JOURNAL OF SOLID STATE CHEMISTRY **98**, 181–186 (1992)

Tin and Antimony Valence States in $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$

M. G. SMITH, J. B. GOODENOUGH, AND A. MANTHIRAM

Center for Materials Science and Engineering, ETC 5.160, The University of Texas at Austin, Austin, Texas 78712-1084

R. D. TAYLOR

Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

AND WEIMIN PENG AND C. W. KIMBALL

Department of Physics, Northern Illinois University, De Kalb, Illinois 60115-2854

Received September 17, 1991; in revised form December 11, 1991

^{119}Sn and ^{121}Sb Mössbauer spectra indicate the presence of Sb^{5+} and $Sn^{(4-x)+}$ ions down to 1.2 K without evidence for disproportionation into Sn^{2+}, Sn^{4+} or Sb^{3+}, Sb^{5+}. It is argued that stabilization of Sb^{5+}, which means a lifting of the donor level above E_F, is accomplished by a static oxide-ion displacement from Sn toward Sb in a 180° Sn–O–Sb link. Placement of E_F within an enhanced density of states at the bottom of the Sn–5$s\,\sigma^*$ band eliminates optical excitations to the conduction band from an impurity band; it is suggested that this situation is a necessary condition for a transparent conductor like In_2O_3 : Sn. The model also permits rationalization of a low, temperature-independent conductivity.

1. Introduction

The observation (*1–4*) that the cubic perovskites $BaPb_{0.75}Sb_{0.25}O_3$, $BaPb_{0.75}Bi_{0.25}O_3$, and $K_{0.4}Ba_{0.6}Bi_{1-x}Sb_xO_3$ are superconductors (T_c = 3.5, 12 and (28 − 0.9x) K, respectively), whereas $BaSn_{1-x}Sb_xO_3$ is not (to 0.05 K), raises a fundamental question concerning the role of covalent bonding in the superconductive mechanism. Moreover, a temperature-independent conductivity in the range $0 \leq x \leq 0.15$ led Cava *et al.* (*4*) to speculate the presence of midgap states associated with the Sb atoms and the possibility of a disproportionation reaction creating Sb^{3+} + Sb^{5+} or Sn^{2+} + Sn^{4+} species. The Mössbauer study reported here was initially motivated by a desire to test the validity of this speculation.

We report ^{119}Sn and ^{121}Sb Mössbauer spectroscopy on $BaSn_{0.85}Sb_{0.15}O_3$, the composition with highest conductivity reported by Cava *et al.* (*4*). This technique directly probes the Sn and Sb valence states. The observation of a single resonance in both probes indicates that electrons are not trapped out via a disproportionation reaction on the time scale (10^{-8} sec) of a Möss-

0022-4596/92 $5.00

bauer experiment. Moreover, the isomer shift (IS) of the ^{121}Sb peak is close to that of Sb_2O_5, whereas that of the ^{119}Sn peak is shifted positive of its value in $BaSnO_3$, which indicates a transfer of electrons from Sb to Sn corresponding to the presence of only Sb^{5+} in this system. We compare this result with the IS found for ^{121}Sb in the superconductive perovskite phases and draw some tentative conclusions about the influence of oxide-ion displacements on the electronic energy levels.

2. Experimental

$BaSnO_3$ and $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ were prepared by solid-state reaction. Stoichiometric amounts of $BaCO_3$, SnO_2 and Sb_2O_3 were mixed in a mortar and pestle and fired at 1200°C for 16 hr. The resulting powders were reground and pressed into pellets. The $BaSnO_3$ sample was annealed in air at 1300°C for 43 hr and slowly cooled to room temperature. $BaSn_{0.85}Sb_{0.15}O_3$ was annealed in air at 1500°C for 65 hr with two intermediate grindings and pressing into pellets. Following Cava *et al.* (*4*), reduced $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ was prepared in flowing N_2 at 950°C for 12 hr with slow cooking to room temperature. The products were all single phase as found by X-ray powder diffraction recorded with Cu$K\alpha$ radiation. The lattice parameter of the white $BaSnO_3$ was a = 4.110(2) Å; those for $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ were 4.114(2) and 4.119(2) Å for the air-fired and N_2-annealed samples, respectively.

^{119}Sn Mössbauer spectroscopy was performed with a $Ca^{119m}SnO_3$ source over the temperature range $1.2 \leq T \leq 300$ K. The source and absorber were both cooled by exchange gas; the temperature was measured and controlled with an integrated thermometer-heater assembly. ^{121}Sb Mössbauer spectroscopy was also performed with a $Ca^{121m}SnO_3$ source. Both source and absorber were held at 78 K. Seebeck measurements were made on polycrystalline pellets with a home-built device in the temperature interval $20 \leq T \leq 320$ K.

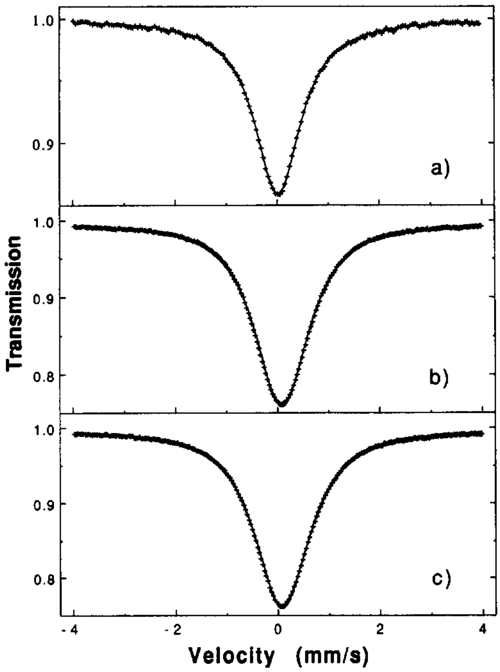

FIG. 1. Room-temperature ^{119}Sn Mössbauer spectra of (a) $BaSnO_3$, (b) $BaSn_{0.85}Sb_{0.15}O_3$, and (c) $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$.

3. Results

Room-temperature ^{119}Sn Mössbauer spectra are shown in Fig. 1; spectra recorded at lower temperatures were essentially identical to those of Fig. 1. The IS with respect to $CaSnO_3$ and the full-width-at-half-maximum linewidths (FWHM) for the single-resonance absorption are given in Table I for both room temperature and 1.2 K.

The 78 K ^{121}Sb Mössbauer spectra for the air- and N_2-annealed $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ samples are compared in Fig. 2 with those for Sb_2O_3 and Sb_2O_5. The fitted IS relative to ^{121}Sb in $CaSnO_3$ at 78 K, the quadrupole splittings ΔE_Q, and the FWHM linewidths are summarized in Table II.

TABLE 1

ISOMER SHIFTS (IS) AND FULL-WIDTH-AT-HALF-MAXIMUM LINEWIDTHS (FWHM) OF FITTED ^{119}Sn MÖSSBAUER SPECTRA OF $BaSnO_3$, $BaSn_{0.85}Sb_{0.15}O_{3-}$, AND $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ MEASURED AT 300 K (Fig. 1)

Sample	Temperature (K)	IS (mm/sec)	FWHM (mm/sec)
$BaSnO_3$	300	0.014(1)	1.10(1)
$BaSn_{0.85}Sb_{0.15}O_3$	300	0.086(1)	1.28(1)
$BaSn_{0.85}Sb_{0.15}O_{3-\delta}$	300	0.083(1)	1.29(1)
$BaSn_{0.85}Sb_{0.15}O_3$	1.2	0.086(2)	1.41(1)
$BaSn_{0.85}Sb_{0.15}O_{3-\delta}$	1.2	0.083(2)	1.30(1)

Note. Isomer shifts are with respect to $CaSnO_3$. The fitted parameters for the spectra of $BaSn_{0.85}Sb_{0.15}O_3$ and $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ recorded at 1.2 K are also given.

Figure 3 shows the temperature dependence of the Seebeck coefficient of the air- and N_2-annealed $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$; it is negative—consistent with *n*-type conduction—with a magnitude that increases nearly linearly with temperature, which is typical for itinerant electrons in a partially filled band. The Seebeck coefficient for undoped $BaSnO_3$ was 2×10^6 μV/K and temperature-independent in the interval $20 \leq T \leq 320$ K.

4. Discussion

The observation of a single absorption peak for both ^{119}Sn and ^{121}Sb eliminates the existence of any static disproportionation into Sn^{2+} and Sn^{4+} or Sb^{3+} and Sb^{5+}. Although the IS for the ^{121}Sb peak is slightly negative of its value for Sb_2O_5, it lies well within the range of values for Sb^{5+} in other oxides (*5*). It would appear that the antimony is essentially present as Sb^{5+} in $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$. This observation has two immediate consequences: first, there are no Sb^{3+} ions present even in the time scale $\tau < 10^{-8}$ sec; second, the electrons transferred from the antimony must manifest themselves in a positive shift of the ^{119}Sn peak from its value in $BaSnO_3$. From Table I, this prediction is seen to be fulfilled. In fact, the magnitude of the IS is consistent with the mean tin valence $Sn^{3.82+}$ predicted for $x = 0.15$ and Sb^{5+} ions.

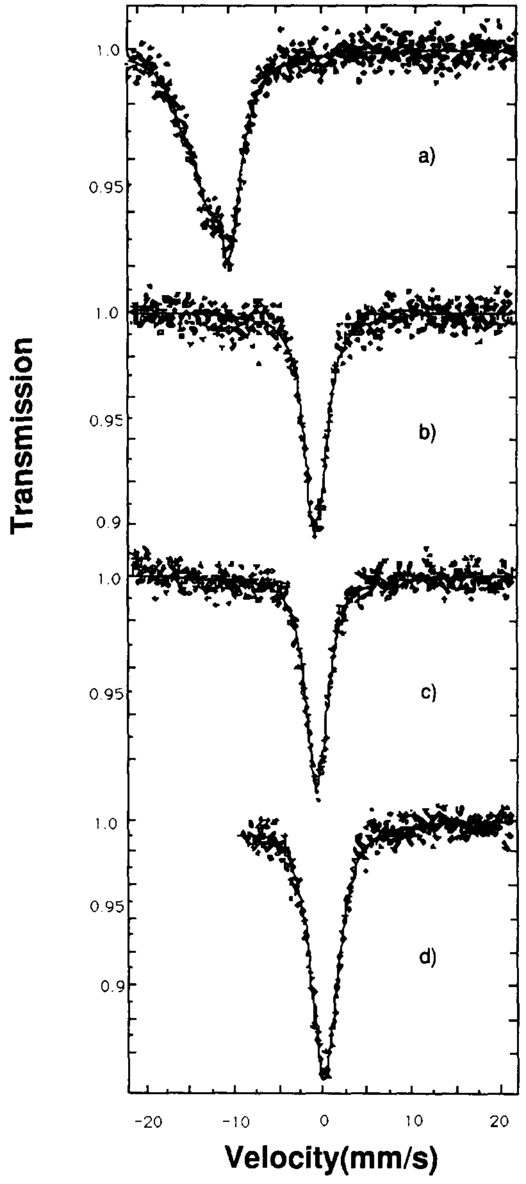

FIG. 2. ^{121}Sb Mössbauer spectra recorded at 78 K of (a) Sb_2O_3, (b) $BaSn_{0.85}Sb_{0.15}O_3$, (c) $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$, and (d) Sb_2O_5.

In a situation where 180° *M*–O–Sb bonds are formed, the transfer of electronic charge from Sb^{4+} to an M^{4+} ion would be accom-

TABLE II

ISOMER SHIFTS (IS), QUADRUPOLE SPLITTINGS (ΔE_Q), AND FULL-WIDTH-AT-HALF-MAXIMUM LINEWIDTHS (FWHM) OF FITTED ^{121}Sb MÖSSBAUER SPECTRA OF Sb_2O_3, Sb_2O_5, $BaSn_{0.85}Sb_{0.15}O_3$, AND $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ MEASURED AT 78 K (Fig. 2)

Sample	IS (mm/sec)	ΔE_Q (mm/sec)	FWHM (mm/sec)
Sb_2O_3	−11.48(5)	18.7(1)	2.9(1)[a]
Sb_2O_5	0.18(5)	−5.52(4)	2.3(1)
$BaSn_{0.85}Sb_{0.15}O_3$	−0.76(5)	−2.89(4)	2.52(6)
$BaSn_{0.85}Sb_{0.15}O_{3-\delta}$	−0.72(5)	−2.96(4)	2.67(6)

Note. Isomer shifts are with respect to ^{121}Sb in $CaSnO_3$ at 78 K.
[a] Thick absorber.

plished by a displacement of the bridging oxygen atoms toward the Sb and away from the *M* atom. Shortening of the Sb–O bonds would raise the antibonding σ^* orbitals of Sb-5*s* parentage; lengthening of the *M*–O bond lowers the corresponding antibonding σ^* orbitals on the *M* atoms. The *M* atom neighboring an Sb^{5+} ion is therefore expected to carry a somewhat higher electron density than an *M* atom having no Sb^{5+} near neighbor, which could account for the somewhat larger FWHM linewidth of the ^{119}Sn resonance in $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ relative to $BaSnO_3$.

The problem faced by Cava *et al.* (*4*) that induced them to propose the existence of midgap states in $BaSn_{1-x}Sb_xO_3$, $0 \leq x \leq 0.2$, was a relatively low and temperature-independent conductivity that is a maximum near $x = 0.15$ and increases with an N_2-anneal, i.e., with the introduction of oxygen vacancies. To address this problem, we construct the semi-empirical energy-density of states versus energy diagrams of Fig. 4.

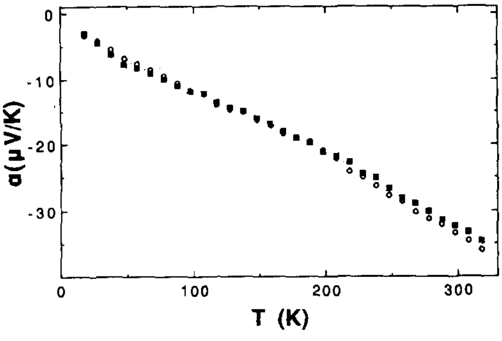

FIG. 3. Seebeck data for $BaSn_{0.85}Sb_{0.15}O_3$ (■) and $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ (○).

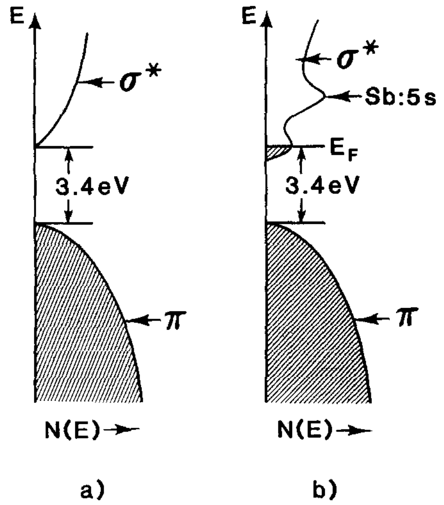

FIG. 4. Schematic energy density of states *N*(*E*) against *E* for (a) $BaSnO_3$ and (b) $BaSn_{0.85}Sb_{0.15}O_3$.

An empirical energy gap of 3.4 eV in $BaSnO_3$ does not shift on substitution of Sb for Sn (*6*). In $BaSnO_3$, the conduction band is an antibonding σ^* band of Sn-5*s* parentage, but with a strong covalent component of O-2*s* and $2p_\sigma$ and a weaker Ba-6*s* admixture; the valence band is a bonding π band of O-$2p_\pi$ parentage with a strong covalent admixture of Sn-$4p_\pi$ and Ba-6*s* and $6p_\sigma$. White $BaSnO_3$ may be doped *n*-type. Antimony is to the right of tin in the periodic table; therefore, substitution of Sb for Sn might be expected to yield a shallow donor state below the conduction-band edge analogous to the substitution of P for Si to dope semiconducting silicon *n*-type. However, such an analogy fails to take into consideration the freedom of the bridging oxygen to adjust the Sn–O and Sb–O bond lengths of a 180° Sn–O–Sb link. The Mössbauer data show that the donor electrons are not trapped at the Sb positions, but are transferred to the Sn atoms even at 1.2 K. Oxygen displacements and polarization toward the Sb atoms that lift the Sb-5*s* donor states above the Fermi energy E_F would also lower the bottom of the σ^* band. This situation places E_F close to the energy E_c of the bottom of the σ^* band in $BaSnO_3$, so Sb doping introduces little change in the energy to excite an electron from the valence π band to the conduction σ^* band, see Fig. 4. More importantly, electrons are located in σ^*-band states, not impurity-band states, which changes the selection rules for optical absorption. We suggest that this may be a condition to be satisfied in transparent conductors such as $In_2O_3:Sn$. $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ is bluish-black and is not a transparent conductor due to the high concentration of Sb; however, smaller levels of Sb doping may make this compound a transparent conductor.

Such a model remains consistent with a mean-free-path of the conduction electron that is determined by the distance between impurity atoms, which are in high concentration. Therefore the mean-free-time τ_s between scattering events would be short and temperature-independent, which would make the electron mobility $\mu = e\tau_s/m^*$ low and temperature-independent. Since the concentration n of mobile charge carriers in the σ^* band is also temperature-independent, it follows that the conductivity $\sigma = ne\mu$ may be low and temperature-independent.

5. Conclusions

Single Mössbauer ^{119}Sn and ^{121}Sb peaks in the compositions $BaSn_{0.85}Sb_{0.15}O_{3-\delta}$ indicate that there is no disproportionation into Sn^{2+} and Sn^{4+} or Sb^{3+} and Sb^{5+} species as had been suggested by Cava *et al.* (*4*) to account for the unusual resistivities they found in the system $BaSn_{1-x}Sb_xO_{3-\delta}$. The IS data indicate a transfer of electronic charge density from Sb^{4+} to Sn^{4+}, so that the dopant atoms are not present as shallow donor centers but as Sb^{5+} species down to 1.2 K. The IS data and the FWHM linewidths for the ^{119}Sn atoms are consistent with a transfer of electron density to the Sn system, but with the Sn atoms neighboring Sb atoms perhaps having a slightly higher electron density.

We argue that local oxygen displacements away from Sn toward Sb neighbors in a 180° Sn–O–Sb bridge make possible the raising of the Sb-5*s* donor states above E_F where they overlap and hybridize with the σ^* band. Placement of E_F within the σ^* band changes the optical-absorption selection rules so as to allow for transparent conductivity at low dopant concentrations; it also gives rise to a low, temperature-independent conductivity.

Acknowledgments

We thank J. Chan for performing the Seebeck measurements. We thank the R. A. Welch Foundation, Houston, Texas, and the National Science Foundation for financial support. One of us (M.G.S.) thanks Los Alamos National Laboratory for financial assistance under the INCOR program, and C.W.K thanks the National Science Foundation under DMR87-19738.

References

1. A. W. Sleight, J. L. Gillson, and P. E. Bierstedt, *Solid State Commun.* **17,** 27 (1975).
2. R. J. Cava, B. Batlogg, G. P. Espinosa, A. P. Ramirez, J. J. Krajewski, W. F. Peck, Jr., L. W. Rupp, Jr., and A. S. Cooper, *Nature* **339,** 291 (1989).
3. B. Dabrowski, D. R. Richards, D. G. Hinks, R. H. Hannon, H. Lee, V. J. Melim, W. Peng, and C. W. Kimball, *Physica C* **162–164,** 91 (1989).

4. R. J. Cava, P. Gammel, B. Batlogg, J. J. Krajewski, W. F. Peck, Jr., L. W. Rupp, Jr., R. Felder, and R. B. van Dover, *Phys. Rev. B* **42,** 4815 (1990).
5. N. N. Greenwood, and T. C. Gibb, "Mössbauer Spectroscopy," pp. 441–452, Chapman and Hall, London (1971).
6. G. Larramona, C. Gutierrez, I. Pereira, M. R. Nunes, and F. M. A. da Costa, *J. Chem. Soc. Faraday Trans.* **85,** 907 (1989).