JOURNAL OF MATERIALS SCIENCE **39** (2004) 5591–5593 LETTERS

Glass formation in the MoO_3–Bi_2O_3–PbO system

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This study is a continuation of a series of investigations concerning glass formation and glass structure in binary and ternary systems, containing MoO_3 and Bi_2O_3 [1–3]. It is aimed at determining the glass formation range in the MoO_3–Bi_2O_3–PbO system and obtaining new amorphous materials. It is known that similar and more complex compositions containing the above oxides are promising candidates for a variety of technological applications such as amorphous semiconductors, waste storage, and infrared transmission components [4–7]. On the other hand, it is important to verify the relation between glass formation ability and glass structure. This is very important for the prediction and design of new technological materials. In this connection, attempts will be made to establish the major building units and their role in the formation of a glass network using infrared spectroscopy (IR).

The homogenized batches prepared from reagent grade MoO_3, Bi_2O_3, and Pb_3O_4 were melted for 10 min in alumina crucibles under air at 900–1200 °C, depending on the melting temperatures of the compositions. Due to a pronounced crystallization tendency of the melts, glass formation was achieved at high cooling rates (10^4–10^5 K/s) using a roller-quenching technique. Fragmented 1–3 mm flat pieces, about 50–100 μm thick, were obtained. Compositions in which the vitreous pieces were prevalent (above 70%) were assumed to determine the glass formation range. The amorphous state of the samples was established by X-ray phase analysis (Philips APT-15 diffractometer, Cu K_α radiation). The glasses were investigated by infrared spectroscopy (Nicolet-320 FTIR spectrometer) using the KBr pellet technique.

The vitreous range established in the ternary MoO_3–Bi_2O_3–PbO system is presented in Fig. 1 where the published data on the binary systems MoO_3–Bi_2O_3 and PbO–Bi_2O_3 are also given [1, 8]. MoO_3–PbO compositions do not form glasses under the experimental conditions. The glasses are situated in a limited concentration range close to the MoO_3–Bi_2O_3 side up to 20 mol% PbO. In this part of the system fall the low melting eutectics E_1 and E_2 of the equilibrium phase diagram [9]. This result is in agreement with a general principle of the production of glasses in a more complex system. Glasses are also obtained in the vicinity of the Bi_2O_3–PbO side, but the introduction of small amounts of MoO_3 (above 5%) drastically deteriorates the glass formation ability. A typical X-ray diffraction pattern of the amorphous sample is shown in Fig. 2a. Besides the fast quenching of melts with compositions $50MoO_3 30Bi_2O_3 20PbO$ and $10MoO_3 20Bi_2O_3 70PbO$ (near the boundary of glass formation), the crystal phases $PbMoO_4$ (JCPDS 08-0475), Bi_2MoO_6 (JCPDS 33-0208), and δBi_2O_3 (JCPDS 16-0654) have been detected (Fig. 2b and c). This result is in agreement with the equilibrium phase diagram [9] as the compositions are in the fields of the primary crystallization of the above compounds.

The IR spectra of the selected key glasses are presented in Fig. 3. The assignment of the infrared bands in the glass spectra is made in the framework of the local point symmetry approach [10, 11]. The obtained spectral data are compared with those of the respective crystalline phases and with data of their crystal structure: MoO_3 [12, 13], PbO [14], Bi_2O_3 [15, 16], $PbMoO_4$ [17, 18], and $Bi_2(MoO_3)_4$, $Bi_2Mo_2O_9$, Bi_2MoO_6 [19–23]. The previous spectral results of the molybdate glasses have also been taken into account [1, 2]. On this basis, the shoulder at 940 cm^{-1} in the spectrum of a glass with 80 mol% MoO_3 (Fig. 3) and the band at 850 cm^{-1} can be attributed to the stretching vibrations of the partially isolated Mo—O bond and of the Mo—O—Mo bridge bonds, respectively, in distorted MoO_6 polyhedra [1, 2, 13]. The displacement of these bands to lower frequencies (920 cm^{-1} and 830 cm^{-1}, respectively) in the glass compositions with 70 mol% MoO_3 is an indication that the Mo—O bonds in the MoO_6 units become longer. More over, the appearance of the band at 780 cm^{-1} in the spectra of the same samples evidences that a part of the MoO_6 polyhedra is transformed into MoO_4 tetrahedra. This band can be attributed to triply degenerated ν_3 vibrations of MoO_4 groups in accordance with the infrared data on the crystalline sheelite-like structures. A typical example is the vibration of the symmetrical MoO_4 tetrahedron in $PbMoO_4$ (ν_3 786 cm^{-1}) [18]. Further formation of a broad absorption band centered at 800 cm^{-1} in the spectrum of the $60MoO_3 30Bi_2O_3 10PbO$ glass can be

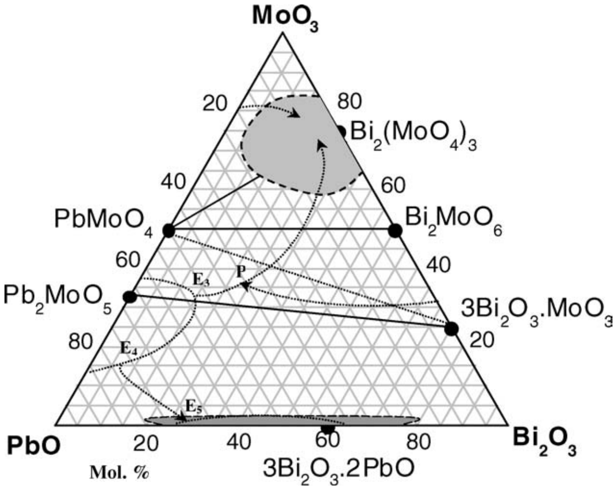

Figure 1 The glass formation ranges (the darker) in the MoO_3–Bi_2O_3–PbO system are indicated by dashed lines. The fields of primary crystallization of the equilibrium phase diagram according to Belyaev and Smolyaninov [9] are given by dotted lines.

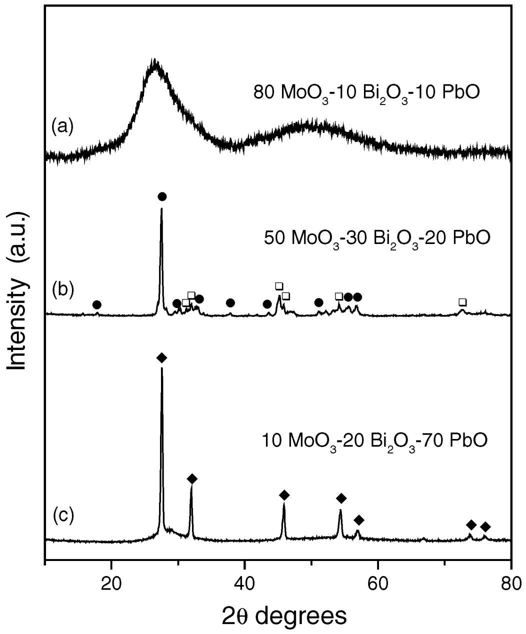

Figure 2 XRD patterns of selected compositions in the MoO_3–Bi_2O_3–PbO system obtained by fast quenching: (a) typical glass (b) and (c) crystallized specimens: (●) $PbMoO_4$; (□) Bi_2MoO_6; (◆) δBi_2O_3.

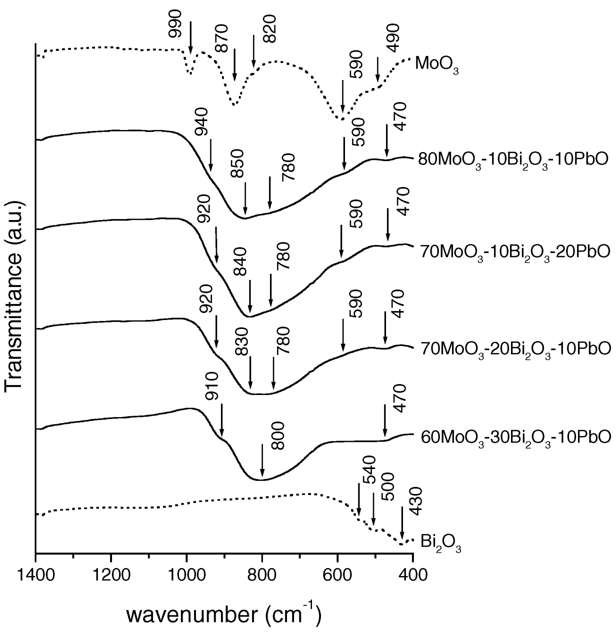

Figure 3 IR spectra of MoO_3–Bi_2O_3–PbO glasses.

considered as a superposition of several low-resolved bands due to elimination of the ν_3 vibrations degeneracy of low-symmetry MoO_4 units. The shoulder at 910 cm^{-1} is attributed to the ν_1 vibrations of the same groups [1, 2, 10, 24]. A similar interpretation of the spectra of the crystalline $Bi_2(MoO_3)_4$, $Bi_2Mo_2O_9$, and Bi_2MoO_6 compounds was made in [1, 23]. The band at 470 cm^{-1} can be assigned mainly to the stretching vibrations of highly distorted BiO_6 polyhedra, as was established for other bismuthate glasses [1, 2, 25–27]. The vibration frequencies of the PbO_n polyhedra in the investigated spectral range could not be detected because it is well known that in the PbO crystal they are located below 400 cm^{-1} [14].

The analysis of the IR spectra shows that in the glass compositions rich in MoO_3 the main structural units of the amorphous network are MoO_6 groups connected by Mo—O—Mo bonds. The introduction of small amounts of Bi_2O_3 and PbO causes a $MoO_6 \rightarrow MoO_4$ transformation. It can be assumed that in the amorphous network of the boundary compositions containing Me_nO_m, (Me = Bi, Pb) above 30 mol%, the content of Mo—O—Mo bridging bonds drastically decreases which is evidenced by the absence of strong bands at 870–830 cm^{-1}. These bonds will be replaced by Mo—$_{short}$O$_{long}$—Bi(Pb) linkages, and the MoO_4 units will be surrounded by another type of MeO_n complexes. We consider these tetrahedra as isolated ones. On the other hand, in these compositions probably mutual linkage of BiO_6 and PbO_n complexes with common edges, similarly to the crystal structure of $PbMoO_4$ and Bi_2MoO_6 phases, will take place [17, 19, 20]. This manner of connecting the polyhedra and depolymerization of the molybdate network are the reasons that a large part of the compositions does not vitrify even at a high cooling rate.

It is proved that (i) the glass formation region is associated with the compositions rich in MoO_3, and this oxide is determined as network former; (ii) Bi_2O_3 and PbO behave as modifiers in this system; (iii) the main structural units forming the glass network are MoO_6, MoO_4, and BiO_6 varying in ratio with the composition; (iv) the formation of isolated MoO_4 groups together with the edges shared of the other polyhedra (BiO_6 and PbO_n) deteriorates the glass formation ability.

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Received 17 September 2003
and accepted 29 March 2004