JOURNAL OF MATERIALS SCIENCE 17 (1982) 2133–2140

On the defect structure of strontium titanate with excess SrO

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The defect structure of strontium titanate with Sr to Ti ratios of 1.002, 1.005 and 1.008 was determined by measuring the equilbrium electrical conductivity at 950 and 1000° C as a function of oxygen partial pressure in the range 10^0 to 10^{-22} atm. The measured conductivity data were similar to those obtained in the sample with Sr/Ti = 1.000. These observations indicate that the incorporation of excess SrO in strontium titanate with ideal composition does not generate any charged defects. A model involving the formation of a shear-structure is considered in order to accommodate the excess SrO in the system.

1. Introduction

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]. Walters and Grace [6] examined the electrical conductivity and Seeback coefficient of $SrTiO_3$ in water–hydrogen atmospheres and concluded that an oxygen vacancy defect model was applicable to $SrTiO_3$ at elevated temperatures. The present authors [7–9] have studied the electrical conductivity in undoped, lanthanum added $SrTiO_3$ and $SrTiO_3$ with excess TiO_2 at elevated temperatures. The structural analogue $BaTiO_3$ has been studied in much detail in both polycrystalline [10–15] and single crystal [16] states. The three polycrystalline samples of $BaTiO_3$ used by Long and Blumenthal [12] were found to be 2.1, 4.6, and 6.0 mol% deficient in BaO by chemical analysis. They noted no systematic variation of the equilibrium electrical conductivity among these samples. Recently, Chan *et al.* [17] studied the defect chemistry of strontium titanate with excess TiO_2 by means of high temperature electrical conductivity as a function of oxygen pressure, P_{O_2}. They concluded that the defects formed due to the presence of excess TiO_2 are unassociated, i.e., V''_{Sr}, and $V_O^{\cdot\cdot}$. The present authors [9], however, found that excess TiO_2 is accomplished by neutral vacancy pairs (V''_{Sr}, $V_O^{\cdot\cdot}$). Strontium titanate, however, has not been studied in the past when the Sr to Ti ratio is greater than unity, i.e., with excess SrO.

The purpose of the present work is to make a detailed study of the electrical conductivity in strontium titanate with excess SrO at elevated temperatures while in equilibrium with the oxygen partial pressure of the surrounding atmosphere. The Sr and Ti ratios selected were 1.002, 1.005 and 1.008 which corresponds to 50.05, 50.125 and 50.199 mol% SrO, respectively. The conductivity data obtained in our previous investigation [7] on samples with Sr/Ti = 1.000 are also given.

2. Experimental procedures

The samples employed in this investigation were prepared by a liquid mix technique [7, 17, 18]. Required amounts of strontium carbonate (Johnson-Matthey Corp., spec. pure) and tetraisopropyl titanate solution (Dupont Co., Tyzor) were dissolved in an ethylene glycol–citric acid solution. There was no evidence of any precipitation in the solutions as they were evaporated to a rigid transparent, uniformly coloured polymeric glass. The glass retains homogeneity on an atomic scale and was calcined at 900° C: there was no evidence of a second phase in the as-calcined samples. These powder samples were pressed into thin circular discs (1.2 cm diameter and 0.1 cm

0022–2461/82/072133–08$03.46/0

thick) under a load of 40 000 psi*, and sintered in air at 1350° C for 12 h. The density of the sintered discs was 94% of the theoretical density. Conductivity specimens were cut from this sintered disc using an airbrasive unit. The specimens were wrapped with four 0.025 cm platinum wires as described in the literature [19, 20]. 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 be 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 pressures 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, CO_2–CO mixtures, and CO_2–H_2 mixtures. The error in volumetric ratio measurements of the gas mixtures resulted in an error of about 1% in the P_{O2} value reported here. The conductivity was measured as a function of P_{O2} at 950° C and 1000° C. The electrical conductivity was determined by measuring the voltage across the potential probes using a high impedance ($> 10^{10}$ ohm) 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. 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 if the conductivity no longer changed, it was assumed that the state of approximately $-1/6$ in the P_{O_2} region $< 10^{-15}$ proved to be attainable reversibly from higher or lower oxygen partial pressures. Equilibium was established as fast as the oxygen pressure could be changed from one value to another (which is usually less than 15 min). The current was varied from 20 μA to 1 mA and no significant change in electrical conductivity was observed. Changing the ratio of the surface area to the volume by varying the size and geometry of the samples produced no detectable difference in the measured conductivity which indicated that the measured quantity was the bulk conductivity. Once the thermodynamic equilibrium was established the conductivity did not change with time after the current was applied to the sample.

3. Results and discussion

The measured electrical conductivities as a function of oxygen partial pressure in strontium titanate with Sr/Ti = 1.000, 1.002, 1.005 and 1.008 at 950° C and 1000° C are given in Figs 1 and 2, respectively. In all the cases, the electrical conductivity changed from p to n-type as the oxygen partial pressure was decreased. The log σ against log P_{O2} data are linear with a slope of approximately $-1/6$ in the P_{O2} region $< 10^{-15}$ atm for all the samples investigated. As the partial pressure of oxygen is increased, the P_{O2} dependence of electrical conductivity changes and the new values of the slopes are about $-1/4$ for the P_{O2} range 10^{-14} to 10^{-8} atm. The measured conductivity in the oxygen partial pressure range $> 10^{-4}$ atm increases with P_{O2}, characteristic of p-type or oxygen excess conduction. The conductivity minima occur at the same P_{O2} for all the samples. The three regions observed in the log σ against log P_{O2} plots are discussed separately in the following.

3.1. Region I, $Po_2 < 10^{-15}$ atm

The slopes observed (about $-1/6$) in the log σ against log P_{O2} plots in this region are similar to that found for $BaTiO_3$ [13–16] and $CaTiO_3$ [21] as well as the results obtained in $SrTiO_3$ with Sr/Ti $\leqslant$ 1.000 in our previous investigations [7, 9]. The phase diagram of Cocco and Massazza [22] for the SrO–TiO_2 system shows that there is a definite phase width for $SrTiO_3$ on the SrO rich side with a single phase region from the ideal composition of $SrTiO_3$ up to about 1.3 mol% excess SrO at 1200° C. The incorporation of excess SrO by a simple point defect model requires the formation of either interstitial strontium and oxygen, Sr_i^{2+} and O_i^{2-}, or titanium and oxygen vacancies, V_{Ti}'''' and $V_0^{\cdot\cdot}$ according to the following

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*10^3 psi = 6.89 N mm^{-2}.

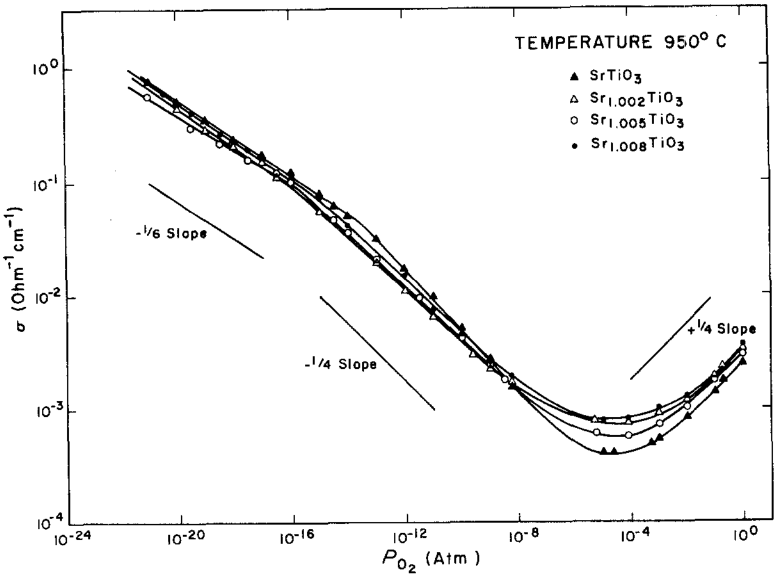

Figure 1 The electrical conductivity as a function of P_{O_2} at 950° C in strontium titanate samples with Sr/Ti = 1.00, 1.002, 1.005 and 1.008.

equations:

$$SrO \rightleftharpoons Sr_i^{2+} + O_i^{2-} \quad (1)$$

and

$$SrO \rightleftharpoons Sr_{Sr}^{x} + O_O^{x} + V_{Ti}^{''''} + 2V_O^{\cdot\cdot} \quad (2)$$

Vacancies of titanium with high formal charges, $V_{Ti}^{''''}$, and the interstitials of strontium and oxygen are energetically unfavourable defects in this close packed structure. The excess SrO can be accomodated in the structure in an ordered fashion between $SrTiO_3$ perovskite blocks so as to form different compounds in a homologous series $n SrTiO_3 \cdot SrO$ [23, 14]. Figure 3 shows the $Sr_3Ti_2O_7$ structure where double $SrTiO_3$ perovskite layers are interleaved with a SrO layer. McCarthy *et al.* [25] and White *et al.* [26] have prepared and identified by X-ray diffraction and Raman spectroscopy the first three members of the series $n SrTiO_3 \cdot SrO$. The present authors [27] have prepared the first six members of this series by employing the liquid mix technique and identified them by Raman laser spectroscopy. The SrO layer formed due to excess SrO represents only the accommodation of strontium and oxygen atoms on certain crystallographic planes for a specific crystal structure. By this type of proposed model, the excess SrO does not generate any electronic defects as can be seen from the observed lack of effect of the Sr to Ti ratio on the electrical conductivity.

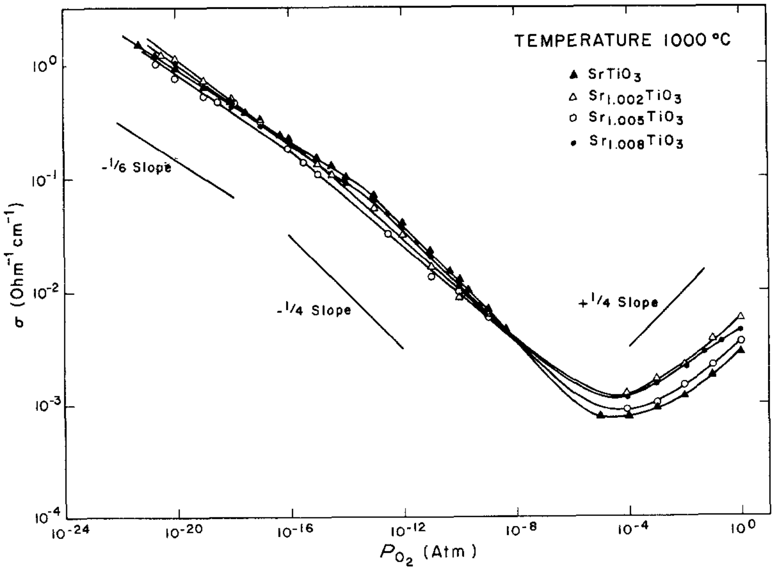

Figure 2 The electrical conductivity as a function of P_{O_2} at 1000° C in strontium titanate samples with Sr/Ti = 1.000, 1.002, 1.005 and 1.008.

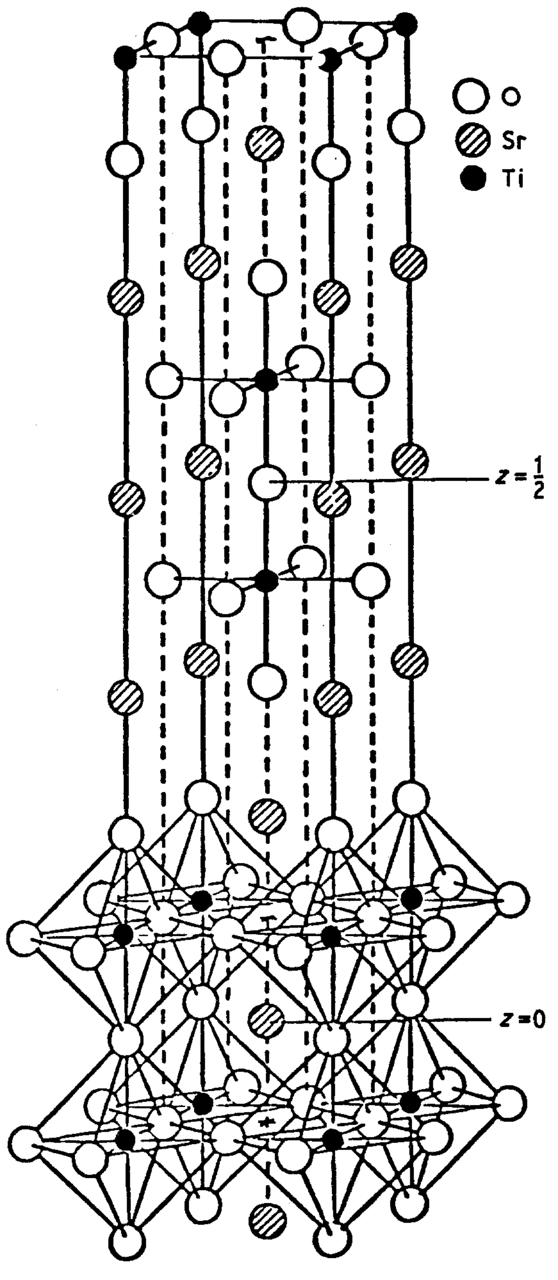

Figure 3 The structure of $Sr_3Ti_2O_7$.

The log σ against log P_{O_2} data (see Figs 1 and 2) are linear for as many as five decades of oxygen partial pressure for a given temperature. This extensive region of linearity affords the opportunity to determine the defect model responsible for the n-type conductivity in this region. The variation of the electrical conductivity with the oxygen partial pressure is calculated in terms of the oxygen vacancy defect model as was done for strontium titanate with Sr/Ti ⩽ 1.000 [7, 9]. One should consider the reaction representing the formation of a doubly ionized oxygen vacancy, $V_O^{\cdot\cdot}$, and two electrons available for electrical conduction by the removal of an oxygen atom from a normal lattice site into the gas phase as shown in Equation 3

$$O_O^x \rightleftharpoons 1/2\,O_2 + V_O^{\cdot\cdot} + 2e' \qquad (3)$$

The equilibrium constant for the Reaction 3 is

$$K_3 \cong [V_O^{\cdot\cdot}]\,[n]^2\,P_{O_2}^{1/2} = \exp\left(\frac{-\Delta G_f}{RT}\right) \qquad (4)$$

where $[n] \equiv [e']$. The Gibbs standard free energy change for Reaction 3 is represented by ΔG_f. With two electrons resulting from each oxygen vacancy, it follows that

$$[n] \cong 2[V_O^{\cdot\cdot}] \qquad (5)$$

Expressing the free energy change in terms of the enthalpy change, ΔH_f, and entropy change ΔS_f and substituting Equation 5 into Equation 4 the result for the electrical conductivity is given by

$$\sigma = 2^{1/3}\,P_{O_2}^{-1/6}\,e\mu\,\exp\left[\frac{\Delta S_f}{3R}\right]\exp\left[\frac{-\Delta H_f}{3RT}\right] \qquad (6)$$

where e is the electronic charge, and μ is the mobility of the conduction electrons. At constant temperature, assuming that the mobility is independent of the change in concentration of oxygen vacancies, a plot of the logarithm of the electrical conductivity against the logarithm of the P_{O_2} should result in a straight line with a slope of $-1/6$. The data in Figs 1 and 2 are in good agreement with the predicted $-1/6$ dependence.

Thermogravimetric work [28] indicates 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} is obtained when the reduction was carried out at an oxygen partial pressure value of 10^{-15} atm. For Equation 5 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 TiO_2 deficiency amounts to 2000 to 8000 ppm. Therefore, from the known levels of TiO_2 deficiency in the samples, the observed relation of $\sigma \propto P_{O_2}^{-1/6}$ could be achieved only when the excess SrO is structurally accommodated in a way not to form any charged defects. We, therefore, suggest the formation of shear structure in the samples with Sr/Ti > 1. The interlayer ordering might not be detected by conventional X-ray powder pattern techniques, because only one (SrO) layer would be required for each five hundred $SrTiO_3$ layers for the case of Sr/Ti = 1.002. In the electrical conductivity studies of samples with Sr/Ti = 1.002, 1.005 amd 1.008, equilibrium was established as fast as it was obtained in the sample with ideal cationic ratio. This indicates that the formation of (SrO) layer did not significantly affect the mass transport mechanism in strontium titanate with excess SrO.

3.2. Region II, $P_{O2} = 10^{-14}$ to 10^{-8} atm

A slope of about − 1/4 is found for the log σ against log P_{O2} data (see Figs 1 and 2). In the same P_{O2} region a slope of about − 1/4 was observed for the sample with ideal cationic ratio [7]. Daniels and Hardtl [29] reported from their log σ against log P_{O2} plot, a slope of about − 1/4 between 700 and 900° C and about − 1/5 at 1200° C for $BaTiO_3$ in the P_{O2} range, 10^{-18} atm. They attributed the − 1/4 slope to singly ionized oxygen vacancies as the cause of conductance and the − 1/5 value to the more frequent occurrence of doubly ionized oxygen vacancies. However, for $SrTiO_3$, it has been shown by earlier investigators [6, 30], that the oxygen vacancies of the quenched samples remain doubly ionized down to liquid nitrogen temperature. The observed slope of − 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 [15] reported net acceptor impurities 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 [14] was able to observe an extensive range of $P_{O2}^{-1/4}$ dependence for conductivity in the oxygen-deficient region below the p–n transition in the $BaTiO_3$ presumably because of greater acceptor impurity content of his samples. We believe that the present samples also contain some unknown acceptor impurities.

In order to discuss the concept of the impurity effect, it is helpful to consider a Kröger-Vink [31] diagram for a ternary oxide of the type ABO_3 with an acceptor impurity. We will, for the purpose of illustration, consider Schottky–Wagner disorder to describe the nonstoichiometry. Fig. 4 illustrates the variation of defect concentrations as a function of oxygen partial pressure for the case of fully ionized atomic defects, electrons [n], and electron holes [p], in a pure ternary oxide ABO_3 with both A and B site vacancies. It is assumed that the A and B content of the oxide is constant. Complete thermodynamic definition of a ternary oxide in equilibrium with only one crystal component, e.g., oxygen, requires the specification of three thermodynamic variables according to the phase rule. If both cationic species are sufficiently non-volatile, the atomic ratio of the cations, A/B, whether known or unknown but assumed constant, can be considered adequate in addition to temperature and total pressure while equilibrating with oxygen if the non–ideal ratio does not lead to charged point defects [32]. The familiar $[n] \propto P_{O_2}^{-1/6}$ in the region with charge neutrality condition $[n] \approx 2[V_O^{\bullet\bullet}]$ is illustrated in Fig. 4. In Fig. 5, an acceptor impurity is added that is always fully ionized, I'_m, to the ternary oxide ABO_3. Note in Fig. 5 that for sufficient departures from stoichiometry it may be possible for the electrical conductivity to be controlled by $[n] \approx 2[V_O^{\bullet\bullet}]$ and to, thereby, mask the effect of the acceptor impurity. The two major points to be derived from Fig. 5 are that the electronic n- to p-type transition has been shifted to lower oxygen partial pressures and the metal-excess to metal-deficit transition has been shifted to higher oxygen partial pressures when an acceptor impurity is added to ABO_3.

In Fig. 5, there is a region with electrical neutrality condition $[I'_m] \approx 2[V_O^{\bullet\bullet}]$ in which the electron concentration varies as the − 1/4 power and the electron hole concentration increases as the + 1/4 power of oxygen partial pressure. In this region, for certain values of P_{O2}, the electron concentration is greater than the electron hole concentration and, hence, the conductivity is n-type with a − 1/4 dependence on P_{O2}. As the oxygen partial pressure increases, the electron hole concentration becomes greater than the electron concentration after a certain

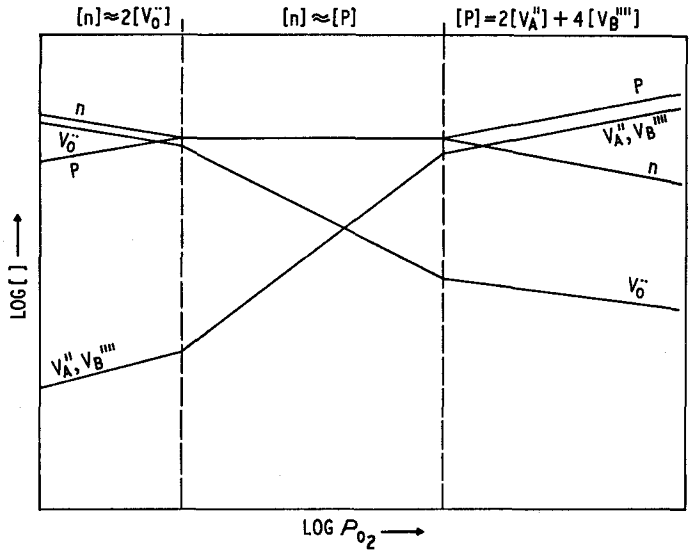

Figure 4 Logarithm of the defect concentration against the logarithm of oxygen pressure in the ternary oxide of the type ABO_3 with Schottky–Wagner disorder.

value of P_{O2} and the compound becomes p-type with a + 1/4 dependence of conductivity on P_{O2}. When the P_{O2} value is increased further, the electron hole concentration becomes equal to the acceptor concentration, which is constant, and, hence, the electrical conductivity is independent of P_{O2}, with the charge neutrality condition, $[I'_m] \approx [p]$, as shown in Fig. 5.

The observed slope of $\sim -1/4$ from the log σ against log P_{O2} data (Figs 1 and 2) in this region of P_{O2} is interpreted in terms of the presence of accidental acceptor impurities, such as Fe, Al or Cr on Ti sites. Thus, the condition of charge neutrality in this region can be

$$[I'_m] \approx 2[V_O^{\cdot\cdot}] \qquad (9)$$

With this neutrality condition and Equations 3 and 4, the electrical conductivity varies with oxygen partial pressure as shown in Equation (10) below.

$$\sigma = 2^{1/2}\,\frac{1}{[I'_m]^{1/2}}\,P_{O2}^{-1/4}\,e\mu \exp\left[\frac{\Delta S_f}{2R}\right]\exp\left[\frac{-\Delta H_f}{2RT}\right] \qquad (10)$$

The observed P_{O2} dependence for all the three samples are in good agreement with the value predicted by the above impurity model.

Incorporation of excess SrO on normal strontium and oxygen sites with the creation of titanium and oxygen site vacancies, Equation 2, will also lead to a $-1/4$ dependence of conductivity in P_{O2} in Region II. The charge neutrality condition will then be

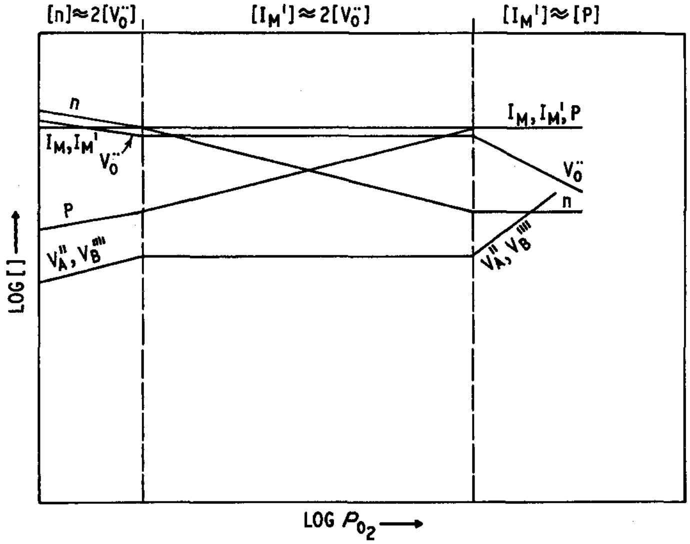

Figure 5 Logarithm of the defect concentration for the ternary oxide ABO_3 with a fully ionized acceptor-impurity, I'_m, and Schottky–Wagner disorder as a function of logarithm of oxygen pressure.

$$[V_0''] \approx 2[V_{Ti}''''] = \text{constant} \tag{7}$$

The mass-action expression for the oxygen extraction reaction, Equation 3, together with the charge neutrality condition, Equation 7, yields,

$$[n] \propto P_O^{-1/4} \tag{8}$$

and, hence, the electrical conductivity will be proportional to $-1/4$ power of P_{O2}.

If the $-1/4$ dependence observed in Region II is due to the creation of titanium and oxygen vacancies, Equation 2, then one should observe the absolute values of the conductivity decrease and the $-1/4$ dependence region extend to much lower P_{O2} values with a concomitant shift of the conductivity minimum to lower P_{O2} as the amount of excess SrO added to the sample is increased. This, in fact, is not observed in the present experiment suggesting that Equation 2, i.e., formation of titanium and oxygen site vacancies, is not a probable defect model for the case of strontium titanate with excess SrO.

If however, the oxygen and titanium vacancies were combined in the form of neutral vacancy pairs, (V_{Ti}'''', $2V_0^{\cdot\cdot}$), then the data would not be able to distinguish between the proposed shear structure model and one involving neutral vacancy pairs. The shear structure model is favoured since Ruddlesden–Popper type phases (nSrTiO$_3$ · SrO) are reported for SrTiO$_3$ with excess SrO [23, 24].

3.3. Region III, $P_{O2} > 10^{-4}$ atm

The measured electrical conductivity in the region for $P_{O2} > 10^{-4}$ atm increases with increasing oxygen partial pressure, indicative of p-type conduction. The oxygen pressure dependence of electrical conductivity for the three samples is $\sim +1/4$. It was shown in BaTiO$_3$ [12, 15, 16], CaTiO$_3$ [21] and SrTiO$_3$ with Sr/Ti $\leqslant 1.000$ [7, 9] that the p-type conductivity arises from the incorporation of oxygen into the impurity-related oxygen vacancies where the reaction is

$$[V_0^{\cdot\cdot}] + 1/2\, O_2 \rightleftharpoons O_0^x + 2h^{\cdot} \tag{11}$$

The charge neutrality condition in this region is the same as observed in region II, i.e.,

$$[I_m'] \approx 2[V_0^{\cdot\cdot}] \tag{12}$$

The chemical mass-action expression for Equation 11 combined with Equation 9 gives

$$\sigma \propto P_{O2}^{+1/4} \tag{13}$$

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.

If one assumes that the incorporation of excess SrO creates the vacancies of titanium and oxygen as given in Equation 2, then one would expect the conductivity in the p-type region to increases as the TiO$_2$-deficiency increases. This is because more oxygen atoms can be incorporated into the oxygen vacancies resulting from Equation 2 and the earlier onset of the $[V_0^{\cdot\cdot}] \approx 2[V_{Ti}'''']$ neutrality condition. No such systematic variation in the absolute values of the conductivity has been observed (see Figs 1 and 2) for the wide range of TiO$_2$ deficiency introduced into the samples used in the present study. If Equation 2, i.e., the formation of titanium and oxygen site vacancies, is the probable defect model, then the expected increase in the p-type region and the decrease in the n-type region of the absolute values of the conductivity as the excess SrO content is increased should result in the shift of the electronic n-p type transition to lower P_{O2} values. The observed data indicate that the conductivity minima for all the samples investigated occur at almost the same P_{O2} value. This again suggests that the incorporation of excess SrO into the strontium titanate lattice does not generate charged defect species. The present authors [9] have concluded that the incorporation of excess TiO$_2$ into strontium titanate is accommodated by forming neutral vacancy pairs (V_{Sr}'', $V_0^{\cdot\cdot}$).

4. Conclusions

The oxygen pressure dependence of the electrical conductivity in the samples with Sr to Ti ratios of 1.002, 1.005 and 1.008 (corresponding to 50.05, 50.125 and 50.199 mol% SrO, respectively) were found to be similar to that observed in strontium titanate with ideal cationic ratio. The absolute values of the conductivity did not change significantly as the Sr to Ti ratio was changed in all three regions. These observations indicate that the incorporation of excess SrO in strontium titanate with ideal composition does not generate any charged defects. The excess SrO can be structurally accommodated by the formation of SrO layers which can be built into the lattice in an ordered fashion. The experimental results indicate that doubly ionized oxygen vacancies, Equation 3, are the dominant defect present at the lowest oxygen pressure region.

For $P_{O2} > 10^{-15}$ atm., the defect chemistry is dominated by accidental acceptor impurities and their related oxygen vacancies, Equation 7. Because of these acceptor impurities, a region in which the electrical conductivity changes as approximately the $-1/4$ power of oxygen pressure is observed. The p-type conductivity observed in the region $P_{O2} > 10^{-4}$ atm is due to fractional filling of the impurity-related oxygen vacancies, Equation 11. The deviation from ideal cationic ratio has no significant role in influencing the observed electrical conductivity.

Acknowledgements

The authors thank the Gas Research Institute for their financial support in carrying out this investigation.

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Received 16 November
and accepted 15 December 1981