Structural characterization of PbO–B$_2$O$_3$–SiO$_2$ glasses

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The effects of silica on the density, boron–oxygen speciation and thermal properties of glasses from the system: PbO–B$_2$O$_3$–SiO$_2$ (PbO concentration: 30, 40, 50 and 60 mol% and silica concentration: 5, 10, 20 and 30 mol%) was studied by ^{11}B MAS NMR and DSC techniques. The incorporation of silica in the borate network steadily increases glass density, decreases the glass transition temperature and increases the thermal stability of glasses against crystallization. SiO$_2$ at low concentrations of up to 20 mol% increases the three dimensional network connectivity by promoting the conversion of BO$_3$ into [BO$_4$]$^-$ units, however at higher silica contents of 30 mol%, the formation of [BO$_4$]$^-$ was suppressed and nonbridging oxygens were rapidly generated in SiO$_4$ and BO$_3$ units. The average number of NBOs per BO$_3$ unit increases with silica concentration and this was indicated in the NMR spectra of glass series with 60 mol% PbO which exhibited a shift in the centre of gravity of the BO$_3$ resonance peak towards more positive ppm values (de-shielding) at a silica concentration of 30 mol%. DSC studies indicated phase separation in the glasses which suggested that the mixing of Pb^{2+} ions , BO$_3$, [BO$_4$]$^-$ and SiO$_4$ units was not completely random.

1. Introduction

Lead borosilicate glasses have a wide glass formation range and low melting points of ~700°C and find application as glass to metal seals due to their good wetting properties with precious metals (such as Ag, Au and Pt), as ceramic sealants, enamels and as transparent x-ray and nuclear radiation shielding windows due to their high densities and large gamma ray attenuation coefficients.[1–4] It is reported that the microhardness and elastic modulus of lead borosilicate glasses containing small amounts of Bi$_2$O$_3$ increase with gamma-ray irradiation.[5] Low melting temperature glasses such as lead borosilicates are of interest for applications in nuclear waste immobilization.[6,7] PbO containing silicate glasses are reported to generate hard x-rays on exposure to femtosecond laser radiation.[8] Therefore lead borosilicate glasses are technologically important materials and require detailed structure-property characterization studies.

Lead borate and lead borosilicate glasses have been studied by variety of techniques such as density measurements,[9,10] microhardness, thermal and dilatometry studies,[11] UV-visible optical,[12] infrared and Raman spectroscopies,[11,13,14] ^{11}B magic angle spinning (MAS) nuclear magnetic resonance (NMR)[10,15–18] and x-ray diffraction.[19] An important structural feature of borate and borosilicate glasses

is the coordination number of boron with oxygen, i.e. n_{BO} which can be either 3 or 4. The fraction of tetrahedral borons, N$_4$ in glasses can be measured by techniques such as ^{11}B MAS NMR spectroscopy, infrared spectroscopy and neutron diffraction. While all the borons in pure B$_2$O$_3$ and binary borosilicate glass are in triangular coordination in BO$_3$ units, borate and borosilicate glasses with alkali, alkaline earth and other metal oxides contain tetrahedrally coordinated [BO$_4$]$^-$ units, the additional oxygens being provided by the metal oxides. The negatively charged [BO$_4$]$^-$ units act as charge balancing centres against positively charged metal ions and enhance the three-dimensional network connectivity. Another charge balancing centre is a nonbridging oxygen (NBO), these are oxygen atoms bonded to only one cation like B^{3+} or Si^{4+} and are denoted as O$^-$; NBOs also carry negative charge and their formation decreases the mechanical strength of glasses, reduces chemical durability and enhances their tendency towards devitrification on heat treatment. The concentration of NBOs in glasses can be measured directly by ^{17}O MAS NMR.[20,21] An estimation of NBO concentration in glasses can be obtained from N$_4$ values by applying the local charge neutrality condition on one glass molecule.[10,22] N$_4$ determines the glass properties such as density, microhardness, coefficient of linear thermal expansion and chemical resistance; it is reported that best chemical resistance of lead borosilicate glasses

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to water is found with highest concentration of four coordinated borons in the glass.[11]

SiO$_2$ like B$_2$O$_3$ is an excellent glass former and SiO$_4$ tetrahedra are the basic structural units in silicate and borosilicate glasses; unlike boron the coordination number of silicon with oxygen is always fixed at 4, although the oxygen atoms in SiO$_4$ tetrahedra can be both bridging oxygens (BO), denoted as O, and nonbridging oxygens denoted as O$^-$. The Q^n nomenclature is used to indicate the number of BOs per SiO$_4$ tetrahedron, where n is the number of bridging oxygens and $(4-n)$ is the number of nonbridging oxygens per SiO$_4$ tetrahedron. The number of BOs in a SiO$_4$ tetrahedron can vary from 0 to 4,[23] therefore there are five types of SiO$_4$ units in silicate and borosilicate glasses, which contain either all BOs, all NBOs or both, and are denoted as Q^4, Q^3, Q^2, Q^1 and Q^0. From the variation of N$_4$ and Q^n, one can determine the polymerization state of the borosilicate network and understand the structural transformations that take place with the addition of network modifiers such as PbO and network formers such as SiO$_2$.

It is interesting to study the effects of silica on the boron–oxygen coordination and the possible inter-tetrahedral avoidance that may exist between [BO$_4$]$^-$ and SiO$_4$ units in borosilicate glasses. Significant inter-tetrahedral avoidance exists between [AlO$_4$]$^-$ and [BO$_4$]$^-$ units in aluminoborate and aluminoborosilicate glasses, in which even small amounts of Al$_2$O$_3$ (2 mol%) drastically reduces N$_4$.[10,24] It is reported that while there is considerable avoidance between [AlO$_4$]$^-$ and [BO$_4$]$^-$ units in aluminoborate glasses, there is more random mixing among BO$_3$, [BO$_4$]$^-$ and SiO$_4$ structural units in sodium borosilicate glasses.[24] The role of silica on the boron–oxygen speciation in lead borosilicate glasses was earlier studied by Kim *et al* who found a small increase in N$_4$ on adding silica to lead borate glasses and concluded that these glasses do not contain BO$_3$ units with NBOs.[17] Sudarsan *et al* reported almost constant N$_4$ in lead borosilicate glasses with varying silica concentrations.[18] These earlier studies used low field ^{11}B NMR which did not fully resolve the resonance peaks of trigonal and tetrahedral borons and restricted the accurate quantification of N$_4$ and f_{NBO}, and hence a full understanding of the effects of silica on the glass structure and properties.

The effect of addition of silica on boron–oxygen speciation in soda lime borosilicate glasses has been analyzed by MAS NMR spectroscopy and it is reported that N$_4$ increases steadily with increase in SiO$_2$ mol%.[25] A two-state statistical model of borosilicate glasses predicts that the conversion of BO$_3$ into [BO$_4$]$^-$ is energetically more favourable than the formation of NBOs in the glass network, moreover the formation of NBOs in SiO$_4$ tetrahedral units (Q^n units) is energetically more favourable than their formation in BO$_3$ units.[25] A second important question

is concerned with the mixing of borate and silicate structural groups in borosilicate glasses. Mixing of the units can occur by the formation of danburite rings each containing two SiO$_4$ and two BO$_4$ units. The formation of danburite rings is the signature of mixing of silicate and borate structural groups. It has been found by Raman studies on alkali borosilicate glasses and melts that the concentration of danburite rings decreases with increasing temperature.[26,27] Lastly, it is important to determine the total concentration of NBOs in borosilicate glasses and their relative fractions in SiO$_4$ and BO$_3$ units.

It is the objective of the present work to study the effects of replacing B$_2$O$_3$ with SiO$_2$ on the density, boron–oxygen coordination number, and fraction of NBOs and glass thermal properties of lead borosilicate glasses containing 30 to 60 mol% PbO. The techniques employed for this purpose are density measurements, ^{11}B MAS NMR spectroscopy and differential scanning calorimetry (DSC). The structure and properties of ternary lead borosilicate glasses are compared with those of binary lead borate glasses studied earlier.[10]

2. Experimental methods

2.1 Glass preparation

Glass samples of the following three lead borosilicate series were prepared by melt quenching:
(1) 30PbO–xSiO$_2$–(70–x)B$_2$O$_3$ (x=5 and 10 mol%)
(2) 40PbO–xSiO$_2$–(60–x)B$_2$O$_3$ (x=5, 10, 20 and 30 mol%)
(3) 60PbO–xSiO$_2$–(40–x)B$_2$O$_3$ (x=5, 10, 20 and 30 mol%)

Binary lead borate glasses and one lead borosilicate glass series containing 50 mol% PbO were prepared and characterized previously,[10] and the results of that study were used here for comparison with properties of glass samples from the three series mentioned above. The procedure used for preparation of glass samples is described elsewhere.[10] The composition, density, structural and thermal properties of all glass samples are given in Table 1.

2.2 Density measurements

The densities (d) of glasses were measured by the Archimedes method using dibutylpthalate (DBP) as the immersion fluid. Density measurements were repeated three to four times on each glass sample; Table 1 gives the average of repeated measurements on each glass. Density measurements were done with a precision better than 0·1%, the maximum error was ±0·004 g cm^{-3}.

2.3 Differential scanning calorimetery (DSC)

DSC measurements were carried out on a SETARAM SETYS 16 TG-DSC system over the temperature range of 200–850°C with a heating rate of 10°C/min. DSC

Table 1. Composition, density, structural and thermal properties of lead borate and borosilicate glasses. Maximum uncertainty in density was ±0.004 g cm⁻³ and uncertainty in temperature was ±1°C

| Sample code | Composition (mol%) | | | Molecular mass, M | Density, d (g cm⁻³) | Molar volume, V_M (cm³mol⁻¹) | N_4 (±0·01) | f_{NBO} (±0·01) | T_g (°C) | T_c (°C) | T_l (°C) |
	PbO	B₂O₃	SiO₂								
Pb30B70	30	70	–	115·69	4·172	27·73	0·35	0·06	487	729	780
Pb30B65Si5	30	65	5	115·21	4·170	27·65	0·41	0·03	–	–	–
Pb30B60Si10	30	60	10	114·74	4·288	26·79	0·42	0·04	–	–	–
Pb40B60	40	60	–	131·05	4·964	26·40	0·43	0·13	454	578	780
Pb40B55Si5	40	55	5	130·57	4·985	26·20	0·47	0·13	448	–	–
Pb40B50Si10	40	50	10	130·09	5·035	25·87	0·48	0·15	445	–	–
Pb40B40Si20	40	40	20	129·14	5·098	25·40	0·49	0·20	442	–	–
Pb40B30Si30	40	30	30	128·19	5·123	25·12	0·48	0·27	439	–	–
Pb50B50	50	50	–	146·41	5·677	25·79	0·45	0·28	406	554	651
Pb50B45Si5	50	45	5	145·93	5·701	25·61	0·45	0·31	406	–	–
Pb50B40Si10	50	40	10	145·45	5·760	25·28	0·44	0·34	402	–	–
Pb50B30Si20	50	30	20	144·50	5·817	24·89	0·44	0·41	399	–	–
Pb50B20Si30	50	20	30	143·54	5·860	24·58	0·41	0·50	396	–	–
Pb60B40	60	40	–	161·76	6·303	25·66	0·39	0·50	351	497	565
Pb60B35Si5	60	35	5	161·29	6·362	25·36	0·42	0·52	345	–	–
Pb60B30Si10	60	30	10	160·81	6·432	25·03	0·41	0·56	341	–	–
Pb60B20Si20	60	20	20	159·85	6·506	24·62	0·37	0·66	338	–	–
Pb60B10Si30	60	10	30	158·9	6·587	24·20	0·29	0·76	341	492	–

studies were done on powdered glass samples in platinum pans under ambient air. Sample sizes of 20–50 mg were used to perform the DSC measurements.

2.4 ¹¹B MAS NMR

Lead borosilicate glass series containing 30, 40 and 60 mol% PbO were analyzed with a 2·5 mm Bruker MAS probe at room temperature on a Bruker Avance NMR spectrometer operating at 16·4 T corresponding to a Larmor frequency at 224·667 MHz for ¹¹B. Single pulse acquisition was applied with spinning rate of 20 kHz and a short RF pulse of 0·4 µs (power of 78·4 kHz) was used with a recycle delay of 5 s. Data were background corrected by subtraction of the empty rotor signal. All the spectra are referenced to the conventional standard, BF₃.O(CH₂CH₃)₂ at 0 ppm.

3. Results

3.1 Density
Density in each of the four lead borosilicate glasses series containing 30, 40, 50 and 60 mol% PbO increased steadily with silica content from 5 to 30 mol% (Table 1 and Figure 1). The density of the binary lead borate glass with 30 mol% PbO (sample Pb30B70) is 4·172±0·001 g cm⁻³ which increases to 4·288±0·003 g cm⁻³ on adding 10 mol% of SiO₂. Similarly density of 60PbO–40B₂O₃ glass (sample Pb60B40) is 6·303±0·003 g cm⁻³ which increases to 6·587±0·002 g cm⁻³ on adding 30 mol% SiO₂ (sample Pb60B10Si30).

3.2 Glass transition and crystallization temperature

The glass transition temperature (T_g) of binary lead borate glasses decreases from 487 to 351°C as PbO concentration increases from 30 to 60 mol%.[10] Figures
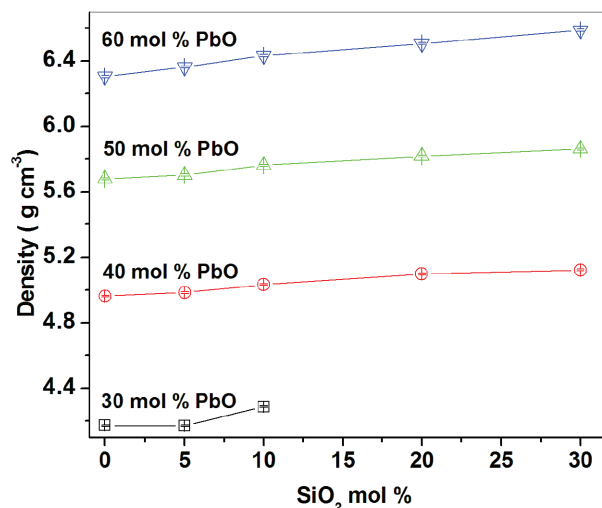

Figure 1. Density of lead borosilicate glasses as a function of PbO and SiO₂ concentrations (error bars are of the same size as the symbols) [Colour available online]

2(a), (b) and (c) are the DSC spectra of lead borosilicate glasses containing 40, 50 and 60 mol% of PbO, respectively. The lead borosilicate glass series with 40 mol% PbO exhibits at least two glass transitions, the sample with 5 mol% SiO₂ shows one strong glass transition at 448°C and a second weak glass transition at 520°C. This in an indication of phase separation in the glasses, which can arise due to incomplete mixing of borate and silicate structural units. The primary glass transition temperature decreases steadily from 448 to 439°C with an increase in silica concentration from 5 to 30 mol%. In the second glass series containing 50 mol% PbO, T_g decreases from 406 to 396°C as the silica concentration increases from 5 to 30 mol% (Figure 3). Glasses with 50 mol% PbO show a single glass transition. Finally the third glass series with 60 mol% PbO shows decrease in T_g from 345 to 341°C as the SiO₂ content was increased from 5 to 30 mol%. This glass series shows weak glass transitions at
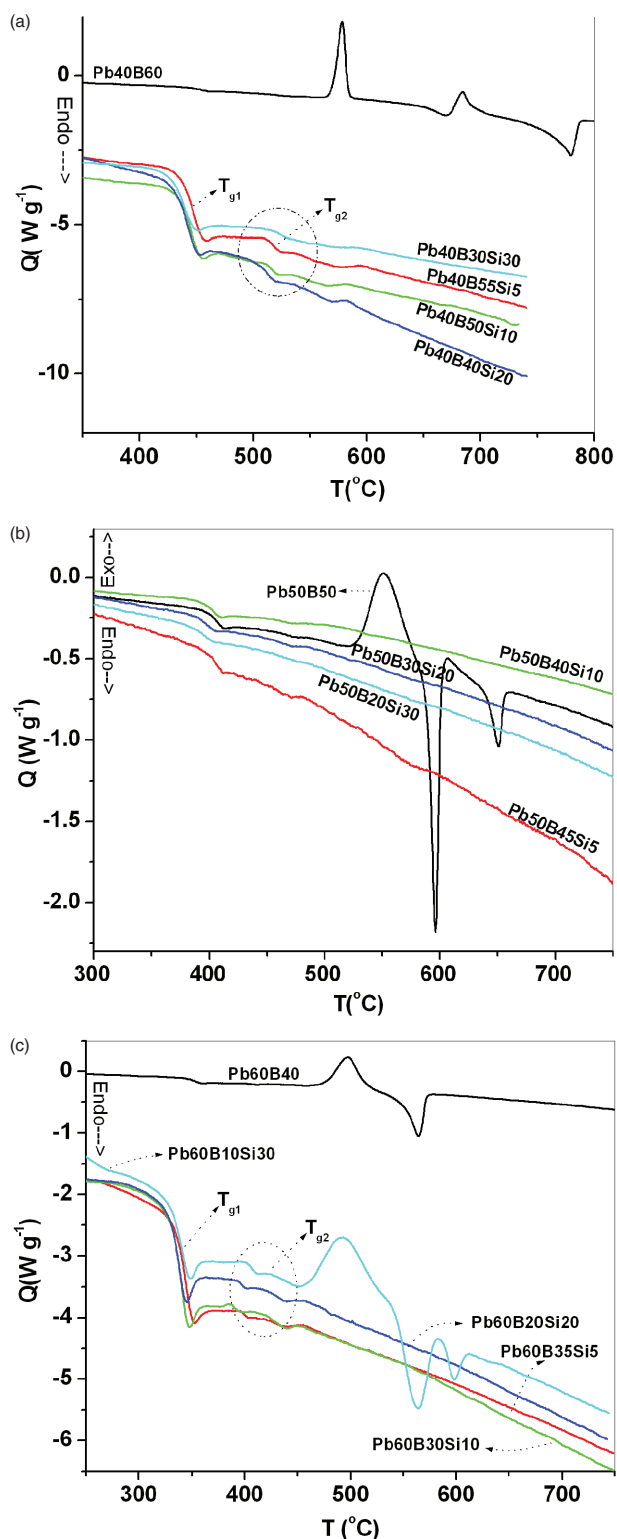
(a)

(b)

(c)

Figure 2(a)–(c). DSC patterns of lead borate and borosilicate glasses (a) 40 mol% PbO (b) 50 mol% PbO (c) 60 mol%. Dotted circles mark the temperature range in which second weak glass transitions are indicated [Colour available online]

higher temperatures of ~400°C. Further while binary lead borate glasses exhibit exothermic crystallization (T_c) and endothermic melting peaks (T_l), these were absent in the lead borosilicate glasses. Therefore it
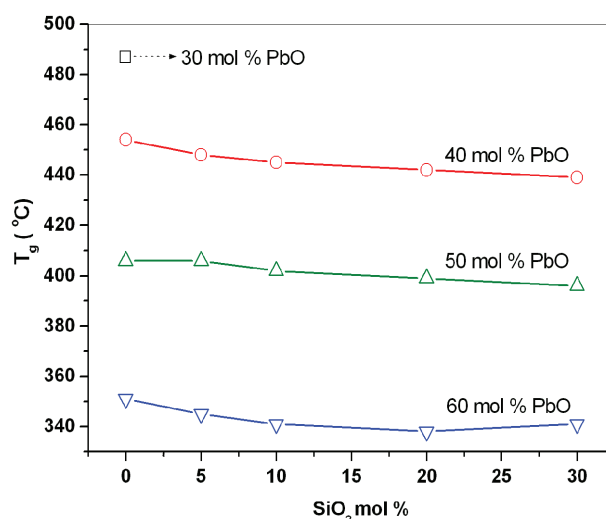

Figure 3. Variation in T_g with silica concentration in lead borosilicate glasses. T_g for binary lead borate glasses corresponding to 0 mol% SiO₂ are also shown [Colour available online]

was concluded that the crystallization tendency is significantly lower for the borosilicate glasses than for the borate glasses.

3.3 Fraction of tetrahedral borons and nonbridging oxygens

^{11}B MAS NMR spectra of lead borosilicate glasses containing 30, 40 and 60 mol% PbO and variable silica contents of 5 to 30 mol% are shown in Figures 4, 5 and 6, respectively. The NMR patterns of binary lead borate glasses and lead borosilicate glasses containing 50 mol% PbO are shown in Ref. 10.

Two well resolved peaks, one relatively sharp peak centred between −0·2 to 0·8 ppm and another broader peak centred in the range of 13·7 to 16·5 ppm were detected in all samples (Figures 4–6). The first peak is due to tetrahedrally coordinated borons while the
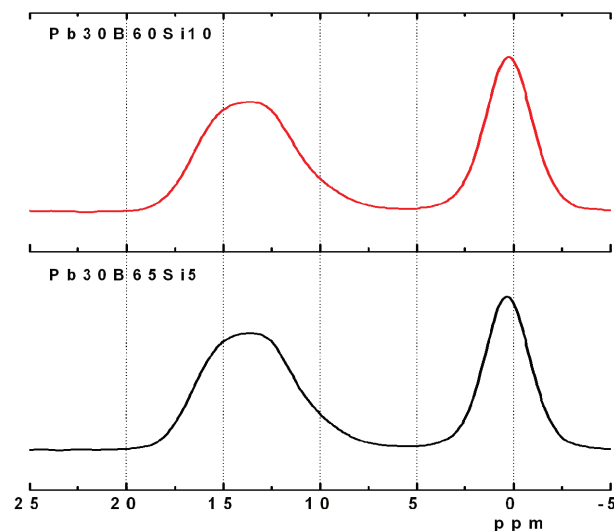

Figure 4. ^{11}B MAS NMR spectra of lead borosilicate glasses containing 30 mol% PbO [Colour available online]
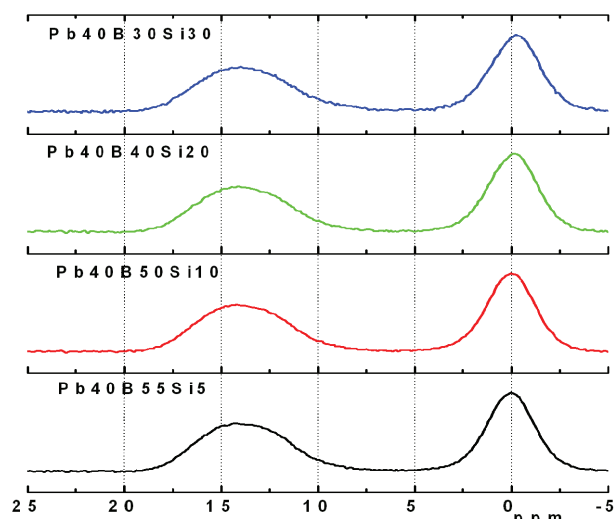
Figure 5. ¹¹B MAS NMR spectra of lead borosilicate glasses containing 40 mol% PbO [Colour available online]

Figure 7. Variation in N_4 with silica concentration in the four lead borosilicate glass series. N_4 in binary lead borate glasses corresponding to 0 mol% of SiO₂ are also shown [Colour available online]

second peak is due to trigonally coordinated borons in the glasses. The fraction of tetrahedral borons (N_4) was calculated from the ratio of integrated area under these two peaks i.e. $N_4 = A_4/(A_3 + A_4)$. The integration of area under these two peaks was done using Origin-6.0 Professional software and the maximum uncertainty in N_4 was ±0·01.
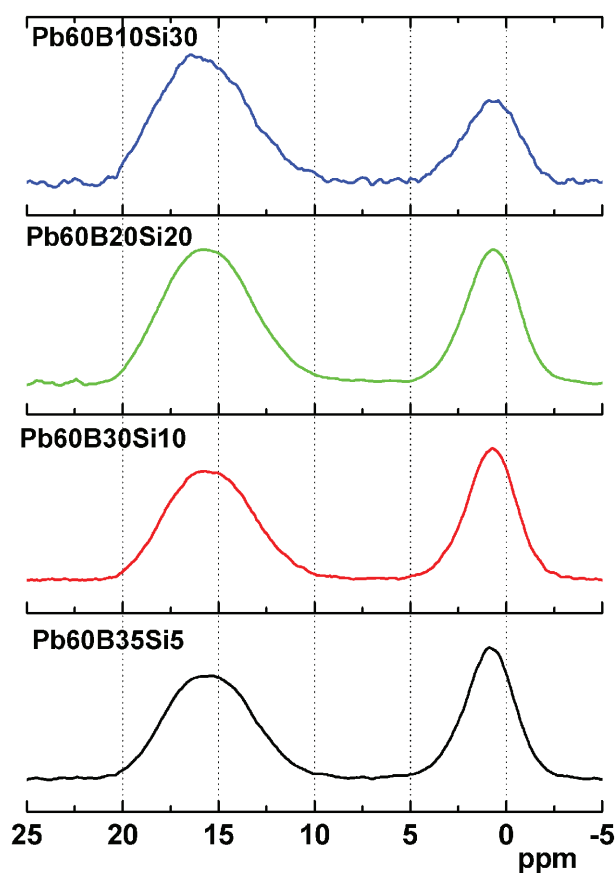

Figure 6. ¹¹B MAS NMR spectra of lead borosilicate glasses containing 60 mol% PbO [Colour available online]
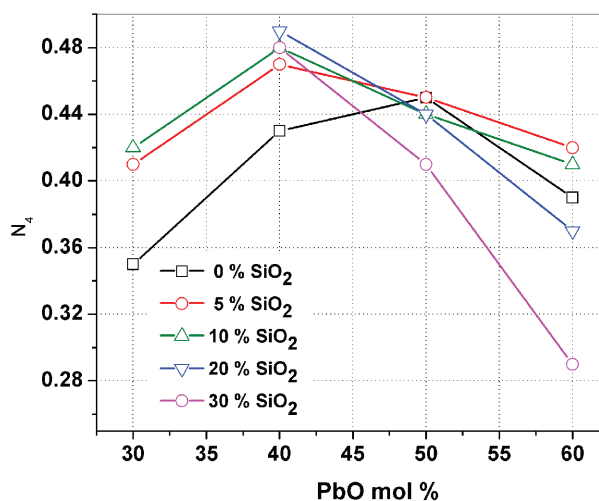
N_4 in glasses with 30, 40 and 60 mol% PbO initially increases with increasing silica concentration. For example, N_4 increases from 0·35 in binary lead borate glass (Sample Pb30B70) to 0·42 in glass with 10 mol% silica (Sample Pb30B60Si10). In the case of lead borate glass with 40 mol% PbO, N_4 even exceeds the maxima of N_4 in binary lead borate glass at 50 mol% PbO (Figure 7), similarly in case of glasses with 60 mol% PbO, N_4 increases from 0·39 to 0·42 on adding 5 mol% SiO₂ and then decreases slowly up to 10 mol% silica and more rapidly at 20 and 30 mol% silica. However the structural changes in lead borosilicate glasses containing 50 mol% PbO were different from those in other lead borosilicate glasses; N_4 remains constant at 0·45 on adding 5 mol% of silica and then decreases slowly to 0·41 on increasing the silica concentration to 30 mol%. The structure of this glass series seemed to be most resistant to changes in N_4 with silica substitution.

Using the measured values of N_4, the average B–O coordination number, $n_{BO} = 3 + N_4$, and the average oxygen–boron coordination, $n_{OB} = n_{BO}(c_B/c_O)$, where c_B and c_O are the molar concentrations of boron and oxygen, respectively, and taking Si–O coordination, n_{SiO}, to be fixed at 4, the average oxygen–silicon co-ordination number, $n_{OSi} = 4(c_{Si}/c_O)$ was calculated and these values were used to determine the fraction of NBOs (f_{NBO}) in the borosilicate network using:

$$f_{NBO} = 2 - (n_{OSi} + n_{OB}) \qquad (1)$$

The above calculation of NBOs is based on the condition of overall charge neutrality of a molecular formula unit, and on the assumptions that there are no oxygen triclusters in the glass network, and that Pb²⁺ is purely ionically bonded with oxygen and does not participate in the network formation. This assumption may not be strictly valid at high PbO
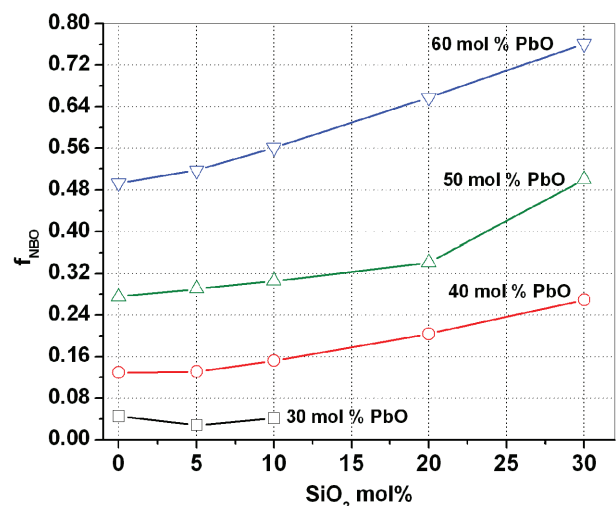
Figure 8. Variation in f_{NBO} with silica concentration in lead borosilicate glasses [Colour available online]

contents of 50 and 60 mol% where PbO begins to act like a network former and its bonding acquires more covalent character.[11,15–17] Small concentrations of oxygen triclusters and covalently bonded Pb atoms will reduce the actual values of f_{NBO} in glasses as compared to values determined from relation (1).

The f_{NBO} values were calculated for all glasses using Equation (1) and it was found that its value decreases from 0·06 to 0·03 on adding 5 mol% of silica in 30PbO–70B₂O₃ glass (sample Pb30B70) and then again increases to a 0·04 with further increase in silica content to 10 mol% (sample Pb30B60Si10).

In the three lead borosilicate glass series containing 40, 50 and 60 mol% PbO, f_{NBO} increases steadily but slowly up to 20 mol% silica and then more rapidly at a silica concentration of 30 mol%. Figure 8 shows the changes in f_{NBO} in all of the glasses.

4. Discussion

The increase of density with increase in silica mol% in the four lead borosilicate glass series can be either due to the increase in molecular mass or due to the decrease in structural volume or both. It is clear from data given in Table 1 that in each lead borosilicate glass series, molar mass decreases by small amounts with increasing silica concentration, for example molar mass deceases from 161·76 to 158·9 g mol⁻¹ on adding 30 mol% silica into lead borate glasses with 60 mol% of PbO. ¹¹B MAS NMR measurements confirmed that the concentration of [BO₄]⁻ units increases with silica additions, which enhances crosslinking and three-dimensional network connectivity. The molar volume data presented in Table 1 for all four glass series clearly shows that silica additions lead to the compaction of the glass structure which leads to increasing glass density.

Earlier Fujino *et al* had prepared and measured the density of several lead borosilicate glasses and melts.

They also reported a small increase in the melt and glass density on adding silica (SiO₂) at the expense of B₂O₃; the density values of our lead borosilicate glasses are in good agreement with the results of Fujino *et al*.[28]

Glass transition temperature decreases by 10 to 15°C with increasing silica concentration; a result which agrees with the findings of Sudarsan *et al* who reported a decrease in T_g on replacing B₂O₃ by SiO₂ in lead borosilicate glasses containing 50 mol% PbO.[18] The decrease in T_g is mostly due to the increase in the concentration of NBOs with the addition of silica. Although network connectivity increases with the formation of [BO₄]⁻ units, the single Bᴵⱽ–O bond strength (373 kJ mol⁻¹) is less than the single Bᴵᴵᴵ–O bond strength (498 kJ mol⁻¹),[29] therefore Bᴵⱽ–O bonds can be broken more easily than Bᴵᴵᴵ–O bonds and hence the increase in N₄ decreases the glass transition temperature.

Borosilicate glasses containing 40 and 60 mol% of PbO exhibit a second weak glass transitions at higher temperatures marked by dotted circles in Figures 2(a)–(c), indicating that small phase separated regions (heterogeneities) were present in these glasses; this could arise due to some amount of demixing of borate and silicate structural units. It is evident from the DSC spectra shown in Figures 2(a)–(c) that the exothermic crystallization peaks are absent in glasses containing silica, while lead borate glasses exhibit crystallization peaks. Therefore the glass stability against crystallization is enhanced with the addition of silica in borate glasses. This enhancement in glass thermal stability can be a direct manifestation of phase separation or heterogeneities in lead borosilicate glasses; the existence of several competing phases is reported to suppress the tendency for crystallization.[30,31] However the size of these phase separated regions (heterogeneities) in lead borosilicate glasses must be very small as all samples were optically clear and transparent.

¹¹B MAS NMR studies provide important insights about the role of silica on boron speciation in lead borosilicate glasses. Firstly, it is important to note that N₄ reaches its maxima at 50 mol% of PbO in binary lead borate glasses (Figure 7). On adding silica to this base glass, N₄ remains nearly constant at 0·45–0·44. This result agrees with findings by Sudarsan *et al* that N₄ is almost constant with silica content in lead borosilicate glasses containing 50 mol% PbO.[18] The f_{NBO} increases steadily from 0·28 in 50PbO–50B₂O₃ glass (sample Pb50B50) to 0·50 in lead borosilicate glass with 50 mol% PbO and 30 mol% of silica (sample Pb50B20Si30).

Although N₄ is nearly constant with increase in silica concentration in the glass series with 50 mol% PbO, the total number of negatively charged [BO₄]⁻ species in the glass network decreases due to partial replacement of B₂O₃ by SiO₂, therefore in order to

maintain local charge neutrality (i.e. compensate the positive charge of Pb^{2+}) additional NBOs in BO$_3$ and SiO$_4$ units are generated by the following reaction mechanisms:

$$2[BO_{3/2}]+O^{2-} \rightleftharpoons 2BO_{2/2}O^- \quad (2)$$

$$2[SiO_{4/2}]+O^{2-} \rightleftharpoons 2[SiO_{3/2}O^-] \quad (3)$$

$$[SiO_{4/2}]+O^{2-} \rightleftharpoons [SiO_{2/2}O^-O^-] \quad (4)$$

where O^{2-} ions are provided by PbO. O$_{x/y}$ denotes x oxygen anions, each coordinated with y network cations (B^{3+} and Si^{4+}), e.g. bridging oxygen when y=2, and O$^-$ denotes nonbridging oxygen (NBO).

^{29}Si MAS NMR studies by Sudarsan *et al* on lead borosilicate glasses containing 50 mol% PbO and 20 to 30 mol% of SiO$_2$ found that about 68% of silica tetrahedra are SiO$_{2/2}$O$_{2/1}^-$ (Q^2), 28% are SiO$_{3/2}$O$^-$ (Q^3) and the remaining 4% are SiO$_{4/2}$ (Q^4) units.[18] Using the measured values of N$_4$, Q^2 and Q^3 in sample Pb50B30Si20 it can be calculated from local charge neutrality condition on one glass "molecule" (50PbO–30B$_2$O$_3$–20SiO$_2$) that the f_{NBO} contribution from BO$_3$ units is 0·23 and f_{NBO} from SiO$_4$ units (Q^2 and Q^3) is 0·18 (total f_{NBO}=0·41). Similarly in the glass sample Pb50B20Si30 while total f_{NBO} is 0·49 (Table 1 and Figure 8), its contribution from NBOs in BO$_3$ units is 0·20 and is 0·29 from Q^2 and Q^3 units. Another interesting question is about the number of NBOs per BO$_3$ unit in these two glasses, this can be calculated from the N$_4$ data; the total number of BO$_3$ units per glass "molecule" in the sample Pb50B30Si20 is 33·6 while total number of NBOs in these units is 41·4, hence average number of NBOs per BO$_3$ unit in this sample is 1·23 which increases to 1·44 in the glass with a higher silica content of 30 mol% (sample Pb50B20Si30). Hence we conclude that number of NBOs in BO$_3$ units increases with the addition of silica. In the earlier work on the lead borosilicate glasses by Kim *et al*, no definite conclusion was made about the changes in f_{NBO} with the variation in silica concentration.[17] The present study shows that NBOs are present not only in Q^n units but also in BO$_3$ units.

The speciation data on three lead borosilicate glass series with 30, 40 and 60 mol% PbO reveal more interesting effects of silica on the glass short range structure; at low silica concentrations the relative concentration of [BO$_4$]$^-$ units increases in all three of these glass series (Figure 7). The increase in N$_4$ without simultaneous increase in f_{NBO} can occur by the reaction:

$$2[BO_{3/2}]+O^{2-} \rightleftharpoons 2[BO_{4/2}]^- \quad (5)$$

In case of glasses with a PbO content of 40 mol%, N$_4$ shows significant increase from the value of 0·43 in 40PbO–60B$_2$O$_3$ glass to 0·49 in 40PbO–40B$_2$O$_3$–20SiO$_2$ glass, this value of N$_4$ is even higher than its maxima of 0·45 in binary 50PbO–50B$_2$O$_3$ glass
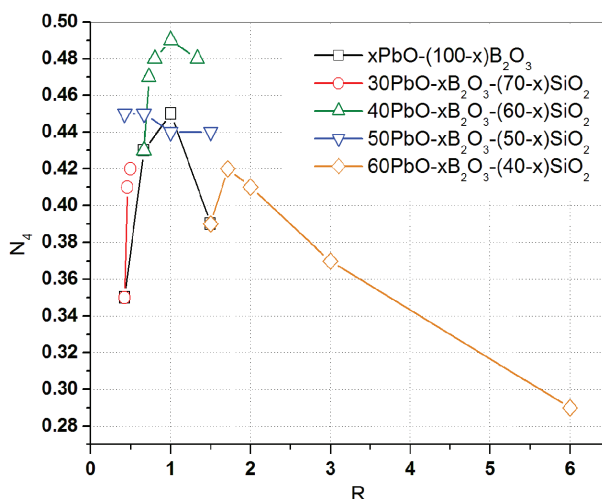

Figure 9. Variation in N$_4$ with molar ratio, R=[PbO]/[B$_2$O$_3$] in lead borate and lead borosilicate glasses [Colour available online]

(sample Pb50B50) which indicates that silica acts like a promoter and enhances the rate of conversion of BO$_3$ into [BO$_4$]$^-$ by the following two step process:

$$2[SiO_{4/2}]+O^{2-} \rightleftharpoons 2[SiO_{3/2}O^-] \quad (6)$$

$$[BO_{3/2}]+[SiO_{3/2}O^-] \rightleftharpoons [BO_{4/2}]^-+[SiO_{4/2}] \quad (7)$$

With the overall reaction as:

$$[SiO_{4/2}]+[BO_{3/2}]+O^{2-} \rightleftharpoons [BO_{4/2}]^-+[SiO_{3/2}O^-] \quad (8)$$

Equation (8) shows that each SiO$_4$ unit produces one [BO$_4$]$^-$ and one Q^3 unit, therefore f_{NBO} increases simultaneously. Similar equations can be written for reactions involving Q^2 units, which contain two NBOs per unit. Since the addition of silica into the glasses also changes the relative concentration of B$_2$O$_3$ by increasing the molar ratio, R=[PbO]/[B$_2$O$_3$], a question arises that whether increase in N$_4$ is due to the increase in R which will increase [BO$_4$]$^-$ units concentration by increasing reaction (5) or whether SiO$_4$ units also play a role in enhancing N$_4$ by the reaction mechanisms such as (8). This can be understood if we analyze the changes in N$_4$ and f_{NBO} in the glasses.

In the first borosilicate glass series containing 30 mol% PbO, N$_4$ increases significantly while f_{NBO} decreases slightly on adding 5 and 10 mol% silica, this indicates that for this particular glass series, increase in R is the dominant factor responsible for increase in N$_4$ via reaction mechanism (5). On analyzing the changes in N$_4$ as a function of R in the three other borosilicate glass series, we realize that borosilicate glass series containing 40 mol% PbO shows variation in N$_4$ quite similar to that in binary lead borate glass series, i.e. it has a maxima at R=1, but the value of maxima is higher, i.e. 0·49 at R=1 (sample Pb40B40Si20) compared to N$_4$=0·45 at same R value in sample Pb50B50 (Figure 9).

In the lead borosilicate glass series with 50 mol%

PbO, N_4 is nearly constant up to 20 mol% silica, while in lead borosilicate glasses with 60 mol% PbO, N_4 initially increases up to a silica content of 10 mol% and then it decreases. It can be therefore concluded that the addition of small concentration of silica (5 to 20 mol%) in borate glasses enhances the fraction of tetrahedral borons in the lead borosilicate network and this enhancement is not only due to changes in molar ratio R, but also due to structural transformations involving SiO_4 units via reaction mechanism (8). Further decrease in N_4 and increase in f_{NBO} at silica concentrations higher than 20 mol%, must be due to reaction mechanisms (2) to (4).

^{11}B MAS NMR spectra of borosilicate glass series containing 30, 40 and 50 mol% PbO do not show any changes in the line shape or in the centre of gravity of the BO_3 resonant peak (Figures 4, 5 and Ref. 10), although NBOs are present in BO_3 units and analysis of NMR data indicates that the average number of NBOs per BO_3 unit increases with SiO_2 concentration. Sodium borosilicate and barium borosilicate glasses show a similar increase in N_4 with increasing silica concentration.[24,27,32] The results of N_4 in lead borosilicate glasses are similar to those reported for soda lime borosilicate glasses, in which N_4 increases from a value of 0·39 to 0·81 as SiO_2 concentration is increased from 0 to 69·3 mol%.[25]

In the glass series with 60 mol% PbO, N_4 rises from 0·39 in the binary $60PbO$–$40B_2O_3$ glass to 0·42 on adding 5 mol% SiO_2 and then decreases slowly to 0·37 at 20 mol% of silica and more rapidly to 0·27 when silica content reaches 30 mol%. It is observed from ^{11}B MAS NMR patterns of these glasses (Figure 6) that there is shift in the centre of gravity of the BO_3 peak from 15·5 to 16·5 ppm at 30 mol% silica, this de-shielding is a signature of generation of more NBOs per BO_3 unit due to the destruction of mixed borate and silicate structural units such as danburite rings.[33] This behaviour is opposite to that reported in sodium borosilicate glasses, which exhibit shifting of the BO_3 NMR peak towards lower ppm values (shielding) with increasing silica concentration.[24] Stentz *et al* had concluded from time of flight mass spectrometry studies that there is a strong random mixing of borate and silicate structural units in lead borosilicate glasses,[34] this conclusion is however not indicated by the NMR studies of the present work. Weak secondary glass transitions (marked as dotted circles and arrows in Figure 2(a)–(c)) observed at temperatures higher than the primary glass transitions in the DSC patterns of lead borosilicate glasses indicate the existence of phase separated regions that can arise due to demixing of borate and silicate structural groups. Petrovskaya concluded from dilatometry studies that lead borosilicates are characterized by a hidden phase separation, which becomes evident with repeated heat treatment.[11] Kim *et al* had also concluded from the study of phase diagram on ternary lead borosilicate glasses that there exist two liquids (phase separation) in lead borosilicate glasses containing 30 to 40 mol% PbO.[17]

Conclusions

Lead borosilicate glasses were prepared and characterized by density, ^{11}B MAS NMR and DSC studies. Silica at low concentrations of 5 to 10 mol% increases N_4 in the borosilicate network and shifts the maxima in N_4 from 50 mol% PbO in binary lead borates to 40 mol% PbO in ternary lead borosilicate glasses. Lead borate glasses containing 50 mol% PbO were resistant to changes in N_4 on adding silica, but glasses with less than and or more than 50 mol% PbO showed enhancement in N_4. The increase in N_4 with silica revealed that the inter-tetrahedral avoidance between SiO_4 and $[BO_4]^-$ units in borosilicate glasses is considerably less than that between $[AlO_4]^-$ and $[BO_4]^-$ units in aluminoborate glasses. The fraction of NBOs in the glass network increases with silica mol% and the number of NBOs per BO_3 unit also increases, this effect was indicated by de-shielding of the BO_3 NMR peak in glass series containing 60 mol% PbO. Silica incorporation in the borate network decreases the glass transition temperature by 10 to 15°C and simultaneously increases the thermal stability of the glasses against devitrification.

Acknowledgements

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