

# Mid-Range Structure of Niobium–Sodium–Phosphate Electro-Optic Glasses

A. A. Lipovskii,<sup>†,‡</sup> D. K. Tagantsev,<sup>‡,§,\*</sup> I. E. Apakova,<sup>||</sup> T. S. Markova,<sup>||</sup> O. V. Yanush,<sup>||</sup> M.G. Donato,<sup>⊥</sup> L. Sirleto,<sup>#</sup> G. Messina,<sup>∇</sup> and G. C. Righini<sup>○,◆</sup>

<sup>†</sup>St. Petersburg Academic University, 195220 St. Petersburg, Russia

<sup>‡</sup>St. Petersburg State Polytechnical University, 195251 St. Petersburg, Russia

<sup>§</sup>Research and Technological Institute of Optical Materials Science, 193171 St. Petersburg, Russia

<sup>||</sup>St. Petersburg Technological University of Plant Polymers, 198095 St. Petersburg, Russia

<sup>⊥</sup>CNR, Istituto per i Processi Chimico-Fisici, 98123 Messina, Italy

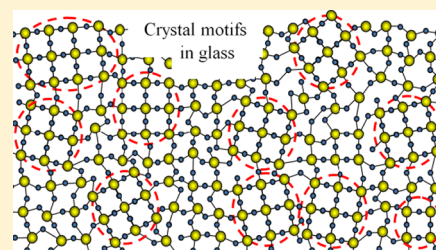
<sup>#</sup>CNR, Istituto per la Microelettronica e Microsistemi, 80131 Napoli, Italy

<sup>∇</sup>Dipartimento MECMAT, Facoltà di Ingegneria, Università “Mediterranea”, 89060 Reggio Calabria, Italy

<sup>○</sup>CNR, Istituto di Fisica Applicata Nello Carrara, 50019 Sesto Fiorentino, Italy

<sup>◆</sup>Museo Storico della Fisica e Centro Studi e Ricerche Enrico Fermi, 00184 Roma, Italy

**ABSTRACT:** The mid-range structure of glasses of the glass-forming system  $x\text{Nb}_2\text{O}_5-(60-x)\text{P}_2\text{O}_5-40\text{Na}_2\text{O}$ , with  $x$  varying from 0 to 40, has been investigated by Raman spectroscopy and electro-optical Kerr measurements. It was found that the mid-range inhomogeneities in the glasses under study vary with  $x$  and their compositions and structures dramatically differ from the gross glass composition. It is shown that inhomogeneities with the  $8\text{NaNbO}_3 + (\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5)$  composition are responsible for the electro-optical sensitivity of the glasses. The electro-optical structural elements of the inhomogeneities of this type are assumed to be fragments of the quasicubic lattice of crystalline  $\text{NaNbO}_3$  demonstrating a rather high electro-optic Kerr coefficient. The obtained results are discussed in terms of the concepts of constant stoichiometric groupings and crystal motifs.



## 1. INTRODUCTION

In the works<sup>1,2</sup> of several authors of this article, it was shown that the combination of data obtained from the study of Raman spectra and electro-optic Kerr coefficients of glasses provides rather useful information about glass structure, in particular about the structure and composition of mid-range inhomogeneities “frozen” in cooling glass melts below the glass transition temperature. To interpret these data, two concepts were used, namely, the concept of constant stoichiometric groupings (CSGs) first stated in refs 3–5 and subsequently developed<sup>6,7</sup> and the concept of crystal motifs (CMs) first described in ref 8 and also developed further.<sup>9</sup>

The former concept is based on the description of the vibrational spectra of glasses as superpositions of relatively small numbers of invariant spectral contours (forms) that are attributed to certain stable products forming in the glass melt from simple oxides included in the initial glass batch. These spectral contours are called principal spectral components (PSCs). Being combined additively, the PSCs form resultant spectra that are those actually recorded in experiments. It is the above-mentioned stable products that are called CSGs. In Raman spectra, each CSG can be generally related to certain spectral bands belonging to one PSC. The set of PSCs (or

CSGs) is determined by processing Raman spectra using the matrix technique introduced by Wallace and Katz.<sup>10</sup>

In accordance with the CM concept, the glass is a quasiheterogeneous system consisting of a continuous disordered glassy network and CMs, where the latter are the ordered regions with crystal-like structure within two to three (no more than four) coordination spheres, the regions having no phase boundaries. By the term “crystal-like”, we suggest, first, that the composition of a CM can differ from the batch glass composition and exactly coincide with the stoichiometry of some chemical compound and, second, that the relative positions of all of the atoms comprising the CM are exactly the same as in one of the crystalline modifications (phases) of this compound. This enables the structure of CMs to be considered as a fragment of a crystalline lattice that is too small to be detected by X-ray diffraction but large enough to attribute its structure to a specific crystalline symmetry or, in other words, to make possible the recognition of the type of crystalline lattice residing in CMs. Following the CM concept, most optical properties of glasses are determined by the composition

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and structure (that is, type of lattice symmetry) of CMs. For example, a glass can demonstrate a high value of the electro-optical Kerr coefficient ( $B$ ) only if the composition and structure of CMs correspond to those of an electro-optic crystal, and a decrease or increase in the concentration (or volume fraction) of electro-optic CMs in a glass is expected to be accompanied by a corresponding decrease or increase in the  $B$  value of the glass.

Application of the CSG concept to Raman spectra provides information about the CM stoichiometry only, whereas values of  $B$  can provide information about the CM structure, that is, about the type (symmetry) of crystalline lattice that could be ascribed to the CM. These statements have been corroborated in studying  $B$  of several alkali niobium silicate glass-forming systems,<sup>1,2</sup> for which a linear correlation was found between  $B$  and the intensity of Raman bands attributed to the collective vibrations in CMs with the composition and structure of lithium or sodium niobate crystals (well-known electro-optic crystals). A simple theory<sup>9</sup> initially developed for glass-ceramics predicts the following dependence of  $B$  on the volume fraction of CMs ( $f$ ):  $B = B_c f / [\alpha + f(1 - \alpha)]^2$ , which, for  $\alpha \gg 1$  and  $f \neq 1$  gives

$$B = \beta \frac{f}{(1 - f)^2} \quad (1)$$

where  $\beta = B_c/\alpha^2$ ;  $\alpha = \epsilon_c/\epsilon_g$ ;  $B_c$  is the electro-optic Kerr coefficient of the crystal with composition and structure of CMs; and  $\epsilon_c$  and  $\epsilon_g$  are the permittivity of such a crystal and the that of the disordered glass matrix, respectively.

The relationship expressed by eq 1 has been found to be in good agreement with experiment<sup>1</sup> if one assumes that the dependence of the volume fraction of CMs on the concentration of CM-former ions is linear. In the above-mentioned case of lithium (sodium) niobate silicate glasses, the CM former was niobium because, in accordance with the Raman study, the CMs found in those glasses had the composition of alkali niobate crystals and the increase of  $B$  with niobium oxide concentration  $x$  in those glasses obeyed just eq 1, where  $f$  was substituted by  $x$ . At the same time, an increase in niobium concentration can result in decreasing  $B$  value if niobium ions do not have partners (say, sodium ions) to form electro-optic CMs. Such a case was observed in our study of electro-optic alkali-free niobium tellurite glasses,<sup>11</sup> where addition of niobium oxide to the glass resulted in diluting the electro-optic Te-based CMs.

The validity of eq 1 was first checked in experiments with electro-optic glass-ceramics for which  $f$  was the volume fraction of alkali niobate nanocrystals.<sup>9</sup> It should be noted that, in accordance with the CM concept, CMs are regarded as nonequilibrium nuclei (prenuclei) of the crystalline phase that precipitate first in heat treatment of the glass above the glass transition temperature. This thesis has been confirmed by our<sup>9</sup> and other studies<sup>12–16</sup> of glass crystallization, where glasses demonstrating a high value of  $B$  formed glass ceramics with electro-optic nanocrystals.

In this article, we present the results of studying the Raman spectra and electro-optic sensitivity of phosphate glasses with a fixed content of sodium and a content of niobium systematically increasing at the expense of phosphorus. The composition and structure of CMs in these glasses were expected to coincide with the composition of either quasicubic  $\text{NaNbO}_3$  or other electro-optical sodium/niobate crystals that would result in a

relatively high electro-optic response of these glasses and a linear dependence of  $B$  on the variable  $x/(100 - x)^2$ , where  $x$  is the molar percentage of niobium oxide.

## 2. EXPERIMENTAL SECTION

**2.1. Glasses.** Recently,<sup>17</sup> the glasses under study were examined to estimate their value as candidate media for Raman optical amplification. The compositions of these glasses can be expressed as  $x\text{Nb}_2\text{O}_5-(60 - x)\text{P}_2\text{O}_5-40\text{Na}_2\text{O}$ , with  $x$  varying from 0 to 40, and  $x\text{Nb}_2\text{O}_5-(50 - x)\text{P}_2\text{O}_5-50\text{Na}_2\text{O}$ , with  $x$  equal to 20 or 30. All glasses were synthesized at 1200–1300 °C by melting an appropriate 150-g batch in silica glass or Pt crucibles for 40 min with 20 min of stirring. Pt crucibles were preferably used for melting glasses with a high content of Nb. The initial reagents were chemically pure  $\text{NaPO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaNO}_3$ , and  $\text{Nb}_2\text{O}_5$ . The melts were poured out into a carbon mold, and each resultant glass was annealed for 2 h at the temperature corresponding to the glass viscosity, equal to  $10^{12 \pm 0.5}$  Pa·s; for the present set of glasses, this temperature depended on glass composition and ranged from 450 to 470 °C. Table 1 summarizes the compositions and corresponding labels of the synthesized glasses.

**Table 1. Compositions (mol %) and Measured Electro-Optic Kerr Coefficients ( $B$ ) of the Glasses under Study**

glass label	$\text{Na}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{Nb}_2\text{O}_5$	$B (\times 10^{16} \text{ m/V}^2)$
24	40	60	0	(0.5)
25	40	55	5	$1 \pm 0.5$
27	40	45	15	$19 \pm 10$
29	40	40	25	$25 \pm 15$
53	40	30	30	$55 \pm 20$
54	40	25	35	$130 \pm 25$
55	40	20	40	$195 \pm 30$
13	50	30	20	$40 \pm 15$
15	50	20	30	$110 \pm 20$

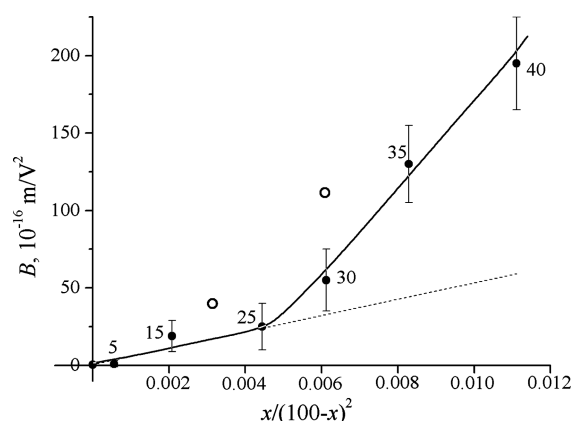
**2.2. Kerr Measurements.** The measurements of the electro-optic Kerr coefficients of these glasses were performed at a HeNe laser wavelength of  $\lambda = 0.63 \mu\text{m}$ . The radiation going through the sample was modulated by a low-frequency electric field (5 kHz, up to 3.0 kV/mm) applied to the sample. The samples were placed between two crossed polarizers, and according to the quadratic character of electro-optic Kerr phenomenon, the output signal was measured at the second harmonic of the input frequency, that is, at 10 kHz. This scheme provided high sensitivity due to the measurements taking place at a frequency range free from typical noises. The measurement accuracy was  $\pm 10\%$  for  $B > 10^{-14} \text{ m/V}^2$  and  $\pm 50\%$  for  $B < 10^{-16} \text{ m/V}^2$ . A detailed description of the technique and apparatus used was reported previously.<sup>18,19</sup> Given the inhomogeneity of the glass samples synthesized under laboratory conditions, five to eight measurements of  $B$  were performed for each sample, with the probe light beam propagating through different regions of the sample in each such measurement; then, the arithmetic mean value of  $B$  and the root-mean-square deviation were calculated, with the latter being considered the experimental error.

**2.3. Raman Measurements.** Unpolarized Raman scattering measurements, that is, without selection of the polarization of the scattered beam, were carried out in a microconfiguration using a Jobin Yvon HR800 monochromator and a thermo-electric cooled CCD detector. The 633-nm line of a HeNe laser

was used as the excitation wavelength. The laser power at the sample surface was approximately 6 mW. An edge filter was used to suppress the Rayleigh line. Raman spectra were collected from the front surface of the samples.

### 3. RESULTS

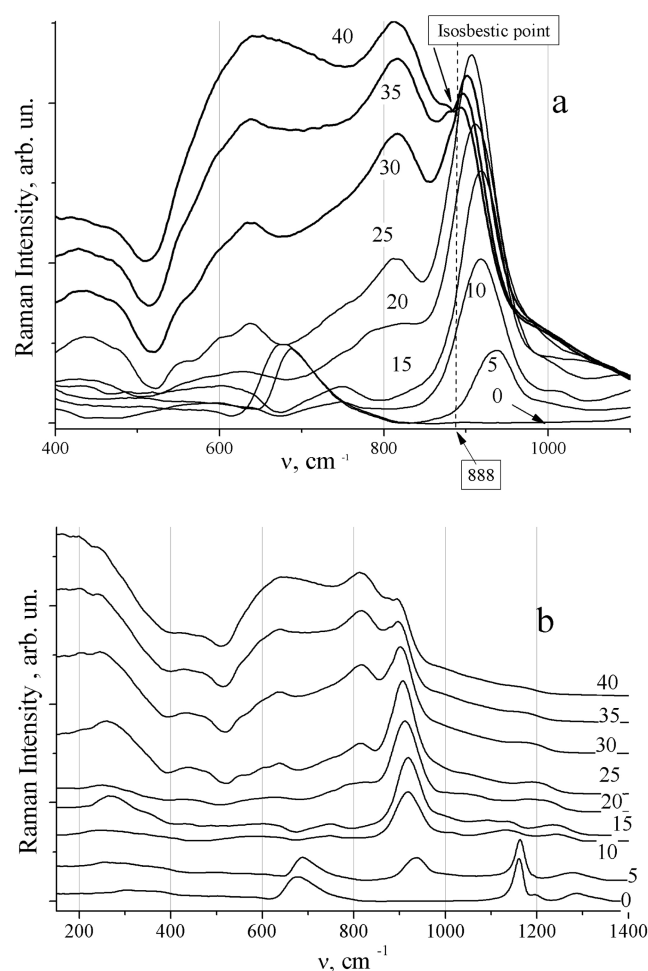
The measured electro-optic Kerr coefficients ( $B$ ) of the glasses under study are presented in Table 1, together with the glass compositions. The dependence of  $B$  on the niobium oxide concentration ( $x$ ) in the glasses is presented in Figure 1; this



**Figure 1.** Dependence of the electro-optic Kerr coefficient  $B$  on  $\text{Nb}_2\text{O}_5$  molar percentage  $x$  (values at the points are equal to  $x$ ).

dependence is plotted as a function of the variable  $x/(100-x)^2$  rather than  $x$ , because, in accordance with the CM concept, the use of such a variable is expected to result in a linear character of the concentration dependence of  $B$ , if niobium ions are considered as the CM formers. Indeed, Figure 1 clearly shows the presence of two intervals where  $B$  varies linearly with  $x/(100-x)^2$ : In the first interval, corresponding to niobium oxide concentration varying from 0 to 25 mol %,  $B$  has a rather slow increase (from  $0.5 \times 10^{-16}$  to  $25 \times 10^{-16}$  m/V<sup>2</sup> with an average increment equal to about  $1 \times 10^{-16}$  m/V<sup>2</sup> per 1 mol %), whereas in the second interval, with niobium oxide concentrations varying from 25 to 40 mol %, the value of  $B$  increases by almost 1 order of magnitude (from  $25 \times 10^{-16}$  to  $195 \times 10^{-16}$  m/V<sup>2</sup> with an average increment of more than  $10 \times 10^{-16}$  m/V<sup>2</sup> per 1 mol %).

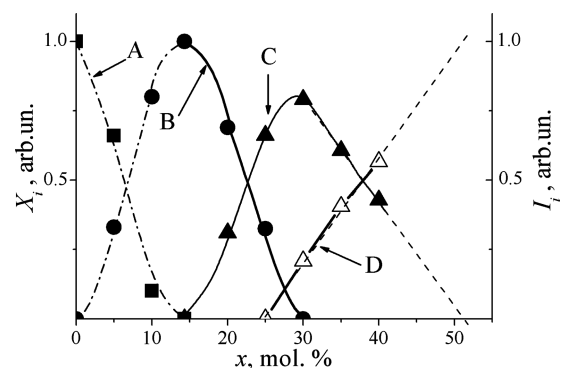
The Raman spectra of the studied glasses are presented in Figure 2. To reveal the PSCs, these Raman spectra were processed by the Wallace–Katz matrix technique.<sup>10</sup> In brief, this procedure<sup>20</sup> consists of finding the minimum number of linearly independent rows of a matrix comprising the set of spectral intensities at fixed frequencies for each experimental Raman spectrum. These frequencies are chosen in the wavelength regions in which the glass spectra demonstrate the greatest alterations with changing glass composition. Processing of the Raman spectra of the studied glasses resulted in revealing four PSCs, labeled A–D. In other words, the Wallace–Katz procedure gives a matrix consisting of four rows (not two or three) that allows the experimental Raman spectra of all studied glasses to be described, with each row presenting the (digital) tabulated spectrum of one PSC only. The tabulated spectra of each type of PSC revealed in different glasses coincide to within a constant factor. The four PSCs were found to appear and disappear one by one (in sequence A–D) according to the increase in the niobium oxide



**Figure 2.** (a) Raman spectra of  $40\text{Na}_2\text{O} \cdot x\text{Nb}_2\text{O}_5 \cdot (60-x)\text{P}_2\text{O}_5$  glasses, (b) the same spectra shifted along the ordinate while keeping the scale unchanged (the values near the spectra indicate  $\text{Nb}_2\text{O}_5$  molar percentage). In a, the isosbestic point and its position (at  $888\text{ cm}^{-1}$ ) are indicated by arrows.

concentration (and the corresponding decrease of the phosphorus concentration).

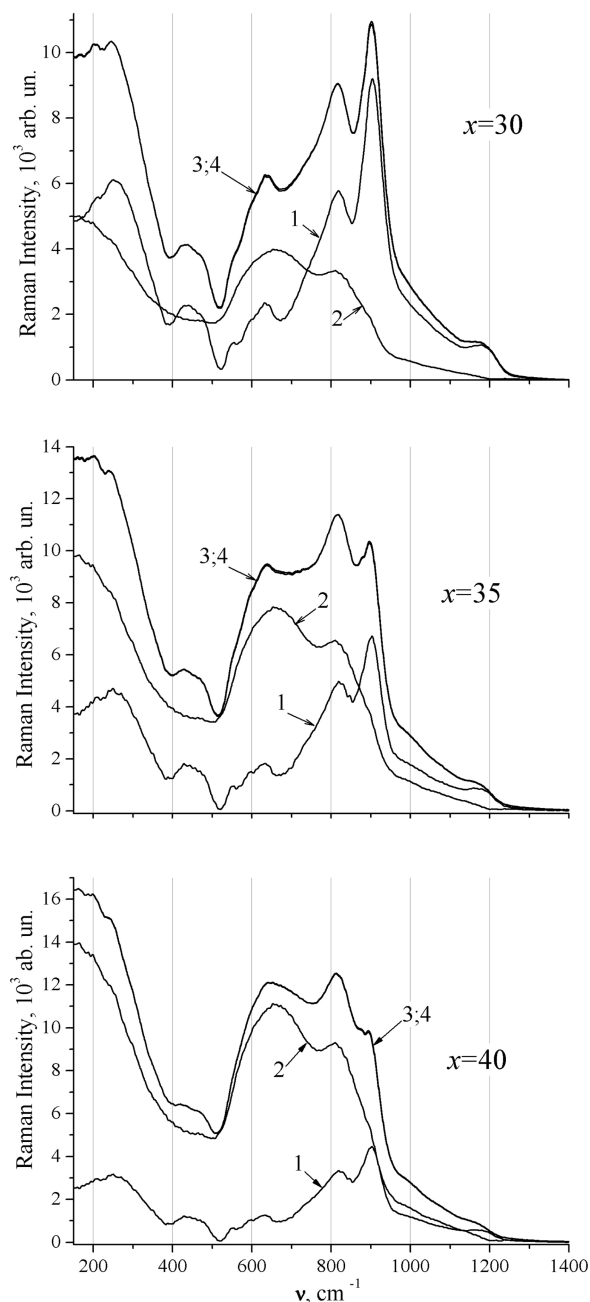
The concentration regions of niobium oxide in which certain PSCs appear (and then disappear) are presented in Figure 3,



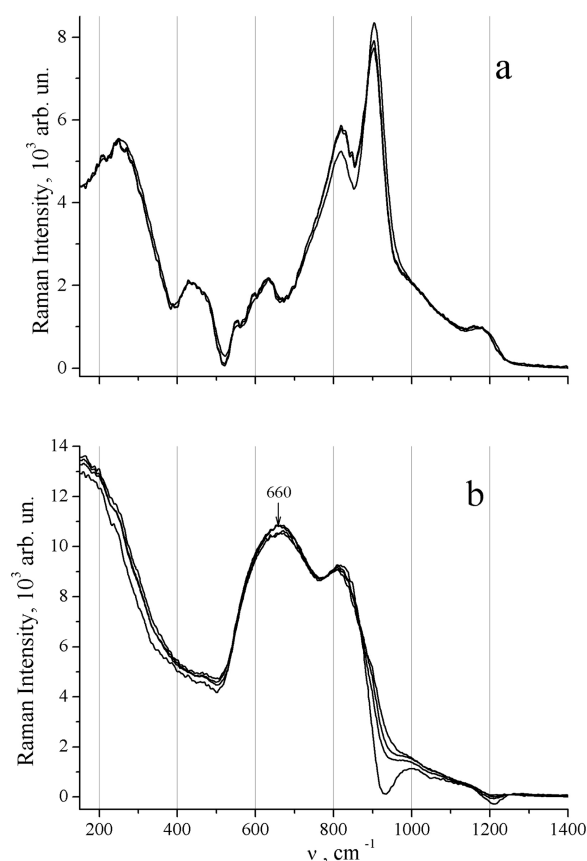
**Figure 3.** Dependences of the molar fraction of CSGs of types A–D ( $X_i$ ) and the intensity of the corresponding PSCs ( $I_i$ ) on the molar percentage of  $\text{Nb}_2\text{O}_5$  in the glass-forming system  $40\text{Na}_2\text{O} \cdot x\text{Nb}_2\text{O}_5 \cdot (60-x)\text{P}_2\text{O}_5$ . It is assumed that  $X_i = I_i$ . Points are experimental data, and lines are guides to the eye.

where the values of  $I_i$  on the left ordinate are the normalized intensities of the found PSCs (for  $i = A-D$ ), namely, the intensities of the PSCs at some fixed wavenumber  $\nu$ . Note that, in accordance with the CSG concept, the values  $I_i$  are functions of  $x$ , and the intensity of the Raman spectrum of a glass at a selected wavenumber  $\nu$  is equal to  $\sum \sigma_i I_i(x)$ , where  $\sigma_i$  is the oscillator strength of the PSC of type  $i$ . In the following section, we show that the values  $I_i$  are proportional to the values  $X_i$ , which are the molar fractions of the CSGs responsible for the appearance of the corresponding PSCs in the Raman spectra of the glasses.

Figures 4 and 5 are presented to confirm the validity of the PSCs found by the Wallace–Katz technique. For this



**Figure 4.** PSCs of types C and D (curves 1 and 2), their superposition (curves 3), and recorded Raman spectra (curves 4) for the glasses with  $x = 30, 35$ , and  $40$ .



**Figure 5.** Demonstration of the invariability (or similarity) of the PSCs belonging to the (a) C- and (b) D-CSGs in the glasses with  $x = 25, 30, 35$ , and  $40$ .

confirmation, only two features should be checked: (1) additivity and (2) invariability (or similarity) of the spectral contours of the found PSCs. Additivity (Figure 4) means that, for each glass (that is, for each  $x$ ), the superposition of the found PSCs should give the experimental spectrum of the corresponding glass. In other words, after being multiplied by the  $X_i$  at given  $x$  and then summed, the found PSCs should form the recorded Raman spectrum of the glass for that value of  $x$ . The second feature, invariability (or similarity) of spectral contours of the found PSCs (Figure 5), means that, being normalized to the maximal intensity, spectral contours of each PSC found in the glasses with different concentrations of niobium oxide should coincide to within the relative accuracy of the Raman spectrum measurements.

The presence of the first feature is confirmed by Figure 4, where the experimental Raman spectra of three glasses containing 30, 35, and 40 mol % niobium oxide (i.e.,  $x = 30, 35$ , and  $40$ , respectively) are compared with the model spectra of the same glasses, that is, with the superpositions of PSCs found by the Wallace–Katz matrix technique for the glasses with these niobium oxide concentrations. Note that, in accordance with the results of the Wallace–Katz technique (see Figure 3), Raman spectra of these glasses comprise only two PSCs, which are types C and D. In Figure 4, one can see the excellent coincidence of the experimental and model spectra.

The presence of the second feature is confirmed by Figure 5, where the normalized C and D PSCs found by the Wallace–Katz technique from the Raman spectra of the glasses with



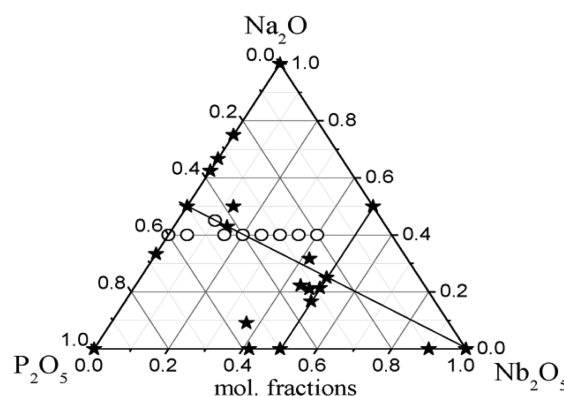
different niobium oxide concentrations are plotted in the same graphs. In this figure, one can see the quite good coincidence of the normalized contours of the PSCs, which evidences their invariability.

#### 4. DISCUSSION

A traditional comprehensive analysis of the Raman spectra of the glasses under study was recently reported by the authors.<sup>17</sup> Most spectral bands were attributed to certain vibration modes known from the literature, but several bands remained under discussion. In particular, a group of bands between approximately 550 and 630  $\text{cm}^{-1}$  and a shoulder at approximately 720  $\text{cm}^{-1}$ , in accordance with the literature data,<sup>6,21</sup> were considered to be associated with the stretching of medium-distance Nb–O bonds coupled to O–P–O deformation modes. However, referring to alkaline niobium silicate glasses,<sup>1,9</sup> in the above-mentioned analysis,<sup>17</sup> it was noted that, in terms of the CSG concept, this group of bands could be attributed to the specific vibrations in the grouping with composition  $\text{R}_2\text{O} \cdot \text{Nb}_2\text{O}_5$  or, equivalently,  $2\text{RNbO}_3$  ( $\text{R} = \text{Na}, \text{Li}$ ). Generally speaking, unlike the silicate glasses, the compositions and structures of CSGs (and therefore CMs) in phosphate glasses containing both sodium and niobium can differ, and CSGs can even incorporate phosphorus. To check this hypothesis, it is necessary to attribute each PSC to the corresponding CSG and find their compositions.

Because the intensity of light scattering is proportional to the concentration of scattering centers and both  $I_i$  and  $X_i$  are normalized to 1, let us consider  $I_i = X_i$ . Compositions of the found CSGs can be identified using the dependence of  $X_i$  or  $I_i$  on  $x$  (Figure 3). In brief, the steps to be undertaken to identify the CSG compositions are the following: At  $x = 0$ , we see that only one CSG (called A, or A-CSG) exists in the glass, and its composition evidently is that of glass 24, that is,  $3\text{P}_2\text{O}_5 \cdot 2\text{Na}_2\text{O}$ ; in addition, the PSC of A-CSG coincides with Raman spectrum of glass 24. The value  $I_A$  decreases with  $x$  and vanishes at  $x = 15$ . This indicates that the glass with  $x = 15$  no longer contains the A-CSGs but rather fully consists of the B-CSGs with the composition coinciding with that of the glass, that is,  $1.5\text{Nb}_2\text{O}_5 \cdot 4.5\text{P}_2\text{O}_5 \cdot 4\text{Na}_2\text{O}$ . To identify compositions of the CSGs called C and D, we used the following deduction. One can see that, in the glasses with  $30 < x < 40$ , there exist only two CSGs (C and D), with  $X_C$  (and  $I_C$ ) linearly decreasing and  $X_D$  (and  $I_D$ ) linearly increasing with  $x$ . Linear extrapolations of these dependences to the abscissa (dashed lines in Figure 3) give two points, namely,  $x = 25 \pm 1$  and  $x = 51 \pm 1$ . It is reasonable to suppose that the hypothetical glass with  $x = 51$  would consist of only D-CSGs, which allows us to identify the composition of the D-CSGs as rather close to  $5\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 4\text{Na}_2\text{O}$ . From Figure 3 ( $X_D = 0$  at  $x = 25$ ), it follows that the glass with  $x = 25$  consists of the two CSGs B and C only. Because the composition of the B-CSGs and  $X_B$  are known, using the obvious equality  $X_C + X_B = 1$ , it is easy to find that the composition of the C-CSGs is  $2.75\text{Nb}_2\text{O}_5 \cdot 3.25\text{P}_2\text{O}_5 \cdot 4\text{Na}_2\text{O}$ . Among the found CSGs, only the composition of the B-CSGs ( $1.5\text{Nb}_2\text{O}_5 \cdot 4.5\text{P}_2\text{O}_5 \cdot 4\text{Na}_2\text{O}$ ) is close to the composition of one of the known crystals, namely,  $1.43\text{Nb}_2\text{O}_5 \cdot 4.28\text{P}_2\text{O}_5 \cdot 4.28\text{Na}_2\text{O}$ .<sup>22</sup> The B-CSG and crystal compositions coincide to within  $\pm 0.07$ , that is, within the possible typical difference in the batch composition and composition of the resultant glass. Chemical compounds with compositions of all of the other CSGs are not mentioned anywhere. However, in accordance with an empirical rule, the

compositions of all real chemical compounds existing in a pseudobinary (actually ternary) system are located on the straight lines of the triangle phase diagram of the system. In the concentration region  $30 < x < 40$ , the ternary glass-forming system under study can actually be considered as a pseudobinary one (the two components are C- and D-CSGs), as corroborated by the presence of the isosbestic point<sup>23</sup> at 888  $\text{cm}^{-1}$  (Figure 2a). The composition of the D-CSGs ( $5\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5 \cdot 4\text{Na}_2\text{O}$ ) is on the straight line  $\text{Na}_2\text{O} = 40$  mol % of the triangle diagram  $\text{Nb}_2\text{O}_5$ – $\text{P}_2\text{O}_5$ – $\text{Na}_2\text{O}$  (see Figure 6), on which one can find a set of known crystals ( $\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ,



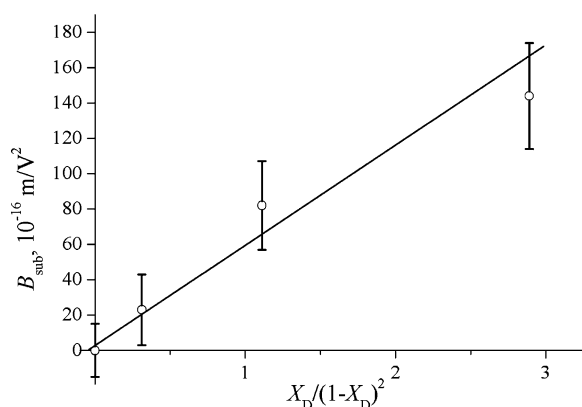
**Figure 6.** Compositions of the studied glasses (○) and known crystals (★) in the  $\text{Na}_2\text{O}$ – $\text{Nb}_2\text{O}_5$ – $\text{P}_2\text{O}_5$  system.<sup>22</sup>

$\text{Na}_2\text{O} \cdot 2\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ ,  $3\text{Na}_2\text{O} \cdot 7\text{Nb}_2\text{O}_5 \cdot 4\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O} \cdot 3\text{Nb}_2\text{O}_5 \cdot 2\text{P}_2\text{O}_5$ , and  $\text{Na}_2\text{O} \cdot \text{Nb}_2\text{O}_5$ ). This fact leads to the prediction of the existence of a crystal with the composition of D-CSG and, on the other side, provides evidence in favor of the formation of stable stoichiometric groupings of just such a composition.

In this study, we were mostly interested in the identification of CSGs in the glasses demonstrating the highest electro-optical Kerr coefficient, that is, in the glasses with niobium oxide concentrations exceeding 25 mol % (see Figure 1). This concentration range has already been shown to be characterized by the presence of only two CSGs (C and D).

Comparing the dependence of  $B$  (Figure 1) and the dependences of  $X_i$  of different CSGs on the niobium oxide concentration (Figure 3) allows determining the CSG that gives the main contribution to the electro-optical sensitivity of the studied glasses. It is obvious that A-, B-, and C-CSGs types are not the groupings of high electro-optical sensitivity because an appreciable rise in  $B$  starts only with the appearance of the D-CSGs. Then, in accordance with the CM concept, one can expect the CMs responsible for the electro-optical sensitivity of glasses to have the composition of the D-CSGs, which should also have a crystal-like structure characterized by high electro-optical sensitivity. Note that high electro-optical sensitivity is revealed when the main contribution to the material polarizability is related to the nuclear polarizability rather than the electronic polarizability. In other words, the D-CMs have a composition and structure of a crystal demonstrating a high value of electro-optical Kerr coefficient. All of the other CMs, corresponding to the A-, B-, and C-CSGs, are assumed to have compositions and structures of crystal lattices characterized by low electro-optical sensitivity and, therefore, mainly by the electronic polarizability. A detailed discussion of the nature of polarizability of electro-optical CMs was previously reported.<sup>9</sup>

The behavior of  $B(x)$  in Figure 1 consists of two linear sections corresponding to the two intervals of niobium oxide concentration: (1) 0–25 mol % and (2) 25–40 mol %. We believe that the first linear part is related to the replacement of phosphorus by niobium, the increase of  $B$  with a rise in niobium concentration being exclusively related to the higher electronic polarizability of the Nb ions with respect to P ions. In Figure 1, this first linear variation is made evident by the dashed line, plotted as a help to the eyes. The CMs with compositions of A-, B-, and C-CSGs existing in the glasses in this concentration interval do not have the structure of any known electro-optical crystals. The second linear part, with a steeper slope, is attributed to the increase in the concentration of electro-optical CMs with composition of D-CSGs, characterized by the strong nuclear polarizability. To separate the contribution of these CMs to electro-optical Kerr coefficient from that due to electronic polarizability, we subtracted from the values of  $B(x)$  the values corresponding to the extrapolated first section. This procedure gave the set of values  $B_{\text{sub}}$ , namely, the electro-optical contributions of the high-polarizable D-CMs to the Kerr coefficients  $B$  of the glasses with  $x > 25$ . Using the data presented in Figure 3, one can deduce the values  $X_D$  in the glasses with  $x > 25$ . Following the CM concept, the dependence of  $B_{\text{sub}}$  on  $X_D/(1 - X_D)^2$  is expected to be a linear one. This dependence is presented in Figure 7; one can see that, indeed, the dependence of  $B_{\text{sub}}$  on



**Figure 7.** Contribution of the D-CSGs to electro-optical Kerr coefficient ( $B_{\text{sub}}$ ) as a function of the molar fraction of the D-CSGs ( $X_D$ ).

$X_D/(1 - X_D)^2$  is linear within the experimental error. Thus, it could be confirmed that the structural (mid-range) entities responsible for the high electro-optical sensitivity of glasses belonging to the  $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$  glass-forming system have the structure and composition of the D-CMs.

Using the data presented in Figure 1, one can also predict a value of the electro-optical Kerr coefficient ( $B_D$ ) of the hypothetical crystal with the same composition as D-CSGs. This value can be determined by a linear extrapolation of the experimental dependence of  $B$  on  $x/(100 - x)^2$  to the value of  $B$  at  $x = 51$  or, more exactly, to the value  $x/(100 - x)^2 = 0.021$ . This calculation is made because the hypothetic glass with  $x = 51$  has been shown to consist of only D-CSGs ( $X_D = 1$ ). As a result, we find  $B_D \approx 450 \times 10^{-16} \text{ m/V}^2$ . At this point, however, the authors of this article have not found any data evidencing the existence of a crystal (or glass) with composition of the D-CSG.

The composition of electro-optical D-CMs, which was found to be  $4\text{Na}_2\text{O} \cdot 5\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ , can be also rewritten as  $8\text{NaNbO}_3$

+  $(\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5)$ . The reason for such a presentation is the form of the D-PSC, which has a broad band with a maximum in the vicinity of  $660 \text{ cm}^{-1}$ ; the width and shape of this band indicate that it presumably consists of a group of bands. Just the same broad band was found in the electro-optical niobium alkaline silicate glasses mentioned in the Introduction of this article; heat treatments of those glasses resulted in the formation of electro-optical glass-ceramics with electro-optical nanocrystals of quasicubic  $\text{NaNbO}_3$ , which was accompanied with a significant growth of this band and Kerr coefficient of glass-ceramics.<sup>2</sup> This fact made it possible to attribute this band in glasses as belonging to a group of collective vibrations in the CMs with the structure and composition of  $\text{NaNbO}_3$  crystal (well-known as electro-optical) and, at the same time, to associate the electro-optical sensitivity of these glasses with the presence of these CMs. Thus, it looks correct to conclude that the D-CMs are based on the crystalline structure of quasicubic  $\text{NaNbO}_3$ , so that the presentation of the D-CMs as  $8\text{NaNbO}_3 + (\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5)$  rather than  $4\text{Na}_2\text{O} \cdot 5\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$  appears to be more reasonable.

Finally, it is sensible to suppose that an increase in sodium oxide concentration at the expense of phosphorus should not lead to a noticeable increase in  $B$ , because the electronic polarizability of sodium ions does not strongly differ from that of phosphorus. However, from Table 1 and Figure 1 one can notice that  $B$  of the glasses in which  $\text{P}_2\text{O}_5$  (10 mol %) is replaced with  $\text{Na}_2\text{O}$  (glasses 13 and 15) increases by about a factor of 2! Such a great increase in  $B$  can be only explained if we assume that, unlike phosphorus, sodium is capable of forming CMs of high electro-optical sensitivity, which, in accordance with the CM concept, should have the structure (lattice symmetry) and composition of an electro-optical crystal. Sodium is known not to form electro-optical crystals with phosphorus, but in the glasses under study, it has a partner (i.e., niobium) to form electro-optical ordered entities with the local structure of crystalline  $\text{NaNbO}_3$ . In other words, replacing  $\text{P}_2\text{O}_5$  with  $\text{Na}_2\text{O}$  would lead to an increase in the concentration of D-CMs and thus result in an increase in  $B$ , that we have actually measured.

## 5. CONCLUSIONS

The mid-range structure of glasses of the glass-forming system  $x\text{Nb}_2\text{O}_5 \cdot (60 - x)\text{P}_2\text{O}_5 \cdot 40\text{Na}_2\text{O}$ , with  $x$  varying from 0 to 40, has been studied in accordance with the concept of constant stoichiometric groupings (CSGs) and the concept of crystal motifs (CMs). This analysis has shown the following:

- Raman spectra of this system in the range  $15 < x < 40$  can be presented as a superposition of three partial spectral components belonging to the stable products called constant stoichiometric groupings (CSGs) or crystal motifs (CMs) that form in the glass melt from the simple oxides included in the initial glass batch;
- The compositions of these CSGs (or CMs) are  $3\text{Na}_2\text{O} \cdot \text{Nb}_2\text{O}_5 \cdot 3\text{P}_2\text{O}_5$ ,  $4\text{Na}_2\text{O} \cdot 2.75\text{Nb}_2\text{O}_5 \cdot 3.25\text{P}_2\text{O}_5$ , and  $4\text{Na}_2\text{O} \cdot 5\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5$ , with the last one [which can also be written as  $8\text{NaNbO}_3 + (\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5)$ ] being responsible for the electro-optical sensitivity of the present glasses;
- CMs with the composition  $8\text{NaNbO}_3 + (\text{Nb}_2\text{O}_5 \cdot \text{P}_2\text{O}_5)$  are based on the crystalline lattice of electro-optical crystal  $\text{NaNbO}_3$ .

We were also able to predict that the glass with composition  $40\text{Na}_2\text{O}\cdot 50\text{Nb}_2\text{O}_5\cdot 10\text{P}_2\text{O}_5$  should exhibit a record electro-optical Kerr coefficient equal to  $450 \times 10^{-16} \text{ m/V}^2$ .

## AUTHOR INFORMATION

### Corresponding Author

\*Tel.: +7-812-560-1878. Fax: +7-812-560-9574. E-mail: tagan@dt1386.spb.edu.

### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Lipovskii, A. A.; Kaganovskii, Yu.; Melehin, V. G.; Tagantsev, D. K.; Yanush, O. V. *J. Non-Cryst. Solids* **2008**, 354 (12–13), 1245–1249.
- (2) Lipovskii, A. A.; Tagantsev, D. K.; Vetrov, A. A.; Yanush, O. V. *Opt. Mater.* **2003**, 21 (4), 749–757.
- (3) Mukhitdinova, I. A.; Yanush, O. V. *Fiz. Khim. Stekla (Sov. J. Glass Phys. Chem.)* **1989**, 15, 34–45.
- (4) Mukhitdinova, I. A.; Yanush, O. V. *Fiz. Khim. Stekla (Sov. J. Glass Phys. Chem.)* **1989**, 15, 45–51.
- (5) Karapetyan, G. O.; Maksimov, L. V.; Yanush, O. V. *Glass Phys. Chem.* **1992**, 18 (6), 412–422.
- (6) Yanush, O. V. In *Proceedings of 18th International Congress on Glass*; The American Ceramic Society: Westerville, OH, 1998; pp 75–80.
- (7) Yanush, O. V.; Markova, T. S. New interpretation of oxide glasses properties on the basis of constant stoichiometry groupings (CSG) concept. In *Properties and Structure of Oxide Glasses*; Klyuev, V. P., Pevzner, B. Z., Eds.; Research Signpost: Kerala, India, 2010; Chapter 1, pp 1–45.
- (8) Karapetyan, G. O.; Lipovskii, A. A.; Loboda, V. V.; Maksimov, L. V.; Svistunov, D. V.; Tagantsev, D. K.; Tatarintsev, B. V.; Vetrov, A. A. *Proc. SPIE* **2001**, 4353, 23–28.
- (9) Lipovskii, A. A.; Tagantsev, D. K.; Tatarintsev, B. V.; Vetrov, A. A. *J. Non-Cryst. Solids* **2003**, 318, 268–283.
- (10) Wallace, R. M.; Katz, S. M. *J. Phys. Chem.* **1964**, 68 (12), 3890–3892.
- (11) Duclere, J. R.; Lipovsky, A. A.; Mirgorodsky, A. P.; Thomas, P.; Tagantsev, D. K.; Zhurikhina, V. V. *J. Non-Cryst. Solids* **2009**, 355 (43–44), 2195–2198.
- (12) Borrelli, N. F.; Herczog, A.; Maurer, R. D. *Appl. Phys. Lett.* **1965**, 7 (5), 117–118.
- (13) Borrelli, N. F.; Layton, M. M. *IEEE Trans. Electron Devices* **1969**, ED-16 (6), 511–514.
- (14) Borrelli, N. F.; Layton, M. M. *J. Non-Cryst. Solids* **1971**, 6 (3), 197–212.
- (15) Layton, M. M.; Herczog, A. *J. Am. Ceram. Soc.* **1967**, 50 (7), 369–375.
- (16) Layton, M. M.; Smith, J. W. *J. Am. Ceram. Soc.* **1975**, 58 (9–10), 435–437.
- (17) Donato, M. G.; Gagliardi, M.; Sirleto, L.; Messina, G.; Lipovskii, A. A.; Tagantsev, D. K.; Righini, G. C. *Appl. Phys. Lett.* **2010**, 97, 231111–1–231111–3.
- (18) Vetrov, A. A.; Lipovskii, A. A.; Tagantsev, D. K. *Instrum. Exp. Techn.* **2002**, 45 (4), 550–554.
- (19) Lipovskii, A. A.; Tagantsev, D. K.; Vetrov, A. A.; Yanush, O. V. *Glastech. Ber. Glass Sci. Technol.* **2002**, 75 (C2), 386–389.
- (20) Apakova, I.; Yanush, O.; Derkacheva, O.; Goncharuk, V.; Maslennikova, I.; Polyakova, I.; Anan'ev, A.; Maksimov, L.; Markova, T. *J. Non-Cryst. Solids* **2011**, 357 (14), 2675–2683.
- (21) El Jazouli, A.; Parent, C.; Dance, J. M.; Le Flem, G.; Hagemuller, P.; Viala, J. C. *J. Solid State Chem.* **1988**, 74 (2), 377–384.
- (22) The data on the compositions of the crystalline compounds existing in the  $\text{Na}_2\text{O}\text{--}\text{Nb}_2\text{O}_5\text{--}\text{P}_2\text{O}_5$  system were gathered by the authors working in the St. Petersburg Technological University of Plant Polymers.
- (23) When an isosbestic plot is constructed by the superposition of the spectra of two species, the isosbestic point corresponds to the wavelength at which these spectra cross each other. If the spectra of two compounds with a constant total concentration cross at any wavelength, all mixtures with the same total concentration will go through that same point. The appearance of isosbestic points in a chemical reaction is good evidence that one main species will be converted to one other major species. See, for instance: Tavker, S.; Kumar, P.; Carlon, H. R.; Milham, M. E. *J. Geophys. Res.* **1997**, 102 (D25), 30017–30022.