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Large thermoelectric response of metallic perovskites: $Sr_{1-x}La_xTiO_3$ $(0\leqslant x\leqslant 0.1)$

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Thermoelectric properties have been investigated for single crystals of $Sr_{1-x}La_xTiO_3$ for $0\leqslant x\leqslant 0.1$. We have found a large power factor (defined as $\mathrm{PF}=S^2/\rho$, S and ρ being the Seebeck coefficient and resistivity, respectively), $28-36\ \mu\mathrm{W/(K^2\ cm)}$, at room temperature in the metallic region with carrier density (n) of $(0.2-2)\times 10^{21}\ \mathrm{cm}^{-3}$. The observed PF is comparable to that of Bi_2Te_3 with much lower n ($\sim 1\times 10^{19}\ \mathrm{cm}^{-3}$). Such an unexpectedly large PF or S at the metallic carrier density is ascribed to the orbital degeneracy (threefold) of the Ti $3d$-t_{2g} conduction band and the relatively large effective mass of conduction electrons as well as to the large energy-dependent scattering rate.

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Thermoelectric properties of solids[1] have long been a fundamental issue in condensed matter physics and is currently attracting a renewed interest as well because of their practical application, such as coolers (Peltier effect) and generators (Seebeck effect). The measure of its performance is the thermoelectric figure-of-merit Z. Z is defined by $Z\equiv S^2\sigma/\kappa$, where S is the Seebeck coefficient, and σ and κ the electronic conductivity and the thermal conductivity, respectively. ($\mathrm{PF}=S^2\sigma$ is called the power factor.) The most urgent need for thermoelectric applications is to find a new thermoelectric material with a high ZT value below the room temperature. $ZT\geqslant 1$ is one of the criteria for practical application, although only a few semiconductors, e.g., bismuth-antimony telluride and bismuth-antimony alloys,[1] have been known to fulfill the condition. Recently, some $3d$ transition-metal oxides have drawn attention as a new category of thermoelectric materials. For example, a large Seebeck coefficient is observed at room temperature in the metallic cobalt oxide, $NaCo_2O_4$.[2] This cobalt oxide has a heavy effective mass of carriers due to the strong electron correlation,[3] which is responsible for the large Seebeck coefficient as in some $4f$ heavy-fermion systems.[1] From a viewpoint of the Mott transition, therefore, the thermoelectric properties in the $3d$ transition-metal oxides are also of great interest.[4]

The materials we have investigated here are single crystals of $Sr_{1-x}La_xTiO_3$ (SLTO), one of the most typical perovskite-type transition-metal oxides in which the carrier density can be systematically controlled over a wide range up to $10^{22}\ \mathrm{cm}^{-3}$. The state in the end compound of $SrTiO_3$ below room temperature is a nonmagnetic band insulator in which the valence band comes from the oxygen $2p$ state and the conduction band from the Ti $3d$-t_{2g} state with threefold orbital degeneracy.[5] The region of $0\leqslant x\leqslant 0.1$ is far from the Mott insulating state ($x=1$) and also from the filling-controlled Mott transition ($x\approx 0.92$).[6] The state in such a lightly electron-doped region is barely metallic with a low Fermi energy and is similar to the situation of the n-type degenerate semiconductor. The low Fermi energy in these compounds is expected to give a large Seebeck coefficient because of a large entropy term arising from the sixfold degeneracy of the Ti $3d$-t_{2g} conduction bands. In an early study,[7] thermoelectric properties of semiconducting $SrTiO_3$ and slightly Nb^{5+}-doped $SrTiO_3$ were investigated. In the present paper, we report a large thermoelectric response in a systematic series of electron-doped metallic titanates with well-controlled carrier densities and investigate its electronic origin by measurements of resistivity, Hall and Seebeck coefficients, thermal conductivity, and specific heat. The large PF observed in SLTO with metallic carrier density (n) of $(0.2-2)\times 10^{21}\ \mathrm{cm}^{-3}$ at room temperature is comparable with that of Bi_2Te_3 compounds, although ZT value is less than unity (about 0.09) because of the large thermal conductivity ($\sim 120\ \mathrm{mW/K\,cm}$). We propose here the possible importance of the orbital degeneracy of carriers in realizing such a large thermoelectric response in the metallic state.

Single crystals of SLTO ($0\leqslant x\leqslant 0.1$) were melt-grown by the floating-zone method at the feeding speed of $15-20$ mm/h.[8] First, a stoichiometric mixture of La_2O_3, $SrTiO_3$, Ti, and TiO_2 was ground and calcined several times at 1400 °C for 12 h. The obtained powder was pressed into a rod with a size of 5 mm $\phi\times 100$ mm and sintered at 1400 °C for 12 h. The ingredient could be melted congruently in a flow of Ar. X-ray-diffraction measurements indicated that all the crystals are single phase with a cubic $Pm3m$ structure. The electronic resistivity ($\rho=1/\sigma$) was measured by a conventional four-probe method. The thermal conductivity (κ) and Seebeck coefficient (S) of the sample were measured in vacuum, about 1×10^{-6} torr. The specific heat was measured by the relaxation method down to 0.5 K. The difference between the actual carrier density n (per Ti atom) determined by meaurements of the Hall effect and the prescribed one (x) was found to be less than 10% for all the crystals (see Table I).

The temperature (T) dependence of resistivity is shown in Fig. 1. In all the crystals shown, the resistivity decreases with the decrease of T and is almost proportional to T^2 below 100 K, which seems to show a Fermi-liquid-like behavior. However, the T^2 coefficient (A) of the resistivity is much enhanced with the decrease of n and the ratio of the A value to the observed electronic specific heat coefficient (γ) (Table I)

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TABLE I. Various physical quantities derived from measurements of the resistivity, specific heat, Hall, and Seebeck coefficients (S) in $Sr_{1-x}La_xTiO_3$ crystals; n is the carrier (electron) density, A is the T^2 coefficient of resistivity, γ is the electronic specific heat coefficient, m^* is the carrier effective mass, T_F is the Fermi temperature, Θ_D is the Debye temperature, and μ is the chemical potential. S_r represents the calculated Seebeck coefficient with use of the scattering parameter r [see Eq. (1) in the text]. n, μ, S, and S_r are the values at 300 K.

x	n (1/Ti)	n (10^{20} cm^{-3})	A (Ω cm/K^2)	γ (mJ/K^2 mol)	m^*/m_b	T_F (K)	Θ_D (K)	μ (eV)	$-S$ (μV/K)	$-S_0$ (μV/K)	$-S_1$ (μV/K)	$-S_2$ (μV/K)
0	0.0052	0.877	3.68×10^{-7}	0.63	1.17	343	402	0.0061	380	190	268	345
0.015	0.014	2.31	2.58×10^{-8}						350			
0.02	0.022	3.73	1.21×10^{-8}	1.04	1.51	697	378	0.0488	260	150	182	247
0.04	0.05	8.41	6.69×10^{-9}						162			
0.05	0.061	10.23	5.14×10^{-9}	1.96	1.62	1273	380	0.102	147	93	118	168
0.1	0.11	19.31	3.08×10^{-9}						88.7			

does not obey the Kadowaki-Woods law characteristic of correlated metals.[9] The behavior is perhaps due to the enhancement of the electron-phonon coupling with the decrease of n, as also manifested by the temperature dependence of the Seebeck coefficients shown in Fig. 2. The resistivity at room temperature drastically decreases with the increase of n as shown in Fig. 3. The room-temperature mobility (μ_c) estimated by using the relation $\sigma = ne\mu_c$ increases with the increase of n until $n \approx 0.03$ per Ti atom as also shown in Fig. 3. The change of μ_c suggests the tendency of localization of the carriers at lower n, which may relate to the above mentioned electron-phonon coupling enhanced toward the low-n region. Above $n \approx 0.03$ per Ti atom, on the other hand, the μ_c saturates and becomes almost constant, about 10 cm^2/V s, which is about two orders of magnitude worse than that of conventional semiconductors but typical of the barely metallic transition-metal oxides. Thus the conductivity in this region is almost proportional to n.

In spite of the fairly low resistivity at room temperature, the observed Seebeck coefficient (Fig. 3) is relatively large in the region of n between 0.02 and 0.06 per Ti atom, whose values are consistent with previous results on the polycrystals.[10] In this regime, we have found that the PF is as large as 36 μW/(K^2 cm) at room temperature (Fig. 3), which is comparable to that of Bi_2Te_3, a typical thermoelectric semiconductor, although the present carrier density (2×10^{20}–1×10^{21} cm^{-3}) is two orders of magnitude larger than that at which the conventional semiconductor usually shows the maximum PF.[1] In the following, we discuss the temperature and doping dependence of the Seebeck coefficient on the basis of the Boltzmann transport in a simplified parabolic band.[11] Given the z-fold degenerate parabolic band [$\epsilon = (hk)^2/2m^*$, k is the wave vector and m^* the effective mass] and the energy–power-dependent relaxation time ($\tau = \tau_0 \epsilon^{r-1/2}$, r is the scattering parameter), one can solve the Boltzmann equation and derive the following expressions for the Seebeck coefficient,[11]

$$S = \frac{k_B}{q}[-y + \delta_r(y)], \tag{1}$$

$$\delta_r(y) = \frac{(r+2)F_{r+1}(y)}{(r+1)F_r(y)}, \tag{2}$$

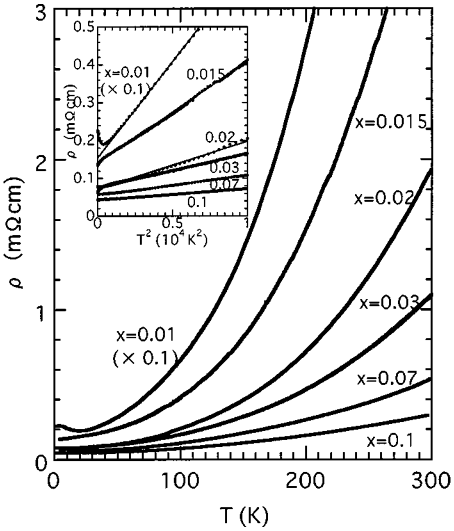

FIG. 1. Temperature (T) dependence of resistivity (ρ) for $Sr_{1-x}La_xTiO_3$ with various x values. Below 100 K, the resisitivites for all compounds are almost proportional to T^2. The inset shows a ρ vs T^2 plot below 100 K.

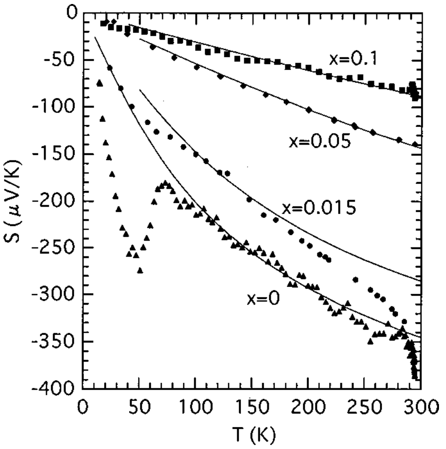

FIG. 2. Temperature (T) dependence of the Seebeck coefficient for $x = 0$, 0.015, 0.05, and 0.1 in $Sr_{1-x}La_xTiO_3$. Solid lines show the calculated results using Eq. (1) with $r = 2$ and experimentally obtained values of chemical potential (see also Table I).

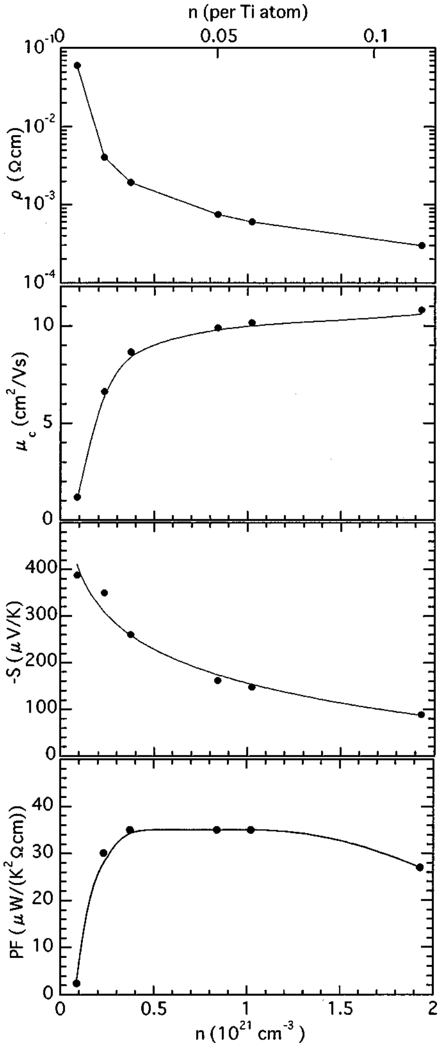

FIG. 3. Carrier doping dependence of resistivity (ρ), mobility (μ_c), Seebeck coefficient (S), and power factor (PF) at room temperature. The PF value takes the maximum at n between 0.02 and 0.06 per Ti atom. Solid lines are guides to the eye.

where q is the charge of the carriers, y the reduced chemical potential (μ/k_BT), and $F_r(y)$ the Fermi integral,

$$F_r(y)=\int_0^\infty \frac{x^r}{1+e^{x-y}}dx. \tag{3}$$

This expression is often used in the case of degenerate semiconductors, semimetals, and metals with a low Fermi energy. It is worth noting that in the limit of $\mu\approx\epsilon_F$, Eq. (1) leads to the well-known T linear dependence of S in the metallic state, $S=-[(\pi k_B)^2/3e\epsilon_F](1+r)T$. In the framework of this model, the Seebeck coefficient can be deduced only by knowing the chemical potential. Therefore, we can test whether Eq. (1) can be applied to the Seebeck coefficient of this system by using the carrier effective mass and concentration estimated from the specific heat and Hall measurements. The obtained physical quantities are shown in Table I. In the low-doped region of SLTO, the bottom of the conduction band is at the Γ point, where the three Ti $3d$-t_{2g} bands are degenerate.[5] Therefore, we assume the sixfold degenerate parabolic conduction band ($z=3\times2$; 2 comes from the spin degree of freedom) to explain the physical properties. As shown in Table I, the derived effective mass is $(1.1-1.7)m_0$ (m_0 being the mass of a bare electron) and the estimated Fermi temperature (T_F) is quite low, $300-1300$ K for $0.005\leqslant n\leqslant0.06$ per Ti atom, which is due not only to the low carrier concentration but also to the high band degeneracy and the relatively heavy electron mass. In such a regime, we cannot use the well-known approximation $\mu\approx\epsilon_F[1-(\pi T/2T_F)^2/3]$, because the relation $T_F\gg T=300$ K no longer holds. The following relation,[1]

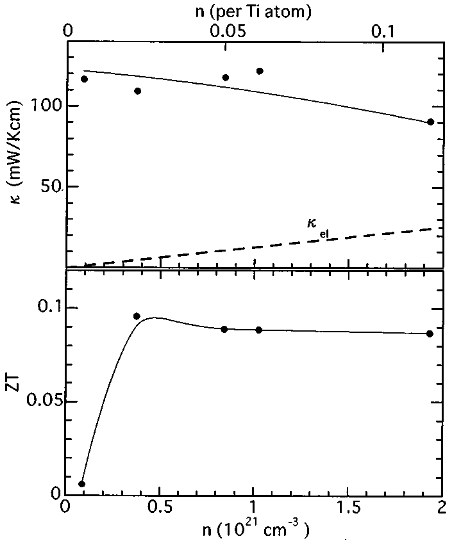

FIG. 4. Carrier doping dependence of the thermal conductivity (κ) and the ZT value at room temperature in $Sr_{1-x}La_xTiO_3$. Solid lines are guides to the eye and a dashed line represents the electronic thermal conductivity (κ_{el}) estimated by the Wiedemann-Franz law.

$$n=z\left(\frac{2\pi m^*k_BT}{h^2}\right)^{3/2}\frac{2}{\sqrt{\pi}}F_{1/2}(y), \tag{4}$$

was used instead to obtain the chemical potential (μ). Then, we estimated the Seebeck coefficients with various scattering parameters r as shown in Table I and found that $r=2$ was most suitable to explain the value of S at room temperature.

With use of the thus obtained values of μ and r, we calculated the temperature dependence of S. In Fig. 2, the calculated results with $r=2$ are shown by solid lines in comparison with the observed ones. We found that the temperature dependencies of S for the respective crystals are well explained by Eq. (1). A discrepancy seen at low temperatures for $n<0.02$ per Ti atom is due to the phonon drag effect. With the decrease of n, the electron-phonon coupling becomes so strong that the the phonon drag effect becomes conspicuous, as manifested by anomalies around 50 K for $x=0$ and 0.015 in Fig. 2. The peak profile of the temperature dependence of the Seebeck coefficient coming from the phonon drag effect should appear at $\Theta_D/5$, Θ_D being the Debye temperature (see Table I). The observed peak temperature

(≈ 50 K) is roughly consistent with that estimated from the observed Θ_D (≈ 380 K; see Table I).

As shown in Fig. 4, the ZT value at room temperature takes the maximum value (≈ 0.09) at $n \approx 0.02$ per Ti atom. The ZT value is much less than unity in spite of the large PF values being comparable to that of Bi_2Te_3. It is because the thermal conductivity is an order of magnitude larger than that of Bi_2Te_3. The thermal conductivity (κ) at room temperature is about $90-120$ mW/K cm and gradually decreases with the increase of n (Fig. 4) perhaps because of the increase of lattice randomness induced by alloying La with Sr. The electronic thermal conductivity (κ_{el}) at room temperature is estimated to be $0-23$ mW/K cm by using the Wiedemann-Franz constant 2.44×10^{-5} V^2/K^2.[12] The κ_{el} increases with the increase of n as indicated by a broken line in Fig. 4(a), in accord with the increase of the conductivity. The electronic contribution is $0-25\%$ to the total thermal conductivity, implying the possibility of increasing the ZT value up to near unity if the lattice contribution (κ_p) could be reduced.

The large PF observed for the carrier concentration of $\approx 10^{21}$ cm^{-3} in the present electron-doped titanates is quite unusual, compared with the conventional semiconductor thermoelectrics with much lower carrier density. The large PF value may be ascribed to the larger effective mass as well as to the high (sixfold) degeneracy of the conduction band. An additional factor to be considered is the large value ($r=2$) of the scattering parameter in this n region. In the framework of Eq. (1), one of the mechanisms that give $r=2$ is the Conwell-Weisskopf scattering[13] by ionized impurities. The poorly screened potential of La ions in SLTO may correspond to such a scatterer, although another possibility is left to be relevant, such as the electron-electron scattering process.

In conclusion, we have investigated transport, thermal, and thermoelectric properties of $Sr_{1-x}La_xTiO_3$ single crystals ($0 \leqslant x \leqslant 0.1$) and found a large PF ($=S^2/\rho$), $28-36$ $\mu W/(K^2$ cm$)$, at room temperature, that is comparable to that observed in Bi_2Te_3, at relatively high carrier concentrations $[(0.2-2)\times 10^{21}$ cm$^{-3}]$. The Seebeck coefficient seems to be well explained by the Boltzmann transport model with use of the experimentally determined chemical potential. The unexpectedly large Seebeck coefficients for $n > 0.02$ per Ti atom (0.3×10^{21} cm^{-3}) may be due to the relatively large effective mass, the high (sixfold) degeneracy of the conduction band, and the large scattering parameter r in the energy (ϵ)-dependent relaxation time expressed as $\tau = \tau_0 \epsilon^{r-1/2}$.

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