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Phase Diagram of the $(CuInTe_2)_{1-x}$–$(2ZnTe)_x$ System and Crystal Growth of $CuZn_2InTe_4$ from Zinc Chloride Flux*

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The phase diagram of the system $(CuInTe_2)_{1-x}$–$(2ZnTe)_x$ has been investigated by microstructure, DTA, and X-ray examinations. It has been found that $CuInTe_2$ and ZnTe form, at elevated temperatures, a continuous series of zincblende solid solutions. The boundaries of the solid-phase fields have been established: At room temperature, the tetragonal chalcopyrite phase α is stable up to about the $x = 0.10$ composition and is followed by a two-phase region $(\alpha + \beta)$, extending from $x = 0.10$ to $x = 0.33$ composition, and by a region $x \geq 0.33$ with the cubic zincblende β structure. Using the flux growth technique with $ZnCl_2$ as solvent, single crystals of the $CuZn_2InTe_4$ composition ($x = 0.50$), closely related to the diamond lattice, have been obtained.

Introduction

Four-component systems of the type $A^{N-1}C^{N+1}D_2^{8-N}$–B^ND^{8-N} ($N = 2$ and 3), where *A*, *B*, *C*, and *D* are elements belonging to four different groups of the periodic table, have been the subject of several investigations (1–22). Special attention in these systems has been paid to crystal chemistry of quaternary diamond-like phases with the general composition $A^{N-1}B_2^NC^{N+1}D_4^{8-N}$ (*22–25*), which belong to the class of normal tetrahedral structures (*26, 27*). These quaternary phases correspond to a specific point of the line connecting a ternary chalcopyrite to a binary zincblende/wurtzite compound. However, since the normal valence and four-electron conditions necessary to form a tetrahedral phase are satisfied for each point of this line, any combination of these binary and ternary compounds can give rise, in principle, to a quaternary tetrahedral phase of definite composition. The $A^{N-1}B_2^NC^{N+1}D_4^{8-N}$ phases might consequently be either solid solution or independent chemical compounds with peculiar chemical and physical properties. The solution to this problem, together with the study of the synthesis processes and structural characterization of such phases, represents another interesting aspect of these researches.

In this paper, as a further contribution to the study of $A^IB_2^{II}C^{III}D_4^{VI}$ chalcogenides, we report the phase diagram of the $(CuInTe_2)_{1-x}$–$(2ZnTe)_x$ system we have obtained in order to define the region of existence and stability of the $CuZn_2InTe_4$ phase and to establish the appropriate crystal growth techniques for this composition.

Experimental

All compositions were prepared by the usual metallurgical techniques by direct

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fusion from stoichiometric mixtures of commercially available high-purity elements (Johnson–Matthey, quoted purity 99.999+ %). The capsules were placed in the center of a vertical furnace and heated in turn above the melting point of each composition, using a programmed linear heating cycle of 20 deg hr^{-1}. During the melting process the samples were mechanically vibrated to enhance a thorough mixing of the elements and to eliminate blowholes and voids in the resultant ingots. After fusion, the samples were crystallized by rapid quenching in air below the solidification point of the component ($CuInTe_2$) with the lower melting temperature (785°C). Soon after this operation, the ampoules were transferred into another vertical furnace, previously regulated at 750°C, and then slowly cooled at room temperature with a speed of 6 deg hr^{-1}. This technique ensured homogeneity of the composition along the ingots. The absence of distilled material and of reaction with the quartz indicated that all samples had the starting composition.

The Phase Diagram

The phase diagram (Fig. 1) was drawn combining the results of DTA measurements, X-ray studies, and microstructural examinations of a large number of samples. The variations with composition of microhardness (Vickers) and lattice parameter of the room-temperature phases are plotted separately in Fig. 2.

The trend of liquid and solid curves is indicative of the existence, at higher temperatures, of a continuous series of solid solutions. This result might appear surprising, since $CuInTe_2$ is commonly known to crystallize only in the tetragonal chalcopyrite ($E1_1$) structure, while ZnTe is a cubic zincblende ($B3$) compound. On the contrary, as previously observed in the analogous $(CuInTe_2)_{1-x}$–$(2CdTe)_x$ and $(CuInTe_2)_{1-x}$–$(2InAs)_x$ systems (*28*), the occurrence of complete solubility suggests the possible existence of a zincblende form of $CuInTe_2$ at elevated temperatures. Such a feature has been experimentally shown by Palatnik and

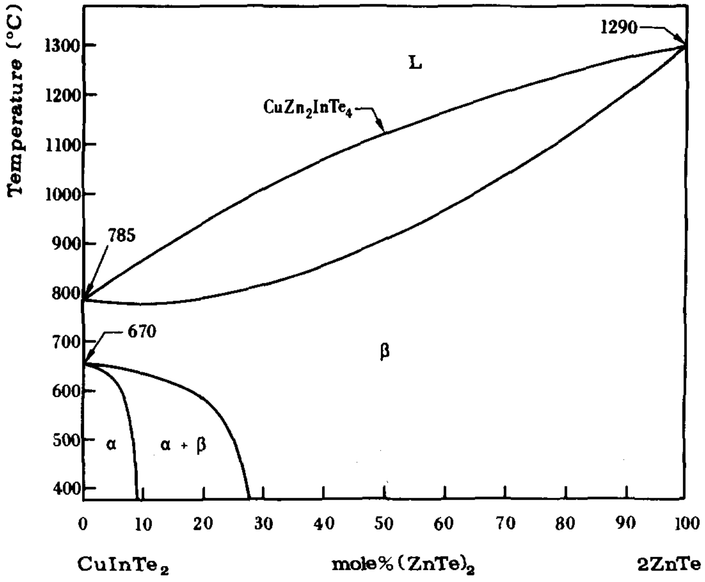

FIG. 1. Phase diagram of the $(CuInTe_2)_{1-x}$–$(2ZnTe)_x$ system.

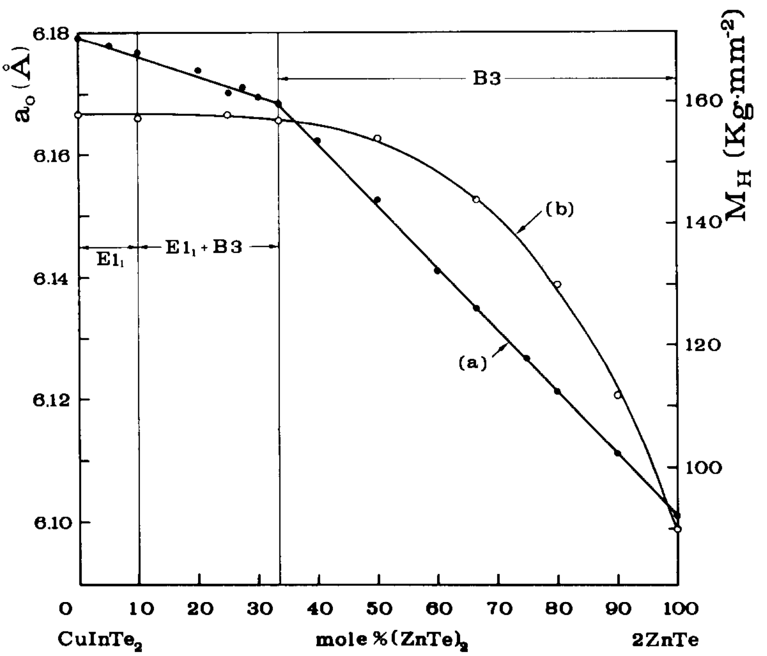

FIG. 2. Lattice parameter (a) and microhardness (b) of the room-temperature phases vs composition. For chalcopyrite phases, we have used the effective cubic lattice constant $a_0 = (a^2c/2)^{1/3}$. For the compositions with $0.10 < x < 0.33$, lattice parameter refers to the main phase.

Rogacheva (*29*). These authors, studying the ternary system Cu–In–Te along the Cu$_2$Te–In$_2$Te$_3$ section, found that CuInTe$_2$ is a chemical compound which melts congruently (789°C) at the stoichiometric composition and shows a solid–solid phase transition at 672°C, characterized as an allotropic transformation from the chalcopyrite to the zincblende structure. These results are in evident disagreement with Zalar (*30, 31*). In fact, on the basis of microstructural examinations on samples annealed for 15 hr at 650°C, he suggested that CuInTe$_2$ is a supersaturated solid solution and the phase transition below the melting point is due to the presence of a small amount of a secondary phase (presumably InTe), which forms locally and, after annealing, precipitates out of the chalcopyritic matrix.

To shed some light on this problem, some CuInTe$_2$ samples were annealed at 720°C for several days and then quickly quenched at −60°C in a CaCl$_2$ saturated solution. Other samples were directly quenched from liquid temperature or slowly lowered to room temperature using different cooling rates. In all cases, the microstructure and microhardness examinations on etched surfaces of the samples (etching CP-4 without bromine) did not reveal foreign phases inside the grains of the main matrix. It should be noted, in this regard, that the $A^{I}C^{III}D_2^{VI}$ compounds are generally stable in very narrow composition ranges and that small deviations from stoichiometry lead to multiphase regions and to additional thermal peaks in the DTA curves (*29, 32, 33*). Unfortunately, all CuInTe$_2$ samples in quenched and slow-cooled forms exhibited only the lines of the chalcopyrite structure and all our attempts to obtain the zincblende form by fast cooling were always unsuccessful. This result, contrary to what happens for several $A^{II}C^{IV}D_2^{V}$ chalcopyrite semiconductors (*34*), is characteristic of the $A^{I}C^{III}D_2^{VI}$ compounds. In fact, for these compounds the high-temperature modification was retained at room temperature only in few cases. These are: $CuFeS_2$, which undergoes a tetragonal to cubic zincblende transformation at 557°C, followed by a second-order transition at ~657°C (*35*), and $AgInS_2$, which transforms from chalcopyrite to wurtzite structure at ~700°C (*36*).

The existence of the zincblende modification in $CuInTe_2$ can be deduced also by examining the works of Range *et al.* on the high-pressure transformations of $A^{I}C^{III}D_2^{VI}$ chalcogenides (*37, 38*). These authors found that $CuInTe_2$ transforms at 20 kbar and 570°C to a high-pressure phase with NaCl ($B1$) structure, although it is not explicitly stated if the NaCl structure directly follows the chalcopyrite structure. However, they observed that the inverse transformation $B1 \rightarrow E1_1$, at high temperature, proceeds via intermediate defect zincblende phases.

As a matter of fact, the general problem of explaining the nature of the phase transitions in $A^{N-1}C^{N+1}D_2^{8-N}$ tetrahedrally coordinated semiconductors requires further investigation and cannot be considered, at present, completely resolved.

The phase diagram of Fig. 1 is characterized by three structural regions, whose boundaries were established by both thermal and X-ray analyses. The tetragonal chalcopyrite phase α exists at temperatures below 670°C and extends, at room temperature, up to the $x = 0.10$ composition. The cubic zincblende phase β, instead, is stable above temperatures ranging from 670°C to room temperature, for compositions with $x < 0.33$, and at any temperature below the solid curve, for $x \geq 0.33$ compositions. The fields of stability of α and β phases are separated by a third region ($\alpha + \beta$) of coexis-

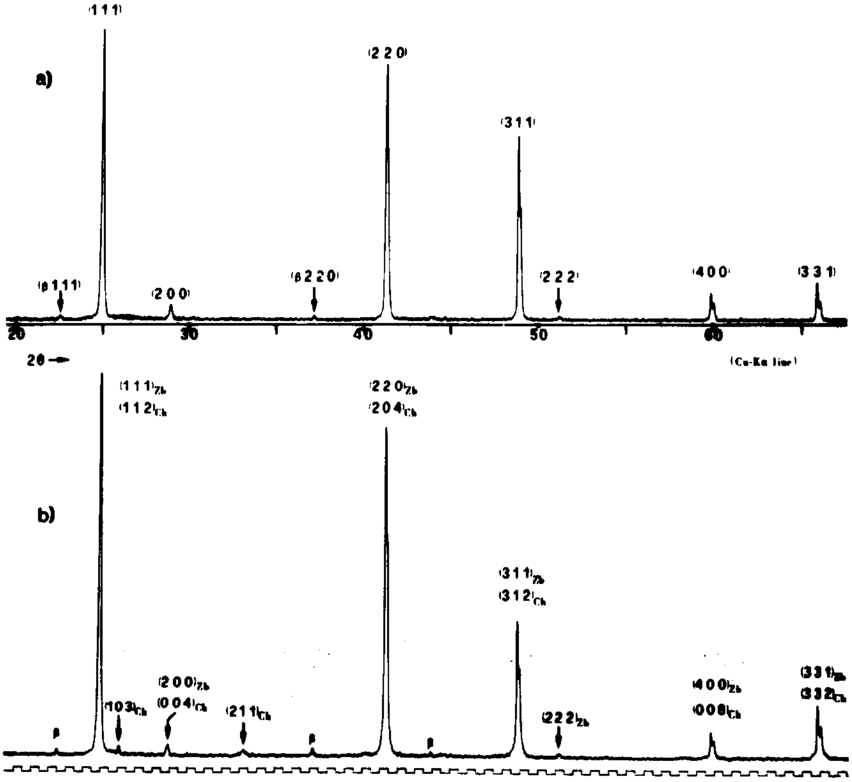

FIG. 3. X-Ray diffractograms of the $x = 0.275$ composition. (a) Quenched form; (b) slow-cooled form.

tence of chalcopyrite and zincblende solid solutions extending, at room temperature, from $x = 0.10$ to $x = 0.33$ compositions. Let us make more clear what happens in the $(\alpha + \beta)$ region with a typical example. Figure 3 shows the X-ray diffractograms of the $x = 0.275$ composition performed on quenched and slow-cooled samples. The quenched form exhibits the cubic zincblende structure entirely; the slow-cooled one shows also the lines of the chalcopyrite structure.

The structure change of the alloys can also be observed in Fig. 4, where the specific heat, at 300°K, of the room-temperature phases is plotted versus composition in arbitrary units.[1] The curve reaches a maximum near the $x = 0.33$ composition, which is the point separating, at room temperature, the zincblende from the chalcopyrite and chalcopyrite–zincblende solid solutions. It is worthy of note that the $x = 0.33$ composition, at which the β phase stably takes place, corresponds to a quaternary phase ($CuZnInTe_3$), in which the anion is evenly surrounded, in the four tetrahedral sites, by an equal number (1.33) of cations.

The results of the present investigation show undoubtedly that the $CuZn_2InTe_4$ quaternary phase ($x = 0.50$) is simply a term of a complete series of solid solutions along the entire phase diagram. Nevertheless, the study of this composition, and in general of all $A^{N-1}B_2^N C^{N+1} D_4^{8-N}$ quaternary phases, is of equally great interest in order to understand the nature and the evolution of the physical properties in more and more complex classes of normal tetrahedral structure semiconductors.

Flux Growth of $CuZn_2InTe_4$

Single crystals of the $CuZn_2InTe_4$ phase were obtained by the flux growth method using $ZnCl_2$ (Merck, pure reagent) as solvent.

The solutions were prepared following the technical procedures reported elsewhere (*41*). The capsules, containing a mixture of 0.05 mole%of $CuZn_2InTe_4$ and 0.95 mole% of $ZnCl_2$, were slowly heated to 710°C with a continuous mechanical vibration and then

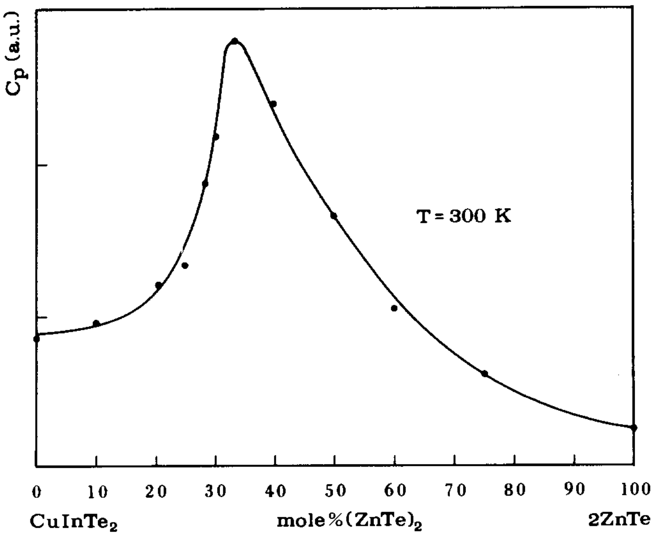

FIG. 4. Trend of the specific heat of the room-temperature phases, at 300°K, vs composition in arbitrary units.

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[1] The specific heat was measured using a slightly modified version of the laser-flash calorimeter described by Takahashi and Murabayashi (*39, 40*).

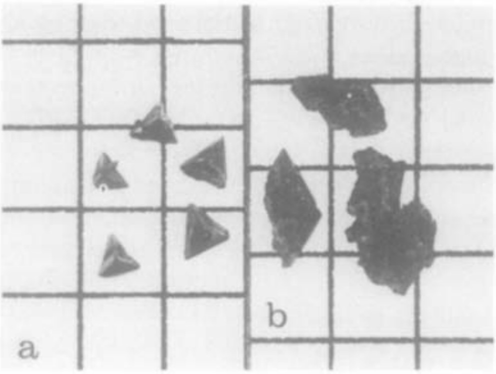

FIG. 5. Pyramids (a) and platelets (b) of $CuZn_2InTe_4$ (1 div = 4 mm).

lowered to room temperature by a programmed cooling rate of 6 deg hr^{-1}. Oscillatory cooling cycles of the type described by Hintzmann and Müller-Vogt (*42*) were also used. The crystals were removed simply by dissolving the flux in doubly distilled water. They grew with two crystal forms, pyramids (Fig. 5a) and platelets (Fig. 5b). The form modification was essentially due to a supersaturation effect of the solution. Some growth runs produced also crystals with a dendritic form (Fig. 6.).

The chemical composition of the grown crystals was checked with X-ray fluorescence and powder diffraction analyses. The former insured the presence of quaternary crystals; the latter, by comparison with the powder diffractograms of polycrystalline samples, was consistent with the $CuZn_2InTe_4$ composition.

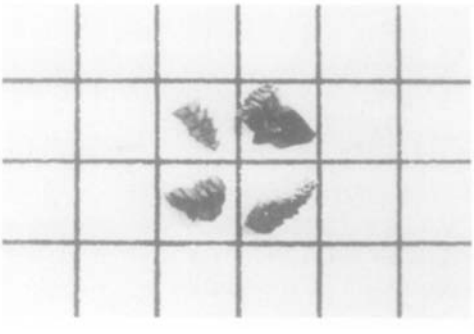

FIG. 6. Dendrite growth of $CuZn_2InTe_4$.

Studies of crystal growth processes by the flux method are now in progress for other $A^{I}B_2^{II}C^{III}D_4^{VI}$ chalcogenides.

Acknowledgments

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