UDC 546 (72.681.682.23)

REFINEMENT OF THE PHASE DIAGRAMS OF THE FeSe–Ga₂Se₃ AND Ga₂Se₃–In₂Se₃ SYSTEMS

F.M.Mammadov

*M.Nagiev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**faikmammadov@mail.ru*

Received 22.02.2018

The quasi-binary systems FeSe–Ga₂Se₃ and Ga₂Se₃–In₂Se₃ were reinvestigated by using DTA as well as RFA methods and their refined T – x phase diagrams were constructed. A comparative analysis of the results obtained with literature data is carried out.

Keywords: FeSe–Ga₂Se₃ and Ga₂Se₃–In₂Se₃ systems, phase diagram, iron, gallium and indium selenides.

Introduction

Multicomponent chalcogenides and phases based on them are advanced functional materials possess thermoelectric, photoelectric, optical, magnetic and other functional properties [1–6].

AB₂X₄ compounds (A – Mn, Fe, Co, Ni; B – p^1 – p^3 elements; X – chalcogen) are characterized by phenomena of electronically or optically governed magnetism; so they are promising materials for the production of wide-gap converters of optical radiations, light modulators, photodetectors, sensors, and data storage devices as well as spintronic and other magnetic-field-controllable functional devices [7–14].

In order to search and develop the physicochemical basis for the production of new magnetic semiconductors, we undertook a phase equilibria study in the MX–Ga₂X₃–In₂X₃ (M – Mn, Fe; X – S, Se, Te) systems. The preliminary results obtained [15, 16] showed the formation of wide regions of solid solutions along the MGa₂X₄–MIn₂X₄ sections of these systems. The analysis of the literature data showed that the phase diagrams of some boundary quasibinary systems of these quasiternary systems need to be refined.

In this paper, new refined T – x diagrams of the quasibinary FeSe–Ga₂Se₃ and Ga₂Se₃–In₂Se₃ systems are presented and compared with literature data.

Results and its discussion

FeSe–Ga₂Se₃ system (Figure 1) belongs to the distectic type. The intermediate γ -phase

with the stoichiometric composition of FeGa₂Se₄ melts at 1285 K and forms eutectics with α - and β -phases based on the initial binary compounds.

Fig.1. Phase diagram of the FeSe–Ga₂Se₃ system.

The eutectics e_1 and e_2 have compositions of 27 and 67 mol% Ga₂Se₃ and crystallize at 1220 and 1175 K, respectively. At the eutectic temperatures, the homogeneity regions of the α -, γ - and β -phases cover the composition intervals of 0–4; 43–59 mol% (1220 K) and 75–100 mol % Ga₂Se₃. At 725 K a eutectoid reaction $\alpha \leftrightarrow (\text{FeSe})_1 + \gamma$ takes place, where $(\text{FeSe})_1$ is a low-temperature modification of iron monoselenide.

The homogeneity regions of the β - and γ -phases decrease slightly with a decrease in temperature and at room temperature are 49–57 and 80–100 mol % of Ga₂Se₃, respectively.

Comparison with the data of [17–19] shows that the T - x diagram of this system constructed by us qualitatively coincides with the results of [17]. However, the temperature of the distectic and eutectoid equilibria, determined by us, significantly differs from those given in [17] (1318 and 1223 K, respectively). We also did not confirm the immiscibility region specified by authors of [17]. Moreover, the data of [19], according to which the FeGa₂Se₄ compound melts by peritectic decomposition are not confirmed by us. Authors of [18] showed congruent melting of FeGa₂Se₄ at 1283 K. This practically coincides with our data.

Ga₂Se₃–In₂Se₃ (Figure 2). A characteristic feature of this system is the presence of wide regions of solid solutions based on Ga₂Se₃ (α -phase), an intermediate modification of In₂Se₃ (γ_1 -phase), and an intermediate γ_2 -phase. The latter decomposes on a solid-phase reaction at 1120 K. The γ_1 -phase is formed by peritectic reaction at 1145 K. The peritectic point (P) has a composition of 65 mol % In₂Se₃. At 1100 K the homogeneity regions of the α - and γ_1 -phases cover the ranges of 0–25 and 55–88 mol % In₂Se₃, respectively.

Fig.2. Phase diagram of the Ga₂Se₃–In₂Se₃ system.

The formation of the γ_1 -phase is accompanied by temperature increasing of the phase transition at 1005 K to 1125 K and a decreasing of the temperature of the phase transition at 920 to 470 K. The latter corresponds to the eutectoid equilibrium $\beta' \leftrightarrow \beta + \gamma_1$. Solubility based on low-temperature modifications of In₂Se₃ does not exceed 2–3 mol %.

Until our investigation, two variants of the phase diagram of the Ga₂Se₃–In₂Se₃ system were known [20, 21]. According to [20], wide areas (45 mol %) of solid solutions (α -phase) and intermediate phase (γ) with a homogeneity region of 50–88 mol % based on Ga₂Se₃ are formed in the system. However, a detailed X-ray study [21] showed that the region of homogeneity of the α -phase does not exceed 20 mol %, while γ -phase is a solid solution based on the intermediate modification of In₂Se₃. In addition, authors of [21] discovered a new intermediate phase with a relatively narrow region of homogeneity (35–42 mol % In₂Se₃). The low-temperature region of the phase diagram in [21] has not been studied.

The phase diagram of Ga₂Se₃–In₂Se₃ system constructed by us, combines the elements of both variants of the phase diagram. In this case, the character of solid-phase equilibria almost completely coincides with the data [21]. However, the distectic maximum of melting of the γ_1 -phase indicated in [21] is not confirmed by us.

Conclusion

FeSe–Ga₂Se₃ and Ga₂Se₃–In₂Se₃ systems were re-studied by means of DTA and RFA methods taking into account the inconsistency of the available literature data on phase equilibria. New refined variants of the phase diagrams of these systems were constructed based on the experimental results obtained, and taking into account earlier data. Comparative analysis with literature data was carried out.

References

1. Ahluwalia G.K. (Ed.). Applications of Chalcogenides: S, Se, and Te. Springer, 2016. 461 p.
2. Kolobov A.V., Tominaga J. Two-Dimensional

- Transition-Metal Dichalcogenides. Springer International Publishing. 2016. 538 p.
- Kanatzidis M.G. Advances in thermoelectrics: From single phases to hierarchical nanostructures and back // Mater. Res. Soc. Bull. 2015. V. 40. Issue 8. P. 687–694.
 - Babanly M.B., Chulkov E.V., Aliev Z.S., Shevelkov A.V., Amiraslanov I.R. Phase diagrams in materials science of topological insulators based on metal chalcogenides // Russ. J. Inorg. Chem. 2017. V. 62. No 13. P. 1703–1729.
 - Gao M-R, Xu Y-F., Jiang J., Yu S-H. Nanostructured metal chalcogenides: synthesis, modification, and applications in energy conversion and storage devices // Chem. Soc. Reviews. 2013. V. 42. P. 2986–3017.
 - Niesner D., Otto S., Hermann V., Fauster Th, Menshchikova T.V., Ereemeev S.V., Aliev Z.S., Amiraslanov I.R., Echenique P.M., Babanly M.B., Chulkov E.V. Bulk and surface electron dynamics in a p-type topological insulator SnSb_2Te_4 // Physical Review B. 2014. V. 89. P. 081404–081404–5.
 - Ohno Y., Young D.K., Beschoten B., Matsukura F., Ohno H., Awschalom D.D. Electrical spin injection in a ferromagnetic semiconductor heterostructure // Nature. 1999. V. 402. P. 790–792.
 - Haeuseler H., Srivastava S.K. Phase equilibria and layered phases in the systems $\text{A}_2\text{X}_3\text{--M}_2\text{X}_3\text{--M}'\text{X}$ ($\text{A} = \text{Ga, In}$; $\text{M} = \text{trivalent metal}$; $\text{M}' = \text{divalent metal}$; $\text{X} = \text{S, Se}$) // Z. Kristallogr. 2000. V. 215. Issue 4. P. 205–221.
 - Ranmohotti K.G., Djieutedjeu H., Lopez J., Page A., Haldolaarachchige N., Chi H., Sahoo P., Uher C., Young D., Poudeu P.F. Coexistence of High-T c Ferromagnetism and n-Type Electrical Conductivity in FeBi_2Se_4 // J. Am. Chem. Soc. 2015. V. 137. Issue 2. P. 691–698.
 - Djieutedjeu H., Makongo J., Rotaru A., Palasyuk A., Takas N.J., Zhou X. Crystal Structure, Charge Transport, and Magnetic Properties of MnSb_2Se_4 // Eur. J. Inorg. Chem. 2011. V. 2011. Issue 26. P. 3969–3977.
 - Torres T., Sagredo V., Chalbauda L.M., Attolin G., Bolzoni F. Magnetic and structural characterization of the semiconductor FeIn_2Se_4 // Physica B. 2006. V. 384. P. 100–102.
 - Niftiyev N.N., Mamedov F.M., Guseynov V.I., Kurbanov S.Sh. AC Electrical Conductivity of FeIn_2Se_4 Single Crystals // Semiconductors. 2018. V. 52. Issue 6. P. 683–685.
 - Niftiyev N.N., Tagiev O.B., Mamedov F.M. Zavisi-mosti dielektricheskikh poter v FeGa_2Se_4 ot chas-toty i temperatury // Izv. NAN Azerbaidzhana (seriya fiziko-tekhnicheskikh i matematicheskikh nauk). 2017. T. 37. № 2. S. 135–138.
 - Bodnar I.V., Truhanov S.V.. Magnitnye svoistva kristallov troinogo soedineniya FeIn_2S_4 // Fizika i tekhnika poluprovodnikov. 2011. T. 45. № 7. S. 890–893.
 - Mammadov F.M., Amiraslanov I.R., Mahmudova M.A., Babanly M.B. Solid-phase equilibria in the $\text{FeS--Ga}_2\text{S}_3\text{--In}_2\text{S}_3$ system and crystal structure of the FeGaInS_4 // Tez. docl. Vseross. konf. s mezhdunarodnym uchastiem "Himiia tverdogo tela i funktsionalnye materialy" i XII Vseross. simpoziuma s mezhdunarodnym uchastiem "Termodinamika i materialovedenie". Sankt-Peterburg. 2018. S. 362.
 - Mamedov F.M., Amiraslanov I.R., Makhmudova M.A., Babanly M.B. Fazovaia diagramma sistemy $\text{FeGa}_2\text{Se}_4\text{--FeIn}_2\text{Se}_4$ i kristallicheskaia struktura FeGaInSe_4 // Vysokochistye veshchestva i materialy. Poluchenie, analiz, primenenie. XVI Vseross. konf. i IX Shkola molodykh uchenykh, posviashchennye 100-letiiu akad. G.G.Deviatykh. Nizhnii Novgorod. 2018. S. 148.
 - Allazov M.R., Babaeva P.K., Rustamov P.G. Issledovanie diagrammy sostoianiia i nekotorykh fizicheskikh svoistv faz sistemy $\text{Ga}_2\text{Se}_3\text{--FeSe}$ // Neorgan. materialy. 1979. T. 15. № 7. S. 1177–1180.
 - Pauliukavets S.A., IBychek V., Patapovich M.P. Specific Features of the Growth, Structure, and Main Physicochemical Properties of FeGa_2Se_4 Single Crystals // Inorg. Materials: Applied Research. 2018. V. 9. No 2. P. 207–211.
 - Pardo M.P., Flahaut J. Systeme $\text{Ga}_2\text{Se}_3\text{--FeSe}$. Etude cristallographique diagramme de phase// Mat. Res. Bull. 1980. V. 15. P. 1043–1048.
 - Abrikosov N.KH., Bankina V.F., Poretckaia L.V., Skudnova E.V., Chizhevskaya S.N. Poluprovodnikovye halkogenidy i splavy na ikh osnove, M.: Nauka, 1975. 220 s.
 - Olekseyuk I.D., Ivanchenko I.A., Gulay L.D., Danulyk I.V. The specify of interaction of components in the $\text{Ga}_2\text{Se}_3\text{--In}_2\text{Se}_3$ system. <http://esnuir.eenu.edu.ua/handle/123456789/1657>

FeSe–Ga₂Se₃ (In₂Se₃) və Ga₂Se₃–In₂Se₃ FAZA DİAQRAMLARININ DƏQİQLƏŞDİRİLMƏSİ

F.M.Məmmədov

FeSe–Ga₂Se₃ (In₂Se₃) və Ga₂Se₃–In₂Se₃ kvazibinar sistemləri DTA və RFA metodları ilə yenidən tədqiq edilmiş və onların dəqiqləşdirilmiş *T-x* faza diaqramları qurulmuşdur. Əldə edilmiş nəticələrin ədəbiyyat məlumatları ilə müqayisəli təhlili aparılmışdır.

Açar sözlər: FeSe–Ga₂Se₃ və Ga₂Se₃–In₂Se₃ sistemləri, faza diaqramı, dəmir, qallium və indiumun selenidləri.

УТОЧНЕНИЕ ФАЗОВЫХ ДИАГРАММ СИСТЕМ $\text{FeSe-Ga}_2\text{Se}_3$ И $\text{Ga}_2\text{Se}_3\text{-In}_2\text{Se}_3$ **Ф.М.Мамедов**

Методами ДТА и РФА повторно изучены квазибинарные системы $\text{FeSe-Ga}_2\text{Se}_3$ (In_2Se_3) и $\text{Ga}_2\text{Se}_3\text{-In}_2\text{Se}_3$ и построены их уточненные T - x -фазовые диаграммы. Проведен сравнительный анализ полученных результатов с литературными данными.

Ключевые слова: системы $\text{FeSe-Ga}_2\text{Se}_3$ и $\text{Ga}_2\text{Se}_3\text{-In}_2\text{Se}_3$, фазовая диаграмма, селениды железа, галлия, индия.

This work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan – Grant EIF/MQM/Elm-Tehsil-1-2016-1(26)-71/01/4-M-33