CRYSTAL STRUCTURE PECULIARITIES OF THE NEW SOLID SOLUTIONS IN THE InSe-GaSe SYSTEM

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The new solid solution phases crystallized in the hexagonal and tetragonal system were revealed in the GaSe-InSe system, and a new orthorhombic phase with a new type of structural blocks has been proposed. The structural features of the $In_{1-x}Ga_xSe$ solid solutions (where $0 \le x \le 1$) were studied using X-Ray Diffraction (XRD).

Keywords: Gallium indium selenide; solid solutions; X-ray diffraction; crystal structure.
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INTRODUCTION

The outstanding electronic properties of graphene inspired researchers to find new 2D layered materials with related exotic properties. The design of the new 2D materials is a very promising area for modern materials science and condensed matter physics. Thanks to intriguing semiconducting properties, the layered binary InSe and GaSe compounds are promising materials for generating broadband radiation in the near, medium, and far-infrared ranges. The ternary compounds based on these binaries have been studied limited, i.e., literature data on the crystal structure of the ternary compound $InGaSe_2$ are very scarce and contradictory [1-4].

The existence of a hexagonal phase for $InGaSe_2$ was first reported by Mobarak et al. [2]. However, the hexagonal lattice parameters *a* and *c* indicated in this work correspond to the tetragonal phase of InGaSe2, rather than the hexagonal one.

In Ref. [7], the authors propose a new van der Waals heterostructure consisting of GaSe and InSe structural slabs, preserving the *P*-6*m*2 space groups for the gallium selenide. No more ternary phases in the GaSe-InSe system were reported up to date. Hence, the only tetragonal phase known so far for the $InGaSe_2$ compound crystallizes in the TlSe-type structure [8-9].

The most specific feature of the InSe and GaSe structures is the presence of intermetallic In-In and Ga-Ga bonds, respectively. Moreover, the Ga-In bond in the crystal structure of the $Ga_{0.9}In_{0.1}$alloy was also found in Ref. [24]. Taking into account that such intermetallic bonds are possible, here we propose new structural models for the $InGaSe_2$ compound.

2. EXPERIMENTAL PART

2.1. Synthesis

Gallium (99.999 mass %), indium (99.99 mass %), and selenium (99.999 mass %) purchased from Alfa Aesar were used for the syntheses of the starting InSe and GaSe as well as for $In_{1-x}Ga_xSe$ (x=0, 0.1, 0.2,…,1.0) solid solution series. The polycrystalline alloys were synthesized by direct melting stoichiometric amounts of the constituent elements in evacuated "graphitized" silica ampoules at 1000°C for 5 h. Each sample was stirred at the synthesis temperature by shaking the furnace and was then cooled down to 400 °C. Further, the samples were kept at this temperature for a fortnight to achieve complete homogenization and were then slowly cooled down to room temperature. The high-temperature phases of the InSe-GaSe system were prepared by the same synthesis technique, but those samples were further water-quenched.

2.2. Analysis

The experimental Powder X-ray Diffraction (PXRD) data were collected on BRUKER D2 Phaser Diffractometer ($5 \le 2\theta \le 120°$; CuK_α) at room temperature and the crystal structure refinement was carried out by the Rietveld method using the BRUKER EVA and TOPAS-4.2 software.

Fig. 1*a* shows the XRPD patterns of all the synthesized ingots along with the InSe-GaSe system, whereas Fig. 1*b* and *c* illustrate the enlarged diffraction peaks profiles of the most intense [002] and [004] lines in the range of 2θ=10-11.5°and 2θ=21-23°, respectively. Fig. 1*e* displays the shifting of the *c* lattice parameter for solid solutions based on InSe (red line), GaSe (blue line), and intermediate phase (green line).

3. DISCUSSION

3.1. Phase compositions of the slowly cooled samples

As seen from Fig. 1*a*, the most intense diffraction peaks [002] and [004] are positioned at 2θ=~11° and 2θ=~22°. Fig. 1*b* and *c* illustrate these areas where a single and symmetric diffraction peak for InSe, GaSe binary compounds, as well as for the following alloys: $In_{0.9}Ga_{0.1}Se$, $In_{0.8}Ga_{0.2}Se$, $In_{0.7}Ga_{0.3}Se$, $In_{0.6}Ga_{0.4}Se$, $In_{0.2}Ga_{0.8}Se$, and $In_{0.1}Ga_{0.9}Se$ are visible. No extra peaks on the diffraction patterns for these alloys were

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observed. Therefore, the theInSe-$In_{0.6}Ga_{0.4}Se$ and $In_{0.2}Ga_{0.8}Se$-GaSe areas highlighted in Fig. 1*b* and *c* with red and blue line scans be considered as solid-solubility fields based on InSe and GaSe, respectively.

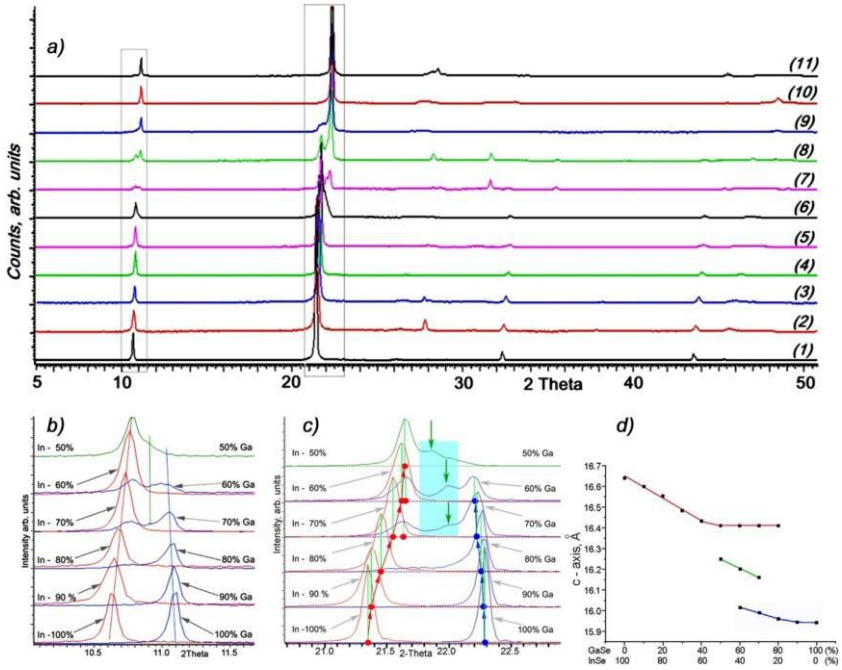

Fig. 1. a), The XRD patterns of the $Ga_{1-n}In_nSe$ (n = 0.1; 0.2 … 1.0): 1, GaSe; 2, $In_{0.1}Ga_{0.9}Se$; 3, $In_{0.2}Ga_{0.8}Se$; 4, $In_{0.3}Ga_{0.7}Se$; 5, $In_{0.4}Ga_{0.6}Se$; 6, $In_{0.5}Ga_{0.5}Se$; 7, $In_{0.6}Ga_{0.4}Se$; 8, $In_{0.7}Ga_{0.3}Se$; 9, $In_{0.8}Ga_{0.2}Se$; 10, $In_{0.9}Ga_{0.1}Se$; 11, InSe; *b*), The enlarged range of 2θ = 10–11.5; *c*), The enlarged range of 2θ = 21–23 ; d), The shifting of the *c* parameter for solid solutions based on InSe (red line), GaSe (blue line), and intermediate phase (green line).

A careful examination of the diffraction patterns for the $In_{0.5}Ga_{0.5}Se$, $In_{0.4}Ga_{0.6}Se$, and $In_{0.3}Ga_{0.7}Se$ samples clearly shows the splitting of the [004] reflection into three peaks. Two of them - left and right - can be considered as peaks for solid solutions based on InSe and GaSe meaning that the InSe-GaSe system does not form a continuous solid solution in the entire range. The third peaks located in the middle and indicated by green arrows in Fig. 1*b* and *c*, do not belong to any of the solid solutions based on the initial compounds. Also, the third peak shown with red arrows in Fig.1*b* cannot belong to solid solutions based on the starting compounds. Apparently, in addition to the mentioned solid solutions series, a new structure is formed in which the amount of In and Ga atoms is equal ($InGaSe_2$). To explain these intermediate peaks, one of the possible ideas would be the formation of a mixed-type structure based on GaSe and InSe structural blocks. In this case, the Se-Ga-Ga-Se and Se-In-In-Se slabs alternate in a single structure with a 1:1 ratio (Fig 1*a*). In Ref. [9], such a model was used for theoretical calculations. Probably, it is a very flexible model that can be suitable for any ratio of blocks or continuous solid solutions. However, as above mentioned, the X-ray analysis showed the absence of continuous solid solutions in the GaSe-InSe section. Thus, the suggestion of alternative models is relevant. We assume that the appearance of these peaks is associated with the formation of new type structural blocks where the gallium and indium atoms are arranged in an orderly manner. In this case, the new models for ternary $InGaSe_2$ may differ significantly from the hexagonal GaSe-type structure. We have proposed three new structural models, which are shown in Figs. 2*b-d*.

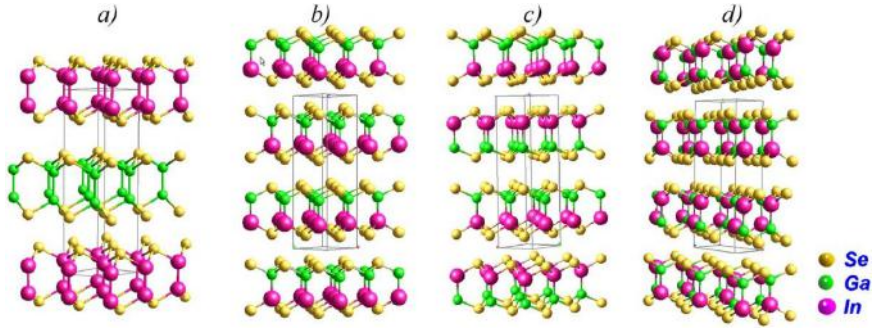

Fig. 2. Various 3D models of the $GaInSe_2$ crystal structure: *a*), hexagonal *P*-6*m*2 configuration used in Ref. [7]; *b*), hexagonal *P*6$_3$*mc*; *c*), trigonal *P*-3*m*1, d), ortho- rhombic *Pnnm*.

CONCLUSIONS

In the InSe-GaSe system, the regions of the solid solution of the hexagonal phase have been refined. It is shown that with the composition $InGaSe_2$, a new phase is formed, which does not belong to solid solutions of the initial components InSe and GaSe. New structural models are proposed for the $InGaSe_2$ phase.

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ОСОБЕННОСТИ КРИСТАЛЛИЧЕСКИХ СТРУКТУР НОВЫХ ТВЕРДЫХ РАСТВОРОВ В СИСТЕМЕ InSe-GaSe

В системе GaSe-InSe обнаружены новые фазы твердого раствора, кристаллизующиеся в гексагональной и тетрагональной системе, и предложена новая орторомбическая фаза с новым типом структурных блоков. Структурные особенности твердых растворов $In_{1-x}Ga_xSe$ (где $0 \le x \le 1$) изучали методом рентгеновской дифракции (РФА).

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InSe-GaSe SİSTEMİNİN YENİ BƏRK MƏHLULLARININ KRİSTALLİK QURLUŞLARININ XÜSUSİYYƏTLƏRİ

GaSe-InSe sistemində heksoqonal və tetraqonal sistemdə kristallaşan yeni bərk məhlul fazaları aşkar edilmiş. Buna əsaslanaraq isə yeni tip struktur blokları ilə yeni ortoromblu faza təklif edilmişdir. $In_{1-x}Ga_xSe$ bərk məhlullarının struktur xüsusiyyətləri (burada $0 \le x \le 1$) rentgen difraksiyasından (XRD) istifadə edilməklə tədqiq edilmişdir.