# Phase Relations in the Zn<sub>3</sub>As<sub>2</sub>–ZnAs<sub>2</sub>–CdAs<sub>2</sub>–Cd<sub>3</sub>As<sub>2</sub> System

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**Abstract**—Phase relations along the  $Cd_3As_2$ – $ZnAs_2$  and  $Zn_3As_2$ – $CdAs_2$  joins are studied by differential thermal analysis, x-ray diffraction, and microstructural analysis. The results, in conjunction with earlier data on the  $CdAs_2$ – $ZnAs_2$ ,  $Zn_3As_2$ – $Cd_3As_2$ ,  $Cd_3As_2$ – $CdAs_2$ , and  $ZnAs_2$ – $Zn_3As_2$  binaries, are used to map out the phase diagram of the liquidus surface in the composition region  $Zn_3As_2$ – $ZnAs_2$ – $CdAs_2$ – $CdAs_2$  of the ternary system Cd–As–Zn. The ternary eutectic revealed in this region has an approximate composition of 26 at. % Cd + 65 at. % As + 9 at. % Zn and melts at 863 K.

## INTRODUCTION

The study of the Zn<sub>3</sub>As<sub>2</sub>–ZnAs<sub>2</sub>–CdAs<sub>2</sub>–Cd<sub>3</sub>As<sub>2</sub> system is of interest for the preparation of solid solutions based on II-V semiconductors. The constituent arsenides, crystallizing in monoclinic (ZnAs<sub>2</sub>) or tetragonal (CdAs<sub>2</sub>, Zn<sub>3</sub>As<sub>2</sub>, Cd<sub>3</sub>As<sub>2</sub>) symmetry [1–6], offer a number of attractive physicochemical, optical, and electrical properties. Owing to the pronounced anisotropy in the thermoelectric power of ZnAs<sub>2</sub> and CdAs<sub>2</sub> single crystals, they are potentially attractive as materials for nonselective radiation detectors [7]. Both ZnAs<sub>2</sub> and CdAs<sub>2</sub> can be used in the fabrication of III– V-based semiconductor devices [8]. Cadmium diarsenide offers high optical activity, which makes it a candidate material for optical modulators and various polarizing devices [9, 10]. Zinc diarsenide can be used as a material for solid-state lasers [11]. In view of this, considerable research effort has recently been concentrated on the preparation and physicochemical studies of perfect single crystals of zinc and cadmium arsenides and related materials.

Perfect ZnAs<sub>2</sub> and CdAs<sub>2</sub> crystals could be prepared by vertical Bridgman growth [12, 13]. The structural perfection of the crystals was shown to depend primarily on the solidification rate, the temperatures of the melting and solidification zones, and the amount of excess arsenic. Single crystals grown under optimal conditions were 20–30 mm in diameter and 100–150 mm in length.

The systems Zn–As and Cd–As, which are the constituent binaries of the ternary system Cd–Zn–As, are known to contain the following compounds: Zn<sub>3</sub>As<sub>2</sub>, ZnAs<sub>2</sub>, Cd<sub>3</sub>As<sub>2</sub>, CdAs<sub>2</sub>, and CdAs<sub>4</sub> [1, 14]. Zn<sub>3</sub>As<sub>2</sub> and ZnAs<sub>2</sub> are isovalent with their Cd analogs. According to Yakimovich *et al.* [15], cadmium tetraarsenide is a metastable phase.

Analysis of earlier results [6, 15–19] indicates that the  $Cd_3As_2$ – $ZnAs_2$  and  $CdAs_2$ – $Zn_3As_2$  joins lie within the quadrangle formed by the  $Cd_3As_2$ – $CdAs_2$ ,  $CdAs_2$ –  $ZnAs_2$ ,  $ZnAs_2$ – $Zn_3As_2$ , and  $Zn_3As_2$ – $Cd_3As_2$  joins. The first three systems are of a eutectic type, while  $Zn_3As_2$ and  $Cd_3As_2$  form a continuous series of solid solutions.

The interest in the  $Zn_3As_2-ZnAs_2-CdAs_2-Cd_3As_2$ system is also motivated by the search for compositions suitable for growing eutectic layers of solid solutions by liquid-phase epitaxy. As in the case of III–V compounds [20], the use of a nonvolatile metal with a relatively low melting point (Zn or Cd) as a solvent in II–V epitaxy is of great benefit.

### **EXPERIMENTAL**

Zn<sub>3</sub>As<sub>2</sub>–ZnAs<sub>2</sub>–CdAs<sub>2</sub>–Cd<sub>3</sub>As<sub>2</sub> samples were prepared from fine-particle ZnAs<sub>2</sub>, Zn<sub>3</sub>As<sub>2</sub>, CdAs<sub>2</sub>, and Cd<sub>3</sub>As<sub>2</sub> powders presynthesized from cadmium and zinc of 99.999+% purity and V5 arsenic via vacuum melting as described in [4, 5, 7, 8]. The process was run in double-wall silica tubes, which were graphitized to prevent reaction between the melt and silica. After loading the starting mixtures, the tubes were pumped down to  $10^{-3}$  Pa and sealed off. The tubes were mounted in a steel block, which was then introduced into a SShchOL vertical furnace. The temperature difference along the length of the tube was ±1 K.

To prepare the constituent arsenides, the temperature was raised at a rate of 20 K/h to the melting point of the corresponding metal (Zn or Cd) and then maintained constant for 10 h. As a result, molten metal spread over arsenic. Next, the metal and arsenic were reacted by raising the temperature at 3–5 K/h to the melting point of the arsenide. After isothermal melt homogenization for 48 h, the temperature was lowered at 10–12 K/h to about 2/3 of the melting temperature of the arsenide, which led to directional solidification by the Tammann process and additional purification of the sample. Next, the sample was annealed at this temperature to relieve thermal stresses.

The other samples were prepared in a similar manner, using the melting temperatures of the constituent arsenides as "reference" points. The highest process temperature was 10–15 K above the melting point of the sample. The reaction was run for 200 h, followed by







**Fig. 1.** (a) Phase diagram of the  $Cd_3As_2$ – $ZnAs_2$  join: (*I*) liquid, (*II*) liquid +  $Cd_{3-x}Zn_xAs_2$ , (*III*) liquid +  $ZnAs_2$ , (*IV*) liquid +  $CdAs_2$  +  $Cd_{3-x}Zn_xAs_2$ , (*V*) liquid +  $ZnAs_2$  +  $Cd_{3-x}Zn_xAs_2$ , (*VI*)  $CdAs_2$  +  $ZnAs_2$  +  $Cd_{3-x}Zn_xAs_2$ . (b) Microstructure of the sample containing 90 mol %  $ZnAs_2$ ; ×200.

homogenization at 823 K (40 K below the melting point of the ternary eutectic) until both the splitting of doublet peaks in the x-ray powder diffraction pattern of the sample and its microhardness remained unchanged.





**Fig. 2.** (a) Phase diagram of the CdAs<sub>2</sub>–Zn<sub>3</sub>As<sub>2</sub> join: (*I*) liquid, (*II*) liquid + CdAs<sub>2</sub>, (*III*) liquid + Cd<sub>3-x</sub>Zn<sub>x</sub>As<sub>2</sub>, (*IV*) liquid + CdAs<sub>2</sub> + Cd<sub>3-x</sub>Zn<sub>x</sub>As<sub>2</sub>, (*V*) liquid + ZnAs<sub>2</sub> + Cd<sub>3-x</sub>Zn<sub>x</sub>As<sub>2</sub>, (*VI*) CdAs<sub>2</sub> + ZnAs<sub>2</sub> + Cd<sub>3-x</sub>Zn<sub>x</sub>As<sub>2</sub>. (b) Microstructure of the sample containing 90 mol % Zn<sub>3</sub>As<sub>2</sub>; ×200.

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**Fig. 3.** Phase diagram of the liquidus surface in the composition region  $Zn_3As_2$ – $ZnAs_2$ – $CdAs_2$ – $Cd_3As_2$  of the Cd–As–Zn system;  $E_s$  is the ternary eutectic at 26 at. % Cd, 65 at. % As, and 9 at. % Zn, with a melting point of 863 K.

The samples were characterized by differential thermal analysis, x-ray diffraction, and microstructural analysis. The composition of individual phases was determined by comparing the measured microhardness H with the known microhardness values of ZnAs<sub>2</sub>, Zn<sub>3</sub>As<sub>2</sub>, CdAs<sub>2</sub>, and Cd<sub>3</sub>As<sub>2</sub> (3.25, 3.00, 2.90, and



Fig. 4. Microstructure of the alloy with the composition  $26 \text{ at. } \% \text{ Cd} + 65 \text{ at. } \% \text{ As} + 9 \text{ at. } \% \text{ Zn}; \times 200.$ 

1.65 MPa, respectively [21–23]). Microstructures were examined in reflected light under an MIM-7 metallurgical microscope (×400) and MIN-9 polarizing microscope (×230). Microhardness was measured on a PMT-3 tester.

## **RESULTS AND DISCUSSION**

Our results indicate that neither the  $Cd_3As_2$ – $ZnAs_2$ nor the  $Zn_3As_2$ – $CdAs_2$  join is pseudobinary. The liquidus along the  $Cd_3As_2$ – $ZnAs_2$  join consists of two pri-



Fig. 5. X-ray scan of the alloy with the composition 26 at. % Cd + 65 at. % As + 9 at. % Zn.

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mary crystallization branches (Fig. 1a). In the composition range 0–85 mol % ZnAs<sub>2</sub>, the primary phase is  $Cd_{3-x}Zn_xAs_2$ . Between 85 and 100 mol % ZnAs<sub>2</sub>, the primary phase is the ZnAs<sub>2</sub>-based solid solution. The join contains a ternary eutectic, which melts at 863 K. Microstructural analysis confirms these phase relations throughout the composition region studied. Figure 1b shows the microstructure of the alloy containing 90 mol % ZnAs<sub>2</sub>. One can see light crystallites of the primary phase ZnAs<sub>2</sub> and precipitates of cocrystallizing  $Cd_{3-x}Zn_xAs_2$  and ZnAs<sub>2</sub>. The ternary eutectic is almost indiscernible because its amount is very small.

In the CdAs<sub>2</sub>–Zn<sub>3</sub>As<sub>2</sub> join (Fig. 2a), the liquidus also consists of two primary crystallization branches. The primary phases are the CdAs<sub>2</sub>-based solid solution in the composition range 0–10 mol % Zn<sub>3</sub>As<sub>2</sub> and the Cd<sub>3-x</sub>Zn<sub>x</sub>As<sub>2</sub> solid solution between 10 and 100 mol % Zn<sub>3</sub>As<sub>2</sub>. Between  $\approx$ 20 and 80 mol % Zn<sub>3</sub>As<sub>2</sub>, Cd<sub>3-x</sub>Zn<sub>x</sub>As<sub>2</sub> and ZnAs<sub>2</sub> cocrystallize. The thermal effect at 863 K is due to the crystallization of the ternary eutectic. The microstructures of CdAs<sub>2</sub>–Zn<sub>3</sub>As<sub>2</sub> samples correlate with the phase diagram of this join. The micrograph of the alloy containing 90 mol % Zn<sub>3</sub>As<sub>2</sub> (Fig. 2b) shows elongated crystallites of the primary phase Cd<sub>3-x</sub>Zn<sub>x</sub>As<sub>2</sub>, embedded in the ternary eutectic.

The dashed lines in Figs. 1a and 2a represent the thermal effects due to the polymorphic transformations of  $Zn_3As_2$  and  $Cd_3As_2$ . Analogous transformations in the ternary system were not studied.

The present and earlier [6, 15–19] results were used to construct the phase diagram of the liquidus surface in the composition region  $Zn_3As_2$ – $ZnAs_2$ – $CdAs_2$ – $Cd_3As_2$ (Fig. 3). The ternary eutectic revealed in this region has an approximate composition of 26 at. % Cd + 65 at. % As + 9 at. % Zn and melts at 863 K. The microstructure and x-ray diffraction pattern of a sample with the eutectic composition are shown in Figs. 4 and 5, respectively.

### CONCLUSIONS

Phase relations in the  $Zn_3As_2$ – $ZnAs_2$ – $CdAs_2$ – $Cd_3As_2$  system were studied by physicochemical analysis. The system was shown to contain a ternary eutectic with an approximate composition of 26 at. % Cd + 65 at. % As + 9 at. % Zn, which melts at 863 K.

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