

Synthesis of BiBO₃ by crystallization of glasses in the Bi₂O₃–MoO₃–B₂O₃ system

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Received January 18, 2011; Revised April 20, 2011

The aim of the present work is to verify the synthesis of bismuth borates by crystallization from glasses. Several bismuth boromolybdate glasses were selected and heat treated at 500–530 °C for different exposure times. Obtaining of BiBO₃ polymorphs, Bi₄B₂O₉, Bi₃B₅O₁₂ and Bi₂MoO₆ has been detected by X-ray diffraction (XRD). Additional information for the formation of BiBO₃ crystal phase was obtained by infrared spectroscopy (IR). There is significant difference in the IR spectra of the glass 50Bi₂O₃.50B₂O₃ and crystal BiBO₃ product. The reason is that in the glass sample the content of BO₄ units is higher than in the crystallized one.

Keywords: crystallization, glasses, X-ray diffraction.

INTRODUCTION

There is significant interest in the preparation and characterization of bismuth borate glasses, glass ceramics and single crystals for their application in non-linear optics [1–5]. An early comprehensive study of several oxide glasses containing Bi₂O₃ as a network former was reported by Dumbaugh [6]. A recent article discussed the effects of melting conditions and crucible materials on the optical properties of oxide glasses containing bismuth [7]. Crystalline bismuth borates, also have received increased attention in recent years due to their outstanding properties like high density, refractive index and very high coefficients of second and third harmonic generation. The phase diagram of Bi₂O₃–B₂O₃ system was first determined by Levin and Daniel [8] and a variety of stable phases are known to exist: Bi₂₄B₁₂O₃₉ (boron sillenite), Bi₄B₂O₉, Bi₃B₅O₁₂, BiB₃O₆ (bismuth triborate), Bi₂B₈O₁₅ (bismuth octaborate). The metastable BiBO₃ phase (bismuth orthoborate) that is missing in the original phase diagram possesses two polymorph modifications (BiBO₃-I and BiBO₃-II) [9–11]. It can be prepared by cooling of a melt with composition of 50B₂O₃.50Bi₂O₃ [9, 10], and it was found that it decomposes into a mixture of the stable Bi₄B₂O₉ and

Bi₃B₅O₁₂ phases at 600 °C [9]. Recently, Egorysheva et al. [12] published a review on the vibrational spectra of bismuth borate crystals. Among several inorganic borate crystals for applications in non-linear optical devices, bismuth triborate (BiB₃O₆) phase is known to have the highest coefficient for second harmonic generation (2.5–7) and numerous studies on its single crystal growth and optical properties have been carried out [10, 13]. Ihara et al. [11] demonstrated for first time that the BiBO₃ phase is also a nonlinear optical crystal with second harmonic intensity about 110 times as large as α-quartz.

Although various studies have been published for obtaining of bismuth borate phases from supercooled melts and glasses some questions still remain open concerning the use of different crucible materials and the influence of preparation conditions [4]. In our previous studies [14–17] it was established that MoO₃ is a suitable component to decrease the melting temperatures in the MoO₃–La₂O₃–B₂O₃, MoO₃–Nd₂O₃–B₂O₃ and MoO₃–ZnO–B₂O₃ systems [15] and the possibility to modify the crystallization processes. That is the reason the ternary system MoO₃–Bi₂O₃–B₂O₃ has been chosen as a subject of this study. The present paper is a continuation of our previous investigations on the ternary Bi₂O₃–MoO₃–B₂O₃ system. The location of the glass formation region was determined, the structure of glasses and optical properties of the glasses and

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glass-crystalline materials were investigated as well [18]. The aim of the present work is to verify the synthesis of BiBO₃ by crystallization from glasses in the presence of MoO₃ as an additional flux agent in the ternary Bi₂O₃-MoO₃-B₂O₃ system.

EXPERIMENTAL

All compositions (10 g) were prepared using reagent grade oxides MoO₃ (Merck, p.a.), Bi₂O₃ (Merck, p.a.) and H₃BO₃ (Reachim, chem. pure) as starting materials. The homogenized batches were melted for 15 min in air in alumina crucibles. The melting temperature was limited to 1000 °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 ~10² K/s). Several glass compositions, situated in different part of the glass formation region were selected: 50Bi₂O₃.50B₂O₃, 50Bi₂O₃.10MoO₃.40B₂O₃, 60Bi₂O₃.5MoO₃.35B₂O₃, 49Bi₂O₃.2MoO₃.49B₂O₃ and 63Bi₂O₃.2MoO₃.35B₂O₃ and additional heat-treatment at 500–530 °C for different exposure times (2–9 h) was performed. The phase transformations of the samples were detected by X-ray diffraction (Bruker D8 Advance diffractometer, Cu K α 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 polished samples. The thermal stability of the selected glasses was verified by differential thermal analysis (LABSYSTM EVO apparatus) with Pt-Pt/Rh thermocouple at a heating rate of 10 K/min in argon flow, using Al₂O₃ as a reference material. The accuracy of the temperature maintenance was determined \pm 5 °C. The optical absorption spectra of the glass and crystalline samples were recorded at room temperature using UV-Vis spectrophotometer (Evolution 300) in the wavelength range 300–1000 nm. The IR spectra were measured using the KBr pellet technique on a Nicolet-320 FTIR spectrometer with a resolution of \pm 1 cm⁻¹, by collecting 16 scans in the range 1600–400 cm⁻¹.

RESULTS AND DISCUSSION

Transparent and homogeneous glass compositions 50Bi₂O₃.50B₂O₃, 50Bi₂O₃.10MoO₃.40B₂O₃, 60Bi₂O₃.5MoO₃.35B₂O₃, 49Bi₂O₃.2MoO₃.49B₂O₃ and 63Bi₂O₃.2MoO₃.35B₂O₃ having a pale yellow to dark yellow color were obtained. The DTA patterns of selected glasses are shown in Fig. 1. It is visible that the increase of MoO₃ content (above 40 mol%) results in the decrease of glass transition tempera-

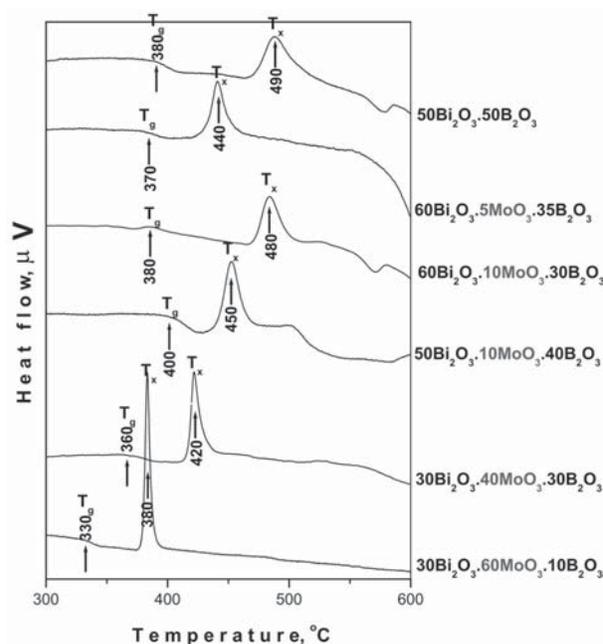


Fig. 1. DTA curves of selected glasses

ture (T_g) and crystallization temperature (T_x) from 370 to 330 °C and from 440 to 380 °C, respectively. The heat treatment regime of the glasses was made having in mind the obtained DTA results and previous reports by Pottier [9], Becker [10] and Ihara [11] as well. In the XRD pattern (Fig. 2) of the binary 50Bi₂O₃.50B₂O₃ composition only the diffraction lines of BiBO₃-II phase, are visible. The addition of 2 mol% MoO₃ leads to the appearance of both BiBO₃ polymorphs: BiBO₃-I (JCPDS 28-0169) and BiBO₃-II (JCPDS 27-0320). Unfortunately, the crystal structures of these two phases have not been determined until now. The increase in MoO₃ content (5 mol%) also leads to the appearance of two phases Bi₄B₂O₉ (JCPDS 70-1458) and Bi₂MoO₆ (koechlinite) (JCPDS 82-2067). Further increase in MoO₃ content (10 mol%) shows only the presence of Bi₂MoO₆ (koechlinite). Another experiment at constant MoO₃ content (2 mol%) was made with varying the ratio of the other two components (Bi₂O₃ and B₂O₃). After heat treatment at 500 °C for 9h in the sample with composition 49Bi₂O₃.2MoO₃.49B₂O₃ both BiBO₃ polymorphs were detected (Fig. 3), while in the other sample with composition 63Bi₂O₃.2MoO₃.35B₂O₃, diffraction lines of several crystal phases were found: BiBO₃-I, BiBO₃-II, Bi₄B₂O₉ and Bi₃B₅O₁₂ (JCPDS 15-0372). According to Pottier [9] the BiBO₃ phase decomposes into a mixture of the stable Bi₄B₂O₉ and Bi₃B₅O₁₂ phases at 600 °C. More experiments are needed in order to elucidate this interesting problem.

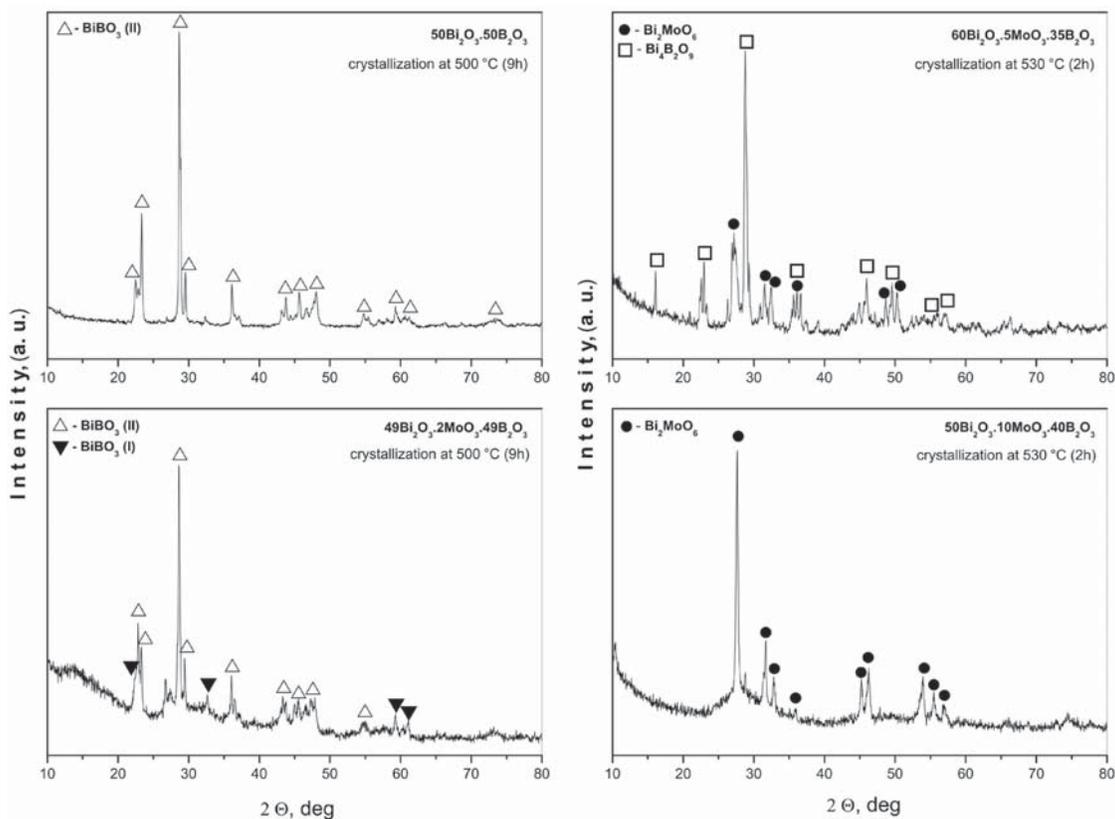


Fig. 2. X-ray diffraction patterns of selected glass compositions after heat treatment

The microstructure of the crystallized sample $50\text{Bi}_2\text{O}_3.50\text{B}_2\text{O}_3$ was examined by SEM analysis (Fig. 4). Partial surface crystallization was observed, while the sample volume is still amorphous. The preliminary microprobe chemical composition analysis showed the presence of BiBO_3 phase that is in agreement with the XRD results (Fig. 2). The UV-Vis spectra of the glass $50\text{Bi}_2\text{O}_3.50\text{B}_2\text{O}_3$ and crystalline BiBO_3 are shown in Fig. 5. The absorption of both samples decreases after 400 nm, but the crystallized sample possesses better transparency than the glass. Besides, a band at 480 nm was observed in the spectrum of the glass sample that could be related to the formation of nanoparticles of elementary bismuth (Bi^0) and their influence on the coloration of the glass. This problem was discussed in details by Sanz et al. for bismuth-silicate glasses [7].

There is significant difference in the IR spectra (Fig. 6) of both samples. The amorphous network contains BO_4 ($930\text{-}880$ and 1040 cm^{-1}), BO_3 (1270 , 1200 cm^{-1}) and BiO_6 (band centered at 470 cm^{-1})

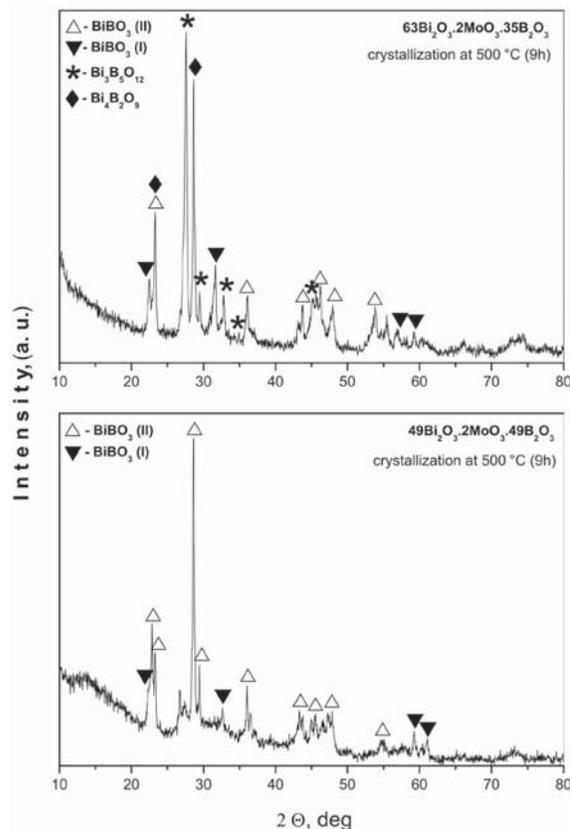


Fig. 3. X-ray diffraction patterns of samples $49\text{Bi}_2\text{O}_3.2\text{MoO}_3.49\text{B}_2\text{O}_3$ and $63\text{Bi}_2\text{O}_3.2\text{MoO}_3.35\text{B}_2\text{O}_3$

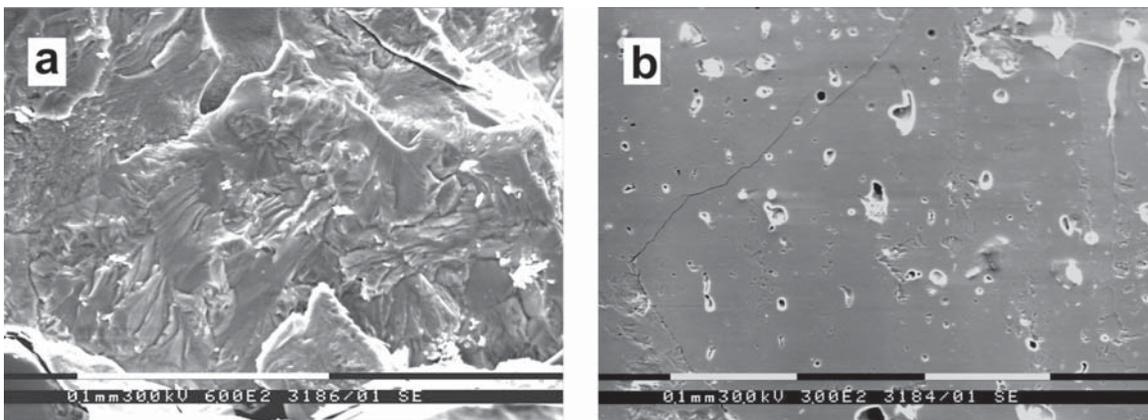


Fig. 4. SEM micrographs of the crystalline BiBO_3 : a) unpolished surface and b) sample volume

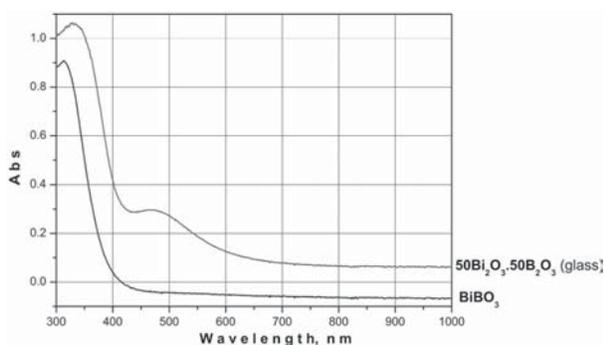


Fig. 5. UV-Vis spectra of the glass and crystalline BiBO_3

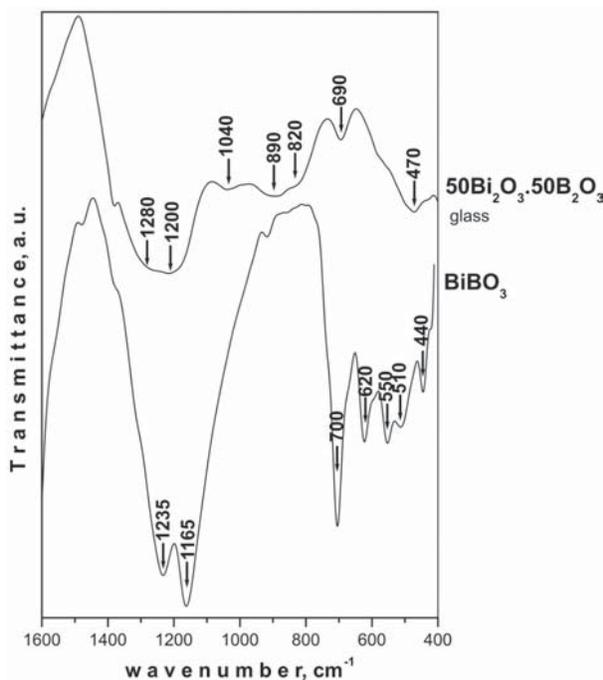


Fig. 6. IR spectra of the glass $50\text{Bi}_2\text{O}_3.50\text{B}_2\text{O}_3$ and crystalline BiBO_3

units. In the IR spectrum of crystalline sample the bands which are related to the BO_4 vibrations are missing and overall it is similar to the results obtained by Egorysheva et al. [12] for the IR spectra of BiBO_3 phase. The obtained results are an additional confirmation that Bi_2O_3 favors the transformation of BO_3 to BO_4 units in the amorphous network [4, 18–21].

CONCLUSIONS

Bismuth borate (BiBO_3) phase was synthesized by crystallization of binary and ternary glass compositions in the $\text{Bi}_2\text{O}_3\text{-MoO}_3\text{-B}_2\text{O}_3$ system. It was established that the addition of 2 mol % MoO_3 leads to the obtaining of $\text{BiBO}_3\text{-I}$ and $\text{BiBO}_3\text{-II}$ bismuth borate polymorphs. The increase in MoO_3 content (2–5 mol%) stimulates the simultaneous crystallization of several phases – BiBO_3 , $\text{Bi}_4\text{B}_2\text{O}_9$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$. Further increase in MoO_3 content (10 mol%) leads to the obtaining of Bi_2MoO_6 (koechlinite) phase, only. IR results established that in the glasses the content of BO_4 units is higher than in the crystallized sample.

Acknowledgements: Authors are grateful to the financial support of the National Science Fund of Bulgaria, Contract No TK-X-1718/07.

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СИНТЕЗ НА BiVO₃ ЧРЕЗ КРИСТАЛИЗАЦИЯ НА СЪТЪКЛА В СИСТЕМАТА MoO₃-Bi₂O₃-B₂O₃

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Постъпила на 18 януари, 2011 г.; приета на 20 април, 2011 г.

(Резюме)

Целта на настоящата работа е да се провери възможността за синтез на BiVO₃ чрез кристализация на стъкла. Няколко трикомпонентни аморфни състава от изследваната система бяха избрани и термично третирани при 500–530 °C с различно време на задръжка. Чрез рентгено-фазов анализ (РФА) бе установено получаването на полиморфните модификации на BiVO₃, както и на Bi₄B₂O₉, Bi₃B₅O₁₂ и Bi₂MoO₆ кристални фази. Допълнителна информация за синтезирания BiVO₃ бе получена и от инфрачервената спектроскопия (ИЧ). Има съществена разлика в ИЧ спектрите на стъклото със състав 50Bi₂O₃.50B₂O₃ и кристалния BiVO₃ продукт. Причината за това е, че в стъклото съдържанието на VO₄ групите е по-високо отколкото в кристалния образец.