



Original articles

Research article

<https://doi.org/10.17308/kcmf.2022.24/9856>Phase equilibria in the $\text{MnTe-MnGa}_2\text{Te}_4\text{-MnIn}_2\text{Te}_4$ systemF. M. Mammadov¹✉, S. Z. Imamaliyeva¹, Ya. I. Jafarov², I. B. Bakhtiyarly¹, M. B. Babanly¹¹Institute of Catalysis and Inorganic Chemistry n.a. M. Nagiyev of the Azerbaijan National Academy of Sciences, 113 H. Javid av., Baku Az1143, Azerbaijan²Baku State University, 23 Z. Khalilova str., Baku Az1148, Azerbaijan

Abstract

A family of compounds with the general formula AB_2X_4 (A – Mn, Fe, Co, Ni; B – Ga, In, Sb, Bi; X – S, Se, Te) and complex phases of variable compositions based on them are among promising functional materials with thermoelectric, photoelectric, optical, and magnetic properties. In this article, we continued the study of multi-component systems based on the chalcogenides of transition metals and presented the results of the study of phase equilibria in the $\text{MnTe-MnGa}_2\text{Te}_4\text{-MnIn}_2\text{Te}_4$ system using differential thermal analysis and X-ray phase analysis.

Based on the experimental results, we built the polythermal cross sections MnTe-MnGaInTe_4 and $\text{MnGa}_2\text{Te}_4\text{-[A]}$ (where [A] is a biphasic alloy of the $2\text{MnTe-MnIn}_2\text{Te}_4$ side system of the 50.0 mol% MnIn_2Te_4 composition) as well as an isothermal section of a phase diagram at 800 K and a projection of the liquidus surface. It was established that the liquidus consists of the fields of primary crystallisation of 4 phases: 1 – Mn-ht; 2 – phases based on various modifications of MnTe; 3 – γ_1 ; 4 – γ_2 . We also identified types and coordinates of non-variant and monovariant equilibria.

Based on triple compounds (MnGa_2Te_4 , MnIn_2Te_4), we determined wide regions of solid solutions that are of particular interest as magnetic materials.

Keywords: Manganese-gallium telluride, Manganese-indium telluride, Phase diagram, Liquidus surface, Solid solutions, Magnetic materials

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1. Introduction

A family of compounds with the general formula AB₂X₄ (A – Mn, Fe, Co, Ni; B – Ga, In, Sb, Bi; X – S, Se, Te) [1–8] and complex phases of variable compositions based on them [9–12] has been of considerable interest over the past thirty years. These magnetic compounds that contain three metal cations around each anion position, while the fourth empty position forms an ordered massif of vacancies, can exist in various crystal structures and show a number of physical and chemical properties related to the crystallographically ordered massif of the vacancies. The magneto-optical properties of these compounds are also of particular interest due to the presence of magnetic ions Fe⁺² and Mn⁺². According to the results of [1–6], these compounds possess thermoelectric, photoelectric, and optical properties.

Recent studies showed that some layered compounds of the AB₂X₄ type exhibit properties of a magnetic and topological insulator [13–24]. Such a combination of magnetic and topological properties potentially leads to the development of multi-functional electronic and spintronic components that offer prospects of better energy efficiency and computing capabilities.

Considering the above, it can be said that the researches aimed at obtaining and studying solid solution based on the compounds of the AB₂X₄ type are relevant.

The search and development of methods for the directed synthesis of new multi-component phases and materials are based on reliable data on the phase equilibria of the corresponding systems [25–27].

In this article, we continued the study of multi-component systems based on the chalcogenides

of transition metals [28–31] and presented the results of the study of phase equilibria in the MnTe–MnGa₂Te₄–MnIn₂Te₄ system.

1.1. Starting compounds

The results of the study of starting binary and ternary compounds of the studied system are presented in [32–35]. MnTe telluride melts incongruently by a peritectic reaction at 1425 K. Several polymorphic transitions are inherent to this compound [32, 33]. The crystallographic parameters of various modifications of this compound are presented in Table 1.

The other two compounds of this system, MnGa₂Te₄ and MnIn₂Te₄, melt congruently at 1083 K [34] and 1025 K [35], respectively. The former crystallises in a pseudo-tetragonal structure, while the latter crystallises in a tetragonal structure (Table 1).

1.2. Boundary quasi-binary systems

A new specified variant of the phase diagram of the MnTe–MnGa₂Te₄ system was presented in [34], according to which was of eutectic type and had the following coordinates of the eutectic point: 84 mol% MnGa₂Te₄ and 1070 K.

The phase diagram of another boundary MnTe–MnIn₂Te₄ system of the eutectic type had the following coordinates of the eutectic point: 90 mol% MnIn₂Te₄ and 1015 K [35].

The authors of [30] studied the MnGa₂Te₄–MnIn₂Te₄ system (Fig. 1). It was established that it is quasi-binary and is characterised by the formation of wide regions of solid solutions based on the starting compounds. The MnGaInTe₄ phase had the highest temperature (1030 K) and crystallises in a tetragonal structure (Table 1). A comparison of MnGaInTe₄ crystal lattices and an MnIn₂Te₄ isostructural ternary compound

Table 1. Crystallographic data of binary and ternary phases of the MnTe–MnGa₂Te₄–MnIn₂Te₄ system

Phases	Crystal system, space group, and lattice parameters, nm	Source
MnTe – rt	hexagonal, $P6_3/mmc$: $a = 0.41498$, $c = 0.67176$ nm	[36]
MnTe – it	cubic, $F\bar{4}3m$: $a = 0.634$ nm	[36]
MnTe – ht	hexagonal, $P6_3/mmc$: $a = 0.4148$, $c = 0.6721$ nm	[36]
MnGa ₂ Te ₄	pseudo-tetragonal: $a = b = 0.847$, $c = 4.83$ nm	[37]
	monoclinic, $C/2c$: $a = b = 1.1999$ nm, $c = 2.4922$ nm	[38]
MnIn ₂ Te ₄	tetragonal, $I-42m$: $a = 0.619490(5)$, $c = 1.23956(2)$ nm	[30]
MnGaInTe ₄	tetragonal, $I-42m$: $a = 0.610293(7)$, $c = 1.21766(2)$ nm	[30]

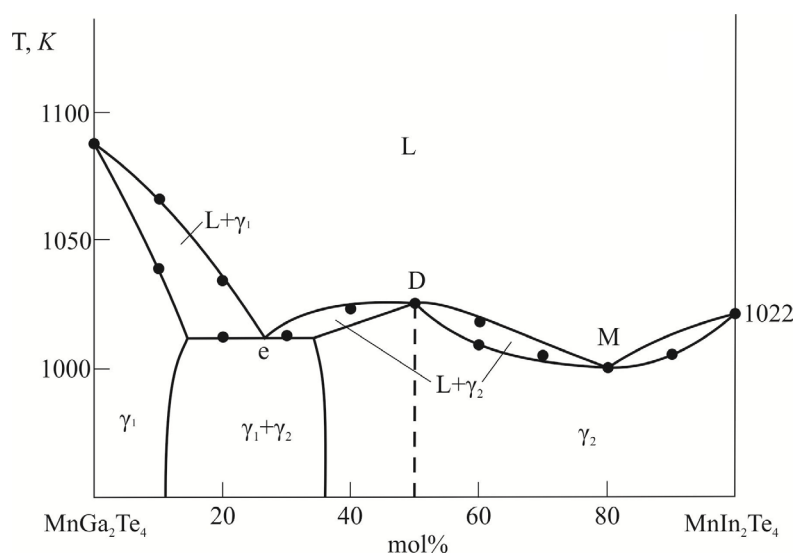


Fig. 1. Phase diagram of the MnGa₂Te₄–MnIn₂Te₄ system [30]

showed [30] that they were considerably different in the nature of colonisation of crystallographic positions and that MnGaInTe₄ could be characterised as an ordered phase.

2. Experimental

2.1. Synthesis

The starting compounds MnTe, MnGa₂Te₄, and MnIn₂Te₄ of the studied systems were synthesised by melting stoichiometric amounts of high purity elementary components (manganese, catalogue number 7439-96-5, indium – 7440-74-6, gallium – 7440-55-3, and tellurium – 13494-80-9) purchased from the German company Alfa Aesar. They were synthesised for 8 hours in sealed quartz ampoules that were evacuated to a residual pressure of 10⁻² Pa. The temperatures were 20 K higher than the melting points. Then the furnace was turned off. To prevent the interaction of quartz with manganese, the starting compounds and intermediate alloys of the studied system were synthesised in graphitised ampoules. The graphitisation was performed by the thermal decomposition of toluene.

The single-phase composition of the synthesised samples was confirmed by means of differential thermal analysis (DTA) and X-ray diffraction (XRD).

According to DTA, the melting points of MnTe, MnGa₂Te₄, and MnIn₂Te₄ were 1425±3 K, 1083±3 K, and 1025±3 K, respectively, which corresponded with the results of [32–35].

Based on the XRD data, we calculated the crystallographic parameters of lattices, which corresponded well with the data from [36, 37, 30], (Table 1):

MnTe-rt – hexagonal, space group *P63/mmc*:
 $a = 0.41488(4)$, $c = 0.67166(6)$ nm;

MnGa₂Te₄ – pseudo-tetragonal
 $a = b = 0.84851(8)$, $c = 4.8402(2)$ nm;

MnIn₂Te₄ – tetragonal, *I-42m*: $a = 0.61949(5)$;
 $c = 1.23956(2)$ nm;

MnGaInTe₄ – tetragonal, *I-42m*: $a = 0.610293(7)$;
 $c = 1.21766(2)$ nm.

The alloys of the MnTe–MnGa₂Te₄–MnIn₂Te₄ system (Fig. 2) were synthesised by melting the above-mentioned compounds in different ratios in evacuated quartz ampoules with further long-term (500 h) thermal annealing at 800 K. In order to develop a diagram for the solid-phase equilibria, some alloys were hardened by dropping ampoules into cold water.

2.2. Research methods

DTA was conducted on a Netzsch STA 449 F3 unit (platinum-platinum/rhodium thermocouples) in the range of temperatures from room temperature to ~ 1450 K with a heating rate of 10 K·min⁻¹.

XRD was conducted by recording powder patterns on a D2 Phaser diffractometer. Crystal lattice parameters were calculated and specified using EVA and TOPAS 4.2 (Bruker, Germany, CuK α radiation, angle range 5° ≤ 2 θ ≤ 80°, recording rate 0.03°×0.2 min).

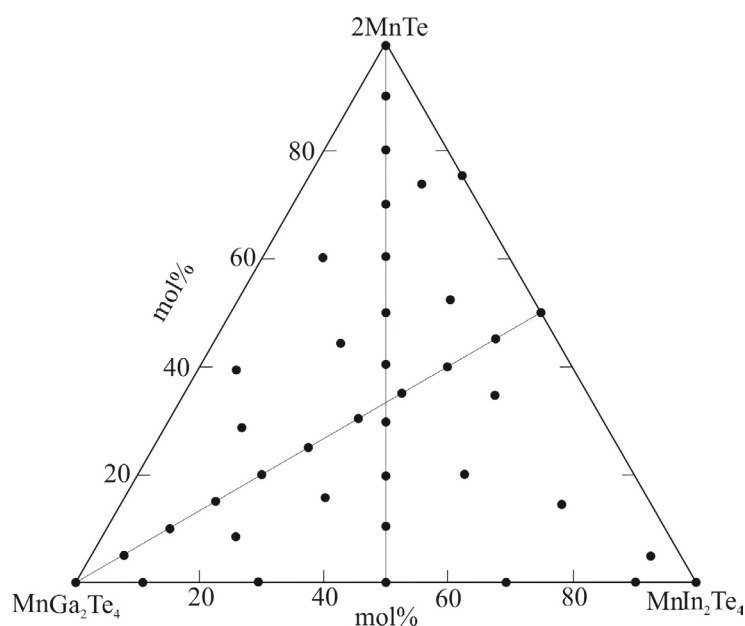


Fig. 2. Compositions of the studied samples in the MnTe–MnGa₂Te₄–MnIn₂Te₄ system

3. Results and discussion

We processed both experimental and published data on boundary systems [30, 34, 35] and obtained a general consistent pattern of phase equilibria in the MnTe–MnGa₂Te₄–MnIn₂Te₄ system. In tables and figures as well as in the article itself, solid solutions based on compounds and their various modifications were designated as follows: α – MnTe-*lt*, γ_1 – MnGa₂Te₄, γ_2 – MnIn₂Te₄.

3.1. Solid-phase equilibria in the MnTe–MnGa₂Te₄–MnIn₂Te₄ system

Based on the XRD data of the samples hardened at 800 K, we developed a diagram for the solid-phase equilibria of the MnTe–MnGa₂Te₄–MnIn₂Te₄ system at 800 K (Fig. 3). As can be seen, wide regions of solid solutions based on ternary MnGa₂Te₄ (γ_1) and MnIn₂Te₄ (γ_2) compounds were formed in the system. These phases had the form of bands 2–4 mol% wide and 15 and 65 mol% long, respectively, along the boundary system MnGa₂Te₄–MnIn₂Te₄. Based on the low-temperature modification of MnTe, the α -phase took up a narrow area (5–6 mol%) of the corresponding angle. The listed phases formed a number of two-phase regions, $\alpha+\gamma_1$, $\alpha+\gamma_2$, and $\gamma_1+\gamma_2$ that were separated by a three-phase region $\alpha+\gamma_1+\gamma_2$.

All the phase regions presented in Fig. 3 were confirmed by XRD. Fig. 4 shows X-ray

powder diffraction patterns of three alloys from different phase regions. It can be seen that the compositions of these samples correspond to the pattern of solid-phase equilibria presented in Fig. 3.

3.2. Liquidus surface

A projection of the liquidus surface of the MnTe–MnGa₂Te₄–MnIn₂Te₄ system consists of four fields of primary crystallisation (Fig. 5). The presence of field (1) corresponding to the primary crystallisation of high-temperature modification of manganese, which was not a component of this

Table 2. Non-variant and monovariant equilibria in the MnTe–MnGa₂Te₄–MnIn₂Te₄ system

Point or curve in Fig. 5.	Equilibrium	<i>T</i> , K
D	$L \leftrightarrow \gamma_2$ (MnGaInTe ₄)	1030
M	$L \leftrightarrow \gamma_2$	1005
e ₁	$L \leftrightarrow \gamma_1 + \gamma_2$	1012
e ₂	$L \leftrightarrow \gamma_1 + \alpha$	1060
e ₃	$L \leftrightarrow \gamma_2 + \alpha$	1015
e ₄	$L \leftrightarrow \gamma_2 + \alpha$	1018
e ₅	$L \leftrightarrow \gamma_2 + \alpha$	1310
E	$L \leftrightarrow \alpha + \gamma_1 + \gamma_2$	997
e ₂ E	$L \leftrightarrow \alpha + \gamma_1$	1060–997
e ₁ E	$L \leftrightarrow \gamma_1 + \gamma_2$	1012–997
e ₄ E	$L \leftrightarrow \alpha + \gamma_2$	1018–997
e ₃ e ₅	$L \leftrightarrow \gamma + \gamma_2$	1015–995
e ₄ e ₅	$L \leftrightarrow \alpha + \gamma_2$	1018–995

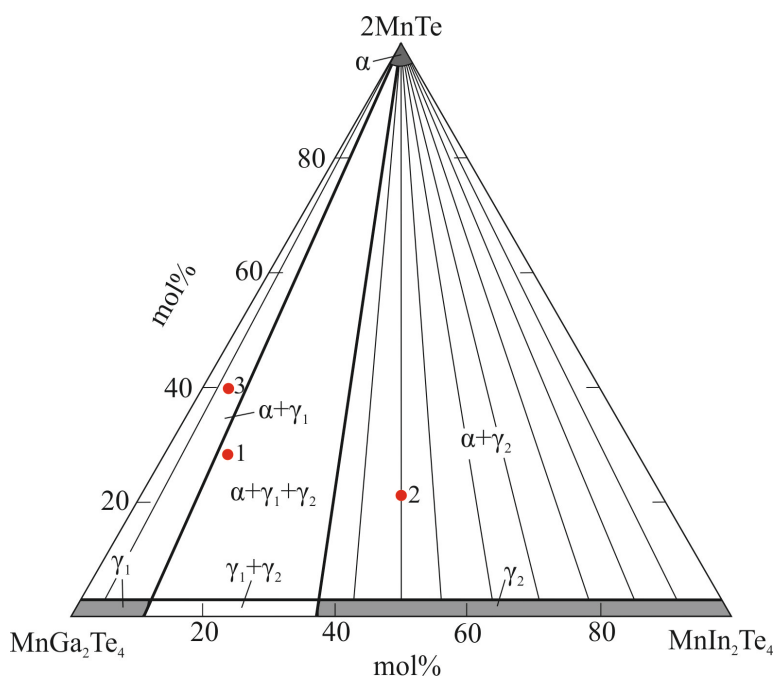


Fig. 3. Diagram of solid-phase equilibria in the MnTe–MnGa₂Te₄–MnIn₂Te₄ system at 800 K · 1-3 alloys for which X-ray powder diffraction patterns are presented in Fig. 4

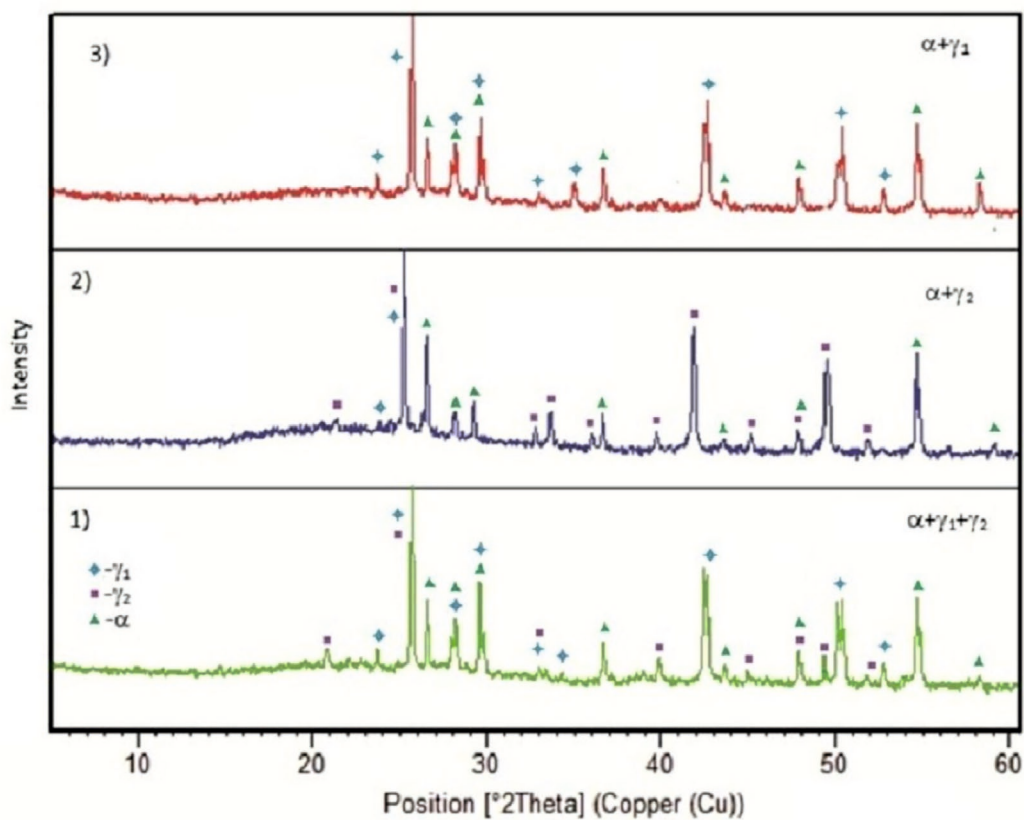


Fig. 4. X-ray powder diffraction patterns of the alloys (1-3) of the MnTe–MnGa₂Te₄–MnIn₂Te₄ system specified in Fig. 3

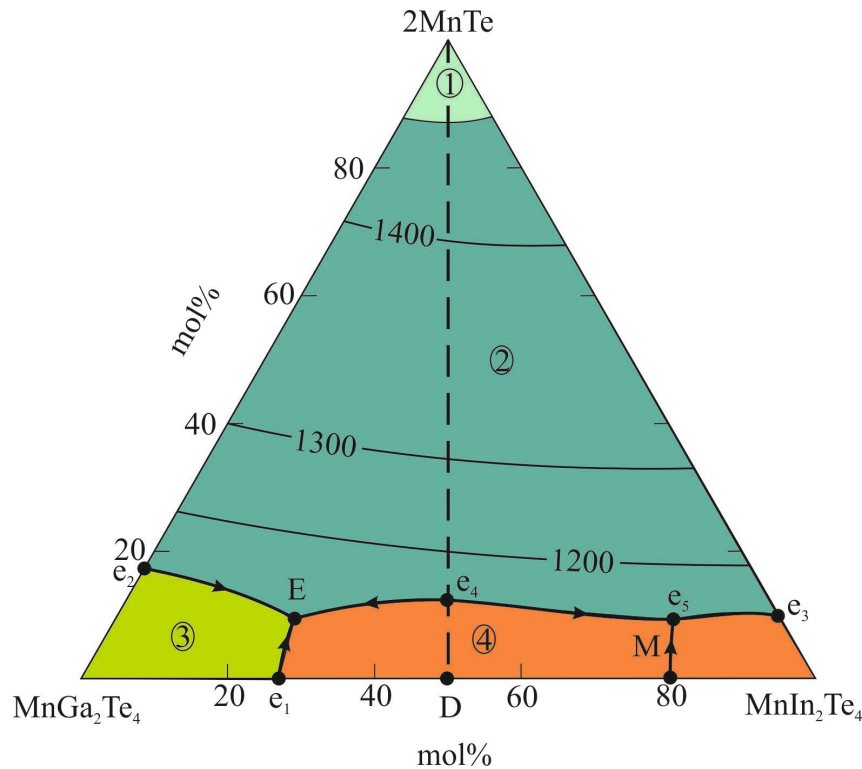


Fig. 5. Projection of the liquidus surface of the MnTe–MnGa₂Te₄–MnIn₂Te₄ system. Primary crystallisation fields of the phases: 1 – Mn-ht; 2 – phases based on various modifications of MnTe; 3 – γ_1 ; 4 – γ_2

system, could be explained by the formation of MnTe by a peritectic reaction $L + \text{Mn-ht} \leftrightarrow \text{MnTe-ht}$ [32]. Field (2) corresponds to the crystallisation of solid solutions based on various modifications of MnTe. The other two fields belong to the γ_1 and γ_2 phases. The specified fields are separated by a number of curves of monovariant equilibria and points of non-variant equilibria. The types and coordinates of non-variant and monovariant equilibria are presented in Table 2.

The MnTe–MnGa₂Te₄–MnIn₂Te₄ system had one partially quasi-binary section (Fig. 5, dotted line) that divided it into 2 subsystems. The MnTe–MnGa₂Te₄–MnGaInTe₄ subsystem belonged to the non-variant eutectic (E) type while the MnTe–MnGaInTe₄–MnIn₂Te₄ subsystem belonged to the monovariant eutectic type. It should be noted that the γ_2 phase of the MnGaInTe₄ composition had the highest melting point of 1030 K. As was shown in [30], the nature of colonisation of crystallographic positions in MnGaInTe₄ allowed considering it as an ordered phase. Taking into account that the MnGaInTe₄ phase was in non-variant eutectic equilibrium with the γ phase based on MnTe-rt (Fig. 5, point e_4), this section could be considered partially quasi-binary.

3.3. Polythermal sections

The **MnTe–MnGaInTe₄** section (Fig. 6) was quasi-binary. The liquidus consists of three curves. Mn-ht crystallises from the melt in the regions of compositions rich in MnTe (> 90 mol%), while solid solutions based on various modifications of manganese monotelluride crystallise in the range of 13–90 mol% MnTe. The γ_2 phase crystallises in the range of 0–15 mol% MnTe. The formation of solid solutions based on MnTe leads to a decrease in temperature of its polymorphic transitions and establishment of metatectic equilibria. The coordinates of the eutectic points (e_4) are 13 mol% MnTe and 1018 K.

The **MnGa₂Te₄–[A]** section (Fig. 7) where [A] is a two-phase alloy of the 2MnTe–MnIn₂Te₄ side system with the 50 mol% MnIn₂Te₄ composition. This section crosses the 2MnTe–MnGaInTe₄ partially quasi-binary section and passes through the primary crystallisation fields of solid solutions based on various crystalline modifications of MnTe and the γ_1 phase. The following monovariant eutectic reactions proceed below the liquidus: $L \leftrightarrow \alpha + \gamma_1$ (55–97 mol% MnGa₂Te₄) and $L \leftrightarrow \alpha + \gamma_2$ (< 55 mol% MnGa₂Te₄). The second reaction is

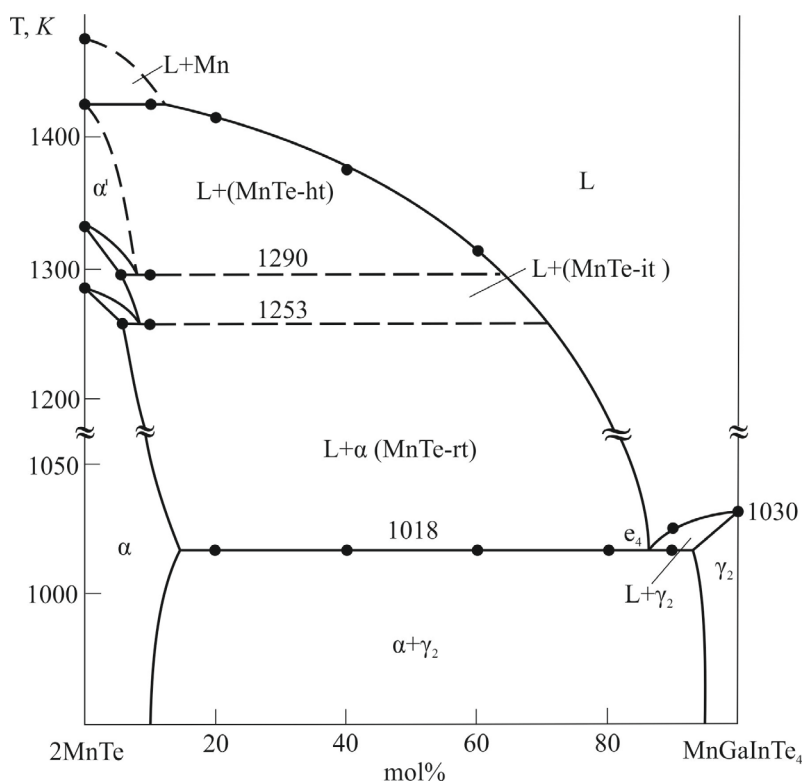


Fig. 6. Polythermal section of 2MnTe–MnGaInTe₄

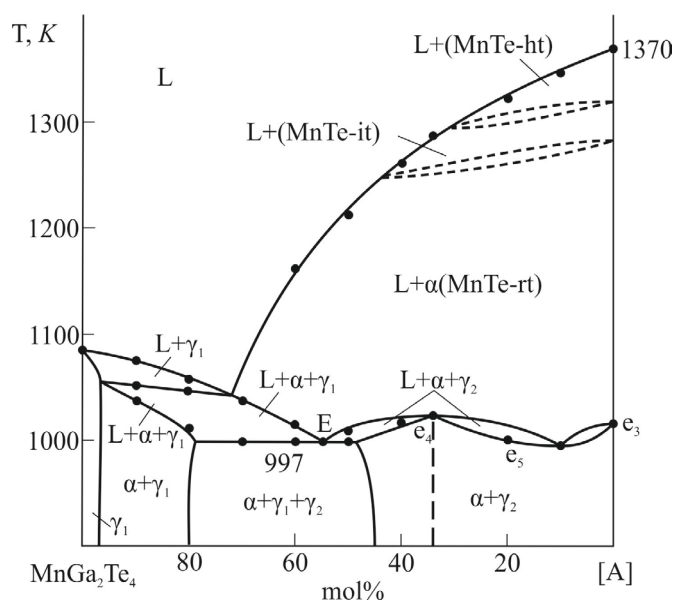


Fig. 7. Polythermal section of MnGa₂Te₄–[A], [A] is the alloy of the 2MnTe–MnIn₂Te₄ system with the composition of 50 mol% MnIn₂Te₄

non-variant in the extremum points (10 and 33.3 mol% MnGa₂Te₄ compositions). Three-phase fields are formed over the course of the specified eutectic processes: L + α + γ₁ and L + α + γ₂ (Fig. 7). In the range of the 0–48 and 80–97 mol% MnGa₂Te₄ compositions crystallisation

ends with the formation of two-phase mixtures, α + γ₂ and α + γ₁, respectively. In the range of 48–80 mol% MnGa₂Te₄ crystallisation proceeds by a L_E ↔ α + γ₁ + γ₂ non-variant eutectic reaction that resulted in the formation of a three-phase region α + γ₁ + γ₂ in the subsolidus.

4. Conclusions

Phase equilibria in the MnTe–MnGa₂Te₄–MnIn₂Te₄ system were studied by DTA and XRD methods. We built a projection of the liquidus surface of this system, an isothermal section at 800 K, and internal polythermal sections of the 2MnTe–MnGaInTe₄ and MnGa₂Te₄–[A] phase diagram. It was shown that the liquidus surfaces corresponded to 4 fields of primary crystallisation fields. We identified the types and coordinates of non-variant and monovariant equilibria. Wide regions of solid solutions along the MnGa₂Te₄–MnIn₂Te₄ section (10 and 65 mol%, respectively) that are of practical interest as potential magnetic materials were determined in the system.

Author contributions

F. M. Mammadov – research concept, writing the article, discussion of results. S. Z. Imamaliyeva – analysis of scientific literature, synthesis of compounds, conducting studies. Ya. I. Jafarov – analysis of scientific literature, discussion of results. I. B. Bakhtiyarly – discussion of results. M. B. Babanly – scientific supervision of research, concept of research, final conclusions.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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