

High-temperature carrier transport and thermoelectric properties of heavily La- or Nb-doped SrTiO₃ single crystals

Shingo Ohta and Takashi Nomura

Nagoya University, Graduate School of Engineering, Nagoya 464-8603, Japan

Hiromichi Ohta and Kunihiro Koumoto^{a)}

Nagoya University, Graduate School of Engineering, Nagoya 464-8603, Japan and CREST, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan

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Electron and thermal transport properties, i.e., electrical conductivity, carrier concentration, Hall mobility, Seebeck coefficient, thermal conductivity, of heavily La- or Nb-doped SrTiO₃ (STO) bulk single crystals were measured at high temperatures, (300–1050 K) to clarify the influence of doping upon the thermoelectric performance of STO. The temperature dependence of Hall mobility and Seebeck coefficient changed at ~ 750 K in all samples because the dominant mechanism for carrier scattering changed with increasing temperature from coupled scattering by polar optical phonons and acoustic phonons to mere acoustic phonon scattering. The density-of-states effective mass of Nb-doped STO, which was estimated from the carrier concentration and Seebeck coefficient, was larger than that of La-doped STO. Thermal conductivity of the samples, which was similar to that of undoped STO single crystal, decreased proportionally to T^{-1} , indicating that the phonon conduction takes place predominantly and the electronic contribution to thermal conductivity is negligible. © 2005 American Institute of Physics. [DOI: 10.1063/1.1847723]

INTRODUCTION

Thermoelectric semiconductors such as SiGe and Bi₂Te₃ are applied to power generators and refrigerators utilizing Seebeck and Peltier effect, respectively.¹ The energy conversion performance of thermoelectric semiconductors is usually evaluated by using the dimensionless figure of merit, $ZT = S^2\sigma/\kappa$, where Z , T , S , σ , and κ are the figure of merit, absolute temperature, Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. Practical applications generally require $ZT \geq 1$. Only a few intermetallic compound semiconductors such as Bi₂Te₃ alloys,² AgPb₁₈SbTe₂₀,³ and filled skutterudite antimonides⁴ are known to fulfill the requirement to date. Although the major thermoelectric materials had been intermetallic compound semiconductors, Na_xCoO₂ was found in 1997 to show high thermoelectric performance⁵ and thermoelectric oxides have drawn great attention and interest since then.

Na_xCoO₂ exhibits a large power factor (PF), $5 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-2}$, which is comparable to that of practical Bi₂Te₃, due to rather large carrier effective mass (m^*), which reflects the large Seebeck coefficient, of Na_xCoO₂. Hence, oxide semiconductors having heavy carriers are expected to be promising candidates for high-performance thermoelectric materials.

Heavily electron-doped SrTiO₃ (STO) is considered to be an appropriate n -type oxide semiconductor for high-temperature thermoelectric application for the following reasons. First, the m^* of the mobile electrons in STO is two orders of magnitude larger ($\sim 10 m_0$) than that of conventional thermoelectric semiconductors ($\sim 0.1 m_0$).⁶ Second,

carrier concentration of STO can be easily controlled to be an insulator to degenerate semiconductor ($\sim 10^{21} \text{ cm}^{-3}$) by appropriate substitutional doping. Accordingly, the absolute value of Seebeck coefficient of heavily doped STO can be maintained large even when the carrier concentration is very high ($\sim 10^{21} \text{ cm}^{-3}$).⁷

Very recently, high-temperature thermoelectric performance of heavily doped ceramic samples of STO has been reported.^{8,9} However, the performance is still low as compared to that of p -type oxide semiconductors,¹⁰ because both electronic and thermal transport would be affected by grain boundaries in polycrystalline ceramics. Therefore, the intrinsic thermoelectric performance of STO at high temperatures is still unknown.

We, therefore, measured high-temperature electron transport and thermoelectric properties of heavily La-doped STO (La-STO) or Nb-doped STO (Nb-STO) single crystals to clarify its intrinsic thermoelectric performance at high temperatures. In this study, we focused on the effect of heavy doping of either Nb at the Ti site or La at the Sr site upon the m^* .

EXPERIMENTAL

Bulk single-crystal samples of La-STO or Nb-STO, which had been grown by a conventional Verneuil method at 2080 °C (Earth Chemical Co.¹¹), were used in this study. The doping levels of the samples are summarized in Table I. The σ of the samples were measured by dc four probe method using the van der Pauw configuration. The S was measured by a conventional steady state method under Ar atmosphere.^{12,13} The κ of the sample was obtained by separate measurements using calorimetry for heat capacity and laser flush for thermal diffusivity under vacuum.

^{a)}Author to whom correspondence should be addressed; electronic mail: g44233a@nucc.cc.nagoya-u.ac.jp

TABLE I. Doping levels of the single-crystal samples of La- and Nb-doped SrTiO₃.

(a)	(b)	(c)	(d)
La-doped ($8.4 \times 10^{19} \text{ cm}^{-3}$)	La-doped ($8.4 \times 10^{20} \text{ cm}^{-3}$)	Nb-doped ($1.6 \times 10^{20} \text{ cm}^{-3}$)	Nb-doped ($3.3 \times 10^{20} \text{ cm}^{-3}$)

RESULTS AND DISCUSSION

Electron transport and thermoelectric properties of the La-STO and Nb-STO samples are summarized in Table II. The n of each sample corresponds very well to the doping level. The μ of the La-STO samples is $6\text{--}7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while that of the Nb-STO samples is $5\text{--}6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The S is negative in all cases indicating n -type semiconductivity. The κ of both the La-STO and Nb-STO was $\sim 12 \text{ W m}^{-1} \text{ K}^{-1}$ comparable to that of undoped-STO.¹⁴

Figure 1 shows the temperature dependence of S for La-STO and Nb-STO. The absolute value of S increased with an increase in temperature in all cases due to an increase in the Fermi integral with temperature. An anomaly of the Seebeck coefficient is clearly observed at $\sim 750 \text{ K}$ in all cases. The reason for this phenomenon can be understood as follows. The S of an n -type semiconductor can be expressed by the following equation as reported by Vining:¹⁵

$$S = -\frac{k_B}{e} \left(\frac{(r+2)F_{r+1}(\xi)}{(r+1)F_r(\xi)} - \xi \right), \quad (1)$$

where k_B , ξ , r , and F_r are the Boltzmann constant, chemical potential, scattering parameter of relaxation time, and Fermi integral, respectively. The F_r is given by

$$F_r(\xi) = \int_0^\infty \frac{x^r}{1 + e^{x-\xi}} dx. \quad (2)$$

The n is given by

$$n_- = 4\pi \left(\frac{2m^* k_B T}{h^2} \right)^{3/2} F_{1/2}(\xi), \quad (3)$$

where h , T , and m^* are the Planck constant, absolute temperature, and density-of-states effective mass, respectively. Above $\sim 750 \text{ K}$, carriers are scattered only by acoustic phonons and the scattering parameter of relaxation time is $r=0$.¹⁶ In contrast, below $\sim 750 \text{ K}$, carriers are scattered by both polar optical phonons and acoustic phonons, and the

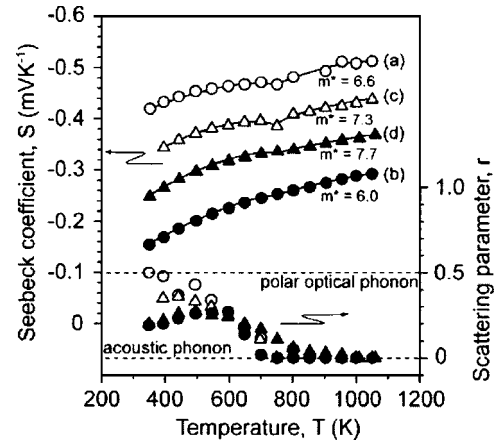


FIG. 1. Temperature dependence of Seebeck coefficient, S , for (a) La-doped ($8.4 \times 10^{19} \text{ cm}^{-3}$), (b) La-doped ($7.9 \times 10^{20} \text{ cm}^{-3}$), (c) Nb-doped ($1.6 \times 10^{20} \text{ cm}^{-3}$), and (d) Nb-doped ($3.3 \times 10^{20} \text{ cm}^{-3}$) SrTiO₃ bulk single crystals. Temperature dependencies of carrier scattering factor, r , calculated from the measured data are also shown.

scattering parameter of relaxation time gradually increases with decreasing temperature reaching 0.5 at room temperature (polar optical phonon scattering) as shown in Fig. 1. The m^* values of the La-STO and Nb-STO, which were estimated using the n and S , are also shown in Fig. 1. The m^* of the Nb-STO ($m^* = 7.3\text{--}7.7 m_0$) is larger than that of La-STO ($m^* = 6.0\text{--}6.6 m_0$).

Figure 2 shows the temperature dependence of σ for La-STO and Nb-STO. The σ decreases proportionally to $T^{-2.0}$ below $\sim 750 \text{ K}$ and $T^{-1.5}$ above $\sim 750 \text{ K}$. The temperature dependencies of n and μ are also shown in the inset. Although n did not show any significant temperature dependence, μ decreased proportionally to $T^{-2.0}$ below $\sim 750 \text{ K}$ and $T^{-1.5}$ above $\sim 750 \text{ K}$, most likely because the dominant mechanism of carrier scattering changed with increasing temperature from coupled scattering by polar optical phonons together with acoustic phonons to mere acoustic phonon scattering.

Figure 3 shows the temperature dependence of κ for La-STO and Nb-STO. The κ decreased proportionally to T^{-1} , indicating that the thermal transport is dominated by phonon conduction. In fact the κ due to the electron contribution (κ_{el}) was $\sim 0.5 \text{ W m}^{-1} \text{ K}^{-1}$, which was estimated using the Wiedemann–Franz law. Although the κ_{el} increases with in-

TABLE II. Electrical conductivity (σ), carrier concentration (n), Hall mobility (μ), Seebeck coefficient (S), power factor ($S^2\sigma$), thermal conductivity (κ), and figure of merit (Z, ZT) for La- and Nb-doped SrTiO₃ measured at room temperature.

	STO	σ (S cm^{-1})	n (10^{20} cm^{-3})	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	S (mV K^{-1})	$S^2\sigma$ ($10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$)	κ ($\text{W m}^{-1} \text{ K}^{-2}$)	Z (10^{-5} K^{-1})	ZT (–)
(a)	La-doped ($8.4 \times 10^{19} \text{ cm}^{-3}$)	54	0.5	7.0	–0.42	9.5	12	7.9	0.02
(b)	La-doped ($8.4 \times 10^{20} \text{ cm}^{-3}$)	1000	6.8	9.2	–0.15	23	9.1	25	0.08
(c)	Nb-doped ($1.6 \times 10^{20} \text{ cm}^{-3}$)	95	1.5	6.2	–0.33	10	11	9.3	0.03
(d)	Nb-doped ($3.3 \times 10^{20} \text{ cm}^{-3}$)	353	3.7	6.0	–0.24	20	9.6	21	0.06

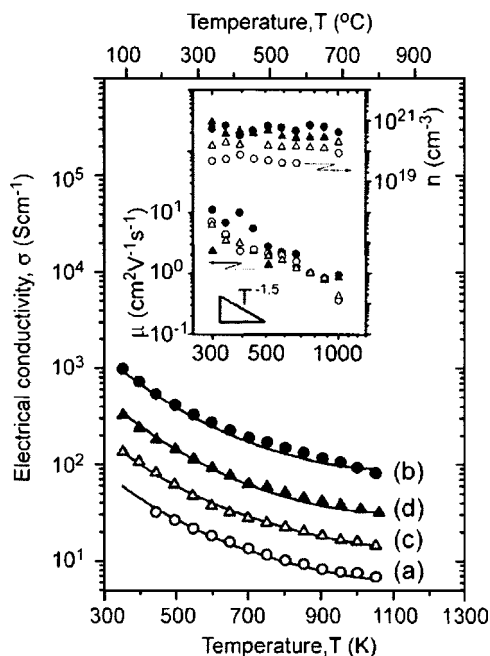


FIG. 2. Temperature dependence of electrical conductivity, σ , for (a) La-doped ($8.4 \times 10^{19} \text{ cm}^{-3}$), (b) La-doped ($7.9 \times 10^{20} \text{ cm}^{-3}$), (c) Nb-doped ($1.6 \times 10^{20} \text{ cm}^{-3}$), and (d) Nb-doped ($3.3 \times 10^{20} \text{ cm}^{-3}$) SrTiO_3 bulk single crystals. Hall mobility, μ , and carrier concentration, n , of the single-crystal samples are also shown in the inset.

creasing n , the κ_{total} shows no significant dependence on the n because the contribution of κ_{lattice} is dominant.

Figure 4 shows the temperature dependence of the Z for La-STO and Nb-STO. The ZT at room temperature of La-STO is ~ 0.03 , which is the largest value so far reported for n -type oxide semiconductors. The absolute value of the S decreases above $\sim 750 \text{ K}$, which leads to a slight decrease in the Z with increasing temperature, in spite of the decrease in

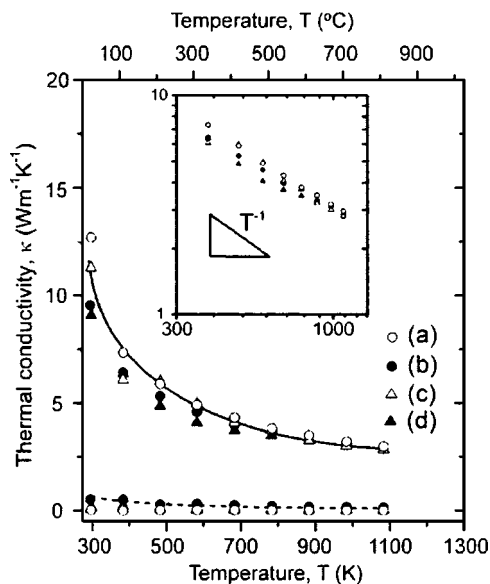


FIG. 3. Temperature dependence of thermal conductivity, κ , for (a) La-doped ($8.4 \times 10^{19} \text{ cm}^{-3}$), (b) La-doped ($7.9 \times 10^{20} \text{ cm}^{-3}$), (c) Nb-doped ($1.6 \times 10^{20} \text{ cm}^{-3}$), and (d) Nb-doped ($3.3 \times 10^{20} \text{ cm}^{-3}$) SrTiO_3 bulk single crystals. Solid lines indicate total thermal conductivity and dotted lines indicate electronic thermal conductivity (κ_e) estimated using the Wiedemann-Franz law. The κ decreasing proportionally to T^{-1} is shown in the inset.

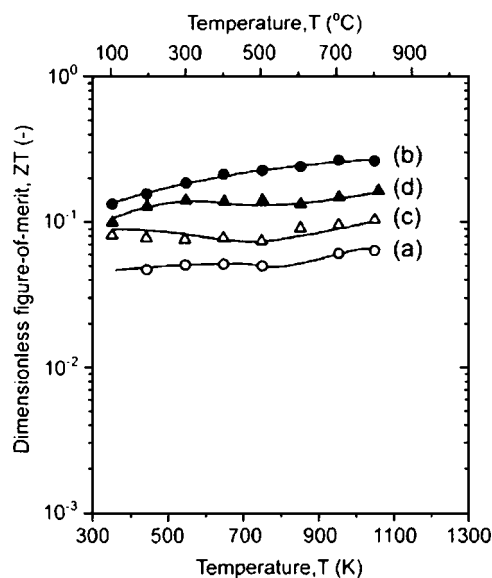


FIG. 4. Dimensionless thermoelectric figure-of-merit, ZT , for (a) La-doped ($8.4 \times 10^{19} \text{ cm}^{-3}$), (b) La-doped ($7.9 \times 10^{20} \text{ cm}^{-3}$), (c) Nb-doped ($1.6 \times 10^{20} \text{ cm}^{-3}$), and (d) Nb-doped ($3.3 \times 10^{20} \text{ cm}^{-3}$) SrTiO_3 bulk single crystals.

κ with increasing temperature. It should be noted that the Z of both La-STO and Nb-STO increased with increasing carrier concentration and the largest ZT of 0.27 at 1073 K was attained in La- $[8.4 \times 10^{20} \text{ cm}^{-3}]$ doped STO which has the largest carrier concentration in all samples. This observation is consistent with our view that heavily doped degenerate semiconductors with large m^* of carriers should demonstrate high thermoelectric performance.

SUMMARY

We clarified herein intrinsic thermoelectric performance of heavily La- and Nb-doped SrTiO_3 bulk single crystals and effect of La- and Nb-doping upon carrier effective mass (m^*). The temperature dependence of μ and S changed at $\sim 750 \text{ K}$ in all samples, indicating that the dominant carrier scattering mechanism changes with increasing temperature from a coupled scattering by polar optical phonons and acoustic phonons to mere acoustic phonon scattering. The κ of the samples, which was similar to that of undoped SrTiO_3 single crystal at room temperature, decreased proportionally to T^{-1} , indicating that the lattice thermal conduction occurs predominantly. The m^* of the Nb-doped STO ($m^* = 7.3\text{--}7.7 m_0$) is larger than that of La-doped STO ($m^* = 6.0\text{--}6.6 m_0$).

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