Effect of the Amount of Vacancies on the Thermoelectric Properties of Cu–Ga–Te Ternary Compounds

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The Cu–Ga–Te ternary compounds: $Cu_3Ga_5Te_9$, $Cu_2Ga_4Te_7$, $CuGa_3Te_5$, $CuGa_5Te_8$, and $CuGaTe_2$ have zinc-blende or chalcopyrite structure. The compounds except for $CuGaTe_2$ contain vacancies in the cation site due to the valence mismatch between cation and anion, and the vacancy concentration is different between these compounds. Here we investigated the effect of the amount of vacancies on the thermoelectric (TE) properties of the Cu–Ga–Te ternary compounds. At room temperature, the presence of vacancies reduced the Hall mobility (μ_H) and the lattice thermal conductivity (κ_{lat}), showing that the vacancies scattered both carriers and phonons. It was found that the decreasing rate of the μ_H was larger than that of the κ_{lat}. Therefore, the presence of vacancies degraded the TE performance of the Cu–Ga–Te ternary compounds. In other words, $CuGaTe_2$ without vacancies would show the best TE figure of merit. The room temperature ZT values for $Cu_3Ga_5Te_9$, $Cu_2Ga_4Te_7$, $CuGa_3Te_5$, $CuGa_5Te_8$, and $CuGaTe_2$ were 2.0×10^{-2}, 2.4×10^{-2}, 8.9×10^{-3}, 1.3×10^{-2}, and 5.6×10^{-3}, respectively.
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1. Introduction

The thermoelectric (TE) technology of energy conversions from waste heat into electrical energy is important to develop alternative energy technologies in the reduction of our dependence on fossil fuels and can be reduced greenhouse-gas emissions.[1] The efficiency of a material used in TE devices is determined by the dimensionless figure of merit, $ZT = S^2 T/\rho/\kappa$, where S, T, ρ, and κ are, respectively, the Seebeck coefficient, absolute temperature, electrical resistivity, and total thermal conductivity ($\kappa = \kappa_{lat} + \kappa_{el}$, where κ_{lat} is the lattice thermal conductivity and κ_{el} is the electronic thermal conductivity).[2] Since the S, ρ, and κ_{el} in bulk materials are interrelated, it is very difficult to control them independently. Therefore, the reduction of κ_{lat} is essential to increase ZT.

Our group has focused attention on the reduction of the κ_{lat} by manipulating the spatial distribution and density of structural vacancies. It is known that Ga_2Te_3 and Ga_2Se_3 have defect zinc-blende cubic structure. Due to the valence mismatch between the cation and anion, one-third of the cation sites are vacancies.[3–6] Such vacancies are expected to affect various physical properties including TE properties. In fact, Ga_2Te_3 exhibits very low κ_{lat} ($= 0.6\,\mathrm{W\,m^{-1}\,K^{-1}}$ at 300 K), most likely due to the effective phonon scattering by the regularly-arranged two-dimensional (2D) vacancy planes.[3] On the other hand, our group has succeeded in preparing two kinds of bulk samples for Ga_2Se_3: one includes 2D vacancy planes and the other contains vacancies as a

point defect. Although these two samples have the same structure with the same chemical composition and the same vacancy density, the values and the temperature dependence of the κ_{lat} of them were distinctly different. The sample with the point type vacancies exhibited relatively high κ_{lat} ($= 1.3\,\mathrm{W\,m^{-1}\,K^{-1}}$ at 300 K) with a T^{-1} temperature dependence, while the sample with the in-plane type vacancies exhibited quite low κ_{lat} ($= 0.6\,\mathrm{W\,m^{-1}\,K^{-1}}$ at 300 K) with rather flat temperature dependence.[6]

In addition to the vacancy distribution described above, the amount of vacancies would also influence the TE properties. However, the effect of the amount of vacancies on the TE properties has not been investigated. In the Cu–Ga–Te ternary system, there exist various compounds with zinc-blende or chalcopyrite structure containing vacancies, viz., $Cu_3Ga_5Te_9$,[7] $Cu_2Ga_4Te_7$,[8,9] $CuGa_3Te_5$,[10] and $CuGa_5Te_8$[11] in addition to $CuGaTe_2$ containing no vacancies. In the crystal of $Cu_3Ga_5Te_9$, $Cu_2Ga_4Te_7$, $CuGa_3Te_5$, and $CuGa_5Te_8$, one-ninth, one-seventh, one-fifth, and one-fourth of the cation sites are structure vacancies. Therefore, the chemical formula of $Cu_3Ga_5Te_9$, $Cu_2Ga_4Te_7$, $CuGa_3Te_5$, $CuGa_5Te_8$, and $CuGaTe_2$ can be described as $Cu_3Ga_5VA_1Te_9$, $Cu_2Ga_4VA_1Te_7$, $CuGa_3VA_1Te_5$, $CuGa_5VA_2Te_8$, and $CuGaVA_0Te_2$, respectively, where VA indicates the vacancy.

In the present study, we tried to clarify the effect of the amount of vacancies on the TE properties of the Cu–Ga–Te ternary compounds. Especially, the relationships between the amount of vacancies and the κ_{lat} or the Hall mobility (μ_H) were investigated.

Table 1 Crystal structure, lattice parameters, and sample densities of the Cu–Ga–Te ternary compounds, together with the literature data.[7,8,10–14]

Compounds	Crystal system	Crystal structure	Lattice parameter (nm)				Ref.	d (g cm^{-3})
			Literature data		Present study			
			a	c	a	c		
CuGaTe$_2$	Tetragonal	chalcopyrite	0.6024	1.1924	0.6016	1.1941	12	5.89
Cu$_3$Ga$_5$Te$_9$	Tetragonal	chalcopyrite	0.5974	1.1875	0.5980	1.1942	7	5.93
Cu$_2$Ga$_4$Te$_7$	Cubic	zinc-blende	0.5930	—	0.5940	—	8	5.78
	Tetragonal	chalcopyrite	0.5960	1.1857	—	—	7	
CuGa$_3$Te$_5$	Tetragonal	chalcopyrite	0.5932	1.1825	0.5933	1.1865	10	5.77
	Tetragonal	chalcopyrite	0.5930	1.1839			13	
CuGa$_5$Te$_8$	Cubic	zinc-blende	0.5914	—	0.5919	—	11	5.57
	Cubic	zinc-blende	0.5918	—		—	14	

2. Experiment

The Cu–Ga–Te ternary compounds were prepared by direct reactions of Cu$_2$Te (99.99%), Ga$_2$Te$_3$ (99.999%), Cu (99.0%), Ga (99.99%), and Te (99.999%) in sealed silica tubes. The ingots obtained after melting of the starting materials were crushed into powders, followed by hot-pressing in a graphite die at 873 K for 3 h in an Ar-flow atmosphere. The samples were characterized using powder X-ray diffraction (XRD) with Cu $K\alpha$ radiation at room temperature. The microstructure and element distribution were observed using the scanning electron microscope (SEM) and the energy-dispersive X-ray (EDX) analyzer. The Seebeck coefficient (S) and the electrical resistivity (ρ) were measured simultaneously around room temperature using the commercially available measurement system (ULVAC, ZEM-1). The Hall coefficient (R_H) was measured at room temperature by the van der Pauw method in vacuum under an applied magnetic field of 0.5 T. The Hall carrier concentration (n_H) and the Hall mobility (μ_H) were calculated from R_H based on the assumptions of a single band model and a Hall factor of 1; i.e., $n_H = 1/(eR_H)$ and $\mu_H = R_H/\rho$, where e is the elementary electric charge. The thermal conductivity (κ) was evaluated from the thermal diffusivity (α), heat capacity (C_p), and density (d) based on the relationship $\kappa = \alpha C_p d$. The α was measured in vacuum using the laser flash thermal constants analyzer (ULVAC, TC-7000) in the temperature range from room temperature to 940 K. The density of the hot-pressed sample was calculated based on the measured weight and dimensions. The C_p was estimated from the Dulong–Petit model, that is, $C_p = 3nR$, where n is the number of atoms per formula unit and R is the gas constant.

3. Results and Discussion

The powder XRD patterns of the polycrystalline samples of the Cu–Ga–Te ternary compounds are shown in Fig. 1. Basically, all the peaks could be indexed in terms of zinc-blende structure with the space group F-43m or chalcopyrite structure with the space group I-42d. Transmission electron microscopy studies revealed that the point-type vacancies
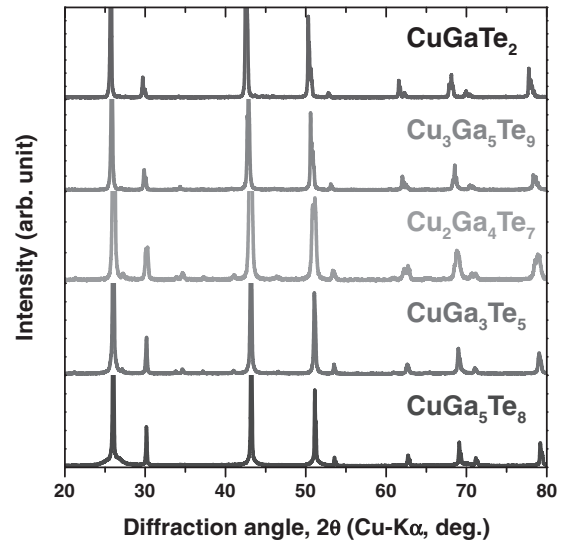

Fig. 1 Powder XRD patterns of polycrystalline samples of the Cu–Ga–Te ternary compounds.

in Cu$_2$Ga$_4$Te$_7$ are regularly arranged,[9] while the vacancy distribution of other Cu–Ga–Te ternary compounds is not determined yet. The lattice parameters calculated from the XRD patterns are summarized in Table 1, together with the literature data.[7,8,10–14] The lattice parameters obtained in the present study are almost identical with those reported in the literatures. The bulk densities of the hot-press samples are also summarized in the table. The densities are approximately 98% of the theoretical value.

The thermal conductivity (κ) of the polycrystalline Cu–Ga–Te ternary compounds as a function of temperature is shown in Fig. 2. The lattice thermal conductivity (κ_{lat}) was roughly evaluated by subtracting the electronic thermal conductivity κ_{el} (= LT/ρ, where L is the Lorentz number = 2.45×10^{-8} W Ω K^{-2}) from the measured κ, i.e., $\kappa_{lat} = \kappa - LT/\rho$. It was confirmed that κ_{lat} was predominant in all the Cu–Ga–Te ternary compounds, equivalent to more than 97% of the measured κ, i.e. $\kappa = \kappa_{lat}$. The κ of CuGaTe$_2$ containing no vacancies decreases with increasing temperature. This means that the typical lattice contribution is
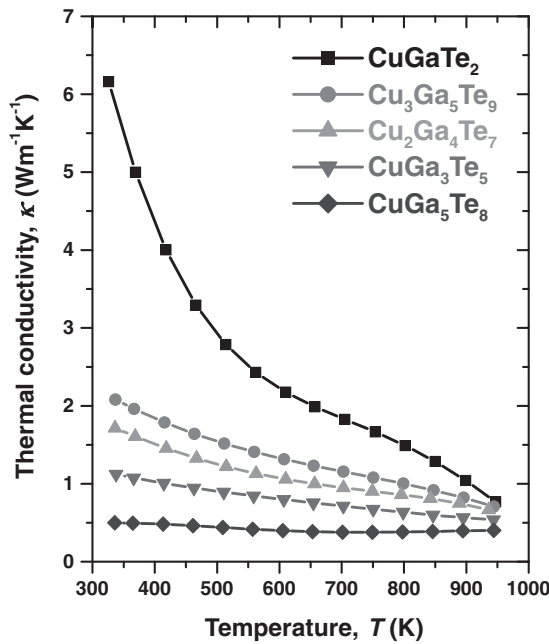
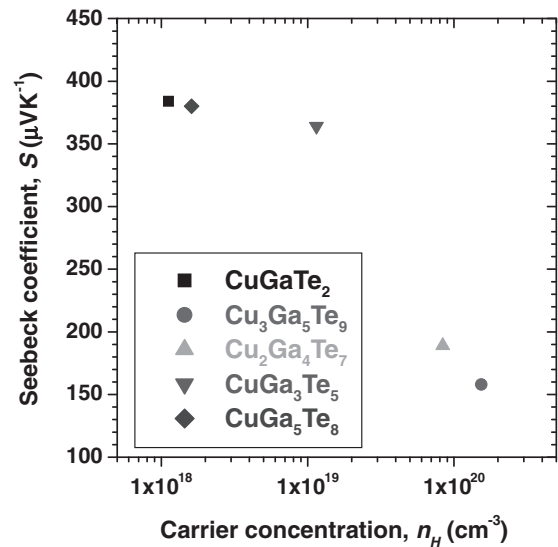Fig. 2 Temperature dependency of the thermal conductivity (κ) of polycrystalline Cu–Ga–Te samples.

Fig. 3 Relationship between the Hall carrier concentration (n_H) and the Seebeck coefficient (S) for the Cu–Ga–Te ternary compounds. The plotted data were obtained around room temperature.

Table 2 Room temperature values of the Hall coefficient (R_H), Hall carrier concentration (n_H), and Hall mobility (μ_H) of the Cu–Ga–Te ternary compounds.

Compounds	Density of vacancy	ρ (Ω cm)	R_H (cm^3 C^{-1})	n_H (cm^{-3})	μ_H (cm^2 V^{-1} s^{-1})
CuGaVA_0Te$_2$	0	6.86×10^{-2}	5.59	1.1×10^{18}	81.5
Cu$_3$Ga$_5$$VA_1Te_9$	1/9 of the cation site	1.43×10^{-2}	4.05×10^{-2}	1.5×10^{20}	2.8
Cu$_2$Ga$_4$$VA_1Te_7$	1/7 of the cation site	5.38×10^{-2}	7.49×10^{-2}	8.3×10^{19}	1.4
CuGa$_3$$VA_1Te_5$	1/5 of the cation site	2.60×10^{-1}	0.54	1.2×10^{19}	2.1
CuGa$_5$$VA_2Te_8$	1/4 of the cation site	3.23	3.89	1.6×10^{18}	1.2

predominant in the κ of CuGaTe$_2$. As shown in Fig. 2, the κ clearly decreases with increasing the amount of vacancies. In addition, the temperature dependence of the κ became flat with increasing the amount of vacancies. These results indicate that the vacancies existing in the crystal scatter phonons efficiently, resulting in well reduced κ with rather flat temperature dependence.

Room temperature values of the electrical resistivity (ρ), Hall coefficient (R_H), Hall carrier concentration (n_H), and Hall mobility (μ_H) of the Cu–Ga–Te ternary compounds are summarized in Table 2. The n_H values of the Cu–Ga–Te ternary compounds were found to be in the orders of 10^{18} to 10^{20} cm^{-3}. CuGaTe$_2$ containing no vacancies exhibits the lowest n_H value. In other compounds containing vacancies, the n_H value increases with decreasing the amount of vacancies. The relationship between the n_H and the S for the Cu–Ga–Te ternary compounds is shown in Fig. 3. Note that here the plotted data are obtained around room temperature. The S values of all the Cu–Ga–Te ternary compounds are positive, meaning that the majority of charge carrier is holes. A reasonable result can be seen in Fig. 3, i.e., the S decreases with increasing n_H. The μ_H values of the Cu–Ga–Te ternary compounds containing vacancies are quite low

compared with that of CuGaTe$_2$, indicating that vacancies scatter carriers efficiently.

The relationships between the amount of vacancies and the μ_H, κ_{lat}, or μ_H/κ_{lat} for the Cu–Ga–Te ternary compounds are shown in Fig. 4. It can be confirmed that the presence of vacancies reduced the μ_H and the κ_{lat}, indicating that the vacancies scatter both carriers and phonons. However, the decreasing rate of the μ_H is clearly larger than that of κ_{lat}, and CuGaTe$_2$ containing no vacancies has the highest μ_H/κ_{lat} in the Cu–Ga–Te ternary compounds. These results mean that the presence of vacancies degrades the TE performance of the Cu–Ga–Te ternary compounds. It is, therefore, CuGaTe$_2$ containing no vacancies would exhibit the highest ZT values in the Cu–Ga–Te ternary compounds.

4. Summary

The effect of the amount of vacancies on the TE properties of the Cu–Ga–Te ternary compounds with zinc-blende or chalcopyrite structure was examined on the polycrystalline samples of Cu$_3$Ga$_5$Te$_9$, Cu$_2$Ga$_4$Te$_7$, CuGa$_3$Te$_5$, CuGa$_5$Te$_8$, and CuGaTe$_2$. The presence of vacancies reduced the μ_H and the κ_{lat}, however, the reduction rate of the μ_H was larger
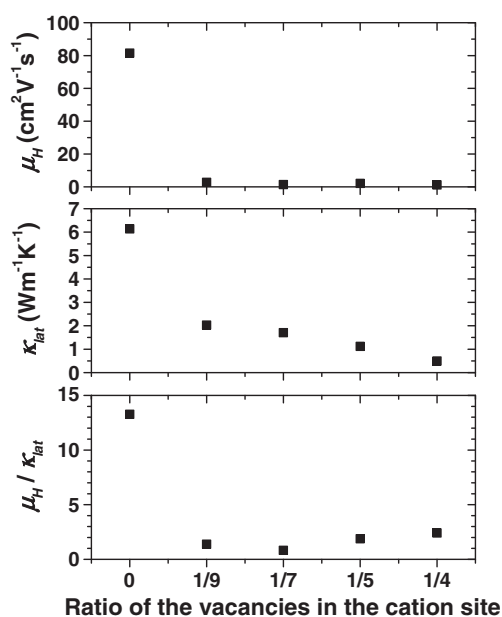
Fig. 4 Relationships between the amount of vacancies and the Hall mobility (μ_H), lattice thermal conductivity (κ_{lat}), or μ_H/κ_{lat} for the Cu–Ga–Te ternary compounds. The plotted data were obtained around room temperature.

than that of the κ_{lat}. These results imply that the presence of vacancies degrades the TE performance of the Cu–Ga–Te ternary compounds; in other words, CuGaTe$_2$ containing no vacancies will show the best TE figure of merit. It should be noted that the spatial distribution of vacancies also affects the TE properties. We have confirmed that vacancies in Cu$_2$Ga$_4$Te$_7$ are regularly arranged as point-type defects.[9] However, it has not been confirmed whether the vacancies exist as in-plane type or point type in other Cu–Ga–Te ternary compounds. More extensive studies are currently underway.

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