

# Structural Change in SiO<sub>2</sub> Glass After Gamma Irradiation

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## Abstract

Silicate glasses KI and KU consist of 2 types of cells, differing in size from 0.5 to 1.5 nm. After irradiation, weak reflections of nanocrystalline phases responsible for UV absorption appear in them. The fact that the absorbed radiation energy is spent on the crystallization of SiO<sub>2</sub> determines their high radiation-optical resistance.

**Keywords:** Silicate Glasses, SiO<sub>2</sub>, Ba, Pb, Gamma and Neutron Irradiation, X-ray Diffraction and Phase Analysis, Reflection.

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## INTRODUCTION

Silicate glass is one of the most interesting materials used by humans since ancient times. Despite its widespread use in science, technology, and everyday life, glass physics has a number of fundamental problems. For example, as is known in science, the structure of a substance has a significant effect on its physical properties. However, the structure of glass, although many models have been proposed, for almost a century has been the subject of controversy among scientists around the world as result of the fact that the main experimental methods for studying the structure of crystalline substances were not fruitful enough due to the lack of long-range order and the multicomponent nature of the most common and interesting types of glass. The degree of applicability of the energy band model and related concepts in glasses also requires substantiation in each specific case. Quartz glass consisting of fused silica with an amorphous structure. Quartz filaments are a rather expensive material, both due to the difficulty of obtaining high-purity quartz, and more complex technology for their production [1]. Glassy materials with ionic conductivity can be used as electrolytes, and in the presence of mixed or electronic conductivity - as electrode materials in electrochemical devices [2]. Lead-silicate glasses are the basis not only for the creation of optical media, optical fibers, but also for the manufacture of electro-optical converters such as microchannel plates [3-5].

The aim of this work was: to elucidate the influence of

structural changes that are caused by irradiation with ionizing gamma rays on SiO<sub>2</sub> glass.

To achieve this goal, it is necessary to solve the following tasks:

1. Study of X-ray spectral properties and regularities of the formation of the energy structure of pure SiO<sub>2</sub> glasses and with Ba impurities.
2. Study of X-ray spectral properties and regularities of the formation of the energy structure of lead-silicate glasses in a wide range of compositions.
3. Study of the structural characteristics of industrial lead-silicate systems.
4. Investigation of the regularities of the formation of intrinsic defects of the glass matrix under the influence of gamma rays.

*Subject of the study:* For the study, we used colorless pure and alkali silicate glass from a warehouse of illiquid materials (GOI St. Petersburg, Russia). X-ray fluorescence analysis with an Am source revealed only a heavy barium impurity of 28%; therefore, the samples were designated by us (SiO<sub>2</sub>-BaO). Using an energy dispersive system in SEM (excitation of the target characteristic radiation by a 100 keV electron beam), elemental analysis was carried out, which revealed the presence of 11 wt% Na, 10 wt% K, and 5 wt% Ba, i.e. in the amount of impurities amounted to 26%. The samples were in the form of polished disks with diameter of 16 mm and thickness of 1 to 2 mm. Highly pure SiO<sub>2</sub> glass with impurities less than 0.001% (grade KU or KSV), which does not stain upon irradiation, which is made

in the form of optically polished laser windows of elliptical shape (5-3 mm<sup>2</sup>) 1 mm thick, was taken as a reference standard. Manual cleavage yielded samples with different masses from 90 to 310 mg to normalize the luminescence intensity in the study of dose dependences. The properties of industrial crystal glass SiO<sub>2</sub> containing PbO were also studied. The interest is due to the fact that lead-containing glasses have high density, which is directly related to the ability of the glass to absorb X-rays, high light transmission in the visible part of the spectrum, and low melting temperature. The samples were in the form of polished plates 10–15 mm in diameter, 2–4 mm and 20 mm thick.

## MATERIALS AND METHODS

X-ray diffraction and phase analysis of silicate glass - structure parameters, formation of dimensional defects and impurity phases, as well as mechanical stresses were investigated by wide-angle and small-angle X-ray structural analysis (XRD) on an improved DRON-3M device (radiation  $\lambda_{\text{CuK}\alpha}=0.1542$  nm) in the range of angles  $2\Theta=10 \div 70^\circ$ , as well as Empyrean (Panalytical) at 5–140 degrees, with a nickel filter and a high-aperture X-tube with a Cu-cathode. Analysis of the obtained X-ray diffraction patterns makes it possible to determine the symmetry of the crystal structure, the crystallographic plane of the sample surface, and the general phase composition. The collimation of the X-ray beam and the use of the small-angle scattering method make it possible to identify both amorphous regions and crystalline inclusions, and to determine their sizes on the nanometer scale according to the well-known Selyakov-Scherrer formula [6-7].

$$L = 0.94 \cdot \lambda / \beta_{hkl} \cos \Theta_{hkl},$$

where L - is the grain size (nm),  $\lambda$  - is the wavelength of the radiation used (nm),  $\theta$  - is the angle of reflection (radians),  $\beta$  - is the half-width of the corresponding reflection (rad).

The error in determining the size of inclusions of nanophases in LiF crystals and glasses was no more than  $\pm$

10% (due to the weak reflection intensity).

**Irradiation with gamma rays:** The samples were wrapped in Al foil for isolation from air, irradiated in a dry channel at 320 K <sup>60</sup>Co on a pool-type installation of the INP AN RUz with gamma quanta at a dose rate of 406 R/s (energy 1.17 and 1.32 MeV) up to 10<sup>9</sup> R and irradiation in the reactor 10<sup>19</sup> n/cm<sup>2</sup>.

## RESULTS AND DISCUSSIONS

### X-ray diffraction and phase analysis

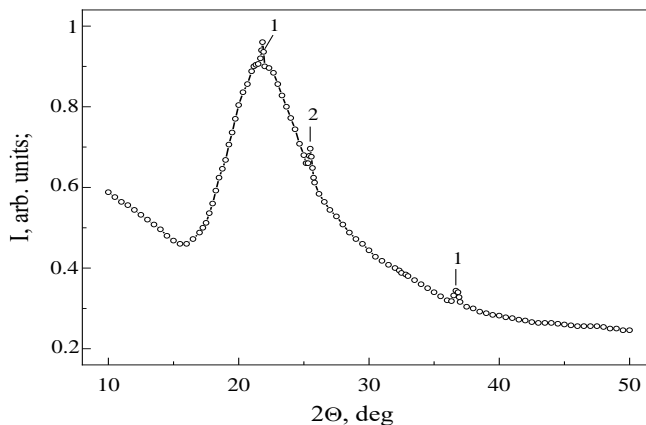


Fig. 1: X-ray standard - pure glass SiO<sub>2</sub>

Fig. 1 shows that an X-ray diffraction pattern of reference - pure SiO<sub>2</sub> glass, where it is shown that, in addition to the diffuse band, 6-SiO<sub>2</sub> nano-rings with a size of 1.4-0.04 nm were found, which are distinguished by selective reflections (111) and (101) from nano -crystals of cristobalite 39 and 28 nm, respectively, as well as the reflection (101) from  $\beta$ -quartz with a size of 35 nm.

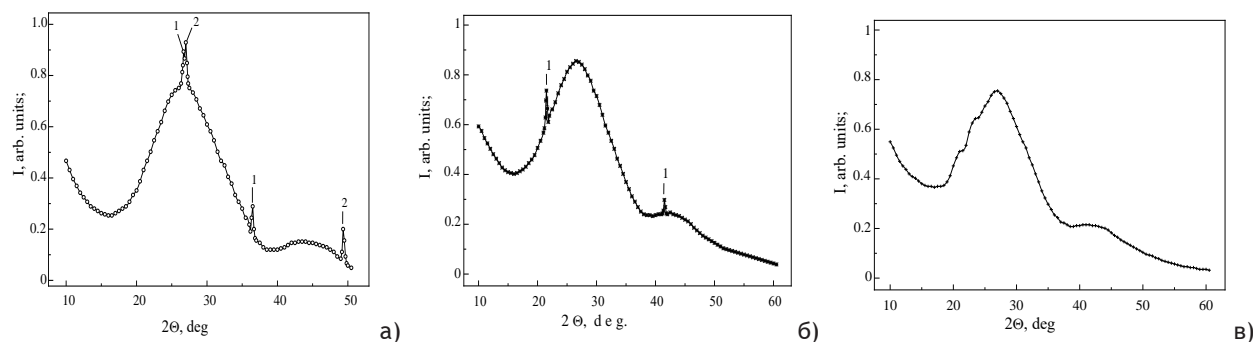


Fig. 2: X-ray diffraction pattern of SiO<sub>2</sub>-BaO before and after gamma irradiation at 210 R/s

The diffraction pattern of unirradiated SiO<sub>2</sub>-BaO is characterized by the presence of two diffuse and four selective reflections (Fig. 2 a). The main diffuse reflex is due to structural fragments of SiO<sub>2-x</sub> with sizes of 0.75  $\pm$

0.02 nm. The weak broad band is apparently associated with the impurity amorphous phases BaO and BaSiO<sub>3</sub> with dimensions of 0.78  $\pm$  0.02 nm. Selective structural lines with low intensity, which are superimposed on diffuse bands,

belong to the crystalline phase of  $\beta$ -quartz SiO<sub>2</sub> with a size of  $14.5 \pm 1.3$  nm and molecular crystals of BaO<sub>2</sub> with a size of  $27.5 \pm 1.8$  nm, which are equally oriented relative to each other. In the X-ray diffraction pattern of gamma-irradiated barium glass at a power of 210 R/s with a dose of  $1.5 \cdot 10^6$  R, only both diffuse reflections are present, and two steps are observed on the left slope of the large one (Fig. 2b), but all selective reflections have disappeared. Dissolution of  $\beta$ -SiO<sub>2</sub> and BaO<sub>2</sub> nanocrystals into the amorphous phase led to an increase in inelastic scattering [6]. The intensity of the diffuse BaO band decreased by 40%, respectively, the size of the nanoparticles increased to  $0.85 \pm 0.02$  nm.

An analysis of the angular positions of the steps showed that they belong to the SiO<sub>2</sub> phase of tridymite with the [110]

and [111] orientations, apparently, at the initial stage of its formation. At a given power and dose (defect density), the rate of introduction of radiation defects does not exceed the rate of their annihilation, which prevents the further formation of this phase [8]. Fig. 2 (c) shows that the X-ray diffraction pattern of a sample irradiated with a higher dose of  $3,5 \cdot 10^7$  R. Both diffuse reflections did not change, but two selective peaks appeared, attributed to the cristobalite SiO<sub>2</sub> phase with crystallite sizes of 50.7-4.5 nm. At such a dose (density of radiation defects), the concentration of localized electrons is high; therefore, the thermal conductivity of the matrix is significantly reduced, which provides local heat release sufficient for crystallization of the high-temperature phase.

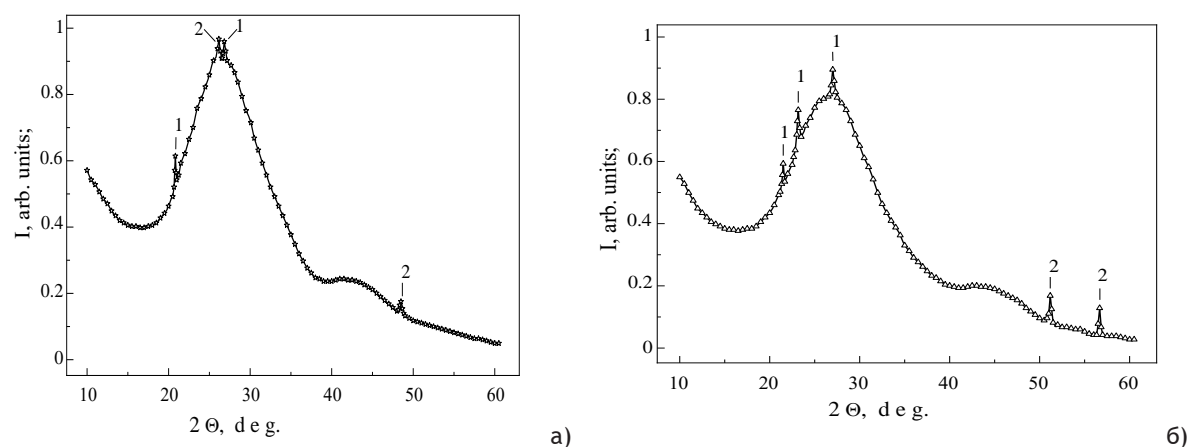


Fig. 3: X-ray diffraction pattern of SiO<sub>2</sub>-BaO before and after gamma irradiation at 600 R/s

Fig. 3 shows X-ray diffraction patterns of glass irradiated at higher dose rate of 600 R/s. After a dose of  $4 \cdot 10^6$  P (a - on the left), a significant decrease in the initial selective reflections from BaO<sub>2</sub> molecular crystals is observed, which indicates their dissolution in the glass matrix to the state of amorphous nanoparticles. This led to an increase in the inelastic background. In addition, a radiation-induced structural-phase transition of 14.5 nm  $\beta$ -SiO<sub>2</sub> nanocrystals into larger tridymite nanocrystals about 40 nm in size occurs. The appearance of an additional peak from this phase with increasing dose to  $10^8$  P (b - right) indicates an increase in size to  $\sim 50$  nm. In addition, at large scattering angles, new selective weak reflections appear, which belong to the perovskite phase BaSiO<sub>3</sub>. It is noteworthy that with the simultaneous formation of two nanocrystalline phases, including heavy ions Ba and Si, a noticeable decrease in the

level of the inelastic background occurs.

The structural and phase composition was determined on a DRON-3M diffractometer with  $\lambda_{\text{CuK}\alpha} = 0.1542$  nm at 300 K, evaluating the interplanar distances  $d/n$  (nm) from reflections. The sizes of nanoparticles were calculated using the Selyakov – Scherrer formula  $D = K\lambda/B \cdot \cos\theta_B$  [9]. For particles  $R < 0.05\lambda$ , scattering can be neglected, then the absorption cross section  $C_a = 18\pi f \epsilon_m^{3/2} (\lambda \epsilon_2)^{-1}$  [10] where  $f$  - is the total volume of the medium filled with metal particles  $\epsilon_m$  and  $\epsilon_2$  are the dielectric constants of the medium (glass) and metal (lead). The nanoparticle size can be estimated from the narrow resonance wavelength responsible for the longitudinal plasmon and its optical density.

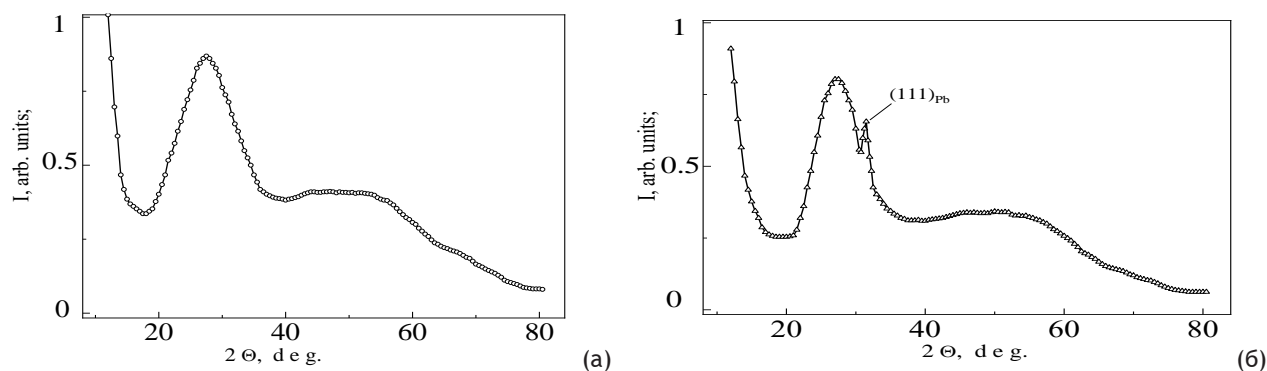


Fig. 4: X-ray diffraction pattern of silicate glass with 24 wt. % PbO: before and after irradiation with a dose of  $3 \cdot 10^8$  R

X-ray of a sample 24 wt. % PbO, is similar to the diffraction of quartz glass and consists of two broad diffuse reflections with different widths and intensities with  $d/n \approx 3.24 \text{ \AA}$  ( $2\Theta \approx 27.5^\circ$ ) and  $d/n \approx 1.70 \text{ \AA}$  ( $2\Theta \approx 54^\circ$ ), respectively (Fig. 4 (a)). It should be noted that the X-ray diffraction pattern of a powder sample obtained by grinding silicate glass in an agate mortar did not differ from the initial X-ray diffraction pattern. The presence of only diffuse reflections indicates that there is no long-range order in the arrangement of the atoms of the silicate glass, but short-range order is retained. The large width of the reflections indicates that the size of the particles causing the diffuse scattering is very small. Analysis of the X-ray diffraction pattern showed that the first diffuse reflection with  $d/n \approx 3.24 \text{ \AA}$  ( $2\Theta \approx 27.5^\circ$ ) is due to the main structural fragments of SiO<sub>2</sub> glass with unsaturated bonds [11]. The sizes of these fragments were  $L_1 \approx 7.5 \text{ \AA}$  with a diffuse peak width  $\omega_1 = 0.1987$  rad. This diffuse reflection is also observed in the X-ray diffraction pattern of pure silica glass at somewhat smaller scattering angles with a width  $\omega_0 = 0.1048$  rad [11]. The observed difference is due to the distortion of the SiO<sub>2</sub> network introduced by the addition of PbO. The second wide peak with  $d/n \approx 1.70 \text{ \AA}$  ( $2\Theta \approx 54^\circ$ ) and width  $\omega_2 = 0.3665$  radians is absent in the X-ray diffraction pattern of pure quartz glass and is possibly associated with the presence of lead-containing cells  $L_2 \approx 4.5 \text{ \AA}$  in size in quartz glass, which can be taken for critical for the investigated composition of silicate glass. Only in this case, a decrease in the bulk free energy of particles is balanced by an increase in their surface free energy, which ensures the stability of the glass network. If the particle size is less than this critical value, then they become unstable and dissolve, then combine with the nearest ones in the matrix. The presence of the second diffuse peak with  $d/n \approx 1.70 \text{ \AA}$  ( $2\Theta \approx 54^\circ$ ) in the X-ray diffraction pattern of unirradiated lead glass can be explained as follows.

As is known, the structure and properties of silica glasses are strongly dependent on the nature of the second oxide, in this case, PbO, which has a large Z and density, which does not form its own structural framework in the matrix, but can partially replace the glass-forming one. As this component is added up to tens of percent, the silicate matrix network

formed from Si–O–Si bridging bonds is increasingly destroyed, non-bridging oxygen atoms appear, Pb<sup>2+</sup> cations are located in relatively large voids of the silicate framework and form lead-containing networks. In an unirradiated sample, the distribution of lead-containing cells in the glass matrix is apparently random. As a result, the disordered three-dimensional matrix mesh structure is preserved in a somewhat distorted form. This conclusion is confirmed by the too large width of the second diffuse maximum with  $d/n \approx 1.70 \text{ \AA}$  ( $2\Theta \approx 54^\circ$ ) and the absence in the X-ray diffraction pattern of selective structural reflections belonging to lead oxide nanocrystals - PbO.

Fig. 4 (b), it can be seen that irradiation with a dose of  $3 \times 10^8$  R by <sup>60</sup>Co gamma source (1.25 MeV) led to a significant difference than the pattern of an unirradiated sample. The level of the inelastic background decreased by 7%, the intensity of the second diffuse reflection also dropped by 13%, the width of the first diffuse peak narrowed by 23% compared to the values of these parameters for the unirradiated sample, and an additional relatively narrow structural reflection with  $d/n \approx 2.840 \text{ \AA}$  ( $2\Theta \approx 31.5^\circ$ ). Narrowing of the first diffuse peak indicates an increase in the critical size of the associated structural fragment to the size  $L_1 \approx 9.5 \text{ \AA}$ . Probably, the process of gamma irradiation causes changes in the distribution of Pb<sup>2+</sup> cations over large cells of the silicate glass network. A decrease in the level of the inelastic background of the irradiated sample in comparison with the unirradiated one indicates the removal of the elastic distortion of the lead-containing cells as a result of the radiation-induced diffusion of Pb<sup>2+</sup> cations towards large cells. First, at low radiation doses, these cations are combined into lead clusters.

In contrast to KI glass, octahedral cells predominate in KB glass, although of smaller sizes, responsible for the 22° band, practically did not change the microstructure of the glass network and the scattering background on nano-sized cells of the glass network. It is seen that large doses of gamma and neutron irradiation give almost equally weak scattering effect from radiation-induced point defects.

This conclusion is also supported by a decrease in the intensity of the second diffuse maximum with  $d/n \approx 1.70 \text{ \AA}$  ( $2\Theta \approx 54^\circ$ ) due to lead-containing cells. In clustering, an

important role is played by the binding energy between like and unlike ions and also depends on their valence. It is possible that the lead-lead bond energy prevails over the lead-oxygen, lead-silicon, and silicon-silicon bond energies. With a further increase in the radiation dose, the clusters self-organize and grow like lead nanocrystals. The analysis showed that the additional reflection (111) with  $d/n \approx 2.840 \text{ \AA}$  ( $2\theta \approx 31.5^\circ$ ) is due to lead nanocrystals  $L_{\text{Pb}} \approx 9 \text{ nm}$  in size. This is evidenced by the relatively narrow width of this reflection  $\omega_3 = 0.0174 \text{ rad}$ . This is the most intense reflection from the crystal lattice of metallic lead.

Gamma irradiation causes the formation of Pb nanocrystals 9 nm in size and the enlargement of silicate cells in the glass matrix to  $L_1 \approx 0.95 \text{ nm}$  due to the completion of oxygen-deficient SiO in SiO<sub>4</sub> due to the reduction of PbO to Pb.

## CONCLUSION

In clustering, an important role is played by the binding energy between like and unlike ions and also depends on their valence. It is possible that the lead-lead bond energy prevails over the lead-oxygen, lead-silicon, and silicon-silicon bond energies. With a further increase in the radiation dose, the clusters self-organize and grow like lead nanocrystals.

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Thus, gamma irradiation with moderate doses of barium in silicate glass provides for the strengthening of the near-surface layer. This is a useful property for glass in vacuum applications.

## REFERENCES

- Kuzmin K.L. Influence of chemical composition and surface modification on mechanical properties of aluminosilicate fibers. Diss. candidate of chemical sciences. -Moscow. 2017. –136 p.
- Saetova N.S. Physicochemical properties of lithium-borate glasses and composites based on them. Diss. candidate of chemical sciences. - Ekaterinburg. 2019. –108 p.
- Fabrication and optical properties of lead silicate glass hole fibers / H. Ebandorff Heidepriem, P. Petropoulos, R. Moore, K. Frampton, D. J. Richardson, T. M. Monro. *Journal of Non-Crystalline Solids*. – 2004. – Vol. 345 & 346. – P. 293–296.
- Dogan, N. Optical and solar parameters of irradiated lead-alkali-silicate glass / N. Dogan, A. B. Tugrul // *Solar Energy Materials & Solar Cells*. – 2001. – Vol. 69. –P. 241–250.
- Wiza, J. L. Microchannel plate detectors / J. L. Wiza // *Nuclear Instruments and Methods*. 1979. – Vol. 162 – № 1-3. – P. 587–601.
- Guinier. X-ray diffraction of crystals. Theory and practice. –Moscow: Fizmatlit. 1961. 604 p.

- Gorelik S.S., Rastorguev L.N., Skakov Yu.A. X-ray and electron-optical analysis. – Metallurgy.
- Phase transformations during irradiation. Ed. Nolfi F.V. / Transl. from English Chelyabinsk, Metallurgy, 1989. –312 p.
- Guozhong Cao. Nanostructures & Nanomaterials: Synthesis, Properties and Applications, London, Imperial College Press. 2004. –433 p.
- Gusev A.I. Nanocrystalline materials: synthesis methods and properties - Yekaterinburg. Ural department RAS. 1998.-175s.
- Ibragimova E.M., and Mussaeva M.A. Electron structure modification of interfaces in SiO<sub>2</sub> glass with PbO nanoparticles at gamma-irradiation // *Journal of Nanoscience and Nanotechnology*, 2012. Vol.12. – P.1–4. doi:10.1166/jnn.2012.6482. doi: <https://doi.org/10.1166/jnn.2012.6482>.