Structural studies on boroaluminosilicate glasses

Jayshree Ramkumar [a], V. Sudarsan [b], S. Chandramouleeswaran [a], V.K. Shrikhande [c],
G.P. Kothiyal [c], P.V. Ravindran [a], S.K. Kulshreshtha [b], T. Mukherjee [d,*]

[a] *Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*
[b] *Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*
[c] *Technical Physics and Prototype Engineering Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*
[d] *Chemistry Group, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India*

Abstract

Two series of boroaluminosilicate glasses having varying mole ratios of B_2O_3/Na_2O (series 1) and B_2O_3/SiO_2 (series II) were prepared by conventional melt-quench method. Based on ^{29}Si and ^{11}B MAS NMR studies, it has been established that for series I glasses up to 15 mol% B_2O_3 content, Na_2O preferentially interacts with B_2O_3 structural units resulting in the conversion of BO_3 to BO_4 structural units. Above 15 mol% B_2O_3 for series I glasses and for all the investigated compositions of the series II glasses, silicon structural units are unaffected whereas boron exist in both trigonal and tetrahedral configurations. Variation of microhardness values of these glasses as a function of composition has been explained based on the change in the relative concentration of BO_4 and BO_3 structural units. These glasses in the powder form can act as efficient room temperature ion exchangers for metal ions like Cu^{2+}. It is seen that the ion exchange does not affect the boron and silicon structural units as revealed by IR studies.
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1. Introduction

Boroaluminosilicate glasses are technologically important due to their high mechanical strength and chemical durability and are widely used in various applications, which include optical communication, glass to metal seals, ion exchange materials, nuclear waste immobilization, etc [1–6]. It is known that the physico-chemical properties of borosilicate/boroaluminosilicate glasses like thermal expansion coefficient, glass transition temperature, chemical durability/thermal stability and ion exchange capacity are strong function of the composition as well as type of the additives incorporated in the glass [3–8]. Composition

of the glass and type of the additives decide the nature of different structural units present in the glass and their interaction and this in turn will decide the properties of the glass. Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy using ^{29}Si and ^{11}B as probe nuclei is an ideal technique to monitor the structural changes in borosilicate glasses. For example, incorporation of B_2O_3 at the expense of PbO in ternary lead borosilicate glasses decreases the thermal expansion coefficient and increases the glass transition temperature [9]. Based on ^{29}Si and ^{11}B MAS NMR and infrared (IR) absorption studies, it has been established that formation of Si–O–B linkages and increase in concentration of Q^4 structural units of silicon (where Q^n represents silicon structural units having *n*-number of bridging oxygen atoms) are responsible for the observed variation in the thermal expansion coefficient and glass transition

* Corresponding author. Tel.: +91 22 25592224; fax: +91 22 25505151.
 E-mail addresses: jrk@barc.gov.in (J. Ramkumar), mukherji@barc.gov.in, tulsi.mukherjee@gmail.com (T. Mukherjee).

temperature. Similarly Bi_2O_3 incorporation at the expense of PbO in $PbO–B_2O_3–SiO_2$ glasses results in the increase of thermal expansion coefficient, deformation and flow temperatures [10]. Addition of network modifiers (alkali/alkaline earth metal oxides) to borosilicate glasses [11–14] results in the initial conversion of BO_3 to BO_4 structural units. With further increase in modifier concentration, BO_4 structural units in the glass are replaced by BO_3^- structural units (planar BO_3 structural units with one nonbridging oxygen atoms). Extensive studies have been reported on the structural aspects of boroaluminosilicate glasses using techniques like IR, Raman and ^{29}Si, ^{11}B MAS NMR [15–18]. Based on these studies existence of structural units like trigonally coordinated boron (BO_3), tetrahedrally coordinated boron (BO_4), silicon atoms with 3 and 4 bridging oxygen atoms, Q^n units with Si–O–B/Si–O–Al linkages, etc., have been well established. It is desirable to correlate these structural aspects with physicochemical properties so that, it will be helpful for developing glasses for various user defined applications. Keeping this in mind, two series of boroaluminosilicate glasses having general formulae $(Na_2O)_{0.27-x}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ (with $0.05 \leqslant x \leqslant 0.22$) (series I) and $(Na_2O)_{0.12}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.84-x}(Al_2O_3)_{0.011}$ (with $0.15 \leqslant x \leqslant 0.28$) (series II) were prepared. Structural aspects were studied using ^{29}Si and ^{11}B MAS NMR techniques. The results obtained are correlated with the variation of microhardness value of the glasses. Room temperature ion exchange property of these glasses, in the powdered form, for Cu^{2+} ion has also been investigated. To the best of authors knowledge no such studies in this direction has been reported for this type of glasses.

2. Experimental

Glass samples were prepared by conventional melt-quench method from reagent grade SiO_2, H_3BO_3, Al_2O_3, $NaNO_3$ and KNO_3 at 1400–1500 °C in platinum crucibles. The structural aspects were studied using X-ray diffraction and NMR techniques.

^{29}Si and ^{11}B MAS NMR patterns of these glasses were recorded using a NMR machine having a magnetic filed of 7.04 T. Powdered samples were packed inside zirconia rotors and subjected to a spinning speed of 5 kHz. Typical 90° pulse durations for ^{29}Si and ^{11}B nuclei are 4.5 and 2.09 μs, respectively with the corresponding delay times of 6 and 2 s. ^{11}B NMR experiments were carried out with lower pulse durations also (up to 0.3 μs) and the line shapes were found to be identical. The chemical shift values for ^{29}Si and ^{11}B NMR spectra are reported with respect to tetramethylsilane and 1M aqueous solution of H_3BO_3, respectively. All the ^{11}B NMR patterns were corrected for the boron nitride (BN) background arising from the Bruker MAS NMR probe. ^{27}Al MAS NMR patterns were recorded for representative glass samples of both the series with a basic frequency of 78.2 MHz. The 90° pulse duration was 3.5 μs with a relaxation delay time of 4 s. Errors

in the relative concentration and chemical shift values of Q^n structural units of Si are calculated by combining the fitting errors and errors obtained form duplicate measurements.

The microhardness of the samples were measured based on indentation technique using Vickers microhardness indenter under a constant load of 50 g for 10 s duration at room temperature. Errors in the microhardness are calculated by duplicate measurements.

For ion exchange studies, Cu^{2+} ion solutions were prepared by dissolving suitable amounts copper chloride in dilute HCl and then standardized by EDTA titrations. Ten milliliter of Cu^{2+} ion solution of known concentration was equilibrated with a weighed amount of glass sample for 5 h and the concentration of metal ions in solution was determined after equilibration by Atomic absorption spectrophotometer. Errors in the exchange capacity have been calculated by duplicate measurements.

For IR investigations, the samples were thoroughly ground with KBr and the fine powder was pressed in the form of thin pellets. IR patterns were recorded using a FTIR machine with a resolution of 4 cm^{-1}. Luminescence studies were carried out using a fluorimeter having 150 W Xe lamp as the excitation source.

3. Results

X-ray diffraction studies revealed the glassy nature of the samples. Fig. 1 shows the ^{29}Si MAS NMR patterns of the $(Na_2O)_{0.27-x}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ glasses (series I) as a function of B_2O_3 concentration. For the glass sample having 5 mol% B_2O_3, an asymmetric peak with maximum around –92 ppm was observed. Deconvolution of this peak assuming a Guassian line shape resulted in two peaks around -102 ppm and -91 ppm. Based on the previous ^{29}Si MAS NMR studies of borosilicate and boroaluminosilicate glasses [11–15], the peaks around -102 and -91 ppm can be attributed to the Q^4 and Q^3 structural units of silicon (i.e. silicon structural units having 4 and 3 bridging oxygen atoms, respectively). As the B_2O_3 concentration increases up to 15 mol%, at the expense of Na_2O, there is a systematic conversion of Q^3 structural units to Q^4 structural units. With further increase in the B_2O_3 content, relative concentration of Q^3 and Q^4 structural units remained same as revealed by the identical ^{29}Si MAS NMR line shapes. Further the chemical shift values of the Q^4 and Q^3 structural units systematically shifted to more negative values (Fig. 2) suggesting the increased chain length (extent of cross linking) of silicate/borosilicate network [19]. Fig. 3 shows the ^{29}Si MAS NMR patterns for $(Na_2O)_{0.12}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.84-x}(Al_2O_3)_{0.011}$ glasses (series II) as a function of B_2O_3 concentration. All the patterns are found to have identical line shape with a broad asymmetric peak around –105 ppm. Deconvolution based on a Guassian fit resulted in two peaks with relative concentration of Q^4 and Q^3 structural units in the ratio 80:20. The relative concentration of Q^4 and Q^3
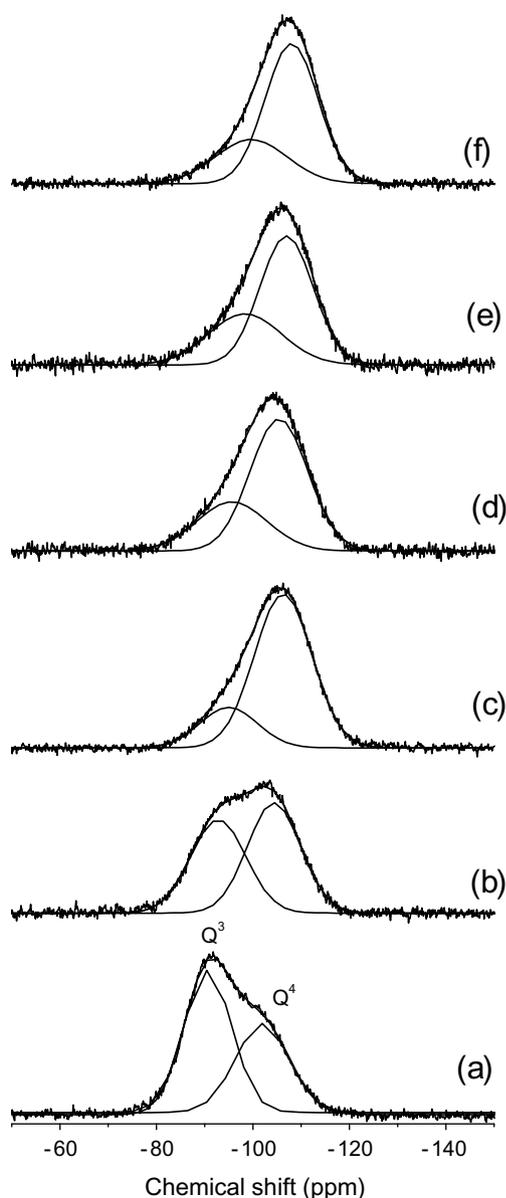
Fig. 1. ^{29}Si MAS NMR patterns for $(Na_2O)_{0.27-x}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ glasses (series I) with (a) $x = 0.05$ (b) $x = 0.10$ (c) $x = 0.15$, (d) $x = 0.17$, (e) 0.20 and (f) $x = 0.22$.

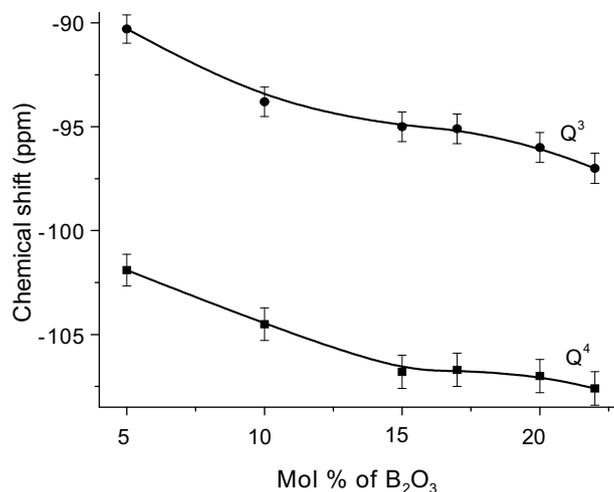Fig. 2. Variation of chemical shift values of Q^n structural units as a function of B_2O_3 concentration for series I glasses. Lines have been drawn as guide to the eyes.

structural units along with their chemical shift values are found to be unaffected (within experimental error) by the increase in B_2O_3 content in the glass as can be seen from Fig. 3.

Fig. 4 shows the ^{11}B MAS NMR patterns for series I glasses as a function of B_2O_3 concentration. As ^{11}B is a quadrupolar nuclei ($I = 3/2$), it will be having a negligible quadrupolar interaction when it occupies environment with cubic symmetry, i.e. tetrahedrally coordinated boron structural units (BO_4). Unlike this boron in trigonal coordination (BO_3 structural unit) is significantly affected by the quadrupolar interaction, giving rise to a broad peak. For the glass containing 5 mol% B_2O_3 (Fig. 4(a)), the NMR pattern consist of a sharp isotropic peak around -22 ppm along with number of side bands characteristic

of tetrahedrally coordinated BO_4 structural units [5,9]. The patterns essentially remained same up to 15 mol% B_2O_3 (Fig. 4(c)). However above 15 mol% B_2O_3 a broad peak appeared as symmetrically placed shoulders around the sharp peak around -22 ppm. Intensity of the broad peak increases with further increase in B_2O_3 concentration. The broad peak has been attributed to the trigonally coordinated boron structural units [5,9]. Fig. 5 shows the ^{11}B MAS NMR patterns of series II glasses as a function of B_2O_3 concentration. All the patterns consist of sharp peak with symmetrically placed broad shoulders on either side, characteristic of BO_4 and BO_3 structural units respectively. The relative intensity of the peak corresponding to BO_3 structural units systematically increase with increase in B_2O_3 concentration in the glass. Accurate determination of BO_3 and BO_4 structural units could not be made due to significant loss of intensity of the peaks corresponding to BO_3 and BO_4 structural units in number of side bands. ^{27}Al MAS NMR studies carried out for these samples revealed only a broad peak around -60 ppm characteristic of tetrahedrally coordinated aluminum (AlO_4) structural units (not shown).

Fig. 6(a) and (b) shows the variation of microhardness as a function of B_2O_3 content for both series I and series II glasses. For series I glasses microhardness value increases up to 15 mol% B_2O_3 and above that it started decreasing. Unlike this for series II glasses the microhardness value systematically decreases with increase in B_2O_3 content in the glass. Similar change in the relative concentration of BO_3 and BO_4 structural units are observed for both the series of glasses as can be seen from the ^{11}B MAS NMR patterns (Figs. 4 and 5).

Cu^{2+} ion exchange studies were carried out at room temperature for two powdered glass samples having composition $(Na_2O)_{0.22}(K_2O)_{0.029}(B_2O_3)_{0.05}(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ (series I with $x = 0.05$) and $(Na_2O)_{0.05}(K_2O)_{0.029}(B_2O_3)_{0.22}(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ (series I with
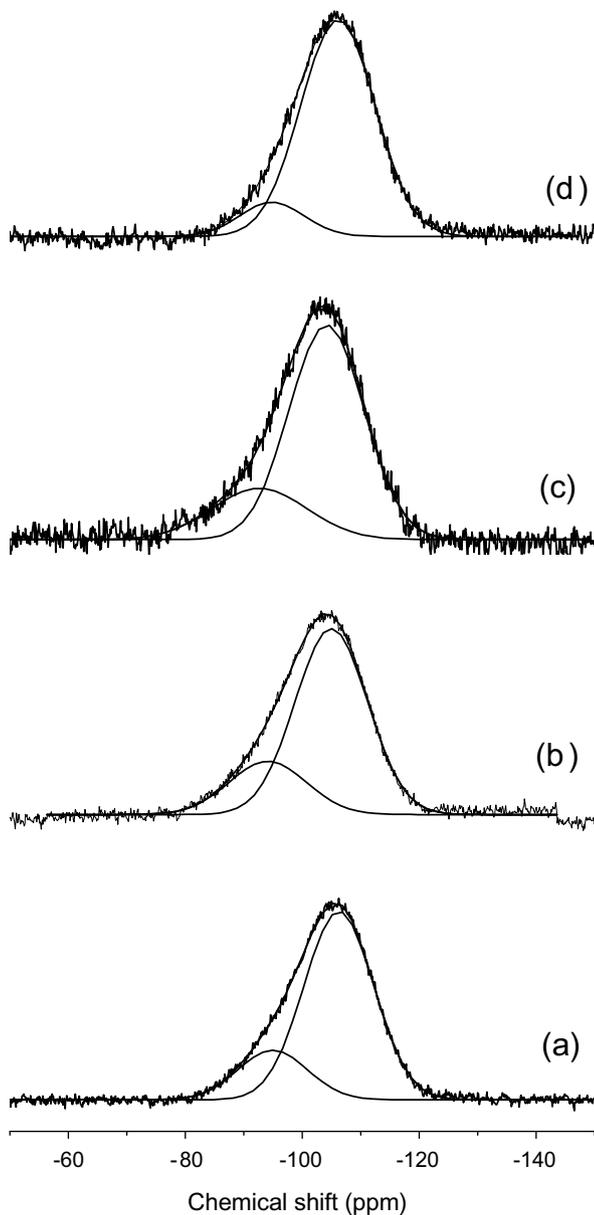
Fig. 3. ^{29}Si MAS NMR patterns for $(Na_2O)_{0.12}(K_2O)_{0.029}(B_2O_3)_x$-$(SiO_2)_{0.84-x}(Al_2O_3)_{0.011}$ glasses (series II) with (a) $x = 0.15$ (b) $x = 0.20$ (c) $x = 0.24$ and (d) $x = 0.28$.

Fig. 4. ^{11}B MAS NMR patterns for $(Na_2O)_{0.27-x}(K_2O)_{0.029}(B_2O_3)_x$-$(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ glasses (series I) with (a) $x = 0.05$ (b) $x = 0.10$ (c) $x = 0.15$, (d) $x = 0.17$, (e) 0.20 and (f) $x = 0.22$. Peaks marked '$*$' are spinning side bands.

$x = 0.22$). These compositions are specifically chosen as they contain maximum and minimum concentrations of Na_2O between both the series of glasses. Ion exchange capacity for series I glass with $x = 0.05$ is found to be 86% ($\pm3\%$) and for series I glass with $x = 0.22$, it is only 12% ($\pm3\%$). As expected ion exchange capacity has been found to be more for sample containing higher amounts of replaceable ions like Na^+ or K^+.

Fig. 7 shows the IR spectra of Cu^{2+} exchanged and unexchanged $(Na_2O)_{0.22}(K_2O)_{0.029}(B_2O_3)_{0.05}(SiO_2)_{0.69}$-$(Al_2O_3)_{0.011}$ glass samples. The patterns are almost same except that the intensity of peaks around $3500 \, cm^{-1}$ and $1600 \, cm^{-1}$ are significantly higher for Cu^{2+} exchanged sample compared to the unexchanged sample and this has been attributed to the water molecules incorporated

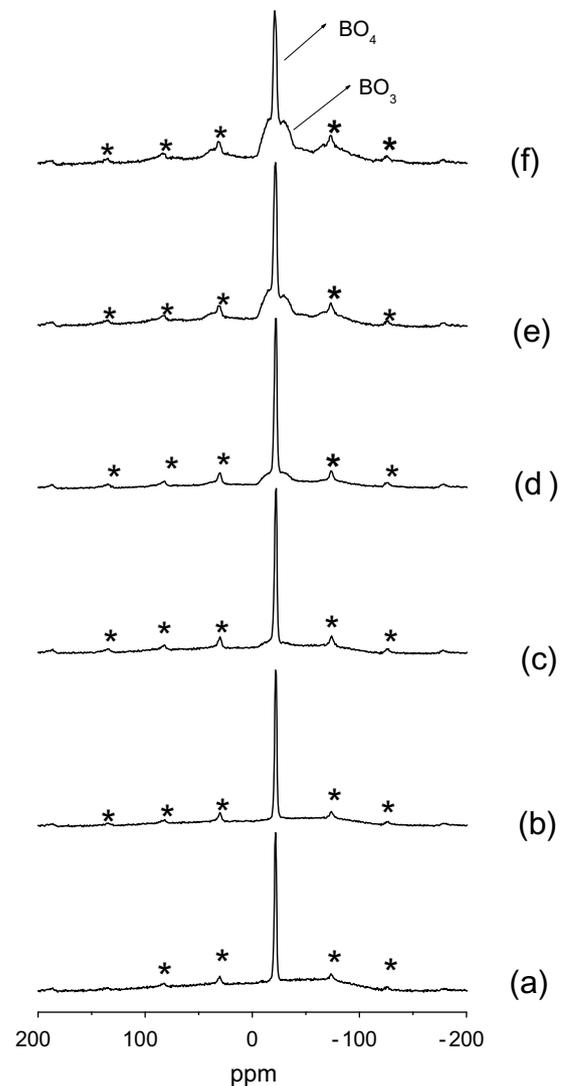into the glass during the room temperature ion exchange process. The peaks around 1050 and $460 \, cm^{-1}$ have been attributed to the stretching and bending vibrations of Si–O–Si/Si–O–B linkages [5,9,13] present in the glass. Photoluminescence measurements were carried out on the samples to check whether any Cu^+ ions are formed in the glass after ion exchange. This is because Cu^{2+} ion in the glass matrix does not give any emission at room temperature, whereas Cu^+ ion gives a broad green emission at room temperature [20].

Fig. 8 shows the emission spectrum of room temperature Cu^{2+} exchanged $(Na_2O)_{0.22}(K_2O)_{0.029}(B_2O_3)_{0.05}(SiO_2)_{0.69}$-$(Al_2O_3)_{0.011}$ glass along with that of the same sample after re-melting. No emission peak is observed for the room temperature ion exchanged sample revealing that all the copper ions exist in the Cu^{2+} state. However, a broad peak around 500 nm is observed from ion exchanged and re-melted glass

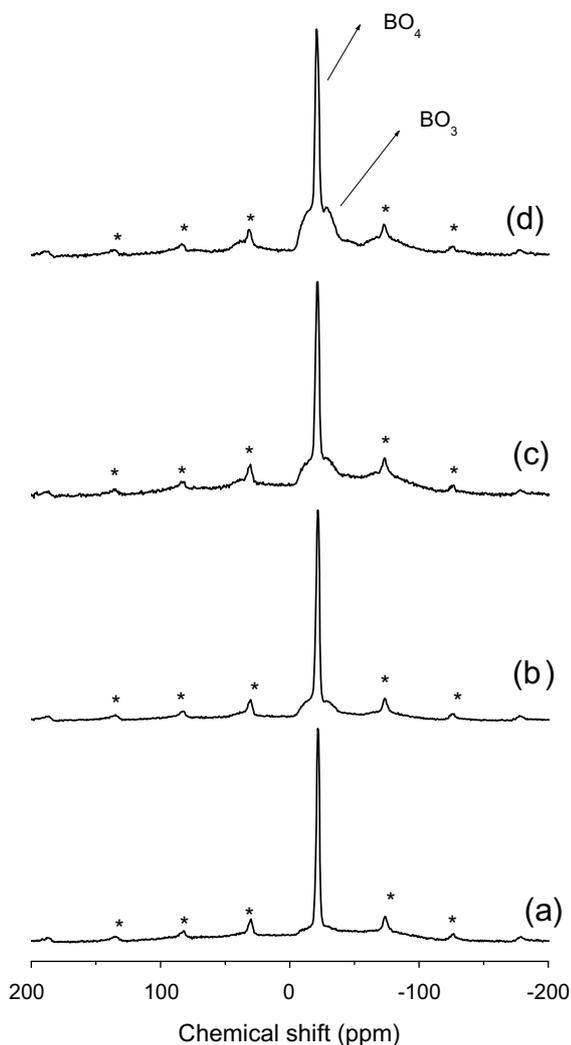Fig. 5. ^{11}B MAS NMR patterns for $(Na_2O)_{0.12}(K_2O)_{0.029}(B_2O_3)_x$-$(SiO_2)_{0.74-x}(Al_2O_3)_{0.011}$ glasses (series II) with (a) $x = 0.15$ (b) $x = 0.20$ (c) $x = 0.24$ and (d) $x = 0.28$. Peaks marked '*' are spinning side bands.
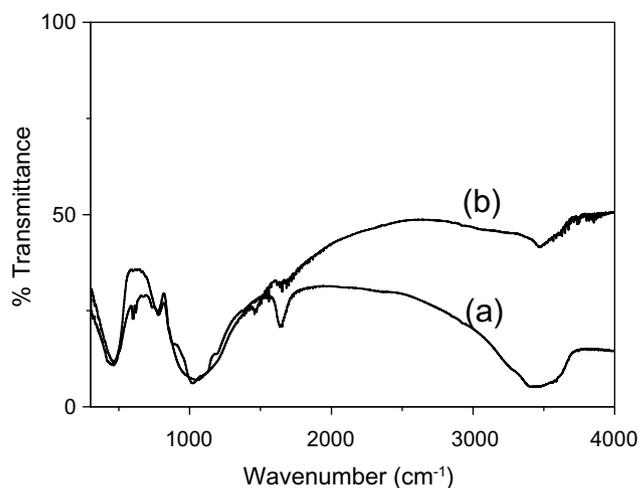

Fig. 7. IR patterns for $(Na_2O)_{0.27-x}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.69}$-$(Al_2O_3)_{0.011}$ glass (a) after (b) before Cu^{2+}exchange.

sample. The broad peak around 500 nm is attributed to the transition between closely non-degenerate T_{1g} and T_{2g} level to the ground state (^1A_g level) of Cu^+ ion [20].

4. Discussion

^{29}Si MAS NMR patterns of series I glasses revealed that Q^3 structural units got converted to Q^4 structural units only up to 15 mol% B_2O_3 concentration, whereas from ^{11}B MAS NMR patterns of the same glasses it is clear that above 15 mol% only BO_3 structural units are formed. Hence by combining ^{29}Si and ^{11}B MAS NMR it can be established that initially when B_2O_3 concentration increases at the expense of Na_2O up to 15 mol%, B_2O_3 preferentially interacts with Na_2O resulting in the conversion of BO_3 to BO_4 structural units. This also leads to the conversion of Q^3–Q^4 structural units of silicon, as Na^+ ions are
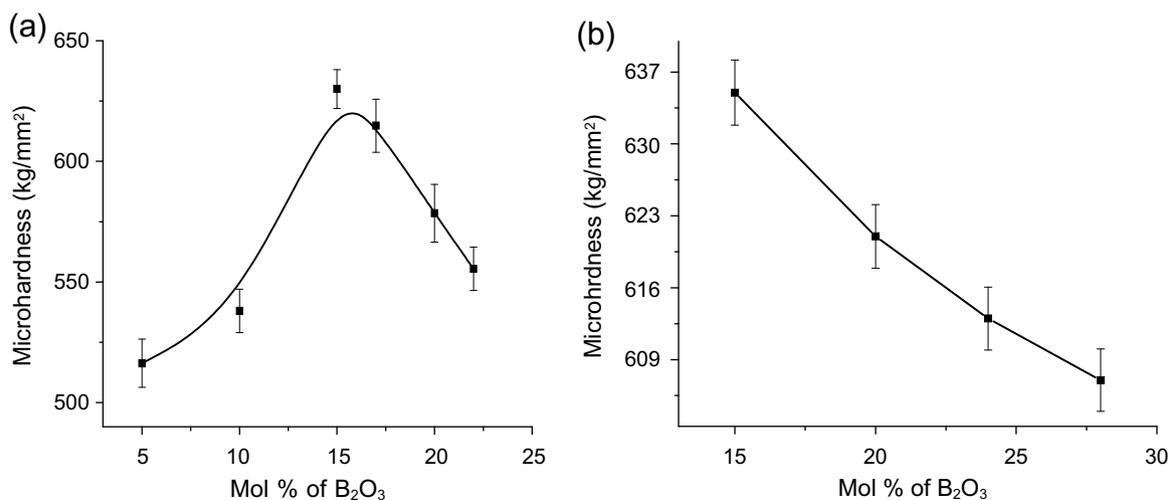

Fig. 6. Variation of microhardness values as a function of composition for (a) $(Na_2O)_{0.27-x}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ glasses and (b) $(Na_2O)_{0.12}(K_2O)_{0.029}(B_2O_3)_x(SiO_2)_{0.84-x}(Al_2O_3)_{0.011}$ glasses. Lines have been drawn as guide to the eyes.
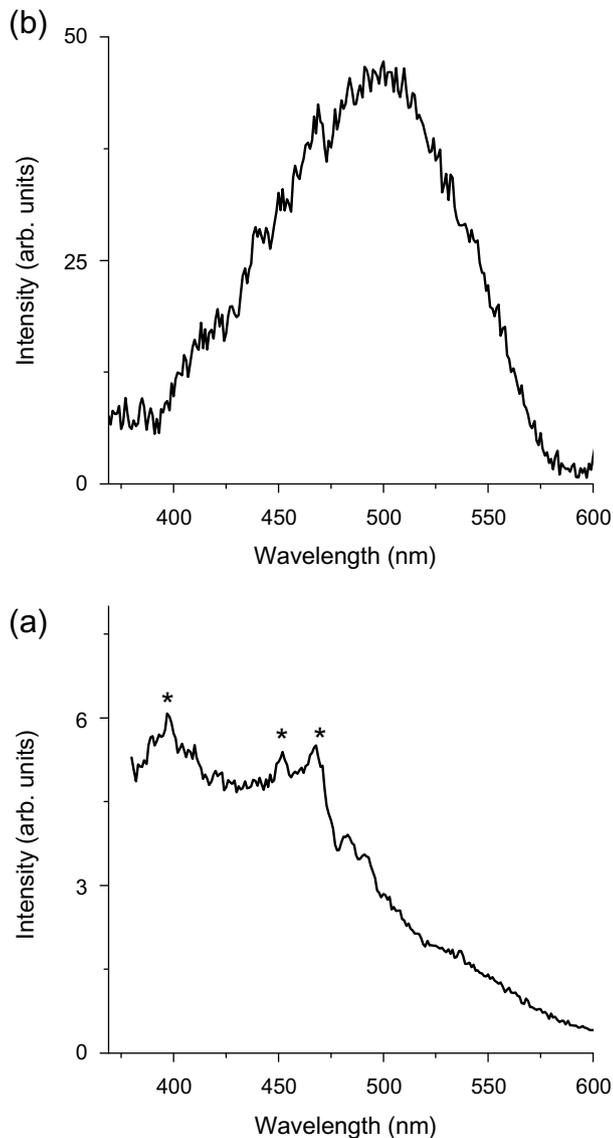
Fig. 8. Emission spectra obtained on 260 nm excitation for (a) as prepared Cu^{2+} exchanged $(Na_2O)_{0.22}(K_2O)_{0.029}(B_2O_3)_{0.05}(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ glass (b) re-melted Cu^{2+} exchanged $(Na_2O)_{0.22}(K_2O)_{0.029}(B_2O_3)_{0.05}(SiO_2)_{0.69}$-$(Al_2O_3)_{0.011}$ glass. Peaks marked '∗' are artefacts.

the ^{11}B MAS NMR patterns. As B_2O_3 concentration increases at the expense of SiO_2, Na^+ ions proportionately get redistributed between the boron and silicon structural units. This results in an increase in BO_3 concentration leaving the silicon structural units unaffected as the Na^+ ions attached with silicon structural units proportionately decreases with decrease in silica content.

Microhardness values of the glass mainly depend on the rigidity of the glass network. Increase in the rigidity of the network is associated with increase in the microhardness values. In both the series of glasses the borosilicate structural units mainly form the network and hence the changes in the boron and silicon structural units decide the rigidity of the glass network. Q^4 structural units of silicon and BO_4 structural units of boron are more rigid compared to Q^3 structural units of silicon and BO_3 structural units of boron. Hence an increase in concentration of Q^4 structural units of silicon and BO_4 structural units of boron will be associated with an increase in microhardness value of the glass. Based on the structural information obtained above, the increase in micro hardness value up to 15 mol% B_2O_3 for series I glasses can be attributed the increase in concentration of Q^4 structural at the expense of Q^3 structural units and presence of more rigid BO_4 structural units. However, above 15 mol%, there is an increase in the concentration of BO_3 structural units whereas silicon structural units remained unaffected. As the Si–O and B–O bonds have got comparable energy, the increase in less rigid BO_3 structural units in the glass is the reason for decrease in microhardness values of the glass. For the series II glasses, silicon structural units are unaffected. But the relative concentration of trigonally coordinated boron structural units increases with increase in B_2O_3 contents. Hence decrease in microhardness with increase in B_2O_3 content for series II glasses is again due to the increase in concentration of less rigid BO_3 structural units. As the Al_2O_3 content is very small and constant and the fact that aluminum exist in the glass as tetrahedrally coordinated AlO_4 structural units irrespective of the composition of the glass, it is reasonable to conclude that Aluminum structural units do not have any effect on the micro hardness variation as a function of composition for both the series of glasses.

Ion exchange capacity has been found to be more when more Na^+ ions are present in the glass sample. High concentration of network modifiers like Na^+, results in the conversion of Si–O–Si to Si–O$^-$ Na^+ or Si–O–H linkages thereby increasing the concentration of nonbridging oxygen atoms in the glass. ^{29}Si MAS NMR patterns clearly show that the glass with composition $(Na_2O)_{0.22}(K_2O)_{0.029}$-$(B_2O_3)_{0.05}(SiO_2)_{0.69}(Al_2O_3)_{0.011}$ has got higher nonbridging oxygen concentration attached to silicon. Also boron in these glasses exist only as BO_4^- structural units whose charge is neutralized by the Na^+ ions. This will result in improved ion exchange capacity for this glass compared to the glass with composition $(Na_2O)_{0.05}(K_2O)_{0.029}$-$(B_2O_3)_{0.22}(SiO_2)_{0.69}(Al_2O_3)_{0.011}$, where mostly Q^4 structural units exist along with BO_3 structural units, which are

insufficient for charge neutralizing the Q^3 structural units of silicon. Na^+ ions are preferentially taken up by B_2O_3 and are used for the conversion of BO_3 to BO_4 structural units. However, above 15 mol% B_2O_3, Na_2O concentration is small and whatever remaining is not sufficient to convert all the BO_3 to BO_4 structural units. Due to this the relative concentration of Q^4 and Q^3 structural units of silicon are unaffected and concentration of BO_3 structural unit increases with increase in B_2O_3 content in the glass. These results agree well with alkali ion behavior observed in sodium borosilicate glasses [11,12].

For series II glasses, the relative concentration of Q^4 and Q^3 structural units are unaffected by the change in the B_2O_3 concentration. Unlike this there is an increase in the relative concentration of BO_3 structural units as revealed by

neutral structural units (does not have any charge). ^{29}Si MAS NMR patterns could not be recorded for the Cu^{2+} exchanged sample due to the significant extent of line broadening brought about by the presence of paramagnetic centers in the glass. IR pattern of the glasses have established that the borosilicate structural units are unaffected by the ion exchange process. This again supports the fact that only the $Na^+/K^+/H^+$ ions are replaced in the glass by Cu^{2+} ions during ion exchange. No Cu^+ ions are formed in the exchanged glass sample, as it would have given a peak centerd around 500–550 nm in the emission spectrum from the sample [20]. However the Cu^{2+} ion in the glass get converted to Cu^+ when the exchanged glass is re-melted and quenched as revealed by a broad peak around 500 nm characteristic of the transition between almost degenerate T_{1g}/T_{2g} levels to ^1A_g level of Cu^+ ions [20].

5. Conclusion

Based on ^{29}Si and ^{11}B MAS NMR studies, it has been concluded that for series I glasses below 15 mol% B_2O_3 content, Na_2O preferentially interacts with B_2O_3 structural units resulting in the conversion of BO_3 to BO_4 structural units along with the conversion of Q^3 to Q^4 structural units of silicon. Above 15 mol% B_2O_3 for series I glass and for all the investigated compositions of the series II glass, silicon structural units are unaffected whereas boron exists in both trigonal and tetrahedral configurations. Variation of microhardness values of these glasses as a function of composition has been explained based on the change in the relative concentration of BO_4 and BO_3 structural units. Room temperature Cu^{2+} ion exchange capacity is highest for glass sample having maximum concentration of exchangeable ions like Na^+ and K^+. Melting of the exchanged glasses results in the formation of Cu^+ ions in the glass.

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