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SIZE DEPENDENT EFFECTS

Optical properties and crystallization of glasses in the system Bi_2O_3–MoO_3–B_2O_3

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Abstract The purpose of this work is to study the optical properties and crystallization of glasses in the ternary system Bi_2O_3–MoO_3–B_2O_3. In order to verify the obtaining of bismuth borate crystal phases several glass compositions have been selected for crystallization. The obtained samples were characterized by X-ray diffraction, scanning electron microscopy and UV–Vis spectroscopy. The UV–Vis spectroscopy showed that the obtained glasses are transparent in the visible region. The values of optical band gap (E_{opt}) and changes in cut-off (λ_c) depending on composition are reported. It was established that the increase in the MoO_3 content led to decreasing the transmittance of the glasses. Moreover, the absorption edge shifts towards longer wavelength.

Introduction

From a structural point of view, it is a challenge to study the glass formation in systems containing a typical glass former (B_2O_3) and conditional network formers (Bi_2O_3, MoO_3, V_2O_5, WO_3, etc.), because they are characterized by different local structure and different connectivity between the polyhedra in the amorphous structure. However, the structural role played by Bi_2O_3 in glasses is complicated and poorly understood. This is because the bismuthate polyhedra are highly distorted due to the presence of lone pair electrons. The interest in heavy metal oxide (HMO) glasses is due to their long infrared cut-off and optical nonlinearity [1, 2]. Egorysheva et al. [3] have mentioned that the correlation between significant structural distortion, the existence of the lone-electron pair of the bismuth ion, and the high nonlinear optical properties shows the direction of the search for new nonlinear optical materials. From this point of view the investigations on multicomponent bismuth-borate compositions are very interesting. Despite the fact that Bi_2O_3 is not a classical glass former, due to high polarizablity and small field strength of Bi^{3+} ions, in the presence of conventional glass formers (such as B_2O_3, SiO_2, etc.) it may build a glass network of BiO_n ($n = 3, 6$) pyramids.

From a practical point of view, the bismuth-borate glasses and glass–ceramics have been widely studied over the years due to their high potential for use in applications such as nonlinear optical devices, laser hosts, tunable waveguides, tunable fiber gratings, etc [4, 5]. It is known that the bismuth oxide glasses usually suffer problems of coloration and crystallization [6], which limits to a great extent the application of bismuth oxide glasses for optical purposes. It was established that oxidizing ions can prevent the process of darkening [6]. Recently, the influence of the third component on the structural transformations in bismuth-borate glasses has been discussed in a few papers [7–12]. Studies on rare earth ions-doped bismuth borate glasses shown that the substitution of rare earth ions by Bi^{3+} ones produce (i) a stabilization of the glass structure and (ii) excellent nonlinear optical properties to the host material [9]. On the other hand this led to increasing the melting temperature of compositions containing above 30 mol% rare earth oxides. But in our previous studies, we

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found that MoO_3 could be a suitable component to improve the melting conditions and modifying the properties of such type of glasses. However, it was established that MoO_3 increases immiscibility tendency in the systems investigated [13, 14] and that is why its content has to be carefully controlled [15].

This article is a continuation of our previous investigations where the location of glass formation region was determined and the structure of the obtained glasses in Bi_2O_3–MoO_3–B_2O_3 system was discussed as well [15]. The aim of this work is to check the optical properties of the as obtained glasses and glass-crystalline materials.

Experimental

All compositions (10 g) were prepared using reagent grade oxides MoO_3 (Merck, p.a.), Bi_2O_3 (Merck, p.a.) and H_3BO_3 (Reachim, chem. pure) as starting materials. The homogenized batches were melted for 15 min in air atmosphere in alumina crucibles. The melting temperature was limited to 1,000 °C in order to decrease the volatility and reduction of the components. The glasses were obtained by press quenching between two copper plates (cooling rate $\sim 10^2$ K/s). The quenched glasses were additionally heat-treated at 450–530 °C for different exposure times (2–9 h). The optical transmission spectra of the unpolished glass and glass-crystalline samples *with the same thickness* were recorded at room temperature using UV–Vis spectrophotometer (Evolution 300) in the wavelength range 400–1000 nm. The uncertainty in the observed wavelength is about ±1 nm. In order to study the crystallization tendency, several glass compositions, situated in different part of the glass formation region were selected: $30Bi_2O_3 \cdot 40MoO_3 \cdot 30B_2O_3$ (**A**), $30Bi_2O_3 \cdot 10MoO_3 \cdot 60B_2O_3$ (**B**), $50Bi_2O_3 \cdot 10MoO_3 \cdot 40B_2O_3$ (**C**), $60Bi_2O_3 \cdot 5MoO_3 \cdot 35B_2O_3$ (**D**), $63Bi_2O_3 \cdot 2MoO_3 \cdot 35B_2O_3$ (**E**), and $50Bi_2O_3 \cdot 50B_2O_3$ (**F**). The structural and phase transformations of the samples were verified by X-ray diffraction (Bruker D8 Advance diffractometer, Cu Kα radiation). The microstructure and the size of the crystals were determined by Scanning Electron Microscopy (SEM 525M). Microprobe analysis (analyze EDAX 9900) were performed on polish samples.

Results and discussion

The location of the investigated glass compositions is illustrated in Fig. 1. The color of glasses changes slightly from light yellow to dark yellow with increasing Bi_2O_3 concentration. Recently, several papers concerning the darkening process of bismuth oxide-containing glasses during the melting were published [6, 16, 17]. It was established that the darkening effect takes place not only by increasing the Bi_2O_3 concentration but also by raising the melting temperature, independently of the material of the employed crucible [16]. According to Sanz et al. [16], the increase of the melting temperature induces a change in the glass color due to the segregation of nanoparticles of elementary bismuth (Bi^0) produced by thermoreduction of the Bi_2O_3. Probably this is one of the reasons for coloration of the obtained by us glasses. The problem is more complicate because of the presence of transition molybdenum ions which could participate in different degree of oxidation without visible absorption effects [18]. By the way, Simon et al. [19] using EPR analysis proved the existence of Mo^{5+} ions in the B_2O_3–Na_2O–MoO_3 vitreous system. Nowadays, Rada et al. [20] suggested reduction of a part of molybdenum ions from the Mo^{6+} to Mo^{5+} and Mo^{4+} to Mo^{3+} states in the system MoO_3–Bi_2O_3–PbO. More experiments are needed in order to elucidate this interesting task in our glasses.

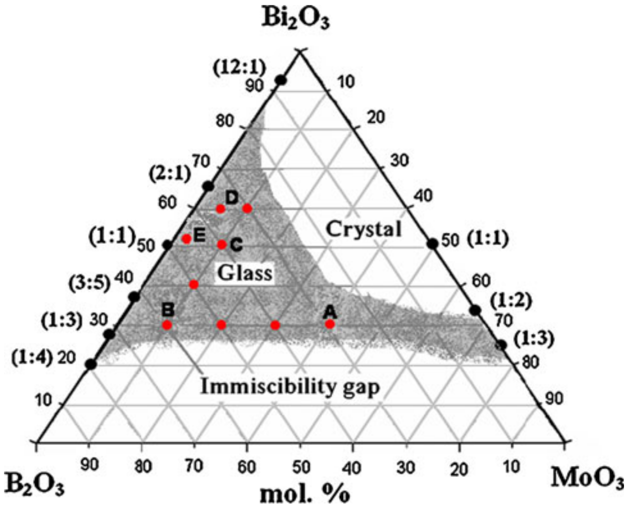

Fig. 1 Glass formation region in the system Bi_2O_3–MoO_3–B_2O_3 according to Iordanova et al. [14]. Location of the investigated glass compositions: $30Bi_2O_3 \cdot 40MoO_3 \cdot 30B_2O_3$ (**A**); $30Bi_2O_3 \cdot 10MoO_3 \cdot 60B_2O_3$ (**B**); $50Bi_2O_3 \cdot 10MoO_3 \cdot 40B_2O_3$ (**C**); $60Bi_2O_3 \cdot 5MoO_3 \cdot 35B_2O_3$ (**D**) and $49Bi_2O_3 \cdot 2MoO_3 \cdot 49B_2O_3$ (**E**)

Optical transmittance spectra in the range 400–1000 nm of the representative glass compositions depend mainly on the MoO_3 and Bi_2O_3 content (Fig. 2). The Bi_2O_3 favors the transmittance in the visible region of the spectra above 700 nm. This result is in good agreement with the fact that bismuthate glasses possess highest transmittance in the NIR region of the spectra [21]. In compositions containing high B_2O_3 content as it can be seen the transmittance shifts toward the UV region in the spectra. The cut-off (λ_c) depends on the glass compositions and shifts towards higher wavelength as the content of MoO_3 and Bi_2O_3 increases. The replacement of B_2O_3 by MoO_3 at constant

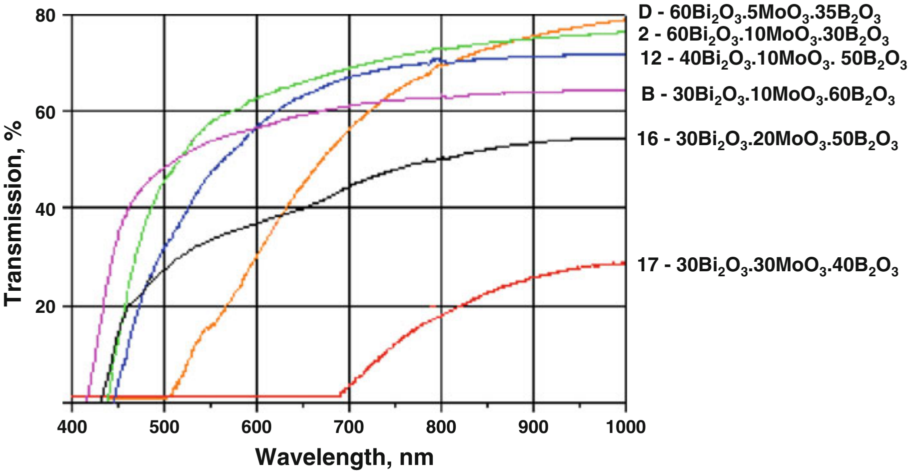

Fig. 2 UV–VIS spectral transmission of selected glasses in the system Bi_2O_3–MoO_3–B_2O_3

Bi_2O_3 content shifts cut-off more drastically (680 nm) than Bi_2O_3 (500 nm). The absorption spectra in the visible range were used for calculations of the optical band gap value (E_{opt}) which are in the range 2.5–2.9 eV (Fig. 3). It is seen that with the increase in the Bi_2O_3 content at constant MoO_3, E_{opt} slightly decreases. Our results were compatible to these obtained by Watanabe et al. [22] for the binary bismuth-borate glasses and Gao et al. [12] for the system Bi_2O_3–B_2O_3–SiO_2. The optical band gap value for sample containing 5 mol% MoO_3 is 2.97 eV close to that of the binary composition ($60Bi_2O_3·40B_2O_3$)—2.92 eV [22]. The addition of 10 mol% MoO_3 leads to decrease in the optical band gap value to 2.65 eV, which is similar to the results obtained by Gao et al. [12], where glass with 10 mol% SiO_2 has E_{opt} of 2.6 eV. Recently it was found that bismuth-borate glasses containing 10 mol% ZnO possess higher value of E_{opt} (2.9–3.5 eV) [23, 24]. Obviously, the influence of the third component on the E_{opt} is also very essential.

The thermal behavior of the investigated glasses was discussed in details elsewhere [15, 25]. Generally, it was established that the increase in MoO_3 content (above 40 mol%) results in decreasing of glass transition temperature (T_g) and crystallization temperature (T_x) from 480 to 360 °C and from 540 to 420 °C, respectively. Selected glass samples were subjected to additional heat treatment. The XRD patterns at different exposure times are shown in Fig. 4. The $BiBO_3$ (JCPDS 27-0320 and 28-0169), $Bi_4B_2O_9$ (JCPDS 70-1458), and orthorhombic Bi_2MoO_6 (JCPDS 76-2388) crystal phases were detected (Fig. 4, samples **C**–**F**). The $BiBO_3$ (II) (JCPDS 27-0320) was obtained after crystallization of composition **F** ($50Bi_2O_3·50B_2O_3$), only. The addition of 2 mol% MoO_3 (sample **E**) led to obtaining of bismuth borate polymorphous (I and II). The $BiBO_3$ (I) and $BiBO_3$ (II) phases were successfully distinguished through the crystallization of binary Bi_2O_3–B_2O_3 glasses [26]. They established that both polymorphous coexist up to 500 °C while above this temperature

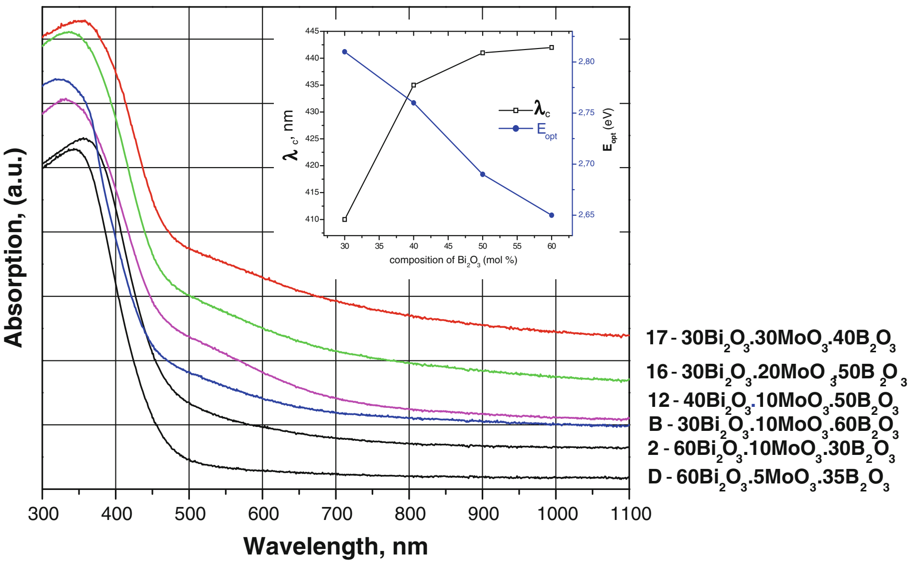

Fig. 3 UV–Vis spectral absorption of selected glasses from the system investigated. The *inset* shows dependence of cut-off wavelength (λ_c) and energy gap (E_{opt}) on Bi_2O_3 mol% composition

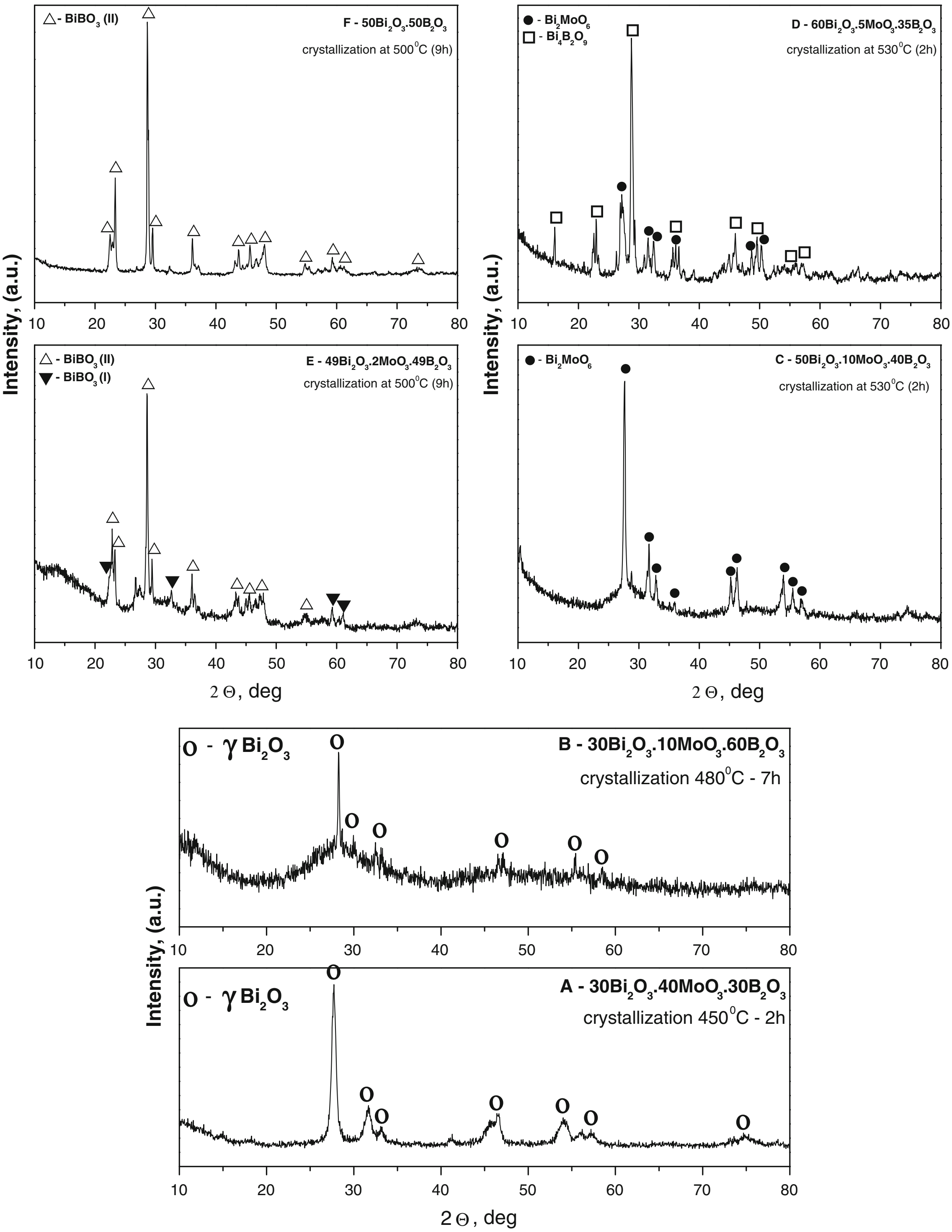

Fig. 4 X-ray diffraction patterns of selected glass compositions after heat treatment

$BiBO_3$ (II) phase only, was obtained. According to Pottier [27], the $BiBO_3$ phase decomposes into a mixture of the stable $Bi_4B_2O_9$ and $Bi_3B_5O_{12}$ phases at 600 °C. In the sample containing above 5 mol% MoO_3 (Fig. 4, sample **C**) bismuth borates were not found and Bi_2MoO_6 (koechlinite) was crystallized, only. Having in mind that the $BiBO_3$ phase possesses the highest coefficient for second harmonic generation [28, 29], it is interesting to continue investigations in this concentration range (below 5 mol% MoO_3). On the other hand, it is well known that Bi_2MoO_6 (koechlinite) is a catalytically active phase and a high oxide ion conductor, also [30, 31]. By the way, this phase was studied recently as a part of the ternary system Bi_2O_3–MoO_3–TiO_2 and different methods for the synthesis and areas of applications of bismuthate molybdates were discussed [32].

In two compositions (**A** and **B**) both situated near the immiscibility gap boundary after crystallization (480 °C, 7 h) γ-Bi_2O_3 (JCPDS 77-0374) phase was observed, only. Probably the MoO_3 and B_2O_3 remain in the amorphous part of these samples. The average crystalline size of as obtained γ-Bi_2O_3 crystals calculated from the broadening of the diffraction line using Sherrer's equation is about 24 nm. The microstructure of the sample B ($30Bi_2O_3 \cdot 10MoO_3 \cdot 60B_2O_3$) was examined by SEM analysis (Fig. 5). Surface crystallization was observed, while the sample

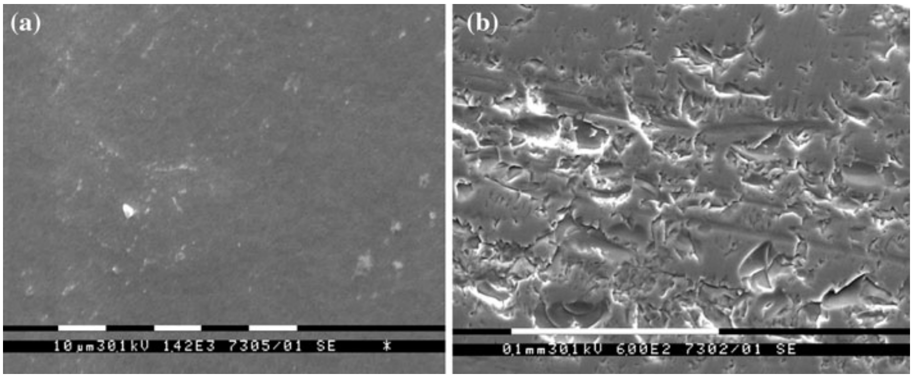

Fig. 5 SEM micrographs of glass B ($30Bi_2O_3 \cdot 10MoO_3 \cdot 60B_2O_3$) after heat treatment at 480 °C for 7 h: **a** cross-section and **b** sample surface

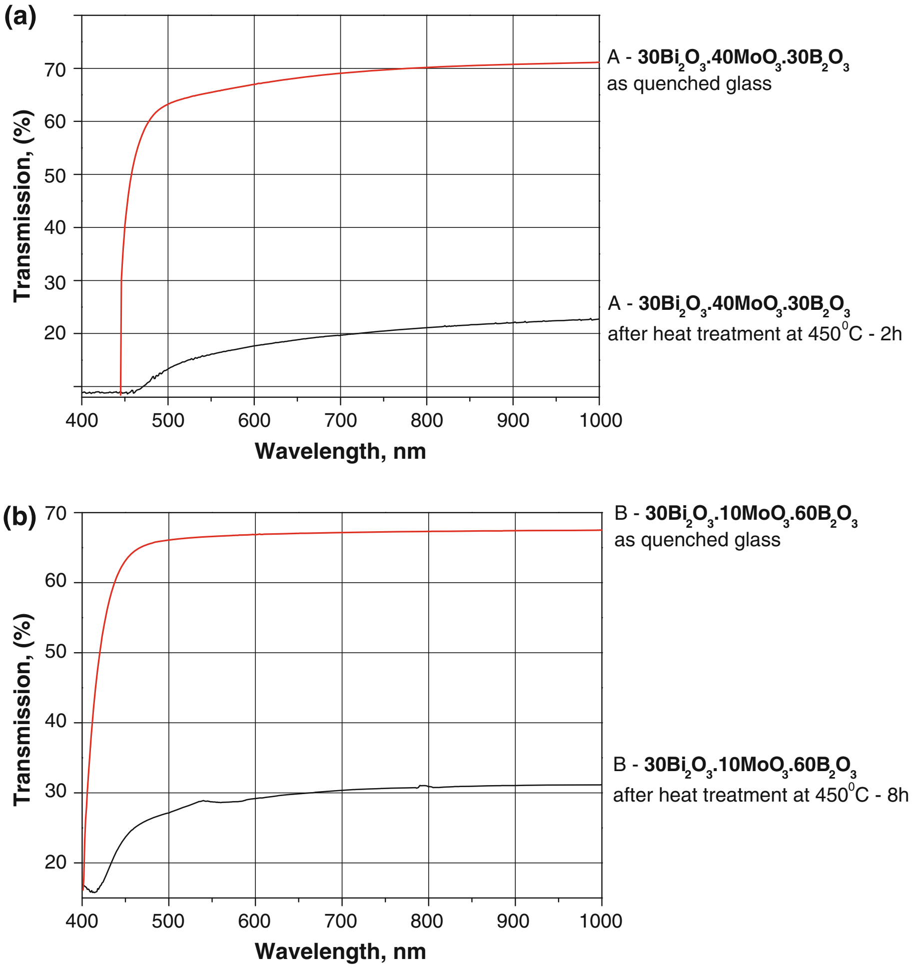

Fig. 6 UV–Vis spectral transmission of glasses **A** and **B** before and after heat treatment

volume is still amorphous. The microprobe analysis exhibits presence of mainly Bi_2O_3 in the crystals that is in agreement with the XRD results (Fig. 4). The UV–Vis spectra of partially crystallized samples **A** and **B** are shown in (Fig. 6). As it is seen the transmittance of both glasses decreases after heat treatment, but the samples are still transparent. Obviously, by the applying procedure semi-transparent glass–ceramic materials could be obtained.

The obtained results on the optical properties of glasses in the ternary Bi_2O_3–MoO_3–B_2O_3 system will be interpreted taking into account structural features of the bismuth-borate glasses [33–36]. Different local structure and different connectivity between the bismuthate, borate, and molybdate units in the amorphous network were established in our previous investigation [15]. The Bi_2O_3 content (up to 50 mol%) favors BO_3 to BO_4 transition [35–37], while MoO_3 preserves the BO_3 units [15, 33, 34]. The structural polyhedra in the amorphous network are connected with the formation of B–O–Bi and Mo–O–Bi bonds. Mixed Mo–O–B bonds were not established in our earlier investigations for different boromolybdate glasses [34, 38, 39]. As it was already found in the systems Bi_2O_3–MoO_3–MeO, the mixed Mo–O···Bi bonds are crucial for the glass formation [32, 40]. The increase in Bi_2O_3 content leads to slight depolymerization of borate network which results in some decreasing of E_{opt} and shifting λ_c towards longer wavelength (Fig. 3). It is well known that when the MoO_3 content is low, it acts as a modifier participates as isolated MoO_4 units and strongly depolymerize the amorphous network. A decrease in the band gap value should be expected also as a result of the partial reduction of molybdenum ions and creation of bonding defects [20]. Obviously, in the obtained glasses, MoO_3 is the decisive factor for decreasing of E_{opt}.

Conclusions

The obtained glasses in the Bi_2O_3–MoO_3–B_2O_3 system are transmittant in the visible range with cut-off near 430–500 nm. The increase in the MoO_3 and Bi_2O_3 content shifts the absorption edge towards the higher wavelengths. The Bi_2O_3 content improved the transmittance above 700 nm. Semitransparent glass–ceramic materials containing γ-Bi_2O_3 crystals were synthesized. It was established that the metastable $BiBO_3$ crystal phase could be obtained at low MoO_3 content (2 mol%) after heat treatment of the glasses. These preliminary results showed that the ternary Bi_2O_3–MoO_3–B_2O_3 glasses are perspective for the development of new multifunctional materials with specific optical properties (E_{opt}, λ_c), colored glasses, flux glasses, and transparent glass–ceramics.

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