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Thermoelectric properties of reduced and La-doped single-crystalline $SrTiO_3$

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Abstract

The thermoelectric properties of single-crystalline reduced and La-doped $SrTiO_3$ were investigated along the [1 0 0]-axis from room temperature to 773 K. The reduced sample showed lower electrical conductivity and thermal conductivity, which indicated that oxygen vacancies acted as strong scattering centers for both electrons and phonons. The thermal conductivity decreased about 40% by the reduction at room temperature. The sound velocity measured at room temperature was almost unaffected by the reductions and La doping, thus the decrease was caused only by the decrease of the mean free path. The reduced and La-doped sample showed almost the same figure of merit in the temperature range considered.

Keywords: Perovskites; Point defects; Electronic transport; Heat conduction

1. Introduction

Thermoelectric conversion is a direct conversion between heat and electric energy, and the efficiency increases with the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature. Since the discovery of $NaCo_2O_4$ [1], the oxide materials have been investigated as non-toxic, low-cost thermoelectric materials. Some layered p-type cobalt oxides showed a large figure of merit that is comparable to conventional materials [2,3]. Also n-type oxide materials has been studied; $CaMnO_3$ [4], Al-doped ZnO [5], (Ba, Sr)PbO_3 [6], and $(ZnO)_mIn_2O_3$ [7] were discovered as a candidate materials.

$SrTiO_3$ is one of the most common ceramics and its transport properties have been intensively studied [8–14]. The high mobility and the large effective mass cause the high electrical conductivity with large negative Seebeck coefficient, which make it prospective as an n-type oxide thermoelectric material. Recently, it was reported that a La-doped $SrTiO_3$ single crystal had a high power factor at room temperature, 28–36 mW/mK^2 [14]. This value is comparable to those of conventional materials such as Bi_2Te_3. However, the high thermal conductivity decreases the figure of merit, thus some substitution has been attempted to improve the situation [15,16]. $SrTiO_3$ is a band insulator, thus reduction and high valence cation doping should be done for carrier generation. Obara et al. reported that Y doping is desirable for improvement of the figure of merit [16]. The electrical properties of La- and Nb-doped single-crystalline $SrTiO_3$ have been investigated and it was reported that Nb doping increases the effective mass [17]. The reduction produced oxygen vacancies, which also generate carrier electrons. As far as we know, the thermoelectric properties of reduced $SrTiO_3$ have not been investigated and compared to those of doped samples. Oxygen vacancies are common defects for oxide materials and are known to affect both their electrical and thermal properties. In this paper, the thermoelectric properties of single-crystalline reduced and La-doped $SrTiO_3$ were investigated from room temperature to 773 K and the differences were discussed.

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Table 1
Heating condition and lattice parameter

Sample	Heating condition	Lattice parameter (nm)
sc-1	10^{-5} Pa, 1173 K, 96 h	0.3904
sc-2	H_2 flow, 1273 K, 12 h	0.3905
sc-3	Ar flow, 1873 K, 12 h	0.3906
pc-3	Ar flow, 1873 K, 12 h	0.3907
$Sr_{0.95}La_{0.05}TiO_3$	–	0.3907

2. Experimental

Single-crystalline substrates of $SrTiO_3$ (15 mm × 15 mm × 1 mm) and rod-shaped La-doped $SrTiO_3$ of 15 mm in length and 10 mm in diameter with a doping level of 3.73 wt.% (5 at.%) were obtained from Furuuchi Chemical Co. The $SrTiO_3$ substrates were reduced by heating at different conditions as described in Table 1, considering the low value of the oxygen diffusion constant [18]. The surfaces of the strongly reduced samples were coated by deposited metal strontium and titanium. They were cut and polished by emery paper for measurements. For comparison, a reduced polycrystalline sample was prepared by a solid-state reaction of 99.9% purity $CaCO_3$ and TiO_2. This sample was sintered at 1873 K in air for 24 h and reduced under the same condition as the sc-3 sample listed in Table 1. The crystal structure and lattice parameter were evaluated from X-ray diffraction data using Cu Kα radiation. The electrical conductivity and the Seebeck coefficient were simultaneously measured in a helium atmosphere up to 773 K, using a ULVAC ZEM-1 equipment. The thermal conductivity was evaluated as the product of the thermal diffusivity, the heat capacity, and the experimental density at room temperature. The thermal diffusivity was measured by a laser flash method using a ULVAC TC-7000 equipment in vacuum. The generated oxygen vacancies were supposed to be small in number for our sample, thus the literature data of $SrTiO_3$ [19] was used for the heat capacity. In addition to the thermoelectric properties, the longitudinal and transverse sound velocities were measured by an ultrasonic pulse-echo method using a NIHON MATECH Echometer 1062 at room temperature. All the properties of single-crystalline samples were measured along the [1 0 0]-axis of $SrTiO_3$. The dimensionless figure of merit was calculated from the above-mentioned values.

3. Results and discussions

The reduced samples have dark blue colors similar to the La-doped sample. All the samples were cubic, belonging to space group *Pm*3*m*. There were no XRD peaks corresponding to the tetragonal phase as reported for strongly oxygen-deficient and quenched $SrTiO_3$ [20]. The lattice parameter calculated from XRD pattern is shown in Table 1. The reductions and La doping slightly increased the lattice constant because of the generated Ti^{3+}. The oxygen vacancies were

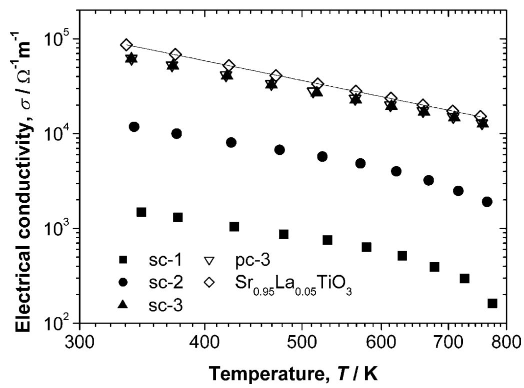

Fig. 1. Temperature dependence of electrical conductivity. The line was fitted to $Sr_{0.95}La_{0.05}TiO_3$ single crystal, changing with a slope of $T^{-2.1}$.

doubly ionized [21] and formed two Ti^{3+}, thus the carrier concentration should be related to the lattice parameter.

The temperature dependence of the Seebeck coefficient is shown in Fig. 1. The Seebeck coefficient of all the samples was negative and decreased proportionally to increasing the temperature. This metallic behavior is in concord with results described in previous reports. The absolute values can be arranged in the sequence sc-1 > sc-2 > sc-3, corresponding to the change of the lattice parameter. The sc-3-, pc-3-, and La-doped samples had almost the same value of the Seebeck coefficient. It indicated that the three samples had a similar carrier concentration, about $8 \times 10^{26}\,m^{-3}$ for $Sr_{0.95}La_{0.05}TiO_3$.

The temperature dependence of the electrical conductivity is shown in Fig. 2. The electrical conductivity showed metallic behavior like the Seebeck coefficient, and decreased with temperature proportionally to $T^{-2.1}$. The power of −2.1 is intermediate to values reported elsewhere: −2.7 to −3.2 [8] at 100–300 K and −1.6 at high temperature [13]. The differences in thermal behavior can be explained by the relative importance of kT relative to E_F, where k, E_F are the Boltzmann constant and the Fermi energy, respectively. The temperature dependence of the electrical properties are same for all the samples, indicating that main scattering mechanism was same for reduced and La-doped samples.

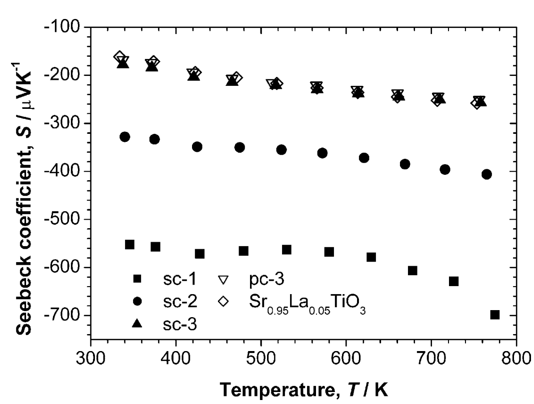

Fig. 2. Temperature dependence of Seebeck coefficient.