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MÖSSBAUER SPECTROSCOPIC STUDIES ON $(\text{Li}_2\text{O}-x\text{B}_2\text{O}_3)_{1-y}(\text{Fe}_2\text{O}_3)_y$ GLASSES

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Abstract

Mössbauer spectra of Fe_2O_3 doped lithium borate glasses have been studied. The spectra exhibit only quadrupole split doublets typical of glasses. Isomer shift (IS), quadrupole splitting (QS), line widths and magnetic hyperfine splitting parameters have been evaluated. It is found that these parameters are dependent on the B_2O_3 and Fe_2O_3 concentration in the glasses. The values IS and QS, indicate that the iron ions are located in the tetrahedral environment.

Keywords: Quadrupole, Isomer Shift (IS), Quadrupole Splitting (QS), Tetrahedral Environment.

1. Introduction

Mössbauer effect is a structure sensitive technique like EPR spectroscopy and has been used extensively to get information on the structure of oxide, chalcogenide and metallic glasses. From Mössbauer measurements, the parameters isomer shift, quadrupole splitting, line widths and magnetic hyperfine splitting can be evaluated. These parameters are structure sensitive and, therefore, provide useful information regarding structure, i.e., coordination number, symmetry, valence and diffusion etc. A number of books and review articles are available in literature giving detailed account of Mössbauer spectroscopy and its applications in chemistry, metallurgy and materials science etc. [01-07]. Review articles by Kurkjian [08] and by Sekhon and Kamal [09] specifically deal with its usefulness and the application of the Mössbauer spectroscopy to oxide glasses. This study gives brief details on our study of the Mössbauer Spectra results on lithium-borate glasses doped with iron oxide.

Kurkjian [08] and Angell & Wong [11] have reviewed early work on Mössbauer spectroscopy (referred MS hereafter) studies in oxide glasses. Recently review articles by Warmuth et al. [12] and Sekhon et al. [09] have also appeared. Some of the earlier important results on a number of oxide glasses are summarized below. MS studies on potassium phosphate glasses [08, 09, 11, 12] show that both Fe^{2+} and Fe^{3+} are present in octahedral sites. The quadrupole splitting, referred QS hereafter, decreases with increase in the alkali content which is attributed to an increase in the symmetry around Fe ions. MS investigations of silicate glasses containing Fe_2O_3 show that (a) iron is present in Fe^{2+} state and/or Fe^{3+} state, (b) Fe^{2+} state prefers to be octahedrally coordinated, i.e., at network modifying positions, whereas Fe^{3+} state is generally tetrahedrally coordinated, i.e., at network forming positions [08, 09, 11, 12]. MS studies on alkali silicate glasses have shown that Fe^{3+} prefers tetrahedral and octahedral sites while Fe^{2+} is found in octahedral sites [08, 09, 11, 12]. In alkaline earth silicate glasses, Fe^{2+} and Fe^{3+} sites depend upon the alkaline earth oxide [13, 14].

Borate glasses have been extensively studied by ^{57}Fe -MS technique and results have been discussed in terms of boron anomaly as well as the role of Fe_2O_3 . Studies on alkali borate and alkaline earth borate glasses containing Fe_2O_3 exhibit some general features: (a) Fe^{3+} prefers to be in tetrahedral and octahedral sites, (b) at high concentrations of Fe_2O_3 in these glasses, crystallites of Fe_2O_3 and Fe_3O_4 may appear, and (c) at intermediate concentration of Fe_2O_3 , a superparamagnetic phase may appear. Sekhon and Kamal [15] observed a continuous decrease in the isomer shift (referred IS hereafter) values with x in $x\text{PbO}-(1-x)\text{B}_2\text{O}_3-10\text{Fe}_2\text{O}_3$ glasses indicating that the s-electron density increases at Fe^{3+} site. The QS values show increase with x for low PbO content (<20 mol%). For the PbO content larger than 20 mol% and up to 50 mol%, QS tends to decrease and shows a small increase on further increase of PbO content. MS studies on $x\text{M}_2\text{O}-(95-x)\text{B}_2\text{O}_3-5\text{Fe}_2\text{O}_3$ glasses, where M = Li, Na or K, by Raman et al. [16] show that IS and QS decrease smoothly with increase in alkali content. They have attributed this to increase in the covalency of Fe-O bond and the site symmetry around Fe^{3+} . Sharp changes in IS and QS in the boron anomaly region were observed by them which are attributed to the change of Fe^{3+} from octahedral to tetrahedral sites.

Nishida et al. [17] observed continuous decrease of IS and QS values with increase in K_2O concentration in $x\text{K}_2\text{O}-(1-x)\text{B}_2\text{O}_3-7\text{Fe}_2\text{O}_3$ glasses. No abrupt changes in IS were observed near the composition corresponding to the boron anomaly. The decrease in IS has been explained by them in terms of a decrease of distance between Fe^{3+} and non-bridging oxygen which leads to an overlap of the 4s-orbital of the Fe^{3+} ion with the p-orbital of the oxygen atom. Further, they suggested that Fe^{3+} ion acts as a network former in this glass system. MS studies on alkaline earth borate glasses, namely, $\text{CaO}-\text{B}_2\text{O}_3-\text{Fe}_2\text{O}_3$ and $\text{BaO}-\text{B}_2\text{O}_3-\text{Fe}_2\text{O}_3$ [18, 19], $x\text{BaO}-(0.9-x)\text{B}_2\text{O}_3-0.1\text{Fe}_2\text{O}_3$ [20] and $(1-y)(\text{BaO}.2\text{B}_2\text{O}_3)-y\text{Fe}_2\text{O}_3$ [20], show that Fe^{3+} ions occupy both tetrahedral and octahedral positions in these glasses. The variation of IS and QS values is observed to be similar as in the lead-borate glasses [15].



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Lithium borate glasses containing Fe₂O₃ have been studied by a few workers [21-23]. Sanchez & Friedel [22] have shown in the Li₂O-B₂O₃-Fe₂O₃ system that Fe³⁺ ions coexist in tetrahedral and octahedral coordination below 8.5 at% Fe and the presence of Fe²⁺ observed in some glasses is related to the preparation conditions. Mostafa et al. [23] studied MS of lithium borate glasses containing 5.66 mol% of Fe₂O₃ in which Li₂O content varied from 15 mol% to 47 mol%. IS was observed to be constant while QS decreased with the Li₂O content in the glasses. They also suggested that iron is present in both tetrahedral and octahedral sites. We present here results of our Mössbauer Spectroscopic studies on (Li₂O-xB₂O₃)_{1-y}(Fe₂O₃)_y glasses and derive some of relevant parameters from the measurements and discuss the results.

2. Experimental details

Analar grade H₃BO₃, Li₂CO₃ and Fe₂O₃ were used as the starting materials to prepare lithium borate glasses with doping iron. Starting chemicals of appropriate proportions were weighed to yield approximately 5 to 7 gm of batches of mixtures. The weighing was done to an accuracy of 0.5 mg using an electronic balance. Chemical mixtures, so prepared, were ground to a fine powder using a good quality agate mortar and an agate pestle to mix the chemicals uniformly using a very small amount of AR-grade acetone. Each batch of these mixtures were placed in a platinum crucible and then transferred to a home-built electric furnace capable of reaching 1150 °C. The temperature of the furnace was controlled using a temperature-control unit capable of controlling temperature within ±5 °C. A chromel-alumel thermocouple was used as the temperature sensor and it was positioned in the furnace so that it was just above the crucible. If the initial mixture contained H₃BO₃, then the mixture was heated to 400-500°C for 24-48 hours first and only then temperature was further increased above melting temperature of the mixture. The melt was kept approximately 10 °C above melting point for 30 minutes to 1 hour depending upon the sample composition. The melt was occasionally shaken for better homogeneous mixing of all the constituent chemicals.

Melts of each batch were quenched by pouring over a hot stainless-steel plate, heated to between 300 and 400 °C, and immediately pressed with another steel plate to obtain glasses of various compositions. A good glass formation was noticed by looking at the transparency and its uniformity. Depending upon the dopant (i.e., Fe₂O₃ etc.) the prepared glasses had distinctive colours. Glasses so produced were kept in another electric furnace immediately to anneal at 300°C for approximately 48 hours. After annealing, each glass sample is ground to make fine powder. This powdered material was used to record a diffraction using a German-make SEIFERT Diffractometer Model “MZ-III” Glassy or amorphous materials do not have long-range atomic order, i.e., atoms are arranged randomly. Therefore, a diffraction pattern containing sharp peaks is not expected as observed in crystalline materials. All the glass investigated here were subjected to the X-ray diffraction measurements to ascertain whether these were really glassy or not. Absence of sharp peaks and the presence of a broad hump indicates the glassy nature of these materials, i.e., long-range atomic order is absent. A physical examination of the glasses prepared also showed that these are “glassy” like. If an X-ray diffraction pattern of any papered glass showed even a small peak, it was rejected and no measurements were made on this particular sample. Fig 1 shows X-ray diffractograms of iron doped lithium borate glasses.

Four sets of glasses prepared: Li₂O-xB₂O₃, where x = 1, 2, 3 and 4. Each set was doped with 10 at%, 15at% and 20 at% of Fe₂O₃. Doping with Fe₂O₃ smaller than 10 at% did not yield good Mössbauer spectra. Each glass was ground to fine powder and was placed in a perspex holder in such a way that the thickness of the sample was uniform. The Mössbauer source was a 10 mCi Co-57 source encapsulated in rhodium matrix. Only room temperature measurements were taken. Total number of counts accumulated were typically 10,00,000. The velocity scale was calibrated using sodium nitroprusside which is used as a standard for Mössbauer spectra exhibiting only quadrupole split doublets. Each Mössbauer spectrum was analyzed into a quadrupole doublet using the least square method described below assuming Lorentzian line shapes.

3. Analysis of Mössbauer Spectrum

The least square fit method has been employed for the analysis of the Mössbauer spectrum in order to obtain the hyperfine parameters, IS and QS. This method fits each Mössbauer spectrum of a sample to a sum of two or more Lorentzian line shapes with a parabolic background as given below.

$$Y = \sum_{i=1}^n \frac{A_i}{1 + \left[\frac{x - P_i}{\Gamma_i} \right]^2} + E + FX + GX^2$$

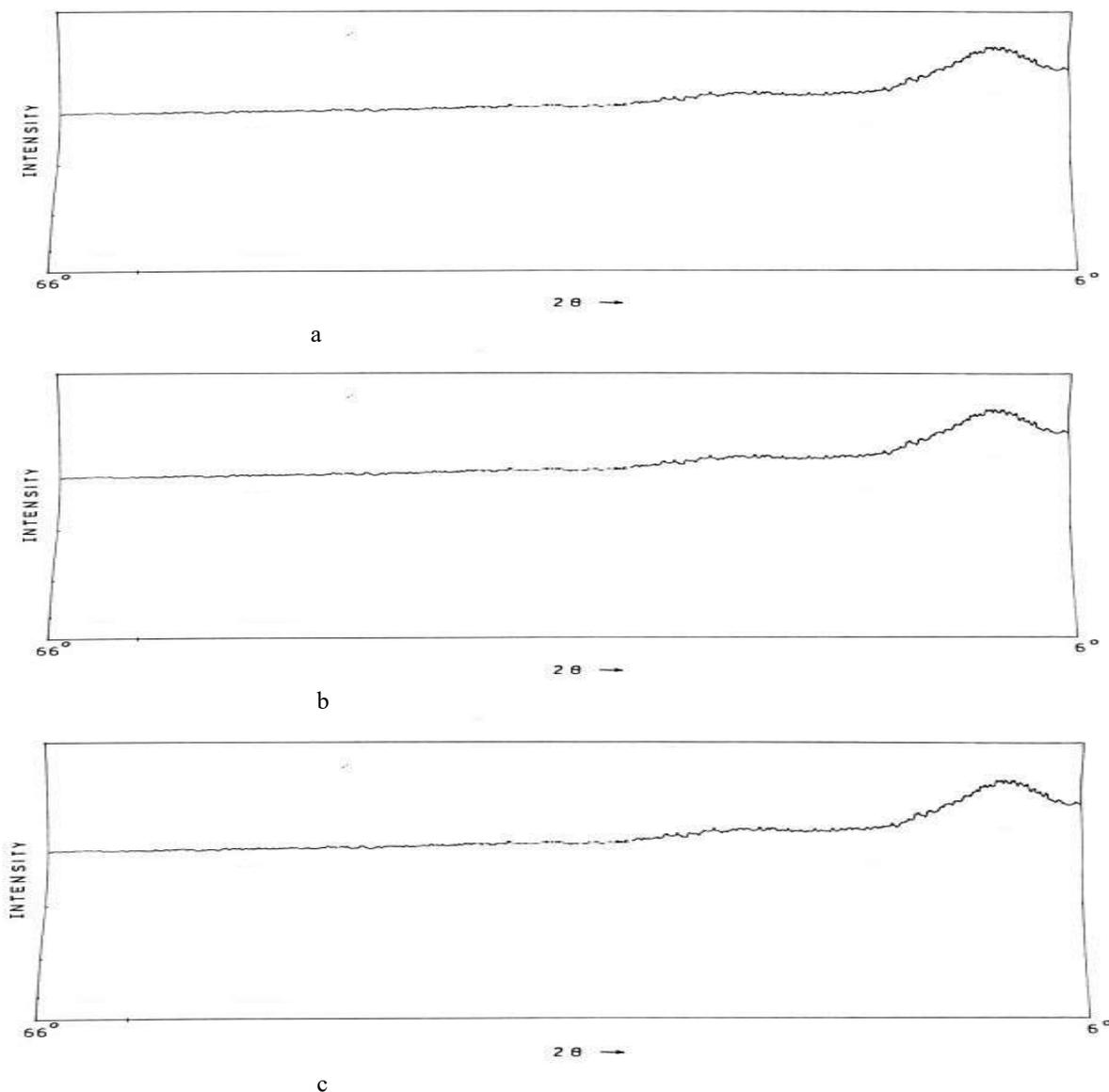


Fig 1: X-ray diffractograms of iron doped lithium borate glasses for (a) $(Li_2O-4B_2O_3)_{0.99}(Fe_2O_3)_{0.01}$, (b) $(Li_2O-4B_2O_3)_{0.985}(Fe_2O_3)_{0.015}$, and (c) $(Li_2O-4B_2O_3)_{0.98}(Fe_2O_3)_{0.02}$

Where A_i is the amplitude of the i^{th} peak (counts), X is the number of the i^{th} channel, P_i is the position of the i^{th} peak(channel), Γ_i is full width of the i^{th} peak at half-maximum amplitude (channels), E , F and G are constants of the parabola which appears as a background. The output of the computer program gives the fitted parameters, namely, the amplitude, the position, half-width and peak area of each line. Using these values, isomer shift and quadrupole splitting values are calculated. Isomer shift values are determined with respect to iron. Since all the glasses studied in this work show a doublet in the spectra, it shows that the spectra are quadrupole interaction split.

4. Results and Discussion

Mössbauer spectra recorded for the glass system $(Li_2O-xB_2O_3)_{1-y}, (Fe_2O_3)_y$, where $x = 1, 2, 3$ and 4 ; $y = 0.1, 0.15$ and 0.2 , show well resolved quadrupole doublets. Figs 2 (a)-(d) show the quadrupole split spectra for the above glass system with $x=1,2,3,4$ and $y=0.15$ and are typical of the spectra. The characteristic feature observed in lithium borate glasses is larger line-width compared to the line-width of the absorption lines in the Mössbauer spectra of either a thin iron foil or sodium nitroprusside, polycrystalline solids.

The larger line widths are due to the random atomic structure of glasses which leads to a distribution in values of electric field gradient and isomer shift at the Mössbauer probe site in the solid. This leads to the larger line widths. The average bond length variations are reflected in the changes of isomer shift values. At a network forming site no appreciable rearrangement is expected. However, at the network modifying site the environment of Fe^{3+} ions becomes rearranged due to the breaking-up of the glass-network.

The two absorptions lines in each spectrum in Fig 2, show some asymmetry in amplitude, that is, amplitude of the two lines differ slightly. This is normally observed in glassy materials including magnetic glasses where the lines in Zeeman split six-line spectra do show similar asymmetry [24]. No evidence of iron clustering is found in any of the samples, even in those samples in which the content of Fe_2O_3 is 20 at%. If clustering of iron oxide were there, the Mössbauer spectra would have shown additional lines, superimposed on the two-line spectrum. Since this is not observed in any of the Mössbauer spectra recorded, it is concluded that the iron oxide does not cluster, at least large enough to produce additional lines due to magnetic effects. Values of IS, QS and line widths for each sample are obtained from the computer fitted programme using two Lorentzians with a parabolic background are given in Table1.

Counts

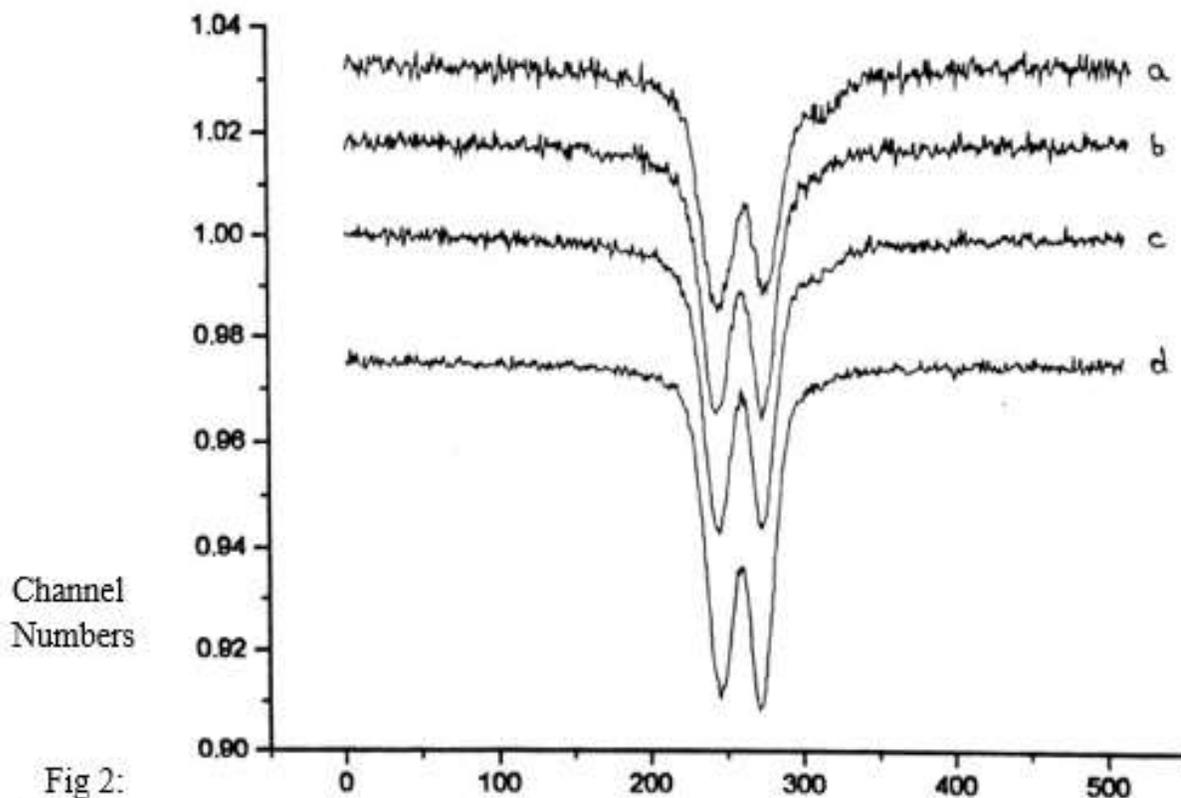


Fig 2:
Mössbauer
spectrum
of $(\text{Li}_2\text{O}-$
 $x\text{B}_2\text{O}_3)_{0.85}$

$(\text{Fe}_2\text{O}_3)_{0.15}$ where (a)x=1, (b) x=2, (c)x=3 and (d)x=4



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Table 1
Calculated Mössbauer parameters

S.No	Sample Name	Isomer Shift With reference to SNP	Quadrupole Splitting	Line width
1	(Li ₂ O-B ₂ O ₃) _{0.99} (Fe ₂ O ₃) _{0.01}	0.33	1.01	0.96
2	(Li ₂ O-2B ₂ O ₃) _{0.99} (Fe ₂ O ₃) _{0.01}	0.35	1.28	0.86
3	(Li ₂ O-3B ₂ O ₃) _{0.99} (Fe ₂ O ₃) _{0.01}	0.40	1.33	0.96
4	(Li ₂ O-4B ₂ O ₃) _{0.99} (Fe ₂ O ₃) _{0.01}	0.35	1.46	1.18
5	(Li ₂ O-B ₂ O ₃) _{0.985} (Fe ₂ O ₃) _{0.015}	0.30	1.00	0.76
6	(Li ₂ O-2B ₂ O ₃) _{0.985} (Fe ₂ O ₃) _{0.015}	0.30	1.14	0.845
7	(Li ₂ O-3B ₂ O ₃) _{0.985} (Fe ₂ O ₃) _{0.015}	0.30	1.10	0.85
8	(Li ₂ O-4B ₂ O ₃) _{0.985} (Fe ₂ O ₃) _{0.015}	0.34	1.18	0.885
9	(Li ₂ O-B ₂ O ₃) _{0.98} (Fe ₂ O ₃) _{0.02}	0.31	1.04	0.79
10	(Li ₂ O-2B ₂ O ₃) _{0.98} (Fe ₂ O ₃) _{0.02}	0.30	1.09	0.80
11	(Li ₂ O-3B ₂ O ₃) _{0.98} (Fe ₂ O ₃) _{0.02}	0.31	1.16	0.80
12	(Li ₂ O-4B ₂ O ₃) _{0.98} (Fe ₂ O ₃) _{0.02}	0.32	1.17	0.73

It has been pointed out earlier that IS and QS give information about the coordination and valence state of the iron in the glass matrix, respectively. Walker et al [10] have calculated the s-electron density at tetrahedral and octahedral sites and have shown that the s-electron density at iron nucleus is higher in the tetrahedral coordination than in the octahedral coordination. In the crystalline compounds such as CaBaFe₄O₈ and KFeO₃ in which high spin Fe³⁺ ion exists in the tetrahedral coordination values of IS are close to 0.15 mm/s [25]. Kurkjian [08] and Kurkjian & Siegty [26] show that IS values in glasses can be as much as 0.32 mm/s. The lowest value for octahedral high spin Fe³⁺ in crystalline materials is exhibited by CaFe₂O₄ and is 0.38 mm/s [26]. For octahedral Fe³⁺ ion in glasses, the value of IS is larger than 0.38 mm/s with an upper limit of 0.48 mm/s. The QS values reported in glasses, where iron is in tetrahedral coordination, usually lie in the range of 0.7 - 1.0 mm/s, whereas for more symmetric environment octahedral coordination, the values are less and lie between 0.32 - 0.88 mm/s.

Table 7.1 shows that values of IS are nearly constant for all the values of x and y for (Li₂O-xB₂O₃)_{1-y}(Fe₂O₃)_y glasses. All glasses have IS ≈ 0.32 ± 0.02 mm/s except for the glass (Li₂O-3B₂O₃)_{0.9}(Fe₂O₃)_{0.1} for which it is 0.4 mm/s. The value of IS ≈ 0.32 mm/s is consistent with the IS values of lithium borate glasses reported by Ohta et al. [27]. Comparing the values of IS in the literature and as described above for iron in tetrahedral coordination with the IS values in Table 1, it is concluded that the iron is in the high spin Fe³⁺ state in the tetrahedral coordination, that is, in the network forming positions in this glass system except for one composition, (Li₂O- 3B₂O₃)_{0.9}(Fe₂O₃)_{0.1}. Since there is hardly any change in IS values regardless of the values of x (B₂O₃ content) and y (Fe₂O₃ content), it is concluded that the s-electron density is not changing much either with x or y., hence, chemical environment seems to remain almost the same.



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Table 1 shows that values of QS for various glasses is larger than 1.00 and there is a trend of increase in its value as x (B_2O_3 content) in $(Li_2O-xB_2O_3)_{1-y}(Fe_2O_3)_y$ increases from 1 to 4 (This means that QS decreases with increase in Li_2O content.). The glasses with $y = 0.1$ (10 mol% of Fe_2O_3) show larger QS values, and the glass with composition $(Li_2O-4B_2O_3)_{0.9}(Fe_2O_3)_{0.1}$ shows the largest QS value (=1.46 mm/s). Ohta et al. [27], who studied iron oxide doped lithium borate and strontium borate glasses using Mössbauer spectroscopy, reported no variation in QS value ~ 1.2 mm/s upto 20 mol% of Li_2O . The QS value was found to decrease linearly on increase of Li_2O content for more than 20 mol%. The QS value for 60 mol% of Li_2O is reported by them to be ~ 0.78 mm/s. The results of $(Li_2O-xB_2O_3)_{1-y}(Fe_2O_3)_y$ glasses here show with increase in B_2O_3 that QS increases (i.e. x values) as shown in Fig 3 (a)-(d), which means that the QS decreases with the increase in Li_2O content which is consistent with the result of Ohta et al. (27). QS also shows a decreasing trend as a function of y for samples with x=3 and x=4, but its variation with y for samples with x=1 and x=2 does not seem to be systematic as shown in Figs 4 (a)-(d). In the literature the QS values for trivalent iron in glasses lie in the range 0.7 to 1.0 mm/s. The large QS values observed in the present glasses are indicative of highly distorted tetrahedral symmetry. Further, the increasing QS values due to changes in the relative compositions of borate and iron seems to increase distortion. The trend of increasing value of QS with B_2O_3 (x) in these glasses indicates that the symmetry is becoming less than that of tetrahedral, i.e., a distorted tetrahedral environment.

Thus, it is concluded that these QS values indicate that the iron is in the tetrahedral coordination, although distorted one, which is also confirmed by the IS values.

5. Conclusions

Lithium borate glasses doped with Fe_2O_3 have been investigated by ^{57}Fe Mössbauer spectroscopy in which relative concentration of Li_2O and B_2O_3 is varied as well as for a given composition of a glass, concentration of Fe_2O_3 is changed. All glasses show Quadrupole split Mössbauer two broad absorption lines typical of nonmagnetic glasses. Isomer shifts and quadrupole splitting (QS) were obtained by analyzing the spectra. It is observed that IS for all the glasses is nearly constant, and its value indicates that the iron ions are tetrahedrally coordinated. The QS values of various glasses show a trend to increase with increase in B_2O_3 content (hence decrease in Li_2O content). These values also indicate that iron ions are located at tetrahedral sites.

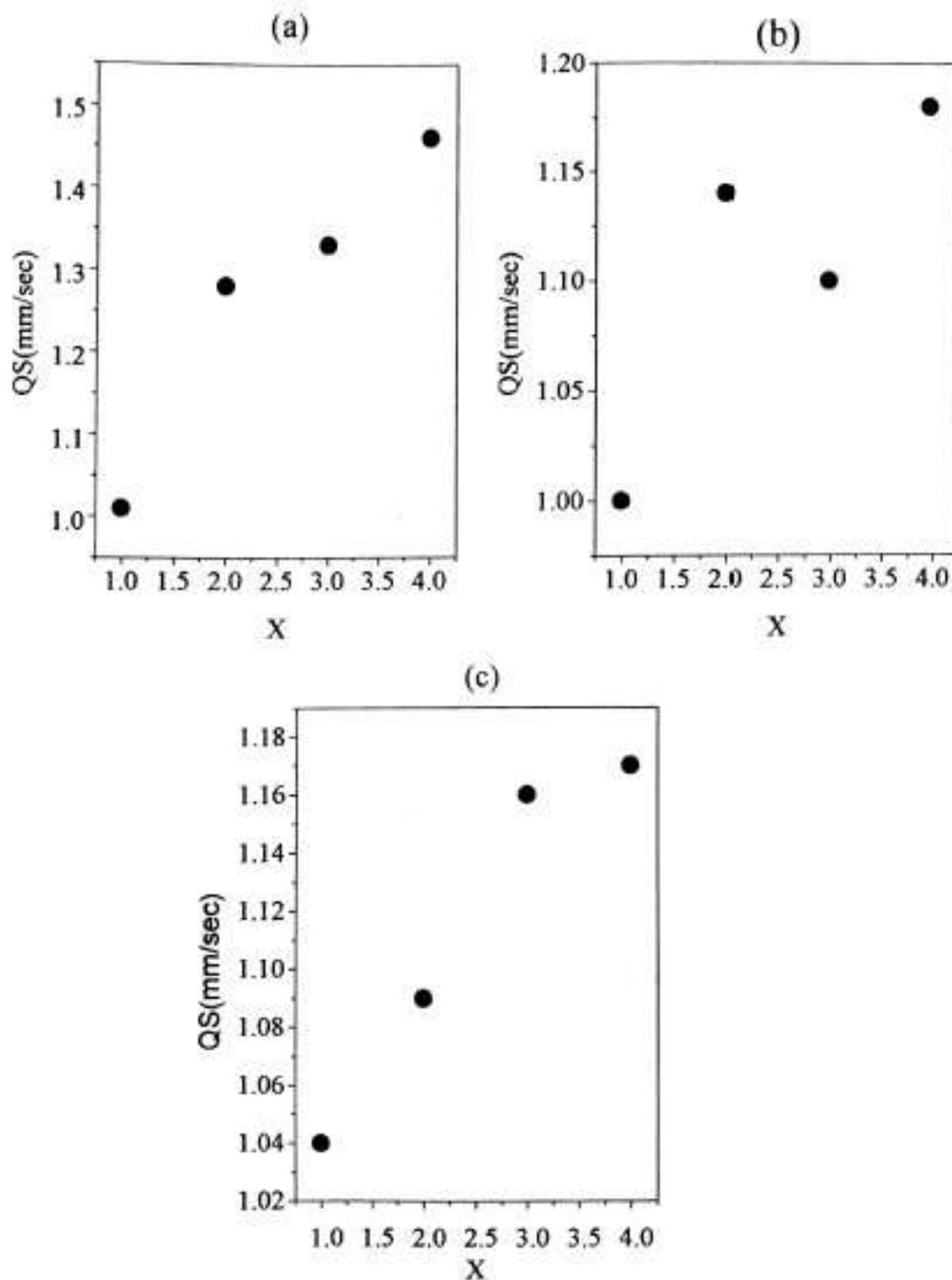


Fig 3: Variation of quadrupole splitting QS with increase in x for $(\text{Li}_2\text{O}-x\text{B}_2\text{O}_3)_{(1-y)}(\text{Fe}_2\text{O}_3)_y$ where (a) $y=0.1$, (b) $y=0.15$, and (c) $y=0.2$

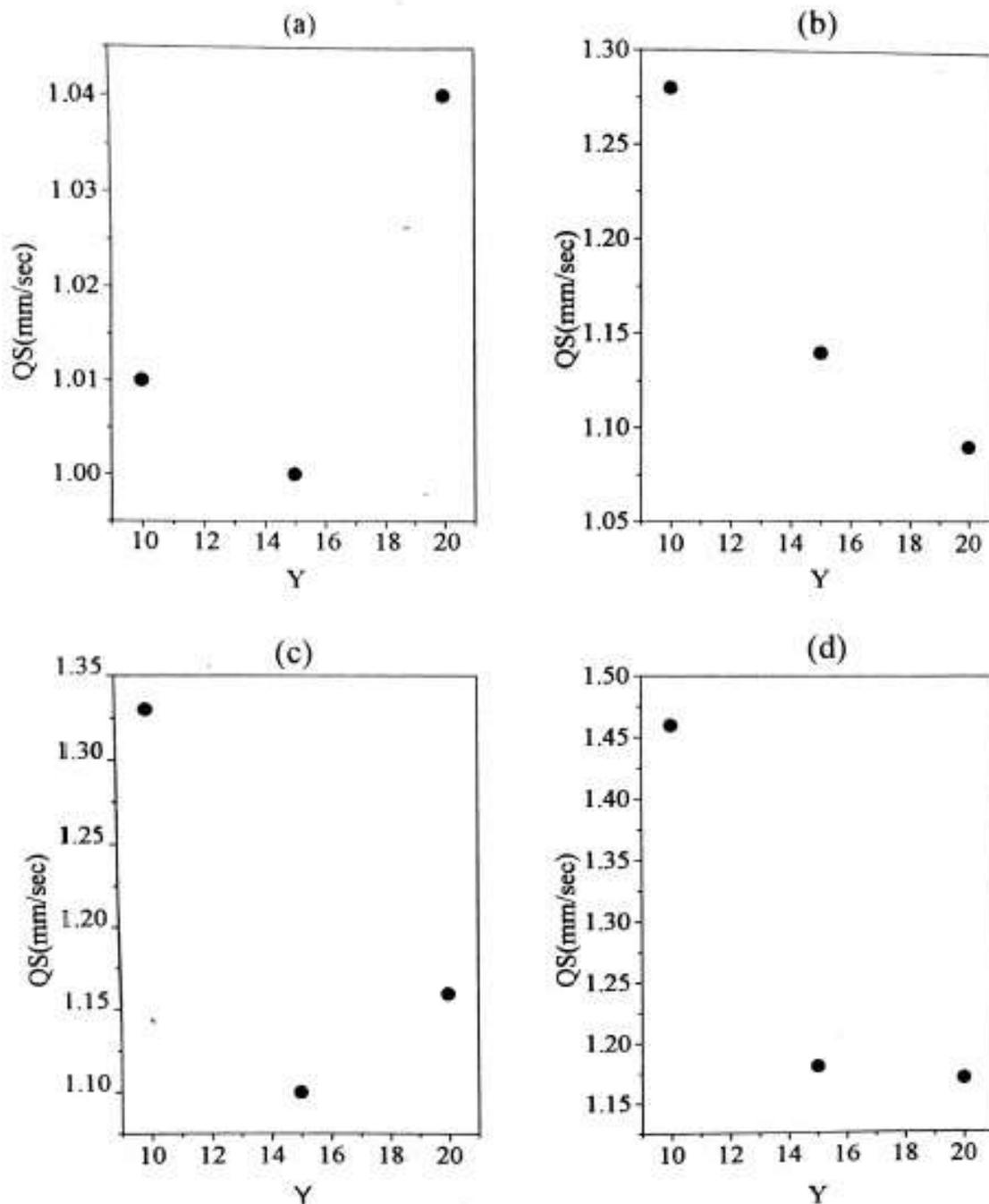


Fig 4 Variation of quadrupole splitting QS with increase in y for $(Li_2O-xB_2O_3)_{(1-y)}(Fe_2O_3)_y$ where (a) x=1, (b) x=2, (c) x=3 and (d) x=4



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References

1. N. N. Greenwood and T. C. Gibbs, "Mössbauer Spectroscopy" (Academic Press, New York, 1964).
2. H. Fraunfelder, "The Mössbauer Effect" (Benjamin, New York, 1962).
3. G. K. Wertheim, "Mössbauer Effect: Principles and Applications" (Academic Press, New York, 1964).
4. U. Gonser (Ed.), "Topics in Applied Physics (Mössbauer Spectroscopy - I)" , Vol. 5
5. Springer, Berlin, 1975and "Topics in Current Physics (Mössbauer Spectroscopy Vol 25,
6. Springer, Berlin, 1981.
7. V. G. Bhide, "Mössbauer Effect", (Tata McGraw Hill, India, 1974).
8. G. M. Bancroft, "Mössbauer Spectroscopy", (McGraw Hill, London, 1973).
9. I. J.Gruverman (Ed.): Mössbauer- Effect Methodology, Vol. 1-9 (Plenum Press,New York, 1965-1974).
10. C. R. Kurkjian, J. Non-crystalline Solids 3 (1970) 157.
11. S. S. Sekhon and R. Kamal, Phys. Chem Glasses 29 (1988) 157.
12. C. A. Angell and C. Wong, Glass Structure by Spectroscopy", (Marcel Dekker, New York, 1976).
13. W. Muller-Warmuth and H. Eckart, Phys. Repts. 2 (1982) 2.
14. J. A. Boon, Chem. Geo. 7 (1971).
15. R. A. Levy, C. H. P. Lupis and P. A. Flinn, Phys. Chem. Glasses 17 (1976) 94. v
16. S. S. Sekhon and R. Kamal, J. Non-Crystalline Solids 33 (1970) 169.
17. T. Raman, G. N. Rao and D. Chakravorty, J. Non-Crystalline Solids 29 (1978) 85
18. T. Nishida, T. Hirai and Y. Takashima, J. Non-Crystalline Solids 43 (1981) 221.
19. A. K. Bandyopadhyay, M. Ribes, F. Pemot and J. Zarzycki, Phys. Chem. Glasses 23 (1982) 31.
20. D. W. Moon, J. M. Aitken, R. K. MacCrone and G. S. Cieloszysk, Phys. Chem. Glasses 16 (1975) 91.
21. N. Kishore, R. Kamal, and R. G. Mendiratta, J. Non-Crystalline Solids 69 (1985) 213.
22. C. Chanmont, A. Derory and J. C. Bernier, Mater. Res. Bull. 15 (1980) 771.
23. J. P. Sanchez and J. M. Freidel, J. Phys. 43 (1982) 1707.
24. A. G. Mostafa, A. M. Sanad, I. Kashif and A. A. El Saghier, J. Mater. Sci. Lett. 4 (1985) 571.
25. A. K. Bhatnagar, Hyperfine Interactions 24-26 (1985) 637.
26. R. Jagannathan and K. N. Shrivastava, Hyperfine Inetractions 7 (1979) 377.
27. C. R. Kurkjian and E. A. Siegty, Phys. Chem. Glasses 9 (1968) 73.
28. Y. Ohta, M. Shimada and M Koizumi, J. Non-Crystalline Solids 51 (1982) 161.