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Phase equilibria in the quasi-ternary system HgSe–Ga_2Se_3–Bi_2Se_3

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The phase equilibria in the quasi-ternary system HgSe–Ga_2Se_3–Bi_2Se_3 were investigated by differential thermal analysis and X-ray diffraction. No quaternary phases were found in the system. The isothermal section of the system at 670 K, part of the section at 520 K, and the liquidus surface projection were constructed. The nature and temperature of the mono- and invariant processes were established.

Semiconductors / Liquid-solid reaction / Phase diagrams / Thermal analysis / X-ray diffraction

Introduction

In recent years considerable attention has been paid to the growth of nonlinear optical crystals for IR and laser technology. Obtaining optical-quality crystals of most of the chalcogenides suitable for this purpose requires relatively complex technology, which greatly affects the economic performance of the working elements and devices made from these crystals.

Compounds with defective chalcopyrite structure are promising materials for semiconductor technology. For instance, their use as nonlinear optical materials ($HgGa_2S_4$ and $Cd_{1-x}Hg_xGa_2S_4$) and photosensitive materials ($ZnGa_2Se_4$), narrow band optical filters ($CdGa_2S_4$), *etc*. is known [1-4]. Important characteristics of the compounds of this group are their low sensitivity to impurities and high resistance to ionizing radiation [4]. The $HgGa_2Se_4$ compound has similar properties [3,5-8]. In particular, it is promising as an optical [3] and nonlinear optical material for parametric light generation [1]. One of the main requirements for such materials is the high optical quality of crystals of suitable dimensions. However, information on the properties of $HgGa_2Se_4$ is rather scarce, and the application is limited by technological difficulties to obtain industrial-size crystals. $HgGa_2Se_4$ melts incongruently and has a high-temperature phase transition, which complicates the growth of single crystals of sufficient size. In most cases, the growth of single crystals is performed by chemical vapor deposition (CVD) using iodine as transport agent, although there are several reports on the production of single crystals by melt methods. One of the most common methods used in such cases is the growth of crystals from non-stoichiometric melts. However, there is a problem of solvent selection. We have previously tested $GeSe_2$ and $SnSe_2$ for this purpose [9-11]. The phase diagrams include a field of primary crystallization of LT-$HgGa_2Se_4$. However, these solvents have a number of disadvantages, including high cost (in the case of $GeSe_2$) and the formation of solid solutions of several mol.% extent. The high value of the ionic radius of Bi^{3+} may be the cause of the virtually absent solid solubility based on $HgGa_2Se_4$. No liquidus curve belonging to $HgGa_2Se_4$ is expected in the $HgGa_2Se_4$–Bi_2Se_3 system, due to the incongruent melting of the ternary phase. Such formation is more probable in the more complex system HgSe–Ga_2Se_3–Bi_2Se_3 with its ternary eutectics, which should, additionally, lower the temperature of crystallization of the alloys. Based on the phase diagram of the Ga_2Se_3–Bi_2Se_3 system, such temperature decrease is likely.

Here we present the results of an investigation of the quasi-ternary system HgSe–Ga_2Se_3–Bi_2Se_3 to determine the most suitable region of the alloys that may be used to obtain $HgGa_2Se_4$ single crystals by the solution-melt method.

The quasi-binary system HgSe–Ga_2Se_3 system was already studied in [12,13]. The phase diagram of the system is of the peritectic type. The system features a ternary compound, $HgGa_2Se_4$, which forms in a peritectic reaction, L+Ga_2Se_3 ⇆ HT-$HgGa_2Se_4$ (peritectic point coordinates 46 mol. % Ga_2Se_3,

1143 K). The homogeneity region of this compound is narrow and shifted towards Ga_2Se_3 (50-52 mol.% Ga_2Se_3 at 470 K). The compound $HgGa_2Se_4$ has a polymorphous transition that takes place in the range 933-913 K. The decrease of the transition temperature corresponds to an increase of the Ga_2Se_3 content. LT-$HgGa_2Se_4$ has a tetragonal thiogallate structure (space group *I*-4) with the lattice periods a = 0.5703, c = 1.076 nm [14], or a = 0.5693, c = 1.0826 nm [15]. HT-$HgGa_2Se_4$ is a disordered form of LT-$HgGa_2Se_4$, and the transition LT-$HgGa_2Se_4$ ⇆ HT-$HgGa_2Se_4$ is accompanied by a significant increase of the unit cell volume.

HgSe forms a solid solution range with disordered sphalerite structure that crystallizes in a narrow temperature range with a minimum at 1058 K and 8 mol.% Ga_2Se_3. The solid solution in the range 20-27 mol.% Ga_2Se_3 forms in a peritectic reaction, L+HT-$HgGa_2Se_4$ ⇆ HgSe at 1093 K. The solid solubility decreases with decreasing temperature and does not exceed 10 mol.% Ga_2Se_3 at 470 K.

Solid-state ordering (α' phase) takes place in the concentration range 12-18 mol.% Ga_2Se_3. Maximum ordering corresponds to the composition $Hg_5Ga_2Se_8$. The diffraction pattern of the corresponding alloy was indexed in [12,13] as an *fcc* lattice with a doubled edge compared to the sphalerite lattice of the solid solution range of HgSe (α phase). The α' phase undergoes a solid-state peritectoid decomposition α' ⇆ α+LT-$HgGa_2Se_4$ at 639 K. The crystal structure of $Hg_5Ga_2Se_8$ was investigated by X-ray powder diffraction in [16]. It was found that the ternary phase crystallizes in the cubic space group *F*-43*m* with the period a = 1.16876 nm.

Solid solutions of Ga_2Se_3 exist in the range 75-100 mol.% Ga_2Se_3 and have defect disordered sphalerite structure. The boundaries of the solid solutions do virtually not vary with temperature.

The Ga_2Se_3–Bi_2Se_3 system was investigated in [17-19]. This is a quasi-binary system of the eutectic type. The system liquidus consists of the curves of primary crystallization of Ga_2Se_3 and Bi_2Se_3. The coordinates of the eutectic point differ slightly between different authors: 60 mol.% Bi_2Se_3 and 880 K [17], or 61 mol.% Bi_2Se_3 and 893 K [18], or 65 mol.% Bi_2Se_3 and 900 K [19]. Only very narrow homogeneity regions of the binary compounds were found in the system.

Experimental

The phase equilibria in the quasi-ternary system HgSe–Ga_2Se_3–Bi_2Se_3 were investigated on alloys located at the boundary side HgSe–Bi_2Se_3 and in four internal sections; additional alloys were synthesized to ascertain the position of the invariant eutectic point (Table 1). Phase and chemical compositions of the alloys are shown in Fig. 1.

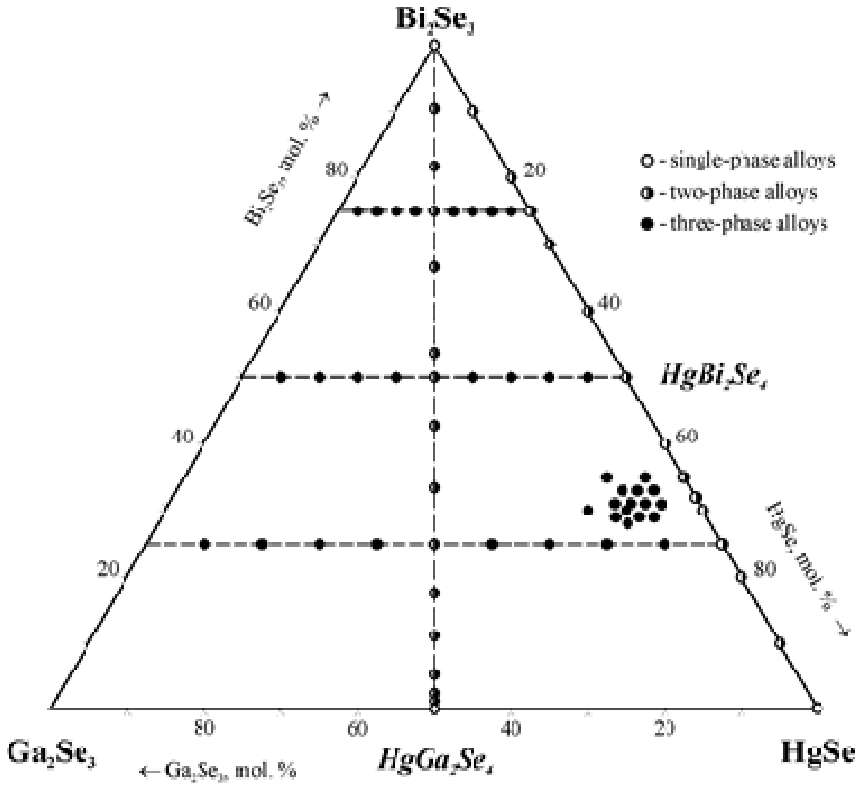

Fig. 1 Composition of the investigated alloys of the HgSe–Ga_2Se_3–Bi_2Se_3 system.

The alloys were synthesized from high-purity elements (at least 99.99 wt.% of the principal element) and previously synthesized HgSe. Appropriate amounts of the raw materials were placed in quartz ampoules that were evacuated to a residual pressure of 10^{-2} Pa and soldered. The synthesis was performed in a shaft-type furnace. The temperature was raised to 1000 K at the rate of 50 K/h, kept for 5 h, and increased to 1200 K at the rate of 15-20 K/h. After exposure at the maximum temperature for 6 h, the alloys were slowly cooled at the rate of 30 K/h to 670 K or 520 K. Homogenizing annealing was carried out for 250 h, followed by quenching into cold water. The synthesis resulted in compact dark-gray ingots.

The obtained alloys were investigated by differential thermal analysis (Paulik-Paulik-Erdey derivatograph, Pt/Pt-Rh thermocouple) and X-ray diffraction (XRD; DRON 4-13 diffractometer, CuK_α radiation, Ni-filter, $\theta/2\theta$ scan in the angle range 10°-70°, scan step 0.05°, exposure time 1 s).

Results and discussion

Triangulation

Triangulation of the HgSe–Ga_2Se_3–Bi_2Se_3 system was performed based on the results of XRD of the alloys annealed at 670 K (Fig. 2).

The $HgGa_2Se_4$–Bi_2Se_3 section is quasi-binary at this temperature and separates the system into two sub-systems, HgSe–$HgGa_2Se_4$–Bi_2Se_3 and $HgGa_2Se_4$–Ga_2Se_3–Bi_2Se_3. The section is non-quasi-binary above the solidus because the ternary compound $HgGa_2Se_4$ melts incongruently.

The system components HgSe and Ga_2Se_3 have solid solution ranges that are stretched along the quasi-binary section HgSe–Ga_2Se_3.

Five alloys of the $Hg_5Ga_2Se_8$–Bi_2Se_3 section were investigated to determine the solid solubility of the $Hg_5Ga_2Se_8$ compound (γ'-solid solutions). This compound forms by a solid-state reaction of ordering of the γ-solid solutions of HgSe below ~640 K. The studied alloys were annealed at 520 K, which is below the temperature of formation of $Hg_5Ga_2Se_8$. All the samples were two-phase, *i.e.* the solid solubility based on $Hg_5Ga_2Se_8$ does not exceed 1 mol.%. The most likely picture of the isothermal section of the HgSe–Ga_2Se_3–Bi_2Se_3 system at 520 K in the region of the existence of the ordered phase is presented in Fig. 3.

The HgSe–Bi_2Se_3 system

The HgSe–Bi_2Se_3 system is a boundary side of the quasi-ternary system HgSe–Ga_2Se_3–Bi_2Se_3. The phase diagram of this system is of the eutectic type with an incongruently melting compound (Fig. 4). The system liquidus consists of the curves of primary crystallization of HgSe, Bi_2Se_3 and $HgBi_2Se_4$. The endothermal compound $HgBi_2Se_4$, which exists in the temperature range 908-848 K, forms by the peritectic reaction $L+Bi_2Se_3 \leftrightarrows HgBi_2Se_4$ at 908 K. The eutectic reaction $L \leftrightarrows HgSe+HgBi_2Se_4$ takes place at 870 K; the composition coordinate of the eutectic point is 32 mol.% Bi_2Se_3.

Typical DTA curves of the alloys of the HgSe–Bi_2Se_3 system (heating effects) are plotted in Fig. 5. Typical XRD patterns of the samples of the HgSe–Bi_2Se_3 system are presented in Fig. 6.

The $HgGa_2Se_4$–Bi_2Se_3 section

The vertical section $HgGa_2Se_4$–Bi_2Se_3 was investigated by DTA and XRD (Fig. 7). The aim was to determine the flow of the monovariant line e_1U_3 (see Fig. 11) and the boundaries of the invariant peritectic processes in the system. The section liquidus is represented by the curves of primary crystallization of the solid solution ranges of Ga_2Se_3 and Bi_2Se_3. At 898 K the section crosses the plane of the invariant peritectic process $L_{U1}+HT\text{-}HgGa_2Se_4 \leftrightarrows LT\text{-}HgGa_2Se_4+Ga_2Se_3$, forming a horizontal line to which the region of the coexistence of three phases, $L+HT\text{-}HgGa_2Se_4+Ga_2Se_3$, converges.

Below this horizontal line there is a region of the monovariant eutectic process $L \leftrightarrows LT\text{-}HgGa_2Se_4+Ga_2Se_3$. This, together with the region of the monovariant eutectic process $L \leftrightarrows Ga_2Se_3+Bi_2Se_3$, converge to the horizontal line that belongs to the plane of another invariant peritectic process $L_{U1}+Ga_2Se_3 \leftrightarrows LT\text{-}HgGa_2Se_4+Bi_2Se_3$, which takes place at 888 K. The horizontal line at 888 K coincides with the connecting line of the plane of the invariant peritectic process $L_{U2}+Ga_2Se_3 \leftrightarrows LT\text{-}HgGa_2Se_4+Bi_2Se_3$. Therefore, the alloys of this section are two-phase below 888 K ($LT\text{-}HgGa_2Se_4+Bi_2Se_3$).

The solid solubility of the system components is negligible, as indicated by the virtually absent shift of the reflections in the diffraction patterns of the alloys.

Table 1 Composition of the invariant points in the quasi-ternary HgSe–Ga_2Se_3–Bi_2Se_3 system.

Invariant point	Composition, mol.%		
	HgSe	Ga_2Se_3	Bi_2Se_3
U_1	34	22	44
U_2	68	10	22
U_3	33	21	46
U_4	52	11	37
E	63	7	30

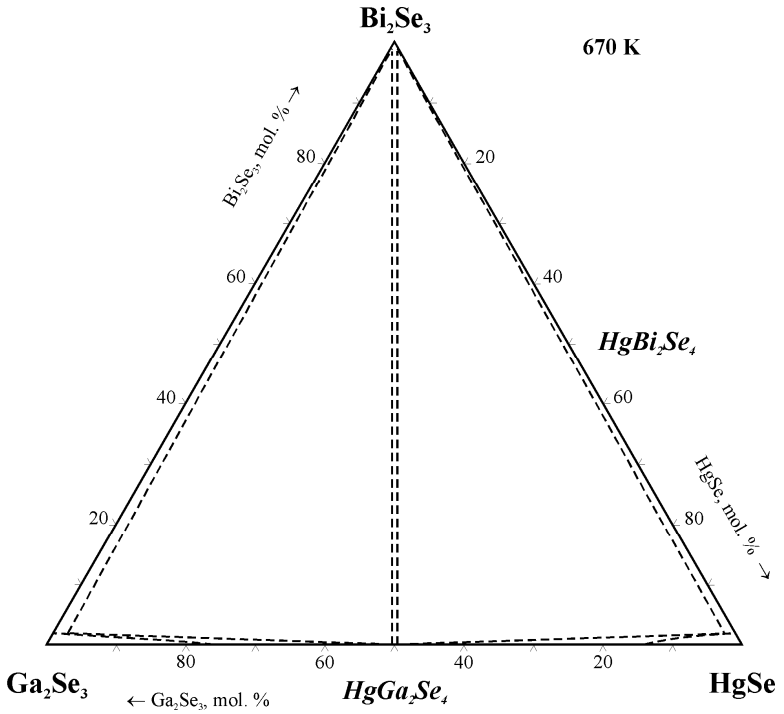

Fig. 2 Isothermal section of the HgSe–Ga_2Se_3–Bi_2Se_3 system at 670 K

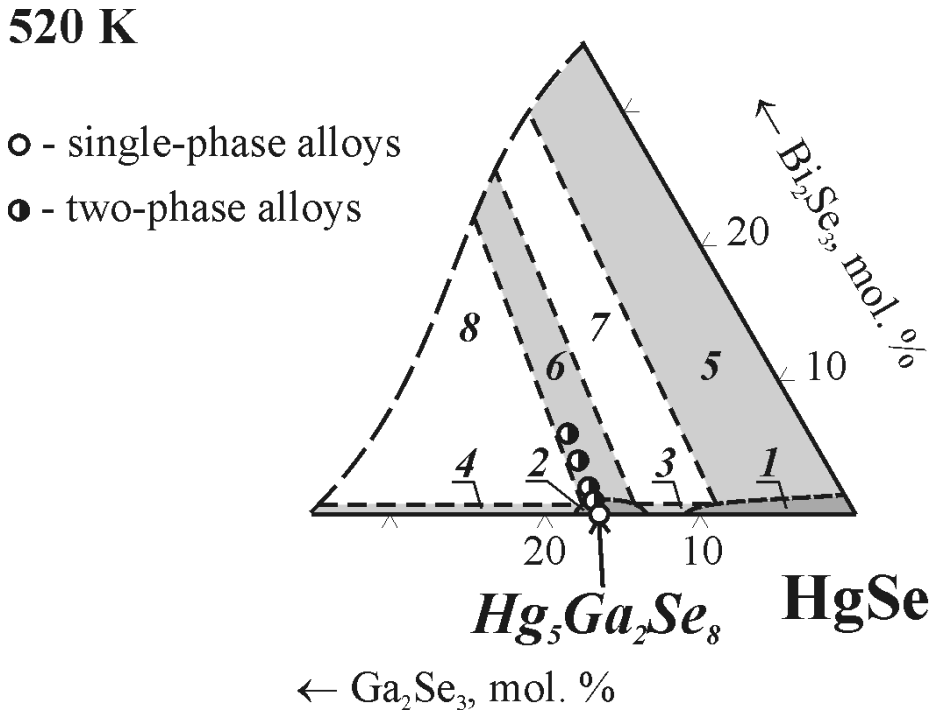

Fig. 3 Isothermal section of the HgSe–Ga_2Se_3–Bi_2Se_3 system at 520 K in the region of existence of the $Hg_5Ga_2Se_8$ phase, including phase and chemical composition of the alloys: ***1*** – γ; ***2*** – γ'; ***3*** – γ+γ'; ***4*** – LT-$HgGa_2Se_4$+γ'; ***5*** – γ+Bi_2Se_3; ***6*** – γ'+Bi_2Se_3; ***7*** – γ+γ'+Bi_2Se_3; ***8*** – LT-$HgGa_2Se_4$+γ'+Bi_2Se_3.

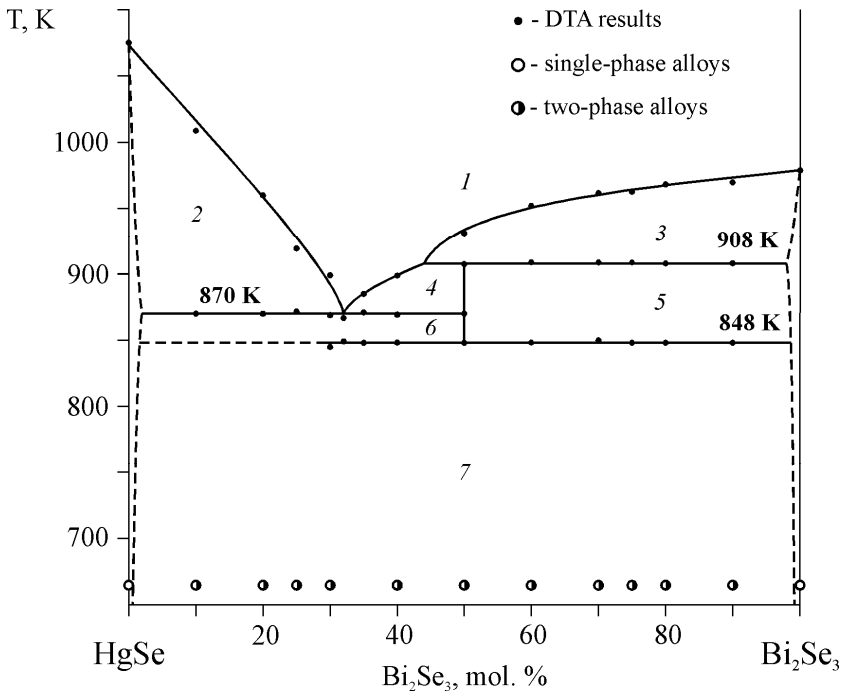

Fig. 4 Phase diagram of the HgSe–Bi_2Se_3 system: ***1*** – L; ***2*** – L+HgSe; ***3*** – L+Bi_2Se_3; ***4*** – L+$HgBi_2Se_4$; ***5*** – $HgBi_2Se_4$+Bi_2Se_3; ***6*** – HgSe+$HgBi_2Se_4$; ***7*** – HgSe+Bi_2Se_3.

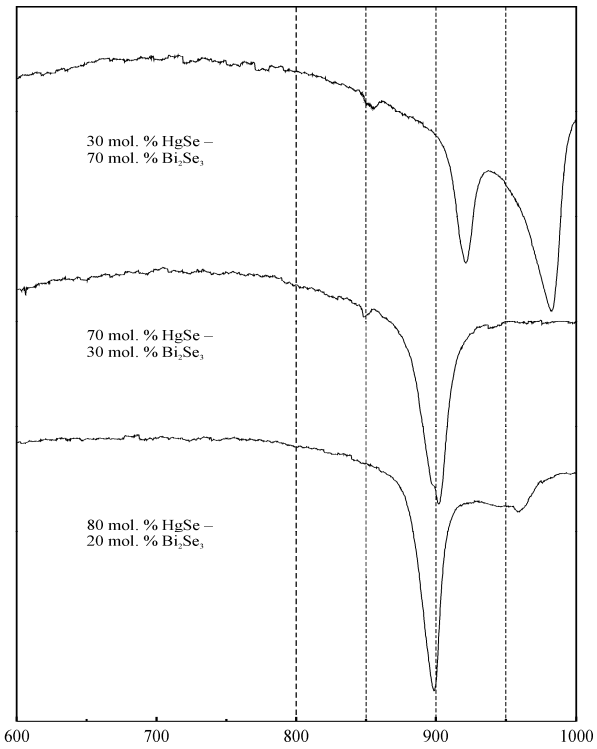

Fig. 5 Typical DTA curves of alloys of the HgSe–Bi_2Se_3 system (heating effects).

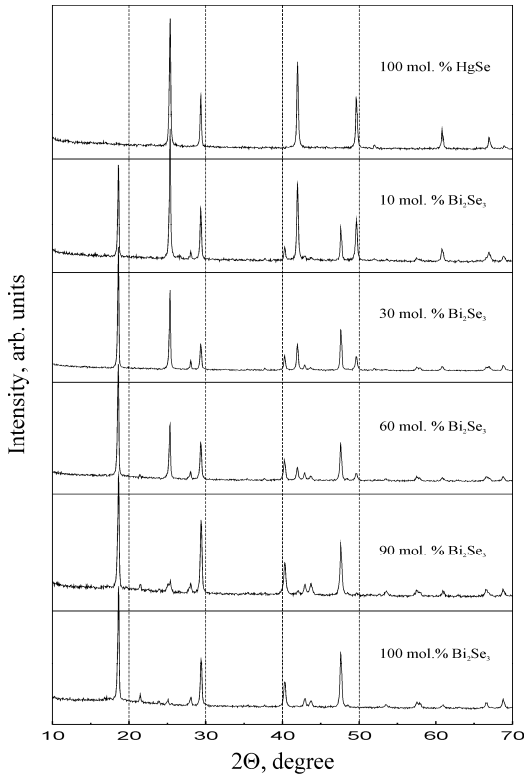

Fig. 6 Typical XRD patterns of alloys of the HgSe–Bi_2Se_3 system.

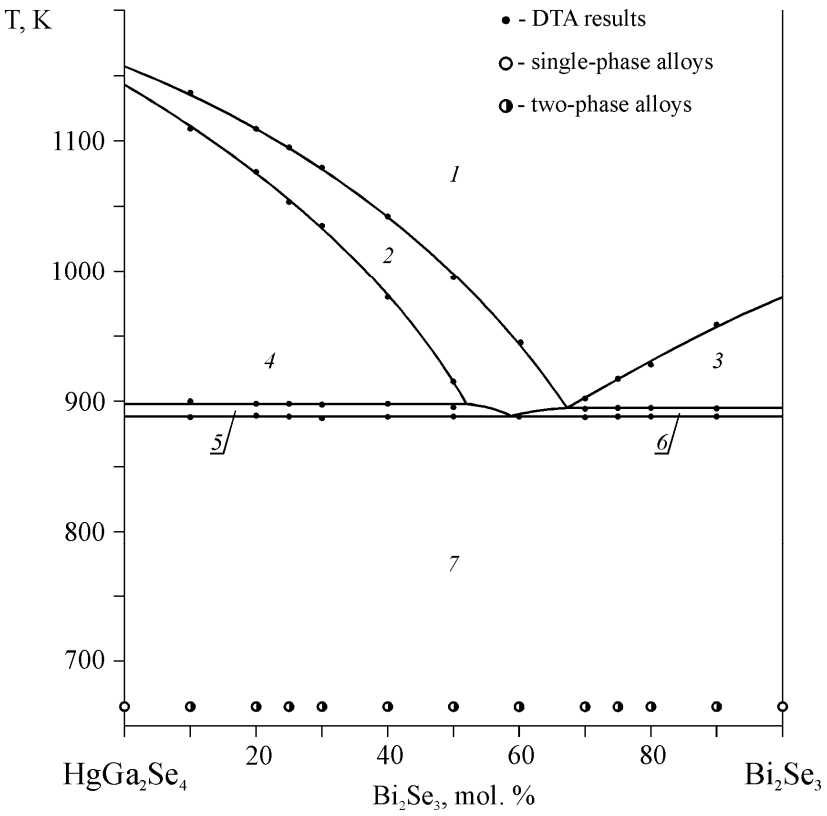

Fig. 7 Vertical section $HgGa_2Se_4–Bi_2Se_3$: ***1*** – L; ***2*** – L+Ga_2Se_3; ***3*** – L+Bi_2Se_3; ***4*** – L+HT-$HgGa_2Se_4$+Ga_2Se_3; ***5*** – L+Ga_2Se_3+LT-$HgGa_2Se_4$; ***6*** – L+Ga_2Se_3+Bi_2Se_3; ***7*** – LT-$HgGa_2Se_4$+Bi_2Se_3.

Sections ‘$Ga_{1.5}Bi_{0.5}Se_3$’–‘$HgBi_{0.5}Se_{1.5}$’, 2‘$GaBiSe_3$’–$HgBi_2Se_4$ and ‘$Ga_{0.5}Bi_{1.5}Se_3$’–‘$Hg_{0.25}Bi_{1.5}Se_{2.5}$’

Vertical sections ‘$Ga_{1.5}Bi_{0.,5}Se_3$’–‘$HgBi_{0.5}Se_{1.5}$’ (Fig. 8), 2‘$GaBiSe_3$’–$HgBi_2Se_4$ (Fig. 9) and ‘$Ga_{0.5}Bi_{1.5}Se_3$’–‘$Hg_{0.25}Bi_{1.5}Se_{2.5}$’ (Fig. 10) were plotted bases on DTA and XRD. These sections were studied to determine the location of the monovariant lines, and the boundaries of the invariant processes that take place in the system.

The ‘$Ga_{1.5}Bi_{0.5}Se_3$’–‘$HgBi_{0.5}Se_{1.5}$’ section (Fig. 8) coincides with the concentration line 25 mol.% Bi_2Se_3. It crosses four regions of primary crystallization, those of the solid solution ranges of Ga_2Se_3, HT-$HgGa_2Se_4$, LT-$HgGa_2Se_4$, and HgSe. Below the liquidus line, in addition to the fields of primary crystallization, the section crosses seven volumes of secondary crystallization. The solidus is represented by the lines of completion of secondary crystallization of the binary eutectics and three horizontal lines of the invariant processes L_{U3}+Ga_2Se_3 ⇆ LT-$HgGa_2Se_4$+Bi_2Se_3 at 888 K, L_{U4}+Bi_2Se_3 ⇆ LT-$HgGa_2Se_4$+$HgBi_2Se_4$ at 870 K, and L_E ⇆ LT-$HgGa_2Se_4$+Ga_2Se_3+$HgBi_2Se_4$+HgSe at 863 K. Two other horizontal lines at 898 K and 840 K belong to the plane of the polymorphous transition of the ternary phase $HgGa_2Se_4$ and the plane of the decomposition of the endothermal compound $HgBi_2Se_4$. All the investigated alloys were three-phase at the annealing temperature, except the alloys containing 0, 50 and 100 mol.% ‘$HgBi_{0.5}Se_{1.5}$’.

The 2‘$GaBiSe_3$’–$HgBi_2Se_4$ section (Fig. 9), which coincides with the concentration line 50 mol.% Bi_2Se_3, crosses the fields of primary crystallization of the solid solution ranges of Ga_2Se_3 and Bi_2Se_3. Below the liquidus line, in addition to the fields of primary crystallization, the section crosses three volumes of secondary crystallization. The solidus is represented by the lines of the completion of the secondary crystallization of the binary eutectics, and two horizontal lines of the invariant processes L_{U3}+Ga_2Se_3 ⇆ LT-$HgGa_2Se_4$+Bi_2Se_3 at 888 K and L_{U4}+Bi_2Se_3 ⇆ LT-$HgGa_2Se_4$+$HgBi_2Se_4$ at 870 K. Another horizontal line at 840 K belongs to the plane of the decomposition of the endothermal compound $HgBi_2Se_4$. The sub-solidus part is similar to that of the ‘$Ga_{1.5}Bi_{0.5}Se_3$’–‘$HgBi_{0.5}Se_{1.5}$’ section (Fig. 8).

The ‘$Ga_{0.5}Bi_{1.5}Se_3$’–‘$Hg_{0.25}Bi_{1.5}Se_{2.5}$’ section (Fig. 10), which coincides with the concentration line 75 mol.% Bi_2Se_3, crosses only the field of primary crystallization of Bi_2Se_3. Otherwise its structure is similar to that of the 2‘$GaBiSe_3$’–$HgBi_2Se_4$ section (Fig. 9).

Liquidus surface projection of the quasi-ternary system $HgSe–Ga_2Se_3–Bi_2Se_3$

The projection of the liquidus surface of the $HgSe–Ga_2Se_3–Bi_2Se_3$ system onto the concentration triangle (Fig. 11) was constructed from literature data on the phase diagrams of the $HgSe–Ga_2S_3$ and $Ga_2S_3–Bi_2S_3$ systems, and our own results on the boundary side $HgSe–Bi_2S_3$ and the four vertical sections described above.

The liquidus surface consists of six fields of primary crystallization belonging to the solid solution ranges of the system components HgSe, Ga_2Se_3 and Bi_2Se_3, and the ternary compounds HT-$HgGa_2Se_4$, LT-$HgGa_2Se_4$ and $HgBi_2Se_4$. The fields of primary crystallization are separated by ten monovariant lines and ten invariant points, of which five are ternary (four ternary peritectics and one ternary eutectic) and five are binary points (two binary eutectics and three binary peritectics). The composition of the ternary invariant points was determined geometrically using the data on the phase equilibria of the vertical sections.

The type and temperature of the mono- and invariant processes in the quasi-ternary system $HgSe–Ga_2Se_3–Bi_2Se_3$ are summarized in Fig. 12.

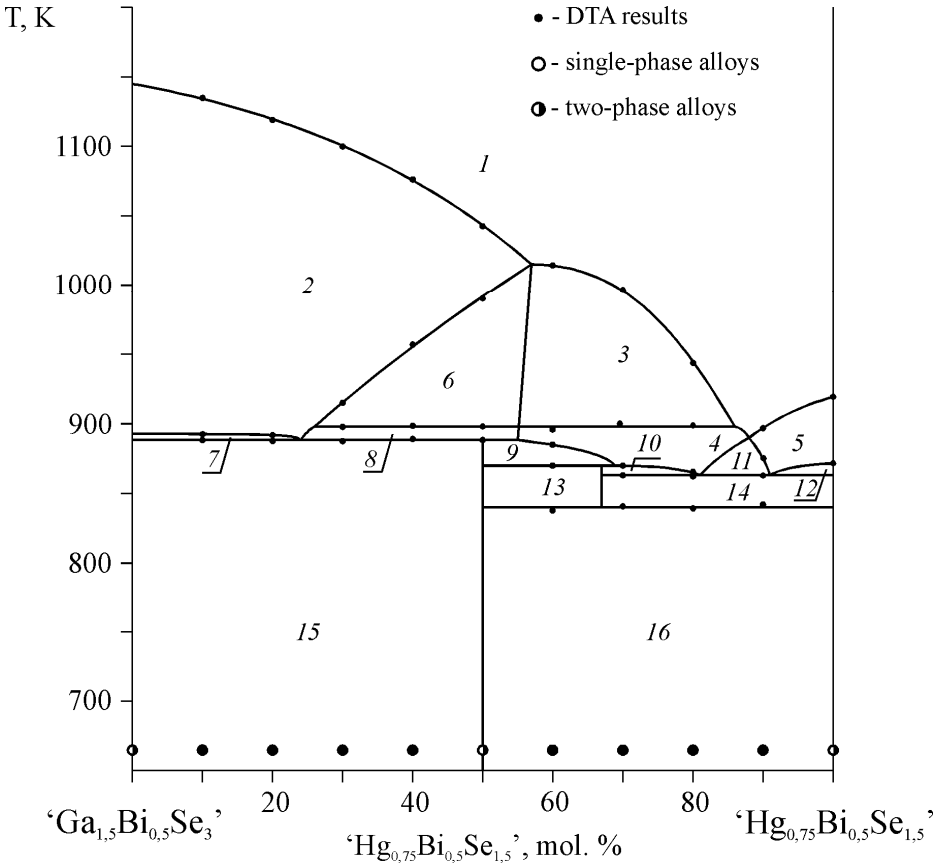

Fig. 8 Vertical section '$Ga_{1,5}Bi_{0,5}Se_3$'–'$HgBi_{0,5}Se_{1,5}$': ***1*** – L; ***2*** – L+Ga_2Se_3; ***3*** – L+HT-$HgGa_2Se_4$; ***4*** – L+LT-$HgGa_2Se_4$; ***5*** – L+HgSe; ***6*** – L+HT-$HgGa_2Se_4$+Ga_2Se_3; ***7*** – L+Ga_2Se_3+Bi_2Se_3; ***8*** – L+LT-$HgGa_2Se_4$+Ga_2Se_3; ***9*** – L+LT-$HgGa_2Se_4$+Bi_2Se_3; ***10*** – L+LT-$HgGa_2Se_4$+$HgBi_2Se_4$; ***11*** – L+LT-$HgGa_2Se_4$+HgSe; ***12*** – L+HgSe+$HgBi_2Se_4$; ***13*** – Bi_2Se_3+LT-$HgGa_2Se_4$+$HgBi_2Se_4$; ***14*** – HgSe+LT-$HgGa_2Se_4$+$HgBi_2Se_4$; ***15*** – LT-$HgGa_2Se_4$+Ga_2Se_3+Bi_2Se_3; ***16*** – LT-$HgGa_2Se_4$+Bi_2Se_3+HgSe.

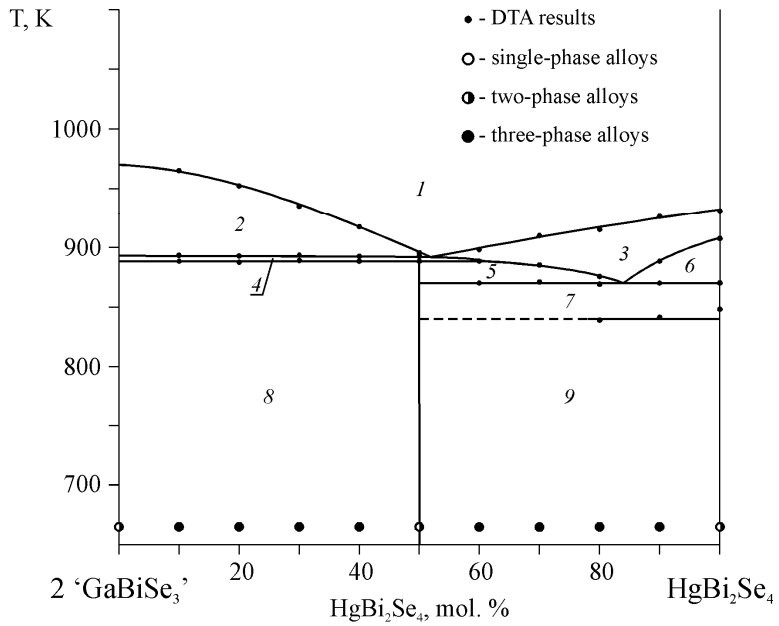

Fig. 9 Vertical section 2'$GaBiSe_3$'–$HgBi_2Se_4$: ***1*** – L; ***2*** – L+Ga_2Se_3; ***3*** – L+Bi_2Se_3; ***4*** – L+Ga_2Se_3+Bi_2Se_3; ***5*** – L+LT-$HgGa_2Se_4$+Bi_2Se_3; ***6*** – L+Bi_2Se_3+$HgBi_2Se_4$; ***7*** – LT-$HgGa_2Se_4$+Bi_2Se_3+$HgBi_2Se_4$; ***8*** – Ga_2Se_3+Bi_2Se_3+LT-$HgGa_2Se_4$; ***9*** – LT-$HgGa_2Se_4$+Bi_2Se_3+HgSe.

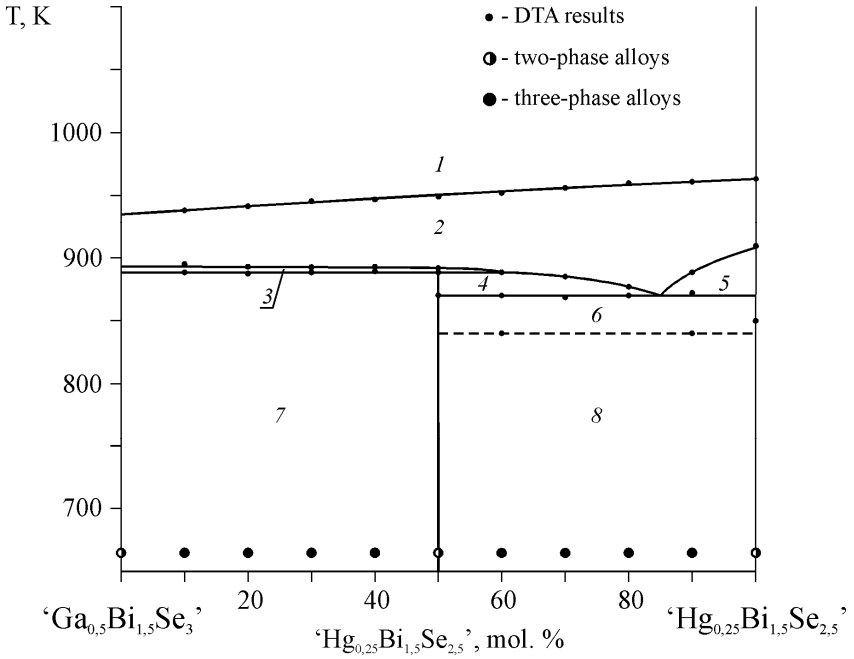

Fig. 10 Vertical section '$Ga_{0,5}Bi_{1,5}Se_3$'–'$Hg_{0,25}Bi_{1,5}Se_{2,5}$': ***1*** – L; ***2*** – L+Bi_2Se_3; ***3*** – L+Ga_2Se_3+Bi_2Se_3; ***4*** – L+LT-$HgGa_2Se_4$+Bi_2Se_3; ***5*** – L+Bi_2Se_3+$HgBi_2Se_4$; ***6*** – LT-$HgGa_2Se_4$+Bi_2Se_3+$HgBi_2Se_4$; ***7*** – Ga_2Se_3+Bi_2Se_3+LT-$HgGa_2Se_4$; ***8*** – LT-$HgGa_2Se_4$+Bi_2Se_3+HgSe.

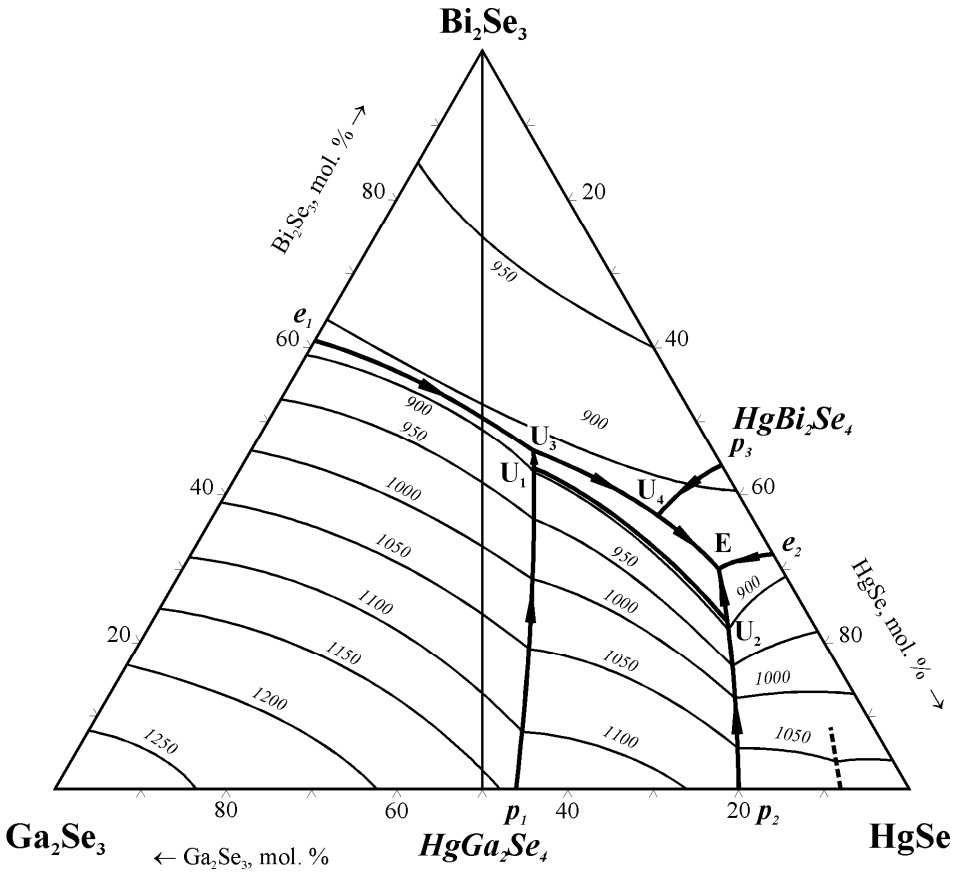

Fig. 11 Liquidus surface projection of the $HgSe–Ga_2Se_3–Bi_2Se_3$ system.

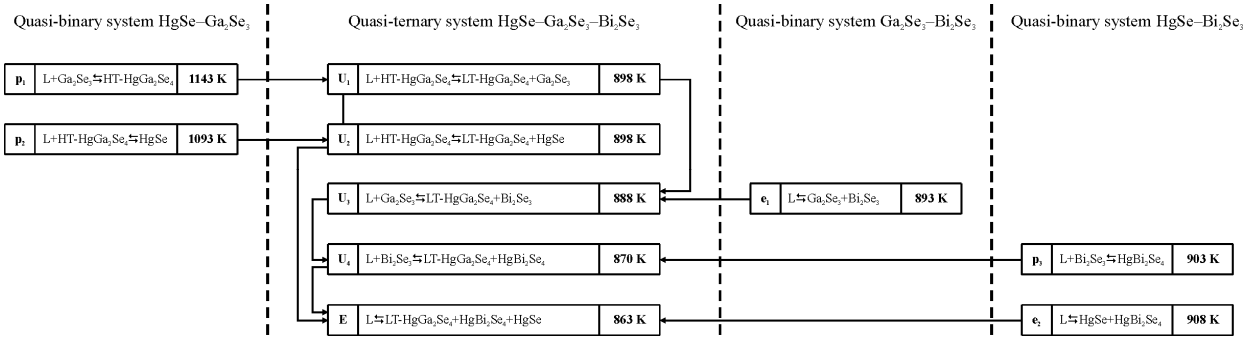

Fig. 12 Liquid-solid equilibria in the $HgSe–Ga_2Se_3–Bi_2Se_3$ quasi-ternary system.

Conclusions

The phase equilibria in the quasi-ternary system $HgSe–Ga_2Se_3–Bi_2Se_3$ were investigated by differential thermal analysis and X-ray diffraction. Five vertical sections and the isothermal section of the system at 670 K (and partly at 520 K) were plotted. Based on these data and literature data on the quasi-binary side systems, the projection of the liquidus surface onto the concentration triangle was constructed. It consists of six fields of primary crystallization. The presence of the field of primary crystallization of $HgGa_2Se_4$ makes it possible to select compositions and conditions for the growth of crystals of this ternary phase by the solution-melt method.

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