

## Synthesis of $\text{BiBO}_3$ by crystallization of glasses in the $\text{Bi}_2\text{O}_3\text{--MoO}_3\text{--B}_2\text{O}_3$ system

R. S. Jordanova<sup>1</sup>, A. D. Bachvarova-Nedelcheva<sup>1\*</sup>, L. I. Aleksandrov<sup>1</sup>, Y. B. Dimitriev<sup>2</sup>

<sup>1</sup> Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,  
“Acad. G. Bonchev”, bld. 11, 1113 Sofia, Bulgaria

<sup>2</sup> University of Chemical Technology and Metallurgy, 8 Kl. Ohridski Blvd., 1756 Sofia, Bulgaria

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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  $\text{BiBO}_3$  polymorphs,  $\text{Bi}_4\text{B}_2\text{O}_9$ ,  $\text{Bi}_3\text{B}_5\text{O}_{12}$  and  $\text{Bi}_2\text{MoO}_6$  has been detected by X-ray diffraction (XRD). Additional information for the formation of  $\text{BiBO}_3$  crystal phase was obtained by infrared spectroscopy (IR). There is significant difference in the IR spectra of the glass  $50\text{Bi}_2\text{O}_3\cdot 50\text{B}_2\text{O}_3$  and crystal  $\text{BiBO}_3$  product. The reason is that in the glass sample the content of  $\text{BO}_4$  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  $\text{Bi}_2\text{O}_3$  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  $\text{Bi}_2\text{O}_3\text{--B}_2\text{O}_3$  system was first determined by Levin and Daniel [8] and a variety of stable phases are known to exist:  $\text{Bi}_{24}\text{B}_{12}\text{O}_{39}$  (boron sillenite),  $\text{Bi}_4\text{B}_2\text{O}_9$ ,  $\text{Bi}_3\text{B}_5\text{O}_{12}$ ,  $\text{BiB}_3\text{O}_6$  (bismuth triborate),  $\text{Bi}_2\text{B}_8\text{O}_{15}$  (bismuth octaborate). The metastable  $\text{BiBO}_3$  phase (bismuth orthoborate) that is missing in the original phase diagram possesses two polymorph modifications ( $\text{BiBO}_3\text{-I}$  and  $\text{BiBO}_3\text{-II}$ ) [9–11]. It can be prepared by cooling of a melt with composition of  $50\text{B}_2\text{O}_3\cdot 50\text{Bi}_2\text{O}_3$  [9, 10], and it was found that it decomposes into a mixture of the stable  $\text{Bi}_4\text{B}_2\text{O}_9$  and

$\text{Bi}_3\text{B}_5\text{O}_{12}$  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 ( $\text{BiB}_3\text{O}_6$ ) 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  $\text{BiBO}_3$  phase is also a nonlinear optical crystal with second harmonic intensity about 110 times as large as  $\alpha$ -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  $\text{MoO}_3$  is a suitable component to decrease the melting temperatures in the  $\text{MoO}_3\text{--La}_2\text{O}_3\text{--B}_2\text{O}_3$ ,  $\text{MoO}_3\text{--Nd}_2\text{O}_3\text{--B}_2\text{O}_3$  and  $\text{MoO}_3\text{--ZnO--B}_2\text{O}_3$  systems [15] and the possibility to modify the crystallization processes. That is the reason the ternary system  $\text{MoO}_3\text{--Bi}_2\text{O}_3\text{--B}_2\text{O}_3$  has been chosen as a subject of this study. The present paper is a continuation of our previous investigations on the ternary  $\text{Bi}_2\text{O}_3\text{--MoO}_3\text{--B}_2\text{O}_3$  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 BiBO<sub>3</sub> by crystallization from glasses in the presence of MoO<sub>3</sub> as an additional flux agent in the ternary Bi<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system.

## EXPERIMENTAL

All compositions (10 g) were prepared using reagent grade oxides MoO<sub>3</sub> (Merck, p.a.), Bi<sub>2</sub>O<sub>3</sub> (Merck, p.a.) and H<sub>3</sub>BO<sub>3</sub> (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 ~10<sup>2</sup> K/s). Several glass compositions, situated in different part of the glass formation region were selected: 50Bi<sub>2</sub>O<sub>3</sub>.50B<sub>2</sub>O<sub>3</sub>, 50Bi<sub>2</sub>O<sub>3</sub>.10MoO<sub>3</sub>.40B<sub>2</sub>O<sub>3</sub>, 60Bi<sub>2</sub>O<sub>3</sub>.5MoO<sub>3</sub>.35B<sub>2</sub>O<sub>3</sub>, 49Bi<sub>2</sub>O<sub>3</sub>.2MoO<sub>3</sub>.49B<sub>2</sub>O<sub>3</sub> and 63Bi<sub>2</sub>O<sub>3</sub>.2MoO<sub>3</sub>.35B<sub>2</sub>O<sub>3</sub> 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 $\alpha$  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<sup>TM</sup> EVO apparatus) with Pt-Pt/Rh thermocouple at a heating rate of 10 K/min in argon flow, using Al<sub>2</sub>O<sub>3</sub> 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<sup>-1</sup>, by collecting 16 scans in the range 1600–400 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

Transparent and homogeneous glass compositions 50Bi<sub>2</sub>O<sub>3</sub>.50B<sub>2</sub>O<sub>3</sub>, 50Bi<sub>2</sub>O<sub>3</sub>.10MoO<sub>3</sub>.40B<sub>2</sub>O<sub>3</sub>, 60Bi<sub>2</sub>O<sub>3</sub>.5MoO<sub>3</sub>.35B<sub>2</sub>O<sub>3</sub>, 49Bi<sub>2</sub>O<sub>3</sub>.2MoO<sub>3</sub>.49B<sub>2</sub>O<sub>3</sub> and 63Bi<sub>2</sub>O<sub>3</sub>.2MoO<sub>3</sub>.35B<sub>2</sub>O<sub>3</sub> 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 MoO<sub>3</sub> content (above 40 mol%) results in the decrease of glass transition tempera-

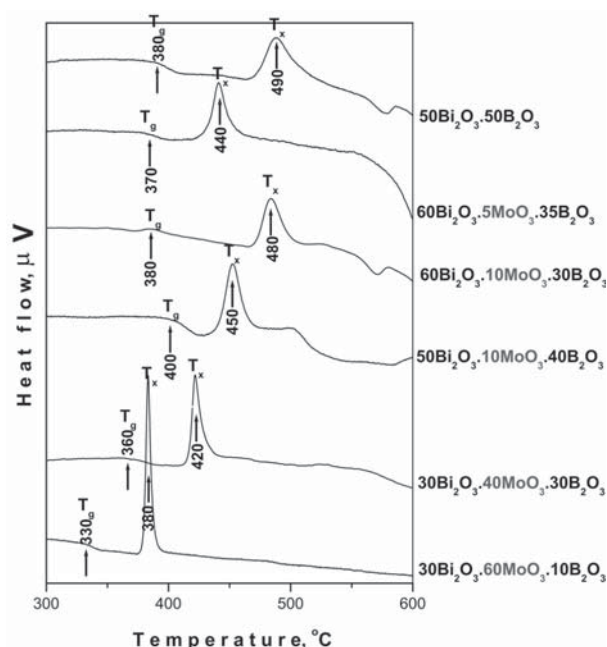
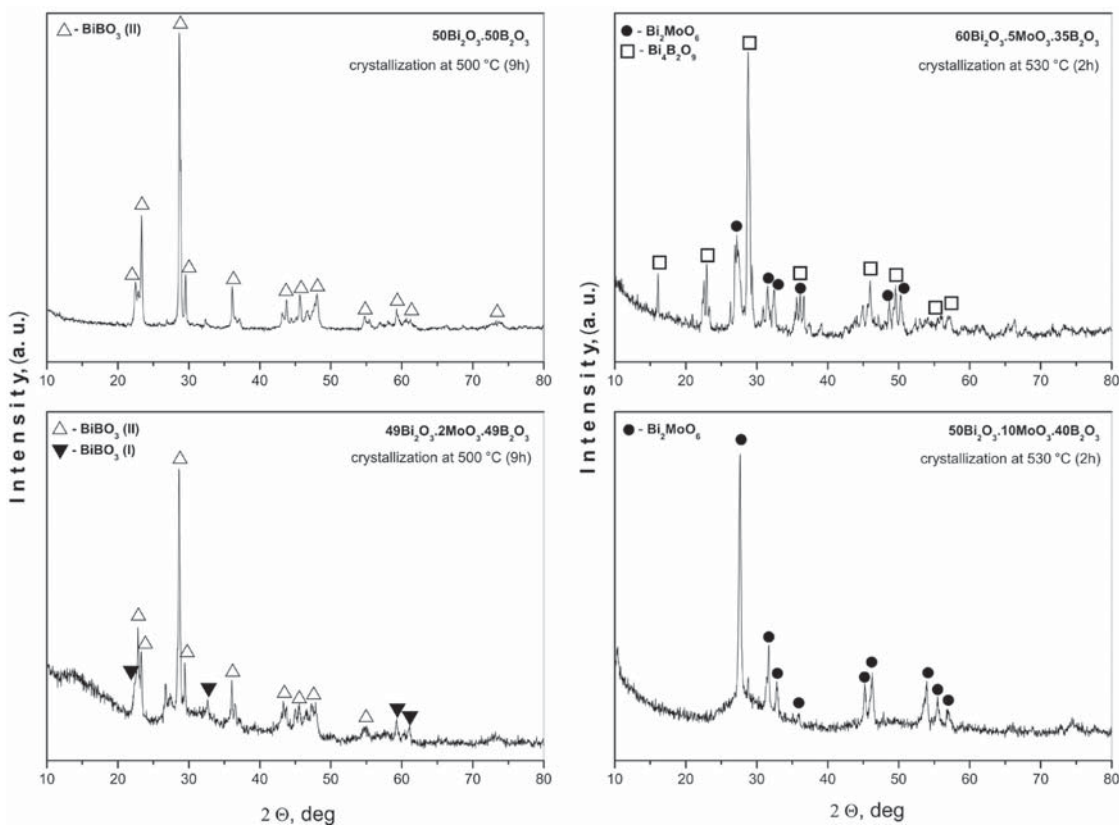


Fig. 1. DTA curves of selected glasses

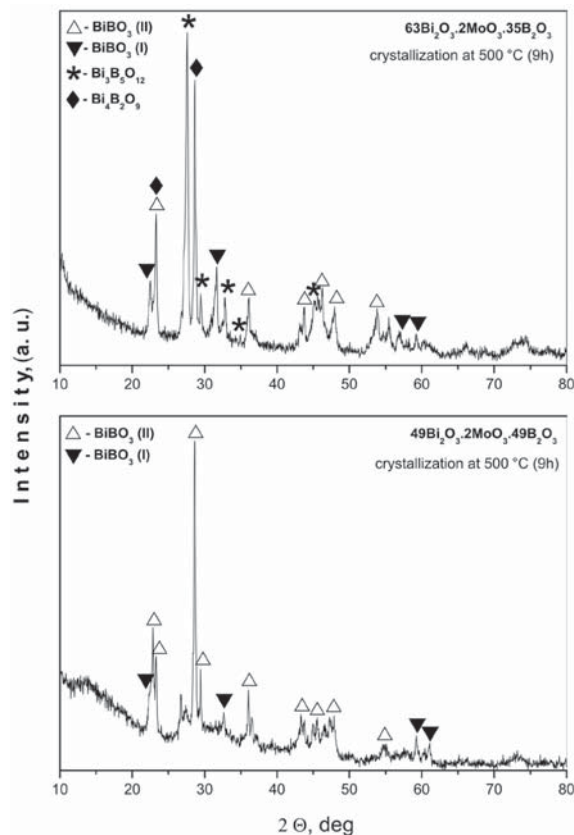
ture ( $T_g$ ) and crystallization temperature ( $T_x$ ) from 370 to 330 °C and from 440 to 380 °C, respectively. The heat treatment regime of the glasses was made having in mind the obtained DTA results and previous reports by Pottier [9], Becker [10] and Ihara [11] as well. In the XRD pattern (Fig. 2) of the binary 50Bi<sub>2</sub>O<sub>3</sub>.50B<sub>2</sub>O<sub>3</sub> composition only the diffraction lines of BiBO<sub>3</sub>-II phase, are visible. The addition of 2 mol% MoO<sub>3</sub> leads to the appearance of both BiBO<sub>3</sub> polymorphs: BiBO<sub>3</sub>-I (JCPDS 28-0169) and BiBO<sub>3</sub>-II (JCPDS 27-0320). Unfortunately, the crystal structures of these two phases have not been determined until now. The increase in MoO<sub>3</sub> content (5 mol%) also leads to the appearance of two phases Bi<sub>4</sub>B<sub>2</sub>O<sub>9</sub> (JCPDS 70-1458) and Bi<sub>2</sub>MoO<sub>6</sub> (koechlinite) (JCPDS 82-2067). Further increase in MoO<sub>3</sub> content (10 mol%) shows only the presence of Bi<sub>2</sub>MoO<sub>6</sub> (koechlinite). Another experiment at constant MoO<sub>3</sub> content (2 mol%) was made with varying the ratio of the other two components (Bi<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>). After heat treatment at 500 °C for 9h in the sample with composition 49Bi<sub>2</sub>O<sub>3</sub>.2MoO<sub>3</sub>.49B<sub>2</sub>O<sub>3</sub> both BiBO<sub>3</sub> polymorphs were detected (Fig. 3), while in the other sample with composition 63Bi<sub>2</sub>O<sub>3</sub>.2MoO<sub>3</sub>.35B<sub>2</sub>O<sub>3</sub>, diffraction lines of several crystal phases were found: BiBO<sub>3</sub>-I, BiBO<sub>3</sub>-II, Bi<sub>4</sub>B<sub>2</sub>O<sub>9</sub> and Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub> (JCPDS 15-0372). According to Pottier [9] the BiBO<sub>3</sub> phase decomposes into a mixture of the stable Bi<sub>4</sub>B<sub>2</sub>O<sub>9</sub> and Bi<sub>3</sub>B<sub>5</sub>O<sub>12</sub> 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  $\text{BiBO}_3$  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  $\text{BiBO}_3$  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 ( $\text{Bi}^0$ ) 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  $\text{BO}_4$  ( $930$ – $880$  and  $1040\text{ cm}^{-1}$ ),  $\text{BO}_3$  ( $1270$ ,  $1200\text{ cm}^{-1}$ ) and  $\text{BiO}_6$  (band centered at  $470\text{ cm}^{-1}$ )



**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  $63\text{Bi}_2\text{O}_3.2\text{MoO}_3.35\text{B}_2\text{O}_3$



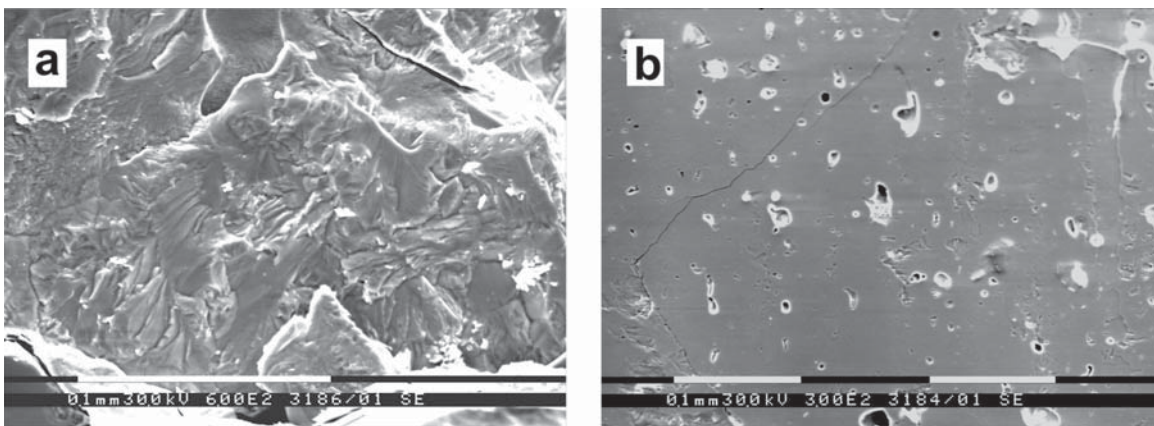


Fig. 4. SEM micrographs of the crystalline  $\text{BiBO}_3$ : a) unpolished surface and b) sample volume

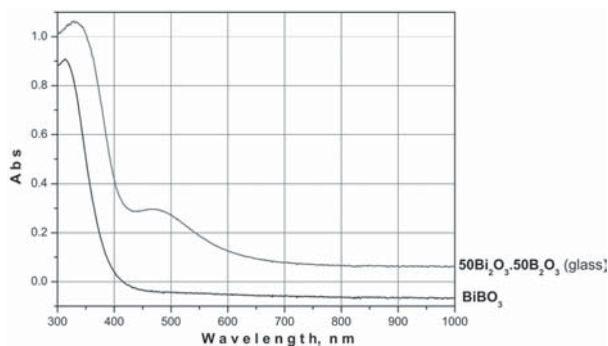


Fig. 5. UV-Vis spectra of the glass and crystalline  $\text{BiBO}_3$

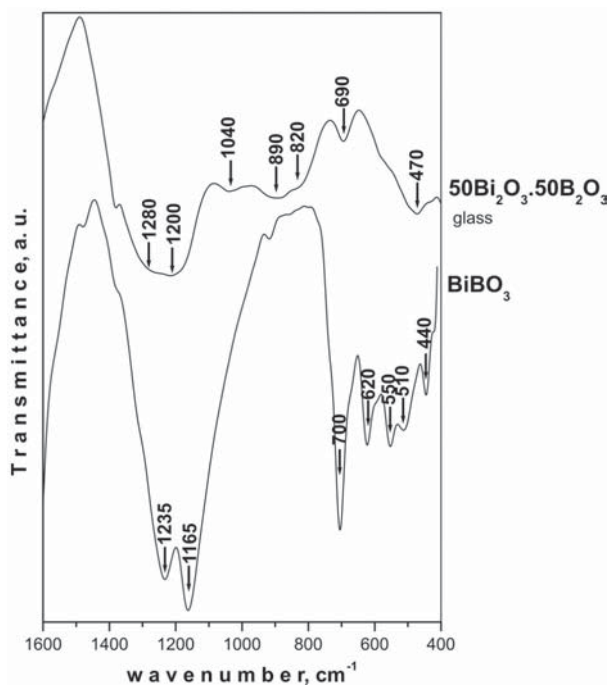


Fig. 6. IR spectra of the glass  $50\text{Bi}_2\text{O}_3.50\text{B}_2\text{O}_3$  and crystalline  $\text{BiBO}_3$

units. In the IR spectrum of crystalline sample the bands which are related to the  $\text{BO}_4$  vibrations are missing and overall it is similar to the results obtained by Egorysheva et al. [12] for the IR spectra of  $\text{BiBO}_3$  phase. The obtained results are an additional confirmation that  $\text{Bi}_2\text{O}_3$  favors the transformation of  $\text{BO}_3$  to  $\text{BO}_4$  units in the amorphous network [4, 18–21].

## CONCLUSIONS

Bismuth borate ( $\text{BiBO}_3$ ) 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 %  $\text{MoO}_3$  leads to the obtaining of  $\text{BiBO}_3\text{-I}$  and  $\text{BiBO}_3\text{-II}$  bismuth borate polymorphs. The increase in  $\text{MoO}_3$  content (2–5 mol%) stimulates the simultaneous crystallization of several phases –  $\text{BiBO}_3$ ,  $\text{Bi}_4\text{B}_2\text{O}_9$  and  $\text{Bi}_3\text{B}_5\text{O}_{12}$ . Further increase in  $\text{MoO}_3$  content (10 mol%) leads to the obtaining of  $\text{Bi}_2\text{MoO}_6$  (koechlinite) phase, only. IR results established that in the glasses the content of  $\text{BO}_4$  units is higher than in the crystallized sample.

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## REFERENCES

1. P. Becker, *Cryst. Res. Technol.*, **38**, 74 (2003).
2. I. Kityk, A. Majchrowski, *Opt. Mater.*, **25**, 33 (2004).
3. L. Li, G. Li, Y. Wang, F. Liao, *Chem. Mater.*, **17**, 4174 (2005).
4. A. Bajaj, A. Khanna, B. Chen, J. G. Longstaffe, U. W. Zwanziger, J. W. Zwanziger, Y. Gomez, F. Gonzalez, *J. Non-Cryst Sol.*, **355**, 45 (2009).

5. A. Bajaj, A. Khanna, N. Kulkarni, S. Aggarwal, *J. Amer. Ceram. Soc.*, **92**(5), 1036 (2009).
6. W. Dumbaugh, *Phys Chem Glasses*, **27**, 119 (1986).
7. O. Sanz, E. Haro-Poniatowski, J. Gonzalo, J. M. Fernandez Navarro, *J. Non-Cryst. Sol.*, **352**, 761 (2006).
8. E. Levin, C. McDaniel, *J. Amer. Ceram. Soc.*, **45**, 355 (1962).
9. M. J. Pottier, *Bull. Soc. Chim. Belg.*, **83**, 235 (1974).
10. P. Becker, R. Frohlich, *Z. Naturforsch.*, **59b**, 256 (2004).
11. R. Ihara, T. Honma, Y. Benino, T. Fujiwara, T. Komatsu, *Opt. Mater.*, **27**, 403 (2004).
12. A. V. Egorysheva, V. Burkov, Yu. Kargin, V. Plotnichenko, V. Koltashev, *Crystallogr. Rep.*, **50**(1) 127 (2005).
13. H. Hellwig, J. Lieberz, L. Bohaty, *J. Appl. Phys.*, **88**, 240 (2000).
14. L. Aleksandrov, R. Iordanova, Y. Dimitriev, *J. Non-Cryst Sol.*, **355**, 2023 (2009).
15. Y. Dimitriev, R. Iordanova, L. Aleksandrov, K. Kostov, *Phys. Chem. Glasses Eur. J. Glass Sci. Technol B*, **50**(3), 212 (2009).
16. Y. Dimitriev, R. Iordanova, *Phys. Chem. Glasses Eur. J. Glass Sci. B*, **50**(2), 123 (2009).
17. M. Krapchanska, R. Iordanova, Y. Dimitriev, A. Bachvarova-Nedelcheva, *J. Optoelect. Adv. Mater.*, **12**(8), 1692 (2010).
18. R. Iordanova, L. Aleksandrov, A. Bachvarova-Nedelcheva, M. AtaaLa, Y. Dimitriev, in: Proc 11-th Internat Conf on the Structure of Non-Cryst. Mater., 2011, in press.
19. E. Gateff, V. Dimitrov, Y. Dimitriev, A. Wright, in: Borate glasses, crystals and melts, A. Wright, S. Feller, A. Hannon (eds.), Society of Glass Technology, Sheffield, 1997, p. 112.
20. Y. Cheng, H. Xiao, W. Guo, *Ceram. Intern.*, **34**, 1335 (2008).
21. C. E. Stone, A. C. Wright, R. N. Sinclair, S. A. Feller, M. Affatigato, D. L. Hogan, C. Vira, Y. Dimitriev, E. Gateff, D. Earth, *Phys. Chem. Glasses*, **41**(6), 409 (2000).

## СИНТЕЗ НА $\text{BiVO}_3$ ЧРЕЗ КРИСТАЛИЗАЦИЯ НА СЪТЪКЛА В СИСТЕМАТА $\text{MoO}_3\text{--Bi}_2\text{O}_3\text{--B}_2\text{O}_3$

Р. С. Йорданова<sup>1</sup>, А. Д. Бъчварова-Неделчева<sup>1\*</sup>, Л. И. Александров<sup>1</sup>,  
Я. Б. Димитриев<sup>2</sup>

<sup>1</sup> *Институт по Обща и Неорганична Химия, Българска Академия на Науките,  
ул. „Акад. Г. Бончев“, бл. 11, 1113 София, България*

<sup>2</sup> *Химикотехнологичен и Металургичен Университет, бул. „Кл. Охридски“ 8,  
1756 София, България*

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(Резюме)

Целта на настоящата работа е да се провери възможността за синтез на  $\text{BiVO}_3$  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  $\text{BiVO}_3$ , както и на  $\text{Bi}_4\text{V}_2\text{O}_9$ ,  $\text{Bi}_3\text{V}_5\text{O}_{12}$  и  $\text{Bi}_2\text{MoO}_6$  кристални фази. Допълнителна информация за синтезирания  $\text{BiVO}_3$  бе получена и от инфрачервената спектроскопия (ИЧ). Има съществена разлика в ИЧ спектрите на стъклото със състав  $50\text{Bi}_2\text{O}_3\text{--}50\text{B}_2\text{O}_3$  и кристалния  $\text{BiVO}_3$  продукт. Причината за това е, че в стъклото съдържанието на  $\text{VO}_4$  групите е по-високо отколкото в кристалния образец.