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PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

State Diagram of the Zn₃As₂–MnAs System

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Abstract—The Zn₃As₂–MnAs system was studied by X-ray powder diffraction, differential thermal, and microstructural analyses. This system is of the eutectic type with the eutectic coordinates (30 wt % (50 mol %) Zn₃As₂, 70 wt % (50 mol %) MnAs, $T_{melt} = 815^{\circ}$ C). The MnAs solubility boundary on the side of Zn₃As₂ is 10 wt %. Zn₃As₂ alloys containing more than 10 wt % MnAs are ferromagnetic with $T_{c} \sim 320$ K. Their magnetization increases with increasing MnAs content.

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Alloys of zinc and manganese arsenides are considered promising materials for granulated structures with giant magnetoresistance [1]. Granulated structures are of interest owing to their possible use in spintronics [2].

Alloys of zinc and manganese arsenides were studied as magnetic materials [3-5], and in those studies they were regarded as solid solutions $(Zn_{1-x}Mn_x)_3As_2$ within the concentration range $0 \le x \le 0.13$. The published [4] temperature dependences of the magnetization of these alloys are characteristic of superparamagnets [6]. From the curves, paramagnetic and ferromagnetic components can be separated. It is well known that introduction of atoms of *d*-elements, in particular, manganese, to a semiconductor leads to a transition of the semiconductor from the diamagnetic to the paramagnetic state. The ferromagnetism of $(Cd_{1-x}Mn_x)_3As_2$, which is isostructural to $(Zn_{1-x}Mn_x)_3As_2$, was attributed [7] to manganese clusters. In our opinion, the samples studied in the discussed works [3-6] were inhomogeneous and contained not only the solid solution $(Zn_{1-x}Mn_{x})_{3}As_{2}$ but also MnAs nanoinclusions. We believe that the presence of such nanoinclusions accounts for the ferromagnetic properties of manganese-containing zinc arsenide alloys [8, 9]. In this context, it was of interest to continue to study alloys of zinc and manganese arsenides, in particular, to determine the nature of the interaction between Zn₃As₂ and MnAs.

EXPERIMENTAL

Samples for studying the phase diagram were prepared at an interval of 10 mol % MnAs. The initial components were Zn₃As₂ and MnAs, which were synthesized in a vacuum in double-wall quartz ampoules from high-purity elemental substances Zn, As, and Mn taken in stoichiometric ratios [10]. The reactants were placed in the inner ampoule, the inner walls of which were lined with pyrolytic carbon for preventing quartz from interacting with melts of components. The processes were carried out in a furnace with automatic temperature control with an accuracy of $\pm 1^{\circ}$ C. To avoid escape of highly volatile components from the evaporation zone because of their evaporation, the ampoules were positioned in the isothermal part of the furnace. The temperature-time conditions of the synthesis were the following: heating at a rate of 50 deg/h to 600°C and treatment at this temperature for 2 h, heating to 1015°C for Zn₃As₂ and to 950°C for MnAs and treatment of melts for better homogenization for no less than 3 h, and cooling of ampoules in switchedoff furnace mode. The samples of intermediate compositions were obtained under the temperature-time conditions similar to those of the Zn_3As_2 synthesis. The samples were investigated by X-ray powder diffraction, differential thermal, and microstructural analyses.

The X-ray powder diffraction analysis was performed with a Bruker D8 ADVANCE diffractometer (Cu K_{α} radiation, $\lambda = 0.1540$ nm, graphite monochromator). Phases were identified based on the ICDD PDF-2 powder diffraction file database using the Diffrac.Suite EVA and Topaz software at the Research Equipment Sharing Center for Physical Methods for Studying Substances and Materials, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia. The X-ray



Fig. 1. X-ray powder diffraction patterns of the reference Zn_3As_2 sample [11], the initial Zn_3As_2 sample, the sample of the composition (90 wt % Zn_3As_2 , 10 wt % MnAs), the sample of the composition (50 wt % Zn_3As_2 , 50 wt % MnAs), the initial MnAs sample, and the reference Zn_3As_2 sample [12].

powder diffraction patterns of the initial phases Zn_3As_2 and MnAs agreed well with those of the reference samples [11, 12]. The X-ray powder diffraction patterns of intermediate samples contained peaks corresponding to both Zn_3As_2 and MnAs; the only exception was the sample of the composition (90 wt % Zn₃As₂, 10 wt % MnÅs), the X-ray powder diffraction patterns of which showed only Zn_3As_2 peaks (Fig. 1). Figure 1 presents the X-ray powder diffraction patterns of the reference Zn_3As_2 sample [11] and the Zn_3As_2 sample that was synthesized in this work and used as a precursor. Figure 1 also shows the X-ray powder diffraction patterns of the reference MnAs sample [12] and the MnAs sample obtained in this work. The X-ray powder diffraction patterns of intermediate samples were presented by the example of the sample of the composition (50 wt % Zn₃As₂, 50 wt % MnAs), which is characterized by peaks assigned both to Zn₃As₂ and MnAs. This coincides with the results of the microstructural studies and is indicative of the formation of solid solutions, which was confirmed by the shift of the Zn_3As_2 peaks in the X-ray powder diffraction patterns of intermediate samples in comparison with that of the reference sample [11] (Fig. 2).



Fig. 2. Fragments of the X-ray powder diffraction patterns of (a) the sample of the composition (50 wt % Zn₃As₂, 50 wt % MnAs) and (b) the reference Zn₃As₂ sample [11].

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Fig. 3. Microstructures of the samples of the compositions (a) (30 wt % Zn_3As_2 , 70 wt % MnAs), (b) (40 wt % Zn_3As_2 , 60 wt % MnAs), and (c) (10 wt % Zn_3As_2 , 90 wt % MnAs).

Figure 3 shows the microstructures of the samples of the compositions (30 wt % Zn_3As_2 , 70 wt % MnAs) (Fig. 3a), (40 wt % Zn_3As_2 , 60 wt % MnAs) (Fig. 3b), and (90 wt % Zn_3As_2 , 10 wt % MnAs) (Fig. 3c). It is

seen from Figs. 3a and 3b that the samples containing more than 10 wt % MnAs are two-phase. The micro-structure of the sample containing 70 wt % MnAs corresponds to the structure of a eutectic.

Composition				Temperatures at events, °C		
wt %		mol %				
Zn ₃ As ₂	MnAs	Zn ₃ As ₂	MnAs	$\alpha \rightarrow \beta - Zn_3As_2$	t _{eut}	t _{liq}
100	0	100	0	651	_	1015
90	10	96	4	635	_	1000
80	20	92	8	594	815	_
70	30	86	14	590	812	980
60	40	80	20	590	816	950
50	50	72	28	585	814	930
40	60	63	37	580	810	920
30	70	53	47	580	810	—
20	80	40	60	575	812	830
10	90	24	76	580	820	925
4	96	10	90	590	820	923
0	100	0	100	-	—	935

Data of differential thermal analysis on the Zn₃As₂-MnAs system



Fig. 4. Temperature dependence of the magnetization of the sample of the composition (80 wt % Zn_3As_2 , 20 wt % MnAs) in a magnetic field at H = 100 Oe.



Fig. 5. State diagram of the Zn₃As₂-MnAs system.

The results of the differential thermal analysis (table) confirmed the data of the X-ray powder diffraction and microstructural analyses on the eutectic nature of the interaction in the Zn_3As_2 -MnAs system. In the thermal curves, thermal events were determined with an accuracy of $\pm 5^{\circ}$ C and assigned as follows: the event at 651°C in the sample containing 100 wt % Zn_3As_2 characterizes the polymorphic transformation of α -Zn₃As₂ to β -Zn₃As₂. In the two-phase samples, the temperature at this event decreased to 590°C. The event at 815°C was attributed to the melting of the eutectic. The higher-temperature events determined the liquidus line.

The magnetic properties of the samples were measured with a Cryogenic vibration magnetometer. Studies showed that alloys in the Zn_3As_2 -MnAs system, except the sample of the composition (90 wt % Zn_3As_2 , 10 wt % MnAs), are ferromagnets with a Curie temperature of ~320 K. The magnetization increased with increasing MnAs content of alloys. As an example, Figure 4 presents the temperature dependence of the magnetization of the sample of the composition (70 wt % Zn_3As_2 , 30 wt % MnAs).

Based on the data of the X-ray powder diffraction, differential thermal, and microstructural analyses, the phase diagram of the Zn_3As_2 -MnAs system was constructed. The diagram characterizes this system as a system of the eutectic type with the eutectic coordinates (30 wt % (50 mol %) Zn_3As_2 , 70 wt % (50 mol %) MnAs, $t_{melt} = 815^{\circ}$ C). The microstructure of the eutectic is lamellar; the MnAs solubility in Zn_3As_2 was approximately estimated at ~10 wt %.

Thus, by X-ray powder diffraction, differential thermal, and microstructural analyses, the Zn_3As_2 -MnAs system was studied. Samples were synthesized in a vacuum in double-wall quartz ampoules. It was shown that the system is of the eutectic type. The X-ray powder diffraction and microstructural studies indicated significant solubility of MnAs in Zn_3As_2 . The alloys, except the sample of the composition (90 wt % Zn_3As_2 , 10 wt % MnAs), are ferromagnetic. Their magnetization increases with increasing MnAs content of the alloys.

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