UDC 546 (711.682.24)

REFINEMENT OF THE PHASE DIAGRAM OF THE MnTe–In₂Te₃ SYSTEM

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Received 11.12.2020

Accepted 15.03.2021

The MnTe–In₂Te₃ system was re-investigated by DTA and XRD methods, and its phase diagram was constructed somewhat differently from the previously known ones. It was found that the system is characterized by the formation of the MnIn₂Te₄ compound congruently melting at 1025 K with a wide (49–67 mol% In₂Te₃) homogeneity region. This phase is in eutectic equilibrium (1015 K) with solid solutions based on *lt*-MnTe (*lt* – low temperature) and in peritectic equilibrium with solid solutions based on In₂Te₃. A comparative analysis of the results obtained with the literature data is carried out.

Keywords: *MnTe–In₂Te₃ system, phase diagram, manganese and indium tellurides, solid solutions.*

doi

Introduction

Ternary and more complex chalcogenides based on 3*d*-elements, in particular manganese, are of great practical interest as materials combining magnetic and semiconducting properties [1–8]. Recent studies have shown that some of them are magnetic topological insulators and extremely promising for use in spintronics and quantum computing [9–15].

The development and creation of new methods for directed synthesis of complex phases and materials require the study of phase equilibria in the corresponding systems [16–19].

With purpose of search and development a physicochemical basis for the creation of new magnetic semiconductors, we have undertaken a study of phase equilibria in MX–Ga₂X₃–In₂X₃ (M – Mn, Fe; X – S, Se, Te) systems. The results obtained for some systems of this type [20–25] displayed the formation of wide areas of solid solutions along the MGa₂X₄–MIn₂X₄ sections. At the same time, an analysis of the literature data has revealed that the phase diagrams of some boundary quasi-binary components of the indicated quasi-ternary systems require clarifying. In papers [26, 27] we presented refined *T*–*x* diagrams of some similar systems.

Our preliminary experimental results obtained under the study of the MnTe–Ga₂Te₃–In₂Te₃ system found out their inconsistency with the known [28] phase diagram of the MnTe–In₂Te₃ boundary system. Taking into

account it the purpose of our work was to re-study phase equilibria in the MnTe–In₂Te₃ system.

The initial compounds of the investigated system have been studied in detail. The MnTe compound melts with decomposition by a peritectic reaction at 1425 K and undergoes polymorphic transitions at 1270 and 1305 K [29]. At the low-temperature modification MnTe (*lt*-MnTe) crystallizes in a hexagonal structure (Sp.Gr. *P63/mmc*) with lattice parameters *a* = 0.41498 nm, *c* = 0.67176 nm [12].

The In₂Te₃ compound melts congruently (940 K) [29] and crystallizes in a cubic structure (Sp.Gr. *F43m*) with lattice parameters *a* = 0.616 nm or 1.850 nm [30].

Experimental part

Materials and synthesis

MnTe and In₂Te₃ compounds were synthesized using high-purity manganese (Mn – 99.99%), indium (In – 99.999%), tellurium in granules (Te – 99.999%) purchased from Alfa Aesar. During the synthesis of In₂Te₃ stoichiometric amounts of elements were placed in an evacuated ~10^{–2} Pa quartz ampoule and melted in a single-zone furnace at 990 K. MnTe synthesis was also carried out under vacuum conditions in a glass-graphite crucible, placed in a quartz ampoule, at 1450 K.

The individuality of both synthesized compounds was controlled by DTA and XRD. The

obtained melting points and crystal lattice parameters coincided within the error limits (± 2 K and ± 0.0003 Å) with the above literature data.

The alloys of the studied system were prepared by melting the initial compounds in various ratios in evacuated quartz ampoules, followed by homogenizing annealing at 850 K for ~500 h.

Research methods

Differential thermal analysis (DTA) was carried out on a Netzsch 404 f1 Pegasus System (chromel-alumel thermocouples) in the temperature range from room temperature to ~1450 K at a heating rate of 10 K/min. Phase and structural studies were carried out based on powder diffraction data obtained on a D2 Phaser diffractometer using the Eva and Topas 4.2 software (Bruker, Germany; $\text{CuK}\alpha$ -radiation, interval of angles $5^\circ \leq 2\theta \leq 80^\circ$, recording rate $0.03^\circ/0.2$ min).

Results and discussion

The analysis of powder diffraction patterns showed that alloys with compositions 50–67 mol% In_2Te_3 have a new diffraction pattern differed from the initial compounds. Figure 1

presents as an example the diffraction patterns of alloys with compositions of 50 and 65 mol% In_2Te_3 . It is also seen from this Figure 1 that the diffractogram of the 80 mol% In_2Te_3 alloy is qualitatively are identical to the diffraction pattern of pure In_2Te_3 with some shift in the reflection angles. Also, according to the XRD data (Figure 1), the diffraction pattern of an alloy containing 30 mol% In_2Te_3 includes accumulation of reflection lines of phases based on MnTe and MnIn_2Te_4 , and an alloy with a composition of 70 mol% In_2Te_3 consists of reflection lines of phases based on In_2Te_3 and MnIn_2Te_4 .

The phase diagram of the MnTe– In_2Te_3 system was constructed using the joint processing of data obtained by methods DTA and RFA (Figure 2). As can be seen, the system is non-quasi-binary due to the incongruent character melting of MnTe, but it is stable below the peritectic temperature (1425 K). The liquidus consists of 5 curves responsible for the primary crystallization of Mn, α' - and α -solid solutions based on two modifications of MnTe, γ -phase based on MnIn_2Te_4 and β -phase based on In_2Te_3 (Figure 2).

Fig.1. Powder diffraction patterns of some alloys of the MnTe– In_2Te_3 system.

Fig.2. Phase diagram of the MnTe–In₂Te₃ system.

The MnIn₂Te₄ compound melts congruently at 1025 K and has a wide (□49–67 mol% In₂Te₃) homogeneity region (γ -phase).

The intermediate γ -phase forms a eutectic with the α -phase (e). Eutectic has coordinates: 45 mol.% In₂Te₃ and 1015 K. The system has a peritectic equilibrium $L+\gamma \leftrightarrow \beta$ at 970 K. The peritectic point (P) has a composition of 83 mol% In₂Te₃. The horizontal lines at 1420 and 1295 K correspond to peritectic ($L+\text{Mn} \leftrightarrow \alpha'$) and metatectic ($\alpha' \leftrightarrow L+\alpha$) equilibria.

The T - x diagram we constructed differs significantly from the one given in [28]. Thus, according to [28], the MnIn₂Te₄ (D) compound melts at ~1040 K and has a constant composition. Moreover, according to [28], MnIn₂Te₄ forms a eutectic with In₂Te₃ at 878 K, which was not confirmed by us. We also obtained data on phase transitions based on MnTe that differ from those given in [28].

Conclusion

In this work, we presented a new scheme of phase equilibria in the MnTe–In₂Te₃ system, which differs from the one presented in the literature. In contrast to literature data, we showed that this system is non-quasi-binary due to the

incongruent melting of MnTe. We have found that the ternary compound MnIn₂Te₄ has a wide homogeneity region and is in peritectic equilibrium with solid solutions based on In₂Te₃, that it is also differed from data [28].

The new phases of the variable composition obtained in this work are of interest as potential magnetic materials.

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MnTe-In₂Te₃ SİSTEMİNİN FAZA DİAQRAMININ DƏQİQLƏŞDİRİLMƏSİ**F.M.Məmmədov**

$\text{MnTe-In}_2\text{Te}_3$ sistemi DTA və XRD metodları ilə yenidən tədqiq edilmiş və əvvəllər ədəbiyyatda göstəriləndən bir qədər fərqlənən faz diaqramı qurulmuşdur. Sistemdə geniş (49–67 mol.% In_2Te_3) homogenlik sahəsi ilə xarakterizə olunan və 1025 K-də konqruent əriyən MnIn_2Te_4 birləşməsinin əmələ gəlməsi aşkar edilmişdir. Bu faza *lt* MnTe əsasında bərk məhlulla evtektik (1015 K), In_2Te_3 əsasında bərk məhlulla isə peritektik tarazlıqdadır. Öldə olunan nəticələrin ədəbiyyat məlumatları ilə müqayisəli təhlili aparılmışdır.

Açar sözlər: $\text{MnTe-In}_2\text{Te}_3$ sistemi, faz diaqramı, manqan və indium telluridləri, bərk məhlullar.

УТОЧНЕНИЕ ФАЗОВОЙ ДИАГРАММЫ СИСТЕМЫ $\text{MnTe-In}_2\text{Te}_3$ **Ф.М.Мамедов**

Система $\text{MnTe-In}_2\text{Te}_3$ повторно исследована методами ДТА и XRD, и построена ее фазовая диаграмма, которая несколько отличается от ранее приведенной в литературе. Установлено, что в системе наблюдается образование конгруэнтно плавящегося при 1025 К соединения MnIn_2Te_4 с широкой (49–67 мол.% In_2Te_3) областью гомогенности. Эта фаза находится в эвтектическом равновесии (1015 К) с твердыми растворами на основе *lt*- MnTe и в перитектическом равновесии с твердыми растворами на основе In_2Te_3 . Проведен сравнительный анализ полученных результатов с литературными данными.

Ключевые слова: система $\text{MnTe-In}_2\text{Te}_3$, фазовая диаграмма, теллуриды марганца и индия, твердые растворы.