THE STRUCTURAL FEATURES OF CRYSTALLINE PHASES OF THE GaSe-InSe SYSTEM

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The phase formation in the GaSe - InSe systems is considered. Synthesized compositions $Ga_xIn_{1-x}Se$ (x = 0, 0.1, 0.2, ..., 1.0) and the regions of mutual solid solutions of these compounds are determined. The investigations were carried out by XRD, DTA and Raman spectroscopic methods. The temperatures of the transitions from the hexagonal phase to the tetragonal phase are determined. The presence of an individual compound of $GaInSe_2$ was confirmed.

It is known that layered compounds of GaSe and InSe crystallize in a hexagonal structure, the slabs of which consist of four atomic layers, such as Se-Me-Me-Se [1-8]. The structures and physical properties of these compounds have been studied quite well. However, the structures of ternary compounds of the type $Ga_xIn_{1-x}X$ (X = S, Se, Te) have been studied little. The information available in the literature is scanty and sometimes contradictory. The only paper devoted to X-ray structure analysis of $GaInSe_2$ was published in 1985 by the authors H.-J. Deiseroth, D. Muller, H.Hahn [9]. To obtain the $GaInSe_2$ compound, Ga and In were first melted in stoichiometric ratios, then adding Se, all the components were re-melted together. Further, the solidified ingot was annealed for a long time at temperatures of 550-650° C. The authors established that the compound crystallizes in the tetragonal system on the structural type $Tl^ITl^{III}Se_2$. It is noted that in the diffraction pattern there are quite a lot of non-indexed peaks, the origin of which was not established.

In [10], the presence of a hexagonal phase for $GaInSe_2$ is reported for the first time. However, the values of the parameters ***a*** and ***c*** given here correspond to the above-mentioned tetragonal phase. A detailed inspection of the work [10] showed that the diffraction indices indicated in this work also correspond to the tetragonal phase, rather than the hexagonal one. Consequently, the representation of this phase as hexagonal is erroneous. This error is corrected in [11], where the diffraction pattern taken from the article [10] is given, but the author characterizes it as tetragonal. In the literature, there are no other data on the structure of $GaInSe_2$ crystalline phases. Consequently, only the tetragonal phase is known for $GaInSe_2$, which crystallizes in the structural type TlSe.

The semiconductor compounds GaSe and InSe are of great practical interest as a promising material for optoelectronics. The study of the phase diagram of GaSe-InSe and the refinement of the solid solution regions of these compounds can contribute to controlling their properties. As is known, the crystal structures of GaSe and InSe contain intermetallic Ga-Ga and In-In bonds, respectively. Another interesting issue is the refinement of the nature of the interactions between Ga and In atoms in $Ga_xIn_{1-x}Se$ solid solutions. Are intermetallic Ga-In bonds formed? To answer these and other similar questions, we synthesized the formulations $Ga_xIn_{1-x}Se$, where x varies in the interval $0 \leq x \leq 1$ in steps of 0.1. Synthesis was carried out by melting the elements in the ratios taken in the appropriate chemical formula and placed in evacuated

quartz ampoules. Further, in order to homogenize, the obtained ingots were annealed at a temperature of 450°C for a period of 14 days. Figure 1 shows the diffraction patterns of all synthesized ingots.
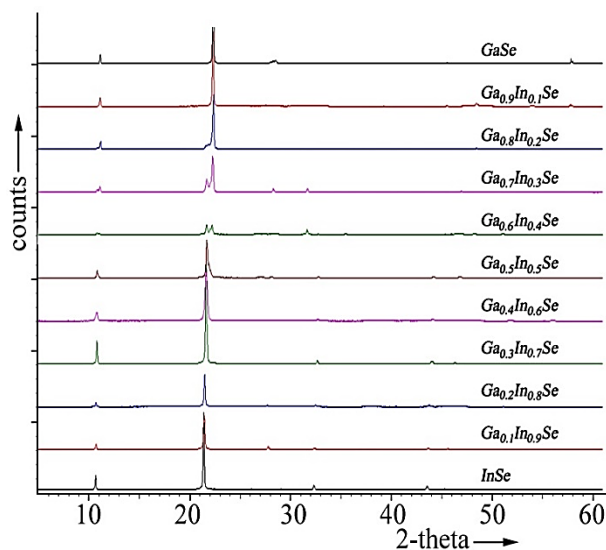

Figure 1. Diffraction patterns of obtained ingots with compositions $Ga_xIn_{1-x}Se$.
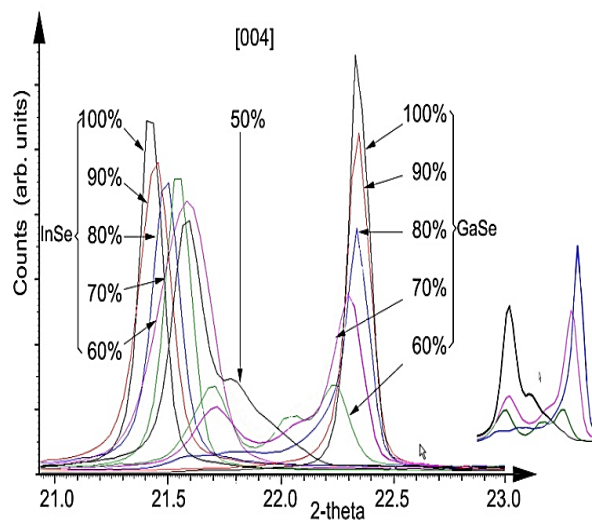

Figure 2. Diffraction peak profiles for the reflex [004], for all received ingots $Ga_xIn_{1-x}Se$

From these diffractograms, we can draw the following conclusions:

- all these diffraction patterns refer to the structural type of GaSe. As is known, this structure is layered, and its blocks consist of four atomic layers of Se-Ga-Ga-Se. Due to the presence of a Ga-Ga bond in it, it is not a stoichiometric compound.

- As can be seen from the figure in the interval between InSe and 0.6InSe-0.4GaSe, the peak profile is symmetrical and looks as one. Apparently, this site can be considered as the solid solution region based on InSe. In this segment, the resulting compounds also belong to the structural type of GaSe.

- On the basis of the obtained diffraction patterns, the values of the parameters of the hexagonal axis "c" were determined. It is found that for GaSe and InSe they differ approximately 0.7 A (15.94 Å and 16.64 Å, respectively). Differences in the parameters of the unit cell led to the individual behavior of these two compounds. As can be seen from Fig. 1, continuously solid solution, covering the whole spectrum, is not observed. This is clearly seen in the central part of the figure, where two peaks are clearly visible. The left of them will refer to solid solutions based on InSe, and the right ones to solid solutions based on GaSe

- With a close examination at the central section of the picture, another peak is visible. (Fig. 2). However, when inspecting the whole diffraction image in general, no peaks were found that did not fit into the overall GaSe type difraction pattern. This suggests that the compound to which these intermediate peaks belong also crystallizes in the structural type of GaSe.
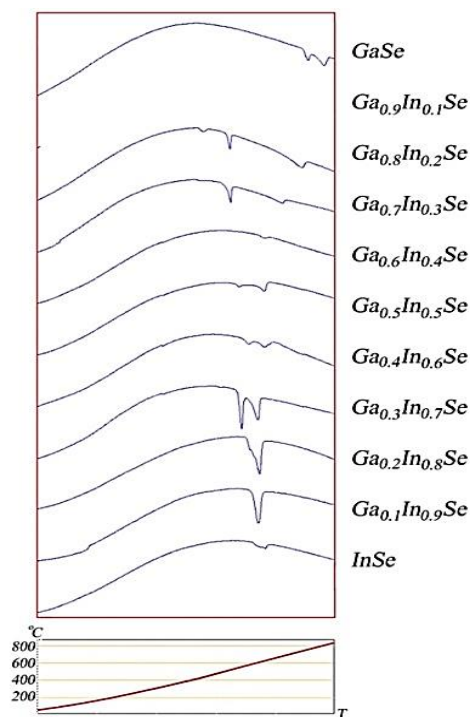
compound of the Se-Ga-In-Se type. Of course, for a convincing proof of this assumption, carrying out additional research is necessary.
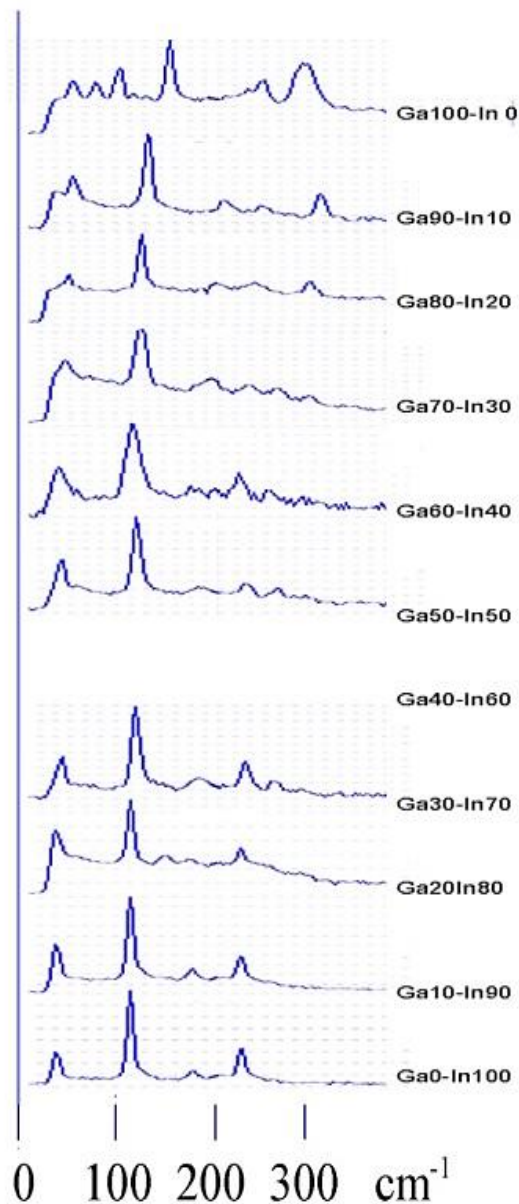

Figure. 4. Raman spectra of all obtained ingots $Ga_xIn_{1-x}Se$.

Figure 3 shows the differential thermal analysis (DTA) curves of synthesized ingots. In the section where the In content predominates, two endo effects are seen. The second one relates to the melting of compounds. Our investigations showed that the first endo-effect relates to the transition to the tetragonal phase, which was noted in [1]. We obtained a tetragonal phase and refined its crystal structure. Figure 4 shows the Raman spectra of the samples obtained. A detailed description of the comparative analysis of the results obtained from x-ray studies, DTA characteristics and Raman spectra will be given in the report.

Figure 3. DTA characteristics of all obtained ingots $Ga_xIn_{1-x}Se$.

We think that under these conditions the appearance of these peaks indicates the formation of an individual

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