Refractive Indices of Glasses of $CaO-Ga_2O_3-GeO_2$ System

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Received: 26.06.2006
After revision: 14.08.2006

Abstract

The results for the refractive indices of undoped and Nd- and Ce-doped glasses of $CaO-Ga_2O_3-GeO_2$ system are obtained and analyzed. The glasses with the garnet ($Ca_3Ga_2Ge_3O_{12}$) and Ca-gallogermanate ($Ca_3Ga_2Ge_4O_{14}$) compositions have been obtained by high-temperature synthesis. Nd and Ce impurities have been added to the garnet-composition glass as Nd_2O_3 and Ce_2O_3 oxides in the amounts of 0.2 and 0.7 wt. %, respectively. The refractive indices of the glasses depend on the basic glass composition. In particular, the refractive index increases with increasing Ge content. The presence of Nd and Ce impurities in the garnet-composition glasses in the amounts larger than 0.1 wt. % gives rise to essential increase of the refractive indices. The average refractive indices for the glasses with $Ca_3Ga_2Ge_4O_{14}$ composition are considerably smaller than those of the corresponding crystals with the garnet and Ca-gallogermanate structure. Significant deviations of the refractive index measured in different parts of $Ca_3Ga_2Ge_3O_{12}$ garnet crystal can be related to inhomogeneous distribution of Ge.

Key words: germanate glasses, optical properties, refractive index, dispersion

PACS: 42.70.Ce; 42.25.Gy; 78.20.Ci

1. Introduction

Crystals and glasses activated with rare-earth metal (Eu, Ho, Er and Nd) ions are still attractive as possible phosphors, active laser media and materials for other applications in optoelectronics. This also concerns the compounds of $CaO-Ga_2O_3-GeO_2$ system activated with rare-earth ions. In particular, crystals and glasses of the $CaO-Ga_2O_3-GeO_2$ system represent materials promising for red phosphors, when activated with Eu^{3+}, and conventional visible and IR lasers, as well as LED (laser emitting diodes) and pumped up-converted lasers, when activated with Ho^{3+}, Er^{3+} and Nd^{3+} ions. From the scientific point of view, the compounds of $CaO-Ga_2O_3-GeO_2$ system are interesting objects for studies of local environments for the impurity luminescence centres in the glass network, since these compounds can be obtained in both crystalline and glassy (or vitreous) states.

Three stable crystalline forms exist in the oxide ternary $CaO-Ga_2O_3-GeO_2$ system: $Ca_3Ga_2Ge_3O_{12}$ (ordered garnet structure, the space group *Ia3d*), $Ca_3Ga_2Ge_4O_{14}$ (compositionally disordered Ca-gallogermanate structure, the space group *P321*) and $Ca_2Ga_2GeO_7$ (gelenite structure, the space group $P\bar{4}2_1m$) [1-3], together with the corresponding glasses [4] possessing stoichiometric compositions similar to those of the crystals.

Single crystals with the garnet and Ca-gallogermanate compositions have been obtained with the Czochralski method and their structures have been described in the works [1-3]. The undoped and rare-earth doped glasses of CaO-Ga_2O_3-GeO_2 system have been prepared by the conventional high-temperature synthesis according to [4]. Structural studies for the obtained glass samples using X-ray scattering and molecular dynamics simulations [5], as well as the XAS (X-ray Absorption Spectroscopy) and EXAFS (Extended X-ray Absorption Fine Structure) analyses [6] have shown that their structure are characterized by a short-range ordering similar to that occurring in the corresponding crystalline compounds and $(Ga/Ge)O_6$ octahedra and $(Ga/Ge)O_4$ tetrahedra built in the glass network.

At the present time, the optical spectra (UV-visible absorption, luminescence excitation and emission) and the decay kinetics of Eu^{3+}, Ho^{3+}, Er^{3+} and Nd^{3+} luminescence centres in Eu-, Ho-, Er- and Nd-doped glasses with the garnet composition have been investigated in a number of papers [7-11]. At the same time, the Judd-Ofelt calculations of spectroscopic and laser parameters of the rare-earth luminescence centres need the values of refractive index and its dispersion for the rare-earth doped glasses. Up to now, the refractive index dispersion in the glasses of CaO-Ga_2O_3-GeO_2 system has not been systematically investigated.

This paper is aimed at measurements and analysis of the refractive indices and their dispersion in the un-doped glasses with the garnet and Ca-gallogermanate compositions and Nd- and Ce-doped glasses with the garnet composition. We will also discuss the obtained results and compare them to the corresponding data known for the crystalline analogues of the mentioned glasses.

2. Experimental details

Undoped glasses of high chemical purity and optical quality with the garnet ($Ca_3Ga_2Ge_3O_{12}$ or $3CaO$-Ga_2O_3-$3GeO_2$) and Ca-gallogermanate ($Ca_3Ga_2Ge_4O_{14}$ or $3CaO$-Ga_2O_3-$4GeO_2$) compositions were obtained in corundum crucibles by conventional high-temperature synthesis technique performed according to [4]. Thus synthesized glass samples were annealed in 500–550^{o}C temperature region for 1 h in order to eliminate internal stresses. Nd- and Ce-doped glasses with the garnet composition were obtained using the same technology. The Nd and Ce impurities were added to the glass constituents as powdered Nd_2O_3 and Ce_2O_3 compounds respectively in the amounts of 0.2 and 0.7 wt. %. Our undoped glasses with the garnet and Ca-gallogermanate compositions were uncoloured, whereas the Nd- and Ce-doped glasses were characterized by lightly blue and intense yellow colours, respectively.

The chemical composition of the obtained glasses was controlled with X-ray microanalysis, using "Camebax" apparatus. The samples for the refractive index measurements of a rectangular prism shape with the approximate size of $9\times7\times3$ mm^3 were cut and then polished. The refractive index dispersion was measured in the spectral range of 420–680 nm at the room temperature, using the immersion method [12] based on commercial refractometer of IRF-23 type. Mixtures of α-bromonaphthalene ($C_{10}H_7Br$) with kerosene and methylene iodide (CH_2J_2) were used as reference immersion liquids respectively for the regions of $1.45<n\leq 1.65$ and $1.65 < n \leq 1.74$. The accuracy of the measurements was $\Delta n = \pm 0.0005$.

3. Experimental results and discussion

Experimental dispersion curves obtained for nominally pure undoped glasses with the $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions are presented in Fig. 1. The data points in Fig. 1 represent the averaged values of the refractive indices, since the investigated glasses of the same composition shows somewhat different refractive indices. That is related to non-identical technological conditions of the synthesis and post-synthesis thermal annealing of the samples. The deviation of the refractive indices from their average values occurring in different samples with the $Ca_3Ga_2Ge_3O_{12}$ and $Ca_3Ga_2Ge_4O_{14}$ compositions does not exceed ±0.01 in the spectral region 420–680 nm. $Ca_3Ga_2Ge_4O_{14}$ composition (Fig. 1, curve 2) is characterized by considerably larger values of refractive index, when compare to $Ca_3Ga_2Ge_3O_{12}$ composition (see Fig. 1, curve 1). Since the glass of Ca-gallogermanate composition ($3CaO-Ga_2O_3-4GeO_2$) contains one additional unit of GeO_2 oxide, in comparison to the glass of the garnet composition ($3CaO-Ga_2O_3-3GeO_2$), one can state that the increase in germanium content in the basic glass leads to increasing refractive index of the glass. On the basis of this result, lower refractive index values for the glasses of the same composition can be related to deficiency of germanium, because the GeO_2 oxide is the most volatile component of the melt during the glass synthesis [13].

The influence of Ce and Nd impurities on the refractive index dispersion of the glass with the garnet $Ca_3Ga_2Ge_3O_{12}$ composition is shown in Fig. 2. Ce and Nd impurities give rise to essential increase in the refractive indices of the doped glasses (Fig. 2, curves 2 and 3), if compare with the results for the undoped glasses of the same composition (see Fig. 2, curve 1). In spite of lower content of Nd (0.2 wt. % of Nd_2O_3), in comparison with that of Ce (0.7 wt. % of Ce_2O_3), the refractive index of Nd-doped

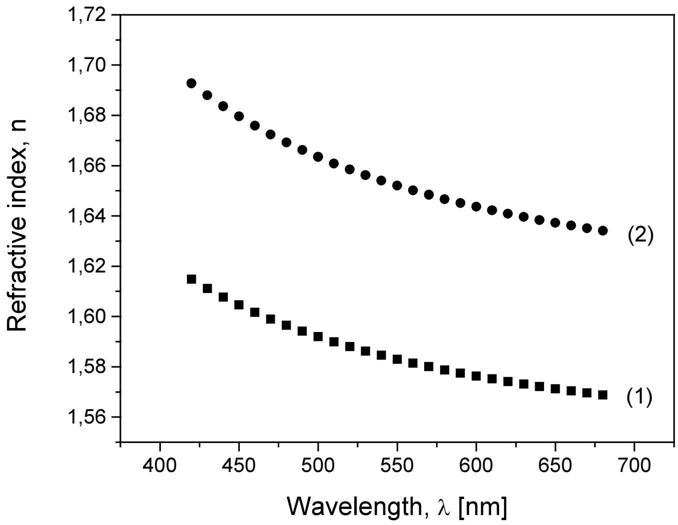

Fig. 1. Refractive index dispersion for the undoped glasses with $Ca_3Ga_2Ge_3O_{12}$ (1) and $Ca_3Ga_2Ge_4O_{14}$ (2) compositions. The data refer to the room temperature.

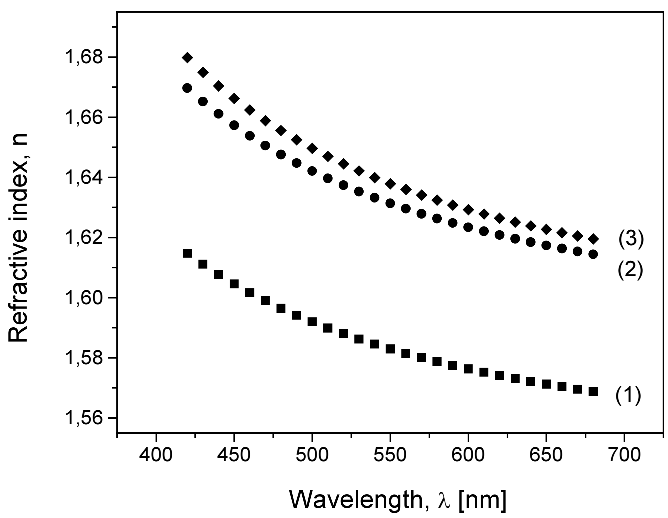

Fig. 2. Refractive index dispersion for the undoped glass with $Ca_3Ga_2Ge_3O_{12}$ composition (1) and the same glass doped with Ce (2) and Nd (3). The data refer to the room temperature.

glass is practically the same as the corresponding parameter of Ce-doped one (Fig. 2, curves 2 and 3). These results demonstrate that the refractive index of rare-earth doped glasses increases with increasing content and atomic number of the dopant impurities. The latter fact should be properly taken into account when using the dispersion data in the Judd-Ofelt analysis of rare-earth luminescence centres.

In order to compare the refractive indices of the undoped glasses and the crystals with the same composition, the dispersion curves for $Ca_3Ga_2Ge_3O_{12}$ garnet crystal have been measured and analyzed. Though the structure of the garnet crystal is cubic (isotropic), the refractive indices measured in different parts of the same garnet sample turn out to be considerably different. The difference between the local refractive index values measured in different parts of the same $Ca_3Ga_2Ge_3O_{12}$ crystal and the average value does not exceed ±0.08 for the spectral region of 420–680 nm. The mentioned differences observed for different parts of the same garnet sample ($\Delta n \le \pm 0.08$) are larger than those characteristic of different glass samples with the $Ca_3Ga_2Ge_3O_{12}$ garnet composition ($\Delta n \le \pm 0.01$). Significant variations of the refractive indices observed for different parts of the same garnet crystal can be associated with inhomogeneous distribution of germanium in the garnet $Ca_3Ga_2Ge_3O_{12}$ lattice. That leads to formation of $Ge^{4+}_{[a]}$ (Ge^{4+} cations in the octahedral [a] sites) and $Ga^{3+}_{(d)}$ (Ga^{3+} cations in the tetrahedral (d) sites) anti-structural (or anti-site) defects [14,15].

The average value of the refractive index for undoped garnet crystal $Ca_3Ga_2Ge_3O_{12}$ ($n=1.64\pm0.08$ at $\lambda = 500$ nm and $T = 300$ K) is notably less than the refractive indices of compositionally disordered Ca-gallogermanate single crystals studied in [16,17]. Anisotropic (trigonal) Ca-gallogermanate crystals are characterized by higher refractive indices ($n_o = 1.813$ and $n_e = 1.838$ at $\lambda = 500$ nm and $T = 300$ K) [16,17] than the glasses of the same ($Ca_3Ga_2Ge_4O_{14}$) composition.

Conclusions

On the basis of results presented in this paper and the analysis of the reference data we conclude the following:

(i) The refractive indices of the glasses and crystals of CaO-Ga_2O_3-GeO_2 system depend on the basic composition. The increasing content of Ge in the glass and crystal compositions leads to significant increase in their refractive indices.

(ii) The presence of Nd and Ce impurities in the amounts larger than 0.1 wt. % leads to essential increase in the refractive index of the $Ca_3Ga_2Ge_3O_{12}$ composition glasses. In general, the refractive index of the rare-earth doped glasses increases with increasing content and atomic number of the doping impurities.

(iii) The differences in the refractive indices observed in the same glasses with the garnet $Ca_3Ga_2Ge_3O_{12}$ composition are related to non-identical technological conditions of the glass synthesis that yield deficiency or excess of germanium in the glass samples. The refractive indices of the crystals with $Ca_3Ga_2Ge_4O_{14}$ compositions are higher than those for the glasses of the same compositions. Essentially larger deviations of the refractive index observed for different parts of the same $Ca_3Ga_2Ge_3O_{12}$ crystal ($\Delta n \le \pm 0.08$), when compare with the corresponding effect peculiar for the glass of the same composition ($\Delta n \le \pm 0.01$), could be associated with inhomogeneous distributions of Ge in the garnet crystals.

Acknowledgements

The authors are thankful to Petro Buchynskii from Lviv Scientific Industrial Amalgamation “MikroTech Karat” for synthesis of the glass samples. Special thanks are to Prof. Rostyslav Vlokh for stimulating discussions. This work has been partly supported by Kazimierz Wielki University of Bydgoszcz under the grant BW / 2006.

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