

EXAFS study of glasses of the CaO–Ga₂O₃–GeO₂ system

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X-ray absorption spectroscopy (XAS) measurements for Ca₃Ga₂Ge₃O₁₂ and Ca₃Ga₂Ge₄O₁₄ glasses are presented. In particular, the extended X-ray absorption fine structure (EXAFS) spectra are analysed and local neighbourhood of Ga and Ge atoms is described in detail. The Ge/Ga atoms neighbourhood in considered glasses is compared with the data available for corresponding crystals. Performed comparative crystal-glass structural analysis confirms correlation between crystalline and glassy structures of the Ca₃Ga₂Ge₃O₁₂ and Ca₃Ga₂Ge₄O₁₄ compounds. Our results provide several new detailed data, and some general suggestions on the CaO–Ga₂O₃–GeO₂ glass structure.

Keywords: oxide glasses, structural analysis, EXAFS.

1. Introduction

Disordered crystals and glass matrices doped with transition and rare-earth metals ions are still very attractive as possible laser media (especially for tunable solid state lasers) [1], [2], optical fibers [3] and for other applications in optoelectronics. In contrast to crystals, the spectroscopic properties and peculiarities due to the incorporation of transition metal ions into glasses have been studied to an insufficient extent, because the valence state and size of glass network formers, modifiers, and

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stabilizers change, which leads to a great variety of different local crystal fields at activator sites. Therefore, experimental investigations and theoretical analysis of spectroscopic properties of transition impurity metal ions in disordered compounds, particularly, compositionally (or substitutionally) disordered oxide crystals and glasses are current topics of solid state physics and optical materials technology. This also concerns CaO–Ga₂O₃–GeO₂ compounds, which can be obtained in crystalline and glassy (vitreous) states. These compounds are novel materials for quantum electronics and other applications. The most promising potential applications of compounds in the CaO–Ga₂O₃–GeO₂ systems are:

- tunable laser materials (also for ultrashort pulses) when doped with Cr³⁺ and Cr⁴⁺ ions;
- scintillators and radiation phosphors when doped with Ce³⁺ ions;
- lasers for telecommunication purposes when doped with Nd³⁺, Ho³⁺ and other rare-earth ions emitting in eye-safe spectral region.

In the Ca–Ga–Ge–O ternary system there exist three stable crystalline forms: Ca₃Ga₂Ge₃O₁₂ (ordered garnet structure, space group *Ia3d*), Ca₃Ga₂Ge₄O₁₄ (substitutionally disordered Ca-gallogermanate structure, space group *P321*), Ca₂Ga₂GeO₇ (gelenite structure, space group *P4̄2₁m*) [4], [5]. Glassy forms with compositions similar to the stoichiometric crystals also exist [6]. The previous structural studies on CaO–Ga₂O₃–GeO₂ glasses by X-ray scattering and molecular dynamics methods have been presented in [7]. Comparative analysis of the X-ray data for CaO–Ga₂O₃–GeO₂ glasses and their crystalline analogs suggests that Ga/GeO₆ octahedra and Ga/GeO₄ tetrahedra form the glass network. The structure of glasses with the Ca₃Ga₂Ge₃O₁₂, Ca₃Ga₂Ge₄O₁₄ and Ca₃Ga₂O₆ compositions are characterised by short-range order similar as in the corresponding crystalline compounds.

In ordered calcium-gallium-germanium garnet crystal, the Ga³⁺ cations occupy, in general, octahedral (*a*)-sites of the lattice. Neutronography technique shows that only a small part (< 0.1 at%) of Ga³⁺ cations occupy tetrahedral (*d*)-sites [8]. In the substitutionally disordered Ca-gallogermanate crystals the Ga³⁺ and Ge⁴⁺ cations are statistically distributed among octahedral (*1a*) and tetrahedral (*3f*)-sites of the lattice. Using X-ray data it was estimated that the average ratio Ga³⁺:Ge⁴⁺ is equal to 1:4 for octahedral sites, and 3:2 for tetrahedral sites of the Ca-gallogermanate lattice [9]. It should be noted that the Ga³⁺:Ge⁴⁺ ratio depends on technological conditions during the crystal growth.

At present we need a detailed structural study of glasses of the CaO–Ga₂O₃–GeO₂ system, particularly of local neighbourhoods of Ga and Ge atoms. The EXAFS method is characterised by atomic selectivity and a high sensitivity to the short-range order, and thus it appears to be the most suitable technique to study the neighbourhood of Ge and Ga atoms in multi-component and disordered systems. For these reasons we performed structural investigations for glasses with garnet (Ca₃Ga₂Ge₃O₁₂), and Ca-gallogermanate (Ca₃Ga₂Ge₄O₁₄) composition, using the X-ray absorption spectroscopy (XAS, *e.g.*, [10]), and the extended X-ray absorption fine structure analysis (EXAFS, *e.g.*, [11]).



The paper is organised as follows. Section 2 contains experimental details. In Section 3, we present and discuss the results of our measurements. Section 4 contains concluding remarks.

2. Experiment

In this section, we present some details on sample preparation technique (Sec. 2.1), XAS measurements (Sec. 2.2) and EXAFS data analysis (Sec. 2.3).

2.1. Sample preparation

The $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ glasses of high optical quality and chemical purity with different compositions were obtained in corundum crucibles by high-temperature synthesis technique according to [6]. Chemical composition of the obtained glasses ($\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$, $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$) was controlled by the X-ray microanalysis method using a Camebax apparatus.

Samples for the EXAFS measurements were obtained by mixing of the powdered glasses with an inert matrix powder (BN of 99% purity) in weigh ratio 1:10, and pressing the resulting mixture into pellets of a typical thickness of 0.5–1 mm, and diameter of 13 mm.

2.2. XAS measurements

The XAFS spectra of $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ and $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ glasses at the Ge and Ga K -edges have been recorded at the BM29 beam-line at the European Synchrotron Radiation Facility, Grenoble [12], using a double-crystal monochromator equipped with Si(311) crystals. An average resolution in the whole range of energy was around 1.5 eV. The room temperature measurements were performed in the energy ranges

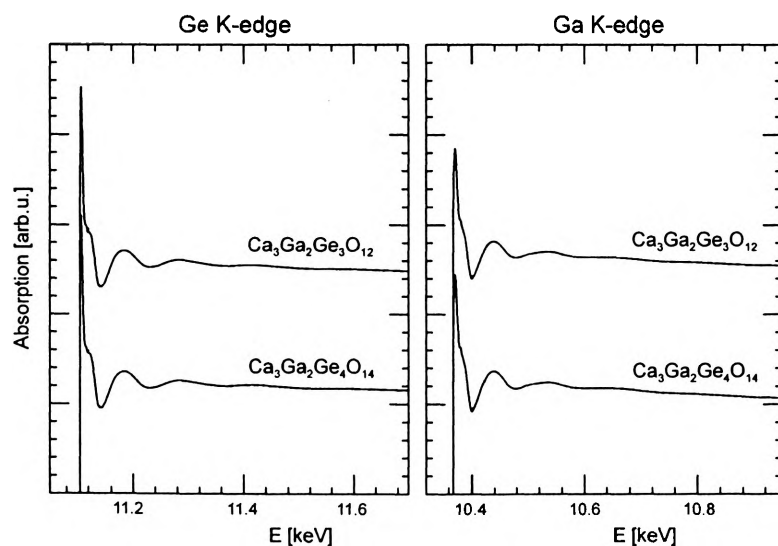


Fig. 1. XANES spectra of the considered glasses recorded at Ge and Ga K -edges.



10980–12300 eV and 10250–11100 eV for Ge and Ga *K*-edges, respectively (the Ge *K*-edge energy amounts to 11104 eV, and Ga *K*-edge to 10367 eV). Obtained XAFS spectra of the glasses are presented in Fig. 1.

2.3. EXAFS data analysis

Experimental data have been analysed with an advanced technique, using theoretical calculations of the X-ray absorption cross-section in the framework of the GNXAS method (GN – refers to the *n*-body distribution function in condensed matter, XAS – as above, for details see [13]–[15]). The method is based on the comparison in the energy space between the experimental signal, $\alpha_{\text{exp}}(E)$, and the theoretical one, $\alpha_{\text{mod}}(E)$, attempting to optimise the relevant structural (R , σ^2 , β , N), and related non-structural (S_0^2 , E_0) parameter values. The meaning of the structural parameters mentioned above is as follows. Parameter R is the mean inter-atomic distance, σ^2 is the Debye–Waller-like parameter, describing both the structural and vibrational disorder, β is the skewness parameter, and N is the co-ordination number. The non-structural parameter S_0^2 , *i.e.*, the amplitude reduction factor, takes into account inelastic processes. Finally, the E_0 parameter gives the difference between experimental and theoretical energy scales. In our GNXAS analysis the theoretical signal was modelled taking into account the following three-shell frequency contributions: Ge–O, Ge–Ca and Ge–Ga for Ge-edge spectra, and Ga–O, Ga–Ca and Ga–Ge for Ga-edge spectra. In addition, the GNXAS method has shown a high flexibility in the modelling of the atomic backgrounds due to the possibility of accounting for multi-electron excitation channels. In our analysis the ($1s_{1/2}3d$), ($1s_{1/2}3p$) and ($1s_{1/2}3s$) channels have been considered.

3. Results and discussion

The results of the fitting procedure are shown in Figs. 2 and 3. The obtained structural parameters are presented in Tabs. 1 and 2.

Preliminary structural investigations (X-ray diffraction and molecular dynamics simulations [7]) of the CaO–Ga₂O₃–GeO₂ glasses show that the structure is characterised by short-range chemical ordering similar to ordering of the corresponding crystalline compounds [4], [5], [9]. For this reason the comparative crystal-glass structural analysis was performed. Let us describe in turn the structure around Ge and Ga atoms in Ca₃Ga₂Ge₃O₁₂ (Sec. 3.1) and Ca₃Ga₂Ge₄O₁₄ (Sec. 3.2) glasses.

3.1. Structure of the Ca₃Ga₂Ge₃O₁₂ glass

As it is seen from Fig. 2 and Tab. 1, for Ca₃Ga₂Ge₃O₁₂ glass, in the Ge-related subsystem, similarly as in the corresponding crystal, regular GeO₄ units are present ($N \approx 4.0$ and small value of σ^2 and β parameters). Disorder parameters of Ge–Ca/Ga correlations also assume similar values as in the ordered garnet structure.

The Ga-related subsystem structure, in the nearest neighbourhood of Ge atoms, is characterised by two types of structural units: GaO₄ (Ga–O₁ correlation) and GaO₆



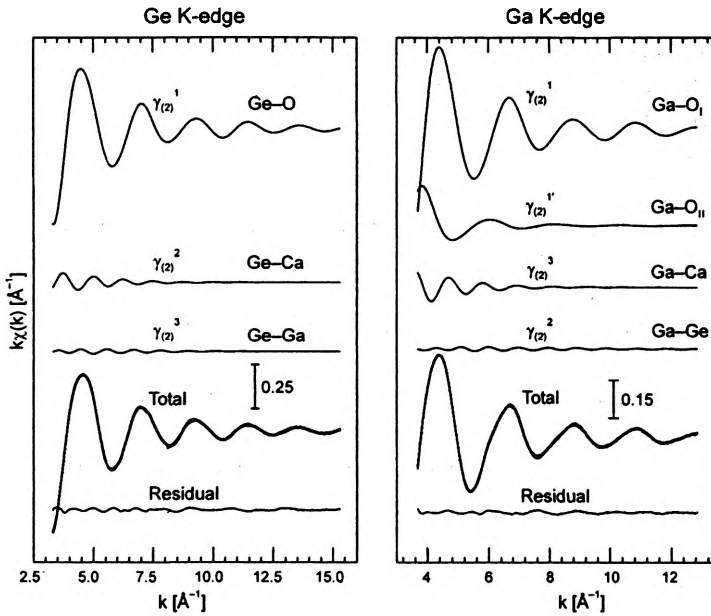


Fig. 2. Results of the GNXAS analysis performed for spectra recorded at Ge and Ga-edges of $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass (solid line – model; dotted – experiment). See also Tab. 1.

Table 1. Structural parameters of $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass derived from Ge and Ga K-edges EXAFS analysis. The symbols are explained in the text.

$\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$	R [Å]	σ^2 [Å ²]	β	N
Ge–O	1.75	0.002	0.47	3.90
Ge–Ca	3.14	0.030	0.78	2.40
Ge–Ga	3.42	0.048	0.80	4.00
Ga–O _I	1.87	0.004	1.32	3.81
Ga–O _{II}	2.29	0.095	1.20	6.00
Ga–Ca	3.51	0.062	0.81	5.90
Ga–Ge	3.97	0.104	1.24	4.19

(Ga–O_{II} correlation). The GaO₄ units dominate, and are more regular than the GaO₆ groups (*cf.* σ^2 parameter values). In the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ garnet crystal, in general, the GaO₆ octahedra are present, and the average Ga–O distance in crystal is smaller by ~ 0.2 Å than $R_{\text{Ga-O}}$ in the GaO₆ units in glass. As was noted above, in the $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ crystals only a small (< 0.1 at%) fraction of GaO₄ tetrahedral groups was detected by neutron diffraction technique [8].

The Ga–Ca two-body spatial correlation, in respect to disorder parameters, is similar as in the corresponding crystal. On the other hand, the Ga–Ge correlation is very irregular (high dispersion, $\sigma^2 > 0.1$ Å²), and is also somewhat different in glass and crystal ($\Delta R \approx 0.55$ Å, $\Delta N \approx 2.0$).

The results of the structural analysis of $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ glass suggest that while the parameters describing the Ge atom neighbourhood in glass have similar values as in the corresponding crystal, the parameters describing the Ga atom neighbourhood in glass and crystal are significantly different. One has to remember that the two-body correlations alone are insufficient to describe the shape of the basic structural units. Unfortunately, in the case of glasses, the three-body correlations are very difficult to extract. Thus, the exact shape of the dominant structural unit in the considered glasses cannot be determined univocally from the EXAFS experiment. Several forms of the basic units are compatible with our results. These might be:

- regular tetrahedra (similarly as in other glasses containing Ga_2O_3 , *e.g.*, [16], [17]);
- square pyramids with oxygen atoms forming the base, and Ga atom in the vertex,
- GaO_6 octahedra, strongly defective due to the presence of vacancies and/or the appearance of elongated Ga–O bonds, characteristic of ordered $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$ garnet crystal; this latter hypothesis is compatible with very high structural unit irregularity found for the GaO_6 groups.

3.2. Structure of the $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ glass

As it is seen from Fig. 3 and Tab. 2, in Ge-related subsystem, like in the corresponding crystal, both GeO_4 (Ga–O_I correlation) and GeO_6 (Ga–O_{II} correlation) units appear. In the glass the GeO_4 units dominate, and are more regular than the GeO_6 groups (*cf.* σ^2 parameters). The $R_{\text{Ge-O}}$ distances in GeO_4 units in crystal and glass are very

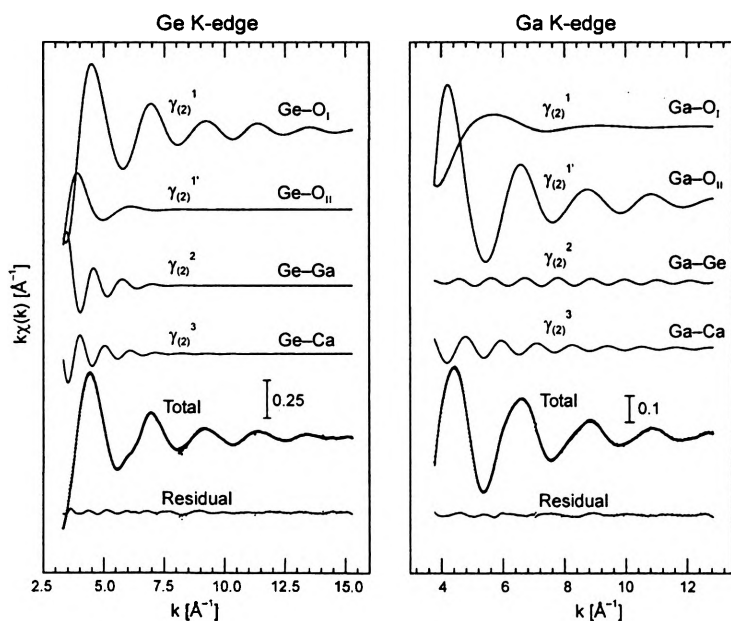


Figure 3. Results of the GNXAS analysis performed for spectra recorded at Ge and Ga-edges of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ glass (solid line – model; dotted – experiment). See also Tab. 2



Table 2. Structural parameters of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ glass derived from Ge and Ga *K*-edges EXAFS analysis. The symbols are explained in the text.

$\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$	R [Å]	σ^2 [Å ²]	β	N
Ge–O _I	1.77	0.002	1.14	4.00
Ge–O _{II}	2.04	0.039	0.32	6.00
Ge–Ca	3.69	0.055	1.11	3.01
Ge–Ga	3.72	0.057	0.75	6.13
Ga–O _I	1.74	0.079	1.20	4.08
Ga–O _{II}	1.91	0.013	1.79	6.05
Ga–Ca	3.61	0.192	1.74	5.71
Ga–Ge	3.55	0.114	1.76	2.99

similar. On the other hand, this distance in GeO_6 units in crystal and glass differ by about 0.1 Å. Ge–Ga/Ca distances reveal rather high dispersion (see σ^2 and β parameters).

In Ga-related subsystem both GaO_4 (Ga–O_I correlation) and GaO_6 (Ga–O_{II} correlation) units have been detected, similarly as in substitutionally disordered Ca-gallogermanate crystal. The structural units in the glass are more compact than in the crystal ($R_{\text{glass}} < R_{\text{crystal}}$, and the β parameter obtained for glass is relatively high). In the glass the GaO_6 units dominate, and are more regular than the GaO_4 groups. Other two spatial correlations (Ga–Ge and Ga–Ca) are highly dispersed (very high values of σ^2 and β parameters).

The results of the structural analysis of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ glass show that the structure around Ge and Ga atoms is characterised by short-range chemical order similar as in the corresponding crystalline compound (substitutionally disordered Ca-gallogermanate crystal). Only one difference exists: GaO_n units in the glass are more compact (the same situation was observed, e.g., for BiO_5 units present in bismuth-silicate glasses [18]).

4. Conclusions

The described results confirm that EXAFS is an efficient probe to investigate the short-range (up to third coordination shell) structure in complex oxide glasses. EXAFS experiment can distinguish between Ge/ GaO_n local environments with various n .

The obtained results confirm also the correlation between crystalline and glassy structures of the considered compounds in the $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$ system. They provide several new detailed data, and also some general suggestions on the glass structure. However, the above preliminary results should be verified using other, independent experimental methods, like solid-state ^{71}Ga magic angle spinning nuclear magnetic resonance.

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