Thermoelectric Properties of CuO-Added AgSbO₃ Ceramics
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The electrical conductivity and Seebeck coefficients of AgSbO₃ with a defect pyrochlore structure were investigated for evaluation as thermoelectric material. In sintering AgSbO₃, CuO was used as a sintering aid, and Cu substituted for Ag in the ceramic during the sintering. AgSbO₃ is an n-type semiconductor, and the addition of Cu increased electrical conductivity and decreased the absolute value of the Seebeck coefficient. The power factor of the 2.5% CuO-added sample was $7.24 \times 10^{-4}$ W m⁻¹ K⁻¹ at 800°C. This value is one of the highest observed in oxide materials.

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1. Introduction

Thermoelectric power generation utilizes thermoelectric devices to convert thermal energy to electric energy using the Seebeck effect. These systems are expected to generate clean energy without any adverse environmental effects, such as the release of exhaust gases or noise pollution caused by driving parts. Because of their thermal durability and chemical stability, oxide thermoelectric materials are better than chalcogenide materials such as Bi₂Te₃, which is one of the more effective materials for thermoelectric energy conversion. Until recently, oxides have been thought to have insufficient conversion efficiencies because of their low carrier mobilities. In 1997, it was found that the layer-structured oxide NaCo₂O₄ was a highly effective thermoelectric material, and the dimensionless figure of merit $Z$ of single crystal of NaCo₂O₄ was shown to exceed unity, which is the standard value for practical applications. Ca₂CoO₄ and related materials were also found to be excellent thermoelectric materials. These new oxide thermoelectric materials are all p-type semiconductors. In general, n-type materials are not as effective as p-type oxides, although some materials such as Zn₂In₂O₅ system homologous materials, Al-doped ZnO, and Ba₁₋ₓSrₓPbO₃, have been found to be quite effective.

AgSbO₃ has a defect pyrochlore structure comprised of linear chains of AgO₆ and SbO₆ octahedra. From this crystal structure and from the fact that both Ag⁺ and Sb⁵⁺ have 4d¹⁰ outermost electron configuration and the conduction band is formed by the wide 5d band, AgSbO₃ is expected to have high mobility and to be a suitable thermoelectric oxide. With high electrical conduction and high optical transparency, AgSbO₃ has been studied as a transparent thin film electrode. From ultraviolet photoemission spectroscopy analysis, Yasukawa et al. reported that the upper valence bands of AgSbO₃ are composed mainly of a mixture of occupied O 2p and Ag 4d orbitals. On the other hand, it was reported that the stoichiometric AgSbO₃ was identified as a channel-type Ag⁺ ion conductor, and with thermal treatment, Ag islands formed and the sample was transformed to be a predominantly electronic conductor.

In this study, sintered samples of pure and CuO-added AgSbO₃ were prepared, and electrical conductivity and Seebeck coefficients of these samples were measured for evaluation of their effectiveness as thermoelectric materials.

2. Experimental

Ag₂O (purity > 99.0%) and Sb₂O₅ (purity > 99.9%) were mixed with a 1:1 atomic ratio of Ag: Sb, and then calcined in aluminum crucibles at 900°C for 2 h. After the addition of 2.5 mass% of poly-vinyl alcohol to the calcined powders as a binder, CuO (2.5 and 5.0 mass%) was added as a sintering agent with the aim of increasing carrier concentration. The powders were mixed, shaped into bars with dimensions of about 1.5 x 4 x 20 mm, and then isostatically pressed under 100 MPa pressure at room temperature. The compact samples thus obtained were then sintered in an electric furnace at 1000°C for 4 h in a powder bed of calcined powders.

The phases in the samples were determined by X-ray diffraction analysis (XRD), and the lattice constant of AgSbO₃ phase was calculated from the 2θ values. The electrical conductivity was measured at temperatures ranging from room temperature to 900°C using the alternate current 4-probe method. Seebeck coefficients were also measured from room temperature to 800°C by measuring the thermoelectric voltage generated by the temperature gradient. The details of the measurements have been described elsewhere.

3. Results and discussion

Figure 1 shows the XRD patterns of the sintered samples. When no CuO was added, a single phase of AgSbO₃ was obtained. As CuO was added, secondary phases of CuSb₂O₄ and metallic Ag formed, the fraction of which increased with increasing quantity of CuO. This suggests that the added Cu reacted with Sb in the AgSbO₃ and formed an oxide compound (CuSb₂O₄), and the abundant Ag was crystallized as a metallic phase. The densities of the sintered samples are listed in Table 1 with lattice constant data. From the results that the density was not larger than 60% of the theoretical one without any additives, it can be concluded that AgSbO₃ is hard to sinter under normal sintering conditions, and the presence of a sintering aid is effective to some degree, since it made the sintering bodies more robust than those with no sintering aid. The main reason for this is thought to be the evaporation of Sb, since the powder bed method was effective for sintering and maintaining the composition. The change in the lattice
constant caused by the addition of CuO indicates that Cu partially substituted for Ag in AgSbO$_3$. 

**Figure 2** shows temperature dependence of electrical conductivity of the samples. AgSbO$_3$ showed semiconducting behavior with increasing conductivity with an increase in temperature. The electrical conductivity of the CuO-added samples was more than one order higher than that of pure AgSbO$_3$, and the conductivity of the 5.0% added sample was higher than that of the 2.5% sample. CuO addition resulted in a step-wise temperature dependence, which suggests multiple conduction mechanisms in these samples. **Figure 3** shows temperature dependence of Seebeck coefficients for these samples. The conduction carriers were electrons since all samples showed negative thermoelectricity. For pure AgSbO$_3$, the carriers seemed to be generated mainly by oxygen defects. However, since the temperature dependence of the Seebeck coefficient for pure AgSbO$_3$ is complicated, another mechanism appears to coexist. Since reproducibility of Seebeck data between 150 and 400°C was lower than for above 400°C, this is likely due to the absorption gas in air. Over 400°C, the absolute value of the Seebeck coefficient decreased as temperature increased, which showed that carrier concentration increased as temperature increased. This explains the temperature dependence of the electrical conductivity. For the CuO-added samples, the carriers seemed to be generated by the substitution of Cu$^{2+}$ ion for Ag$^+$ in AgSbO$_3$. The activation energy of the conductivity between 300 and 900°C of 2.5 and 5.0% CuO-added samples are 42 and 32 kJ mol$^{-1}$, respectively, which are comparable to the data for AgSbO$_3$ obtained by Wiggers et al., wherein nano-sized metallic Ag particles were dispersed. 

**Figure 4** shows temperature dependence of the thermoelectric power factors ($\alpha^2\sigma$) of the samples as a function of temperature.
Thermoelectric Properties of CuO-Added AgSbO₃ Ceramics

coefficient and electrical conductivity, $\sigma^2\alpha$, which yields the electrical contribution of thermoelectric energy conversion. If the cost of the supplied heat energy is negligibly small, this factor would be more important than the thermoelectric figure of merit, Z. For all temperatures between 100 and 800°C, the 2.5% CuO-added sample showed the highest performance as a thermoelectric material in the samples examined in this study. The temperature dependence shows that these materials are suitable for use in the high temperature region of thermoelectric conversion. At 800°C, the value of the power factor of the sample was $7.24 \times 10^{-4}$ Wm$^{-1}$K$^{-2}$, which is one of the highest values observed in oxide materials. Though thermal conductivity measurements of these materials are needed to judge usefulness for thermoelectric energy conversion, this study indicates that an optimized material of Ag–Cu–Sb–O system is the most hopeful candidate for an n-type oxide thermoelectric material.

4. Conclusions

For the sintering of AgSbO₃, CuO was used as a sintering aid. The Cu addition formed secondary phases of CuSb₂O₆ and Ag, and changed the lattice constants of AgSbO₃, which indicated that Cu substituted for Ag in AgSbO₃. With CuO addition, electrical conductivity increased and the absolute value of Seebeck coefficient decreased for AgSbO₃. This can be explained by the increase of the carrier (electron) concentration. The power factor of 2.5% CuO-added sample was $7.24 \times 10^{-4}$ Wm$^{-1}$K$^{-2}$ at 800°C. This value is one of the highest observed for oxide materials. This study also suggests that an optimized material of Ag–Cu–Sb–O system is the most hopeful candidate for an n-type oxide thermoelectric material.

References