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Structural features of the $AgGaGe_3Se_8$ crystal doped with Er, Dy and Nd

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In the work, the effect of changes of structural properties by doping with rare-earth metals (REM) (Nd, Dy, Er) of the $AgGaGe_3Se_8$ has been investigated. According to the results of the X-ray analysis, it is obvious that adding REM to the structure is the point of local distortion and stress, which manifests itself in the modification of diffraction reflections. Microstructural analysis based on SEM and EPMA confirmed the single-phase morphology and chemical homogeneity of the crystals within the analysis area. The presence of the basic structural unit of the $(Ga,Ge)Se_4$ tetrahedrons has been indicated by Raman Spectroscopy. Although rare-earth doping has little effect on the position of the fundamental vibrational modes, an increase in the intensity of individual bands is observed. The obtained results indicate that the key properties of the material are preserved after doping, which makes it possible to use such modified crystals in nonlinear optics and photonics devices, in particular where fine-tuning of the optical parameters is required.

Keywords: alloying, rare-earth elements, crystal structure, Raman spectra.

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Introduction

Recently, there has been an increasing interest in the development of infrared (IR) optically activated and controlled devices based on chalcogenides. Special attention is drawn to ternary and quaternary crystals [1–5]. Chalcogenide crystals, unlike oxides, have a wider transparency range that also covers the mid-infrared region of the spectrum [6]. As one moves from S to Se to Te, the chalcogenides become more polarized, the energy of the band gap decreases, and the nonlinear optical susceptibility of the both second and third order increases. At the same time, the introduction of rare earth atoms generally leads to a reduction of the band gap and a decrease in transparency, which is a key parameter for optoelectronics.

It is well known that $AgGaSe_2$ crystals are effective nonlinear ones used for creating coherent light emitters [7]. However, these crystals have a significant drawback: a low laser damage threshold. To overcome this problem, quaternary crystals $AgGaGe_3Se_8$ are obtained, which can be viewed as a solid solutions between $AgGaSe_2$ and $(GeSe_2)_n$, where n =1, 2, 3, 4, and 5. Crystals with $n = 4$ – $AgGaGe_3Se_8$, have a significantly higher laser damage threshold. Moreover, such crystals can be as transfer matrix for point sources, particularly for rare earth metals incorporated within them.

Therefore, the aim of this work is to study the effect of doping with rare earth elements Er, Dy, and Nd on the structural and optical properties of $AgGaGe_3Se_8$ crystals.

I. Experimental section

The crystal has been synthesized by the Bridgman-Stockbarger method. The conditions of process are the following: temperature in the crystallization zone – 1250 K; annealing temperature – 720 K; temperature gradient at the solid-liquid interface – 5 K/mm; growth rate – 0.1 mm/h; annealing time – 150 hours; cooling rate to room temperature – 5 K/h. The AgGaGe$_3$Se$_8$ single crystals obtained in this way had the shape of cylinders with a diameter of 18 mm and a length of 30 mm. The Dy/Nd/Er impurity (approximately 0.2%) was introduced into the initial mixture to achieve a concentration close to the concentration of intrinsic structural defects.

To determine the quantitative and qualitative composition of the crystals, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) methods are used (Tescan Vega 3 LMU scanning electron microscope (Oxford Instruments AZtec ONE System) and REMMA-102-02 with an elemental microanalyzer).

To record the Raman spectra, we used an MDR-23 spectrometer equipped with an iDus 420 Andor (UK) cooled CCD detector. The Raman signals were excited by a solid-state laser line with a wavelength of 671 nm. The laser power density on the sample surface was less than 10^3 W/cm^2, which excluded thermal modification of the samples. A spectral resolution for all excitation radiation wavelengths did not exceed 2 cm $^{-1}$ and as determined from the Si phonon peak width of a Si single crystal. The Si phonon peak position of 520.5 cm^{-1} was used as a reference for determining the position of the peaks in the Raman spectra.

II. Experimental results

The crystal structure of the AgGaGe$_3$Se$_8$ selenides belongs to the GeS$_2$ (SG *Fdd*2 [8]) structural type. The Ag atoms are the nodal points in the AgGaGe$_3$Se$_8$ structure, and the isotropic parameters indicate their significant fluctuation, leading to the appearance of defects and migration of Ag$^+$ ions. In the AgGaGe$_3$Se$_8$ structure (Fig. 1), the Ag and Se atoms form the significant deformed tetrahedral (distortion index (bond length) = 0.0271; effective coordination number = 3.87). The atom of statistical mixture {0.25Ga:0.75Ge} with Selenium atoms has also tetrahedral environment [Ga,Ge 4Se]. It is worth noticing that these tetrahedrals are enough symmetric (distortion index (bond length) = 0.00038; effective coordination number = 4.0).

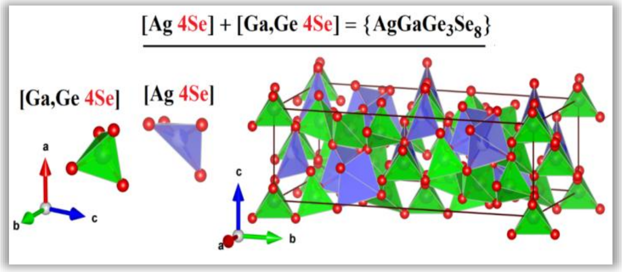

Fig. 1. Coordinational environment of Ag and {Ga,Ge}and the AgGaGe$_3$Se$_8$ crystal structure.

The radii of the Ag^+ ion is 1.13 Å, the distance – δ(Ag – Se), that is calculated as the sum of ionic radii and is equal 3.04 Å [9]. The ionic radii $r(Nd^{+3}) = 1.04$ Å, $r(Dy^{+3}) = 0.91$ Å i $r(Er^{+3}) = 0.89$ Å are quite close to the ionic radii of the Ag^{+1}. In fact, such feature opens the opportunity for doping of the AgGaGe$_3$Se$_8$ crystals with REM and obtaining the chalcogenides with stoichiometric composition Ag$_{1-3x}$R$_x$GaGe$_3$Se$_8$.

In Fig 2, the theoretical, experimental and difference patterns of the AgGaGe$_3$Se$_8$ doped with Ne, Dy and Er are presented.

According to the X-ray analysis, the doping with Nd, Dy, Er does not lead to change of the unit cell of the

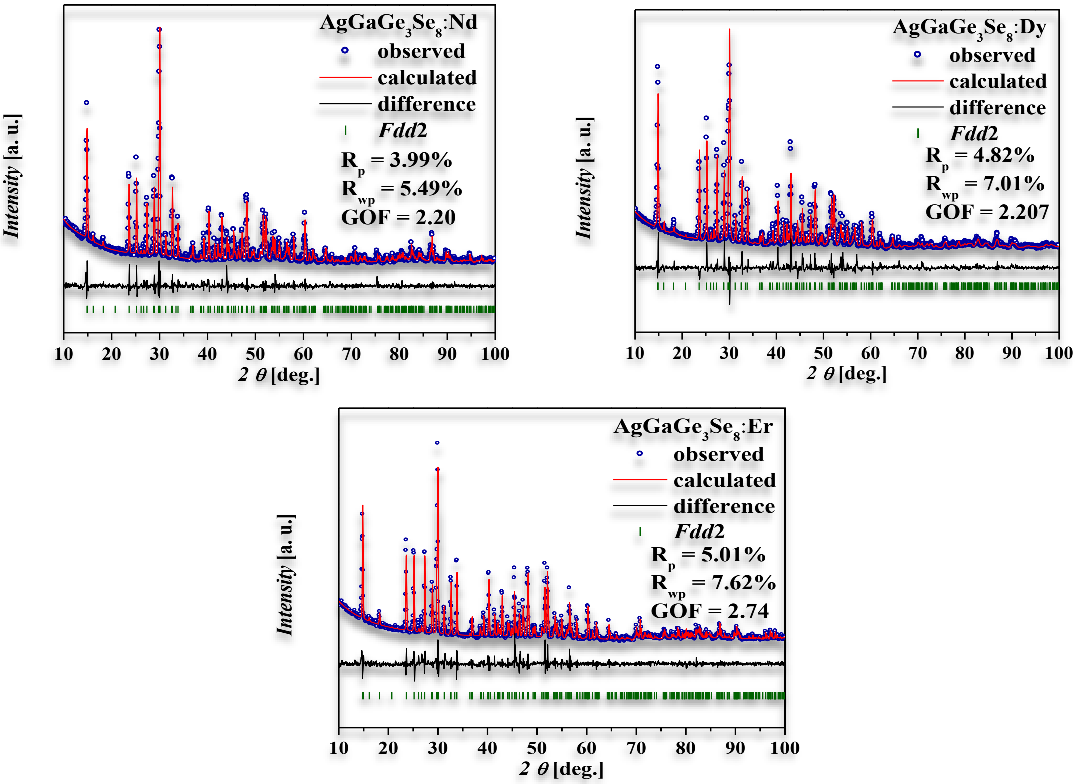

Fig 2. The calculated, observed and difference patterns of the AgGaGe$_3$Se$_8$ doped with Ne, Dy and Er.

$AgGaGe_3Se_8$ crystal. However, a noticeable change in the height and width of the diffraction patterns was observed. The observed transformation of the X-ray pattern indicates the distortions caused by the impurity and the appearance of a strained state of the matrix lattice.

The phase analysis and determination of chemical compositions were performed for the studied crystals using a TESCAN scanning electron microscope (SEM) equipped with WDS/EDXS detectors for electron probe microanalysis (EPMA). For example, Fig. 3 shows an SEM microimage of a part of the $AgGaGe_3Se_8$:Nd crystal.

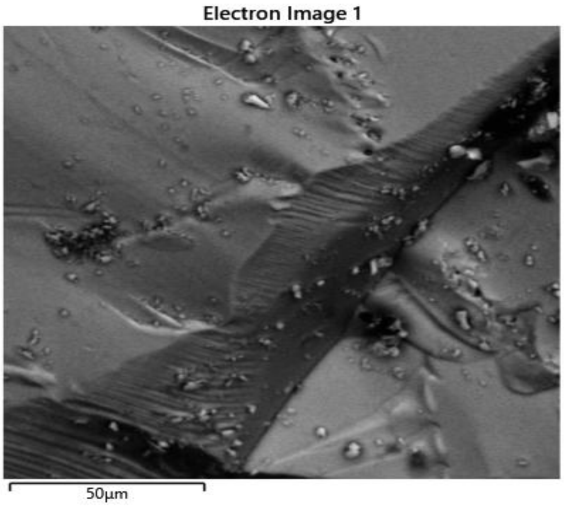

Fig 3. The result of the SEM analysis of the part of the $AgGaGe_3Se_8$:Nd crystal.

EDS images and element distribution for the $AgGaGe_3Se_8$:Nd crystal are presented in Fig. 4 and 5.

It can be seen that the crystals have a single-phase morphology, although all the objects of study exhibit visible dark spots, as well as lighter and darker areas, which arise due to the inhomogeneous roughness of the surface caused by cutting and polishing. The content of components determined by the EPMA method is in good agreement with the initial composition of the synthesized sample. This method confirms a qualitative assessment of the elemental composition and the uniformity of the samples on the scale of the selected scanning area.

The $AgGaGe_3Se_8$ crystals have a non-centrosymmetric orthorhombic structure and belong to the space group *Fdd*2 [10]. The structure of the solid solutions $Ag_xGa_xGe_{1-x}Se_2$ is formed by "adding" $AgGaSe_2$ to $GeSe_2$ through the substitution of Ge^{4+} with Ga^{3+} in the cation sublattice of $GeSe_2$, while the resulting charge deficiency is compensated by Ag^+ ions. As we demonstrated in our previous work [11], when doping $AgGaGe_3Se_8$ crystals with rare earth ions, these ions are incorporated into the crystal lattice at positions occupied by Ag^+ ions. In our study [12], we conducted a detailed study of the Raman spectra of $AgGaGe_2Se_6$, $AgGaGe_3Se_8$, $AgGaGe_4Se_{10}$, and $AgGaGe_5Se_{12}$ crystals, and assigned the main bands of the Raman spectra to specific vibrational modes.

The similarity of the experimental Raman spectra of the aforementioned crystals indicates that the basic structural unit for all the compounds is the $(Ga,Ge)Se_4$ tetrahedron. The most intense vibrational modes in the spectra of these compounds, at frequencies of 199 and 210 cm^{-1}, are associated with vibrations of $GeSe_2$ structural units, while the band at 192 cm^{-1} corresponds to a vibrational mode in $AgGaSe_2$ structural units. The same study demonstrated that the phonon spectrum of the mixed compound $Ag_xGa_xGe_{1-x}Se_2$ simultaneously exhibits bands characteristic of both end-member compounds: $AgGaSe_2$ $(x = 1)$ and $GeSe_2$ $(x = 0.5)$.

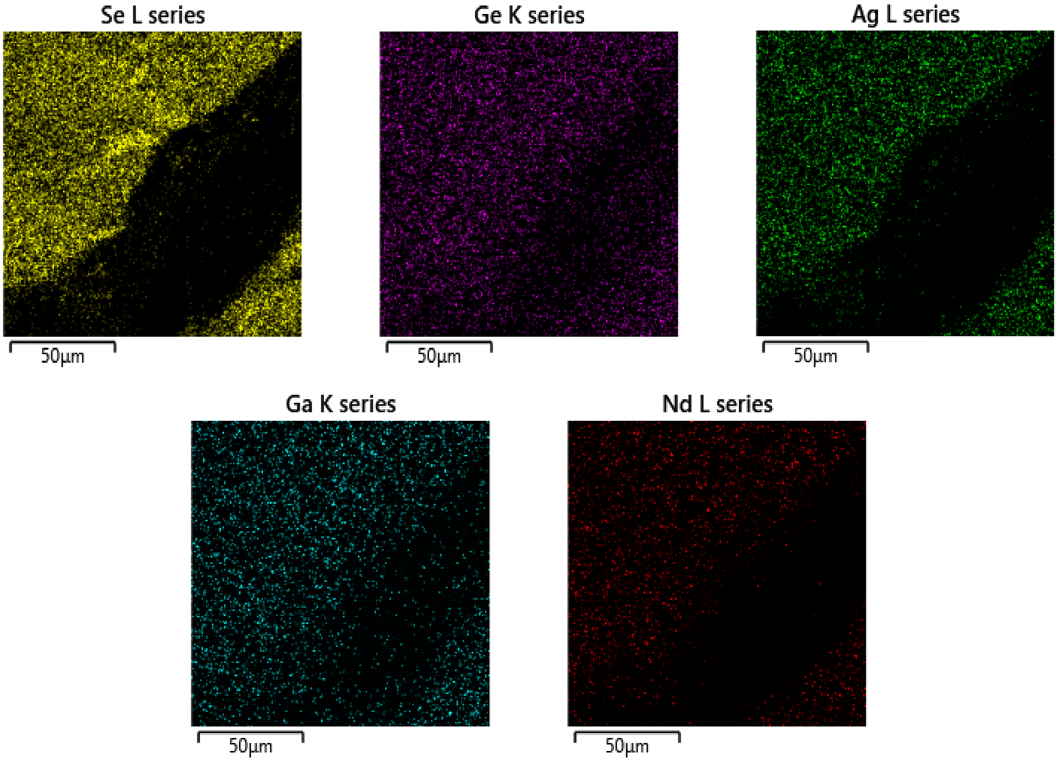

Fig. 4. EDS map of the reflected region in $AgGaGe_3Se_8$:Nd.

Furthermore, the spectral transformation with varying component composition follows a two-mode behavior.

Fig. 6 presents Raman spectra normalized to the intensity of the band at 199 cm⁻¹ for the undoped $AgGaGe_3Se_8$ crystal and for the same type of crystals doped with rare-earth ions Nd^{3+}, Dy^{3+}, and Er^{3+}. Doping the crystals with rare-earth elements in such small amounts (0.2 wt%) does not significantly affect the vibrational modes that may appear in the Raman spectra. Indeed, as shown in Fig. 6, all spectra are quite similar. Nevertheless, let us examine specific regions of these spectra in more detail.

Fig. 7(a) shows the Raman spectra of the aforementioned crystals in the spectral region of the most intense bands at 199 and 210 cm⁻¹, which correspond to the vibrational modes of the $GeSe_2$ structural units in the $AgGaGe_3Se_8$ crystal, and the band at 192 cm⁻¹, which corresponds to the vibrational mode of the $AgGaSe_2$ structural units. The spectra indicate that doping the crystals with rare-earth elements results in a slight decrease in the intensity of the 192 cm⁻¹ band. These changes may be due to a reduction in the number of Ag^+ ion bonds in $AgGaSe_2$. At the same time, their substitution with bonds involving rare-earth ions is still insufficient for them to appear as a separate, lower-frequency band (since the atomic mass of rare-earth elements is significantly higher than that of Ag).

Fig. 7(b) presents the Raman spectra of the undoped $AgGaGe_3Se_8$ crystal and the Raman spectra of similar crystals doped with Nd^{3+}, Dy^{3+}, and Er^{3+} ions. As expected, minor changes occur (an increase in intensity) in the region of the band at 60 cm⁻¹, which corresponds to the vibrational modes of $AgGaSe_2$ [12]. A more intriguing effect of doping the crystals with rare-earth ions is the significant increase in the intensity of the band at 75 cm⁻¹, which is attributed to vibrations of $GeSe_2$ structural units [12]. These intensity changes may result from the indirect influence of rare-earth ions on the vibrations of Se atoms in $GeSe_4$ tetrahedra, as interatomic distances change significantly when Ag^+ ions are replaced with rare-earth ions [11].

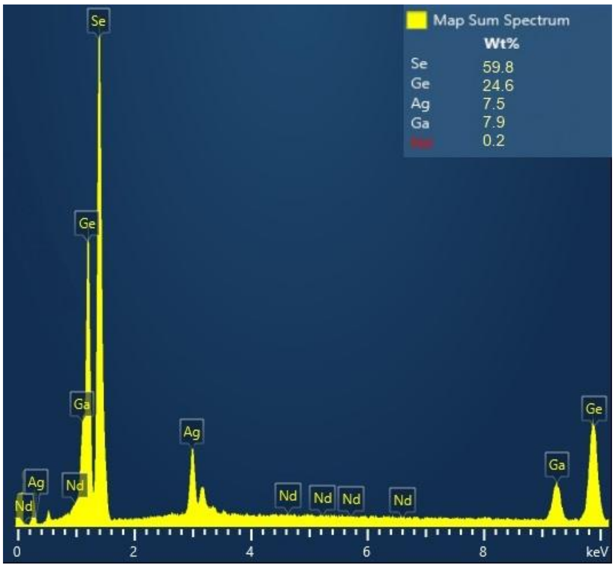

Fig. 5. The element analysis of the $AgGaGe_3Se_8$:Nd structure.

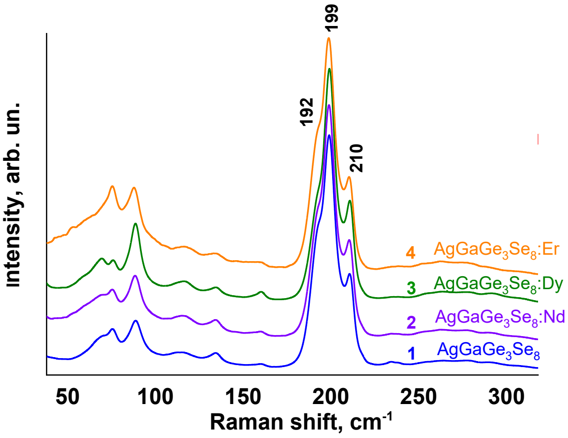

Fig. 6. Raman spectra of crystalline compounds normalized to the intensity of the band at 199 cm⁻¹: undoped $AgGaGe_3Se_8$ (spectrum 1) and $AgGaGe_3Se_8$ doped with rare-earth ions – Nd^{3+} (spectrum 2), Dy^{3+} (spectrum 3), and Er^{3+} (spectrum 4).

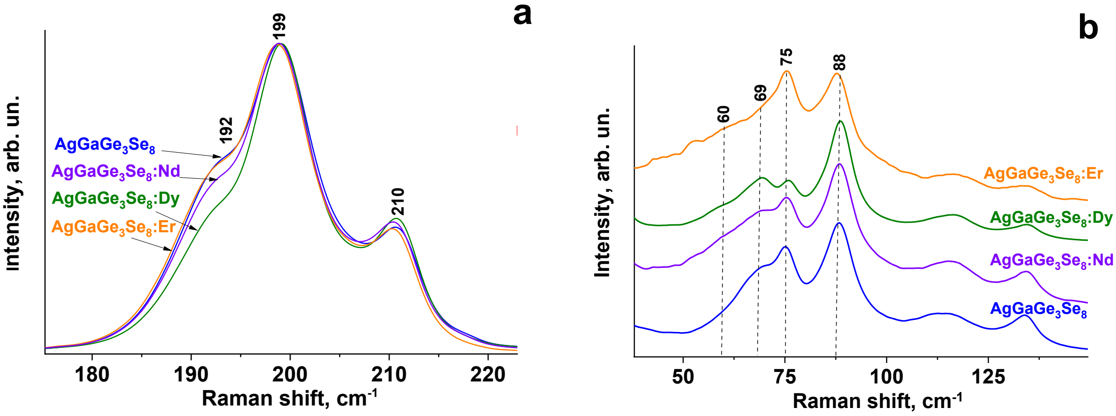

Fig. 7. Raman spectra of crystalline compounds: undoped AgGaGe$_3$Se$_8$ and AgGaGe$_3$Se$_8$ doped with rare-earth ions Nd^{3+}, Dy^{3+}, and Er^{3+} in different spectral regions.

Conclusions

The work investigates the influence of doping with rare earth elements Er, Dy, and Nd on the structural and optical properties of AgGaGe$_3$Se$_8$ crystals. X-ray diffraction analysis revealed that doping with Nd, Dy, and Er did not affect the crystal structure of AgGaGe$_3$Se$_8$; however, it led to distortions and stress in the lattice, as evidenced by changes in the diffraction patterns. Results from SEM and EPMA analyses confirm the single-phase morphology and chemical homogeneity of AgGaGe$_3$Se$_8$:Nd crystals within the studied area. The study of Raman spectra showed that AgGaGe$_3$Se$_8$ crystals have a basic structural unit of (Ga,Ge)Se$_4$. Doping with rare earth ions (Nd^{3+}, Dy^{3+}, Er^{3+}) has minimal impact on the main vibrational modes; however, it causes an increase in the intensity of certain bands, indicating an indirect influence on the structural vibrations in the GeSe$_4$ tetrahedra due to changes in interatomic distances. Thus, the work establishes that doping AgGaGe$_3$Se$_8$ crystals with rare earth elements (Nd, Dy, Er) does not disrupt their structural integrity and chemical homogeneity, allowing for the preservation of key optical properties while simultaneously opening possibilities for fine-tuning vibrational characteristics and potential optimization of the material for applications in nonlinear optics and photonics.

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Структурні особливості кристалів $AgGaGe_3Se_8$ легованих Er, Dy та Nd

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У даній роботі досліджено вплив легування рідкоземельними елементами (Nd, Dy, Er) на структурні характеристики кристалів $AgGaGe_3Se_8$. За допомогою рентгеноструктурного аналізу встановлено, що додавання зазначених іонів викликає локальні спотворення та напруження, що проявляється в модифікації дифракційних відбиттів. Мікроструктурний аналіз методами SEM та EPMA підтвердив однофазну морфологію та хімічну однорідність кристалів у межах зони аналізу. Раманівська спектроскопія виявила наявність базової структурної одиниці у вигляді тетраедрів $(Ga,Ge)Se_4$. Незважаючи на те, що легування рідкоземельними елементами незначно впливає на положення основних коливних мод, спостерігається зростання інтенсивності окремих смуг. Отримані результати свідчать про збереження ключових властивостей матеріалу після легування, що робить можливим використання таких модифікованих кристалів у пристроях нелінійної оптики та фотоніки, зокрема там, де потрібне тонке налаштування оптичних параметрів.

Ключові слова: легування, рідкоземельні елементи, кристалічна структура, раманівські спектри.