



The Similar Defect Chemistry of Highly-Doped $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$

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Abstract. The equilibrium electrical conductivities of undoped $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) have been shown to behave quite differently. SBT has the behavior expected for a 1% acceptor-doped oxide, while SBN behaves like a 1% donor-doped oxide. This difference has been related to the substantial cation place exchange that occurs between the Bi^{+3} and Sr^{+2} ions in the alternating layers of the structure. It was proposed that this place exchange is not entirely self-compensating, as would be expected for a simple, isotropic oxide, but that there is some local compensation within each layer by lattice and/or electronic defects. It is now shown that the equilibrium conductivity of 3% donor-doped SBT is similar to that of undoped SBN, while the equilibrium conductivity of 3% acceptor-doped SBN resembles that of undoped SBT. Thus the defect chemistries of the two compounds are quite similar, but the equilibrium conductivities are displaced along a doping axis.

Keywords: defects, doping, acceptor dopants, donor dopants, place exchange, equilibrium conductivity, seebeck, conductivity jump, SBT, SBN

Introduction

Ferroelectric metal oxides are of great interest because their spontaneous polarization, which can be reversed by an applied voltage, allows them to be used as nonvolatile memories on Si-based computer chips [1, 2]. Early studies involving the PbTiO_3 - PbZrO_3 system found that these materials suffer from polarization fatigue, whereby the amount of switchable charge eventually decays after many cycles to the point that the polarization direction can no longer be reliably determined [3, 4]. It was subsequently found that $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) are highly resistant to such fatigue, and they have become prime candidates for use in nonvolatile memories [5]. Studies of the defect chemistry of such materials can give insight into the nature of the ionic and electronic defects present, and hence can contribute to an understanding

of the basis for the resistance to fatigue. The basic tool for such studies is the measurement of the high temperature equilibrium electrical conductivity as a function of oxygen activity and temperature. Our previous studies of the equilibrium conductivities of undoped and lightly-doped SBT and SBN showed that they behave very differently, as shown in Figs. 1 and 2 [6–8]. This is surprising since the two compounds are isostructural and since Nb^{+5} and Ta^{+5} have very similar chemical behavior.

SBT and SBN are ferroelectric members of the Aurivillius family of crystal structures. They have layered structures in which fluorite-like $\text{Bi}_2\text{O}_2^{+2}$ layers alternate with perovskite-like $\text{SrM}_2\text{O}_7^{-2}$ layers, where $M = \text{Ta}$ or Nb . Detailed structural studies of both compounds have shown that there is substantial, i.e. several percent, cation place exchange between the Bi^{+3} and the Sr^{+2} [9,10]. This place exchange creates $\text{Bi}_{\text{Sr}}^{\cdot}$ donor centers and $\text{Sr}_{\text{Bi}}^{\cdot}$ acceptor centers and these should be self-compensating in an isotropic structure. However, in these layered structures, the acceptor

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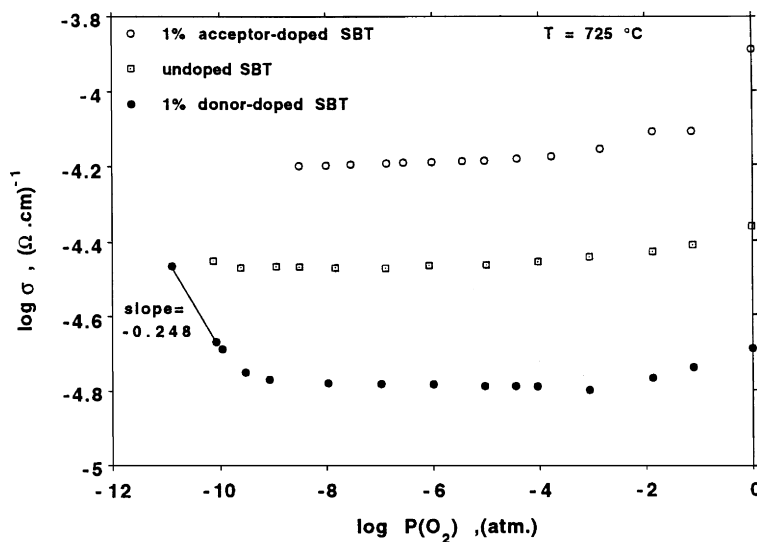


Fig. 1. The equilibrium electrical conductivity of undoped, 1% acceptor-doped ($\text{Ti}_{\text{Ta}}^{\text{IV}}$), and 1% donor-doped SBT ($\text{Bi}_{\text{Sr}}^{\text{III}}$) at 725°C (adapted from Ref. 6).

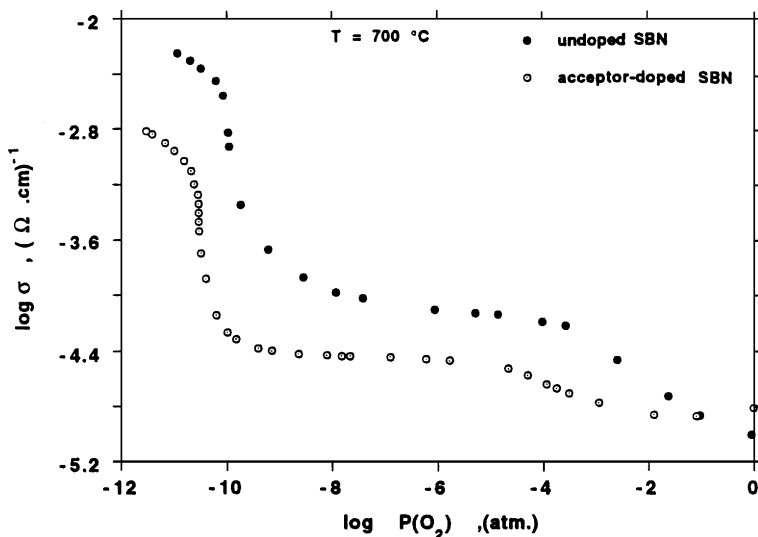


Fig. 2. The equilibrium electrical conductivity of undoped, and 1% acceptor-doped ($\text{Ti}_{\text{Nb}}^{\text{IV}}$) SBN at 700°C (adapted from Ref. 6).

centers are in the Bi layers, while the donor centers are in the perovskite layers. In our earlier papers, we postulated that this results in incomplete self-compensation, with the acceptors in the Bi layer being at least partially compensated locally by oxygen vacancies, while the donors in the perovskite layers are at least partially compensated locally by electrons or cation vacancies [7, 8]. Doping studies indicated that the resulting self-doping levels are of the order of 1–2% in each layer. The equilibrium con-

ductivity is then dominated by the better conducting layer.

Experimental Procedure

The compounds were prepared by the mixed oxide technique with calcination at 1050°C (SBN) and 1100°C (SBT) for one hour in air. Hydrostatically pressed samples were then sintered in air at 1150°C for one hour (SBN) and at 1200°C for 1/2 hour (SBT). The

dc conductivity measurements were made by the standard 4-point technique using platinum electrodes. The samples were equilibrated with a flowing gas stream composed of Ar-O₂ mixtures or Ar depleted of oxygen by means of an electrochemical oxygen pump based on calcia-doped zirconia. The oxygen activity near the sample was measured with an yttria-doped zirconia electrochemical sensor. Measurements made on multiple samples of the undoped materials indicated good reproducibility. The consistent trends observed as a function of dopant kind and concentration indicated that measurements on single samples of the doped compounds were adequate. Equilibration times varied greatly with temperature and oxygen activity. Care was taken to insure that measured values could be reproduced from different starting conditions. The conductivity was periodically measured at a reference condition, usually pure oxygen, to insure that no irreversible changes had occurred. This indicated that exposure to extremely low oxygen activities should be avoided. The temperature range was restricted to 600–800°C in order to minimize the risk of loss of Bi₂O₃ by volatilization.

Thermoelectric power (Seebeck) measurements were made using a heat pulse technique similar to that described by Eklund and Matabah [11]. A temporary thermal gradient was created across the sample by passing an ac current for less than two minutes through a Pt wire wrapped around one end of the sample. The thermoelectric voltage across the sample, and the voltage developed by a thermocouple placed across the sample (proportional to the temperature gradient), were measured as a function of time as the gradient gradually decreased. More detailed descriptions of the experimental procedure can be found in the earlier publications [7, 8].

Undoped and Lightly Doped SBT and SBT

The equilibrium electrical conductivity of SBT as a function of oxygen activity at 725°C is shown in Fig. 1. Data are shown for undoped, 1% acceptor-doped (Ti_{Nb}⁴⁺), and 1% donor-doped (La_{Sr}³⁺) SBT. The conductivity in the broad, central plateau was shown to be ionic with an activation energy of 0.94 eV, while the ionic transport number gradually decreased as the oxygen activity approached 1 atm [7]. This is consistent with oxygen vacancy conduction with an increasing contribution from holes as some of the vacancies are filled with oxygen

at the higher oxygen activities. The contribution from holes was confirmed by the sign of the Seebeck coefficient in pure oxygen. The shape of the conductivity profile was similar for the doped samples, but the level of conductivity was increased by the acceptor dopant while it was decreased by the donor dopant. The decrease in ionic conductivity caused by the donor dopant exposed a greater rise in conductivity at the lowest oxygen activities. This contribution is attributed to electrons that result from the loss of oxygen. The observed log-log slope of $-1/4$ is that expected for electrons when charge neutrality is dominated by acceptors and their compensating oxygen vacancies. The effect of the dopants is consistent with the presence of 1–2% acceptor centers in the undoped material with compensation by oxygen vacancies. This background acceptor content was attributed to the Sr_{Bi}²⁺ centers in the Bi layers that result from the cation place exchange between the two alternating layers [7]. Thus the ionic conductivity of SBT appears to be localized in the Bi layers. This model was described in greater detail in an earlier paper [7].

The equilibrium conductivity of undoped and 1% acceptor-doped (Ti_{Nb}⁴⁺) SBN as a function of oxygen activity at 700°C is shown in Fig. 2. The shape of the conductivity profile is totally different from that of SBT. The acceptor-dopant reduced the level of the conductivity without changing its general appearance. For comparison, the effect of the addition of 3% donor-dopant (La_{Sr}³⁺) to SBN is shown in Fig. 3.

The level of the conductivity is uniformly increased while the general shape of the conductivity profile remains unchanged. For all three compositions, as the oxygen activity decreases from 1 atm, there is first a region with log-log slope $-1/4$, then a plateau that is followed by an abrupt jump in conductivity, and finally a brief region of shallower slope. The $-1/4$ slope and plateau are consistent with *n*-type conduction in a donor-doped oxide as discussed in our earlier paper [8]. The former region is consistent with charge compensation of the donor centers by cation vacancies, while in the plateau region, compensation appears to be by electrons. It is proposed that the activation energy of the conductivity in these two regions, about 1.6 eV, is almost entirely due to the electron mobility. The *n*-type conduction is viewed as a hopping process that is highly thermally activated. It is proposed that the abrupt increase in conductivity results from a decrease in the activation energy of the electron mobility that occurs near where the oxygen vacancy concentration reaches

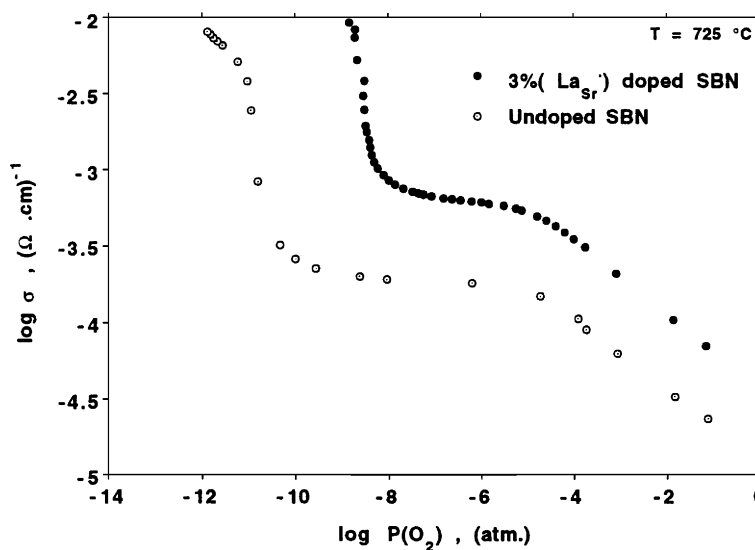


Fig. 3. The equilibrium electrical conductivity of undoped and 3% donor-doped (La_{Sr}) SBN at 725° .

the donor concentration. It will be shown that the log-log slope at the lowest oxygen activities is $-1/6$, which is characteristic of heavy reduction with the condition of charge neutrality being dominated by electrons and oxygen vacancies. Thus the behavior is that expected for a typical donor-doped oxide with the exception of the abrupt increase in the electron mobility. The effect of the dopants suggests that the undoped SBN has a donor center content of 1–2%, and this is attributed to Bi_{Sr} centers in the perovskite-like layer that result from the cation place exchange between the two alternating layers. Thus the n -type conduction in these samples of SBN appears to be localized in the perovskite-like layers. A more detailed analysis of the defect chemistry of SBN appears elsewhere in this journal [8].

In this paper we explore higher dopant concentrations. It is shown that with sufficient added donor impurities, SBT can be made to behave like undoped SBN, while with sufficient added acceptor impurities SBN can be induced to behave like undoped SBT. Thus the two compounds do not behave so differently after all. Their equilibrium conductivities are just displaced laterally along a donor-acceptor doping axis.

Donor Doped SBT

Figure 4 shows the progression of the equilibrium conductivity of SBT from 1% acceptor-doped ($\text{Ti}_{\text{Ta}}^{\text{I}}$), to un-

doped, to 1, 3, and 3.5% donor-doped (La_{Sr}). As shown in Fig. 1, the addition of 1% acceptor dopant approximately doubled the ionic conductivity of the undoped material, while the addition of 1% donor dopant reduced it by about half. But the 3% donor addition was sufficient to suppress the ionic conductivity enough to expose the n -type conductivity characteristic of an oxide having a net excess of donor centers. This more heavily donor-doped SBT now has a conductivity profile similar to that of undoped SBN. All of this behavior is consistent with the proposal that undoped SBT has a net acceptor content of about 1–2% in the Bi layers due to the cation place exchange. It is to be expected that the donor dopant would also increase the n -type conduction, which is postulated to occur in the perovskite layers. Note that even though the dopants were substituted for host cations in the perovskite layers, they also suppressed the ionic conduction in the Bi layers. Thus while the main hypothesis of our model is that the defect chemistry of the alternating layers of the structure are somewhat independent, this cannot be entirely true, and there must be some interaction between the layers. If there were no such interaction, then the addition of donor dopants to the perovskite layers should result only in an increase in the n -type conductivity in those layers. It is also possible that the added dopant modifies the amount of cation place exchange, or the portion of the displaced cations that are locally compensated by lattice or electronic defects. The extent of

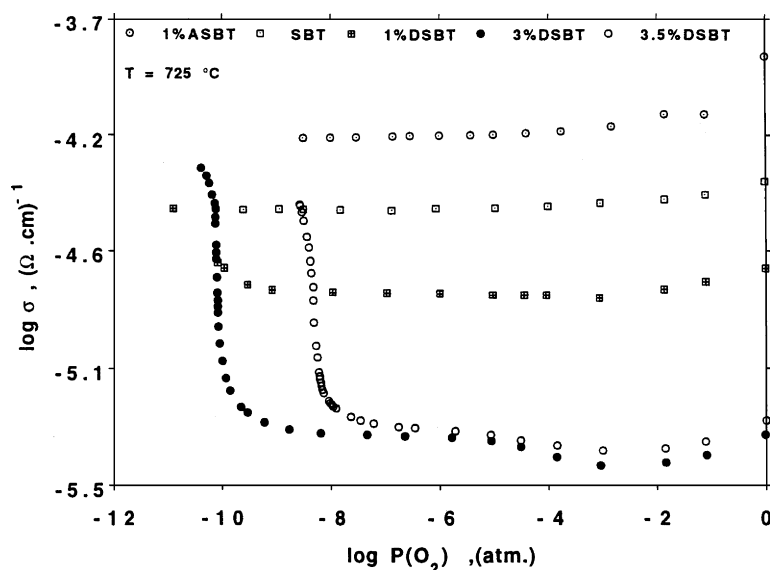


Fig. 4. The equilibrium electrical conductivities of 1% acceptor-doped, undoped, and 1, 3, and 3.5% donor-doped SBT at 725°C.

place exchange should be established during the sintering process, and is expected to be essentially invariant during the conductivity measurements. No additional information is available about these possibilities.

If the equilibrium conductivity of SBN as shown in Fig. 2 could have been measured at oxygen activities substantially above 1 atm, one would expect to see the $-1/4$ slope flatten out, and then for the conductivity to pass through a minimum value followed by a trend toward a $+1/4$ slope as p -type conduction due to oxidation takes over. In fact, the data for the undoped sample do show a slight flattening of the slope, and for the 1% acceptor doped sample a very shallow minimum appears to have moved into view. Indeed, the minimum is expected to move toward lower oxygen activities with increasing acceptor content. In the case of the 3% donor-doped SBT, as shown in Fig. 4, there also appears to be a very shallow minimum. This is confirmed by the positive sign of the Seebeck coefficient for this sample, measured in 1 atm oxygen at 725°C, which indicates that the charge carriers are positively charged. This is further evidence that the 3% donor-doped SBT is behaving as a conventional donor-doped oxide in the region of higher oxygen activities. The vertical distance between the minimum and the plateau is so small that the log-log slope of $-1/4$ is not fully developed. This implies that the conductivity associated with the condition $n = p$ is only slightly lower than that of the plateau region. There may also

be a significant contribution from the ionic conduction in the Bi layers that will further flatten the conductivity minimum.

Acceptor Doped SBN

The equilibrium conductivity of SBN at 700°C, undoped and with 1 and 3% acceptor dopant, ($Ti_{Nb}^{1/}$), is shown in Fig. 5.

The 3% acceptor-doped SBN now shows the same kind of conductivity profile as undoped SBT, and the conductivity now appears to be mostly ionic conduction in the Bi layers. In fact, as seen in Fig. 6, the level of ionic conductivity in the 3% acceptor-doped SBN is about an order of magnitude higher than that in undoped SBT. As in the case of doped SBT, doping in the perovskite layers of SBN seems to have primarily affected the oxygen vacancy conduction in the Bi layers, although, at the 3% acceptor level, the perovskite layer should have excess acceptor centers and thus might make some additional ionic contribution to the conduction. As shown in Fig. 6, the n -type conductivity at 725°C in the highly acceptor-doped SBN is much more prominent than in undoped SBT. This is to be expected if the band gap of SBN is lower than that of SBT. It is now possible to assign a log-log slope of $-1/4$ to this region, as was also noted for the case of 1% donor-doped SBT, Fig. 1. This is anticipated for the case of n -type

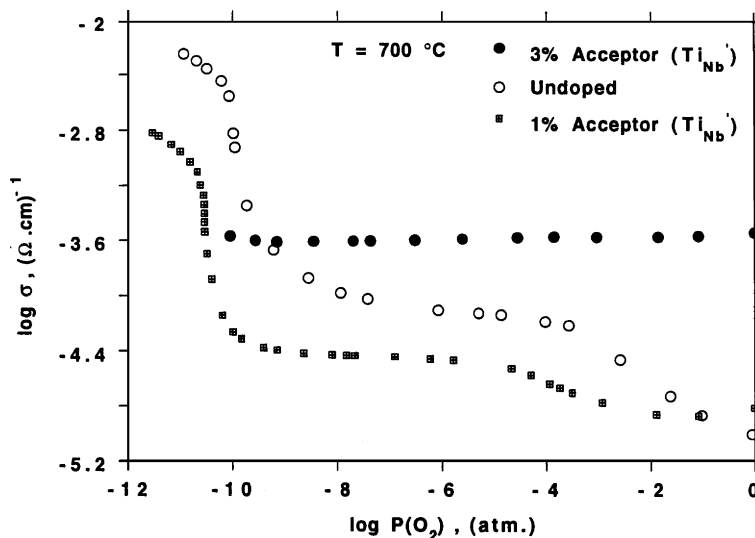


Fig. 5. The equilibrium electrical conductivities of undoped and 1% and 3% acceptor-doped SBN at 700°C.

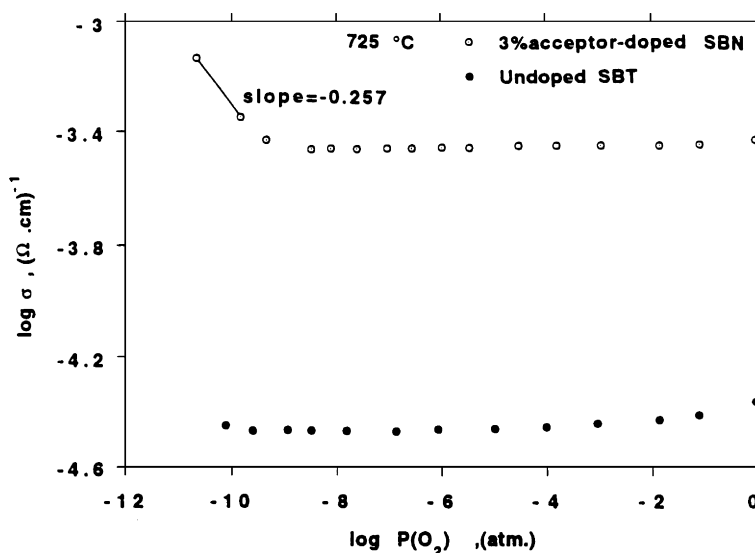


Fig. 6. Comparison of the equilibrium conductivity of undoped SBT and 3% acceptor-doped SBN at 725°C (adapted from Ref. 6).

conduction that results from reduction for the case that charge neutrality is determined by the acceptor centers and their compensating oxygen vacancies.

Comparison of SBT and SBN

We have postulated that in both undoped SBT and undoped SBN the perovskite layers are 1–2% donor doped, and the Bi layers are 1–2% acceptor doped

as a result of cation place exchange and the absence of complete self-compensation. In undoped SBT the equilibrium conductivity is dominated by ionic conductivity due to compensating oxygen vacancies in the acceptor-doped Bi layers. In undoped SBN the equilibrium conductivity is primarily due to *n*-type conduction in the donor-doped perovskite layers. But with sufficient added donors the dominant conductivity in SBT switches to the perovskite layers, and the behavior is similar to that of undoped SBN. Likewise, with

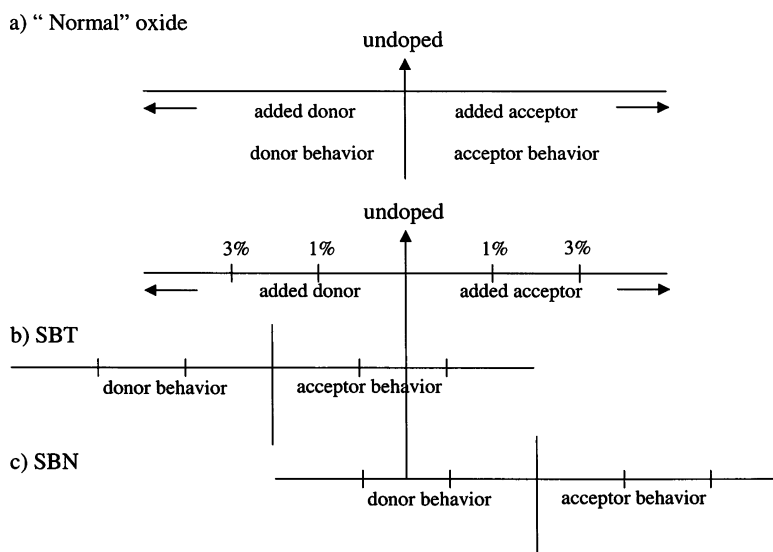


Fig. 7. Schematic representation of the behavior of oxides as a function of added acceptor and donor dopants. a. A “normal” oxide, b. SBT, and c. SBN.

sufficient added acceptors the dominant conductivity in SBN switches to the Bi layers, and the behavior becomes similar to that of undoped SBT. Thus in the most general sense, SBT and SBN behave very similarly, but the different facets of their behavior occur at different balances of the conductivity in each layer. They can be viewed as being displaced laterally from one another along a doping axis as shown schematically in Fig. 7, because of the intrinsic doping that results from the extensive cation place exchange. The effect of doping a normal, isotropic oxide is depicted in Fig. 7a. For the undoped oxide, the behavior is displaced only very slightly from the intrinsic case due to the presence of accidental impurities. With increasing addition of acceptor dopants the behavior is increasingly acceptor-like, while with increasing addition of donor dopants the behavior is increasingly donor-like. The case of SBT is shown in Fig. 7b. Because of the cation place exchange between Sr⁺² in the perovskite layers and Bi⁺³ in the Bi layers, and due to the dominance of the ionic conduction in the Bi layers, the undoped material already acts as if it has 1–2% acceptor content. Addition of more acceptor dopant accentuates the acceptor-doped behavior, but the initial additions of donor dopant merely reduces the net acceptor behavior. Only for donor additions in excess of about 2% do the properties switch over to donor-doped behavior, as control of the conductiv-

ity is taken over by the perovskite layers. As shown in Fig. 7c, the behavior of SBN is just the opposite, since the perovskite layers initially control the conductivity. The undoped material behaves like a material with 1–2% donor content. Addition of more donor dopant accentuates the donor-doped behavior, while the initial additions of acceptor dopant merely reduces the net donor behavior. Only for acceptor additions in excess of about 2% do the properties switch over to acceptor-doped behavior, as control of the conductivity is taken over primarily by the Bi layers. The difference in behavior between the two compounds is attributed to a lower band gap in SBN. The electronic states in solid compounds derive from the electronic states in the constituent atoms. Thus band gaps correlate with the redox behavior of those atoms. Since Nb⁺⁵ is much more easily reduced than Ta⁺⁵, it is expected that niobates will have smaller bandgaps than the analogous tantalates. This is supported by the measured band gaps at 300 K for LiNbO₃ (3.64 eV) and LiTaO₃ (3.93 eV) [12]. Because of the lower band gap in SBN, its behavior is more strongly influenced by electronic defects.

The temperature dependence of the equilibrium conductivity in undoped SBT is attributed to the thermally-activated mobility of the oxygen vacancies in the Bi layers [7]. In undoped SBN the temperature dependence of the equilibrium conductivity appears to be

primarily due to the highly activated mobility of the electrons in the perovskite layers [8].

The Effect of Thermal History

The equilibrium conductivities of SBT and SBN are largely determined by the amount of cation place exchange that occurs between the Bi and perovskite layers. The equilibrium amount of place exchange is most likely dependent on the temperature and time duration of the sintering process. It is probably not practical to determine the equilibrium amounts of exchange, but it may be possible to vary the temperature at which the exchange is frozen in. Figure 8 shows the equilibrium conductivity profiles for undoped SBN sintered in air at 1150°C with two different heating and cooling rates: 9°C per minute for both heating to the sintering temperature and cooling back to room temperature in one case, and 5°C per minute for both heating and cooling for the other. The conductivity in the two regions at the highest oxygen activities were not significantly affected, but the abrupt jump in conductivity occurred at an oxygen activity almost two orders higher for the sample with the slower ramp rate. This shift was repeatable.

As seen in Figs. 2, 3, and 4, a similar shift of the conductivity jump to higher oxygen activity resulted from the donor-doping of SBN, and from increasing the added donor content of SBT from 3 to 3.5%. It appears

that the conductivity jump moves toward higher oxygen activities as the donor concentration is increased. Since increased donor concentrations and slower heating and cooling rates have similar effects on the location of the conductivity jump, the slower heating and cooling rates may be resulting in an increase in the concentration of locally compensated donors in the perovskite layers. This could result from increased cation place exchange, or an increase in the amount of local compensation of the donors, or both. The ability to shift the location of the jump is useful. As seen in Fig. 9, a combination of donor-doping and slow ramp rates during sintering of SBN results in a shift in the abrupt jump that exposes a much wider region for oxygen activities below the jump, before the sample starts to decompose at about $\log P(\text{O}_2) = -10$. It is then possible to assign a log-log slope of $-1/6$ to that region. That is the slope expected when the products of reduction, oxygen vacancies and electrons, dominate the expression for charge neutrality. This suggests that the abrupt jump occurs near the boundary between normally-behaved regions where charge neutrality is determined by $[\text{donor}'] = n$ and $2[V_{\text{O}}^{\bullet}] = n$.

As discussed previously [8], the electron mobility in the region with oxygen activities above that of the jump appears to be extremely small and highly thermally activated, with an activation energy of about 1.6 eV in SBN. We suggest that the jump results from a partial release from this restricted mobility and that this release occurs as the oxygen vacancy and electron

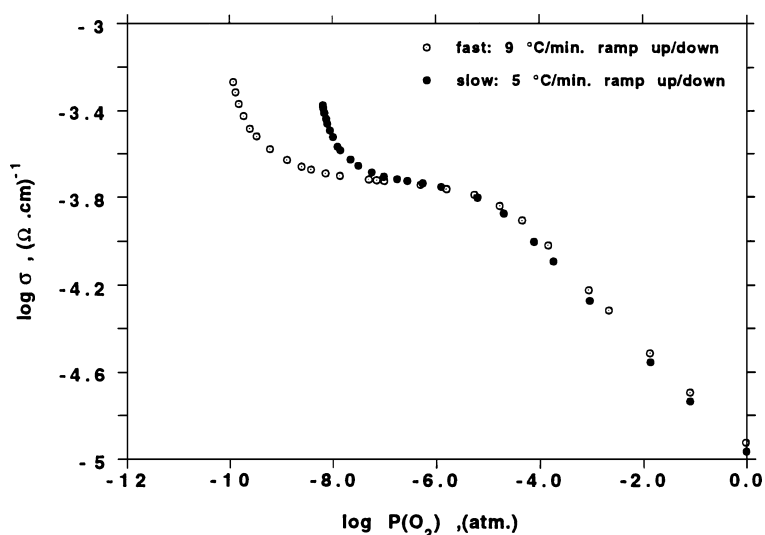


Fig. 8. The equilibrium electrical conductivities at 700°C of undoped SBN sintered with different heating and cooling rates.

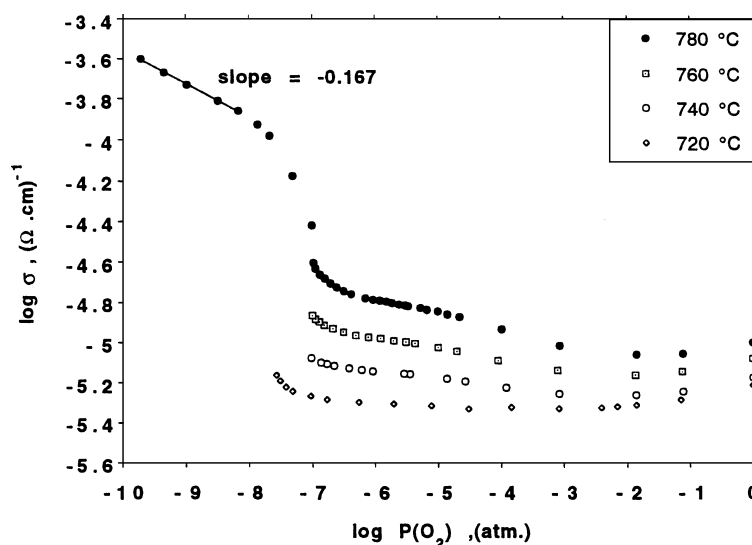


Fig. 9. The equilibrium electrical conductivity of 3% donor-doped SBT sintered with the slower heating and cooling rates. The log-log slope for oxygen activities below that of the sharp increase in conductivity is revealed to be $-1/6$.

concentrations rise above the donor level. A decrease in the activation energy of mobility from 1.6 to 1.4 eV at 1000 K would account for the approximate height of the jump. The full development of the jump is very slow, taking about 8 hours, and this suggests that there may be some atomic rearrangement that results in the change in electron mobility. However, this rearrange-

ment is insufficient to be detected by powder X-ray diffraction measurements made on quenched samples, and thus may be a highly localized effect. According to this model, the behavior of the *n*-type conductivity in SBN and donor-doped SBT is equivalent to that of any simple, donor-doped oxide with the exception of the change in the activation energy of mobility that results in the conductivity jump. This behavior is summarized schematically in Fig. 10 which depicts the oxygen activity dependence of the electron concentration, the electron mobility, and the resulting conductivity. Conductivity profiles similar to those reported here for SBN have also been observed in SrTiO₃, particularly when donor-doped. These reports have been summarized in our earlier paper on SBN [8].

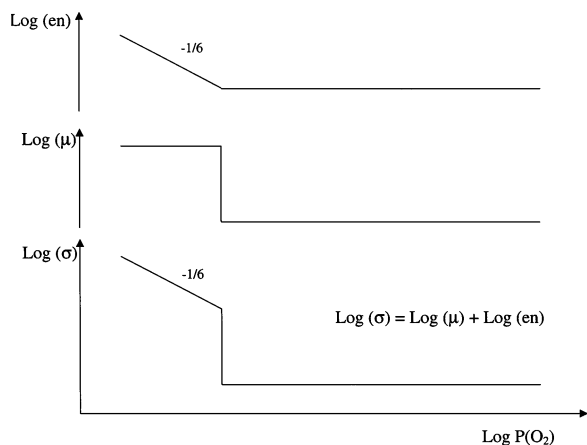


Fig. 10. Schematic representation of the contributions of the concentration of charge carriers, *n*, and the mobility, *μ*, to the *n*-type conductivity as a function of the oxygen activity. The electron concentration behaves like that of a “normal” donor-doped oxide, while the mobility undergoes a transition.

Summary

Undoped and acceptor-doped SBT, and SBN with more than 2% added acceptors, behave as normal highly acceptor-doped oxides, such as acceptor-doped ZrO₂ or CeO₂. The equilibrium conductivity is dominated by a broad plateau of ionic conductivity due to oxygen vacancies in the Bi layers. As the oxygen activity approaches 1 atm, there is an increasing *p*-type contribution due to partial filling of the vacancies. At the lowest oxygen activities, *n*-type conductivity begins to

increase with further reduction due to increasing oxygen loss.

Undoped and donor-doped SBN, and SBT with more than 2% added donors, behave as normal donor-doped oxides, such as donor-doped TiO₂ or Nb₂O₅, with *n*-type conduction that generally increases with reduction. As the oxygen activity decreases from 1 atm or above, the equilibrium conductivity is initially *p*-type and decreases to a shallow minimum. Below the minimum, the conductivity is *n*-type and initially increases. These two regions correspond to charge compensation of the donor centers by an ionic defect. The conductivity then levels out as electrons become the major charge-compensating species. Finally, the concentrations of oxygen and electrons due to reduction rise above the donor level, and the log-log slope changes to the familiar $-1/6$ characteristic of a change in the approximate condition of charge neutrality to $n = 2[V_{\text{O}}^{\bullet\bullet}]$. This behavior can be summarized in the form of the Kroger-Vink diagram for a generic donor-doped oxide [12]. The only exception to this normal behavior is the abrupt increase in the equilibrium conductivity at low oxygen activities. It is proposed that the electrons are deeply trapped and move with a hopping-like motion that is highly thermally activated. The jump in the conductivity is attributed to a small decrease in the activation energy of the electron mobility.

The behavior of both compounds is dominated by significant cation place exchange between Bi⁺³ and Sr⁺², with incomplete self-compensation. This leaves some fraction of the Bi_{Sr}[•] in the perovskite layers, and Sr_{Bi}[•] in the Bi layers, that must be locally compensated by lattice or electronic defects. The equilibrium con-

ductivity is then dominated by the more highly conducting layer.

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References

1. J.F. Scott and C.A. Paz de Araujo, *Science*, **246**, 1400 (1989).
2. O. Auciello, J.F. Scott, and R. Ramesh, *Physics Today*, **51**, 22 (1998).
3. W.L. Warren, B.A. Tuttle, and D. Dimos, *Appl. Phys. Lett.*, **67**, 1426 (1995).
4. W.Y. Pan, C.F. Yue, and B.A. Tuttle, *Ceram. Trans.*, **25**, 385 (1992).
5. B.M. Melnick, J. Gregory, and C.A. Paz de Araujo, *Integrated Ferroelectrics*, **11**, 145 (1995).
6. A.C. Palanduz and D.M. Smyth, *J. Euro. Ceram. Soc.*, **19**, 731 (1999).
7. A.C. Palanduz and D.M. Smyth, *J. Electroceram.*, **5**(1), 21 (2000).
8. A.C. Palanduz and D.M. Smyth, *J. Electroceram.*, **11**, 191 (2003).
9. A.D. Rae, J.G. Thompson, and R.L. Withers, *Acta Crystallogr., Sect. B*, **48**, 418 (1992).
10. S.M. Blake, M.J. Falconer, M. McCready, and P. Lightfoot, *J. Mater. Chem.*, **7**(8), 1609 (1997).
11. P.C. Eklund and A.K. Matabah, *Rev. Sci. Instrum.*, **48**, 775 (1977).
12. S. Cabuk and A. Mamedov, *J. Opt. A: Pure Appl. Opt.*, **1**, 424 (1999).
13. D.M. Smyth, *Prog. Solid St. Chem.*, **15**, 145 (1984).