

## Thermoelectric properties of $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$ ( $x \leq 0.02$ )

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**Abstract.** A set of polycrystalline samples of  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$  ( $x < 0.02$ ) were prepared with special care taken in controlling the La content to within 0.2%. The measured resistivity ( $\rho$ ) and thermopower ( $S$ ) change systematically with  $x$ , and the  $x$ -dependences are explained consistently on the basis of a rigid-band picture in a single parabolic band. The carrier concentration evaluated ranges from  $10^{19}$  to  $10^{20}$   $\text{cm}^{-3}$ , while the scattering time and the mobility do not appreciably change with the La substitution. The power factor ( $S^2/\rho$ ) takes a maximum at a carrier concentration of  $4 \times 10^{19}$   $\text{cm}^{-3}$ , which is nearly the same value as for conventional thermoelectric semiconductors. These data clearly indicate that carrier doping in  $\text{SrPbO}_3$  is as controllable as that in conventional semiconductors.

### 1. Introduction

Thermoelectrics (energy conversion between heat and electricity via thermoelectric phenomena in solids) has long been one of the fields of application of semiconductors [1, 2]. For good thermoelectric conversion, a large thermopower ( $S$ ) and a low resistivity ( $\rho$ ) are required. In the presence of a temperature gradient  $\Delta T$ , the Seebeck effect can convert heat into electricity, where  $S \Delta T$  and  $\rho$  correspond to the voltage and internal resistance of a battery, respectively. Then the upper limit of the electric power is proportional to the so-called ‘power factor’  $S^2/\rho$ .  $S$  and  $\rho$  are larger for smaller carrier concentration, and  $S^2/\rho$  takes a maximum at an optimal concentration of the order of  $10^{19}$   $\text{cm}^{-3}$ , which corresponds to that for degenerate semiconductors. For a given carrier concentration, one way to maximize  $S^2/\rho$  is to find a material with a low  $\rho$ , or, equivalently, a material of high mobility ( $\mu$ ). Consequently high-mobility semiconductors have been used for thermoelectric applications.

In spite of their chemical stability in air at high temperature, oxide semiconductors have been regarded as unsuitable for thermoelectric applications because of their low mobility. The thermoelectric performance of oxides was indeed poorer than that of conventional thermoelectric materials such as  $\text{Bi}_2\text{Te}_3$ . Very recently, however, we have found a large thermopower of  $100 \mu\text{V K}^{-1}$  and a low resistivity of  $200 \mu\Omega \text{cm}$  at room temperature in a layered cobalt oxide,  $\text{NaCo}_2\text{O}_4$  [3]. This suggests that yet another thermoelectric oxide might still be unknown to us.

One problem is that the thermopower of  $\text{NaCo}_2\text{O}_4$  is always positive (P type) above room temperature, and an oxide with a negative thermopower (N type) is indispensable to thermoelectric device use. A possible candidate is  $\text{SrPbO}_3$  [4].  $\text{SrPbO}_3$  has the  $\text{GdFeO}_3$ -type perovskite structure, and the three-dimensional network of Pb–O octahedra forms a wide

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conduction band of Pb 6s–O 2p character. Itoh *et al* [5] measured the Hall effect for SrPbO<sub>3</sub>, and found that it is an N-type conductor with a carrier concentration of 10<sup>18</sup> cm<sup>-3</sup>. The carrier concentration can be controlled by the substitution of Ba for Sr [5, 6], or La for Sr [7, 8]. The former substitution modifies the tilting angle of the Pb–O octahedra to change the overlap between Pb 6s and O 2p, while the latter one decreases the formal valence of Pb to supply one electron per La. In this paper we report on the thermoelectric properties of Sr<sub>1-x</sub>La<sub>x</sub>PbO<sub>3</sub> from 4.2 to 300 K. We strictly controlled the amount of La substitution to within 0.2%, in order to achieve a carrier concentration of the order of 10<sup>19</sup> cm<sup>-3</sup>.

## 2. Experimental procedure

Polycrystalline samples of Sr<sub>1-x</sub>La<sub>x</sub>PbO<sub>3</sub> were prepared through a solid-state reaction. For the precise control of the La content to within 0.2%, SrPbO<sub>3</sub> and Sr<sub>0.95</sub>La<sub>0.05</sub>PbO<sub>3</sub> ( $x = 0.05$ ) were synthesized in advance. A stoichiometric mixture of SrCO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and PbO was calcined at 750 °C for 32 h in air. The powders of SrPbO<sub>3</sub> and Sr<sub>0.95</sub>La<sub>0.05</sub>PbO<sub>3</sub> obtained were used as precursors to Sr<sub>1-x</sub>La<sub>x</sub>PbO<sub>3</sub> ( $x \leq 0.02$ ). They were then appropriately mixed, pressed into pellets, and sintered at 900 °C for 12 h in air. The x-ray diffraction of the samples showed essentially the same patterns as in reference [4], showing that our samples are single phase with no trace of unwanted impurity phases. The resistivity was measured through a four-probe method in a liquid-helium cryostat. The thermopower was measured using a steady-state method, where the temperature gradient (typically 1 K cm<sup>-1</sup>) was measured by a differential copper–constantan thermocouple.

## 3. Results and discussion

The dependence on the temperature ( $T$ ) of the resistivities of the prepared samples is shown in figure 1(a). As reported previously [5, 7, 8], the resistivity for SrPbO<sub>3</sub> ( $x = 0$ ) shows an upturn near 100 K. This peculiar  $T$ -dependence is not yet understood, but the localization may play an important role [7]. The measured resistivity for SrPbO<sub>3</sub> is in the range of reported values, 0.02 Ω cm [7] to 0.4 Ω cm [5]; these depend on the different oxygen vacancy caused by the different preparation conditions. The highest resistivity is observed for the sample prepared under high oxygen pressure [5], which has the fewest oxygen vacancies. This suggests that SrPbO<sub>3</sub> is an extrinsic semiconductor, and the electrons are doped from the oxygen vacancies. With the La substitution, the resistivity monotonically decreases and the low-temperature upturn is systematically suppressed. Since the substitution of La<sup>3+</sup> for Sr<sup>2+</sup> supplies carriers, the carrier is an electron in Sr<sub>1-x</sub>La<sub>x</sub>PbO<sub>3</sub>. It should be noted that the  $\rho$ - $T$  curves in figure 1(a) are nearly parallel with one another above 100 K, which means that the  $T$ -dependences of the resistivities are essentially identical above 100 K.

Figure 1(b) shows the thermopowers of Sr<sub>1-x</sub>La<sub>x</sub>PbO<sub>3</sub>. The sign is negative, and the magnitude decreases with increasing  $x$ , which is consistent with the N-type conduction of this system. The temperature dependence is roughly proportional to  $T$  near 4.2 K, and saturates at higher temperatures. The saturation is more remarkable for smaller  $x$ . This  $T$ -dependence is well understood on the basis of a single-band picture. In the low-temperature limit where the Fermi energy  $E_F$  is much larger than  $k_B T$ , electrons can be treated as a degenerate Fermi gas, and the diffusive part of the thermopower is written as [9]

$$S = \frac{\pi^2 k_B k_B T}{2 e E_F}. \quad (1)$$

In the high-temperature limit of  $k_B T \gg E_F$ , the electron gas is classical, to obey the Boltzmann

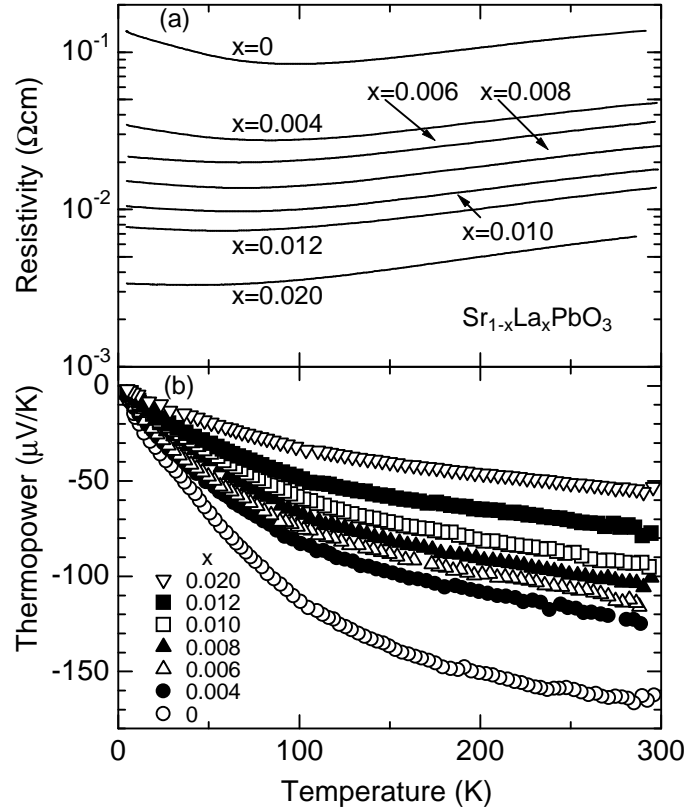


Figure 1. (a) The resistivity and (b) the thermopower of  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$ .

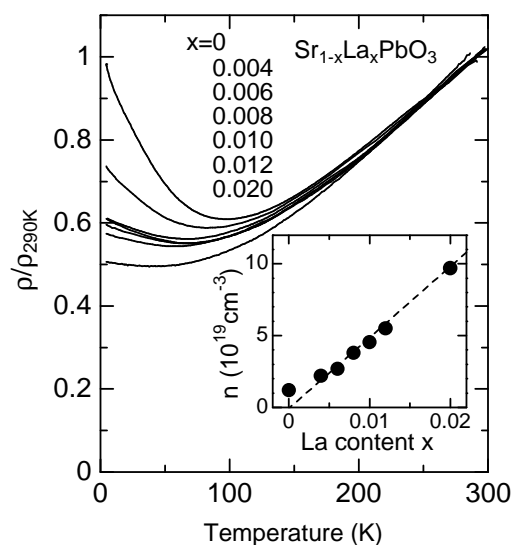
distribution, and the thermopower is independent of temperature [10]. Since  $E_F$  is smaller for smaller  $x$ , the saturation is seen at lower temperatures for smaller  $x$ .

In a single parabolic band,  $E_F$  is expressed through the carrier concentration  $n$  by

$$E_F = \frac{1}{2m} \hbar^2 k_F^2 = \frac{1}{2m} \hbar^2 (3\pi^2 n)^{2/3} \quad (2)$$

where  $m$  and  $k_F$  are the effective mass of the carriers and the Fermi wavenumber, respectively. Assuming that  $m$  is equal to the electron mass  $m_0$ ,  $n$  is evaluated from the  $T$ -linear part of  $S$  at low temperatures using equations (1) and (2). The  $n$  obtained is shown in the inset of figure 2, where  $n$  is roughly proportional to the La content  $x$ . This clearly indicates that the substituted La ions supply electrons as mobile carriers. If one electron per La is doped in the conduction band,  $n$  is calculated to be  $1.2 \times 10^{20} \text{ cm}^{-3}$  at  $x = 0.01$ , which is of the same order of magnitude as the observed  $n$ . This coincidence is rather surprising in view of our rough assumptions. The disagreement in the magnitude of  $n$  is attributable to the effective mass ( $m \sim 3m_0$ ).

One may notice that a completely different conclusion could be derived from equation (2) on the assumption that the carrier concentration is constant. This would be the case for a Mott insulator, where electrons in a partially filled band are localized owing to the strong Coulomb repulsion. We emphasize that  $\text{SrPbO}_3$  is a band insulator. The formal valence of Pb is 4+, and



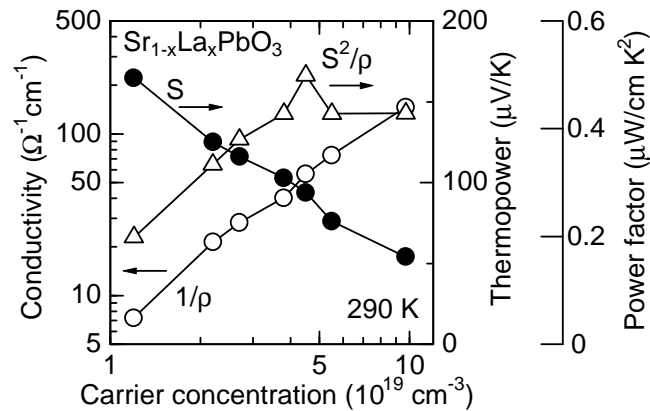
**Figure 2.** The resistivities of  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$  normalized at 290 K. The inset shows the carrier concentration evaluated from the low-temperature thermopower (see the text).

the Pb 6s band is nearly empty. Thus the substitution of a trivalent La for a divalent Sr can decrease the Pb valence toward 3+, which introduces an electron per La. In fact, it is established that a rigid-band picture is valid for slightly doped  $\text{APbO}_3$  ( $A = \text{Ba}$  and  $\text{Sr}$ ) [5, 11, 12]. In addition, the change of the lattice parameter is not detected in the x-ray diffraction, which implies that the overlap integral and the band mass remain unchanged by La doping. We further applied our analysis to  $\text{Sr}_{1-x}\text{Ba}_x\text{PbO}_3$ , where the carrier concentration increases with  $x$ , and found that the  $n$  evaluated is in excellent agreement with  $n$  measured through the Hall effect [5, 6]. Thus we think that the above results justify our assumption well.

As already seen in figure 1(a), the  $T$ -dependence of the resistivity above 100 K is nearly independent of  $x$ . To see this more clearly, we normalize the resistivities at 290 K ( $\rho/\rho_{290K}$ ) in figure 2, where all of the data fall on a single curve above 100 K. This indicates that the La substitution alters neither the scattering time nor the mobility appreciably. We conclude that, together with the relation  $n \propto x$ , the substitution of La for Sr is consistently understood through a rigid-band picture in a single parabolic band. This implies that the carrier concentration in  $\text{SrPbO}_3$  is controlled as precisely as that in conventional thermoelectric semiconductors.

The conductivity ( $=1/\rho$ ), the thermopower ( $S$ ), and the power factor ( $S^2/\rho$ ) at 290 K are plotted as functions of  $n$  in figure 3. Similarly to the case for conventional thermoelectric materials,  $S^2/\rho$  is maximized at an optimized carrier concentration of around  $4 \times 10^{19} \text{ cm}^{-3}$ . Yasukawa and Murayama [6] found that the thermoelectric properties for  $\text{Ba}_{1-x}\text{Sr}_x\text{PbO}_3$  are optimized at  $x = 0.6$ . Since  $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{PbO}_3$  shows nearly the same  $S$  as  $\text{Sr}_{0.99}\text{La}_{0.01}\text{PbO}_3$  ( $80 \mu\text{V K}^{-1}$  at room temperature), the optimized carrier concentrations of the two are nearly equal. We emphasize that  $\text{Sr}_{0.99}\text{La}_{0.01}\text{PbO}_3$  is metallic from room temperature down to 70 K, while  $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{PbO}_3$  is nonmetallic at all temperatures [5, 6]. This is because the small amount of La substitution introduces less disorder than the solid solution of Sr and Ba.

Let us estimate the mobility and the mean free path for  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$ , and compare them with those for conventional thermoelectric materials. At room temperature,  $\rho$  and  $n$  for  $\text{Sr}_{0.99}\text{La}_{0.01}\text{PbO}_3$  are  $16 \text{ m}\Omega \text{ cm}$  and  $4.5 \times 10^{19} \text{ cm}^{-3}$ , respectively. Then the mobility is



**Figure 3.** The conductivity ( $1/\rho$ ), the thermopower ( $S$ ), and the power factor ( $S^2/\rho$ ) of  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$  plotted as functions of the carrier concentration. All of the data were taken at 290 K.

calculated as  $\mu = 1/nep \sim 8.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Although this is reasonably high in comparison with the mobility for other conducting oxides, it is more than 10 times lower than the mobility for  $\text{Bi}_2\text{Te}_3$  [13]. Using the Fermi velocity  $v_F = \sqrt{2E_F/m}$ , the mean free path  $\ell$  is calculated as  $\ell = v_F\tau = v_F m\mu/e \sim 7 \text{ \AA}$ , which is comparable to the lattice parameters. According to these results, we conclude that  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$  is barely metallic, and in the presence of some disorders it will lose the metallic conduction. This would be the reason for the nonmetallic conduction of  $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{PbO}_3$ . We further point out that the short  $\ell$  explains why the substituted La does not decrease  $\mu$ . In the  $x = 0.01$  sample, for example, the average distance between the La ions is  $19 \text{ \AA}$  ( $>\ell$ ), indicating that impurity scattering is less dominant.

The origin of the scattering mechanism for  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$  is yet to be understood. A possible candidate is the strong electron–phonon interaction. Since the stable valence of a Pb ion in oxides is  $2+$  or  $4+$ , the doped electrons are likely to exist in pairs as  $\text{Pb}^{2+}$  in  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$ . The ionic radius of  $\text{Pb}^{2+}$  is larger than that of  $\text{Pb}^{4+}$ , and thus the electron pair will enlarge the Pb–O octahedra where they are. If this happens, the breathing mode of the Pb–O octahedra will strongly interact with the hopping electrons to act as a strong scatterer. This is a similar situation to that seen for  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ , where the charge separation between  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  is believed to play a crucial role in the pairing mechanism of the superconductivity [12].

#### 4. Summary

We prepared a set of polycrystalline samples of  $\text{Sr}_{1-x}\text{La}_x\text{PbO}_3$  for  $x \leq 0.02$ . The measured resistivity and thermopower are consistently explained on the assumption that the trivalent  $\text{La}^{3+}$  substituted for the divalent  $\text{Sr}^{2+}$  supplies one electron as a carrier in a rigid-band manner. The carrier concentration evaluated ranges from  $10^{19}$  to  $10^{20} \text{ cm}^{-3}$ , while the scattering time and the mobility are not appreciably modified by the La substitution. The present study clearly indicates that the carrier concentration of  $\text{SrPbO}_3$  is controlled as easily as that of conventional thermoelectric semiconductors, which indicates a possibility of fabricating thermoelectric devices from just oxide conductors.

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