SYNTHESIS OF SELENITE GLASSES IN AIR*

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ABSTRACT

The aim of the present investigation is to obtain SeO₂-containing oxide glasses under air. The batches were prepared using the previously synthesized multicomponent glasses and selenites (ZnSeO₄, Ag₅SeO₆, and CuSeO₄). They were heated at 700-800°C for 15 min. The melting was performed in different crucibles depending on their corrosion resistance. Compositions containing more than 50 mass % selenites showed a strong trend to evaporation. Transparent low-melting glasses were obtained in the systems ZnSeO₄-TeO₂-B₂O₃-SrO, ZnSeO₄-TeO₂-Nd₂O₃-ZnO, ZnSeO₄-TeO₂-CeO₂-BaO-ZnO, ZnSeO₄-TeO₂-Na₂O-μO-BaO and ZnSeO₄-TeO₂-Al₂O₃. The detection of SeO₂ group vibrations (850-830 cm⁻¹, 760-730 cm⁻¹) confirmed that SeO₂ had remained in the samples after melting. A very simple reproducible scheme for the preparation of multicomponent selenite glasses under conventional circumstances was developed.

Keywords: selenites, glasses, air conditions, units, amorphous network.

INTRODUCTION

Homogeneous multicomponent selenite glasses containing other non-traditional network formers V₂O₅, TeO₅, MoO₃ and Bi₂O₃ have been obtained [1-3]. They are interesting mainly from scientific point of view in order to investigate the glass formation ability and the network structure of glasses depending on their compositions. The main difficulty with the preparation of this type of glasses is their volatilization near the liquidus temperature and the sublimation of SeO₂ at atmospheric pressure and temperatures above 315°C. Besides the volatility, another obstacle for the practical applications of these glasses is their hygroscopicity. Since 1981 the glass formation and structure of different selenite systems have been investigated in the Department of Silicate Technology of the University of Chemical Technology and Metallurgy, Sofia. The results obtained during the last 20 years have been reviewed by Dimitriev et al. [3]. In our earlier investigations [4] glasses were obtained under high pressure using an autoclave or silica glass ampoules (volume 5 cm³), which were evacuated and sealed at pressure P = 0.1 Pa. Except for the first results of Rawson and Stanworth [5, 6], until now the synthesis of selenite glasses in air has not been investigated.

The purpose of the present work is to obtain selenite glasses in air and to determine the conditions of melting as well as to develop an appropriate technological scheme.

EXPERIMENTAL

Previously synthesized selenites (Ag₅SeO₆, CuSeO₃ and ZnSeO₄) and glasses were used as starting...
materials in order to decrease the volatilization. The selenites were prepared by the classical method [7] from saturated aqueous solutions containing: Ag(NO₃)₂, Cu(NO₃)₂, Zn(NO₃)₂, and SeO₂ in an appropriate ratio. The products were dried and heated up to 250°C. The identification of the compounds was performed by X-ray diffraction: ICDD file No 34-0382 was used for Ag₂SeO₃, CuSeO₃ [8-10] and file No 75-0718, for ZnSeO₃. The batches were prepared by mixing selenites with previously synthesized multicomponent glasses in different ratios. The melting of the batches was performed in suitable crucibles (platinum, quartz, corundum, porcelain), in order to prevent corrosion. A maximum temperature of melting was not higher than 700 - 800°C, and was achieved by an appropriate selection of the initial oxide glasses. During heating, the evaporation of the melts was controlled, as an indication of SeO₂ loss. According to the preliminary results in spite of their high thermal stability (530°C for Ag₂SeO₃ and 550°C for CuSeO₃) these compounds were not suitable due to their high evaporation rate. The use of ZnSeO₃ is more appropriate. The amorphous state was determined by X-ray diffraction (TUR M65, Cu Kα radiation) and the amorphous network was studied by IR spectroscopy (FTIR spectrophotometer, computer controlled “Bruker” EQUINOX 55) using the KBr pallets method in the wave number range 4000-400 cm⁻¹.

RESULTS AND DISCUSSION

Table 1 shows the samples that were amorphous and transparent after melting only. Stable glasses were obtained with the participation of barium borate, zinc borate and tellurite compositions. The ZnSeO₃ addition to the molybdenum and tungstate compositions led to formation of glass-crystalline materials only, which were not interesting in a view of further investigations. Visual observations show an upper glass formation boundary of 40 - 50 wt % SeO₂ for barium-borate and zinc-borate compositions. The glass formation regions are shifted to 60 - 70 wt % ZnSeO₃ after addition of tellurite compositions. Infrared spectroscopy was used as a qualitative test to prove the presence of selenite units (SeO₃) in the amorphous network. The IR spectrum of ZnSeO₃ (Fig. 1) is characterized by intense bands at 690, 720, 760 and 850 cm⁻¹, which can be assigned to the vibrations of the isolated SeO₃ groups. Absorption at 700 cm⁻¹ increases, which is an indication of the pres-

Table 1. Temperature and visual characterization of selected multicomponent compositions containing SeO₂.

<table>
<thead>
<tr>
<th>№</th>
<th>Compositions, mass %</th>
<th>Visual characterization</th>
<th>Melting temperature and kind of the crucibles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30ZnSeO₃ + 70(60ZnO:40B₂O₃)</td>
<td>Yellow glass</td>
<td>1030°C, Platinum</td>
</tr>
<tr>
<td>2</td>
<td>70ZnSeO₃ + 30(40TeO₂:30B₂O₃:30CaO)</td>
<td>Yellow glass</td>
<td>900°C, porcelain</td>
</tr>
<tr>
<td>3</td>
<td>30ZnSeO₃ + 70(40TeO₂:30B₂O₃:30CaO)</td>
<td>Yellow glass</td>
<td>900°C, porcelain</td>
</tr>
<tr>
<td>4</td>
<td>70ZnSeO₃ + 30(50TeO₂:30B₂O₃:20SrO)</td>
<td>Yellow glass</td>
<td>900°C, porcelain</td>
</tr>
<tr>
<td>5</td>
<td>30ZnSeO₃ + 70(50TeO₂:30B₂O₃:20SrO)</td>
<td>Yellow glass</td>
<td>900°C, porcelain</td>
</tr>
<tr>
<td>6</td>
<td>40ZnSeO₃ + 60(78.3TeO₂:1.7Nd₂O₃:20ZnO)</td>
<td>Yellow glass</td>
<td>900°C, porcelain</td>
</tr>
<tr>
<td>7</td>
<td>30ZnSeO₃ + 70(77.2TeO₂:13.8BaO:8.2ZnO)</td>
<td>Orange glass</td>
<td>900°C, porcelain</td>
</tr>
<tr>
<td>8</td>
<td>30ZnSeO₃ + 70(70TeO₂:2.5Na₂O:25Ag₂O:2.5BaO)</td>
<td>Red glass</td>
<td>850°C, porcelain</td>
</tr>
<tr>
<td>9</td>
<td>50ZnSeO₃ + 50(70TeO₂:2.5Na₂O:25Ag₂O:2.5BaO)</td>
<td>Red glass</td>
<td>850°C, porcelain</td>
</tr>
<tr>
<td>10</td>
<td>50ZnSeO₃ + 50(97.3TeO₂:2.5Al₂O₃)</td>
<td>Yellow glass</td>
<td>850°C, porcelain</td>
</tr>
<tr>
<td>11</td>
<td>30ZnSeO₃ + 70BaO</td>
<td>Yellow glass</td>
<td>850°C, porcelain</td>
</tr>
<tr>
<td>12</td>
<td>50ZnSeO₃ + 50(50TeO₂:7Nd₂O₃:3ZnO)</td>
<td>Yellow glass</td>
<td>850°C, porcelain</td>
</tr>
</tbody>
</table>

Fig. 1. IR spectra of ZnSeO₃·2H₂O and ZnSeO₃.
Fig. 2. IR spectra of multicomponent glasses containing barium-borate and zinc-borate compositions.

Fig. 3. IR spectra of multicomponent glasses containing tellurite compositions.

Fig. 4. IR spectra of multicomponent glasses containing tellurite compositions.

Fig. 5. IR spectra of multicomponent glasses containing tellurite compositions.
Preliminary synthesis of selenites

Grinding and homogenization

Melting (porcelain, quartz and corundum crucibles)

Cooling (at room temperature)

Characterization

Fig. 6. Scheme for synthesis of selenite glasses in air atmosphere.

ence of $\text{SeO}_3^2$ groups in the glass structure (Fig. 2). Figs. 3, 4 and 5 show the IR data for the selected compositions. Introduction of 30 to 50 mass % $\text{ZnSeO}_3$ provokes a strong absorption in the range 720-650 cm$^{-1}$, which can be regarded as a proof of the presence of isolated $\text{SeO}_3$ groups: $v''$ (720 cm$^{-1}$), $v'$ (690 - 650 cm$^{-1}$). The bands, which are typical of borate group vibrations [11, 12] are not intense in the investigated glasses. The band intensity increase at 1360 cm$^{-1}$ is connected with the formation of $\text{BO}_3$ and $\text{BO}_2$ complexes, which take part in superstructural units. Figs. 3 and 4 show the IR spectra of the multicomponent compositions containing $\text{TeO}_2$. The bands at 640-600 cm$^{-1}$ are due to the vibration of deformed $\text{TeO}_2$ groups and are shifted to higher frequencies (680-660 cm$^{-1}$), depending on the compositions. That is an indication of the transformation of $\text{TeO}_4$ into $\text{TeO}_3$ groups [13-15]. Typical examples of IR spectra are shown on Fig. 5. With the introduction of $\text{ZnSeO}_3$ the 700 cm$^{-1}$ band intensity produced by $\text{SeO}_3$ units vibrations increases, which agrees with the foregoing. There is some coincidence of $\text{TeO}_3$ and $\text{SeO}_3$ bands vibrations in the region at 680 cm$^{-1}$.

The results obtained allow us to propose a simple scheme (Fig. 6) for the preparation of multicomponent selenite glasses, applying the following stages:

1. Preliminary synthesis of selenites and low melting telluride, borate, molybdenum and tungstate glasses;
2. Mixing and homogenization;
3. Melting at 700 - 800°C, during which the batches evaporation and evolution of $\text{SeO}_2$ gas phase is followed.

CONCLUSIONS

The possibility for obtaining multicomponent selenite glasses in air using different combinations of compositions containing previously synthesized selenites and low melting oxide glasses (tellurite and borate) has been proved. An appropriate scheme for the synthesis of the glasses has been developed.

REFERENCES