

# Effects of Nanosized Silver Particles on Thermoelectric Properties of CuO-added AgSbO<sub>3</sub> Ceramics

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CuO addition to AgSbO<sub>3</sub> caused the deposition of Ag nanoparticles and CuSb<sub>2</sub>O<sub>6</sub> as secondary phases during sintering. A sample with 2.5mass% CuO addition showed an anomalous increase in thermoelectric power. The power factor of the specimen was  $7.24 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$ , which is one of the highest values in *n*-type oxide materials. The anomalous increase of Seebeck coefficients appears to depend on the size and distribution of the Ag nanoparticles. In this study, the preparation processes, such as when CuO was added, the sintering duration, and the amount of CuO, were controlled and varied, and the effects of the size and distribution of the silver particles were investigated. A suitable distribution of Ag particles was realized by CuO addition after AgSbO<sub>3</sub> was prepared. This means that Ag particles which were formed from decomposed AgSbO<sub>3</sub> crystals were necessary for the high performance. The effect of the sintering duration was important for the high temperature electrical conductivity which was caused by channeling between the Ag particles.

Key words: silver antimony oxide, silver particles, metal semiconductor composites, Seebeck coefficients, ceramic processing

## 1. INTRODUCTION

Oxide thermoelectric materials are excellent candidates for thermoelectric power generation since they have good thermal durability as well as chemical stability at high temperatures compared to metal alloy compounds such as Bi<sub>2</sub>Te<sub>3</sub>. Until recently, oxides have been thought to have insufficient conversion efficiencies because of their low carrier mobilities. Recently, it was found that the layered oxide NaCo<sub>2</sub>O<sub>4</sub> was a highly effective thermoelectric material [1], and the dimensionless figure of merit *ZT* of a single crystal of NaCo<sub>2</sub>O<sub>4</sub> was shown to exceed unity [2], which is the criterion for practical applications. Ca<sub>2</sub>Co<sub>2</sub>O<sub>5</sub> and related materials were also found to be excellent thermoelectric materials [3, 4]. These oxide thermoelectric materials are all *p*-type semiconductors. To date, *n*-type oxide thermoelectric materials have not been as effective as *p*-type oxides, although some materials, such as Zn-In-O system homologous materials [5, 6], Al-doped ZnO [7, 8], and Ba<sub>1-x</sub>Sr<sub>x</sub>PbO<sub>3</sub> [9], have been found to be effective to some degree.

AgSbO<sub>3</sub> has a defect pyrochlore structure comprised of linear chains of AgO<sub>6</sub> and SbO<sub>6</sub> octahedra. From this crystal structure, and from the fact that both Ag<sup>+</sup> and Sb<sup>5+</sup> have a 4d<sup>10</sup> outermost electron configuration and the conduction band is formed by the wide 5s band, AgSbO<sub>3</sub> is expected to have high mobility and to be a suitable thermoelectric oxide. With high electrical conduction and high optical transparency, AgSbO<sub>3</sub> has been studied as a transparent thin film electrode [10-13]. From ultraviolet photoemission spectroscopy analysis, Yasukawa et al. [14] reported that the upper valence bands of AgSbO<sub>3</sub> are composed mainly of a mixture of occupied O 2p and Ag 4d orbitals. On the other hand, it was reported that the stoichiometric AgSbO<sub>3</sub> was identified as a channel-type Ag<sup>+</sup> ion conductor, and with

thermal treatment, Ag islands were formed and the sample was transformed into a predominantly electronic conductor [15].

We have found that CuO-added AgSbO<sub>3</sub> ceramics have high electrical conductivities and Seebeck coefficients, and 2.5mass%-CuO-added samples showed a power factor of  $7.24 \times 10^{-4} \text{ Wm}^{-1}\text{K}^{-2}$  at 800°C [16]. This value is one of the highest observed in *n*-type oxide materials. In this system, the sample consisted mainly of AgSbO<sub>3</sub>, with CuSb<sub>2</sub>O<sub>6</sub> and Ag as secondary phases. It was also found that nanosized particles of metallic Ag play an important role in the thermoelectric performance of the oxide. In the present study, in order to control the size and distribution of the Ag particles, preparation processes such as the timing of addition of CuO, sintering duration and the CuO amount were varied, and the effects of nanosized Ag particles on thermoelectric properties are investigated.

## 2. EXPERIMENTAL DETAILS

Ag<sub>2</sub>O (>99.0% purity), Sb<sub>2</sub>O<sub>3</sub> (>99.9% purity) and CuO (special grade) were used as starting materials. Two methods were used to prepare CuO-added AgSbO<sub>3</sub> sintered samples. In method I, Ag<sub>2</sub>O and Sb<sub>2</sub>O<sub>3</sub> were mixed with a 1:1 atomic ratio of Ag:Sb, and then calcined in aluminum crucibles at 900°C for 2 h. After that, CuO was added as a dopant, and the powders were mixed thoroughly. In method II, Ag<sub>2</sub>O and Sb<sub>2</sub>O<sub>3</sub> were weighed so that Ag:Sb = 1:1, and CuO was added to be the same amount as method I, and mixed together for 1 h. The powders were then calcined at 900°C for 2 h.

In both cases, the powders obtained were mixed with 2mass% of poly-vinyl alcohol (PVA), shaped into rectangular bars with dimensions of 1.5×4×20 mm, and then isostatically pressed with 100 MPa pressure. The compacted samples thus obtained were berried in a

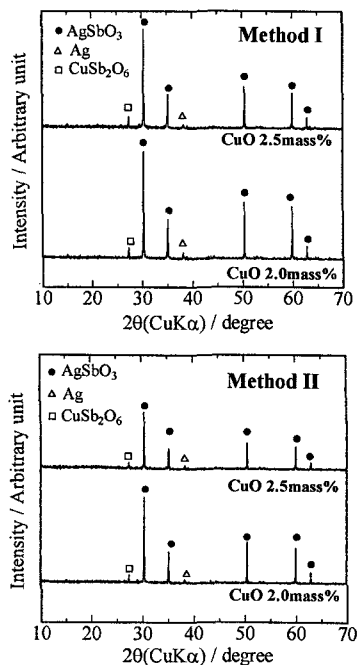


Fig. 1 XRD patterns of the sintered bodies of CuO-added AgSbO<sub>3</sub> prepared by methods I and II.

powder bed of calcined powders and sintered in an electric furnace at 1000°C. The amount of CuO (0 – 10 mass%) and the sintering duration (2 – 48 h) were controlled and varied to change the size and distribution of the Ag particles in the samples.

The phases in the samples were determined by X-ray diffraction analysis (XRD), and the crystallite size of the Ag particles was determined using Scherrer's method. The electrical conductivity was measured at temperatures ranging from room temperature to 900°C using the alternating current 4-probe method. Seebeck coefficients were also measured from room temperature to 800°C by measuring the thermoelectric voltage generated by the temperature gradients. Details of the electrical measurements have been described elsewhere [17].

### 3. RESULTS AND DISCUSSION

#### 3.1 Effects of preparation method

Figure 1 shows the XRD patterns of the sintered bodies prepared using the two methods I and II. The CuO content was selected to be 2.0 and 2.5 mass% of AgSbO<sub>3</sub>. All samples were found to consist of three phases, AgSbO<sub>3</sub>, Ag and CuSb<sub>2</sub>O<sub>6</sub>, and the ratio of these phases were similar for all samples. For method I, the calcined powders before CuO addition consisted of a single phase of AgSbO<sub>3</sub>. Thus, the metallic Ag phase detected by XRD shown in Fig. 1 precipitated from the AgSbO<sub>3</sub> phase during sintering.

Figure 2 shows the temperature dependence of electrical conductivity of the samples prepared by the two methods. All samples showed stepwise temperature dependence, which suggests multiple conduction mechanisms. For each preparation method, the samples with more CuO showed higher conductivity, which indicates that the added CuO induced conducting carriers by the substitution of Cu<sup>2+</sup> ion for Ag sites in

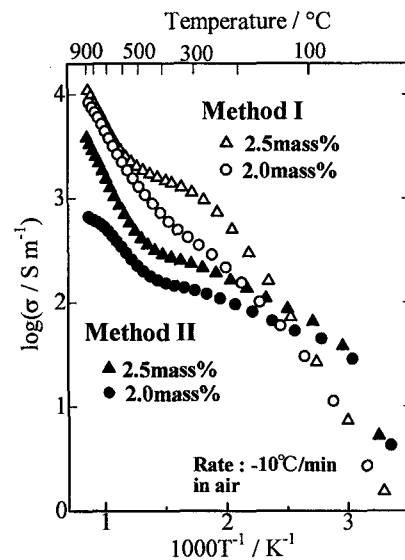


Fig. 2. Temperature dependence of electrical conductivity ( $\sigma$ ) of the sintered bodies prepared by methods I and II.

AgSbO<sub>3</sub>.

Comparing methods I and II, it was found that the sample prepared by method I showed higher conductivity above around 200°C. Fig. 3 shows the temperature dependence of the Seebeck coefficients of the samples; a larger thermoelectric voltage is in the upper y-axis. The absolute values of the Seebeck coefficients of the samples prepared by method I increased with increasing temperature, and samples prepared by method II showed decreasing thermoelectric power with increasing temperature. These results indicate that more carriers were generated, and thus, more Cu<sup>2+</sup> ion substituted Ag sites were formed, by the addition of CuO after formation of the AgSbO<sub>3</sub> phase, than by simultaneous preparation. In terms of the

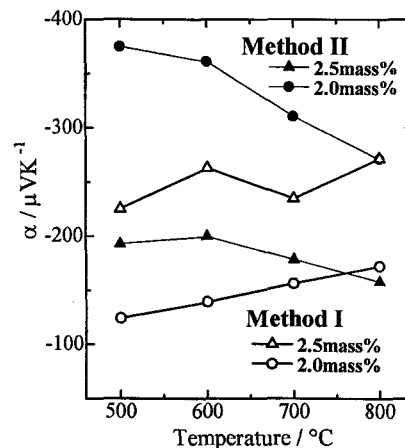


Fig. 3 Temperature dependence of the Seebeck coefficient ( $\alpha$ ) of the sintered bodies prepared by methods I and II.

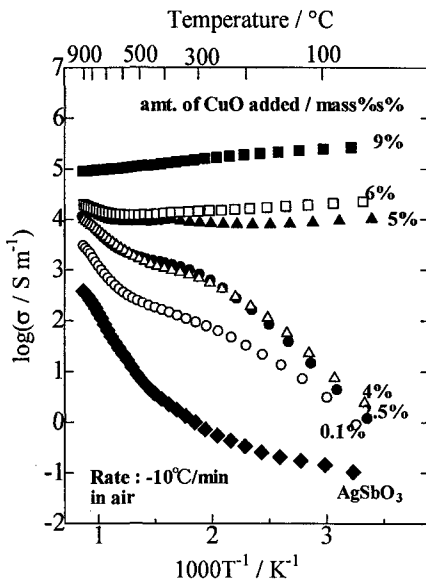


Fig. 4 Temperature dependence of the electrical conductivity ( $\sigma$ ) of the sintered bodies for various CuO additions.

samples prepared by method II, as more CuO was added, the absolute value of the Seebeck coefficient was lowered, which is normal since a large carrier concentration decreases thermoelectric power in principle. For method I, however, the opposite result was obtained. This phenomenon could not be explained by the concentration of carriers alone. Therefore, the effects of the dispersed Ag particles generated as a secondary phase by the addition of CuO might be concerned.

### 3.2 Effects of the amount of CuO addition

In order to clarify the effects of the CuO addition, samples with various amounts of CuO were prepared using method I and the thermoelectric properties were measured. When a CuO concentration greater than 0.5mass% of  $\text{AgSbO}_3$  was added, secondary phases of  $\text{CuSb}_2\text{O}_6$  and Ag were detected by XRD.

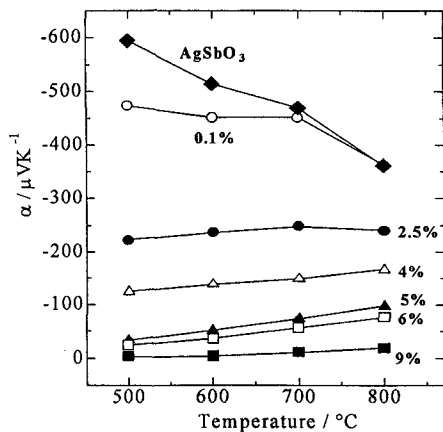


Fig. 5 Seebeck coefficients ( $\alpha$ ) of sintered bodies measured at 800°C as a function of the amount of CuO added.

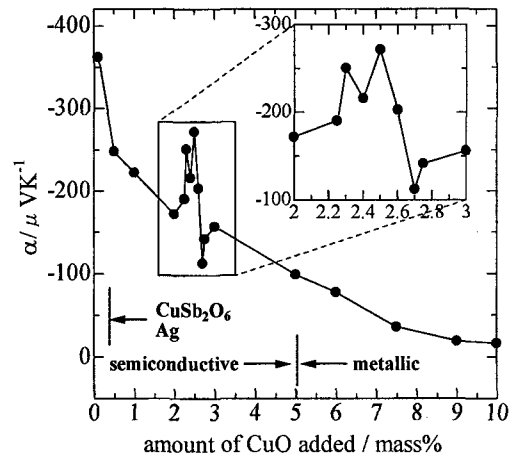


Fig. 6 Dependence of Seebeck coefficients ( $\alpha$ ) of the sintered bodies measured at 800°C on the amount of CuO added.

Figure 4 shows the temperature dependence of the electrical conductivity of the samples prepared with various quantities of CuO. As the amount of CuO increased, the conductivity increased, and tended to show metallic behavior. The samples with 0.1, 2.5 and 4.0 mass% of CuO added showed a stepwise dependence. It appears that hopping or tunneling conduction occurred above 500°C. Fig. 5 shows Seebeck coefficients of these samples. For the samples with CuO addition greater than or equal to 2.5mass%, metallic behavior, *i.e.*, increasing thermoelectric voltage with increasing temperature, was observed. As the amount of CuO addition increased, the absolute value of the Seebeck coefficients decreased as in the general tendency. However, this tendency is contrary to the results of Fig. 3. Fig. 6 shows the detailed dependence of the Seebeck coefficient on the amount of CuO measured at 800°C. Though the absolute value of the Seebeck coefficient decreased with CuO addition in general, very peculiar large values of thermoelectric power were seen in the region of 2.5 mass%, which is in the middle of the metal and semiconductor region in Fig. 4. It seems that the very high thermoelectric power of this material system is generated under optimum conditions of nano-sized Ag particles precipitated during sintering. This phenomenon appears to be very sensitive to the amount, size and the distribution of the Ag particles.

Table 1 Crystallite size of Ag particles determined by Sherrer's method

sample	peak position/deg	peak width/deg	crystallite size/pm
standard	38.28	0.167	
2h-sintered	38.07	0.262	874
6h-sintered	38.09	0.272	818
48h-sintered	38.08	0.286	759

### 3.3 Effects of sintering duration

The sintering duration was varied from 2 to 48 h, in order to prepare samples with different sizes and distributions of the secondary Ag phase, and the effects on the electrical properties were investigated. All samples were prepared by method I with the addition of 2.5 mass% CuO. From the XRD analysis, they consisted of three phases, *i.e.*, AgSbO<sub>3</sub>, CuSb<sub>2</sub>O<sub>6</sub> and Ag, and the ratio was almost the same from sample to sample.

Table 1 shows the diffraction peak data of the Ag (111) reflection and the calculated crystallite size of metal Ag phase in the samples sintered for various durations. The crystallite size of the Ag particles decreased as sintering duration increased. This suggests that the deposited Ag particles in the AgSbO<sub>3</sub> phase were melted and excluded from grains during sintering, and reminded particles having relatively large crystallite size were lost. Fig. 7 shows the electrical conductivity of these samples. The samples sintered for 2, 4 and 6 h showed an increase in conductivity with increasing temperature above 400°C. When sintered for more than or equal to 8 h, no increase in conductivity was observed. These results can be explained as follows. In samples sintered for short durations, Ag particles were spread in the AgSbO<sub>3</sub> phase, and the hopping length of electrons between the Ag particles was short; therefore the hopping occurred easily. On the contrary, as sintering progressed, the melted Ag segregated to grain boundaries and the distance between the Ag phases was too long for the hopping. Consequently, it was found that the optimum sintering duration was 4 h at 1000°C.

### 4. CONCLUSIONS

- (1) The samples prepared by CuO addition after calcination showed higher electrical conductivity and more metallic dependence of thermoelectric power on temperature than the samples with simultaneous preparation. It seems that the former samples had a greater carrier concentration and are suitable for thermoelectric applications.
- (2) The electrical conductivity at high temperature of the CuO-added AgSbO<sub>3</sub> sintered body was affected by the sintering duration. This was explained by the size and distribution of Ag particles.
- (3) Peculiar large values of thermoelectric power were observed near 2.5 mass% of CuO addition. This phenomenon is very sensitive to the amount, size and the distribution of the Ag particles.

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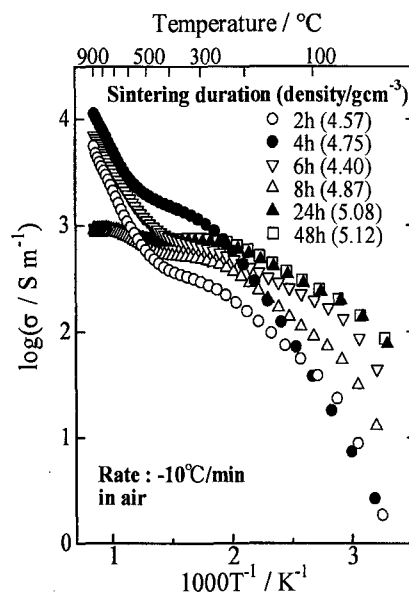


Fig. 7 Effects of sintering duration on electrical conductivity ( $\sigma$ ) of the sintered bodies.