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# INVESTIGATION OF THE Se–$SrGa_2Se_4$ SYSTEM

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To synthesize alloys of the Se–$SrGa_2Se_4$ system, the $SrGa_2Se_4$ compound was first obtained from the binary compounds SrSe and $Ga_2Se_3$ via the ampoule method in the temperature range of 1000–1200°C. Subsequently, alloys were synthesized based on Se and $SrGa_2Se_4$. Single crystals of the Sr thiogallate were grown using the Bridgman method. For the first time, the phase equilibria of the Se–$SrGa_2Se_4$ system were studied through differential thermal analysis (DTA), X-ray phase analysis (XRD), microstructural analysis (MSA), as well as density and microhardness measurements, and the T–x phase diagram was constructed. A eutectic reaction was identified within the $Ga_2Se_3$ concentration range. The $SrGa_2Se_4$ compound was found to melt congruently at 1110°C, crystallizing in the orthorhombic system, with lattice parameters determined as a = 21.56 Å, b = 21.45 Å, and c = 12.75 Å. The physical properties were determined on a solid solution based on $SrGa_2Se_4$ containing 6 mol% Se. The $SrGa_2Se_4$ compound has potential applications in optoelectronics, lasers, radiation detectors, dosimetric systems, photovoltaic materials, solar panels, and can also be used in the synthesis of phosphor materials when activated with rare earth elements.

**Keywords:** system, density, microhardness, phase, solid solution, photoconductivity, quasibinary, eutectic, solid solution.

## INTRODUCTION

Currently, complex selenide compounds of the $A^2B^3{}_2C^6{}_4$ type, particularly $SrGa_2Se_4$ crystals, are attracting significant scientific interest due to their pronounced nonlinear optical properties. Such materials are considered suitable candidates for applications in photovoltaics, infrared optics, and thermophotovoltaic converters. However, the phase behavior and crystal structure changes of the Se–$SrGa_2Se_4$ system have not been fully explored in existing studies, which highlights the relevance and novelty of the present research.

High-purity elements of selenium (Se), strontium (Sr), and gallium (Ga) were used for the synthesis of alloys within the Se–$SrGa_2Se_4$ system. Initially, the $SrGa_2Se_4$ compound was synthesized from SrSe and $Ga_2Se_3$ precursors via the sealed ampoule method at temperatures ranging from 1000 to 1200 °C.

## EXPERIMENTAL

Subsequent synthesis of Se–$SrGa_2Se_4$ system alloys was carried out using elemental Se and the pre-synthesized $SrGa_2Se_4$ compound. The mixtures were sealed in evacuated quartz ampoules (to a residual pressure of 0.133 Pa) and subjected to heat treatment within the temperature range of 500 to 1000 °C.

The synthesized samples were subjected to thermal treatment at 200°C for a duration of 240 hours. The alloys in equilibrium were studied using physicochemical analysis methods.

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The alloys of the Se-$SrGa_2Se_4$ system are compact, black-colored substances. The extended application period of semiconductor materials is attributed to their resistance to external environmental effects and other chemical influences. It has been found that Se-rich samples containing 0–40% $SrGa_2Se_4$ are resistant to atmospheric oxygen, water, and organic solvents. Although the samples rich in $SrGa_2Se_4$ remain stable against atmospheric moisture in solid form, when crushed and exposed to open air for a long time, they absorb moisture and undergo hydrolysis. All the alloys of the Se-$SrGa_2Se_4$ system dissolve well in strong acids such as $HNO_3$, $H_2SO_4$, and HCl.

The results of the thermal analysis of the Se-$SrGa_2Se_4$ system alloys show that two endothermic effects are observed in the thermograms of the alloys. This indicates that the system has a quasibinary character.

The simplest and most convenient method for studying phase composition is microstructural analysis. It enables the construction of phase diagrams and the determination of the number of phases and the sequence of their crystallization regions. This method allows for:
a) monitoring the quality of the alloy obtained during single crystal growth;
b) identifying the structure of displacements, defects, and the formation of single-phase crystals.

Microstructural analysis is a more reliable and visually observable method for distinguishing between phases present in the studied systems, as well as for identifying homogeneous and heterogeneous regions.

By performing microstructural analysis of the system's alloys, the phase composition of the alloys was determined. The microstructure of samples containing 40, 70, and 94 mol% $SrGa_2Se_4$ was studied using a microscope. The microstructures of these samples are shown in Figures 3.23 a, b, and c.

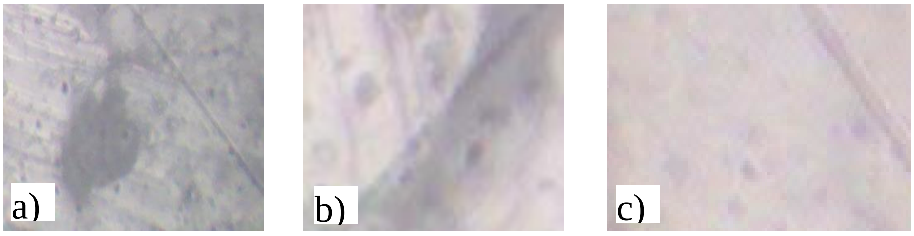


**Fig.1.** Microstructure of alloys in the Se–$SrGa_2Se_4$ system: **a)**40 mol % $SrGa_2Se_4$,**b)**70 mol % $SrGa_2Se_4$, **c)** 94 mol % $SrGa_2Se_4$.

As seen in alloys with the compositions shown in Fig. 1. a and b, these samples belong to the two-phase region. The single-phase 94 mol% $SrGa_2Se_4$ sample, on the other hand, is a solid solution alloy based on the $SrGa_2Se_4$ compound.

To confirm the results of differential thermal and microstructural analyses, diffraction patterns of alloys containing 80 and 94 mol% $SrGa_2Se_4$ were obtained and compared with the diffraction patterns of the initial substances (Fig.2). It was found that the diffraction pattern of the 80 mol% $SrGa_2Se_4$ alloy consists of a mixture of diffraction maxima from the initial substances, indicating the presence of a two-phase alloy.

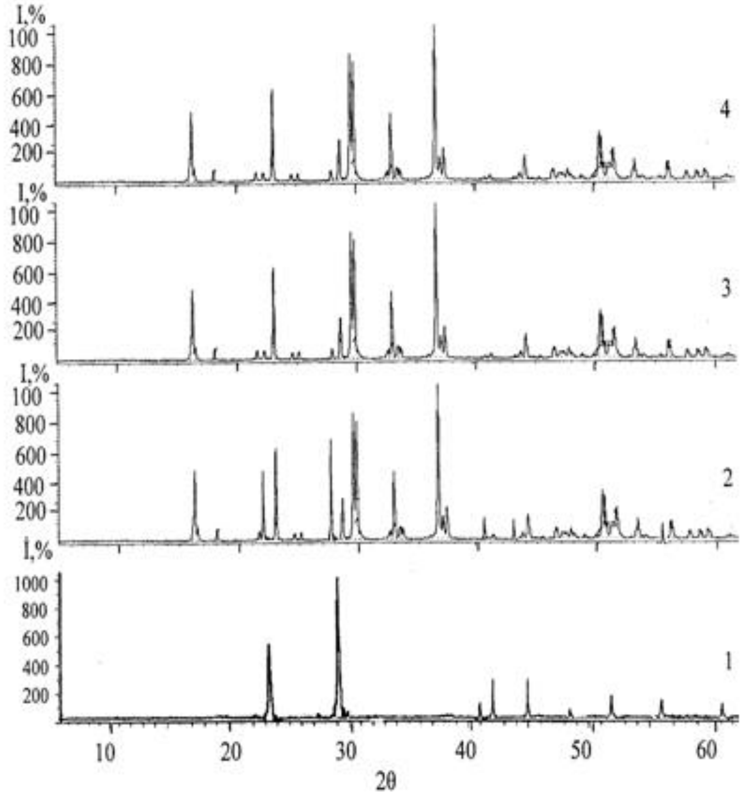


**Fig.2**. Diffractograms of alloys of the Se-$SrGa_2Se_4$ system. 1) Se, 2) 80 mol %, 3) 94 mol %, 4) 100 mol % $SrGa_2Se_4$.

The diffraction maxima observed in the pattern of the 94 mol% $SrGa_2Se_4$ sample correspond exactly to those of the $SrGa_2Se_4$ compound. They differ slightly only in terms of interplanar spacings. The 94 mol% $SrGa_2Se_4$ sample is a solid solution alloy based on the $SrGa_2Se_4$ compound.

Based on the results of comprehensive physicochemical analyses, the T-x phase diagram of the Se–$SrGa_2Se_4$ system was constructed (Fig.3). The phase diagram of the Se–$SrGa_2Se_4$ system is a quasibinary section of the Sr–Ga–Se ternary system and is of the eutectic type. The composition of the binary eutectic formed between the Se and $SrGa_2Se_4$ components is 5 mol% $SrGa_2Se_4$, and the eutectic temperature is 200°C. At room temperature, only 6 mol% $SrGa_2Se_4$ solubility in the $SrGa_2Se_4$ system was detected. The liquidus of the Se–$SrGa_2Se_4$ system is bounded by monovariant equilibrium curves of the α-solid solution based on Se and the $SrGa_2Se_4$ compound. Below the solidus line, two-phase alloys consisting of (Se + α) are crystallized.

During the measurement of microhardness of the alloys in the Se–$SrGa_2Se_4$ system, two different values were obtained. The microhardness of the Se element is 600 MPa. The microhardness of the α-solid solution based on the $SrGa_2Se_4$ compound varies in the range of 2400–2460 MPa. Table 1 presents some physicochemical data of the Se–$SrGa_2Se_4$ system.

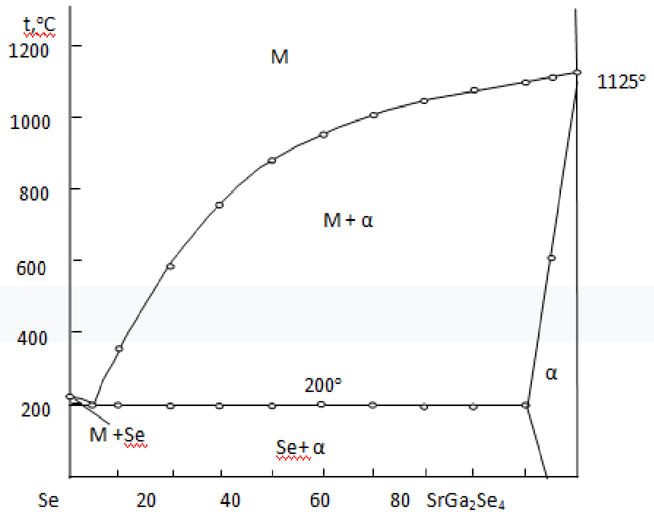


**Fig.3.** T-x phase diagram of the Se-SrGa2Se4 system

**Table 1.** Composition of the alloys of the Se-$SrGa_2Se_4$ system, results of DTA, density, and microhardness measurements.

| Composition, mol % | | Thermal heating effects, °C | Density, g/cm$^3$ | Microhardness of phases, MPa | |
|---|---|---|---|---|---|
| Se | $SrGa_2Se_4$ | | | $SrGaSe_2$ | α |
| | | | | P=0,05 N | P=0,15N |
| 100 | 0,0 | 220 | 4,80 | 600 | – |
| 95 | 5,0 | 200 | 4,80 | Evtek. | Evtek. |
| 90 | 10 | 200,360 | 4,76 | 600 | – |
| 80 | 20 | 200,585 | 4,72 | 600 | – |
| 70 | 30 | 200,750 | 4,70 | 600 | 1460 |
| 60 | 40 | 200,880 | 4,67 | 600 | 1460 |
| 50 | 50 | 200,950 | 4,65 | – | 1460 |
| 40 | 60 | 200,1000 | 4,60 | – | 1460 |
| 30 | 70 | 200,1050 | 4,57 | – | 1460 |
| 20 | 80 | 200,1075 | 4,52 | – | 1460 |
| 10 | 90 | 200,1100 | 4,52 | – | 1460 |
| 5,0 | 95 | 610,1110 | 4,55 | | 1450 |
| 0,0 | 100 | 1125 | 4,50 | – | 1400 |

Thus, in order to study the phase equilibrium in the Se–$SrGa_2Se_4$ system, alloys were synthesized and thermally treated over a wide compositional range.

## RESULTS AND DISCUSSIONS

The phase equilibrium of the system was investigated using differential thermal analysis (DTA), X-ray phase analysis (XRD), microstructural analysis (MSA), as well as density and microhardness measurements, and its T–x phase diagram was constructed. The phase diagram of the Se–$SrGa_2Se_4$ system is a quasibinary section of the Sr–Ga–Se ternary system and is of eutectic type. The eutectic composition formed between the Se and $SrGa_2Se_4$ components is 5 mol% $SrGa_2Se_4$, and its temperature is 200°C. At room temperature, the solid solution region based on the $SrGa_2Se_4$ compound is 6 mol% Se, while the solid solution region based on Se has not been determined. The $SrGa_2Se_4$ compound was found to melt congruently at 1110°C, crystallizing in the orthorhombic system, with lattice parameters determined as a = 21.56 Å, b = 21.45 Å, and c = 12.75 Å.

The measurement of the physical properties of the $SrGa_2Se_4$ compound has revealed that this material primarily functions as a semiconductor and holds potential applications in various advanced technological fields. This compound can be utilized in optoelectronics-for photodetectors and light-emitting diodes (LEDs) operating in the invisible (infrared) and near-infrared range, as well as in lasers, particularly as an active medium in those working in the mid- and near-infrared regions. Additionally, it can be used as a phosphor material-for instance, as a phosphor component in white light-emitting LEDs, in X-ray or cathodoluminescent display systems [4-6].

In radiation detectors, $SrGa_2Se_4$ can serve as a semiconductor material due to its radiation resistance, making it suitable for the detection of gamma and X-rays, as well as in dosimetric systems. As a photovoltaic material, its wide band gap and low defect density make it promising for use in solar panels. Furthermore, by doping the $SrGa_2Se_4$ crystal with rare-earth ions such as $Er^{3+}$, $Tm^{3+}$, and $Yb^{3+}$, it can be used to develop components for optical fiber amplifiers, infrared imaging, and optical communication systems [5-8].

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