

STRUCTURE STUDY OF Se-As CHALCOGENIDE GLASSY SEMICONDUCTOR SYSTEM DOPED BY EuF₃ IMPURITY

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The local structure and surface morphology of film samples of chalcogenide glassy semiconductor (CGS) Se₉₅As₅ and Se₉₅As₅(EuF₃)_x(x=0.01÷1 at%) have been studied by X-ray diffraction, Raman scattering and atomic-force microscopy. The “quasi-period” of the structure, the correlation length, the structural elements and chemical bonds that form the amorphous matrix, and the surface morphology of the films of the CGS materials studied have been determined. Interpretation of results obtained has been carried out within the framework of the Elliot voids-cluster model, taking into account the chemical activity of europium ions and the peculiarities of their distribution.

Keywords: amorphous, x-ray diffraction, Raman spectrum, non-crystalline semiconductor, disorder.

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1. INTRODUCTION

Chalcogenide glasses are promising optical materials for creating devices for fiber and integrated optics, as well as for use in information processing systems. This is due to low losses in the transmission band, with a high refractive index (~2–4.5), transparency in the IR spectral region (~0.5–12 μm) and photosensitivity, with high values of nonlinear optical parameters, together with the ability to change the physicochemical properties by variation of the composition, and doping [1-3]. It is known that the electronic properties of CGS material are controlled by negative effective correlation energy (so called U⁻ centers), the beneficial states of which are D⁺ and D⁻ centers with two holes and electrons, respectively [4]. It is possible to change the relative concentration of D⁺ and D⁻ centers by doping with impurities manifested in the form of ions. For this purpose, it is advisable to use rare-earth elements [5], since they mainly manifest themselves as positive ions. In non-crystalline materials, the order in the arrangement of atoms is performed only on a scale covering areas of the order of tens angstroms, there are a short and medium range order of an atoms. Therefore, structure studies of CGS materials consist in determining the short and medium order to which the presented work is devoted.

In this paper the structure of the Se₉₅As₅ and Se₉₅As₅(EuF₃)_x(x=0.01÷1at%) chalcogenide glassy semiconductor (CGS) by the methods of X-ray diffraction, Raman scattering and atomic force microscopy have been investigated. The choice of this composition as a research object is due to the fact that replacing part of the selenium atoms with arsenic atoms whose coordination number is greater than that of selenium results in partial destruction of the Se₈ rings, stitching the ends of the chain molecules and branching of the chain structure. At the same time, the

average value of the coordination number increases and the crystallization-resistant glassy material with stable matrix is obtained. Advantage of study of such objects is due to the fact that the determined parameters of the local structure will be stable, which will make it possible to express promising areas of their application. The use of EuF₃ for doping is due to the fact the Eu, as a chemically active element, can form new structural elements with selenium atom, as well as participating, as a positive ion will contribute to a change in the relative concentration of charged centers, which will affect its electronic properties. This will help to find ways for the practical application of the specified CGS material successfully, i.e. to expand its use.

2. EXPERIMENTAL AND SAMPLE PREPARATION

The samples were obtained by fusing elementary substances of special purity in vacuumed to 10⁻³ Torr quartz cells. The synthesis was carried out at a temperature of 1200 K for 10 hours in a rotating furnace followed by cooling in the off-furnace mode with a holding time of at least 5 hours. The impurity concentration was used within 0.001÷1 at %. Samples for measurements were films of thickness 0.5 μm±2 mm. The films were fabricated by thermal evaporation at rate of 0.2–0.5 μm/s in a vacuum of 10⁻⁴ Torr onto cold glass substrates. The Raman spectra were studied on a three-dimensional confocal Raman microscope Nanofinder 30 (Tokyo Instr.) with the excitation wavelength 532nm. The radius of the laser beam incident on the film was ~4 μm. The radiation receiver was a cooled CCD camera (-70°C) operating in the photon counting mode, an exposure time of 20 s with a laser power of 4 mW, and an error in the spectral

resolution of 0.5 cm^{-1} . The x-ray analysis was performed using the D2Phaser diffractometer “Bruker” and using CuK α -rays ($\lambda = 1,5406 \text{ \AA}$) at $2\theta = 5^\circ\text{-}80^\circ$ angular interval. Structural studies, calculations were performed on EVA and TOPAZ programs. The surface morphology of the films has been investigated by atomic-force microscope. All experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

In this paper, the structure of film samples of $\text{Se}_{95}\text{As}_5$ and $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_x(x=0.01\div 1\text{at}\%)$ chalcogenide glassy semiconductor have been studied by X-ray diffraction, Raman scattering and atomic force microscopy. Fig. 1 indicates the angular distributions of X-ray diffraction intensity for $8 \mu\text{m}$ thick film samples $\text{Se}_{95}\text{As}_5$, $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_{0.25}$, $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_1$ in the range of diffraction angles 2θ from 5 to 80° (θ is the Bragg angle). It can be seen that the general shape of these patterns is the same for pure and doped by EuF_3 impurity for glassy system Se-As. In the range of X-ray diffraction patterns (from 5° to 80°), the glasses look similar because they exhibit two halo (or broad) diffraction peaks located at different values of 2θ between $18^\circ\text{-}38^\circ$ and $46^\circ\text{-}60^\circ$, where the broad highs indicate their amorphous.

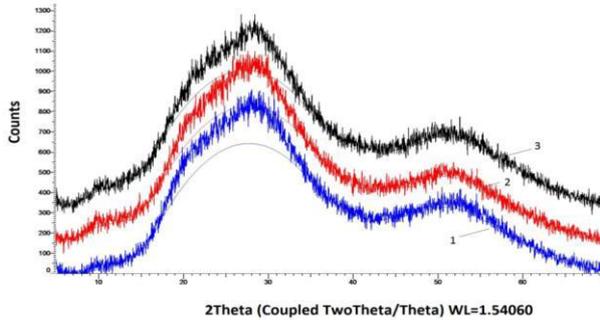


Fig.1. X-ray diffraction patterns of glassy films 1 - $\text{Se}_{95}\text{As}_5$, 2 - $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_1$, 3- $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_{0.25}$

X-ray diffraction patterns of CGS, as in most other glasses [6-8], has a narrow maximum, the so-called first sharp diffraction peak (FSDP), which

differs from others by an anomalous temperature dependence and pressure [9-12]. FSDP on the x-ray diffraction patterns of CGS is usually associated with the existence of ordering on the scales of medium order [6, 13–18]. For glassy materials with tetrahedral structural units, Elliott proposed the void –cluster model [13,14]. According to this model, in such materials, groups of atoms forming clusters are separated from each other by voids or regions with a reduced atomic density. According to [20], a void-cluster model is acceptable for most CGSs. Due to the mutual repulsion of electrons of solitary pairs on the chalcogen atoms, they have a low packing density, and the presence of voids is a characteristic feature of their structure. In this regard, the analysis of the results on x-ray diffraction in the region corresponding to the FSDP was carried out within the framework of the nanostructured features of chalcogenide glasses. Structure parameters, i.e. R - “quasi-period” of structure or atomic density fluctuations [13,14,20], the repeatability of which in a certain region of correlation may cause the appearance of FSDP, L is the correlation length (size of MRO regions) in which the periodicity of the fluctuations of atoms is maintained, were calculated according to the formulas [17]

$$R \approx 2\pi/Q_1, \quad (1)$$

$$L \approx 2\pi/\Delta Q_1, \quad (2)$$

where Q_1 is the value of the scattering vector, corresponding to the position of FSDP and defined by the formula $Q_1=4\pi\sin\theta/\lambda$, ΔQ_1 is the width corresponding to half the amplitude of the FSDP maximum. The obtained values of the parameters characterizing the FSDP and the structure of the films studied are listed in the table. Using the formula proposed in [11,15] and connecting the position of the FSDP Q_1 with the diameter of the nanovoids (D),

$$Q_1 = 2\pi/D, \quad (3)$$

we estimated the values of D . The results obtained are also presented in the table.

Table

The values of the parameters of the short range and medium orders of pure and doped by EuF_3 impurity of $\text{Se}_{95}\text{As}_5$ glassy semiconductor

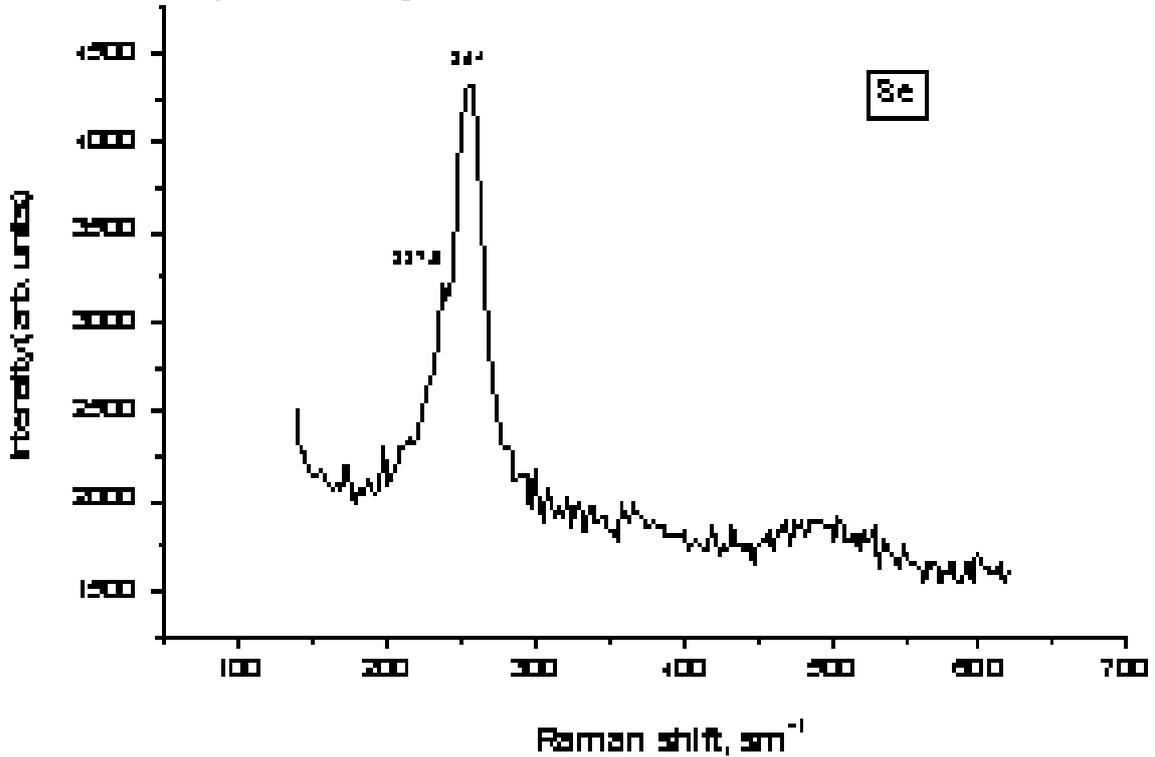
XCI	$2\theta,^\circ$	$FWHH,^\circ$	$Q_1, \text{ \AA}^{-1}$	$\Delta Q_1, \text{ \AA}^{-1}$	$R, \text{ \AA}$	$L, \text{ \AA}$	$D, \text{ \AA}$
$\text{Se}_{95}\text{As}_5$	28,05	13,895	1,9763	0,9597	3,1776	6,54437	3,654
$\text{Se}_{95}\text{As}_5+0.25\text{at}\%\text{EuF}_3$	27,536	13,628	1,9408	0,9418	3,2357	6,668	3,7211
$\text{Se}_{95}\text{As}_5+1\text{at}\%\text{EuF}_3$	26,837	14,819	1,8924	1,0406	3,3184	6,0349	3,81619

The authors [10] analyzed the formulas proposed by various researchers [13,14] to determine the distances of interatomic correlations or distances between voids, and showed that, in all cases, the results obtained are close to the values of the diameter of voids obtained from formula (3).

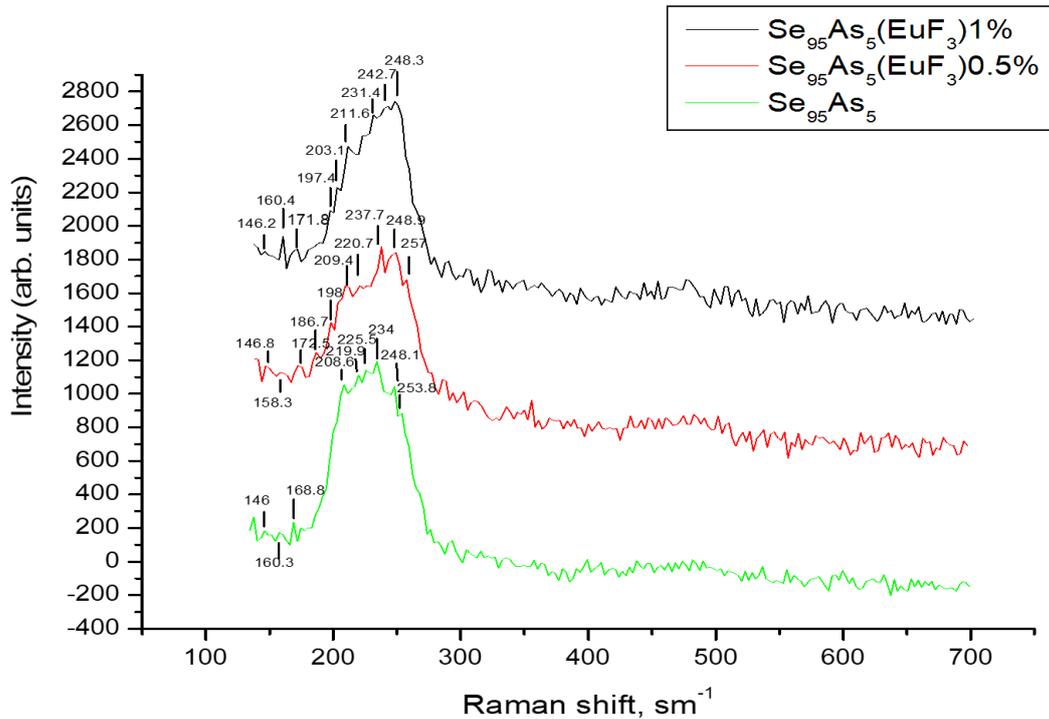
Fig. 2 shows the Raman spectrum of amorphous selenium (fig. 2a) and $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_x(x=0;0.5;1 \text{ at}\%)$ systems films (fig. 2b). The spectrum of amorphous selenium consists of a wide at 254 cm^{-1} and narrow maximum at 236.8 cm^{-1} frequency corresponding to the vibration of Se_8 ring molecules and –Se-Se- chain

molecules [21, 22]. Doping selenium by arsenic the maximum at 254 cm⁻¹ (curve 1 in fig. 2b) is weakened which is due to the rupture of part of the ring molecules. The emerging peaks in the frequency range of 209÷220 cm⁻¹ are associated with the As₄Se₄ type of molecular fragment, and the peak 225 cm⁻¹ also observed in all CGS systems containing As and Se

atoms and is attributed to the AsSe₃ structural elements [21,23]. The weak peak at 170 cm⁻¹ is observed in all spectra shown in fig. 2b which is the associated with oscillations of homopolar coupling As – As [24].



a)



b)

Fig. 2. Raman spectra of the Se (a) and glassy systems Se- As, Se-As-EuF₃ (b)

Adding of EuF_3 impurity in the $\text{Se}_{95}\text{As}_5$ system leads to change in the spectra (curve 2 and 3 in fig. 2b). The peak at 254 cm^{-1} disappears completely, which is apparently due to the fact that europium, as chemically active, more effectively causes destruction of ring molecules and forms bridging bonds between the chains, promotes the polymerization of macromolecules, stitches the ends of polymer chains into a pyramidal structure. Europium due to its high chemical activity has a stronger effect on the structure than arsenic atoms and contributes to the establishment of grid-chain structure. New peaks appearing in the frequency range $170 \div 240\text{ cm}^{-1}$ appear to be related to the formation of the new structural elements with the participation of europium atoms, since europium as chemically active element in different structural elements can replace arsenic.

For defining of the electronic processes mechanism and the use of the film for practical purposes, an important role is played by the structure and quality of the surface. For this purpose, the effect of the EuF_3 impurity on the relief and surface

properties of $\text{Se}_{95}\text{As}_5$ has been investigated. In fig. 3 shows the AFM 3D image of the relief of the $\text{Se}_{95}\text{As}_5$ CGS composition (a) and $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_x$ ($x=0.01;0.1$ at.%) (b,c). The AFM study of the relief shows that the relief of the samples varies greatly when the impurity of the rare-earth compound EuF_3 is introduced into the initial $\text{Se}_{95}\text{As}_5$ composition. The relief of the $\text{Se}_{95}\text{As}_5$ samples containing EuF_3 is gradually smoothed out. As can be seen, from fig. 3(c) the surface becomes even smoother with increasing EuF_3 content. This gives us reason to judge that EuF_3 at a high content (0.5-1at%) leads to the formation of a homogeneous surface of the sample. It can be seen that the surface of the composition $\text{Se}_{95}\text{As}_5$ and $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_x$ ($x=0.01;0.1$ at.%) is different, that is, structural changes occur [17].

The histogram of the surface heterogeneity (fig. 4) shows that the introduction of EuF_3 into the $\text{Se}_{95}\text{As}_5$ composition smoothes the relief of the sample. It is also shown that the *rms* roughness of the surface of the sample $\text{Se}_{95}\text{As}_5$ is 50-250 nm, $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_{0.01}$ is 100-300 nm, and for the $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_{0.1}$ is 150-250 nm.

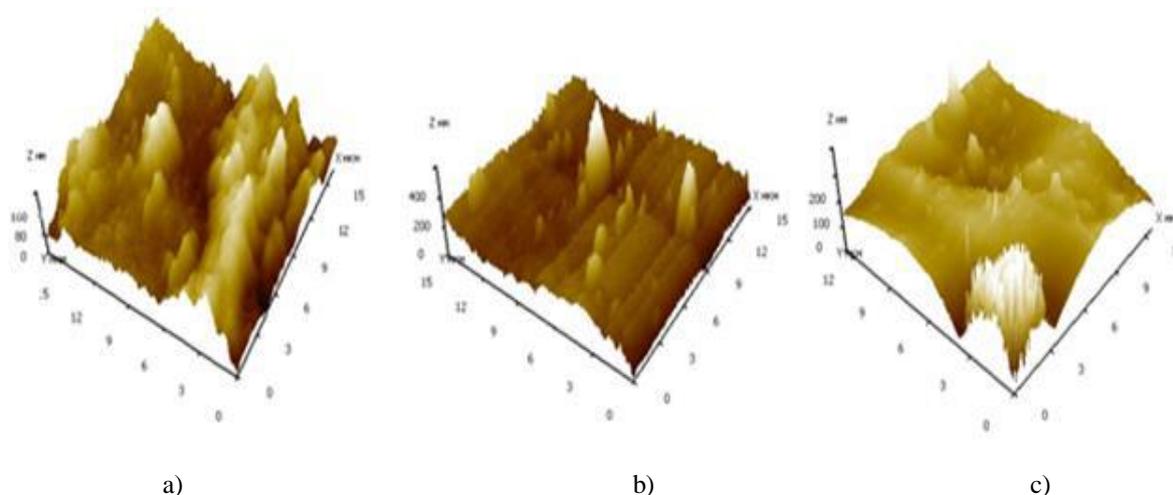


Fig.3. AFM 3D relief image of the $\text{Se}_{95}\text{As}_5$ (a), $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_{0.01}$ (b), $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_{0.1}$ (c)

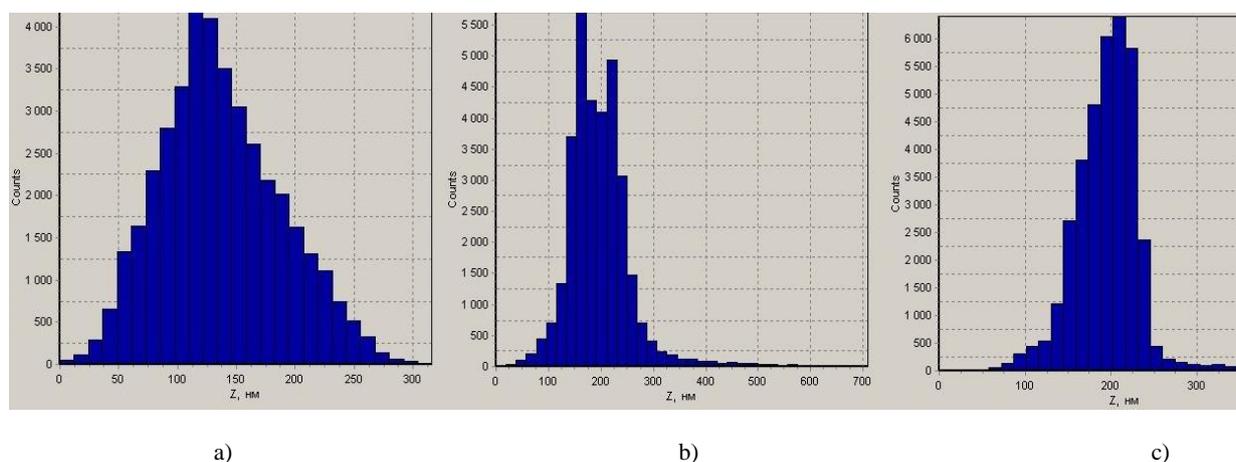


Fig.4. The histogram of the values of the image elements and the surface roughness of $\text{Se}_{95}\text{As}_5$ (a), $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_{0.01}$ (b), $\text{Se}_{95}\text{As}_5(\text{EuF}_3)_{0.1}$ (c)

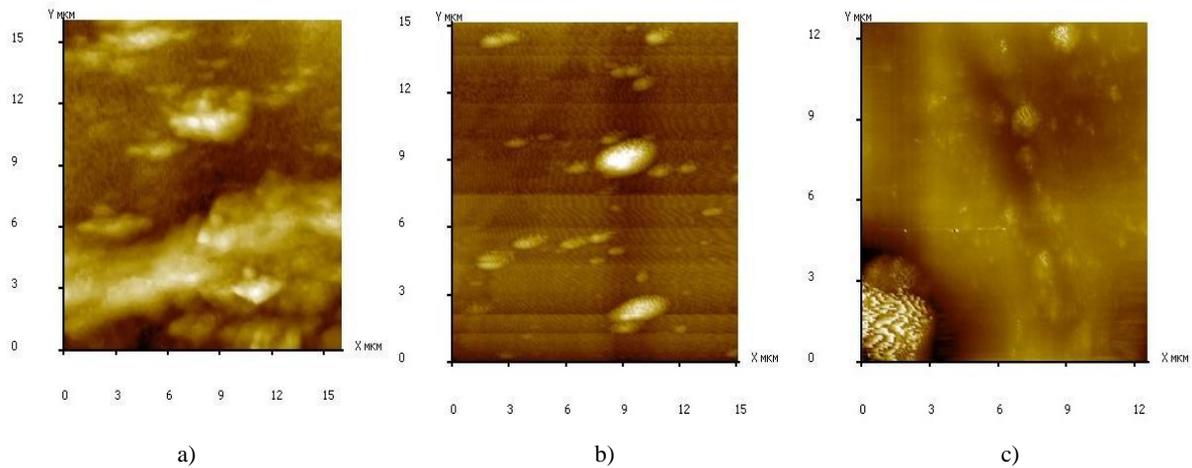


Fig.5. AFM 2D relief images of the Se₉₅As₅ (a), Se₉₅As₅(EuF₃)_{0.01} (b), Se₉₅As₅(EuF₃)_{0.1} (c)

Fig. 5 shows the AFM 2D relief images of Se₉₅As₅ and samples containing EuF₃ in various percentages. From fig. 5 that with an increase in the EuF₃ content, the relief of the sample changes markedly. This picture is a consequence of the fact that at low content of EuF₃ appears as ions Eu³⁺, F⁻ and fills the existing voids. This eliminates the inhomogeneities associated with the density deficit, and also reduces the concentration of broken bonds, which leads to a decrease in the density of localized states in the mobility gap associated with charged defects (*U*⁻ centers). If we assume that the introduced EuF₃ appear as Eu³⁺ and F⁻ ions and in small quantities, mainly fill the existing voids, then they will help to eliminate the heterogeneity associated with the density deficit in these areas and at the same time due to chemical activity contribute to the formation of the EuSe₃, SeF₆ type of structural element as a result of which the concentration of dangling bonds decreases, accompanied by a decrease in the density of localized states in the mobility gap associated with charged defects (*U*⁻ centers) and about weakening of electrostatic potential fluctuations.

4. CONCLUSION

The structure of the Se₉₅As₅(EuF₃)_x (*x* = 0; 0,5; 1 at%) CGS systems have been studied by X - ray diffraction, Raman scattering and atomic force microscopy. Interpretation of the results obtained have been carried out within the framework of the Elliott void-cluster model and the model of charged defects, the parameters of the local structure, in particular, the “quasi-period” density fluctuations, the correlation length (sizes of MRO regions), and diameters of nanovoids have been determined. A comparative analysis of the Raman spectra of the investigated films by literature data on Raman scattering of such materials the base structure elements and chemical bonds forming the amorphous matrix of Se₉₅As₅ CGS have been determined. Changes in the spectrum of Se₉₅As₅ doped by EuF₃ impurity were attributed to the destruction of some bonds and structural elements, and by the formation the new bonds with participation of europium atoms.

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