On relationship of atomic structure, nano-sized inhomogeneities and second-order optical non-linearity of K$_2$O–TiO$_2$–P$_2$O$_5$ glasses

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Abstract

Glasses at early stages of phase separation, while remaining amorphous, are shown to possess or not to possess second-order optical nonlinearity (SON) depending on specific features of their short-range/medium range order and nanoinhomogeneous structure characterized with IR and Raman spectroscopy, X-ray diffraction, small-angle X-ray and neutron scattering and second harmonic generation (SHG). In the present work it is demonstrated by the example of potassium titanium phosphate glasses of composition near KTiOPO$_4$ stoichiometry. Formation of nanoinhomogeneities, structure of which is similar to the structural motif of some non-linear optical (NLO) crystal, favors SON. Heat treatment of such glasses at temperatures near glass-transition temperature $T_g$ stimulates remarkable SON enhancement keeping transparency and amorphous state. While temperature is increasing SHG grows up to values, comparable with those of NLO crystals with rise of Bragg reflections in the X-ray diffraction pattern of the glass and decrease of its transparency. Revealing correlations between structural peculiarities of glasses and their SON argues preference of description of short- and medium-range order in glasses with composition close to boundaries of glass-forming regions from the position of quasi-crystallite models.

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1. Introduction

Glass is a centrosymmetric media and therefore does not possess optical non-linearity of even orders. For recent years several ways of second-order optical non-linearity (SON) stimulation in glasses were developed. One of them is homogeneous or heterogeneous nucleation of non-centrosymmetric crystals in the glass bulk [1,2]. Such nano- or microstructured glasses allow second harmonic generation (SHG) keeping transparency. On account of relatively small concentration and chaotic orientation of nanocrystals SHG signal is considerably weaker than that in single crystals of the same composition. Thus to obtain nanostructured glasses with high SON it is advantageous to match glass composition and heat-treatment procedure so as to precipitate a maximum quantity of non-linear optical (NLO) crystalline phase, and to get precise refractive index
matching between glass matrix and crystals. The latter condition is crucial at the stage of crystal growth, up to a sub-micron size, where producing glass–ceramics with SHG yield comparable to that of crystals becomes possible.

Homogeneous nucleation often satisfies both conditions mentioned above when composition is similar for the initial glass and for the precipitating phase. Hence one of the most promising glass-forming systems is \( \text{K}_2\text{O} \cdot \text{TiO}_2 \cdot \text{P}_2\text{O}_5 \) (KTP) system in the composition range close to stoichiometry of \( \text{KTiOP} \) ferroelectric crystal, potassium titanil phosphate, possessing very high SON. Yet \( \text{K}_2\text{O} \cdot \text{2TiO}_2 \cdot \text{P}_2\text{O}_5 \) composition lies outside glass-forming region of KTP system, and it is necessary to add some extra amount of glass-forming oxide to the stoichiometric composition. D. Li and co-workers [3] obtained sol–gel nanocomposite glasses and glass–ceramics \( \left( \text{K}_2\text{O} \cdot 2\text{TiO}_2 \cdot \text{P}_2\text{O}_5 \right) \cdot \text{SiO}_2 \) which showed SHG. Other papers [4–8] described synthesis, crystallization behavior and NLO properties of glasses of \( \text{K}_2\text{O} \cdot \text{2TiO}_2 \cdot \text{P}_2\text{O}_5 \) composition with addition of \( \text{SiO}_2 \), \( \text{P}_2\text{O}_5 \) and \( \text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 7\text{SiO}_2 \). Both crystallization process and NLO properties appeared to depend strongly on the added oxide. It is shown that, depending on type and quantity of addition, the first precipitating nanocrystalline phase can be either KTiOP or centrosymmetric crystalline phases; this is a decisive factor for SON stimulation in transparent glasses [4,5].

In our opinion the most effective way to gain information on glass structure and structural changes during nanostructuring is a comparison of X-ray and neutron diffraction curves, vibrational spectra, Nuclear Magnetic Resonance and Electron Spin Resonance spectra, physical and NLO properties of the same substance in crystalline and vitreous states. In this paper we carry out a comparative analysis of vibrational spectra of \( \text{KTiOPO}_4 \) crystal already published [9–12] and vibrational spectra of KTP glasses taking into account data of small-angle neutron (SANS) and X-ray (SAXS) scattering, high resolution electron microscopy and SHG.

2. Experimental

In order to reveal SON nature at early stages of phase separation in glasses we studied by means of IR and Raman spectroscopy the structure of KTP glasses, possessing different crystallization properties and different SON, respectively. For our study we chose \( 90\left( \text{K}_2\text{O} \cdot \text{2TiO}_2 \cdot \text{P}_2\text{O}_5 \right) \cdot 10\text{B}_2\text{O}_3 \) (KTP–10B), \( 90\left( \text{K}_2\text{O} \cdot \text{2TiO}_2 \cdot \text{P}_2\text{O}_5 \right) \cdot 10\text{SiO}_2 \) (KTP–10Si) and \( 93\left( \text{K}_2\text{O} \cdot \text{2TiO}_2 \cdot \text{P}_2\text{O}_5 \right) \cdot 7\text{P}_2\text{O}_5 \) (KTP–7P) glasses, studied previously [4,5]. Glass samples were prepared by fast cooling of the melt. A detailed description of their preparation can be found in [4,5]. X-ray diffraction (XRD) patterns were recorded at the X-ray diffractometer DRON-3M (CuK\( \alpha \) line). Nano-inhomogeneity of the glasses was examined by SAXS at the European Synchrotron Radiation Facility (ESRF) (Grenoble, France) in the range of scattering vector \( q = 4\pi\sin\theta/\lambda \) (\( \theta \) – scattering angle, \( \lambda \) – synchrotron radiation wavelength) from 0.015 to 0.25 Å\(^{-1}\). Moreover SANS curves were obtained for KTP–10B glasses heat treated at different times, \( q \) ranging from 0.01 to 0.25 Å\(^{-1}\) at the KWSI diffractometer at FRJ-2 Reactor of Institut für Festkörperforschung, Forschungszentrum Jülich GmbH.

Inhomogeneities sizes were determined from SANS and SAXS curves under the Guinier approximation [13] of the monodisperse system of spherical particles having the same nuclear and electron density, situated into the uniform glassy matrix.

Raman spectra were measured in the range 20–1700 cm\(^{-1}\) using T64000 triple spectograph (Jobin Ivon) with 2 cm\(^{-1}\) resolution. Raman scattering was stimulated by the Ar-ion laser Stabilite 2017 (Spectra Physics) emission (green line, \( \lambda = 514.5 \) nm) through Olympus BH2-UMA microscope.

IR \( \varepsilon' \) spectra were obtained by submillimeter spectrometer ‘Epsilon’ (10–33 cm\(^{-1}\)) and IR Fourier-spectrometer Bruker IFS-113v (\( \sim 30–1000 \) cm\(^{-1}\)). Direct measurement of \( \varepsilon' \) was held in the frequency range 10–33 cm\(^{-1}\). In the range 30–1000 cm\(^{-1}\) IR reflectivity spectra were measured and then \( \varepsilon' \) spectra were calculated by dispersion analysis with normalization according to direct measurement data at the low-frequency range. The detailed description of this technique is given in [14].

SHG was measured at room temperature by the conventional YAG:Nd laser (\( \lambda = 1064 \) nm). Crystalline \( \alpha \)-quartz powder was used as a reference standard, so units of all SHG data listed below are relative to quartz: \( I_{2\omega}/I_{2\omega} \) (Si\(_2\)O\(_5\)), where \( I_{2\omega} \) is the SHG intensity in the studied sample and \( I_{2\omega} \) (Si\(_2\)O\(_5\)) is the SHG \( \alpha \)-quartz powder SHG intensity at the same conditions, for more details see [4].

3. Results and discussion

3.1. XRD patterns, SAXS and SANS

XRD patterns of as-quenched KTP glasses and KTP–10B glass, heat-treated at 580 °C for 30 min (KTP–10B–T)

![Fig. 1. X-ray diffraction patterns of KTP-10B, KTP-10B-T, KTP-10Si and KTP-7P glasses.](image-url)
on Fig. 1, contain no pronounced peaks. That confirms absence of any crystalline phase in both as-quenched and heat-treated samples.

SAXS and SANS curves of KTP glass samples are presented in Fig. 2. Analysis of these curves proves as-quenched KTP–10B and KTP–7P glasses to be homogeneous i.e., to contain no phase inhomogeneities since $I_{\text{SAXS}}$ and also $I_{\text{SANS}}$ for KTP–10B does not depend on the scattering vector $q$. KTP–10Si shows an increase of the scattering below 0.05 Å$^{-1}$. Calculation according to Guinier approximation [13] shows that it contains inhomogeneities less than 10–40 Å in size. Since scattering intensity is very small, these inhomogeneities can be characterized either by small amount or extremely small electron density difference between matrix and particles. Electron microscopy confirms absence of inhomogeneities in this glass [4]. KTP–10B–T glass reveals well-developed nanostructure with a typical size of inhomogeneities $\approx$45 Å according to SAXS data and about 50 Å from SANS (Fig. 3). Presence of a maximum in the SAXS curve suggests well-correlated distance between inhomogeneities (about 300 Å).

### 3.2. Wide range IR spectra

IR $\tilde{\nu}$ spectra of as-quenched KTP glasses and heat-treated KTP–10B–T glass are shown in Fig. 4. $\tilde{\nu}$ spectra of the KTP–10B and KTP–10B–T (i.e., homogeneous and phase-separated ones according to Fig. 3) are almost the same. The main difference consists in slight changes of relative intensities of some bands in the glass spectrum after heat treatment; intensities of peaks increased at $\approx$475 and $\approx$620 cm$^{-1}$, and diminished at $\approx$712 and 370 cm$^{-1}$ (in the last case frequency of the maximum also shifted to 360 cm$^{-1}$). The small difference between of as-quenched and heat-treated glasses lies in conservation of coordination numbers of all atoms during heat treatment. From this we can conclude, that a majority of boron atoms in the initial glass are threefold coordinated since during developing of inhomogeneous structure peaks at 1200 and 1380 cm$^{-1}$ do not change and boron concentration in KTP–10B glass is small. Strong bands (taking into account small concentration of boron in KTP–10B glass) at 1200 and 1380 cm$^{-1}$ which are not observed in KTP glasses without boron also confirm this assumption since threefold coordinated boron atoms do not involve potassium atoms building mixed titanium–phosphate–borate network but build their own network, formed by BO₃ triangles. Actually we can assume nanoinhomogeneous structure to be already formed in as-quenched KTP–10B glass at such a small scale (less than 10 Å) that SANS and SAXS curves obtained in the experiments performed give poor information on it. Hence we can conclude that as-quenched KTP–10B glass has the same atomic structure as phase-separated

![Fig. 2. SANS data for initial and heat treated KTP–10B glasses. SAXS data for KTP–10B, KTP–10B–T, KTP–10Si and KTP–7P glasses.](image)

![Fig. 3. Effective diameter of inhomogeneities in KTP–10B glass samples heat-treated at 580 °C for different times, calculated from SANS and SAXS data.](image)
one and during the heat treatment size of inhomogeneities increases from 5–10 Å to ~50 Å in our case. A certain frequency shift and change of intensities can be explained with the composition shift resulting from phase separation. The similar dependence are described for some other glasses, e.g., for sodium–silicate one[15].

Spectrum of KTP–10Si glass also reveals similarity with KTP–10B spectra. Analysis of available publications shows that some features of KTP–10Si $\epsilon''$ spectrum are concerned with vibrations of silicon–oxygen bonds, and absence of such features confirms that they are related to silicon atoms. The peak at $\approx 1000$ cm$^{-1}$ is much stronger than in KTP–10B and KTP–10B–T spectra, which evidently results from antisymmetric stretching mode Si–O: the most intensive peak in $\epsilon''$ spectrum of silica glass, antisymmetric stretching vibration Si–O–Si has a maximum at 1068 cm$^{-1}$[16]. A broad strong peak at 350 cm$^{-1}$ (370 cm$^{-1}$ and 360 cm$^{-1}$ in KTP–10B and KTP–10B–T spectra, respectively) increases in KTP–10Si spectrum and a shoulder appears at the high-frequency slope of this peak at $\approx 440$ cm$^{-1}$ (a shoulder also is present at $\approx 470$ cm$^{-1}$ in KTP–10B and KTP–10B–T spectra). In the range 340–370 cm$^{-1}$ $\epsilon''$ spectra of all the samples studied contain an intensive peak which can be due to the $v_3$ vibrational mode of PO$_4$ tetrahedra: in the $\epsilon''$ spectrum of the KTiOPO$_4$ crystal this mode is represented by two peaks 364–385 cm$^{-1}$ and 400–404 cm$^{-1}$, respectively, depending on the orientation of the sample [10]. On the contrary, the shoulder at $\approx 440$ cm$^{-1}$ is a characteristic feature of KTP–10Si glass and is related to the bending mode at 446 cm$^{-1}$ in the spectrum of vitreous silica[16]. Moreover a weak band lies at $\approx 1150$ cm$^{-1}$ in KTP–10Si spectrum which does not appear in the spectra of the other KTP glasses, while the $\epsilon''$ spectrum of vitreous SiO$_2$ contains a band at 1164 cm$^{-1}$[16]. Thus we can suggest that in KTP–10Si glass as well as in KTP–10B glass, silicon atoms do not modify titanium–phosphate network which remains close to the structural motif of KTiOPO$_4$ crystal but build independent silicate structure. This conclusion agrees with the phase nanoinhomogeneity of this glass detected by SAXS and one more time confirms the above mentioned model of KTP–10Si structure, suggested in papers [4,7].

Broad peaks are present at $\approx 60$ and $\approx 100$ cm$^{-1}$ in the low-frequency range of $\epsilon''$ spectra of glasses discussed above. $\epsilon''$ spectra of KTiOPO$_4$ crystal also contain a large number of vibrational bands in the range 75–140 cm$^{-1}$, their position depending on the measurement geometry. This is in agreement with the assumption of a structural similarity of the short- and medium-range order of KTP–10Si and KTP–10B glasses with the structural motif of KTiOPO$_4$ crystal. This conclusion is supported by the fact that low-frequency range of the spectrum of KTP–7P glass significantly differs from that of other glasses. Splittings of the peak at $\approx 60$ cm$^{-1}$ in the KTP–10B–T glass IR spectrum is expected to connect with phase separation phenomenon.

IR spectrum of KTP–7P glass differs from the other spectra, represented in Fig. 4. This difference consists both in the absence of peaks related to silicate or borate component and in the absence of some features common for KTP–10Si and KTP–10B, obviously related to the structure of potassium–titanium–phosphate component. The difference can be observed in the ranges 650–800 and 900–1100 cm$^{-1}$: a broad intensive peak at $\approx 1000$ cm$^{-1}$ in contrast to the other spectra is formed by the two strongly overlapping bands. It should be emphasized that the
low-frequency part (<150 cm⁻¹) of the KTP–7P spectrum also differs from those in spectra of other KTP glasses. It becomes apparent in the frequency shift of the low-frequency maximum as well as in remarkable decreasing of its intensity. It may be result of the fact that KTP–7P is the only homogeneous glass, composition of which lies outside the immiscibility region. In contrast to other glasses studied, a centrosymmetric crystalline phase KTi₂(PO₄)₃ precipitates from the KTP–7P glass during its heat treatment [8], which can form via homogeneous crystallization without subsequent amorphous phase separation taking into account similarity of composition of the glass and of the precipitating crystalline phase.

3.3. Raman spectra

Raman spectra of KTP glasses are shown in Fig. 5, which also includes Raman spectrum of KTiOPO₄ crystal, measured by Kugel et al. [10].

Raman spectra of KTP–10B and KTP–10B–T glasses agree with suggested above structural model of KTP–10B glass based on IR data: Raman spectra of the as-quenched and heat treated samples are very close to each other, and the spectrum of the heat-treated sample reveals a process of ordering of the potassium–titanium–phosphate phase approaching to crystalline KTiOPO₄: in the Raman spectrum of KTP–10B–T glass in comparison with that of as-quenched KTP–10B glass common peaks sharpen (peak at 505 cm⁻¹ sharpens strongly and shifts to 512 cm⁻¹) and new ones appear at ~560 and ~620 cm⁻¹ possessing analogues in KTiOPO₄ spectrum. The boson peak sharpens as well, and the frequency of its maximum (~80 cm⁻¹) nears to the frequency of KTiOPO₄ band (90 cm⁻¹) as compared to the boson peak of the as-quenched sample (~70 cm⁻¹).

Fig. 5 shows that Raman spectra of KTP–10B and KTP–10Si glasses are similar and their peaks mostly correspond to bands or groups of bands in the spectrum of KTiOPO₄. The strongest band in the spectra of these glasses having maximum at 715 cm⁻¹ for KTP–10B and at 730 cm⁻¹ for KTP–10Si conforms to the strongest band at 700 cm⁻¹ resulting from ν₁ vibration of TiO₆ octahedra in KTiOPO₄ [10]. A broad intense peak with the maximum at ~270 cm⁻¹ agrees with a number of bands in the crystal spectrum in the range 200–400 cm⁻¹ mainly concerned with K–O vibrations and various modes of TiO₆ octahedra [10]. A band at ~930 cm⁻¹ and a shoulder at ~770 cm⁻¹, do not have evident analogues in crystalline KTiOPO₄ spectrum but according to [11] Raman spectrum of KTiOPO₄ melt contain intensive bands at 920 and 770 cm⁻¹ presumably corresponding to vibrations of PO₄ tetrahedra and titanium–oxygen complexes in the melt. In the low-frequency range of glasses spectra boson peaks are present at ~70 cm⁻¹ whereas KTiOPO₄ low-frequency spectrum contains a relatively strong band at 90 cm⁻¹ and a number of weak bands nearby.

Thus we can conclude that both short- and medium-range orders of KTP–10B and KTP–10Si glasses are close to each other and to the structural motif of KTiOPO₄ crystal.

The Raman spectrum of KTP–7P on the contrast to the discussed above ones does not reveal similarity with the spectrum of KTiOPO₄ crystal. According to [10,17] we can assign the peaks of KTP–7P spectrum at ~500, ~980 and ~1230 cm⁻¹ to various vibrations of P–O complexes. The boson peak can be observed in the low-frequency region at 58 cm⁻¹ which also differs from the position of the main low-frequency band of KTiOPO₄ (90 cm⁻¹). Hence the medium-range order of KTP–7P glass is formed in compliance with some crystalline phase, other than KTiOPO₄, most probably a centrosymmetric phase KTi₂(PO₄)₃ which crystallizes during heat treatment of this glass at certain conditions [8] and in the direction of which KTP–7P composition is shifted from KTiOPO₄ stoichiometry.

3.4. SHG

SHG data for KTP–10Si glass were reported in part in papers [4,8]. They are shown in Fig. 6–8. Fig. 6 represents SHG signal dependence on the heat treatment temperature with a constant duration of 1 h. KTP–10Si glass remains transparent at temperatures below 650 °C. It should be
noticed that this point lies near glass-transition temperature of this glass $T_g = 634$ °C [7]. SHG dependence on the heat-treatment time at 640 °C near the edge of the transparency region is shown in Fig. 7. SHG intensity appears to grow along with the heat-treatment time increase, glass preserving transparency.

In Fig. 8 XRD patterns of the as-quenched and heat-treated at different temperatures and times KTP–10Si samples are shown together with corresponding SHG values of these samples. XRD patterns of samples, heat-treated at temperatures 727 °C and higher (Fig. 8(d)–(f)) contain narrow peaks, indicating appearing crystalline structure, and position of these peaks coincides with the XRD pattern of KTiOPO$_4$ [18].

Yet SHG signal, though smaller one, is obtained in the samples heat-treated at temperatures below 650 °C and remaining amorphous (Fig. 8(b) and (c)), and even in the as-quenched sample (Fig. 8(a)), that agrees with SAXS data detecting nanoinhomogeneities in the as-quenched KTP–10Si glass. SHG values for KTP–10B glass at different heat-treatment temperatures for 1 h are shown in Fig. 9. This dependence is evidently similar to that for KTP–10Si except difference in boundary temperatures of transparency levels. KTP–10B glass remains transparent after 1 h of heat treatment at temperatures below 600 °C, which also lies near the glass-transition temperature $T_g = 585$ °C.

SHG does not appear in KTP–7P glass both in as-quenched and in heat-treated at different conditions samples.

Hence we can infer that SON origin in KTP–10B and KTP–10Si glasses during heat treatment results from discussed above similarity of short- and medium-range order of KTP–10B and KTP–10Si and the structural motif of KTiOPO$_4$ crystal. On the contrary KTP–7P glass does not possess SON in the initial homogeneous state as well as in the phase-separated one, that agrees with its suggested similarity to the crystalline KTi$_2$(PO$_4$)$_3$ phase precipitating in it.

Thus in the present work correlation between the atomic structure of the as-quenched glass, its phase separation and crystallization and developing SON of this glass is shown for the first time. Revealing correlation between structural properties of amorphous glasses and their SON argues advantages of description of short- and medium-range order in glasses with composition close to edges of glass-forming regions from the position of quasi-crystallite models.

4. Conclusion

Transparent glasses of $90(K_2O \cdot 2TiO_2 \cdot P_2O_5) \cdot 10B_2O_3$ (KTP–10B), $90(K_2O \cdot 2TiO_2 \cdot P_2O_5) \cdot 10SiO_2$ (KTP–10Si) and $93(K_2O \cdot 2TiO_2 \cdot P_2O_5) \cdot 7P_2O_5$ (KTP–7P) molar composition are obtained nearby the stoichiometry of well-known NLO phase potassium titanil–phosphate KTiOPO$_4$ by means of rapid cooling of the melt. KTP–10B and KTP–7P glasses are nano-homogeneous according to SAXS data.
and KTP–10Si glass contains nanoinhomogeneities less than 40 Å in size. A monodisperse nanostructure with the particle diameter ~50 Å is formed in KTP–10B glass by heat treatment at 580 °C (KTP–10B–T glass).

A study of atomic structure of these glasses by XRD, IR and Raman spectroscopy together with SON measuring by SHG allowed ascertaining structural similarity of the short- and medium-range order of KTP–10B and KTP–10Si glasses and KTiOPO₄ crystal, whereas KTP–7P glass differs a lot from them by its structure. Crystallization of these glasses differs in accordance with the difference in atomic structure: KTiOPO₄ precipitates as a first crystalline phase in glasses with B₂O₃ and SiO₂ additions, while the first crystallizing phase in KTP–7P glass is centrosymmetric KTi₂(PO₄)₃ showing no yield of SHG. KTP–10B and KTP–10Si reveal SHG effect which is not observed in KTP–7P glass.

It follows from the obtained results that at the stage of amorphous phase separation where glass is characterized by diffuse XRD pattern it can possess or not possess SON: that depends on the structure of the short-range and medium-range order. Similarity of these orders to the structural motif of some NLO crystalline phase is favorable for SON origin. Enlargement of polar inhomogeneities results in a remarkable SHG increase and at the stage of rise of Bragg reflections in the XRD pattern, SHG signal grows along with the concentration of NLO crystalline phase and average size of NLO crystals.

Discovery of correlation between structure of glass and its SON confirms the hypothesis of existence of a crystalline analogue with the same or nearby composition, structural motif of which is similar not only to a short-range but also to a medium range order of the glass.

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