Micro inhomogeneities of alkali niobate germanate glasses studied by light scattering spectroscopy.

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Li_2O-Na_2O-GeO_2-Nb_2O_5 glasses were studied by means of Rayleigh and Mandel'shtam-Brillouin and Raman scattering spectroscopy. Composition dependencies of Landau-Placzek ratios and Rayleigh scattering losses were found. Raman spectra were processed and constant stoechiometry groupings were identified. Growth of Kerr coefficient with Nb concentration was explained by forming of groupings with stoichiometry of well-known electrooptical crystals.

Introduction

Recently interest in niobate glasses has been caused by their peculiarities attractive for some up-to-date applications. It was found that niobate glasses and glass-ceramics were characterized by high Kerr coefficients relative to other glasses and may be used to form electrically controlled optical devices [1-3]. In addition, it was found that niobate glasses and glass-ceramics doped with rare-earth ions may be considered as promising luminescent and laser materials [4,5]. However, the studies were restricted to niobosilicate and niobophosphate [6] glass systems. Our research is targeted on the analysis of structure of alkali niobogermanate glasses on the base of light scattering spectroscopy data.

Theoretical background

As is well-known, Rayleigh and Mandel'shtam-Brillouin scattering (RMBS) spectroscopy gives us an opportunity to spectrally separate contributions from isobaric density fluctuations (Rayleigh scattering - RS) and from adiabatic density (ρ) fluctuations (Mandel'shtam-Brillouin scattering - MBS) into the light scattered by a single component matter and to estimate the role of fluctuations of different origins into the light scattering through the ratio of component intensities ($R_{L\text{-}P} = R_\rho + R_{anis} = I^{RS}/I^{MBS}$).

In the case of multicomponent system, $R_{L\text{-}P} = I^{RS}/I^{MBS} = R_\rho + R_C + R_{anis} = I_\rho^{RS}/I^{MBS} + I_C^{RS}/I^{MBS} + R_{anis}$, where R_ρ, R_C, I_ρ^{RS}, I_C^{RS}, R_{anis} are the contributions of isobaric density, concentration (C), and anisotropy fluctuations into $R_{L\text{-}P}$ and I^{RS}. Hence, $R_{L\text{-}P}$ may be considered as a measure of physical and chemical microinhomogeneity of a medium while I^{MBS} plays the role of inner reference that ensures estimation of Rayleigh scattering losses through $R_{L\text{-}P}$.

Glasses are characterized by increased I^{RS} because of "freezing" of isobaric density, concentration, and anisotropy fluctuations in the process of glass transition. It was found that “frozen-in” concentration fluctuations dominate in Rayleigh scattering by multicomponent glasses [7].

Comparison of RMBS and Raman spectroscopy data for the two component glass forming systems showed that concentration fluctuations were built of constant stoichiometry groupings (CSG) found from Raman spectra [8].

It was proposed to extend this approach to niobate glasses supposedly containing CSGs with stoichiometry of electrooptical (EO) crystals $NaNbO_3$ or $LiNbO_3$ because the main problem to be solved was to design EO glasses with high Kerr coefficient and low Rayleigh scattering losses.

Experimental

$5Li_2O – 5Na_2O – (90 – x) GeO_2 – x Nb_2O_5$, $10Li_2O – 10Na_2O – (80 – x) GeO_2 – x Nb_2O_5$, and $x (0.5 Li_2O – 0.5 NaO_2 – Nb_2O_5) – (100 – 2x) GeO_2$ glass series were synthesized and studied by Rayleigh and Mandel’shtam-Brillouin (RMBS) and Raman scattering spectroscopy. RMBS was excited by a helium-neon laser (λ= 633 nm) and the spectra were taken with RMBS spectrometer at the 90^o scattering angle. To enhance the contrast of the spectra, computer processing based on deconvolution technique was used [9]. Polarized spectra of Raman scattering excited by an argon laser (λ= 483 nm) were measured by the two-beam spectrometer. The spectral width of the slit was no greater than 2 cm^{-1}. The spectra of studied glasses were strongly polarized. Relative intensities of Raman spectra were measured at 80 and 800 cm^{-1}. Silica glass was used as a reference.

Results and discussion

Fig.1 shows that Rayleigh scattering losses increase with Nb content in glasses. Having in mind the data on RMBS spectra of alkali-germanate and alkali nioboborosilicate glasses [8], one can suppose that the curves in Fig.1 should be explained by the growth of light scattering by Nb containing “frozen-in” concentration fluctuations. Similarity of composition dependencies and Rayleigh scattering intensities confirms the possibility to use intensity of MBS components in RMBS spectra as an inner reference.

Growth of total percentage of alkali oxides leads to the extension of glass forming area in alkali niobogermanate systems. It resulted in the forming of glasses with high concentration of niobium.

The next question concerns internal structure of these Nb containing micro inhomogeneitites in niobate glasses. To answer it, the Raman spectra were decomposed by the technique of subsequent extraction of band intensities of one spectrum from another described elsewhere [10]. It was found that the residual spectral form was characterized by unchangeable contour ascribed to the CSG (Li, Na) $NbO_3 \cdot nGeO_2$ (Fig.2).

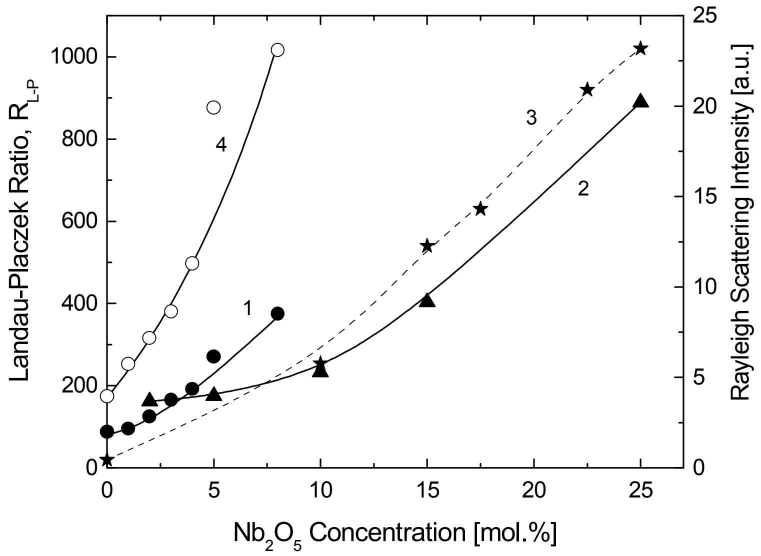

Fig. 1. Landau-Placzek ratio, R_{L-P}, as functions of Nb_2O_5 concentration in ($5Li_2O$–$5Na_2O$)–(90-x)GeO_2–$x Nb_2O_5$ (1), ($10Li_2O$–$10Na_2O$)–(80-x)GeO_2–$x Nb_2O_5$ (2), and x($0.5Li_2O$–$0.5NaO_2$–Nb_2O_5)–(100–2x)GeO_2 (3) glasses. Curve 4 is the Rayleigh scattering intensity measured relative to that of silica glass versus composition of ($5Li_2O$–$5Na_2O$)–(90-x)GeO_2–$x Nb_2O_5$ glasses . Curves are drawn as a guide for eye.

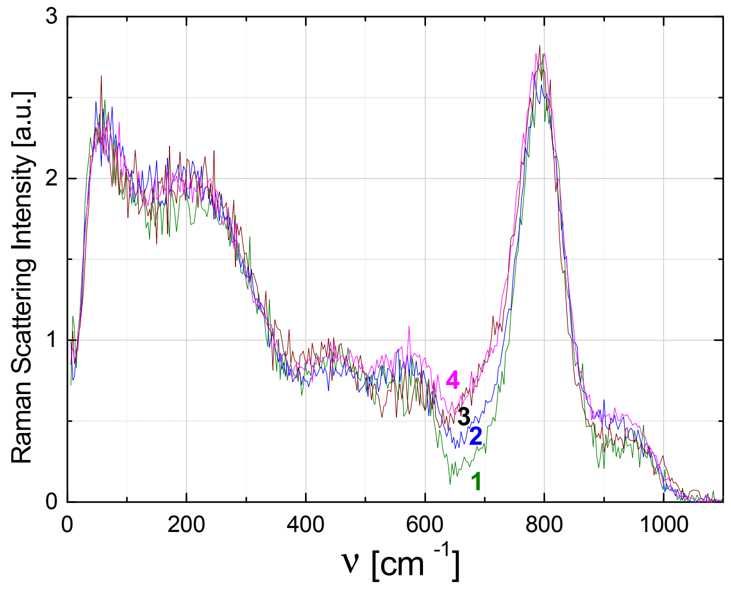

Fig. 2. Contour of the bands extracted from Raman spectra of ($5Li_2O$–$5Na_2O$)–(90-x)GeO_2–$x Nb_2O_5$ glasses ascribed to CSGs (Li, Na) $NbO_3 \cdot nGeO_2$. HV polarization. Numbers at the curves are Nb_2O_5 concentrations (mol%).

Processing of Raman spectra led to determination of partial spectral forms ascribed to CSGs listed in capture to Fig. 3. As opposed to the two component germanate systems, the exact compositions of CSGs (that is m, n) in the glasses under study could not be identified.

Similarly to alkali niobosilicate glasses, one can suppose that the appearance of Nb in alkali germanate glasses causes formation of (Li, Na) $NbO_3 \cdot nGeO_2$ CSGs that leads to Raman scattering in 800 cm^{-1} range. Additional portions of Nb promote their decomposition under the scheme: (Li, Na) $NbO_3 \cdot nGeO_2 \rightarrow$ (Li, Na)NbO_3 + (Li_2O, Na_2O)$\cdot pGeO_2$ that results in Raman scattering in the 730 cm^{-1} range.

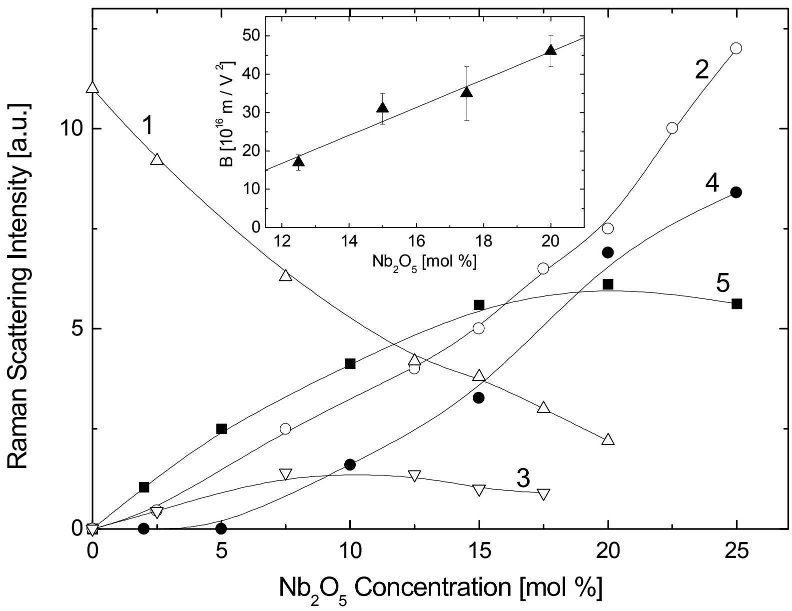

Fig. 3. Intensity of partial spectral forms in Raman scattering spectra taken at HH-polarization versus Nb_2O_5 concentration. The curves are related to the forms ascribed to CSGs (Li_2O, Na_2O)$\cdot mGeO_2$ (curve 1), (Li, Na)NbO_3 (2), (Li, Na)$NbO_3 \cdot nGeO_2$ (3) in x($0.5Li_2O$–0.5 NaO_2–Nb_2O_5)–(100–2x)GeO_2 glasses and CSGs (Li, Na)NbO_3 (4) and (Li, Na)$NbO_3 \cdot nGeO_2$ (5) in ($10Li_2O$–$10Na_2O$)–(80-x)GeO_2–$x Nb_2O_5$ glasses. In the insert: the Kerr coefficient of x($0.5Li_2O$–$0.5NaO_2$–Nb_2O_5)–(100–2x)GeO_2 glasses versus Nb_2O_5 concentration. Curves are drawn as a guide for eye.

Hence, one can expect that increase in amount of CSGs Nb containing groupings structurally similar to the well-known EO crystals should cause the growth of Kerr coefficient and "frozen-in" fluctuations of their concentration determining Rayleigh scattering losses. Experimental data shown in Figs. 1 and 3 does not contradict to this hypothesis but the role of other structural microinhomogeneities in EO properties of the glasses should be studied in more detail in future.

Conclusions

Incorporation of Nb in composition of alkali germanate glasses leads to the growth of both Rayleigh scattering and the Kerr coefficient with Nb percentage that is caused by the fluctuation microinhomogeneities formed from constant composition groupings with stoichiometry of well-known electrooptical crystals.

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[1] A.A.Zhilin, G.O.Karapetyan, A.A.Lipovskii, L.V.Maksimov, G.T.Petrovsky, D.K.Tagantsev "Vitreous Materials for Electrooptics" Glass Physics and Chemistry 2000, 26, n 1, pp. 242-246.

[2] G.O.Karapetyan, A.A.Lipovskii, V.V.Loboda, L.V.Maksimov, D.V.Svistunov, D.K.Tagantsev, B.V.Tatarintsev, A.A.Vetrov "Electrooptic Glasses and Glass-Ceramics for Elements Controlling Laser Radiation" SPIE v.4323, pp. 23-28, 2001.

[3] G.S.Maciel, N.Rakov. Cid B.de Araujo, A.A.Lipovslii, D.K.Tagantsev "Optical limiting behavior of a glass-ceramics containing sodiun niobate crystallites" Applied Phys. Lett. 2001, v.79, n 5, pp. 284-286.

[4] Zhidong Yao, Yong Ding, Tokuro Nanda, Yoshinari Miura "Photoluminescence Increase of Er^{3+} in Na_2O-Nb_2O_5-SiO_2 Glasses after Crystallization" J.Non-Crystal. Solids, 1999, 259, pp. 45-50.

[5] Chung Jiang, Qingji, Zeng, Hua Liu, Xiaodong Tang, Junzhou Zhang, Fuxi Gan "Yb:niobosilicate Glass with High-Emission Cross Section" J. Amer.Ceram.Soc. 2000, 83, n 7, pp.1709-1712.

[6] Cid B.de Araujo, J.A.C.Laiva, A.S.B.Sombra "The Properties and Crystallization of $LiNbO_3$ in Lithium Niobophosphate Glasses" J. Phys.: Condens. Matter 1995, 7, pp.9723-9730.

[7] J. Schroeder "Light Scattering by Glass" Treatise on Material Science and Technology. V.12, Glass 1. Acad. Press. New York, N.Y., 1977, pp.157-222.

[8] G.O.Karapetyan, L.V. Maksimov, O.V. Yanush "Physical Consequences of Inhomogeneous Glass Structure from Scattered Light Spectroscopy Data" J. Non-Crystal. Solids, 1990, v.123, n 1-2. pp.286-290.

[9] G.O.Karapetyan, A.B.Konstantinov, L.V.Maksimov, P.V.Reznichenko "Bayessian Deconvolution of Spectra for Rayleigh and Brillouin Scattering in Glasses" Sov. J. Appl.Spectroscopy 1985, 43, n 5, pp.1243-1247.

[10] A. Lipovskii, D. Tagantsev, B. Tatarintsev, A.Vetrov, O.Yanush "Raman Spectroscopy and the Origin of Electrooptical Kerr Phenomenon in Niobium Alkali-Silicate Glasses" Optical materials (in press).