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Crystallization of bismuth borate glasses

Anu Bajaj and Atul Khanna¹

Department of Applied Physics, Guru Nanak Dev University, Amritsar 143005, Punjab, India

E-mail: ak.ap@gndu.ac.in

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Abstract

Bismuth borate glasses with Bi_2O_3 concentration of 20–66 mol% were prepared by melt quenching and devitrified by heat treatment above their glass transition temperatures. All glasses show a strong tendency towards crystallization on annealing that increases with Bi_2O_3 concentration. The crystalline phases formed on devitrification were characterized by FTIR absorption spectroscopy and DSC measurements. Our studies reveal that phases produced in glasses are strongly determined by initial glass composition and the two most stable crystalline phases are: $\text{Bi}_3\text{B}_5\text{O}_{12}$ and $\text{Bi}_4\text{B}_2\text{O}_9$. The metastable BiBO_3 phase can also be formed by devitrification of glass with 50 mol% of Bi_2O_3 . This phase is, however, unstable and decomposes into $\text{Bi}_3\text{B}_5\text{O}_{12}$ and $\text{Bi}_4\text{B}_2\text{O}_9$ on prolonged heat treatment.

1. Introduction

Bismuth borate crystals and glasses have attracted significant interest in recent years due to their several outstanding properties like wide glass formation range of 20–80 mol% Bi_2O_3 , high density and refractive indices [1–4], and large coefficients for second and third harmonic generation [5–10]. At least five stable crystalline phases of the Bi_2O_3 – B_2O_3 system: bismuth octaborate ($\text{Bi}_2\text{B}_8\text{O}_{15}$) [11–13], bismuth triborate (BiB_3O_6) [11, 14–17], $\text{Bi}_3\text{B}_5\text{O}_{12}$ [11, 18, 19], $\text{Bi}_4\text{B}_2\text{O}_9$ [11, 20] and boron sillenite ($\text{Bi}_{24}\text{B}_2\text{O}_{39}$) [11, 21], and metastable bismuth orthoborate (BiBO_3) phases are known to exist [22–24]. $\text{Bi}_2\text{B}_8\text{O}_{15}$, BiB_3O_6 and BiBO_3 phases exhibit polymorphism. BiB_3O_6 is reported to have at least three polymorphs, one which has only tetrahedrally coordinated borons and another with only triangularly coordinated borons [17]. The metastable BiBO_3 has two polymorphs: BiBO_3 -I and BiBO_3 -II; the latter is a low temperature and more disordered crystalline phase [22, 24] with very high coefficients for nonlinear optical effects [24]. It is likely that polymorphism exists in other bismuth borate compounds as a function of temperature or pressure, a phenomenon which is strongly facilitated by two B–O coordination numbers of 3 and 4. The boron–oxygen coordination in borates can be significantly tailored by changes in composition [25–27], temperature [28–32] and pressure [33, 34]. Single crystals of all the above phases have been successfully grown and characterized with the primary objective of application of these materials in nonlinear optical devices [7, 8, 12, 19–21, 23].

¹ Author to whom any correspondence should be addressed.

The study of crystallization of glasses (devitrification) is important from a fundamental point of view as it provides insights about the relationship between a glass and its corresponding crystalline structure. According to Krogh-Moe's model of borates the short-range order (SRO) of glasses is identical to that of corresponding crystalline phases and that randomly oriented crystal-like entities exist in borate glasses [35]. The identification and characterization of crystalline phases formed on heat treatment of borate glasses and their correlation with initial glass structure and properties can test the validity of this model. Several borate and borosilicate glasses show phase separation on annealing above the glass transition temperature. Therefore the study of heat treatment effects on glasses is also important for understanding their thermal stability.

In this paper we report the preparation of glasses from the system: $x\text{Bi}_2\text{O}_3$ – $(100 - x)\text{B}_2\text{O}_3$ ($20 \leq x \leq 66$ mol%). Glass-ceramic samples were prepared by annealing the glasses at temperatures above their glass transition temperature for several hours and characterized by vibrational (FTIR) absorption spectroscopy and DSC measurements.

2. Experimental procedure

2.1. Glass preparation

Glass samples from the system $x\text{Bi}_2\text{O}_3$ – $(100 - x)\text{B}_2\text{O}_3$ ($x = 20, 25, 30, 33, 37.5, 40, 42, 47, 50, 55, 60$ and 66) were prepared by the melt quenching method. Appropriate amounts of Bi_2O_3 (Aldrich 99.9%) and H_3BO_3 (Merck, ACS grade)

Table 1. Composition of bismuth borate glasses prepared and devitrified.

Glass sample no.	Composition (mol%)	
	Bi ₂ O ₃	B ₂ O ₃
1	20	80
2	25	75
3	30	70
4	33	67
5	37.5	62.5
6	40	60
7	42	58
8	47	53
9a	50	50
9b	50	50
10 ^a	50	50
11 ^b	50	50
12	53	47
13	55	45
14	60	40
15	66	34

^a Doped with 1000 ppm of Li₂O.^b Doped with 5000 ppm of Al₂O₃.

were weighed and thoroughly mixed in an agate mortar–pestle and transferred to a platinum crucible (25 ml capacity) and sintered at 250 and 450 °C for 24 h each to completely dehydrate H₃BO₃. The furnace temperature was then raised (250 °C h⁻¹) and the batch mixture was melted in a temperature range of 700–950 °C. The platinum crucible was occasionally swirled inside the furnace to homogenize the glass melt and quenched on a massive brass block. Button-shaped samples were obtained and immediately transferred to an annealing furnace maintained at 300–350 °C. Glasses were annealed for about 30 min to reduce thermal stresses generated by non-uniform cooling of the melt. Bismuth borate glasses with 66 mol% of Bi₂O₃ were prepared by the splat quenching technique to prevent crystallization. Glasses prepared by splat quenching were not given an annealing treatment. Two 50Bi₂O₃–50B₂O₃ glass samples were prepared by doping with 1000 and 5000 ppm of Li⁺ and Al³⁺ ions, respectively. Table 1 gives the composition of bismuth borate glasses that were prepared and subsequently devitrified (crystallized) in this study.

2.2. Preparation of crystalline phases

Bismuth borate glasses prepared as above were devitrified by heat treatment in the temperature range of 500–625 °C for several hours. This temperature is above the reported glass transition temperature of all bismuth borate glasses [1, 3, 4, 26]. The first glass containing 20 mol% of Bi₂O₃ (sample 1) was annealed for 41 h as it produced only small amounts of crystallinity after its initial heat treatment for 17 h. We crystallized two samples of bismuth borate glass containing 50 mol% of Bi₂O₃. One glass (sample 9a) of this composition was devitrified by annealing at 500 °C for 5 h while its second glass sample with the same nominal composition (sample 9b) was annealed at 550 °C for 17 h. Table 2 gives preparation details of all devitrified samples.

Table 2. Heat treatment conditions for devitrification of bismuth borate glasses.

Sample no.	Heat treatment
1CR	Glass sample 1 heat-treated at 550 °C for 41 h
2CR	Glass sample 2 heat-treated at 550 °C for 17 h
3CR	Glass sample 3 heat-treated at 550 °C for 17 h
4CR	Glass sample 4 heat-treated at 550 °C for 17 h
5CR	Glass sample 5 heat-treated at 550 °C for 17 h
6CR	Glass sample 6 heat-treated at 615 °C for 38 h
7CR	Glass sample 7 heat-treated at 550 °C for 17 h
8CR	Glass sample 8 heat-treated at 550 °C for 17 h
9aCR	Glass sample 9a heat-treated at 500 °C for 5 h
9bCR	Glass sample 9b heat-treated at 550 °C for 17 h
10CR	Glass sample 10 heat-treated at 550 °C for 17 h
11CR	Glass sample 11 heat-treated at 550 °C for 17 h
12CR	Glass sample 12 heat-treated at 550 °C for 17 h
13CR	Glass sample 13 heat-treated at 550 °C for 17 h
14CR	Glass sample 14 heat-treated at 550 °C for 17 h
15CR	Glass sample 15 heat-treated at 550 °C for 17 h

2.3. FTIR absorption spectroscopy

The mid-infrared absorption spectra of all crystallized samples were measured on a Shimadzu (Model 8400S) Fourier-transform infrared (FTIR) spectrophotometer in the wavenumber range of 2000–400 cm⁻¹ by the KBr pellet technique with a spectral resolution of 4 cm⁻¹.

2.4. DSC measurements

Thermal properties of crystallized samples were measured on a Perkin-Elmer Diamond Pyris differential scanning calorimeter (DSC). Measurements were performed on powdered samples in Pt pans at a heating rate of 10 K min⁻¹ under air ambient (200 ml min⁻¹). Sample amounts of 15–20 mg were used during DSC experiments.

3. Results and discussion

We have reported detailed structure–property correlations in bismuth borate glasses elsewhere [26]. In this study we focus on the characterization of crystalline phases produced by devitrification of glasses by FTIR and DSC measurements.

Figures 1(a)–(d) display the FTIR absorption spectra of all crystallized glasses. The vibrational spectra of crystalline

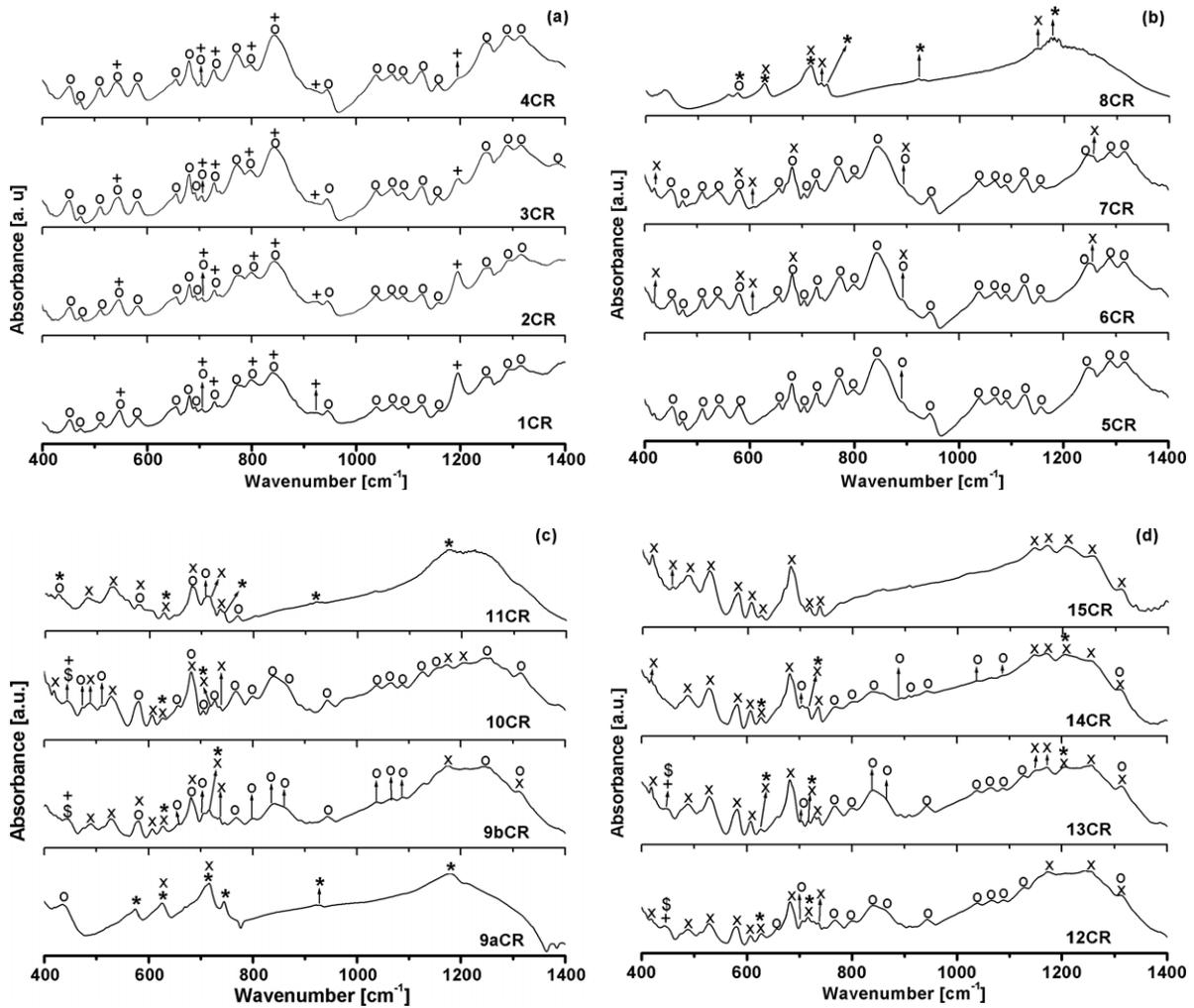


Figure 1. (a)–(d) FTIR absorption spectra of crystallized bismuth borate glasses. ((+) $\text{Bi}_2\text{B}_8\text{O}_{15}$, (\$) BiB_3O_6 , (o) $\text{Bi}_3\text{B}_5\text{O}_{12}$, (*) BiBO_3 and (x) $\text{Bi}_4\text{B}_2\text{O}_9$.)

phases of bismuth borates: $\text{Bi}_2\text{B}_8\text{O}_{15}$, BiB_3O_6 , $\text{Bi}_3\text{B}_5\text{O}_{12}$, BiBO_3 , $\text{Bi}_4\text{B}_2\text{O}_9$ and $\text{Bi}_{24}\text{B}_{20}\text{O}_{39}$ have absorption peaks at characteristic wavenumbers. Egorysheva *et al* prepared single crystals of bismuth borates and measured their mid-IR absorption spectra [36]. We have used the reported IR spectral data [36] to identify the crystalline phases that are formed in devitrified glasses (samples 1CR–15CR). Tables 3 and 4 give the IR absorption peak positions (in cm^{-1}) and the crystalline phases that are formed in each sample.

The first glass (sample 1CR) has a composition that equals the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase and expectedly produces this phase on annealing. The most prominent and distinct peak due to $\text{Bi}_2\text{B}_8\text{O}_{15}$ is the strong absorption peak at 1195 cm^{-1} (figure 1(a) and table 3). We also observe a strong absorption shoulder centered at about 928 cm^{-1} that can be attributed to $\text{Bi}_2\text{B}_8\text{O}_{15}$. Other peaks that can be due to the bismuth octaborate phase are centered at 548, 704, 729, 799 and 843 cm^{-1} . These peaks can also be due to the $\text{Bi}_3\text{B}_5\text{O}_{12}$ phase, which seems to be present at significantly higher concentration than the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase (table 3 and figure 1(a)). The formation of $\text{Bi}_3\text{B}_5\text{O}_{12}$ indicates that, besides the following

crystallization mechanism:



Other reactions, like thermal decomposition of the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase, may also be occurring during the thermal annealing process as below:



It is, however, reported that the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase is thermally stable right up to its melting temperature of $715 \pm 5^\circ\text{C}$ [11–13]. Therefore it is likely that $\text{Bi}_2\text{B}_8\text{O}_{15}$ actually does not decomposes on heat treatment at 550°C (for 41 h) according to equation (2) but some regions of the initial glass crystallize directly into the $\text{Bi}_3\text{B}_5\text{O}_{12}$ phase and B_2O_3 precipitates by the following mechanism:



In other words, parts of the initial glass crystallize into the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase while some parts crystallize into the $\text{Bi}_3\text{B}_5\text{O}_{12}$ phase and B_2O_3 precipitates. This in turn indicates the

Table 3. IR absorption peak positions of crystalline phases in devitrified bismuth borate glasses. Maximum uncertainty in peak position is $\pm 2 \text{ cm}^{-1}$. ('s' denotes an absorption shoulder).

Sample no.	IR absorption bands (cm^{-1})	Crystal phases
1CR	548, 704, 729, 799, 843, 928(s), 1195 453, 473, 511, 548, 581, 656, 681, 691, 704, 729, 773, 799, 841, 945, 1037, 1069, 1089, 1126, 1159, 1248, 1289, 1316	$\text{Bi}_2\text{B}_8\text{O}_{15}$ $\text{Bi}_3\text{B}_5\text{O}_{12}$
2CR	548, 704, 729, 799, 843, 928(s), 1195 453, 473, 511, 548, 581, 656, 681, 691, 704, 729, 773, 799, 843, 945, 1040, 1069, 1089, 1126, 1159, 1248, 1289, 1315	$\text{Bi}_2\text{B}_8\text{O}_{15}$ $\text{Bi}_3\text{B}_5\text{O}_{12}$
3CR	548, 704, 729, 799, 843, 928(s), 1195 453, 473, 511, 548, 581, 656, 681, 691, 704, 729, 773, 799, 843, 945, 1040, 1069, 1089, 1126, 1159, 1248, 1289, 1315, 1386	$\text{Bi}_2\text{B}_8\text{O}_{15}$ $\text{Bi}_3\text{B}_5\text{O}_{12}$
4CR	545, 704, 729, 799, 843, 928(s), 1195(s) 453, 473, 511, 545, 581, 656, 681, 704, 729, 773, 799, 843, 945, 1040, 1069, 1089, 1126, 1159, 1248, 1289, 1315	$\text{Bi}_2\text{B}_8\text{O}_{15}$ $\text{Bi}_3\text{B}_5\text{O}_{12}$
5CR	453, 473, 511, 545, 580, 655, 681, 705, 729, 773, 799, 843, 892, 944, 1039, 1069, 1089, 1127, 1157, 1249, 1288, 1316	$\text{Bi}_3\text{B}_5\text{O}_{12}$
6CR	453, 473, 511, 540, 580, 655, 681, 705, 729, 773, 799, 843, 892, 944, 1039, 1069, 1089, 1127, 1157, 1249, 1288, 1316 420, 580, 606, 681, 892, 1257	$\text{Bi}_3\text{B}_5\text{O}_{12}$ $\text{Bi}_4\text{B}_2\text{O}_9$
7CR	453, 473, 511, 540, 580, 656, 681, 705, 728, 773, 799, 843, 892, 944, 1039, 1069, 1089, 1127, 1157, 1249, 1288, 1316 420, 580, 606, 681, 892, 1257	$\text{Bi}_3\text{B}_5\text{O}_{12}$ $\text{Bi}_4\text{B}_2\text{O}_9$
8CR	576 576, 627, 716, 747, 925, 1180 627, 716, 736, 1150	$\text{Bi}_3\text{B}_5\text{O}_{12}$ BiBO_3 $\text{Bi}_4\text{B}_2\text{O}_9$
12CR	447 447 659, 706, 771, 800, 841, 865, 943, 1037, 1067, 1088, 1129, 1312 627, 716 420, 490, 528, 581, 608, 627, 681, 716, 737, 1175, 1254, 1312	$\text{Bi}_2\text{B}_8\text{O}_{15}$ BiB_3O_6 $\text{Bi}_3\text{B}_5\text{O}_{12}$ BiBO_3 $\text{Bi}_4\text{B}_2\text{O}_9$
13CR	447 447 706, 770, 799, 839, 865, 943, 1037, 1066, 1088, 1127, 1312 627, 718, 1206 420, 488, 529, 583, 607, 627, 682, 718, 737, 1150, 1171, 1206, 1254, 1312	$\text{Bi}_2\text{B}_8\text{O}_{15}$ BiB_3O_6 $\text{Bi}_3\text{B}_5\text{O}_{12}$ BiBO_3 $\text{Bi}_4\text{B}_2\text{O}_9$
14CR	704, 770, 800, 839, 890, 909, 943, 1037, 1088, 1313 628, 718, 1208 420, 487, 531, 581, 607, 628, 684, 718, 736, 1149, 1171, 1208, 1257, 1313	$\text{Bi}_3\text{B}_5\text{O}_{12}$ BiBO_3 $\text{Bi}_4\text{B}_2\text{O}_9$
15CR	421, 458, 488, 528, 581, 609, 628, 683, 718, 737, 1149, 1174, 1209, 1254, 1313	$\text{Bi}_4\text{B}_2\text{O}_9$

existence of structural heterogeneities in bismuth borate glass containing 20 mol% of Bi_2O_3 (sample 1). The DSC pattern of this crystallized sample (1CR) is displayed in figure 2 and the values of various endothermic and exothermic transition temperatures (peak points) are presented in table 5. We observe one broad endothermic transition peak centered at 117°C . It is known that $\text{Bi}_2\text{B}_8\text{O}_{15}$ crystals suffer a broad, sluggish and reversible phase transition between 100 and 117°C [12]. Therefore the peak at 117°C is due to this phase transition phenomenon of $\text{Bi}_2\text{B}_8\text{O}_{15}$. This sample also exhibits a glass transition at 460°C , indicating that it has significant amounts of glassy phase, which did not fully crystallize even after 41 h of heat treatment at 550°C . Because the sample is not fully crystalline, it shows a broad exothermic crystallization peak at 596°C and a liquidus peak at 665°C . $\text{Bi}_2\text{B}_8\text{O}_{15}$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$ phases have melting points of 715 ± 5 and

$722 \pm 5^\circ\text{C}$, respectively [11]. We do not observe sharp melting peaks at these two temperatures since there exists a mixture of $\text{Bi}_2\text{B}_8\text{O}_{15}$, $\text{Bi}_3\text{B}_5\text{O}_{12}$ and B_2O_3 along with the remaining glassy phase in the devitrified sample.

Sample 2CR is devitrified bismuth triborate glass containing 25 mol% of Bi_2O_3 . This glass (sample 2) interestingly does not form the crystalline bismuth triborate (BiB_3O_6) phase on its heat treatment although its composition is equal to it, but rather $\text{Bi}_3\text{B}_5\text{O}_{12}$ and $\text{Bi}_2\text{B}_8\text{O}_{15}$ phases. These two phases can be produced from the initial glass (sample 2) by the following mechanism:



The crystallized sample 2CR is predominantly $\text{Bi}_3\text{B}_5\text{O}_{12}$ but it also contains the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase. The latter's presence is proved by the observation of a strong absorption peak at

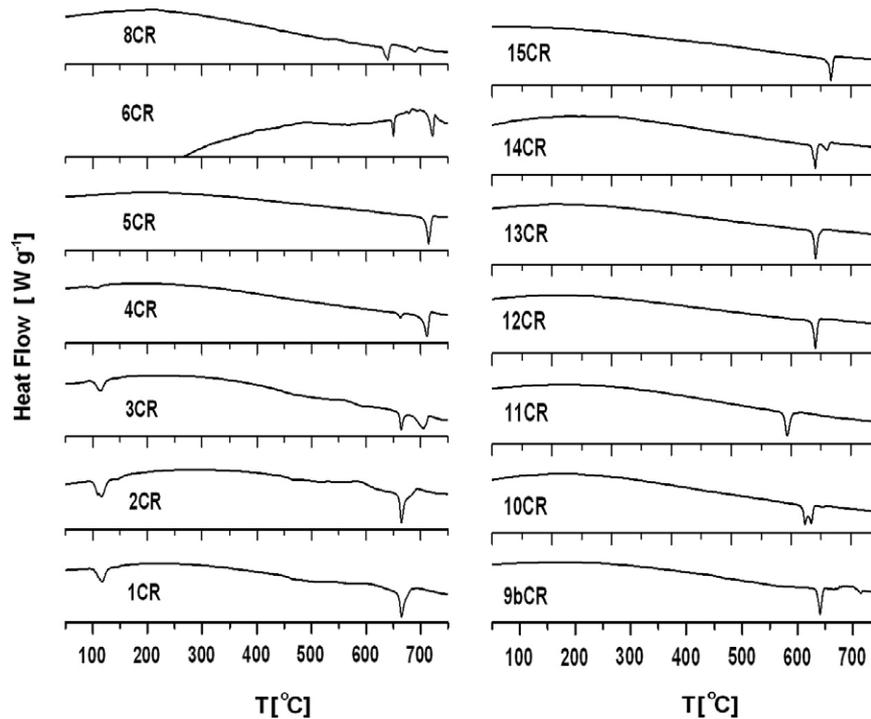


Figure 2. DSC patterns of crystallized bismuth borate glasses.

Table 4. IR absorption peaks of crystalline phases in devitrified $50\text{Bi}_2\text{O}_3\text{-}50\text{B}_2\text{O}_3$ glasses doped with Li and Al ions ((s) denotes an absorption shoulder).

Sample no.	IR absorption bands (cm^{-1})	Crystal phases
9aCR	436 575, 628, 717, 747, 929, 1180 628, 717	$\text{Bi}_3\text{B}_5\text{O}_{12}$ BiBO_3 $\text{Bi}_4\text{B}_2\text{O}_9$
9bCR	447 447 581, 658, 682, 704, 769, 799, 839, 861, 944, 1039, 1067, 1090, 1249, 1312 628, 717 489, 528, 579, 607, 628, 682, 717, 737, 1174, 1312	$\text{Bi}_2\text{B}_8\text{O}_{15}$ BiB_3O_6 $\text{Bi}_3\text{B}_5\text{O}_{12}$ BiBO_3 $\text{Bi}_4\text{B}_2\text{O}_9$
10CR	447 447 474, 513, 580, 657, 681, 704, 728, 770, 800, 841, 864, 943, 1037, 1067, 1087, 1126, 1157, 1248, 1314 627, 717 420, 486, 528, 606, 627, 681, 717, 737, 1173, 1207	$\text{Bi}_2\text{B}_8\text{O}_{15}$ BiB_3O_6 $\text{Bi}_3\text{B}_5\text{O}_{12}$ BiBO_3 $\text{Bi}_4\text{B}_2\text{O}_9$
11CR	426, 581, 681, 709, 771 426, 627, 745, 928(s), 1178 486, 531, 581, 627, 681, 718, 737	$\text{Bi}_3\text{B}_5\text{O}_{12}$ BiBO_3 $\text{Bi}_4\text{B}_2\text{O}_9$

1195 cm^{-1} and an absorption shoulder at $\sim 928\text{ cm}^{-1}$ and other peaks at $548, 704, 729, 799$ and 843 cm^{-1} in its FTIR spectrum (figure 1(a) and table 3). The DSC pattern of this sample (2CR) shows endothermic transitions at 110 and $116\text{ }^\circ\text{C}$, which is the signature of the bismuth octaborate phase (figure 2 and table 5). We also observe a glass transition at $458\text{ }^\circ\text{C}$ (midpoint value) indicating that this crystallized sample has a significant remnant glassy phase.

It is reported that crystallization of $\text{Bi}_2\text{O}_3\text{-}3\text{B}_2\text{O}_3$ melt depends strongly on its thermal history [37]. In particular, bismuth triborate melt does not crystallize into the BiB_3O_6

phase but instead forms $\text{Bi}_2\text{B}_8\text{O}_{15}$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$ phases on solidification, if the initial melt is overheated. Therefore the reason why our glass sample 2 did not crystallize into the BiB_3O_6 phase on heat treatment could be due to its melt history, which was such that it produces $\text{Bi}_3\text{B}_5\text{O}_{12}$ and $\text{Bi}_2\text{B}_8\text{O}_{15}$ crystal-like entities in the glass which act as nucleating centers and cause crystallization according to equation (4).

FTIR studies reveal that $\text{Bi}_3\text{B}_5\text{O}_{12}$ is the predominant phase in samples 3CR and 4CR with small amounts of $\text{Bi}_2\text{B}_8\text{O}_{15}$, as evidenced by the IR absorption peak at

Table 5. Thermal properties of crystallized bismuth borate glasses (all temperature values are in °C and maximum error is ±1 °C).

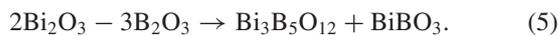
Sample no.	T_{d1}	T_{d2}	T_g	T_{c1}	T_{m1}	T_{m2}	T_{m3}	T_{m4}
1CR	117	143	460	596	665	—	—	—
2CR	110	116	458	582	665	—	—	—
3CR	115	142	451	557	664	705	742	—
4CR	107	—	—	—	662	712	—	—
5CR	107	—	—	—	634	715	—	—
6CR	—	—	—	—	650	679	722	—
8CR	—	—	436	547	635	639	690	718
9bCR	—	—	458	—	641	666	715	—
10CR	—	—	—	—	623	634	653	—
11CR	—	—	—	—	—	593	—	—
12CR	—	—	—	—	641	660	—	—
13CR	—	—	—	—	641	—	—	—
14CR	—	—	—	—	638	641	660	—
15CR	—	—	—	—	—	668	—	—

1195 cm^{-1} (figure 1(a) and table 3). The intensity of this peak decreases as Bi_2O_3 concentration is increased from 20 to 33 mol%. Sample 4CR exhibits an absorption shoulder at 1195 cm^{-1} . Similarly the intensity of an absorption shoulder centered at $\sim 928 \text{ cm}^{-1}$ (attributed to the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase) also decreases on moving from sample 1CR to 4CR.

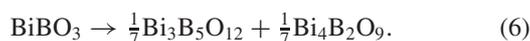
On comparing the FTIR spectra of samples 1CR to 4CR (figure 1(a)) we note that the intensity of the peak at 548 cm^{-1} (due to both $\text{Bi}_2\text{B}_8\text{O}_{15}$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$) is relatively greater than the intensity of peaks at 511 and 581 cm^{-1} (only due to $\text{Bi}_3\text{B}_5\text{O}_{12}$). This strongly indicates that the peak at 548 cm^{-1} in sample 1CR is mostly due to the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase. The relative intensity of this peak decreases as we move from sample 1CR to 4CR, because the formation of $\text{Bi}_2\text{B}_8\text{O}_{15}$ decreases in comparison to $\text{Bi}_3\text{B}_5\text{O}_{12}$. The DSC patterns of devitrified glasses containing 30 and 33 mol% of Bi_2O_3 (samples 3CR and 4CR) exhibit broad, endothermic transition peaks centered at 115 and 107 °C, respectively, which again indicates that the $\text{Bi}_2\text{B}_8\text{O}_{15}$ phase is indeed produced on devitrification of glass samples 3 and 4.

Sample 5CR, which is formed by crystallization of glass sample 5 (37.5 mol% of Bi_2O_3), is entirely the $\text{Bi}_3\text{B}_5\text{O}_{12}$ phase as determined by FTIR measurements (figure 1(b)). The DSC pattern of this sample exhibits one very weak liquidus peak at 634 °C and another very strong peak at 715 °C: the latter is attributed to the melting of the $\text{Bi}_3\text{B}_5\text{O}_{12}$ phase [11].

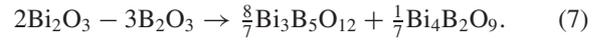
The glass sample with 40 mol% of Bi_2O_3 ($2\text{Bi}_2\text{O}_3 - 3\text{B}_2\text{O}_3$, sample 6) produces $\text{Bi}_3\text{B}_5\text{O}_{12}$ and $\text{Bi}_4\text{B}_2\text{O}_9$ phases on crystallization. This can be understood by the following mechanism:



The BiBO_3 (bismuth orthoborate) phase produced by equation (5) is metastable and decomposes into $\text{Bi}_3\text{B}_5\text{O}_{12}$ and $\text{Bi}_4\text{B}_2\text{O}_9$ phases on heat treatment for an extended time period of 17 h at 550 °C by the following reaction:



The overall devitrification reaction of glass 6 can therefore be written as

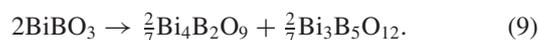


FTIR studies do not provide any clear evidence for the formation of the $\text{Bi}_4\text{B}_2\text{O}_9$ phase in samples 6CR and 7CR as their spectra are very similar to that of sample 5CR. The latter is expected to be entirely the $\text{Bi}_3\text{B}_5\text{O}_{12}$ phase due to the composition ($37.5\text{Bi}_2\text{O}_3 - 62.5\text{B}_2\text{O}_3$) of its initial glass (sample 5). Samples 6CR and 7CR exhibit two very weak peaks at 420 and 606 cm^{-1} which can be attributed only due to the $\text{Bi}_4\text{B}_2\text{O}_9$ phase (figure 1(b)). The DSC results for sample 6CR, however, strongly suggest that the $\text{Bi}_4\text{B}_2\text{O}_9$ phase is indeed present in it. We observe three liquidus peaks at 650, 679 and 722 °C in sample 6CR (figure 2 and table 5). The peaks at 650 and 722 °C are very strong compared to the peak at 679 °C, which is weak. It is known that the $\text{Bi}_4\text{B}_2\text{O}_9$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$ phases have a eutectic point at 648 °C [11], therefore the peak at 650 °C is likely to be this eutectic temperature. The peak at 722 °C is clearly the melting peak of the $\text{Bi}_3\text{B}_5\text{O}_{12}$ phase while the peak at 679 °C is in all probability the melting peak of the $\text{Bi}_4\text{B}_2\text{O}_9$ phase [11, 20]. The glass sample with 47 mol% of Bi_2O_3 (sample 8) produces mostly the metastable BiBO_3 phase on crystallization along with small amounts of the $\text{Bi}_3\text{B}_5\text{O}_{12}$ and $\text{Bi}_4\text{B}_2\text{O}_9$ phases.

Two glasses with initial composition of 50 mol% of Bi_2O_3 (samples 9a and 9b) were crystallized by heat treatment. One glass (sample 9a) was annealed at 500 °C for 5 h while the second glass with the same composition (sample 9b) was annealed at 550 °C for 17 h. The FTIR spectra of crystallized sample 9aCR shows that it is mostly the metastable BiBO_3 phase with small amounts of $\text{Bi}_4\text{B}_2\text{O}_9$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$ phases (figure 1(c) and table 4). BiBO_3 is metastable and has two known polymorphs: $\text{BiBO}_3\text{-I}$ and $\text{BiBO}_3\text{-II}$. Interestingly BiBO_3 was missing in the original phase diagram of the $\text{Bi}_2\text{O}_3 - \text{B}_2\text{O}_3$ system [11], but its existence was first proved by Pottier [22]. Growth of single crystals of the $\text{BiBO}_3\text{-I}$ phase has been reported in the literature [23].

The second crystalline sample 9bCR obtained by heat treatment of the $50\text{Bi}_2\text{O}_3 - 50\text{B}_2\text{O}_3$ glass (sample 9b) for a longer time of 17 h is predominantly $\text{Bi}_3\text{B}_5\text{O}_{12}$ and $\text{Bi}_4\text{B}_2\text{O}_9$ phases with small traces of the BiBO_3 phase. This is because BiBO_3 decomposes to $\text{Bi}_4\text{B}_2\text{O}_9$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$ phases on heat treatment for 17 h according to the reaction shown in equation (6). We also prepared two $50\text{Bi}_2\text{O}_3 - 50\text{B}_2\text{O}_3$ glasses doped with 1000 ppm and 5000 ppm of Li_2O and Al_2O_3 (glasses 10 and 11, respectively) to study how the formation of the metastable BiBO_3 phase is influenced by the presence of Li^+ and Al^{3+} dopant ions in the glass matrix. Both glass samples 10 and 11 were devitrified by annealing at 550 °C for 17 h. FTIR studies found that devitrification produces $\text{Bi}_4\text{B}_2\text{O}_9$ and $\text{Bi}_3\text{B}_5\text{O}_{12}$ phases in both glasses. The devitrified glass doped with Al^{3+} (sample 11CR) contains significant amounts of the BiBO_3 phase but one doped with Li^+ (sample 10CR) exhibits only two weak peaks at 627 and 717 cm^{-1} which can be attributed to both BiBO_3 and $\text{Bi}_4\text{B}_2\text{O}_9$ phases. We therefore conclude that Li^+ doping suppresses the formation of the crystalline BiBO_3 phase.

The glass with 53 mol% of Bi₂O₃ (sample 12) produces mostly Bi₃B₅O₁₂ and Bi₄B₂O₉ phases on devitrification. As we increase Bi₂O₃ content, crystallization of glasses produces increasing amounts of Bi₄B₂O₉ phase (figure 1(d) and table 3). The glass with 60 mol% of Bi₂O₃ (3Bi₂O₃–2B₂O₃, sample 14) produces primarily Bi₃B₅O₁₂ and Bi₄B₂O₉ phases. These phases can be formed by the following mechanisms:



The overall reaction is



The DSC pattern of this crystallized sample (14CR) exhibits three endothermic liquidus peaks at 638, 641 and 660 °C, which arise due to eutectic points of the Bi₄B₂O₉, Bi₃B₅O₁₂ and BiBO₃ phases.

The last glass sample 15 (66 mol% Bi₂O₃) produces only the Bi₄B₂O₉ phase on heat treatment at 550 °C for 17 h. This is expected as the initial glass (sample 15) has a composition which is very close to Bi₄B₂O₉. The DSC pattern of the devitrified sample (15CR) shows one very sharp melting peak at 668 °C. This peak is due to the melting of the Bi₄B₂O₉ phase whose melting point is reported to be in the range of 666–679 °C [11, 20].

All bismuth borate glasses crystallize on heat treatment. The tendency towards crystallization increases with Bi₂O₃ concentration. These findings are different from the earlier results on devitrification properties of bismuth borate glasses. It has been reported that bismuth borate glasses (doped with 0.5 mol% of Mn²⁺ ions) with Bi₂O₃ content ≤37.5 mol% do not crystallize even after 90 h of heat treatment at 550 °C [38]. In contrast, our experiments conclude that heat treatment at 550 °C for 17 h is sufficient to crystallize all bismuth borate glasses: only the first glass sample containing 20 mol% of Bi₂O₃ (sample 1) required a longer annealing time of about 41 h for crystallization. This difference in crystallization behavior is explained by the fact that, in the earlier study, the authors prepared glasses by melting the batch mixture in alumina crucibles at 1100 °C, the latter reacting vigorously with bismuth borate melts and introducing large concentrations (several mol%) of alumina impurities in the final glasses. Alumina impurities in lead and bismuth borates are known to strongly suppress the crystallization tendency of these glasses [25, 39]. A recent study reports the effects of Gd³⁺ ion doping on the crystallization properties of 2Bi₂O₃–B₂O₃ glasses by FTIR spectroscopy and x-ray diffraction [40]. The preparation of these glasses was also performed in alumina crucibles which, as mentioned above, introduce significant Al³⁺ impurity concentration in bismuth borate glasses and drastically modify their crystallization properties.

4. Conclusions

Bismuth borate glasses were crystallized by heat treatment at temperatures in the range of 550–615 °C for several hours.

All glasses crystallize on annealing and the tendency for crystallization increases with Bi₂O₃ concentration. The crystalline phases produced in devitrified samples were identified by FTIR and DSC measurements. The Bi₂B₈O₁₅ phase is formed in devitrified glasses with Bi₂O₃ content ≤33 mol%. Our studies reveal that crystalline phases produced by devitrification of bismuth borate glasses are determined not only by composition but also by structural heterogeneities that seem to be present in glasses at lower Bi₂O₃ concentrations of ≤25 mol%. Bi₃B₅O₁₂ and Bi₄B₂O₉ are the two phases which are formed most easily; the latter is produced at Bi₂O₃ content ≥40 mol%. The metastable bismuth orthoborate (BiBO₃) phase can be produced by short duration (about 5 h) annealing of glass with 50 mol% of Bi₂O₃. This phase is thermally unstable and decomposes to Bi₃B₅O₁₂ and Bi₄B₂O₉ phases on heating for longer times and/or at higher temperatures.

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