Enhanced Phonon Scattering by Oxygen Defects in Metal Oxides

Hideaki Hirobe[1] and Michitaka Ohtaki[1,2]

[1]Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580,
Fax: 092-583-8835, e-mail: ohtaki@mm.kyushu-u.ac.jp
[2]CREST, Japan Science and Technology Agency, Kawaguchi, Saitama, 332-0012

The thermal diffusivity, α, of $SrCo_{1-x}Fe_xO_{3-\delta}$ was investigated in terms of order-disorder transition of oxygen vacancies accompanying with the brownmillerite-perovskite structural phase transition. On quenching the sample after holding at various temperature T_q in air, the α values of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$ measured at room temperature decreased drastically with increasing T_q. Re-annealing of the sample at 1200°C in air recovered the initial values of α, ρ, and C_p. These results suggest that randomly distributed oxygen vacancies in the perovskite structure of the high-temperature phase effectively enhance the phonon scattering.

Key words: oxide thermoelectric material, thermal conductivity, perovskite, brownmillerite, oxygen nonstoichiometry

1. INTRODUCTION

Thermoelectric conversion is a technology that can directly convert heat energy into electricity by the Seebeck effect or the Peltier effect of semiconductors. Thermoelectric power generation is unique in the following aspects: able to obtain electrical power even from a minimal temperature difference; no noise, no vibration, no emission, no moving parts; small size, light weight; outstandingly high reliability. To solve environmental and energy problems and the global warming issues, the thermoelectric conversion attracts much attention as an energy-recycling technology which can upgrade the thinly distributed waste heat energy to electric energy.

The thermoelectric materials now in practical use mainly consist of heavy elements like Bi, Te, Se and Pb. They have many problems such as low durability and high toxicity in high temperature atmospheres. On the other hand, oxides are stable even at high temperature, highly reliable, and much less costly. Although oxides had been considered to be unsuitable for thermoelectric materials due to their low carrier mobility, recent discoveries of oxide thermoelectric materials and their rapidly increasing performance have revealed the limitations of the conventional material design strategy [1-5].

The performance of thermoelectric power generation is estimated from the figure of merit, Z, represented as $Z=S^2\sigma/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. A large S, a high σ, and a low κ are therefore required simultaneously. However, $\kappa = \kappa_{el} + \kappa_{ph}$, and κ_{el}, the thermal conductivity by carriers, is generally proportional to σ according to the Wiedemann-Franz law; $\kappa_{el} = L\sigma T$, where L is the Lorenz number. It is important to reduce κ_{ph}, the thermal conductivity due to the lattice vibrations.

A p-type thermoelectric oxide $NaCo_2O_4$, which exhibits the highest performance in the oxide thermoelectric materials at present, has the thermal conductivity lower than that of quartz glass. Selective phonon scattering due to the partially deficient disordered Na layers spatially distant from the carrier-conducting CoO_2 layers, is believed to be responsible for such a low thermal conductivity. Nevertheless, any experimental evidence has not been reported so far.

Many metal oxides lose oxygen at high temperature. In the field of oxide semiconductors, oxygen deficiency at high temperature is an inevitable phenomenon, and its influence on the carrier concentrations must always be taken into consideration. Although the relation between the oxygen partial pressure and the electrical conductivity has been extensively studied for many years, the relation between the oxygen defects and the thermal properties has scarcely been known.

A perovskite-type oxide $SrCo_{1-x}Fe_xO_{3-\delta}$ shows a large oxygen nonstoichiometry. This material is known to show an order-disorder transition of oxygen vacancies depending on the composition x and temperature. The transition is observed between the high temperature cubic perovskite structure in which the oxygen vacancies are distributed randomly, and the low

temperature orthorhombic brownmillerite structure in which the oxygen vacancies are ordered in the (110) direction. The brownmillerite-to-perovskite transition temperature decreases with increasing the amount of substitution at the B site, x, and the perovskite structure stabilizes at room temperature at x=0.5~0.6 [6-9].

This work aims at investigating the phonon scattering by the oxide ion defects, which is inevitable for oxide thermoelectric materials at high temperature.

On order-disorder transitions of the oxygen vacancies, only the arrangement of the anion sublattice changes with remaining the arrangement of the cations ions unchanged, being contrasting to $NaCo_2O_4$.

In this paper, compositional and temperature dependences of the thermal conductivity of $SrCo_{1-x}Fe_xO_{3-\delta}$ are investigated in order to examine the possibility of selective phonon scattering by the order-disorder transition of oxygen defects.

2. EXPERIMENTAL

2.1 Sample preparation. $SrCo_{1-x}Fe_xO_{3-\delta}$ was prepared from nitrate or acetates of constituent metals. An aqueous solution dissolving the appropriate amounts of the metal salt was evaporated to dryness by heating up to about 350°C, followed by calcining at 850°C for 5 h in air. The product was ground in an agate mortar and the powder was pressed into a disk under a pressure of 120 MPa, and sintered at 1200°C for 5 h following by furnace cooling [6][7]. The crystal structure of the final product was identified by X-ray diffraction analysis (XRD) with the CuKα radiation.

2.2 Measurement of thermal conductivity. The thermal conductivity was measured by the laser-flash technique in vacuum on an LFA-502 (Kyoto Electronics Manufacturing). The disk sample was cut into a square plate (5 x 5 x 1 mm) and both faces were blackened using a carbon spray. The thermal diffusivity α and the specific heat C_p were measured, and the thermal conductivity κ was obtained by multiplying these values with the density ρ as $\kappa = \alpha \cdot C_p \cdot \rho$ (ρ was the bulk density measured by the dimensions and the weight of the samples).

2.3 Measurement of oxygen nonstoichiometry. Based on the experimental procedure by Liu et al. [8], the thermogravimetric analysis was carried out to determine the equilibrium nonstoichiometry of oxygen in $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$ as a function of temperature within the range of 300°C ≤ T ≤ 800°C. All of the samples for the thermogravimetric studies were pretreated by the following procedure. Samples of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$ were heated in oxygen at 900°C for 1 h, cooled to a given temperature and held for 24 h, then quenched in liquid nitrogen.

The oxygen content of the samples was determined by hydrogen reduction method [8].

The oxygen stoichiometry (3-δ) of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$ was determined by reducing the samples in a mixed gas of 5% H_2 and 95% N_2 at a flow rate of 50 ml/min. Samples were first heated in a thermobalance at 110°C for 2 h to remove absorbed water, and then heated at a rate of 2°C /min to 900°C and held until constant weight was obtained. The oxygen content was calculated from the weight loss by assuming that the final products were SrO, Co, and Fe metals.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the obtained samples. The brownmillerite-perovskite phase transition temperature of $SrCo_{1-x}Fe_xO_{3-\delta}$ decreases with increasing amount of x. The brownmillerite structure slightly remained at x=0.3, the samples were single phase of the perovskite structure at x=0.6.
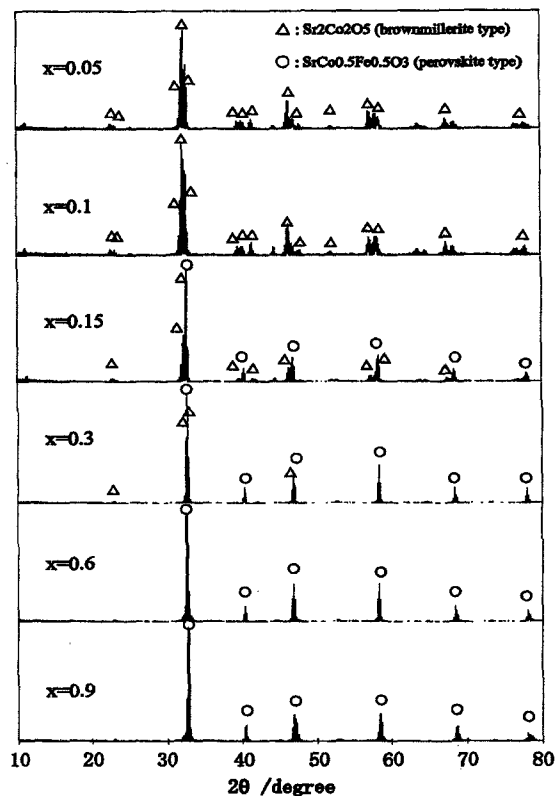

Fig. 1. The XRD patterns of $SrCo_{1-x}Fe_xO_{3-\delta}$. (X=0.05, 0.1, 0.15, 0.3, 0.6 and 0.9)

As shown in the section 2.2, the thermal conductivity is derived from three experimental values, α, C_p and ρ. In order to discuss the phonon scattering behavior more directly, we will focus on the thermal diffusivity, α, which is directly measured by the laser flash technique and is free from the influence of C_p, and ρ. Figure 2 shows the temperature dependence of the thermal
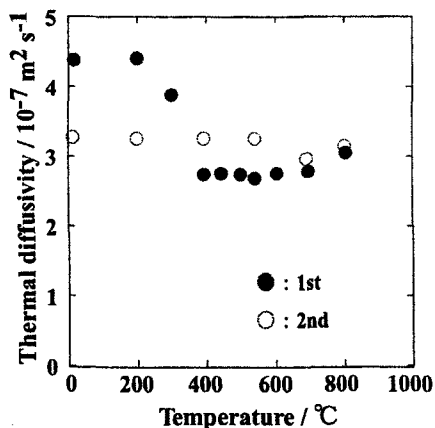
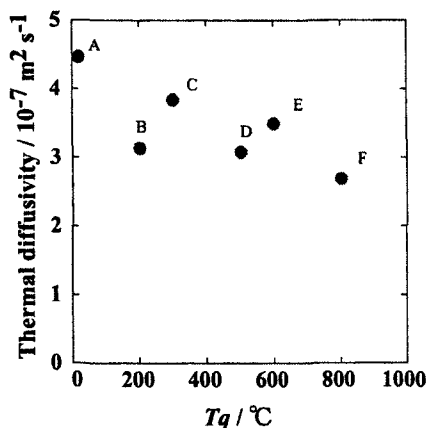**Fig. 2.** The thermal diffusivity of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$. Open circles represent the 2nd measurement.

Fig. 3. The thermal diffusivity of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$ as a function of quenching temperature T_q. Samples A to F are different samples cut out from one sample pellet.

diffusivity of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$. The open symbols show the results of the 2nd run subsequently carried out after the 1st run. One can see an abrupt decrease of α in the 1st run at about 300°C. This behavior cannot be explained by the T^{-1} dependence usually observed for the phonon thermal conduction, and suggests a possible phase transition from ordered to random phase. Unlike the 1st run, the α values at the 2nd run were much lower at room temperature, and converged to the same value to the 1st run at 800°C with no abrupt decrease. This behavior would be consistent if one can assume that the sample cooled in vacuum after the 1st run would retain the high temperature phase down to room temperature without recovering oxygen desorbed at high temperature during the 1st run; the frozen high temperature phase which may have a random structure would be seen even at room temperature at a low α value similar to those observed at high temperature.

Figure 3 shows the thermal diffusivity of quenched samples of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$. The six sample pieces were cut out from one pellet and quenched in liquid nitrogen
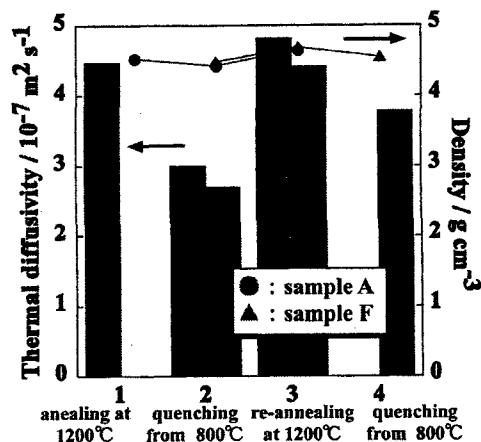
Fig. 4. The thermal diffusivity and density of the samples A and F in Fig.3. The samples were treated by the following procedure; annealing at 1200°C (1) → quenching from 800°C (2) → re-annealing at 1200°C (3) → quenching from 800°C (4).
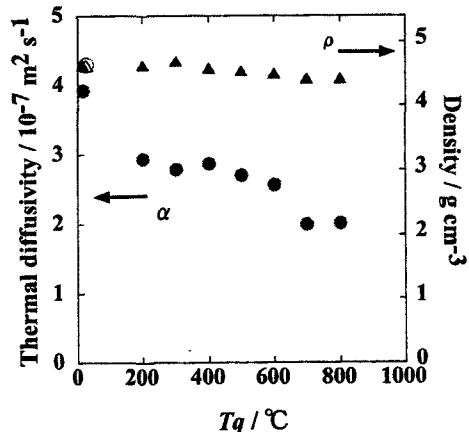

Fig. 5. The thermal diffusivity of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$ as a function of the quenching temperature T_q. Being different from Fig. 3, one sample piece was used throughout the experiment.

after holdling at the given temperature in air. The thermal diffusivity was measured at room temperature. Since each sample pieces were not completely the same, the results may contain experimental errors varying over the samples. Even so, we can clearly see a decrease in α with increasing quenched temperature, T_q. It is considered that the phonons were scattered more effectively in the high temperature random structure frozen down to room temperature. To confirm this, the samples A (slowly cooled from 1200°C) and F (quenched from 800°C) were subsequently subject to the following cycle: annealing at 1200°C (followed by slow cooling) → quenching from 800°C → re-annealing at 1200°C → quenching from 800°C. The results of the measurements of α and ρ after each step are shown in Figure 4.

The sample A, which was obtained by annealing at 1200°C, showed a large decrease in α after quenching from 800°C. However, after re-annealing at 1200°C in air, α returned to the initial value. On the other hand, the α values of the sample F, obtained by quenching from 800°C, increased largely after re-annealing at 1200°C, and decreased again after the 2nd quenching. In addition, even the changes in ρ were small, a reversible behavior was also observed for ρ. The reversible behavior of α and ρ was considered to be caused by reversible absorption and desorption of oxygen.

Figure 5 shows the thermal diffusivity and density of $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$ repeatedly measured for a single sample piece. An open circle and open triangle represent the results after re-annealing at 1200°C, which was subsequently carried out after the concecutive measurements with increasing T_q from 200°C to 800°C with an increment of 200°C. As obviously seen in Figure 4, a clear decrease in α with increasing T_q occurs. Moreover, α and ρ recovered the initial values after re-annealing at 1200°C. Because the changes in α (and ρ) were completely reversible in air but irreversible in vacuum (see Fig. 2), the reversible absorption and desorption of oxygen must be responsible for the phenomena, and it is strongly suggested that the random arrangement of the oxygen sublattice in the high temperature perovskite structures scatters phonon effectively.

The oxygen content in $SrCo_{0.7}Fe_{0.3}O_{3-\delta}$ decreased with increasing temperature, and for example, $3-\delta=2.78$ at 400°C and 2.56 at 600°C.

Since formal oxygen content, $3-\delta$, of 2.5 roughly corresponds to the lower limit of the oxygen content, further decrease in $3-\delta$ at higher temperatures is expected to be negligible. The large decrease in α at the temperature higher than 600°C seen in Figure 5 therefore cannot be explained by a further oxygen defects, and reversible structural changes of the oxygen sublattice may provide a plausible explanation.

4. CONCLUSIONS

Reduction of the thermal diffusivity, α (and hence the thermal conductivity), of $SrCo_{1-x}Fe_xO_{3-\delta}$ is investigated with respect to phonon scattering by the oxygen defects. The thermal diffusivity showed an abrupt decrease in vacuum. The dependence of α on the oxygen partial pressure and temperature shows that the changes in the thermal diffusivity are reversible in the oxygen-containing atmospheres, and suggests that the randomly distributed oxygen defects would be responsible for the reduction of the thermal diffusivity. The order-disorder transition of the oxygen sublattice is thereby reported for the first time as an effective scattering center for phonons.

5. REFERENCES

[1] M. Ohtaki, et al., *Proc. 12th Int. Conf. Thermoelectrics*, p.212 (1993).

[2] H. Ohta, et al., *J. Am. Ceram. Soc.*, **79**, 2193 (1996).

[3] M. Ohtaki, et al., *J. Appl. Phys.*, **79**, 1816 (1996).

[4] I. Terasaki, et al., *Phys. Rev.* **B,56**, R12685 (1997).

[5] W. Koshibae, et al., *Phys. Rev.* **B,62**, 6869 (2000).

[6] H. Kusaba, G. Sakai, K.Shimanoe, N. Miura, N. Yamazoe, *Solid State Ionics*, **152**, 689 (2002).

[7] H. Kusaba, G. Sakai, N. Miura, N. Yamazoe, *Ionics*, **6**, 47 (2000).

[8] H. Kruidhof, H. J. M. Bouwmeester, R. H. E. v. Doorn, A. J. Burggraaf, *Solid State Ionics*, **63-65**, 816 (1993).

[9] N. Grunbaum, L. Mogni, F. Prado, A. Caneiro, *J. Solid State Chem*, **177**, 2350 (2004).

[10] L. M. Liu, T. H. Lee, L. Qiu, Y. L. Yang, A. L. Jacobson, *Mater. Res. Bull.*, **31**, 29 (1996).