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Vitrification ability in the system CuO-SeO_2-MoO_3

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The vitrification ability in the three component system CuO-SeO_2-MoO_3 has been studied. Stable glasses were obtained near the SeO_2 corner. The simultaneous presence of CuO and MoO_3 leads to deterioration of the glass formation, because isolated MoO_4 groups were formed. Associated SeO_3 groups were established in the compositions with a higher SeO_2 content (70 mol %). New knowledge of the design of the amorphous network with a definite degree of polymerization and an appropriate ratio of different coordination polyhedra was obtained.

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1. Introduction

Molybdate and selenite glasses are a new family of non-traditional glasses which have been interesting mainly from a scientific point of view. Some of them possess a variety of specific properties due to which they are potential candidates for technological applications as amorphous semiconductors, infrared transmission components, in non linear optical devices, sensors, reflecting windows, soluble microfertilizers, for nuclear waste storage, etc. [1-9]. The main difficulties in the preparation of molybdate glasses are connected with the high crystallization tendency of the compositions, because MoO_3 is not able to form a glass itself at a slow cooling rate. All many-component molybdate glasses are characterized by two (upper and lower) boundaries of glass formation. From a structural point of view, the first one is related to the possibility to depolimerize the sheet structure of MoO_3 containing edge shared MoO_6 octahedra. The other is determined by the compositions containing isolated MoO_4 tetrahedra. This peculiarity is important for their practical applications. For example, one of the particular difficulties with the vitrification of the waste storage is the presence of molybdenum in tetrahedral coordination against the oxygen in the compositions [9]. That is why it is interesting to control the coordination of molybdenum in the glasses. This study is a continuation of a series of investigations concerning glass formation and glass structure in binary and more complex molybdate systems [10]. The other non-traditional glass former is SeO_2, which decreases the melting temperature of the glass compostions [11].

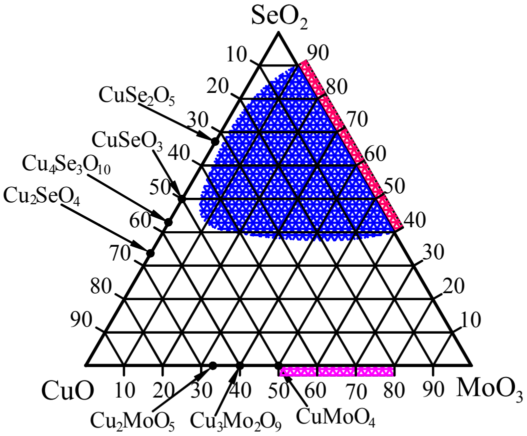

Fig. 1. Glass formation region in the system CuO-SeO_2-MoO_3.

The paper deals with the vitrification ability in the three component system MoO_3-CuO-SeO_2 and is aimed at obtaining more information about different structural units participating in the amorphous network. The three-component model system has been selected upon establishing the glass formation regions in the binary systems SeO_2-MoO_3 [12] and CuO-MoO_3 [10] as well as in the section $CuSeO_3$-MoO_3 [13] and the vitrification of some three-component compositions at a high oxygen pressure [14]. In this case by combination of the components it is possible to compare the polymerization tendencies depending on the compositions.

2. Experimental

Copper selenite ($CuSeO_3$) was used as a starting compound in order to decrease the volatilization of selenium. It was prepared by the classical method [15] from saturated aqueous solutions of $CuSO_4.5H_2O$ with SeO_2. The product was dried and heated up to 250^0C and was identified by X-ray diffraction using JCPDS files № 48-0374 ($CuSeO_3$). The other compounds were CuO (Merck) and MoO_3. Molybdenum trioxide (MoO_3) was obtained by thermal treatment of ammonium heptamolybdate tetrahydrate (Aldrich) at 550 ^{o}C for 5 h. The melting of the batches was performed in silica ampoules (volume 5 cm^3) sealed at a pressure P = 0.1 Pa. They were situated in a metal container and heated at a temperature of 750^0C. The melted samples were cooled with a rate of 100 K/s. The differential thermal analyses (DTA) and thermogravimetry (DTA-TG) were carried out on a Stanton Redcroft STA 780 apparatus with a heating rate of 10 K/s in argon flow, using Al_2O_3 as reference material. The phase transformations of the samples were verified by X-ray diffraction (Bruker D8 Advance, Cu Kα radiation) and IR spectroscopy using the KBr pellets method (Nicolet-320 - FTIR spectrometer with a resolution of $\pm 1cm^{-1}$, by collecting 64 scans in the range 1400–400 cm^{-1}).

3. Results

The glass formation region of the system is presented in fig. 1. The stable glasses were situated near the SeO_2 corner. The content of the components reached 10-20 mol% MoO_3, 10-45 mol% CuO and 45-70 mol% SeO_2. Fig. 2 shows the XRD results on some typical samples from the system. Compositions representing a mixture of glass and crystals are observed in the central part of the system, and are not included in the glass formation region.

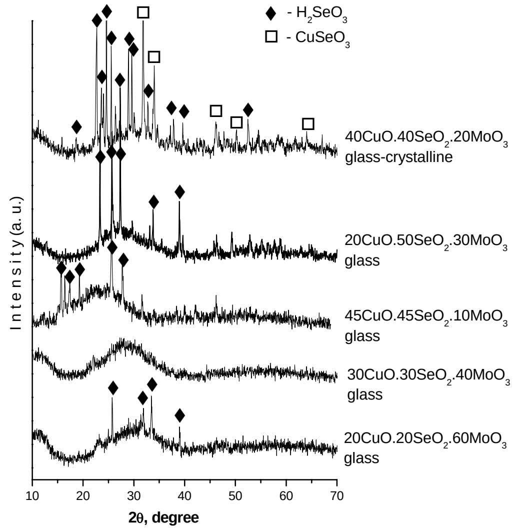

Fig. 2. XRD of the samples from the system.

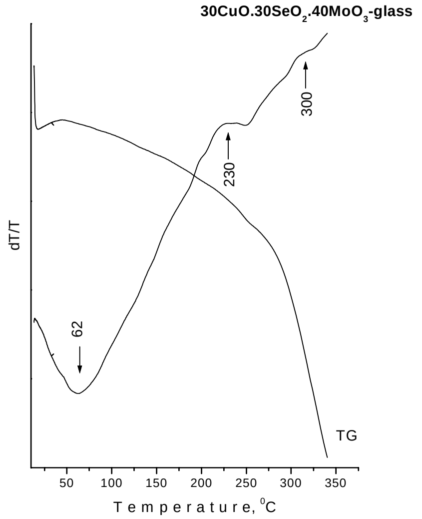

Fig. 3. DTA analysis of the glass sample $30CuO.30SeO_2.40MoO_3$.

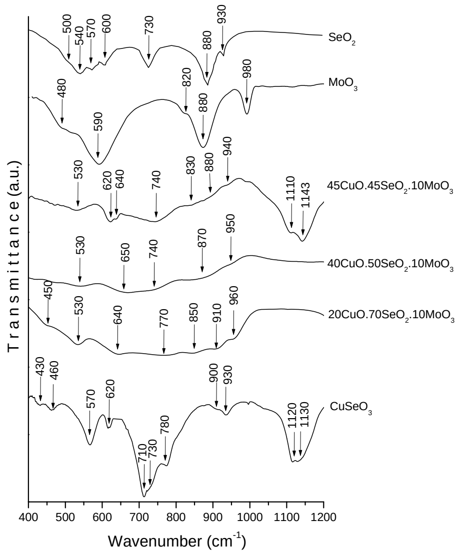

Fig. 4. IR spectra of the glasses with 10 mol % MoO_3.

The crystal phases $CuSeO_3$, MoO_3, SeO_2 or H_2SeO_3 (as a result of the hydration processes) were identified in them. DTA analysis of an amorphous sample of $30CuO.30SeO_2.40MoO_3$ showed it to be thermally stable up to 200^0C (Fig. 3). The crystallization started at 230^0C, and was accompanied by fast mass loss. The infrared spectra of the samples situated in different sections of the system are presented in figs. 4, 5 and 6. The spectra of all glass samples are not well resolved and have a broad absorption region at about 900-600 cm^{-1}. The compositions containing 10 mol % MoO_3 showed a broad absorption plateau situated near 740 cm^{-1} (Fig. 4). With increasing SeO_2 content (from 45 to 70 mol %), the bands at 740 cm^{-1} and a shoulder at 870 cm^{-1} were shifted to 770 and 910 cm^{-1}, respectively. The band at 640 cm^{-1} did not change with varying composition. The absorption band at 620 cm^{-1} along with those at 1140 and 1110 cm^{-1} appeared in the composition containing 45 mol % SeO_2 (Fig. 4). The band at 530 cm^{-1} did not change its position with varying composition either. The IR spectra of the compositions containing 20 mol % MoO_3 showed no essential change (fig. 5) and are not well resolved either, while those with a higher MoO_3 content (40 and 70 mol %) demonstrated a different behavior (fig. 6). The band at about 850 cm^{-1} (fig. 5) was shifted to 870 cm^{-1} (fig. 6) and its intensity decreased. The composition with 70 mol % MoO_3 (fig. 6), being out of the glass formation region, was characterized by two strong bands at 870, 580 cm^{-1} and a small band at 980 cm^{-1}.

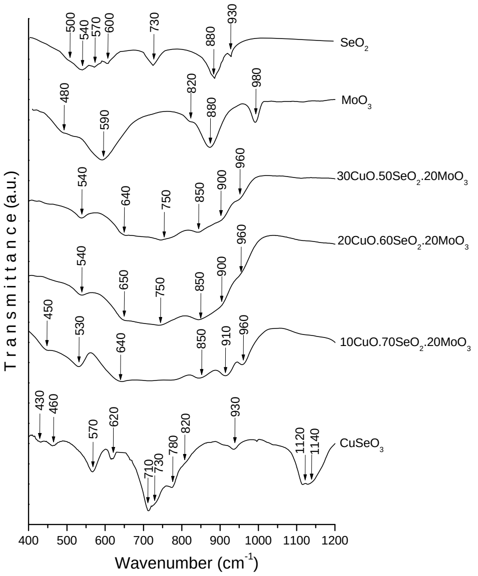

Fig. 5. IR spectra of the glasses with 20 mol % MoO_3.

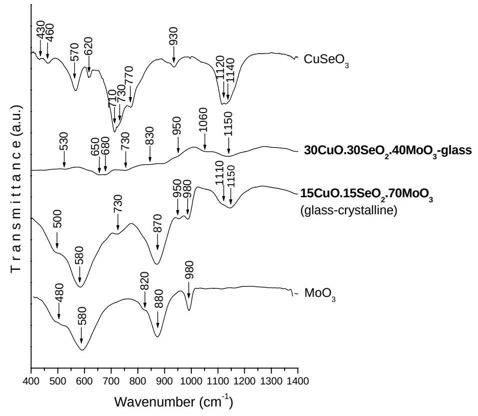

Fig. 6. IR spectra of the compositions with higher MoO_3 content.

4. Discussion

The results obtained about the vitrification tendency in the system investigated are in good agreement with our previous studies [13,14]. The differences are due to the different cooling rates. The cooling rate which was used in the present study, did not allow obtaining glasses near the CuO-MoO_3 site because, as was mentioned in [10], the binary compositions can be vitrificated of a high cooling rate. The IR spectra obtained give some preliminary information about the network formation. Their interpretation is based on spectral data from the literature concerning selenite glasses [11] as well as on spectral data concerning crystalline phases [10, 12, 13, 16 and 17]. The hydration processes (bands at 1140, 1120 and 620 cm^{-1}) and the overlapping of the bands, which is connected with the vibration of different building units are additional difficulties associated with the interpretation. These facts in combination with the not well resolved bands in IR spectra of the glasses prevent their more precise interpretation.

The absorption area at about 770-740 cm^{-1} is due to the vibration of various units such as Se-O-Se units and isolated SeO_3 groups (ν^{as}). The indication of the polymerization of SeO_3 units is the shoulder near 900 cm^{-1}, related with the vibration of isolated Se=O bonds, which are not present in isolated SeO_3 pyramids. There are no absorption bands in the range between 800-600 cm^{-1} in the spectrum of pure MoO_3. The MoO_6 units do not vibrate in this region. In the spectrum of a partially crystallized sample (containing 70 mol % MoO_3, fig. 6), the band at 980 cm^{-1} can be attributed to the vibration of a Mo=O bond in edge shared MoO_6 octahedra. The band at 870 cm^{-1} is due to the vibration of Mo-O-Mo bonds. The other band at 580 cm^{-1} is related to the vibration of Mo_2O_2 bridge. The bands at 980 and 880 cm^{-1}, which are characteristic of pure MoO_3 are absent in the spectra of the glasses with lower MoO_3 content. Instead of that a band about 850 cm^{-1} remained and it can be assigned to the vibration of MoO_4 groups.

The bands in the range 570-450 cm^{-1} in the spectra of all samples may be assigned to the vibration of CuO_n polyhedra. It is well known that the band at 560 cm^{-1} is assigned to the vibrations of a CuO_4 "square" with D_{4h} point symmetry [18, 19]. In this case another band centered at 530 cm^{-1} appeared and it is absent in the spectra of $CuSeO_3$ and MoO_3. That is why its interpretation is unclear. The band at 640 cm^{-1} is probably produced by vibrations of linear Cu^+O_2 groups [10]. Hence, during the glass formation, $Cu^{2+} \rightarrow Cu^+$ partial reduction takes place. Despite the CuO_n polyhedra formation they did not form strong bridging bond with other polyhedra. Obviously, from analysis of the IR spectra it can be concluded that CuO as a modifier stimulates the formation of more flexible isolated SeO_3 and MoO_4 units. This process prevents MoO_3 being a network former.

5. Conclusions

The present investigations indicate that stable glasses are obtained near the SeO_2 corner. The simultaneous presence of CuO and MoO_3 leads to deterioration of the glass formation, because isolated MoO_4 groups are formed. With the SeO_2 content increase, polymerization of SeO_3 units is established (band near 900 cm^{-1}). The results obtained contribute to design new glasses, where the appropriate ratio of different structural polyhedra in the amorphous network is very important.

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