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## Raman spectra of glasses of CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> system

Padlyak B.

Institute of Physical Optics, 23 Dragomanov St., 79005 Lviv, Ukraine  
e-mail: bpadlyak@ifp.lviv.ua

Received: 29.12.2007

### Abstract

Raman spectra of undoped glasses of CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> system with the garnet (Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>) and Ca-gallogermanate (Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>4</sub>O<sub>14</sub>) structures are measured and analyzed. The spectra are interpreted on the basis of comparison to the well known Raman spectra of the garnet crystals with Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> and Ca<sub>3</sub>Sc<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> structures. It is shown that the spectra observed for the glasses of CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> system are almost independent of the basic glass composition. They consist of two broad bands centred near 535 and 825 cm<sup>-1</sup>, which belong to totally symmetric vibrational modes A<sub>1g</sub> of the mixed tetrahedral groups (structural units) (Ge/Ga)O<sub>4</sub> available in the glass network. The interpretation of our results shows good correlation with the structural data obtained with EXAFS spectroscopy.

**Keywords:** germanate glasses, garnet crystals, Raman spectroscopy, vibrational properties.

**PACS:** 42.70.Ce, 78.30.Ly, 63.50.+x.

**UDC:** 535.36

### Introduction

In the recent works [1–6] it has been shown that the glasses of CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> system activated with Cr<sup>3+</sup>, Nd<sup>3+</sup>, Er<sup>3+</sup> and Ho<sup>3+</sup> ions are promising materials for active elements of solid-state lasers. Spectroscopic properties of activator ions in the host materials strongly depend on electron-phonon interaction. Therefore, studies of the vibrational (infrared absorption and Raman) spectra of crystals and glasses should enable better understanding of spectroscopic properties of the transition and rare-earth luminescence centres in the above host materials.

The first communication related to the Raman spectra of the glasses of CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> system has been reported by the authors [7]. In the present work we present more detailed investigations of the Raman spectra of CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> glasses with different compositions and their interpretation obtained on the basis of comparison to the well known Raman and infrared (IR) absorption spectra of their crystalline analogues, in particular those of the garnet crystals Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>.

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## Experimental details

Undoped CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> glasses of different compositions were obtained in corundum crucibles by standard high-temperature synthesis technique employed according to [8]. They were characterized by high chemical purity and optical quality. The basic chemical composition of our samples was controlled by X-ray microanalysis method, using a “Camebax” apparatus. For investigation of Raman spectra we selected a number of typical glass samples with the basic compositions of garnet (Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>) and Caggallogermanate (Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>4</sub>O<sub>14</sub>).

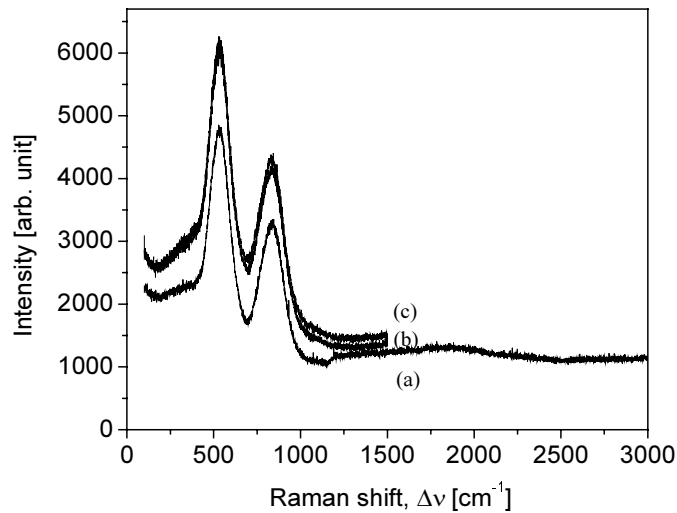
For comparative analysis we used well identified Raman spectra of the undoped garnet crystals Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub>, Ca<sub>3</sub>Sc<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> and R<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub> (with R = Sm, Gd and Nd) reported in [9–14], together with the spectra of the garnet crystal Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> obtained with the same spectrometer. Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> and the other garnet crystals were obtained by a standard Czochralski technique. Samples for the Raman studies were cut and polished to the shape of rectangular parallelepipeds, with the approximate sizes of 10×5×3 mm<sup>3</sup>. Samples of the garnet crystals were oriented with respect to specific crystallographic planes, in order to obtain a controlled light-scattering geometry. In particular, we used the samples of Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> crystals with the oriented (100) and (110) crystallographic planes, when measuring the Raman spectra.

The Raman spectra were recorded using a standard “Jobin-Yvon” spectrometer of T64000 type. We worked at the room temperature in the 100–3000 cm<sup>-1</sup> range and set the frequency step of 0.2 cm<sup>-1</sup>. Spectral resolution of the spectrometer did not exceed the value 4 cm<sup>-1</sup>. We used an ion Ar laser ( $\lambda_{exc} = 514.5$  nm and  $P_{exc} = 500–800$  mW) for exciting the Raman spectra. All the spectra for the glasses and crystals were detected in the back-scattering geometry for a number of parts of the samples under test.

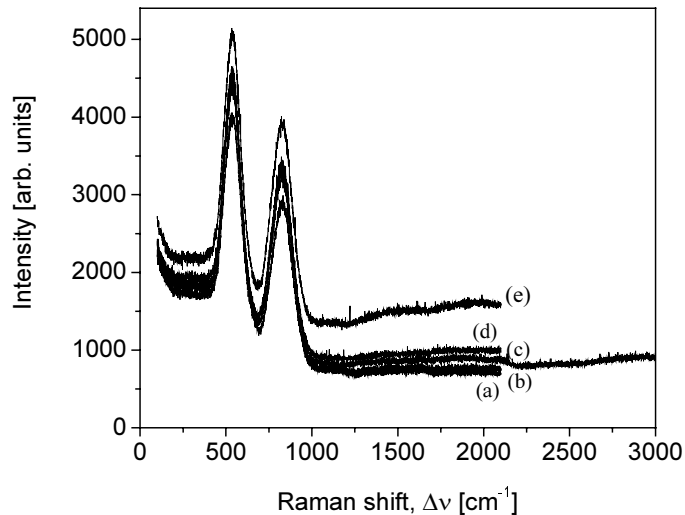
## Results and discussion

The Raman spectra of the glass samples with Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>4</sub>O<sub>14</sub> and Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> compositions are presented in Fig. 1 and 2, respectively. They are almost independent of the basic glass composition and consist of two broad bands centred near 535 and 825 cm<sup>-1</sup>. As seen from Fig. 1 and 2, different parts of samples with the garnet and Caggallogermanate compositions yield practically the same Raman spectra, thus evidencing high structural homogeneity of the glasses under studies. As shown by the EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy in [15], local structures of the glasses and crystals of CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> system with the same chemical composition are closely related. Then the two broad bands observed in the Raman spectra of the glasses could be identified on the basis of comparative analysis with the spectra measured and identified earlier for the single crystals with the same or similar chemical compositions.

For comparative analysis of the Raman spectra obtained for the glasses of CaO-Ga<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> system we have used the spectra of the garnet crystals with Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> [9, 10] and Ca<sub>3</sub>Sc<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> [11] compositions, since the corresponding results for



**Fig. 1.** Raman spectra detected at the room temperature for three different parts of the glass sample with  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  composition (curves a–c).



**Fig. 2.** Raman spectra detected at the room temperature for five different parts of the glass sample with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  composition (curves a–e).

compositionally-disordered Ca-gallogermanate crystal [16] are rather complicated and have not yet been interpreted unambiguously. To compare the frequencies and symmetry of the lines observed in the Raman spectra of  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  garnet, we have also involved the spectra of rare-earth gallium garnets with the compositions of  $\text{R}_3\text{Ga}_5\text{O}_{12}$  ( $\text{R} = \text{Sm}, \text{Gd}$  and  $\text{Nd}$ ), which have been measured and identified in the studies [12–14].

Let us consider basic results of the factor-group analysis for the garnet structure described in [17–19]. This structure is characterized by the cubic space group  $Ia\bar{3}d (O_h^{10})$  and the body-centred Bravais cell, with  $Z = 8$ . The possible sites, their local symmetry

and some other crystallographic characteristics of the garnet  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  structure are presented in Table 1.

**Table 1.** Crystallographic characteristics of cation and anion positions in the garnet crystals  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  (the space group  $Ia3d$  or  $O_h^{10}$  and the unit cell parameter  $a = 12.251 \text{ \AA}$ ).

General chemical formula of the garnet structure	$\{\text{C}_3\}$	$[\text{A}_2]$	$(\text{D}_3)$	$(\text{H}_{12})$
Ideal stoichiometric formula of $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ garnet	$\{\text{Ca}^{2+}\}_3$	$[\text{Ga}^{3+}]_2$	$(\text{Ge}^{4+})_3$	$(\text{O}^{2-})_{12}$
Type of sites, $\alpha$	$\{\text{c}\}$	$[\text{a}]$	$(\text{d})$	$\text{h}$
Local symmetry group of sites, $G_\alpha$	$\text{D}_2$	$\text{C}_{3i}$	$\text{S}_4$	$\text{C}_1$
Unit cell multiplicity, $K_\alpha$	24	16	24	96
Coordination to oxygen, $N$	8	6	4	–
Type of oxygen polyhedron	dodecahedron	<i>octahedron</i>	<i>tetrahedron</i>	–

The structure of the garnet crystals  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  can be represented as a spatial network of  $\text{GaO}_6$  octahedra and  $\text{GeO}_4$  tetrahedra, which are linked through the corners and form three-dimensional chains along the three crystallographic directions. These polyhedral chains form cavities, among which structural dodecahedral sites occupied by  $\text{Ca}^{2+}$  cations are located. Description of the garnet structure presented above shows that vibrations of polyhedral units are strongly coupled one to another.

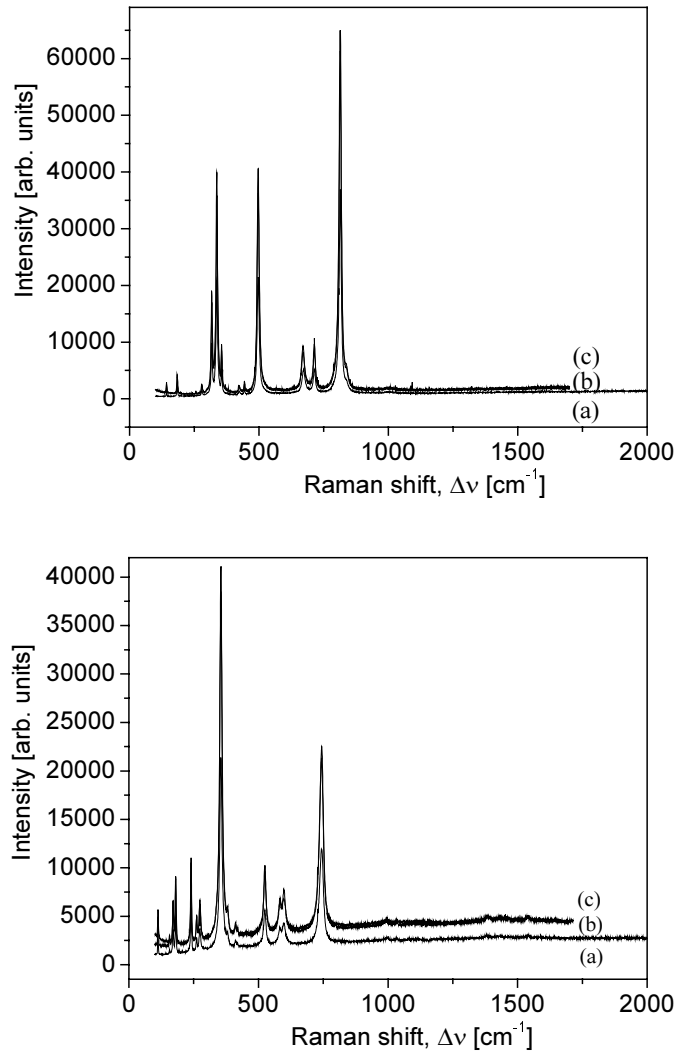
Group-theoretical analysis of the garnet lattice in [17] has been carried out on the basis of assumption of a primitive unit cell, instead of the conventional body-centred one. The primitive cell under consideration consists of four formula units (80 atoms) and has the same symmetry elements as the factor group  $\text{O}_h$ .  $\Gamma$  representation of the factor group  $\text{O}_h$  for the unit cell mentioned above, which has 240 degrees of freedom, can be reduced to the following:

$$\Gamma = 3A_{1g} + 5A_{2g} + 8E_g + 14T_{1g} + 14T_{2g} + 5A_{1u} + 5A_{2u} + 10E_u + 18T_{1u} + 16T_{2u}. \quad (1)$$

According to symmetry selection rules, the  $T_{1u}$  modes reveal themselves in the IR absorption spectrum, while the  $A_{1g}$ ,  $E_g$  and  $T_{2g}$  modes in the Raman spectrum. Let us notice that one of the  $18T_{1u}$  modes belongs to translation motions and does not reveal itself in the IR absorption. Thus, the results [17] testify that, at the most, 17 vibrational modes should be observed in the IR absorption and 25 modes in the Raman spectra of crystals with the garnet structure.

As for the experimental Raman spectra, the number and the intensity of lines

depends essentially on the geometry of light scattering, the excitation wavelength and the temperature. The experimental spectra obtained for the single crystals  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  are presented in Fig. 3. 12 lines are observed in the case of scattering in (100) crystallographic plane (Fig. 3, a) and 15 lines for the case of (110) plane (Fig. 3, b).



**Fig. 3.** Raman spectra detected at the room temperature for three different parts of the crystal samples with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{13}$  composition (curves a–c). Figures (a) and (b) refer to the scattering in (100) and (110) crystallographic planes, respectively.

In Table 2 we present the line positions measured for the Raman spectra of  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  garnet crystal (Fig. 3, a, b). For comparison, we have also displayed there the referenced data for the frequencies and symmetry of optical phonons referred to the spectra of  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  garnet and rare-earth gallium garnets with  $\text{R}_3\text{Ga}_5\text{O}_{12}$  (R = Sm, Gd and Nd) compositions.

**Table 2.** Vibrational frequencies and symmetry of optical phonons in the Raman spectra obtained at the room temperature for the garnets with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  and  $\text{R}_3\text{Ga}_5\text{O}_{12}$  (R = Sm, Gd and Nd) compositions.

Vibrational frequencies, $\nu$ [ $\text{cm}^{-1}$ ]					Optical phonon symmetry
$\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$		$\text{Sm}_3\text{Ga}_5\text{O}_{12}$	$\text{Gd}_3\text{Ga}_5\text{O}_{12}$	$\text{Nd}_3\text{Ga}_5\text{O}_{12}$	
This work $\lambda_{\text{exc}}=514.5$ nm	[10] $\lambda_{\text{exc}}=441.6$ nm	[12] $\lambda_{\text{exc}} = 514.5$ nm	[13] $\lambda_{\text{exc}} = 514.5$ nm	[14] $\lambda_{\text{exc}} = 441.6$ nm	
113	–	113	112	113	$E_g$
144	145	–	–	142	$E_g$
157	153	159	156	161	$T_{2g}$
170	185	171	170	174	$T_{2g}$
180	198	180	179	185	$T_{2g}$
–	–	–	–	230	$T_{2g}$
240	–	240	240	238	$T_{2g}$
261	–	264	262	262	$E_g$
274	280	274	275	278	$T_{2g}$
–	301	–	–	298	–
–	319	–	–	331	$T_{2g}$
355	338	353	356	350	$A_{1g}$
–	356	372	–	364	$E_g$
390	382	382	384	395	$T_{2g}$
412	424	408	–	404	$T_{2g}$
418	443, 479	415	–	416	$E_g$
525	497	523	–	520	$A_{1g}$
–	518	–	–	566	$T_{2g}$
584	671	581	588	582	$T_{2g}$
597	–	595	600	–	$T_{2g}$
744, 815	814	736	742	728	$A_{1g}$
840	839	–	–	–	$T_{2g}$

It should be noted that the authors [9] and [10] have observed respectively 21 and 19 lines in the Raman spectra of  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  crystal. For comparison with the referenced data, Table 2 comprises also the frequencies and symmetry of all modes present in the Raman spectra of  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  garnet, which are measured at the scattering in (100) and (110) crystallographic planes. The line frequencies obtained in this work for the Raman spectra of  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  crystal are close to those of the Raman lines found for  $\text{Sm}_3\text{Ga}_5\text{O}_{12}$  [12] and  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  [13] garnets and detected at the same excitation ( $\lambda_{\text{exc}} = 514.5$  nm) and the light scattering geometry. At the same time, they are slightly

different from the corresponding frequencies obtained for the  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  [10] and  $\text{Nd}_3\text{Ga}_5\text{O}_{12}$  [14] garnets and detected at  $\lambda_{\text{exc}} = 441.6 \text{ nm}$  (see Table 2).

The line frequencies and the assignments of lines observed in the Raman spectra of the glass and crystal with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  composition and the crystal with  $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$  composition are gathered in Table 3.

Table 3. Line frequencies and identification of the lines present in the Raman spectra of the glass and crystal with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  composition and the  $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$  garnet (detected at  $\lambda_{\text{exc}} = 514.5 \text{ nm}$  and  $T = 300 \text{ K}$ ).

$\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ (glass) This work	$\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ (crystal) This work	$\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ (crystal) [11]	Identification of Raman lines [11]
Frequency, $\nu$ [ $\text{cm}^{-1}$ ]	Frequency, $\nu$ [ $\text{cm}^{-1}$ ]	Frequency, $\nu$ [ $\text{cm}^{-1}$ ]	Phonon symmetry
	$144 \pm 4$	$133 \pm 1$ (w)	lattice
	$185 \pm 4$	$169 \pm 1$	
	$281 \pm 4$	$267 \pm 1$	$\nu_2, \nu_4$
	$318 \pm 4$	$295 \pm 1$	
	$338 \pm 4$	$330 \pm 1$	
	$357 \pm 4$	$402 \pm 1$	
$535 \pm 10$	$424 \pm 4$	$468 \pm 1$	( $A_{1g}$ )
	$445 \pm 4$	$500 \pm 1$ (w)	
	$498 \pm 4$	$688 \pm 1$	$\nu_1, \nu_3$
	$672 \pm 4$	$\sim 705$ (w)	
	$715 \pm 4$	$730 \pm 1$	
$825 \pm 10$	$815 \pm 4$	$804 \pm 1$	( $A_{1g}$ )
	$\sim 840$ (w)	$\sim 830$ (w, sh)	

- Notes: 1. Vibrational frequencies for the  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  garnet are measured at the light scattering in (100) crystallographic plane.  
2. Weak peaks are denoted as 'w' and shoulders of lines as 'sh'.

As seen from Table 3, only 13 lines are detected [11] in the  $100 - 900 \text{ cm}^{-1}$  region of the Raman spectra of single  $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$  crystal. In the study [11] the Raman spectrum observed in the  $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$  garnet has been identified basing on the following rules suggested in [17, 19]: (1) all the normal modes  $\nu_1(A_1)$ ,  $\nu_2(E)$ ,  $\nu_3(T_2)$  and  $\nu_4(T_2)$  of the regular tetrahedra (the symmetry  $T_d$ ) are active in the Raman spectra, (2) the frequencies of the stretching modes ( $\nu_1$  and  $\nu_3$ ) are higher than those of the bending modes ( $\nu_2$  and  $\nu_4$ ), (3) only the factor-group representations corresponding to  $\nu_1$  and  $\nu_2$

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modes contain totally symmetric terms, and (4) all the modes ( $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$ ) of the regular tetrahedral units, which give rise to the factor-group representation containing two components ( $A_{1g}$ ,  $E_g$  or  $T_{2g}$ ), reveal themselves in the Raman spectra.

Let us again issue from the comparison of the line positions for the Raman spectra of glass and crystal with the composition  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  and the garnet crystal  $\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$ , which are presented in Table 3. Then one can conclude that the broad bands with the maxima located near 535 and 825  $\text{cm}^{-1}$  belong to totally symmetric vibrational modes  $A_{1g}$  of  $(\text{Ga}/\text{Ge})\text{O}_4$  tetrahedral groups (structural units) of the glass network. Significant width of the observed Raman bands can be explained as a result of wide distribution of the local structure parameters of the mixed tetrahedral groups  $(\text{Ga}/\text{Ge})\text{O}_4$  in the glass structure. This fact has been confirmed by the EXAFS spectroscopy in the study [15].

### Conclusions

Let us summarize in brief the main results derived in this work. The Raman spectra of the glasses of  $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$  system with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  and  $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$  compositions are experimentally measured and analyzed. In particular, we have shown that the Raman spectrum of the glasses of  $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$  system is practically independent of the basic glass composition. It consists of the two broad bands with the maxima located near 535 and 825  $\text{cm}^{-1}$ . The broad bands observed in the Raman spectra belong to totally symmetric modes  $A_{1g}$  of the mixed tetrahedral groups  $(\text{Ga}/\text{Ge})\text{O}_4$  (the phonon symmetry  $A_{1g}$ ), which represent basic structural units of  $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$  glass network.

The Raman spectroscopic results obtained by us can be used for interpretation of multiphonon relaxation of the excited states of  $\text{Cr}^{3+}$  [1, 2] and  $\text{Er}^{3+}$  [6] luminescence centres in the glasses with  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  garnet composition. This will be a subject of our future work.

### Acknowledgement

The author thanks Petro Buchynskii from Lviv Scientific Industrial Amalgamation “MikroTech Karat” for synthesis of glass samples.

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