The quasi-ternary CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system

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Differential-thermal analysis, X-ray diffraction, and metallography were used to study the interaction between the components of the quasi-ternary CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system. Phase diagrams of four polythermal sections, the isothermal section at 670 K, as well as a projection of the liquidus surface have been constructed. The projection of the liquidus surface consists of six fields of primary crystallization of the phases, which are separated by 12 monovariant curves and 11 invariant points. The type of mono- and invariant processes in the system has been investigated and the coordinates of the invariant points have been determined. The system is triangulated by the quasi-binary section CdGa$_2$Se$_4$-Bi$_2$Se$_3$ into two sub-systems CdSe–CdGa$_2$Se$_4$–Bi$_2$Se$_3$ and CdGa$_2$Se$_4$–Ga$_2$Se$_3$–Bi$_2$Se$_3$. The present results can be employed for the growth of CdGa$_2$Se$_4$ single crystals from non-stoichiometric melts.

Introduction

Compounds A^{II}B$^{III}_2$C$^{VI}_4$ with defect chalcopyrite structure (CdGa$_2$S$_4$ structure type) are promising materials for non-linear optics. For instance, non-linear properties of HgGa$_2$S$_4$ [1,2] and Hg$_{1-x}$Cd$_x$Ga$_2$S$_4$ [2] have been extensively studied during recent years. Some of their parameters, like resistance against laser radiation, exceed by far those of the chalcogenide compounds that are presently used for the parametric frequency conversion of CO$_2$ lasers [2]. Among the numerous representatives of this group, we focus on CdGa$_2$Se$_4$. A comprehensive review of its optical properties can be found in [3]. The ternary cadmium gallium selenide has been known for a long time [4], but its industrial application is limited due to difficulties in growing large bulk crystals. Although the CdGa$_2$Se$_4$ compound melts congruently, it undergoes a polymorphous transformation, which hinders the single crystal growth using directional crystallization of the stoichiometric solution. There were attempts to grow CdGa$_2$Se$_4$ single crystals using chemical transport reactions with iodine as a transport agent [5-9]. Furthermore, the growth of single crystals from different melts is described in several studies [10-15], since non-stoichiometric melts can offer growth temperatures lower than the polymorphous transformation temperature. In this respect, the selection of the solvent is an important issue. We have tested a series of different solvents: SnSe$_2$ [12], SnSe [13], Sb$_2$Se$_3$ [14], Bi$_2$Se$_3$ [15], and PbSe [16]. The corresponding binary phase diagrams exhibit a primary crystallization field of the low-temperature CdGa$_2$Se$_4$ modification. Unfortunately, the formation of undesirable solid solutions on the basis of CdGa$_2$Se$_4$ occurs in all the above systems, except Bi$_2$Se$_3$ and PbSe. Therefore, we conclude that the two latter solvents seem to be the most promising for successful crystal growth [15]. The part of the liquidus that belongs to the low-temperature CdGa$_2$Se$_4$ modification in the CdGa$_2$Se$_4$–Bi$_2$Se$_3$ system is not large though. However, there may exist a possibility to widen the primary crystallization region by using the more complex CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system, where possible ternary eutectics should lower the crystallization temperature of intermediate alloys inside the system.

The binary compounds CdSe, Ga$_2$Se$_3$, and Bi$_2$Se$_3$ melt congruently at 1512 K, 1278 K [17], and 979 K [18], respectively; they possess narrow homogeneity ranges, and therefore, act as components of a quasi-ternary system. Cadmium selenide crystallizes in the wurtzite structure type, space group $P6_3mc$ with lattice parameters $a = 0.42999$ and $c = 0.70109$ nm [19]. Ga$_2$Se$_3$ crystallizes in the zinc blende structure type, space group $F\bar{4}3m$, $a = 0.5422$ nm [20], whereas

Bi$_2$Se$_3$ exhibits a trigonal structure, space group $R\bar{3}m$, with $a = 0.41404(7)$, $c = 2.8640(6)$ nm [15].

The boundary systems CdSe–Ga$_2$Se$_3$, CdSe–Bi$_2$Se$_3$, and Ga$_2$Se$_3$–Bi$_2$Se$_3$ were investigated in [21-25]. There is one congruently melting compound CdGa$_2$Se$_4$ in the CdSe–Ga$_2$Se$_3$ system. According to [21], the coordinates of the two eutectic points are 39 mol.% Ga$_2$Se$_3$ / 1208 K and 64 mol.% Ga$_2$Se$_3$ / 1206 K, which are in agreement with those given in [23]. The polymorphous transformation of CdGa$_2$Se$_4$ takes place at 1090 K. The solid solubility in Ga$_2$Se$_3$ extends to 17 mol.% CdSe at 1206 K; on the CdSe side the solid solution contains 32 mol.% Ga$_2$Se$_3$ at the eutectic temperature. The solid solubility in CdGa$_2$Se$_4$ is ~2 mol.% and is shifted to the Ga$_2$Se$_3$ side. Monotectoid decomposition of the solid solution at 988 K is observed for alloys in the concentration range of 5-25 mol.% Ga$_2$Se$_3$. According to [22], the coordinates of the eutectic points are 45 mol.% and 55 mol.% Ga$_2$Se$_3$ for 1203 and 1213 K, respectively. The solid solubility in the system components is 13 and 25 mol.% Ga$_2$Se$_3$ [23]. The low-temperature modification of CdGa$_2$Se$_4$ crystallizes in a defect chalcopyrite structure (space group $I\bar{4}$) with unit cell parameters $a = 0.57430$ and $c = 1.0752$ nm [15].

The CdSe–Bi$_2$Se$_3$ system was investigated in [24]. In this system, a peritectic reaction results in the formation of the CdBi$_2$Se$_4$ compound, which is stable only in the temperature interval 877-1009 K. The coordinates of the peritectic point are 95 mol.% Bi$_2$Se$_3$ / 1009 K. The solid solution based on CdSe contains 0.25 mol.% Bi$_2$Se$_3$ at 723 K; when raising the temperature it extends to 1 mol.% at 1000 K. The solid solution of Bi$_2$Se$_3$ contains up to 3 mol.% CdSe at 723 K.

The Ga$_2$Se$_3$–Bi$_2$Se$_3$ system is described in [18,25]. The system is quasi-binary and of the eutectic type. The liquidus consists of the primary crystallization fields of the Ga$_2$Se$_3$ and Bi$_2$Se$_3$ solid solutions. The coordinates of the eutectic point are 65 mol.% Bi$_2$Se$_3$ / 900 K [18] or ~61 mol.% Bi$_2$Se$_3$ / 893 K [25]. The solid solubility of the components does not exceed 5 mol.% [25].

The CdGa$_2$Se$_4$–Bi$_2$Se$_3$ phase diagram is of the eutectic type [15]. Its liquidus consists of three fields of primary crystallization of solid solutions based on the high- and low-temperature modifications of CdGa$_2$Se$_4$ and Bi$_2$Se$_3$. The eutectic point is located at ~86 mol.% Bi$_2$Se$_3$ and 929 K. A horizontal line at 1092 K corresponds to the polymorphous transformation of high-temperature CdGa$_2$Se$_4$ into low-temperature CdGa$_2$Se$_4$.

Analyzing the above phase diagrams, we expect that lowering the crystallization temperature is feasible in the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ quasi-ternary system because of the possible formation of ternary eutectics. This work is focused on the investigation of phase equilibria in the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system, performed in order to find concentration regions that are suitable for the growth of single crystals of the low-temperature modification of CdGa$_2$Se$_4$ using the solution-melt method.

Experimental

For the investigation of the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system, 54 alloys were prepared, the compositions of which are plotted on the concentration triangle shown in Fig. 1. Their synthesis was carried out by fusing calculated amounts of the elements (purity better than 99.99%) in evacuated quartz ampoules. The alloys were held for 3 hours at the maximum temperature, which was 1320-1170 K depending on the composition. Afterwards, the ampoules were cooled slowly (10 K/h) down to 670 K. At this temperature, the alloys were annealed for 250 hours and then rapidly quenched in cold water.

The obtained alloys were investigated with differential-thermal analysis (DTA), X-ray diffraction (XRD), and metallography. DTA signals were recorded on a Paulik-Paulik-Erdey derivatograph (Pt/Pt-Rh thermocouple). XRD was performed on powders using a DRON–4-13 diffractometer (CuK_α-radiation), and the microstructure of polished alloys was examined on a Leica VMHT Auto microhardness tester.

Triangulation

The isothermal section of the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system at 670 K was constructed using XRD and metallography results (Fig. 2). The CdGa$_2$Se$_4$ compound forms a quasi-binary section with Bi$_2$Se$_3$. The section divides the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system into two sub-systems, namely Ga$_2$Se$_3$–Bi$_2$Se$_3$–CdGa$_2$Se$_4$ and CdSe–Bi$_2$Se$_3$–CdGa$_2$Se$_4$. The CdBi$_2$Se$_4$ compound is formed by a peritectic reaction in the CdSe–Bi$_2$Se$_3$–CdGa$_2$Se$_4$ sub-system. This compound is stable only in a limited high-temperature interval and does not exist at the annealing temperature 670 K. Within the range of existence of CdBi$_2$Se$_4$, the CdSe–Bi$_2$Se$_3$–CdGa$_2$Se$_4$ sub-system could be conventionally triangulated into CdGa$_2$Se$_4$–Bi$_2$Se$_3$–CdBi$_2$Se$_4$ and CdGa$_2$Se$_4$–CdBi$_2$Se$_4$–CdSe sub-systems.

Results

The common section at 75 mol.% Bi$_2$Se$_3$: 'GaBi$_3$Se$_4$'–'CdBi$_6$Se$_{10}$' section (Fig. 3)

The liquidus of the 'GaBi$_3$Se$_4$'–'CdBi$_6$Se$_{10}$' section consists of the primary crystallization fields of γ^*, δ,

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* α, β, γ, ξ, δ' and δ are solid solution ranges of Ga$_2$Se$_3$, CdSe, Bi$_2$Se$_3$, CdBi$_2$Se$_4$, hight-temperature and low-temperature CdGa$_2$Se$_4$ modifications, respectively.
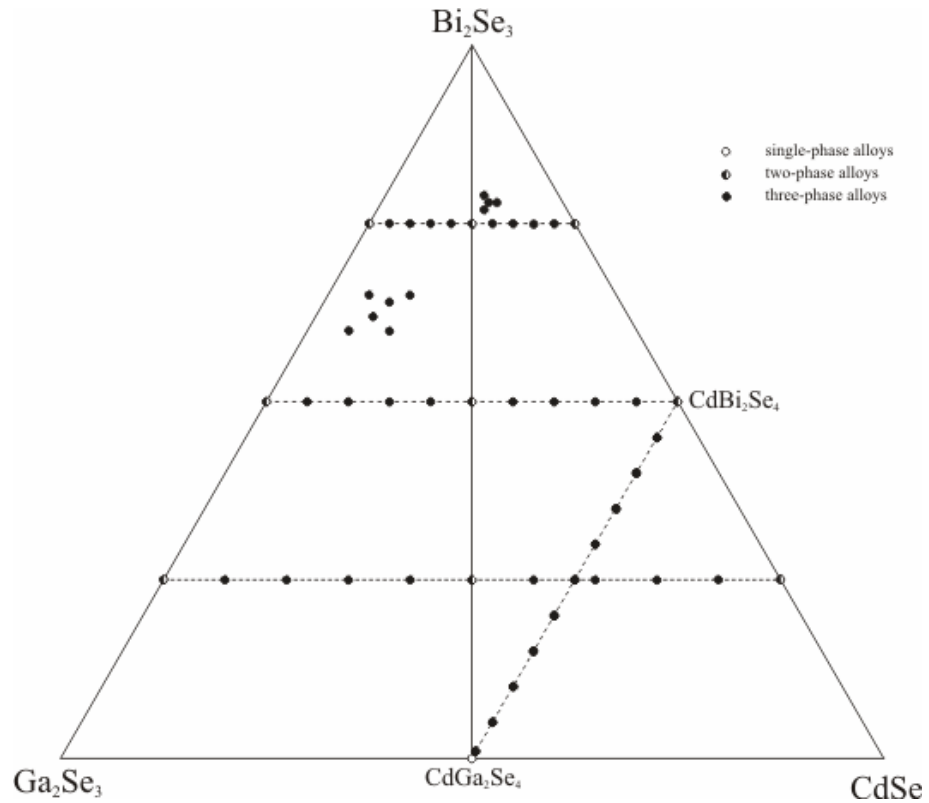
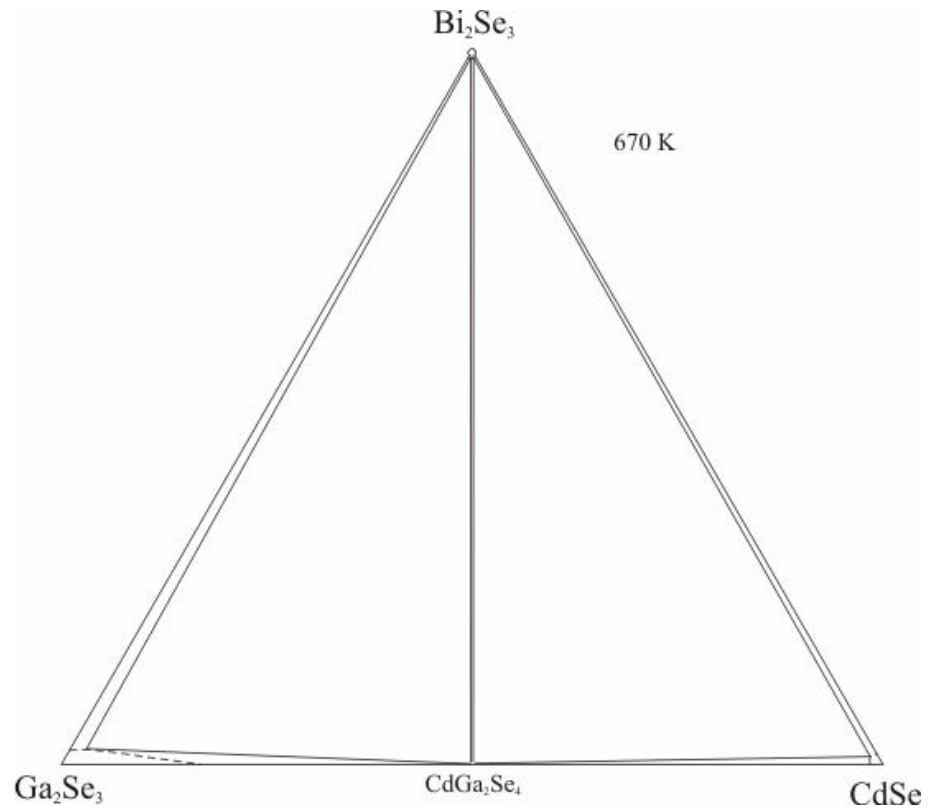**Fig. 1** Composition of the investigated alloys of the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system.

Fig. 2 Isothermal section of the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system at 670 K.

and β. The secondary crystallization involves two binary eutectics ([L⇔α+γ (field 5), L⇔δ+γ (6)] in the sub-liquidus part of the Ga$_2$Se$_3$–CdGa$_2$Se$_4$–Bi$_2$Se$_3$ sub-system (0-50 mol.% 'CdBi$_6$Se$_{10}$' in the section). The crystallization in this part of the section is completed by a eutectic reaction at 892 K (point E$_1$ in Fig. 7). The alloy with 50 mol.% 'CdBi$_6$Se$_{10}$' is a two-phase one (e$_4$, Fig. 7). For the alloys from the concentration interval ~55-62 mol.% 'CdBi$_6$Se$_{10}$', the L+β⇔δ+ξ peritectic reaction is observed at 942 K, as well as the secondary crystallization fields, L+δ+β (field 7) and L+ξ+β (field 8). Since the alloys of this part of the section are located in the CdGa$_2$Se$_4$–Bi$_2$Se$_3$–CdBi$_2$Se$_4$ sub-system, the primary crystallization field of the solid solution of the ternary compound ξ (field 10) can be found in the sub-liquidus part. The lowering of the CdBi$_2$Se$_4$ decomposition temperature indicates the existence of a certain homogeneity region based on CdBi$_2$Se$_4$, and one additional invariant solid-state process ξ⇔β+γ+δ. Crystallization of these alloys completes with the L⇔δ+γ+ξ ternary eutectic process (922 K, E$_2$).

The common section at 50 mol.% Bi$_2$Se$_3$: 'BiGaSe$_3$'– CdBi$_2$Se$_4$ (Fig. 4)

The 'BiGaSe$_3$'–CdBi$_2$Se$_4$ section contains three fields of primary crystallization: L+α (field 2), L+δ (3), and L+β (4). There are 5 regions of secondary crystallization involving the liquid phase (L+α+γ (field 5), L+α+δ (6), L+δ+γ (7), L+δ+β (8), L+β+ξ (9)) in the sub-liquidus part. The alloys located in the Ga$_2$Se$_3$–CdGa$_2$Se$_4$–Bi$_2$Se$_3$ sub-system (0-50 mol.% CdBi$_2$Se$_4$) solidify according to the ternary eutectic reaction L⇔α+δ+γ at 892 K (E$_1$, Fig. 7). The alloy containing 50 mol.% Bi$_2$Se$_3$ contains two phases (e$_4$, Fig. 7). For most samples from the CdGa$_2$Se$_4$– CdBi$_2$Se$_4$–CdSe sub-system, the crystallization continues with the invariant peritectic horizontal, which belongs to the δ–U$_3$–ξ–β plane (942 K) and finishes with the ternary eutectic reaction L⇔δ+γ+ξ at 922 K (E$_2$, Fig. 7). The horizontal line at 853 K corresponds to the eutectoid decomposition of CdBi$_2$Se$_4$.

The common section at 25 mol.% Bi$_2$Se$_3$: 'BiGa$_3$Se$_6$'– 'Cd$_3$Bi$_2$Se$_6$' (Fig. 5)

Although the diagram of the 'BiGa$_3$Se$_6$'–'Cd$_3$Bi$_2$Se$_6$' section is similar to the previous one, it has several peculiarities. One difference is that the section contains a primary crystallization field of δ' (field 3). Fields 4 correspond to the simultaneous existence of the low- and high-temperature modifications of CdGa$_2$Se$_4$. Together with the liquidus isotherms they are used to determine geometrically the position of the two ternary peritectics U$_1$ and U$_2$ (Fig. 7). Another difference is that the section crosses the CdGa$_2$Se$_4$– CdBi$_2$Se$_4$–CdSe sub-system (67-100 mol.% 'Cd$_3$Bi$_2$Se$_6$'), where the crystallization is completed

by a peritectic reaction at 942 K. The thermal decomposition of CdBi$_2$Se$_4$ takes place at 853 K, however, a liquid phase is not required for the reaction.

The CdGa$_2$Se$_4$–CdBi$_2$Se$_4$ section (Fig. 6)

The CdGa$_2$Se$_4$–CdBi$_2$Se$_4$ section is not quasi-binary. Its liquidus consists of primary crystallization fields of solid solutions based on high-temperature and low-temperature CdGa$_2$Se$_4$, and CdSe. The horizontal line at 1078 K corresponds to the beginning of the
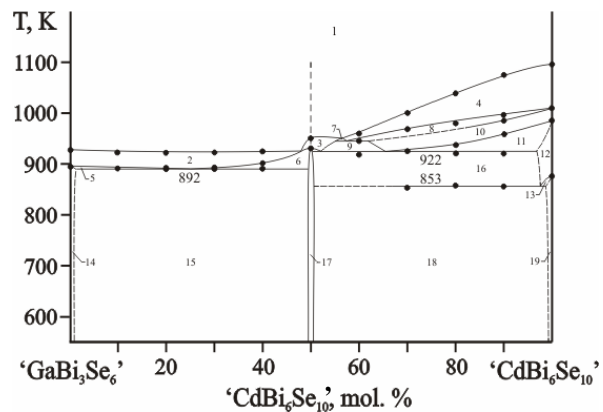

Fig. 3 Phase diagram of the 'GaBi$_3$Se$_4$'– 'CdBi$_6$Se$_{10}$' section: (1) L; (2) L+γ; (3) L+δ; (4) L+β; (5) L+γ+α; (6) L+γ+δ; (7) L+δ+β; (8) L+β+ξ; (9) L+δ+ξ; (10) L+ξ; (11) L+ξ+γ; (12) ξ+γ; (13) γ+ξ+β; (14) γ+α; (15) γ+α+δ; (16) β+δ+ξ; (17) γ+δ; (18) β+δ+γ; (19) γ+β.
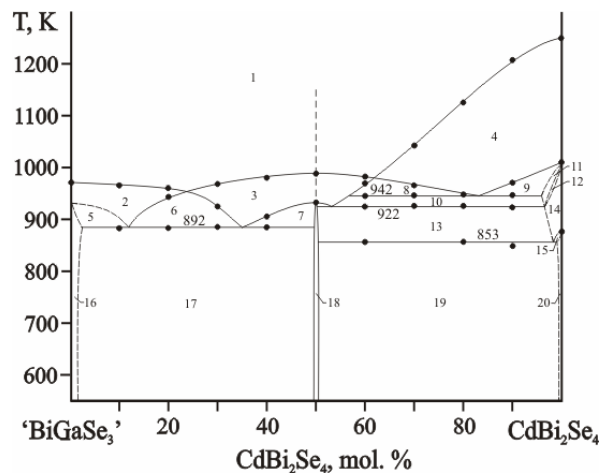
Fig. 4 Phase diagram of the 'BiGaSe$_3$'– CdBi$_2$Se$_4$ section: (1) L; (2) L+α; (3) L+δ; (4) L+β; (5) L+α+γ; (6) L+δ+α; (7) L+δ+γ; (8) L+β+δ; (9) L+β+ξ; (10) L+δ+ξ; (11) L+ξ; (12) L+γ+ξ; (13) δ+γ+ξ; (14) γ+ξ; (15) β+γ+ξ; (16) α+γ; (17) α+γ+δ; (18) γ+δ; (19) δ+γ+β; (20) β+γ.

secondary crystallization of δ with ξ (field 5). The peritectic reaction L+β⇔δ+ξ at 942 K is typical for all the alloys from the CdGa$_2$Se$_4$–CdBi$_2$Se$_4$–CdSe sub-system. In turn, the decomposition of CdBi$_2$Se$_4$ is the reason why all intermediate alloys are three-phase ones at the annealing temperature of 670 K.
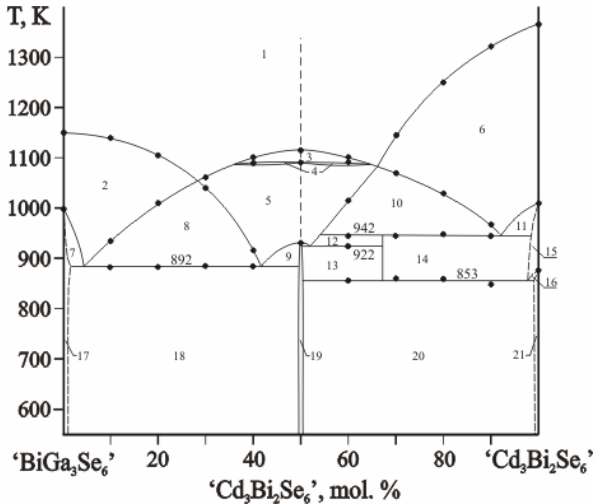

Fig. 5 Phase diagram of the 'BiGa$_3$Se$_6$'– 'Cd$_3$Bi$_2$Se$_6$'section: (1) L; (2) L+α; (3) L+δ′; (4) L+δ′+δ; (5) L+δ; (6) L+β; (7) L+α+γ; (8) L+α+δ; (9) L+δ+γ; (10) L+β+δ; (11) L+β+ξ; (12) L+δ+ξ; (13) δ+γ+ξ; (14) δ+β+ξ; (15) β+ξ; (16) γ+ξ+β; (17) α+γ; (18) α+δ+γ; (19) γ+δ; (20) δ+γ+β; (21) γ+β.
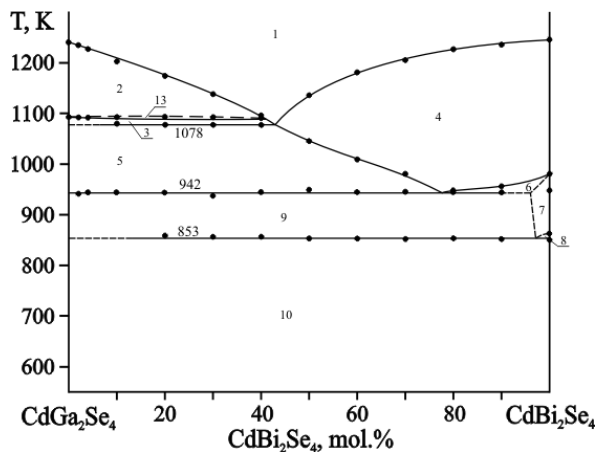
Fig. 6 Phase diagram of the CdGa$_2$Se$_4$– CdBi$_2$Se$_4$ section: (1) L; (2) L+δ′; (3) L+δ; (4) L+β; (5) L+δ+β; (6) L+β+ξ; (7) ξ; (8) ξ+β; (9) β+γ+ξ; (10) δ+ξ; (11) δ+γ+β; (12) β+γ; (13) L+ δ+ δ′

Projection of the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ liquidus surface

Based on the described phase diagrams of the boundary systems and four sections, a projection of the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ liquidus surface on the concentration triangle has been constructed (Fig. 7). The liquidus surface is represented by six fields of primary crystallization. Three of them belong to the solid solutions based on the system components: β, α, and γ. The other three fields correspond to the primary crystallization of the ternary compounds: δ′, δ, and ξ. The fields are separated by 11 monovariant lines. There are 7 binary and 5 ternary points in the system, among them 3 ternary peritectics and 2 ternary eutectics. The type and temperature of all invariant processes are given as a scheme in Fig. 8. The coordinates of the eutectic point (Table 1) were estimated geometrically and further refined during metallographic observations of specific alloys. The ternary peritectic compositions were evaluated geometrically using the relevant phase diagrams and liquidus isotherms.

The CdGa$_2$Se$_4$–Bi$_2$Se$_3$ quasi-binary section divides the system into two sub-systems, Ga$_2$Se$_3$–Bi$_2$Se$_3$– CdGa$_2$Se$_4$ and CdSe–Bi$_2$Se$_3$–CdGa$_2$Se$_4$. Three binary eutectics and one binary peritectic are located on the sides of the Ga$_2$Se$_3$–Bi$_2$Se$_3$–CdGa$_2$Se$_4$ triangle; two ternary peritectic processes occur inside the triangle. Point U$_1$ corresponds to the peritectic L+δ′⇔α+δ (1089 K). The ternary eutectic reaction E$_1$ (892 K) takes place in the plane limited by α–γ–δ.

Point U$_2$ in the CdGa$_2$Se$_4$–Bi$_2$Se$_3$–CdSe sub-system corresponds to the ternary peritectic process L+δ′⇔δ+β (1088 K), which takes place within the δ–p$_3$–U$_2$–β plane. The invariant process U$_3$, L+β⇔δ+ξ, exists because of the incongruent melting of CdBi$_2$Se$_4$, and is located within the ξ–U$_3$–δ–β plane. The CdGa$_2$Se$_4$–Bi$_2$Se$_3$–CdSe sub-system is divided by the non-quasi-binary section CdGa$_2$Se$_4$– CdBi$_2$Se$_4$ into the CdGa$_2$Se$_4$–CdBi$_2$Se$_4$–CdSe and CdGa$_2$Se$_4$–Bi$_2$Se$_3$–CdBi$_2$Se$_4$ sub-systems. The crystallization of all alloys from the CdGa$_2$Se$_4$– CdBi$_2$Se$_4$–CdSe sub-system is completed by a ternary eutectic reaction (E$_2$, L⇔β+δ+γ). In the other sub-system, the solidified alloys exhibit a mixture of the solid solutions based on CdGa$_2$Se$_4$, Bi$_2$Se$_3$, and CdSe, because the CdBi$_2$Se$_4$ compound is not stable below 853 K.

The polymorphous transformation of CdGa$_2$Se$_4$ appears on the liquidus surface as the invariant curve U$_1$p$_3$U$_2$. Both modifications of CdGa$_2$Se$_4$ possess their own primary crystallization field.

Comparing the investigated system with earlier studied systems [12-16], we can recognize the absence of quaternary phases and the limited solid solubility based on CdGa$_2$Se$_4$, and the presence of primary crystallization fields of both the HT- and LT-modification of the ternary phase. The section joining CdGa$_2$Se$_4$ and the third component is quasi-binary of the eutectic type in all the systems. The field of primary crystallization of the LT modification is in all cases rather large and depends on the melting point of the third component of these systems. As the solid solubility based on CdGa$_2$Se$_4$ is limited, the temperatures of the invariant processes related to
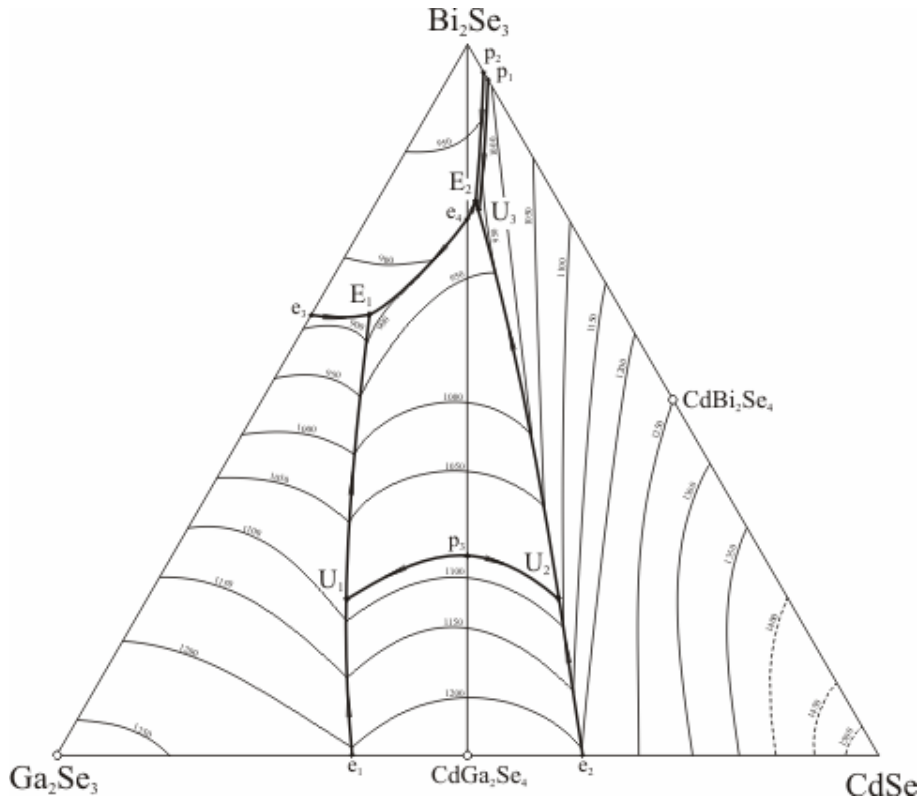
Fig. 7 Projection of the liquidus surface of the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system.
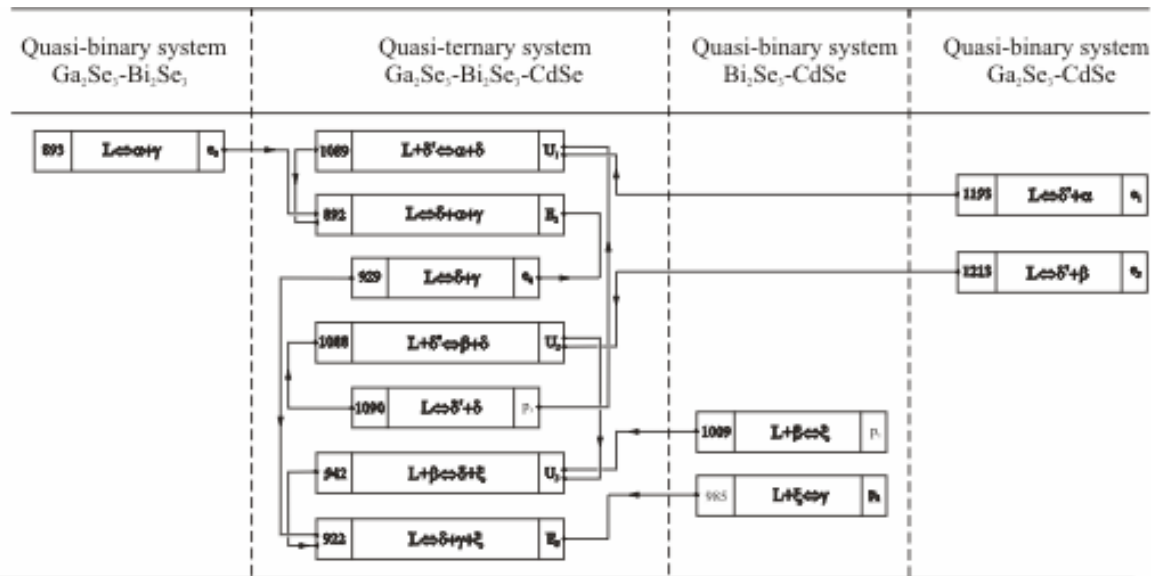

Fig. 8 Liquid-solid equilibria in the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ quasi-ternary system.

Table 1 Composition of the invariant points in the quasi-ternary CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system.

Invariant point	Composition, mol.%		
	CdSe	Ga$_2$Se$_3$	Bi$_2$Se$_3$
E$_1$	7	31	62
E$_2$	12	10	78
U$_1$	24	54	22
U$_2$	28	50	22
U$_3$	13	10	77

the phase transition are very close (within 20 K). Taking into account that the solid solution ranges in the systems with GeSe$_2$, SnSe$_2$, Sb$_2$Se$_3$ extend by less than 2-3 mol.%, but are practically absent in the systems with PbSe and Bi$_2$Se$_3$, the latter two are of the most interest as solvents for the solution-melt technique. However, the use of PbSe for crystal growth requires special equipment due to high viscosity of the melts (indicated by the possibility of glass-formation of certain alloys of this system). Thus the use of Bi$_2$Se$_3$ as the solvent is expected to produce the best crystals among all the investigated systems.

Conclusion

The constructed phase diagram of the CdSe–Ga$_2$Se$_3$–Bi$_2$Se$_3$ system exhibits a considerably large region of primary crystallization of the low-temperature CdGa$_2$Se$_4$ modification, and therefore, can be used when selecting the initial composition of the melt for the growth of single crystals of the low-temperature CdGa$_2$Se$_4$ by the solution-melt method.

References

[1] V.V. Badikov, A.K. Don, K.V. Mitin, A.V. Seryogin, V.V. Sinaiskii, N.I. Shchebetova, *Kvantovaya Elektron.* 33 (2003) 831.

[2] Yu.M. Andreev, V.V. Badikov, V.G. Voevodin, L.G. Geiko, P.P. Geiko, M.V. Ivashchenko, A.I. Karapuzikov, I.V. Serstov, *Kvantovaya Elektron.* 31 (2001) 1075.

[3] L.M. Suslikov, V.Yu. Slivka, M.P. Lisitsa, *Solid-State Optical Filters on Gyropropic Crystals*, Interpress LTD, Kiev, 1998 (in Russian).

[4] H. Hahn, G. Frank, W. Klinger, A. Stoerger, J. Stoerger, Z. *Anorg. Allg. Chem.* 279 (1955) 241.

[5] Y.O. Derid, S.I. Radautsan, I.M. Tiginyanu, *Multicomponent chalcogenides* $A^{II}B^{III}_2C^{VI}_4$, Shtiintsa, Kishinev, 1998 (in Russian).

[6] C.-D. Kim, H.-M. Jeong, H.-G. Kim, W.-T. Kim, *J. Korean Phys. Soc.* 27 (1994) 440.

[7] J.A. Beun, R. Nitsche, M. Lichtensteiger, *Physica*, 27 (1961) 448.

[8] T.G. Kerimova, Sh.S. Mamedov, E.Y. Salaev, *Solid State Commun.* 48 (1983) 597.

[9] V. Tezlevan, I. Mushkutariu, S. Radantsan, V. Tsurkan, *Proc. First Int. Conf. "Material Science of Chalcogenide and Diamond-Structure Semiconductors", Chernivtsi*, 1994, Vol. 1, p. 28.

[10] H. Horinaka, A. Uemura, N. Yamamoto, *J. Cryst. Growth* 99 (1990) 785.

[11] A.A. Vaipolin, Y.A. Nikolaev, I.K. Polushina, V.Y. Rud', Y.V. Rud', E.I. Terykov, N. Fernelius, *Fiz. Tekh. Poluprovodn.* 37 (2003) 572.

[12] I.D. Olekseyuk, O.V. Parasyuk, *Proc. First Int. Conf. "Material Science of Chalcogenide and Diamond-Structure Semiconductors", Chernivtsi*, 1994, Vol. 1, p. 111.

[13] I.D. Olekseyuk, O.V. Parasyuk, O.M. Yurchenko, L.V. Piskach, V.Z. Pankevych, *Abstr. 14th Int. Conf. Crystal Growth, Grenoble, France*, 2004, p. 283.

[14] S.M. Sosovska, O.M. Yurchenko, Y.E. Romanyuk, I.D. Olekseyuk, O.V. Parasyuk, *Chem. Met. Alloys* 2 (2009) 55-58.

[15] S.M. Sosovska, O.M. Yurchenko, Y.E. Romanyuk, I.D. Olekseyuk, O.V. Parasyuk, *J. Alloys Compd.* 417 (2005) 127-130.

[16] S.M Sosovska, I.D. Olekseyuk, O.V. Parasyuk, *VII Vseukr. Konf. Stud. Aspir.*, 2006, p. 67.

[17] T.B. Massalski (Ed.), *Binary Alloy Phase Diagrams*, Vol. 1-3, ASM, Ohio, 1985, P. 3589.

[18] R. Eholie, J. Flahaut, *Bull. Soc. Chim. Fr.* 4 (1972) 1250-1254.

[19] R.R. Reeber, *J. Mater. Sci.* 11 (1976) 590-591.

[20] P.H. Hamilton, *Semicond. Prod. Solid State Technolog.* 7(6) (1964) 15-20.

[21] S.M. Sosovska, I.D. Olekseyuk, O.V. Parasyuk, *J. Alloys Compd.* 453 (2008) 115–120.

[22] A.M. Loireau-Lozac'h, M. Guittard, J. Flahaut, *Mater. Res. Bull.* 20 (1985) 443-451.

[23] M.P. Tyrziu, S.I. Radautsan, M.M. Markus, S.M. Kolosenko, *Phys. Status Solidi A* 3 (1970) 293-296.

[24] A.A. Sher, I.N. Odin, A.V. Novoselova, *Zh. Neorg. Khim.* 24 (1979) 2509-2515.

[25] S.M. Sosovska, O.V. Gurska, L.V. Piskach, O.V. Parasyuk, *Nauk. Visn. Volyn. Nats. Univ.* 4 (2006) 66-70.