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Electrical Conductivity in Strontium Titanate with Nonideal Cationic Ratio

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The electrical conductivity of polycrystalline strontium titanate with (Sr/Ti) = 0.996, 0.99, and 0.98 was determined for the oxygen partial pressure range of 10^0 to 10^{-22} atm and the temperature range of 850–1050°C. These data were found to be similar to that obtained for the sample with ideal cationic ratio. The observed data were proportional to the $-\frac{1}{6}$ power of oxygen partial pressure for $P_{O_2} < 10^{-15}$ atm, proportional to $P_{O_2}^{-1/4}$ for the pressure range 10^{-8}–10^{-15} atm, and proportional to $P_{O_2}^{+1/4}$ for $P_{O_2} > 10^{-4}$ atm. The deviation from the ideal Sr-to-Ti ratio was found to be accommodated by neutral vacancy pairs, $(V_{Sr}'' V_O^{\cdot\cdot})$. The results indicate that the single-phase field of strontium titanate extends beyond 50.505 mole% TiO_2 at elevated temperatures.

Introduction

Strontium titanate has technological importance as a dielectric, in the photolysis of water, as an oxygen sensor, and in magnetohydrodynamic (MHD) operations. Also, in recent years, strontium titanate has attracted much attention, both experimental and theoretical, due to its many and varied properties, including superconductivity (*1–3*), a second-order structural phase transition (*4*), and a stress-induced phase transition (*5*). The electrical transport properties of semiconducting *n*-type $SrTiO_3$ were first investigated by Frederikse *et al.* (*6*), who found a band-type conduction process with an electron effective mass much greater than the free-electron mass. The high-temperature electrical conductivity in undoped $SrTiO_3$ was investigated recently for an oxygen partial pressure range of 10^0–10^{-22} atm and a temperature range of 750–1050°C (*7, 8*). A theoretical examination of the electronic energy bands of strontium titanate has been carried out by Kahn and Leyendecker (*9*). Their calculations led to filled valance bands derived primarily from oxygen 2*p* orbitals and empty conduction bands derived predominantly from titanium 3*d* orbitals. From the optical transmission studies on single-crystal strontium titanate which was heated in vacuum, Gandy (*10*) determined a band gap of 3.15 eV. Walters and Grace (*11*) examined the electrical conductivity and Seebeck coefficient of Sr TiO_3 in water–hydrogen atmospheres for a narrow range of oxygen partial pressure and concluded that an oxygen vacancy defect model was applicable to $SrTiO_3$ at elevated temperatures. The structural analog, $BaTiO_3$, has been studied in much detail in both polycrystalline (*12–17*) and single-crystal (*18*) states. The three polycrystalline samples of $BaTiO_3$ used by Long and

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Blumenthal (*14*) were found to be 2.1, 4.6, and 6.0 mole% deficient in BaO by chemical analysis. They noted no systematic variation of the equilibrium conductivity among these samples. A comparison of the sample with an ideal cationic ratio with one 0.1 mole% deficient in BaO showed no major differences in the equilibrium conductivity values (*17*). Eror and Smyth (*18*) have investigated the electrical conductivity of single-crystal $BaTiO_3$ pulled from a TiO_2-rich melt in order to lower the solidus temperature below that of the disruptive hexagonal to cubic transition. Recently, Chan *et al.* (*8*) studied the defect chemistry of strontium titanate with different Sr/Ti ratios by means of the high-temperature electrical conductivity as a function of P_{O_2}. They concluded that $SrTiO_3$ saturates with TiO_2 at less than 50.1 mole% and the defects formed due to the deviation from ideal cationic ratio are unassociated.

The purpose of the present work was to make a detailed study of the electrical conductivity in strontium titanate with different Sr-to-Ti ratios at elevated temperatures while in equilibrium with the oxygen partial pressure of the surrounding atmosphere. The Sr-to-Ti ratios selected were 0.996, 0.99, and 0.98, which correspond to 50.10, 50.251, and 50.505 mole% TiO_2. The conductivity data obtained on samples with Sr/Ti = 1.000 in our previous investigation (*7*) are also given.

Experimental

The specimens used in this investigation were prepared by a liquid mix technique (*7, 19, 20*). The powder samples were pressed into thin rectangular slabs (2.1 × 0.6 × 0.05 cm) under a load of 40,000 psi and sintered in air at 1350°C for 12 hr. Electrical conductivity specimens were cut from the sintered slabs using an airbrasive unit. The specimens were wrapped with four 0.025-cm platinum wires as described in the literature (*21, 22*). Small notches were cut in the edges of the sample to aid in holding the platinum wires in place.

A conventional four-probe direct current technique was employed for all electrical conductivity measurements. The four platinum leads were insulated from one another by recrystallized high-purity alumina insulators. A standard taper Pyrex joint to which capillary tubes had been sealed was mounted on top of the furnace reaction tube assembly. The platinum wires exited through the capillary tubes and were glass-sealed vacuum tight into the tubes.

The oxygen partial presssures surrounding the samples were controlled by flowing metered mixtures of gases past the sample. The gases were oxygen, compressed air, argon with known amounts of oxygen, and CO_2/CO mixtures. The conductivity was measured as a function of P_{O_2} in the temperature range 850–1050°C and was determined by measuring the voltage across the potential probes using a high-impedance ($>10^{10}$ ohms) digital voltmeter (Keithley 191 Digital Multimeter). The current was supplied between the two outer leads by a constant-current source (Keithley 225 current source). The voltage was measured with the current in both forward and reverse directions, and the conductivity was calculated from the average values. Current was varied from 20 μA to 1 mA and no significant change in conductivity was observed. After each variation of the gas atmosphere surrounding the sample, the conductivity was measured as it changed to the new equilibrium value. The process of change in conductivity was recorded and when the conductivity no longer changed, it was assumed that the state of equilibrium had been attained. This state proved to be attainable reversibly from higher or lower oxygen partial pressures. Changing the ratio of the surface area-to-volume by varying the size and geometry of the samples produced no detectable difference in the measured conductivity, which indicated that

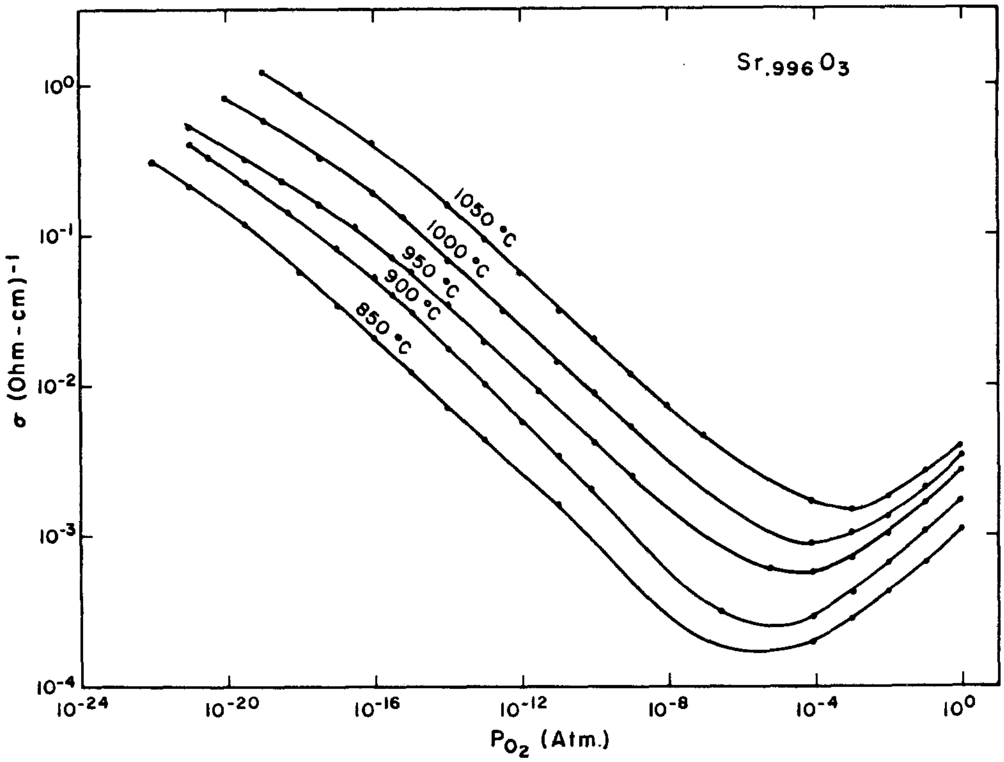

FIG. 1. The electrical conductivity of $Sr_{0.996}TiO_3$ as a function of P_{O_2} at constant temperature.

the measured quantity was the bulk conductivity.

Results and Discussion

The electrical conductivity of polycrystalline strontium titanate with Sr/Ti = 0.996, 0.99, and 0.98 in the temperature range 850–1050°C and in equilibrium with oxygen partial pressures between 10^0 to 10^{-22} atm, is shown in Figs. 1–3. In all the cases, the electrical conductivity changes from *p* to *n* type as the oxygen partial pressure is decreased. Three regions were observed as the P_{O_2} value was decreased at any given temperature. Figures 4–6 show the conductivity of $SrTiO_3$, $Sr_{0.996}TiO_3$, $Sr_{0.99}TiO_3$, and $Sr_{0.98}TiO_3$ at 900, 950, and 1000°C, respectively.

The log σ vs log P_{O_2} data are linear with a slope in the range $(-1/5.4)$ to $(-1/6.3)$ in the P_{O_2} region less than 10^{-15} atm for the three samples with excess TiO_2 (see Table I). As the oxygen activity is increased further, the P_{O_2} dependence of the conductivity changes for all the samples and this change in slope is also observed in strontium titanate with ideal cationic ratio (*7*). The new values of the slopes of log σ vs log P_{O_2} are in the range $(-1/4.2)$ to $(-1/4.6)$ for the P_{O_2} region of 10^{-15}–10^{-8} atm. These data are shown in Table II.

The region of linearity in the *p*-type region increases in width with decreasing temperature as the *p*–*n* transition moves to lower P_{O_2}. The P_{O_2} at the conductivity minimum, P_{O_2}(min), moves slightly (less than one decade in oxygen pressure) to the higher P_{O_2} values for the samples with Sr/Ti < 1 as compared with the sample with Sr/Ti = 1.000 (Figs. 4–6). This is in disagreement

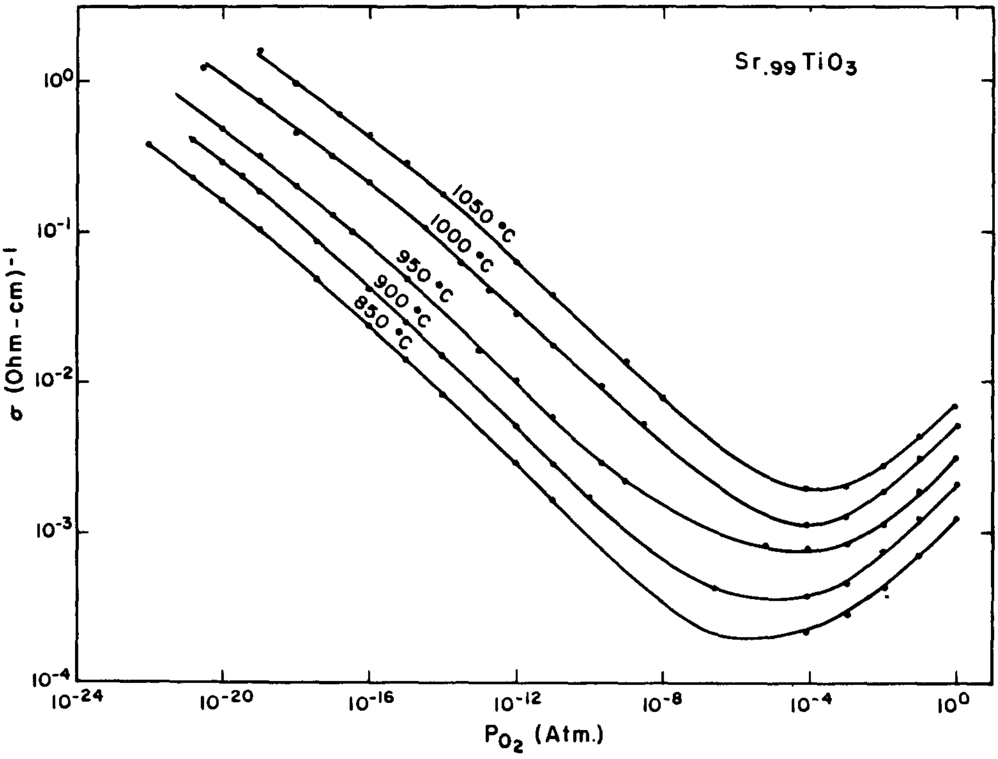

FIG. 2. The electrical conductivity of $Sr_{0.99}TiO_3$ as a function of P_{O_2} at constant temperature.

with the prediction of Chan *et al.* (*8*) that the conductivity minimum moves to lower P_{O_2} by two orders of magnitude for each order of magnitude increase in the extrinsic $V_O^{\cdot\cdot}$ concentration present as an unassociated defect in the samples with excess TiO_2. Table III gives the oxygen pressure dependence for conductivity in the *p*-type region for the three samples.

Region I: [$P_{O_2} < 10^{-15}$ *atm*]

The log σ vs log P_{O_2} data (Figs. 1–3) are linear for as many as five decades of oxygen partial pressure for a given temperature. The slopes obtained ($\simeq -\frac{1}{6}$) for the log σ vs log P_{O_2} plots in this region are similar to those found for $BaTiO_3$ (*15–18*) and $CaTiO_3$ (*23*), as well as the results obtained for polycrystalline $SrTiO_3$ (*7*).

TABLE I

P_{O_2} DEPENDENCE OF ELECTRICAL CONDUCTIVITY IN $Sr_{0.996}TiO_3$, $Sr_{0.99}TiO_3$, AND $Sr_{0.98}TiO_3$ IN THE REGION LESS THAN 10^{-15} atm

T (°C)	m for $\sigma_n \propto P_{O_2}^{-1/m}$ in:	$Sr_{0.996}TiO_3$	$Sr_{0.99}TiO_3$	$Sr_{0.98}TiO_3$
850		6.0	5.4	5.9
900		5.8	5.5	6.0
950		6.4	5.5	6.2
1000		6.2	5.5	6.2
1050		6.2	5.7	6.3

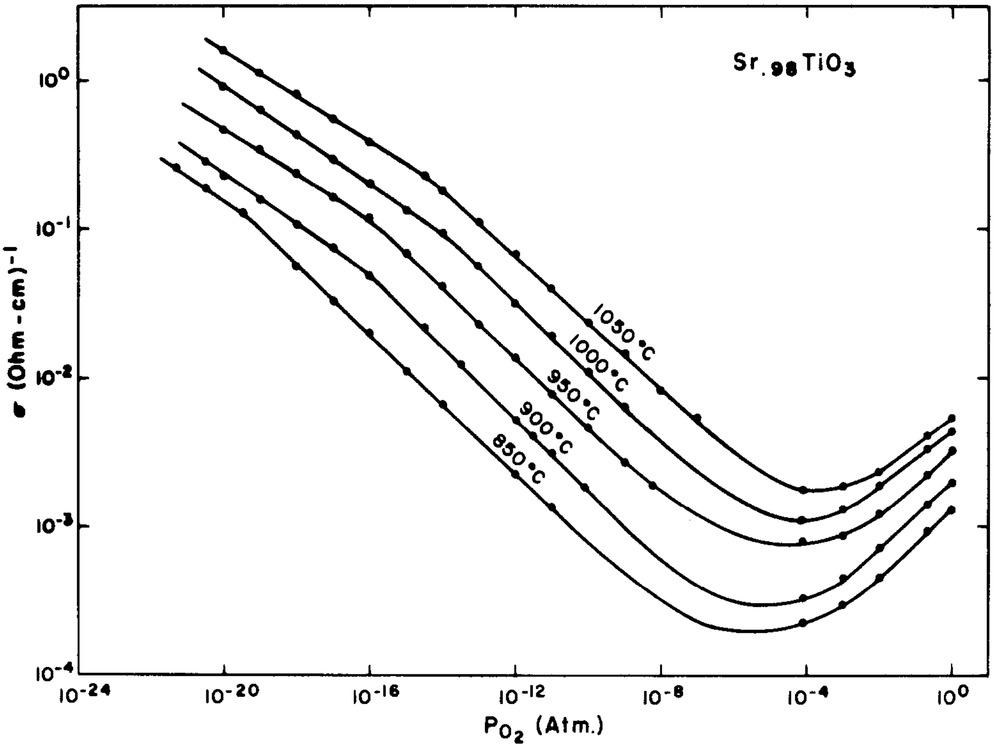

FIG. 3. The electrical conductivity of $Sr_{0.98}TiO_3$ as a function of P_{O_2} at constant temperature.

Deviation from the ideal Sr/Ti ratio must be accommodated by point defects (*18*). A number of mechanisms can be envisioned for the incorporation of excess TiO_2 into $SrTiO_3$ of ideal composition so as to make the Sr/Ti ratio less than unity. The mechanisms include:

$$TiO_2 \rightleftharpoons Ti_i^{+4} + 2O_i^{-2}, \qquad (1)$$

$$TiO_2 \rightleftharpoons Ti_i^{+4} + O_2 + 4e', \qquad (2)$$

$$2TiO_2 \rightleftharpoons Ti_{Sr}^{+2} + Ti_{Ti} + 3O_0 + O_i^{-2}, \qquad (3)$$

$$2TiO_2 \rightleftharpoons Ti_{Sr}^{+2} + Ti_{Ti} + 3O_0 + 2e' + \tfrac{1}{2}O_2, \qquad (4)$$

$$TiO_2 \rightleftharpoons Ti_{Ti} + 2O_0 + V_{Sr}'' + V_0^{\cdot\cdot}, \qquad (5)$$

$$TiO_2 + \tfrac{1}{2}O_2 \rightleftharpoons Ti_{Ti} + 3O_0 + V_{Sr}'' + 2h^{\cdot}. \qquad (6)$$

The reactions [Eqs. (2), (4), and (6)] which generate electronic defects can be excluded

TABLE II

P_{O_2} DEPENDENCE OF ELECTRICAL CONDUCTIVITY IN $Sr_{0.996}TiO_3$, $Sr_{0.99}TiO_3$, AND $Sr_{0.98}TiO_3$ IN THE REGION 10^{-15}–10^{-8} atm

T (°C)	*m* for $\sigma_n \propto P_{O_2}^{-1/m}$ in:	$Sr_{0.996}TiO_3$	$Sr_{0.99}TiO_3$	$Sr_{0.98}TiO_3$
850		4.4	4.4	4.3
900		4.2	4.4	4.2
950		4.4	4.4	4.2
1000		4.5	4.6	4.2
1050		4.6	4.4	4.5

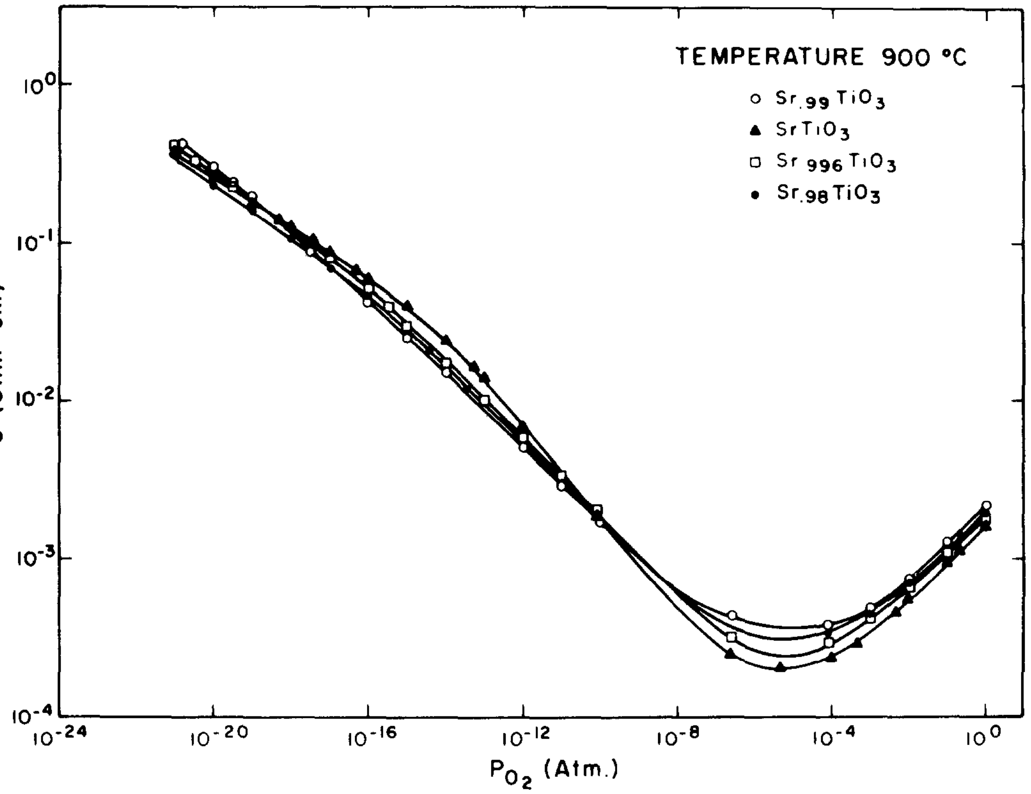

FIG. 4. Electrical conductivity of strontium titanate with Sr/Ti = 1.0, 0.996, 0.99, and 0.98 as a function of P_{O_2} at 900°C.

because of the observed lack of the effect of the Sr/Ti ratio on the electronic conductivity (Figs. 4–6). Both Ti_i^{+4} and O_i^{-2} are unfavorable defects in the close-packed perovskite structure, so Eq. (5), involving the formation of V''_{Sr} and $V_O^{\cdot\cdot}$, is the most probable choice. They appear to be the dominant ionic defect in the closely related $BaTiO_3$ (*14, 15, 18*) in the oxygen-deficient region and this is in accord with the electrical conductivity measurements for $SrTiO_3$ (*7, 8*) which showed that $V_O^{\cdot\cdot}$ is the preferred defect for oxygen deficiency in $SrTiO_3$.

The assignment of double effective

TABLE III

P_{O_2} DEPENDENCE OF ELECTRICAL CONDUCTIVITY IN $Sr_{0.996}TiO_3$, $Sr_{0.99}TiO_3$, AND $Sr_{0.98}TiO_3$ IN THE *p*-TYPE REGION

T (°C)	*m* for $\sigma_p \propto P_{O_2}^{+1/m}$ in:	$Sr_{0.996}TiO_3$	$Sr_{0.99}TiO_3$	$Sr_{0.98}TiO_3$
850		4.5	4.4	4.4
900		4.4	4.3	4.3
950		4.4	4.4	4.4
1000		4.4	4.8	4.5
1050		4.8	4.8	4.8

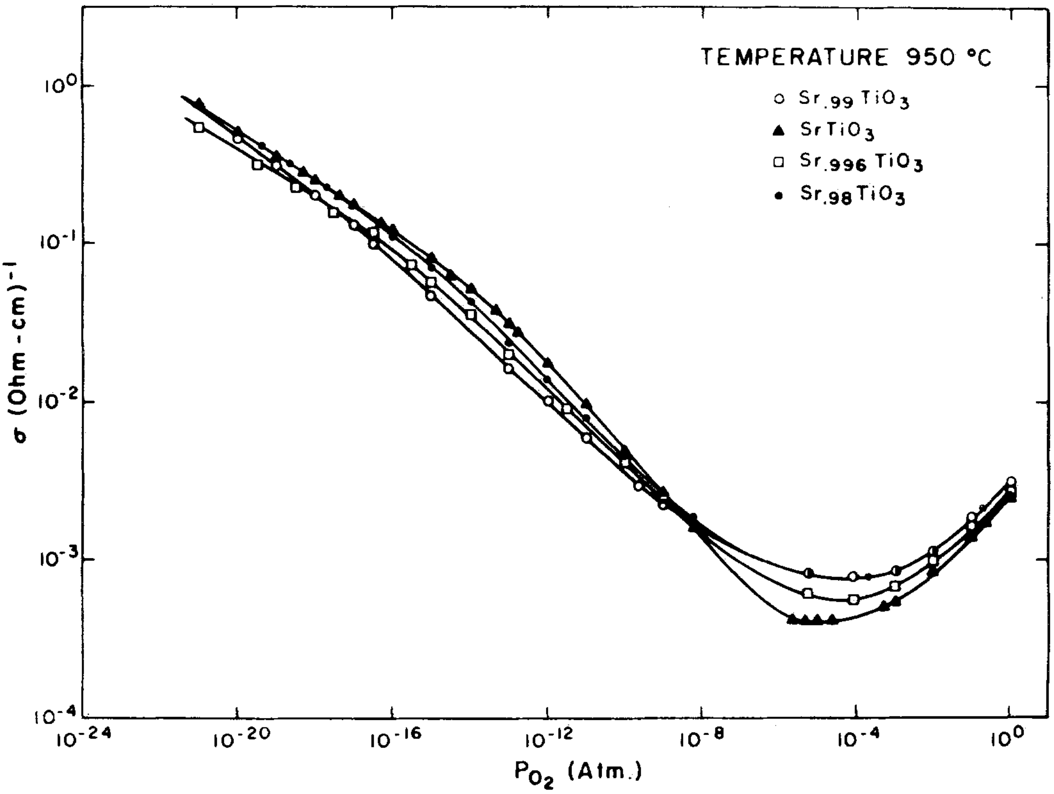

FIG. 5. Electrical conductivity of strontium titanate with Sr/Ti = 1.0, 0.996, 0.99, and 0.98 as a function of P_{O_2} at 950°C.

charges to both kinds of vacancies, $V_O^{\cdot\cdot}$ and V''_{Sr}, implies that both donor levels associated with oxygen vacancies lie above both acceptor levels associated with strontium vacancies. This is supported by evidence that the oxygen vacancies in the similar compound $BaTiO_3$ are either substantially (*14*) or entirely (*18*) doubly ionized at temperatures of 800°C and above, and that the oxygen vacancy levels in $SrTiO_3$ are extremely close to the conduction band (*6*).

The equilibrium incorporation reaction, Eq. (5), can be characterized by the mass-action expression

$$[V''_{Sr}]\,[V_O^{\cdot\cdot}] = K_5 a_{TiO_2}, \qquad (7)$$

where a_{TiO_2} is the equilibrium activity of TiO_2.

When oxygen deficiency is also incorporated into such a system by reducing the oxygen activity in equilibrium with the SrO-deficient $SrTiO_3$, we should consider

$$O_O^x \rightleftharpoons \tfrac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e' \qquad (8)$$

and

$$[V_O^{\cdot\cdot}]\,[n]^2 = K_8 P_{O_2}^{-1/2}, \qquad (9)$$

where $[n]^2 \equiv e'$.

It is clear that a substantial built-in SrO deficiency will initially exceed the disorder from the oxygen loss described in Eq. (8). For this case the electrical neutrality condition will read

$$[V''_{Sr}] \approx [V_O^{\cdot\cdot}] \approx K_5^{1/2} a_{TiO_2}^{1/2}. \qquad (10)$$

From Eqs. (9) and (10) we can then obtain

$$[n] = \left[\frac{K_8^{1/2}}{K_5^{1/4} a_{TiO_2}^{1/4}}\right] P_{O_2}^{-1/4}. \qquad (11)$$

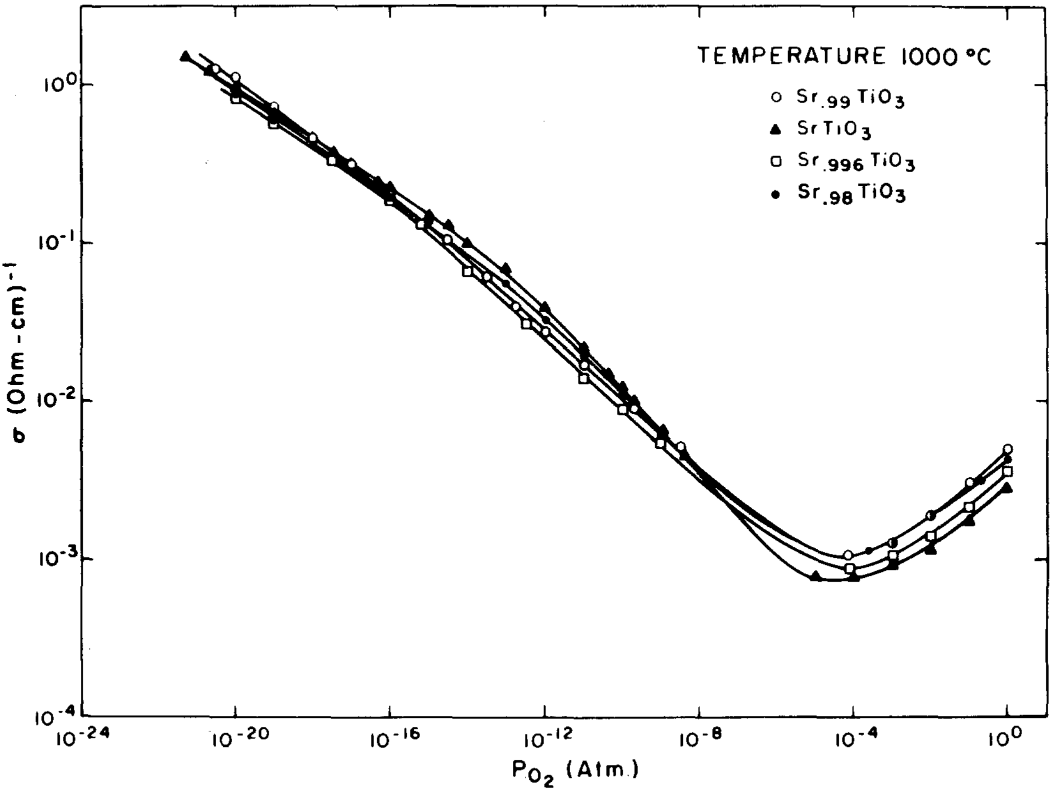

FIG. 6. Electrical conductivity of strontium titanate with Sr/Ti = 1.0, 0.996, 0.99, and 0.98 as a function of P_{O_2} at 1000°C.

The data in Figs. 1–3 and Table I indicate that in the low P_{O_2} region, the electrical conductivity varies as the $\approx -\frac{1}{6}$ power of oxygen partial pressure, similar to the value found in strontium titanate with ideal cationic ratio. This indicates that at low P_{O_2} the electrical neutrality condition should be

$$[n] \approx 2[V_O^{\cdot\cdot}] \qquad (12)$$

to give

$$[n] \approx (2K_8)^{1/3}P_{O_2}^{-1/6} \approx K_{13}P_{O_2}^{-1/6} \exp\left(\frac{-\Delta H_n}{3RT}\right), \qquad (13)$$

where ΔH_n is the enthalpy of reaction for Eq. (8). For Eq. (12) to hold, the oxygen deficiency must greatly exceed the built-in SrO deficiency.

Thermogravimetric work (*24*) indicated a maximum value of about 4.5×10^{-3} for x in $SrTiO_{3-x}$ when reduction was carried out in hydrogen (corresponds to the most extreme conditions used in this study) at 1050°C and a value of about 1.2×10^{-3} was obtained when the reduction was carried out at an oxygen partial pressure value of 10^{-15} atm. For Eq. (12) to be a valid expression for the dominant charged defects, no other charged defect can be present in excess of about 4×10^{-4} per cation site (400 ppm atomic). But for the samples under consideration the SrO deficiency amounts to 4,000–20,000 ppm. Our experimental results show a slope of $\approx -\frac{1}{6}$ for the oxygen pressure dependence in the lower P_{O_2} range and this could be possible only when the defects related to the SrO deficiency are associated into neutral complexes, such as vacancy pairs, to such an extent that the residual, isolated, charged defects from this source do not affect the condition of charge neutrality, Eq. (12), and thus have no influence on the oxygen-deficient defect chemistry. This association can be represented as

$$V_{Sr}'' + V_O^{\cdot\cdot} \rightleftharpoons (V_{Sr}''\,V_O^{\cdot\cdot}), \qquad (14)$$

where the parentheses indicate that the enclosed species are electrostatically bound to adjacent lattice sites. It has been reported in the literature (*17, 18*) that the defects formed due to excess TiO_2 in $BaTiO_3$ are associated into neutral vacancy pairs, $(V_{Ba}''\,V_O^{\cdot\cdot})$.

The mass-action expression for Eq. (14) gives

$$\frac{[(V_{Sr}''\,V_O^{\cdot\cdot})]}{[V_{Sr}''][V_O^{\cdot\cdot}]} = K_{14} = K_{15}\exp\left(\frac{-\Delta H_a}{RT}\right), \qquad (15)$$

where ΔH_a, the enthalpy of association, is a negative number for this exothermic process. From Eq. (15) one can estimate the value of ΔH_a necessary to keep the concentration of the dissociated vacancies below, say, the 10-ppm level for the experimental temperature range. Kröger (*25*) has reviewed published parameters for defect association and showed that the entire preexponential term in the association relationships such as Eq. (15), i.e., the entropy factor, is generally close to unity. With this assumption, Eq. (15) reduces to $\Delta H_a = -18.4RT$ for Sr/Ti = 0.99 with $[V_{Sr}''] = [V_O^{\cdot\cdot}] = 10$ ppm. The calculated values of $-\Delta H_a$ then range from 2.1 eV at 1050°C to 1.78 eV at 850°C for the sample with Sr/Ti = 0.99. Similar to the results of Eror and Smyth (*18*) for BaO-deficient $BaTiO_3$, it can be shown that for the case of Sr/Ti = 0.99, $[V_O^{\cdot\cdot}] = 100$ ppm would reduce the absolute value of the calculated values of ΔH_a by about 15%. Moreover, the values will be even smaller if the entropy term favors the dissociation, which is not unlikely. An association enthalpy of ≈2 eV would be adequate to provide the association required in the experimental temperature range used in this investigation. This value is not an unrealistic magnitude for doubly charged defects such as V_{Sr}'' and $V_O^{\cdot\cdot}$ on adjacent lattice sites, when it is recalled that the association enthalpies for divalent impurity cations and cation vacancies in alkali halides, e.g., $[Sr_{Na}^{\cdot}, V_{Na}']$ in NaCl, are about −0.5 eV (*26, 27*), and there is enough evidence to suggest that ΔH_a for cation and anion vacancies in these crystals, e.g., $(V_{Na}', V_{Cl}^{\cdot})$ in NaCl, are about −1 eV (*26–28*). The latter value is larger than the former because these defects involve adjacent lattice sites and is thus the closer analog of the $(V_{Sr}'', V_O^{\cdot\cdot})$ complex discussed here. The degree of association can be significant to quite high temperatures even when only one of the defects is doubly ionized. It has been proposed that defect pairs of the type $(M_{Ni}^{\cdot}\,V_{Ni}'')$ make significant contributions to the diffusion of Al^{+3} and Cr^{+3} in NiO up to nearly 1800°C (*28–30*).

There is no significant increase in conductivity between the samples with different Sr-to-Ti ratios. From the known levels of oxygen and SrO deficiencies in the samples, this condition of $\sigma \propto P_{O_2}^{-1/6}$ could not be achieved without substantial association of the SrO-deficient defects. Otherwise, reaction (8) could not become the dominant source of $[V_O^{\cdot\cdot}]$ at low pressures and the relationship $\sigma \propto P_{O_2}^{-1/6}$ would not be observed.

Chan *et al.* (*8*) observed the minimum in the conductivity for Sr/Ti = 0.999 and 0.995 samples at similar P_{O_2} values in the log σ vs log P_{O_2} plot, and based on this they concluded that the $SrTiO_3$ saturates with TiO_2 at less than 50.1 mole%. The phase information available to date for the $SrO-TiO_2$ system (*31*) gives no indication of any solubility for excess TiO_2 in $SrTiO_3$. The phase diagram for the structural analog, $BaO-TiO_2$, shows that there is a definite phase width for $BaTiO_3$ on the TiO_2-rich side and a single-phase region from the ideal composition of $BaTiO_3$ up to about 1 mole% excess TiO_2 at 1400°C (*32*). In disagreement with the above results, Sharma *et al.* (*33*) reported that the solubility of TiO_2 in Ba TiO_3 is <0.1 mole%. The available phase study in the system $SrO-TiO_2$ (*31*) suggests that the second phase formed for excess TiO_2 in $SrTiO_2$ should be TiO_2. The presence of second phase in the polycrystalline samples should have some effect on transport properties, such as electrical conductivity or oxygen self-diffusion. In the electrical conductivity studies of samples with Sr/Ti = 0.996, 0.99, and 0.98, equilibrium was established as fast as it was obtained in the sample with ideal cationic ratio. Also, in the samples with 50.505 mole% TiO_2 (Sr/Ti = 0.98) no second phase was observed optically, by X-ray diffraction, or by laser Raman spectroscopy, a technique which is more sensitive than the first two. This indicated that for the conditions under which the present samples were sintered, $SrTiO_3$ did not saturate with TiO_2 even at 50.505 mole%.

The magnitude of ΔH_n, the enthalpy of the oxygen extraction reaction, is obtained from Arrhenius plots of the conductivity, as deduced from Eq. (13). This procedure neglects the contributions from the temperature dependence of the carrier mobility or density of states. The values of ΔH_n calculated from the slopes of the Arrhenius plots (see Fig. 7 for the sample with Sr/Ti = 0.996) are listed in Table IV. Average values of 4.89 eV (112.72 kcal/mole), 4.98 eV (114.96 kcal/mole), and 5.0 eV (115.3 kcal/mole) are obtained for the samples with Sr-to-Ti ratios of 0.996, 0.99, and 0.98, respectively. An average value of 4.85 eV (111.8 kcal/mole) was obtained for the same P_{O_2} region in strontium titanate with ideal cationic ratio (*7*).

TABLE IV

ACTIVATION ENTHALPIES FOR CONDUCTION IN $Sr_{0.996}TiO_3$, $Sr_{0.99}TiO_3$, AND $Sr_{0.98}TiO_3$ IN THE REGION LESS THAN 10^{-15} atm

P_{O_2} (atm)	Activation enthalpies (kcal/mole)		
	$Sr_{0.996}TiO_3$	$Sr_{0.99}TiO_3$	$Sr_{0.98}TiO_3$
10^{-21}	109.75	109.75	—
10^{-20}	109.75	109.75	115.31
10^{-19}	109.75	112.49	115.31
10^{-18}	115.24	120.73	115.31
10^{-17}	115.24	122.10	115.31
10^{-16}	116.60	—	115.23

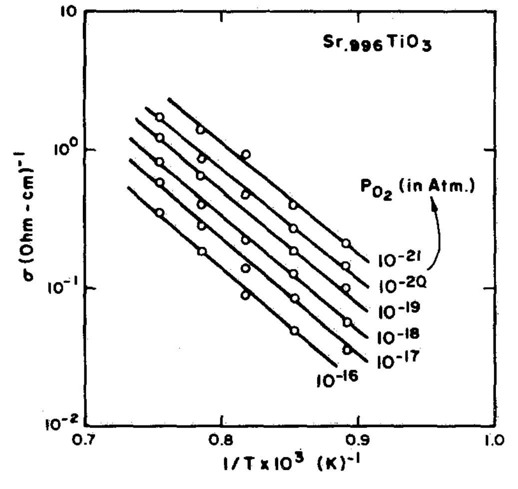

FIG. 7. Temperature dependence of conductivity in $Sr_{0.996}TiO_3$ in the *n*-type, oxygen-deficient region.

Region II: [P_{O_2} = 10^{-8}–10^{-15} *atm*]

A slope of $\approx -1/4.4$ was found for the log σ vs log P_{O_2} data (see Table II). In the same P_{O_2} region a slope of $\approx -\frac{1}{4}$ was observed for the sample with ideal cationic ratio (*7*). Daniels and Hardtl (*34*) reported from their log σ vs log P_{O_2} plot a slope of $\approx -\frac{1}{4}$ between 700 and 900°C and $\approx -\frac{1}{5}$ at 1200°C for Ba TiO_3 in the P_{O_2} range 10^{-18}–10^{-8} atm. They attributed the $-\frac{1}{4}$ slope to singly ionized oxygen vacancies as the cause of conductance and the $-\frac{1}{5}$ value to the more frequent occurrence of doubly ionized oxygen vacancies. However, for $SrTiO_3$, it has been shown by earlier investigators (*35, 36*) that the oxygen vacancies of the quenched samples remain doubly ionized down to liquid nitrogen temperature. The observed slope of $-\frac{1}{4}$ in this region must, therefore, be due to the presence of an unknown, negatively charged impurity, i.e., an acceptor impurity such as Al, Fe, or Cr on Ti sites. For the case of undoped $BaTiO_3$ prepared by the same technique as the one used here, Chan and Smyth (*17*) reported a net acceptor impurity concentration of about 130 ppm (atomic). They proposed that all undoped material ($BaTiO_3$) studied to date had a net excess of acceptor impurities, and attributed this to the fact that potential acceptor elements are naturally much more abundant than potential donor elements. The present authors (*7*) estimated the unknown acceptor impurity concentration of about 170 ppm in the strontium titanate sample with Sr/Ti = 1.0000. Seuter (*16*) was able to observe an extensive range of $P_{O_2}^{-1/4}$ dependence for conductivity in the oxygen-deficient region below the *p–n* transition in the $BaTiO_3$, presumably because of a greater acceptor impurity content of his samples. We believe that the present samples also contain some unknown acceptor impurities which are singly ionized. Thus, the condition of charge neutrality in this region can be

$$2[V_O^{\cdot\cdot}] \approx [A'], \qquad (16)$$

where A′ is the singly ionized acceptor impurity, such as Al'_{Ti}. With this neutrality condition, the electrical conductivity varies as the $-\frac{1}{4}$ power of oxygen partial pressure. The observed P_{O_2} dependence for all three samples is in agreement with the predicted value by the above impurity model. The activation enthalpies of conduction derived from the Arrhenius slopes are shown in Table V. Average values of 4.04 eV (93.06 kcal/mole), 4.45 eV (102.5 kcal/mole), and 4.22 eV (97.28 kcal/mole) are estimated for the samples with Sr/Ti = 0.996, 0.99 and 0.98, respectively.

TABLE V

ACTIVATION ENTHALPIES FOR CONDUCTION IN $Sr_{0.996}TiO_3$, $Sr_{0.99}TiO_3$, AND $Sr_{0.98}TiO_3$ IN THE REGION 10^{-15}–10^{-8} atm

P_{O_2} (atm)	Activation enthalpies (kcal/mole) $Sr_{0.996}TiO_3$	$Sr_{0.99}TiO_3$	$Sr_{0.98}TiO_3$
10^{-15}	92.74	97.85	96.03
10^{-14}	90.54	99.69	97.17
10^{-13}	94.20	101.52	97.23
10^{-12}	94.20	104.26	97.17
10^{-11}	93.56	104.72	97.25
10^{-10}	92.37	103.92	98.31
10^{-9}	93.84	105.63	97.83

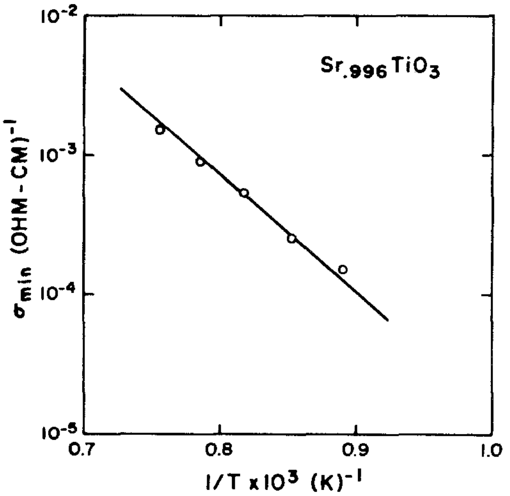

FIG. 8. Temperature dependence of conductivity minima in $Sr_{0.996}TiO_3$.

Transition Region

Becker and Frederikse (*37*) showed that the band gap (extrapolated to zero temperature) of a semiconductor which exhibits a *p*-to-*n* transition may be determined from the Arrhenius plots of the conductivity minima. The log σ_{min} vs $1/T$ data in Fig. 8 indicate a value of $E_g^\circ = 3.34$ eV (77.05 kcal/mole) as the band gap for polycrystalline $Sr_{0.996}TiO_3$ extrapolated to 0°K. This is in good agreement with the range of 3.2–3.4 eV reported from optical absorption data (*38–40*) on single crystalline $SrTiO_3$, and the value of 3.36

eV (77.54 kcal/mole) observed for polycrystalline strontium titanate with ideal Sr-to-Ti ratio (7). Values of 3.31 eV (76.33 kcal/mole) and 3.40 eV (78.40 kcal/mole) are obtained for the band gap at 0°K for $Sr_{0.99}TiO_3$ and $Sr_{0.98}TiO_3$ samples, respectively. Assuming band conduction for both electrons and holes, the full expression for the Arrhenius plot is

$$\frac{\partial \ln \sigma_{\min}}{\partial (RT)^{-1}} = \frac{\partial}{\partial (RT)^{-1}} \times \left(\frac{\ln \mu_n \mu_p}{2} + \ln N_c N_v\right) - \frac{E_g^\circ}{2}. \quad (17)$$

Assuming that the temperature dependence of the mobilities is the same for electrons and holes, and if both N_c and N_v, the density of states near the conduction and valence band edge, respectively, are proportional to $T^{+3/2}$, the mobility and density of state terms cancel each other, and the Arrhenius slope is directly proportional to E_g°.

Region III: [$P_{O_2} > 10^{-4}$ *atm*]

The conductivity in this region increased with increasing oxygen partial pressure (see Figs. 1–3), indicative of *p*-type, or oxygen-excess, conductivity. The oxygen pressure dependence of electrical conductivity (see Table III) for the three samples is in the range (1/4.4)–(1/4.8). The activation enthalpies of conduction, ΔH_p, derived from the Arrhenius slopes are given in Table VI. Values of 1.73 eV (39.9 kcal/mole), 2.3 eV (53.5 kcal/mole), and 1.86 eV (42.98 kcal/mole) are typical for the samples with Sr/Ti = 0.996, 0.99, and 0.98, respectively.

Stoichiometric excess of oxygen can be incorporated into strontium titanate by a favorable process (*7, 18*). The SrO deficiency makes available systematic oxygen vacancies which might accommodate a stoichiometric excess of oxygen according to

$$(V_{Sr}'' V_0^{\cdot\cdot}) + \tfrac{1}{2}O_2 \rightleftharpoons O_0^x + V_{Sr}' + h^{\cdot}, \quad (18)$$

TABLE VI

ACTIVATION ENTHALPIES FOR CONDUCTION IN THE *p*-TYPE REGION

P_{O_2} (atm)	Activation enthalpies (kcal/mole)		
	$Sr_{0.996}TiO_3$	$Sr_{0.99}TiO_3$	$Sr_{0.98}TiO_3$
10^0	38.96	50.85	41.16
2.1×10^{-1}	—	—	42.30
9.78×10^{-2}	39.51	53.41	—
10^{-2}	40.24	53.96	43.44
10^{-3}	39.63	54.87	44.58
8.45×10^{-5}	41.16	54.42	43.44

$$\frac{[V_{Sr}'][p]}{[(V_{Sr}'' V_0^{\cdot\cdot})]} = K_{18}P_{O_2}^{1/2} = K_{19}P_{O_2}^{1/2} \exp\left(\frac{-\Delta H_p}{RT}\right), \quad (19)$$

where $[p] \equiv h^{\cdot}$.

$[(V_{Sr}''V_0^{\cdot\cdot})]$ can be taken as constant in Eq. (19) for a given composition. The unassociated strontium vacancies that result when the oxygen vacancy in the neutral strontium vacancy–oxygen vacancy complex is filled must be singly ionized in order to lead to the $+\frac{1}{4}$ oxygen partial pressure dependence of the electrical conductivity data when Eq. (19) is combined with the corresponding charge neutrality condition

$$[V_{Sr}'] \approx [p]. \quad (20)$$

The combination of Eqs. (19) and (20), however, indicates that $[p]$ and, therefore, the conductivity in this region should be proportional to $[(V_{Sr}''V_0^{\cdot\cdot})]^{1/2}$. No such variation in the electrical conductivity has been observed (Figs. 4–6), which suggests that the bound $V_0^{\cdot\cdot}$ related to the SrO deficiency does not offer the sites for the incorporation of oxygen atoms, leading to the observed *p*-type behavior. If one assumes that the defects formed due to the SrO deficiency are unassociated, then one would expect the conductivity in the *p*-type region to increase as the SrO deficiency increases. This is because more oxygen atoms can be incorporated into the oxygen vacancies from the unassociated defects. No such systematic variation in the absolute values of the conductivity has been observed (see Figs. 4–6) for the wide range of SrO deficiency introduced into the samples used in the present study.

The observed p-type behavior, therefore, is due to the incorporation of oxygen into the impurity-related oxygen vacancies, and the reaction is

$$[V_0^{\cdot\cdot}] + \tfrac{1}{2}O_2 \rightleftharpoons O_0^x + 2h^{\cdot}. \qquad (21)$$

The charge neutrality condition near the stoichiometric region is given by [Eq. (16)]

$$[A'] \approx 2[V_0^{\cdot\cdot}].$$

The chemical mass-action expression for Eq. (21) combined with Eq. (16) gives

$$\sigma \propto P_{O_2}^{1/4} \qquad (22)$$

as long as only a minor fraction of the impurity-related $V_0^{\cdot\cdot}$ is filled. This model fits the observed oxygen pressure dependence of conductivity in this region. The trend toward shallower slopes at higher temperatures represents an intrusion of the transition region leading to the conductivity minima which are moving toward higher P_{O_2} with increasing temperature. The ready availability of oxygen vacancies explains the unusual ease with which the material accepts a stoichiometric excess of oxygen. The shift to lower P_{O_2} values of the conductivity minimum observed by Chan *et al.* (*8*) for Sr/Ti = 0.999 and 0.995 could be due to higher concentrations of unknown acceptor impurities present in those samples as compared with the sample with ideal cationic ratio. These acceptor impurities will lead to higher conductivity values, as observed by Chan *et al.* (*8*), in the p-type region. They have also reported that the conductivity minimum for the SrO-deficient samples occurred at similar P_{O_2} values. It may very well be that the defects formed due to deviation from ideal cationic ratio are associated into neutral vacancy pairs, $(V_{Sr}''V_0^{\cdot\cdot})$, and not because of the saturation of $SrTiO_3$ with TiO_2.

The question of the limit of TiO_2 solubility in $SrTiO_3$ is an interesting one. Smyth (*41*) reports that recent results showed the presence of a second phase, apparently TiO_2, in samples with Sr/Ti = 0.995. As discussed above, our experimental results show a significant region of $\sim -\frac{1}{6}$ oxygen partial pressure dependence of the electrical conductivity for $P_{O_2} \leq 10^{-14}$ atm, that is indistinguishable from stoichiometric Sr TiO_3—even for very large excesses of TiO_2. Chan *et al.* (*42*) have referred to the extent of the $P_{O_2}^{-1/6}$ dependence of the electrical conductivity as a measure of the intrinsic or impurity-insensitive region for the titanates. Chan *et al.* (*8*), however, reported a significant difference when excess TiO_2 was added to stoichiometric $SrTiO_3$. It is not clear, however, why their results at high $P_{O_2}(>10^{-4}$ atm) were identical for Sr/Ti = 0.9990 and 0.9950, while they differed, according to their model, for $P_{O_2} < 10^{-4}$ atm. The conductivity profiles of donor-doped $SrTiO_3$ are also confusing. For 498 ppm Nb, Sr/Ti = 1.0000, they reported a very large ($P_{O_2} \geq 10^{-15}$ atm) oxygen partial pressure range where the electrical conductivity has very little dependence upon P_{O_2}. We have found (*43*), however, for 1000 ppm La, (La + Sr)/Ti = 1.000, that only for $P_{O_2} \leq 10^{-20}$ atm does the electrical conductivity have little dependence upon P_{O_2} and for $P_{O_2} \geq 10^{-6}$ atm the electrical conductivity is proportional to $P_{O_2}^{-1/4.5}$. In fact, even for 20,000 ppm (2 at.%) La there is a $P_{O_2}^{-1/4.3}$ dependence of the electrical conductivity for $P_{O_2} \geq 10^{-6}$ atm.

Conclusions

The oxygen pressure dependence of electrical conductivity for the samples with Sr-to-Ti ratios of 0.996, 0.99, and 0.98 (corresponds to 50.10, 50.251, and 50.505 mole% TiO_2, respectively) was found to be similar to that obtained in strontium titanate with ideal cation–cation ratio. The absolute values of the conductivity in all three regions did not change significantly as the Sr/Ti ratio was changed. These observations indicate that defects related to the deviation from ideal cationic ratio are associated into neutral vacancy pairs, $(V''_{Sr}\ V_{O}^{\cdot\cdot})$, and this conclusion is similar to that obtained for the structural analog, $BaTiO_3$, with excess TiO_2 by earlier investigators (*17, 18*). The experimental results indicate that doubly ionized oxygen vacancies are the dominant defect present at the lowest P_{O_2} and temperature range of 850–1050°C.

For $P_{O_2} > 10^{-15}$ atm the defect chemistry of strontium titanate is dominated by accidential acceptor impurities and their related oxygen vacancies, Eq. (16). Because of these acceptor impurities, a region in which the conductivity changes as the $\approx -1/4.4$ power of oxygen partial pressure is observed.

The *p*-type conductivity observed in the region $P_{O_2} > 10^{-4}$ atm is due to fractional filling of the impurity-related oxygen vacancies, Eq. (21), and the defects present due to the deviation from ideal cationic ratios have no significant role in influencing the observed electrical conductivity. Thus, a stoichiometric excess of oxygen is achieved even while not all of the available oxygen sites are occupied. The ready availability of oxygen vacancies results in a low enthalpy for the oxygen incorporation reaction.

The band gap values estimated for the SrO-deficient strontium titanate samples were found to be close, within the experimental error, to the value obtained for the sample with Sr/Ti = 1.0. The defects formed due to deviation from ideal cationic ratio have no influence on the intrinsic band gap of the material.

The results indicate that for the conditions under which the present samples were sintered, $SrTiO_3$ does not saturate with TiO_2 even at 50.505 mole%, and this is in disagreement with the results of Chan *et al.* (*8*), who predicted that the phase boundary for single-phase $SrTiO_3$ is less than 50.1 mole% TiO_2. The effect on the defect chemistry of $SrTiO_3$ with excess SrO is currently under investigation.

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