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# NEW VERSION OF THE PHASE DIAGRAM OF THE MnTe- $Ga_2Te_3$ SYSTEM

**Faik M. Mammadov**[*]

Institute of Catalysis and Inorganic Chemistry, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan

**Abstract.** The MnTe-$Ga_2Te_3$ system was re-investigated by differential-thermal analysis and X-ray diffraction methods and its phase diagram was constructed, which slightly differs from that previously presented in the literature. The system is characterized by the formation of the $MnGa_2Te_4$ compound congruently melting at 1083 K with a wide (48-58 mol.% $Ga_2Te_3$) homogeneity region, as well as ~ 30 mol% solid solutions based on $Ga_2Te_3$. $MnGa_2Te_4$ compound is in eutectic equilibrium (1060 K) with solid solutions based on low-temperature MnTe and in peritectic equilibrium with solid solutions based on $Ga_2Te_3$. A comparative analysis of the results obtained with the literature data was carried out.

***Keywords:*** *phase diagram, manganese-gallium tellurides, solid solutions.*

***Corresponding Author:*** *Faik M. Mammadov, Institute of Catalysis and Inorganic Chemistry, National Academy of Sciences of Azerbaijan, Baku, Azerbaijan, e-mail: faikmamadov@mail.ru*

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## 1. Introduction

Complex chalcogenides of transition metals, in particular, compounds of the $AB_2X_4$ type (A-Mn, Fe, B-Ga, In, Sb, Bi, X-S, Se, Te) are important functional materials that possess magnetic, optical, photoelectric, thermoelectric, and other properties (Yang *et.al.*, 2019; Ranmohotti *et.al.*, 2015; Djieutedjeu *et.al.*, 2011; Torresa *et.al.*, 2006; Bodnar *et.al.*, 2010, 2011; Niftiyev *et.al.*, 2018; Myoung *et.al.*, 2017; Yang *et.al.*, 2019; Karthikeyan *et.al.*, 2017). Recent studies have shown that some of these compounds are magnetic topological insulators and are promising for creating ultrafast memory elements, spintronic devices, quantum computers, detectors, etc. (Klimovskikh *et.al.*, 2020; Estyunin *et.al.*, 2020; Yonghao *et.al.*, 2020; Zhou *et.al.*, 2020; Yujun *et.al.*, 2020).

The development of methods for the synthesis of new complex phases is based on reliable data on phase equilibria in the corresponding systems (Zlomanov *et.al.*, 2013; Babanly *et.al.*, 2017, 2019; Imamaliyeva *et.al.*, 2018).

To search and develop the physicochemical basis for obtaining new magnetic semiconductors, we undertook a study of phase equilibria in the AX - $Ga_2X_3$ - $In_2X_3$ systems (Mammadov *et.al.*, 2019b, 2020; Mammadov *et.al.*, 2019a) and showed the formation of wide areas of solid solutions along the $AGa_2X_4$ – $AIn_2X_4$ sections of these systems.

The preliminary experimental results obtained by us during the study of the MnTe- $Ga_2Te_3$- $In_2Te_3$ system showed their inconsistency with the known (Babaeva *et.al.*, 1983; Rustamov *et.al.*, 1978; Garbato *et.al.*,1993) phase diagrams of the boundary MnTe-$In_2Te_3$ and MnTe-$Ga_2Te_3$ quasi-binary systems. In (Mammadov *et.al.*, 2021), we presented the refined T - x diagram of the MnTe-$In_2Te_3$ system.

The present paper is aiming to obtain new data on phase equilibria in the MnTe-$Ga_2Te_3$ system.

The initial binary compounds of this system have been studied in detail (Massalski *et.al.*, 1990; Aliev *et.al.*, 2019; Mukherjee *et.al.*, 1980).

MnTe compound melts at 1425 K with decomposition by a peritectic reaction and undergo polymorphic transitions at 1270 and 1305 K (Massalski *et.al.*, 1990). Low-temperature (LT) -MnTe crystallizes in a hexagonal structure (Sp.Gr. *P*63/*mmc*) with lattice parameters $a$ = 0.41498 nm, $c$ = 0.67176 nm (Aliev *et.al.*, 2019 ).

The $Ga_2Te_3$ compound melts congruently (1065 K) (Massalski *et.al.*, 1990) and crystallizes in a cubic structure (Sp.Gr.*F*-43*m*) with a lattice period $a$ = 0.58980 nm (Mukherjee *et.al.*, 1980).

## 2. Experimental part

### *Materials and synthesis*

$Ga_2Te_3$ and MnTe compounds were synthesized by using high-purity manganese (Mn-99.99%), indium (Ga-99.999%), and tellurium (Te-99.999%) purchased from Alfa Aesar. Stoichiometric mixtures of elementary components were placed in a quartz ampoule, which was evacuated to a residual pressure of ~ $10^{-2}$ Pa and sealed. The synthesis of $Ga_2Te_3$ was carried out at 1070 K. Taking into account the interaction of manganese with quartz, the synthesis of MnTe was carried out in a glass-graphite crucible placed in a quartz ampoule. The ampoule was heated to 1450 K and then kept at 1300 K for 10 h. Then the ampoule was cooled by turning off the furnace.

The individuality of both synthesized compounds was controlled by differential-thermal analysis (DTA) and X-ray diffraction (XRD) methods. The obtained melting temperatures and crystal lattice parameters coincided within the error limits (± 2 K and ± 0.0003 Å) with the above literature data (Massalski *et.al.*, 1990, Aliev *et.al.*, 2019, Mukherjee *et.al.*, 1980).

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 900 K for 500 h.

### *Research methods*

For the investigations, differential-thermal analysis and X-ray diffraction methods were used. DTA was performed on a Netzsch STA449 F3 device (platinum-platinum/rhodium thermocouple) 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 programs (Bruker, Germany; CuKα radiation, angle interval $5° \leq 2\theta \leq 80°$, recording rate 0.03 ° / 0.2 min ).

## 3. Results and its discussion

The powder diffraction patterns of the annealed samples are shown in Fig. 1. As can be seen, the diffraction patterns of the samples containing 40 and 60 mol% $Ga_2Te_3$ consist of sets of reflection lines of the phases based on LT- MnTe and $MnGa_2Te_4$ (α+γ) and $Ga_2Te_3$, $MnGa_2Te_4$ (β + γ) respectively. According to Fig. 1, an alloy with a composition of 50 mol% $Ga_2Te_3$, ($MnGa_2Te_4$) has an individual diffraction pattern that is different from the initial compounds. For samples containing 55 and 70 mol% $Ga_2Te_3$, the diffraction patterns are qualitatively the same for $MnGa_2Te_4$ and $Ga_2Te_3$ and are characterized by some shift in the reflection angles. This shows broad ranges of homogeneity based on these compounds.

The phase diagram of the MnTe- $Ga_2Te_3$ system was constructed using the DTA data, taking into account the XRD results (Fig. 2). As can be seen, it is non-quasi-binary due to the incongruent character of melting of the MnTe compound, but stable below the peritectic (1425 K). Liquidus consists of 4 curves of the primary crystallization of Mn, α′-, and α-solid solutions based on two modifications of MnTe, γ-phase based on $MnGa_2Te_4$ and β-phase based on $Ga_2Te_3$ (Fig. 2).

$MnGa_2Te_4$ compound melts congruently at 1083 K and has a wide (~49-58 mol.% $Ga_2Te_3$) region of homogeneity (γ-phase). This phase forms a eutectic with MnTe, which has a composition of 42 mol% $Ga_2Te_3$ and crystallizes at 1060 K. At a temperature of 1070 K, a β-solid solution based on $Ga_2Te_3$ is formed by the peritectic reaction $L + \gamma \leftrightarrow \beta$. The peritectic point (p) has a composition of 72 mol% $Ga_2Te_3$. On the liquidus and solidus curves of the β-phase, a minimum point (M) at 1050 K was observed.

The T-x diagram constructed by us differs significantly from those given in (Rustamov *et al.*, 1978; Garbato *et.al.*,1993). Thus, according to (Rustamov *et.al.*, 1978), the $MnGa_2Te_4$ compound has an almost constant composition and melts congruently at 1118 K. The coordinates of the $MnGa_2Te_4$ eutectic with MnTe (38 mol% $Ga_2Te_3$ and 1033 K) differ significantly from our data. In addition, according to (Rustamov *et.al.*, 1978), $MnGa_2Te_4$ forms a eutectic with $Ga_2Te_3$, which was not confirmed by us.

The data (Garbato *et.al.*,1993) on the melting point of $MnGa_2Te_4$ (1093 K) and solid-phase equilibria are close to ours, however, the T - x diagram given in this work is constructed in violation of the known provisions.

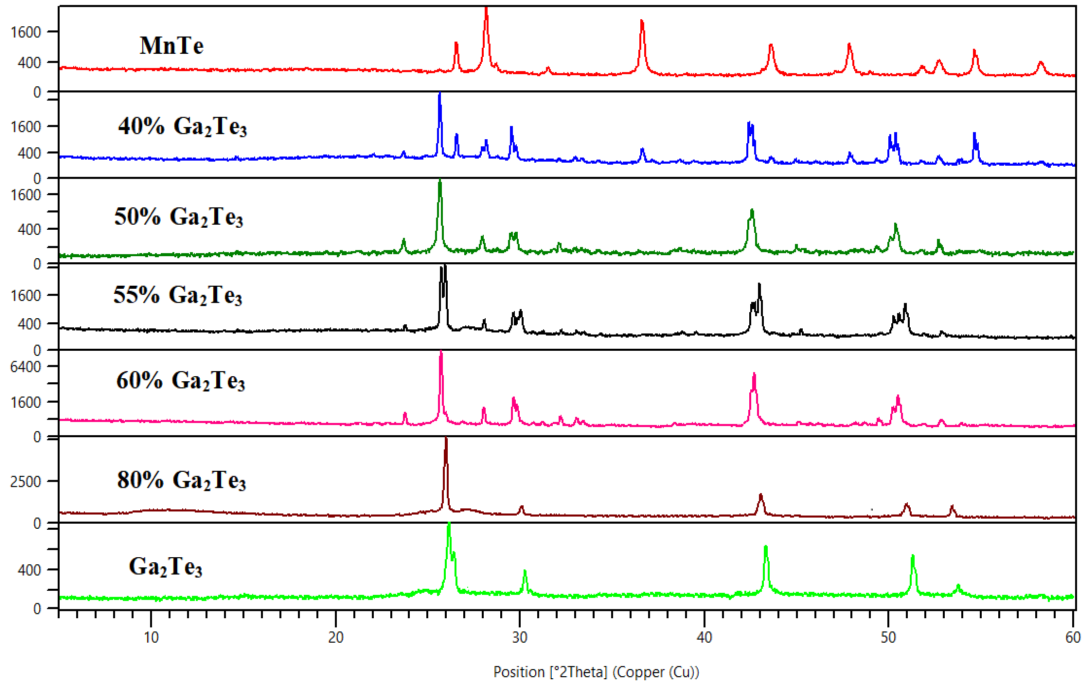

**Figure 1.** Diffraction patterns of some alloys MnTe-$Ga_2Te_3$ system

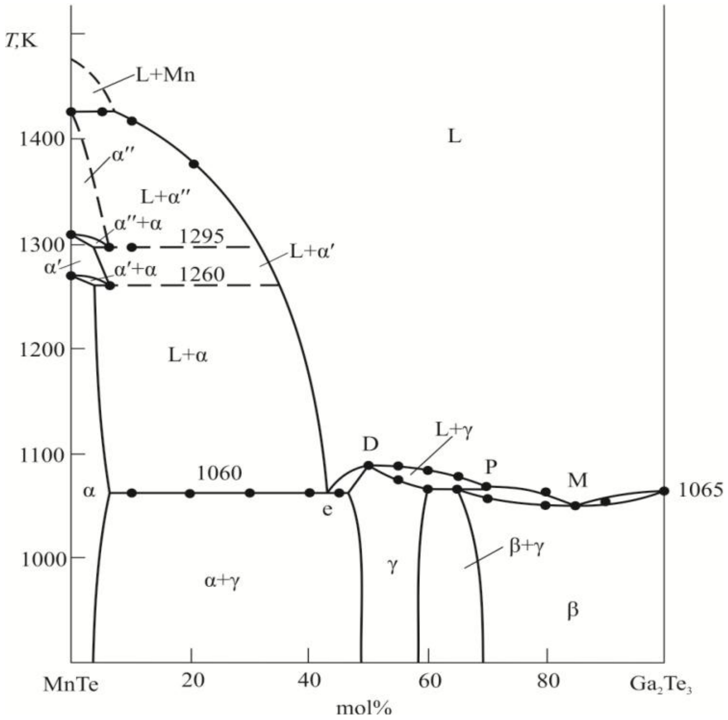

**Figure 2.** Phase diagram of the MnTe-$Ga_2Te_3$ system

## 4. Conclusion

Based on the DTA and XRD data of the carefully homogenized by prolonged thermal annealing samples, we obtained a new version of the T-x phase diagram of the MnTe- $Ga_2Te_3$ system, which differs from the two previously known variants. It was found that the $MnGa_2Te_4$ ternary compound melts congruently to 1083 K and has a wide homogeneity range (at 900 K from 48 to 58 mol% $Ga_2Te_3$). A wide range (up to 30 mol%) of solid solutions based on $Ga_2Te_3$ was revealed also. The new phases obtained in this work are of interest as potential magnetic materials.

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