CZU: 621.315.592:548.55

GROWTH AND CHARACTERIZATION OF *Eu* DOPED *GaSe* SINGLE CRYSTALS BY X-RAY DIFFRACTION AND RAMAN SPECTROSCOPY

Dumitru UNTILA[*,**], *Igor EVTODIEV*[*,**], *Iuliana CARAMAN*[***],
Valeriu KANTSER[*,**], *Nicolae SPALATU*[****], *Liliana DMITROGLO*[*],
Silvia EVTODIEV[*], *Dorin SPOIALĂ*[*], *Irina ROTARU*[*], *Petru GAŞIN*[*]

[*]*Moldova State University*
[**]*Ghitu Institute of Electronic Engineering and Nanotechnologies, ASM*
[***]*Vasile Alecsandri University of Bacau (Romania)*
[****]*Tallinn University of Technology (Estonia)*

GaSe single crystals doped with *Eu* (0.025, 0.05, 0.5, 1.0 and 3.0 at%) were grown by Bridgman method using *Ga*, *Se* and *Eu* elementary components. The crystalline structure and vibration modes of the *GaSe*: *Eu* crystals lattice were studied by X-ray diffraction and Raman spectroscopy. *Eu* atoms arranged in the van der Waals space of *GaSe*: *Eu* crystals form *Eu-Se* valence bonds and restructure hexagonal lattice of *GaSe* leading to $EuGa_2Se_4$ crystallites formation. Defects generated by $EuGa_2Se_4$ crystallites lead to broadening and shifting of single phonon peaks present in Raman spectra towards shorter wavenumbers, and at the same time, activate the longitudinal optical vibrations of *EuSe* sublattice.

Keywords: GaSe, doping, Eu, XRD, Raman.

CREŞTEREA ŞI CARACTERIZAREA MONOCRISTALELOR DE *GaSe*: *Eu* PRIN DIFRACŢIA RAZELOR X ŞI SPECTROSCOPIA RAMAN

Monocristalele de *GaSe* nedopate şi dopate cu *Eu* în cantităţi de 0.025, 0.05, 0.5, 1.0 şi 3.0% at. au fost crescute prin metoda Bridgman din componente elementare *Ga*, *Se* şi *Eu*. Structura cristalină şi modelele de vibraţie a reţelei cristalelor de *GaSe*:*Eu* au fost studiate prin difracţia razelor X şi spectroscopia Raman. Atomii de *Eu* localizaţi în spaţiul van der Waals al cristalelor de *GaSe*:*Eu* creează legături de valenţă *Eu-Se* şi restructurează reţeaua hexagonală a compusului *GaSe,* conducând la formarea cristalitelor de $EuGa_2Se_4$. Defectele generate de cristalitele de $EuGa_2Se_4$ duc la lărgirea şi deplasarea benzilor monofononice de difuzie Raman spre numere de undă mici şi, totodată, activează vibraţiile optice longitudinale ale subreţelei *EuSe*.

Cuvinte-cheie: GaSe, dopare, Eu, XRD, Raman.

Introduction

Ga and *In* compounds with chalcogens (*S*, *Se*, *Te*), and in particular the gallium monoselenide (*GaSe*), are semiconductors revealing mechanical, electrical and optical anisotropies [1-5]. Materials anisotropy is determined by their lamellar structure. They are composed of elementary planar packings arranged in the *Se-Ga-Ga-Se* order. These packings are bonded one to another by van der Waals forces [6]. Packings are bonded inside by ionic-covalent forces [7]. The elementary layers are packed along C_6 crystallographic axis. This arrangement as well as weak forces between the packings allows the single crystals cleavage in parallel lamellae, having smooth surfaces and sub micrometric thicknesses. Anisotropy of the structural properties, along with the optical and luminescent ones, determines the researchers' interest on physical properties of *GaSe* compound.

Four polymorphic modifications of *GaSe* crystals depending on layers stacking mode and their number in the elementary cell are known. XRD analysis of the gallium selenide grown by Bridgman method demonstrates the prevalent growth of *ε-GaSe* modification [8], although a low content of *γ –GaSe* is present as well. *ε-GaSe* polytype being a semiconductor without inversion center belongs to 6m2 point group and is a material with high nonlinear susceptibility in the range from 600-650 nm up to 18 μm [9, 10]. The structural characteristics of *GaSe* crystals determine the intercalation mode of heterogenic atoms in the crystal lattice. Lattice defects curing process results in the storage of the impurity atoms into van der Waals space localized between packings, contributing in this way to the strengthening of bonds between *Se* atomic planes. At certain concentrations and certain crystal preparation temperatures the impurity atoms form compounds with *Se* atoms belonging to neighboring packings and clusters which modify properties of basic crystals. Both structural changes and the

presence of heterogeneous compounds in the $A^{III}B^{VI}$ semiconductors, and *GaSe* in particularly, are identified by XRD and Raman methods [11-16].

Both structural and composition changes which occur in *Eu* doped *GaSe* single crystals (doping range 0.025 at% up to 3.0%).

Experimental details

Undoped *GaSe* and *Eu* doped single crystals were grown by Bridgman method [17]. *Eu* doping was made during the synthesis process. Ingots of 15-20 g mass were obtained. *Eu* distribution homogeneity was verified by atomic emission spectroscopy. Phase composition, crystalline structure and interaction mechanisms of *Eu* atoms with compound elements (*Ga* and *Se*) were studied by XRD using a Rigaku Ultima IV diffractometer (radiation *CuK$_\alpha$*, $\lambda = 1.5406$ Å, 40 kV at 40 mA; silicon strip detector D/teX Ultra, Rigaku, Japan) in the Bragg–Brentano (θ–2θ) geometry and by Raman spectroscopy using a high resolution micro-Raman spectrometer Horiba Jobin Yvon HR800, equipped with multichannel CCD detection system in backscattering configuration. The incident *Nd-YAG* laser ($\lambda = 532$ nm) and 10 μm spot size diameter, was used for excitation.

Experimental results and discussions

Preparation of undoped and Eu doped GaSe single crystals. Undoped and *Eu* doped *GaSe* single crystals were grown by vertical Bridgman method in quartz ampoules (~15 mm internal diameter). The quartz ampoules were etched for 30 min by acid solution (*HF*: *HNO*3 = 1:1), and rinsed in distilled and double-distilled water, the purifying process ending with a thermal annealing for few hours at 1250K. Ampoules have been filled in with primary elements (*Ga* (5N) and *Se* (4N)) taken in stoichiometric quantities and *Eu* (3N) in quantities of 0.025, 0.05, 0.5, 1.0 and 3.0 at%. Ampoules have been pumped down to the pressure of residual gases - 10^{-6} Torr and sealed afterwards. The compounds synthesis was made in a furnace having three temperature zones, and tilted to ~30˚ relative to horizon. The temperature increased for 2 hours up to 700K in the first temperature zone (and set as constant), where the ampoule was placed initially, while in the second temperature zone (containing melted *Ga*) it was set to 1350K. The ampoule containing melted materials was moved through the second zone (1350K) with a velocity of 2 cm/h. The compound synthesis time was 12 hours. The furnace was moved into vertical position immediately after the synthesis process ended, and the temperature was decreased down to 1280K. The melt was moved between zones 2 and 3 with a velocity of 2.0 mm/h. The temperature gradient of 30˚C/cm was set for zone 3. The typical image of an obtained single crystal is shown in Fig.1.

Fig.1. The image of *GaSe* single crystal doped with 0.025 at% *Eu*.

GaSe samples (25 mg), coming from three regions of the single crystal, have been used for Atomic Emission Spectroscopy (AES) analysis. The emission spectra of the atoms were excited by electric discharge in-between graphite electrodes. The emission line of *Eu* atoms with $\lambda = 2906.68$ Å was taken in the quality of analytic spectral line. The line characteristic for *Ga* atoms emission ($\lambda = 2943.64$ Å) was taken as spectral comparison line. The *Eu* concentration determination demonstrated that its concentration differs max 3% along the crystal's ingot.

Crystalline structure of undoped and Eu doped GaSe single crystals Diffraction peaks from the planes systems perpendicular to C_6 crystallographic axis are present in the XRD patterns of undoped *GaSe* crystals (Fig.2). The maximal relative intensity corresponds to the X ray diffraction from planes system (0 0 4).

XRD pattern of *GaSe* single crystals doped with 0.025% at *Eu* (Fig.3, a) contain both intense peaks from the planes characteristic for ε-*GaSe* and few peaks corresponding to *β* and *δ-GaSe* phases, and Ga_2Se_3 compound. The filling of *Ga* vacancy with *Eu* leads to both crystalline lattice deformation and to widening of XRD lines since the *Eu* atomic radius is about 1.4 times bigger than *Ga* atomic radius. The broadening by 0.005˚ of XRD

peaks from the plane system with the Miller indexes (0 0 4) was observed at *GaSe* crystals doping with 0.5 at% *Er* [18].
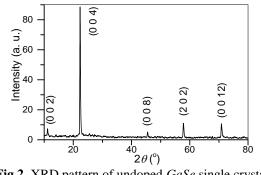

Fig.2. XRD pattern of undoped *GaSe* single crystal.

To be underlined that diffraction peaks resulting from the crystallographic planes characteristic for Ga_2Se_3 compound and those oblique oriented to the C_6 axis of *GaSe* crystals doped with 0.025 at% *Eu* are well highlighted at high diffraction angles and have a relatively low intensity being compared to the ones resulting from the perpendicularly oriented planes to C_6 axis. It can be seen (Fig.3, b), the XRD patterns of *GaSe* crystals doped with 0.05 at% *Eu* reveal both the reflexes characteristic for β and δ-*GaSe* polytypes present in crystals doped with 0.025 at% *Eu* and few new peaks determined by the crystallographic planes (4 2 4), (0 0 8) and (6 10 2) characteristic for $EuGa_2Se_4$. In Fig.3, c, the XRD pattern of *GaSe* crystals doped with 1.0 at% is presented. As can be observed from the comparison of this pattern with those presented in Fig.3, b, a 20 times concentration increase results in new peaks formation at $2\theta = 28.20°$, $33.18°$ and $51.78°$. These peaks are identified as diffraction from (1 0 1), (8 0 0), and (6 10 2), planes respectively, characteristic for $EuGa_2Se_4$ crystals. Moreover, new low intensity peaks are formed in the immediate proximity of reflexes observed at $2\theta = 22.30$ and $71.06°$ determined by the presence of β and δ-*GaSe* polytype.
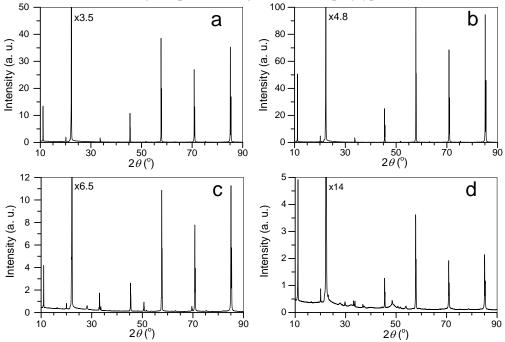

Fig.3. XRD patterns of *GaSe* crystals doped with 0.025 at%, 0.05 at%, 1.0 at% and 3.0 at% *Eu*.

As mentioned above, the filling of *Ga* vacancies with *Eu* atoms leads to elementary cell deformation. This fact can contribute to both the atomic planes displacement and formation of these two polytype. These changes are observed much better in the XRD pattern of *GaSe* crystals doped with 3.0 at% *Eu* (Fig.3, d). This pattern has peaks belonging to the $EuGa_2Se_4$ compound which are more numerous and intense. The systematized results of XRD analysis are presented in the Table 1.

Thus as a result of *Eu* doping in the *GaSe* lattice the composite *EuGa$_2$Se$_4$* is formed. Some reflexes of this compound are present starting with concentration of 0.05 at%. These crystallites presence increase at *Eu* concentration increase. It is well known that atomic impurities cure defects in the *Ga* sublattice, while their excess is accumulated in the van der Waals space between packings. *Eu*, being located in the van der Waals space of two neighboring *Se* planes, form clusters of *EuGa$_2$Se$_4$* crystallites. Probably, the formation process of these crystallites occurs in a few steps. Initially under influence of *Eu* atoms located in the van der Waals space both the formation of *EuSe* bonds occur and translation of elementary *Se-Ga-Ga-Se* packings, which resulted in *Ga$_2$Se$_3$* crystallites formation. Thus by combining of *Ga$_2$Se$_3$* with *EuSe* pair the stable *EuGa$_2$Se$_4$* compound is formed.

Table 1

Interpretation of XRD patterns of *GaSe* crystals doped with *Eu*

2θ (°), experimental				ICDD-JCPDS cards				
0.025	0.05	1.0	3.0	Compound	PDF	2θ (º)	I	h k l
		22.20		*β-GaSe*	A	22.21	71.7	0 0 4
				δ-GaSe	B	22.217	100	0 0 8
22.30	22.30	22.30		*GaSe*	C	22.26	100.0	0 0 4
22.34				*GaSe*	D	22.338	999	0 0 6
				EuGa$_2$Se$_4$	E	22.34	6.6	1 5 1
			23.14	*EuGa$_2$Se$_4$*	E	23.14	75.2	4 2 2
		27.86		*GaSe*	C	27.60	4.0	1 0 0
	28.20			*GaSe*	C	28.00	6.0	1 0 1
			29.70	*β-GaSe*	A	29.67	2.0	1 0 2
				EuGa$_2$Se$_4$	E	29.71	51.9	6 2 2
		29.90		*EuGa$_2$Se$_4$*	E	29.92	57.0	2 6 2
		32.24		*β-GaSe*	A	32.25	100	1 0 3
		32.86		*EuGa$_2$Se$_4$*	E	32.73	8.9	0 4 4
		33.10		*Ga$_2$Se$_3$*	F	33.074	23	$\overline{2}$ 0 2
		33.18	33.18	*EuGa$_2$Se$_4$*	E	33.19	32.2	8 0 0
		33.62		*EuGa$_2$Se$_4$*	E	33.57	13.1	0 8 0
			33.70	*GaSe*	C	33.80	2.0	0 0 6
				EuGa$_2$Se$_4$	E	33.79	6.8	4 2 4
			36.82	*EuGa$_2$Se$_4$*	E	36.83	100	5 7 1
		37.16		*EuGa$_2$Se$_4$*	E	37.14	8.4	8 2 2
			37.34	*EuGa$_2$Se$_4$*	E	37.33	15.1	8 4 0
			37.60	*EuGa$_2$Se$_4$*	E	37.59	24.5	4 8 0
33.78	33.70			*δ-GaSe*	B	33.800	25	1 0 7
				EuGa$_2$Se$_4$	E	33.79	6.8	4 2 4
				GaSe	C	33.8	2.0	0 0 6
		45.16		*EuGa$_2$Se$_4$*	E	45.13	1.0	2 8 4
45.32	45.34			*β-GaSe*	A	45.321	7	0 0 8
				δ-GaSe	B	45.320	1	0 0 16
45.46	45.48	45.44		*GaSe*	D	45.587	18	0 0 12
				β-GaSe	A	45.32	0.7	0 0 8
	45.60		45.58	*GaSe*	C	45.62	10.0	0 0 8
				EuGa$_2$Se$_4$	E	45.58	1.2	3 9 3
		48.18		*EuGa$_2$Se$_4$*	E	48.21	3.5	3 7 5
		48.30	48.44	*EuGa$_2$Se$_4$*	E	48.5	0.3	9 5 3
			48.56	*GaSe*	C	48.54	17.0	1 1 0
				β-GaSe	A	48.51	61.4	1 1 0
		50.64		*GaSe*	D	50.651	40.2	0 1 11
				EuGa$_2$Se$_4$	E	50.62	20.2	6 2 6
			50.72	*Ga$_2$Se$_3$*	G	50.716	<1	1 1 6
		50.76		*EuGa$_2$Se$_4$*	E	50.76	19.3	12 0 0
51.46	51.46			*Ga$_2$Se$_3$*	H	51.204	10	0 1 6
				EuGa$_2$Se$_4$	E	51.35	2.6	0 12 0
	51.66			*EuGa$_2$Se$_4$*	E	51.53	11.7	10 6 2
	51.78		51.78	*EuGa$_2$Se$_4$*	E	51.81	18.6	6 10 2
			53.90	*EuGa$_2$Se$_4$*	E	53.75	8.2	12 4 0
				β-GaSe	A	53.97	28.1	1 1 4
57.50	57.50			*GaSe*	D	57.537	51	2 0 2
57.68		57.66		*Ga$_2$Se$_3$*	F	57.686	4	$\overline{4}$ 2 1
57.74				*GaSe*	D	57.725	48	1 0 13
57.90	57.94	57.82	57.92	*GaSe*	C	57.92	27.0	2 0 2
				EuGa$_2$Se$_4$	E	57.87	7.8	0 0 8
		63.08		*EuGa$_2$Se$_4$*	E	63.16	0.3	7 5 7
		69.38		*GaSe*	D	69.352	53	1 0 16
		69.58		*Ga$_2$Se$_3$*	F	69.549	15	$\overline{1}$ 5 4
70.58		70.76		*β-GaSe*	A	70.60	1.3	0 0 12
				δ-GaSe	B	70.620	2	0 0 24
70.76				*Ga$_2$Se$_3$*	F	70.745	2	$\overline{1}$ 7 3
70.82	70.86			*Ga$_2$Se$_3$*	G	70.847	<1	6 14 4
70.96		70.96		*β-GaSe*	A	70.96	7.7	1 0 11
				δ-GaSe	B	70.963	9	1 0 22
71.02	71.06		71.04	*GaSe*	C	71.02	17	0 0 12
				δ-GaSe	B	71.099	20	2 0 14
75.30	75.36	75.24		*β-GaSe*	A	75.34	0.1	2 0 8
84.82				*β-GaSe*	A	84.79	1.7	0 0 14
				δ-GaSe	B	84.779	2	0 0 28
85.06	85.12	85.02		*β-GaSe*	A	85.06	0.8	2 0 10
85.32	85.38	85.28	85.34	*GaSe*	C	85.36	20.0	0 0 14

*A - 01-078-1927; B - 29-0628; C - 00-037-0931; D - 81-1971; E - 01-070-2524; F - 76-0975; G - 33-0568; H - 20-0437.

Raman scattering Lattice vibration modes and in particularly Raman spectra of ε-*GaSe* crystals are well studied in many works [12, 19-21]. The symmetry center is missing for the elementary cell of ε-*GaSe* polytype, so some vibration modes of the lattice are active in both absorption/reflection FTIR and in Raman spectra. The Raman spectra of ε-*GaSe* crystals at room temperature consists of bands active at 19 cm^{-1} (E'), 59 cm^{-1} (E''), 134 cm^{-1} (A$_1$'), 213 cm^{-1} (E'$_{TO}$), 253 cm^{-1} (E'$_{LO}$), and 308 cm^{-1} (A$_1$') [21]. The Raman spectra of *GaSe* crystals doped with 0.025 at% and 0.05 at% *Eu* are presented in Fig.4. Raman spectrum of *GaSe* single crystal doped with 0.025 at% *Eu* (Fig.4, curve 1) contains four intense bands with peak intensities at 132.7 cm^{-1}, 211.9 cm^{-1}, 251.0 cm^{-1}, and 306.9 cm^{-1}, which are identified as basic vibrations of *ε-GaSe* polytype lattice. Moreover, in this spectrum a low intensity band appears at 156.6 cm^{-1}. This band is assigned to the LO phonons ($\nu \sim_{LO}$) of *EuSe* crystals (156 cm^{-1}) [22].

The low quantity of metal atoms, and especially those of groups II and III, cures the structure defects of *GaSe* lattice. A proof of this fact is the amplification of absorption band of the *n* = 1 excitonic band [1]. The excess of impurity atoms is accumulated in the van der Waals space and in some concentrations and temperature conditions generate bonds with *Se* atoms of the neighboring packings.
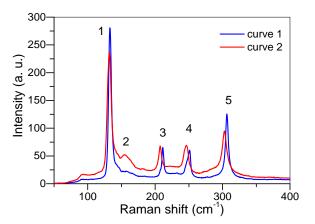
Fig.4. Raman spectra of *GaSe* crystals doped with 0.025 at% (curve 1) and 0.05 at% *Eu* (curve 2).

Table 2

Assignment of the Raman bands observed in *GaSe:Eu* crystals (0.025 at% and 0.05 at.%)

C_{Eu} Nr.	0.025 at% Wave number, cm^{-1}	I, a. u.	0.05 at% Wave number, cm^{-1}	I, a. u.	Assignment		Wave number, cm^{-1}	Ref.
1	132.7	280.8	132.2	237.0	*GaSe*	E'	134	[12, 19, 21]
2	156.6	22.8	155.1	52.5	*EuSe*	LO phonon	156	[22]
3	211.9	65.4	207.4	68.2	*GaSe*	E'	214	[19, 23]
4	251.0	60.3	246.4	69.2	*GaSe*	E' (LO)	253	[12, 19, 21]
5	306.9	125.7	302.8	94.9	*GaSe*	A'_1	307	[12, 19]

An intensity increase of the band assigned to the single phonon vibration of *EuSe* (156 cm^{-1} [22]) is observed in Raman spectra (Fig.4, Table 2) for *Eu* concentration increase (0.025 - 0.05 at%). Thus one can conclude that $EuGa_2Se_4$ compound is formed. This fact is also confirmed by XRD measurements (Table 1). Both Raman bands broadening and their shift towards shorter wavenumbers (by 4-5 cm^{-1}) prove $EuGa_2Se_4$ crystallites formation. As it is known from literature [24], intense single peaks (A'_1 and E'), in Raman spectra of *GaSe:S* single crystals, shift towards shorter wavelength with increasing *S* content. A confined phonons model [25] was considered for the understanding of the experimental results, as well as data given in [26, 27].

Conclusions

The growth of *GaSe* single crystals, both undoped and *Eu* doped was done by Bridgman method and use of *Ga*, *Se* and *Eu* elementary components. The dopant concentration was: 0.025, 0.05, 0.5, 1.0 and 3.0 at%. The cure of *Ga* vacancies in *GaSe* occurs at low dopant concentration (0.025 at%), while at concentration increase, the *Eu* atoms are accumulated in the van der Waals space of the crystals. So, at concentrations of 0.05-3 at% *Eu* atoms form $EuGa_2Se_4$ crystallites in *GaSe* single crystals, fact confirmed by XRD. The formation process of $EuGa_2Se_4$ crystallites probably occurs in a few steps. Initially under the influence of *Eu* atoms, located in the van der Waals space, both the formation of *EuSe* bonds and translation of elementary *Se-Ga-Ga-Se* packings occur. This fact leads to Ga_2Se_3 crystallites formation. The stable $EuGa_2Se_4$ compound is formed by combination of Ga_2Se_3 with *EuSe*. The presence of $EuGa_2Se_4$ crystallites create a distortion of the hexagonal lattice of *GaSe* compound, fact that leads to the broadening and shifting of phonon peaks present in Raman spectra towards shorter wavenumbers. The arrangement mode of atomic planes of the $EuGa_2Se_4$ crystallites determines LO vibrations of *EuSe* sublattice, the latter being active in Raman spectra.

References:

1. EVTODIEV, I. Anisotropy of the exciton processes in *GaSe* crystals with low *S* and *Te* concentrations. In: *J. Nano-electron. Optoelectron*, 2009, vol.4, p.76-88.
2. AUGELLI, V., MANFREDOTTI, C., MURRI, R., VASANELLI, L. Hall-mobility anisotropy in *GaSe*. In: *Phys. Rev. B: Condens. Matter: Condens. Matter.*, 1978, vol.17, no.8, p.3221-3226.
3. ALLAKHVERDIEV, K., FERNELIUS, N., GASHIMZADE, F., GOLDSTEIN, J., SALAEV, E., SALAEVA, Z. Anisotropy of optical absorption in *GaSe* studied by midinfrared spectroscopy. In: *J. Appl. Phys.*, 2003, vol.93, no.6, p.3336-3339.
4. CUCULESCU, E., EVTODIEV, I., CARAMAN, I. The anisotropy of the optical properties of ternary semiconductors formed by elements of III and VI groups. In: *Phys. Status Solidi C*, 2009, vol.6, no.5, p.1207-1212.
5. MOLLOY, J.F., NAFTALY, M., ANDREEV, Y., KOKH, K., LANSKII, G., SVETLICHNYI, V. Absorption anisotropy in sulfur doped gallium selenide crystals studied by THz-TDS. In: *Opt. Mater. Express*, 2014, vol.4, no.11, p.2451-2459.
6. DZYALOSHINSKII, I.E., LIFSHITZ, E.M., PITAEVSKII, L.P. General theory of van der Waals forces. In: *Phys. Usp.*, 1961, vol.4, no.2, p.153-176.
7. BREBNER, J.L. The optical absorption edge in layer structures. In: *J. Phys. Chem. Solids*, 1964, vol.25, no.12, p.1427-1433.
8. GOBBI, G., STAEHLI, J.L., GUZZI, M., CAPOZZI, V. Spectres excitoniques et propriétés structurales de *GaSe*. In: *Helv. Phys. Acta*, 1979, vol.52, p.337-341.
9. ABDULLAEV, G.B., KULEVSKII, L.A., PROKHOROV, A.M., SAVEL'EV, A.D., SALAEV, E.Y., SMIRNOV, V.V. *GaSe*, a new effective material for nonlinear optics. In: *JETP Lett.*, 1972, vol.16, no.3, p.90-95.
10. ABDULLAEV, G.B., ALLAKHVERDIEV, K.R., KARASEV, M.E., KONOV, V.I., KULEVSKII, L.A., MUSTAFAEV, N.B., PASHININ, P.P., PROKHOROV, A.M., STARODUMOV, Y.M., CHAPLIEV, N.I. Efficient generation of the second harmonic of CO_2 laser radiation in a *GaSe* crystal. In: *Sov. J. Quantum Electron*, 1989, vol.19, nr.4, p.494-498.
11. BELEN'KII, G.L., STOPACHINSKII, V.B. Electronic and vibrational spectra of III-VI layered semiconductors. In: *Sov. Phys. Usp.,* 1983, vol.26, no.6, p.497-517.
12. ALLAKHVERDIEV, K., BAYKARA, T., ELLIALTIOGLU, S., HASHIMZADE, F., HUSEINOVA, D., KAWAMURA, K., KAYA, A.A., KULIBEKOV (GULUBAYOV), A.M., ONARI, S. Lattice vibrations of pure and doped *GaSe*. In: *Mater. Res. Bull.*, 2006, vol.41, p.751-763.
13. MANDAL, K.C., CHOI, M., KANG, S.H., RAUH, R.D., WEI, J., ZHANG, H., ZHENG, L., CUI, Y., GROZA, M., BURGER, A. *GaSe* and *GaTe* anisotropic layered semiconductors for radiation detectors. In: *Proc. of SPIE.*, 2007, vol.6706, p.67060E.
14. CERDEIRA, F., MENESES, E.A., GOUSKOV, A. Splittings and correlations between the long-wavelength optical phonons in the layer compounds *GaSe*, *GaTe*, and $GaSe_{1-x}Te_x$. In: *Phys. Rev. B: Condens. Matter.*, 1977, no.16, p.1648-1654.
15. ERRANDONEA, D., MARTÍNEZ-GARCÍA, D., SEGURA, A., HAINES, J., MACHADO-CHARRY, E., CANADELL, E., CHERVIN, J.C., CHEVY, A. High-pressure electronic structure and phase transitions in mono-clinic *InSe*: X-ray diffraction, Raman spectroscopy, and density functional theory. In: *Phys. Rev. B: Condens. Matter: Condens. Matter.*, 2008, vol.77, no.4, p.045208.
16. HIROHATA, A., MOODERA, J.S., BERERA, G.P. Structural and electrical properties of *InSe* polycrystalline films and diode fabrication. In: *Thin Solid Films*, 2006, vol.510, p.247-250.
17. DHANARAJ, G., BYRAPPA, K., PRASAD, V., DUDLEY, M. *Crystal growth techniques and characterization: an overview.* Springer handbook of crystal growth. Springer, Heidelberg/ Dordrecht/London/New York, 2010.
18. HSU, Y.K., CHEN, C.W., HUANG, J.Y., PAN, C.L., ZHANG, J.Y., CHANG, C.S. Erbium doped *GaSe* crystal for mid-IR applications. In: *Opt. Express*, 2006, vol.14, nr.12, p.5484-5491.
19. HOFF, R.M., IRWIN, J.C., LIETH, R. M.A. Raman scattering in *GaSe*. In: *Can. J. Phys.*, 1975, vol.53, no.17, p.1606-1614.
20. JANDL, S., BREBNER, J.L., POWELL, B.M. Lattice dynamics of *GaSe*. In: *Phys. Rev. B: Condens. Matter.*, 1976, vol.13, p.686-693.
21. GAUTHIER, M., POLIAN, A., BESSON, J.M., CHEVY, A. Optical properties of gallium selenide under high pressure. In: *Phys. Rev. B: Condens. Matter.*, 1989, vol.40, nr.6, p.3837-3854.
22. OUSAKA, Y., SAKAI, O., TACHIKI, M. Theory of Raman scattering in magnetically ordered phases of *EuSe* and *EuTe*. In: *Solid State Commun.*, 1977, vol.23, no.8, p.589-592.
23. ALLAKHVERDIEV, K.R., SALAEV, E.Y., TAGYEV, M.M., BABAEV, S.S., GENZEL, L. Davydov doublets in Raman spectra of *ε-GaSe*. In: *Solid State Commun.*, 1986, vol.59, no.3, p.133-136.

24. KOKH, K.A., MOLLOY, J.F., NAFTALY, M., ANDREEV, Y., SVETLICHNYI, V.A., LANSKII, G.V., LAPIN, I.N., IZAAK, T.I., KOKH, A.E. Growth and optical properties of solid solution crystals $GaSe_{1-x}S_x$. In: *Mater. Chem. Phys.*, 2015, vol.154, p.152-157.
25. ANAND, K., KAUR, J., SINGH, R.C., THANGARAJ, R. Effect of terbium doping on structural, optical and gas sensing properties of In_2O_3 nanoparticles. In: *Mater. Sci. Semicond. Process.*, 2015, vol.39, p.476-483.
26. ARORA, A.K., RAJALAKSHMI, M., RAVINDRAN, T.R., SIVASUBRAMANIAN, V. Raman spectroscopy of optical phonon confinement in nanostructured materials. In: *J. Raman Spectrosc.*, 2007, vol.38, no.6, p.604-617.
27. SINGH, J.P., SRIVASTAVA, R.C., AGRAWAL, H.M., KUMAR, R. Micro-Raman investigation of nanosized zinc ferrite: effect of crystallite size and fluence of irradiation. In: *J. Raman Spectrosc.*, 2010, vol.42, no.7, p.1510-1517.

Prezentat la 05.07.2017