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The Effect of Cation Place Exchange on the Electrical Conductivity of $SrBi_2M_2O_9$ (M = Ta, Nb)

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Abstract

The defect chemistry and charge transport in undoped and doped $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) has been studied by measurement of the equilibrium electrical conductivity as a function of oxygen activity at temperatures between 600 and 800°C. Undoped SBT appears to contain about 1% excess acceptor centers, while undoped SBN appears to contain about 1% excess donor centers. The behavior is attributed to substantial place exchange between Sr^{+2} and Bi^{+3} in the alternating layers of the structure with partial local compensation by oxygen vacancies in the bismuth layers and by electrons in the perovskite-like layers. The total conductivity is then dominated by the better conducting layer, i.e. ionic conductivity by oxygen vacancies in the bismuth layers in SBT, and electron conduction in the perovskite-like layers in SBN. The major determining factor is the larger band gap and greater electron trapping in SBT. © *1999 Elsevier Science Limited. All rights reserved*

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1 Introduction

The bismuth-layer ferroelectrics have become leading candidates for nonvolatile thin film memories on silicon based computer chips. In particular, $SrBi_2Ta_2O_9$ (SBT) has been extensively investigated and is beginning to be incorporated into practical devices. While the remanent polarization is substantially less than that of the competing PZT-based materials, the bismuth-layer compounds are much more resistant to polarization fatigue, i.e. the loss of switchable charge after many cycles of polarization reversal.

The electrical conductivity of the ferroelectric is of importance in determining the level of leakage currents, and in the degradation of dielectric properties under prolonged temperature-voltage stress. The level and the nature of the electrical conductivity will be determined by the presence of electronic and ionic defects in the crystalline lattice. Accordingly, we have undertaken a study of the defect chemistry of $SrBi_2Ta_2O_9$ and its niobium analogue.

The structure of SBT consists of perovskite-like layers, having the net composition ${SrTa_2O_7}^{-2}$, and bismuth oxide layers, of composition ${Bi_2O_2}^{+2}$. Recent detailed structural studies indicate that there is significant place exchange, several percent, between the Sr^{+2} and Bi^{+3} ions.[12] This can be viewed as an attempt to reduce the charge imbalance between the layers. In a homogeneous material, such place exchange should be self-compensating and not require the presence of any other compensating defects.

2 Experimental

The compounds were prepared by the mixed oxide technique with calcination at 1050 (SBN) and 1100°C (SBT) for 1 h in air. Pressed samples were then sintered in air at 1150°C for 1 h (SBN) and 1200°C for 1/2 h (SBT). The dc conductivity measurements were made by the standard 4-point technique using platinum electrodes in a flowing gas stream composed of Ar–O_2 mixtures or argon depleted of oxygen by means of an electrochemical oxygen pump using acceptor-doped ZrO_2. The oxygen activity near the sample was measured with a doped zirconia electrochemical sensor.

3 Results

The equilibrium electrical conductivities of undoped, acceptor-doped, and donor-doped $SrBi_2$-

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$\mathrm{Ta_2O_9}$ as a function of oxygen activity at 725 °C are shown in Fig. 1. The broad plateau with slight upturns at the highest and lowest oxygen activities is typical of acceptor-doped oxides.[3] The plateau is attributed to ionic conductivity due to compensating oxygen vacancies, and this was confirmed by determination of the ionic transport number by oxygen concentration cell measurements. The upturn at high oxygen activities is caused by an increasing hole conduction due to partial filling of the compensating vacancies, while that at low oxygen activities is caused by an increasing electron concentration due to reduction. The ionic conductivity has an activation energy of 90 kJ mol (0.94 eV) which is typical of oxygen vacancy conduction in perovskite oxides.

The equilibrium conductivities of 1% acceptor-doped (Ti^{+4} substituted for Ta^{+5}) and 1% donor-doped (La^{+3} substituted for Sr^{+2}) SBT are also shown in Fig. 1. As expected for an oxide with a

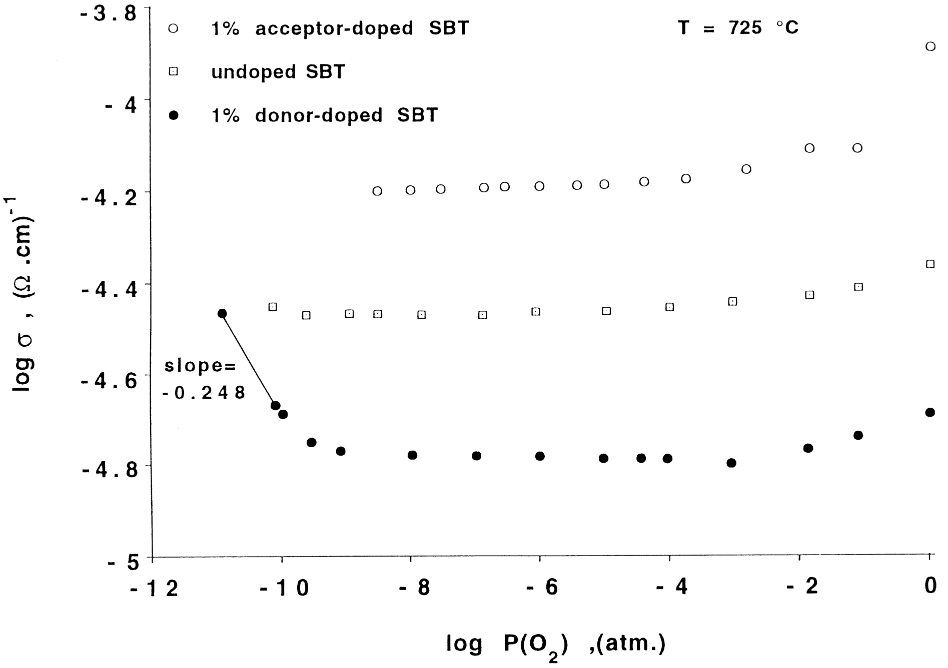

Fig. 1. The equilibrium electrical conductivity of undoped, 1% acceptor-doped ($\mathrm{Ti}'_{\mathrm{Ta}}$), and 1% donor-doped ($\mathrm{La}^{\bullet}_{\mathrm{Sr}}$) SBT as a function of oxygen activity at 725 °C.

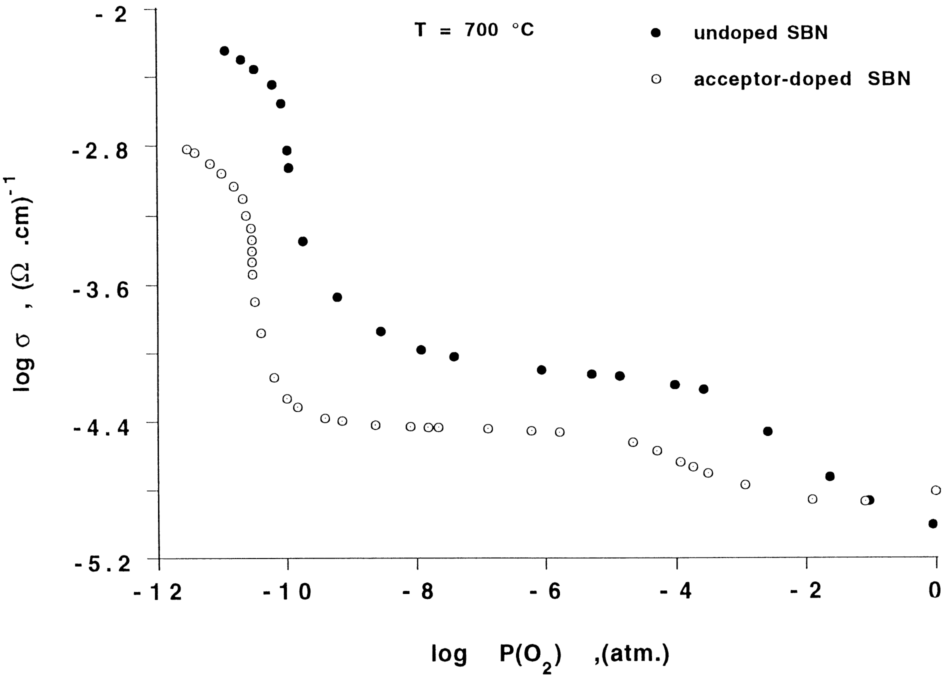

Fig. 2. The equilibrium electrical conductivity of undoped and 1% acceptor-doped ($\mathrm{Ti_{Nb}}'$) SBN as a function of oxygen activity at 700 °C.

net excess of acceptor-centers, the addition of more acceptors increases the ionic conductivity, while the addition of donor impurities reduces it. Note that the n-type region is enhanced in the donor-doped sample, because the oxygen vacancy concentration drops linearly with decreasing net acceptor excess while the electron concentration increases as the square root. The magnitude of the changes caused by the doping is consistent with a net acceptor content of the order of 1% in the undoped material; this is far in excess of any expected impurity content or error in composition.

It was anticipated that the isostructural $SrBi_2Nb_2O_9$ (SBN) would have a smaller band gap than the tantalum analog because of the easier reducibility of Nb^{+5} compared with Ta^{+5}, and would thus show more electronic disorder. (The greater ease of reduction should reduce the enthalpy of reduction, and since the band gap can be derived from the sum of the enthalpies of reduction and oxidation, this should result in a smaller band gap for SBN compared with that of SBT.) The equilibrium conductivities of undoped and 1% acceptor-doped SBN at 700 °C are shown in Fig. 2. The results are surprisingly different from that of SBT. With decreasing oxygen activity from 1 atm, the conductivity rises with a log–log slope of $-1/4$ and then levels out. This is characteristic of donor-doped oxides with ionic compensation of the donors at high oxygen activities and compensation by electrons at lower oxygen activities.[3] The effect of the added acceptor is consistent with the presence of a net excess of donors in the undoped SBN of the order of 1%, again far in excess of any expected impurity content or error in composition. For the doped sample it appears that a shallow minimum has moved into view at an oxygen activity of about 10^{-2} atm. This is the expected direction of shift for a reduction in the net donor content. At very low oxygen activities the conductivity undergoes an abrupt rise in value. This seems to be an unrelated phenomenon that is not yet understood and it will not be discussed further in this report.

4 Discussion

The initial results just described raise the questions as to why SBT and SBN behave so differently when Ta^{+5} and Nb^{+5} have very similar chemical behaviors, and as to the origin of the approximately 1% acceptor and donor concentrations in the undoped materials. Some further information is obtained by the use of higher dopant concentrations. It is seen in Fig. 3 that the equilibrium conductivity of SBT with 3% added donor has the general appearance of undoped SBN, i.e. both now act as donor-excess materials. Moreover, as seen in Fig. 4, the equilibrium conductivity of SBN with 3% added acceptor now has the general appearance of undoped SBT, i.e. both now behave as acceptor-excess materials. Thus the two compounds do not act completely differently, they are merely displaced along the doping axis. The apparent acceptor content of undoped SBT can be over-powered by added donor to give donor-doped behavior, while the apparent donor content of undoped SBN can

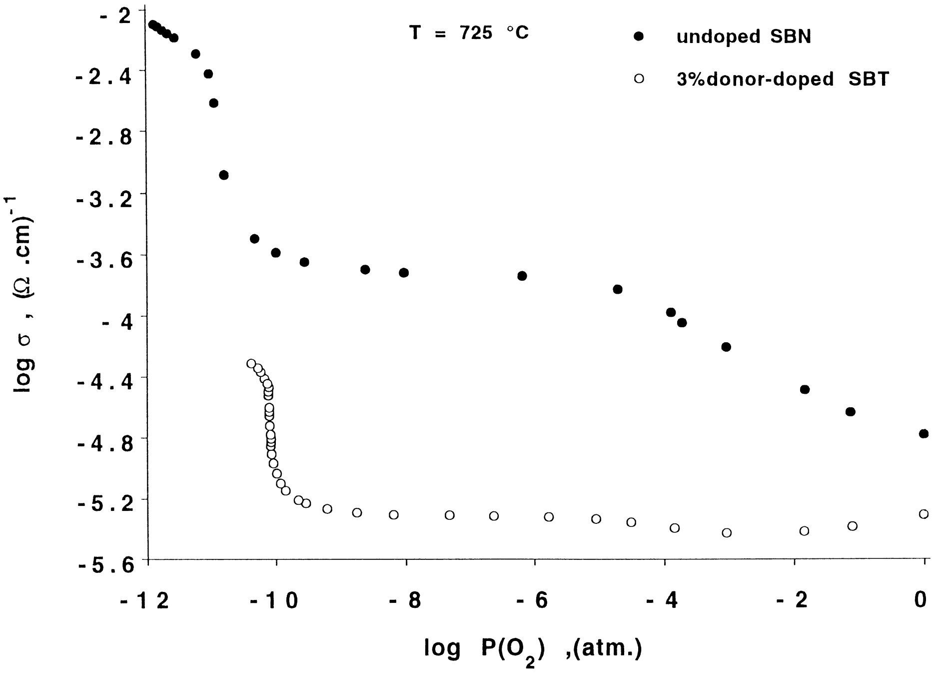

Fig. 3. The equilibrium electrical conductivity of undoped SBN and 3% donor-doped ($La^{\bullet}_{Sr}$) SBT as a function of oxygen activity at 725 °C.

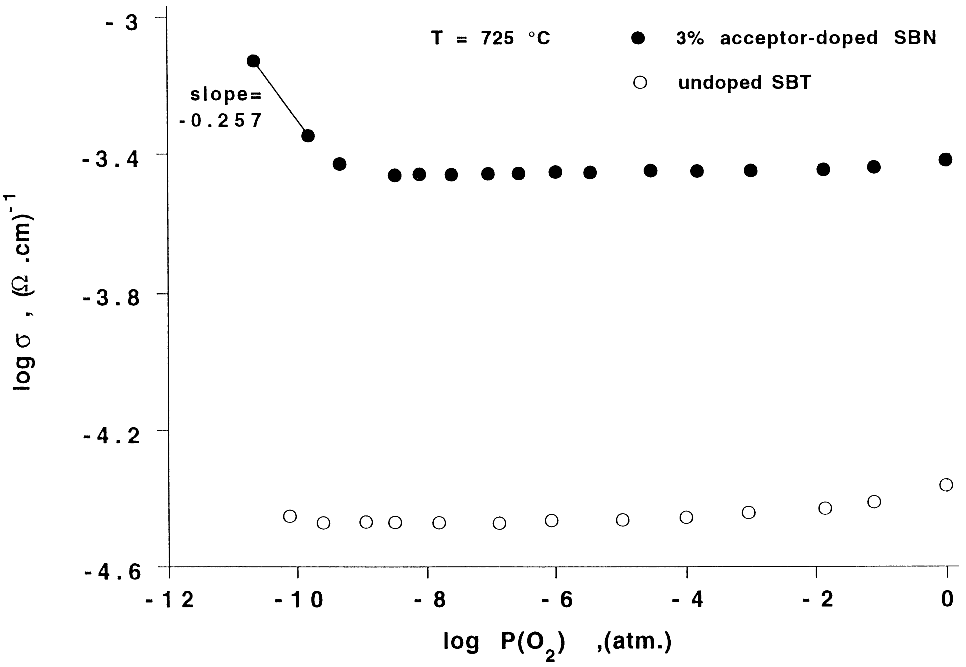

Fig. 4. The equilibrium electrical conductivity of undoped SBT and 3% acceptor-doped (Ti_{Nb}') SBN as a function of oxygen activity at 725 °C.

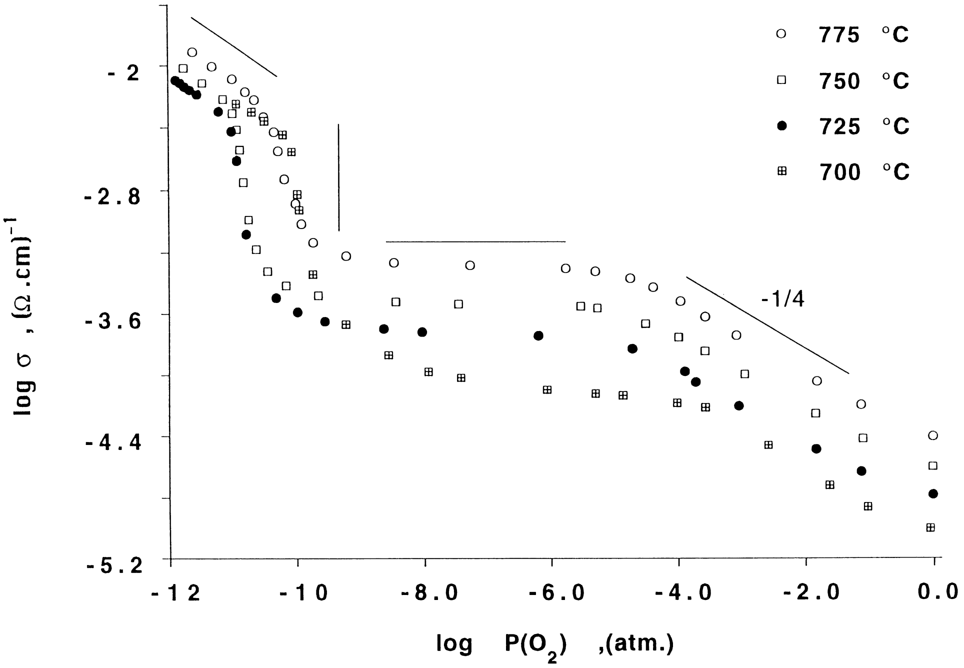

Fig. 5. The equilibrium electrical conductivity of undoped SBN as a function of oxygen activity at several temperatures.

be over-powered by added acceptor to give acceptor–doped behavior.

It is suggested that the key to the behavior of the two compounds originates in the extensive place-exchange between Sr^{+2} and Bi^{+3} in the two layers of the structure. A recent structural study found 13% exchange in $BaBi_22Nb_2O_9$ and 5% in $CaBi_2Nb_2O_9$.[2] In a homogeneous structure such place-exchange would be self-compensating, but perhaps that is not completely true when the impurity centers are in different layers. Thus some fraction of the Sr'_{Bi}, in the bismuth layers might be compensated by oxygen vacancies, while some fraction of the $Bi^{\bullet}_{Sr}$ in the perovskite layers might be compensated by electrons. The electrical conductivity would then be dominated by the layer that makes the larger contribution to the total conductivity. This would appear to be ionic conductivity in the bismuth layers of undoped SBT, and electronic conductivity in the perovskite layers of undoped SBN. The fact that the amount of excess acceptor and excess donor in undoped SBT and SBN is about the same, approximately 1%, implies that the amount of place exchange and of self-compensation is about the same in the two compounds.

Why do different layers dominate the conductivity in the two compounds? Figure 5 shows the equilibrium electrical conductivity of undoped SBN at several temperatures. Note that the conductivity in the plateau region, where the total concentration of electron species should be determined by the net donor excess, shows a substantial temperature dependence, i.e. an activation energy of about 200 kJ mol^{-1} (2·1 eV). This implies that the electrons are mostly immobilized in deep traps, presumably the impurity centers, or have a highly activated mobility, or both. SBT is expected to have the higher band gap and thus most likely deeper electron traps. If the electrons are more deeply trapped in SBT, then the ionic conductivity of the bismuth layers may be dominant, while the shallower electron traps in SBN result in a larger contribution by electrons in the perovskite layers. Thus the strikingly different behavior of the apparently very similar undoped compounds can be completely explained by the presence of deeper electron traps in SBT, as would be expected if it has the wider band gap due to the greater difficulty in reducing Ta^{+5} compared with Nb^{+5}.

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