EFFECT OF TEMPERATURE ON THE RADIAL DISTRIBUTION FUNCTION OF ATOMS IN THE SILICATE GLASS $2SiO_2 \cdot PbO$

ABSTRACT

In this article, results of investigation of the effect of temperature on radial distribution function of atoms in lead-silicate glass are reported. Radial distribution functions of atoms in the lead-silicate glass $2SiO_2 \cdot PbO$ were calculated via Mathematica 5.1 Wolfram Research from high-temperature X-ray diffraction patterns. It turned out that in the range of 773-973 K mainly variations of the location of atoms in the third coordination sphere have observed, while in the range of 973-1123 K, changes in the first and second coordination spheres take place.

Keywords: temperature dependence of resistivity, thermopower coefficient, high-temperature X-ray diffraction, coordination spheres

1. INTRODUCTION

In doped lead-silicate glass, at temperatures higher than 700 K, a sharp increase in resistivity *ρ* and thermopower coefficient *S* was observed (Fig.1) [1]. Based on the assumption that these changes caused by the structural transitions of the glass itself and the nanocrystals present in it, these dependences in the range from the temperature of liquid helium to 1200 K was explained qualitatively [2] .

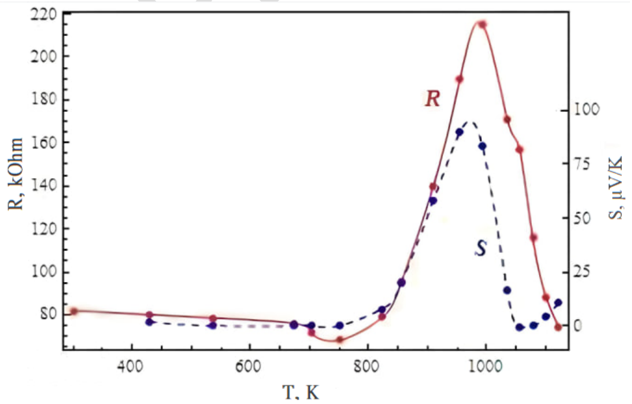

Figure 1. Temperature dependences of resistance *R* and coefficient of thermopower *S* in $2SiO_2 \cdot PbO$ glass doped with RuO_2 [1]

However, there was no direct experimental basis for this assumption, since the nanocrystals in the glass are very small (1-2 nm in size), so it is not possible to determine the changes in their structure directly (for example, using X-ray diffraction).

It is known that when studying the structure of non-crystalline substances by diffraction methods, only the radial distribution function $\rho(r)$ of its atoms can be determined [3, 4]. Here r is the distance from the central atom to other atoms. [9] In essence, heavy atoms play the main role in X-ray diffraction [5]. The meaning of $\rho(r)$ is that the $4\pi r^2 \rho(r) dr$ is number of atoms located on spherical layer of radius from r to $r + dr$ centered at given (heavy) atom.

Here, $4\pi r^2$ is the surface of a sphere with a radius r, $4\pi r^2 dr$ is the volume of a spherical layer of thickness dr on the surface of this sphere.

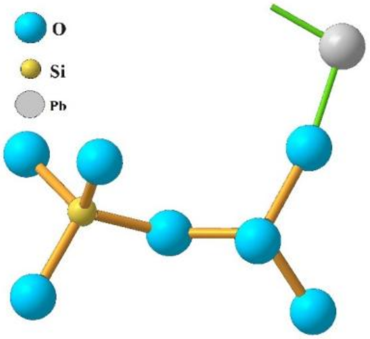

Figure 2. Spatial arrangement of atoms in lead-silicate glass (model)

For the radial distribution function, calculations using Fourier transforms give the following formula [6]:

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^\infty s\{\frac{I(s)}{Nf^2} - 1\}\sin sr\, ds. \qquad (1)$$

Here $\rho_0 = \rho(r\rightarrow\infty)$, $I(s)$ is the intensity distribution in the X-ray diffraction image, $s = (2\pi\sin\theta)/\lambda$ is the change of the X-ray wave vector during the scattering process, N is the number of atoms in the studied substance, f is the shape coefficient of atoms. Formula (1) gives the average value of the spatial radial distribution of atoms in space and time. If the studied sample consists of several types of atoms, then formula (1) has the following form:

$$\sum_{\mathrm{m}} 4\pi r^2\rho_m(\mathrm{r}) = \sum_{\mathrm{m}} k_m\, 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^\infty s\left\{\frac{I(s)}{\sum_{\mathrm{m}} f_m^2} - 1\right\}\sin srds. \qquad (2)$$

In this case, k_m is the effective number of X-ray scattering electrons in a m-type atom, often determined by the k_m-type atomic shape coefficient f_m graph. This method is universal and applies to all types of isotropic substances, only for amorphous substances it is necessary to subtract the intensity of incoherent scattering from the experimentally obtained (s). Above, the presence of nanocrystals in lead-silicate glass and the physical basis of studying structural transitions in them using X-ray diffraction in the range of 300-1123 K were assumed. In order to test these assumptions in practice, X-ray diffraction images of the sample in the range of 300-1123 K have obtained and atomic arrangement has studied.

It should be noted that in all silicates, including vitreous silicate glasses silicon atoms are surrounded by oxygen atoms in $[SiO_4]^{4-}$ tetrahedra (Figure 2), which are connected to each other and another atoms only through their ends [8].

2. MATERIAL AND METHODS

Lead silicate glass was fired in a furnace at 1123 K for 60 minutes. The finished glass was turned into powder-like particles with a diameter of 0.2-0.5 μm in a grinder. X-ray patterns of silicate glass at temperatures of 293, 773, 973 and 1123 K (Fig. 3) were skiagraphed on a Siemens D500 X-ray diffractometer with the Anton Parker HTK16N high-temperature chamber. The temperature points 293, 773, 973 and 1123 K were chosen for the experiment because at these points *R(T)* and *S(T)* (Fig. 1) start to increase sharply, reach a maximum and return almost to their initial values. One can see from Figure 3, the X-ray diffraction images of the sample affected by temperature, but it is impossible to say variations on arrangement of which atoms led to these changes. Therefore, it is necessary to calculate the radial distribution function $\rho(r)$ of atoms. [10]

3. RESULTS AND DISCUSSION

The radial distribution functions of atoms calculated according to formula (1) are presented in Fig. 3.

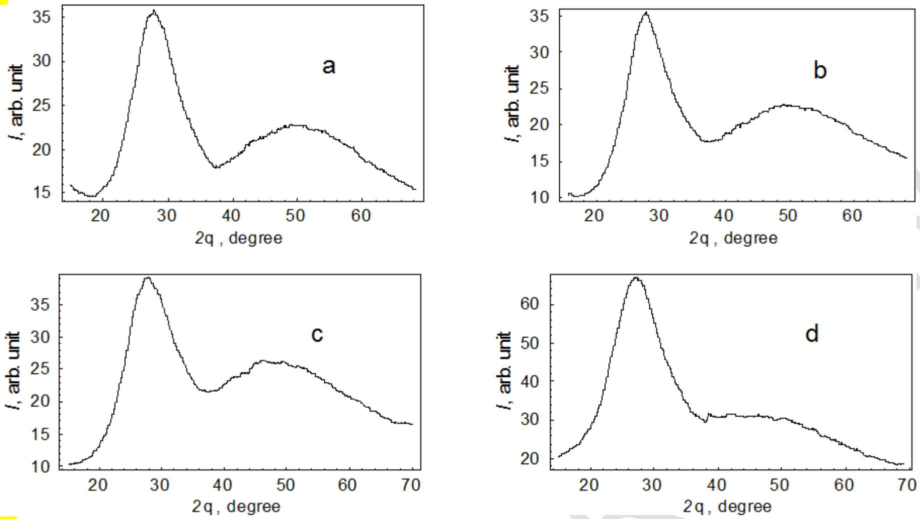

Figure 3. X-ray scattering image of $2SiO_2 \cdot PbO$ glass at different temperatures: 300 *K* (a), 773 *K* (b), 973 *K* (c) and 1123 *K* (d)

It can be seen that the changes in the radial distribution function at 300 and 773 K (Fig. 3a) are hardly noticeable, that is, there was no change in the glass structure up to 773 K. The radial distribution function at 973 and 1123 K (Fig. 3b) differs from the previous one, especially this difference is clearly visible in the maximum near 2.2 Å.

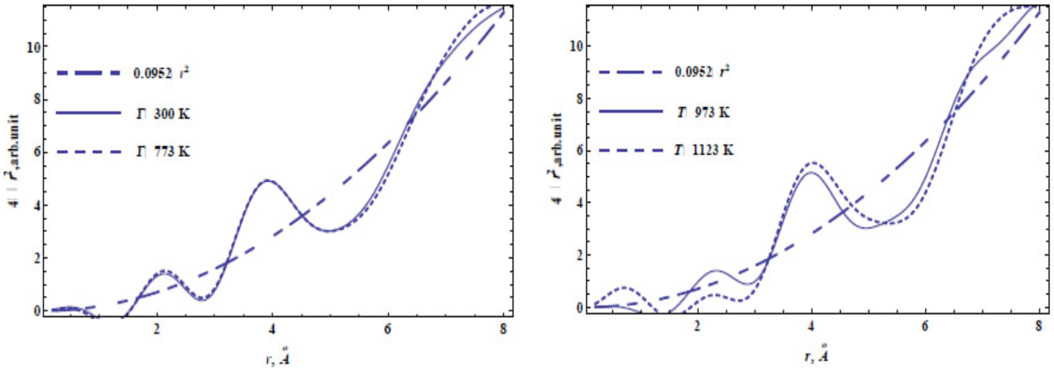

Figure 4. Radial distribution functions in 2SiO2·PbO glass at different temperatures: a) 293K and 773K, b) 973K and 1123K

The radial distribution function was calculated for lead atoms [5]. Accordingly, structural transitions in nanocrystals begin, reach a maximum, and end at these points. In this case, due to the increase in the distance between the atoms, the overlap of their wave functions decreases.

It is known [7] that heavy atoms make the main contribution to X-ray diffraction in amorphous substances consisting of several types of atoms. Accordingly, in Fig. 4, the radial distribution functions are calculated starting from the heaviest atom in the glass - lead atoms, that is, these atoms are located at the beginning of the coordinates.

4. CONCLUSION

It was detected that increasing the temperature up to 773 K causes small changes in third coordination sphere (maximum at 7 Å, arrangement of oxygen atoms beyond the silicon atoms), while change in the first (2.2 Å) and the second (4 Å) coordination spheres observed mainly at 973 and 1123 K, where nearest oxygen and silicon atoms displaced around lead atoms.

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