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Electrical properties of $BaSnO_3$ in substitution of antimony for tin and lanthanum for barium

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Polycrystalline materials of $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$ were prepared. Substitutional solubilities of antimony for tin and lanthanum for barium, respectively, in $BaSnO_3$ were obtained to be $x=0.18$ for $BaSn_{1-x}Sb_xO_{3-\delta}$ and $y < 0.052$ for $Ba_{1-y}La_ySnO_{3-\delta}$. The X-ray photoemission spectroscopy measurements showed the valence of antimony and tin is mixed in our samples of $BaSn_{1-x}Sb_xO_{3-\delta}$. At lower temperature, magnetic susceptibilities of $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$ satisfy the Curie law, indicating the existence of non-interacting localized electrons at the Sn^{4+} site, and forming a $Sn^{4+}+e^-$ state in these systems. By substitution of antimony and lanthanum in $BaSnO_3$, the conductive properties are semiconductor-like. To explain this conductive behaviour, three types of mechanism were taken into consideration.

1. Introduction

$BaSnO_3$ is an insulator [1] ($\rho > 10^8 \Omega$ cm [2]) with a cubic perovskite structure. In this compound, Ba^{2+} ions are at the corners of this cubic cell and Sn^{4+} ions are coordinated octahedrally by six oxygen anions, making a 5s–2p type metal-oxygen bonding. It has been pointed out [3] that the conduction band in $BaSnO_3$ is an antibonding σ^* band of Sn–5s parentage, and the valence band is bonding π band of O–2pπ parentage. Singh *et al.* [4] calculated the energy band structure of $BaSnO_3$ by using an extension of the general linearized augmented-plane-wave method. The result shows that the bottom of the conduction band in $BaSnO_3$ is at Γ point and the top of the valance band is at R point with an indirect band gap of 0.79 eV, whereas the band gap measured by the experiment is 3.4 eV [5].

Since materials of $BaPb_{0.75}Bi_{0.25}O_3$ and $BaPb_{0.75}Sb_{0.25}O_3$ are superconductors with a metal–oxygen bonding of 6s–2p and 6s(5s)–2p respectively, Cava *et al.* [6] have investigated the conductive properties of the $BaSn_{1-x}Sb_xO_{3-\delta}$ perovskites, in which the metal–oxygen bonding is solely of the 5s–2p type. However, they failed to find superconductivity in this system even though the temperature was down to 0.05 K. Otherwise, it has also been reported in their work that the solubility of antimony in $BaSn_{1-x}Sb_xO_{3-\delta}$ is less than 0.2, and in the middle of the solubility range the resistivities are essentially temperature independent from 5 to 300 K. To explain the behaviour of resistivities with temperature, Cava *et al.* speculated that the carriers were present in narrow impurity-like midgap states associated with the antimony atoms, whereas another research group [3] suggested that the Sb–5s donor state could be lifted above the Fermi level and located in the conduction band by considering the oxygen displacement and polarization toward the antimony in Sn–O–Sb link.

Otherwise, the conductive property of substitution of lanthanum in $SrSnO_3$ was studied by Shimizu *et al.* [7]. They have reported that there are two valent states of tin in $Sr_{1-y}La_ySnO_{3-\delta}$, and the increase of the electrical conductivity in this system is due to electron transfer between these different valent states of tin.

In this work, we report the results on lattice parameter, d.c. resistivity, magnetic susceptibility and X-ray photoemission spectroscopy (XPS) for $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$, and discuss the possible mechanisms which affect the conduction in these systems.

2. Experimental procedure

Samples of $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$ were synthesized with appropriate amounts of $BaCO_3$(99.9%), SnO_2(99.99%), Sb_2O_3(99.99%) and La_2O_3(99.99%) from $x = 0$ to 0.3 and $y = 0$ to 0.08, respectively. The powders were thoroughly mixed in an agate mortar and fired in air at 1000 °C for 12 h in a pure Al_2O_3 crucible. The products were pulverized, pressed into pellets of 10 mm in diameter. Samples of $BaSn_{1-x}Sb_xO_{3-\delta}$ were sintered in flowing N_2 gas at 1300 °C for 12 h on a pure Al_2O_3 boat, then slowly cooled down to room temperature. Samples of $Ba_{1-y}La_ySnO_{3-\delta}$ were sintered in air at 1580 °C for 16 h in a platinum crucible and quenched to room temperature in a few minutes. A sample of $BaSnO_3$ was sintered at 1250 °C for 12 h in air. Surfaces of all sintered samples were polished before experiments.

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All samples were examined by the powder X-ray diffraction analysis (XRD) using the monochromatized CuK_α radiation with a Rigaku diffractometer. Lattice parameters of these samples were refined from the d-spacings measurement. In order to get the correct values of the lattice parameter, silicon powder (99.99%) was used as an internal standard.

The composition of the samples was determined by the inductive coupled plasma (ICP, Seiko model SPS 1500) for $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$ which were recognized as single phases by the powder XRD method.

Resistivity measurements (d.c.) were performed by the standard four-probe technique on the single-phase samples from 10 K to room temperature. The samples cut from the pellets, which had rectangular cross sections ($3 \times 3 \times 8\ mm^3$), were connected to four silver probes by indium. The measuring current was chosen to be 100 μA.

The magnetic susceptibility was measured for some samples by the Quantum Design MPMS-2 SQUID magnetometer from temperatures of 5 to 300 K under a magnetic field of 1 tesla. Electron binding energies of antimony and tin in $BaSn_{1-x}Sb_xO_{3-\delta}$ were measured by the XPS (Shimadzu ESCA-850) at room temperature and the binding energies were corrected by the peak of Au $4f_{7/2}$.

3. Results and discussion

The variation of lattice parameters for $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$ is shown in Fig. 1, in which solid lines mean the single phase and dash lines the multiphase. The lattice parameter of $BaSnO_3$ ($x = y = 0$) is $\alpha = 0.41165 \pm 0.00002$ nm, confirmed to agree with the literature data $\alpha = 0.41163$ nm [8] within the error of our lattice parameter calculation. With substitution of antimony for tin, the lattice parameter of $BaSn_{1-x}Sb_xO_{3-\delta}$ increases nonlinearly from $x = 0$ to 0.18, then is constant above $x = 0.18$. In addition, the powder XRD pattern shows a coexistence of $BaSb_2O_6$ and other known phases for $x = 0.25$. Therefore, it is considered that $x = 0.18$ is a solubility limit in our samples. The lattice parameter of $Ba_{1-y}La_ySnO_{3-\delta}$ shows a linear increase from $y = 0$ to 0.052, however, diffraction peaks of BaO appear in the XRD pattern for $y = 0.052$, indicating the solubility of lanthanum in $Ba_{1-y}La_ySnO_{3-\delta}$ is less than 0.052 in our samples.

Electron binding energies of antimony and tin in $BaSn_{1-x}Sb_xO_{3-\delta}$ are summarized in Tables I and II, respectively. Table I shows the binding energies of Sb $3d_{3/2}$. Because the peaks of the spectrum of Sb $3d_{5/2}$ and O 1s overlap in this system, only the binding energies of Sb $3d_{3/2}$ for $BaSn_{0.927}Sb_{0.073}O_{3-\delta}$ and $BaSn_{0.82}Sb_{0.18}O_{3-\delta}$ are shown in the table, compared with those for Sb_2O_3 and Sb_2O_5 in which antimony is solely trivalent or pentavalent, respectively. The shift of the binding energies for Sb $3d_{3/2}$ in $BaSn_{1-x}Sb_xO_{3-\delta}$ indicates the valence of antimony is mixed in our samples. As reported earlier [9], it seems impossible for antimony to disproportionate into a trivalent state and a pentavalent one in a 6-coordination site of the perovskite structure. Therefore, the valence state of antimony in $BaSn_{1-x}Sb_xO_{3-\delta}$ is probably a mixture of Sb^{5+} and $Sb^{5+} + e^-$. Table II shows the binding energies of Sn $3d_{3/2}$. The peaks of Sn $3d_{3/2}$ shift to lower energy with increasing of the antimony composition, indicating a mixed valence state of tin in $BaSn_{1-x}Sb_xO_{3-\delta}$.

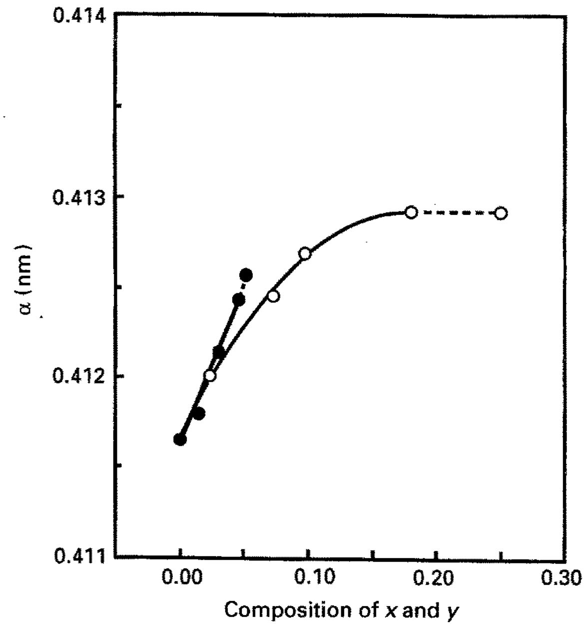

Figure 1 Cubic lattice parameters for $BaSn_{1-x}Sb_xO_{3-\delta}$ (○) and $Ba_{1-y}La_ySnO_{3-\delta}$ (●) measured at room temperature. Lines are guides to the eye, solid lines indicate the single phase; dashed lines indicate the multiphase.

TABLE I Binding energies of Sb $3d_{3/2}$ core level and the valence of Sb

Material	Sb $3d_{3/2}$(eV)	Valence
Sb_2O_5	540.30	+5
$BaSn_{0.927}Sb_{0.073}O_{3-\delta}$	540.05	mixed
$BaSn_{0.820}Sb_{0.180}O_{3-\delta}$	539.95	mixed
Sb_2O_3	539.90	+3

Table II Binding energies of Sn $3d_{3/2}$ core level and the valence of Sn

Material	Sn $3d_{3/2}$(eV)	Valence
$BaSnO_3$	495.15	+4
$BaSn_{0.927}Sb_{0.073}O_{3-\delta}$	494.85	mixed
$BaSn_{0.820}Sb_{0.180}O_{3-\delta}$	494.45	mixed

It has been reported [6] that the lattice parameter of $BaSn_{1-x}Sb_xO_{3-\delta}$ is independent of the oxygen vacancy in the samples over the composition range. Thus, the variation of the lattice parameter is mainly due to the valence change through the substitution. In $BaSn_{1-x}Sb_xO_{3-\delta}$, as discussed above, the valence of antimony and tin is all mixed. The nonlinear variation of the lattice parameter is probably due to the complicated valence change of antimony and tin in the composition range. The linear increase of the lattice parameter for $Ba_{1-y}La_ySnO_{3-\delta}$ from $y = 0$ to 0.046

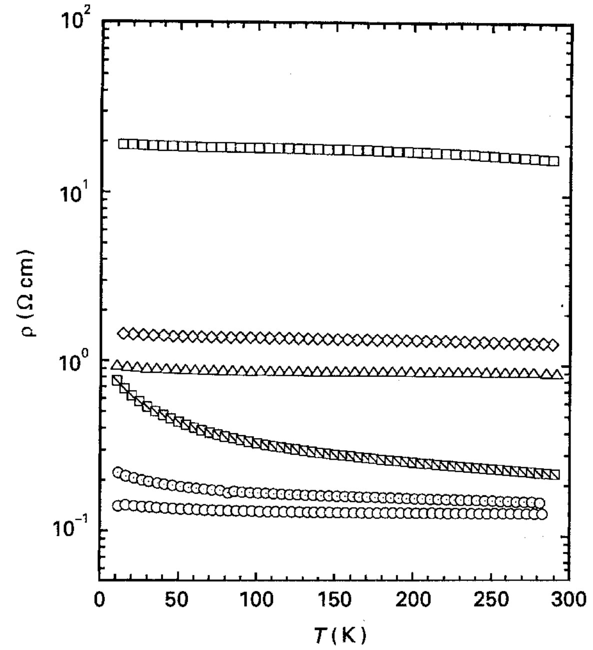

Figure 2 Temperature dependence of resistivities for $BaSn_{1-x}Sb_xO_{3-\delta}$. □, $x = 0.010$; ◇, $x = 0.024$; △, $x = 0.030$; ▧, $x = 0.180$; ⊙, $x = 0.097$; ○, $x = 0.073$.

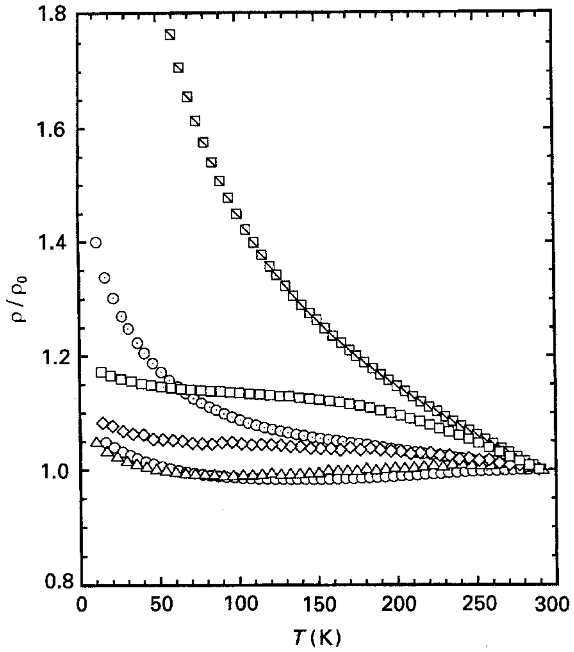

Figure 3 Temperature dependence of relative resistivities for $BaSn_{1-x}Sb_xO_{3-\delta}$. ρ_0 indicates the resistivity at room temperature. □, $x = 0.010$; ◇, $x = 0.024$; △, $x = 0.030$; ▧, $x = 0.180$; ⊙, $x = 0.097$; ○, $x = 0.073$.

may indicate the valence change of tin because the ionic radii of La^{3+} (0.136 nm) is smaller than Ba^{2+} (0.161 nm) [10]. The lattice parameter above $y = 0.046$ is probably a result of the vacancy [] at the Ba sites, since a part of Ba^{2+} ions get out from $Ba_{1-y}La_ySnO_{3-\delta}$ to form a two-phase mixture $(Ba_{1-y-z}La_y[]_z)SnO_{3-\delta} + zBaO$.

Resistivities (d.c.) of $BaSn_{1-x}Sb_xO_{3-\delta}$ are plotted in Fig. 2 from 10 K to room temperature. The behaviour of resistivity versus temperature in our samples is similar to what has been got by a.c. resistivity measurements [6], in which the resistivities are vitually temperature independent except the sample for $x = 0.2$. Fig. 3 shows the temperature dependence of relative resistivities for $BaSn_{1-x}Sb_xO_{3-\delta}$. From $x = 0.01$ to 0.024, a negative temperature dependence was observed. At $x = 0.03$ and 0.073, a change from metal-like behaviour to semiconductor-like one is apparent near 100 K and 150 K, respectively. Above $x = 0.097$ the semiconductor-like behaviour is obvious. No semiconductor–metal transition was observed with the composition of antimony above $x = 0.073$. It was considered [5, 11] that the conductive electrons are donated by the antimony. In addition, the resistivity of $BaSn_{1-x}Sb_xO_{3-\delta}$ is semiconductor-like and the band gap is 3.4 eV which does not shift with the composition of x [5]. Therefore, the conductivity is probably related to the following aspects. One is the oxygen vacancy. The oxygen vacancy can be considered to be one type of donor state since each oxygen vacancy is connected with two residual electrons. It was observed [6] that the oxygen vacancy considerably influences the resistivity in this system, in which the resistivity of $BaSnO_3$ annealed in N_2 is only 1% of that annealed in O_2. The second is the excitation of electrons to the conduction band. The antimony atoms in $BaSn_{1-x}Sb_xO_{3-\delta}$ give up four of their five electrons of the outer shell to the lattice bonds, while the fifth electron which is only loosely bound, as discussed above, forming a $Sb^{5+} + e^-$ state. It was claimed [12] that this electron can be excited thermally to the conduction band because the binding energy of this electron is weak (less than 0.03 eV in SnO_2). This means it is easy for this electron to be in a delocalized state. The third one is the hopping of electrons. The XPS measurements showed the valence of tin is mixed in our samples. It was considered [3] that the change of the valence for tin is related to the transfer of electrons from antimony to tin. As mentioned before, the conduction band in this system is an antibonding σ^* band of Sn 5s parentage. If the energy of these electrons is located at the bottom of the conduction band the hopping of the electrons between tin atoms would be possible. At present, there is no further evidence to prove which mechanism is more important in this system.

Resistivities and relative resistivities of $Ba_{1-y}La_ySnO_{3-\delta}$ from $y = 0.015$ to 0.046 are shown in Fig. 4(a) and (b), respectively. The behaviour of the resistivities, similar to that of $BaSn_{1-x}Sb_xO_{3-\delta}$, is nearly temperature independent and the variation of their values is less than 10% for all samples between 10 K and room temperature. The Hall coefficients on $Ba_{1-y}La_ySnO_{3-\delta}$ for $y = 0.03$ and 0.046 have been measured at room temperature and the sign is negative, indicating the conductive carriers are electrons in this system. No significant decrease of the resistivity was observed as with that of $BaSn_{1-x}Sb_xO_{3-\delta}$. In $Ba_{1-y}La_ySnO_{3-\delta}$, the oxygen vacancy is probably also present, since the ABO_3 perovskite oxide can lose oxygen easily [2]. Otherwise, the substitution of lanthanum for barium results in the valence change of tin, indicating the

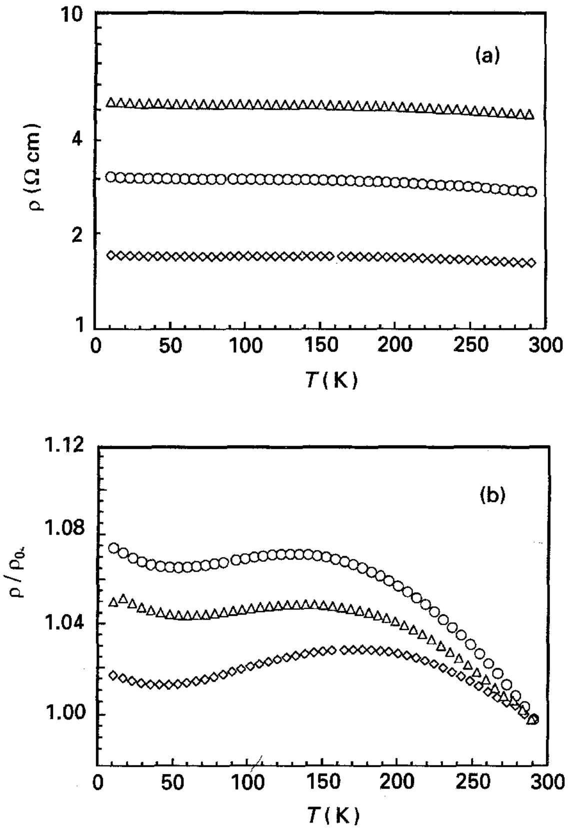

Figure 4 (a) Temperature dependence of resistivities for $Ba_{1-y}La_ySnO_{3-\delta}$. (b) Temperature dependence of relative resistivities for $Ba_{1-y}La_ySnO_{3-\delta}$. ρ_0 indicates the resistivity at room temperature. △, $y = 0.015$; ○, $y = 0.046$; ◇, $v = 0.030$.

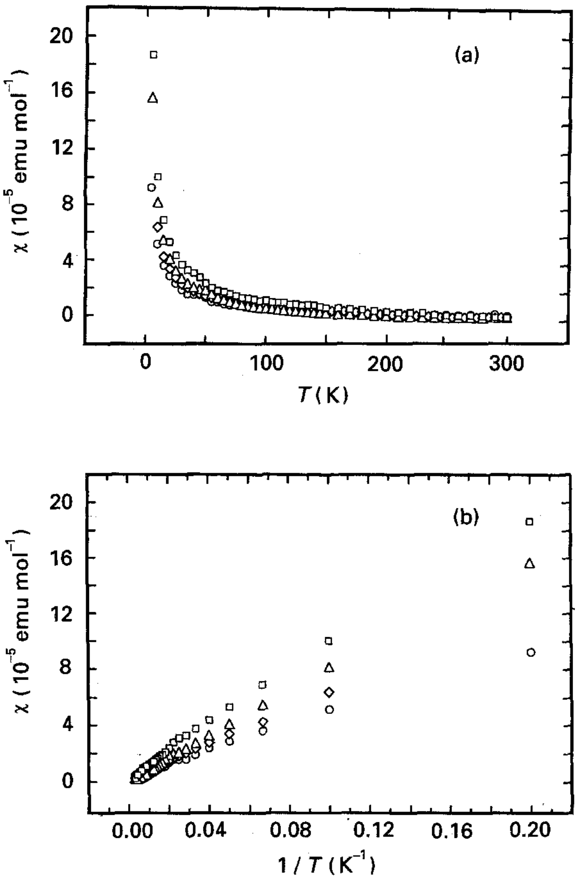

Figure 5 (a) Temperature dependence of magnetic susceptibilities for $BaSn_{1-x}Sb_xO_{3-\delta}$ with $x = 0.01$, 0.073 and 0.18 and $Ba_{1-y}La_ySnO_{3-\delta}$ with $y = 0.046$. (b) Reciprocal temperature dependence of magnetic susceptibilities for $BaSn_{1-x}Sb_xO_{3-\delta}$ with $x = 0.01$, 0.073 and 0.18, and $Ba_{1-y}La_ySnO_{3-\delta}$ with $y = 0.046$. ○, $BaSn_{0.820}Sb_{0.180}O_{3-\delta}$ ◇, $BaSn_{0.927}Sb_{0.073}O_{3-\delta}$; △, $BaSn_{0.990}Sb_{0.010}O_{3-\delta}$; □, $Ba_{0.954}La_{0.046}SnO_{3-\delta}$.

TABLE III Curie constant of $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$

Material	$C(10^{-4}$e.m.u. K mol$^{-1})$	Temperature region (K)
$Ba_{0.954}La_{0.046}SnO_{3-\delta}$	9.53	< 300
$BaSn_{0.990}Sb_{0.010}O_{3-\delta}$	8.04	< 220
$BaSn_{0.927}Sb_{0.073}O_{3-\delta}$	6.44	< 250
$BaSn_{0.820}Sb_{0.180}O_{3-\delta}$	4.69	< 220

transfer of electrons from lanthanum to tin. If the energy of the transferred electrons is situated below the mobility edge of the conduction band, hopping of the electrons is possible. The above two mechanisms (oxygen vacancy and hopping of electrons) probably play an important role in this system.

Fig. 5(a) shows magnetic susceptibilities of $BaSn_{1-x}Sb_xO_{3-\delta}$ for $x = 0.01$, 0.073 and 0.18, and $Ba_{1-y}La_ySnO_{3-\delta}$ for $y = 0.046$. The data shown in the figure were corrected by subtracting the orbital diamagnetism of relevant ions from measured values. At lower temperatures, it was found that the magnetic susceptibilities satisfy the Curie Law

$$\chi = C/T \qquad (1)$$

where C is the Curie constant. To illustrate the agreement between the data and the Curie Law, the magnetic susceptibilities were replotted against reciprocal temperature in Fig. 5(b). The graphs of all samples are straight lines at low temperature, indicating there are non-interacting localized electrons in $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$. The calculated Curie constants and the temperature region, in which the Curie Law is satisfied, are listed in Table III. In the table, the Curie constant increases with the composition of tin in $BaSn_{1-x}Sb_xO_{3-\delta}$ and has a maximum in an antimony-free material $Ba_{0.954}La_{0.046}SnO_{3-\delta}$. This fact indicates the electrons, transferred from antimony or lanthanum, are localized at the Sn^{4+} site, forming a $Sn^{4+} + e^-$ state in $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$. Unfortunately, there is no further evidence to illustrate whether these non-interacting localized electrons are the conductive electrons.

Fig. 6 shows the composition dependence of the room-temperature resistivity ρ_0 in $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$. With substitution of antimony for tin, the resistivity drops obviously from $x = 0.01$ to 0.073, then increases slowly above $x = 0.073$. At $x = 0.073$, the resistivity has a minimum. The variation of the resistivity with x is very similar to that of $SrPb_{1-x}Sb_xO_{3-\delta}$ and $SrPb_{1-x}Bi_xO_{3-\delta}$ [9], in which the resistivities have minima at $x = 0.075$ and 0.05, respectively. The resistivity curve of $Ba_{1-y}La_ySnO_{3-\delta}$ in the figure shows the same tendency as that of $BaSn_{1-x}Sb_xO_{3-\delta}$, however, the values of the resistivity in its composition range are not influenced

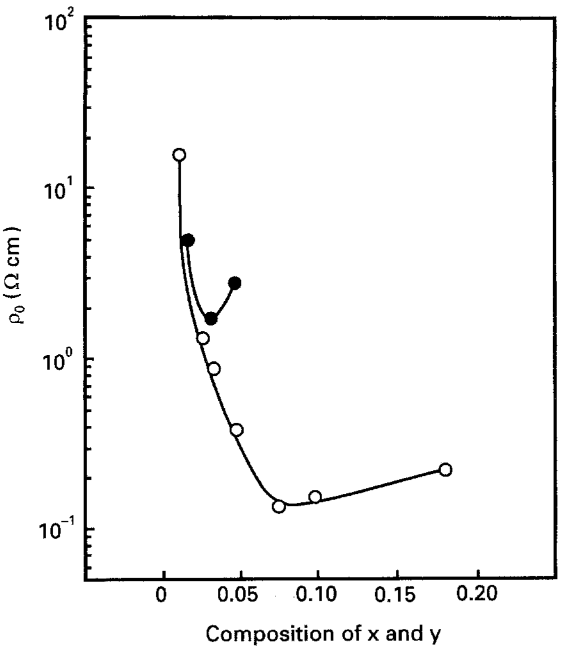

Figure 6 Composition dependence of resistivities at room temperature for $BaSn_{1-x}Sb_xO_{3-\delta}$ (○) and $Ba_{1-y}La_ySnO_{3-\delta}$ (●). Lines are guides to the eye.

obviously through the substitution. At the lower composition range ($x, y \leq 0.03$), the values of the resistivity for $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$ are similar and the temperature dependence of the resistivity in Figs 2, 3 and 4 shows the same tendency, probably indicating the same conductive mechanism in this range.

4. Conclusions

Substitutional solubilities of antimony for tin and lanthanum for barium, respectively, in $BaSnO_3$ were $x = 0.18$ for $BaSn_{1-x}Sb_xO_{3-\delta}$ and $y < 0.052$ for $Ba_{1-y}La_ySnO_{3-\delta}$. These substitutions convert an insulating $BaSnO_3$ into semiconductor-like ones with fairly temperature-independent resistivities of $1 \sim 10^{-1}$ Ω cm at the optimized compositions. The magnetic susceptibilities show the existence of non-interacting localized electrons in $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$, and the Curie constant increases with the composition of tin, indicating a $Sn^{4+} + e^-$ state in these materials. From our XPS measurements, the valence of antimony and tin is mixed in $BaSn_{1-x}Sb_xO_{3-\delta}$. It is considered the expected states for antimony in $BaSn_{1-x}Sb_xO_{3-\delta}$ are Sb^{5+} and $Sb^{5+} + e^-$, and for tin in $BaSn_{1-x}Sb_xO_{3-\delta}$ and $Ba_{1-y}La_ySnO_{3-\delta}$ are $Sn^{4+} + e^-$ and Sn^{2+}. To interpret the semiconductor-like conductivity, three types of mechanism (oxygen vacancy, excitation of electrons to the conduction band and hopping of electrons) were taken into consideration in these systems.

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