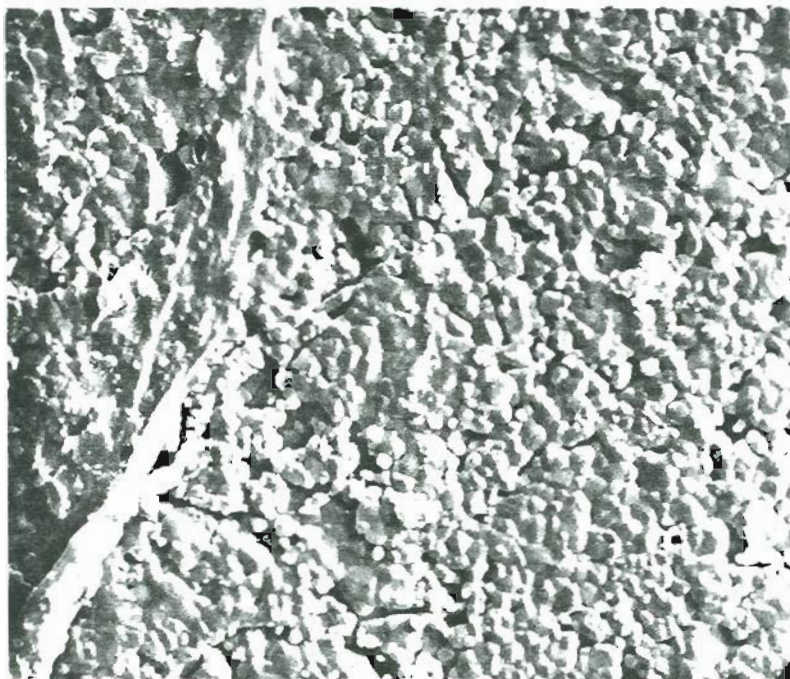


Figure 5.5. SEM picture of untreated Ta(4%)TiO₂, reduced in $P(O_2) = 10^{-16}$ atm. Magnification = 1,000X.

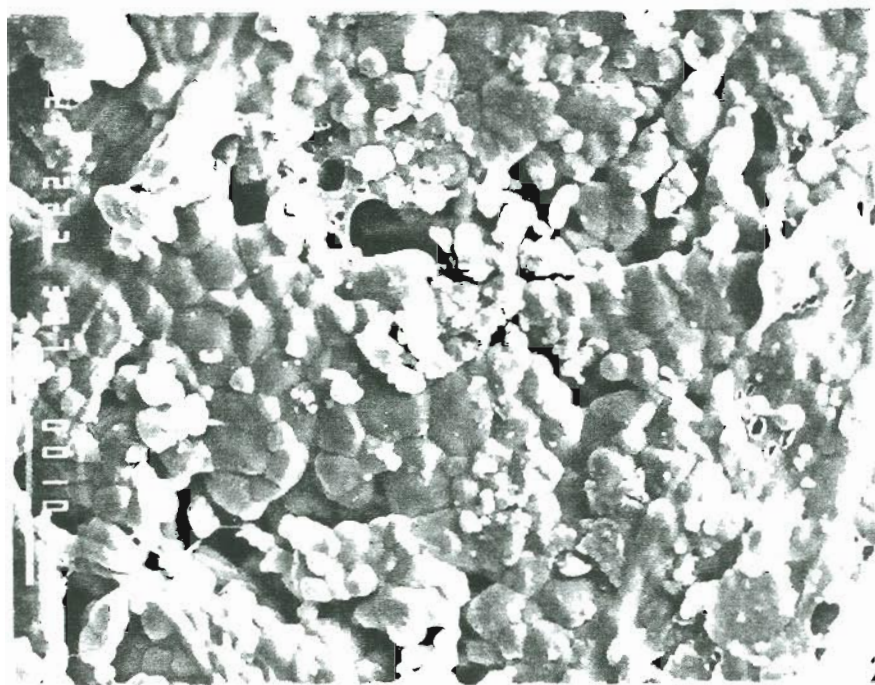


Figure 5.6. SEM picture of untreated Ta(4%)TiO₂ sample shown in Fig. 5.1.5, with magnification = 2,200X.

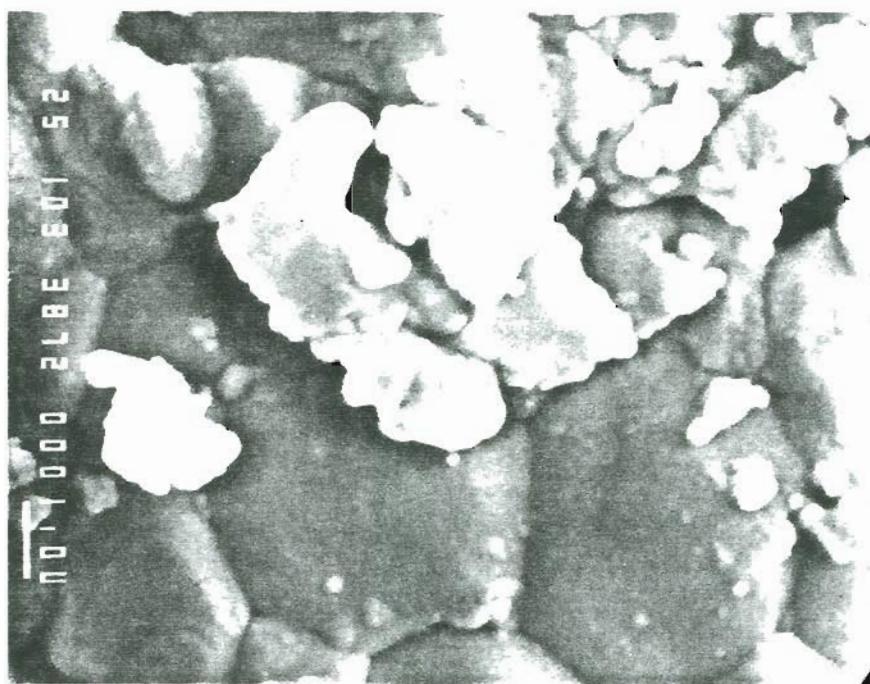


Figure 5.7. SEM picture of untreated Ta(4%)TiO₂ surface shown in Fig. 5.1.5 and 5.1.6, magnification = 10,000X.

Again, doping and reduction produced no observable changes in grain structure.

The large grain size found in the TiO_2 samples is dramatically demonstrated in Figure 5.7, taken with a magnification of $10^4\times$. Figure 5.6, along with Figure 5.7, establishes this size to be in the range 1-4 μm , or about one order of magnitude greater than that found in SrTiO_3 . This is in keeping with the differences in T_m .

To insure that these apparent grain sizes weren't merely the typical powder dimensions, samples were examined under SEM after polishing and etching. Figure 5.8 shows the typical general surface structure thus seen, in this case for a TiO_2 sample doped with 0.1 at.% Ta and reduced in $P_{\text{O}_2} = 10^{-8}\text{atm}$ at 1323 K. It was found in all cases that the pretreatment tended to blur the structural boundaries rather than enhance them; nevertheless, careful examination of these materials under greater magnification supported the findings discussed above. The picture in Figure 5.9 was taken of the same sample displayed in Fig. 5.8, but with a magnification of 2000X: grain sizes can be seen to be in the range 1-3 μm .

5.2 TiO_2 Single Crystal Orientation

A 1 mm thick slice was cut from the TiO_2 single crystal boule, using the high speed diamond saw, for X-ray Laue back-reflection crystal orientation. TiO_2 is a positive, uniaxial crystal (348); visual inspection down the axis of the boule revealed a small degree of birefringence. Consequently, direct c-axis orientation can be eliminated.

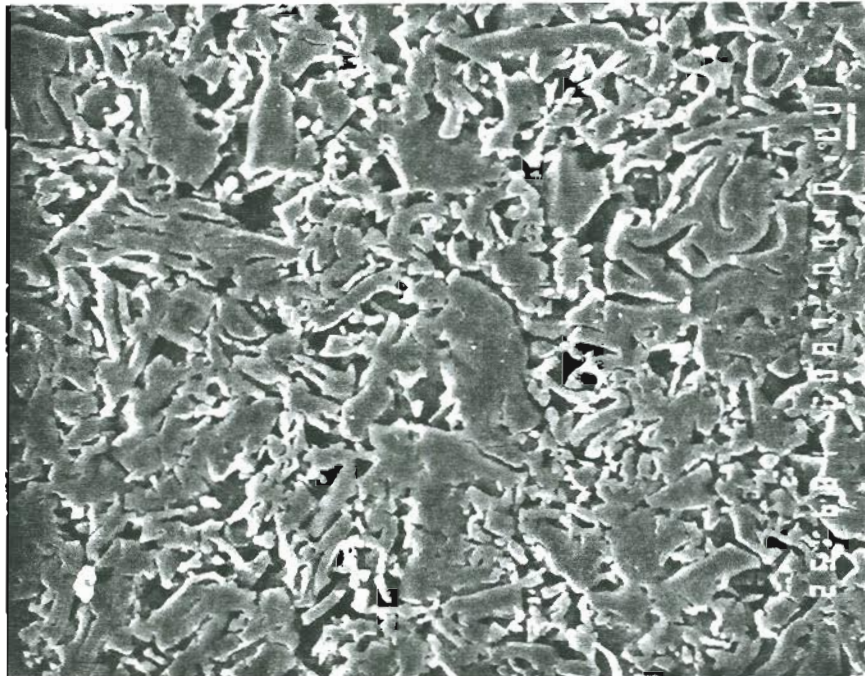


Figure 5.8. SEM picture of polished and etched (60 min, in hot concentrated H_2SO_4) $\text{Ta}(0.1\%)\text{TiO}_2$, reduced in $\text{P}(\text{O}_2) = 10^{-8}$ atm. Magnification = 600X.

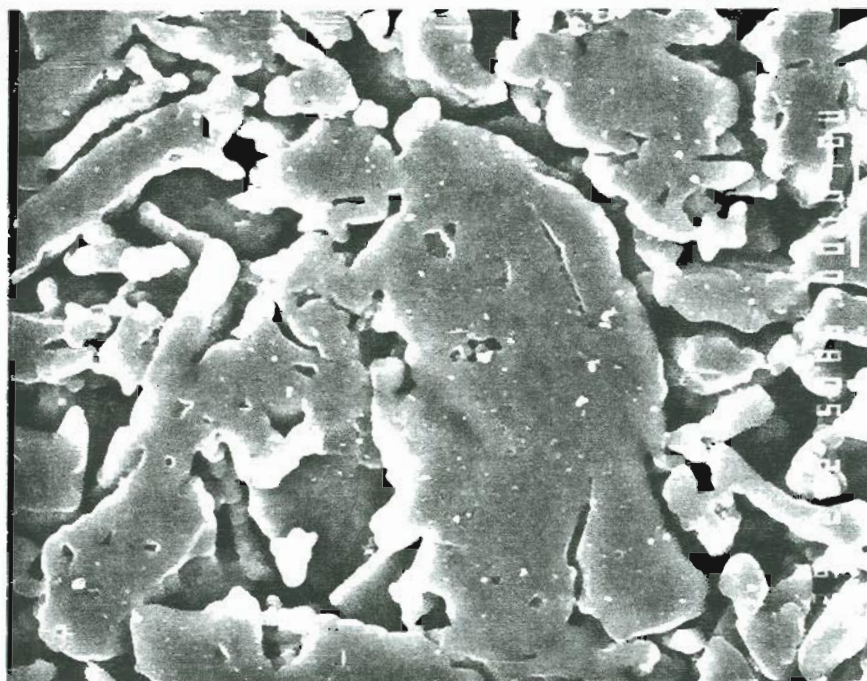


Figure 5.9. SEM picture of Ta(0.1%)TiO₂ sample shown in Fig. 5.1.8. Magnification - 2,000X.

The TiO_2 slice was mounted using black apiezon wax onto the Laue camera sample holder, and manually aligned on a flat table by visually sighting along a flat surface. The sample holder was then mounted on the Laue camera rail such that the sample face was situated 5 cm from the film plane. A 50 kV, 14 mA electron beam was used to generate the X-rays from a molybdenum target. It was immediately apparent that incoherent (Compton) backscattering from the sample was fogging the resultant picture to the extent that analysis could not be done. To overcome this, the picture was overexposed and underdeveloped to bring out the less intense regions of the photograph. This resulted in an adequate picture.

Further improvements were obtained by polishing the slice by hand and replacing the Mo target tube in the X-ray unit with a Cu target tube, which provides a better white spectrum for Laue work. In addition, a beam collimator was used to minimize Compton scattering problems.

Analysis of the resulting photographs with the aid of a Greninger-Bond 5 cm net (349) showed two points of high symmetry (4-fold) separated by an angle of about 30° . The lowest order indice point was found to be about 9° off the beam axis. Hence the orientation of this crystal appears to be about 9° off the c-axis.

5.3 Stability and Behavior of Electrical Contacts

Indium-based contacts have been reported as ohmic and of low resistance when applied to oxide semiconductors (343-346), but problems of contact aging have been identified (345). It was thus a

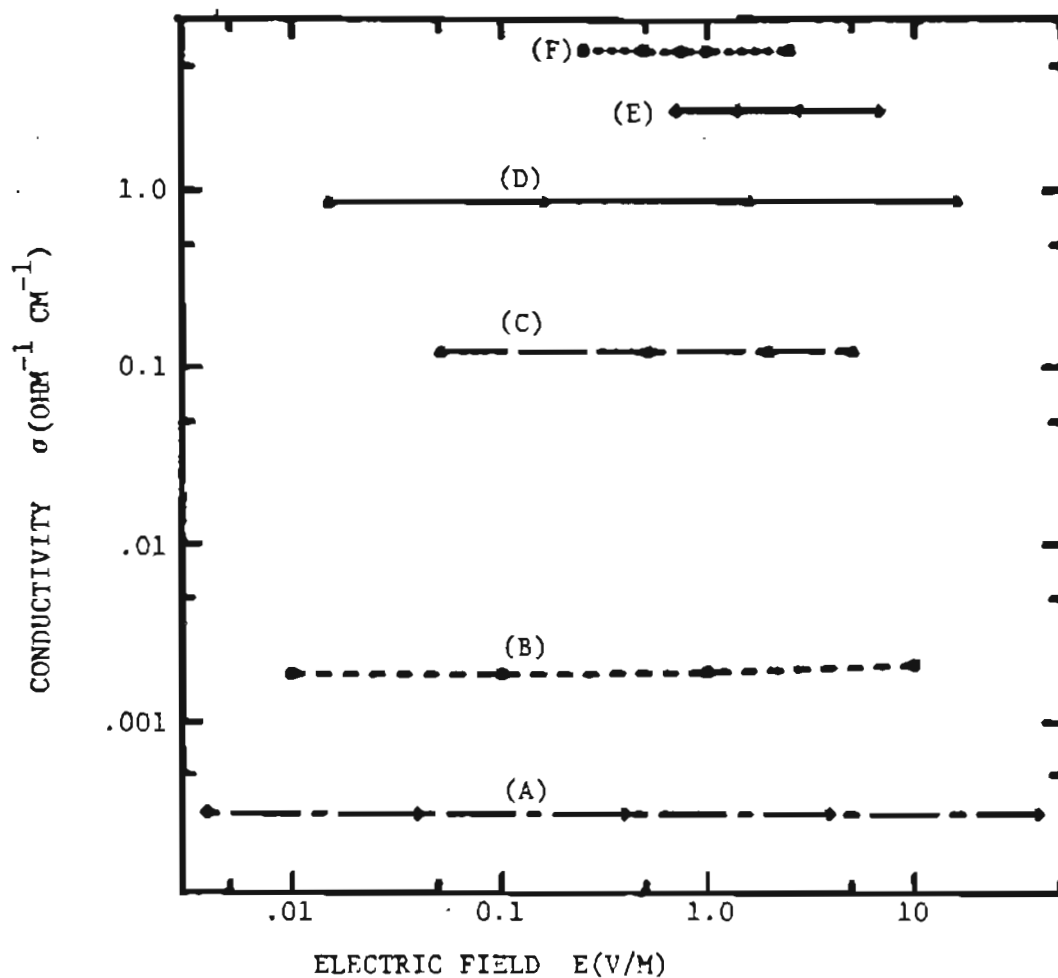
matter of immediate concern to check for ohmic behavior in the contacts applied as described in Section 4.2 (pp. 121-124), as well as to estimate the contact resistivity, ρ_c , and to check for signs of aging problems.

Figures 5.10 and 5.11 show the measured conductivity versus field strength for a number of SrTiO_3 and TiO_2 samples, plus one sample of reduced Nb_2O_5 . As can be seen, ohmic behavior was obtained in all cases over a 3 to 5 order of magnitude change in applied field. All of the samples studied in this investigation were similarly tested after the application of contacts, and all of these contacts were found to be ohmic in the field range of interest. In addition, check for ohmic behavior was done at the high and low temperature ends of the experimental range, with similarly positive results.

A limiting value can be assigned to the contact resistivity, ρ_c , by evaluating the apparent resistivity and contact size of some of the more conducting samples. For SrTiO_3 -based samples, σ_{max} was found for fully reduced samples of $[\text{La}] = 0.2 \text{ at.}\%$, where for the case of reduction in $P_{\text{O}_2} = 10^{-20} \text{ atm}$ (at 1323 K), it was found that $\sigma(300 \text{ K}) \approx 8.5 \Omega^{-1} \text{ cm}^{-1}$. Contact size was typically about 0.5 mm^2 .

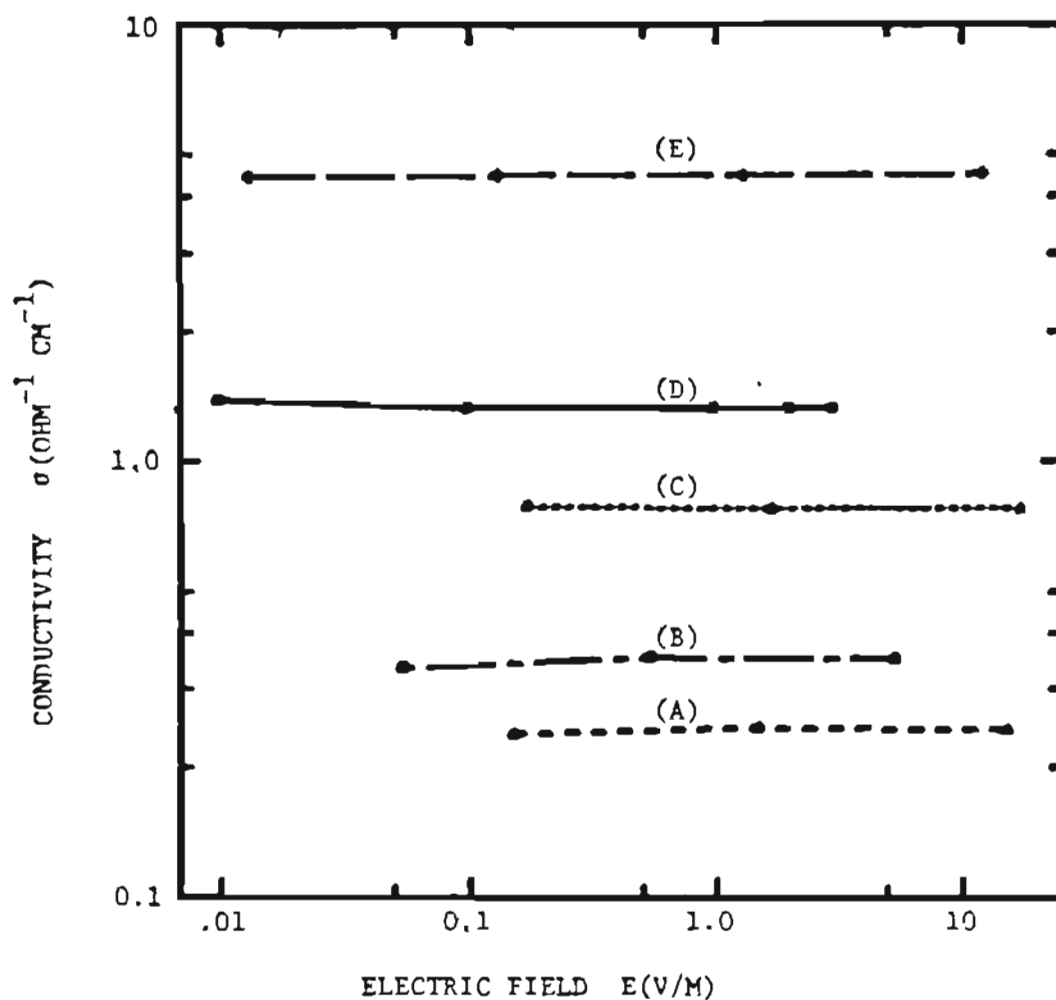
The voltage drop recorded between the two contact points in the measurements of σ can be viewed as the result of three series resistances:

$$\Delta V = \Delta V_{c1} + \Delta V_{\text{bulk}} + \Delta V_{c2} \quad (5.1)$$



A: $\text{La}(0.5\%)\text{SrTiO}_3$, $P(\text{O}_2)=10^{-8}$ atm D: $\text{La}(0.3\%)\text{SrTiO}_3$, $P(\text{O}_2)=10^{-17}$ atm
 B: SrTiO_3 , $P(\text{O}_2)=10^{-16}$ atm E: $\text{La}(0.2\%)\text{SrTiO}_3$, $P(\text{O}_2)=10^{-18}$ atm
 C: $\text{La}(0.5\%)\text{SrTiO}_3$, $P(\text{O}_2)=10^{-18}$ atm F: $\text{La}(0.2\%)\text{SrTiO}_3$, $P(\text{O}_2)=10^{-19}$ atm

Figure 5.10. Electrical conductivity versus applied field for ceramic samples of La-doped and undoped SrTiO_3 of various reduction states. Electrical contacts were made using an In:Ga alloy.



A: TiO_2 , monocrystal, $P(\text{O}_2)=10^{-12}$ atm D: $\text{Ta}(0.1\%)\text{TiO}_2$, $P(\text{O}_2)=10^{-16}$ atm
 B: $\text{Ta}(0.1\%)\text{TiO}_2$, $P(\text{O}_2)=10^{-12}$ atm E: Nb_2O_5 , $P(\text{O}_2)=10^{-18}$ atm
 C: $\text{Ta}(0.2\%)\text{TiO}_2$, $P(\text{O}_2)=10^{-12}$ atm

Figure 5.11. Electrical conductivity versus applied field for various samples of monocrystal and ceramic TiO_2 , undoped and Ta-doped, and reduced; also included is the curve for one sample of reduced, ceramic Nb_2O_5 . Electrical contacts were all made using an In:Ga alloy.

where Δv_{C1} , Δv_{C2} are the voltage drops at the two contacts. If the assumption is made that the bulk resistance is negligible for the high conductivity materials, an upper limit to ρ_c can be established. For the sample just quoted, this works out to:

$$\rho_c(\text{SrTiO}_3) < 10^{-4} \Omega\text{-cm}^2 \quad (5.2)$$

or:

$$R_c(\text{SrTiO}_3) < 0.01 \Omega \quad (5.3)$$

A similar calculation for the set of TiO_2 -based samples yields:

$$\rho_c(\text{TiO}_2) < 10^{-5} \Omega\text{-cm}^2 \quad (5.4)$$

or:

$$R_c(\text{TiO}_2) < 0.002 \Omega \quad (5.5)$$

Aging effects on In:Ga contacts were examined by periodically remeasuring the conductivity of several samples. Table 5.1 presents the results found for In:Ga alloy contacts on TiO_2 -based ceramics. The changes in the measured room temperature conductivity after over 250 days of exposure to air are clearly negligible; the fluctuations of $< 2\%$ are well within the range of experimental precision.

TABLE 5.1. The effects of extended atmospheric exposure on room temperature conductivity measurements of TiO_2 -based ceramics, contacted with In:Ga alloy.

Sample	Reduction State P_{O_2} (atm)	σ_{t_0} $(\Omega\text{-cm})^{-1}$	$\sigma_{\Delta t}$ $(\Omega\text{-cm})^{-1}$	Δt (days)	$\frac{\sigma_{t_0} - \sigma_{\Delta t}}{\sigma_{t_0}}$
Ta(1.0%) TiO_2	10^{-8}	0.704	0.693	259	+0.016
Ta(1.0%) TiO_2	10^{-12}	2.81	2.83	289	-0.007
Ta(0.19%) TiO_2	10^{-12}	0.783	0.781	285	+0.003
Ta(0.1%) TiO_2	10^{-12}	0.351	0.355	281	-0.011

TABLE 5.2. The effects of extended atmospheric exposure on room temperature conductivity measurements of $\text{La}(0.3\%)\text{SrTiO}_3$ (reduced in $P(\text{O}_2) = 10^{-20}$ atm), contacted with In:Ga alloy.

σ_{t_0} $(\Omega\text{-cm})^{-1}$	$\sigma_{\Delta t}$ $(\Omega\text{-cm})^{-1}$	Δt (days)	$\frac{\sigma_{t_0} - \sigma_{\Delta t}}{\sigma_{t_0}}$
3.31	3.314	1	-0.001
3.31	3.318	2	-0.002
3.31	3.296	6	+0.004
3.31	3.34	112	-0.009
3.31	3.31	415	0.0

A similar controlled aging test was done on a ceramic SrTiO_3 sample doped with 0.3 at.% La and reduced in $P_{\text{O}_2} = 10^{-20}$ atm. The results are presented in Table 5.2. Again the fluctuations in σ with exposure to room atmosphere are utterly trivial, and it can safely be concluded that electrical contacts applied to these materials with the method outlined in Section 4.2 are stable.

5.4 Electrical Conductivity in Reduced SrTiO_3

The high temperature (1123–1323 K) electronic characteristics of ceramic undoped SrTiO_3 were examined by U. Balachandran (228). His results are presented in Figures 5.12–5.13, where it can be seen that at high temperature, σ increases uniformly with reduction and with temperature. The slopes found in the high temperature Kroger-Vink diagram (Fig. 5.13) coupled with weight loss measurements, support the view that reduction results in oxygen vacancy creation, with a concomitant rise in free carrier concentration. As mentioned previously (pp. 73–74), these vacancies can be readily quenched-in, and carrier freeze-out is known to occur at low temperatures for lightly reduced samples. On the other hand, strong reduction tends to defer carrier freeze-out to liquid helium temperatures, which is suggestive of impurity banding.

The conductivity measurements performed in this study on quenched samples of nominally undoped SrTiO_3 of various reduction states display all of these characteristics. Figure 5.14 shows the behavior of σ in the temperature range 10–300 K. Previous investigators (192–193) have shown that oxygen vacancy energy levels

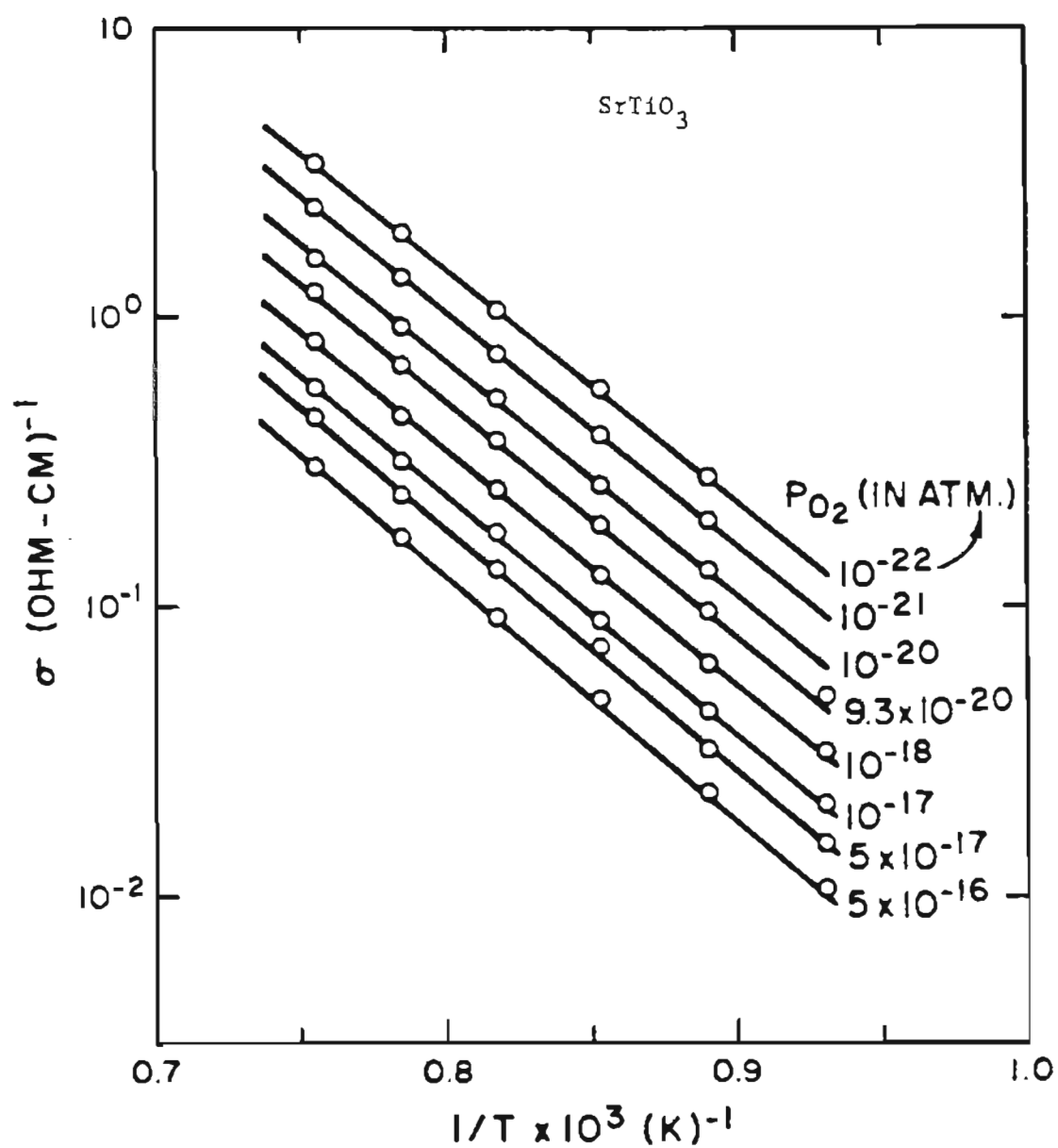
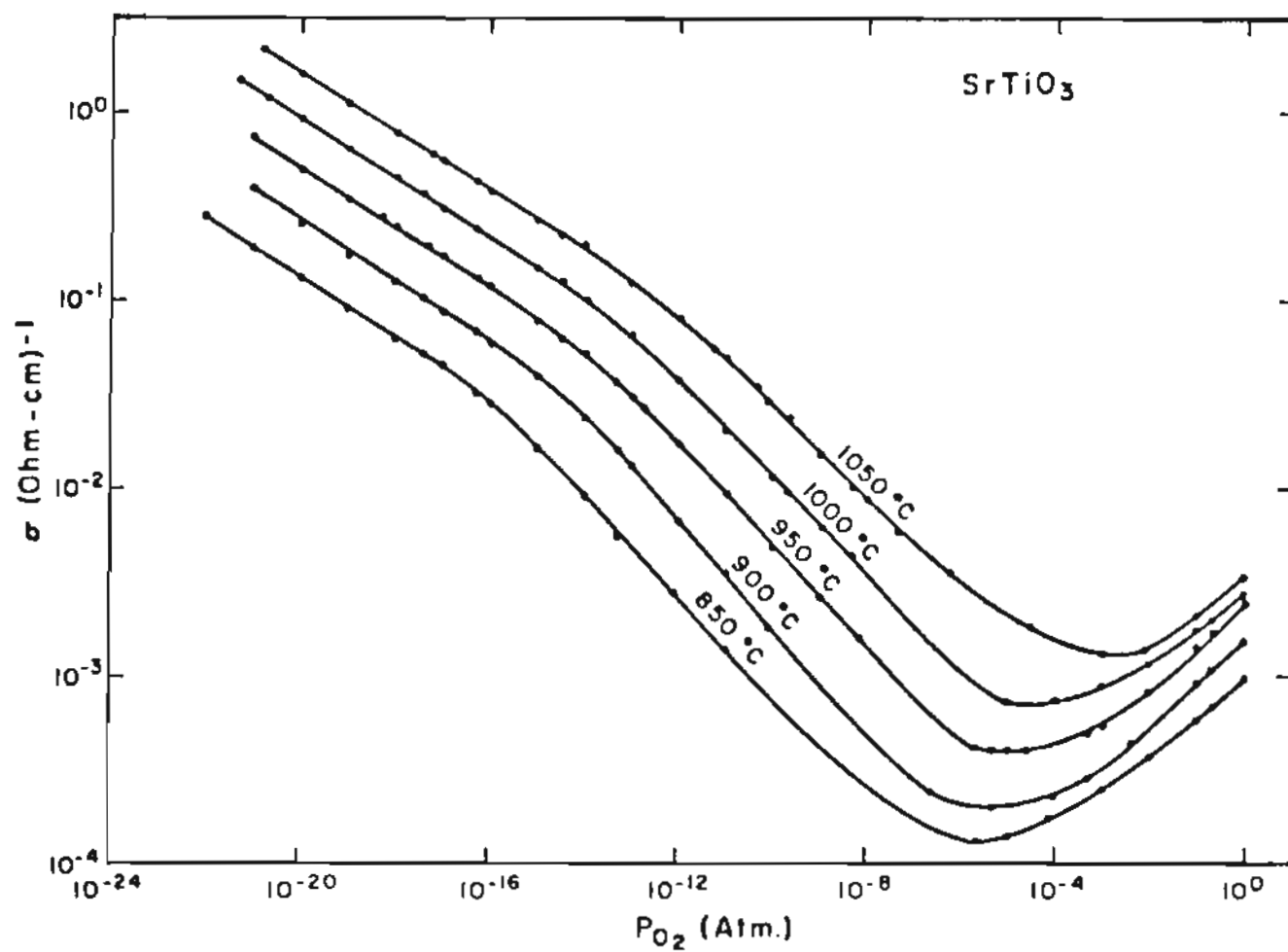


Figure 5.12. Temperature dependence of conductivity of polycrystalline SrTiO_3 in the n-type, oxygen-deficient region. (From reference 228).

Figure 5.13. The electrical conductivity of polycrystalline SrTiO_3 . High temperature region. (From reference 228).



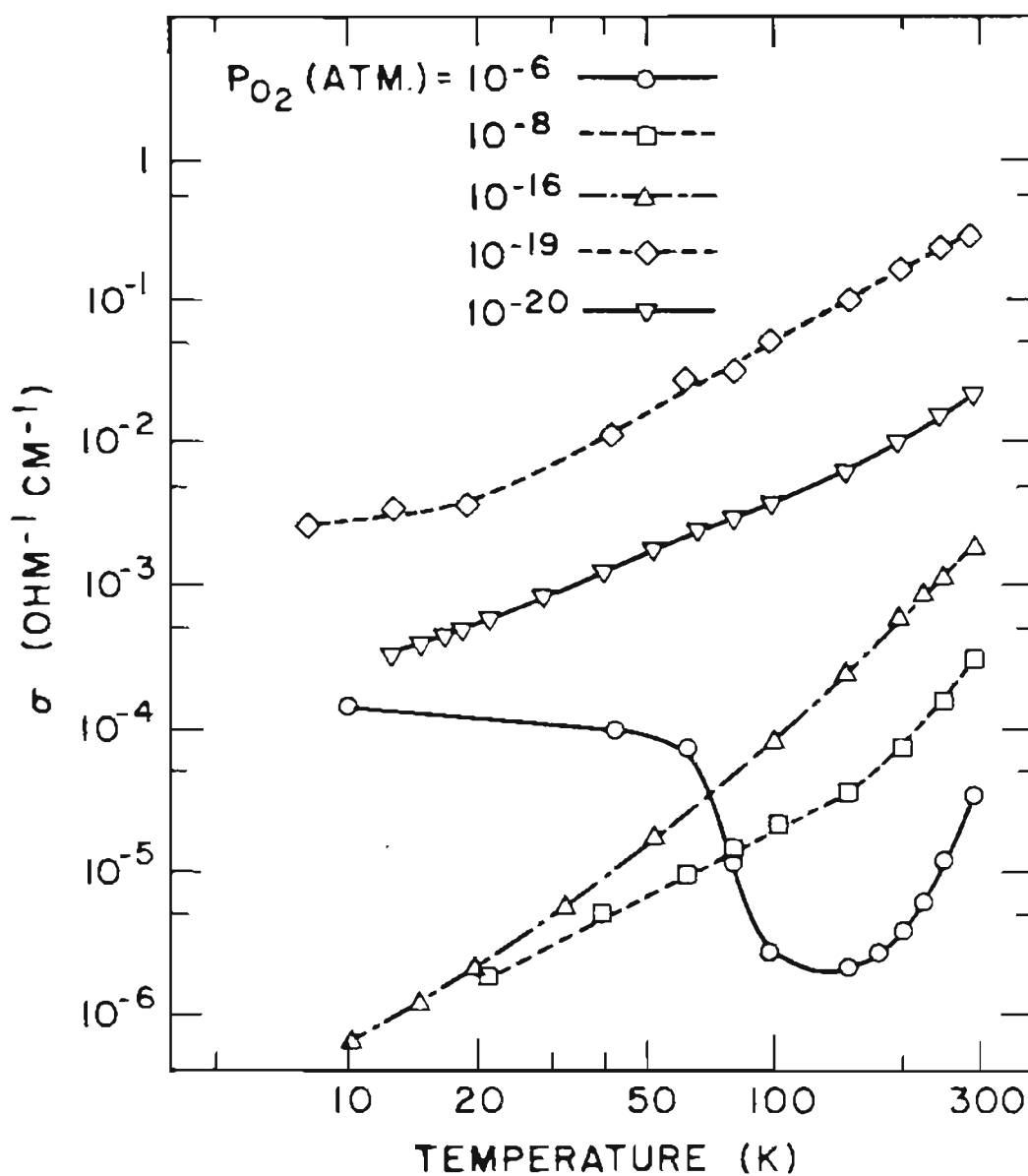


Figure 5.14. Electrical conductivity versus temperature in the range 10-300 K for ceramic, undoped SrTiO_3 after quenching from high temperature (1323 K) equilibration to various oxygen partial pressures.

in undoped or lightly doped SrTiO_3 tend to form impurity bands, separated from the conduction band by about 0.04–0.08 eV. These O_v -related impurity bands merge with the conduction band when free carrier concentrations in excess of 10^{17} cm^{-3} are obtained; for $n < 10^{17} \text{ cm}^{-3}$, conduction occurs predominantly within the impurity band. Hall measurements on single crystal specimens indicated that at room temperature, these low- n materials display mobilities in the range $1\text{--}10 \text{ cm}^2/\text{V}\cdot\text{sec}$. (192–194). Comparing this with the measured σ for the samples of Figure 5.14, it is seen that n lies in the range $10^{13}\text{--}10^{17} \text{ cm}^{-3}$.

The SrTiO_3 sample reduced in $P_{O_2} = 10^{-6} \text{ atm}$ is clearly at the low end of this n -range, and displays interesting temperature behavior that has been noted also for lightly reduced monocrystal SrTiO_3 (193). The explanation proposed by Lee et al. (193) was that the following steps occur on cooling: (1) Conductivity initially decreases with falling T , due to carrier freeze-out, i.e., decreasing n ; (2) when n is small enough to be dominated by impurity electrons, it becomes essentially constant; (3) that below that temperature, σ increases, since μ_n rises with the reduction in lattice phonon scattering. (The third step in that hypothesis has to assume that impurity scattering will be relatively unimportant). For sufficiently low T , μ_n approaches a constant value, and so does σ .

The curves for the samples reduced in the P_{O_2} range $10^{-8}\text{--}10^{-20} \text{ atm}$ exhibit the behavior noted by other investigators and alluded to above. An increase in σ with reduction is seen up to reduction in $P_{O_2} = 10^{-19} \text{ atm}$; further reduction results in a decrease in σ . At

high T this is not the case (Fig. 5.13), where it was seen that σ uniformly increases with reduction. This is due to the constancy of mobility with reduction at high T (1123-1323 K), since optical phonon scattering predominates. The formation of impurity-related conduction bands changes the scattering characteristics at low T (10-300 K), resulting in the conductivity behavior noted. Figure 5.15 is an Arrhenius plot for these materials in the temperature range 200-300 K, where activated transport is clearly seen. The activation energies implied by these curves fall in the range 0.03-0.075 eV, and are seen to decrease with increasing n. These results are in quantitative agreement with those of Lee et al. (193) and Tufte and Chapman (192), and seem to confirm their impurity band model for oxygen vacancies in SrTiO_3 .

5.5 Electrical Conductivity in La-Doped SrTiO_3

5.5.1 Dependence of σ on Temperature

The temperature behavior of La-doped SrTiO_3 shows somewhat more complexity than that found in the undoped case. For all but the most heavily doped materials, reduction in $P_{\text{O}_2} \leq 10^{-12}$ atm results in the appearance of a conductivity maxima in the range 300-500 K. The La concentration demarcation for this effect seems to fall at about 0.3 at.%, as can be seen by comparing Figures 5.16A and 5.17. Comparison of the two parts of Figure 5.16 demonstrates the influence of reduction on the occurrence of this maxima. In this figure, a log-log plot of σ versus T in this temperature range (300-500 K)

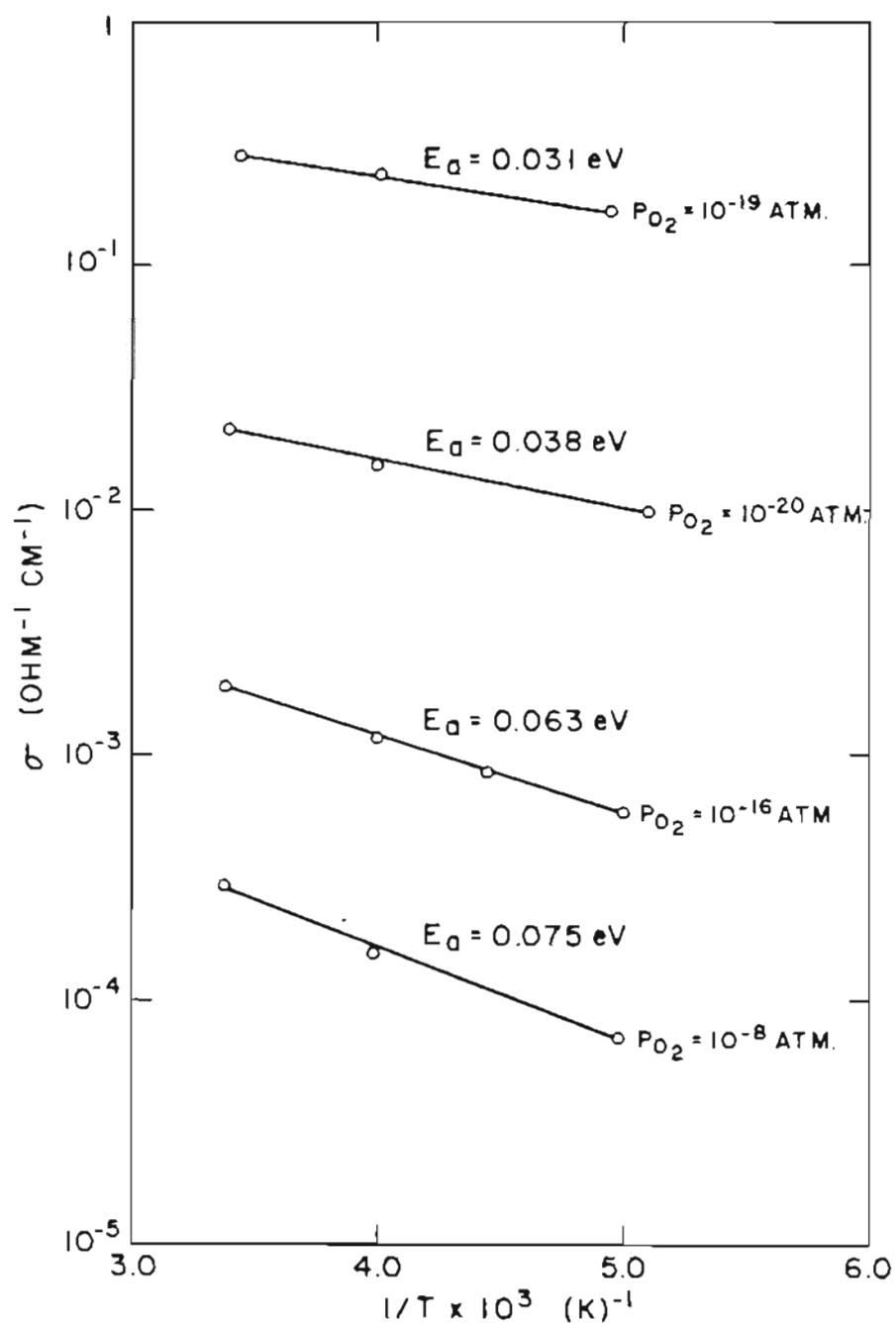


Figure 5.15. $\text{Log}(\sigma)$ versus $1000/T$ for ceramic, undoped SrTiO_3 in the temperature range 200-300 K, for four different reduction states.

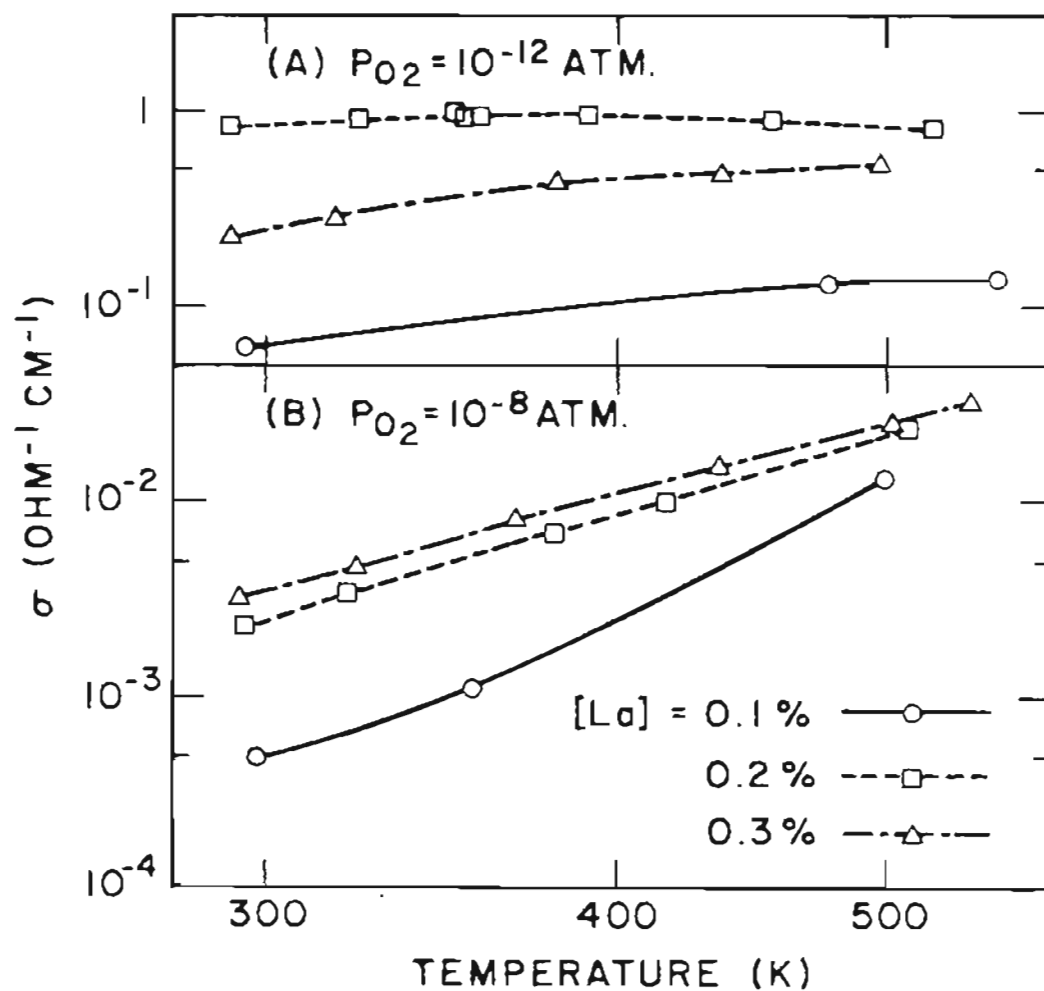


Figure 5.16. Electrical conductivity versus T (300–500 K) for lightly doped, ceramic SrTiO_3 for two different reduction states. These curves illustrate the appearance of a conductivity maxima as reduction is increased.

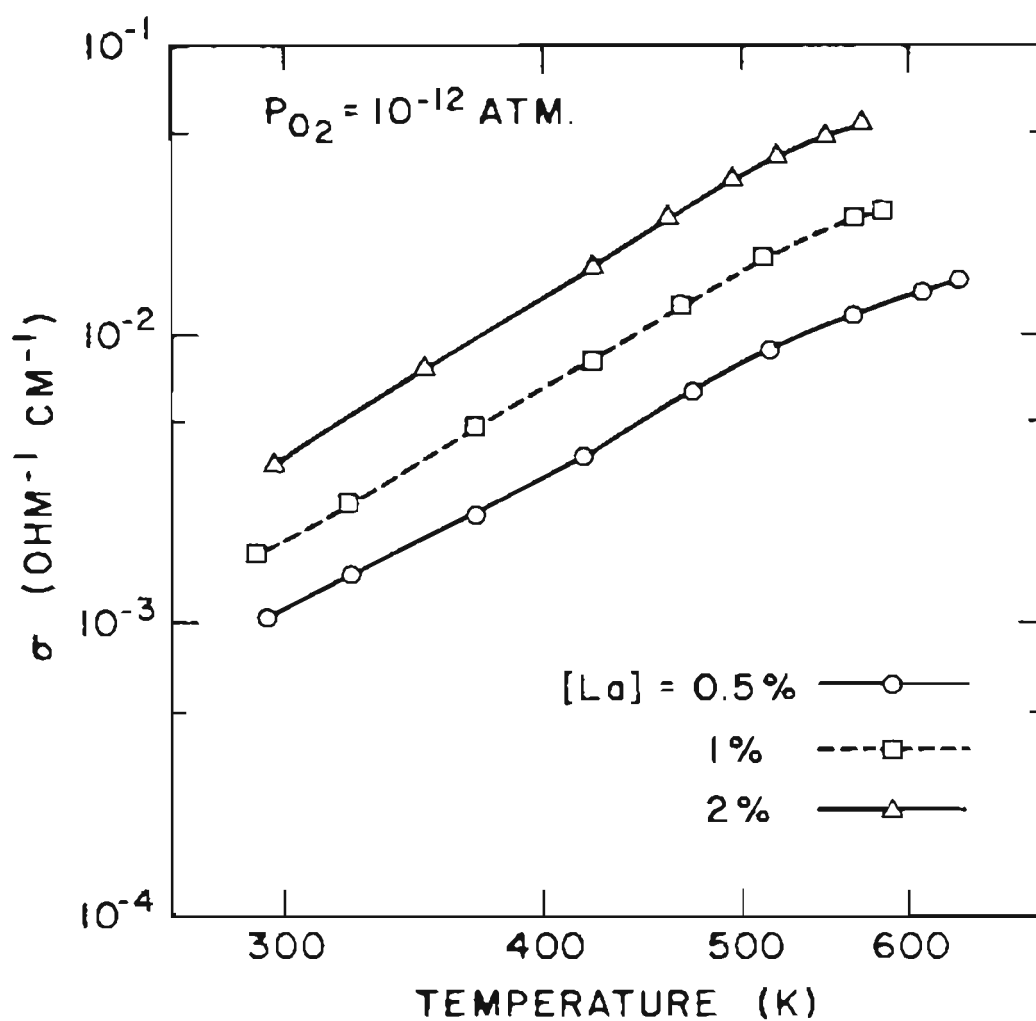


Figure 5.17. Electrical conductivity versus T (300-600 K) for highly doped, ceramic SrTiO_3 reduced in $\log(P_{O_2}) = -12$. No maxima is found for these materials.

clearly shows a maxima for those lightly doped samples ($[La] \leq 0.3\%$) reduced in $P_{O_2} = 10^{-12}$ atm, but not for those reduced in $P_{O_2} = 10^{-8}$ atm.

Figure 5.18 shows a log-log plot of σ versus T over the temperature range 10-500 K for those highly doped ($[La] \geq 0.5\%$) and lightly reduced samples of Fig. 5.17. Log-log coordinate systems have been selected for use in this section since this gives a balanced view of changes at lower temperature ($T < 300$ K), as compared with those evident for room temperature and above. Moreover, there would be no advantage in expressing these data in the conventional semiconductor Arrhenius form ($\log(\sigma)$ versus $1/T$), since they show no long straight "activated" regions.

Figures 5.19-5.23 are graphs of $\log(\sigma)$ versus $\log T$ in the T range 10-500 K for $La: SrTiO_3$ (with $[La] = 0.1, 0.2, 0.3, 0.5, 1.0$ and 5.0 at.%) ceramic samples quenched from five different oxygen equilibration pressures (10^{-16} atm $\geq P_{O_2} \geq 10^{-20}$ atm). Comparing these curves with Figure 5.18, it can be seen that carrier freeze-out is prominent in the more lightly reduced samples, but that this effect becomes much less significant as the sample reduction increases. In the case of $[La] = 0.2\%$ equilibrated to $P_{O_2} \leq 10^{-18}$ atm, carrier freeze-out appears to be deferred to $T < 10$ K. These results are suggestive of impurity banding.

Figures 5.24-5.28 show an expanded view of σ for these materials in the T range 300-500 K, and are provided to give a clearer picture of the conductivity maxima. It can be seen in these figures that σ_{max} is obtained for $[La] = 0.1, 0.2$, and 0.3% , but not for concentra-

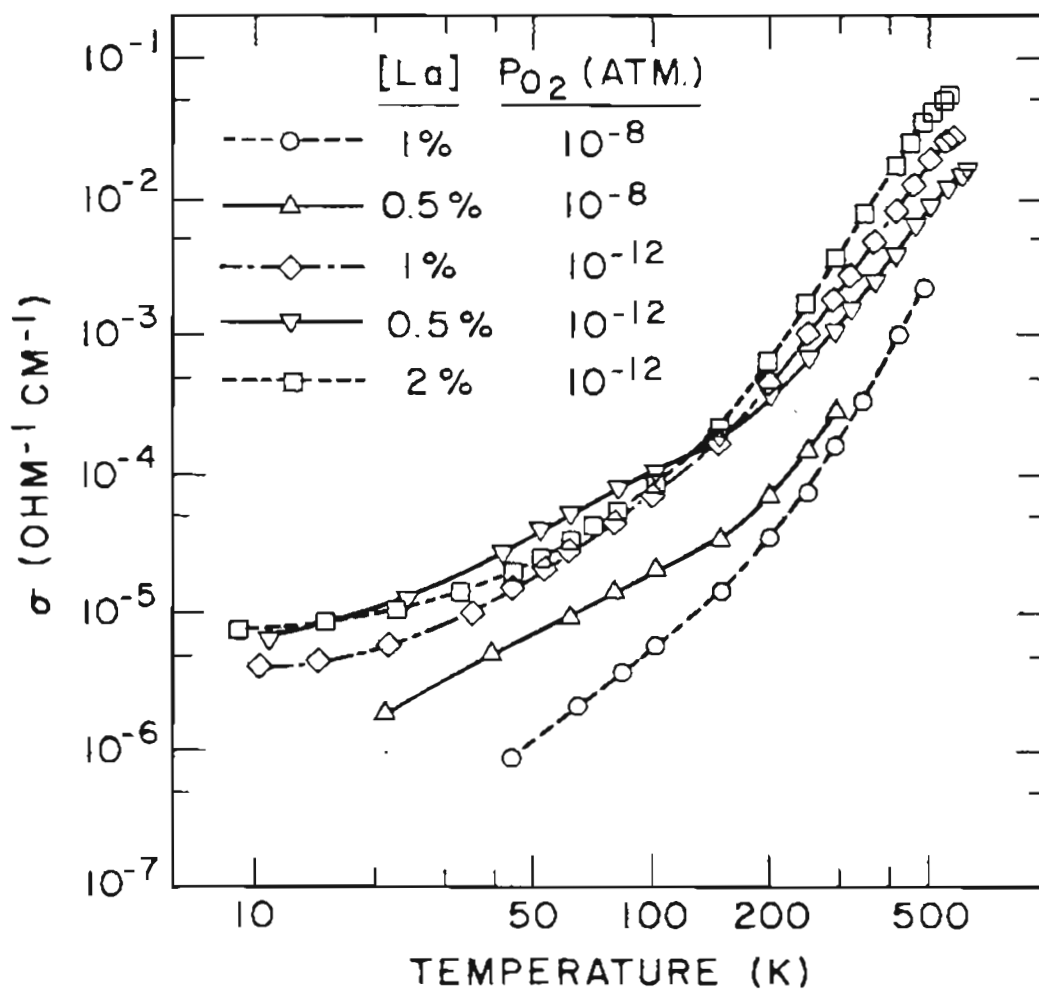


Figure 5.18. Electrical conductivity versus temperature (log-log plot) over the range 10-500 K for the highly doped ceramic SrTiO_3 samples of Fig. 5.17 at two different reduction states.

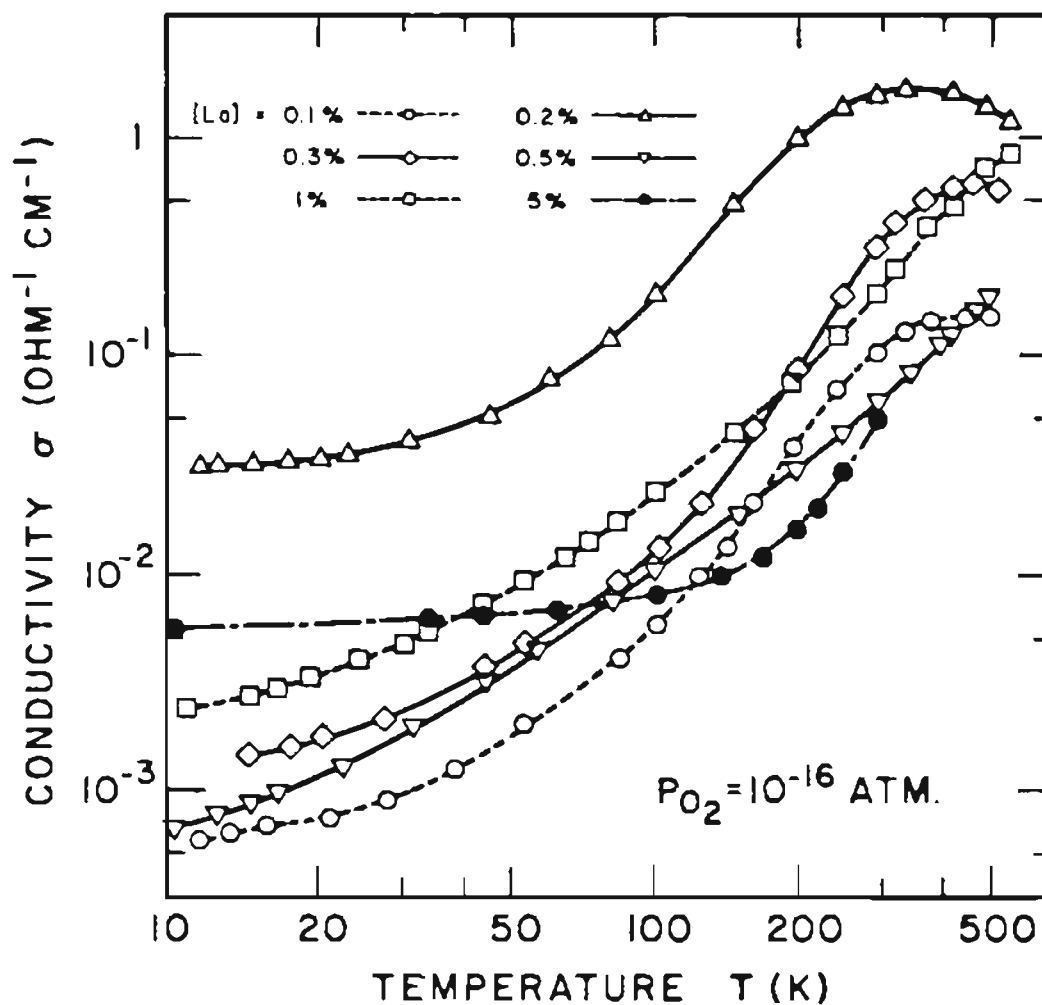


Figure 5.19. Electrical conductivity versus temperature (log-log plot) over the range 10-500 K for six La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

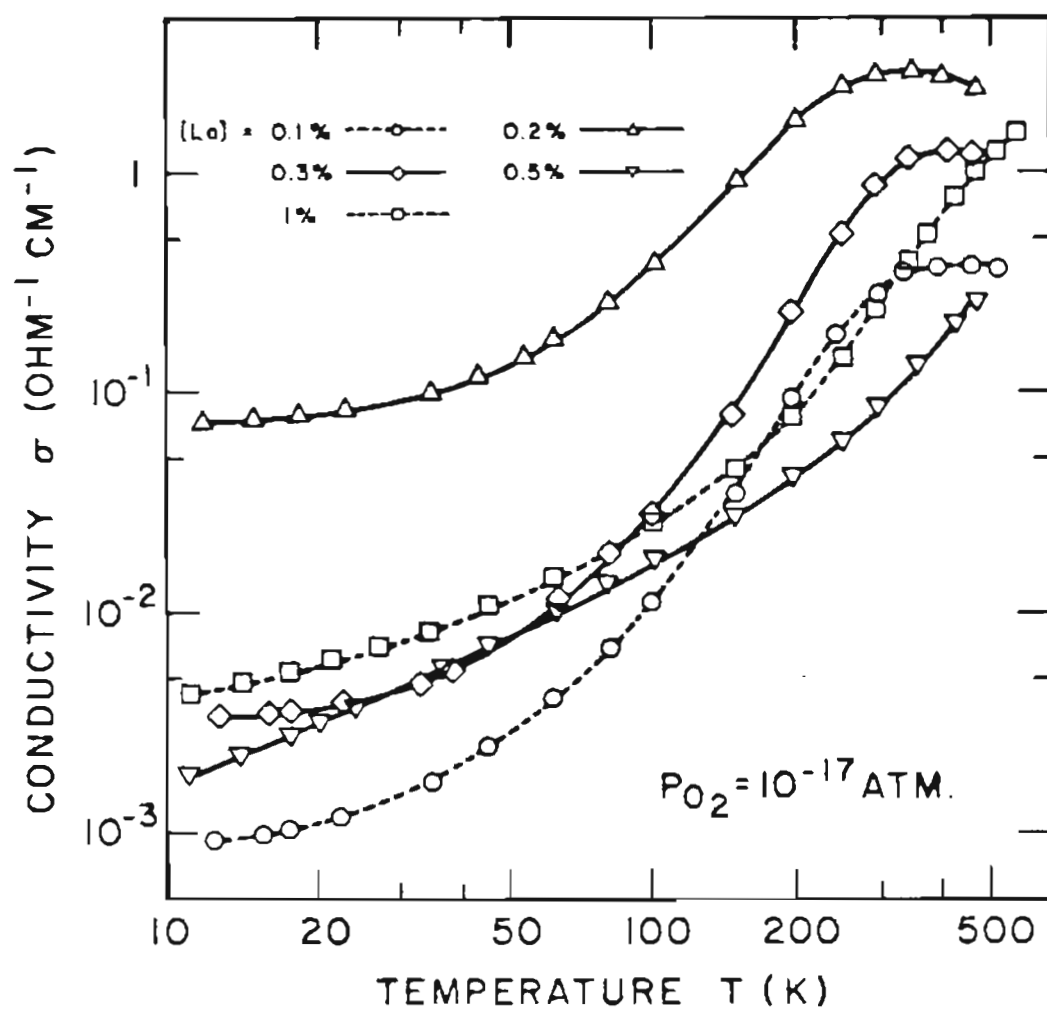


Figure 5.20. Electrical conductivity versus temperature (log-log plot) over the range 10-500 K for five La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

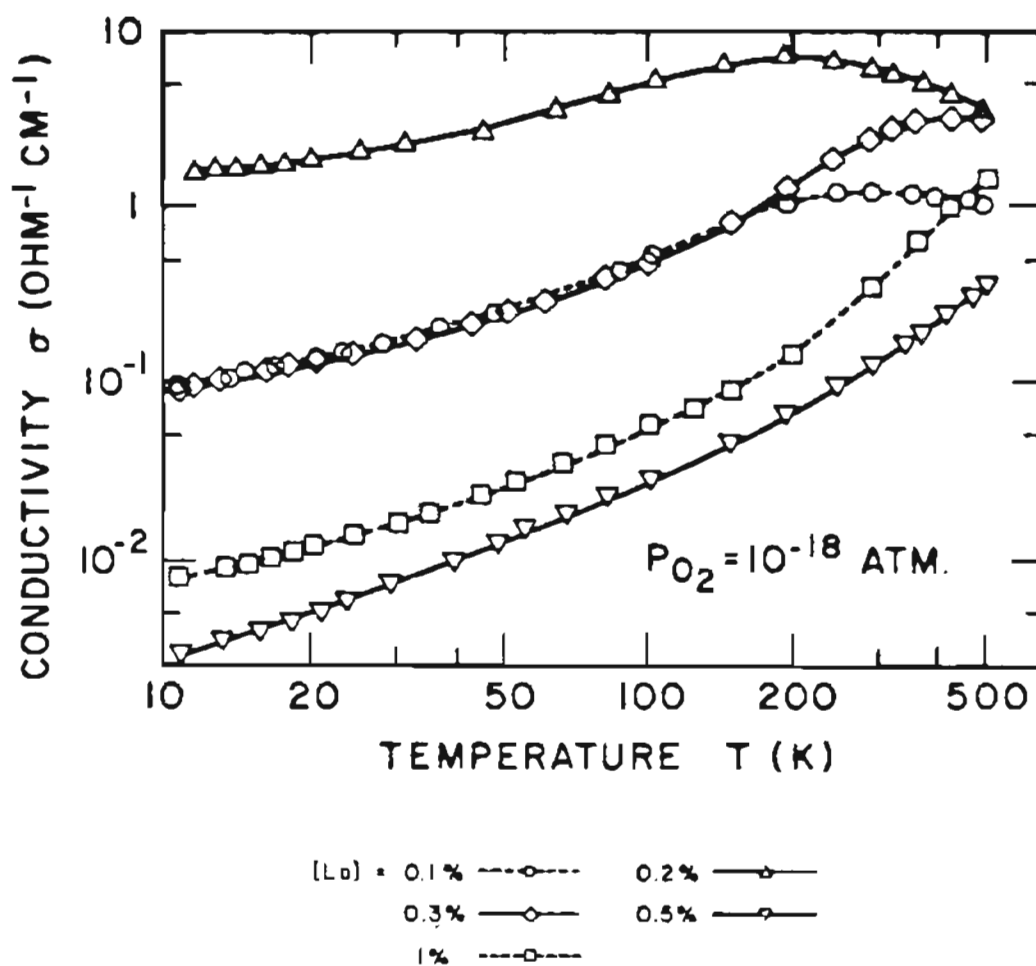


Figure 5.21. Electrical conductivity versus temperature (log-log plots) over the range 10-500 K for five La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

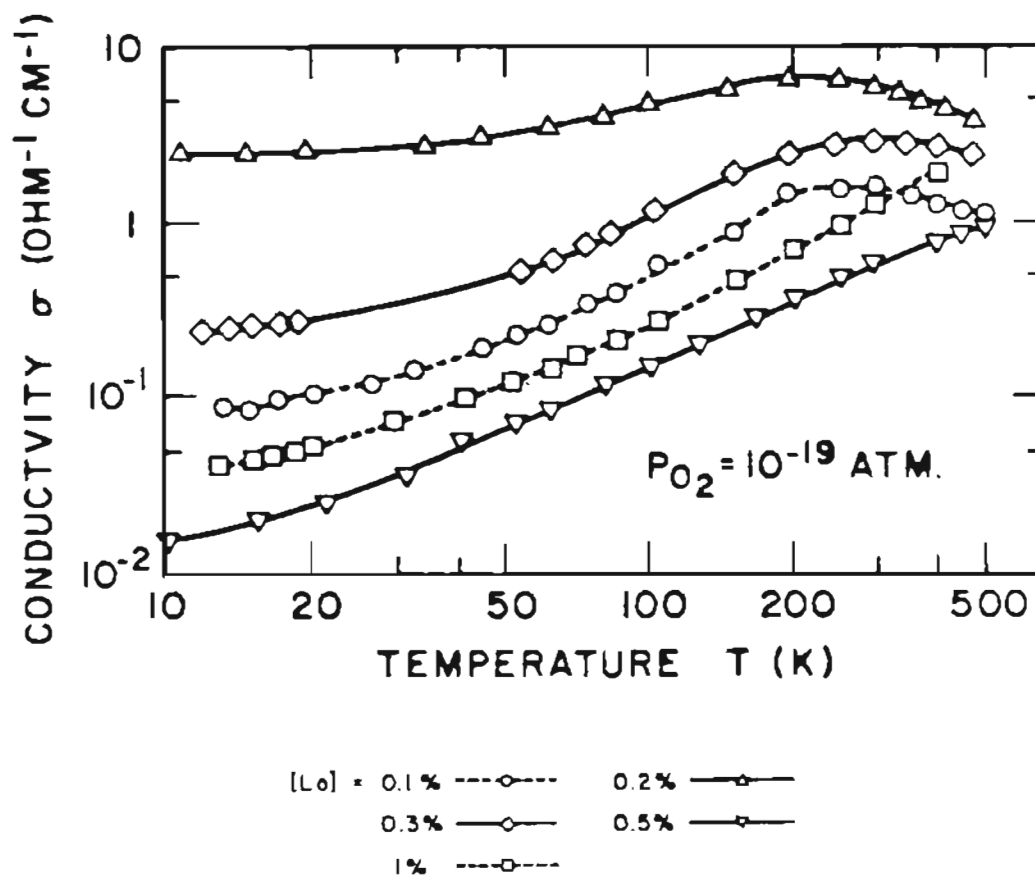


Figure 5.22. Electrical conductivity versus temperature (log-log plots) over the range 10-500 K for five La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

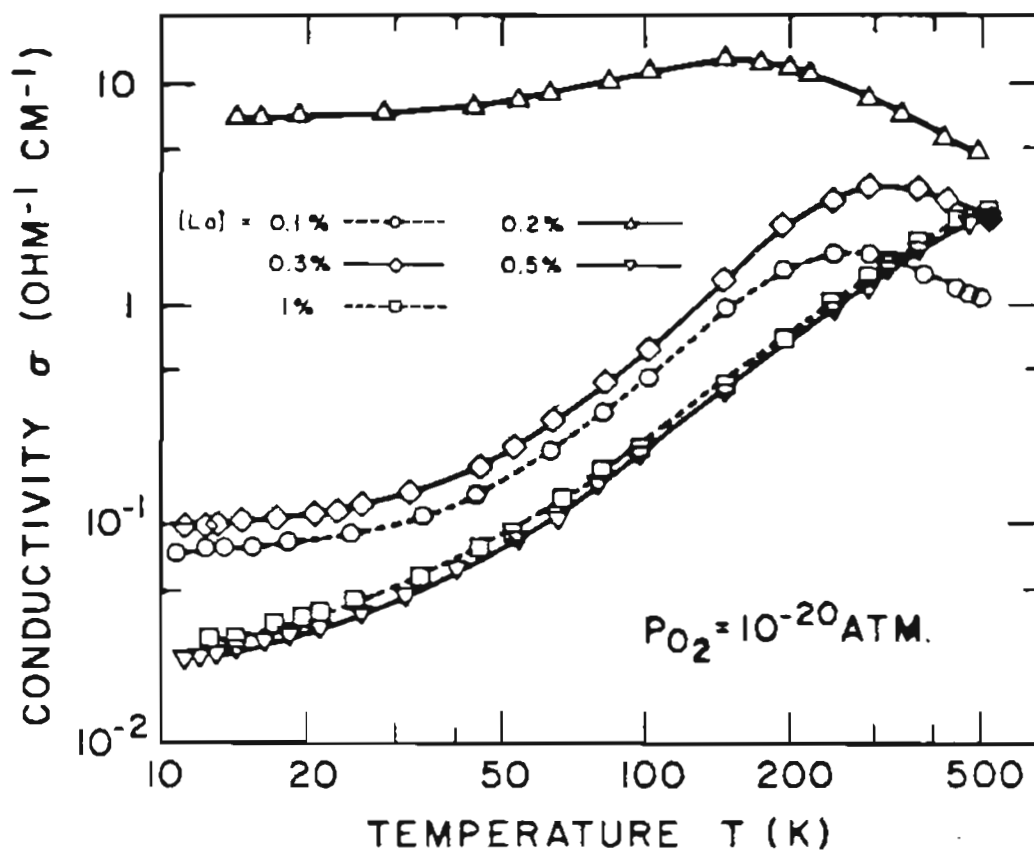


Figure 5.23. Electrical conductivity versus temperature (log-log plots) over the range 10-500 K for five La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

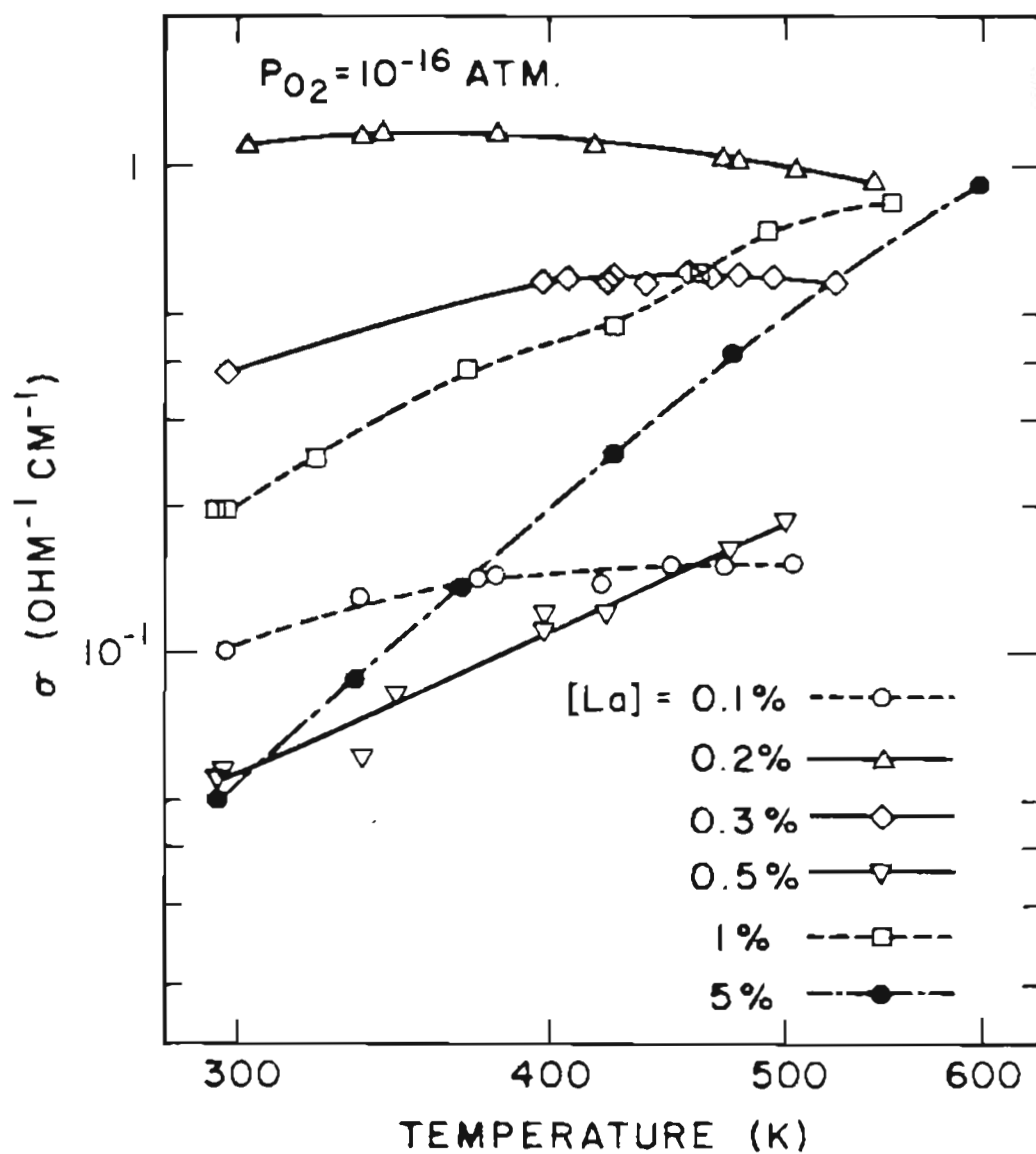


Figure 5.24. Electrical conductivity versus temperature over the range 300-500 K for six La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

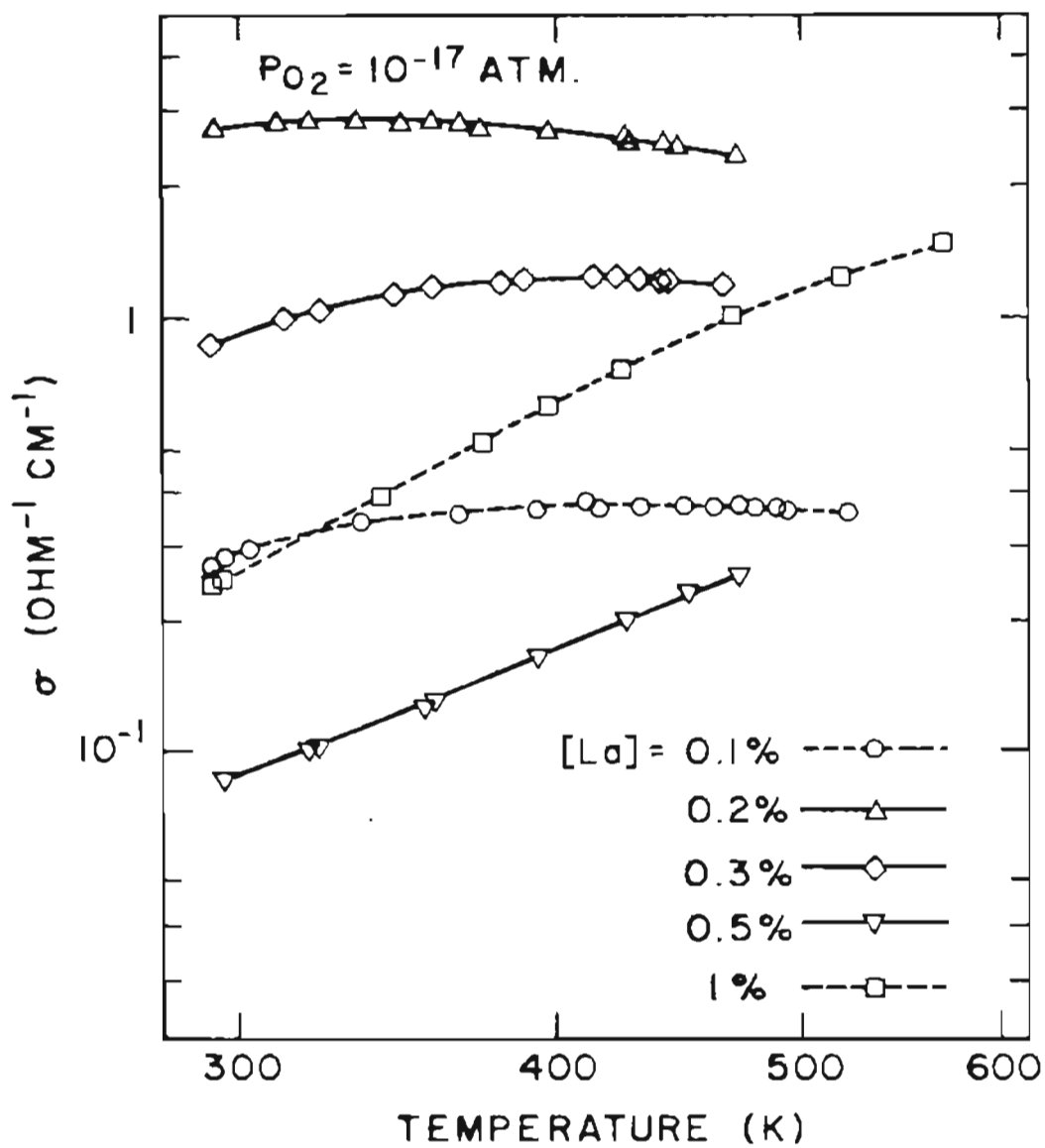


Figure 5.25. Electrical conductivity versus temperature over the range 300-500 K for five La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

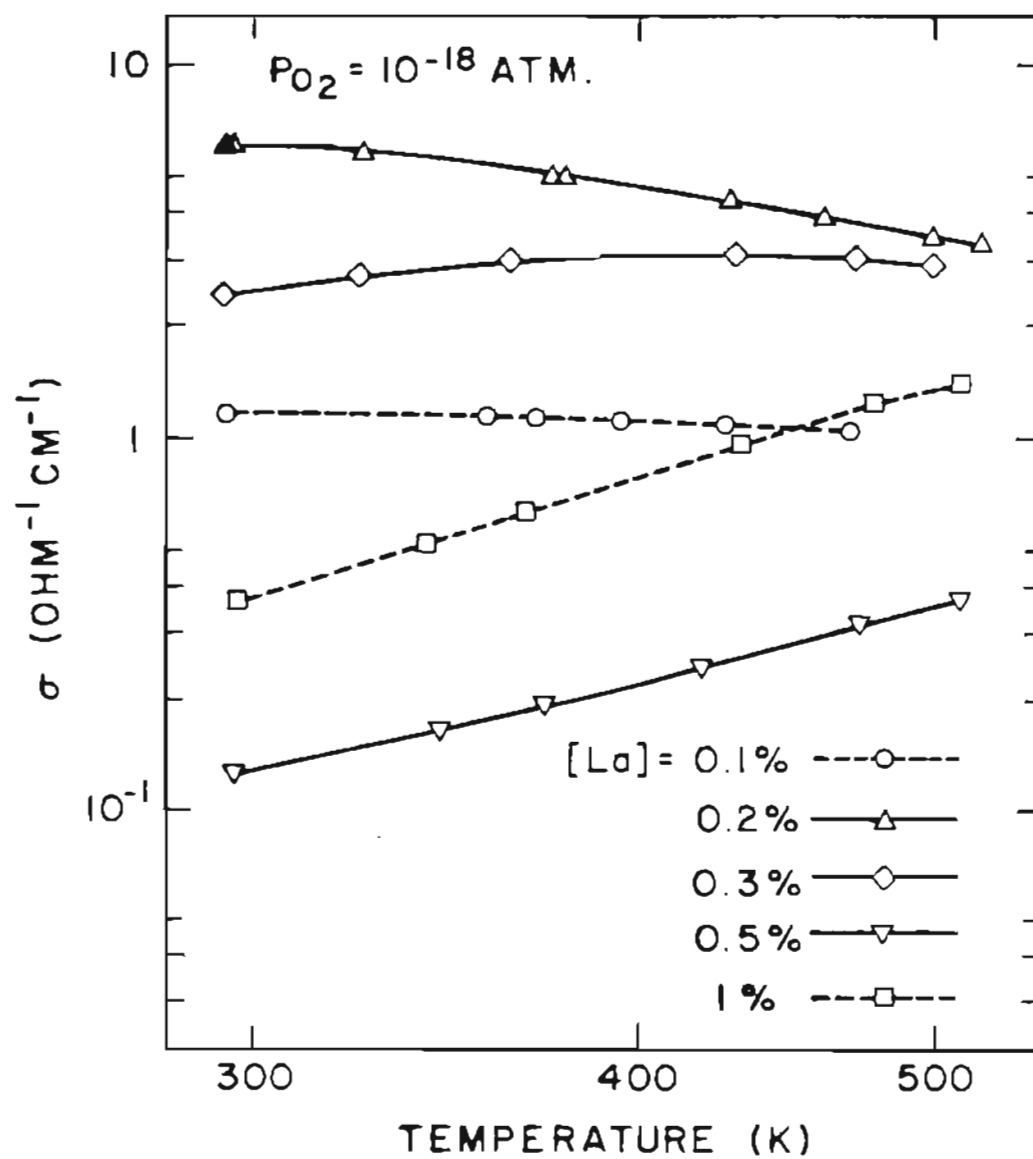


Figure 5.26. Electrical conductivity versus temperature over the range 300-500 K for five La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

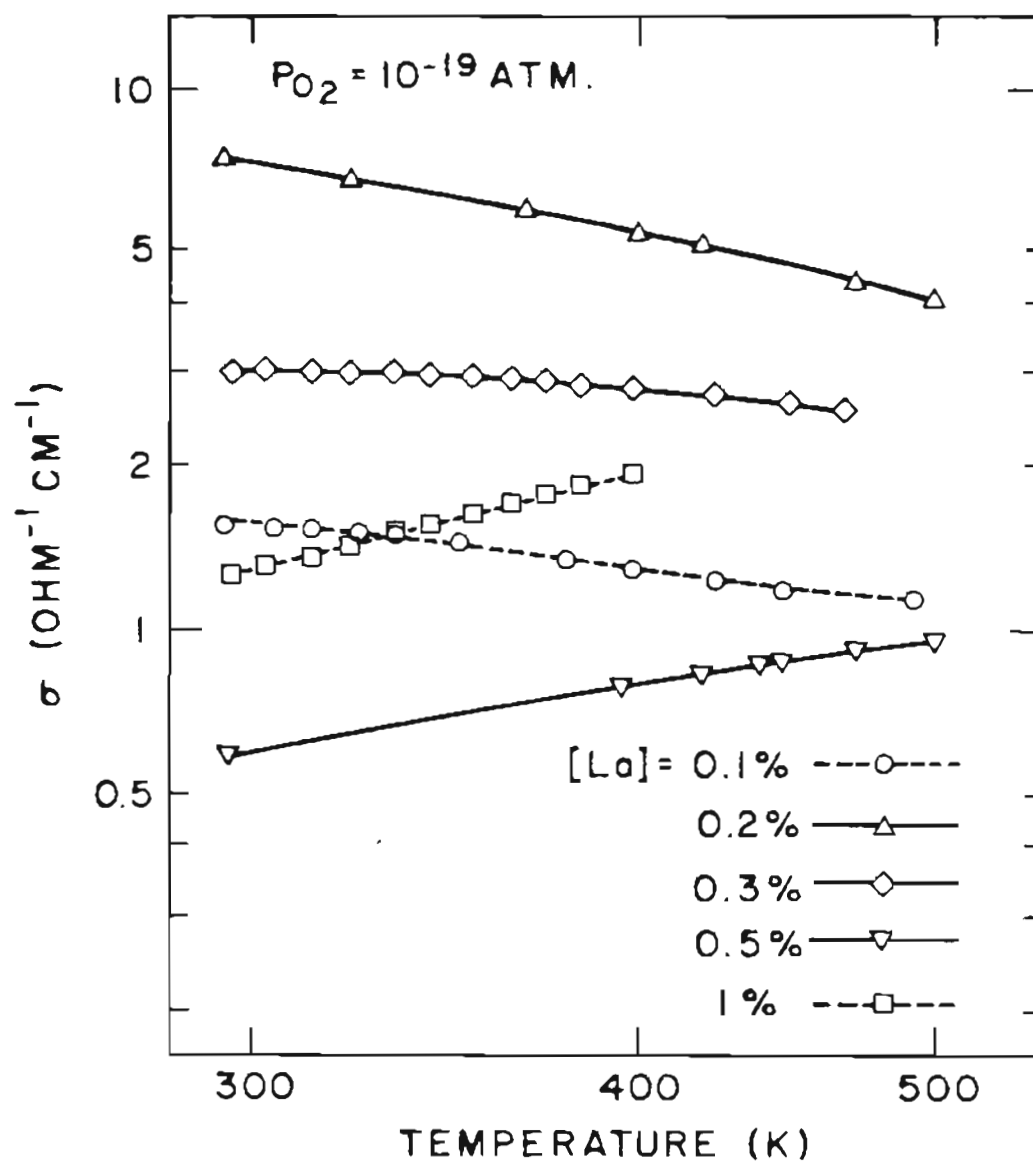


Figure 5.27. Electrical conductivity versus temperature over the range 300-500 K for five La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

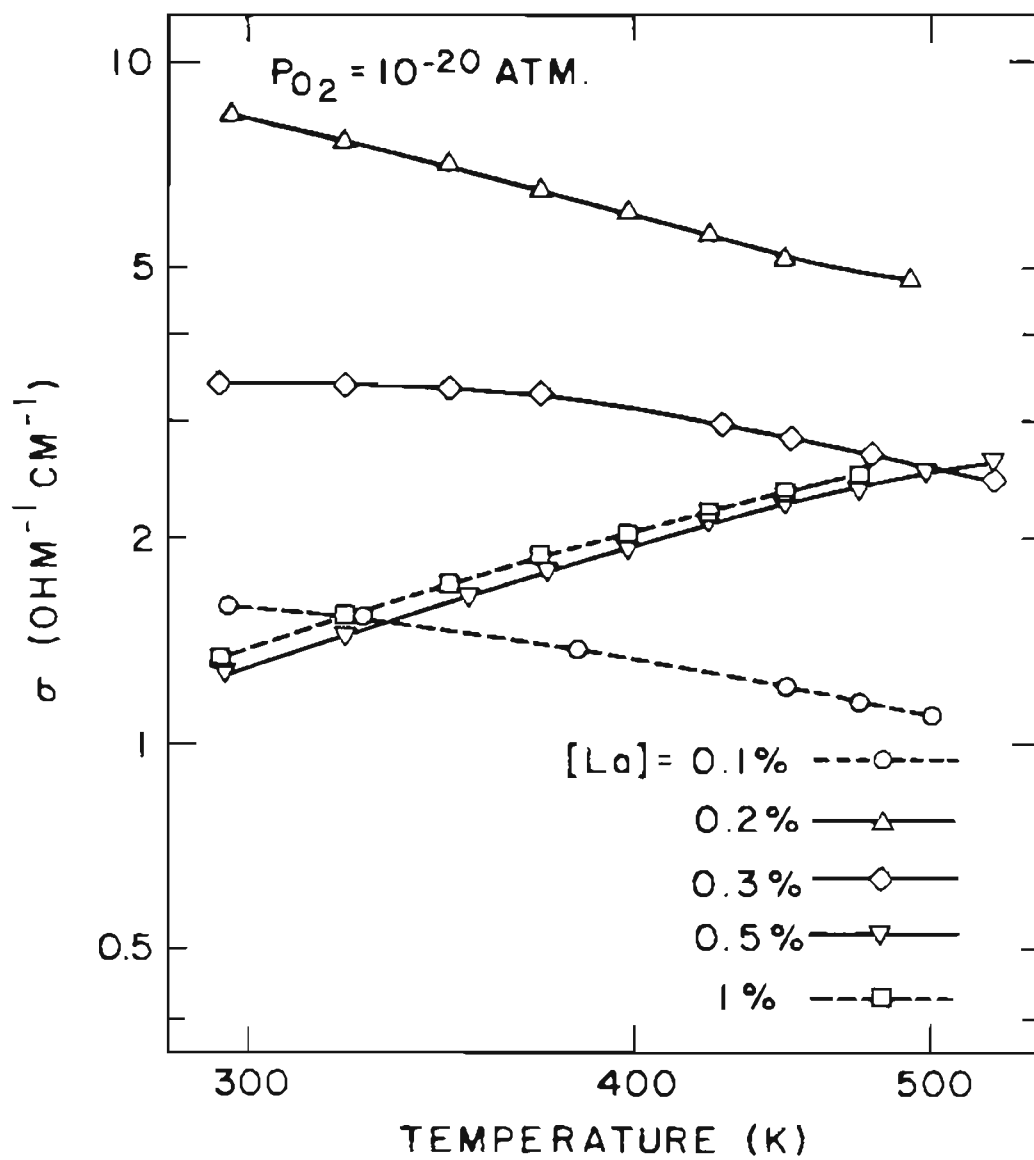


Figure 5.28. Electrical conductivity versus temperature over the range 300-500 K for five La doping concentrations, reduced under oxygen partial pressure indicated at 1325 K.

tions $> 0.3\%$. There is also a tendency for this maxima to shift to lower temperatures as the sample reduction is increased. This behavior is illustrated in Figures 5.29-5.31, wherein $\log(\sigma)$ versus $\log T$ curves for four different reduction states are given for each of the three lowest doping levels. The temperature range was selected for each set of curves to include $T(\sigma_{\max})$.

5.5.2 Dependence of σ on La-Doping

The variation of σ with lanthanum doping for samples reduced, quenched, and measured at lower temperatures proved to be fundamentally different from that found by Balachandran and Eror (238) at high temperatures. Balachandran and Eror (Figure 5.32) found that high temperature conductivity increased linearly with $[\text{La}]$ for the entire P_{O_2} range 10^{-22} to 1 atm. This was not unexpected from the defect model of Eqn. (2.9). Figures 5.33-5.34 present the low temperature results (300 K and 10 K, respectively) as found in this investigation.

The weakest doping shown in Figures 5.33 and 5.34 is $[\text{La}] = 1.7 \times 10^{19} \text{ cm}^{-3} = 0.1 \text{ at.}\%$ for strontium replacement. Even for this smallest La concentration, the typical La-La (or Ti^{3+} - Ti^{3+}) distance is less than 50 Å. Thus effects related to impurity bands can be expected (350).

A careful examination of Figures 5.19-5.23 shows that σ maximizes around $[\text{La}] \approx 0.2\%$, for each selected P_{O_2} during prequench reduction, and throughout the temperature range 10-500 K. That feature is further demonstrated by Figures 5.33-5.34, showing the variation of

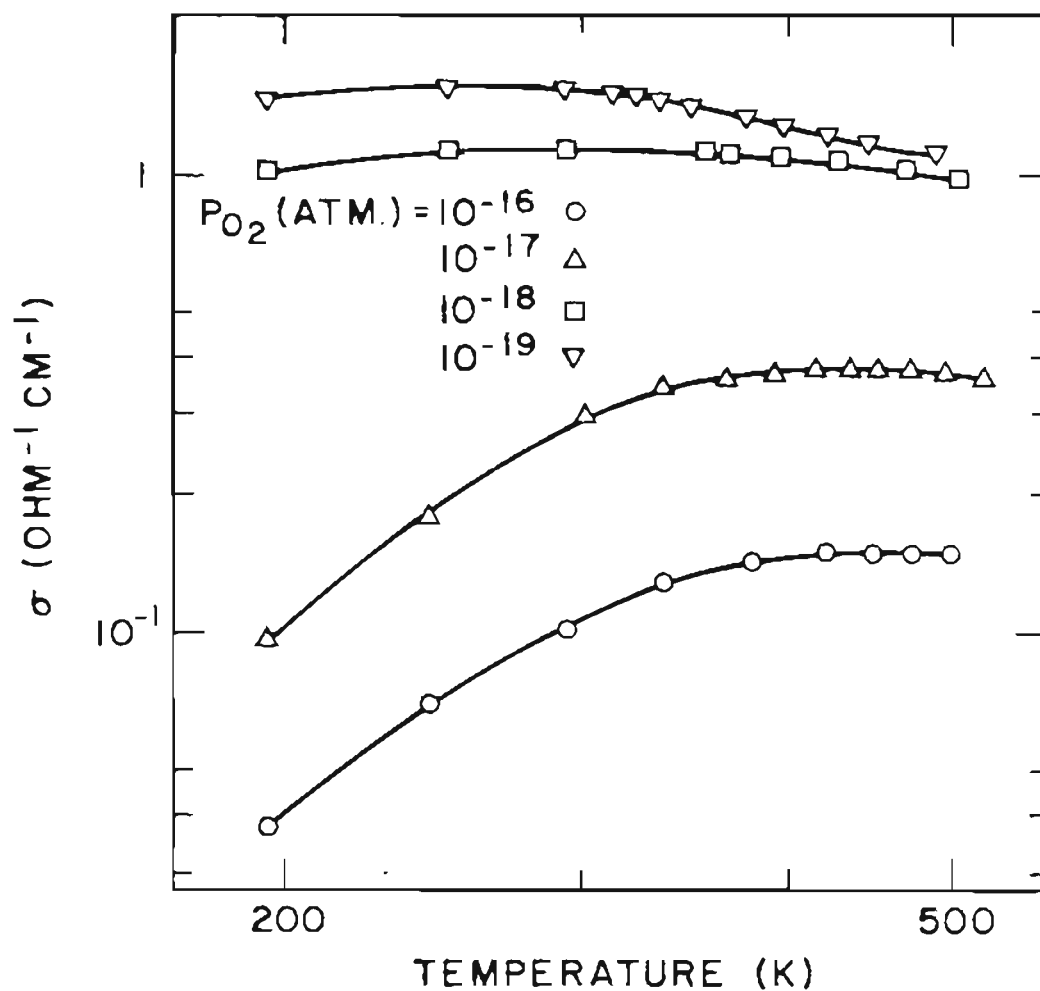


Figure 5.29. Electrical conductivity versus temperature over the range 200–500 K for $\text{La}(0.1\%)\text{SrTiO}_3$, after high temperature (1325 K) reduction in four different partial pressures of oxygen.

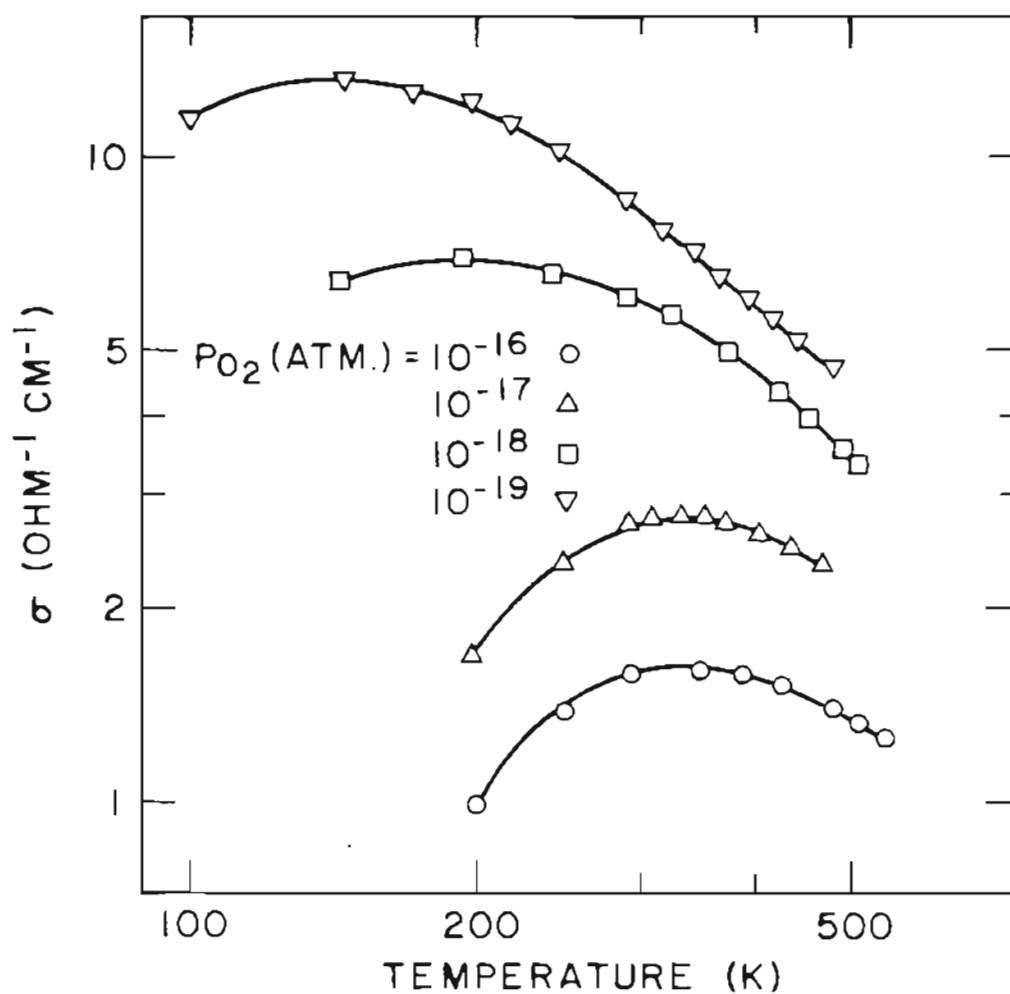


Figure 5.30. Electrical conductivity versus temperature over the range 100-500 K for $\text{La}(0.2\%)\text{SrTiO}_3$, after high temperature (1325 K) reduction in four different partial pressures of oxygen.

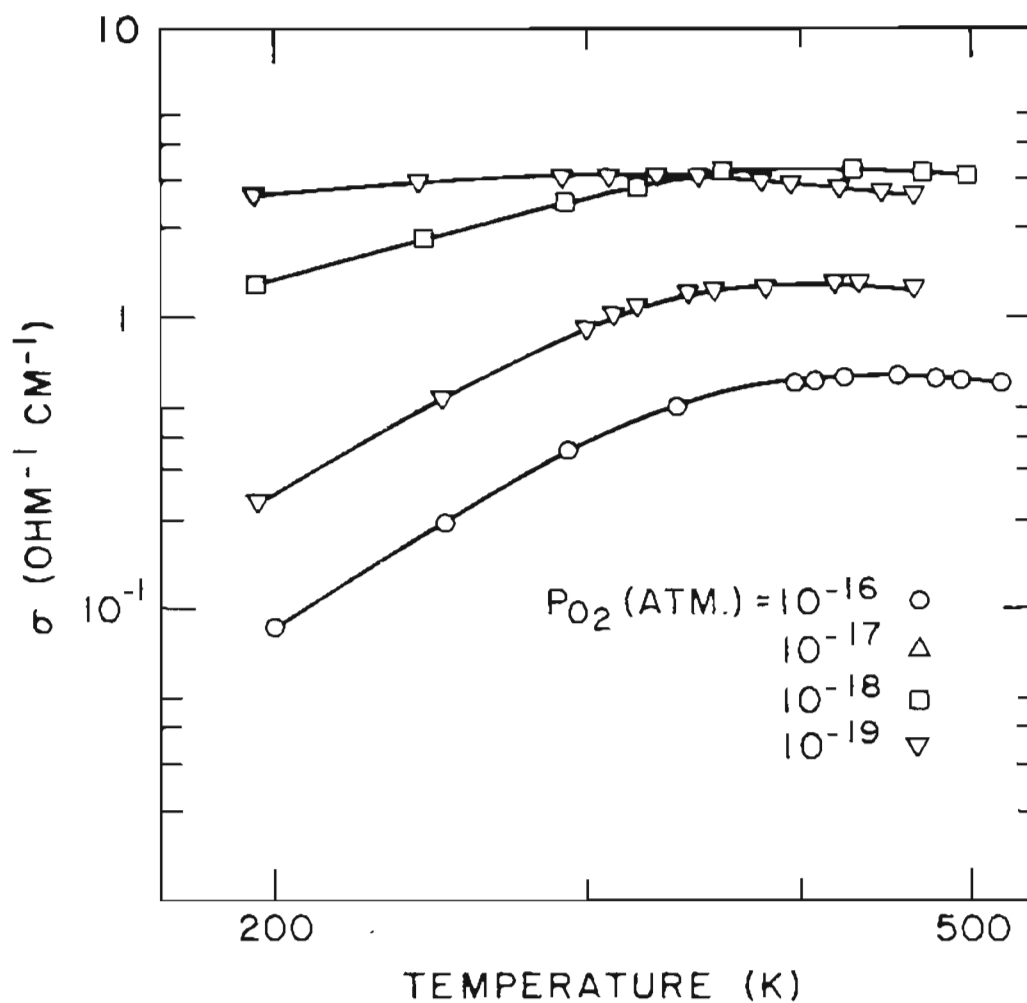


Figure 5.31. Electrical conductivity versus temperature over the range 200-500 K for La(0.3%)SrTiO₃, after high temperature (1325 K) reduction in four different partial pressures of oxygen.

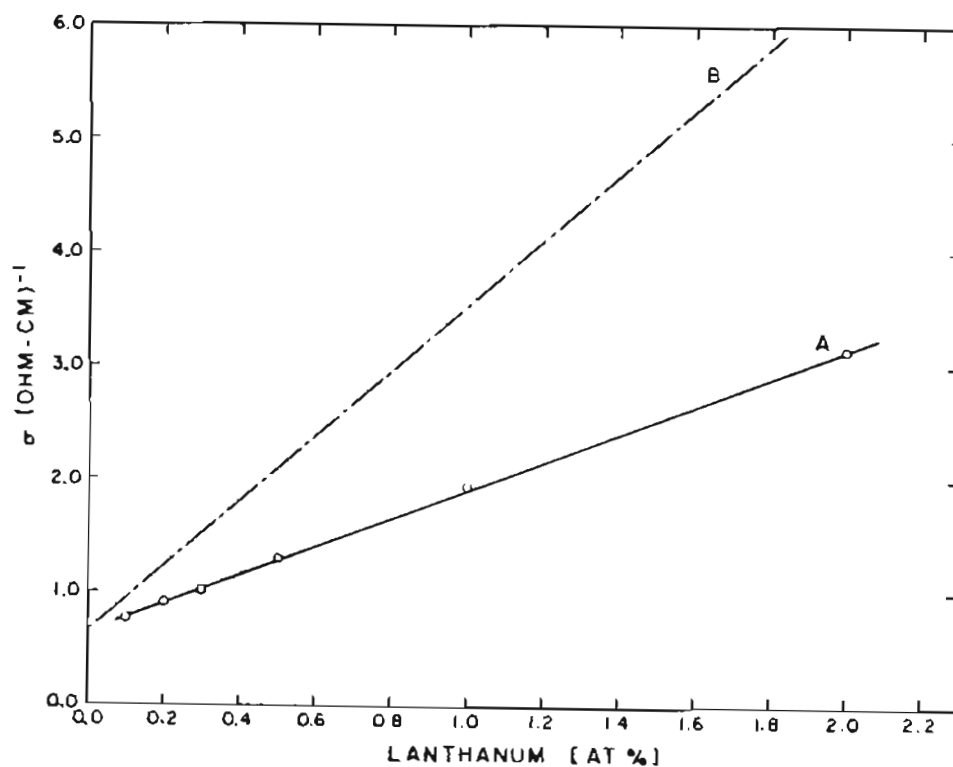


Figure 5.32. Electrical conductivity of La-Doped SrTiO_3 at 1325 K and 10^{-16} atm. oxygen partial pressure as a function of the La concentration. Curve A: Experimental points; Curve B: Conductivity based on the assumption $\mu_n = 0.1 \text{ cm}^2/\text{V-s}$ and $n = [\text{La}]$. (From reference 238).

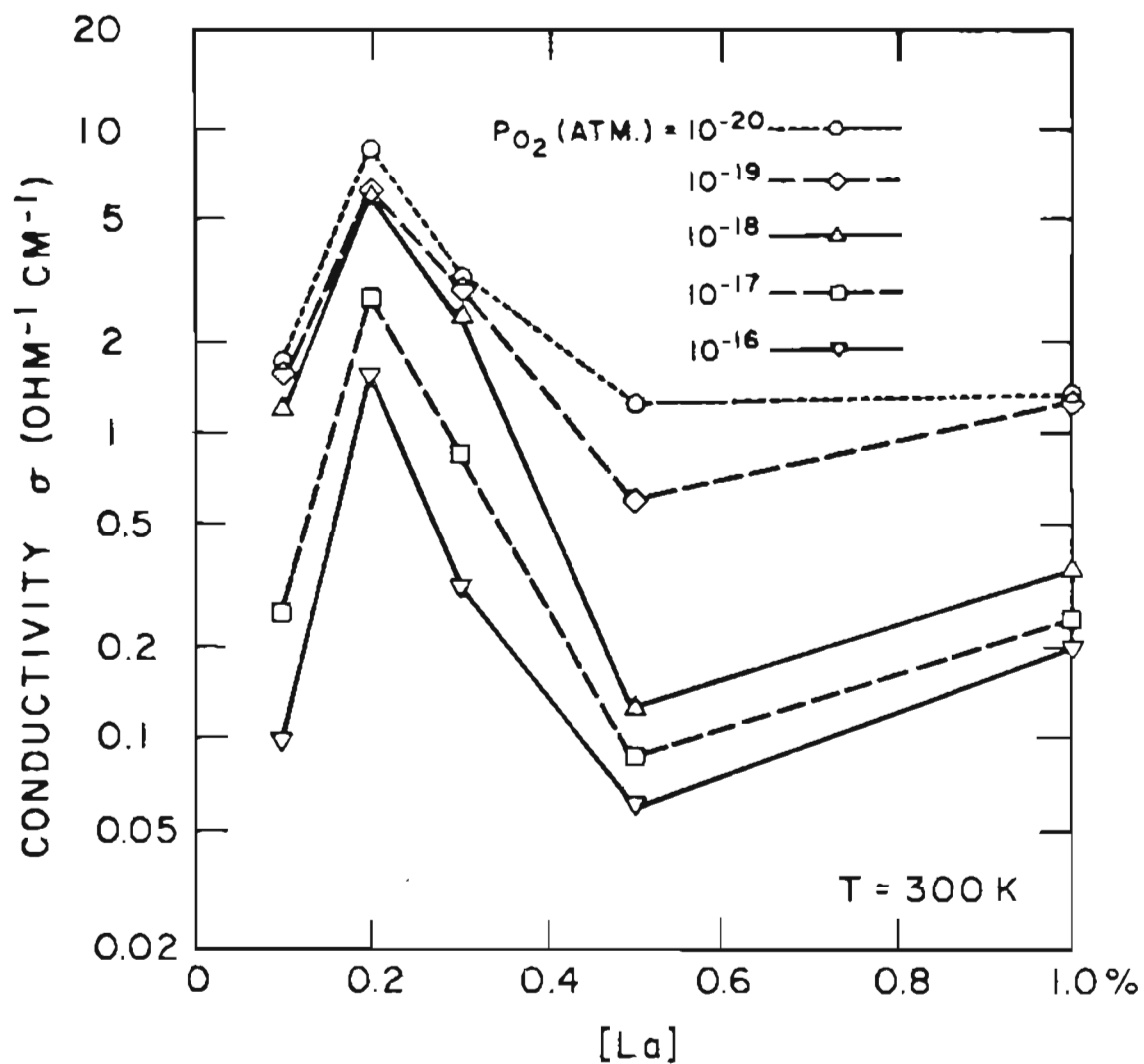


Figure 5.33. Isothermal plots of conductivity versus lanthanum doping, for various stages of reduction, for the temperature $T = 300 \text{ K}$.

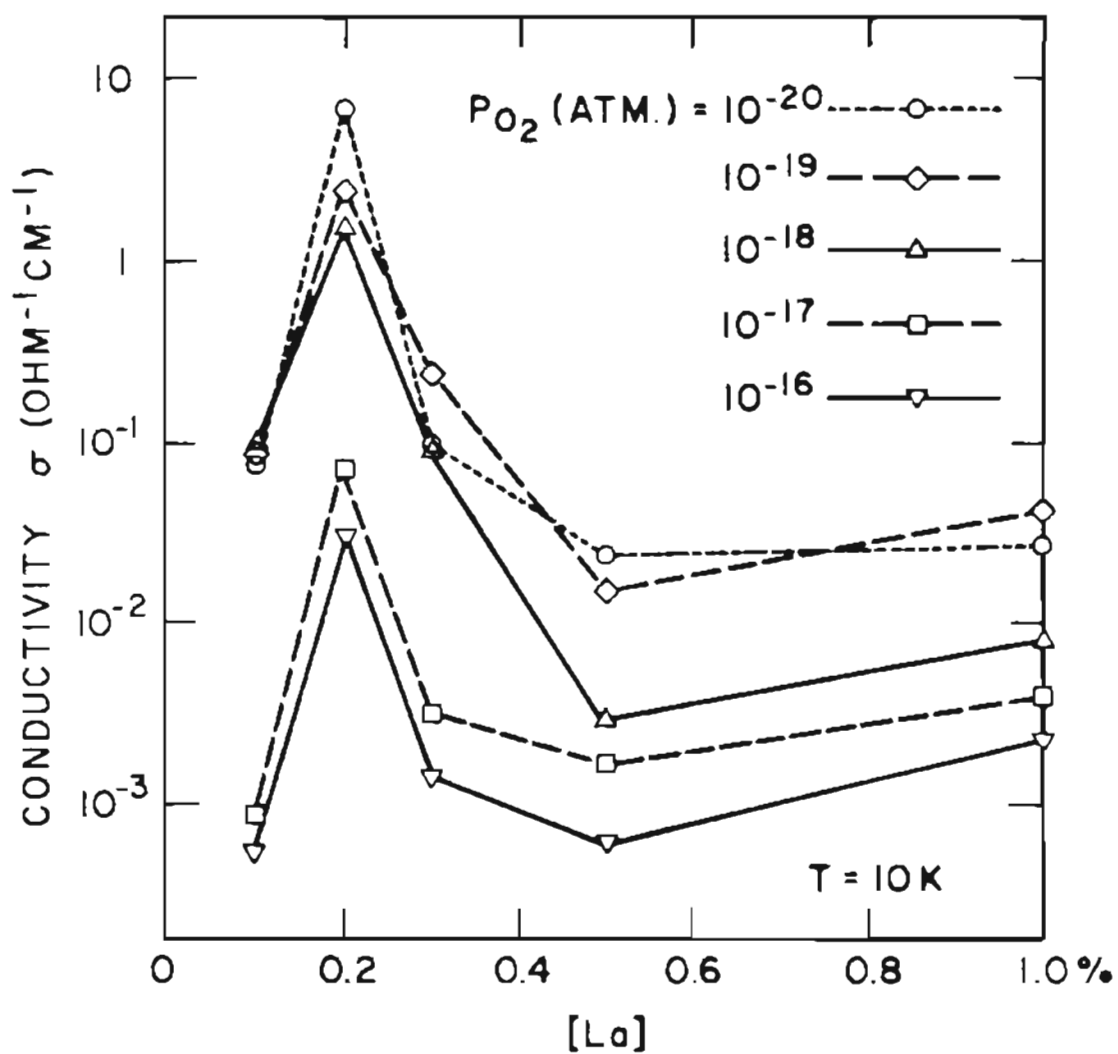


Figure 5.34. Isothermal plots of conductivity versus lanthanum doping, for various stages of reduction, for the temperature $T = 10 \text{ K}$.

conductivity with doping, for two very different temperatures, as influenced also by the various choices for P_{O_2} during pre-quench equilibration. For each of the ten curves in Fig. 5.33-5.34, the conductivity shows a prominent maximum for $[La] = 0.2\%$. In each of these cases, the subsequent fall of σ with increasing doping can be seen to be arrested for $[La] > 0.5\%$.

Table 5.3 shows results for thermopower measurements near room temperature. These show that, for a given reduction state, the magnitude of the (negative) Seebeck coefficient Θ tends to decrease with increasing $[La]$. Such numbers for Θ can not readily be converted into reliable numbers for the conduction electron density, n . For, as remarked in Section 2.1, multiband conduction in several conduction band minima can be expected. One may also anticipate conduction by low-mobility carriers in an impurity band. Particularly for carriers of the latter class, the "heat of carrier transfer" would be a very questionable multiple of (k/e) . Even so, one may reasonably expect that $|\Theta|$ will decrease as n increases within a family of samples.

For an extrinsic semiconductor at a given temperature, it can happen (for weak doping) that n rises linearly with dopant concentration. However, the rise of n is a monotonic but sublinear one (48) if increased doping forces ϵ_F high enough so that many of the added donors must remain neutral. A further (low mobility) class of carrier has its effect modified above a critical La concentration, when a donor impurity band merges with the conduction band(s). Mott (350)

{La} at. %	P_{O_2} atm	Θ $\mu V/K$
0.2	10^{-18}	-800
0.5	10^{-18}	-605
1.0	10^{-19}	-320
0.1	10^{-20}	-340
0.2	10^{-20}	-310

Table 5.3. Values of Thermopower (Seebeck Coefficient, Θ) for $T \approx 290$ K.

estimated that this could happen in the mid- 10^{18} cm^{-3} range for shallow donors in SrTiO_3 . Thus the conventional decomposition of one-band conduction:

$$\log(\sigma/e) = \log(n) + \log\mu_n \quad (5.6)$$

oversimplifies things even for monocrystal reduced La-doped SrTiO_3 . The intergranular contact resistances of microcrystalline material add another complication to the analysis. Despite this, Figs. 5.19-5.23 and 5.33-5.34 can still reflect trends that La doping and reduction have on the numbers and mobilities for various classes of extrinsically-derived electron. The following points can be made:

(1) For heavy doping, $[\text{La}] > 0.3\%$, $(d\sigma/dT) > 0$ throughout the 10-500 K range covered by the curves of Figs. 5.19-5.23, and for each of the five stages of reduction. The lines of Figs. 5.33-5.34 also show that conduction for $[\text{La}] = 1\%$ modestly exceeds that for $[\text{La}] = 0.5\%$; true for each stage of reduction and for both 10 K and 300 K. That behavior is consistent with fully merged conduction and impurity bands, and with some combination of impurity scattering and intra-band scattering. Mott (350) noted that the high dielectric constant of SrTiO_3 makes ionized impurity scattering (351) weak compared with most other semiconductors.

(2) For weaker doping - and with some features retained in part even up to $[\text{La}] \cong 0.3\%$ - conductivity maximizes near 300 K. There are indications of σ starting to fall off in the range 300-500 K; and

high temperature data (238) shows that, by $T \approx 1100$ K, conductivity has already passed through a minimum several times smaller, and has resumed $(d\sigma/dT) > 0$ behavior. The temperature range of negative $(d\sigma/dT)$ would fit conventional LO mode scattering models (189).

(3) Conductivity falls off more emphatically for low temperatures in these less heavily doped samples. As previously remarked, the relation between $\log(\sigma)$ and $(1/T)$ is not linear. [Neither is a plot of $\log(\sigma)$ vs. $(1/T)^{1/4}$.] It is likely that donor de-ionization plays a role in the low-temperature $\sigma(T)$ for the less strongly doped material, compounded with other influences.

(4) The $[La] \cong 0.2\%$ condition gives the highest conductivity, for each reduction state, and throughout the 10-500 K temperature range. This indicates that any overlap of impurity and conduction bands for this doping strength is insufficient to cause much scattering of conduction electrons into impurity band states. For the stronger examples of reduction (i.e., $P_{O_2} \leq 10^{-18}$ atm), $(d\sigma/dT)$ is small throughout the 10-500 K range. Assuming the applicability of Eqn. (2.9), and one mobile electron per La atom, σ for these samples has a magnitude consistent with $\mu_n \cong 1 \text{ cm}^2/\text{V s}$. For comparison, Frederikse and Hosler (188) deduced $\mu_n \cong 5 \text{ cm}^2/\text{V s}$ for their lanthanum-doped single crystal samples.

It could well be that the bulk value of the "mean μ_n " rises substantially on cooling below 300 K, for the "weakly doped" samples of $[La] = 1.7 \times 10^{19} \text{ cm}^{-3}$. Such a rise of μ_n was seen in the single crystal work (188). For these ceramic samples, that tendency would

be at least partly offset by the influence of intergranular contacts. Nonetheless, one could reasonably conjecture that (σ/en) itself rises on cooling for these weakly-doped samples. In that case, σ itself falls on cooling only because $n(T)$ has a stronger dependence. If that hypothesis is correct, then the steepness of $n(T)$ is smallest for the samples that were most strongly reduced: $P_{O_2} \leq 10^{-18}$ atm during pre-quench high temperature equilibration.

5.5.3 Dependence of σ on Oxygen Partial Pressure

Figures 5.35-5.36 demonstrate the dependence of σ on P_{O_2} for various concentrations of lanthanum impurities at the temperatures, 300 and 500 K. It was largely on the basis of such figures generated under equilibrium conditions at elevated temperatures ($T \geq 1000$ K), that Balachandran and Eror (238) were able to confirm the defect structure of Eqn. (2.9). They found that the conductivity is largely independent of P_{O_2} for $P_{O_2} \leq 10^{-16}$ atm, and that in the range $1 - 10^{-16}$ atm, $\sigma \propto P_{O_2}^{-1/m}$, with m scattered between 4.0 and 4.7. A theoretical analysis based on Eqn. (2.9) using the same techniques outlined in Section 2.2.4 leads to the prediction that $m = 4.0$ in this P_{O_2} region.

Table 5.4 shows the values for m determined from linear regression analysis of the data plotted in Figures 5.35-5.36. As indicated in the previous sections, the formation of impurity bands with doping causes the influence of carrier mobility on the conductivity to be substantial after quenching; consequently, the distinctions between the regimes of Eqn. (2.9) for small P_{O_2} and for larger P_{O_2} are less clear-cut, and the parameter m can no longer be readily predicted.

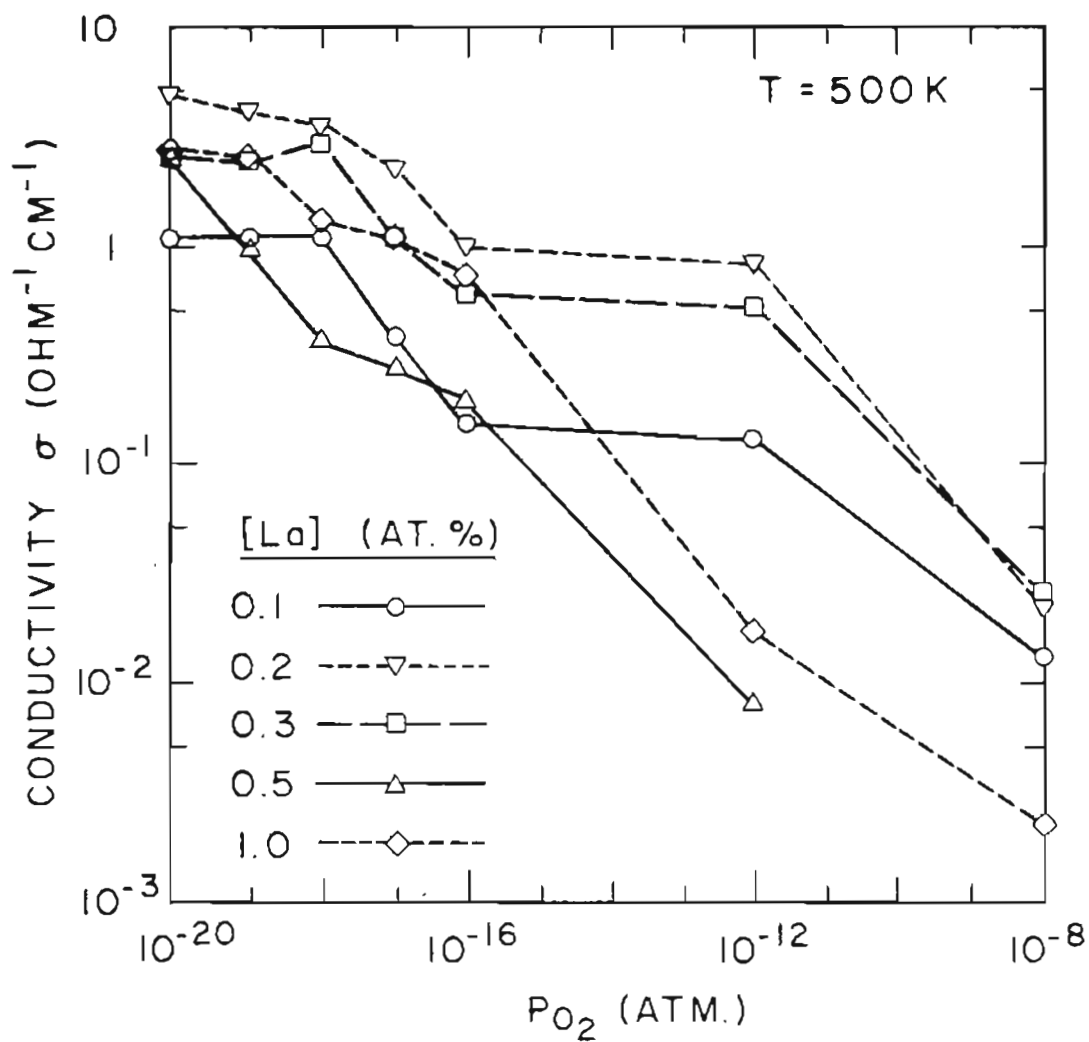


Figure 5.36. Electrical conductivity vs. pre-quench oxygen equilibration pressure for various $[\text{La}]$ at $T = 500 \text{ K}$.

Table 5.4. The Defect Structure Index m , from the equation:
 $\sigma \propto P_{O_2}^{-1/m}$, as derived from slopes of data in Figs.
 5.35-5.36.[†]

{La} Doping Atomic Percent	Defect Structure Index m	
	T = 300 K (Fig. 5.35)	T = 500 K (Fig. 5.36)
0.1	3.5	6.3
0.2	3.3	5.1
0.3	4.0	5.7
0.5	3.5	3.6
1.0	2.8	3.3

[†]Based on linear regression analysis of data for the oxygen partial pressure range $10^{-18} \leq P_{O_2} \leq 10^{-8}$ atm. All samples measured as quenched from 1325 K equilibration.

Nevertheless, selecting $P_{O_2} = 10^{-18}$ atm as the demarcation between the two regimes of Eqn. (2.9) for quenched samples leads to values of m falling between 2.8 and 4.0 at 300 K, and between 3.3 and 6.3 at 500 K. The average value for m taken from all ten curves of Figs. 5.35-5.36 is 4.1, with an average correlation of 0.96 and a standard deviation of 1.0. Considering the complications added by impurity banding and the non-constant mobility term, this is in good agreement with the high temperature results quoted above. This result supports the conclusion that the defect structure found at high temperatures is retained in form upon quenching.

5.6 Spectral Response of Reduced and La-Doped Ceramic $SrTiO_3$

The initial attempts to record the photoconductive response of these materials were accomplished in the traditional fashion, as outlined in Section 4.5. These yielded true spectral response curves for only one sample (undoped $SrTiO_3$ reduced in $P_{O_2} = 10^{-16}$ atm), and at that only for temperatures below about 35 K. Other samples produced only bolometric response curves, and these also required low temperatures.

The fundamental problem in this experimental arrangement (wherein a modulated photovoltage was to be selected out of a large DC background voltage) appeared to be intrinsic to the materials. The fluctuating photovoltage, ΔV , is related to other functional parameters in the following way:

$$\Delta V \propto \Delta n_{th} + \Delta n_{ph} \quad (5.7)$$

where Δn_{th} represents thermally induced charge carriers (bolometric response) and Δn_{ph} represents photo-induced charge carriers. These terms in turn have the following dependencies:

$$\Delta n_{th} \propto d\rho/dT, \kappa \quad (5.8)$$

$$\Delta n_{ph} \propto \alpha, \tau_n \quad (5.9)$$

In the above two relations, ρ is the resistivity, κ the coefficient of lattice heating, α the absorption coefficient, and τ_n the carrier lifetime. In general, $\tau_n \ll \kappa$; hence at moderate chopping frequencies the lattice heating effects can dominate absorption effects and it may be necessary to chop at very high frequencies in order to filter out the heating effects.

The room temperature spectral response measurement technique outlined in Section 4.5 did not suffer from this problem, and good photoconductive scans were obtained for a variety of photoanode materials. Figure 5.37 shows these scans for four of those samples, recorded in a working PEC cell and corrected for instrumentation optical throughput. These show quantum efficiency η (response per incident photon) versus λ , with the logarithmic ordinate scale a relative one. The vertical separations of the four curves have been reduced, but are in the correct order: thus curve (A) is for a weakly responsive anode (undoped SrTiO_3), while samples with $[\text{La}] = 0.5$ and 1.0% as in curves (C) and (D) showed a larger responsivity -

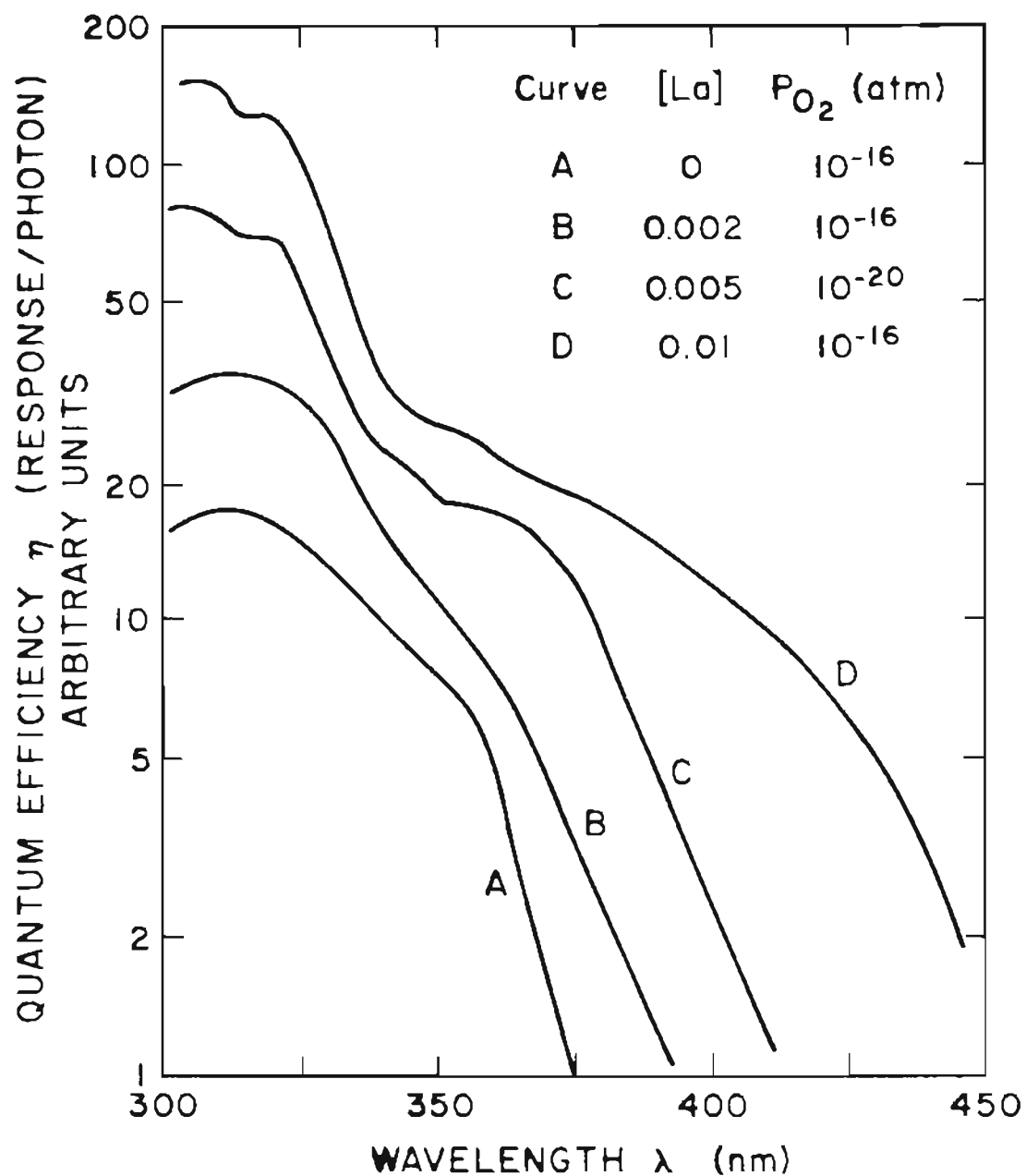


Figure 5.37. Semilogarithmic spectral response plots for four extrinsic SrTiO_3 ceramic samples, as identified above for doping and reduction state, measured in 1M NaOH PEC. The curves have been moved closer together than their actual responsivities would have placed them, to make the figure more compact.

as well as an extended spectral response.

The dark conductivity of La:SrTiO₃ through the temperature range 10-500 K was found to be maximized for [La] = 0.2%. This was attributed to the formation of a donor impurity band, with significant overlap occurring with the conduction band for [La] $\approx$ 0.3%. That interpretation of dark conductivity data is supported by the change of spectral response with doping illustrated by the various curves of Fig. 5.37.

Thus curve (A) shows the characteristic spectral response of undoped SrTiO₃ that has been sufficiently reduced to provide enough dark conductivity in the bulk for facilitation of the measurement. The quantum efficiency η falls off rapidly for $h\nu < 3.5$ eV ($\lambda > 355$ nm), as the actual "edge" of intrinsic transitions is approached.

Koffyberg et al. (352) and Dwight and Wold (89) have both analyzed comparable data for the rapid fall-off of responsivity with decreasing $h\nu$ for monocrystal SrTiO₃, using a (quite) simplified form of the expression (47) appropriate for an indirect (phonon-aided) transition. Thus if one assumes that $\eta \approx (A/h\nu)(h\nu - E_g)^2$, then E_g is obtained as the intercept in a plot of $(\eta h\nu)^{1/2}$ versus $h\nu$. In this way, Koffyberg et al. deduced $E_g = 3.21$ eV, and Dwight and Wold reported $E_g = 3.2$ eV ($\lambda_g \approx 388$ nm). A similar value is obtainable with the comparable plot for the undoped ceramic sample of Curve (A). The shorter-wave length features of curve (A) [i.e., the decrease of slope at 355 nm (3.5 eV), and the maximum near 310 nm (4.0 eV)] both correspond to those features as seen by Dwight and Wold (89) for un-

doped single crystal material.

Several differences are apparent between curves (A) and (B). It is important to keep in perspective those arising from lanthanum doping ($[La] = 0.2\%$), ones influenced by the oxygen defect chemistry [$P_{O_2} = 10^{-16}$ atm for the samples of both curves (A) and (B)], and those influenced by other variables: mean crystallite size, and the granule surface characteristics. Thus, compared with curve (A), one can say of curve (B) that:-

- (i) The overall responsivity is larger for all wavelengths.
- (ii) The quantum efficiency changes more between 310 and 355 nm.
- (iii) The "edge" region for $\lambda > 355$ nm is less steep, and extrapolates to an E_g some 0.1 eV smaller.

That small evidence of gap reduction is greatly amplified by the spectral curves for samples (C) and (D), with their stronger lanthanum doping, and is consistent with electrical conductivity data presented previously concerning the formation of an impurity band, which merges with the conduction band and provides a low energy tail to that band.

Thus curve (C), compared with curve (B), shows a distinct extension of the long wavelength response, with a perceptible structure at the spectral location ($h\nu \cong 3.37$ eV, $\lambda \cong 368$ nm) where Dwight and Wold (89) had speculated about one of the indirect thresholds. For longer wavelengths, the quantum efficiency of curve (C) has an exponential slope similar to that in curve (B). However, the more heavily doped sample of curve (D) ($[La] = 1.0\%$) shows a large extension of the long-wave response, still detectable at 440 nm (2.8 eV).

One may note also that separate maxima near 310 nm (4.0 eV) and 320 nm (3.9 eV) are apparent for both curves (C) and (D) of Fig. 5.37. Koffyberg et al. (352) and Dwight and Wold (89) both inferred a direct gap for SrTiO_3 between 3.7 and 3.8 eV, and one can expect the optical absorption coefficient α to exceed 10^4 cm^{-1} for shorter wavelengths. One might expect some maximization of the quantum efficiency for a ceramic sample when the optical penetration depth α^{-1} is comparable with the average particle radius ($\sim 0.2 \text{ }\mu\text{m}$), provided that minority carriers can have a diffusion length at least this large, even for strong doping.

5.7 Photoactivity of Extrinsic Ceramic SrTiO_3

Figure 5.38 shows 300 K data of photocurrent density J versus any applied bias V , for microcrystalline ceramic $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ photoanodes in aqueous electrolytes of various pH. Each of the photoanodes for Fig. 5.38 had been strongly reduced ($P_{\text{O}_2} = 10^{-20}$ atm at 1325 K) and quenched.

The trend shown in parts (A) and (B) of Fig. 5.38, that photoactivity is most pronounced for a high pH electrolyte in both undoped SrTiO_3 and 1% La-doped material, was found also to be the case for other doping strengths and reduction conditions. This is also in agreement with previous work (103,244-245) on single crystal SrTiO_3 (see Section 2.1.8). Accordingly, almost all subsequent PEC cell tests used a 1M NaOH electrolyte.

The two parts of Fig. 5.38 have very different ordinate scales, so that part (B) could show the large photocurrent resulting from

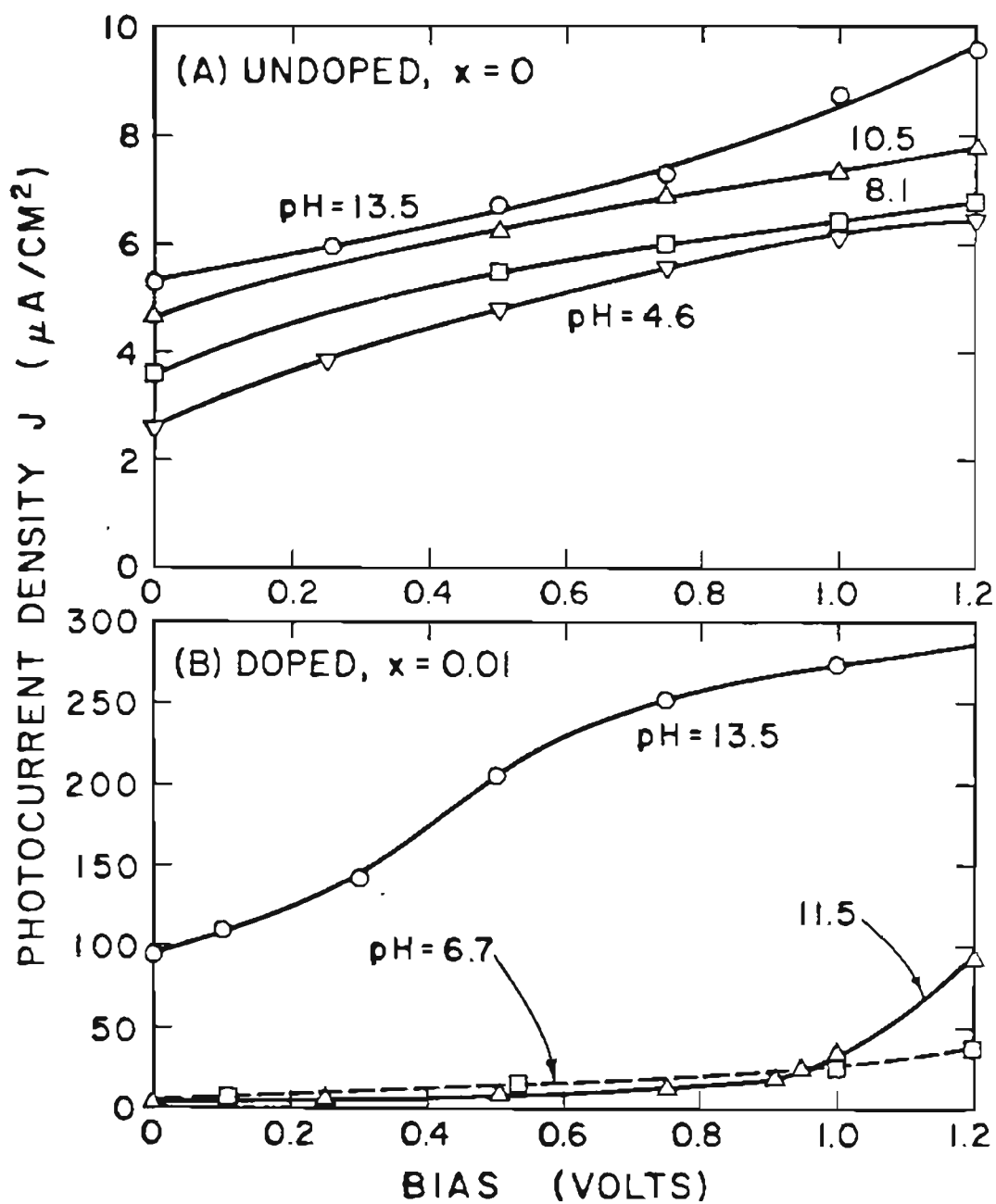


Figure 5.38. Photocurrent density J ($\mu\text{A}/\text{cm}^2$) versus applied bias for PEC_{26} cells using ceramic photoanodes reduced in $\text{P}(\text{O}_2) = 10^{-20}$ atm, and aqueous electrolytes of various pH. (A) Undoped SrTiO_3 . (B) $\text{La}(1\%)\text{SrTiO}_3$. (AM2 illumination).

external bias to a PEC cell with a strongly basic electrolyte, and a strongly-doped, strongly-reduced photoanode. This should not obscure the experimental observation of zero-bias photocurrent densities of from 2.5 to 95 $\mu\text{A}/\text{cm}^2$ for variously prepared photoanodes and electrolytes under AM2 illumination.

All photoanode materials reported on here were reduced by a 1325 K equilibration under conditions in the range $10^{-20} \leq P_{\text{O}_2} \leq 10^{-16}$ atm prior to quenching. Figures 5.39-5.41 illustrate the dependence of the illuminated J - V characteristic (in 1M NaOH electrolyte) on lanthanum doping strength for this reduction range. For the strongest reduction, $P_{\text{O}_2} = 10^{-20}$ atm, Fig. 5.41 shows a monotonic increase of photoactivity with doping. This contrasts with the situation in Figs. 5.39-5.40, for less severe reduction ($P_{\text{O}_2} = 10^{-16}$ and 10^{-18} atm, respectively).

That contrast is not incongruous, since the defect chemistry of quenched $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ has been shown (234,353) to change form within the reduction range $10^{-20} \leq P_{\text{O}_2} \leq 10^{-16}$ atm. At the upper end of that P_{O_2} range, the lattice contains excess oxygen, has Sr vacancies in the perovskite cells, and parts of SrO planes interleaving those perovskite units. For more severe reduction, the oxygen content is forced back to stoichiometry, lanthanum incorporation promotes $\text{Ti}^{\text{IV}} \rightarrow \text{Ti}^{\text{III}}$ (controlled-valency mechanism), and an extra electron from donor doping can become available for conduction. High temperature (234) and low temperature conductivity measurements indicate that this requires $P_{\text{O}_2} < 10^{-18}$ atm for the 1325 K equili-

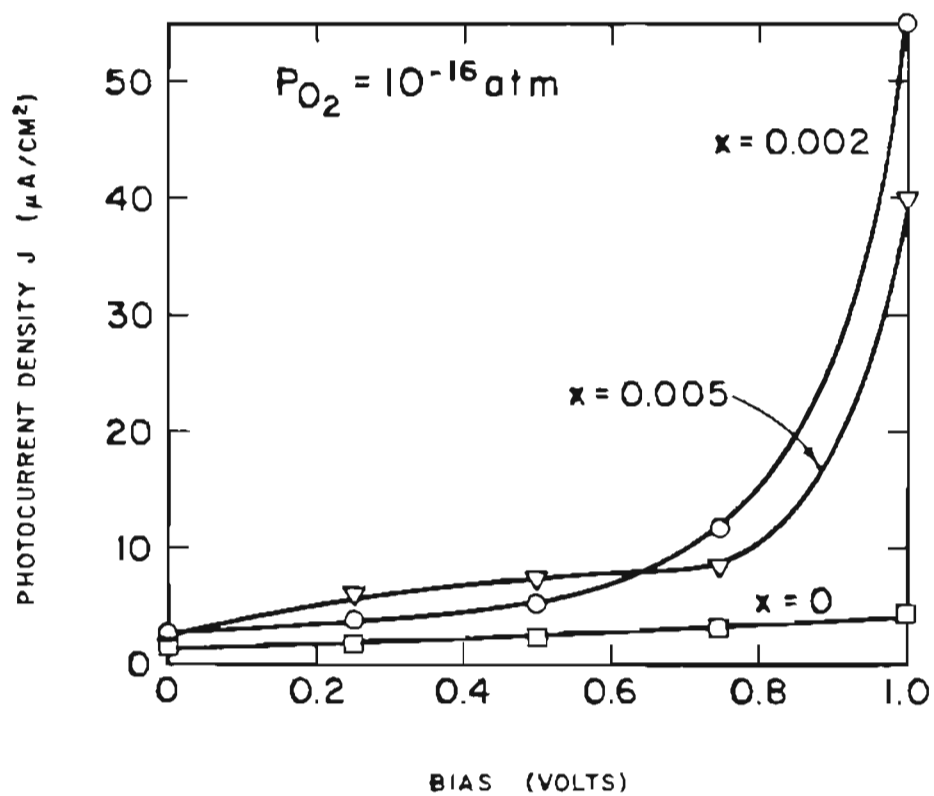


Figure 5.39. Photocurrent density versus applied bias for ceramic $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ photoanodes reduced at $P_{\text{O}_2} = 10^{-16} \text{ atm}$, in 1M NaOH PEC cells under AM2 illumination.

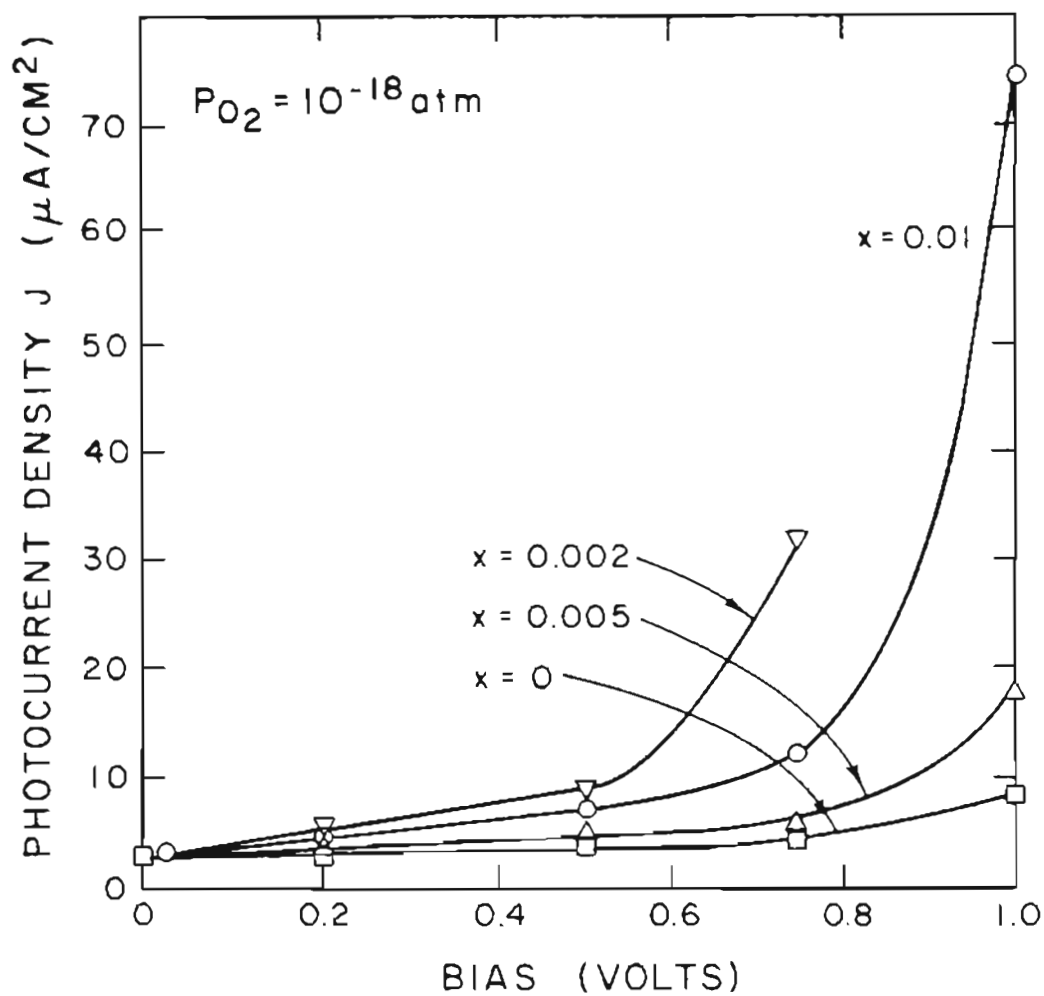


Figure 5.40. Photocurrent density versus applied bias for ceramic $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ photoanodes reduced at $P_{\text{O}_2} = 10^{-18} \text{ atm}$, in 1M NaOH PEC cells under AM2 illumination.

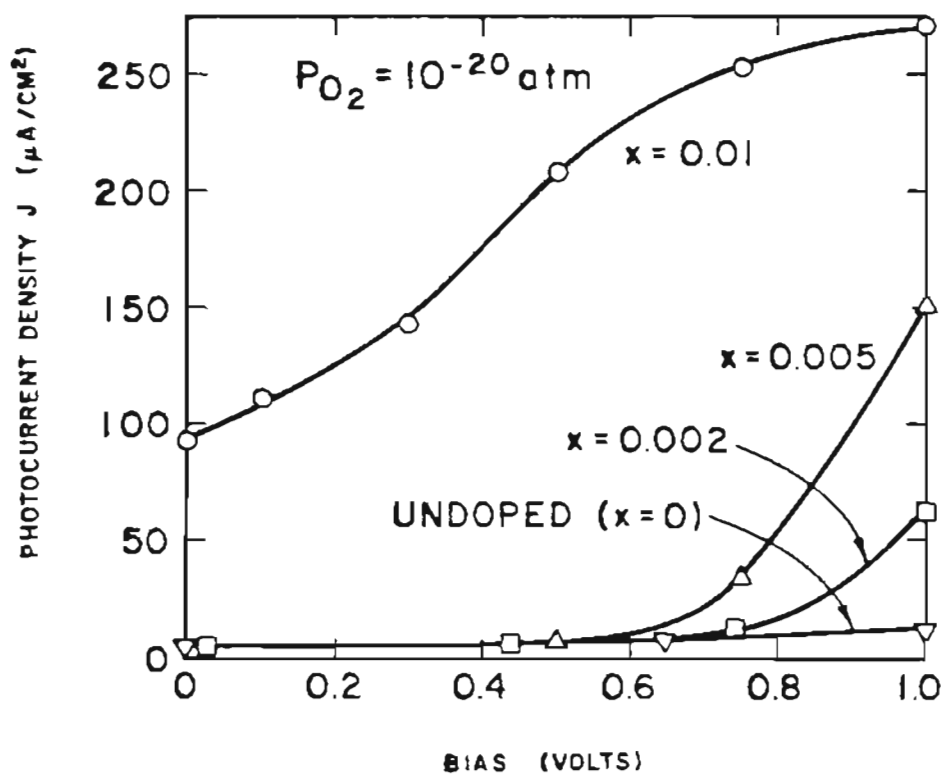


Figure 5.41. Photocurrent density versus applied bias for ceramic $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ photoanodes reduced at $P_{\text{O}_2} = 10^{-20} \text{ atm}$, in 1M NaOH PEC cells under AM2 illumination.

bration, a conclusion supported by Figs. 5.39-5.41.

In order to maximize the useful photoactivity of a material, it is desirable to minimize the optical bandgap, while at the same time allowing efficient separation of charge carriers within the depletion region. The latter is controlled by V_{fb} of the material, in the solution to be used. It is also important that the dark bulk conductivity be large enough not to detract from the expectation of a high quantum efficiency. As pointed in the Introduction, there must additionally be a mechanism by which photo-generated holes can communicate with the appropriate species in the electrolyte. This is presumably accomplished via surface states with energies in the semiconductor bandgap (see Section 2.1.4).

As has been shown, the conductivity itself is maximized by moderate doping ($[La] \cong 0.2\%$), and the room temperature conductivity is some ten times smaller for $[La] = 1.0\%$. On the other hand, extension of the spectral response is accomplished by lanthanum doping up to 1%. These competing effects are best reconciled by use of heavy doping and quenching from a fully reduced state - since reduction assists σ_{300} for a given $[La]$ until exhaustion is reached. This is confirmed by the performance of $La_{0.01}Sr_{0.99}TiO_3$ reduced at $P_{O_2} = 10^{-20}$ atm, as epitomized by the curves in Figs. 5.38 (B) and 5.41. Hence the decrease of the optical bandgap brought about by the impurity band tail overcomes the deleterious effect that impurity band-scattering has on the electron mobility.

Figures 5.42 and 5.43, and Table 5.5, address the question of electrode stability. Figure 5.42 shows the dark electrical conductance (expressed as the equivalent bulk conductivity in $\text{ohm}^{-1} \text{cm}^{-1}$ of homogeneous material) for $\text{La}_{0.002}\text{Sr}_{0.998}\text{TiO}_3$ that was quenched from $P_{\text{O}_2} = 10^{-20}$ atm equilibration. Curve (A) in Fig. 5.42 shows $\log(\sigma)$ versus $100/T$ over the range 10-300 K for this material as quenched. Curve (B) displays the conductance (expressed as equivalent conductivity) for a similarly prepared sample that was then operated in a PEC cell for 13.6 hours, using 1M NaOH electrolyte and AM2 illumination. It can be seen that this operation in a cell has lowered the conductance, by a factor of some 3:1 for the higher temperatures, and by some 5:1 for low temperatures. Curve (C) is for the same sample as in curve (B), but after a second high temperature equilibration/reduction/quench sequence. Note that the room temperature conductivity has been restored to essentially the original value, though this is not so for low temperatures.

The tests illustrated in Fig. 5.42 are not perfectly quantitative, since all three curves could not be obtained with the identical sample. Moreover, sample cleaning after PEC cell use (30 minute ultrasonic bath in 37% HCl, and running deionized water rinse) may not have removed all of the indium and silver contact material. Subsequent reduction at 1325 K could then have allowed in-diffusion of these impurities, where they would serve as acceptors, and reduce especially the low temperature conductivity. Thus the most interesting aspect of Fig. 5.42 is that, despite that source of po-

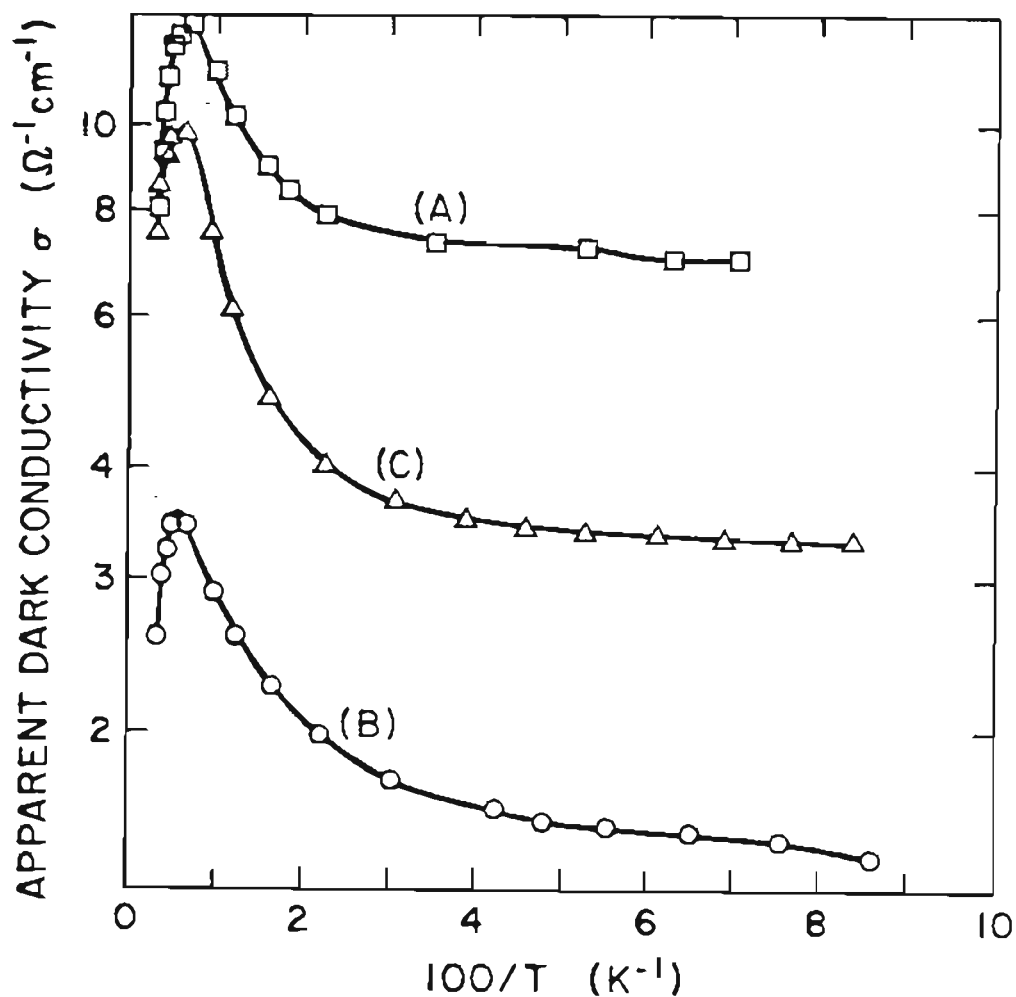
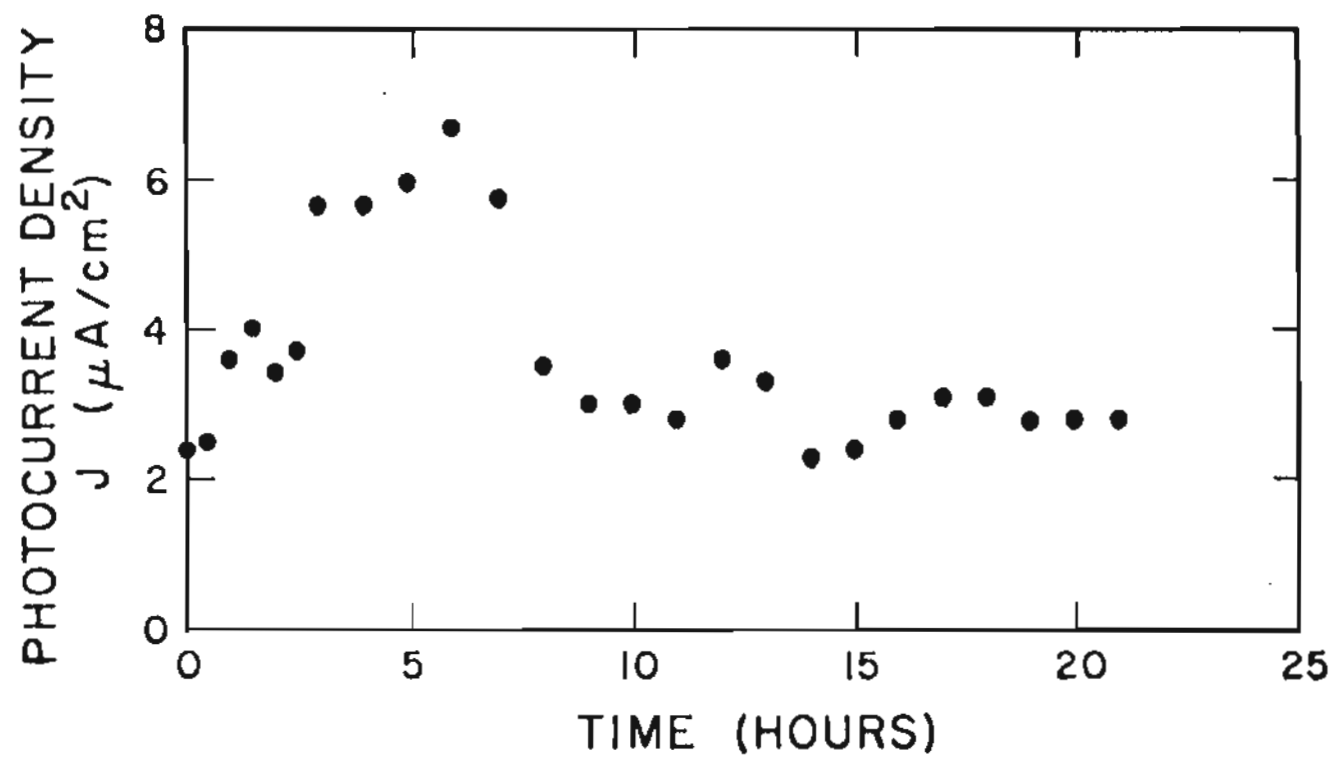


Figure 5.42. Electrical conductance (expressed as equivalent to bulk conductivity for homogeneous material), versus reciprocal temperature for ceramic $\text{La}(0.2\%)\text{SrTiO}_3$ reduced at $P_{\text{O}_2} = 10^{-20}$ atm. (A) Material as prepared, reduced and quenched. (B) Material similarly prepared, after preparation in PEC cell at AM2 illumination and 1M NaOH electrolyte for 13.6 hours. (C) The sample of curve (B), after a re-reduction at 1325 K with $P_{\text{O}_2} = 10^{-20}$ atm.

Table 5.5. A comparison of 300 K conductance (expressed as apparent bulk conductivity) for samples before and after use as a photoanode in a PEC cell.

Material Preparation		Time in PEC Cell (hours)	Apparent Bulk Conductivity σ_{300} ($\Omega^{-1} \text{ cm}^{-1}$)		Comments
La Doping x	Reduction P_{O_2} (atm)		Before	After	
0.002	10^{-18}	12.3	6.0	1.8	Different Samples
0.002	10^{-20}	13.6	8.5	2.6	" "
0.005	10^{-18}	27.6	0.56	0.48	Identical Sample
0.005	10^{-20}	49.1	0.66	0.50	" "
0.01	10^{-18}	28.4	0.64	0.73	Different Samples
0.01	10^{-20}	20.8	1.3	1.7	" "

Figure 5.43. Photocurrent density versus time of illumination (at AM2) for undoped ceramic SrTiO_3 , reduced in $P_{\text{O}_2} = 10^{-16}$ atm, in 1M NaOH.



tential contamination, re-reduction did restore the room temperature conductivity to almost its original value.

Thus electrode photo-oxidation may be occurring to some extent, but as a reversible process. Similar tests done with more strongly doped $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ anodes showed an interesting reversal of the trend. Table 5.5 gives values for the apparent σ_{300} of six representative doped samples, before and after PEC cell operation. Note that samples doped with $x = 0.005$ show a quite small drop in conductance after operation in a cell, while samples doped with $x = 0.01$ actually show a small conductance increase. This suggests that photo-oxidation may occur only for weakly doped material, and may be precluded for $[\text{La}] \geq 0.5\%$. That is indeed fortuitous, in the light of the finding that strong doping is advantageous for optimizing the quantum efficiency and the spectral response.

Figure 5.43 plots photocurrent versus time for a ceramic photoanode. These data happen to be for undoped SrTiO_3 reduced in $P_{\text{O}_2} = 10^{-16}$ atm; one of the less responsive samples. The figure shows that zero-bias photocurrent for AM2 illumination tends to rise to a maximum after some 4 to 6 hours, followed by a fairly rapid decline to a steady level. No further change in performance was observed out to 22 hours of operation.

Various other photoanodes have been monitored for periods of from 12 to 50 hours of simulated solar illumination, and showed only modest changes in photoactivity, mostly less prominent than those in Fig. 5.43. Visual and microscopic examination showed no apparent

changes, supporting an interpretation that SrTiO_3 and $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ in reduced ceramic form are stable to photodecomposition in 1M NaOH.

5.8 Electrical Conductivity in Extrinsic TiO_2

Figures 5.44-5.49 are log-log plots of σ versus T for Ta-doped ceramic TiO_2 samples in the temperature range 10-500 K, with doping levels ranging from 0.1-4.0 at.%, and for six different high temperature (1325 K) reducing conditions ($10^{-20} \leq p_{\text{O}_2} \leq 10^{-8}$ atm). Figure 5.50 is a similar plot for the same six reduction states of undoped, polycrystalline TiO_2 . The results for the undoped, single crystal samples are shown in Figure 5.51, for four reduction states in the range $10^{-12} \leq p_{\text{O}_2} \leq 10^{-20}$ atm.

Log-log plots are again used to give a more balanced representation of the conductivity data throughout the full temperature range under investigation.

As can be seen by comparing Figs. 5.44-5.46 (high temperature equilibration at $p_{\text{O}_2} = 10^{-8}, 10^{-12}, 10^{-16}$ atm) with Figs. 5.48-5.49, the sensitivity of σ to doping level diminishes drastically with reduction. For $p_{\text{O}_2} \leq 10^{-16}$ atm, it can be seen that σ increases slowly with $[\text{Ta}]$ in the range $0.1\% \leq [\text{Ta}] \leq 4\%$. On the other hand, for $p_{\text{O}_2} > 10^{-18}$ atm it becomes difficult to distinguish the curves for TiO_2 from those for $\text{Ta}(0.1\%)\text{TiO}_2$. Figure 5.48 includes the curve obtained for a lightly Nb-doped ($[\text{Nb}] = 0.05\%$) sample for comparison.

Noting that a doping level of $[\text{Ta}_{\text{Ti}}] = 0.1\%$ corresponds to $[\text{Ta}] \approx 3.3 \times 10^{19} \text{ cm}^{-3}$, and that these are shallow donors ($E_a < 0.2 \text{ eV}$;

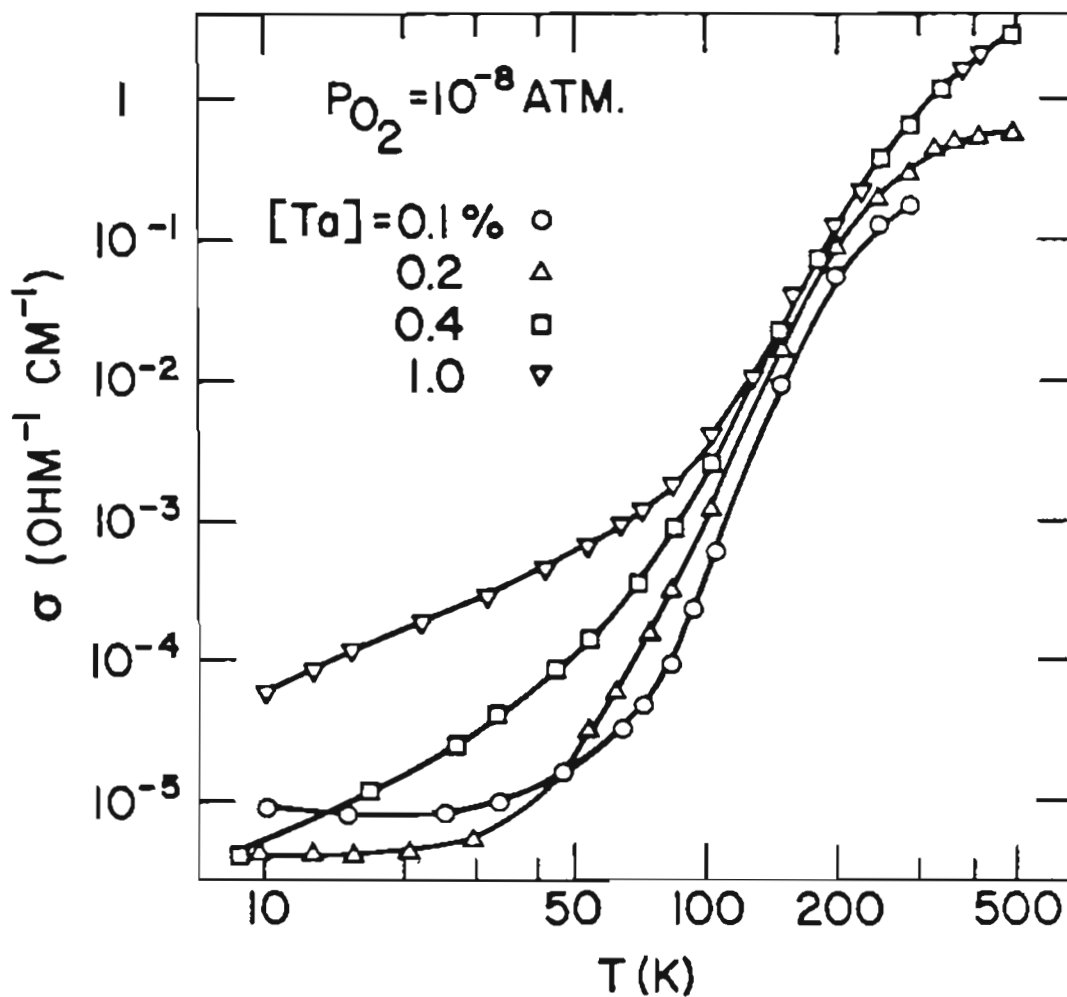


Figure 5.44. Electrical conductivity versus temperature over the range 10-500 K for Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

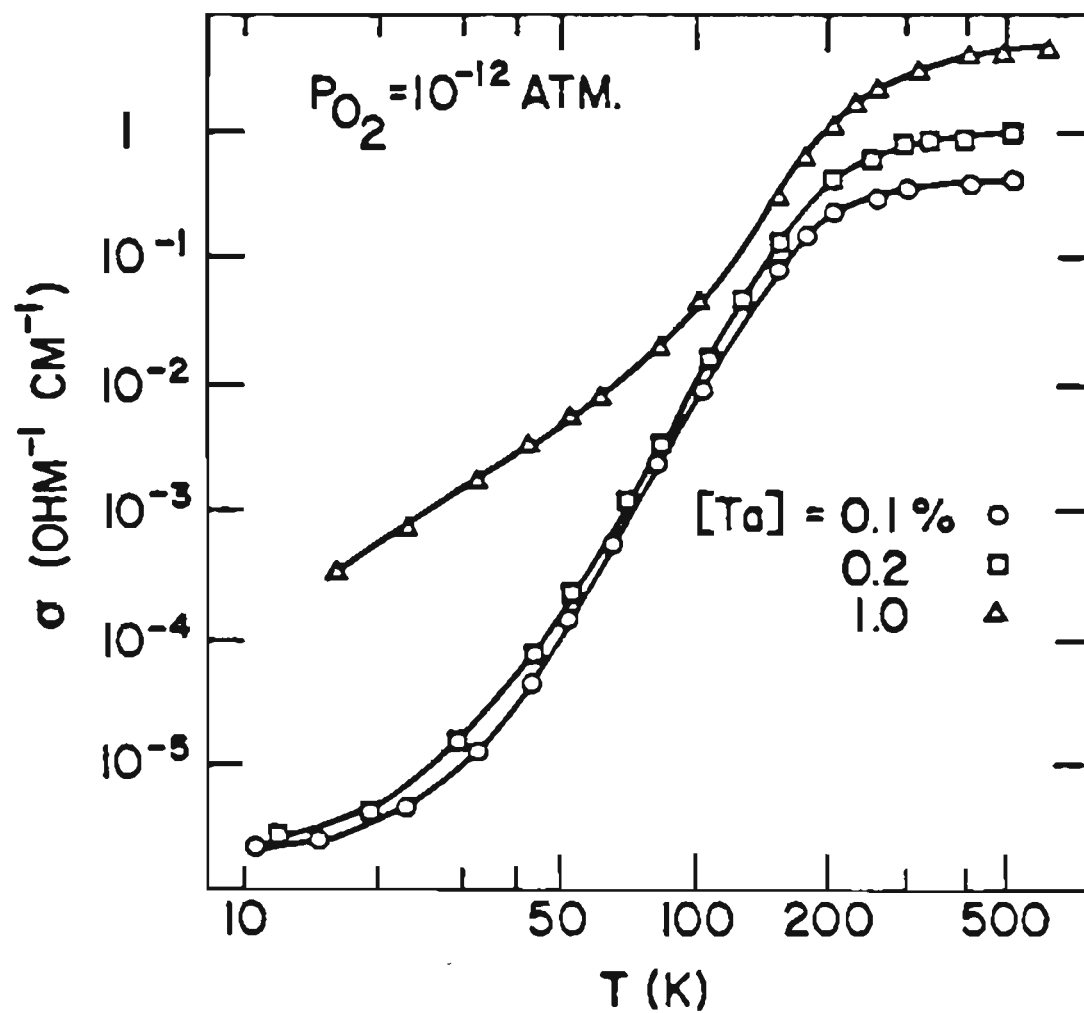


Figure 5.45. Electrical conductivity versus temperature over the range 10-500 K for Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

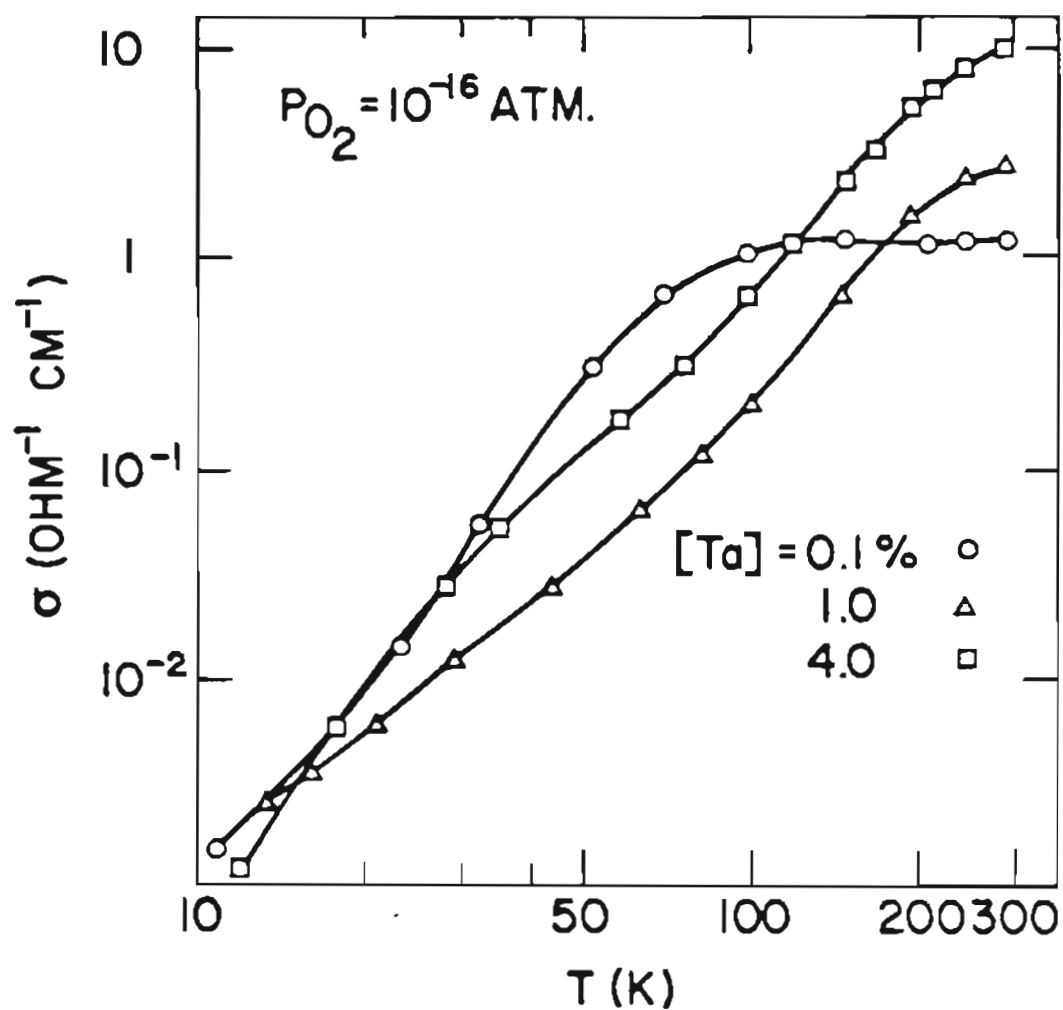


Figure 5.46. Electrical conductivity versus temperature over the range 10-300 K for Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

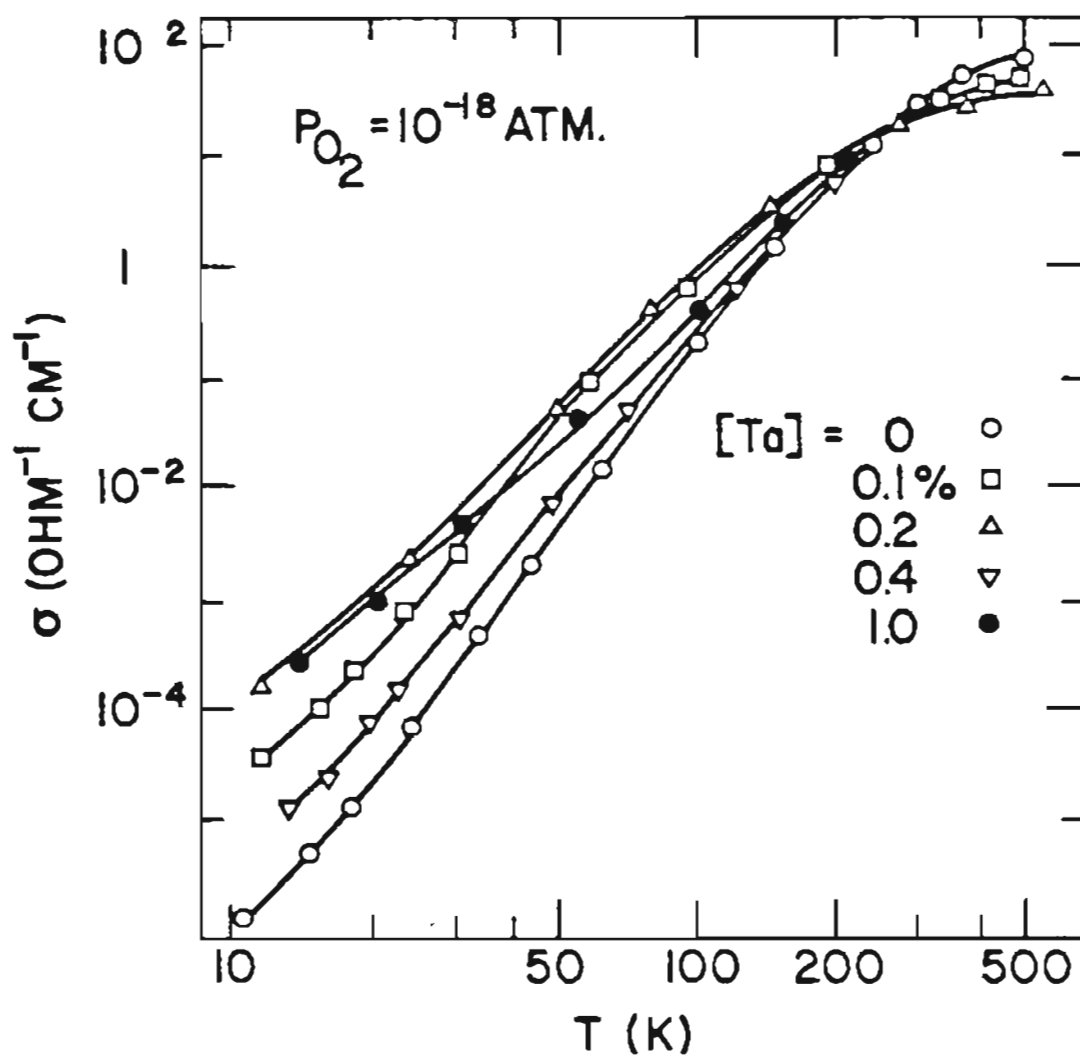


Figure 5.47. Electrical conductivity versus temperature over the range 10–500 K for undoped and Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

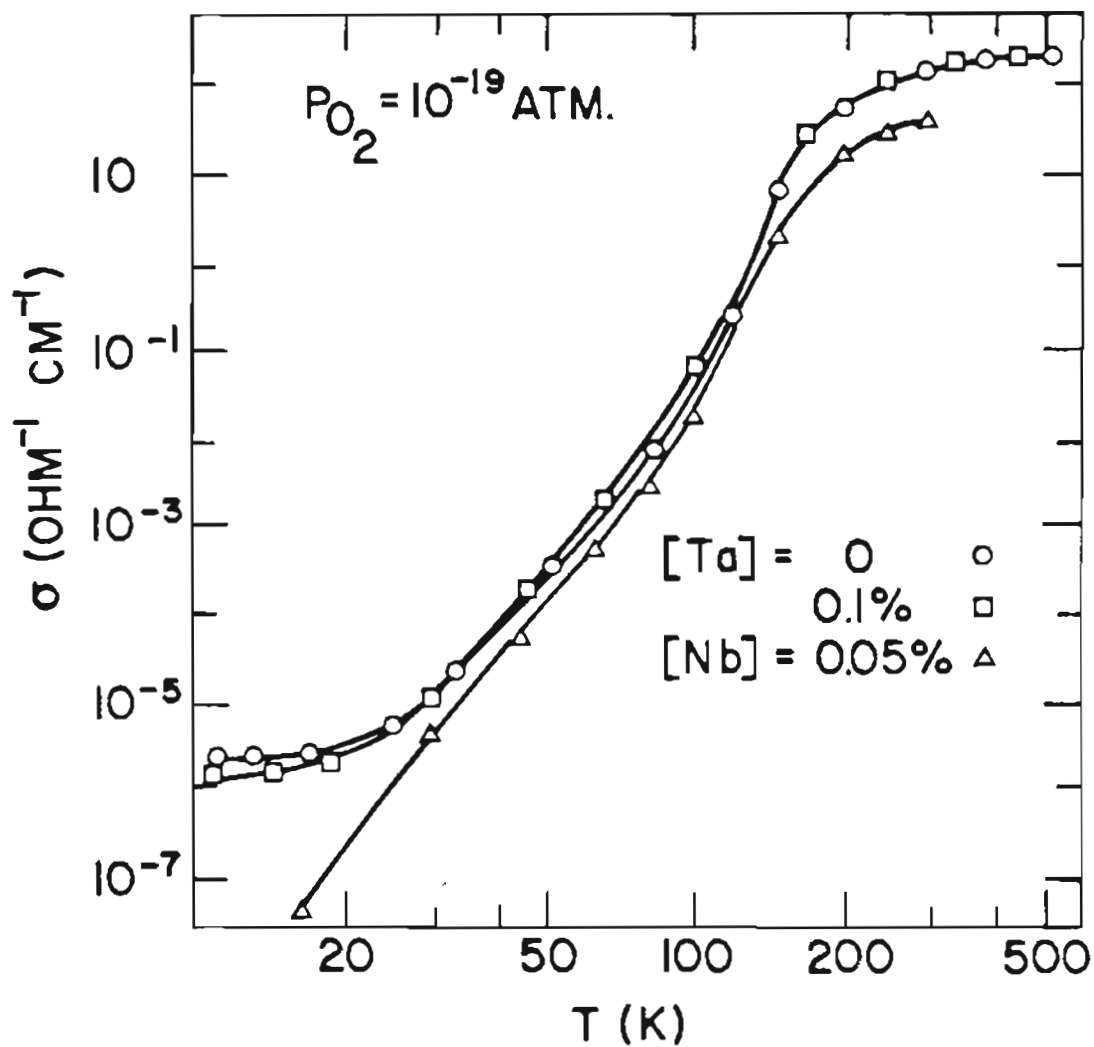


Figure 5.48. Electrical conductivity versus temperature over the range 10-500 K for undoped, Ta- and Nb-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

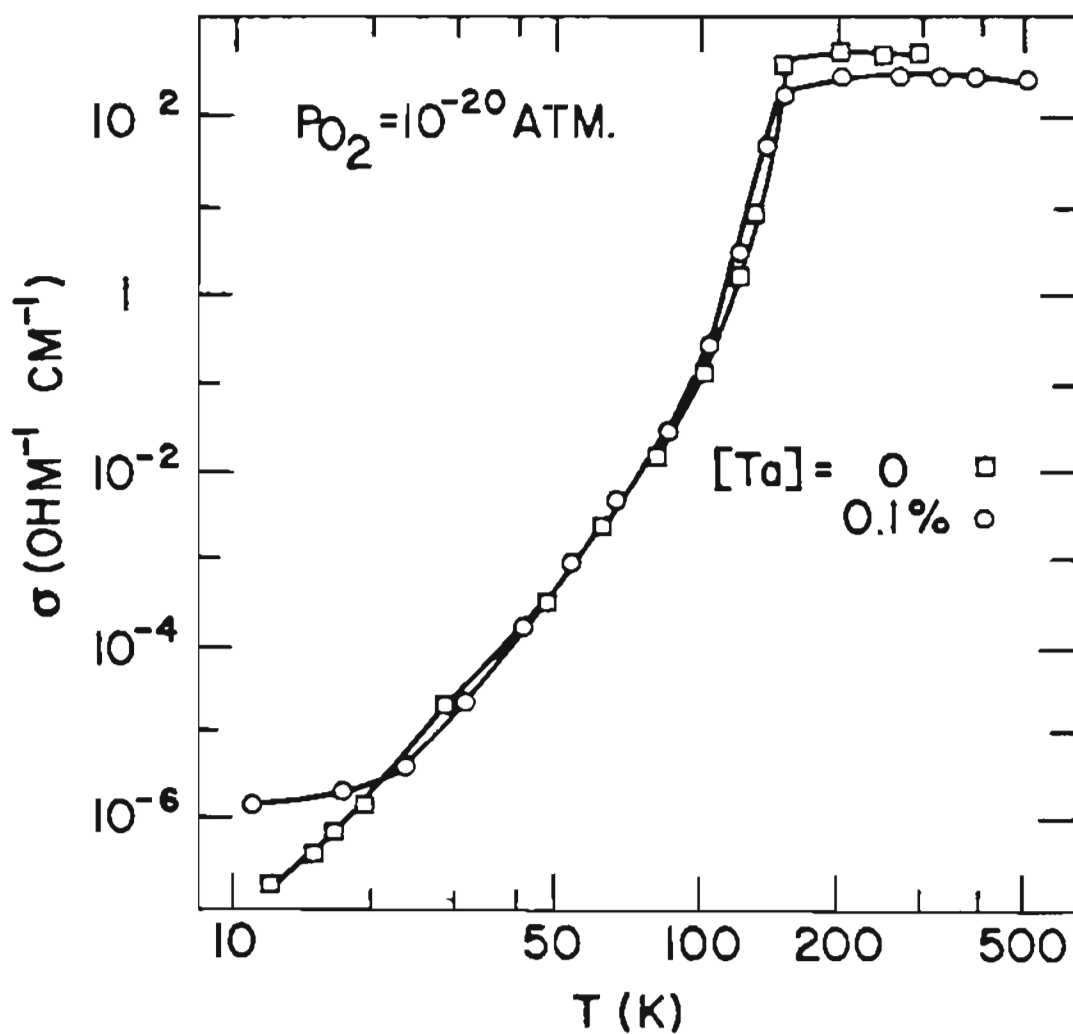


Figure 5.49. Electrical conductivity versus temperature over the range 10–500 K for undoped and Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

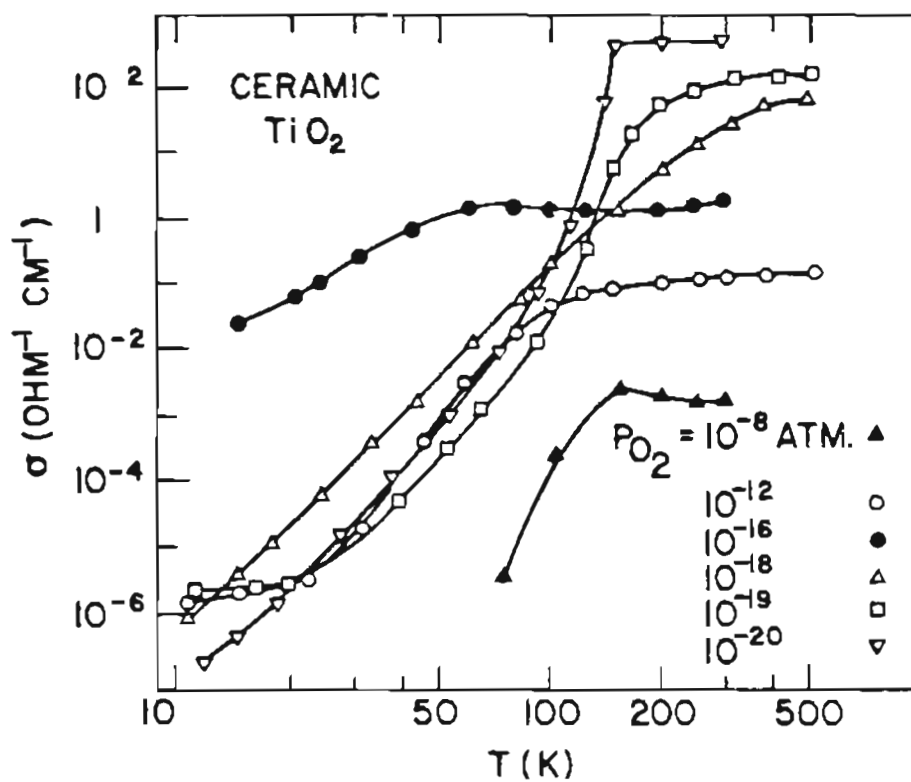


Figure 5.50. Electrical conductivity versus temperature over the range 10-500 K for undoped, ceramic TiO_2 , after high temperature equilibration to six different reducing environments.

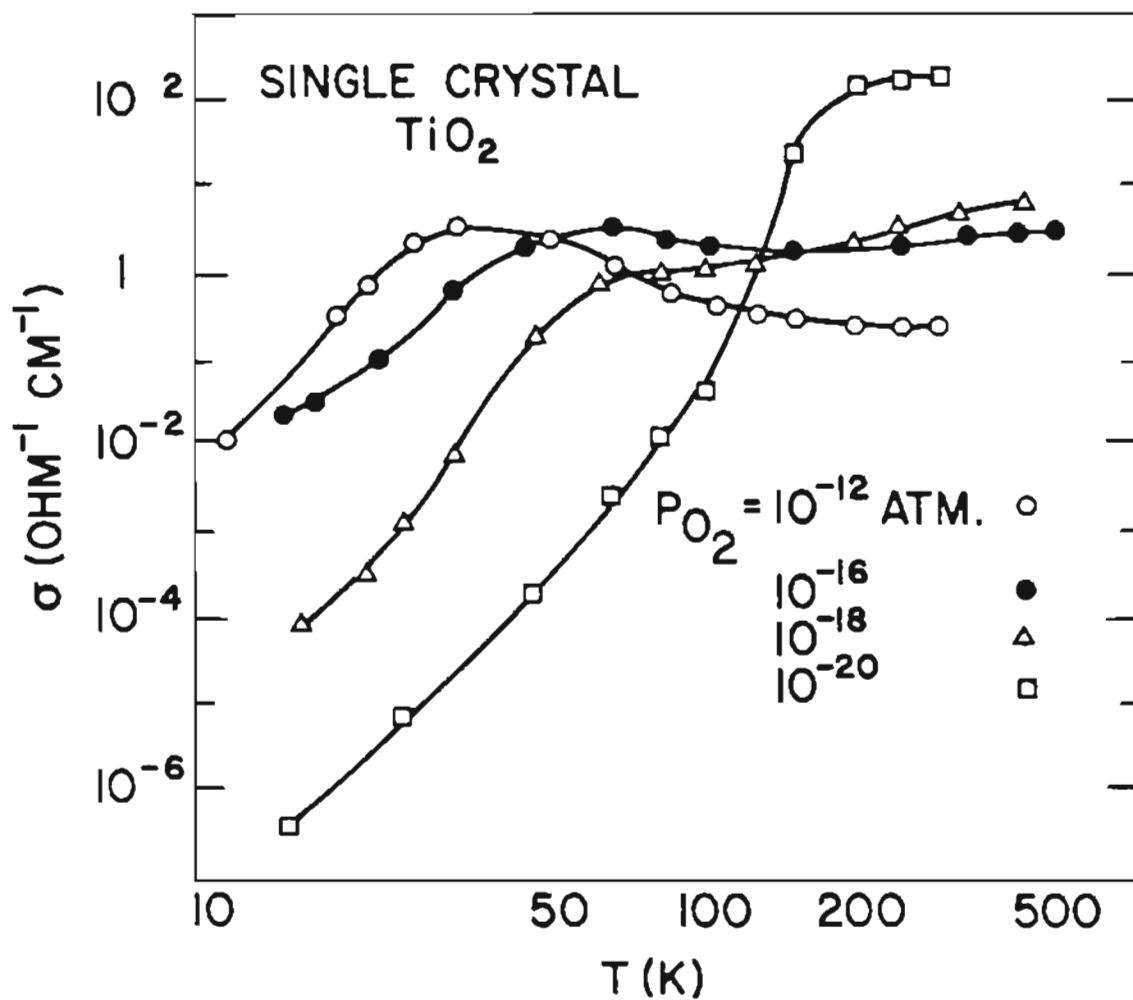


Figure 5.51. Electrical conductivity versus temperature over the range 10-500 K for undoped, single crystal TiO_2 , after high temperature equilibration to four different reducing environments.

see below), it can be concluded that high temperature reduction produces anion-deficiency-related donor defects quite efficiently, such that $n \approx 10^{19} \text{ cm}^{-3}$ is readily obtainable.

Figures 5.52-5.59 reproduce these conductivity data in Arrhenius ($\log[\sigma]$ vs. $1/T$) form. In these figures it can be seen that activated transport regions occur in the mid-temperature range (generally subsequent to a local conductivity maxima), often followed by a region characterized by thermal stability down to 10 K. These activation energies tend to increase with reduction and, to a lesser extent, with doping, as can be seen by examining Table 5.6.

An interesting difference between the behavior of polycrystalline TiO_2 and single crystal TiO_2 can be seen in Figures 5.58-5.59. Figure 5.59 clearly demonstrates the existence of a local maximum in σ for the single crystal samples, and that this maxima occurs at increasing temperature as the sample reduction (and hence n) is increased. This behavior is seen in Fig. 5.58 for only one ceramic sample. Furthermore, E_a is seen to increase uniformly with reduction for monocrystalline materials, but not for their ceramic counterparts. It appears that the rate of thermal quenching of defect-related charge carriers in TiO_2 is dependent not only on point defect concentration (and hence n for single crystal material), but also very much so on the concentrations of extended defects (such as grain boundaries). These two types of defects can interact, leading to complex electronic properties such as those depicted in Fig. 5.58. This is not unexpected, as anion-deficiency-related point defects

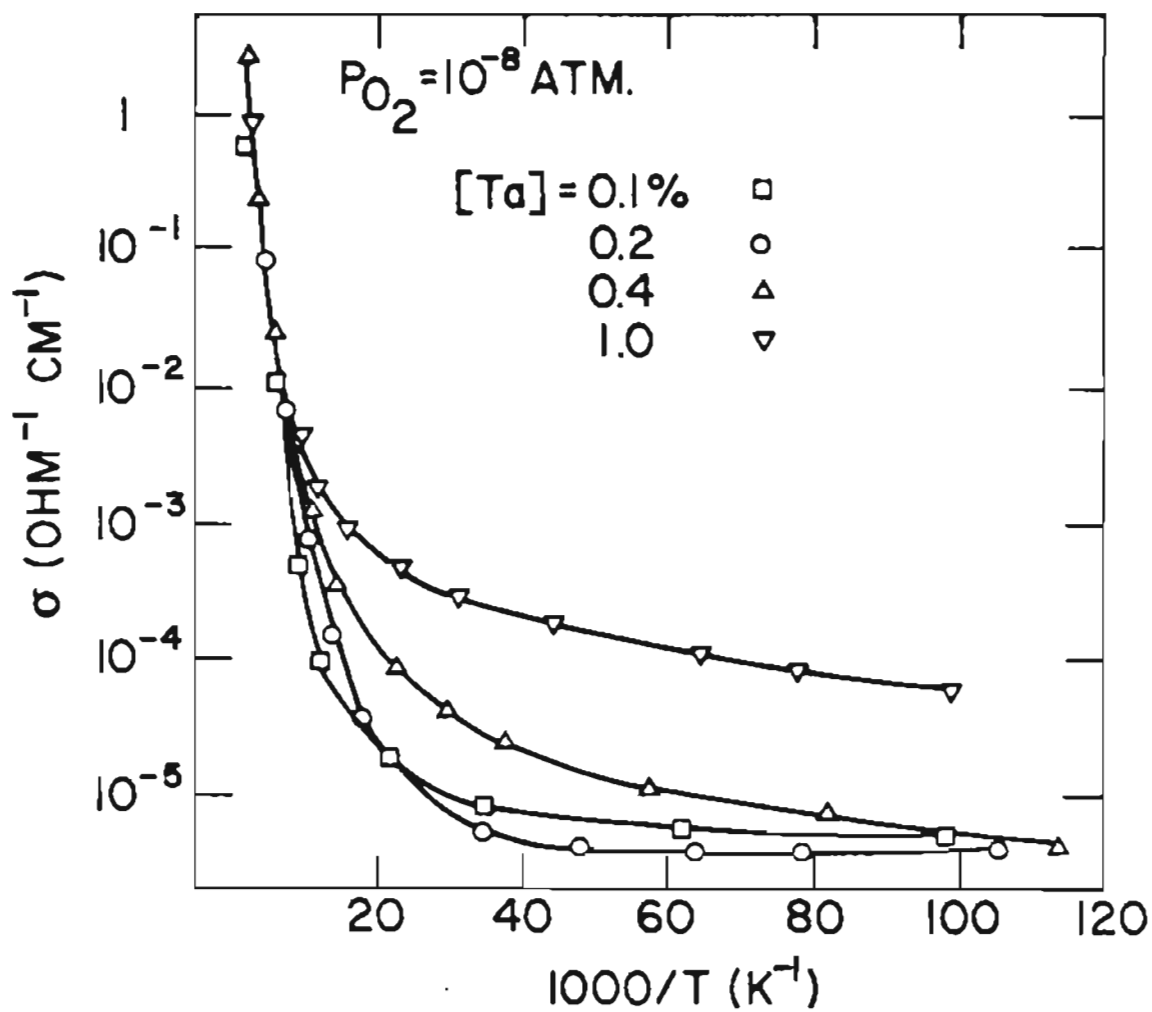


Figure 5.52. Plot of $\log(\sigma)$ versus $1000/T$ for Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

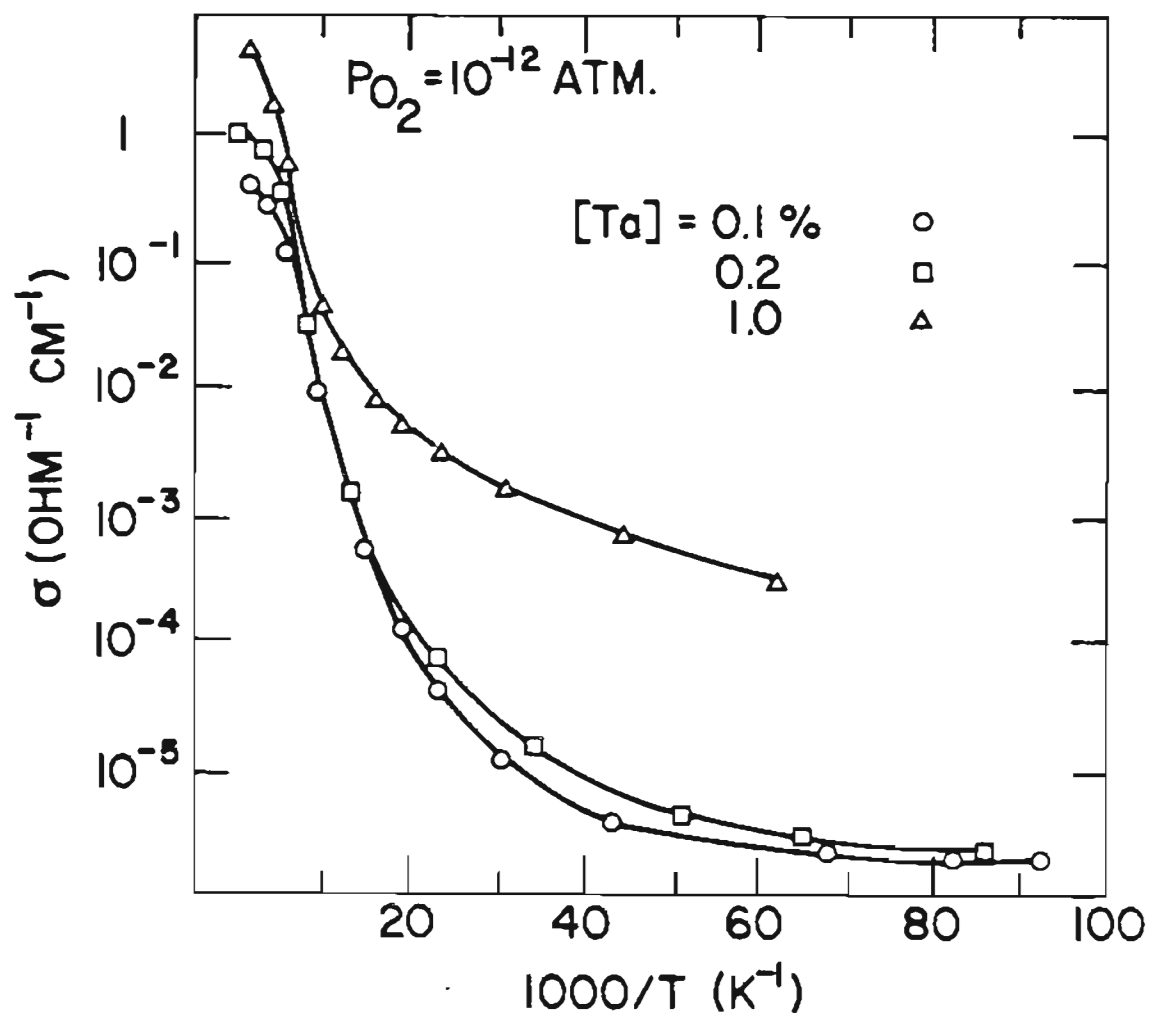


Figure 5.53. Plot of $\log(\sigma)$ versus $1000/T$ for Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

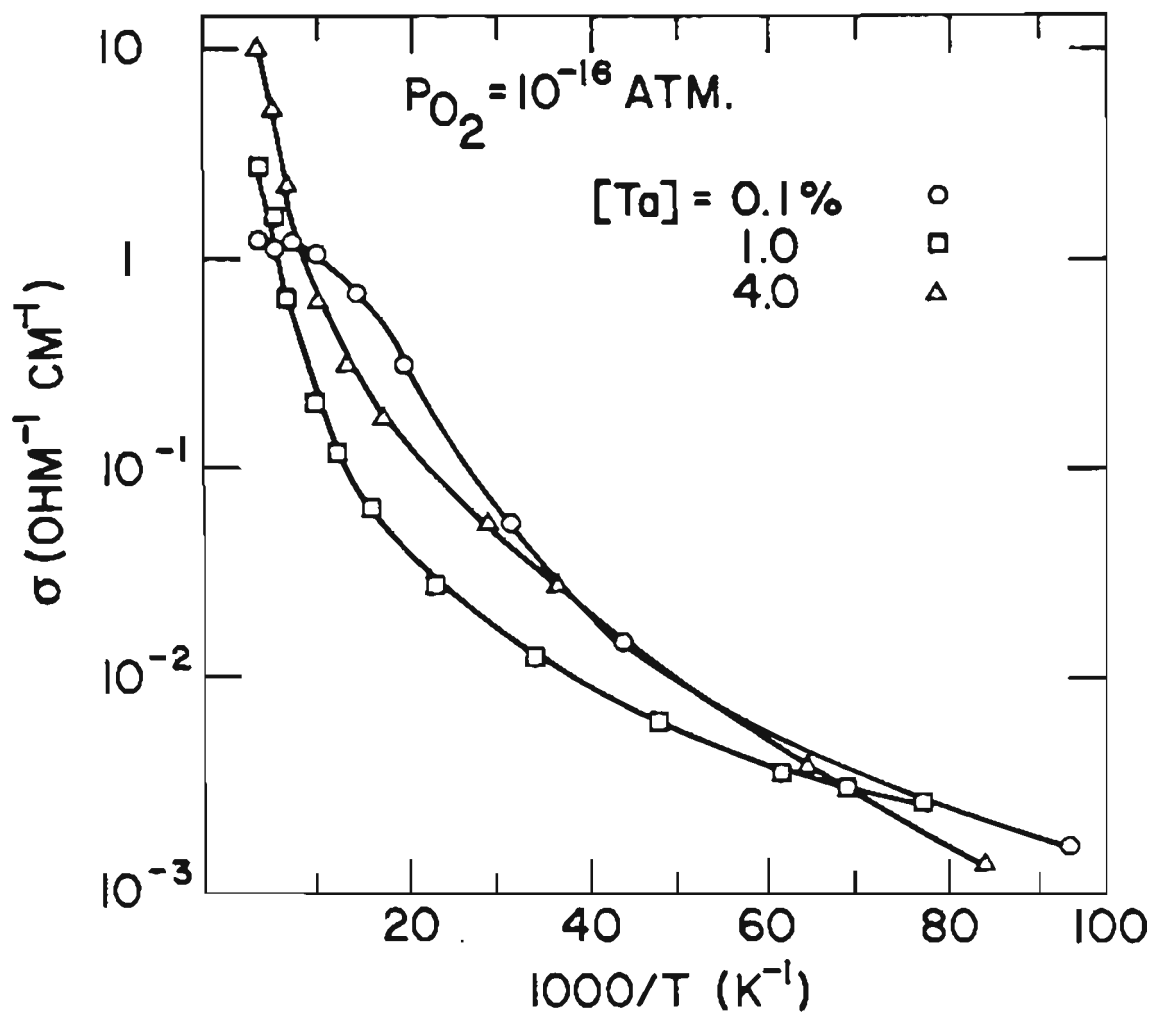


Figure 5.54. Plot of $\log(\sigma)$ versus $1000/T$ for Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

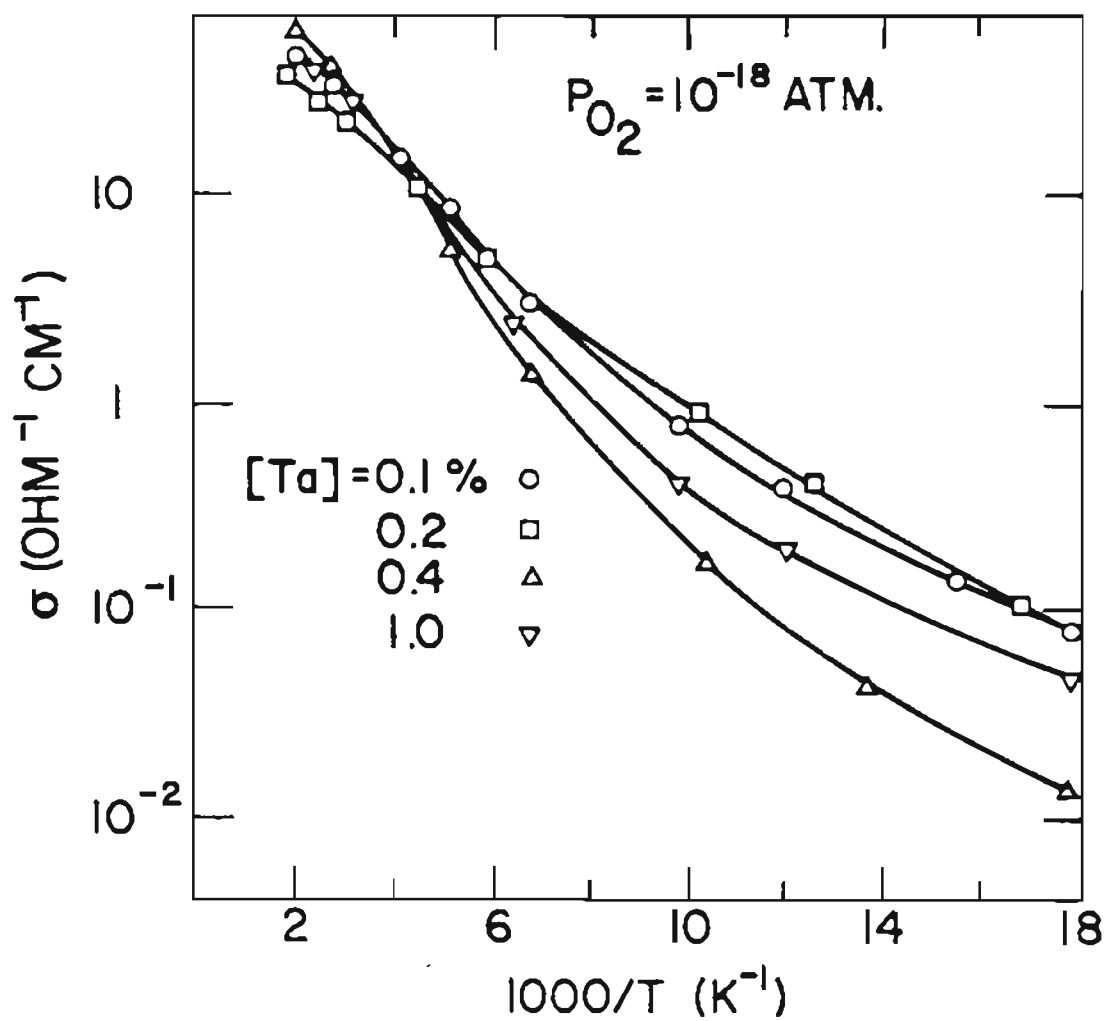


Figure 5.55. Plot of $\log(\sigma)$ versus $1000/T$ for Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

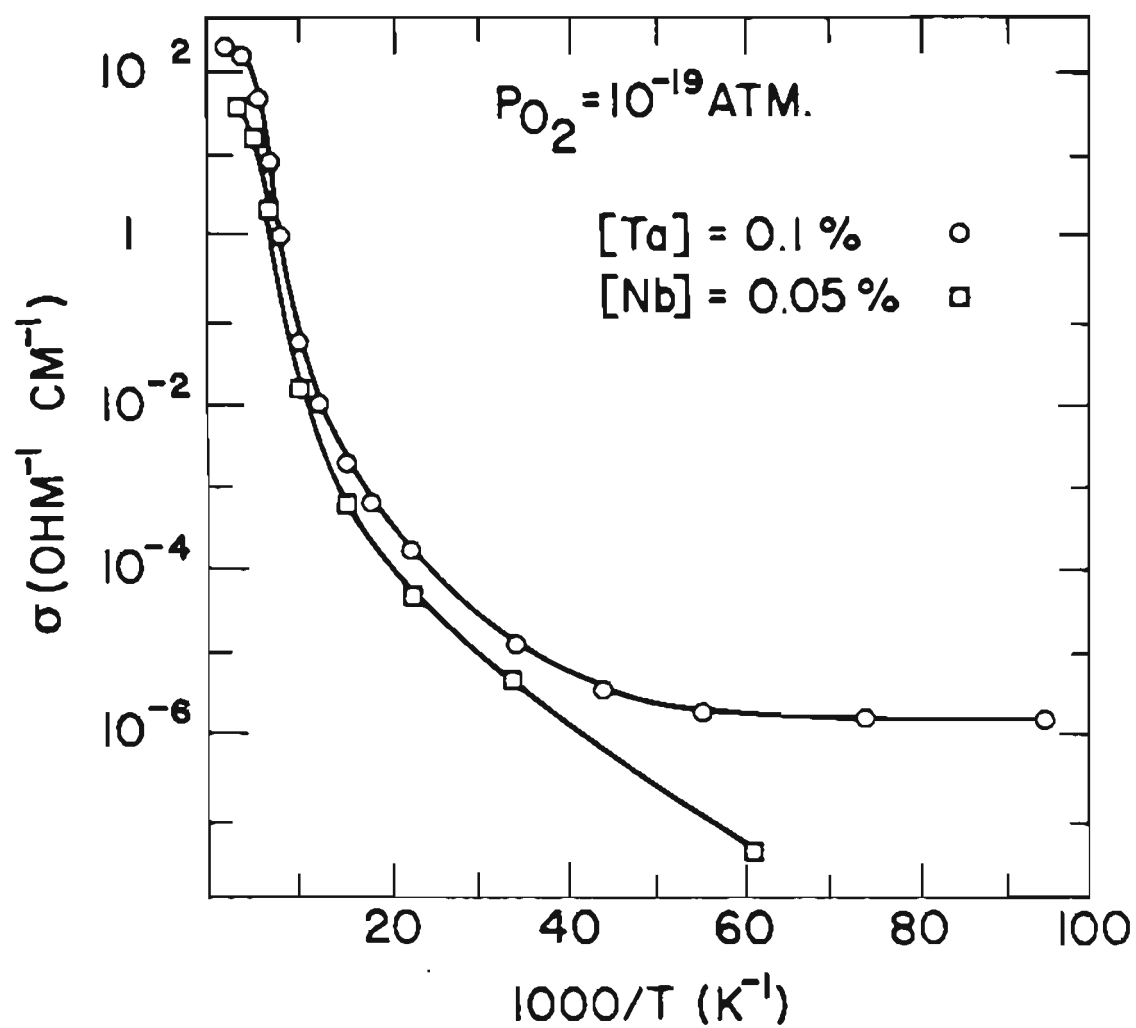


Figure 5.56. Plot of $\log(\sigma)$ versus $1000/T$ for Ta- and Nb-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

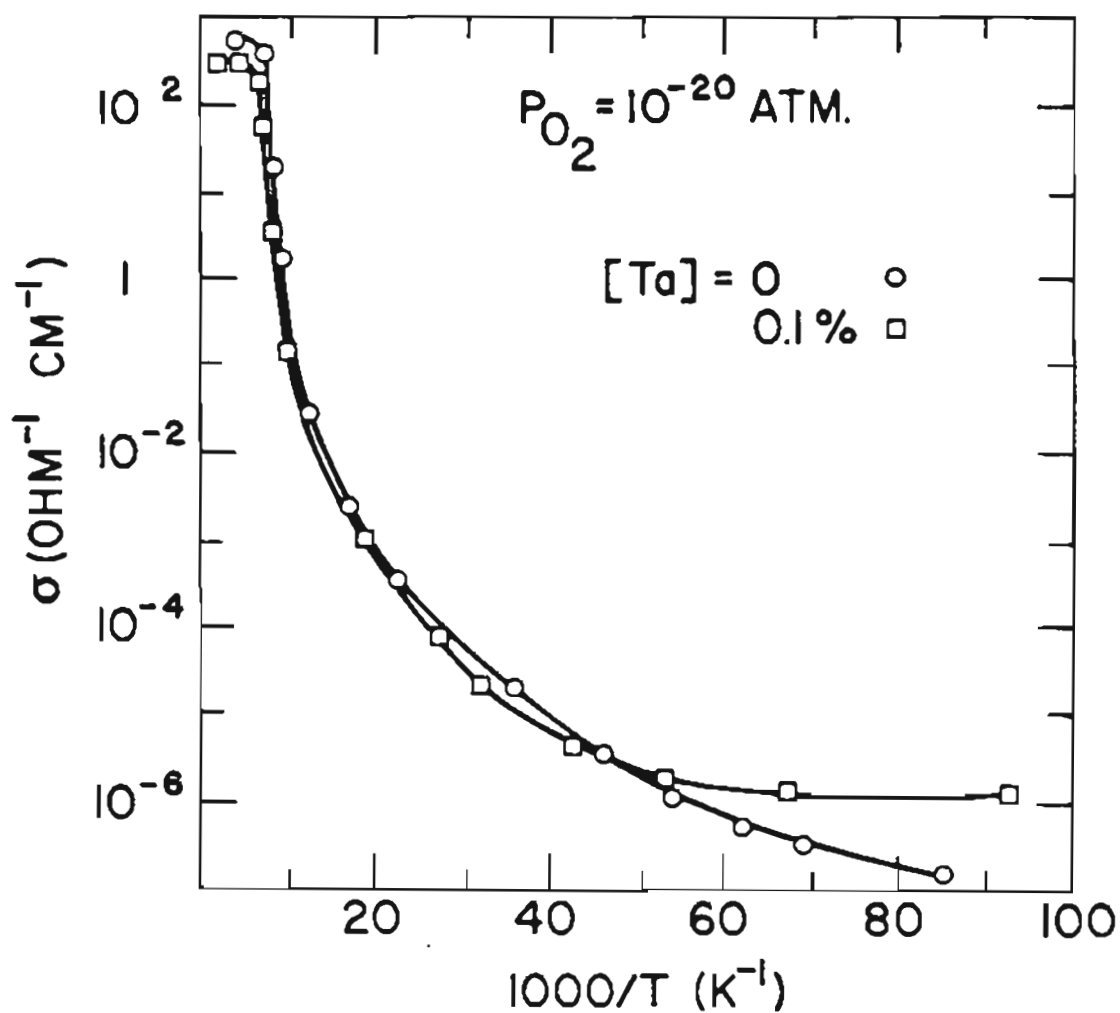


Figure 5.57. Plot of $\log(\sigma)$ versus $1000/T$ for undoped and Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated at 1325 K.

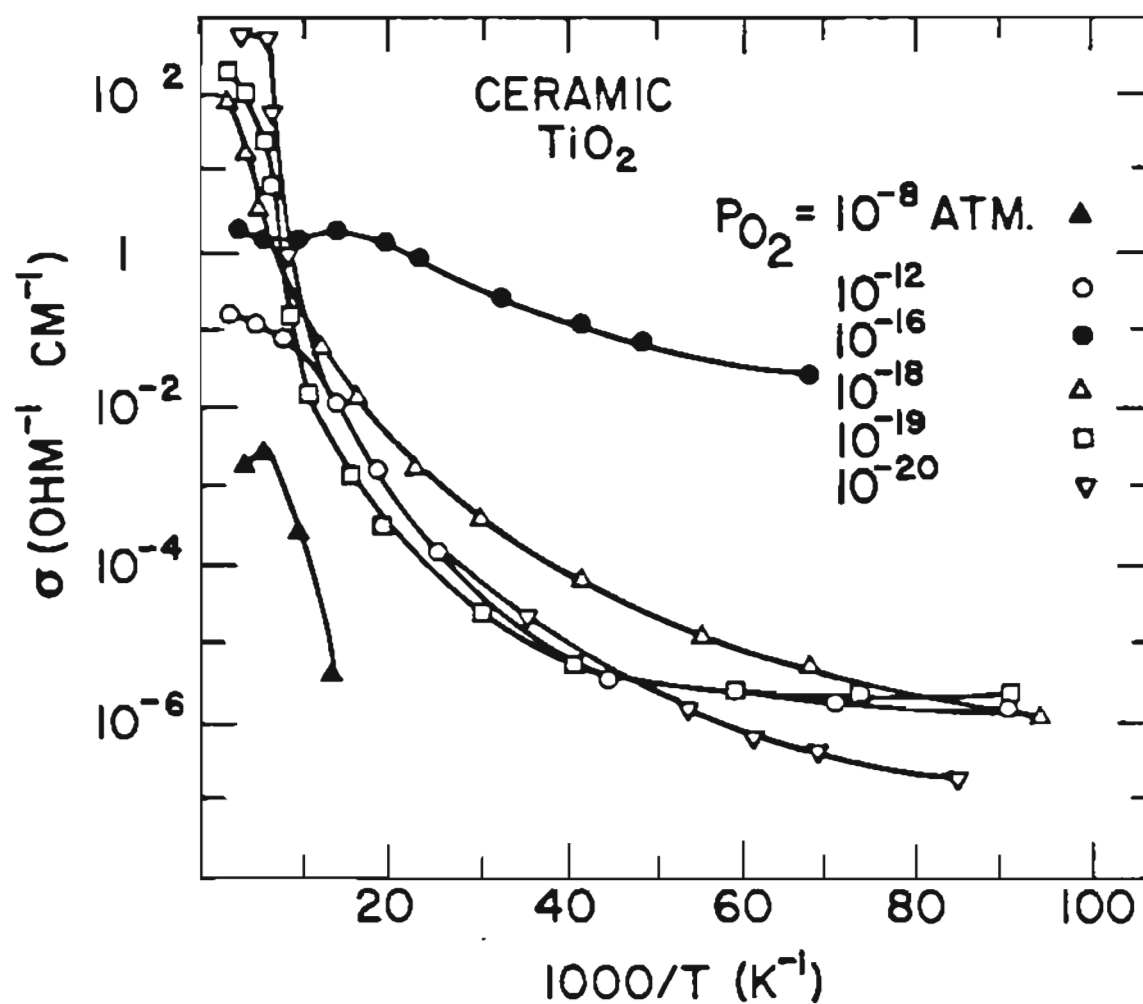


Figure 5.58. Plot of $\log(\sigma)$ versus $1000/T$ for undoped TiO_2 ceramic materials, reduced under the oxygen partial pressures indicated at 1325 K.

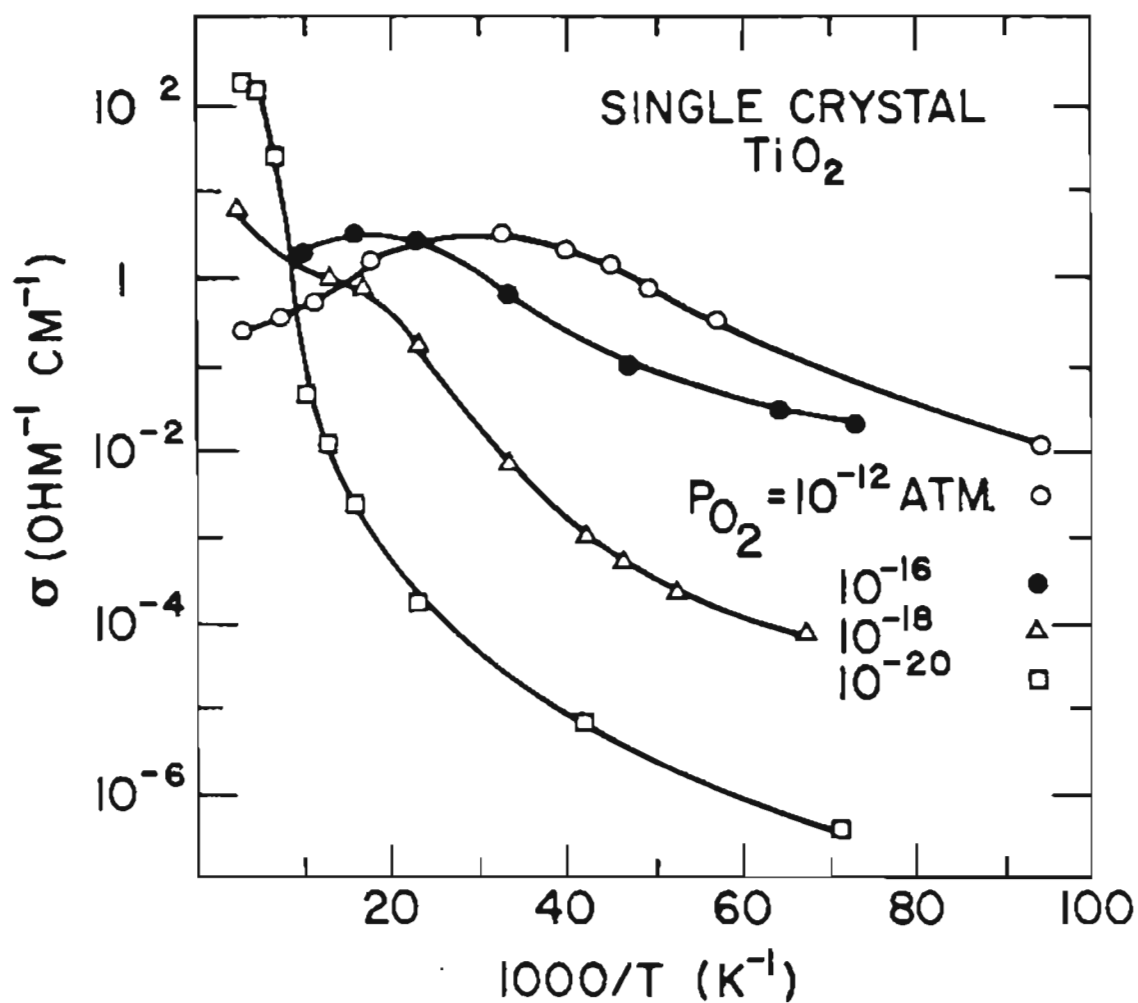


Figure 5.59. Plot of $\log(\sigma)$ versus $1000/T$ for undoped TiO_2 single crystal materials, reduced under the oxygen partial pressures indicated at 1325 K.

Material	P_{O_2} (atmospheres)					
	10^{-8}	10^{-12}	10^{-16}	10^{-18}	10^{-19}	10^{-20}
TiO ₂ (ceramic)	.08	.03	.01	.057	.12	.17
TiO ₂ (single crystal)		.008	.012	.028		.14
Ta(0.1%)TiO ₂	.08	.06	.012	.05	.13	.17
Ta(.19%)TiO ₂	.08	.06		.044		
Ta(.42%)TiO ₂	.08			.073		
Ta(1.0%)TiO ₂	.08	.056	.036	.062		
Ta(4.0%)TiO ₂			.04			
Nb(.05%)TiO ₂					.12	

Table 5.6. Activation energies in eV for extrinsic TiO₂. Inferred from Arrhenius plots, Figs. 5.52-5.59.

are known to aggregate at and diffuse along extended defect sites such as grain boundaries (354-357).

It can also be seen in Table 5.6 that E_a decreases with reduction in the P_{O_2} range 10^{-8} - 10^{-16} atm (for ceramic materials), and then increases with reduction for $P_{O_2} < 10^{-16}$ atm. It is also apparent that E_a is insensitive to doping up to $[Ta] = 3 \times 10^{19} \text{ cm}^{-3}$.

Levin and Rosa (358-359) found that charge compensation at high P_{O_2} in Ta or Nb-doped TiO_2 is accomplished by negatively charged lattice defects; however, they were careful to point out that conductivity data alone could not be used to distinguish oxygen interstitials from titanium vacancies in pentavalent-oxide-doped rutile. They found that at low doping levels the contribution to σ from native defects becomes significant for $P_{O_2} \leq 10^{-13}$ atm (at $T = 1273 \text{ K}$).

Figure 5.60 reproduces the $\log(\sigma)$ vs $\log(P_{O_2})$ (K-V diagram) results for Ta: TiO_2 obtained by Tani and Baumard (287). Their high temperature results show three distinct regions, of slopes $-1/5$, 0 , and $-1/4$, representative of reduced rutile $(Ta,Ti)O_{2-x}$, nearly stoichiometric $Ta_y^{5+}Ti_y^{3+}Ti_{1-2y}^{4+}O_2$, and overstoichiometric $Ta_y^{5+}Ti_{1-y}^{4+}O_{2+y/2}$ solid solutions, respectively. The latter region corresponds to oxidizing conditions ($P_{O_2} \geq 10^{-4}$ atm).

Tani and Baumard found that the native-defect-dominated region for $[Ta] = 0.3\%$ (at $T = 1273 \text{ K}$) occurs when $P_{O_2} \leq 10^{-13}$ atm, in agreement with the results of Levin and Rosa. As can be seen in Fig. 5.60, the impurity-dominated (zero slope) region extends to considerably lower P_{O_2} at higher doping. In general, it appears that

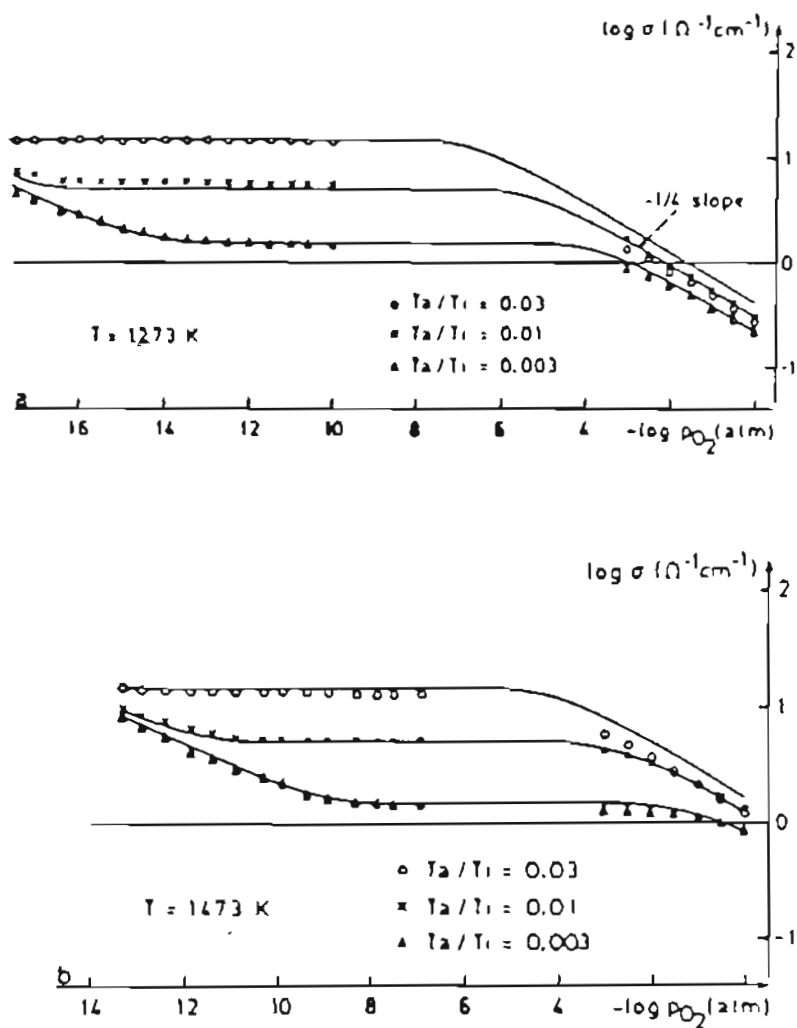


Figure 5.60. Electrical conductivity of Ta-doped TiO_2 versus oxygen pressure at different temperatures. (A) $T = 1273 \text{ K}$; (B) $T = 1473 \text{ K}$. (From reference 287).

boundary and ionized impurity scattering can be expected to contribute

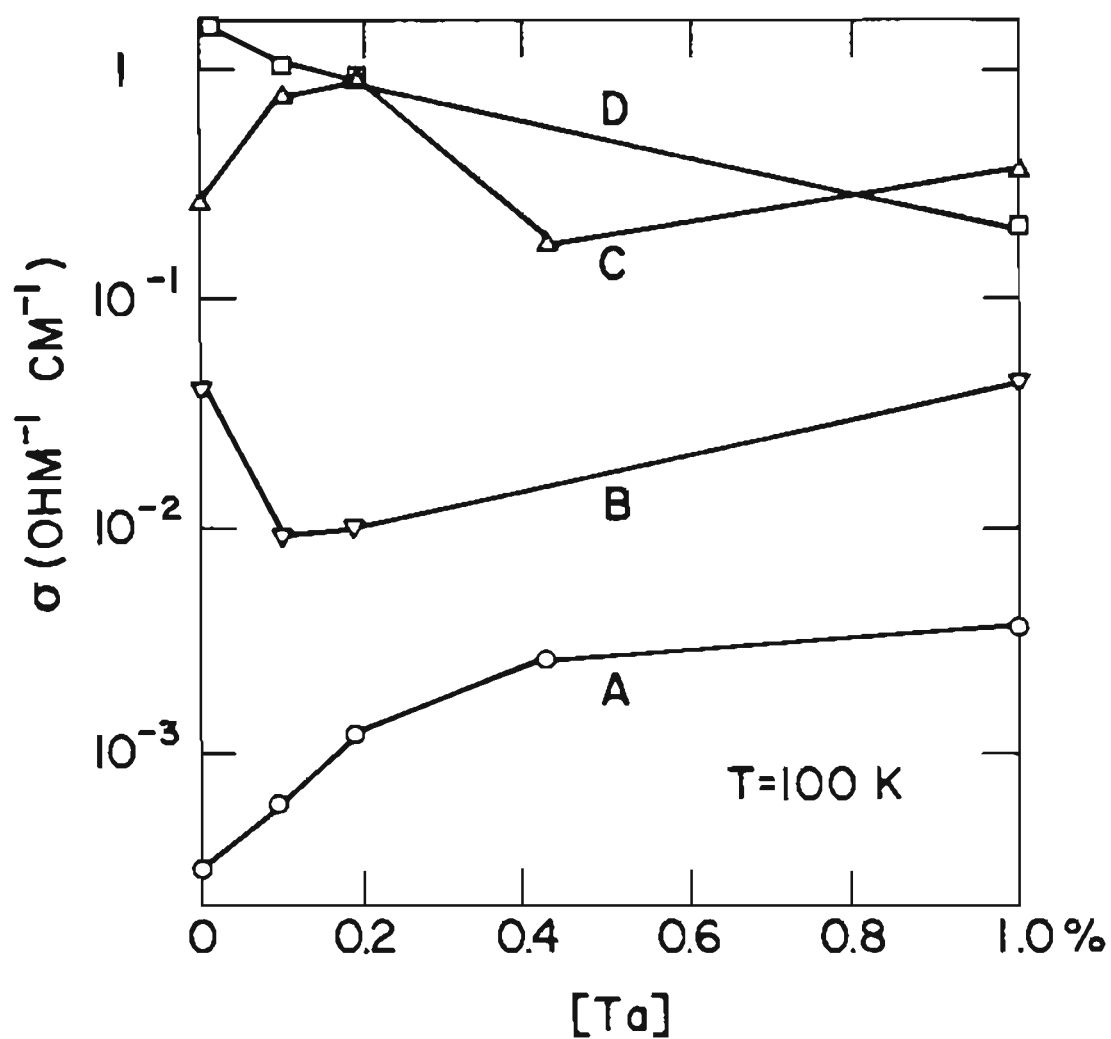


Figure 5.61. Electrical conductivity versus Ta-dopant concentration for ceramic TiO_2 materials, reduced in:
 (A) $P_{\text{O}_2} = 10^{-8} \text{ atm}$; (B) $P_{\text{O}_2} = 10^{-12} \text{ atm}$;
 (C) $P_{\text{O}_2} = 10^{-18} \text{ atm}$; (D) $P_{\text{O}_2} = 10^{-16} \text{ atm}$.

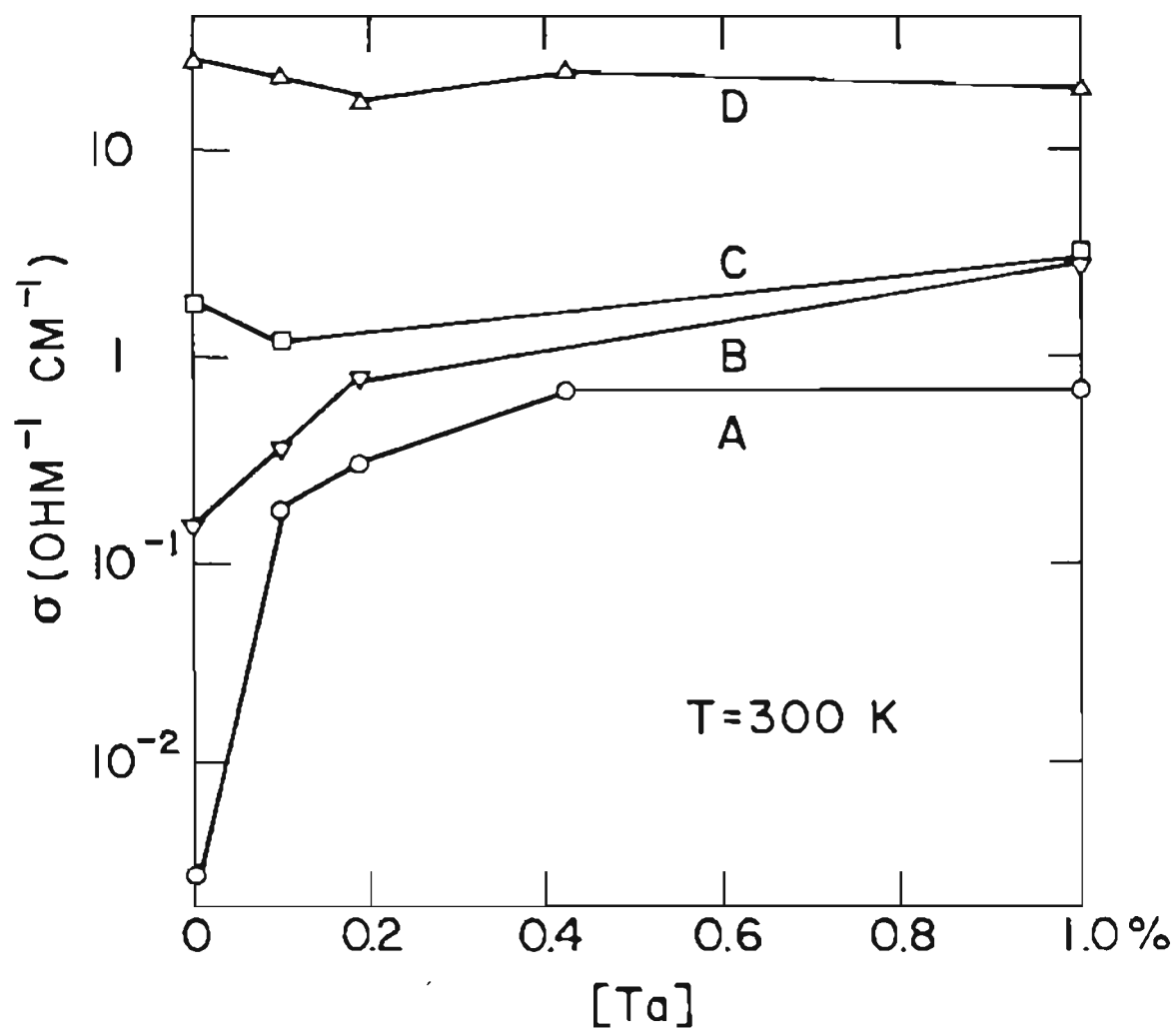


Figure 5.62. Electrical conductivity versus Ta-dopant concentration for ceramic TiO_2 materials, reduced in:
 (A) $P_{\text{O}_2} = 10^{-8} \text{ atm}$; (B) $P_{\text{O}_2} = 10^{-12} \text{ atm}$;
 (C) $P_{\text{O}_2} = 10^{-16} \text{ atm}$; (D) $P_{\text{O}_2} = 10^{-18} \text{ atm}$.

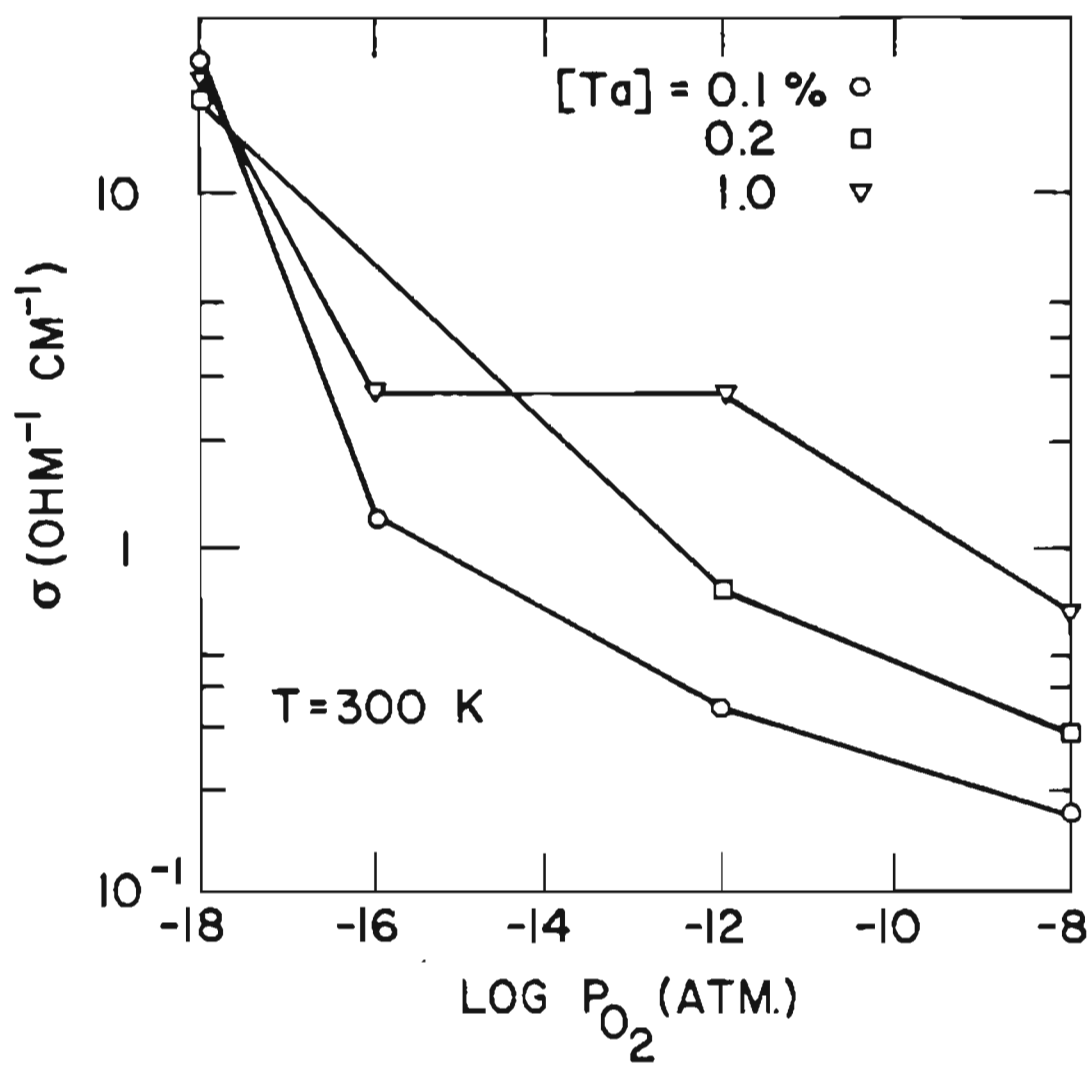


Figure 5.63. Kroger-Vink diagram for Ta-doped TiO_2 ceramic materials at $T = 300\text{ K}$.

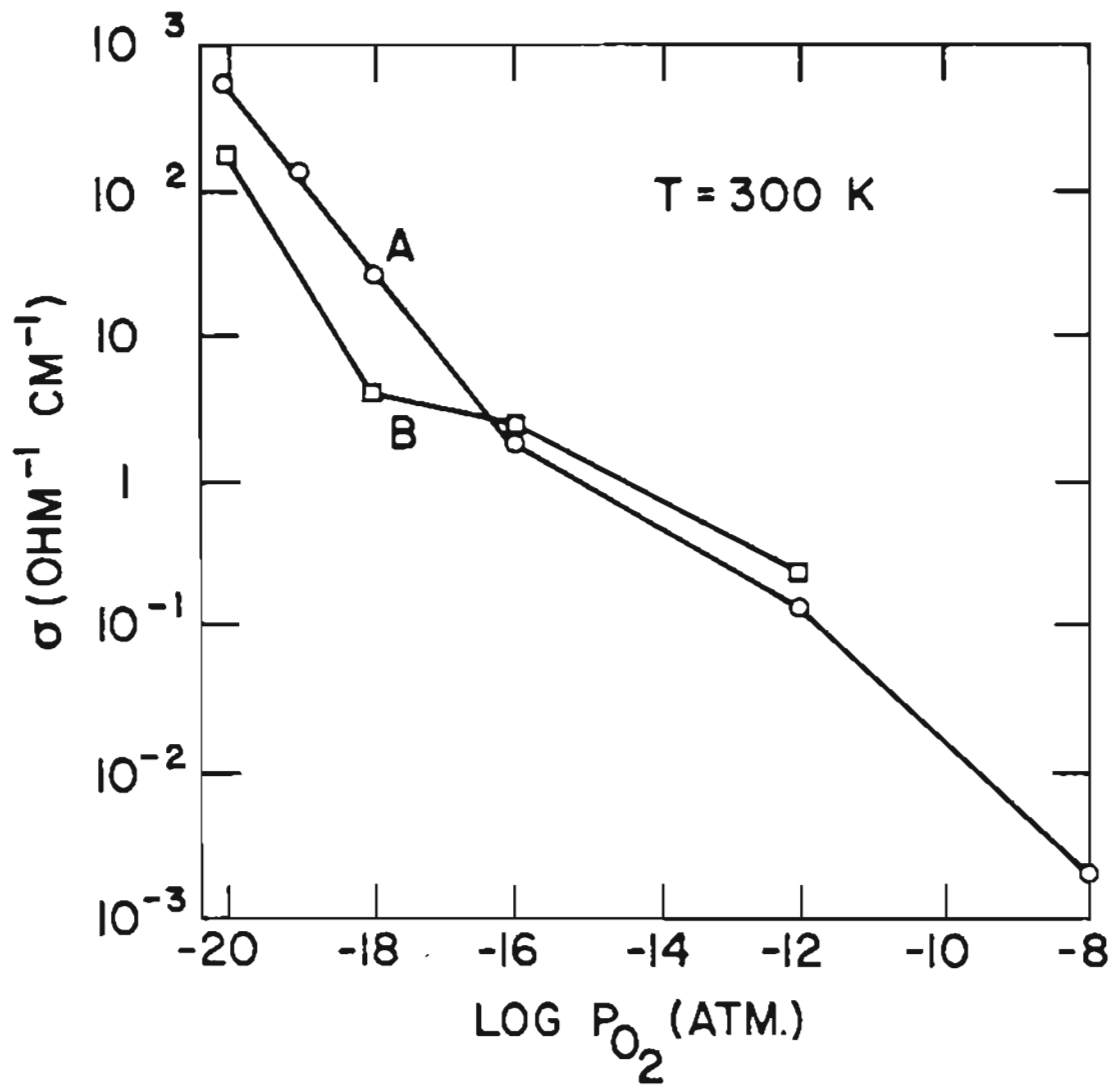


Figure 5.64. Kroger-Vink plot for undoped (A) ceramic and (B) single crystal TiO_2 materials, at $T = 300 \text{ K}$.

to the mobility term, and μ_n can not reasonably be expected to remain independent of reduction. Keeping these reservations in mind, it is nevertheless interesting to note that the curves of Fig. 5.64 seem to split into two regions of distinctly differing slopes. For ceramic materials, curve A shows a slope of $m = 0.83$ for the P_{O_2} range 10^{-8} - 10^{-16} atm, and of $m = 1.49$ for the range 10^{-16} - 10^{-20} atm. If one were to (with great caution) suppose a relation of the form:

$$\sigma \propto P_{O_2}^{-1/n} \quad (5.10)$$

then the model would have to be consistent with the values of $n = 1.21$ ($P_{O_2} = 10^{-8}$ - 10^{-16} atm) and $n = 0.67$ ($P_{O_2} = 10^{-16}$ - 10^{-20} atm). These values do not fit any simple defect models commonly proposed for TiO_2 , and hence are not immediately of support towards any general conclusions along these lines.

5.9 Spectral Response of Extrinsic TiO_2

5.9.1 Undoped TiO_2

Figure 5.65 shows the spectral response in terms of an arbitrary response per incident photon, corrected for the light source (75 Watt Xenon arc lamp) and optics, for both single crystal and ceramic undoped TiO_2 . These materials were all strongly reduced ($10^{-18} \leq P_{O_2}$ (atm) $\leq 10^{-12}$) at 1325 K. It can be seen that the single crystal sample displays a somewhat broader absorption shoulder near the cutoff edge (404 nm, 3.07 eV) than the ceramic materials.

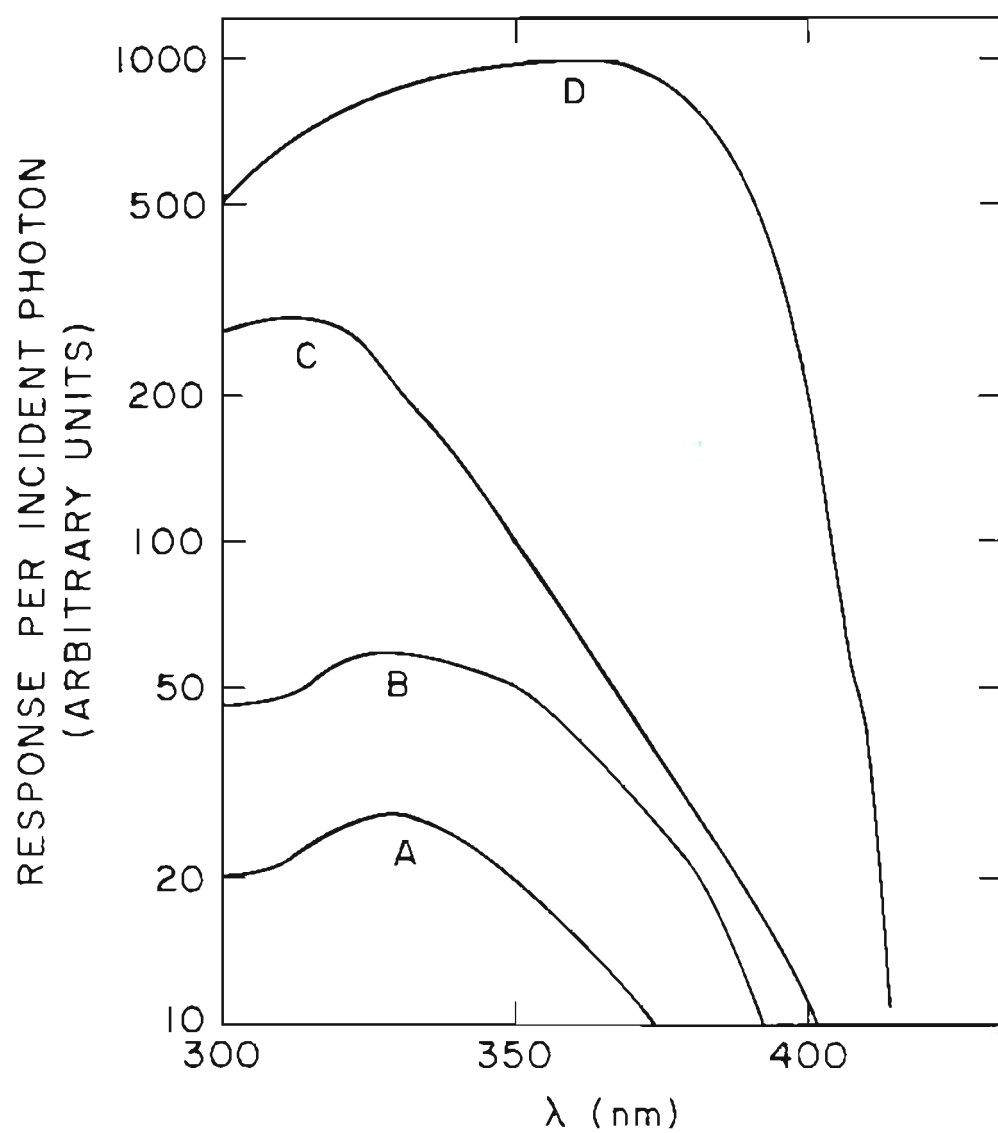


Figure 5.65. Spectral response plots for undoped TiO_2 photoanodes, as measured in 1M NaOH PEC cell. (A) ceramic, $P(\text{O}_2) = 10^{-12}$ atm; (B) ceramic, $P(\text{O}_2) = 10^{-16}$ atm; (C) ceramic, $P(\text{O}_2) = 10^{-18}$ atm; (D) single crystal, $P(\text{O}_2) = 10^{-16}$ atm.

Other than the above observation, however, the spectral characteristics are quite ordinary for TiO_2 material. All of the samples studied demonstrate an optical bandgap of ≈ 3.1 eV. This is in agreement with optical values in the standard literature (260,262), and with the thermal E_g calculated by Balachandran and Eror (284) for these materials. Sample reduction appears to have very little influence on the spectral response.

5.9.2 Tantalum Doped TiO_2

Figure 5.66 shows the (arbitrary) response per incident photon versus wavelength for Ta-doped TiO_2 , with $[\text{Ta}] = 0.1, 0.4$ and 1.0% . It can be seen by comparison with Figure 5.65 that light doping ($[\text{Ta}] = 0.1\%$) results in a response curve that differs only slightly from that of the corresponding undoped material. That difference shows up in a somewhat shorter wavelength peak, occurring at $\lambda = 310$ nm for $[\text{Ta}] = 0.1\%$, as opposed to $\lambda = 330$ nm for $[\text{Ta}] = 0$. The long wavelength drop-off is of the same form, displaying an optical bandgap of $E_g \approx 3.1$ eV.

At increased doping levels, it can be seen that the optical cutoff remains unchanged (3.1 eV), but that the low-wavelength response becomes somewhat altered. A local absorption minima now shows at $\lambda \approx 310$ nm (4.0 eV). This is interesting behavior, but it must be noted that the change in form of the curve is quite gentle and would not be expected to have any measurable impact on PEC performance. The inability of Ta-doping to decrease E_g is the primary point of interest in these curves, and should be considered in evaluating

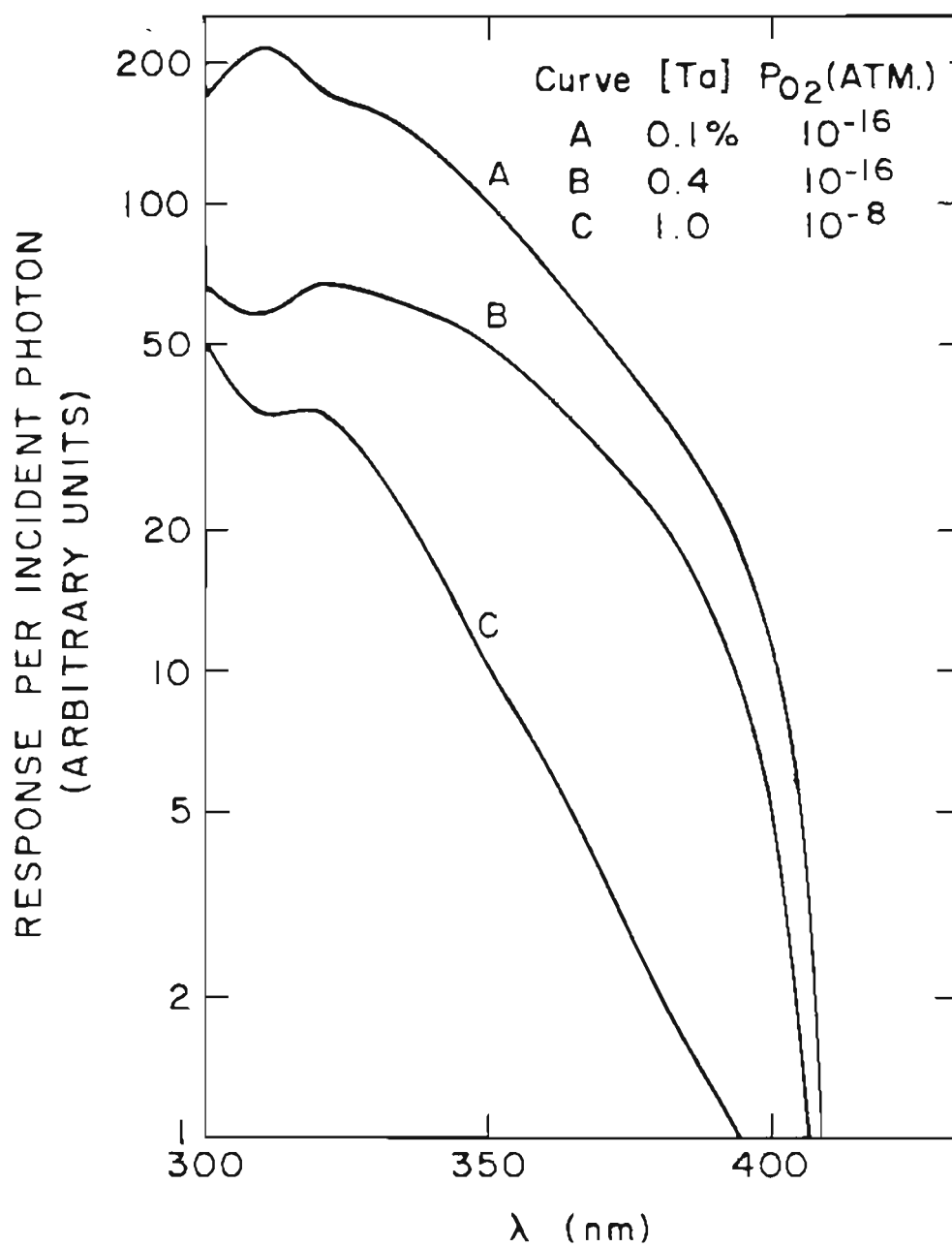


Figure 5.66. Spectral response plots for Ta-doped TiO_2 ceramic photoanodes, as measured in 1M NaOH PEC cell.

the usefulness of these materials as photoanodes in a PEC.

5.9.3 Acceptor Doped TiO_2

Several ceramic samples doped with the 3-d transition metal acceptor impurities Cr, Fe and Al were examined for their spectral response. It has previously been found that a diminished photore-sponse can sometimes be seen in Cr-doped TiO_2 (322,325,327-331); however, this effect often requires large biasing to be seen (329).

Figure 5.67 presents the results for Cr-doped TiO_2 , with four [Cr] levels (0.02, 0.05, 0.1 and 0.3%), and with reduction in $P_{\text{O}_2} = 10^{-16}$ atm at 1325 K. These scans were taken with no biasing voltage. Scans were also done with $V_b = 1.0\text{V}$, and yielded similar results. In all cases, the optical bandgap was unchanged from the undoped and Ta-doped cases ($E_g \approx 3.1$ eV).

The same negative results were obtained for Al and Fe-doped TiO_2 ceramics (Figure 5.68). In this case, doping levels of 0.05 and 0.5% were used, and reduction was carried out at 1325 K in $P_{\text{O}_2} = 10^{-18}$ atm. It appears that useful extension of E_g in ceramic TiO_2 is not easily obtained.

5.10 Photoactivity of Extrinsic TiO_2

As a PEC working anode, ceramic undoped and Ta-doped TiO_2 behaved just as expected from the abundant literature (86,290-306,318-331). Figure 5.69 demonstrates that PEC performance is indeed optimized by increasing the electrolyte pH. Ta-doped materials showed the same general trend, and pH = 14 solutions were used exclusively for per-

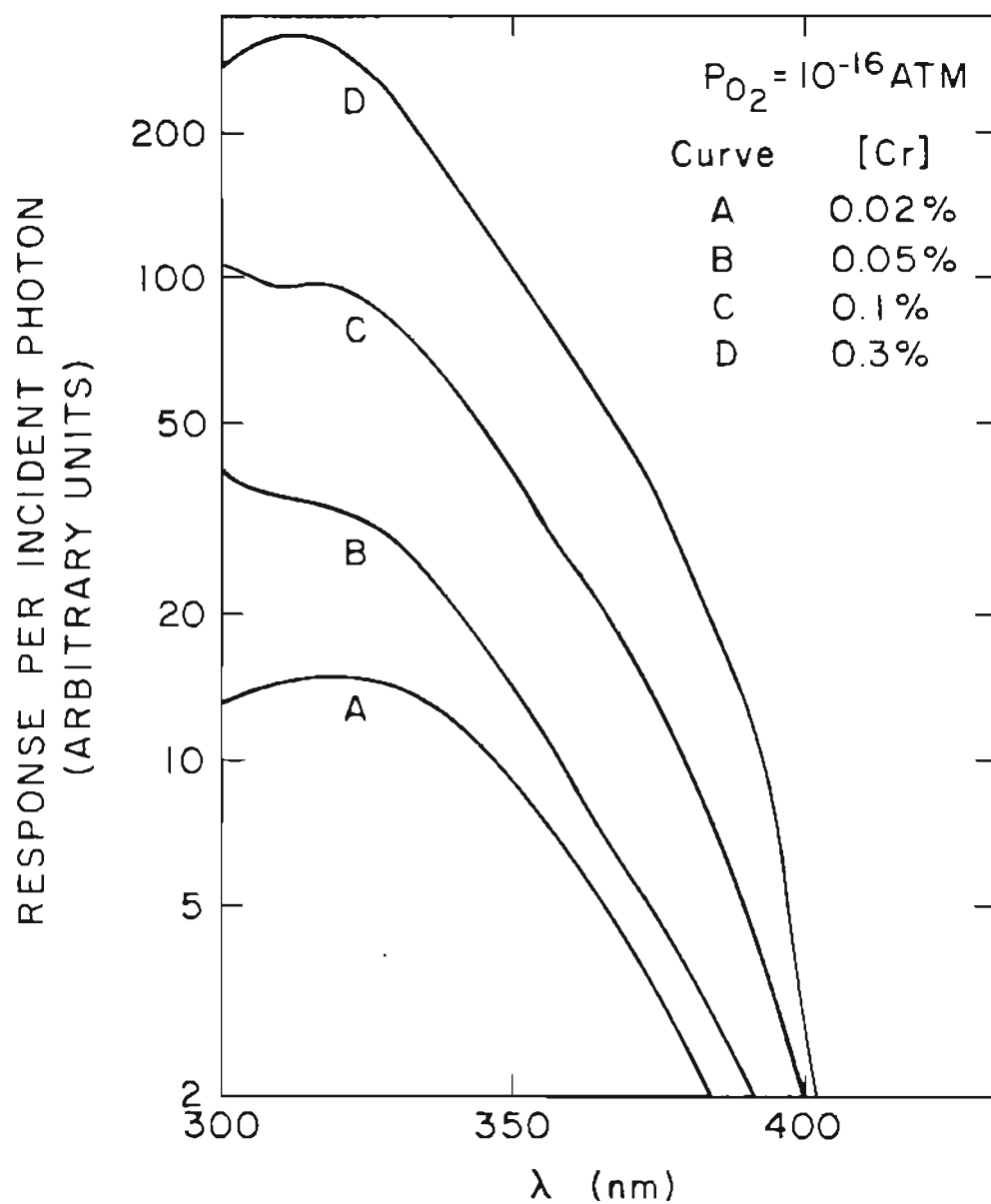


Figure 5.67. Spectral response plots for Cr-doped TiO_2 ceramic photoanodes, as measured in 1M NaOH PEC cell.

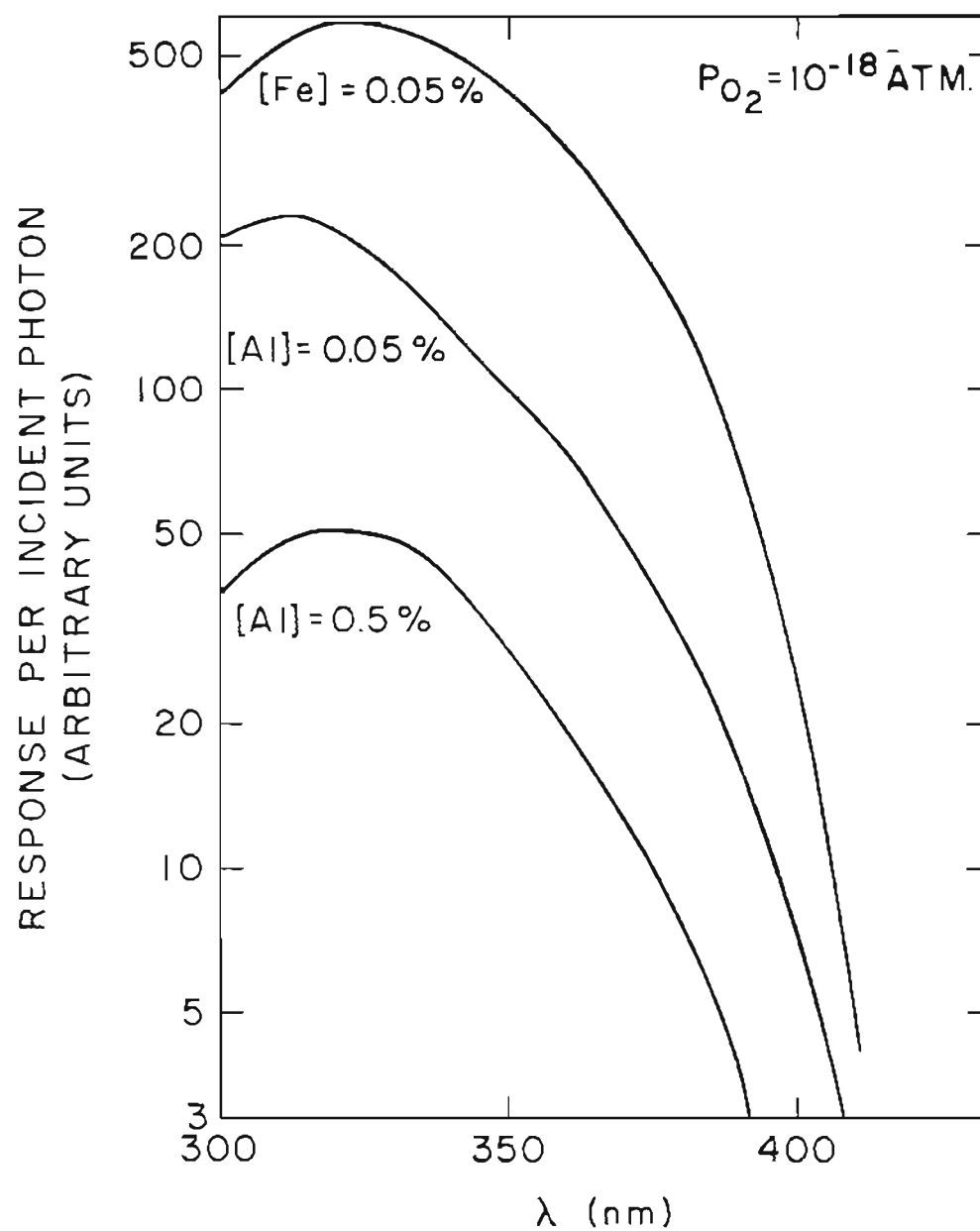


Figure 5.68. Spectral response plots for Al- and Fe-doped TiO_2 ceramic photoanodes, as measured in 1M NaOH PEC cell.

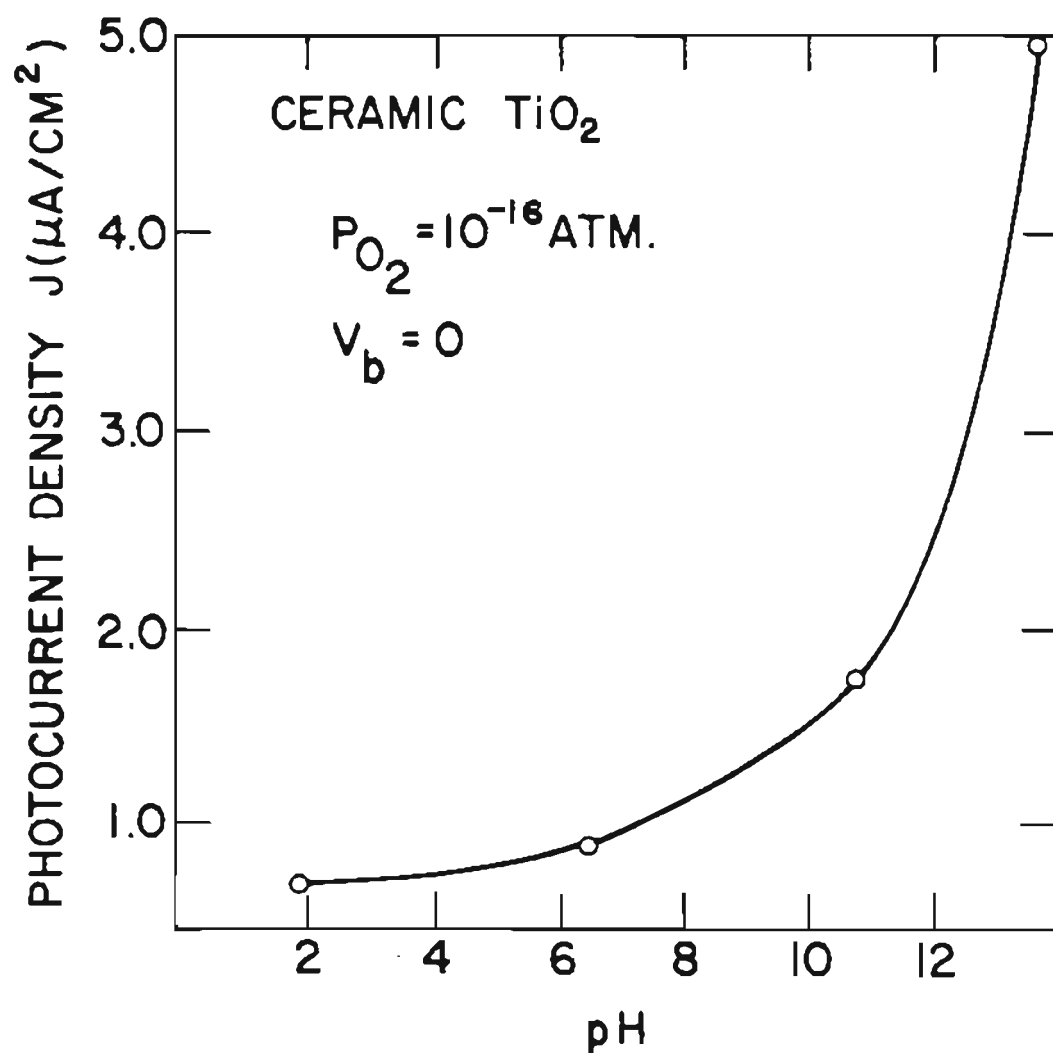


Figure 5.69. Photocurrent density versus electrolyte pH for undoped, ceramic TiO₂ photoanode, reduced under the oxygen partial pressure indicated. Measurements performed with no applied bias and under AM2 illumination.

formance comparisons after this initial test.

Figure 5.70 shows the clear superiority of a single crystal specimen over ceramic material, throughout the biasing range investigated (0-1 V). It should be noted that photocurrents generated in these devices at low bias did not result in hydrogen formation at the cathode. The response in this region ($V_b < 0.5$ V) was photovoltaic rather than photoelectrochemical.

Ta-doping was found to have very little effect on PEC performance. Figure 5.71 shows only a slight increase in J as [Ta] is increased from 0.1 to 1.0%, and that may be due simply to the modest decline in room temperature resistivity (from 0.83 to 0.36 Ω -cm.). Comparing the two curves of Fig. 5.71 with the range of curve A of Fig. 5.70, it can be seen that there is very little difference between the response of the Ta-doped samples and the undoped (ceramic) sample. The undoped TiO_2 sample depicted in curve A of Fig. 5.70 displayed a resistivity of $\rho \approx 0.7$ Ω -cm. Ta-doping is thus seen to be an ineffective means for increasing the photoactivity of ceramic TiO_2 .

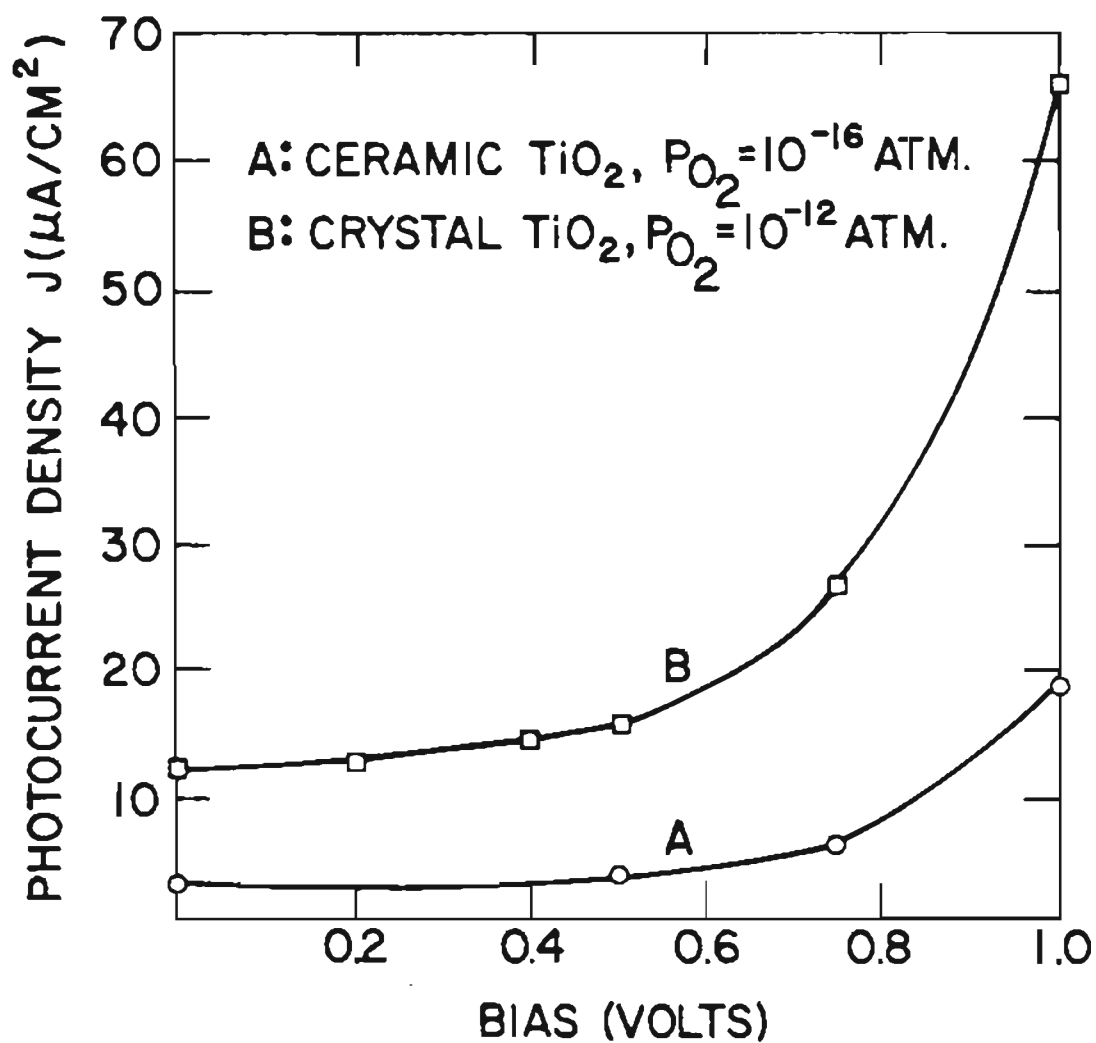


Figure 5.70. Photocurrent density versus applied bias for undoped TiO_2 photoanodes, reduced under the oxygen partial pressures indicated. Measurements performed in 1M NaOH PEC cells under AM2 illumination.

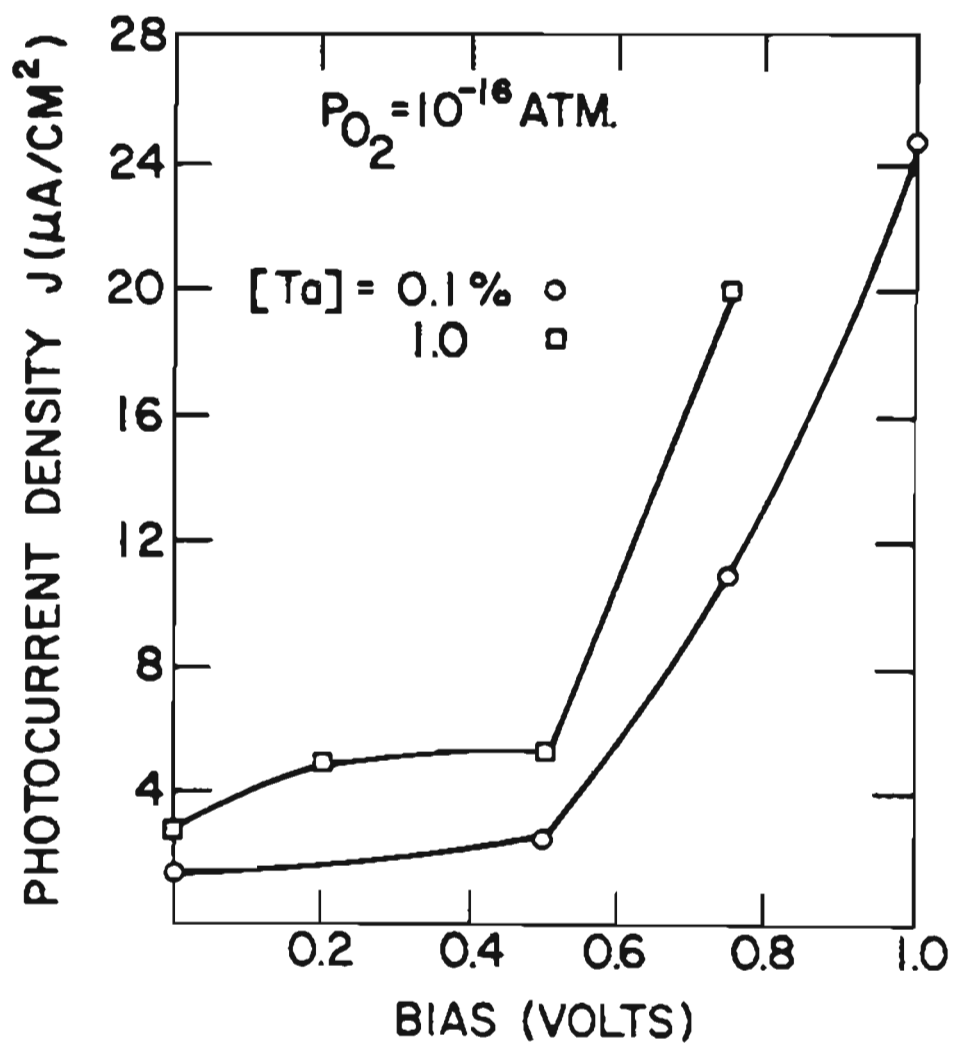


Figure 5.71. Photocurrent density versus applied bias for Ta-doped TiO_2 ceramic materials, reduced under the oxygen partial pressure indicated. Measurements performed in 1M NaOH PEC cells under AM2 illumination.

CHAPTER SIX

CONCLUSIONS

Well defined, reproducible semiconductors can be made from ceramic SrTiO_3 and TiO_2 -based materials, quenched from a high temperature, reducing atmosphere. By using the liquid mix technique (233,332), a wide variety of doped and undoped samples can be quickly, efficiently and cheaply made, thus allowing the completion of a thorough analysis of any given oxide system within a reasonable time frame. In particular, the electronic and optical characteristics can be readily studied in the temperature range 10-500 K without having to maintain a controlled atmosphere. This allows for a quick and easy comparison of the "quenched-in" low temperature behavior with high temperature (1000-1500 K) equilibrium results. High temperature measurements have been done on many oxides, primarily for the purpose of defining the defect structures of the materials as a function of anion and dopant concentrations. One result of this investigation is that valuable information concerning the defect structure of some oxides can also be obtained from quenched samples, despite the complications introduced by the non-constant mobility term and the inherent problems of dealing with a non-equilibrium system.

It has been shown that stable, ohmic contacts can be easily applied to these ceramic oxides using In:Ga alloy solder coated with conducting silver paste, and that no contact aging is seen after periods of time greater than 500 days.

6.1 Ceramic SrTiO_3

It has been established that the primary defect structure in reduced, undoped SrTiO_3 consists of oxygen vacancies, and that these vacancies are readily quenched-in. Carrier freeze-out has been shown to be substantial for lightly reduced samples ($n_{300} < 10^{17} \text{ cm}^{-3}$), with this effect decreasing with increasing reduction. This behavior has been associated with O_v -impurity band formation, and the identification of activation energies in the range 0.03–0.075 eV (for $n = 10^{17} - 10^{13} \text{ cm}^{-3}$) is in agreement with results previously obtained using single crystal samples (192–193).

The performance of ceramic SrTiO_3 photoanodes, modified by both donor doping and reduction, has been investigated for use in the photodissociation of water. The monitoring of photocurrents (produced in the photovoltaic mode) as a function of materials defect chemistry, in conjunction with measurements of electrical conductivity and of spectral response, provide the following conclusions:

- (i) These materials function best in a high pH environment.
- (ii) Lanthanum doping promotes formation of an impurity band for $[\text{La}] \geq 0.002$, and the spectral response confirms expectations from dark conductivity that the conduction and impurity bands are fully merged with a substantial band tail by the time $[\text{La}] \approx 0.01$.
- (iii) As a result of (ii), and the fact that conductivity increases with reduction until complete reduction ($P_{\text{O}_2} \leq 10^{-18} \text{ atm}$) is attained, optimal photoanode performance requires strong lanthanum doping and strong reduction prior to quenching.

(iv) No significant photodecomposition effects were seen as a result of operation in a PEC cell at AM2 illumination for periods of up to 50 hours.

(v) Modest photo-oxidation appears to occur for samples with $[La] \leq 0.002$, but not for stronger doping.

(vi) Ceramic $La_xSr_{1-x}TiO_3$ doped with $x \approx 0.01$, and fully reduced ($P_{O_2} \approx 10^{-20}$ atm) shows a vigorous photoactivity in 1M NaOH, without requirement for any external bias. It is assisted in this regard by the amply adequate dark conductivity, by the effect of conduction/impurity band tailing in reducing the optical bandgap, and evidently by the presence of a substantial density of midgap surface states.

6.2 Ceramic TiO_2

High temperature reduction has been shown to be a remarkably efficient means of producing donor defects in undoped, ceramic TiO_2 , to the extent that conduction-band electron concentrations in the range $n = 10^{17} - 10^{19} \text{ cm}^{-3}$ are readily obtainable.

Regions of activated transport are seen in both Ta-doped and undoped TiO_2 in the temperature range 100-300 K, with the activation energy (E_a) showing a minimum for ceramic materials equilibrated to $P_{O_2} = 10^{-16}$ atm. At that oxygen pressure, $E_a \approx 0.01-0.04$ eV, and increases with $[Ta]$. Monocrystalline, undoped TiO_2 samples exhibited a uniform increase in E_a with reduction, contrary to the behavior of their polycrystalline analogs. This indicates that the concentration of extended defects may play a strong role in determining the rate of thermal quenching of defect-related charge carriers.

Medium temperature (100-300 K) conduction in ceramic Ta:TiO₂ does not appear to be impurity-dominated for [Ta] ≤ 0.4% in the oxygen pressure range of this investigation (10⁻⁸ - 10⁻¹⁸ atm); consequently, σ is fairly insensitive to [Ta] in these materials. For higher doping ([Ta] = 1.0%), impurity-dominated conduction is obtained in the P_{O₂} range 10⁻¹² - 10⁻¹⁶ atm, with an activation energy of 0.04-0.06 eV. However, Ta-doping in the range studied (0.1-1.0%) showed no ability to substantially alter the photoresponse of ceramic TiO₂, and photoanode performance was left essentially unchanged. Ceramic TiO₂ homogeneously doped with the acceptor impurities Cr, Al, and Fe, and reduced in the P_{O₂} range 10⁻¹⁶-10⁻²⁰ atm, also showed no significant extension of the spectral response.

CHAPTER SEVEN

RECOMMENDATIONS FOR FUTURE WORK

The unusual behavior of σ at low temperatures for lightly reduced SrTiO_3 ($n \approx 10^{13} \text{ cm}^{-3}$) has been pointed out (Fig. 5.14), along with a previously proposed (193) explanation. Further study of SrTiO_3 in this range of reduction would be of interest. Hall effect studies throughout the temperature range 10-300 K would be needed to determine $\mu(T)$, and for this, suitable single crystal specimens would be required.

Another matter of continued interest is the study of the singly ionized oxygen vacancy defect ($\text{O}_V^\cdot$). The possibility of the formation of $\text{O}_V^\cdot$ defects in both SrTiO_3 and TiO_2 plays a significant role in the determination of the defect structure of these materials from the high temperature Kroger-Vink diagrams. Determination of the activation energy of the $\text{O}_V^\cdot - \text{O}_V^{\cdot\cdot}$ transition from low temperature (4-100 K) studies would provide information about the likelihood of the occurrence of this defect in either of these families of materials.

The formation of impurity bands in La:SrTiO_3 as $[\text{La}]$ exceeds 0.2% is a very interesting result, and bears further study. Conductivity and photoconductivity measurements in the temperature range 10-500 K for La-doping levels up to the solid solubility limit of 40% (239) would be of great general interest.

In particular, the photoelectrochemical performance of fully reduced $\text{La}(1.0\%)\text{SrTiO}_3$ single crystal and ceramic anodes in a closed

PEC cell should be evaluated and reported. It is the hope of this study that such an undertaking will be initiated.

And finally, a study such as that reported here should be accomplished on a similar family of ceramic materials based on Fe_2O_3 . Fe_2O_3 has been shown to be a stable photoanode material (96-102), and has a more favorable bandgap (2.20 eV). The problems of low absorption coefficients and poor diffusion lengths mentioned in Section 1.3.1 can be evaluated quickly and relatively cheaply over a wide range of material modification by employing the techniques outlined in this work.

REFERENCES

1. S. Wagner, in "Solid State Chemistry of Energy Conversion and Storage", edited by J. B. Goodenough and M. S. Whittingham (Advances in Chemistry Series #163), (Amer. Chem. Soc., Wash. D.C., 1977), p. 109.
2. H. Pauwels and A. De Vos, Sol. St. Elec. 24, 835 (1981).
3. J. B. Goodenough, A. Hamnett, M. P. Dare-Edwards, G. Campet and R. D. Wright, Surf. Sci. 101, 531 (1980).
4. S. M. Sze, in "Physics of Semiconductor Devices", 2nd edition, (Wiley, New York, 1981), p. 245.
5. J. F. Dewald, in "Semiconductors", edited by N. B. Hannay (ACS Monograph 140), (Amer. Chem. Soc., Wash. D.C., 1959), p. 727.
6. H. Gerischer, in "Physical Chemistry: An Advanced Treatise", Vol. 9A, edited by H. Eyring, D. Henderson and W. Jost, (Academic Press, New York, 1970), p. 463.
7. J. O'M. Bockris and K. Uosaki, in "Solid State Chemistry of Energy Conversion and Storage", edited by J. B. Goodenough and M. S. Whittingham (Advances in Chemistry Series #163), (Amer. Chem. Soc., Wash. D.C., 1977), p. 33.
8. A. Fisher, Pop. Sci., June 1978, 66 (1978).
9. H. P. Maruska and A. K. Ghosh, Solar Energy 20, 443 (1978).
10. A. J. Nozik, in "Annual Reviews of Physical Chemistry", Vol. 29, (Annual Reviews Inc., Palo Alto, Calif., 1978), p. 189.
11. L. A. Harris and R. H. Wilson, in "Annual Reviews of Material Science", Vol. 8, (Annual Reviews Inc., Palo Alto, Calif., 1978), p. 99
12. W. A. Gerrard and L. M. Rouse, J. Vac. Sci. Technol. 15, 1155 (1978).
13. M. Tomkiewicz and H. Fay, Appl. Phys. 18, 1 (1979).
14. M. S. Wrighton, C&EN, Sept. 3, 1979, 31 (1979).

15. H. Gerischer, in "Solar Energy Conversion: Solid State Physics Aspects", edited by B. O. Seraphin (Topics in Applied Physics Series, Vol. 31), (Springer-Verlag, New York, 1979), p. 115.
16. B. V. Tilak, P. W. T. Lu, J. E. Colman and S. Srinivasan, in "Electrochemical Processing", edited by J. O'M. Bockris, B. E. Conway, E. Yeager and R. E. White (Comprehensive Treatise of Electrochemistry, Vol. 2), (Plenum Press, New York, 1981), p. 1.
17. R. L. LeRoy, C. T. Bowen and D. J. LeRoy, J. Electrochem. Soc. 127, 1954 (1980).
18. G. De Beni, J. Electrochem. Soc. 129, 67 (1982).
19. R. A. Marcus, J. Chem. Phys. 24, 966 (1956).
20. R. A. Marcus, J. Chem. Phys. 24, 979 (1956).
21. R. A. Marcus, J. Chem. Phys. 26, 867 (1957).
22. R. A. Marcus, J. Phys. Chem. 67, 853 (1963).
23. R. A. Marcus, J. Chem. Phys. 41, 2624 (1964).
24. R. A. Marcus, J. Chem. Phys. 43, 679 (1965).
25. J. W. Conley, C. B. Duke, G. D. Mahan and J. J. Tiemann, Phys. Rev. 150, 466 (1966).
26. H. Gerischer, Surf. Sci. 18, 97 (1969).
27. S. R. Morrison, Surf. Sci. 15, 363 (1969).
28. R. De Gryse, W. P. Gomes, F. Cardon and J. Vennik, J. Electrochem. Soc. 122, 711 (1975).
29. R. H. Wilson, J. Appl. Phys. 48, 4292 (1977).
30. J. O'M. Bockris and K. Uosaki, J. Electrochem. Soc. 125, 223 (1978).
31. H. A. Laitinen, C. A. Vincent and T. M. Bednarski, J. Electrochem. Soc. 115, 1024 (1968).
32. W. P. Gomes, T. Freund and S. R. Morrison, J. Electrochem. Soc. 115, 818 (1968).
33. P. J. Boddy, Surf. Sci. 13, 52 (1969).

34. R. Memming, J. Electrochem. Soc. 116, 785 (1969).
35. R. A. L. Vanden Berghe, F. Cardon and W. P. Gomes, Surf. Sci. 39, 368 (1973).
36. S. N. Frank and A. J. Bard, J. Am. Chem. Soc. 97, 7427 (1975).
37. B. J. Baliga, R. Bhat and S. K. Ghandhi, J. Appl. Phys. 46, 3941 (1975).
38. R. Memming, J. Electrochem. Soc. 125, 117 (1978).
39. M. Nishida, Nature 277, 202 (1979).
40. W. Göpel, in "Advances in Solid State Physics", Vol. XX, edited by J. Treusch (Vieweg, W. Germany, 1980), p. 177.
41. J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry", (Plenum Press, New York, 1970).
42. H. Reiss, J. Electrochem. Soc. 125, 937 (1978).
43. A. J. Nozik, Appl. Phys. Lett. 30, 567 (1977).
44. K. Ohashi, J. McCann and J. O'M. Bockris, Nature 266, 610 (1977).
45. R. A. Smith, in "Semiconductors", 2nd edition, (Cambridge University Press, New York, 1978), pp. 270-286.
46. J. S. Blakemore, in "Solid State Physics", 2nd edition, (Saunders, Philadelphia, 1974), pp. 387-393.
47. J. I. Pankove, in "Optical Processes in Semiconductors", (Dover, New York, 1975), pp. 160-169.
48. J. S. Blakemore, in "Semiconductor Statistics", (Dover, New York, 1982), ch. 6-9.
49. A. Haug, Phys. Stat. Sol. (b) 97, 481 (1980).
50. A. Haug, Phys. Stat. Sol. (b) 108, 443 (1981).
51. S. R. Morrison, Phys. Rev. 104, 619 (1956).
52. W. Shockley and W. T. Read, Jr., Phys. Rev. 87, 835 (1952).
53. R. N. Hall, Phys. Rev. 83, 228 (1951).
54. J. P. McKelvey and R. L. Longini, Phys. Rev. 99, 1227 (1955).

55. D. M. Cook, in "The Theory of the Electromagnetic Field", (Prentice-Hall, Englewood Cliffs, N.J., 1975), p. 363.
56. J. W. Coltman, J. Appl. Phys. 18, 536 (1947).
57. M. Born and E. Wolf, in "Principles of Optics", 5th edition, (Pergamon Press, New York, 1975), p. 59.
58. E. Hecht and A. Zajac, in "Optics", (Addison Wesley, Menlo Park, Calif., 1976), p. 312.
59. S. G. Davison and J. D. Levine, in "Solid State Physics", Vol. 25, edited by H. Ehrenreich, F. Seitz, and D. Turnbull, (Academic Press, New York, 1970), p. 1.
60. J. Pollmann, in "Advances in Solid State Physics", Vol. XX, edited by J. Treusch, (Vieweg, W. Germany, 1980), p. 117.
61. M. L. Cohen, in "Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems", edited by J. Pask and A. Evans (Materials Science Research Vol. 14), (Plenum Press, New York, 1981), p. 1.
62. A. K. Ghosh and H. P. Maruska, J. Electrochem. Soc. 124, 1516 (1977).
63. W. W. Gärtner, Phys. Rev. 116, 84 (1959).
64. D. Laser and A. J. Bard, J. Electrochem. Soc. 123, 1828 (1976).
65. D. Laser and A. J. Bard, J. Electrochem. Soc. 123, 1833 (1976).
66. D. Laser and A. J. Bard, J. Electrochem. Soc. 123, 1837 (1976).
67. S. W. Feldberg, J. Phys. Chem. 74, 87 (1969).
68. J. P. McKelvey, R. L. Longini and T. P. Brody, Phys. Rev. 123, 51 (1961).
69. J. P. McKelvey and J. C. Balogh, Phys. Rev. 137, A1555 (1965).
70. E. F. Pulver and J. P. McKelvey, Phys. Rev. 149, 617 (1967).
71. J. Thomchick, J. Appl. Phys. 49, 3609 (1978).
72. W. J. Albery, P. N. Bartlett, A. Hamnett, and M. P. Dare-Edwards, J. Electrochem. Soc. 128, 1492 (1981).
73. S. R. Morrison, in "Electrochemistry at Semiconductor and Oxidized Metal Electrodes", (Plenum Press, New York, 1980), pp. 189-263.

74. R. K. Kalia, M. F. Weber, L. Schumacher and M. J. Dignam, *Surf. Sci.* 101, 214 (1980).
75. Y. Maeda, A. Fujishima and K. Honda, *J. Electrochem. Soc.* 128, 1731 (1981).
76. W. L. Ahlgren, *J. Electrochem. Soc.* 128, 2123 (1981).
77. M. A. Butler and D. S. Ginley, *J. Electrochem. Soc.* 125, 228 (1978).
78. A. S. Grove, in "Physics and Technology of Semiconductor Devices", (Wiley, New York, 1967), pp. 169-172.
79. A. van der Ziel, in "Solid State Physical Electronics", 3rd edition, edited by N. Holonyak Jr. (Solid State Physical Electronics Series), (Prentice-Hall, Englewood Cliffs, New Jersey, 1976), pp. 284-286.
80. D. Elliott, D. L. Zellmer, and H. A. Laitinen, *J. Electrochem. Soc.* 117, 1343 (1970).
81. A. M. Goodman, *J. Appl. Phys.* 34, 329 (1963).
82. L. J. Handley and A. J. Bard, *J. Electrochem. Soc.* 127, 338 (1980).
83. M. A. Butler, *J. Appl. Phys.* 48, 1914 (1977).
84. J. R. Wilson and S-M Park, *J. Electrochem. Soc.* 128, 2369 (1981).
85. J. F. McCann and J. Pezy, *J. Electrochem. Soc.* 128, 1735 (1981).
86. A. Fujishima and K. Honda, *Nature* 238, 37 (1972).
87. "Solid State Chemistry of Energy Conversion and Storage", edited by J. B. Goodenough and M. S. Whittingham (Advances in Chemistry Series No. 163), (Amer. Chem. Soc., Wash. D.C., 1977).
88. "Interfacial Photoprocesses: Energy Conversion and Synthesis", edited by M. S. Wrighton (Advances in Chemistry Series No. 184), (Amer. Chem. Soc., Wash. D.C., 1980).
89. "Photoeffects at Semiconductor-Electrolyte Interfaces", edited by A. J. Nozik (ACS Symposium Series #146), (Amer. Chem. Soc., Wash. D.C., 1981).

90. M. Tomkiewicz and J. M. Woodall, *Science* 196, 990 (1977).
91. M. J. Madou, F. Cardon, and W. P. Gomes, *J. Electrochem. Soc.* 124, 1623 (1977).
92. A. Heller, K. C. Chang, and B. Miller, *J. Electrochem. Soc.* 124, 697 (1977).
93. J. Manassen, G. Hodes, and D. Cahen, *J. Electrochem. Soc.* 124, 532 (1977).
94. W. J. Danaher and L. E. Lyons, *Nature* 271, 139 (1978).
95. M. S. Wrighton, A. B. Ellis and S. W. Kaiser, in "Solid State Chemistry of Energy Conversion and Storage", edited by J. B. Goodenough and M. S. Whittingham (Advances in Chemistry Series #163), (Amer. Chem. Soc., Wash. D.C., 1977), p. 71.
96. R. K. Quinn, R. D. Nasby, and R. J. Baughman, *Mat. Res. Bull.* 11, 1011 (1976).
97. K. L. Hardee and A. J. Bard, *J. Electrochem. Soc.* 123, 1024 (1976).
98. L-S. R. Yeh and N. Hackerman, *J. Electrochem. Soc.* 124, 833 (1977).
99. J. H. Kennedy and K. W. Frese, Jr., *J. Electrochem. Soc.* 125, 723 (1978).
100. J. H. Kennedy and K. W. Frese, Jr., *J. Electrochem. Soc.* 125, 709 (1978).
101. P. Iwanski, J. S. Curran, W. Gissler, and R. Merming, *J. Electrochem. Soc.* 128, 2128 (1981).
102. J. H. Kennedy, M. Anderman, and R. Shinar, *J. Electrochem. Soc.* 128, 2371 (1981).
103. M. S. Wrighton, A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Abrahamson, and D. S. Ginley, *J. Amer. Chem. Soc.* 98, 2774 (1976).
104. K. L. Hardee and A. J. Bard, *J. Electrochem. Soc.* 124, 215 (1977).
105. H. H. Kung, H. S. Jarrett, A. W. Sleight, and A. Ferretti, *J. Appl. Phys.* 48, 2463 (1977).
106. J. F. McCann and J. O'M. Bockris, *J. Electrochem. Soc.* 128, 1719 (1981).

107. R. S. Yeo, J. Orehotsky, W. Visscher, and S. Srinivasan, J. Electrochem. Soc. 128, 1900 (1981).
108. R. D. Nasby and R. K. Quinn, Mat. Res. Bull. 11, 985 (1976).
109. H. Tributsch, J. Electrochem. Soc. 125, 1086 (1978).
110. G. Blasse, G. J. Dirksen, and P. H. M. de Korte, Mat. Res. Bull. 16, 991 (1981).
111. W. D. K. Clark and N. Sutin, J. Amer. Chem. Soc. 99, 4676 (1977).
112. N. Alonso, V. M. Beley, P. Chartier, and V. Ern, Revue Phys. Appl. 16, 5 (1981).
113. P. A. Kohl, S. N. Frank, and A. J. Bard, J. Electrochem. Soc. 124, 225 (1977).
114. F-T. Liou, C. Y. Yang, and S. N. Levine, J. Electrochem. Soc. 129, 342 (1982).
115. J. G. Mavroides, J. C. Fan, and H. J. Zeiger, reference 89, pp. 217-230.
116. R. Williams, J. Vac. Sci. Technol. 13, 12 (1976).
117. H. Gerischer, J. Vac. Sci. Technol. 15, 1422 (1978).
118. M. S. Wrighton, J. M. Bolts, A. B. Bocarsly, M. C. Palazzotto, and E. G. Walton, J. Vac. Sci. Technol. 15, 1429 (1978).
119. K. W. Frese Jr., M. J. Madou, and S. R. Morrison, J. Electrochem. Soc. 128, 1939 (1981).
120. F-R. F. Fan, B. L. Wheeler, A. J. Bard, and R. N. Noufi, J. Electrochem. Soc. 128, 2042 (1981).
121. L. B. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 65 (1936).
122. S. L. Altmann and A. P. Cracknell, Rev. Mod. Phys. 37, 19 (1965).
123. R. A. Cowley, Phys. Rev. 134, A981 (1964).
124. T. Sakudo and H. Unoki, Phys. Rev. Ltr. 26, 851 (1971).
125. M. Cardona, Phys. Rev. 140, A651 (1965).

- 126. A. H. Kahn and A. J. Leyendecker, Phys. Rev. 135, A1321 (1964).
- 127. E. Simanek and Z. Sroubek, Phys. Stat. Sol. 8, K47 (1965).
- 128. H. P. R. Frederikse, W. R. Hosler, and W. R. Thurber, Phys. Rev. 143, 648 (1966).
- 129. Z. Sroubek, Phys. Rev. B 2, 3170 (1970).
- 130. R. A. Smith, in "Semiconductors", 2nd edition, (Cambridge University Press, New York, 1978), p. 85.
- 131. O. N. Tufte and E. L. Stelzer, Phys. Rev. 141, 675 (1966).
- 132. T. F. Soules, E. J. Kelly, D. M. Vaught, and J. W. Richardson, Phys. Rev. B 6, 1519 (1972).
- 133. L. F. Mattheiss, Phys. Rev. B 6, 4718 (1972).
- 134. T. Wolfram, Phys. Rev. Ltr. 29, 1383 (1972).
- 135. S. Ellialtioglu and T. Wolfram, Phys. Rev. B 15, 5909 (1977).
- 136. I. Gyemant and M. J. Kelly, J. Phys. C 11, L193 (1978).
- 137. W. A. Harrison, in "Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond", (W. H. Freeman and Co., San Francisco, 1980), pp. 438-452.
- 138. E. Poindexter and A. A. Giardini, Phys. Rev. 110, 1069 (1958).
- 139. J. C. Phillips, in "Bonds and Bands in Semiconductors", edited by A. M. Alper and A. S. Nowick (Materials Science and Technology Series), (Academic Press, New York, 1973), p. 81.
- 140. W. Cochran, Advan. Phys. 9, 387 (1960).
- 141. W. Cochran, Advan. Phys. 10, 401 (1961).
- 142. E. Fatuzzo and W. J. Merz, in "Ferroelectricity", edited by E. P. Wohlfarth (Series of Monographs on Selected Topics in Solid State Physics), (North-Holland Pub. Co., Amsterdam, 1967), pp. 148-170.
- 143. M. I. Cohen, R. C. Casella, R. F. Blunt, and R. A. Forman, Phys. Rev. 186, 834 (1969).
- 144. B. N. N. Achar, G. R. Barsch, and L. E. Cross, Phys. Rev. B 24, 1209 (1981).

- 145. H. Thomas and K. A. Müller, Phys. Rev. Ltr. 21, 1256 (1968).
- 146. P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Ltr. 21, 16 (1968).
- 147. K. Otnes, T. Riste, G. Shirane, and J. Feder, Sol. St. Comm. 9, 1103 (1971).
- 148. H. Unoki and R. Sakudo, J. Phys. Soc. Japan 23, 546 (1967).
- 149. J. Zak, J. Math. Phys. 1, 165 (1960).
- 150. L. F. Mattheiss, Phys. Rev. B 6, 4740 (1972).
- 151. G. F. Koster, in "Solid State Physics", edited by F. Seitz and D. Turnbull, (Academic Press, New York, 1957), p. 173.
- 152. Y. T. Sihvonen, J. Appl. Phys. 38, 4431 (1967).
- 153. L. Grabner, Phys. Rev. 177, 1315 (1969).
- 154. M. S. Kozyreva, Opt. Spectrosc. (USSR) 43, 51 (1977).
- 155. P. S. Narayanan and K. Vedam, Z. Physik 163, 158 (1961).
- 156. R. F. Schaufele and M. J. Weber, J. Chem. Phys. 46, 2859 (1967).
- 157. W. G. Nilsen and J. G. Skinner, J. Chem. Phys. 48, 2240 (1968).
- 158. W. Taylor and A. F. Murray, Sol. St. Comm. 31, 937 (1979).
- 159. U. Balachandran and N. G. Eror, J. Amer. Ceram. Soc. 65, in press (1982).
- 160. S. B. Levin, N. J. Field, F. M. Plock, and L. Merker, J. Opt. Soc. Am. 45, 737 (1955).
- 161. H. W. Gandy, Phys. Rev. 113, 795 (1959).
- 162. R. C. Casella, Phys. Rev. 154, 743 (1967).
- 163. G. A. Barbosa, R. S. Katiyar, and S. P. S. Porto, J. Opt. Soc. Am. 68, 610 (1978).
- 164. M. I. Cohen and R. F. Blunt, Phys. Rev. 168, 929 (1968).
- 165. F. Urbach, Phys. Rev. 92, 1324 (1953).
- 166. G. D. Mahan, Phys. Rev. 145, 602 (1966).

167. D. L. Dexter, Phys. Rev. Ltr. 19, 1383 (1967).
168. D. Dunn, Phys. Rev. 174, 855 (1968).
169. M. Capizzi and A. Frova, Phys. Rev. Ltr. 25, 1298 (1970).
170. K. W. Blazey, Phys. Rev. Ltr. 27, 146 (1971).
171. H. E. Weaver, J. Phys. Chem. Sol. 11, 274 (1959).
172. A. S. Barker Jr. and M. Tinkham, Phys. Rev. 125, 1527 (1962).
173. A. S. Barker Jr., Phys. Rev. 145, 391 (1966).
174. W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. 126, 1710 (1962).
175. E. A. Kraut, T. Wolfram, and W. Hall, Phys. Rev. B 6, 1499 (1972).
176. F. J. Morin and T. Wolfram, Phys. Rev. Ltr. 30, 1214 (1973).
177. T. Wolfram, E. A. Kraut, and F. J. Morin, Phys. Rev. B 7, 1677 (1973).
178. T. Wolfram and F. J. Morin, Appl. Phys. 8, 125 (1975).
179. T. Wolfram, R. Hurst, and F. J. Morin, Phys. Rev. B 15, 1151 (1977).
180. S. Ellialtioglu and T. Wolfram, Phys. Rev. B 18, 4509 (1978).
181. R. A. Powell and W. E. Spicer, Phys. Rev. B 13, 2601 (1976).
182. V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, Phys. Rev. B 17, 4908 (1978).
183. W. J. Lo and G. A. Somorjai, Phys. Rev. B 17, 4942 (1978).
184. J. G. Mavroides and D. F. Kolesar, J. Vac. Sci. Technol. 15, 538 (1978).
185. V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, Sol. St. Comm. 24, 623 (1977).
186. V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, J. Vac. Sci. Technol. 15, 534 (1977).
187. M. Tomkiewicz, Surf. Sci. 101, 286 (1980).

188. H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, Phys. Rev. 134, A442 (1964).
189. H. P. R. Frederikse and W. R. Hosler, Phys. Rev. 161, 822 (1967).
190. H. P. R. Frederikse and G. A. Candela, Phys. Rev. 147, 583 (1966).
191. W. S. Baer, Phys. Rev. 144, 734 (1966).
192. O. N. Tufte and P. W. Chapman, Phys. Rev. 155, 796 (1967).
193. C. Lee, J. Yahia, and J. L. Brebner, Phys. Rev. B 3, 2525 (1971).
194. D. Parker and J. Yahia, Phys. Rev. 169, 605 (1968).
195. C. S. Koonce, M. L. Cohen, J. F. Schooley, W. R. Hosler, and E. R. Pfeiffer, Phys. Rev. 163, 380 (1967).
196. E. Ambler, J. H. Colwell, W. R. Hosler, and J. F. Schooley, Phys. Rev. 148, 280 (1966).
197. G. Binnig, A. Baratoff, H. E. Hoenig, and J. G. Bednorz, Phys. Rev. Ltr. 45, 1352 (1980).
198. J. F. Schooley, H. P. R. Frederikse, W. R. Hosler, and E. R. Pfeiffer, Phys. Rev. 159, 301 (1967).
199. K. A. Müller, Phys. Rev. Ltr. 2, 341 (1959).
200. L. Rimai and G. A. DeMars, Phys. Rev. 127, 702 (1962).
201. M. J. Weber and R. F. Schaufele, Phys. Rev. 138, A1544 (1965).
202. E. S. Kirkpatrick, K. A. Müller, and R. S. Rubins, Phys. Rev. 135, A86 (1964).
203. V. G. Bhide and H. C. Bhasin, Phys. Rev. 172, 290 (1968).
204. B. W. Faughnan and Z. J. Kiss, Phys. Rev. Ltr. 21, 1331 (1968).
205. Z. J. Kiss, IEEE J. Quant. Elec. QE-5, 12 (1969).
206. B. W. Faughnan and Z. J. Kiss, IEEE J. Quant. Elec. QE-5, 17 (1969).
207. B. W. Faughnan, Phys. Rev. B 4, 3623 (1971).
208. K. A. Müller, T. von Waldkirch, W. Berlinger, and B. W. Faughnan, Sol. St. Comm. 9, 1097 (1971).

- 209. J. Blanc and D. L. Staebler, Phys. Rev. B 4, 3548 (1971).
- 210. R. L. Wild, E. M. Rockar, and J. C. Smith, Phys. Rev. B 8, 3828 (1973).
- 211. F. J. Morin and J. R. Oliver, Phys. Rev. B 8, 5847 (1973).
- 212. K. A. Müller, W. Berlinger, and R. S. Rubins, Phys. Rev. 186, 361 (1969).
- 213. D. L. Dexter, in "Solid State Physics", Vol. 6, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), p. 355.
- 214. S. E. Stokowski and A. L. Schawlow, Phys. Rev. 178, 457 (1969).
- 215. S. E. Stokowski and A. L. Schawlow, Phys. Rev. 178, 464 (1969).
- 216. W. J. Burke and R. J. Pressley, Phys. Rev. 182, 395 (1969).
- 217. A. K. Ghosh, R. R. Addiss Jr., and R. B. Lauer, J. Appl. Phys. 44, 3798 (1973).
- 218. Q. Kim, R. C. Powell, M. Mostoller and T. M. Wilson, Phys. Rev. B 12, 5627 (1975).
- 219. T. C. Ensign and S. E. Stokowski, Phys. Rev. B 1, 2799 (1970).
- 220. J. B. Hastings, S. M. Shapiro, and B. C. Frazer, Phys. Rev. Ltr. 40, 237 (1978).
- 221. N. E. Phillips, J. C. Ho, D. P. Woody, J. K. Hulm and C. K. Jones, Phys. Lett. 29A, 356 (1969).
- 222. P. P. J. Van Engelen and J. C. M. Henning, Phys. Lett. 25A, 733 (1967).
- 223. O. F. Schirmer and K. A. Müller, Phys. Rev. B 7, 2986 (1973).
- 224. T. Feng, Phys. Rev. B 25, 627 (1982).
- 225. A. E. Paladino, L. G. Rubin and J. S. Waugh, J. Phys. Chem. Sol. 26, 391 (1965).
- 226. A. E. Paladino, Bull. Amer. Ceram. Soc. 48, 476 (1965).
- 227. L. C. Walters and R. E. Grace, J. Phys. Chem. Sol. 28, 239 (1967).
- 228. U. Balachandran and N. G. Eror, J. Sol. St. Chem. 39, 351 (1981).

- 229. F. A. Kroger and H. J. Vink, in "Solid State Physics", Vol. 3, edited by H. Ehrenreich, F. Seitz, and D. Turnbull, (Academic Press, New York, 1956), p. 307.
- 230. H. Yamada and G. R. Miller, J. Sol. St. Chem. 6, 169 (1973).
- 231. M. A. A. Franco and M. V. Regi, Nature 270, 706 (1977).
- 232. B. C. Tofield, Nature 272, 713 (1978).
- 233. N. G. Eror and D. M. Smyth, in "Chemistry of Extended Defects in Non-Metallic Solids", edited by L. Eyring and M. O'Keefe (North-Holland, 1970), p. 62.
- 234. N. G. Eror and U. Balachandran, J. Sol. St. Chem. 40, 85 (1981).
- 235. S. N. Ruddlesden and P. Popper, Acta Cryst. 10, 538 (1957).
- 236. S. N. Ruddlesden and P. Popper, Acta Cryst. 11, 54 (1958).
- 237. E. J. W. Verwey, P. W. Haayman, F. C. Romeyn and G. W. van Oosterhout, Philips Res. Repts. 5, 173 (1950).
- 238. U. Balachandran and N. G. Eror, J. Electrochem. Soc. 129, 1021 (1982).
- 239. U. Balachandran and N. G. Eror, Comm. Amer. Ceram. Soc. 64, C-75 (1981).
- 240. N.-H. Chan, R. K. Sharma, and D. M. Smyth, J. Electrochem. Soc. 128, 1762 (1981).
- 241. U. Balachandran and N. G. Eror, J. Sol. St. Chem. 42, in press.
- 242. U. Balachandran and N. G. Eror, J. Am. Ceram. Soc. 65, in press.
- 243. U. Balachandran and N. G. Eror, J. Less Common Metals, in press.
- 244. J. G. Mavroides, J. A. Kafalas, and D. F. Kolesar, Appl. Phys. Lett. 28, 241 (1976).
- 245. T. Watanabe, A. Fujishima, and K. Honda, Bull. Chem. Soc. Jap. 49, 355 (1976).
- 246. A. B. Bocarsly, J. M. Bolts, P. G. Cummins, and M. S. Wrighton, Appl. Phys. Lett. 31, 568 (1977).

- 247. J. Vandermolen, W. P. Gomes, and F. Cardon, *J. Electrochem. Soc.* 127, 324 (1980).
- 248. M. A. Butler, M. Abramovich, F. Decker, and J. F. Juliao, *J. Electrochem. Soc.* 128, 200 (1981).
- 249. B. Reichman and C. E. Byvik, *J. Electrochem. Soc.* 128, 2601 (1981).
- 250. R. E. Schwerzel, E. W. Brooman, H. J. Byker, E. J. Drauglis, D. D. Levy, L. E. Waaler, and V. E. Wood, in "Photoeffects at Semiconductor-Electrolyte Interfaces", edited by A. J. Nozik (ACS Symposium Series #146), (Amer. Chem. Soc., Wash. D. C., 1981), pp. 191-206.
- 251. F. A. Grant, *Rev. Mod. Phys.* 31, 646 (1959).
- 252. H. P. R. Frederikse, *J. Appl. Phys. Suppl.* to 32, 2211 (1961).
- 253. A. Von Hippel, J. Kalnajs, and W. B. Westphal, *J. Phys. Chem. Sol.* 23, 779 (1962).
- 254. Z. M. Jarzebski, in "Oxide Semiconductors", edited by B. R. Pamplin (International Series of Monographs in the Science of the Solid State Vol. 4), (Pergamon Press, New York, 1973), ch. 12.
- 255. J. S. Blakemore, in preparation (unpublished).
- 256. N. Daude, C. Gout, and C. Jouanin, *Phys. Rev. B* 15, 3229 (1977).
- 257. D. W. Fischer, *Phys. Rev. B* 5, 4219 (1972).
- 258. M. L. Knotek and J. E. Houston, *Phys. Rev. B* 15, 4580 (1977).
- 259. K. Vos and H. J. Krusemeyer, *J. Phys. C* 10, 3893 (1977).
- 260. K. Vos, *J. Phys. C* 10, 3917 (1977).
- 261. H. Mathieu, J. Pascual, and J. Camassel, *Phys. Rev. B* 18, 6920 (1978).
- 262. J. Pascual, J. Camassel, and H. Mathieu, *Phys. Rev. B* 18, 5606 (1978).
- 263. J. G. Traylor, H. G. Smith, R. M. Nicklow, and M. K. Wilkinson, *Phys. Rev. B* 3, 3457 (1971).
- 264. D. C. Cronmeyer, *Phys. Rev.* 87, 876 (1952).

- 265. R. G. Breckenridge and W. R. Hosler, Phys. Rev. 91, 793 (1953).
- 266. M. D. Earle, Phys. Rev. 61, 56 (1942).
- 267. H. P. R. Frederikse, W. R. Hosler, and J. H. Becker, in "Semi-conducting Materials I" (Proceedings Internat. Semicond. Conf., Prague, 1960), p. 868.
- 268. J. Yahia, J. Phys. Chem. Sol. 25, 881 (1964).
- 269. J. H. Becker and W. R. Hosler, Phys. Rev. 137, A1872 (1965).
- 270. M. Itakura, N. Nizeki, H. Toyoda, and H. Iwasaki, Jap. J. Appl. Phys. 6, 311 (1967).
- 271. E. Iguchi, K. Yajima, T. Asahina, and Y. Kanamori, J. Phys. Chem. Sol. 35, 597 (1974).
- 272. V. E. Henrich, G. Dresselhaus, and H. J. Zeiger, Phys. Rev. Ltr. 36, 1335 (1976).
- 273. Y. W. Chung, W. J. Lo, and G. A. Somorjai, Surf. Sci. 64, 588 (1977).
- 274. C. N. Sayers and N. R. Armstrong, Surf. Sci. 77, 301 (1978).
- 275. J. Rudolph, A. Natruf 14a, 727 (1959).
- 276. P. Kofstad, J. Phys. Chem. Sol. 23, 1579 (1962).
- 277. R. Assayag, M. Dodem, and R. Faivre, C. R. Acad. Sci. Paris 240, 1212 (1955).
- 278. D. S. Tannhauser, Sol. St. Comm. 1, 223 (1963).
- 279. E. H. Greener, F. J. Barone, and W. M. Hirthe, J. Amer. Ceram. Soc. 48, 623 (1965).
- 280. J. Yahia, Phys. Rev. 130, 1711 (1963).
- 281. R. N. Blumenthal, J. Coburn, J. Baukus, and W. M. Hirthe, J. Phys. Chem. Sol. 27, 643 (1966).
- 282. A. K. Ghosh, F. G. Wakim, and R. R. Addiss Jr., Phys. Rev. 184, 979 (1969).
- 283. J. F. Marucco, J. Gautron, and P. Lemasson, J. Phys. Chem. Sol. 42, 363 (1981).

284. U. Balachandran and N. G. Eror, to be published.
285. N. G. Eror and D. M. Smyth, in "The Chemistry of Extended Defects in Non-Metallic Solids", edited by L. Eyring and M. O'Keeffe (Proceedings of the Institute for Advanced Study of the Chemistry of Extended Defects in Non-Metallic Solids), (North-Holland, 1970), p. 62.
286. J. F. Baumard and E. Tani, J. Chem. Phys. 67, 857 (1977).
287. E. Tani and J. F. Baumard, J. Sol. St. Chem. 32, 105 (1980).
288. A. Inoue and E. Iguchi, J. Phys. C: Sol. St. Phys. 12, 5157 (1979).
289. P. O. Andersson, E. L. Kollberg, and A. Jelenski, J. Phys. C: Sol. St. Phys. 7, 1868 (1974).
290. P. J. Boddy, J. Electrochem. Soc. 115, 199 (1968).
291. M. S. Wrighton, D. S. Ginley, P. T. Wolczanski, A. B. Ellis, D. L. Morse, and A. Linz, Proc. Nat. Acad. Sci. USA 72, 1518 (1975).
292. J. G. Mavroides, D. I. Tchernev, J. A. Kafalas, and D. F. Kolesar, Mat. Res. Bull. 10, 1023 (1975).
293. A. J. Nozik, Nature 257, 383 (1975).
294. R. H. Wilson, L. A. Harris, and M. E. Gerstner, J. Electrochem. Soc. 126, 844 (1979).
295. L. A. Harris, M. E. Gerstner, and R. H. Wilson, J. Electrochem. Soc. 126, 850 (1979).
296. J. Keeney, D. H. Weinstein, and G. M. Haas, Nature 253, 719 (1975).
297. J. F. Houlihan, D. P. Madacsi, E. J. Walsh, and L. N. Mulay, Mat. Res. Bull. 11, 1191 (1976).
298. W. L. Ahlgren and S. O. Sari, Surf. Sci. 76, 148 (1978).
299. K. L. Hardee and A. J. Bard, J. Electrochem. Soc. 122, 739 (1975).
300. D. Laser and A. J. Bard, J. Electrochem. Soc. 123, 1027 (1976).
301. L. A. Harris and R. H. Wilson, J. Electrochem. Soc. 123, 1010 (1976).

- 302. L. A. Harris, D. R. Cross, and M. E. Gerstner, J. Electrochem. Soc. 124, 839 (1977).
- 303. J. O'M. Bockris and K. Uosaki, J. Electrochem. Soc. 124, 98 (1977).
- 304. M. E. Gerstner, J. Electrochem. Soc. 126, 944 (1979).
- 305. J-L. Desplat, J. Appl. Phys. 47, 5102 (1976).
- 306. J. H. Carey and B. G. Oliver, Nature 259, 554 (1976).
- 307. H. Morisaki, M. Hariya, and K. Yazawa, Appl. Phys. Ltr. 30, 7 (1977).
- 308. F. Decker, J. F. Juliao, and M. Abramovich, Appl. Phys. Ltr. 35, 397 (1979).
- 309. L. M. Rouse, Mat. Res. Bull. 13, 861 (1978).
- 310. M. Tomkiewicz, J. Electrochem. Soc. 126, 1505 (1979).
- 311. M. Tomkiewicz, J. Electrochem. Soc. 126, 2220 (1979).
- 312. M. Tomkiewicz, J. Electrochem. Soc. 127, 1518 (1980).
- 313. J. Schoonman, K. Vos, and G. Blasse, J. Electrochem. Soc. 128, 1154 (1981).
- 314. H. Morisaki, T. Baba, and K. Yazawa, Phys. Rev. B 21, 837 (1980).
- 315. P. Salvador, J. Electrochem. Soc. 128, 1895 (1981).
- 316. W. Siripala and M. Tomkiewicz, J. Electrochem. Soc. 128, 2491 (1981).
- 317. W. J. Lo, Y. W. Chung, and G. A. Somorjai, Surf. Sci. 71, 199 (1978).
- 318. D. S. Ginley and M. L. Knotek, J. Electrochem. Soc. 126, 2163 (1979).
- 319. J. Augustynski, J. Hinden, and C. Stalder, J. Electrochem. Soc. 124, 1063 (1977).
- 320. S. N. Subbarao, Y. H. Yun, R. Kershaw, K. Dwight, and A. Wold, Mat. Res. Bull. 13, 1461 (1978).

- 321. J. F. Houlihan, R. F. Bonaquist, R. T. Dirstine, and D. P. Madacsi, *Mat. Res. Bull.* 16, 659 (1981).
- 322. R. Wang and C. H. Henager Jr., *J. Electrochem. Soc.* 126, 83 (1979).
- 323. C. Stalder and J. Augustynski, *J. Electrochem. Soc.* 126, 2007 (1979).
- 324. J. F. Houlihan, J. R. Hamilton and D. P. Madacsi, *Mat. Res. Bull.* 14, 915 (1979).
- 325. A. Monnier and J. Augustynski, *J. Electrochem. Soc.* 127, 1576 (1980).
- 326. P. Salvador, *Mat. Res. Bull.* 15, 1287 (1980).
- 327. Y. Matsumoto, J. Kurimoto, Y. Amagasaki, and E. Sato, *J. Electrochem. Soc.* 127, 2148 (1980).
- 328. J. F. Juliao, F. Decker, and M. Abramovich, *J. Electrochem. Soc.* 127, 2264 (1980).
- 329. G. Campet, J. Verniolle, J-P. Doumerc, and J. Claverie, *Mat. Res. Bull.* 15, 1135 (1980).
- 330. Y. Matsumoto, J. Kurimoto, T. Shimizu, and E. Sato, *J. Electrochem. Soc.* 128, 1040 (1981).
- 331. J. Claverie, J. Verniolle, G. Campet, J-P. Doumerc, and P. Hagenmuller, *Mat. Res. Bull.* 16, 1019 (1981).
- 332. U. Balachandran, Ph.D. Thesis, Oregon Graduate Center, Ch. 4 (1980).
- 333. L. J. van der Pauw, *Phil. Tech. Rev.* 20, 220 (1958).
- 334. L. J. van der Pauw, *Phil. Res. Rpt.* 13, 1 (1958).
- 335. S. Amer, *Sol. St. Elec.* 6, 141 (1963).
- 336. W. L. V. Price, *Sol. St. Elec.* 16, 753 (1973).
- 337. R. Chwang, B. J. Smith, and C. R. Crowell, *Sol. St. Elec.* 17, 1217 (1974).
- 338. D. M. Boerger, J. J. Kramer, and L. D. Partain, *J. Appl. Phys.* 52, 269 (1981).

339. C. Y. Chang, Y. K. Fang, and S. M. Sze, *Sol. St. Elec.* 14, 541 (1971).
340. V. L. Rideout, *Sol. St. Elec.* 18, 541 (1975).
341. R. S. Popović, *Sol. St. Elec.* 21, 1133 (1978).
342. S. S. Flaschen and L. G. van Uitert, *J. Appl. Phys.* 27, 190 (1956).
343. H. M. Landis, *J. Appl. Phys.* 36, 2000 (1965).
344. J. E. Carnes and A. M. Goodman, *J. Appl. Phys.* 38, 3091 (1967).
345. J. W. Fleming Jr. and H. M. O'Bryan Jr., *Ceram. Bull.* 55, 715 (1976).
346. J. Narayan and V. N. Shukla, *J. Appl. Phys.* 51, 3444 (1980).
347. "Handbook of Optics", edited by W. G. Driscoll (Optical Soc. of Amer.), (McGraw-Hill, New York, 1978), p. 7-23.
348. E. A. Wood, in "Crystals and Light", (Van Nostrand, New York, 1964), pp. 84-87.
349. E. A. Wood, in "Crystal Orientation Manual", (Columbia Univ. Press, New York, 1963), p. 32.
350. N. F. Mott, in "Metal-Insulator Transitions", (Taylor and Francis, London, 1974), Sec. 6.4.
351. H. Brooks, *Advances in Elec. and Elec. Phys.* 7, 85 (1955).
352. F. P. Koffybert, K. Dwight, and A. Wold, *Sol. St. Comm.* 30, 433 (1979).
353. B. Odekirk, U. Balachandran, N. G. Eror, and J. S. Blakemore, *Mater. Res. Bull.* 17, 199 (1982).
354. B. Tuck, in "Introduction to Diffusion in Semiconductors", (IEE Monograph Series 16), (Peter Peregrinus Ltd., Stevenage, England, 1974).
355. S. Amelinckx and W. Dekeyser, in "Solid State Physics", Vol. 8, edited by H. Ehrenreich, F. Seitz, and D. Turnbull, (Academic Press, New York, 1961), p. 325.
356. R. A. Swalin, in "Thermodynamics of Solids", 2nd edition, (Wiley & Sons, New York, 1972), ch. 10.

- 357. J. H. Brophy, R. M. Rose, and J. Wulff, in "The Structure and Properties of Materials, Vol. II: Thermodynamics of Structure", (Wiley & Sons, New York, 1964), ch. 5.
- 358. G. Levin and C. J. Rosa, Z. Metallkunde 70, 601 (1979).
- 359. G. Levin and C. J. Rosa, Z. Metallkunde 70, 646 (1979).
- 360. B. G. Hyde and L. A. Bursill, in "The Chemistry of Extended Defects in Non-Metallic Solids", edited by L. Eyring and M. O'Keefe, (North Holland, Amsterdam, 1970), pp. 347-378.
- 361. M. A. Butler and D. S. Ginsley, Chem. Phys. Lett. 47, 319 (1977).
- 362. U. Balachandran, B. Odekirk, and N. G. Eror, J. Sol. St. Chem. 41, 185 (1982).
- 363. J. F. McCann and S. P. S. Badwal, J. Electrochem. Soc. 129, 551 (1982).
- 364. C. H. Perry, J. H. Fertel, and T. F. McNelly, J. Chem. Phys. 47, 1619 (1967).
- 365. "Handbook of Optics", edited by W. G. Driscoll (Optical Society of America), (McGraw-Hill, New York, 1978), p. 7-106.

APPENDIX I
PHOTOELECTRODE MATERIALS

Table AI.1. Bandgap and flatband potentials for various semiconductors studied as electrodes for photodecomposition of water.

Material	Bandgap (eV)	Flatband Potential vs. SCE (pH = 13)	Remarks	Reference
TiO ₂	3.0	-0.80	Stable	291-295
SrTiO ₃	3.2	-1.15	Stable	103
BaTiO ₃	3.3	-0.80	Stable	101,105
FeTiO ₃	2.2	-0.59	Corrodes	361
CaTiO ₃	3.46	-1.2	Stable	11,362
KTaO ₃	3.5	-1.2	Stable	9
Pb(La)TiO ₃	3.0	-	Insulating	9
Pb(Zr)TiO ₃	2.9	-	Insulating	9
Fe ₂ TiO ₄	2.1	0.2	Corrodes	9
Fe ₂ TiO ₅	2.2	0.5	Stable	9
FeNbO ₄	2.2	-0.1		89
Fe ₂ O ₃	2.2	-0.67	Stable	97,102-108
Cu ₂ O	2.2		Corrodes	9
CuO	1.7	-0.11	Corrodes	97
WO ₃	2.7	-0.54	Stable, low pH	77,83,97
ZnO	3.2	-1.09	Corrodes	77
SnO ₂	3.7	-0.82	Stable	77
SiC	3.0	-2.3	Corrodes	9
V ₂ O ₅	2.75	0.13	Corrodes	97
PbO	2.8	-0.54	Corrodes	97

GaP	1.7	0.07	Stable, low pH	85,90-91
CdS	2.42	-0.74	Corrodes	92
CdSe	1.71	-0.44	Corrodes	92-93,95
ZnSe	2.6-2.7	-	Corrodes	9,115
CdFe ₂ O ₄	2.3	-0.2	Stable	105
PbFe ₁₂ O ₁₉	2.3	0.0	Stable	105
Pb ₄ Ti ₃ WO ₁₃	2.4	-0.6	Stable	105
Hg ₂ Ta ₂ O ₇	1.8	0.1	Stable	105
Hg ₂ Nb ₂ O ₇	1.8	0.2	Stable	105
ZrO ₂	5.0	-2.0	Stable	9
Ta ₂ O ₅	4.0	-1.44	Stable	9,77
Nb ₂ O ₅	3.4	-1.0	Stable	9
Sr ₂ Nb ₂ O ₇	3.9	-1.3		89
Fe ₂ O ₃ /TiO ₂	2.2	-0.7		363
In ₂ O ₃	2.4	-0.7	Stable	99
NaNbO ₃		-1.28		85
CdTe	1.4	-0.08		85,94-95
GaSe		-0.2		85
CuInS ₂		0.06		85
InSe		-1.02		85
BaSrNb ₄ O ₁₂	3.4	-0.9		89
MoS ₂	1.75		Corrodes	109
MoSe ₂	1.4		Corrodes	109
p-WSe ₂	1.35			110
BiOCl	3.5			110
Bi ₄ Ti ₃ O ₁₂	3.4			110
Bi ₂ O ₂	3.5			110
Bi ₂ WO ₆	3.1			110
NiNb ₂ O ₆	3.6			110
MgNb ₂ O ₆	4.5			110
Ti _{0.9} Nb _{0.1} O ₂	1.8			115

Bi ₂ O ₃	2.8	-0.25	Corrodes	97
YFeO ₃	2.6	-0.5	Stable	9
CdO	2.3	-0.22	No Response	9,77
Si	1.1	-1.7	Corrodes	9
InP	1.25	-1.2	Corrodes	9,95
GaAs	1.42	-0.3	Corrodes	82,95

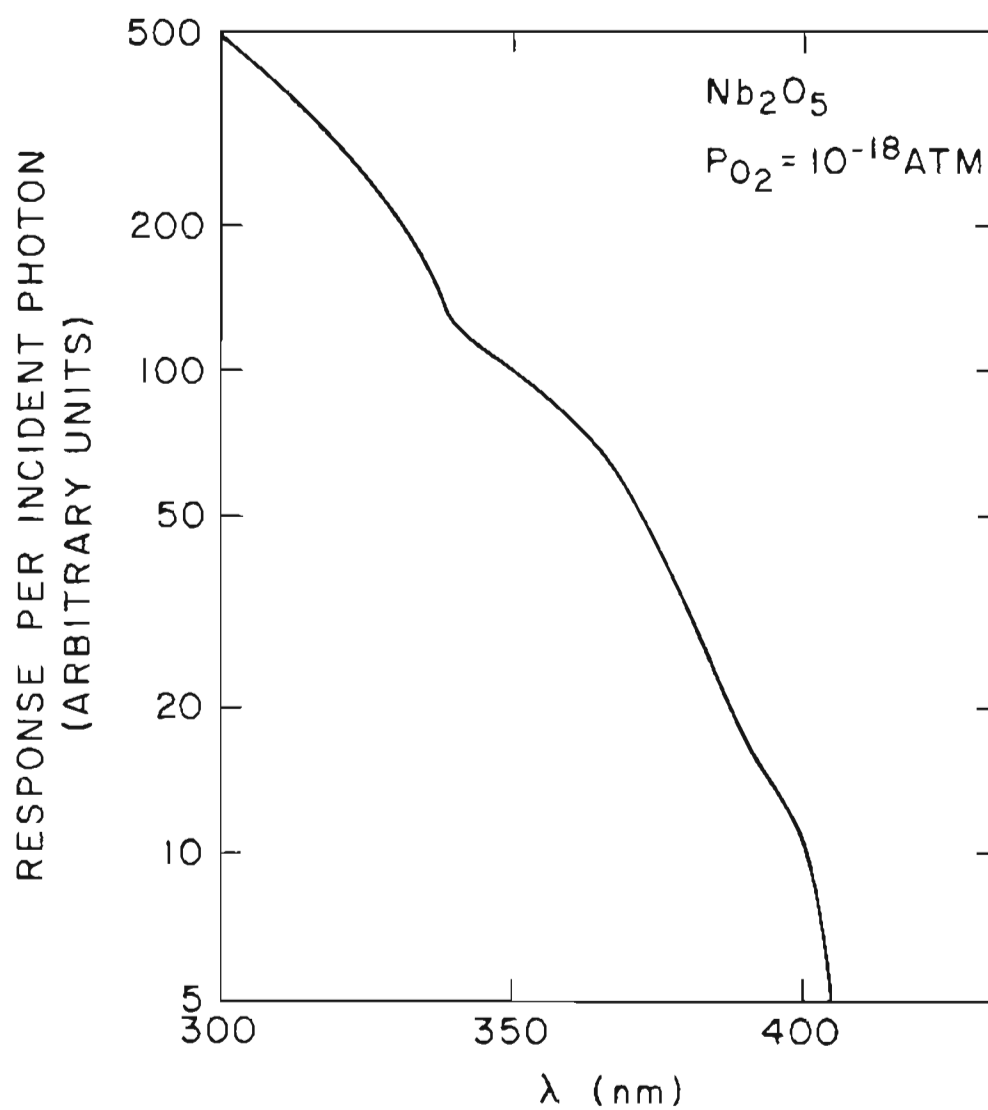


Figure A1.1. Spectral response plot of ceramic Nb₂O₅ photoanode, as measured in 1M NaOH PEC cell, as discussed in Section 4.5.

APPENDIX II

 SrTiO_3 BAND STRUCTURE DIAGRAMS

Figure A2.1 demonstrates the TiO_6 -octahedra found in the crystal structure of SrTiO_3 (219).

The E-k plots derived from various models for SrTiO_3 are reproduced below as follows:

Figure A2.2. Kahn and Leyendecker (126) LCAO model.

Figure A2.3. Soules et al. (132) self-consistent-field (SCF) LCAO model.

Figure A2.4. Mattheiss (133) nonrelativistic APW model, fitted to the Slater and Koster LCAO interpolation scheme.

Figure A2.5. Wolfram et al. (177) LCAO, generalized-Seitz-ionic model.

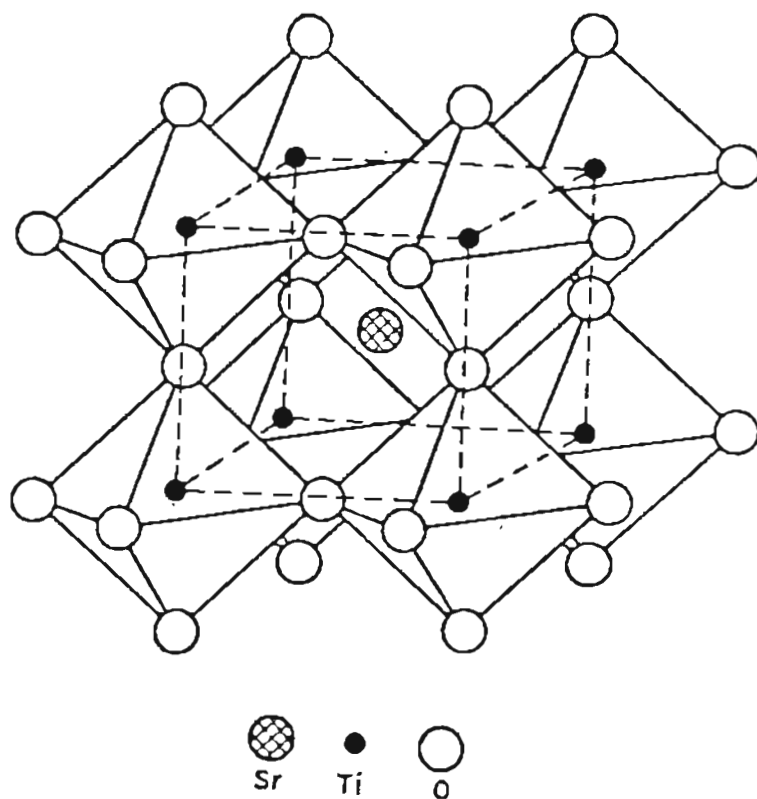


Figure A2.1. The crystal structure of SrTiO₃, displaying the TiO₆ octahedra. (From Ensign and Stokowski, reference 219).

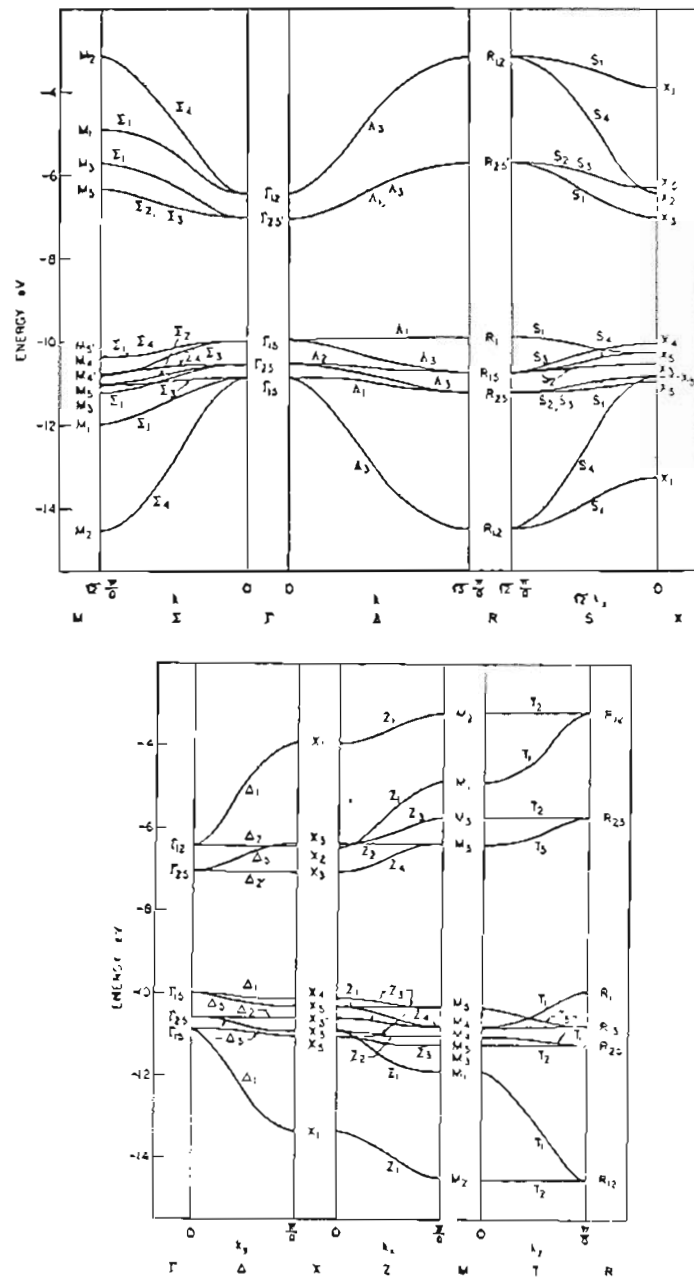


Figure A2.2. Plot of energy versus wave vector for lines of symmetry of the Brillouin zone. (From Kahn and Leyendecker, reference 126).

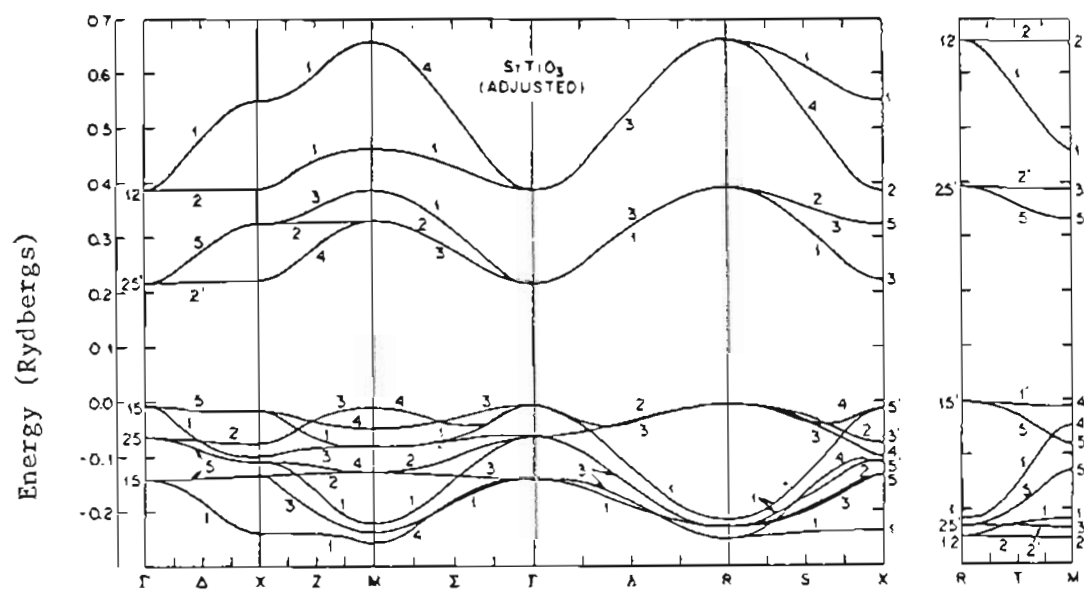


Figure A2.4. Plot of energy vs. wave vector along symmetry lines.
(From Mattheiss, reference 133).

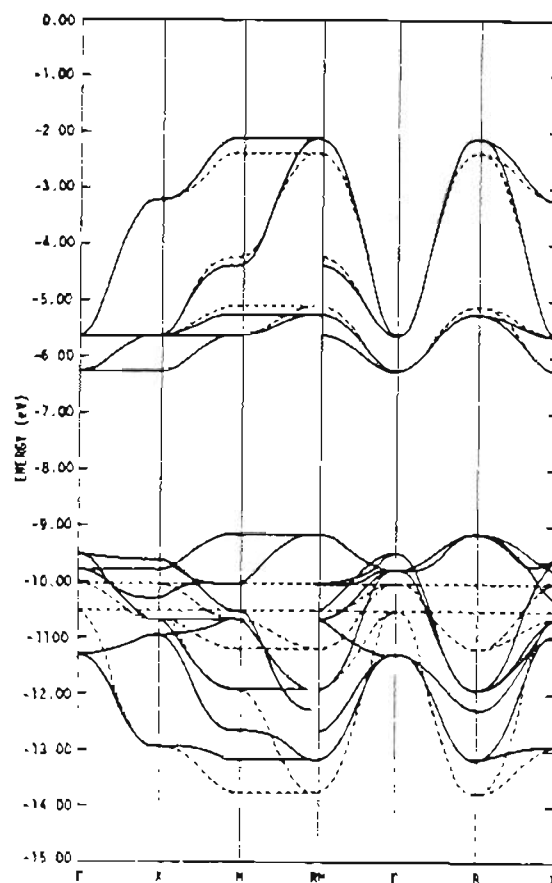


Figure A2.5. Energy vs. wave vector along symmetry lines of the Brillouin zone. The dashed curves neglect the $(pp\sigma)$ and $(pp\pi)$ interactions. (From Wolfram et al., reference 177).

APPENDIX III
SUPERCONDUCTING SrTiO_3

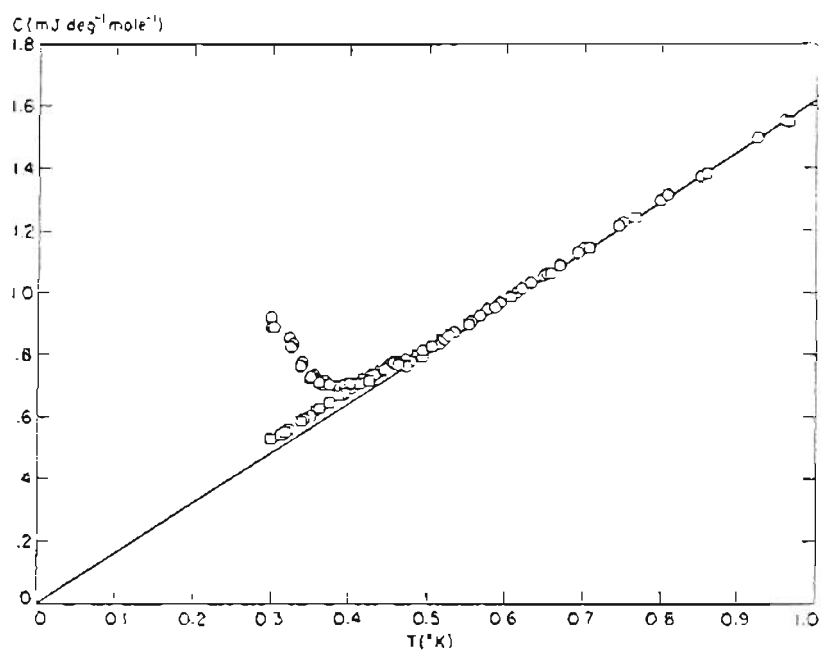


Figure A3.1. Heat capacity of polycrystalline Nb-doped SrTiO_3 ($n_c = 1.4 \times 10^{20} \text{ cm}^{-3}$) below 1 K in the earth's field (open circles) and in 260 Oe (open squares). The solid curve is given by:

$$C = 1.60T + 2.1 \times 10^{-2} T^3 + 9 \times 10^{-4} T^5$$

(From Ambler et al., reference 196).

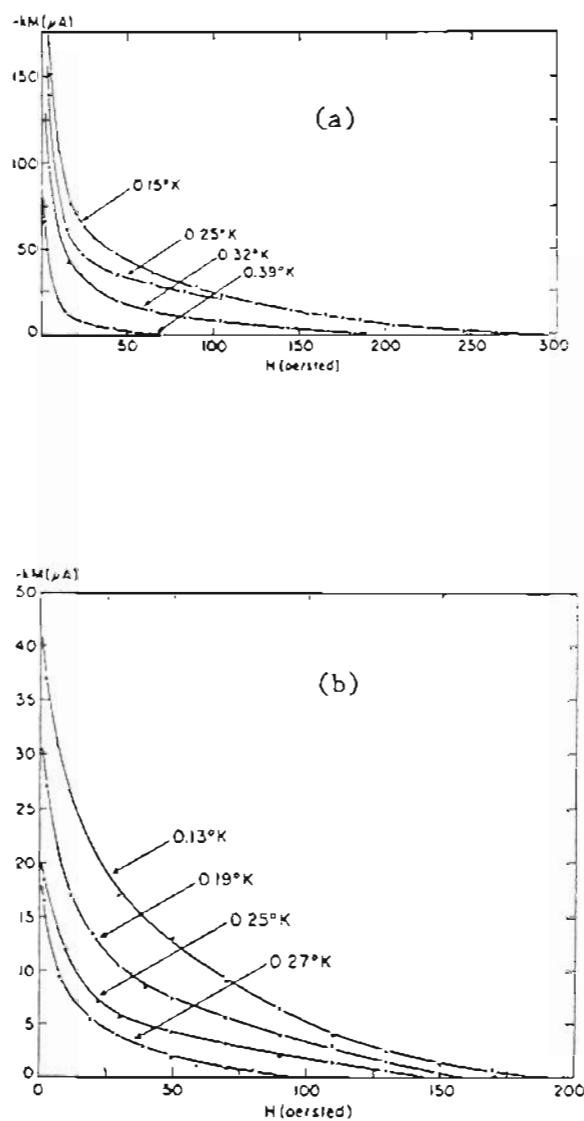


Figure A3.2. Magnetization curves for (a) single crystal Nb-doped SrTiO_3 ($n_c = 1.7 \times 10^{20} \text{ cm}^{-3}$) and (b) single crystal reduced SrTiO_3 ($n_c = 1.0 \times 10^{20} \text{ cm}^{-3}$). (From Ambler et al., reference^c196).

APPENDIX IV
PHONON SPECTRUM OF SrTiO_3

Table A4.1. Raman bands observed in SrTiO_3 as a function of temperature (frequencies are all in cm^{-1}). (From Balachandran and Eror, reference 159).

	78K	100K	120K	175K	223K	273K	295K	333K	393K
A	48	48	49						
B	71	73	73	75	75	77	77	81	83
C	148	146	146						
D	169	169	172	174	170	171	171	170	
E	235	238	236						
F	255	255	253	250	250	250	250	252	256
G	293	297	299	305	308	311	313	316	320
H	378	372	370	368	372	374	375	380	381
I	450	450	450						
J	561	562	561	560	561	561	561	561	561
K	620	616	617	619	619	620	620	620	623
L	676	674	678	680	680	678	678	678	678
M	719	718	714	716	720	721	723	725	725
N	784	779	793						
P	1040	1043	1046	1040	1038	1033	1036	1040	1040
Q	1320	1312	1315	1316	1318	1320	1320	1320	1320
R	1620	1600	1600	1606	1610	1610	1607	1610	1610

Table A4.2. Frequencies (cm^{-1}) of phonon branches at the edge of the Brillouin zone for SrTiO_3 (295 K).

Phonon Branch	Reference 159	Reference 123	Reference 364
TO_1	122	117	120
TO_2	196	194	190
TO_3	339	328	330
TO_4	508	544	540
LO_1	233	270	
LO_2	518	473	
LO_3	576	550	
LO_4	804	807	
TA	122	117	110
LA	147	150	

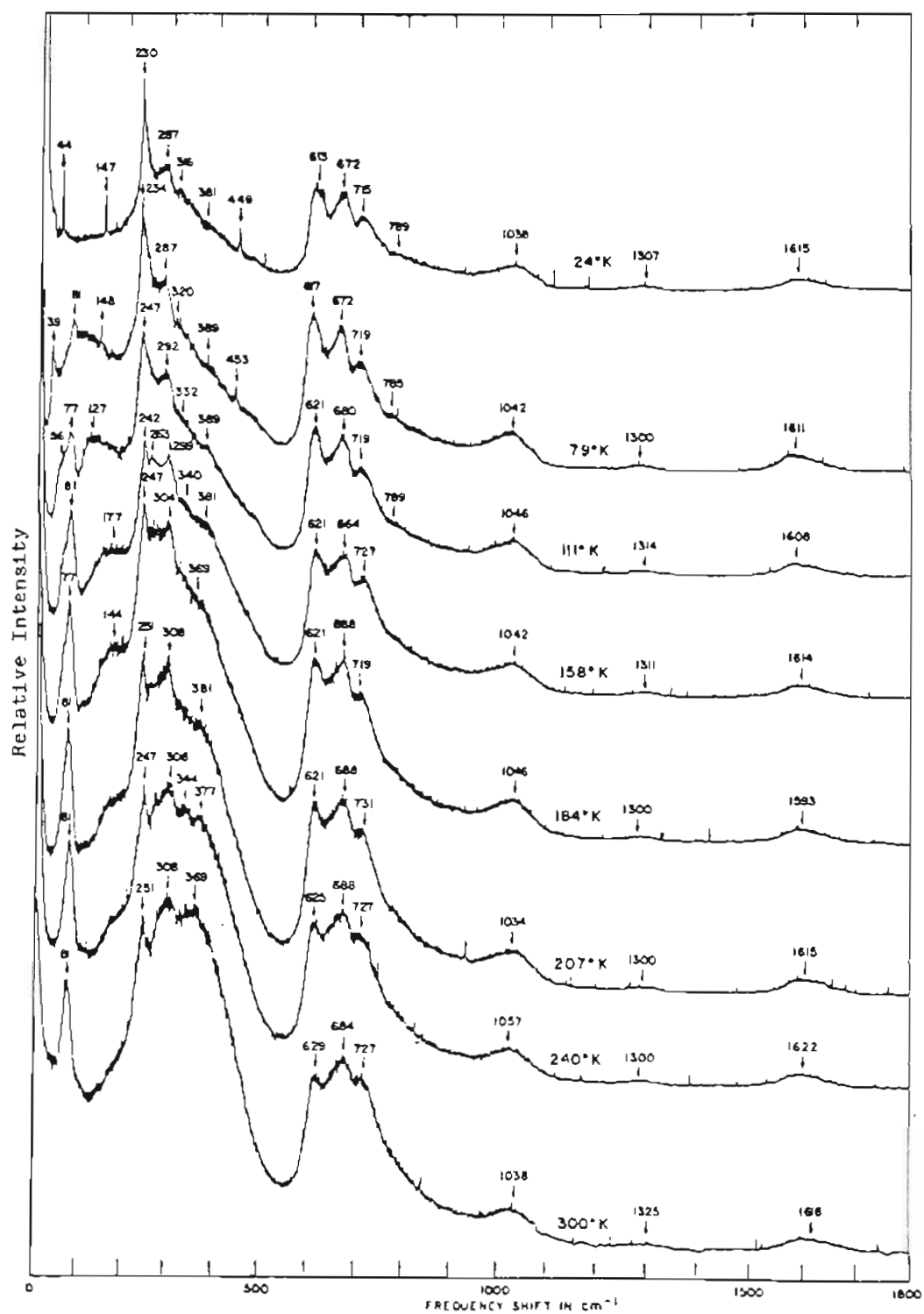


Figure A4.1. The Raman spectrum of pure SrTiO_3 as a function of temperature using the 488 nm laser line. (From ref. 156).

$\lambda, \mu\text{m}$	n	$\lambda, \mu\text{m}$	n	$\lambda, \mu\text{m}$	n	$\lambda, \mu\text{m}$	n
0.40	2.66386	0.68	2.37135	0.96	2.32035	3.40	2.21370
0.44	2.56007	0.72	2.35998	1.00	2.31633	3.80	2.19428
0.48	2.49751	0.76	2.35055	1.40	2.29073	4.20	2.17265
0.52	2.45553	0.80	2.34260	1.80	2.27498	4.60	2.14865
0.56	2.42544	0.84	2.33583	2.20	2.26109	5.00	2.12212
0.60	2.40285	0.88	2.32997	2.60	2.24676	5.40	2.09290
0.64	2.38532	0.92	2.32486	3.00	2.23111		

Dispersion Equation

$$n = A + BL + CL^2 + DL^3 + EL^4$$

where

$$A = 2.28355 \quad D = -0.0061335$$

$$B = 0.035906 \quad E = -0.00001502$$

$$C = 0.001666 \quad L = \frac{1}{\lambda^2 - 0.028}$$

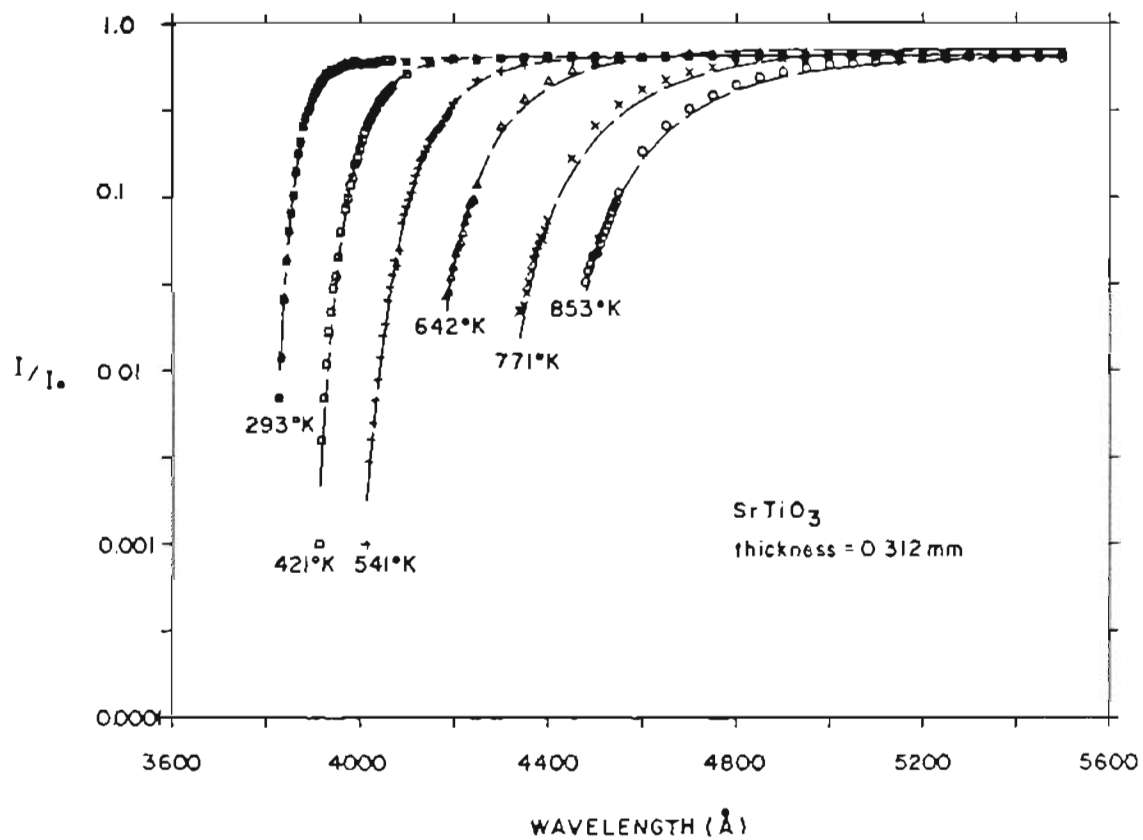


Figure A5.1. Transmitted intensity of SrTiO_3 single crystal of thickness = 0.312 mm. (From Barbosa et al., reference 163).

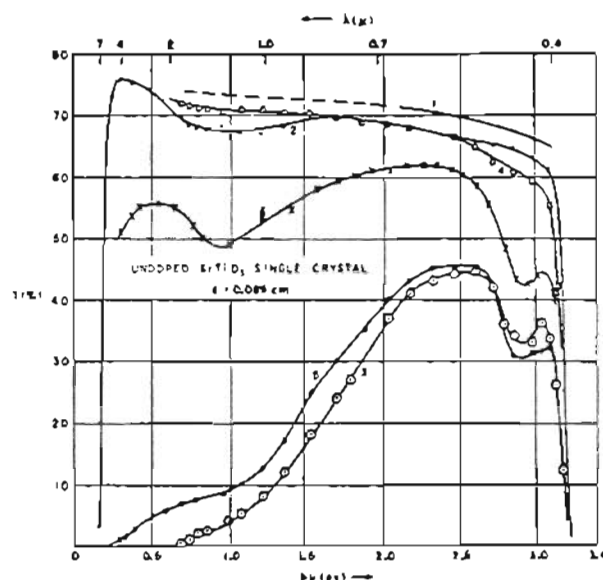


Figure A5.2. Transmission spectra of heat-treated pure SrTiO_3 . (1) plot of $T = 2n/(n^2+1)$; (2) untreated crystal; (3) 3 hrs at 1315 K in vacuum; (4) 5.25 hrs at 1525 K in oxygen; (5) 2 hrs at 1315 K in vacuum; crystal brought back to stoichiometry by oxygen heating, then (6) 2 hrs at 1225 K in vacuum. (From Gandy, reference 161).

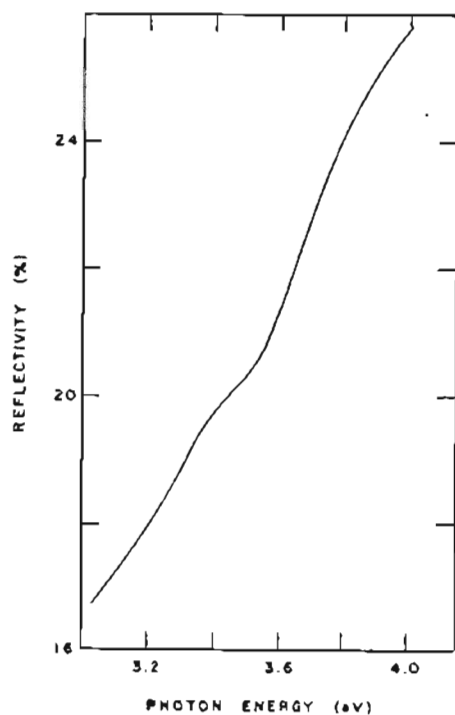


Figure A5.3.

Room temperature reflectivity of SrTiO_3 in the range 3.0-4.0 eV. (From Cohen and Blunt, reference 164).

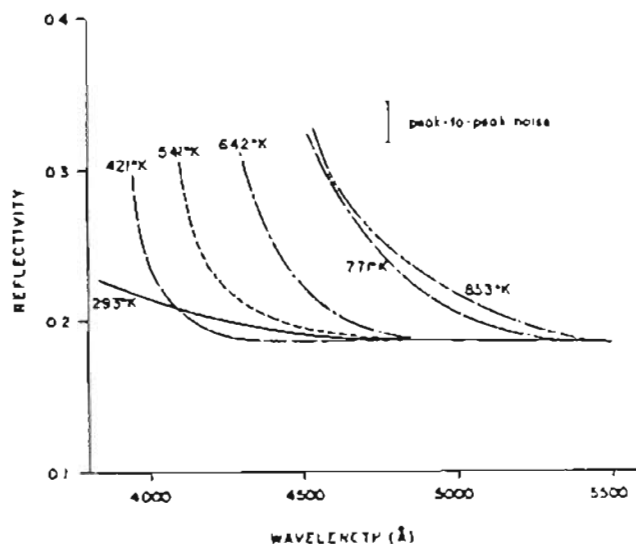


Figure A5.4.

Reflectivity of SrTiO_3 as a function of temperature and energy (2.2-3.1 eV). (From Barbosa et al., reference 163).

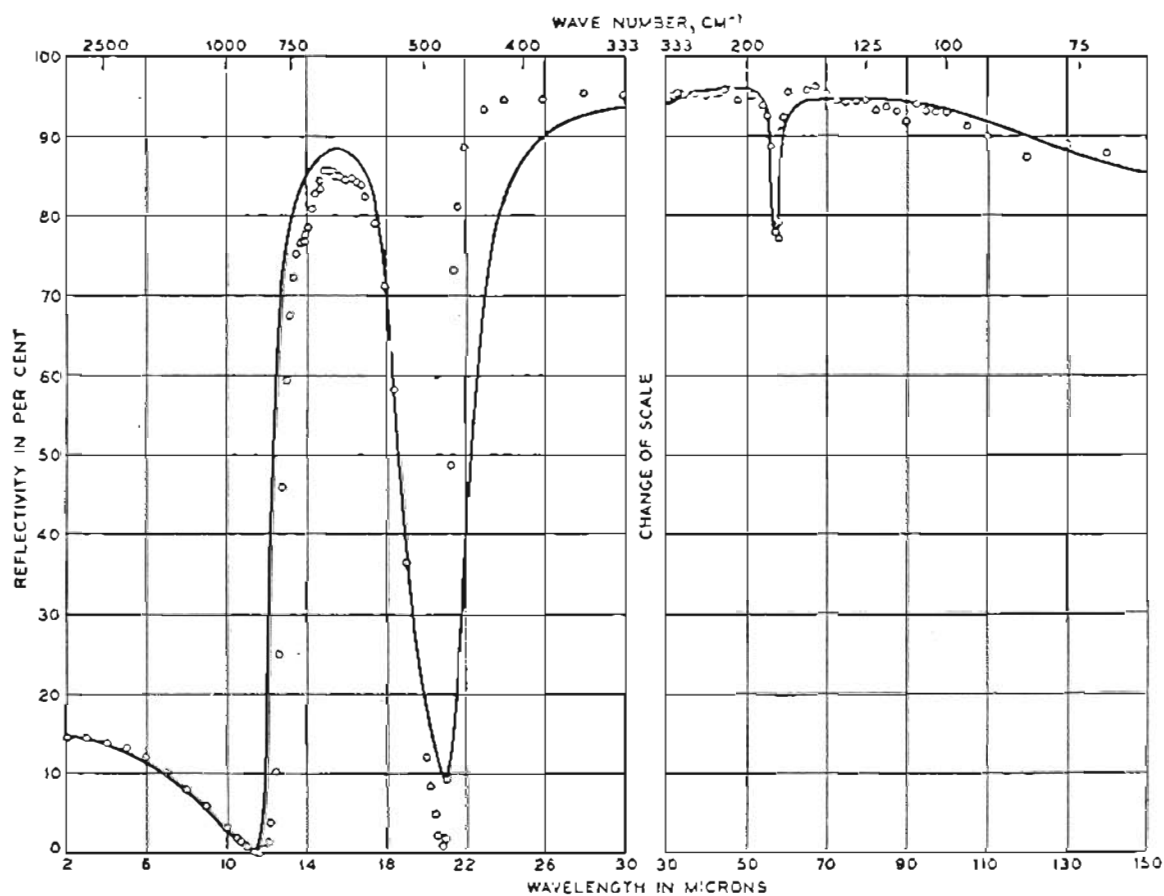


Figure A5.5. Reflectivity in the infrared. Solid curve was calculated using dispersion theory. (From reference 174).

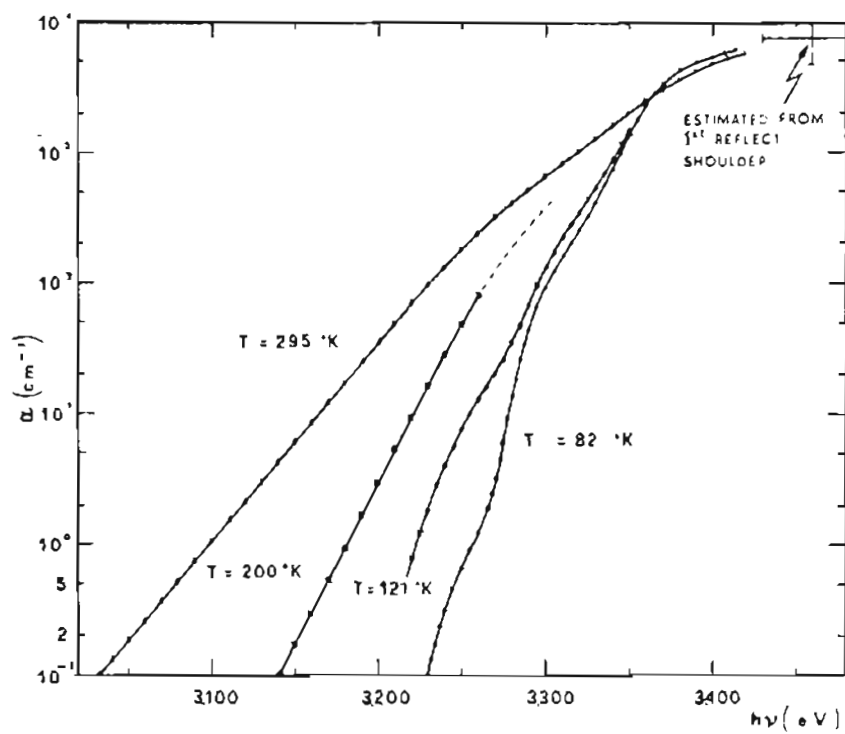


Figure A5.6. Absorption coefficient of SrTiO_3 for four different temperatures near the intrinsic edge (3.0–3.4 eV). (From Capizzi and Frova, reference 169).

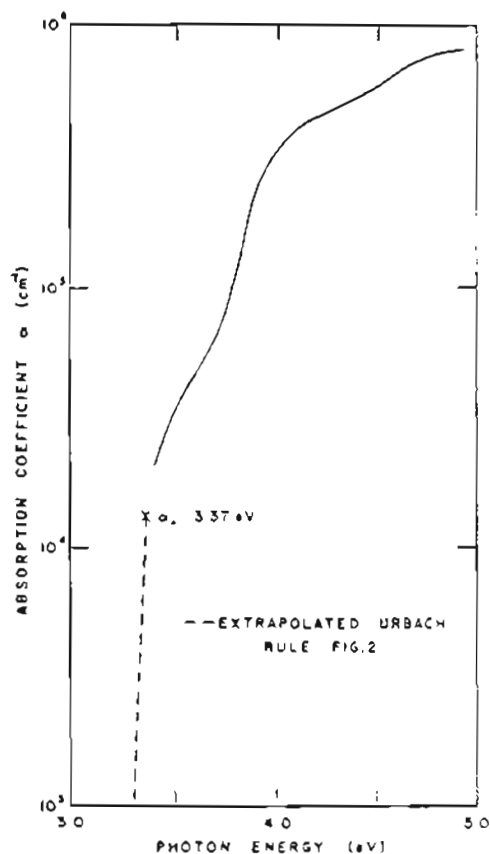


Figure A5.7.

Absorption coefficient in the range 3.4-5.0 eV. (From Cohen and Blunt, reference 164).

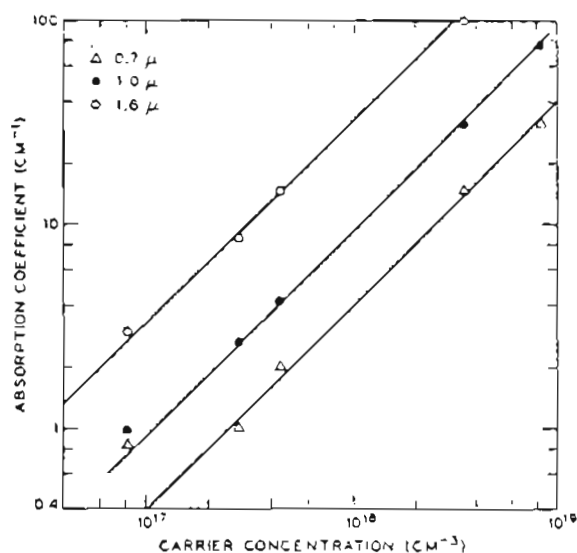


Figure A5.8.

Room temperature absorption coefficient as a function of carrier concentration at 3 different wavelengths. The lines drawn have unity slope. (From Baer, reference 191).

APPENDIX VI

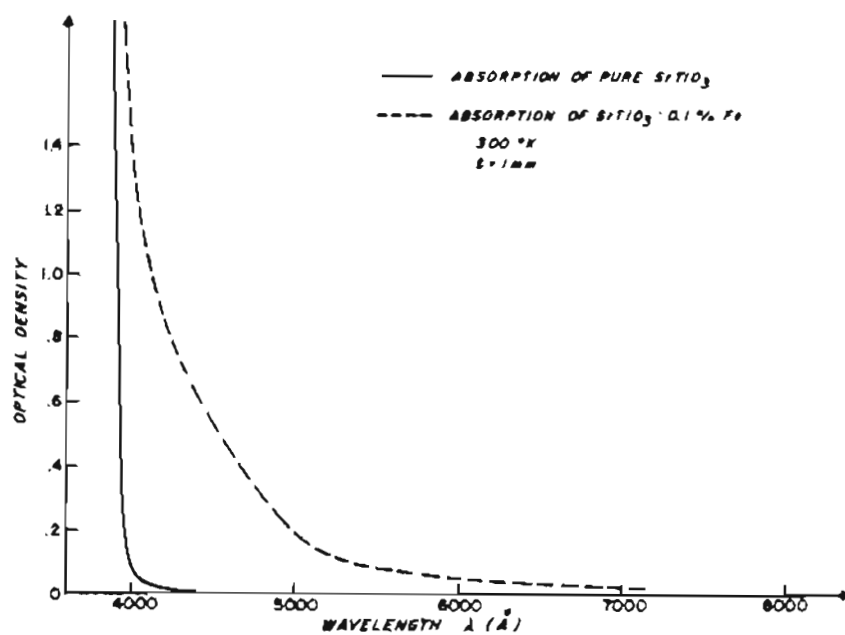
OPTICAL DENSITY OF PHOTOCHROMIC SrTiO_3 

Figure A6.1. Absorption spectra of pure and Fe-doped SrTiO_3 . (From Kiss, reference 205).

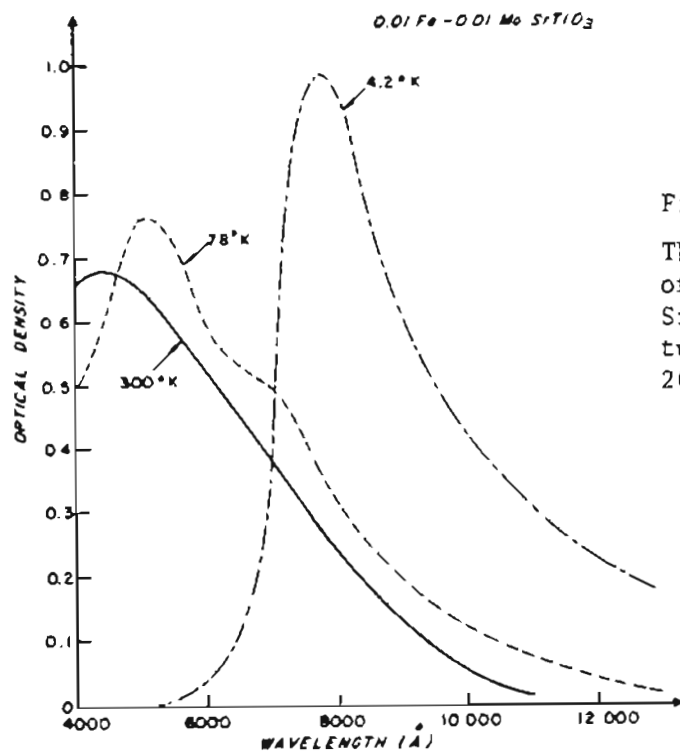


Figure A6.2.

The induced-absorption spectra of low-concentration Fe-doped SrTiO_3 at different temperatures. (From Kiss, reference 205).

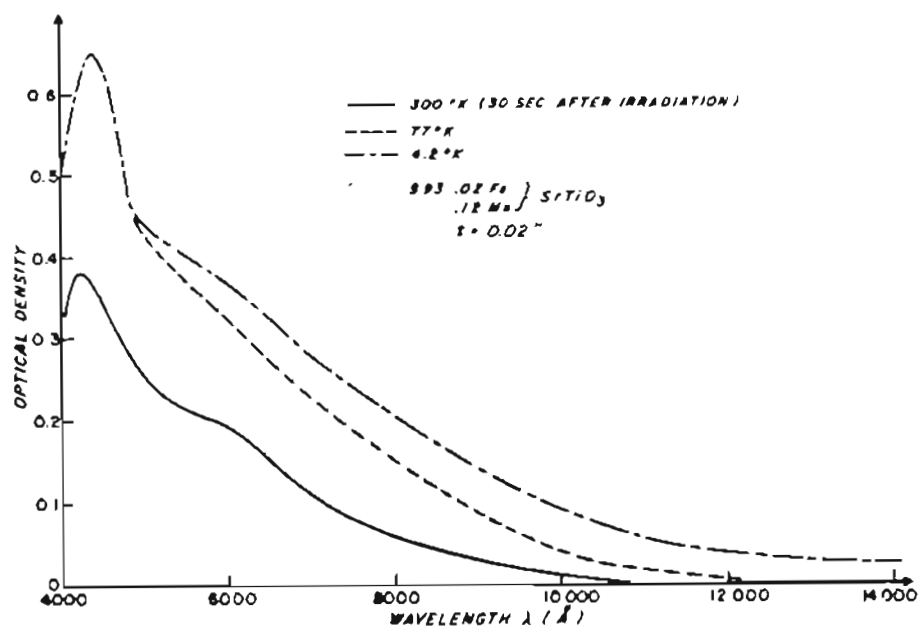


Figure A6.3. The induced-absorption spectra of Fe/Mo-doped SrTiO_3 at various temperatures. (From Kiss, reference 205).

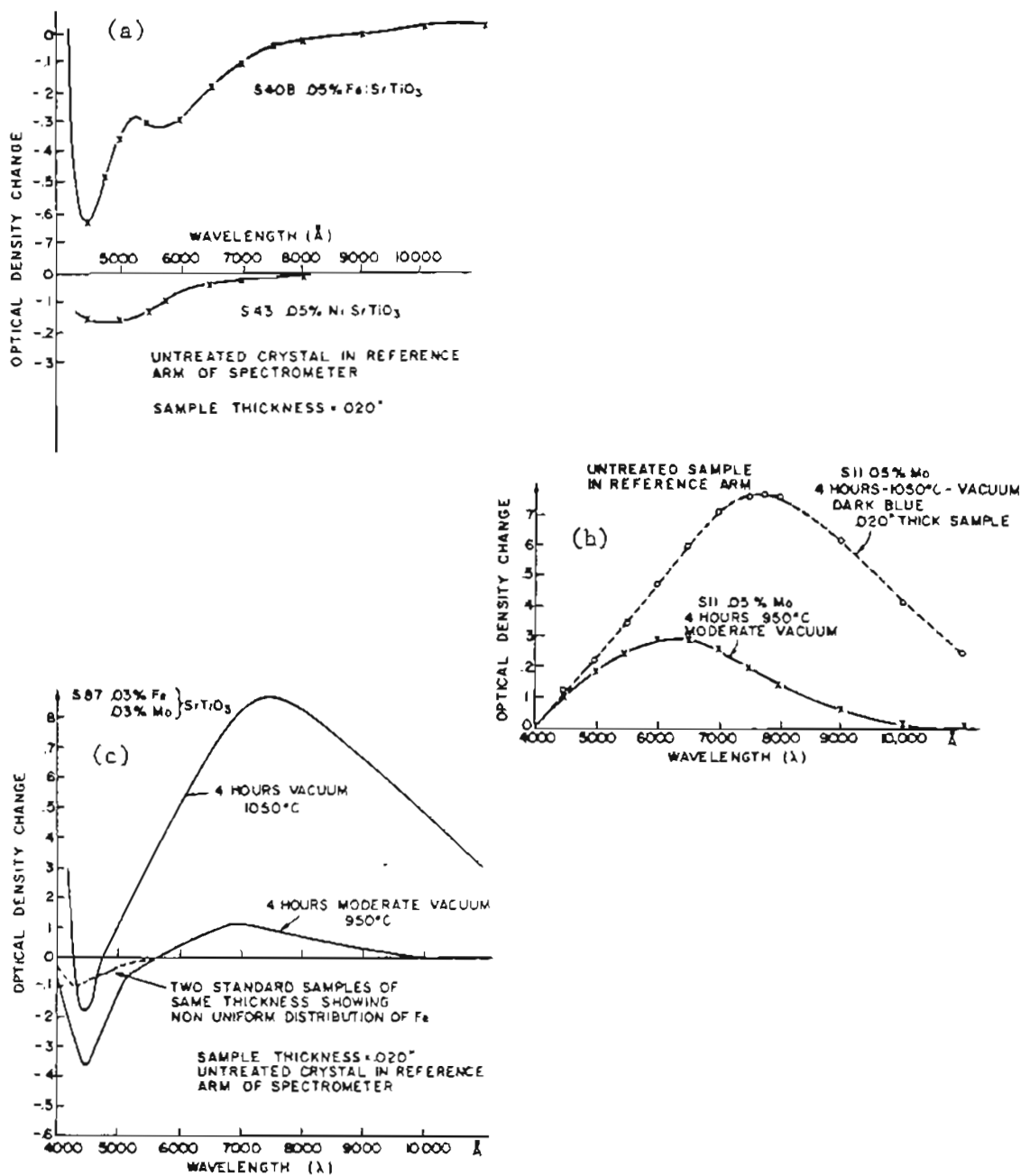


Figure A6.4. Optical density changes in reduced (a) Fe- and Ni-doped, (b) Mo-doped, and (c) Fe/Mo-doped SrTiO_3 . (From Faughnan and Kiss, reference 206).

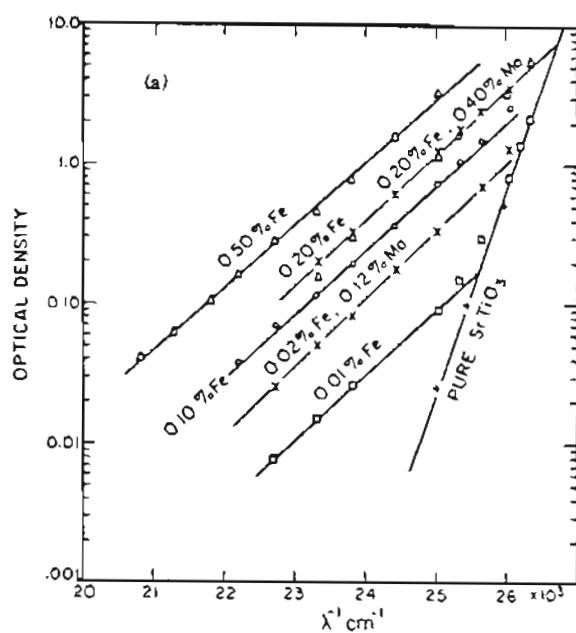
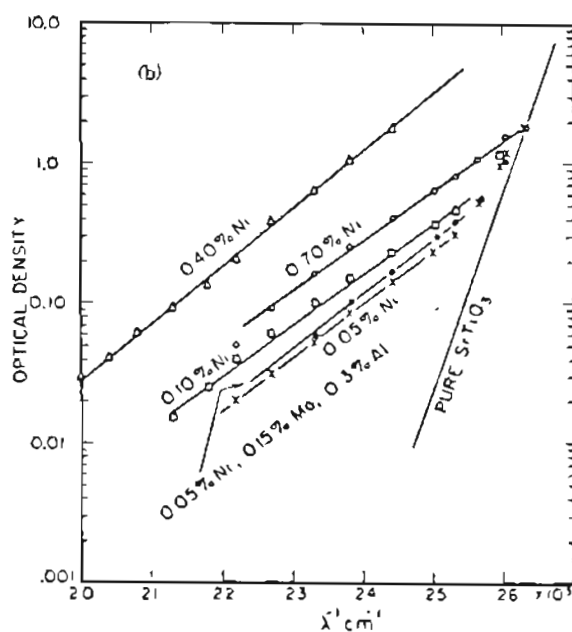


Figure A6.5.

Absorption band near the band edge in (a) Fe:SrTiO₃ and (b) Ni:SrTiO₃. (From Faughnan, reference 207).



APPENDIX VII
ELECTRONIC PROPERTIES OF SINGLE CRYSTAL SrTiO_3

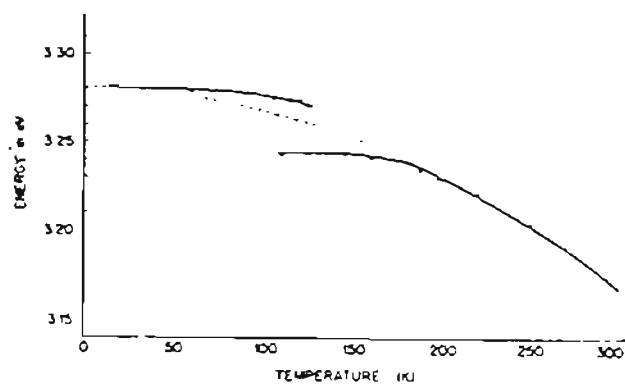


Figure A7.1. Variation of bandgap of SrTiO_3 with temperature.
(From Blazey, reference 170).

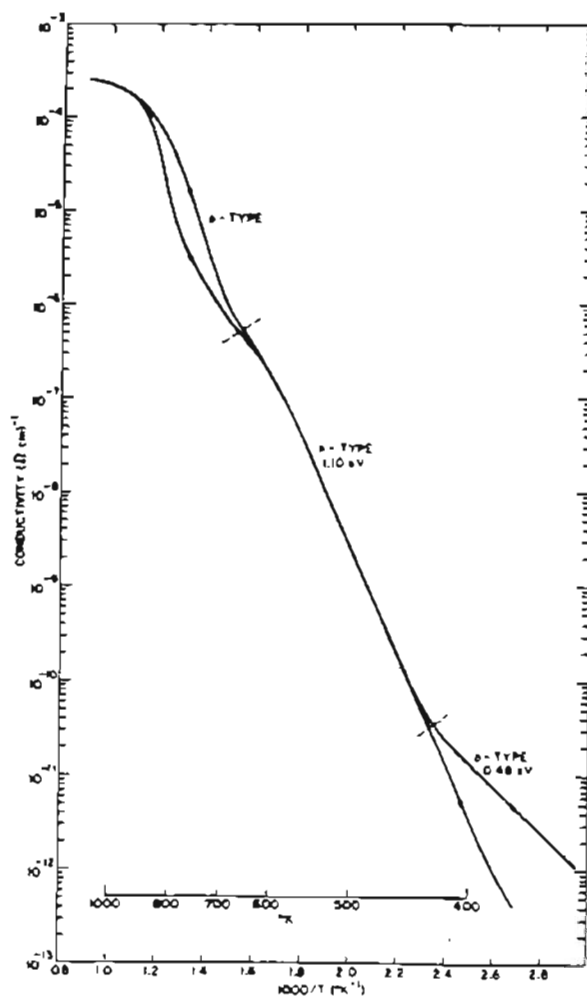
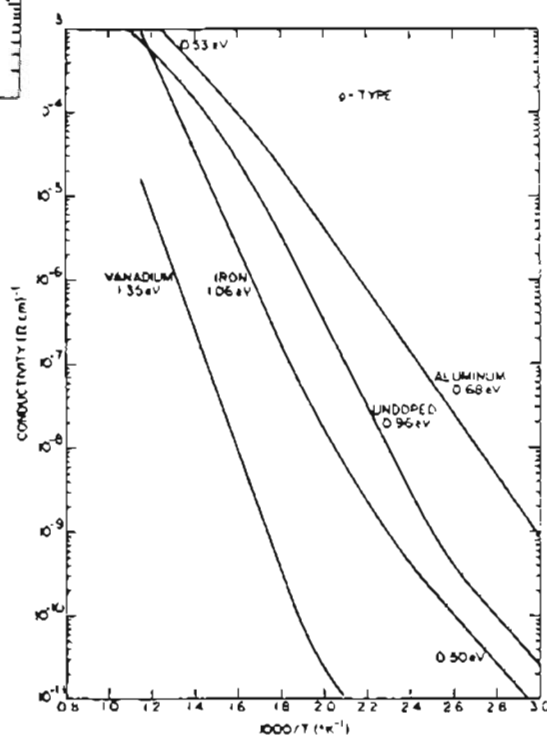


Figure A7.2.

σ vs. $1000/T$ for an as-grown crystal SrTiO_3 sample. (From Morin and Oliver, reference 211).

Figure A7.3.

σ vs. $1000/T$ for oxidized samples of undoped, and Va-, Fe-, and Al-doped SrTiO_3 crystals. (From Morin and Oliver, reference 211).



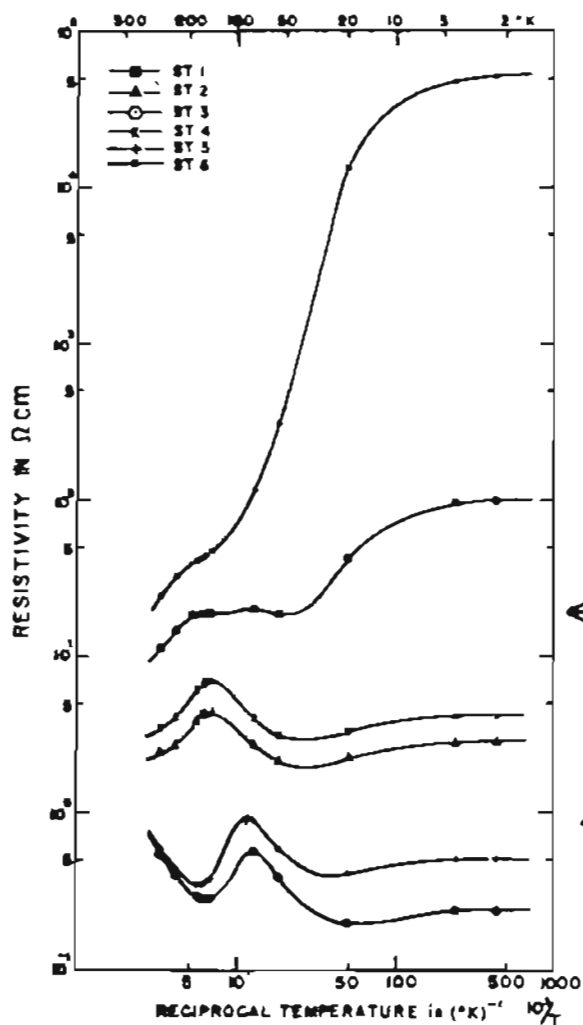


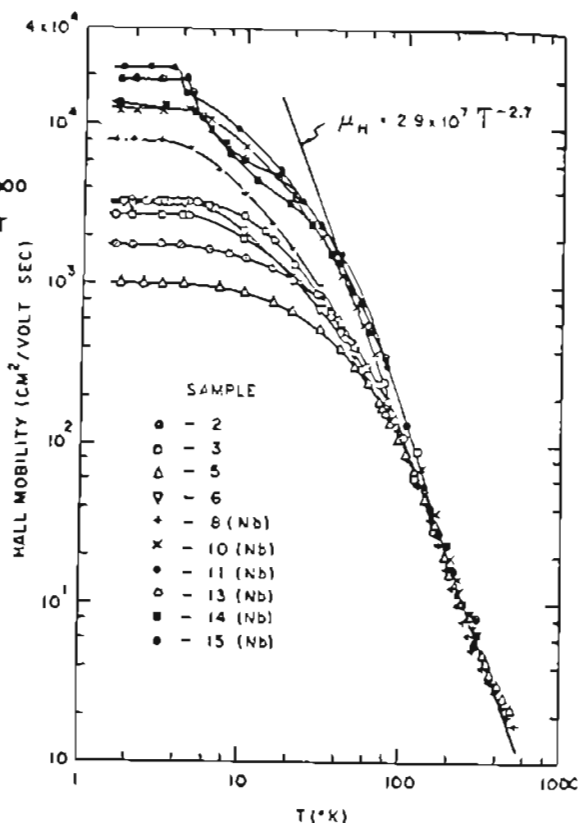
Figure A7.4.

Resistivity vs. $1000/T$ for slightly reduced samples of SrTiO_3 single crystal. (From Lee et al., reference 193).

Sample No.	n (cm^{-2})
ST3	2.08×10^{18}
ST5	3.25×10^{18}
ST2	5.87×10^{17}
ST4	4.94×10^{17}
ST1	1.18×10^{17}
ST6	7.72×10^{16}

Figure A7.5.

Temperature dependence of the Hall mobility in SrTiO_3 . (From Tufte and Chapman, reference 192).



APPENDIX VIII
 SrTiO_3 PHOTOANODES

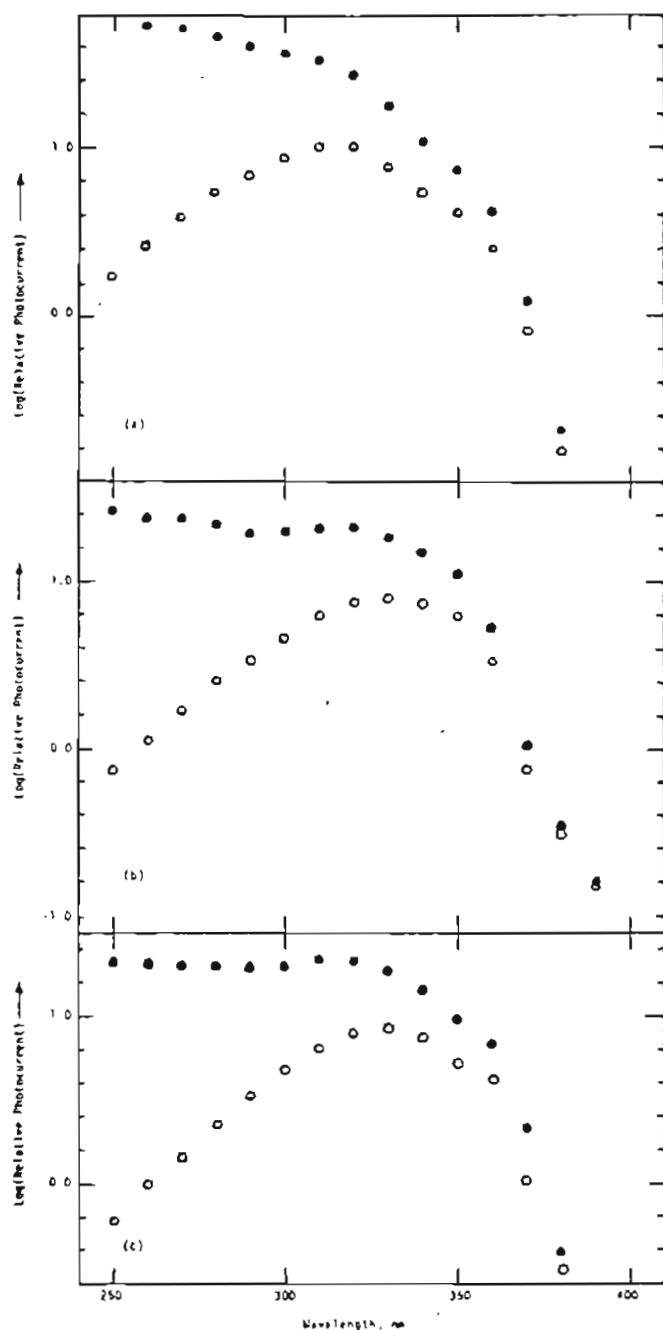


Figure A8.1.

Relative photocurrent vs. wavelength for three SrTiO_3 crystal photoanodes. Open circles are observed response, closed circles are corrected for incident light intensity. (From Wrighton et al., reference 103).

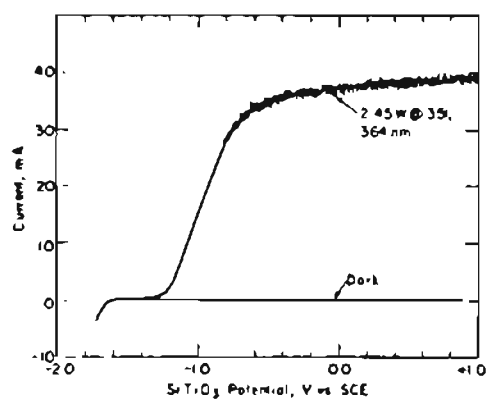


Figure A8.2. Current-voltage curve for SrTiO_3 crystalline photoanode. (From Bocarsly et al., reference 246).

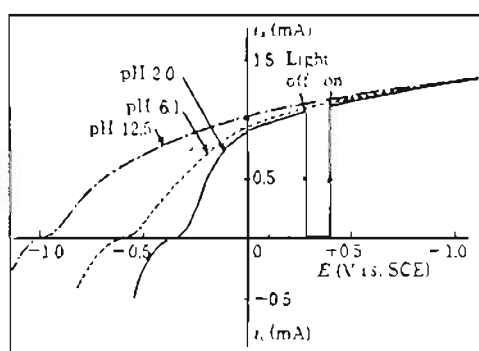


Figure A8.3. Current-voltage characteristics of SrTiO_3 electrode. (From Watanabe et al., reference 245).

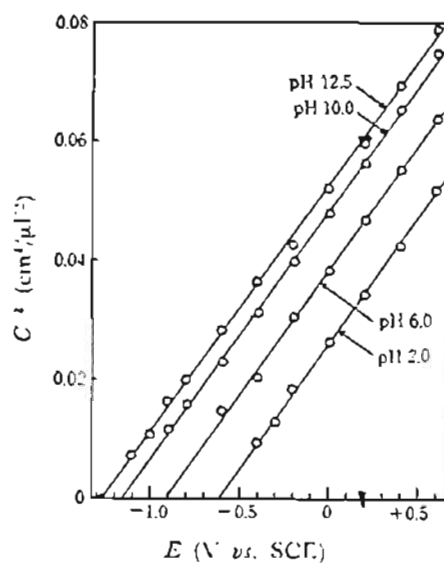


Figure A8.4. Mott-Schottky plots for SrTiO_3 electrode. (From Watanabe et al., reference 245).

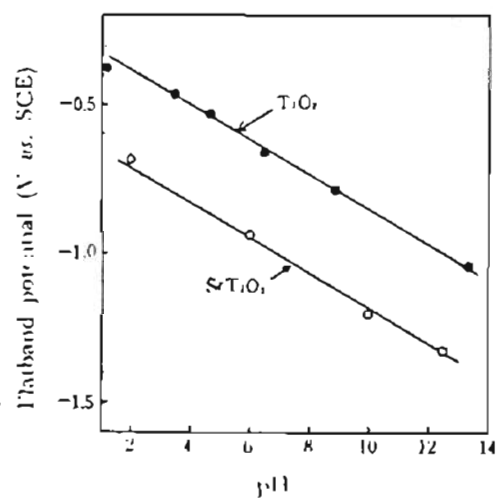


Figure A8.5. Dependence of the flatband potentials of SrTiO_3 and TiO_2 single crystal electrodes on pH. (From Watanabe et al., reference 245).

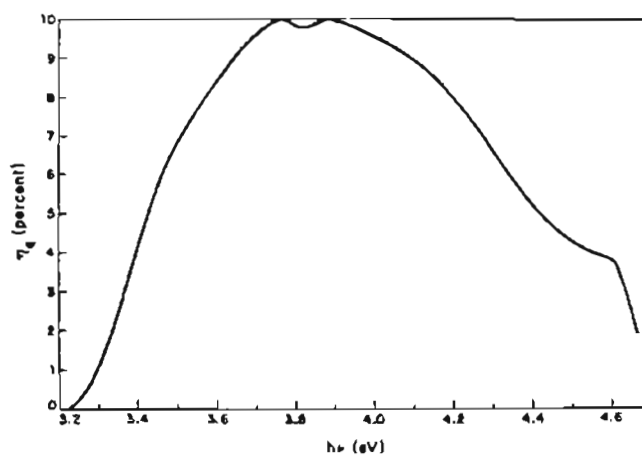


Figure A8.6. External quantum efficiency at zero bias vs. photon energy for SrTiO_3 photoanode in 10N NaOH. (From Mavroides et al., reference 244).

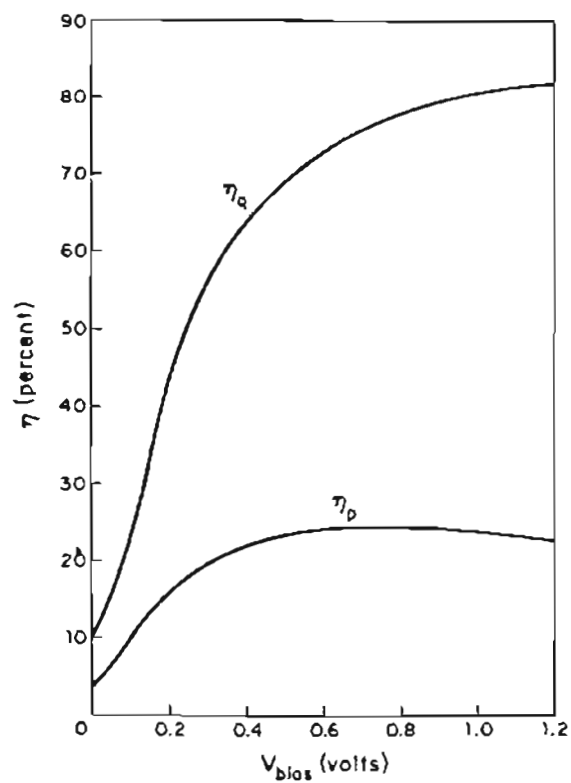


Figure A8.7.

External quantum efficiency (η_e) and power conversion efficiency (η_p) vs. bias voltage for SrTiO_3 photoanode in 10N NaOH. Photon energy was 3.8 eV. (From Mavroides et al., reference 244).

BIOGRAPHICAL NOTE

The author was born April 17, 1951 in Washington D.C., and spent most of his childhood in Ontario, California. He graduated from Hempfield Area Senior High School in Greensburg, Pennsylvania in 1969. This was followed by a four year enlistment in the U.S. Air Force, most of which was spent working in the Air Force Hospital at Edwards AFB in southeastern California.

The author's college career began in 1974, when he attended Chaffey College in Alta Loma, California. There he received the CRC Freshman Chemistry Achievement Award. In 1975-76, he attended Foothill College in Los Altos Hills, California, after which he enrolled in Sonoma State University, Rohnert Park, California. He received his Bachelor of Science degree in Physics from the latter school in June, 1978.

In July, 1978, the author began study at the Oregon Graduate Center where he completed the requirements for the degree Doctor of Philosophy in Applied Physics in August 1982. In 1981-82, he was elected to Who's Who Among Students in American Universities and Colleges.

The author is married to the former Rose Marie Murray and has one child, Brandy Danielle, age 4.

He is leaving the Graduate Center to accept a post doctoral position at Southern Methodist University, Dallas, Texas.

PUBLICATIONS

B. Odekirk, U. Balachandran, N. G. Eror, and J. S. Blakemore, "Conductivity of Ceramic La-Doped SrTiO_3 , Strongly Reduced and Quenched," Comm. Amer. Ceram. Soc., in press.

B. Odekirk and J. S. Blakemore, "Ceramic SrTiO_3 Photoanodes: Enhancement of Photoactivity Through Donor Doping," J. Electrochem. Soc., in press.

B. Odekirk, U. Balachandran, N. G. Eror, and J. S. Blakemore, "Electronic Conduction in Quenched Ceramic Samples of Highly Reduced Lanthanum Doped SrTiO_3 ," Mat. Res. Bull. 17, 199 (1982).

U. Balachandran, B. Odekirk, and N. G. Eror, "Defect Structure of Acceptor Doped Calcium Titanate at Elevated Temperatures," J. Mat. Sci. 17, 1656 (1982).

U. Balachandran, B. Odekirk, and N. G. Eror, "Electrical Conductivity in Calcium Titanate," J. Sol. St. Chem. 41, 185 (1982).