Semiconductor physics

Fabrication and performance characterization of Sb_2Se_3-GaSe eutectic systems

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Abstract. Sb_2Se_3-GaSe eutectic composites were synthesized by the vertical Bridgman method. XRD analysis and structural study of the Sb_2Se_3-GaSe eutectics showed that Sb_2Se_3 inclusions were uniformly distributed in the GaSe matrice. Three eutectic points in the Sb_2Se_3-GaSe system were studied. The compositions of the three eutectics of 80, 55 and 40 wt.% Sb_2Se_3 formed in the Sb_2Se_3-GaSe systems, and the corresponding melting points of 776, 725 and 698 K were determined. Anisotropy of the electrical properties of the eutectic systems was observed. The anisotropy degree was $\sim 10^3$ depending on the crystallization direction.

Keywords: XRD, SEM and EDX analysis, differential scanning calorimetry, Raman spectra, eutectic system.

https://doi.org/10.15407/spqeo27.02.184
PACS 07.20.Fw, 61.05.cp, 68.37.Hk, 78.30.Fs, 81.30.-t

Manuscript received 14.12.23; revised version received 21.03.24; accepted for publication 19.06.24; published online 21.06.24.

1. Introduction

Obtaining semiconductor based composite materials with controlled physical properties depends not only on the materials composition but also on their structure. All of the distribution, size and shape of the phases as well as the interface characteristics are important in defining the composite properties [1–3]. Significant improvements of the properties of composite materials are often achieved by developing new microstructures. In this regard, eutectics is a paradigm of composite materials with very fine microstructures that enables combining the properties of each component to optimize the overall material physical properties [4, 5].

Antimony selenide (Sb_2Se_3) receives ever more attention of solid-state materials physicists due to broad range of its applications in optics, electronics, mechanics, energy and environmental protection [6–8]. These applications include a new generation of photovoltaic converters, photo-catalysts, sensors, functional smart coatings, smart membranes and separation devices, and micro-optical and photonic components [9]. In solar energetics, photovoltaic conversion using solar cells is considered to be the most efficient way to harness solar energy by converting it directly into electricity [10, 11].

In recent years, Sb_2Se_3 has attracted great interest due to its high thermoelectric efficiency and good photovoltaic properties [9]. On the other hand, GaSe crystals are widely used as a photoconductive and non-linear optical material [6, 7]. GaSe is a good candidate to use in photodetectors due to its strong absorption in the UV-visible spectral range [19].

Eutectic systems retain the physical properties of their constituent compounds [13], and these properties can be controlled [12, 18]. Therefore, study of Sb_2Se_3-GaSe eutectic systems that combine the properties of both Sb_2Se_3 and GaSe components [14–16] is important.

In this work, properties of Sb_2Se_3-GaSe eutectic systems are studied by Raman scattering, physical-chemical characterization, and electrical measurements. Moreover, possible applications of such systems are suggested.

2. Experimental

Sb_2Se_3-GaSe eutectic composites were prepared by the vertical Bridgman method. The rate of the crystallization front was about 1.7 mm/min. X-ray spectra of the Sb_2Se_3-GaSe eutectic systems were measured by an Advance-D8 diffractometer (“Bruker”). The radiation source was a CuK_α anode operating at a voltage of 40 kV and a current of 40 mA. The radiation wavelength was λ = 1.5406 Å, and the angle between the incident X-rays and the sample was 2Θ = 5...80. A Zeiss ΣIGMA field emission scanning electron microscope (FESEM) was used to characterize the morphology of the specimens and to obtain qualitative

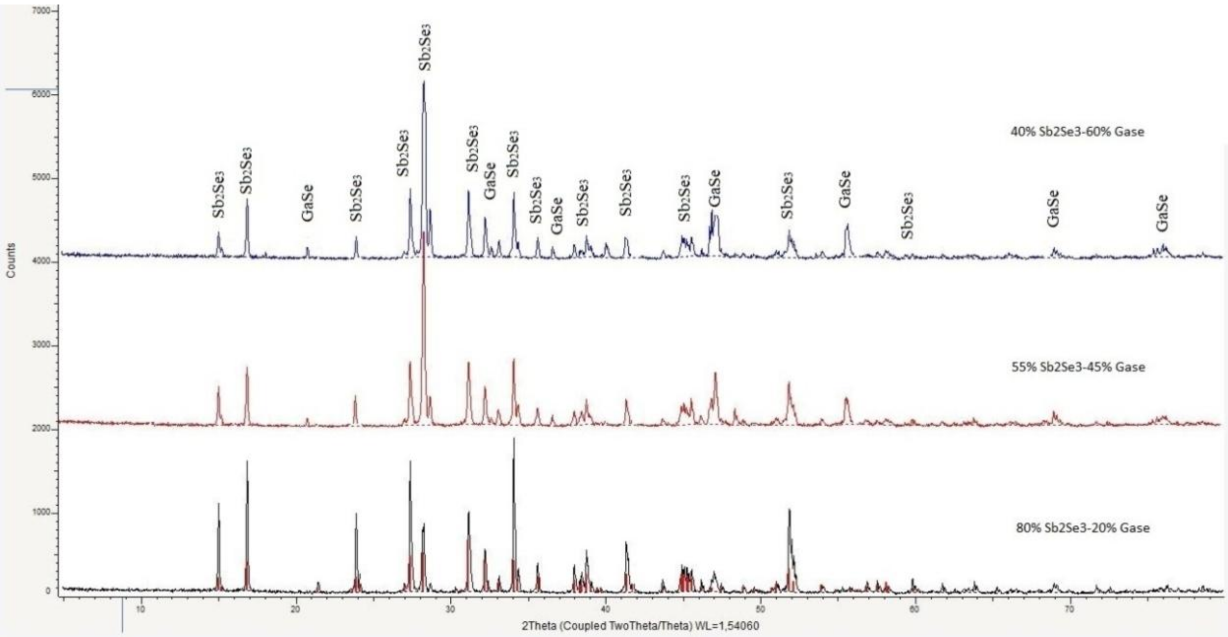

Fig. 1. XRD patterns of Sb_2Se_3-GaSe eutectic systems.

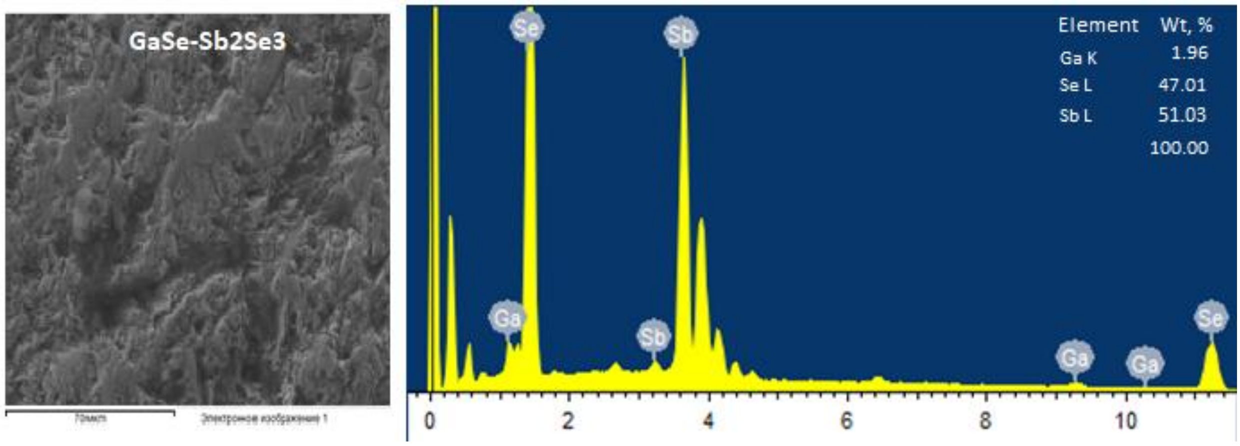

Fig. 2. X-ray spectra of Sb_2Se_3-GaSe systems obtained with SEM–EDX.

information about their elemental composition. Raman scattering from the samples was studied using a Nanofinder 30 confocal setup (Tokyo Instruments, Japan) with a diffraction grating with 1800 lines/mm and a spectral resolution of 0.5 cm^{-1}. The excitation was induced by a second harmonic of a Nd:YAG laser (λ = 532 nm) operating at a maximum power of 10 mW. Thermal analysis of the Sb_2Se_3-GaSe eutectic systems was performed in an Ar atmosphere using a NETZSCH DSC 204 F1 (Germany) differential scanning calorimeter. Nitrogen was used as a shielding gas. A 40 mg composite sample was placed in an Al socket. In the same slot, a piece of sapphire was placed as a standard sample. Both cells were heated at a rate of 10 K/min under totally identical conditions. The Ar flow rate was 20 ml/min. The studies were carried out in the temperature range of 273 to 873 K.

3. Results and discussion

The Sb_2Se_3-GaSe composites were obtained in the form of light grey compact ingots. Three eutectic points of the Sb_2Se_3-GaSe system were studied. The diffraction patterns of the composites under study are shown in Fig. 1. Analysis of the XRD spectra confirmed that this system is diphasic. The most intense peaks correspond to (020), (120), (130), (230), (240), (211), (301), (041), (141), (520), (002), and (061) planes. The Muller indices are identical to those of Sb_2Se_3. The orthorhombic structure with the lattice parameters a = 3.81, b = 12.82, c = 15.06 is revealed. At the same time, the weak peaks at 2θ = 22°, 34°, 45.5°, 58° and 71° coincide with the GaSe lines. Gallium monoselenide melts congruently at 960 °C, crystallizes in a hexagonal syngony with the lattice parameters a = b = 0.375 nm and c = 1.591 nm,

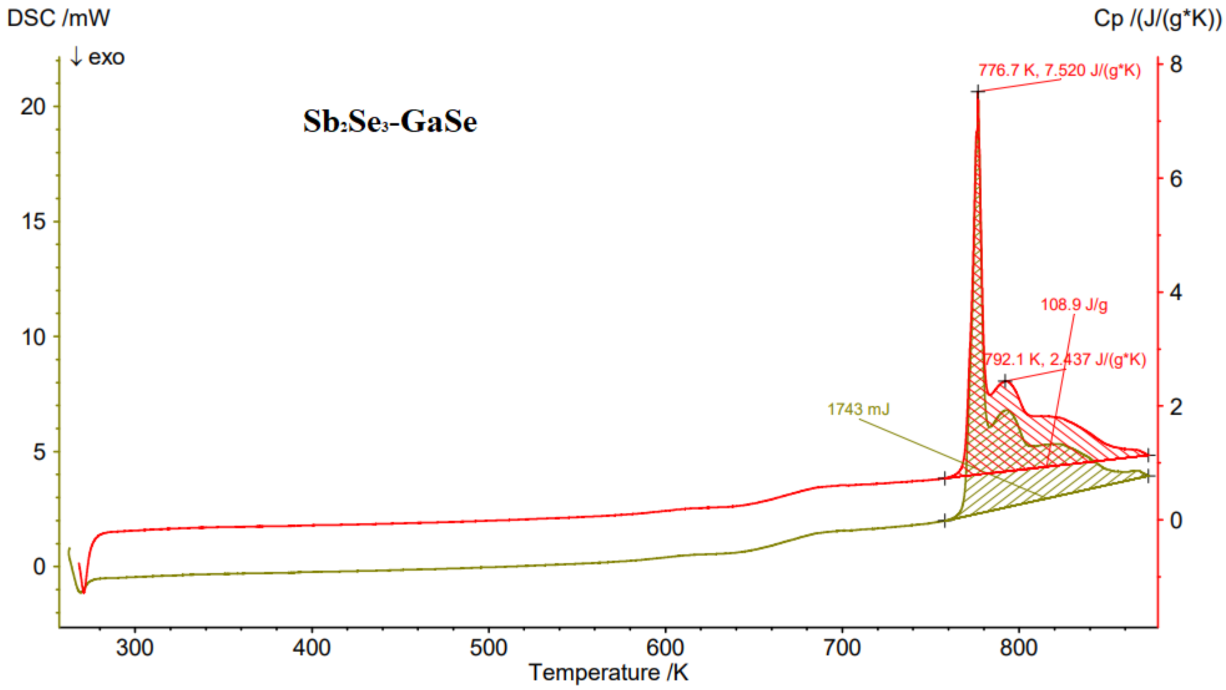

Fig. 3. DSC curves for Sb_2Se_3-GaSe eutectic composite.

Z = 4, which belongs to the space group P63/mmc-D4 6h, and has the density ρ = 5.03 g/cm^3. It was determined that the compositions of the three eutectics formed in the Sb_2Se_3-GaSe systems were 80, 55 and 40 wt.% Sb_2Se_3, the respective melting points were 776, 725 and 698 K.

The structure of the Sb_2Se_3-GaSe eutectic systems was studied by electron microscopy (FESEM) and X-ray spectrography (Fig. 2). SEM and EDX analysis showed that the obtained eutectics were two phase systems. Fig. 2 shows an image of the Sb_2Se_3-GaSe system containing 51.03 wt.% of Sb, 47.01 wt.% of Se and 1.96 wt.% of Ga. The data correspond to the stoichiometric compositions of the matrix and inclusions.

High temperature phase change was studied by differential thermal analysis (DSC), which was used to monitor endothermic behavior of the sample during scanning. The obtained results are shown in Fig. 3.

Fig. 3 shows the DSC curves for the Sb_2Se_3-GaSe eutectic composite in the temperature range of 0 to 873 K.

The specific heat capacity was calculated from the data presented in this figure using the following expression:

$$C_p = \frac{m_{\text{standart}}}{m_{\text{sample}}} \frac{DSC_{\text{sample}} - DSC_{\text{bas}}}{DSC_{\text{standart}} - DSC_{\text{bas}}} C_{p\,\text{standart}},$$

where DSC_{sample}, DSC_{bas} and DSC_{standard} are the ordinates of the DSC curves corresponding to the sample, blank specimen, and standard specimen, respectively, $C_{p\,\text{sample}}$ and $C_{p\,\text{standard}}$ are the specific heat of the sample and standard specimen, respectively, and m_{sample} and m_{standard} are the sample and sapphire masses, respectively [1].

As can be seen from Fig. 3, two endothermic peaks at 776 and 792 K are present on the temperature dependence of heat flow. It is established therefore that the initial and the final melting temperatures are 776 and 792 K, respectively, and the enthalpy of melting is equal to 108.9 J/g.

Two phases and interphases in the Raman spectra of the GaSe-Sb_2Se_3 eutectic composite were investigated at room temperature for both GaSe-Sb_2Se_3 and Sb_2Se_3 to confirm presence of the zones. Figs 4 and 5 show the Raman spectra of the Sb_2Se_3 compound and the GaSe-Sb_2Se_3 eutectic system. Raman spectroscopy was used to study the structure of the samples. As can be seen from Fig. 4, the Raman spectrum shows more intense peaks around 153 and 191.3 cm^{-1}, which are usually attributed

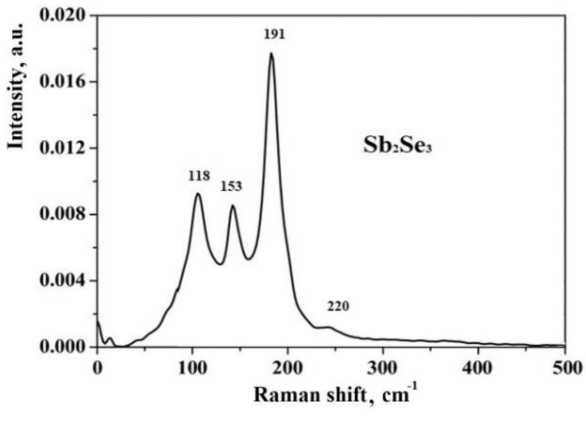

Fig. 4. Raman spectrum of Sb_2Se_3 milled powder.

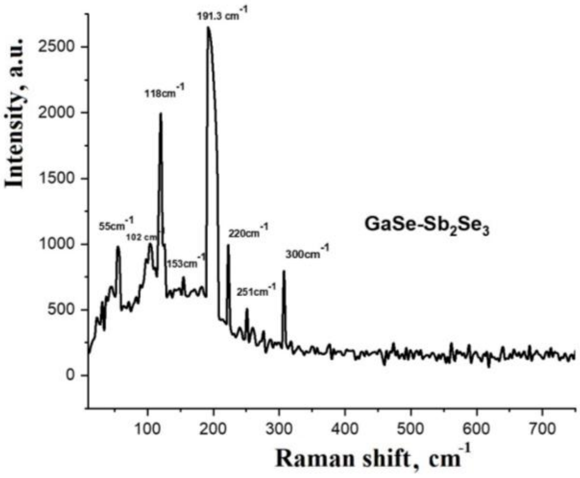

Fig. 5. Raman spectrum of Sb_2Se_3-GaSe eutectic system.

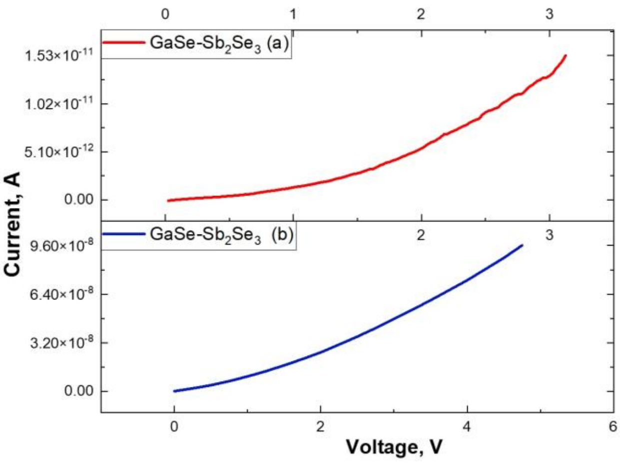

Fig. 6. Current-voltage characteristics of Sb_2Se_3-GaSe eutectic system.

to Sb_2Se_3 phase. In particular, the first peak corresponds to the A_{2u} mode of Sb-Sb bonds, and the second one to the A_g mode of Sb-Se-Sb chains.

The peaks at 220 cm^{-1} were detected for Sb_2Se_3. These peaks were attributed to the strong Sb-Se modes. The Raman modes at 102 and 118 cm^{-1} were assigned to Se-Se bonds [10]. The peaks at 251 and 300 cm^{-1} were detected and attributed to a strong GaSe compound [14, 17]. Absence of peaks related to any of the supplement phases reconfirms purity of the synthesized material.

Fig. 6 presents the current-voltage characteristics of the Sb_2Se_3-GaSe systems. As can be seen from this figure, the current-voltage dependences show an anisotropy between the directions parallel and perpendicular to the crystallization direction of the studied system. The current is larger in the direction perpendicular to the crystallization direction. The anisotropy degree is ~10^3. The observed anisotropy may be attributed to inclusions short-circuiting. We conclude as well that the current in the nonlinear region is caused by the field effect.

4. Conclusions

In summary, we have investigated the structural and electrophysical properties of Sb_2Se_3-GaSe eutectic systems taking into account all possible configurations. Two congruent melting compounds have been obtained for the Sb_2Se_3-GaSe system. The compositions of the three eutectics formed in the system are 40, 55 and 80 mol.% Sb_2Se_3, and their melting temperatures are 470, 425 and 450 °C, respectively. The SEM and XRD studies have confirmed that the Sb_2Se_3-GaSe eutectic systems consist of a semiconductor matrix and oriented inclusions. The initial and the final melting temperatures for this eutectic composite are 776 and 792 K, respectively. It has been found out that the peaks detected in the Raman spectra correspond to the Sb_2Se_3-GaSe alloys and Se-Se bonds.

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Виготовлення та характеристика евтектичних систем Sb_2Se_3-GaSe

M.V. Kazimov, G.B. Ibragimov

Анотація. Евтектичні композити Sb_2Se_3-GaSe було синтезовано вертикальним методом Бріджмена. Рентгенівський аналіз і структурні дослідження евтектики Sb_2Se_3-GaSe показали рівномірний розподіл включень Sb_2Se_3 у матриці GaSe. У системі Sb_2Se_3-GaSe було досліджено три точки евтектики. Було визначено, що склад трьох евтектик, утворених у системах Sb_2Se_3-GaSe, становить 80, 55 та 40 мас.% Sb_2Se_3, а відповідні температури плавлення становлять 776, 725 та 698 K. Спостерігали анізотропію електричних властивостей евтектичних систем. Ступінь анізотропії становив ~10^3 залежно від напрямку кристалізації.

Ключові слова: XRD, SEM та EDX аналіз, диференціальна скануюча калориметрія, раманівські спектри, евтектична система.