

INVESTIGATION OF THE Se–SrGa₂Se₄ SYSTEM

Nagi Yaqubov, Aytan Sultanova, Yasin Jafarov, Malahat Bagiyeva, Humay Huseynova

Baku State university, Baku, Azerbaijan

Received: 15 november 2024

Accepted: 09 december 2024

Published: 24 december 2024

To synthesize alloys of the Se–SrGa₂Se₄ system, the SrGa₂Se₄ compound was first obtained from the binary compounds SrSe and Ga₂Se₃ via the ampoule method in the temperature range of 1000–1200°C. Subsequently, alloys were synthesized based on Se and SrGa₂Se₄. Single crystals of the Sr thiogallate were grown using the Bridgman method. For the first time, the phase equilibria of the Se–SrGa₂Se₄ 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 Ga₂Se₃ concentration range. The SrGa₂Se₄ compound was found to melt congruently at 1110°C, crystallizing in the orthorhombic system, with lattice parameters determined as $a = 21.56 \text{ \AA}$, $b = 21.45 \text{ \AA}$, and $c = 12.75 \text{ \AA}$. The physical properties were determined on a solid solution based on SrGa₂Se₄ containing 6 mol% Se. The SrGa₂Se₄ 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 A²B³₂C⁶₄ type, particularly SrGa₂Se₄ 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–SrGa₂Se₄ 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–SrGa₂Se₄ system. Initially, the SrGa₂Se₄ compound was synthesized from SrSe and Ga₂Se₃ precursors via the sealed ampoule method at temperatures ranging from 1000 to 1200 °C.

EXPERIMENTAL

Subsequent synthesis of Se–SrGa₂Se₄ system alloys was carried out using elemental Se and the pre-synthesized SrGa₂Se₄ 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.

The alloys of the Se-SrGa₂Se₄ 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% SrGa₂Se₄ are resistant to atmospheric oxygen, water, and organic solvents. Although the samples rich in SrGa₂Se₄ 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-SrGa₂Se₄ system dissolve well in strong acids such as HNO₃, H₂SO₄, and HCl.

The results of the thermal analysis of the Se-SrGa₂Se₄ 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% SrGa₂Se₄ 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-SrGa₂Se₄ system: **a)** 40 mol % SrGa₂Se₄, **b)** 70 mol % SrGa₂Se₄, **c)** 94 mol % SrGa₂Se₄.

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% SrGa₂Se₄ sample, on the other hand, is a solid solution alloy based on the SrGa₂Se₄ compound.

To confirm the results of differential thermal and microstructural analyses, diffraction patterns of alloys containing 80 and 94 mol% SrGa₂Se₄ 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% SrGa₂Se₄ alloy consists of a mixture of diffraction maxima from the initial substances, indicating the presence of a two-phase alloy.

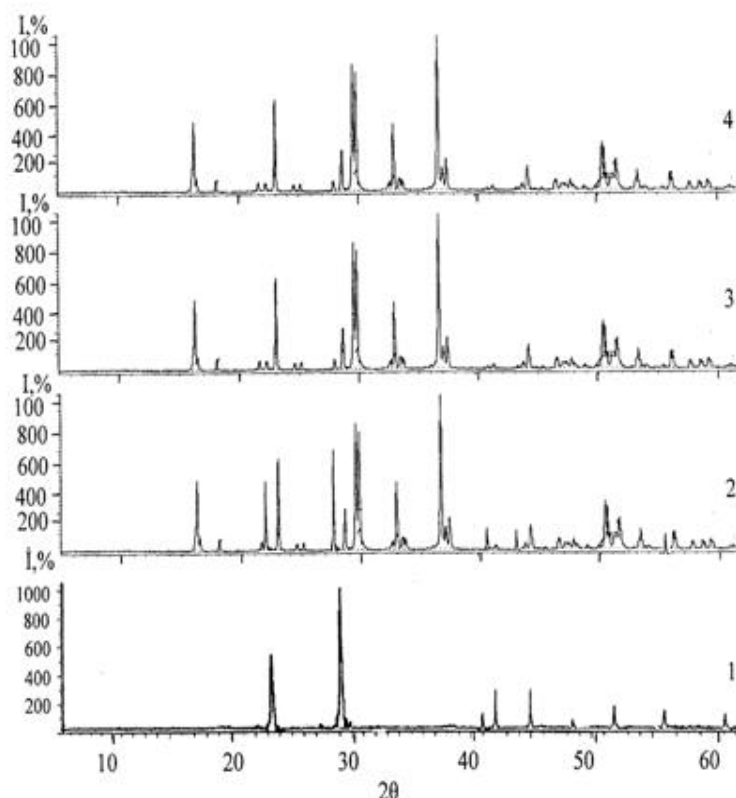


Fig.2. Diffractograms of alloys of the Se-SrGa₂Se₄ system. 1) Se, 2) 80 mol %, 3) 94 mol %, 4) 100 mol % SrGa₂Se₄.

The diffraction maxima observed in the pattern of the 94 mol% SrGa₂Se₄ sample correspond exactly to those of the SrGa₂Se₄ compound. They differ slightly only in terms of interplanar spacings. The 94 mol% SrGa₂Se₄ sample is a solid solution alloy based on the SrGa₂Se₄ compound.

Based on the results of comprehensive physicochemical analyses, the T-x phase diagram of the Se-SrGa₂Se₄ system was constructed (Fig.3). The phase diagram of the Se-SrGa₂Se₄ 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 SrGa₂Se₄ components is 5 mol% SrGa₂Se₄, and the eutectic temperature is 200°C. At room temperature, only 6 mol% SrGa₂Se₄ solubility in the SrGa₂Se₄ system was detected. The liquidus of the Se-SrGa₂Se₄ system is bounded by monovariant equilibrium curves of the α-solid solution based on Se and the SrGa₂Se₄ 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-SrGa₂Se₄ 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 SrGa₂Se₄ compound varies in the range of 2400–2460 MPa. Table 1 presents some physicochemical data of the Se-SrGa₂Se₄ system.

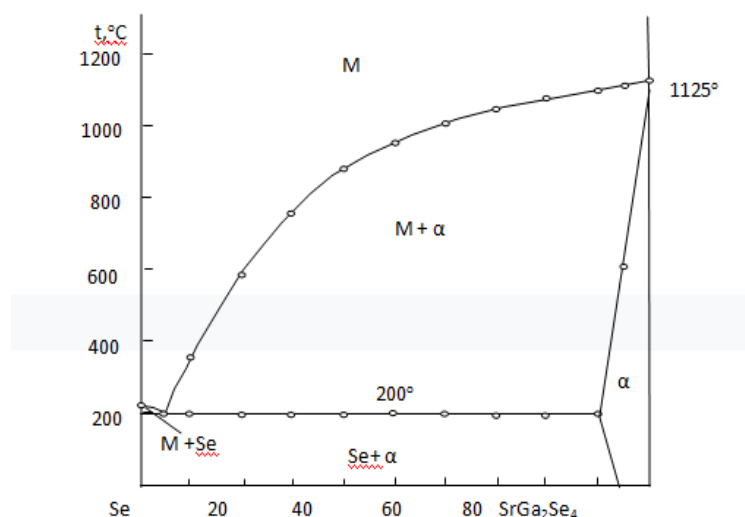


Fig.3. T-x phase diagram of the Se-SrGa₂Se₄ system

Table 1. Composition of the alloys of the Se-SrGa₂Se₄ system, results of DTA, density, and microhardness measurements.

Composition, mol %		Thermal heating effects, °C	Density, g/cm ³	Microhardness of phases, MPa	
Se	SrGa ₂ Se 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–SrGa₂Se₄ 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–SrGa₂Se₄ 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 SrGa₂Se₄ components is 5 mol% SrGa₂Se₄, and its temperature is 200°C. At room temperature, the solid solution region based on the SrGa₂Se₄ compound is 6 mol% Se, while the solid solution region based on Se has not been determined. The SrGa₂Se₄ compound was found to melt congruently at 1110°C, crystallizing in the orthorhombic system, with lattice parameters determined as $a = 21.56 \text{ Å}$, $b = 21.45 \text{ Å}$, and $c = 12.75 \text{ Å}$.

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].

REFERENCES

- [1] Sultanova, A.N.; Yaqubov, N.I.; Əliyev, İ.I.; Ahmedova C .A. and Gafarova G. Physico-chemical investigation of phase equilibrium, *Norwegian Journal of development of the International Science*, **2024**, №133, pp. 28-31, <https://doi.org/10.5281/zenodo.11390460>
- [2] Yagubov. N.I.et al.Study of chemical interaction in the ga-srse system, *Proceedings Chemistry* 78 2, **2023**, 78-82; <https://doi.org/110.61413/Pfhq7389>
- [3] Yagubov, N.I.; Sultanova A.N.; Aliyev I.I. The phase diagram of the In_2Se_3 - SrInSe_2 system and the photo- and electrophysical properties of the obtained phases, *Jomard publishing journal*, **2020**, 8(3) pp.402-411, <https://doi.org/10.62476/nmca83402>
- [4] Chiharu, H.; Nobuyasu. M.; Takeo, T. Determination of a pseudo-binary SrSe – Ga_2Se_3 phase diagram and single crystal growth of SrGa_2Se_4 compounds, *Journal of Physics and Chemistry of Solids*, **2003**, 64(9-10), pp.1797-1800, [https://doi.org/10.1016/S0022-3697\(03\)00096-9](https://doi.org/10.1016/S0022-3697(03)00096-9)
- [5] Nakanishi, Y.; Shiba, K.; Sowa,H.; Tatsuoka, H.; Kuwabara,T. and Nakamura,Y. Preparation of blue-emitting $\text{SrGa}_2\text{Se}_4\text{:Ce}$ thin films by multi-source deposition, *Applied Surface Science*, **1996**, 100-101, pp. 639-64, [https://doi.org/10.1016/0169-4332\(96\)00354-6](https://doi.org/10.1016/0169-4332(96)00354-6)
- [6] Yagubov, N.I.; Aliyev. I.I.; Veliyev, C.A.; Ali, R. Likvidu Surface Projection for the CaTe-In-Te Quasi-ternary sustem, *Journal of Allous and Compound*, **2015**. p.319-324. <http://www.sciencedirect.com/science/article/pii/S0925838814017198>
- [7] Chiharu, H. et al. Determination of a pseudo-binary SrSe – Ga_2Se_3 phase diagram and single crystal growth of SrGa_2Se_4 compounds, *Journal of Physics and Chemistry of Solids*, **2003**, 64(9), pp. 797-1800, [https://doi.org/110.1016/S0022-3697\(03\)00096-9](https://doi.org/110.1016/S0022-3697(03)00096-9)
- [8] Wilfried, K. and Herbert, S. Die Struktur des SrGa_2Se_4 , eine neue Besetzungsvariante des TlSe -Typs, **1983**, <https://doi.org/10.1002/zaac.19834990416>