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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

Join Si–$ZnAs_2$ of the Ternary System Zn–Si–As

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Abstract—The quasi-binary join Si-$ZnAs_2$ of the system Zn–Si–As was studied by physicochemical methods. The congruently melting compound $ZnSiAs_2$ and eutectics Si + $ZnSiAs_2$ and $ZnSiAs_2$ + $ZnAs_2$ are formed along this join. The composition of the eutectic Si + $ZnSiAs_2$ is 90 mol % $ZnAs_2$ and 10 mol % Si; T_m = 630°C. The composition of the eutectic $ZnSiAs_2$ + Si is 55 mol % Si and 45 mol % $ZnAs_2$. The component solubilities in $ZnSiAs_2$ do not exceed 1 mol %.

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The goal of spintronics, a promising line of solid-state electronics, is the discovery and preparation of high-temperature ferromagnetic semiconductors structurally compatible with silicon and providing injection of highly mobile, polarized electrons into the semiconductor [1].

Ferromagnets with above-room Curie points were prepared by doping chalcopyrites $CdGeP_2$, $ZnGeAs_2$, and $CdGeAs_2$ with manganese [2–4].

Here, we study the compound $ZnSiAs_2$, which is formed from zinc diarsenide and silicon.

The crystal structure of $ZnSiAs_2$ is shown in Fig. 1. To choose the parameters of $ZnSiAs_2$ synthesis, we considered the ternary system Zn–Si–As. Analysis of the binary subsystems Zn–As, Si–As, and Si–Zn [5] showed that Si–$ZnAs_2$ and Zn–$SiAs_2$ are the most likely quasi-binary joins of the system Zn–Si–As. Proceeding from the physical and chemical properties of the components of the joins Si–$ZnAs_2$ and Zn–$SiAs_2$, the optimal version of $ZnSiAs_2$ synthesis is the reaction between $ZnAs_2$ and Si; therefore, to refine the synthesis parameters, it is relevant to study the join Si–$ZnAs_2$ of the system Zn–Si–As.

EXPERIMENTAL

Samples with compositions lying along the join Si–$ZnAs_2$ were alloyed from high-purity silicon (Kr-00 type) and presynthesized $ZnAs_2$ in 10 mol % steps. Zinc diarsenide was prepared by reacting high-purity zinc and arsenic in the stoichiometric proportion, as described in [6].

RESULTS AND DISCUSSION

The investigative tools used were X-ray powder diffraction (XRD), differential thermal analysis (DTA), X-ray fluorescence analysis (XFA), and microstructure observation (MS).

X-ray powder diffraction was measured on a DRON-1 diffractometer (CuK_α radiation, Ni filter). Samples were identified with reference to the JCPDS

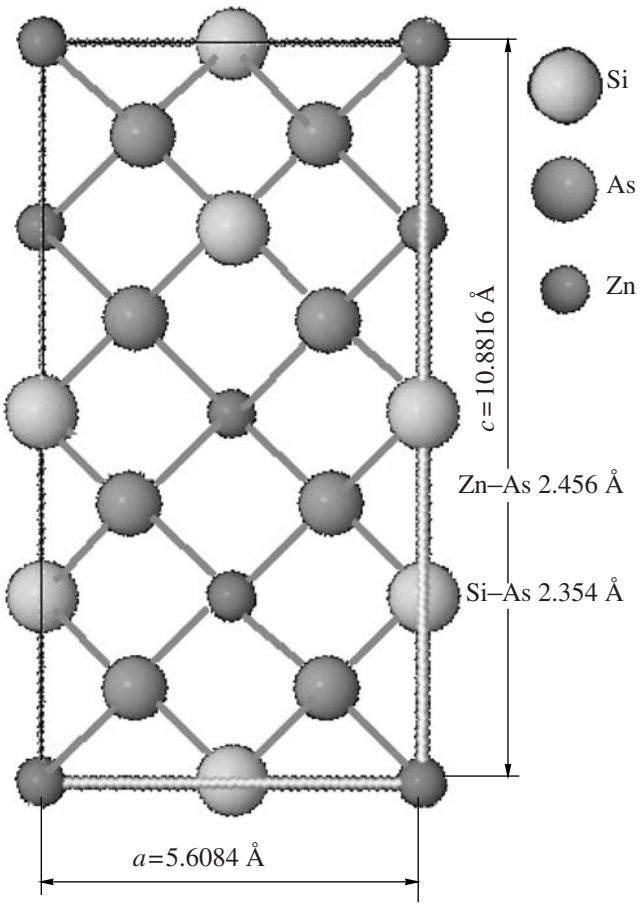

Fig. 1. $ZnSiAs_2$ crystal structure.

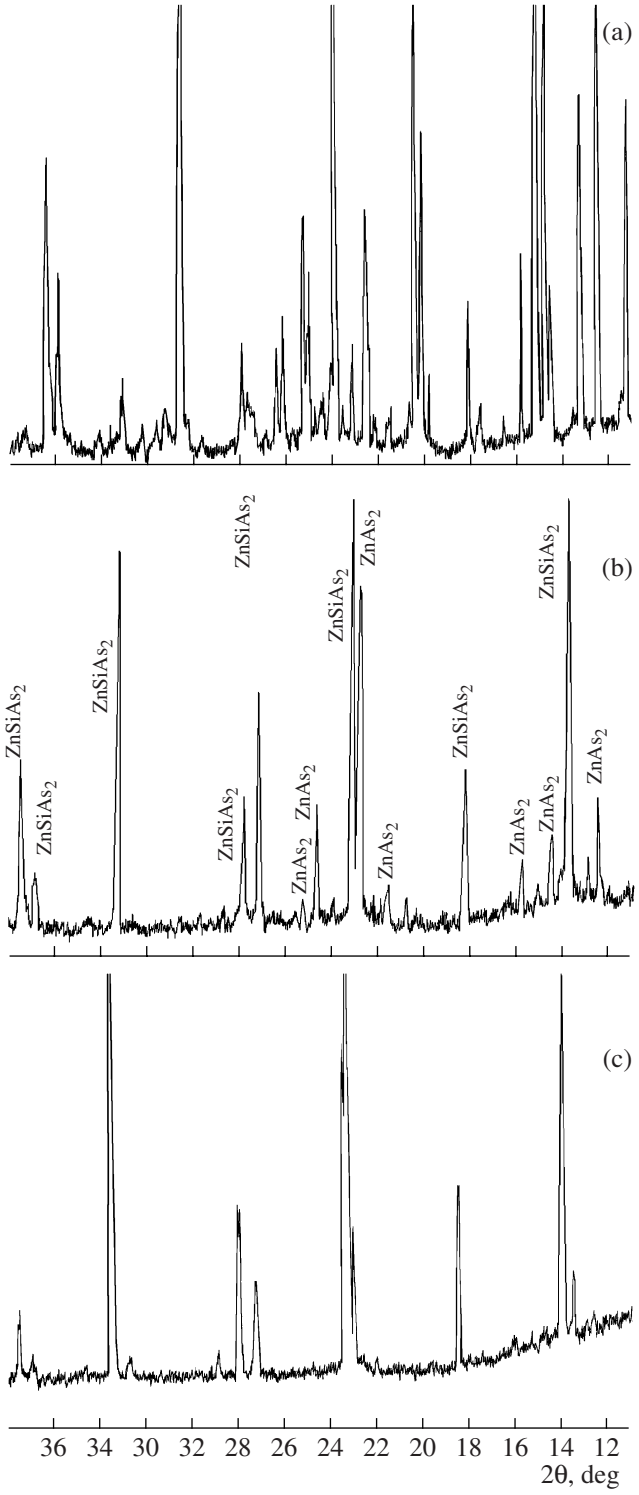

Fig. 2. X-ray diffraction patterns for (a) $ZnSiAs_2$, (b) 50 mol % $ZnSiAs_2$ + 50 mol % $ZnAs_2$, and (c) $ZnSiAs_2$.

data base. The precision of phase composition determination by XRD was ±4%. Examination of diffraction patterns (Fig. 2) showed that the samples contained Si, $ZnSiAs_2$, and $ZnAs_2$ phases solely. For $ZnSiAs_2$ samples containing excess $ZnAs_2$, X-ray diffraction patterns did not show noticeable shifts of diffraction peaks in the 2θ range of 10° to 90° (Fig. 2b); this signifies the low component solubilities and the existence of a narrow homogeneity range for $ZnSiAs_2$. Microstructure and XFA data support XRD data.

Figure 3 displays the micrographs of alloys with overstoichiometric $ZnSiAs_2$ proportion relative to $ZnAs_2$. All samples, except for the sample in Fig. 3a, contain $ZnSiAs_2$ (the light phase) and the eutectic $ZnSiAs_2 + ZnAs_2$ (the dark phase). The eutectic prevalence increases with rising $ZnAs_2$ concentration to reach a maximum in the alloy containing 18 mol % $ZnSiAs_2$ + 82 mol % $ZnAs_2$ or 9 mol % Si + 91 mol % $ZnAs_2$ (Fig. 3a).

Differential thermal analysis was carried out on an NTR-70 Kurnakov's pyrometer. A Pt–Pt/Rd thermocouple graduated against the reference points of chemically pure compounds was the temperature gage. The references used were zinc (692 K), antimony (903 K), sodium chloride (1074 K), and germanium (1210 K). The measurement accuracy was ±4°C K. The DTA trace for the 9 mol % Si + 91 mol % $ZnAs_2$ sample contains a single peak at 630°C.

X-ray fluorescence analysis was performed on an EAGLE III μ-probe X-ray fluorescence analyzer at the Microscopy and Analysis Systems Company. Linear scanning was carried out along four lines 11–13 mm long from both sizes of the sample. X-ray spectra from 100-μm spots were obtained using a tube with an Rh anode at U = 40 kV and I = 250 μA at 50 points lying at equal distances from one another along each line. The accumulation time per spectrum was 10 s. Concentrations of chemical elements were determined by the fundamental parameters method without references using software "No Standards" (EDAX). This program gives an error of 5% for the major components (30–100%), 10% for low concentrations (5–30%), and 50% for traces (<3%).

Figure 4a is the micrograph of the cross section of 97 mol % $ZnSiAs_2$ + 3 mol % Si ingot (x200). Figures 4b–4d show the zinc, arsenic, and silicon distributions in X-rays in the same region. These distributions are nonuniform.

Zinc and arsenic concentrations decrease and silicon precipitates along block joins in polycrystals. The composition of the eutectic $ZnSiAs_2$ + Si is ~ 80 $ZnSiAs_2$ + 20 mol % Si, as shown by quantitative XFA (Fig. 5).

The join Si–$ZnAs_2$ was constructed on the basis of our study (Fig. 6). The join Si–$ZnAs_2$ is quasi-binary. The congruently melting compound $ZnSiAs_2$ (T_m = 1096°C) and two eutectics (Si + $ZnSiAs_2$ and $ZnSiAs_2$ + $ZnAs_2$) are formed along this join.

To summarize, proceeding from the earlier analysis of the binary subsystems Zn–As, Si–As, and Si–Zn [5], here we have analyzed the Zn–Si–As ternary diagram.

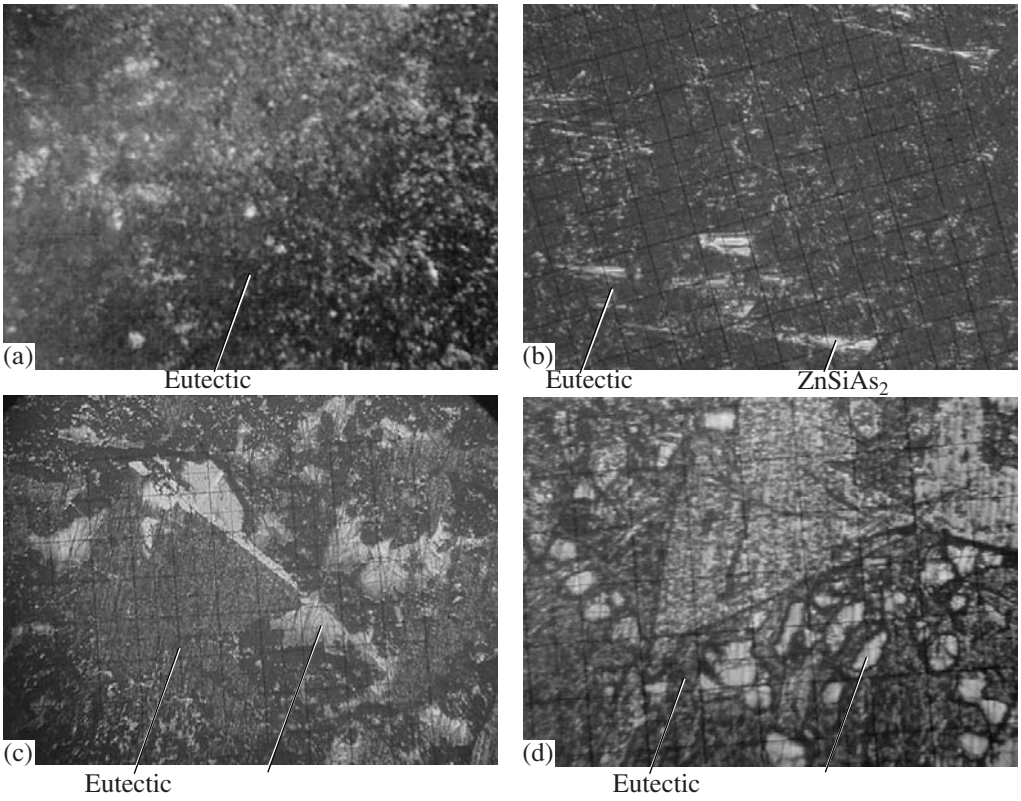

Fig. 3. Micrographs (x400) of samples containing (a) 9 mol % Si + 91 mol % $ZnAs_2$, (b) 10 mol % Si + 90 mol % $ZnAs_2$, (c) 20 mol % Si + 80 mol % $ZnAs_2$, and (d) 30 mol % Si + 70 mol % $ZnAs_2$.

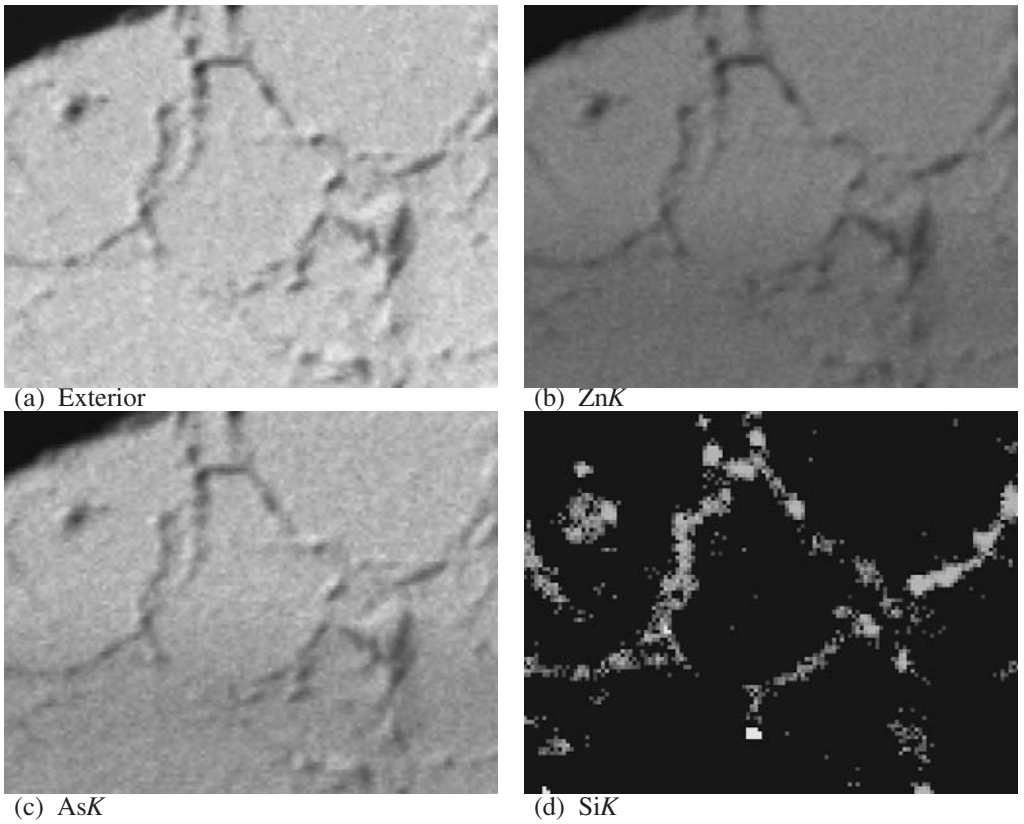

Fig. 4. Panel (a): micrograph (×200) of the cross section of an ingot containing 97 mol % $ZnSiAs_2$ + 3 mol % Si. Panels (b–d): distribution of (b) zinc, (c) arsenic, and (c) silicon.

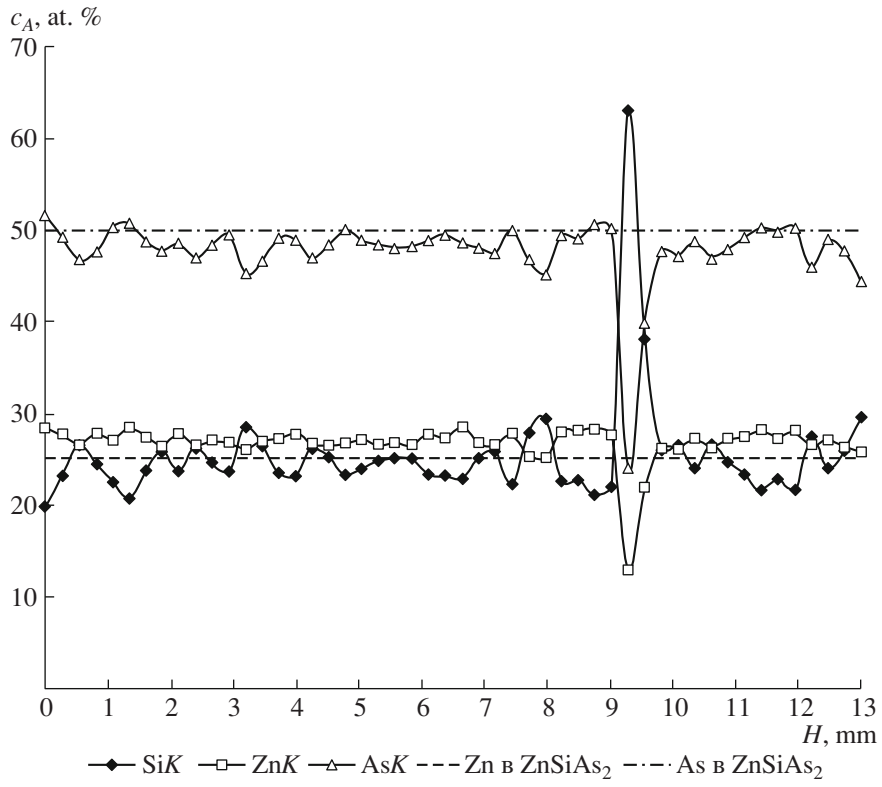

Fig. 5. Element distribution along the length of an ingot containing 97 mol % $ZnSiAs_2$ + 3 mol % Si.

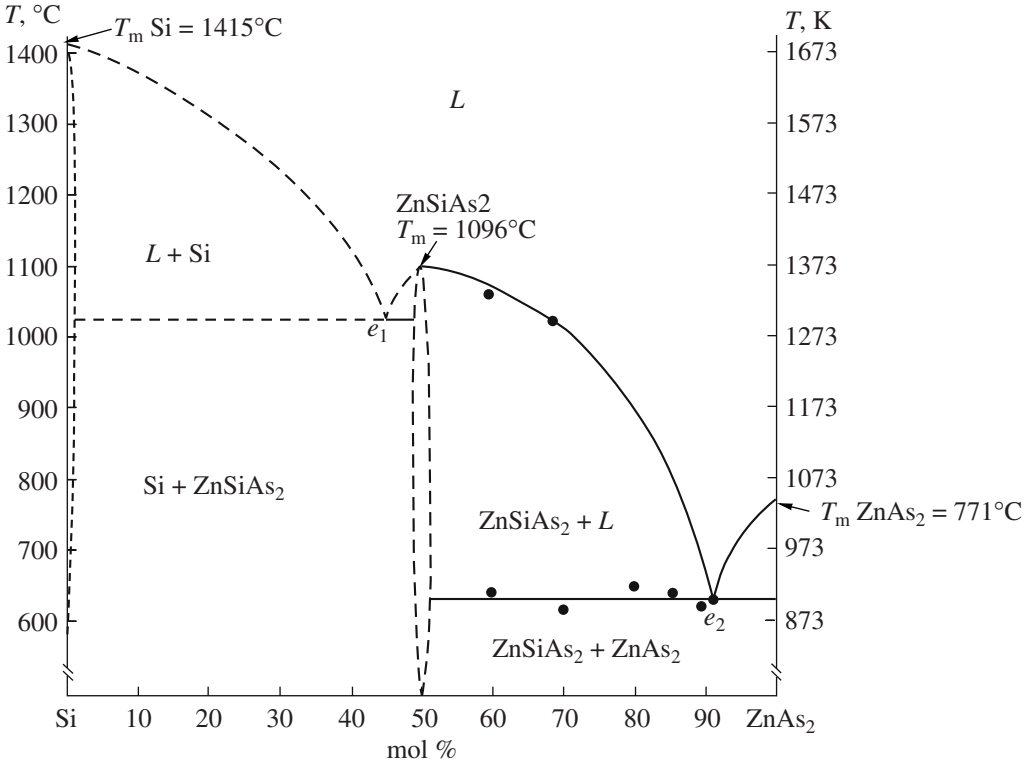

Fig. 6. Join Si–$ZnAs_2$ of the system Zn–Si–As.

The join Si–$ZnAs_2$ is quasi-binary; the ternary compound $ZnSiAs_2$ with T_m = 1096°C is formed along this join, flanked by eutectics on both the silicon and zinc diarsenide sides.

The composition of the eutectic $ZnSiAs_2 + ZnAs_2$ is 18 mol % $ZnSiAs_2$ + 82 mol % $ZnAs_2$ or 9 mol % Si + 91 mol % $ZnAs_2$ (T_m = 630°C). The composition of the eutectic $ZnSiAs_2$ + Si is ~ 88 mol % $ZnSiAs_2$ + 12 mol % Si or 44 mol % $ZnAs_2$ + 56 mol % Si. The component solubilities in $ZnSiAs_2$ do not exceed 1 mol %.

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REFERENCES

1. V. A. Ivanov, T. G. Aminov, V. M. Novotortsev, and V. T. Kalinnikov, Izv. Akad. Nauk, Ser. Khim., No. 11, 2255 (2004).
2. G. A. Medvedkin, T. Ishibashi, T. Nishi, and K. Sato, Fiz. Tekh. Poluprovodn. **35**, 305 (2001).
3. V. M. Novotortsev, S. A. Varnavskii, S. F. Marenkin, et al., Zh. Neorg. Khim. **48** (8), 1 (2006) [Russ. J. Inorg. Chem. **48** (8), 1153 (2006)].
4. S. Choi, J. Choi, S. C. Hong, and S. Cho, J. Korean Phys. Soc **42**, S739 (2003).
5. *Phase Diagrams for Binary Metal Systems*, Ed. by N. P. Lyakishev (Mashinostroenie, Moscow, 1997) [in Russian].
6. S. F. Marenkin, A. B. Maimasov, and A. V. Popov, Neorg. Mater. **33** (4), 394 (1997).