

Glass formation in the system $\text{SeO}_2\text{-CuO-B}_2\text{O}_3$

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The glass formation region in the system $\text{SeO}_2\text{-B}_2\text{O}_3\text{-CuO}$ has been determined using the melt quenching method of sealed silica ampoules. Crystallization of CuB_2O_4 only has been observed in a wide concentrate region near the glass formation boundary. The formation of three-component compounds was not proved. It was suggested that the section $\text{SeO}_2\text{-CuB}_2\text{O}_4$ is the only quazi-binary one as a simple eutectic type. The presence of SeO_3 ($\nu = 820 \text{ cm}^{-1}$; $760\text{-}750 \text{ cm}^{-1}$) units in the amorphous samples has been confirmed by IR spectroscopy. A band at 540 cm^{-1} appears in the spectra, which may be assigned to the CuO_4 "square planar" units.

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1. Introduction

Selenite glasses were obtained in multicomponent systems with the participation of non-traditional network formers such as MoO_3 , Bi_2O_3 , V_2O_5 and TeO_2 [1, 2]. They are interesting mainly from a fundamental point of view in order to verify the glass formation ability and their structure. The main difficulties of their preparation are the sublimation of SeO_2 (at atmospheric pressure) and the hygroscopicity of the samples. Up to now selenite glasses with the participation of B_2O_3 have not been studied systematically. In our earlier investigations [3] we obtained amorphous materials and glass-crystalline products in section $\text{CuSeO}_3\text{-B}_2\text{O}_3$ as part of the system $\text{SeO}_2\text{-B}_2\text{O}_3\text{-CuO}$ and the glasses in the binary system $\text{SeO}_2\text{-B}_2\text{O}_3$ [4]. Some peculiarities concerning the phase formation of the samples obtained by super-cooling of the melts remain unclear yet. The questions arose stimulated our investigations over wider concentration ranges.

The purpose of the present work is to obtain information about the glass formation region in the system $\text{SeO}_2\text{-B}_2\text{O}_3\text{-CuO}$ and to identify the crystal phases, which were separated from the melts near the glass formation boundary.

2. Experimental

Copper selenite (CuSeO_3) was used as starting compound in order to decrease the volatilization of SeO_2 . It was prepared by the classical method [5] from saturated aqueous solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with SeO_2 , dried and heated up to 250°C . It was identified as single phase products by ICDD file № 48-0374. The batches were prepared by mixing previously synthesized compound (CuSeO_3) and B_2O_3 in different ratios. They were dried at 200°C for 6h in a vacuum drying-oven. The melting of the

batches was performed in silica ampoules (volume 5 cm^3) evacuated at a pressure $P = 0.1 \text{ Pa}$. The ampoules were situated in a metal container and heated at a temperature of 800°C . The melted samples were cooled with a rate of $100^\circ\text{C}/\text{min}$. The structural and phase transformation of the samples were verified by X-ray diffraction (TUR M65, Cu $K\alpha$ radiation) and IR spectroscopy (FTIR spectrophotometer, computer-controlled Bruker EQUINOX 55, in the wave range $1400\text{-}400 \text{ cm}^{-1}$) using the KBr pellets method. Scanning Electron Microscopy (JEOL Superprobe 733) was used to observe the microheterogeneities in the structure of the compositions selected from the system investigated. Electron microprobe analysis EMRA (JEOL Superprobe 733) was performed on polish samples.

3. Results and discussion

The glass formation regions of the systems are presented in Fig. 1.

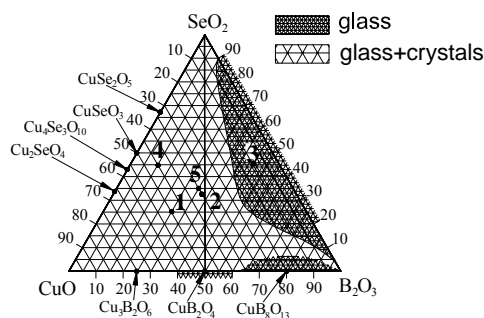


Fig. 1. Glass formation region in the system $\text{SeO}_2\text{-CuO-B}_2\text{O}_3$.

The stable glasses are situated near the $\text{SeO}_2\text{-B}_2\text{O}_3$ site. The content of the third component in the glasses reaches 30 mol% CuO. Comparing the both systems $\text{SeO}_2\text{-CuO-B}_2\text{O}_3$ and $\text{SeO}_2\text{-Ag}_2\text{O-B}_2\text{O}_3$ it can be concluded that the glass formation region in the second one is extended to the B_2O_3 corner due to the role of the silver ion (Ag^+) as modifier, which stimulate the BO_3 to BO_4 transitions [6]. In the system $\text{SeO}_2\text{-CuO-MoO}_3$ the glass formation region is extended to the CuO-SeO_2 site, because the simultaneously presence of CuO and MoO_3 stimulate the formation of isolated and mobile MoO_4 units in wider concentration range. Most of the investigated compositions possess a high hygroscopicity, which makes experiments with them difficult. This was confirmed by X-ray diffraction patterns (Fig. 2) of the glass samples, where H_3BO_3 was detected only. A mixture of glass and crystals is observed in a set of compositions near the glass boundary (Fig. 3).

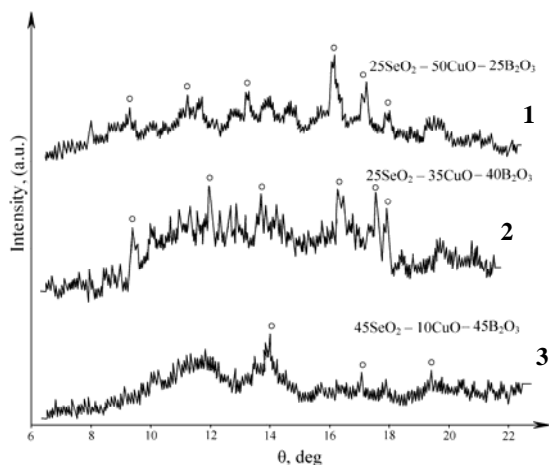


Fig. 2. XRD patterns of the selected glasses from the system $\text{SeO}_2\text{-CuO-B}_2\text{O}_3$; o - H_3BO_3 .

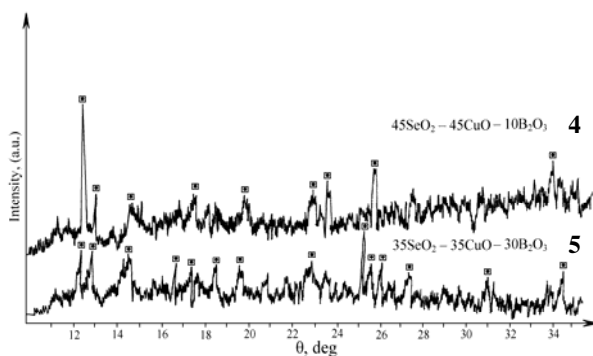


Fig. 3. XRD patterns of the crystalline samples from the system $\text{SeO}_2\text{-CuO-B}_2\text{O}_3$; ■ - $\text{Cu}_2\text{B}_2\text{O}_4$.

It is well known that in the binary system $\text{CuO-B}_2\text{O}_3$ there is a broad liquid phase separation region, which is not spread out in the three-component compositions and is limited in the binary system. A composition,

$25\text{SeO}_2.35\text{CuO}.40\text{B}_2\text{O}_3$ (composition 2, Fig. 1) situated far from the binary system $\text{CuO-B}_2\text{O}_3$, was selected. At slow cooling a heterogeneous structure was observed: formation of layers and droplets (Fig. 4a). According to the preliminary Electron microprobe analysis established that the first layer contains B_2O_3 , SeO_2 and CuO oxides, the second layer is rich in B_2O_3 and CuO oxides and droplets containing selenium only, probably they are a result of SeO_2 reduction (Fig. 4b).

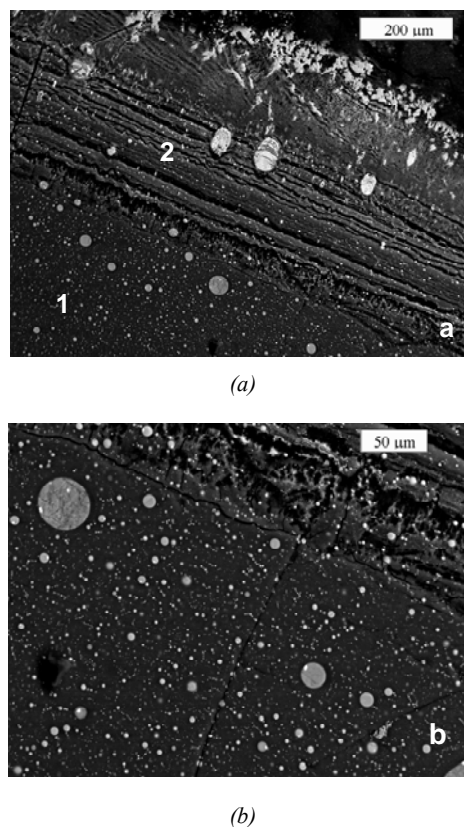


Fig. 4. SEM micrographs of the sample with composition $25\text{SeO}_2.35\text{CuO}.40\text{B}_2\text{O}_3$.

Fig. 5 shows the IR spectra of a slowly cooled sample (3, Fig. 1) in the $\text{SeO}_2\text{-CuO-B}_2\text{O}_3$ system. According to the X-ray diffraction data of this sample, $\text{Cu}_2\text{B}_2\text{O}_4$ was identified only. The interpretation of the IR spectra is based on spectral data from the literature concerning CuSeO_3 selenite [7] as well as other selenites containing isolated SeO_3 units [3] and spectra of selenite glasses [1, 2]. The bands at 820 , 700 and 420 cm^{-1} are attributed to the vibrations of isolated SeO_3 groups [7, 8]. Probably these selenite units take part in the amorphous network formation. As it was pointed out $\text{Cu}_2\text{B}_2\text{O}_4$ phase only crystallized which confirmed our suggestion that SeO_3 units remain mainly in the amorphous matrix. The bands at 1230 and 670 cm^{-1} are too weak, because of the low B_2O_3 concentration (10 mol %) and it is difficult to be assigned. They can be attributed to the associated or isolated BO_3 groups [9]. As it is well known the crystalline copperborate phase ($\text{Cu}_2\text{B}_2\text{O}_4$) contains BO_3 units only [10]. This

is in contrast to the $\text{SeO}_2\text{-B}_2\text{O}_3\text{-Ag}_2\text{O}$ system, where the formation of BO_4 units was discussed [6]. While in the investigated $\text{SeO}_2\text{-CuO-B}_2\text{O}_3$ system a stronger tendency to formation of isolated SeO_3 and BO_3 units under the influence of modifier ion (Cu^{2+}) instead of polymerization was observed. This process leads to deterioration of the glass formation ability over a wide concentration range. In contrast to our results, Lucacel et al. established that the CuO content favors the obtaining of homogeneous glasses [11]. It is interesting that a band at 530 cm^{-1} appears which may be assigned to the vibration of CuO_4 "square planar" units [3, 8].

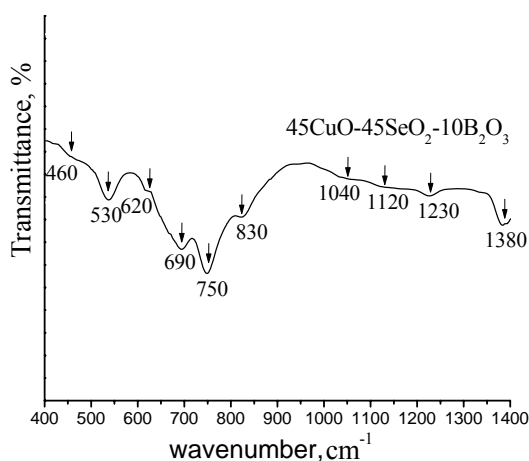


Fig. 5. IR spectra of selected glass-crystalline sample with CuB_2O_4 crystals.

On the basis of the IR spectra for the main building units, detected in the amorphous part of the samples and the fact that CuB_2O_4 crystals only have been identified over a wide concentration range, a model has been proposed for the glass structure transformation in the system $\text{SeO}_2\text{-B}_2\text{O}_3\text{-CuO}$ [12]. On the other hand, in the binary system $\text{SeO}_2\text{-CuO}$, compounds CuSeO_3 and CuSe_2O_5 are formed, which can dissociate easier at higher temperatures. They contain isolated SeO_3 pyramids and pyrogroups, respectively [3, 7 and 13]. That is why the glass formation is extended toward $\text{SeO}_2\text{-B}_2\text{O}_3$ boundary in compositions where the depolymerization processes were not developed.

4. Conclusions

The present investigation shows that in the systems $\text{SeO}_2\text{-B}_2\text{O}_3\text{-CuO}$ glasses can be obtained near the $\text{SeO}_2\text{-B}_2\text{O}_3$ site. The IR spectra reveal the presence of SeO_3 , BO_3 and CuO_n groups. These structural peculiarities of the network explain the unsatisfactory glass formation ability of the systems investigated.

Acknowledgments

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References

- [1] Y. Dimitriev, St. Yordanov, L. Lakov, J. of Non-Crystall. Solids, **293-295**, 410 (2001).
- [2] Y. Dimitriev, St. Yordanov, L. Lakov, J. of Non-Crystall. Solids, **192-193**, 179 (1995).
- [3] A. Bachvarova, Y. Dimitriev, R. Iordanova, J. of Non-Crystall. Solids, **351**, 998 (2005).
- [4] A. Bachvarova, Y. Dimitriev, Y. Ivanova, R. Iordanova, J. University of Chemical Technology and Metallurgy, XXXVIII, **4**, 1271 (2003).
- [5] L. Gmelin, E. Best, I. Hinz, H. Wendt, GMELIN Se – Bd.A1 Element, 1979.
- [6] Y. Dimitriev, A. Bachvarova-Nedelcheva, R. Iordanova, Mater. Res. Bull. **43**, 1905 (2008).
- [7] G. Gospodinov, L. Sukova, K. Petrov, J. Inorg. Chem. **33**, 1975 (1988) (in Russian).
- [8] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination compounds, Wiley, New York, 1978.
- [9] C. P. Varsamis, E. I. Kamitsos, G. D. Chryssikos, Solid State Ionics **136-137** (2000) 1031-1039.
- [10] V. V. Kondrateva, Rentgenometricheskij opredelitel boratov, Leningrad, 1969 (in Russian).
- [11] R. Lucacel, I. Ardelean, Phys. Chem. Glass.: Europ. J. Glass Sci. Technol., part B **47**(4), (2006).
- [12] A. Bachvarova-Nedelcheva, R. Iordanova, Y. Dimitriev, Proc. Third Balkan Conference of Glass Science and Technology, ed. by B. Samuneva, Y. Dimitriev, S. Bachvarov, I. Gutzow, sept. 26 – 30, Varna, **I**, 2008 (in press).
- [13] A. Bachvarova-Nedelcheva, PhD Thesis, Sofia 2005.

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