

## Nonsuperconducting $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$ : The $5s$ -orbital analog of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$

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The  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$  perovskite solid solution exists for  $0.0 \leq x \leq 0.2$ . The best electrical conductivity occurs for  $x$  near 0.15, and is essentially temperature independent from 300 to 5 K. The materials, although conductive, do not become superconducting to temperatures as low as 0.05 K. We propose that the difference between metal  $5s$ -oxygen  $2p$  and metal  $6s$ -oxygen  $2p$  bonding in solids accounts for this behavior.

For the copper oxide based high-temperature superconductors, there are very few who argue that the microscopic pairing mechanism is conventional electron-phonon coupling. The same is not the case, however, for the small family of simple perovskites based on  $\text{BaBiO}_3$  and  $\text{BaPbO}_3$ . For these materials, with a maximum  $T_c$  of 30 K for  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ ,<sup>1,2</sup> there is still considerable disagreement as to whether they are "conventional" superconductors, or whether the special electronic characteristics of the constituent metal-oxygen bonds plays a critical role in the underlying superconducting mechanism.<sup>3-7</sup> The family also includes the superconductors  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$  ( $T_c = 12$  K) (Ref. 8) and  $\text{BaPb}_{0.75}\text{Sb}_{0.25}\text{O}_3$  ( $T_c = 3.5$  K),<sup>9</sup> all three members having very high  $T_c$ 's relative to their densities of electronic states at the Fermi level.<sup>10</sup> All involve metal-oxygen bonding based either solely on metal  $6s(\text{Bi,Pb})$ -oxygen  $2p$ , or metal  $6s$ - $5s(\text{Sb})$ -oxygen  $2p$  overlap.<sup>11</sup> In order to investigate further the importance of the metal-oxygen band for the occurrence of superconductivity in this class of materials, we have investigated the properties of the  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$  perovskite, in which the metal-oxygen bonding is solely of the  $5s$ - $2p$  type. The same tendencies for electronically driven charge disproportionation might be expected for Sn-Sb based perovskites as are present for Pb-Sb, Pb-Bi, or Bi-based perovskites. Surprisingly, we find that the  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$  perovskites, even though conducting, are not superconducting to temperatures as low as 0.05 K. The results suggest that subtle differences in the relative energies of the oxygen  $2p$  and metal valence orbitals in the solid are critical to the occurrence of superconductivity in this class of materials.

The  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$  perovskites were prepared from stoichiometric mixtures of  $\text{BaCO}_3$ ,  $\text{Sn}_2\text{O}_4$ , and  $\text{Sb}_2\text{O}_3$ , for  $x = 0-0.5$ , at intervals of  $\Delta x = 0.05$ . They were initially slowly heated to  $1200^\circ\text{C}$  in air as powders are fired for 16 h. After mechanical grinding, they were pressed into pellets ( $\frac{1}{2}$  inch diameter) which were then deeply buried (in dense  $\text{Al}_2\text{O}_3$  crucibles) in powder of their own composition to prevent volatilization for subsequent heatings. They were heated ( $600^\circ\text{C}/\text{h}$ ) to  $1450^\circ\text{C}$  and reacted for 60 h in air. An additional reaction at  $1550^\circ\text{C}$  in air for 8 h was found to yield the best quality materials. For  $x \neq 0$ , pellets and powders were very well sintered and were separable only with considerable effort. The separated pel-

lets were then treated under a variety of atmospheres at different temperatures to obtain the most conductive materials. A postreaction anneal at  $950^\circ\text{C}$  in flowing  $\text{N}_2$  for 16 h was found to yield the best results. Surfaces were ground and polished on all samples before final x-ray, magnetic, and resistivity studies, to insure bulk characterization.

We found that the perovskite solid solution  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$  only exists for  $0 \leq x \leq 0.20$ . This is a considerably smaller solubility range than is found for the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  ( $x_{\text{max}} = 1$ ) and  $\text{BaPb}_{1-x}\text{Sb}_x\text{O}_3$  ( $x_{\text{max}} = 0.45$ ) perovskites. The solubility limit was determined by the disappearing phase method, and the composition dependence of the cubic-lattice parameter, both by powder x-ray diffraction. This composition boundary is in good agreement with that found by others.<sup>12,13</sup> The cubic-cell parameter is shown in Fig. 1 for samples postannealed in either oxygen at  $550^\circ\text{C}$ , or nitrogen at  $950^\circ\text{C}$ . The parameter changes relatively little over the composition range, and, within the precision of the measurements, is independent of the conditions of the post anneal.

Figure 2 shows the resistivity of  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$  samples at room temperature. Resistivities were measured at 100 Hz on bar samples with four indium contacts. The resistivity is a strong function of both Sb content and the nature of the postanneal. Samples were weighed to a precision of one part in  $10^5$  before and after postannealing.

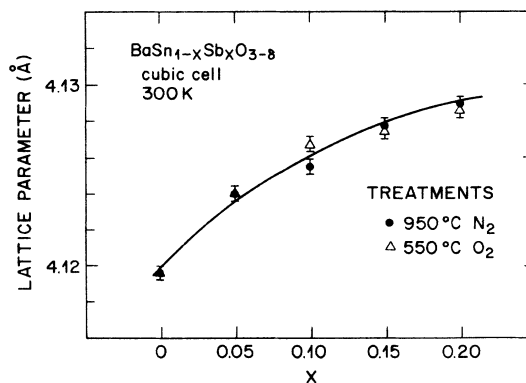


FIG. 1. Cubic unit-cell parameters for the  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$  perovskite solid solution, measured at 300 K.

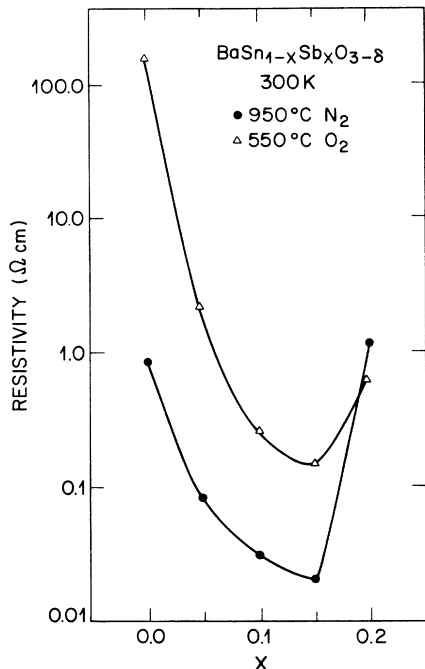


FIG. 2. Composition and postanneal dependence of the room-temperature resistivities of the  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_{3-\delta}$  perovskite solid solution.

The small weight changes observed indicated that the differences in oxygen stoichiometry for the two sets of samples were less than  $\delta=0.01$  in  $\text{Ba}(\text{Sn,Sb})\text{O}_{3-\delta}$ . There is, however, a significant decrease in the resistivity for the  $\text{N}_2$  annealed series, especially for the antimony free material. The resistivity decreases by a factor of 40 with increasing Sb content up to  $x=0.15$ . We did not observe extra peaks in powder-x-ray-diffraction patterns which might indicate the presence of extra phases or large-scale structural distortion in the composition region between  $x=0.15$  and 0.20, where the resistivity abruptly increases. This increase in resistivity is either an intrinsic property of the phase, as is suggested by the results shown in Fig. 1, or is due to the appearance of a very small amount of highly resistive material concentrated at the grain boundaries of the ceramic, not observable in the x-ray patterns.

The temperature dependencies of the resistivities from 300–4.2 K are shown in Fig. 3. For  $x=0-0.15$  the resistivities are virtually temperature independent. Only at  $x=0.2$  is semiconductinglike behavior observed. The resistivity versus temperature behavior of these materials is very similar to what is observed for high-quality ceramic samples of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ .<sup>14</sup> The resistivities in the present case are, however, several orders of magnitude larger than for the Pb-Bi analog.  $\text{BaPbO}_3$  is a semimetal with a resistivity (in polycrystalline form) of  $2 \times 10^{-4} \Omega \text{ cm}$ . Stoichiometric ceramic  $\text{BaSnO}_3$  appears to have a resistivity of  $10^2 \Omega \text{ cm}$ , and, when slightly reduced,  $1 \Omega \text{ cm}$ , making it  $10^4-10^6$  times more resistive than  $\text{BaPbO}_3$ . At  $x=0.15$  the resistivity of the  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_{3-\delta}$  ceramic is  $20 \text{ m} \Omega \text{ cm}$ , whereas that of the  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  ceramic is  $4 \text{ m} \Omega \text{ cm}$ . (The resistivity of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  ceramics increases with increasing  $x$  over the whole solid-

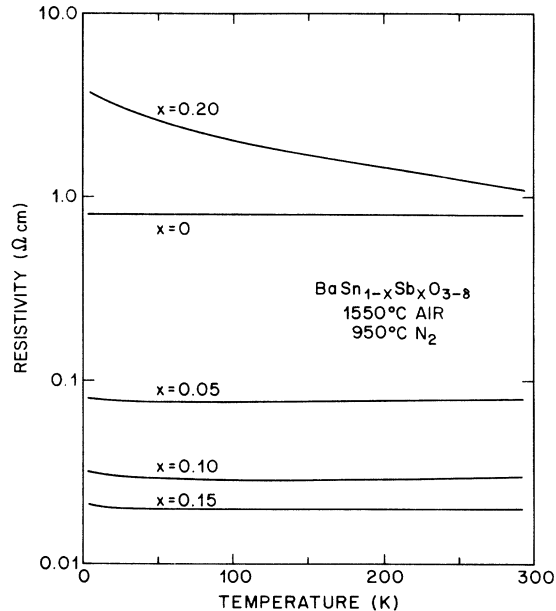


FIG. 3. Temperature-dependent resistivities of polycrystalline samples of  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$  from 300–4.2 K.

solution range). Superconducting  $\text{SrTiO}_{3-\delta}$ ,  $T_c \approx 0.3 \text{ K}$ , for comparison, has a metallic temperature dependent resistivity between 300 and 4.2 K, and a resistivity of approximately  $0.4 \text{ m} \Omega \text{ cm}$  at 4.2 K.<sup>15</sup>

The  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_{3-\delta}$  samples were tested for superconductivity magnetically. They were first tested in a dc field of 5 Oe down to 2 K in a superconducting quantum interference device (SQUID) magnetometer. They were then mounted in a dilution refrigerator and cooled to 0.05 K in a 1 kHz ac magnetic field of approximately 1 Oe. The sensitivity employed was approximately 1000 times greater than was necessary to observe the superconducting transition in a test sample of polycrystalline  $\text{BaPb}_{0.9}\text{Sb}_{0.1}\text{O}_3$ . No transitions were observed. Figure 4 shows our low-temperature data for  $\text{BaSn}_{0.85}\text{Sb}_{0.15}\text{O}_3$  compared to the results of our measurements for optimal ( $x=0.25$ ) and nonoptimal ( $x=0.15$ ) compositions of polycrystalline and single-crystal  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  and  $\text{BaPb}_{1-x}\text{Sb}_x\text{O}_3$ .

To understand why we might expect that the  $\text{Ba}(\text{Sn,Sb})\text{O}_3$  perovskite might be superconducting and the inferences that can be drawn from its failure to do so, we consider first the electronic similarities of the elements in question. The electronic configurations of Sn and Sb are  $[\text{Kr}]4d^{10}5s^2p^2$  and  $[\text{Kr}]4d^{10}5s^2p^3$ , and those of Pb and Bi are  $[\text{Xe}]4f^{14}5d^{10}6s^2p^2$  and  $[\text{Xe}]4f^{14}5d^{10}6s^2p^3$ . Thus the bonding orbitals are 5s for Sn and Sb and 6s for Pb and Bi. Estimates of the energies of those orbitals for both free atoms and atoms in solids are very similar<sup>16,17</sup> without relativistic effects, but relativistic local-density-approximation calculations reveal that the 5s levels are approximately 1.5 eV higher than their 6s counterparts.<sup>18</sup> Thus one might expect that the metal-oxygen covalency is not as good for the 5s as it is for the 6s based perovskites.

By considering the differences between  $\text{BaPbO}_3$  and  $\text{BaSnO}_3$  we can make a proposal as to what the critical weak or missing factor is that prevents the current materi-

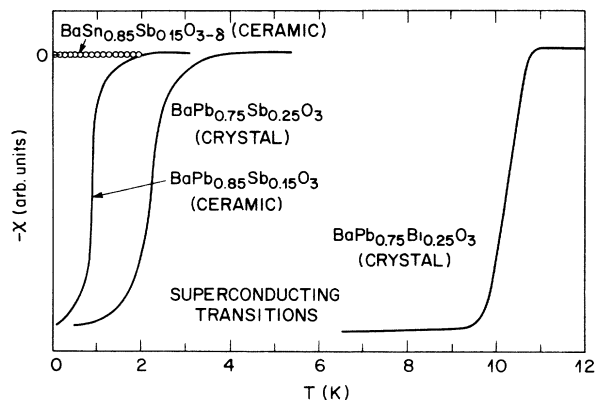


FIG. 4. Comparison of the superconducting transitions for  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ ,  $\text{BaPb}_{0.85}\text{Sb}_{0.15}\text{O}_3$ ,  $\text{BaPb}_{0.75}\text{Sb}_{0.25}\text{O}_3$ , and the susceptibility data for  $\text{BaSn}_{0.85}\text{Sb}_{0.15}\text{O}_3$  between 2 and 0.05 K.

als from becoming superconducting.  $\text{BaPbO}_3$  has a metallic resistivity due to an "accident" of the band structure. Like white insulating  $\text{BaSnO}_3$ , by electron count alone it would not be expected to be conductive. Conductivity arises because of the overlap of the narrow oxygen  $p_{\perp}$  band (from oxygen  $2p$  states perpendicular to the metal-oxygen bonds) with the broad antibonding  $sp_{\parallel}\sigma^*$  metal-oxygen band (from metal-oxygen states parallel to the metal-oxygen bond). When electrons are added to  $\text{BaPbO}_3$  by additions of Bi or Sb they go into the antibonding  $sp_{\parallel}\sigma^*$  band. The  $s$ - $p$   $\sigma^*$  band is approximately 16-eV wide in  $\text{Ba}(\text{Pb,Bi})\text{O}_3$  due to the closeness in energy of the Pb  $6s$  and O  $2p$  levels.<sup>11</sup> The bare energies of the  $5s$  orbitals, as seen in Table I, are significantly different from the  $6s$  orbitals. Therefore the primary difference in band structures between the  $5s$  and  $6s$  cases might be a smaller  $5s$ - $2p$  overlap, leading to a narrower  $sp\sigma^*$  band and a gap between this band and the oxygen  $p_{\perp}$  band.

$\text{BaSnO}_3$  is a white, poorly conducting material, indicating that a 1.5 eV difference in Sn and Pb bonding orbital energies has resulted in the fact that there is no longer any overlap of the  $sp_{\parallel}\sigma^*$  and  $p_{\perp}$  bands. The measured band gap is 3.4 eV, and is apparently independent of Sb concentration for  $\text{BaSn}_{1-x}\text{Sb}_x\text{O}_3$ .<sup>19</sup> Because the gap between the  $p_{\perp}$  and  $sp_{\parallel}\sigma^*$  bands is so wide, it is likely that the carriers that are introduced by Sb substitution never get into the  $\sigma^*$  band. The difference between the Sn and Sb orbital energies suggests that the carriers are found in a narrow impuritylike midgap band. Further, the minimum conductivity expected to result in a metallic temperature dependence, estimated based on an expectation of 0.15  $e/f.u.$  in  $\text{BaSn}_{0.85}\text{Sb}_{0.15}\text{O}_3$  and a scattering length of one

TABLE I. Relative Electronic Energies of Sn, Pb, Sb, and Bi.

Free-Atom Ionization Potentials (eV) <sup>a</sup>					
Atom	Ionization State				
	I	II	III	IV	V
Sn	7.3	14.6	30.5	40.7	
Pb	7.4	15.0	31.9	42.3	
Sb	8.6	16.5	25.3	44.2	56.0
Bi	7.3	16.7	25.6	45.3	56.0

Energies of $s$ and $p$ Orbitals (eV)		
Atom	$-E_s$	$-E_p$
Sn	10.77	3.73,4.19
Pb	12.19	3.32,4.81
Sb	13.03	4.81,5.44
Bi	14.61	4.27,6.20

<sup>a</sup>From Ref. 16.

lattice parameter, is approximately  $10^{-3} \Omega \text{ cm}$ , a factor of 20 larger than we observe. Because the temperature-dependent conductivity does not show the localization expected for such a situation, we suggest that most of the carriers are trapped, leading to a serious underestimation of their number from the Sb stoichiometry. Such trapping could, for instance, be due to microscopic  $\text{Sb}^{3+}$ - $\text{Sb}^{5+}$  or  $\text{Sn}^{2+}$ - $\text{Sn}^{4+}$  charge disproportion. The few carriers that are available for conductivity travel in a narrow impuritylike band and display a peculiar, nearly temperature independent  $\rho$ . Thus, we propose that carrier doping in  $\text{BaSnO}_3$  by Sb substitution never leads to the presence of carriers in the hybridized  $sp_{\parallel}\sigma^*$  band, even though it does lead to conductivity. It is the nearness of that band in energy to the  $p_{\perp}$  oxygen bands in the  $6s$  bonding systems that makes it accessible to doping.

The present results clearly point to the special situation in  $\text{Ba}(\text{Pb,Bi})\text{O}_3$  which leads to superconductivity and which is obviously rooted in the unique combination of metal and oxygen energy levels. The change from  $6s$  to  $5s$  metal states destroys the delicate balance. The same rationale holds true for the cuprate superconductors, as can be seen, e.g., by comparing  $(\text{La,Sr})_2\text{CuO}_4$  with  $(\text{La,Sr})_2\text{NiO}_4$ , where the slightly higher Ni  $3d$  energy levels apparently also change the properties profoundly.

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