



Synthesis and thermal conductivities of ZnIn_2Te_4 and CdIn_2Te_4 with defect-chalcopyrite structure

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ABSTRACT

ZnIn_2Te_4 and CdIn_2Te_4 have a defect-chalcopyrite tetragonal crystal structure with structural vacancies. In order to investigate the effects of vacancies on the lattice thermal conductivity (κ_{lat}), single phase samples of ZnIn_2Te_4 and CdIn_2Te_4 were synthesized and their κ_{lat} values were examined in the temperature range from room temperature to 850 K. The κ_{lat} data for ZnIn_2Te_4 and CdIn_2Te_4 were compared with those of Zn- and Cd-series chalcopyrite compounds with no vacancies. The results revealed that the presence of vacancies alone in the defect-chalcopyrite structure does not result in effective phonon scattering.

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1. Introduction

Thermoelectric (TE) technology, for converting waste heat into useful electricity, is expected to play an important role in meeting today's energy challenges [1]. The efficiency of the device is linked to the TE properties of the generator materials and the temperature gradient across the device. The effectiveness of the TE conversion is determined by the dimensionless figure of merit, $ZT = S^2 \sigma T / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the total thermal conductivity ($\kappa = \kappa_{lat} + \kappa_{el}$, the lattice and the electronic contributions, respectively). Since S , σ , and κ_{el} in bulk materials are interrelated, it is very important to reduce κ_{lat} so that ZT can be increased [2]. Contemporary developments in low dimensional materials and new bulk TE materials are leading to breakthroughs in TE research [3]. Recently, low- κ_{lat} materials, such as Ag_9TlTe_5 [4], have been proposed as next-generation advanced TE materials.

Our group has focused on vacancies in the crystal as one way to reduce κ_{lat} . Good examples of compounds with vacancies include Ga_2Te_3 and In_2Te_3 with a defect zinc-blend structure (space group: $F-43m$) [5–7]. Due to valence mismatch between the cation and the anion, a third of the cation sites are structural vacancies; i.e., the chemical formula $A_2\text{Te}_3$ ($A = \text{Ga}, \text{In}$) can be written as $A_2VA_1\text{Te}_3$,

where VA indicates a vacancy. These vacancies are thought to be distributed in various states and are also expected to affect various physical properties including TE properties. Kurosaki et al. revealed that Ga_2Te_3 exhibits very low- κ_{lat} , most likely due to effective phonon scattering by two-dimensional vacancy planes that exist throughout the bulk sample [5]. Pei and Morelli have shown that a significant reduction in κ_{lat} occurs in $\text{InSb-In}_2\text{Te}_3$ solid solutions due to strong phonon–vacancy scattering [8].

Against this background, in the present study, we focused our attention on defect-chalcopyrite compounds (tetragonal structure, space group: $I-4$). Defect-chalcopyrite compounds contain a large number of vacancies in the crystal similar to defect zinc-blend compounds. The general chemical formula of defect-chalcopyrite compounds considered here is $\text{II-III}_2\text{-VI}_4$ where $\text{II} = \text{Zn}$ or Cd , $\text{III} = \text{In}$ or Ga , and $\text{VI} = \text{S}, \text{Te},$ or Se . In order to maintain the valence mismatch, half of the II sites in $\text{II-III}_2\text{-VI}_4$ compounds should be vacant; in other words, the chemical formula $\text{II-III}_2\text{-VI}_4$ can be written as $\text{II-VA-III}_2\text{-VI}_4$ [9]. The $\text{II-III}_2\text{-VI}_4$ defect-chalcopyrite compounds are closely related to parent II-IV-V_2 chalcopyrite compounds that contain no vacancies in the crystal, such as ZnGeAs_2 . The band structure and optical properties of the defect-chalcopyrite compounds ZnIn_2Te_4 [10,11] and CdIn_2Te_4 [12,13] have been previously reported. However, little research has been done on the κ (and κ_{lat}) values of these compounds. In the present study, therefore, we attempted to synthesize ZnIn_2Te_4 and CdIn_2Te_4 and investigate the temperature dependence of κ_{lat} . The obtained κ_{lat} values of ZnIn_2Te_4 and CdIn_2Te_4 were compared with those of

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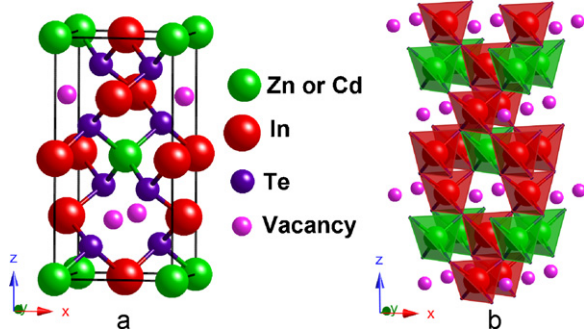


Fig. 1. (a) Crystal structure of ZnIn_2Te_4 . (b) Zn or Cd and In atoms exist at the center of tetrahedra surrounded by Te atoms.

the parent II-IV-V₂ chalcopyrite compounds from literature. The effects of vacancies on κ_{lat} of the chalcopyrite-series compounds are discussed in this report.

2. Experimental

ZnIn_2Te_4 and CdIn_2Te_4 ternary compounds were synthesized by direct reactions of mixtures of stoichiometric ratios of Zn (3N), Cd (6N), In_2Te_3 (5N), and Te (5N) in sealed silica tubes. These mixtures were slowly heated to 1173 K for ZnIn_2Te_4 and 1053 K for CdIn_2Te_4 , held at these temperatures for 3 days before quenching in an ice water bath. The products were crushed and milled into fine powders. Bulk samples were then produced by hot-pressing using a 10 mm graphite die under 45 MPa sintering pressure at 873 K for 2 h in an argon-flow atmosphere. The phases, morphologies, and chemical compositions of these samples were characterized by powder X-ray diffraction (XRD) technique using $\text{Cu K}\alpha$ radiation on a Rigaku RINT 2000 instrument and a scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) analyzer (Hitachi, S2600H) at room temperature. The densities of the bulk samples were calculated based on the measured weight and dimensions. Longitudinal and shear sound velocities were measured by the ultrasonic pulse echo method at room temperature in air, and the Debye temperature (θ_D) was evaluated from the measured sound velocities. Thermal conductivity (κ) was calculated from thermal diffusivity (α), heat capacity (C_p) and sample density (d) based on the relationship $\kappa = \alpha C_p d$. α was measured under vacuum using a laser flash apparatus (ULVAC, TC-7000). C_p was estimated using the Dulong-Petit model, $C_p = 3nR$, where n is the number of atoms per formula unit and R is the gas constant. κ was evaluated in the temperature range from room temperature to 850 K.

Table 1

Lattice parameter, sample bulk density, and chemical composition of the ZnIn_2Te_4 and CdIn_2Te_4 samples, as determined by EDX analysis.

	ZnIn_2Te_4	CdIn_2Te_4
Lattice parameter		
a (nm)	0.6132	0.6220
c (nm)	1.2292	1.2453
Theoretical density d_{th} (g cm^{-3})	5.79	5.88
Measured density d_{ex} (g cm^{-3})	5.76	5.83
Relative density d_{ex}/d_{th} (%)	99	99
Chemical composition determined by EDX analysis		
Zn (at.%)	15	–
Cd (at.%)	–	13
In (at.%)	29	30
Te (at.%)	56	57

3. Results and discussion

Powder XRD patterns of the prepared samples were in good agreement with the JCPDS database (Reference codes: 74-0218 for ZnIn_2Te_4 and 74-0219 for CdIn_2Te_4) [14,15]. It was confirmed from the XRD data that chemical reactions of all the raw materials used were completed and single phase samples of ZnIn_2Te_4 and CdIn_2Te_4 were successfully produced.

The crystal structures of the compounds are shown in Fig. 1(a). This crystal system is known as the defect-chalcopyrite structure. Details of this structure are reported in Refs. [10,14], wherein the atomic positions in the unit cell were reported as follows: (1) A Zn or Cd atom occupies the (0, 0, 0) position; (2) the In atom occupies the (0, 0, 0.5) and (0, 0.5, 0.25) positions; (3) the Te atom occupies the (0.26, 0.24, 0.13) position; (4) a vacancy occupies the (0.5, 0, 0.25) position. Two Zn or Cd atoms are present with two vacancies, four In atoms, and eight Te atoms in the unit cell. Zn or Cd and In atoms are present in the center of the tetrahedra created by four Te atoms, as shown in Fig. 1(b).

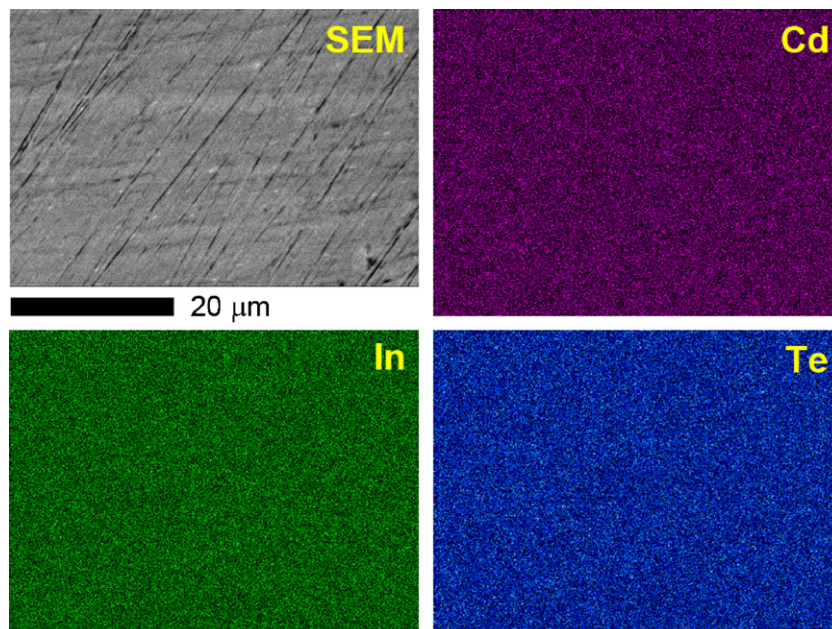


Fig. 2. SEM and EDX mapping images of the CdIn_2Te_4 sample.

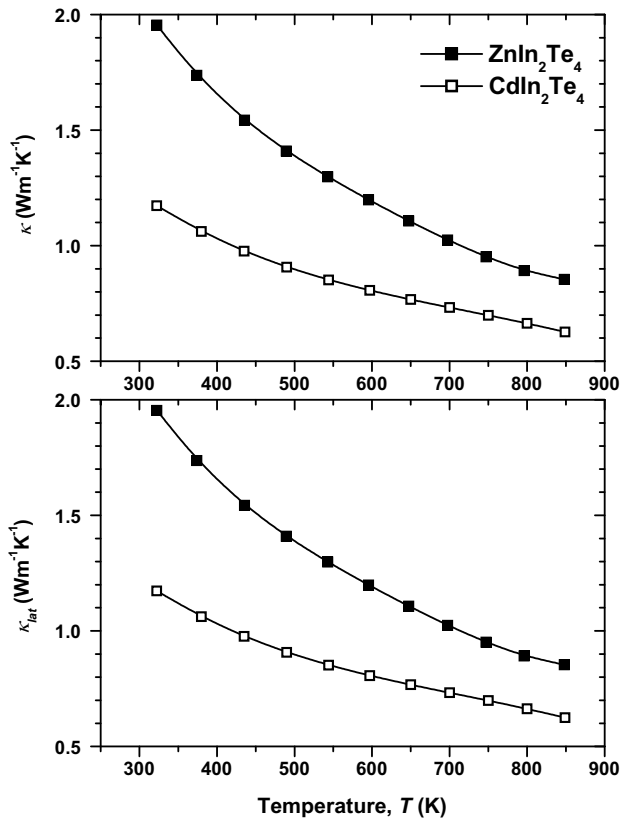


Fig. 3. Temperature dependence of the thermal conductivity of ZnIn_2Te_4 and CdIn_2Te_4 . (a) Total thermal conductivity (κ) and (b) lattice thermal conductivity (κ_{lat}).

The lattice parameters, sample bulk density, and chemical composition of the samples are summarized in Table 1. The tetragonal lattice parameters and the theoretical densities of these compounds were in good agreement with those reported by Hahn et al. [14]. The densities of the polycrystalline samples taken from the sintered specimens were 99% of the theoretical density. All the samples appeared to be stable in air at room temperature.

Table 2

Average atomic weight of the crystal (M), third root of the average volume occupied by an atom (δ), Debye temperature (θ_D), number of atoms in the unit cell (n), parameter ($M\delta(\theta_D)^3/n^{2/3}$) and lattice thermal conductivity (κ_{lat}) at room temperature for the II-III₂-VI₄ n defect-chalcopyrite compounds ZnIn_2Te_4 and CdIn_2Te_4 and the II-IV-V₂ chalcopyrite compounds ZnSiAs_2 , ZnGeAs_2 , ZnGeP_2 , CdGeP_2 , and CdSnAs_2 .

	ZnIn_2Te_4	CdIn_2Te_4	ZnSiAs_2	ZnGeAs_2	ZnGeP_2	CdGeP_2	CdSnAs_2
Average atomic weight of the crystal M (u)	115.1	121.8	60.8	72.0	50.0	61.7	95.2
Third root of the average volume occupied by an atom δ (nm)	0.321	0.325	0.278 ^a	0.282 ^a	0.271 ^b	0.281 ^c	0.302 ^d
Debye temperature θ_D (K)	175	166	339 ^e	302 ^e	392 ^e	304 ^e	255 ^e
Number of atoms in the unit cell n	14	14	16	16	16	16	16
Parameter $M\delta(\theta_D)^3/n^{2/3}$ (μm^3)	0.0341	0.0312	0.1036	0.0879	0.1286	0.0767	0.0752
Lattice thermal conductivity at room temperature κ_{lat} ($\text{Wm}^{-1}\text{K}^{-1}$)	2.1	1.2	14.0 ^f	11.4 ^f	18.0 ^f	11.0 ^f	9.2 ^e

^a Ref. [17].

^b Ref. [18].

^c Ref. [19].

^d Ref. [20].

^e Ref. [21].

^f Ref. [22].

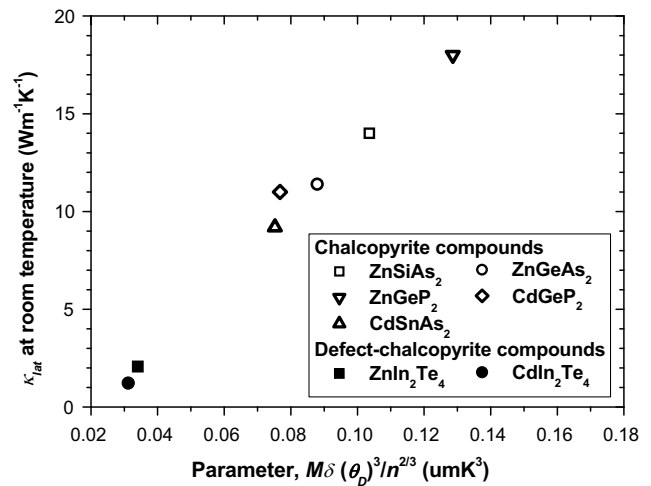


Fig. 4. Relationship between the parameter ($M\delta(\theta_D)^3/n^{2/3}$) and the lattice thermal conductivity (κ_{lat}) at room temperature for the II-III₂-VI₄ defect-chalcopyrite compounds, ZnIn_2Te_4 and CdIn_2Te_4 , together with the data of the II-IV-V₂ chalcopyrite compounds, ZnSiAs_2 , ZnGeAs_2 , ZnGeP_2 , CdGeP_2 , and CdSnAs_2 .

SEM and EDX mapping images of the bulk CdIn_2Te_4 sample are shown in Fig. 2. The SEM image indicated that the sample was homogeneous. EDX analysis revealed that Cd, In, and Te were uniformly distributed on the sample surface. In the case of ZnIn_2Te_4 , similar results to those for CdIn_2Te_4 were obtained. The SEM and EDX analyses confirmed that the ZnIn_2Te_4 and CdIn_2Te_4 samples were homogeneous, without any impurity phases. The quantitative EDX analysis confirmed that the chemical compositions of the bulk sintered samples were roughly in accordance with the stoichiometric compositions, as summarized in Table 1.

The temperature dependence of κ for ZnIn_2Te_4 and CdIn_2Te_4 is shown in Fig. 3(a). The κ values of both compounds were relatively low and decreased with temperature. κ_{lat} was obtained by subtracting κ_{el} from the total thermal conductivity. The value of κ_{el} can be calculated as $\kappa_{el} = L\sigma T$, where σ is the electrical conductivity and L is the Lorentz number ($L = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$). By using the σ values obtained experimentally by our group, κ_{lat} for ZnIn_2Te_4 and CdIn_2Te_4 was calculated as shown in Fig. 3(b). It was confirmed that κ_{lat} was predominant in these compounds. The κ_{lat} values for

ZnIn₂Te₄ and CdIn₂Te₄ at room temperature were approximately 2.1 and 1.2 Wm⁻¹ K⁻¹, respectively. ZnIn₂Te₄ yielded higher κ_{lat} values than CdIn₂Te₄ over the whole temperature range considered. As summarized in Table 2, CdIn₂Te₄ exhibited a lower Debye temperature ($\theta_D = 166$ K) than ZnIn₂Te₄ ($\theta_D = 175$ K). Since ZnIn₂Te₄ and CdIn₂Te₄ have the same crystal structure, the larger molecular weight of CdIn₂Te₄ would lead to lower θ_D and thus lower κ_{lat} compared to ZnIn₂Te₄.

In order to discuss the effect of vacancies on κ_{lat} in the defect-chalcopyrite compounds, the κ_{lat} values obtained for ZnIn₂Te₄ and CdIn₂Te₄ were compared with those of the chalcopyrite compounds with no vacancies. Among various chalcopyrite compounds, we chose the Zn- and Cd-series II-IV-V₂ compounds for this purpose, as summarized in Table 2.

Generally, under the assumptions that none of optical phonons carry heat and that the temperature is above the Debye temperature θ_D , κ_{lat} can be expressed as [16]:

$$\kappa_{lat} \propto \frac{M\delta(\theta_D)^3}{n^{2/3}T}$$

where M is the average atomic weight of the crystal, δ is the third root of the average volume occupied by an atom, n is the number of atoms in the unit cell, and T is the absolute temperature. M can be obtained from the molecular weight. δ can be calculated from the lattice parameter. The lattice parameter, θ_D , and κ_{lat} values for ZnSiAs₂, ZnGeAs₂, ZnGeP₂, CdGeP₂, and CdSnAs₂ have been reported in Refs. [17–22]. We calculated the parameter ($M\delta(\theta_D)^3/n^{2/3}$) at 300 K for the II-IV-V₂ chalcopyrite compounds, ZnSiAs₂, ZnGeAs₂, ZnGeP₂, CdGeP₂, and CdSnAs₂, and the II-III₂-VI₄ defect-chalcopyrite compounds, ZnIn₂Te₄ and CdIn₂Te₄. The values of M , δ , n , θ_D , ($M\delta(\theta_D)^3/n^{2/3}$) and κ_{lat} at room temperature for these compounds are summarized in Table 2. The relationship between the parameter ($M\delta(\theta_D)^3/n^{2/3}$) and κ_{lat} at room temperature is shown in Fig. 4. From the figure, it is observed that (1) decreasing the value of the parameter ($M\delta(\theta_D)^3/n^{2/3}$) leads to a decrease in the value of κ_{lat} and (2) the κ_{lat} values of ZnIn₂Te₄ and CdIn₂Te₄ are on the extrapolated line which expresses the relationship between the parameter ($M\delta(\theta_D)^3/n^{2/3}$) and κ_{lat} for the II-IV-V₂ chalcopyrite compounds. These results demonstrate that the magnitude relation of the κ_{lat} values of the II-IV-V₂ chalcopyrite compounds as well as the II-III₂-VI₄ defect-chalcopyrite compounds can be explained by the general κ_{lat} theory, viz. the vacancies in the defect-chalcopyrite compounds have little effect on the reduction of κ_{lat} .

4. Summary and conclusion

In the present study, polycrystalline single phase samples of ZnIn₂Te₄ and CdIn₂Te₄ with the defect-chalcopyrite structure were

successfully synthesized and κ was examined in the temperature range from room temperature to 850 K. The XRD patterns and the lattice parameters are in good agreement with previously reported data. The κ values of both samples were relatively low and decreased with temperature, and CdIn₂Te₄ yielded lower κ values than ZnIn₂Te₄. For both compounds, κ_{lat} was predominant, equivalent to more than 99% of the measured κ . CdIn₂Te₄ exhibited a lower Debye temperature ($\theta_D = 166$ K) than ZnIn₂Te₄ ($\theta_D = 175$ K), which would lead to a lower κ_{lat} for CdIn₂Te₄ than for ZnIn₂Te₄. The obtained κ_{lat} values for ZnIn₂Te₄ and CdIn₂Te₄ were compared to those of the Zn- and Cd-series chalcopyrite compounds with no vacancies. These results revealed that the vacancies in the defect-chalcopyrite compounds are not responsible for the reduction in κ_{lat} , in other words, the presence of vacancies alone in the defect-chalcopyrite structure does not result in effective phonon scattering.

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