Glass formation in the system MoO_3-TiO_2-Bi_2O_3

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Melt quenching technique was applied to study the glass formation in the MoO_3-TiO_2-Bi_2O_3 system. A narrow glass formation area was situated around the MoO_3 corner. The thermal stability of the glasses was determined by DTA, the glass transition temperature (T_g) was about 350 ºC and the crystallization peak temperature (T_k) is about 400 ºC. By IR spectroscopy was shown that the main structural units in the glass network were MoO_6 and MoO_4 polyhedra.

1. Introduction

Molybdate glasses are one of the so called non-traditional glasses. The Molybdenum oxide (MoO_3) is well-known as a conditional network former but it is not able to form a glass itself at slow cooling rates. The main problems of the preparation of molybdate glasses without participation of classical network formers are connected with the high crystallization tendency of the components. By introducing other glass network formers, more complicated molybdate glasses have been obtained. The results concerning structure of non-traditional molybdate glasses have been recently summarized [1]. This study is a continuation of a series of investigations about glass formation and glass structure in binary and ternary systems, containing MoO_3 and Bi_2O_3 [2]. The selected components of the system investigated, are three non traditional network formers. Every one of them determines independently a separate family of amorphous materials. From a fundamental point of view their competitive action on the network formation is useful to be verified. This is very important for the prediction and design of new technological materials. The glasses containing both MoO_3 and Bi_2O_3 oxides are of great interest because of the simultaneous presence of two non-traditional network formers. The glass formation region in the binary system MoO_3-Bi_2O_3 is situated mainly around MoO_3 [3-5]. That is why it can be concluded that MoO_3 is a stronger network former than is Bi_2O_3 oxide. On the other hand, TiO_2 is also an interesting non-traditional network former. Binary glasses containing up to 30-50 wt % TiO_2, in the system Bi_2O_3-TiO_2 were obtained [6, 7]. Glasses from the Bi_2O_3-TiO_2-B_2O_3 system were prepared and crystallized recently in order to obtain a $Bi_4Ti_3O_{12}$ crystal phase. This phase is a well-known ferroelectric material and it is anticipated to be an excellent candidate for the next generation of ferroelectric random-access memories [8, 9]. In order to study the glass formation ability, Ruessel et al. investigated more complex compositions with the participation of Nb_2O_5, SiO_2, Bi_2O_3, and TiO_2 [10, 11].

Recently, the ternary system MoO_3-TiO_2-Bi_2O_3 was intensively studied by our team [12, 13]. During the experiments on the phase formation in the section $Bi_4Ti_3O_{12}$-Bi_2MoO_6 it was established that both $Bi_4Ti_3O_{12}$ and Bi_2MoO_6 phases were separated but the glasses were not obtained. Among the various molybdate compositions Bi_2MoO_6 and $Bi_2Mo_2O_9$ have been found to be catalytically active phases [14]. Having all this in mind, it can be concluded that from a fundamental point of view it is interesting to clarify the glass formation tendency in the system MoO_3-TiO_2-Bi_2O_3 taking into account all data obtained on the binary systems. The problem of the role of network former is still disputable. That is why the system MoO_3-TiO_2-Bi_2O_3 is suitable to elucidate the connection between the glass formation ability and the possibility to form different topological networks.

The purpose of this study is to determine the glass formation range in the MoO_3-TiO_2-Bi_2O_3 system, to define the main building units and their role in the formation of a glass network.

2. Experimental

All batches were prepared using reagent grade oxides MoO_3 (Merck, p.a.), Bi_2O_3 (Merck, p.a.) and TiO_2 (Merck, p.a.) as starting materials. The homogenized batches (10 g) were melted for 15 min in air at low temperature (near 800^oC) in alumina crucibles. In order to get amorphous samples, two methods for cooling of the melts were applied: fast quenching using roller-technique (10^4-10^5K/s). By visual and optical observations it was assumed that those compositions in which vitreous pieces were prevalent (above 70-80 mol %) were in the glass formation area. The phase transformations have been identified by X-ray diffraction (Philips APT 15 diffractometer, Cu Kα radiation) at room temperatures. The differential thermal analysis and thermogravimetry (DTA-TG) were carried out on a Stanton Redcroft STA 780 apparatus with a heating rate of 10°/min in a stream of air flow and Al_2O_3

as a reference material. IR spectroscopy was performed by a Nicolet-320-FTIR spectrometer with a resolution of $\pm 1\,\text{cm}^{-1}$, by collecting 64 scans in the range 1400–400 cm⁻¹.

3. Results

The location of the glass formation region in the system investigated is shown in Fig. 1. The three component glasses were obtained near the MoO₃ corner

(Fig. 1). We confirmed the glass formation range in the binary Bi₂O₃-MoO₃ system which is situated between 95 and 65 mol % MoO₃ [1, 15]. In the TiO₂-MoO₃ system in the narrow concentrate region glasses near 90 mol % MoO₃ were obtained (Fig. 3). Near the binary system Bi₂O₃-TiO₂ three component glasses were not obtained. Compositions containing below 5 mol % MoO₃ were vitrified, only. The crystalline phases Bi₄Ti₃O₁₂, Bi₂Mo₂O₉ and Bi₂MoO₆ were separated in a wide concentration region. Typical X-ray diffraction patterns of the three component amorphous samples are presented in Fig. 2.
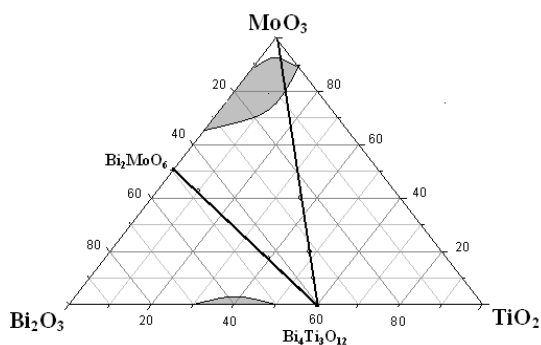
by a high crystallization ability and the crystallization (T_k) starts near 370-410 °C (Fig. 3). The melting temperatures of the crystalline samples are in the range 640-670°C. The registered two endothermic effects on the DTA curves could be related to the solidus and liquidus temperatures of the corresponding compositions. A well-defined endothermic effect at 640 °C could be related to the eutectic temperature.

The assignments of the IR spectra (Fig. 4) were made on the basis of our previous study [1]. In the IR spectra of the obtained glasses, intensive absorption in the range 870-550 cm⁻¹ was observed (Fig. 5). The strong band at 870 cm⁻¹ is dominant in the compositions with a high MoO₃ content (85 mol % MoO₃). In the composition with a lower MoO₃ content (65 mol %) the intensity of bands at 770 and 830 cm⁻¹ increased and a shoulder at 930-920 cm⁻¹ was observed. Band at 570 cm⁻¹ is present in all compositions.

Fig. 3. DTA curves of the glasses in the MoO₃-Bi₂O₃-TiO₂.

Fig. 1. Glass formation region in the system MoO₃-Bi₂O₃-TiO₂.
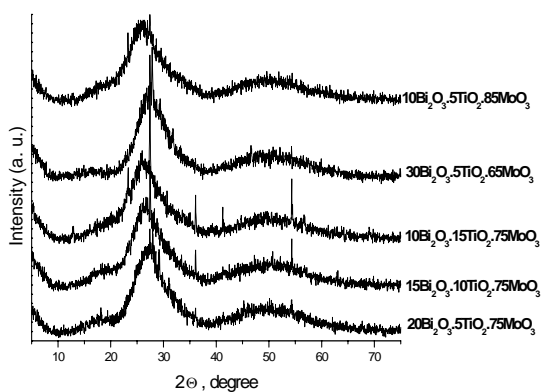
Fig. 2. XRD patterns of amorphous samples from the system MoO₃-Bi₂O₃-TiO₂.

DTA curves of selected glasses are presented in Figure 3. The glass transition temperature (T_g) for most of the glasses is at about 350°C. The glasses are characterized

Fig. 4. IR spectra of molybdate glasses with high MoO₃ content.

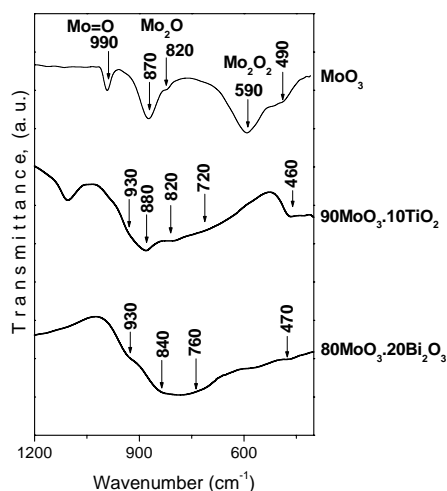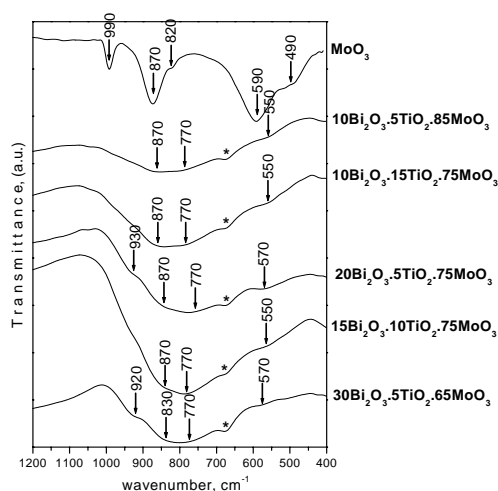*Fig. 5. IR spectra of glasses in the system MoO_3-Bi_2O_3-TiO_2. * denotes CO_2 absorption.*

4. Discussion

The obtained glass formation region and the existence of partially amorphous samples outside the glass formation region, raise some basic questions concerning the glass formation in non-traditional molybdate glasses:

1. How to explain the existence of upper and lower glass formation boundaries in systems with the participation of Bi_2O_3, TiO_2 and MoO_3?

2. Is it possible to apply the main hypothesis for the network formation in oxide systems to the glasses containing Bi_2O_3, TiO_2 and MoO_3?

There are several structural models, which we consider as a cornerstone in elucidating the tendency of the glass formation in oxide systems [1]. The most popular are only a few hypotheses: the Zahariazen's classical model for the "random network", Porai-Koshitz's model for the microheterogeneous structure, Polak and Bernal's model for the close packing. Some other hypotheses were developed more recently: Greaves [16, 17], Gaskell [18, 19], Gupta and Cooper [20-23]. The above structural models for the glass forming ability are based on one or another important parameter essential for the creation of an amorphous network. Actually they were developed taking into account some specific materials only. Despite their significance they are not in a position to solve all problems concerning different type of glasses. That is why we accept them as useful orientate rules for discussion. In this paper our discussion will be limited using mainly the classical model of "random network" of Zahariasen and its extension as a "topologically disordered network" (TD) developed latter by Cooper & Gupta.

The main points that follow the above hypothesis are: **(a)** which are the structural units building the amorphous network (short range order) and do they change with the compositions in a given system; **(b)** what is the connectivity between the polyhedra corner, edge or face

sharing (middle range order)? The obtained IR data on the vibration of the main polyhedra in the amorphous network and the literature data on the crystal structure of the compounds as well, are a good base for the suggestion of structural models. It is well known that pure orthorhombic MoO_3 is impossible to be vitrified but the addition of a second component stabilizes glass formation.

In our previous papers [1] it was established that more stable glasses were obtained when amorphous network was built up by corner shared octahedral units irrespective that it is not satisfied one of the Zachariazen's criteria. The important role of bridging bonds in the generation of amorphous network was confirmed. A typical example of corner shared octahedra is the network of molybdate glasses with highest MoO_3 content (80-90 mol %) (Fig. 4). The characteristic band in the IR spectra of these glasses is at 880 cm^{-1} (νMo-O-Mo) and the band at 590 cm^{-1} corresponding to the vibration of edge-shared octahedra absent [1]. The presence of TiO_2 in the three component glasses under investigation preserves the MoO_6 octahedra (strong band at 870 cm^{-1}), (Figs. 5, 6). This explains the existence of the upper boundary of glass composition. But it is not sufficient for stabilization of the amorphous network and extending the glass formation boundary. That is why the nature of the second component is important for the processes of structural transformations. Bi_2O_3 is one of the components that stimulate the $MoO_6 \rightarrow MoO_4$ transition. The characteristic bands of MoO_4 groups are at 840 and 760 cm^{-1} and shoulder at 930 cm^{-1} (Fig. 4). In the spectra of glasses under investigation the increasing of the band intensity at 770 cm^{-1} instead of 870 cm^{-1} along with the appearance of band at 830 cm^{-1} and a shoulder at 930 – 920 cm^{-1} indicate formation of MoO_4 with lower symmetry (Fig. 5). The creations of Mo–O–Bi mixed bonds, which are not typical bridging, ones do not deteriorate the glass formation in a limited concentration range. The increase of the number of Mo–O–Me mixed bonds leads to an increase in the number of small mobile units in the melt (isolated MoO_4 tetrahedra). The accumulation of a critical number of MoO_4 tetrahedra makes the stability of amorphous network questionable. This defines the lower glass formation boundary. The weak bands at about 570-550 cm^{-1} are ascribed to the stretching vibrations of Bi-O$^-$ (of non-bridging oxygen) in BiO_6 pyramidal units [24-26].
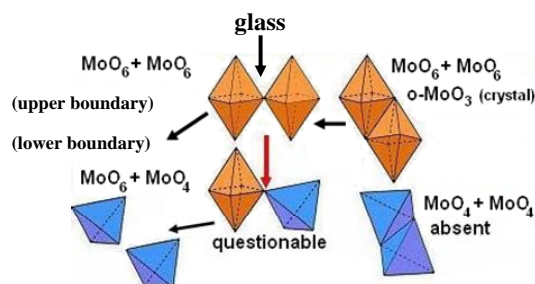

Fig. 6. Formation of the amorphous network, different ways for connection of tetrahedra and octahedra based on the IR spectra.

The above hypothesis on the transformations of different types of MoO_n polyhedra is presented in Fig. 6.

5. Conclusions

Molybdate glasses with the participation of Bi_2O_3 and TiO_2 were obtained. Molybdenum trioxide (MoO_3) is the main network former. The glass network of the three component glasses is built up by MoO_4 and MoO_6 units. The increase in Bi_2O_3 content leads to $MoO_6 \rightarrow MoO_4$ transformations. The obtained molybdate glass structure is incompatible with the bismuth-titanate one because there is no connection between the obtained glass formation regions.

Acknowledgments

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