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Structural study of glasses in the system B_2O_3-Bi_2O_3-La_2O_3-WO_3☆

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ABSTRACT

New multicomponent $(100-(x-y))\cdot(0.6B_2O_3\cdot0.4Bi_2O_3)\cdot xLa_2O_3\cdot yWO_3$, x = 0, 10; y = 0 ÷ 40 mol% glasses were obtained by melt quenching technique and its structure were examined by infrared and Raman spectroscopies. Based on the obtained spectral data it was suggested that in the absence of La_2O_3, tungsten incorporates into boro-bismuthate network in small quantities through Bi^{3+} and B—O—W bonds are not formed. Accumulation of Bi—O—W bonds stimulates crystallization processes. La_2O_3 is crucial to connect tungstate units with boro-bismuthate glass matrix and to realize amorphous network with their participation. It was supposed that in glasses with higher WO_3 content (30 and 40 mol%) two inconsisted glass networks are formed bismuth-borate one built up by BO_3, BO_4, BiO_6 units and tungstate one, built up mainly by WO_6. These networks are interconnected through lanthanum.

1. Introduction

Vitrification and glass stability in the Bi_2O_3–B_2O_3 system have been the object of many studies [1–10]. According to the literature the binary Bi_2O_3–B_2O_3 system is characterized with a large glass formation range of 20–88 mol% Bi_2O_3 [1–3]. However, depending on the preparation conditions, crucible materials, and cooling rates different glass formation regions and microheterogeneities have been obtained. Recently bismuth-borate glasses have attracted considerable interest as host materials for laser-active ions like Er^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+} [11–15], and can find applications as white light emitting diodes, and optoelectronic devices [16,17]. It has been reported that the glass structure of bismuth borate glasses can be stabilized by doping with RE oxides. In particular, $Bi_2O_3\cdot B_2O_3$ glasses doped with suitable amount of La_2O_3 could tighten the glass network structure and improve the microhardness of bismuth-borate glass [13,14,15]. The optical properties of rare-earth ions in bismuth borate glasses can be affected by varying the glass compositions (structural changes in the host glass matrix). There are a few papers [18–20] available in the literature, investigating the influence of WO_3 content on the optical properties of pure bismuth-borate and Eu^{2+} doped and Er^{3+}/Yb^{3+} co-doped bismuth-borate glasses. It is shown that introducing a suitable amount of WO_3 improves the optical characteristic of glasses. On the other hand tungsten oxide containing glasses have recently attracted increasing scientific interest as promising technological materials because of the specific thermal, mechanical, electrical and optical properties obtained by insertion of tungsten atoms inside the glass network. The extent and ability of incorporating WO_3 in glasses strongly depend on the glass former, size of ions in the glass structure, mobility of the modifier cation, etc. Stable glasses, having a high WO_3 content, where WO_3 can be regarded as glass-forming oxide are obtained in the systems, with participation of alkali metal oxides, TeO_2, P_2O_5 and Sb_2O_5 [21–24]. Glasses with high WO_3 content within a narrow concentration range (60–75 mol%) are obtained in tungstate systems containing simultaneously and other non-traditional glass formers such as V_2O_5, MoO_3, Bi_2O_3 [25,26]. Although B_2O_3 is a classical network former, glasses in binary B_2O_3-WO_3 systems were not obtained and liquid –phase separation is observed [27]. According to Vogel borate glasses containing fifth and sixth column elements (Nb, Ta, Mo, W) show a pronounced tendency toward unmixing [28]. Recently we have established that the introduction of La_2O_3 improves glass formation in the WO_3-B_2O_3. Stable glasses in the La_2O_3-WO_3-B_2O_3 system, containing up to 50 mol% WO_3 were obtained. It was suggested that tungsten ions are bounded to the BO_3 units through LaO_{10} polyhedra [29]. On the other hand it was reported that stable immiscibility prevents the formation of clear glasses over range 0 to 20 mol% La_2O_3, but excellent quality glasses could be formed between 20 and 28 mol% La_2O_3 in the B_2O_3-La_2O_3 system [30]. Therefore it is interesting from both fundamental and technological point of view to check the possibility of obtaining multicomponent bismuth-borate glass compositions with simultaneously participation of La_2O_3 and WO_3. The present work describes results over synthesis and structural characterization of $(100-(x-y))\cdot(0.6B_2O_3\cdot0.4Bi_2O_3)\cdot xLa_2O_3\cdot yWO_3$ glasses,

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☆ In memoriam of our teacher, Professor Yanko Dimitriev.

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Table 1
Nominal compositions of the samples (mol%).

Sample ID	B_2O_3	Bi_2O_3	La_2O_3	WO_3
BB1	60	40	–	–
BBW2	57.5	37.5	–	5
BBW2′	55	35	–	10
BBL3	55	35	10	–
BBLW4	48	32	10	10
BBLW5	42	28	10	20
BBLW6	36	24	10	30
BBLW7	30	20	10	40
BBLW8	24	16	10	50

$x = 0, 10$; $y = 0 \div 40$ mol%.

2. Materials and methods

The glass formation ability of the selected compositions, with a constant ratio $B_2O_3/Bi_2O_3 = 1.5$, without or containing 10 mol% La_2O_3 and varying WO_3 concentration of 0, 5, 10, 20, 30, 40, 50 mol% is investigated by applying of the melt quenching method. The nominal compositions of the glass samples and their sample ID's are given in Table 1. All specimens were prepared using reagent grade Bi_2O_3, H_3BO_3, La_2O_3 and WO_3. The homogenised batches were melted at the temperature range between 1000 and 1250 °C for 30 min in a platinum crucible in air. The melts were quenched by pouring and pressing between two copper plates (cooling rates 10^1–10^2 K/s). The phase formation of the samples was established by x-ray phase analysis with a Bruker D8 Advance diffractometer, using Cu K_α radiation in the $10 < 2\theta < 60$ range. The IR spectra of the glasses were measured using KBr pellet technique on a Nicolet-320 FTIR spectrometer with a resolution of ± 1 cm^{-1} in the range 1600–400 cm^{-1}. Each of the IR spectra was fitted with a sum of Gaussian curves by means of the least square method with the fit correlation coefficient - R^2 in the range $0.99916 \div 0.99978$. Raman scattering studies were performed on samples with Renishaw In-Via Reflex micro-Raman spectrometer using 514.5 nm argon ion laser (50 mW) as excitation source, diffraction grating having 2400 lines mm^{-1}, an edge filter for Stokes spectra and a Peltier cooled CCD detector. Measurements were carried out in an unpolarized mode, at room temperature in the backscattering geometry, in the Raman shift range from 100 to 2000 cm^{-1} with a spectral resolution of 1 cm^{-1}.

3. Results

3.1. X-ray phase analysis

Transparent yellowish glasses that change their color to pale orange with increasing WO_3 content were obtained in the system B_2O_3-Bi_2O_3-La_2O_3-WO_3. According to the XRD data (Fig. 1), binary BB1, ternary BBW2, BBL3 and quaternary BBLW4, BBLW2, BBLW3 and BBLW4 samples were x-ray amorphous. Glass-crystalline material exhibits an amorphous hallo and diffraction peaks corresponding to Bi_2WO_6 (JCPDS-00-039-0256) was quenched from the melt containing over 5 mol% of WO_3 without La_2O_3 (sample ID - BBW2′). Quenched quaternary sample containing 50 mol% WO_3 (sample ID - BBLW8) was amorphous but on its surface light droplets were observed. Probably the process of liquid phase separation occurs during the cooling of the melt. Future investigations are needed to clarify this phenomenon.

3.2. Result and analysis of IR spectra

The structure of the glasses is studied by IR and Raman spectroscopies (Figs. 2–5). Generally the IR spectra of borate glasses can be divided into three infrared regions [31–36]. The first groups of bands which are located in the 1500–1200 cm^{-1} spectral region are due to the B—O stretching vibrations in BO_3 units participating in different borate groups. The bands situated in the 1100–800 cm^{-1} frequency range are connected with the vibrations of B—O bonds in BO_4 units and the bands observed around 700 cm^{-1} are due to the bending vibrations of B—O—B linkages.

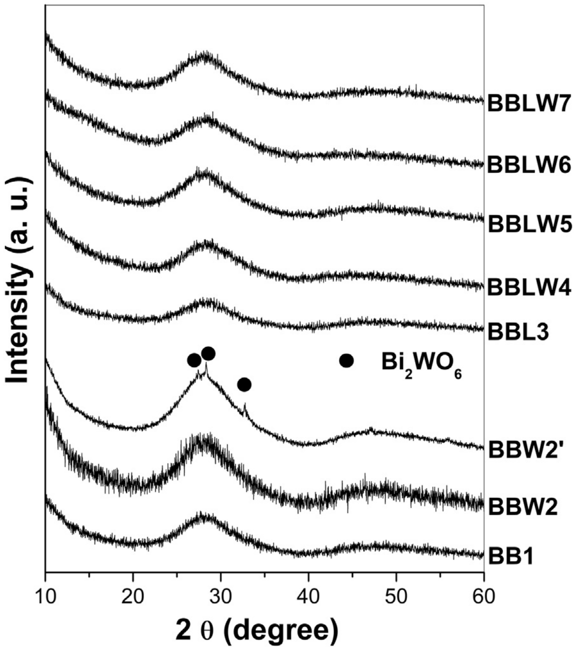

Fig. 1. XRD patterns of glasses in the B_2O_3-Bi_2O_3-La_2O_3-WO_3 system (see Table 1).

The observed absorption bands in the IR spectra of binary BB1 glass obtained by us are in agreement with the known short range order of bismuth-borate glasses with a similar composition [2,10,11,37,38]. The glass spectrum is characterized by broad and unresolved bands due to the overlapping of the vibrations of different borate groups (Fig. 2a, spectrum BB1). That is why a deconvolution of the spectrum should be made to separate the vibrations of different structural units. In this way in the broad band between 1500 and 1200 cm^{-1} three peaks at 1392 cm^{-1}, 1314 cm^{-1} and 1213 cm^{-1} are observed (Fig. 2b, Glass BB1). The most intense band at 1314 cm^{-1} is due to the stretching vibration of BO_3 groups involved in superstructural units (BO_3 + BO_4) [31,34,39–42]. The band at 1213 cm^{-1} can be associated with the BO_3 stretching vibration in meta-, pyro- and orthoborate structures [31,34,39–41]. The band at 1392 cm^{-1} can be attributed to the stretching vibration of non-bridging $B—O^-$ bonds (NBOs) in BO_3 from various type borate groups [31,34,39–41]. In the absorption region of BO_4, four bands at 1042 cm^{-1}, 990 cm^{-1}, 915 cm^{-1} and 825 cm^{-1} are evident. These bands are attributed to the vibrations of BO_4 units from di-, tri-, tetra- and penta-borate groups [34,42]. The band at 685 cm^{-1}, is due to the bending vibration of B—O—B bonds in superstructural units, containing BO_3 and BO_4 groups [11,43]. The assignment of the band at 627 cm^{-1} is complicated. This band could be attributed to the bending vibration of B—O—B bonds in meta- and pyroborates built up by BO_3 units [44,45]. On the other hand, the vibrations of distorted BiO_6 units are at about 620 cm^{-1} and 480 cm^{-1} [10,11,25,46–49]. The appearance of several bands in the low frequency region at about 475 cm^{-1}, 503 cm^{-1} and 627 cm^{-1} can be due to the vibrations of highly distorted BiO_6.

The addition of 5 mol% WO_3 in the $60B_2O_3{\cdot}40Bi_2O_3$ glass matrix, produces some changes in the IR spectrum (Fig. 2a, spectrum BBW2). More precise after the deconvolution of the spectrum of BBW2 glass (Fig. 2c), the bands in the 1500 cm^{-1}–1200 cm^{-1} range slightly shift to the higher wavenumbers. The bands at 1217 cm^{-1} and 1405 cm^{-1} rise in intensity while the band at 1325 cm^{-1} decreases. These spectral