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Glass formation in the systems Ag_2SeO_3–M_nO_m and $CuSeO_3$–M_nO_m ($M_nO_m = B_2O_3$, MoO_3)

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Abstract

The purpose of this study is to determine glass formation regions in the sections Ag_2SeO_3–M_nO_m and $CuSeO_3$–M_nO_m ($M_nO_m = B_2O_3$, MoO_3). It is a continuation of our previous works where binary and multi component selenite glasses with the participation of non-traditional network formers such as: MoO_3, V_2O_5, TeO_2 and Bi_2O_3 have been obtained. The existence of several structural units SeO_3, MoO_4, MoO_6, CuO_4 and BO_3, forming the amorphous network have been determined by IR spectroscopy. Conclusions about the glass-forming tendency in the Ag_2SeO_3–M_nO_m and $CuSeO_3$–M_nO_m ($M_nO_m = B_2O_3$, MoO_3) systems are drawn on the basis of their structural peculiarities.

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1. Introduction

The idea of synthesizing selenite glasses belongs to Rawson [1] and Stanworth [2] who obtained glasses in the K_2O–SeO_2 and SeO_2–TeO_2–PbO systems. The main difficulty with the preparation of this type of glass is their volatilization from selenite at the liquidus and the sublimation of SeO_2 at atmospheric pressure and temperatures above 315 °C. Besides the volatility, the other main obstacle to the practical application of these glasses is their hygroscopicity. Since 1981 the glass formation and structure of different selenite systems have been investigated in the 'Silicate Technology' Department of the University of Chemical Technology and Metallurgy of Sofia [3]. The results obtained during the last 20 years have been reviewed [4]. There are a few papers [5–13] in which the synthesis and properties of similar materials are considered. Data on new oxide complex selenites have been reported recently [14,15].

The purpose of this paper is to study the glass formation in the systems Ag_2O–SeO_2–M_nO_m and CuO–SeO_2–M_nO_m ($M_nO_m = B_2O_3$, MoO_3). The experiments were limited to the sections Ag_2SeO_3–M_nO_m and $CuSeO_3$–M_nO_m.

2. Experimental procedure

Previously synthesized selenites Ag_2SeO_3 and $CuSeO_3$ were used as starting materials in order to decrease the volatilizaton. The compounds were prepared by the classical method [16] from saturated aqueous solutions of $AgNO_3$ and $CuSO_4 \cdot 5H_2O$ with SeO_2. The products were dried and heated up to 250 °C. They were measured by X-ray diffraction, using ICDD files No. 34-0382 (Ag_2SeO_3) and No. 48-0374 ($CuSeO_3$). The batches were prepared by mixing of previously synthesized compounds ($CuSeO_3$ and Ag_2SeO_3) with MoO_3 or B_2O_3 in different ratio. All selected compositions were calculated by this manner. For example in the section $CuSeO_3$-MoO_3 the composition $70CuSeO_3 \cdot 30MoO_3$ corresponds to $35CuO \cdot 35SeO_2 \cdot 30MoO_3$ mol%; for the other section

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Ag_2SeO_3–MoO_3 the composition $30Ag_2SeO_3 \cdot 70MoO_3$ corresponds to $15Ag_2O \cdot 15SeO_2 \cdot 70MoO_3$ mol% and s.o. All compositions are shown in Figs. 3–5. The melting of the batches was performed in sealed silica glass ampoules (volume 5 cm^3), evacuated at a pressure $P = 0.1$ Pa [3,4]. They were situated in metal containers and heated in the temperature range 750–880 °C depending on the compositions. The melted samples were cooled with a rate of 100 °C/min and characterized by X-ray diffraction (TUR M65, Cu Kα radiation) and IR spectroscopy (FTIR spectrophotometer, computer controlled 'Bruker' EQUINOX 55) using the KBr pallets method in the wave number range 4000–400 cm^{-1}.

3. Results and discussion

The glasses obtained in the compositional range 30–70 mol% Ag_2SeO_3 corresponded to the section Ag_2SeO_3–MoO_3, while those of the 40–90 mol% $CuSeO_3$ range belonged to the $CuSeO_3$–MoO_3 section. Replacement of MoO_3 by B_2O_3 in the Ag_2SeO_3–MoO_3 section led to a decreasing glass formation ability and only a mixture of glass and crystalline products were obtained in the Ag_2SeO_3–B_2O_3 system. Replacement of MoO_3 by B_2O_3 in the $CuSeO_3$–MoO_3 section resulted in the appearance of crystalline products only. The initial crystal phases (Ag_2SeO_3 and $CuSeO_3$) were identified in all sections after thermal treatment. Fig. 1 shows the diffractogram of the selected compositions, which are predominantly amorphous, bearing in mind the course of the X-ray patterns. Only these kinds of samples are subjected to the IR spectral study.

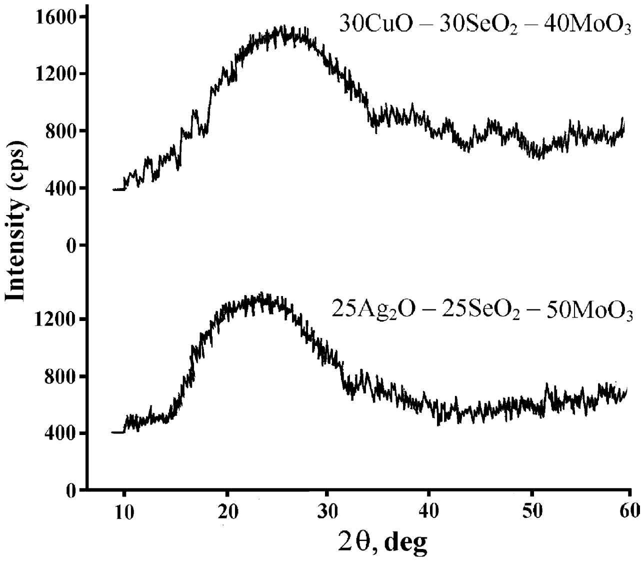

Fig. 1. X-ray diffraction of the glasses in the systems CuO–SeO_2–MoO_3 and Ag_2O–SeO_2–MoO_3.

Figs. 2–4 show the IR absorption spectra of some selected compositions. They were interpreted on the basis of structural and spectral data [17–22] on crystalline phases within the framework of the point group symmetry limitations [18]. The crystal structure of $CuSeO_3$ consists of SeO_3 pyramidal groups with an average value of the Se–O distances equal to 1.71 Å where one of them is shorter. Cu atoms are in 'square planar' oxygen environment with Cu–O < 2.10 Å [23,24]. A weak shoulder at 830 cm^{-1} (ν_1^s) (Fig. 2), and bands at 770 cm^{-1} (ν_2), 720 cm^{-1} (ν_5) and 430 cm^{-1} (δ), in the IR spectra of $CuSeO_3$ are assigned to the vibrations of SeO_3 pyramidal groups with low C_s symmetry [17,18] (Table 1). The ν_2 and ν_5 bands are a result of the splitting of ν_3^{as} (C_{3v}–C_s transition). The band at 560 cm^{-1} is assigned to the vibrations of a CuO_4 'square' with D_{4h} point symmetry [18,22].

According to the crystallographic data, Ag_2SeO_3 forms monoclinic crystals with space group $P2_1/c$. There are no significant differences in the Se–O distances within the SeO_3^{2-} ion and the average value is 1.70 Å [25].

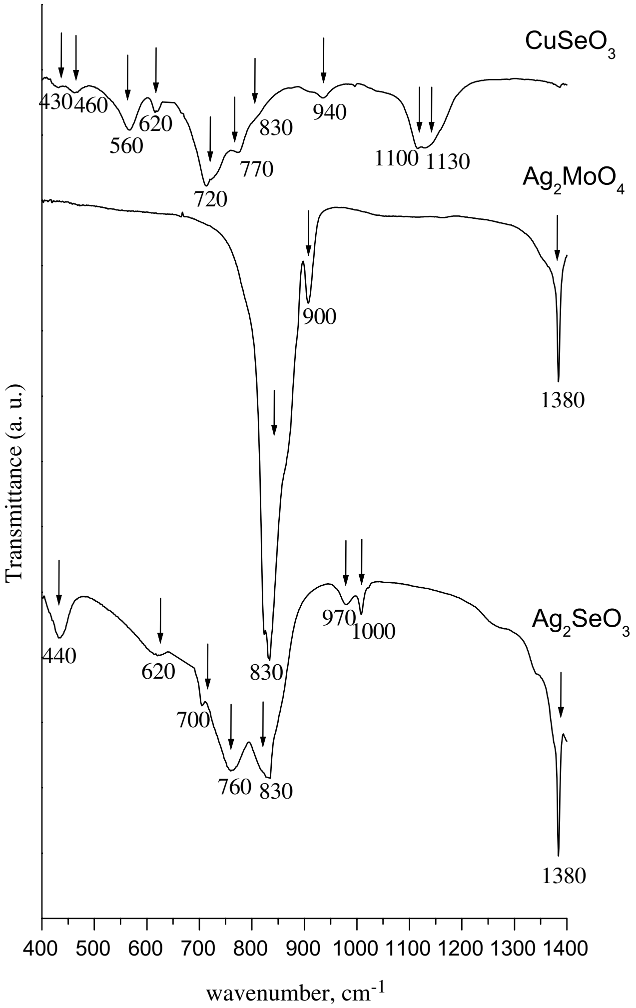

Fig. 2. IR spectra of the crystalline products.