
Raman spectra of glasses of CaO-Ga₂O₃-GeO₂ system

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Abstract

Raman spectra of undoped glasses of CaO-Ga₂O₃-GeO₂ system with the garnet (Ca₃Ga₂Ge₃O₁₂) and Ca-gallogermanate (Ca₃Ga₂Ge₄O₁₄) compositions are measured and analyzed. The spectra are interpreted on the basis of comparison to the well known Raman spectra of the garnet crystals with Ca₃Ga₂Ge₃O₁₂ and Ca₃Sc₂Ge₃O₁₂ compositions. It is shown that the spectra observed for the glasses of CaO-Ga₂O₃-GeO₂ system are almost independent of the basic glass composition. They consist of two broad bands centred near 535 and 825 cm⁻¹, which belong to totally symmetric vibrational modes A_{1g} of the mixed tetrahedral groups (structural units) (Ge/Ga)O₄ 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.

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Introduction

In the recent works [1–6] it has been shown that the glasses of CaO-Ga₂O₃-GeO₂ system activated with Cr³⁺, Nd³⁺, Er³⁺ and Ho³⁺ 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-Ga₂O₃-GeO₂ system has been reported by the authors [7]. In the present work we present more detailed investigations of the Raman spectra of CaO-Ga₂O₃-GeO₂ 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 Ca₃Ga₂Ge₃O₁₂ garnet crystals.

Experimental details

Undoped CaO-Ga₂O₃-GeO₂ 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 (Ca₃Ga₂Ge₃O₁₂) and Ca-gallogermanate (Ca₃Ga₂Ge₄O₁₄).

For comparative analysis we used well identified Raman spectra of the undoped garnet crystals Ca₃Ga₂Ge₃O₁₂, Ca₃Sc₂Ge₃O₁₂ and R₃Ga₅O₁₂ (with R = Sm, Gd and Nd) reported in [9–14], together with the spectra of the garnet crystal Ca₃Ga₂Ge₃O₁₂ obtained with the same spectrometer. Ca₃Ga₂Ge₃O₁₂ 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 mm³. 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 Ca₃Ga₂Ge₃O₁₂ 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⁻¹ range and set the frequency step of 0.2 cm⁻¹. Spectral resolution of the spectrometer did not exceed the value 4 cm⁻¹. 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 Ca₃Ga₂Ge₄O₁₄ and Ca₃Ga₂Ge₃O₁₂ 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⁻¹. As seen from Fig. 1 and 2, different parts of samples with the garnet and Ca-gallogermanate 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-Ga₂O₃-GeO₂ 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-Ga₂O₃-GeO₂ system we have used the spectra of the garnet crystals with Ca₃Ga₂Ge₃O₁₂ [9, 10] and Ca₃Sc₂Ge₃O₁₂ [11] compositions, since the corresponding

results for 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 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 $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ garnet structure are presented in Table 1.

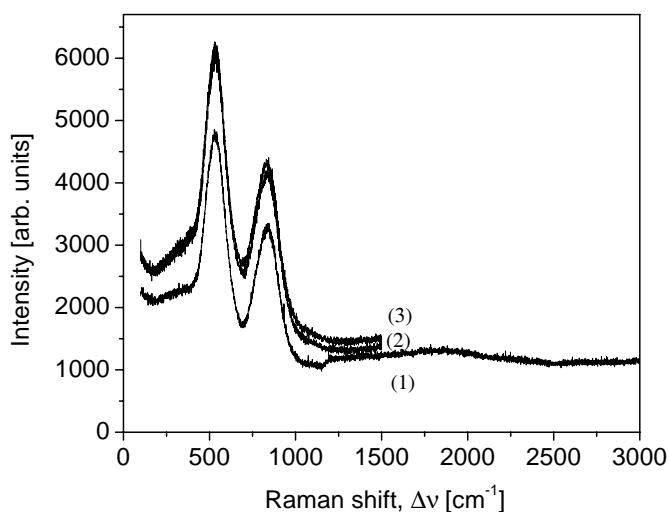


Fig. 1. Raman spectra detected at the room temperature for three different parts of the glass sample with $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ composition (curves 1–3).

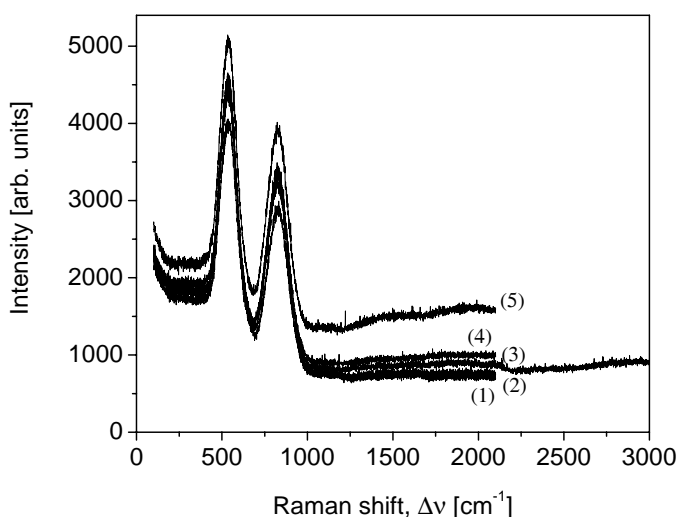


Fig. 2. Raman spectra detected at the room temperature for five different parts of the glass sample with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition (curves 1–5).

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	$\{\text{C}_3\}$	$[\text{A}_2]$	(D_3)	(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, α	$\{\text{c}\}$	$[\text{a}]$	(d)	h
Local symmetry group of sites, G_α	D_2	C_{3i}	S_4	C_1
Unit cell multiplicity, K_α	24	16	24	96
Coordination to oxygen, N	8	6	4	–
Type of oxygen polyhedron	dodecahedron	octahedron	tetrahedron	–

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 GaO_6 octahedra and 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 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 O_h . Γ representation of the factor group 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).

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.

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

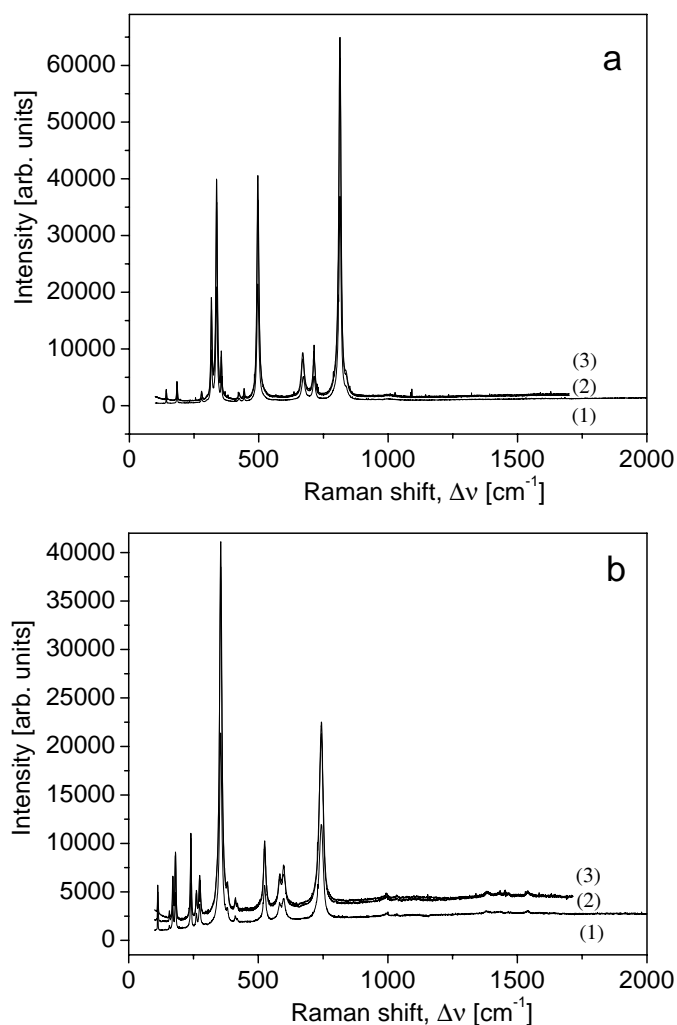


Fig. 3. Raman spectra detected at the room temperature for three different parts of the crystal samples with $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ composition (curves 1–3). Figures (a) and (b) refer to the scattering in (100) and (110) crystallographic planes, respectively.

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, ν [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}

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 of lines 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 at $\lambda_{\text{exc}} = 441.6$ 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.

As seen from Table 3, only 13 lines are detected by authors [11] in the $100-900$ 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

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 $\lambda_{exc} = 514.5 \text{ nm}$ 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, ν [cm^{-1}]	Frequency, ν [cm^{-1}]	Frequency, ν [cm^{-1}]	Phonon symmetry
	144 ± 4	133 ± 1 (w)	lattice
	185 ± 4	169 ± 1	
	281 ± 4	267 ± 1	ν_2, ν_4
	318 ± 4	295 ± 1	
	338 ± 4	330 ± 1	
	357 ± 4	402 ± 1	
535 ± 10	424 ± 4	468 ± 1	(A_{1g})
	445 ± 4	500 ± 1 (w)	
	498 ± 4	688 ± 1	ν_1, ν_3
	672 ± 4	~ 705 (w)	
	715 ± 4	730 ± 1	
825 ± 10	815 ± 4	804 ± 1	(A_{1g})
	~ 840 (w)	~ 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'.

[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 (ν_1 and ν_3) are higher than those of the bending modes (ν_2 and ν_4), (3) only the factor-group representations corresponding to ν_1 and ν_2 modes contain totally symmetric terms, and (4) all the modes (ν_1, ν_2, ν_3 and ν_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 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 (Ga/Ge)O₄ 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 CaO-Ga₂O₃-GeO₂ system with Ca₃Ga₂Ge₃O₁₂ and Ca₃Ga₂Ge₄O₁₄ compositions are experimentally measured and analyzed. In particular, we have shown that the Raman spectrum of the glasses of CaO-Ga₂O₃-GeO₂ system is practically independent of the basic glass composition. It consists of the two broad bands with the maxima located near 535 and 825 cm⁻¹. The broad bands observed in the Raman spectra belong to totally symmetric modes of the mixed tetrahedral groups (Ga/Ge)O₄ (the phonon symmetry A_{1g}), which represent basic structural units of CaO-Ga₂O₃-GeO₂ glass network.

The Raman spectroscopic results obtained by us can be used for interpretation of multiphonon relaxation of the excited states of Cr³⁺ [1, 2] and Er³⁺ [6] luminescence centres in the glasses with Ca₃Ga₂Ge₃O₁₂ garnet composition. This will be a subject of our future work.

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