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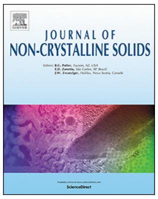

Enhanced thermal stability of high-bismuth borate glasses by addition of iron

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ABSTRACT

Glasses with nominal molar composition $20B_2O_3-(80-x)Bi_2O_3-xFe_2O_3$ (where x = 0–40) were successfully prepared by melt-quenching. These glasses were characterised by multiple techniques including density, X-ray diffraction (XRD), X-Ray fluorescence (XRF), Raman, FT-IR and Mössbauer spectroscopies, dilatometry and differential thermal analysis (DTA). Partial replacement of Bi_2O_3 by Fe_2O_3 leads to decreasing density and molar volume and a substantial increase in thermal stability, as measured by several parameters, with maximum improvements achieved when x = 10–20. These improvements are accompanied by modest increases in dilatometric softening point. FT-IR and Raman spectra confirm the presence of BO_3 and BiO_6 structural units in all glasses, with glass structure apparently little affected by Fe_2O_3. Mössbauer spectroscopy confirms that iron is present partly as 4-fold coordinated Fe^{3+} in all glasses, with some 5- and/or 6- coordinated Fe^{3+} sites also present.

1. Introduction

Low-melting glasses have a wide range of applications and are essential to providing hermetic sealing in many applications including electronic, semiconducting, optical and photovoltaic devices, amongst many others [1–4]. Some of the lowest-melting and lowest-sealing temperature glasses, often referred to as solder glasses, were traditionally based on the lead borate system [1–4]. Freiser [2] noted that the viscosity-temperature profile of solder glasses should be such that the “preferred zone” of viscosity enabling viscous flow of the solder glass, should leave the work piece (metal or glass) unaffected. Takamori [3] considered solder glasses on the basis of their thermal expansion coefficient. However, in recent years legislation has effectively banned the use of lead in sealing glasses [1] and in many other glasses, and manufacturers continue to search for alternative, lead-free sealing glasses capable of delivering low sealing temperatures and acceptable thermal expansion behaviour.

Other low-melting borate glasses include alkali borates [5–8] and in order to access glass transition temperatures, T_g, of < 573 K, alkali borate glasses with high alkali contents are required [6]. However, such high-alkali glasses display high thermal expansion coefficients ($15–25 \times 10^{-6} K^{-1}$) [6], which will render them unsuitable for some sealing applications. Lower alkali borate glasses exhibit T_g's of ca. 623 - 723 K [8]. Binary alkaline earth borate glasses and ternary alkali-alkaline earth borate glasses exhibit even higher values of T_g, as discussed by Wozniak and James [9]. Furthermore, alkali borate glasses exhibit poor chemical durability and are therefore less attractive as potential lead-free sealing glasses. Zinc in borate sealing glasses has also received considerable attention [1–4], however, ZnO was traditionally a third component in B_2O_3-PbO glasses and comparable high-zinc glasses in the binary B_2O_3-ZnO system typically exhibit higher T_g's > 773 K, too high for some sealing applications.

One family of glasses that may be capable of replacing lead with a non-toxic alternative in some applications occurs in the B_2O_3-Bi_2O_3 system. In his recent, very thorough review of bismuth-containing glasses Maeder [1] noted that Bi_2O_3 “appears a quite promising drop-in replacement for PbO” but “the somewhat lower fluxing ability…leads to higher processing temperatures”. Despite this, bismuth-rich low temperature sealing glasses have been successfully developed [10–12]. Bismuth borates have been stated to form transparent glasses over a particularly wide range of Bi_2O_3 contents, from 20 to 85 mol% [13]. Bajaj et al. [13] undertook a detailed investigation of the structure and properties of glasses in the system $xBi_2O_3 - (100 - x)B_2O_3$ where x = 20 to 66 (mol %), and noted the interest in this system for non-

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Table 1
Nominal (analysed) glass compositions, density, molar volume and thermal parameters.

Sample	Nominal (analysed) composition/mol%				Density, ρ/g cm^{-3} ($\pm$ 0.01)	Molar Vol., V_m cm^{-3} ($\pm$ 0.5)	T_g/K ($\pm$ 3)	T_x/K ($\pm$ 3)	T_c/K ($\pm$ 3)	T_m/K ($\pm$ 3)	ΔT/K ($\pm$ 6) [28]	S [29]	K_{gl} [30]	T_d/K ($\pm$ 3)
	B_2O_3	Fe_2O_3 ($\pm$ 3)	Bi_2O_3 ($\pm$ 3)	Al_2O_3 ($\pm$ 3)										
0Fe	20.0[a]	0.0 (0.0)	80.0 (73.7)	0.0 (6.3)	7.88	49.1	603	635	655	861	32	1.06	0.142	600
10Fe	20.0[a]	10.0 (6.8)	70.0 (65.9)	0.0 (7.3)	7.58	47.0	635	701	715	858	66	1.46	0.420	635
20Fe	20.0[a]	20.0 (14.5)	60.0 (61.0)	0.0 (4.5)	7.25	44.9	662	723	755	923[b]	61	2.95	0.305[b]	665
30Fe	20.0[a]	30.0 (21.5)	50.0 (52.7)	0.0 (5.7)	6.99	42.2	692	731	752[b]	948[b]	39	1.18	0.180[b]	675
40Fe	20.0[a]	40.0[a]	40.0[a]	0.0[a]	6.63	39.9	690	745	777[b]	904[b]	55	2.55	0.346[b]	680

[a] not measured.
[b] DTA traces showed multiple phase formation/melting.

linear optics. Shaaban et al. [14] studied glasses with compositions xBi_2O_3 – (100 − x)B_2O_3 where x = 35 to 60 mol%. They carefully characterised thermal properties, crystallisation behaviour and structure, demonstrating that thermal stability decreased with increasing Bi_2O_3 content.

A wide range of additional components to the B_2O_3-Bi_2O_3 glass system has been studied previously, as summarised by Maeder [1]. However, a dopant that has received relatively little attention, particularly in the context of high-bismuth sealing glasses, is iron. Dumbaugh [15] showed that the binary system Bi_2O_3-Fe_2O_3, which contains no classical glass formers, is capable of forming glasses over a considerable range of iron contents, given the inclusion of a third component (in Dumbaugh's case CdO and/or PbO). This offered a tantalising clue to the potential for incorporating iron in high-bismuth glasses. Qiu et al. [16] studied glass formation and DC conductivity in the system B_2O_3-Bi_2O_3-Fe_2O_3, and confirmed that high-Bi_2O_3, low-B_2O_3 glasses containing up to 40 mol% Fe_2O_3 can be formed by press-quenching the melt between two copper blocks. Baia et al. [17, 18] studied the structure of a wide range of compositions in the systems (mol%) 95[xB_2O_3.(1 − x)Bi_2O_3]-5Fe_2O_3 where 0.07 ≤ x ≤ 90 and 90[xB_2O_3.(1 − x)Bi_2O_3]-10Fe_2O_3 where 0.07 ≤ x ≤ 0.625 using Raman and FT-IR spectroscopies. They found that Bi^{3+} cations are incorporated in the glass network as BiO_6 polyhedra, and iron doping can stabilise the glass network at intermediate bismuth contents. El-Desoky and colleagues [19–21] studied doping of iron into B_2O_3-Bi_2O_3-R_2O (R = Li, Na, K) glasses, however, they were primarily investigating electrical properties and their glasses were relatively high in B_2O_3 and low in Bi_2O_3. Akamatsu et al. [22] studied the magnetic and structural properties of glasses with nominal molar composition xFe_2O_3 - (80 − x) Bi_2O_3 -·20 B_2O_3 (where x = 18.2–40.0). These glasses exhibit unusual magnetic behaviour which they explained in terms of coexisting spin glass phases and magnetic clusters. Another application area of interest in high-bismuth glasses is for radiation shielding/dosimeter applications, and these have also received recent attention [23–24]. The presence of boron and bismuth could enable potential applications in the nuclear arena, due to the high absorption cross-section for thermal-neutrons (B) and γ-radiation (Bi). In terms of iron-free bismuth borate glasses, Yawale and Pakade [25] studied the physical and electrical transport properties of Bi_2O_3-B_2O_3 glasses, and further detailed studies of the physical properties of Bi_2O_3-B_2O_3 glasses, across a wide range of compositions, were carried out by Stehle et al. [26] and George et al. [27]. The high densities of bismuth-rich borate glasses are inherently linked to all of the above applications. As noted by Maeder [1], anomalies in density and T_g can also suggest structural information, hence knowledge of the density and molar volume of bismuth borate glasses is important. One additional property requirement of sealing glasses is that they exhibit sufficient chemical durability for the application in question. As discussed by Maeder [1], some high-lead borate glasses and high-bismuth borate glasses exhibit chemical durabilities that are considered acceptable for many low-temperature sealing applications.

Understanding the effects of iron additions to the structure and properties of high-bismuth borate glasses is therefore of interest, not only from the perspective of developing new lead-free sealing glasses, but also within the wider context of understanding the structure of high-bismuth oxide glasses, and in terms of new potential applications requiring novel electrical, nuclear or other properties. Here we have studied the effects of iron doping on the structure and physical properties of glasses with nominal molar composition 20 B_2O_3 – (80 − x) Bi_2O_3 – xFe_2O_3 (where x = 0–40).

2. Experimental procedures

Batches to provide 50 g of glass were produced using the reagent-grade chemicals boric acid (H_3BO_3, 99.5%), bismuth oxide (Bi_2O_3, 99%) and iron oxide (Fe_2O_3, 98%). Raw materials were carefully dried overnight prior to weighing (H_3BO_3 at 323 K so as not to decompose; and Bi_2O_3 and Fe_2O_3 at 393 K). Batches were weighed out using a calibrated 2 decimal-place balance, and were then mixed thoroughly. Nominal glass compositions are listed in Table 1. The mixed batches were then placed in recrystallised Al_2O_3 crucibles, with an Al_2O_3 lid placed over the crucible to reduce volatilisation losses during heating and melting. Crucibles were placed in an electric furnace and heated at 5 K/min in air to 1373 K, and held at this temperature for 30 min. The lids were then removed from the crucibles and the crucibles removed from the furnace and their contents press-quenched between two steel plates. Resulting samples were then stored in sealed bags. Samples were powdered in an attrition mill for 1 min to provide samples for XRD, XRF, Mössbauer spectroscopy, DTA and FT-IR spectroscopies. Density measurements, Raman spectroscopy and dilatometry were performed on bulk glass samples.

Densities have been measured by the Archimedes method using deionised water as the suspension medium. Archimedes densities are calculated using Eq. (1):

$$\text{Density} = ((W_A/(W_A–W_W)) \times \delta_W \qquad (1)$$

where W_A = weight in air, W_W = weight in water and δ_W = temperature correction. Averages of three measurements were taken for each sample. Molar volumes have been calculated using measured densities and analysed compositions.

Elemental analysis was performed using a PANalytical MagiX Pro XRF spectrometer equipped with a Rh anode. Powdered samples were mixed with cellulose binder and pressed into pellets using a 20 t force in a Retsch PP40 hydraulic press. A semi-quantitative XRF analysis program, IQ+ for standardless data analysis, was used here. Boron was not detected by XRF and so to enable useful analysis it had to be assumed that no boron losses had occurred during melting, and analysed content