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Structural, thermodynamical and optical properties of Cu_2-II-IV-VI_4 quaternary compounds

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The Cu_2-II-IV-VI_4 compounds (II = Zn, Cd; IV = Si, Ge, Sn; VI = S, Se, Te) with a tetrahedral coordinated structure have been investigated, as compared with the results of the products synthesized from respective elemental mixtures. These crystal structures and melting points are determined, using differential thermal analysis and powder X-ray diffraction, respectively. The optical band gaps of these balk crystals grown by the horizontal gradient freezing or Iodine transport method are also measured by optical absorption. These melting points, lattice constants and band gaps are found to vary linearly with increasing of mean atomic weight, and can be established from the empirical equations.

1. Introduction

Tetrahedrally coordinated ternary and quaternary compound semiconductors, for examples, defect chalcopyrite, spinel, stannite and famatinite, were derived by Pamplin [1] from various combinations of elements in the vicinity of the IV group element. Such multinary compounds are characterized by offering an extensive field for material design, and hence are important to develop new materials for devices application. Among those materials, a lot of Cu_2-II-IV-VI_4 quaternary compounds are known to have a stannite structure [2, 3], and a part of these compounds have a potential for application in photovoltaic cells [4–6]. However, it is very difficult to prepare high-quality crystals as compared with ternary chalcopyrite compound semiconductors. Thus, it is necessary to establish structural and thermodynamical properties to obtain single crystals with suitable size, compositional homogeneity and high purity, and the reliable databases on the physical properties should be constructed.

Until now, we have studied the synthesis from the stoichiometric melts of Cu_2-II-IV-Se_4 (II = Zn, Cd; IV = Ge, Sn), and primitive structural and optical properties of these four compounds have been characterized [4]. On the other hand, Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ thin films were prepared by the spray [5] and evaporation [6], and the electrical resistivity of only Cu_2ZnSnS_4 thin films were measured [5, 6]. However, the crystal structures, and thermodynamical and optical properties of many quaternary compounds have been yet unknown. In this study, the melting points of Cu_2-II-IV-VI_4 compounds (II = Zn, Cd; IV = Si, Ge, Sn; VI = S, Se, Te) are determined by the differential thermal analysis (DTA) as exactly as possible, and the lattice constants of these synthesized products are determined using powder X-ray diffraction (XRD). Furthermore, their crystals are grown by the horizontal gradient freezing (HGF) or Iodine transport (IT) method, and the energy gaps are also measured. It is shown that linear relationships exist between these values and the mean atomic weight, as same reported by Nomura *et al.* [7] and Matsushita *et al.* [8] about lattice constants, optical band gaps and melting points of chalcopyrite semiconductors.

2. Experimental

The melting points were observed using DTA. The mixture of the elements, weighed about 0.5 g, was sealed in a quartz ampoule having dimensions of 7 mm $\phi \times 40$ mm under a vacuum. The difference in temperature between a sample and a reference material, i.e., DTA signal, was directly measured by thermocouples (CA). The rate of DTA in the heating and cooling processes was held at a constant value of 2 K/min. Here, the systematic error of the observed temperature was confirmed to be within 2 K at the most. The products synthesized after DTA were identified by powder XRD using the Cu-K_α characteristic line (1.5405 Å). The reference materials were naturally prepared during the DTA, and used for comparison of XRD patterns. Furthermore, the XRD patterns were also compared with the JCPDS files [9]. The lattice constants were calculated from XRD lines using the method of least squares.

Bulk crystals were grown using the HGF method from the respective melts. The starting materials weighed to 3–5 g in total were sealed in a quartz tube having dimensions of 8 mm $\phi \times 80$ mm under vacuum of $\sim 10^{-6}$ Torr. The samples sealed in a quartz tube were first heated to the temperatures above 50–100 K of the melting point of respective compounds, and held at this temperature for 6 h. Then, the whole zone was cooled electrically at a speed of 20 K/h, keeping the temperature gradient of 3 K/cm. Since Cu_2ZnGeS_4 and Cu_2CdGeS_4 have higher melting point, these samples were prepared by means of the IT method. The starting materials weighed to 1–3 g in total and the iodine of 5, 10 or 20 mg/cm^3 were sealed in a quartz tube having dimensions of 8 or 15 mm $\phi \times 150$ mm under vacuum of $\sim 10^{-6}$ Torr. The samples sealed in a quartz tube were heated to 1073–1273 K in the high-temperature zone and 873–1023 K in the low-temperature zone, and held for 120 h.

The single crystal blocks of grown bulk crystals, having near stoichiometric compositions clarified by electron probe microanalyzer (EPMA), were investigated by the optical absorption. Transmission spectra of the samples, having a few kinds of thickness raging from 20 to 50 μm, were measured using Jasco V-570 with a Halogen lamp as the light source at room temperature, and the optical energy gaps were determined.

3. Results and discussion

3.1. Lattice constants

The examples of determining the lattice constants are shown in the case of Cu_2-II-IV-S_4 (II = Zn, Cd; IV = Ge, Sn) as follows. The Cu_2ZnSnS_4 and Cu_2CdSnS_4 compounds have the tetrahedral structure, and the atomic arrangement in a unit cell can be analogically derived from that of the chalcopyrite semiconductor. In addition, these two compounds can be confirmed to have the stannite structure for ordering I-II and ordering I-IV by the Rietved Method [10]. On the other hand, the Cu_2ZnGeS_4 and Cu_2CdGeS_4 compound has an orthorhombic structure which can be analogical from that of "JCPDS: No.43-1387" [9]. The lattice constants determined from all of XRD lines in Fig. 1 are shown in Table I, the values are in good agreement with the data of the samples prepared by the iodine transport method as reported by Nitsche *et al.* [3]. We have also measured structural properties of another Cu_2-II-IV-VI_4 compounds by the above-mentioned method, as summarized in Table I. Among these materials, four following materials were not synthesized: $Cu_2ZnGeTe_4$ have the mixed phases of ZnTe and Cu_2GeTe_3, $Cu_2ZnSnTe_4$ have these of ZnTe, SnTe and Cu_2SnTe_3, $Cu_2CdGeTe_4$ have these of CdTe and Cu_2GeTe_3, and $Cu_2CdSnTe_4$ have these of CdTe, SnTe and Cu_2SnTe_3. Fig. 2 shows the lattice constant "*a*" as a function of mean atomic weight for Cu_2-II-IV-VI_4 compounds, and the value increases linearly with increasing of mean atomic weight for two kinds of compounds with the tetrahedral or orthorhombic structure as follows: tetrahedral system; a (Å) $= 0.015\langle M\rangle + 4.592$ and orthorhombic system: a (Å) $= 0.017\langle M\rangle + 6.739$, where a is the lattice constant "*a*", and $\langle M\rangle$ the mean atomic weight.

TABLE I Some physical properties for Cu_2-II-IV-VI_4 compounds (*:ref. [2, 3])

Materials	Mean atomic weight ⟨M⟩	Melting point (°C)	Crystal system	a (Å)	b (Å)	c (Å)	E_g (eV)
Cu_2ZnSiS_4	43.6		ortho.*	7.435*	6.396*	6.135*	3.25*
$Cu_2ZnSiSe_4$	67.1		ortho.*	7.823*	6.720*	6.440*	2.33*
$Cu_2ZnSiTe_4$	91.4	700	tetra.	5.98	–	11.78	1.47
Cu_2ZnGeS_4	49.2	1120	ortho.	7.57	6.47	6.13	2.10*
$Cu_2ZnGeSe_4$	72.6	890	tetra.	5.606	–	11.04	1.63
$Cu_2ZnGeTe_4$	96.9						
Cu_2ZnSnS_4	54.9	990	tetra.	5.43	–	10.81	1.39
$Cu_2ZnSnSe_4$	78.4	805	tetra.	5.693	–	11.33	1.44
$Cu_2ZnSnTe_4$	102.7						
Cu_2CdSiS_4	49.5		ortho.*	7.598*	6.486*	6.258*	
$Cu_2CdSiSe_4$	72.9		ortho.*	7.990*	6.824*	6.264*	
$Cu_2CdSiTe_4$	97.3	650	tetra.	6.12	–	11.79	
Cu_2CdGeS_4	55.0	1020	ortho.	7.70	6.55	6.28	
$Cu_2CdGeSe_4$	78.5	840	ortho.	8.088	6.875	6.564	1.20
$Cu_2CdGeTe_4$	102.8						
Cu_2CdSnS_4	60.8	926	tetra.	5.59	–	10.84	1.37
$Cu_2CdSnSe_4$	84.3	780	tetra.	5.832	–	11.39	0.96
$Cu_2CdSnTe_4$	108.6						

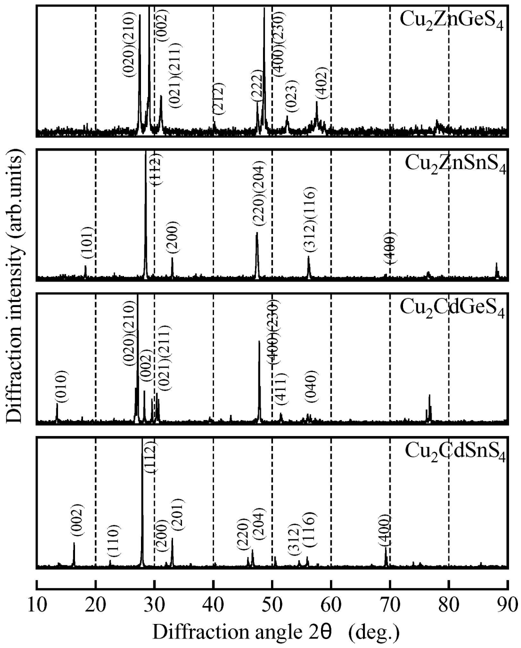

Figure 1 Powder X-ray diffraction patterns of Cu_2-II-IV-S_4 compounds (II = Zn, Cd; IV = Ge, Sn).

3.2. Melting points

As the examples of DTA curves, Fig. 3 shows these of Cu_2-II-IV-S_4 compounds (II = Zn, Cd; IV = Ge, Sn)

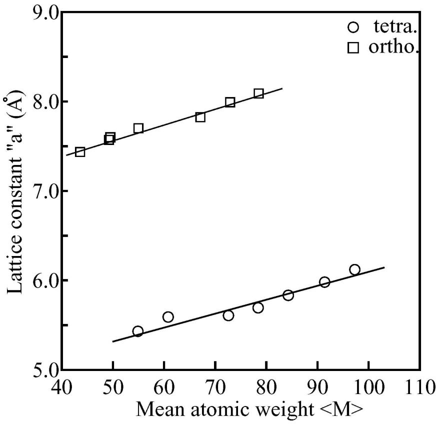

Figure 2 Lattice constant "*a*" as a function of mean atomic weight for Cu_2-II-IV-VI_4 compounds.

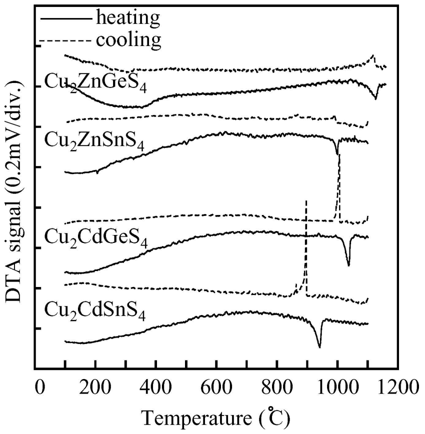

Figure 3 DTA curves of Cu$_2$-II-IV-S$_4$ compounds (II = Zn, Cd; IV = Ge, Sn) in the heating and cooling processes.

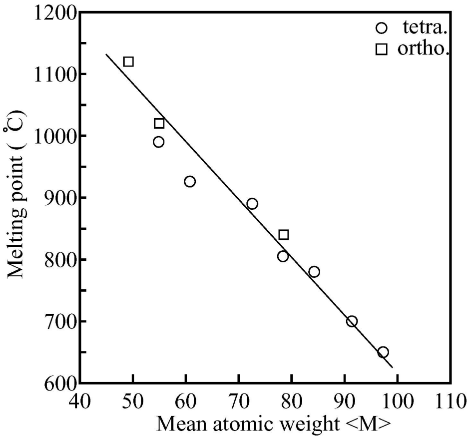

Figure 4 Melting point as a function of mean atomic weight for Cu$_2$-II-IV-VI$_4$ compounds.

in the heating and cooling processes. All of these four compounds were evaluated to have the melting points as shown in Table I, because respective DTA curves exhibit only one peak in both the heating and cooling processes. We also measured the melting points of another Cu$_2$-II-IV-VI$_4$ compounds by the above-mentioned method, as summarized in Table I. Fig. 4 shows the melting point as a function of mean atomic weight for Cu$_2$-II-IV-VI$_4$ compounds, and the value decreases linearly with increasing of mean atomic weight as follows, T_{m} (°C) $= -8.72\langle \mathrm{M}\rangle + 1500$, where T_{m} is the melting point, and $\langle \mathrm{M}\rangle$ the mean atomic weight. Dependencies of the melting points of the Cu$_2$-II-IV-VI$_4$ are compared with those for Cu-III-VI$_2$ group chalcopyrite semiconductor [8]. It can be seen that Cu$_2$-II-IV-VI$_4$ has a similar tendency to their ternary analog system, and additionally, the values the quaternary system is a little lower than these of their ternary analogs.

3.3. Optical band gaps

The values of the band gaps determined from the results of the optical absorption are summarized in Table I, and those of some compounds are found to be suitable for optimum conversion efficiency for photovoltaic cells (1.2–1.5 eV). Fig. 5 shows the optical band gap as a function of mean atomic weight for Cu$_2$-II-IV-VI$_4$ compounds, and the value decreases linearly with increasing of mean atomic weight for three kinds of compounds Cu$_2$-II-IV-S$_4$, Cu$_2$-II-IV-Se$_4$ or Cu$_2$-II-IV-Te$_4$ system as follows: Cu$_2$-II-IV-S$_4$ system; E_{g} (eV) $= -0.06\langle \mathrm{M}\rangle + 4.81$ and Cu$_2$-II-IV-Se$_4$ system: E_{g} (eV) $= -0.06\langle \mathrm{M}\rangle + 6.05$, where E_{g} is the optical band gap, and $\langle \mathrm{M}\rangle$ the mean atomic weight.

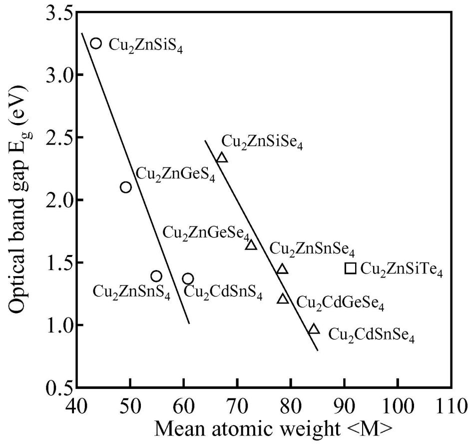

Figure 5 Optical band gap as a function of mean atomic weight for Cu$_2$-II-IV-VI$_4$ compounds.

4. Summary

Tetrahedrally coordinated quaternary semiconductors Cu$_2$-II-IV-VI$_4$ compounds (II = Zn, Cd; IV = Si, Ge, Sn; VI = S, Se, Te) were investigated about these structural and thermodynamical properties to obtain better-quality single crystals The physical properties of the above-mentioned compounds were grown by the horizontal gradient freezing or Iodine transport method, and determined from the results of differential thermal analysis, powder X-ray diffraction, optical absorption. It was found that these melting points, lattice constants and band gaps could be established from the empirical linear equations with these mean atomic weights.

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