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Electrooptical Kerr phenomenon and Raman spectroscopy of one lithium–niobium–silicate glass-forming system

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Abstract

Raman spectra and electrooptical Kerr coefficients of glasses belonging to one lithium–niobate–silicate glass-forming system $x\mathrm{Nb_2O_5} \cdot (66 - x)\mathrm{SiO_2} \cdot 19\mathrm{Li_2O} \cdot 11\mathrm{K_2O} \cdot 2\mathrm{B_2O_3} \cdot 2\mathrm{CdO}$ are studied. It has been found that these glasses demonstrate a record value of electrooptical Kerr coefficient; the glass with $x = 35$ showed electrooptical Kerr coefficient equal to 266×10^{-16} m/V^2. Using Raman spectroscopy combined with the concept of Constant Stoichiometric Groupings, a correlation of electrooptical Kerr coefficients of these glasses with the content of $\mathrm{Li_2O} \cdot \mathrm{Nb_2O_5}$ (or $2\mathrm{LiNbO_3}$) groupings has been demonstrated. The hypothesis that electrooptical Kerr sensitivity of glasses is related to the ordered regions with composition and symmetry corresponding to some of known electrooptical crystals has been verified. These regions, which the authors called 'Crystal Motifs', are identified with the groupings found in studying Raman spectra of the glasses.

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1. Introduction

Recently [1,2] the authors have suggested that enhanced (if any) electrooptical Kerr sensitivity of glasses originates in their microinhomogeneous structure, that is, in the concentration and density fluctuations native to glasses. It is considered that if a glass demonstrates an increased electrooptical Kerr sensitivity, these fluctuations are the ordered regions with the structure (composition and symmetry) corresponding to some Kerr electrooptical crystal, the regions' size being about 2–3 coordination spheres, that is, 1–2 nm. These regions have been called the Crystal Motifs (CMs) [1]. In different designations, the very similar hypotheses are proposed by other researchers [3–7] as well. Due to small sizes of the CMs it is hardly possible to observe CMs directly, and, by now, only indirect methods have been developed (for example, Mandel'shtam–Brillouin light scattering or small angle X-ray scattering), but they give too general information about the regions, like their average size or electron density. However, for the basic and applied reasons, it is of interest to characterize the CMs by two additional parameters: composition and symmetry (or type of 'crystalline' lattice of ordered regions). In our previous work [2], it has been shown that Raman spectroscopy can give information on the composition of typical entities, which are identified with the CMs responsible for electrooptical sensitivity of glasses. The approach used is based on the presentation of vibration spectra of oxide

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glasses as a superposition of relatively small number of unchangeable spectral components (partial spectra), which, being additively summarized, form the glass spectrum. These partial spectra result from the stable products of the interaction between initial simple oxides, like those in the glass batch. Such products are called the Constant Stoichiometric Groupings (CSG); in Raman spectra, these groupings can be related to a set of the partial spectra, which are called the Principle Spectral Components (PSC) [8]. However, CSGs found from Raman spectra supply us with information on the CMs' composition only and do not give any information on crystalline (symmetry) structure of the CMs. The lack of this information can be filled by knowledge on electrooptical Kerr coefficients of the same glasses, for a difference in crystalline symmetry of the CMs of the same composition conditions their different electrooptical response. All this makes reasonable to perform systematic study of Raman spectra and electrooptical Kerr coefficients (or other glass properties dependent on the structure of CMs, like, e.g., non-linear refractivity, which is linearly proportional to electrooptical Kerr coefficient [9]) of glasses depending on their compositions. In the present work we apply this approach to study a lithium–niobium–silicate glass-forming system. We call these glasses LiS glasses.

2. Experimental

Compositions of LiS glasses can be formalized as $x\mathrm{Nb_2O_5}\cdot(66-x)\mathrm{SiO_2}\cdot 19\mathrm{Li_2O}\cdot 11\mathrm{K_2O}\cdot 2\mathrm{B_2O_3}\cdot 2\mathrm{CdO}$ with x ranging from 0.5 to 35. The glasses were produced by melting an appropriate 180-g batch in platinum crucible at 1400–1450 °C for 2 h with stirring. The melts were poured out onto a pre-heated brass plate, and each resultant glass was annealed for 2 h at their glass transition temperature, T_G, with this temperature corresponding to the glass viscosity equal to $10^{12\pm0.2}$ Pa s. The anneal temperatures varied from 495 °C to 550 °C. The glasses were characterized by differential thermal analysis. Optical absorption spectroscopy and refractometry were used to characterize transparency and refractivity of the glasses. Experiments on crystallization of the glasses in the course of their annealing at temperatures above T_G (600–650 °C) have been performed as well, and formed crystalline phases were characterized by X-ray diffractometry (XRD) using powdered samples and Cu Kα radiation.

Polarized Raman spectra of synthesized glasses were measured with 2 $\mathrm{cm^{-1}}$ step at room temperature by two-beam spectrometer using photomultipliyer in photon counting mode. In the calculations of spectra derivatives, smoothing interval was chosen in such a way that for several spectra of glasses with close compositions the same maxima could be clearly observed. Raman scattering was excited by argon laser ($\lambda = 0.488$ μm, power 1 W). Relative intensities of Raman spectra were measured at frequencies 80 and 800 $\mathrm{cm^{-1}}$, the sample made of fused silica being used as a reference. The set of CSG was found using the matrix Wallace–Katz technique [10].

The measurements of electrooptical Kerr coefficient of the glasses were performed using the technique earlier developed by authors. The description of the technique is presented in [11] in detail and in [1,2] in brief.

3. Results

The glasses demonstrated refractive index increasing from 1.55 to 1.95 (in visible optical range) with a rise in niobium oxide content. In parallel, the glasses changed from fully transparent in visible range (except Fresnel losses) to yellowish that, in accordance with optical absorption spectra, was conditioned by shifting their fundamental absorption edge.

Fig. 1 displays the dependence of electrooptical Kerr coefficient on niobium oxide content (x) in LiS glasses. One can see that electrooptical Kerr coefficient does not change up to x equal to ~10, and then it rises with acceleration. It should be noted that for $x = 35$ electrooptical Kerr coefficient achieves its maximal value, equal to 266×10^{-16} $\mathrm{m/V^2}$, which, by our knowledge, is the absolutely maximal one for glasses at all.

Fig. 2 depicts Raman spectra of LiS glasses depending on x. (For this figure to be not overcharged, we do not present spectra of all the LiS glasses studied.) One can observe that first portions of niobium oxide lead to the appearance of a vibration band at about 850 $\mathrm{cm^{-1}}$. The next portions of niobium oxide (over 10 mol%) result in two other bands in the vicinities of 800 $\mathrm{cm^{-1}}$ and 650 $\mathrm{cm^{-1}}$, which, on the background of the already unchangeable band laying in the region of 850 $\mathrm{cm^{-1}}$, profoundly rise with niobium content, with the band at 650 $\mathrm{cm^{-1}}$ rising faster than the one at 800 $\mathrm{cm^{-1}}$. Fig. 3

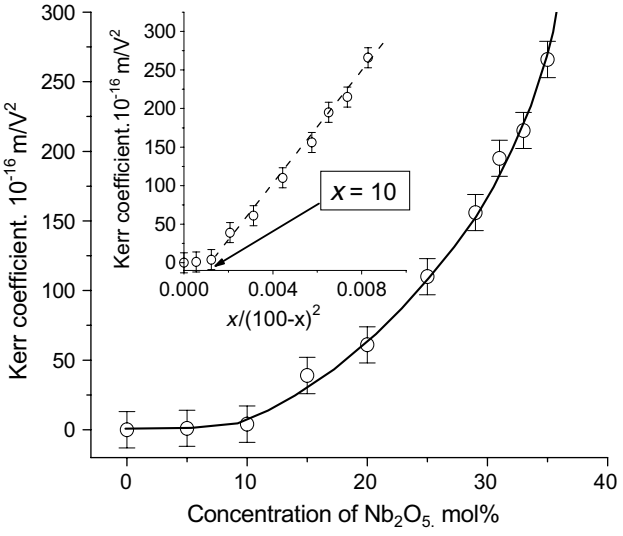

Fig. 1. Electrooptical Kerr coefficient of LiS glasses via niobium oxide content x. Insert: the dependence of electrooptical Kerr coefficient on $x/(100-x)^2$.