Synthesis of BiBO$_3$ by crystallization of glasses in the Bi$_2$O$_3$–MoO$_3$–B$_2$O$_3$ system

R. S. Iordanova$^1$, A. D. Bachvarova-Nedelcheva$^{1*}$, L. I. Aleksandrov$^1$, Y. B. Dimitriev$^2$

$^1$ Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, “Acad. G. Bonchev”, bld. 11, 1113 Sofia, Bulgaria

$^2$ University of Chemical Technology and Metallurgy, 8 Kl. Ohridski blvd., 1756 Sofia, Bulgaria

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 BiBO$_3$ polymorphs, Bi$_4$B$_2$O$_9$, Bi$_3$B$_5$O$_{12}$ and Bi$_2$MoO$_6$ has been detected by X-ray diffraction (XRD). Additional information for the formation of BiBO$_3$ crystal phase was obtained by infrared spectroscopy (IR). There is a significant difference in the IR spectra of the glass 50Bi$_2$O$_3.50$B$_2$O$_3$ and crystal BiBO$_3$ product. The reason is that in the glass sample the content of BO$_4$ 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 Bi$_2$O$_3$ 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 Bi$_2$O$_3$–B$_2$O$_3$ system was first determined by Levin and Daniel [8] and a variety of stable phases are known to exist: Bi$_2$B$_2$O$_7$ (boron sillenite), Bi$_4$B$_2$O$_9$, Bi$_3$B$_5$O$_{12}$, BiB$_3$O$_6$ (bismuth triborate), Bi$_2$B$_8$O$_{15}$ (bismuth octaborate). The metastable BiBO$_3$ phase (bismuth orthoborate) that is missing in the original phase diagram possesses two polymorph modifications (BiBO$_3$-I and BiBO$_3$-II) [9-11]. It can be prepared by cooling of a melt with composition of 50B$_2$O$_3.50$Bi$_2$O$_3$ [9, 10], and it was found that it decomposes into a mixture of the stable Bi$_2$B$_2$O$_7$ and Bi$_2$B$_2$O$_7$ 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 (BiB$_3$O$_6$) 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 BiBO$_3$ 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 MoO$_3$ is a suitable component to decrease the melting temperatures in the MoO$_3$–La$_2$O$_3$–B$_2$O$_3$, MoO$_3$–Nd$_2$O$_3$–B$_2$O$_3$ and MoO$_3$–ZnO–B$_2$O$_3$ systems [15] and the possibility to modify the crystallization processes. That is the reason the ternary system MoO$_3$–Bi$_2$O$_3$–B$_2$O$_3$ has been chosen as a subject of this study. The present paper is a continuation of our previous investigations on the ternary Bi$_2$O$_3$–MoO$_3$–B$_2$O$_3$ system. The location of the glass formation region was determined, the structure of glasses and optical properties of the glasses and

* To whom all correspondence should be sent:
E-mail: albenadb@svr.igic.bas.bg
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 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 polished samples. The thermal stability of the selected glasses was verified by differential thermal analysis (LABSYS 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 ± 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 ±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 temperature (Tg) and crystallization temperature (Tx) 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 leds 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 leds to the appearance of two phases Bi₂B₂O₆ (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, Bi₂B₂O₆ and Bi₂B₅O₁₂ (JCPDS 15-0372). According to Pottier [9] the BiBO₃ phase decomposes into a mixture of the stable Bi₂B₂O₆ and Bi₂B₅O₁₂ phases at 600 °C. More experiments are needed in order to elucidate this interesting problem.
The microstructure of the crystallized sample 50Bi₂O₃.50B₂O₃ 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 BiBO₃ phase that is in agreement with the XRD results (Fig. 2). The UV-Vis spectra of the glass 50Bi₂O₃.50B₂O₃ and crystalline BiBO₃ 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 (Bi⁰) 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 BO₄ (930–880 and 1040 cm⁻¹), BO₃ (1270, 1200 cm⁻¹) and BiO₆ (band centered at 470 cm⁻¹).
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 Bi_2O_3-MoO_3-B_2O_3 system. It was established that the addition of 2 mol % MoO_3 leads to the obtaining of BiBO_3-I and BiBO_3-II bismuth borate polymorphs. The increase in MoO_3 content (2–5 mol%) stimulates the simultaneous crystallization of several phases – BiBO_3, Bi_4B_2O_9 and Bi_3B_5O_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_3 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.

REFERENCES


СИНТЕЗ НА BiBO₃ ЧРЕЗ КРИСТАЛИЗАЦИЯ НА СТЪКЛА В СИСТЕМАТА MoO₃–Bi₂O₃–B₂O₃

Р. С. Йорданова¹, А. Д. Бъчварова-Неделчева¹*, Л. И. Александров¹,
Я. Б. Димитриев²

¹ Институт по Обща и Неорганична Химия, Българска Академия на Науките,
ул. „Акад. Г. Бончев”, бл. 11, 1113 София, България
² Химикотехнологичен и Металургичен Университет, бул. „Кл. Охридски” 8,
1756 София, България

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 BiBO₃ 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 BiBO₃, както и на Bi₄B₂O₉, Bi₃B₅O₁₂ и Bi₂MoO₆ кристални фази. Допълнителна информация за синтезираната BiBO₃ бе получена и от инфрачервена спектроскопия (ИЧ). Има съществена разлика в ИЧ спектрите на стъклото със състав 50Bi₂O₃:50B₂O₃ и кристалния BiBO₃ продукт. Причината за това е, че в стъклото съдържанието на BO₃ групите е по-високо отколкото в кристалния образец.