Thermoelectric Properties of Silver Antimonate with Mixed Valency of Antimony

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Abstract
Silver (Ag) and silver antimonate (AgSbO₃) composites with different amounts of Sb³⁺ were synthesized by normal sintering with the aim of realizing a thermoelectric material. The electrical conductivity (σ) increased in the sample containing larger amount of Sb³⁺, whereas Seebeck coefficient (S) decreased. Producing Sb³⁺ caused the generation of oxygen vacancies in the material, and thus the corresponding donor levels are created in the bandgap, providing more conduction electrons. The conductive Ag particles would contribute to the conduction path as bypasses for carrier transport. The thermal conductivity (κ) was slightly lower in the presence of Ag defects in AgSbO₃.

Keywords
Thermoelectric Material, Silver Antimonate, Seebeck Coefficient, Electrical Conductivity, Thermal Conductivity

1. Introduction
Thermoelectric (TE) materials have been attracting attention due to their potential for recycling energy using exhausted heat through the thermal-electric conversion effect, generating clean energy without polluting the environment. Recently, several oxides have been recognized as potential thermoelectric materials [1] [2] [3] [4]. TE conversion efficiency is represented by a dimensionless figure of merit, \( ZT = S^2\sigma T / \kappa \), where \( S \), \( \sigma \), \( \kappa \), and \( T \) are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. From these equations, large \( S \) and \( \sigma \) values and a low \( \kappa \) are necessary for high TE performance.

It is known that typical oxides have a low mobility (\( \mu \)) and high \( \kappa \) (particularly, \( \kappa_{ph} \) which is the thermal conductivity mediated by phonons), originating from
their ionic bonding between light atoms and high electronegativity of oxygen. Different from these oxides, silver antimonite (AgSbO₃), which has a defect pyrochlore structure composed of linear chains of AgO₆ and SbO₆, possesses rather high μ originating from its highly-dispersed valence band and conduction band composed of Ag 5s and Sb 5s orbitals, respectively [5] [6]. In addition, AgSbO₃ has low stacking density and thus its κₚₐ is significantly lower than those of other oxides [7] [8]. So, AgSbO₃ has been investigated as a candidate n-type TE material, e.g., by addition of CuO [5] and by using a spark plasma sintering (SPS) method to prepare dense AgSbO₃ [7]. According to Wiggers et al., aggregated Ag islands are formed in the thermally treated AgSbO₃, causing the increase in σ by the electron hopping between such metallic islands [9]. However, the previous studies, regarding TE properties of AgSbO₃, did not mention the existence of metallic Ag. Moreover, the valency of Sb (Sb³⁺ (4d¹⁰), Sb⁵⁺ (4d¹⁰5s²)) should affect σ due to generation of oxygen vacancy in the presence of Sb³⁺; however such discussion has not been performed. Thus, in the present paper, we characterize the AgSbO₃ in details, prepared by the combination of a solid state reaction (SSR) method and a nitric acid (HNO₃) treatment [10]. In addition, the existence of metallic silver and the ratio of Sb³⁺/Sb⁵⁺ in AgSbO₃ are discussed in connection with σ, S, and κ.

2. Experimental

AgSbO₃ was synthesized by SSR using Ag₂O (>99.0%, Kanto Kagaku) and Sb₂O₃ (>98.0%, Kanto Kagaku) as raw materials. The raw materials were weighed to the stoichiometric molar ratio, and were mixed by ball milling (200 rpm, milling rate) for 20 h, and then the mixed powder was calcined at 900°C for 2 h. The partial calcined powder was uniaxially pressed into a rectangular pellet with the dimensions ~ 4 × 5 × 20 mm, followed by calcination in an electric furnace (HPM-1N, AS-ONE) in air at 900°C for 2 h (denoted by NS). The remaining calcined powder was washed by HNO₃ (5.0 mol/L, Kanto Kagaku), then dried at 90°C for 20 h. The obtained powder was pressed into a pellet followed by calcination in the electric furnace under the same conditions, and obtained sample was denoted by NAT-NS.

The obtained calcined powders and sintered bodies, after grounding powders and pulverizing bodies, respectively, into fine powders were characterized by conventional X-ray diffraction analysis (XRD) with CuKα radiation (PANalytical, PW-1700). Synchrotron radiation powder diffraction patterns were obtained at BL02B2 in SPring-8 after pulverizing bodies into fine powders. The patterns were collected in the 2θ range of 3° - 73° in a step scanning mode, with a step length of 0.01°. The Rietveld analyses using a RIETAN-FP software (a multipurpose pattern-fitting system) were performed on the synchrotron radiation diffraction patterns. For the analysis, the space groups Fd3m (cubic, No. 227) and Fm-3m (cubic, No. 225) were used as the starting structural model of AgSbO₃ (a = 10.23 nm) and Ag (a = 4.0857 nm). A scanning electron microscope (SEM; JSM-6500F, JEOL) was used to observe the morphology of cross-sectional
surfaces of the samples. The valency of Ag and Sb ions was evaluated by X-ray photoelectron spectroscopy (XPS; Axis-Ultra, Shimadzu).

To measure $\sigma$ and $S$, either two or four Pt wires, respectively, were attached by an Ag-conductive region to the prepared rectangular pellet samples. The temperature dependence of $S$ (Yokogawa, Model 7563) with a temperature gradient of 5 - 20 K and that of $\sigma$ (Agilent Technologies, E5273A) were measured from 473 K to 873 K by conventional two-probe steady-state and four-probe methods, respectively. We then calculated the power factor ($PF$), as expressed by $S^2\sigma$, for each sample. A modified Harman method was used to measure $ZT$ at 600°C [11] and then we calculated $\kappa$ by using the equation, $ZT = S^2\sigma T/\kappa$.

3. Results and Discussion

3.1. Characterizations

The observed diffraction patterns for NS and NAT-NS by synchrotron radiation are shown in Figure 1(a) and Figure 1(b), respectively, and indicated it adopted double phases of cubic AgSbO$_3$ and Ag. Not shown here, but calcined AgSbO$_3$ indicated the homogeneous defect pyrochlore structure by the conventional XRD. The detection of Ag was reasonably expected as Ag$_2$O is thermally decom-

![Figure 1](https://example.com/f1.png)

**Figure 1.** Measured synchrotron radiation diffraction patterns and patterns calculated by Rietveld analysis for the prepared samples, (a) NS and (b) NAT-NS. The dotted red plots, black lines, and blue lines represent measured patterns, calculated patterns, and the differences between the measured and calculated patterns, respectively. Crystallographic data determined by the Rietveld analysis are shown in Table 1.
posed to Ag at ~280˚C. Figure 1 also includes the calculated pattern involving AgSbO₃ and Ag, and the difference between the observed and calculated values. The molar percentages of AgSbO₃ and Ag in both samples, their lattice parameters, and their compositions were determined by Rietveld refinement and are summarized in Table 1. In the NS sample, the Ag/Sb ratio is unity, in good agreement with the stoichiometric ratio (Ag₁.₀₀Sb₁.₀₀O₃), although Ag exists separately in spite of the stoichiometric ratio of starting materials, Ag₂O and Sb₂O₃. This is reasonable because Sb element volatilized during sintering [5] [8]. In contrast, in the NAT-NS sample, the Ag/Sb ratio is less than unity (Ag₀.₉₈Sb₁.₀₀O₃), reflecting the HNO₃ treatment which extracted Ag from the AgSbO₃ lattice, causing the Ag defect in AgSbO₃. The amounts of the separated Ag in both samples were observed to be similar. The relative densities of NS and NAT-NS pellets were also quite similar, 58.9 and 56.6%, respectively (Table 2). Those values were small, ~60% of the theoretical ones, which is considered to be attributable to the evaporation of Sb [5].

SEM images of the fracture surfaces of NS and NAT-NS are shown in Figure 2(a) and Figure 2(b), respectively. The NS and NAT-NS powders, with particle sizes of ~100 - 200 nm in diameter, appeared to be aggregated, indicating that both of them were porous. The binding energies corresponding to Ag 3d₅/₂ of Ag⁰ (Ag), Ag⁺ (Ag₂O), and Ag²⁺ (AgO) are quite similar, and are 368.0 - 368.3, 367.6 - 367.8, and 367.3 - 367.4 eV, respectively [12]. Since all the energies are in such a narrow range, it is quite difficult to perform a quantitative analysis of the Ag oxidation states from a deconvolution analysis of XPS spectra with high certainty. However, qualitatively, as shown in Figure 3(a), the spectrum peak of HNO₃-treated sample (NAT-NS) shifted to the higher binding energy side (inset in Figure 3(a)), and also the spectrum had tailing in the lower binding energy region. These observations indicate that the HNO₃-treated sample has more Ag

### Table 1. Crystallographic data determined by the Rietveld analysis.

| Sample | NS      | NAT-NS |
|--------|---------|---------|
| Rwp    | 8.90    | 10.1    |
| S      | 6.19    | 6.86    |
| Ag content/mol% | 0.79 | 0.83 |
| Lattice parametrt of Ag, a/nm | 4.078 | 4.081 |
| Lattice parametrt of AgSbO₃, a/nm | 10.22 | 10.25 |
| Composition of AgSbO₃⁺ | Ag₁.₀₀Sb₁.₀₀O₃ | Ag₀.₉₈Sb₁.₀₀O₃ |

*a. Estimated from the occupancies of Ag and Sb in AgSbO₃.*

### Table 2. Characterization data of NS and NAT-NS, SPS samples.

| Sample   | NS     | NAT-NS |
|----------|--------|--------|
| Relative density/% | 58.9  | 56.6   |
| Sb⁺⁺/Sb⁺⁺⁺ ratio | 1.5   | 0.23   |
in AgSbO₃ including Ag⁰ and Ag²⁺ oxidation states. The Sb 3d₃/₂ XPS spectra of NS and NAT-NS are shown in Figure 3(b) and Figure 3(c), respectively. As for the oxidation states of Sb, the peaks at 540.7 and 539.7 eV are assigned to the 3d₃/₂ orbital of Sb⁵⁺ and Sb³⁺, respectively [13]. To quantitatively evaluate the Sb³⁺/Sb⁵⁺ atomic ratios, peak deconvolution was performed using a Gaussian lineshape. The component Sb³⁺ and Sb⁵⁺ spectra determined by deconvolution and fitted peaks are also shown in Figure 3(b) and Figure 3(c). The atomic ratios of Sb³⁺/Sb⁵⁺, which were determined by the area of Sb 3d₃/₂ for Sb³⁺ divided by that for Sb⁵⁺, are also shown in Table 2. When we compare the Sb³⁺/Sb⁵⁺ ratio between NS and NAT-NS, the amount of Sb⁵⁺ increased after HNO₃ treatment. This is also reasonable because HNO₃ acts as an oxidant. So, it could be considered that Ag²⁺ also increased, and then Ag⁰ in AgSbO₃ might increase to maintain charge neutrality (Figure 2 & Figure 3).
3.2. Thermoelectric Properties

Figure 4(a) shows the temperature dependence of $\sigma$ for NS and NAT-NS. The $\sigma$ values of both samples increased with increasing temperature, which is typical semiconductor behavior. In Figure 4(a), NS containing larger amount of Sb$^{3+}$ with the similar amount of the separated Ag, compared to NAT-NS, indicated the higher $\sigma$. So, producing Sb$^{3+}$ is the key to increase $\sigma$. This could be plausible because generating Sb$^{3+}$ caused the generation of more oxygen vacancies in the material, and thus the corresponding donor levels are created in the band gap. This can provide more conduction electrons than in the case of no donor levels in the gaps. It should be noted that the Sb$^{3+}$/Sb$^{5+}$ ratio did affect $\sigma$ more greatly than the Ag/Sb ratio. As mentioned above, NAT-NS containing Ag-defect (Ag$_{0.98}$Sb$_{1.00}$O$_{y}$) has more amounts Ag$^0$ (4d$^10$5s$^1$) and Ag$^{2+}$ (4d$^9$), meaning the increase in $\sigma$ due to their open electronic-shell configurations than NS (Ag$_{0.98}$Sb$_{1.00}$O$_{y}$, Ag$^+$ (4d$^{10}$), closed electronic-shell configuration). However, the opposite experimental results were observed.

Temperature dependence of $S$ for NS and NAT-NS is shown in Figure 4(b). $S$ values of both samples were negative, indicating the occurrence of n-type conduction. The trend of the absolute values of $S$ almost covers the Ioffe’s theory, that is, the absolute value of $S$ decreases when $\sigma$ increases. So, NAT-NS had the higher absolute values of $S$. Figure 4(c) shows the temperature dependence of power factor ($PF$), which was calculated from the formula $\sigma \times S^2$. The $PF$ observed in this study ($\sim 1 \times 10^{-5}$ W·m$^{-1}$·K$^{-2}$) was obtained for NS at 600˚C.

Finally, we examined the value of $ZT$ for the NS and NAT-NS samples at 600˚C using the modified Harman method and then $\kappa$ was calculated. The $ZT$ values for NS and NAT-NS were 0.009 and 0.007, respectively. The $\kappa$ value for NS was calculated to be 0.42 W·m$^{-1}$·K$^{-1}$, which is reasonably consistent with the previously reported values of 1.1 and 0.8 W·m$^{-1}$·K$^{-1}$ at room temperature and
400˚C, respectively [8]. The κ value for NAT-NS was 0.38 W ∙m−1∙K−1, which is slightly smaller than that for NS. This might be attributable to the presence of Ag defects, causing the phonon scattering by the defect site. Although these ZT values need to be increased by around two orders of magnitude to be suitable for practical use, this study provides that the introduction of Sb3+ in AgSbO3 enhanced the thermoelectric property.

4. Conclusion

We prepared AgSbO3-based thermoelectric materials with and without the HNO3 treatment. Then the sample that had higher σ indicated the higher Z, attributable to the generation of Sb3+, in spite of smaller S and larger κ. The ZT value for NS was observed to be ~0.009 at 600˚C, which is two orders of magnitude smaller than the minimum value considered being required for practical use, which is greater than 1. To achieve a higher ZT value, we are now trying to prepare dense AgSbO3 with and without HNO3 treatment using the SPS method because it is well-known that the SPS method allows the production of dense samples, resulting in the enhanced TE properties.

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