Paper

Thermoelectric Properties of *P*-Type BaSnO₃ Ceramics Doped with Cobalt

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SYNOPSIS

Perovskite-type BaSn_{1-x}Co_xO_{3-δ} ceramics were prepared by a solid state reaction, and the electrical conductivity σ and Seebeck coefficient S were measured in the temperature range 373–1073 K to evaluate the thermoelectric power factors $S^2\sigma$. Dense ceramics with relative densities of ~98% were obtained by firing at 1573 K for the BaSn_{1-x}Co_xO_{3-δ} with $x = 0.03$ –0.15. Temperature dependence of σ and S showed that the BaSn_{1-x}Co_xO_{3-δ} ceramics with $x = 0.03$ –0.15 were *p*-type semiconductors. A possible origin of the *p*-type conduction is hopping of holes between localized states of Co ions. The $S^2\sigma$ values were in the orders of 10^{-11} – 10^{-7} Wm⁻¹K⁻² and the highest value was 2.7×10^{-7} Wm⁻¹K⁻² at 1073 K for $x = 0.15$.

KEY WORDS

BaSnO₃, perovskite, electrical conductivity, Seebeck coefficient, thermoelectric properties

1 Introduction

Thermoelectric energy conversion is a very important technology for effective utilization of waste heat. The key issue for the technology is to develop thermoelectric oxide ceramics having performance high enough to convert waste heat from incinerators or combustion engines into electricity^{1,2)}. Thermoelectric performance of a material is evaluated by the figure of merit Z expressed by the equation $Z = S^2\sigma/\kappa$, where S , σ , κ are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. The power factor $S^2\sigma$, instead of Z , is frequently estimated for the plain evaluation of the thermoelectric performance.

Barium stannate, BaSnO₃, is a simple cubic perovskite and an electrical insulator with a wide band gap of 3.1 eV³⁻⁶⁾. The barium stannate is known to become an *n*-type conductor by doping with La or Sb and the electrical properties have been investigated in previous studies⁷⁻¹³⁾. As a candidate of thermoelectric oxide ceramics, the barium stannate has several advantages such as manufacturing ease, chemical stability, and thermal stability at high temperatures. We reported thermoelectric properties of La-doped BaSnO₃ ceramics exhibiting *n*-type degenerate semiconducting behavior at high temperatures¹⁴⁾. The

Ba_{0.99}La_{0.01}SnO₃ ceramic showed power factors of 2×10^{-4} – 3×10^{-4} Wm⁻¹K⁻² at temperatures 773–1073 K¹⁴⁾. In addition to the *n*-type thermoelectric properties, it is worth investigating thermoelectric properties of *p*-type BaSnO₃-based ceramics, since combination of *n*-type and *p*-type oxides consisting of the same mother phase has some advantages such as equal thermal expansion coefficient when used as a thermoelectric device. Parkash *et al.*¹⁵⁾ reported that BaSnO₃ ceramics doped with cobalt showed *p*-type conductivity and the conduction was due to hopping of charge carriers between localized states such as Co²⁺ and Co³⁺, which were formed with compensation for loss of oxygen during the sintering. However, the thermoelectric power factors were not reported in the paper.

In this study, dense ceramics of BaSn_{1-x}Co_xO_{3-δ} were prepared by a solid state reaction, and the electrical conductivity and Seebeck coefficient were measured at high temperatures to evaluate the power factors.

2 Experimental

Perovskite-type BaSn_{1-x}Co_xO_{3-δ} ceramics were prepared by a solid state reaction. Reagent powders of BaCO₃ (99.9%) (Wako Pure Chemical Industries, Ltd.), SnO₂ (99.9%) (Kojundo Chemical Laboratory Co., Ltd.), and Co₃O₄ (99.9%)

(Kojundo Chemical Laboratory Co., Ltd.) were weighed stoichiometrically and mixed thoroughly with ethanol. The mixed powder was pressed into a disc and calcined at 1273 K for 6 h in air flow. The disc was ground and pressed again at a pressure of 200 MPa using a cold isostatic press. The disc was buried in the calcined powder and fired at 1273–1673 K for 3 h in air flow.

To identify the obtained phases and evaluate the lattice parameter of the perovskite phase, X-ray powder diffraction (XRD) patterns were measured with $\text{CuK}\alpha$ radiation (Rigaku, Ultima-III, 40 kV, 40 mA). Relative density of the ceramics was estimated as a ratio of the bulk density to the theoretical one; the bulk density was estimated from the mass and volume of the ceramics, while the theoretical one was from the lattice parameter assuming the compositions as $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-x/2}$. Microstructure of the ceramics was observed by scanning electron microscopy (JEOL JSM-6701F). Diffuse reflectance spectra were measured for the powdered samples of the ceramics in the wavelength range from 240 nm to 800 nm using a spectrophotometer (Hitachi U-3900H). MgO powder was used as a reference. Kubelka-Munk (KM) function spectra

were calculated using the equation $f(R) = (1-R)^2/2R$, where $f(R)$ is the KM function and R is the diffuse reflectance, respectively. Electrical conductivity and Seebeck coefficient were measured at several steady temperatures from 1073 K to 373 K in air. The electrical conductivity was measured by a direct current (dc) four-probe method. The Seebeck coefficient was evaluated by estimating the linear gradient of $\Delta V/\Delta T$, where ΔV and ΔT are the thermoelectromotive force and temperature difference between the two ends of a sample measured using Pt leads and Pt/Pt-Rh thermocouples, respectively, with a correction of the thermopower of platinum¹⁶⁾.

3 Results and discussion

Samples of $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ with $x = 0.00$ –0.60 were prepared. Fig. 1 shows XRD patterns for the ceramics with $x = 0.00$ –0.20 after sintering at 1573 K for 3 h in air flow. The XRD patterns for the ceramics with $x = 0.00$ –0.15 were completely indexed on the basis of a simple cubic lattice, while that with $x = 0.20$ showed an additional peak due to an impurity phase as indicated by an arrow. The intensity of this peak increased with increasing Co content from $x = 0.20$ to $x = 0.60$. Fig. 2 shows Co content dependence of the lattice parameter a . The lattice parameter decreased with increasing Co content, indicating systematical substitution of the Co ions at the Sn site up to $x = 0.15$. The relative density of the BaSnO_3 was 52 %, while those of the Co-doped ceramics with $x = 0.03$ –0.15 were ~ 98 %. Therefore, the dense ceramics of the perovskite-type $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ were obtained for $x = 0.03$ –0.15. Fig. 3 shows an FE-SEM image for a polished surface of a

Fig.1 X-ray powder diffraction patterns for the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics with $x = 0.00$ –0.20 after firing at 1573 K for 3 h in air flow. The arrow indicates a diffraction peak due to an impurity phase.

Fig.2 Co content dependence of the lattice parameter a for the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics with $x = 0.00$ –0.15.

Fig.3 FE-SEM image for a polished surface of a BaSn_{0.90}Co_{0.10}O_{3-δ} ceramic.

Fig.4 Firing temperature dependence of the relative density for the BaSn_{1-x}Co_xO_{3-δ} ceramics with $x = 0.03$ and 0.05 .

BaSn_{0.90}Co_{0.10}O_{3-δ} ceramic. The ceramic had a well-densified structure consisting of grains with sub-microns in size.

Fig. 4 shows firing temperature dependence of the relative density after firing in the temperature range 1273–1673 K for the samples with $x = 0.03$ and 0.05 . All the samples plotted in the figure were the perovskite-type single phases. The relative density increased with increasing firing temperature and reached to 95% after firing at 1523 K for both the samples. Thus, the samples doped with a small amount of Co ions were densified by firing at high temperatures, but the non-doped BaSnO₃ was not densified

Fig.5 Kubelka-Munk function spectra for the powdered samples of the BaSn_{1-x}Co_xO_{3-δ} ceramics. The spectra were obtained from the diffuse reflectance spectra which were measured with MgO powder as a reference.

even after firing at temperatures up to 1673 K. Since all the Co-doped samples with $x = 0.03$ – 0.15 became the perovskite-type single phases by the calcinations at 1273 K, it is considered that the densification during the firing was promoted by the solid state reaction among the BaSn_{1-x}Co_xO_{3-δ} particles, which might be activated by active diffusion/migration of the ions due to the presence of oxygen vacancies.

Fig. 5 shows KM function spectra for the powdered samples of the BaSn_{1-x}Co_xO_{3-δ} ceramics with $x = 0.00$ – 0.15 . An optical absorption edge was clearly observed at ~ 3 eV for the non-doped BaSnO₃, corresponding to the optical band gap between the valence band (VB) composed of O2p nonbonding orbitals and the conduction band (CB) composed of Sn5s–O2p σ^* antibonding orbitals^{5,6}. For the BaSn_{1-x}Co_xO_{3-δ} with $x = 0.03$ – 0.15 , a weaker absorption band was observed in the energy range 1.5–3.0 eV. The dark brown color of the Co-doped samples originated from this absorption. Energy levels of $3d\ t_{2g}$ and e_g of the Co ions are located in the band gap between the VB and CB. If the Co ions have a mixed valence state of Co²⁺ and Co³⁺ in a low spin state, charge transfer transition from Co²⁺ ($t_{2g}^6 e_g^1$) to Co³⁺ ($t_{2g}^6 e_g^0$) as well as d – d transition in each Co ion is responsible for the weak absorption.

Fig. 6 shows reciprocal temperature dependence of the electrical conductivity σ for the BaSn_{1-x}Co_xO_{3-δ} ceramics with $x = 0.03$ – 0.15 . The σ values were 10^0 – 10^2 Sm⁻¹ in the

Fig.6 Reciprocal temperature dependence of the electrical conductivity σ for the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics. The inset shows the $T^{-1/4}$ dependence of $\log \sigma$.

measured temperature range and increased with increasing temperature for all the ceramics, indicating that all the ceramics were semiconductors. The σ values also increased with increasing Co content from $x=0.03$ to 0.15 . The inset shows the plots of $\log \sigma$ vs $T^{-1/4}$. The plots showed good linearity for all the ceramics. This linearity suggests that the electrical conduction in the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ may be due to a variable range hopping (VRH) of the carriers. Fig. 7 shows reciprocal temperature dependence of the Seebeck coefficient S for the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics with $x=0.03$ – 0.15 . The signs of the S values were positive. The S values showed nearly equal temperature dependence among the ceramics except for the data at high temperatures for $x=0.15$; The temperature dependence of S was small at temperatures higher than ~ 623 K, but the S values decreased with decreasing temperature at temperatures lower than ~ 623 K, and the values of some samples changed to negative at ~ 373 K.

Electrical conduction behavior of the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics is discussed. The p -type electrical conduction of the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ is clearly related to the doped Co ions, since non-doped BaSnO_3 is insulating. The observed VRH-like behavior suggests the presence of some localized states in the band gap. It is considered that the observed electrical conducting behavior is attributed to hopping conduction between Co^{2+} and Co^{3+} ions, as Parkash *et al.*¹⁵⁾

Fig.7 Reciprocal temperature dependence of the Seebeck coefficient S for the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics.

also pointed out. Koshibae *et al.*¹⁷⁾ showed Seebeck coefficient for cobalt oxides having a mixed valence state of Co ions. According to the theory, S for electronic transport between Co^{2+} and Co^{3+} is written as

$$S = \frac{k_B}{e} \ln \frac{g_3 [\text{Co}^{2+}]}{g_2 [\text{Co}^{3+}]} \quad (1)$$

where e and k_B are the electronic charge and Boltzmann constant, respectively, and $\frac{k_B}{e}$ gives $86.17 \mu\text{VK}^{-1}$. The $[\text{Co}^{2+}]$ and $[\text{Co}^{3+}]$ express the concentrations of Co^{2+} and Co^{3+} ions to the total Co ions, respectively, and the g_2 and g_3 are the numbers of configuration determined by the spin and orbital degrees of freedom of the Co^{2+} and Co^{3+} ions, respectively. The equation (1) indicates that S does not depend on the Co concentration x but depends on the ratio of $\frac{[\text{Co}^{2+}]}{[\text{Co}^{3+}]}$, which is determined by oxidation-reduction equilibrium of the Co ions at each temperature. The theory agrees well with the experimental results that S showed no significant dependence on the Co concentration in the range $x=0.03$ – 0.15 . On the other hand, S showed clear temperature dependence in the temperature range 373 – 623 K as shown in Fig. 6. According to the theory, the temperature dependence of S is qualitatively explained by the variation of the $\frac{[\text{Co}^{2+}]}{[\text{Co}^{3+}]}$ ratio. Since oxygen vacancies are generally easy to form at elevated temperatures, Co^{2+} concentration increases with increasing temperature due to the reduction of Co^{3+} and the increase in $[\text{Co}^{2+}]$ results in the increase of S . Moreover, the change in the sign of S to negative at ~ 373 K is caused

by the decrease in $[\text{Co}^{2+}]$ due to the oxidation of Co^{2+} with decreasing temperature.

Fig. 8 shows temperature dependence of the power factor $S^2\sigma$ for the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics with $x = 0.03-0.15$. The power factors increased with increasing temperature for all the ceramics, and also increased gradually with increasing Co content at high temperatures reflecting the Co content dependence of the electrical conductivity. The maximum value was $2.7 \times 10^{-7} \text{ Wm}^{-1}\text{K}^{-2}$ at 1073 K for $x = 0.15$. Although the power factors for the present $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics were quite low, the *p*-type conductivity may be useful when combined with *n*-type BaSnO_3 ceramics as a thermoelectric device.

4 Conclusions

Perovskite-type $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics were prepared by a solid state reaction, and the electrical conductivity σ and Seebeck coefficient S were measured in the temperature range 373–1073 K to evaluate the power factors $S^2\sigma$.

- (1) Dense ceramics with the relative densities of $\sim 98\%$ were obtained for the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ with $x = 0.03-0.15$.
- (2) Temperature dependence of σ and S showed that the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics with $x = 0.03-0.15$ were *p*-type semiconductors.
- (3) Hopping of holes between localized states of Co ions was proposed as a possible origin of the *p*-type conduction.
- (4) The $S^2\sigma$ values were in the orders of $10^{-11}-10^{-7} \text{ Wm}^{-1}\text{K}^{-2}$ and the highest value was $2.7 \times 10^{-7} \text{ Wm}^{-1}\text{K}^{-2}$ at 1073 K for $x = 0.15$.

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Fig. 8 Temperature dependence of the power factor $S^2\sigma$ for the $\text{BaSn}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ ceramics.

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