Structural and Thermoelectric Properties of (Zn$_{1-x}$M$_x$)$_{13}$Sb$_{10}$ (*M* = Cu, Ag, Au and Ga)

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Abstract: Effect of substitution for Zn by its neighboring elements of Cu, Ag, Au and Ga in the periodic table on the thermoelectric property has been investigated for the Zn$_{13}$Sb$_{10}$ compound prepared by a quenching method. A small amount of Ga is successfully substituted for the Zn site with the solubility limit of 10%, and enhances metallic conduction. The improvement of the power factor has been achieved by 25% at 340 K for the 10% Ga-substituted system. n-type conduction is not obtained by the Ga substitution. On the other hand, the substitution of the other elements of Cu, Ag and Au has led to the formation of totally different phases from the 13:10 phase.

Key words: Thermoelectric properties, zinc antimonide, substitution.

1. Introduction

The β-Zn$_4$Sb$_3$ compound, which has recently refined to be Zn$_{13}$Sb$_{10}$, has attracted much attention since the discovery of the high *ZT* value of 1.3 at 670 K [1]. Many research works have been devoted to optimize the thermoelectric performance by substitution of the constituent elements [2-14]. Among the many substitution studies, the effect of Cd substitution has been investigated most intensively because the Cd substitution is the most effective to optimize the thermoelectric property. Russian groups have firstly reported that the effect of Cd substitution on the transport properties of Zn$_4$Sb$_3$ [2-4]. Caillat *et al*. have reported the thermoelectric property of the Cd-substitution system [5]. Kuznetsov and Rowe have reported that details of the structural property of the hot-pressed (Zn$_{1-x}$Cd$_x$)$_4$Sb$_3$ samples [7]. Nakamoto *et al*. have reported the thermoelectric and structural properties of the Cd-substitution system prepared by rapid quenching and gradient freeze methods [8, 13].

On the other hand, the effect of substitution by the other neighboring elements than Cd in the periodic table on the structural and thermoelectric properties has not been fully understood because of the smaller solubility limit than 10%. It is also of our particular interest to realize an inversion to n-type conduction in the Zn$_{13}$Sb$_{10}$ compound by substitution.

In the present study, in order to examine the substitution effect for Zn by its neighboring elements on the thermoelectric property of the Zn$_{13}$Sb$_{10}$ compound, we have investigated structural and thermoelectric properties of the (Zn$_{1-x}$M$_x$)$_{13}$Sb$_{10}$ (*M* = Cu, Ag, Au and Ga) compounds.

2. Experiments

(Zn$_{0.9}$M$_{0.1}$)$_{13}$Sb$_{10}$ (*M* = Cu, Ag, Au and Ga) compounds were prepared by a quenching method. For the Ga-substituted system, the sample with *x* = 0.05 and 0.15 were also prepared. The high-purity constituent elements of Zn (6N), *M* (Cu:4N, Ag:6N, Au:4N and Ga:6N) and Sb (6N) were loaded into a double quartz ampoule and sealed under vacuum. The elements were melted at 1,023 K for several hours by a

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vertical electric furnace and then quenched into ice water. The ingots were cut into several pieces with suitable shapes for various physical measurements using a spark erosion cutter (SANKYO Eng. Ltd., DE-60).

The powder XRD (X-ray diffraction) measurement was performed at room temperature by a Rigaku RINT-2500 using Cu Kα radiation. The electrical resistivity, Seebeck coefficient and thermal conductivity measurements were carried out by a Physical Property Measurement System (Quantum Design Ltd.) in the temperature range between 5 and 340 K.

3. Results and Discussion

3.1 X-Ray Diffraction Profile

Figs. 1-4 show the powder XRD profiles at room temperature for the Cu-, Ag-, Au- and Ga-substituted samples, respectively. The Cu-, Ag- and Au-substituted samples with $x = 0.1$ possess totally different phases from the 13:10 one as shown in Figs. 1-3. No 13:10 phase is found at all in these XRD profiles. The XRD profiles of the Cu-, Ag- and Au-substituted systems are very similar to one another, suggesting that a similar kind of impurity phases are formed in these substituted systems. However, these impurity phases are not identified at present. The Ga-substituted samples with $x = 0.05$ and 0.10 are found to be of single phase. The reflections from impurity phases are observed at the top part of the sample with $x = 0.10$. Thus, the solubility limit of Ga is found to be about 10% in the $(Zn_{1-x}Ga_x)_{13}Sb_{10}$.

3.2 Thermoelectric Properties

3.2.1 Electrical Resistivity

Fig. 5 shows the electrical resistivity ρ of the $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga) systems as a function of temperature. $\rho(T)$ and the β to α structural phase transition at 250 K are significantly modified by these substitutions. ρ of the Au-substituted sample has larger resistivity than the non-substituted sample by a

factor of 2.6 at room temperature. In contrast, the other substituted systems with Cu and Ga show more metallic
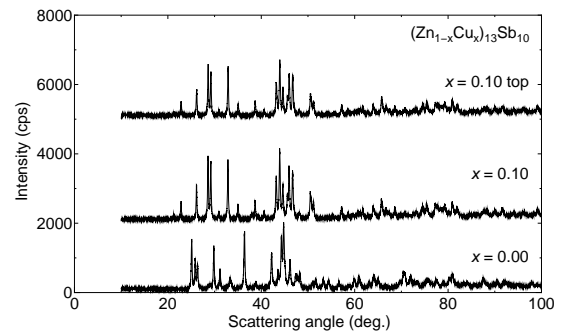

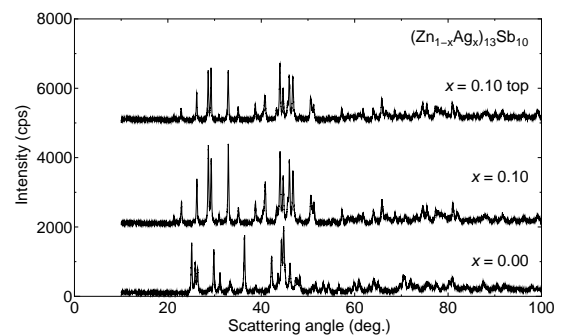**Fig. 1 Powder X-ray diffraction profiles of $(Zn_{1-x}Cu_x)_{13}Sb_{10}$ with $x = 0.00$ and 0.10.**

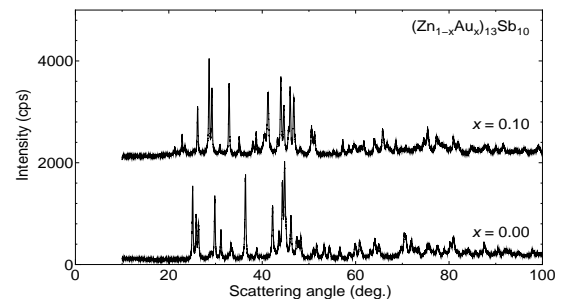**Fig. 2 Powder X-ray diffraction profiles of $(Zn_{1-x}Ag_x)_{13}Sb_{10}$ with $x = 0.00$ and 0.10.**

Fig. 3 Powder X-ray diffraction profiles of $(Zn_{1-x}Au_x)_{13}Sb_{10}$ with $x = 0.00$ and 0.10.

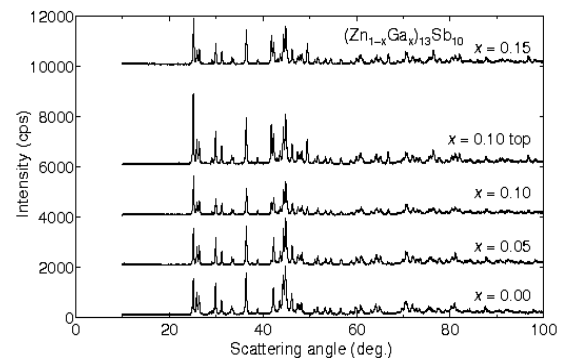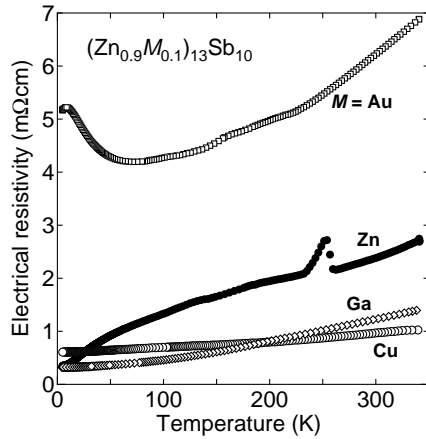**Fig. 4 Powder X-ray diffraction profiles of $(Zn_{1-x}Ga_x)_{13}Sb_{10}$ ($x = 0.00$, 0.05, 0.10 and 0.15).**

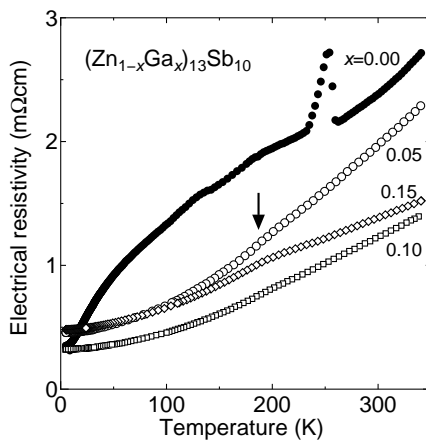**Fig. 5   Electrical resistivity of $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga) as a function of temperature.**

Fig. 6   Electrical resistivity of $(Zn_{1-x}Ga_x)_{13}Sb_{10}$ (x = 0.00, 0.05, 0.10 and 0.15) as a function of temperature.

behavior with smaller resistivity. It should be noted that the β to α structural transition is totally suppressed by these substitutions.

Fig. 6 shows the electrical resistivity as a function of temperature for the Ga-substitution system. ρ decreases with increasing Ga content x up to 0.10. The slight increase in ρ for x = 0.15 is attributable to the formation of impurity phases. It should be emphasized again that the β to α structural transition is also not prominent by the Ga substitution. Only a small kink in ρ is found around 190 K in the Ga-substituted samples, as indicated by an arrow.

3.2.2 Seebeck Coefficient

Fig. 7 shows the Seebeck coefficient S as a function of temperature for $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga). All the substituted samples have a smaller

Seebeck coefficient than the non-substituted one. The Seebeck coefficient of the Au-substituted sample is not so enhanced irrespective of the large resistivity value. The large ρ value in the Au-substituted sample may be caused by cracks. The Cu substituted sample has one half magnitude of the non-substituted one. The anomaly associated with the β to α structural transition is totally smeared out by these substitutions.

The Seebeck coefficient of the Ga-substituted system is shown in Fig. 8 as a function of temperature. All the Ga-substituted $Zn_{13}Sb_{10}$ compounds show p type conduction. S is decreased by the Ga substitution; about 80% and 50% for the β- and α-phases, respectively. Any anomalies indicative of the structural phase transition are not observed for the Ga-substituted samples.
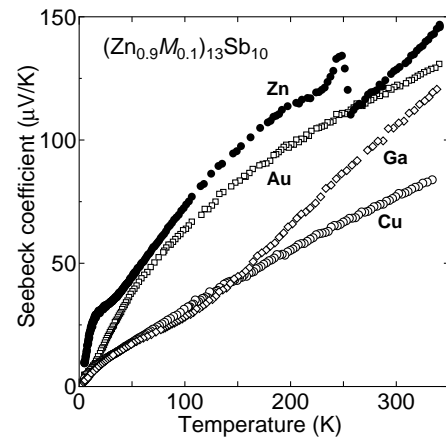

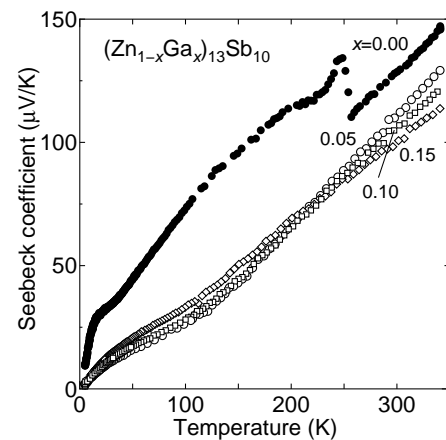**Fig. 7   Seebeck coefficient of $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga) as a function of temperature.**

Fig. 8   Seebeck coefficient of $(Zn_{1-x}Ga_x)_{13}Sb_{10}$ (x = 0.00, 0.05, 0.10 and 0.15) as a function of temperature.

3.2.3 Power Factor

Figs. 9 and 10 show the power factor *P.F.* as a function of temperature for $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga) and $(Zn_{1-x}Ga_x)_{13}Sb_{10}$ (x = 0.00, 0.05, 0.10 and 0.15) respectively. The improvement of the *P.F.* is observed above 250 K only in the Ga-substituted system. The maximum *P.F.* is found in the Ga-substituted sample with x = 0.10 as shown in Fig. 10. The *P.F.* of the Ga-substituted sample with x = 0.10 has larger by 25% than that of the non-substituted one at 340 K, whereas it is smaller below 250 K.

3.2.4 Thermal Conductivity

The thermal conductivity of $(Zn_{0.9}M_{0.1})_{13}$ Sb_{10} (M = Cu, Au and Ga) is displayed as a function of temperature in Fig. 11. The non-substituted sample shows a large peak in the $\kappa(T)$ at 15 K. The strong suppression of the
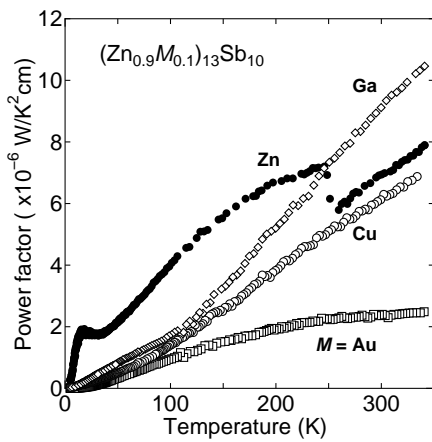

Fig. 9   Power factor of $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga) as a function of temperature.

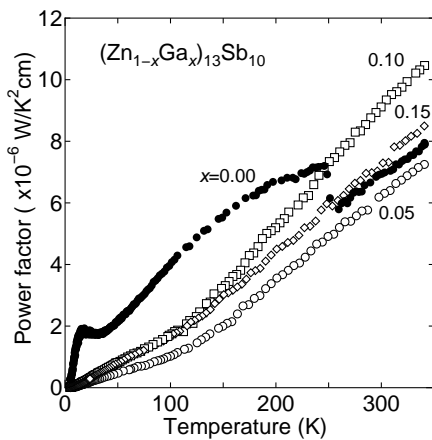**Fig. 10   Power factor of $(Zn_{1-x}Ga_x)_{13}Sb_{10}$ (x = 0.00, 0.05, 0.10 and 0.15) as a function of temperature.**

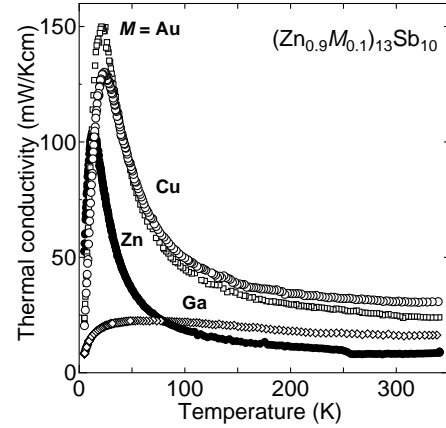**Fig. 11   Thermal conductivity of $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga) as a function of temperature.**

low-temperature peak in $\kappa(T)$ is found only in the Ga-substituted sample, indicating the disturbance of the lattice periodicity due to the substitution. On the contrary, the Cu- and Au-substituted systems have larger κ than the non-substituted sample; the peaks exceeding 100 mW/Kcm are observed at 20 K. This is caused by the formation of metallic impurity phases in these samples. This is also supported by the results of ρ and S. The anomaly associated with the β to α structural phase transition is not visible in the $\kappa(T)$ for all the substituted samples.

Fig. 12 shows the $\kappa(T)$ for the Ga-substituted system. The low-temperature peak around 15 K is strongly suppressed by the Ga-substitution, indicating that Ga is introduced into the regular lattice sites of the 13:10 phase. However, κ increases with increasing Ga content at higher temperatures than 150 K. The sample with x = 0.10 has about two times larger value than the non-substituted one at room temperature.

3.2.5 Dimensionless Figure of Merit

Figs. 13 and 14 show temperature dependence of the dimensionless figure of merit *ZT* for $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga) and $(Zn_{1-x}Ga_x)_{13}Sb_{10}$ (x = 0.00, 0.05, 0.10 and 0.15) respectively. No improvement of the thermoelectric performance is achieved by the 10% substitution of Au, Cu and Ga in the present study. A systematic dependence of *ZT* on the Ga content is found; the *ZT* is decreased with Ga substitution.
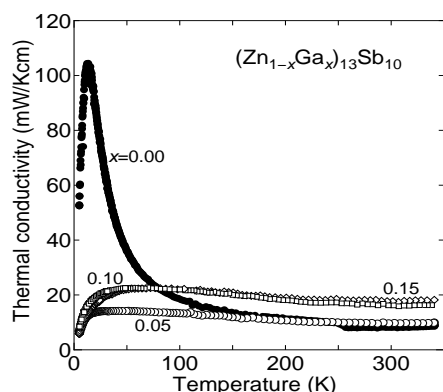
Fig. 12   Thermal conductivity of $(Zn_{1-x}Ga_x)_{13}Sb_{10}$ (x = 0.00, 0.05, 0.10 and 0.15) as a function of temperature.

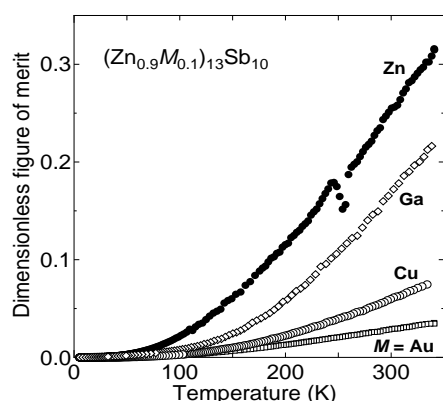**Fig. 13   Dimensionless figure of merit of $(Zn_{0.9}M_{0.1})_{13}Sb_{10}$ (M = Cu, Au and Ga) as a function of temperature.**

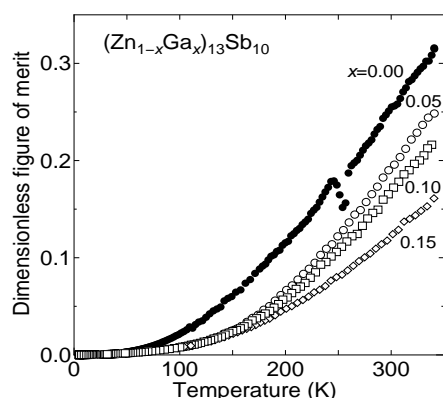**Fig. 14   Dimensionless figure of merit of $(Zn_{1-x}Ga_x)_{13}Sb_{10}$ (x = 0.00, 0.05, 0.10 and 0.15) as a function of temperature.**

4. Conclusions

$(Zn_{1-x}M_x)_{13}Sb_{10}$ compounds (M = Cu, Ag, Au and Ga) have been prepared and their structural and thermoelectric properties have been investigated.

The single phase of the 13:10 phase is obtained only for the Ga-substituted system. The solubility limit is 10%

for the Ga substitution. The β to α structural phase transition is perfectly suppressed by the 5% substitution of Ga. The power factor is enhanced by 25% in the β-phase, whereas it is lowered by the Ga substitution below 250 K. On the other hand, the power factor is appreciably lowered by Cu and Au substitutions. It is also concluded that n-type conduction is not observed by the Ga substitution. The 13:10 phase is not formed by the substitution of the other elements of Cu, Ag and Au.

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