X-ray Study of the Structure of Multicomponent Glasses Based on Mining-Industry Waste

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Abstract—The short-range order and microinhomogeneity structure of laboratory samples of glasses belonging to the diopside–orthoclase–apatite system with different percentages of components were investigated by X-ray diffraction and small-angle scattering. A correlation between a change in the chemical composition of a glass, causing its segregation, and the short-range order parameters was ascertained: an increase in the apatite content leads to a change in the short-range order parameters. The use of the X-ray small-angle scattering technique made it possible to reveal inhomogeneities of electron density in the glasses under study and the dependence of the sizes of inhomogeneities on the glass composition. © 2004 MAIK “Nauka/Interperiodica”.

INTRODUCTION

In recent years, the field of application of basalt fibers and casting has been significantly widened. In particular, they can be used for production of heat-insulating mats and cords and sound-absorbing and filter materials. Due to its high chemical durability, basalt casting can be used in the chemicals industry. The application of mining-industry waste significantly reduces the cost of such materials. The development of industrial technologies in this field depends on obtaining glasses with the desired properties. In this context, prediction of these properties—depending on the chemical composition of a glass and conditions of its preparation—plays an important role. In particular, multicomponent glasses are of interest. Information on the structure of these glasses is important both from the scientific point of view and for their practical use in new material production technologies. To date, information obtained in this field is rather scarce.

In this paper, we report the results of investigations of the short-range order and microinhomogeneities in diopside–orthoclase–apatite glasses by X-ray diffraction analysis. Previous studies [1] showed that, when the content of apatite in the glasses of this system is increased to a certain value, a transition from the homogeneous state to a state characterized by two immiscible phases occurs. It is of interest to find out how this phenomenon is related to changes in the microstructure of the objects studied.

EXPERIMENTAL SAMPLES

Figure 1 shows the phase diagram of the diopside–orthoclase–apatite system, where points 1, 2, 3, and 4 denote the chemical composition of the studied glass samples. The curve in the diagram represents the boundary, below which (at a corresponding concentration of the components) the glass structure is homogeneous; above this boundary, the glass separates into two immiscible phases.

Samples of apatite (Ca₅(PO₄)₃F), diopside (CaMgSi₂O₆), and orthoclase (KAlSi₃O₈) were prepared, respectively, from apatite concentrate (AO Apatite), a monomineral fraction of diopside extracted from phlogopite–diopside rocks of the

Fig. 1. Solubility of apatite in the apatite–orthoclase–diopside system. (○) Homogeneous melt at 1400°C, (■) two liquid immiscible phases, (■) melt and crystals at the same temperature.
Kovdor phlogopite deposit [1], and a monomineral fraction of potassium feldspar from the Kovdor deposit. The chemical compositions of diopside and potassium feldspar (orthoclase) somewhat differ

\[ \begin{align*}
1: & \text{O}_{0.608}\text{Si}_{0.154}\text{Al}_{0.012}\text{K}_{0.005}\text{Ti}_{0.008}\text{Ca}_{0.029}\text{Fe}_{0.007}\text{P}_{0.013}\text{Mg}_{0.005}\text{Na}_{0.002} \\
2: & \text{O}_{0.610}\text{Si}_{0.154}\text{Al}_{0.016}\text{K}_{0.005}\text{Ti}_{0.007}\text{Ca}_{0.029}\text{Fe}_{0.005}\text{P}_{0.011}\text{Mg}_{0.055}\text{Na}_{0.002} \\
3: & \text{O}_{0.612}\text{Si}_{0.154}\text{Al}_{0.011}\text{K}_{0.008}\text{Ti}_{0.007}\text{Ca}_{0.102}\text{Fe}_{0.006}\text{P}_{0.013}\text{Mg}_{0.051}\text{Na}_{0.002} \\
4: & \text{O}_{0.613}\text{Si}_{0.146}\text{Al}_{0.011}\text{K}_{0.008}\text{Ti}_{0.006}\text{Ca}_{0.103}\text{Fe}_{0.005}\text{P}_{0.047}\text{Mg}_{0.048}\text{Na}_{0.002}
\end{align*} \]

With regard to the effect of temperature on the solubility of apatite in aluminosilicate melts, the blend was prepared in corundum crucibles at the same temperature (1400°C) [1]. The melt was kept at this temperature for 3 h for complete homogenization. In order to relieve stresses, the prepared glass was annealed at 600°C. The glass-transition temperature was approximately the same for all the samples (in the vicinity of 750°C).

**EXPERIMENTAL AND CALCULATION TECHNIQUES**

The short-range order parameters were determined by X-ray diffraction analysis on a DRON-3.0 automated diffractometer in MoKα radiation with monochromatization of the primary and diffracted beams in reflection geometry and in the s range \( s = 4\pi\sin\theta/\lambda \), where \( s \) is the diffraction vector, \( \theta \) is the diffraction angle, and \( \lambda \) is the radiation wavelength) from 0.35 to 16.6 Å\(^{-1}\). Fused quartz was used as a reference. The experimental values of the reflection intensities were corrected to scattering from air, polarization, and Compton scattering, after which the short-range order parameters were calculated by the Warren–Finback method.

Table 1. Chemical compositions of diopside and orthoclase

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Weight content, %</th>
<th>diopside</th>
<th>orthoclase</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>55.36</td>
<td>62.93</td>
<td></td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.40</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>1.30</td>
<td>17.75</td>
<td></td>
</tr>
<tr>
<td>FeO + Fe(_2)O(_3)</td>
<td>3.50</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>14.51</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>24.63</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.20</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.10</td>
<td>16.76</td>
<td></td>
</tr>
</tbody>
</table>

According to Warren [2, 3], the distribution of pair functions is constructed in the form

\[
\sum_{i} \sum_{j} \frac{N_{ij}}{r_{ij}} P_{ij}(r) = 2\pi^{2} r_{ij} \frac{Z_{j}}{Z_{i}} \int_{0}^{r_{ij}} I_{i}(s) \exp(-\alpha^{2} s^{2}) g^{-2}(s) \sin(sr) ds,
\]

where \( N_{ij} \) is the number of atoms of type \( j \) on the \( i \)th coordination sphere; \( r_{ij} \) is the radius of the \( ij \)th coordination sphere for \( j \)-type atoms; \( s \) is the electron density; \( Z_{j} \) is the atomic number of the elements forming a material; \( I_{i}(s) \) is the interference function of the \( i \)-type atoms; \( \exp(-\alpha^{2} s^{2}) \) is the decay factor, the action of which manifests itself in the reduction of the influence of experimental errors; and \( g^{-2}(s) \) is the sharpening factor, which ensures a higher contrast of the interference pattern at large values of \( s \). The pair functions have the form

\[
P_{ij}(r) = \int_{0}^{r_{ij}} f_{i} f_{j} \sin(sr_{ij}) \exp(-\alpha^{2} s^{2}) g^{-2}(s) \sin(sr) ds,
\]

where \( f_{i} f_{j} \) are the atomic scattering functions of the \( i \) and \( j \)-type atoms.

The pair function characterizes the distribution of the electron density of a particular pair of atoms and depends on the types of atoms forming the pair. The left-hand side of (1) is calculated from the experimental intensities. Let us denote it as \( D(r) \) and the integrand as \( H(s) \). Then, \( D(r) = 2\pi^{2} r_{ij} \frac{Z_{j}}{Z_{i}} \int_{0}^{r_{ij}} H(s) \sin(sr) ds \). \( D(r) \) is the distribution of the sum of pair functions \( P_{ij}(r) \) and characterizes the distribution of electron density in a material. The positions of peaks on the curve \( D(r) \) give the corresponding interatomic distances. In real noncrystalline materials, the widths of the maxima of the pair functions \( P_{ij}(r) \) increase due to the dispersion \( \sigma_{r} \) of interatomic distances with respect to the average value of \( r_{ij} \). These values are fitted by the method of successive approximations; the criterion is a sufficiently good coincidence between the left- and the

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