CHAPTER 5

Mössbauer Spectroscopy

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MÖSSBAUER SPECTROSCOPIC STUDIES

RESULTS AND DISCUSSION

5.1 INTRODUCTION:

Mössbauer spectroscopy has been recognized as a powerful tool to investigate the short range structural details in several inorganic oxide glasses [1,5]. The Mössbauer effect is used to determine the valence state and coordination of iron ion and to observe any segregation of iron in crystallite form. The observed parameters such as isomershift (δ), quadrupole splitting (ΔE), fractional area and line width give insight into the nature of bond, the crystal structure and the internal magnetic field H_{int}, in the glass, if present. It has been reported that the oxidation state and coordination number can be known from the amplitude of the isomershift. The quadrupole splitting is also very useful to obtain such information. The value of quadrupole moment for tetrahedral Fe^{+3} is larger than the corresponding value for octahedral symmetry in the oxide glasses[6]. Several workers[2-8] have discussed the identification of crystallite formation in several glass systems above a certain concentration of Fe_2O_3.

The studies on borate and vanadate glasses containing varying amounts of network modifier exhibit certain unique features [5] such as observation of maxima, minima or marked changes in many physical properties like thermal expansion, UV absorption, IR absorption, mean B-O and V-O distance, coordination number of Vanadium and Boron with oxygen, intensity of four fold coordinated boron band in NMR spectrum, ionic conductivity, dc conductivity etc. at a certain value of modifier in borate glass systems. It is basically because of boron anomaly present in borate glasses. There have been some attempts[7-10] to investigate, using Mössbauer spectroscopy, boron anomaly effect with regard to valence and conduction states of iron cations. Raman et.al., [7] have noted sharp changes in isomershift, δ, value near the boron anomaly in Soda-broate glasses, while Sekhon et. al., [4-5] observed no sharp change in δ in lead borate. Ohta et. al.,[10] too have observed boron anomaly in Lithium borate and strontium borate glasses.

Mössbauer studies on several borate glasses namely sodium[11-13], lithium[14-15], calcium[16] and lead[4,5,17-18], vanadate glasses such as barium borovanadate glasses containing Fe_2O_3[19-20], have been reported. A common feature in all published spectra has been a broadened doublet corresponding to an isomershift value somewhere between the ones for Fe^{+3} at tetrahedral network forming and octahedral network modifying sites. Kawamoto et. al.,[21] and Hiroshima et. al.,[22] have reported the results of their studies of the electrical and magnetic properties of glasses in the system V_2O_5-BaO-ZnO-K_2O including the binary BaO-V_2O_5 and P_2O_5-V_2O_5-Fe_2O_3 systems respectively. Levy et. al.,[23] in their work have shown that the increased precision in Mössbauer spectral recording and the improved computer analysis of spectral lines, it is possible to estimate correctly the fractions of Fe^{+3} ions, which may occupy both substitutional as well as interstitial sites in the V_2O_5 lattice. The knowledge of these fractions is of help in explaining the observed changes in physical properties such as optical properties, viscosity, refractive index and electrical conductivity.

In the present chapter, the results of Mössbauer spectroscopic studies in the following systems are discussed and have been tried to understand the effect of K^+ cations on vanadium and boron polyhedra surrounding it and on surrounding environment of Fe^{+3} ions.

(1) xK_2O: $(95-x)[2V_2O_5:B_2O_3]$: $5Fe_2O_3$

Where x=0 to 30 in step of 5 mole %.

(2) $20K_2O$: yV_2O_5: $(75-y)B_2O_3$: $5Fe_2O_3$

Where y=40 to 75 in step of 5 mole %.

(3) $xK_2O: (100-x-y)[(1+n)V_2O_5:B_2O_3]: yFe_2O_3$

Where x=0 to 20 in step of 5 mole %.

y =5 to 15 mole % in step of 2.5 mole %.

n = 0.2 to 1 in step of 0.2.

Analysis of Spectra:

Mössbauer spectra of the samples of series (1), (2) and (3) are taken at room temperature and are analysed by computer fitting the data as described in Section 3.32. A set of two broadened lines is a characteristic feature of all the recorded spectra. A close examination of the observed spectra clearly indicates the asymmetry in heights, widths and shapes in two lines of quadrupole doublet. The sum of the natural line width, absorber thickness broadening and experimental condition broadening is ≈0.23 mm/sec for Fe_2O_3 polycrystalline absorber containing 5 mg/cm^2 of Fe^{57} for calibrating the velocity scale of the drive. An attempt is made to fit quadrupole doublet with the help of Meerwal program[23a] which as been converted to run on smaller personal computers. The experimental and fitted parameters (data) obtained, after the execution of this Meerwall's program (FORTRAN), have been plotted by using a program written in BASIC language graphics. This program in BASIC not only plots the spectra equal to computer screen size with velocity scale on x-axis and relative intensity at y-axis, but also calculates the Mössbauer parameters like isomershift, quadrupole splitting, line width, fractional intensity etc. An attempt is also made to fit more than two doublets. On doing so, much higher values of chi-square and misfit parameters are observed than the ones expected from statistical consideration and instrumental errors.

5.2 Studies of xK_2O: $(95-x)[2V_2O_5:B_2O_3]$: $5Fe_2O_3$ series:

Figure 5.21 shows the Mössbauer spectra of all glass samples in series-1. The spectra of the present glass series showed a broadened doublet for K_2O=0 to 30 mole %, which is resolved into a single doublet as in the case of K_2O-V_2O_5 [23] and Na_2O-V_2O_5 [11] glasses containing 10 mole % Fe_2O_3. No hyperfine splitting is observed in any of the glasses in the present series. The Mössbauer parameters calculated for this series of glasses are listed in the Table 5.21. It can be seen that the isomershift values change from 0.270 mm/sec to 0.482 mm/sec. Similar type of results were also reported for alkali vanadate glasses[24] and P_2O_5-V_2O_5 glasses[25]. This broad line width in glass samples is ascribed to the non uniformity of the steric configuration around the Mössbauer nucleus (^{57}Fe) in the glasses[1]. Mössbauer spectra of amorphous materials can, therefore, be considered as superposition of many absorptions of which the peak positions are gradually and continuously shifted.

Variation of Quadrupole Splitting:

While isomershift values depend on first few coordinated ions, quadrupole splitting depends on distant ions as well, therefore, quadrupole splitting, rather than isomershift is expected to be more sensitive to K^+ ions. Therefore, in the present studies the quadrupole splitting rather than isomershift is seen to be the parameter to distinguish tetrahedral and octahedral sites. It is observed from the Table 5.21 that for zero amount of K_2O, Fe^{+3} ions show octahedral symmetry surrounded by more symmetrical group of VO_4 and BO_4 tetrahedra. Fe_2O_3 being amphoteric in nature, behaves as a glass modifier in the glass when K_2O=0 mole % and Fe^{+3} ions go to the interstitial sites in octahedral environment. Now as the amount of glass modifier K_2O is added, it

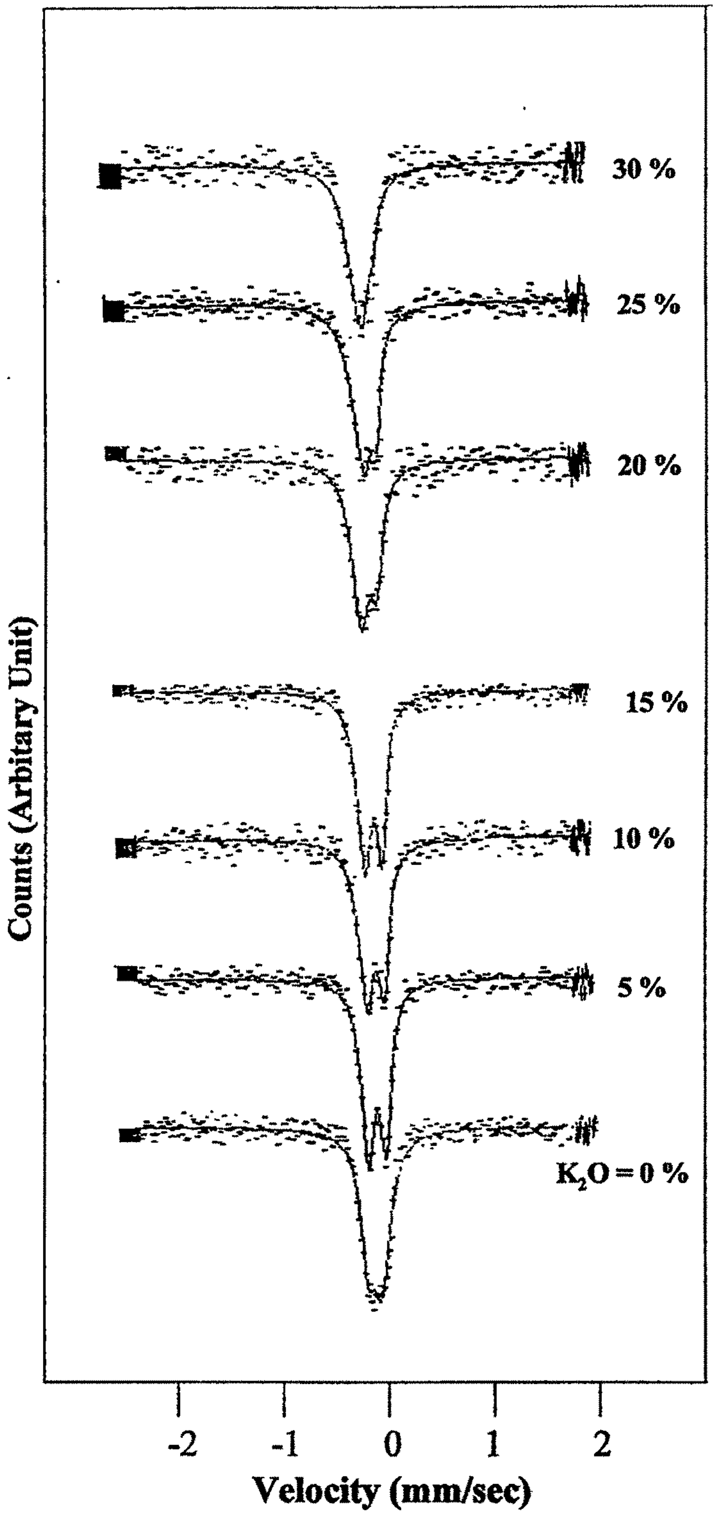


Figure 5.21: Mössbauer spectra of glasses of series 1.

Table : 5.21 Mössbauer Paameters of xK_2O: $(95\text{-}x)[2V_2O_5{:}B_2O_3]$: $5Fe_2O_3$ Glass series.

K_2O Mole %	Fr. Int. Peak-1 ± 3 %	Fr.Int. Peak-2 ± 3 %	Width 1 mm/sec	Width 2 mm/sec	I.somershift (δ) mm/sec (± 3 %)	Quadrupole Splitting (ΔE) mm/sec (± 3 %)
0	0.320	0.680	0.561	0.812	0.270	0.511
5	0.516	0.485	0.579	0.594	0.352	0.645
10	0.534	0.462	0.555	0.520	0.405	0.648
15	0.580	0.418	0.597	0.484	0.404	0.637
20	0.639	0.361	0.716	0.594	0.426	0.590
25	0.800	0.201	0.876	0.438	0.469	0.516
30	0.889	0.110	0.873	0.466	0.482	0.502

opens the structure three dimensionally and added Fe^{+3} ions found in a tetrahedral environment at network forming sites indicated by the values of the quadrupole splitting for K_2O= 5, 10 and 15 mole % glasses. The tetrahedral symmetry of Fe^{+3} ions is less than those in octahedral symmetry therefore, quadrupole splitting at tetrahedral symmetry is greater than octahedral symmetry. The variation of quadrupole splitting with K_2O amount is shown in Figure 5.22. The continuous decrease of quadrupole splitting means that the introduction of the alkali oxide is accompanied by the increase of the symmetry around the Fe^{+3} ions. The effect of valence electron on the quadrupole splitting is negligible, since each 3d orbital of Fe^{+3} (high spin) is occupied by one electron respectively. The reason for the decrease of the quadrupole splitting is, therefore, attributed to the decrease of the value of q_{latt}. The following reason may be assigned for decrease of quadrupole splitting in the present glass system.

The addition of K_2O to vanadate and borate structure changes VO_5 polyhedra and BO_3 into VO_4 and BO_4 (above 20 mole %) as evident from IR studies, Section 4.22. Also, the addition of K^+ ion produces non-bridging oxygens in the network. If the oxygen connected to iron becomes non-bridging, the electric field gradient at iron sites would change. The direction of change of asymmetry would depend upon the particular oxygen which becomes non-bridging and the already existing electric field gradient at the iron. For any potassium oxide concentration, the iron ions are surrounded by both VO_5 and VO_4 groups as well as BO_3 and BO_4 polyhedra. V-O and B-O separation is larger in length in case of VO_4 and BO_4 polyhedra than in VO_5 and BO_3 polyhedra and gives rise to lower electric field strength at oxygen sites in case of VO_4 and BO_4 tetrahedra than VO_5 and BO_3 polyhedra. This difference in electric field strength at different oxygen ions connecting the iron may give rise to different Fe-O bond separation for each corner of the oxygen polyhedra of iron or twisting of bonds. These factors cause deviations from

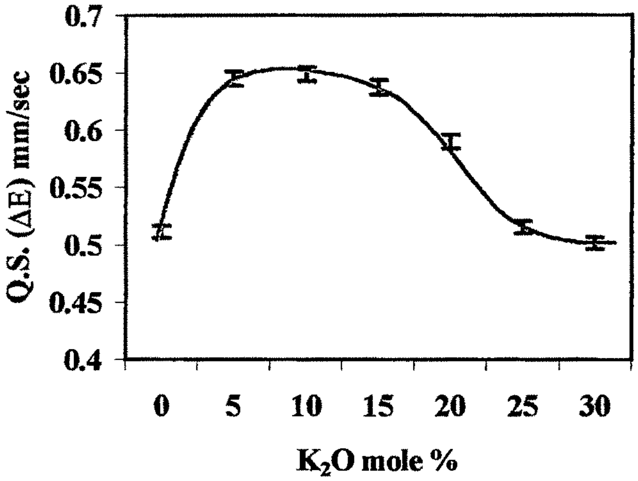


Figure 5.22 : Plot of Quadrupole Splitting versus K_2O mole %.

cubic symmetry of the iron oxygen octahedron, culminating in an electric field at the iron nucleus. As the K^+ concentration is increased, some of the VO_5 and BO_3 polyhedra connected with Fe^{+3} ions are converted into VO_4 and BO_4 polyhedra. This, in general, changes the symmetry around the iron ions surrounded by VO_5 or VO_4 and BO_4 or BO_3 polyhedra. Here again, whether the symmetry increases or decreases would depend upon particular polyhedra surrounding the Fe^{+3} ion which undergoes $VO_5 \rightarrow VO_4$ and $BO_3 \rightarrow BO_4$ transformation. The observed variation of quadrupole splitting, Figure 5.22, indicates that the net effect of the above phenomenon is to decrease the electric field gradient at octahedral sites. Similar trend has been observed in case of K_2O-V_2O_5[25] glasses containing Fe_2O_3. At very low concentration of K_2O, glass structure consists of BO_3, BO_4 and VO_5 and VO_4 polyhedras. It means iron is surrounded by different polyhedra groups to produce more asymmetric environment around Fe^{+3}. The transformation of BO_3 to BO_4 and VO_5 to VO_4 takes place with the increase of K_2O as is evident by the IR spectra [27].

Incase of low K_2O glasses, i.e., K_2O less than 15 mole %, each Fe^{+3} ion seems to be surrounded by four bridging oxygens which constitute the borate and vanadate polyhedra and the iron shows the tetrahedral symmetry. A distinct decrease of quadrupole splitting for alkali vanadate glasses was also reported by Nishida et. al. [25] and observed that Fe^{+3} ions are present at tetrahedral environment in vanadate glasses either at substitutional sites of V^{+5} or V^{+4} ions constituting the glass matrix or at the interstitial sites. The similar results were obtained by Dimitriev et. al.[28] by IR studies. As the amount of K_2O is increased from 20 mole % to 30 mole %, K^+ ions further break the chains and create the non-bridging oxygens not only in boron and vanadium chains but in iron-oxygen chains too. As Fe^{+3} is very weak glass former (amphoteric nature), it is compelled to leave the chain in substitutional position i.e., tetrahedral site and pushed to interstitial site in octahedral environment. Now Fe^{+3} ions in octahedral environment are surrounded by more symmetric polyhedra groups of BO_4 and VO_4 units. Hence, the decrease of q_{latt} is observed which is attributed to the decrease of quadrupole splitting now in octahedral sites. The similar results are also reported by Nishida et.al. [26] and observed that a distinct decrease in quadrupole splitting of the Fe^{+3} ions with increasing alkali oxides contents is due to gradual change of the alkali vanadate glasses from the layer structure composed of the VO_5 tetrahedral pyramids to the chain structure composed of tetrahedra.

The Variation of Isomershift :

Figure 5.23 shows the variation of isomershift with the K_2O amount. It is observed that the isomershift of the Fe^{+3} ions in the present glass samples increases with the increase of K_2O contents lying in the range of 0.270 mm/sec to 0.482 mm/sec. The increase of isomershift means the decrease of s-electron density at the iron nucleus due to increase of the distance between Fe^{+3} ions and oxygen atoms. According to Zachariasen's random network model[29] the addition to the network structure of a monovalent oxide such as K_2O, the cation takes up an interstitial position in the structure when it gives up its oxygen. This is also supported by IR studies, Section 4.22. Potassium ions with an ionic radius 1.33 Å are coordinated with six oxygens for a close packing. The introduction of potassium in the network forming V_2O_5 and B_2O_3, thus, ruptures the V_2O_5 and B_2O_3 units. Fe_2O_3, being amphoteric in nature, is incorporated in the form of Fe^{+3} ions at tetrahedral network-forming and/or octahedral network-modifying sites depending upon the amount of glass constituents. As the K^+ ion possesses a polarization power, which depends upon its charge/radius ratio, it will interact with neighbouring non-bridging oxygens electrostatically which are bound to Fe^{+3} ions. The added K_2O, occupy only the interstitial sites available in vanadate and borate polyhedra. Besides, as already indicated, number of tetrahedral sites increases on addition

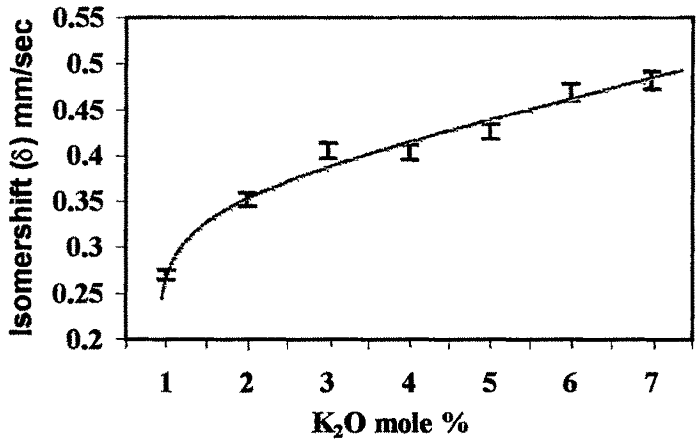


Figure 5.23 : Plot of Isomershift versus K_2O mole %.

of K_2O initially upto 15 mole %. This leads to the change in hybridization of iron-oxygen bonding from d^2sp^3, which is typical of an octahedral site, to sd^3 of tetrahedral environment. On further addition of K_2O, more BO_4 and VO_4 units are formed [30] and more space is formed due to the presence of K^+ ions at interstitials. Also, K^+ ions push the structure apart and increase the bond length of vanadium and borate polyhedra increasing Fe-O bond distance, which decreases the s-electron density at iron nucleus. As iron is shifted to more spacious interstitial sites where the distance between oxygens of BO_4 and VO_4 chains and Fe^{+3} ions continues to increase with increase of K_2O, isomershift is expected to increase.

The Variation of Fractional Intensity:

Figure 5.24 shows the variation of fractional intensity with K_2O amount. The fractional intensity of one of the peak continuously increases while amount of iron at other peak decreases. The Mössbauer spectra for K_2O=0 mole % (Figure 5.21) shows the peak intensities as 0.32 for one of the peak and 0.68 for the other. These intensities increase and become 0.89 for first and 0.11 for the other peak respectively when K_2O is increased to 30 mole % in the glasses. Kishore et. al.[31] discussed a similar effect for BaO-B_2O_3-Fe_2O_3 glass system, where the iron goes at the interstitial O-sites with the increase of BaO content. According to Kishore et. al.,[31] , the higher amount of alkali oxide provides sufficient oxygen to enable a larger portion of Fe^{+3} to form tetrahedra. Fe_2O_3 also converts VO_5 into VO_4 and BO_3 into BO_4 as is evident from IR spectra, Section 4.22. At low concentration of K^+ ions, the tendency to change vanadium from 5-fold to 4-fold is satisfied by the oxygen of K_2O as electronegativity of Fe^{+3}(1.8) is more than that of potassium (0.8), the release of oxygen of K_2O will be comparatively easier and iron remains in network-forming tetrahedral sites. For larger values of K_2O (more than 15 mole %),

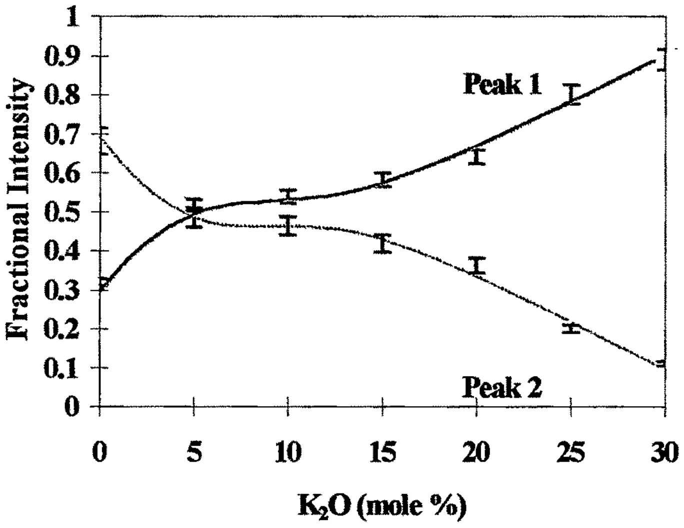


Figure 5.24 : Plot of Fractional Intensity versus K_2O mole %.

K_2O starts utilizing its oxygen in converting BO_3 to BO_4 polyhedra too and Fe_2O_3 starts participating in network-modifying the structure of vanadium from VO_5 to VO_4 and BO_3 to BO_4. After leaving its oxygens iron ions now starts acquiring interstitial octahedral positions. Therefore, the observed asymmetric behaviour in peak intensity is observed due to the variation of K_2O in the present glass series.

Linewidth:

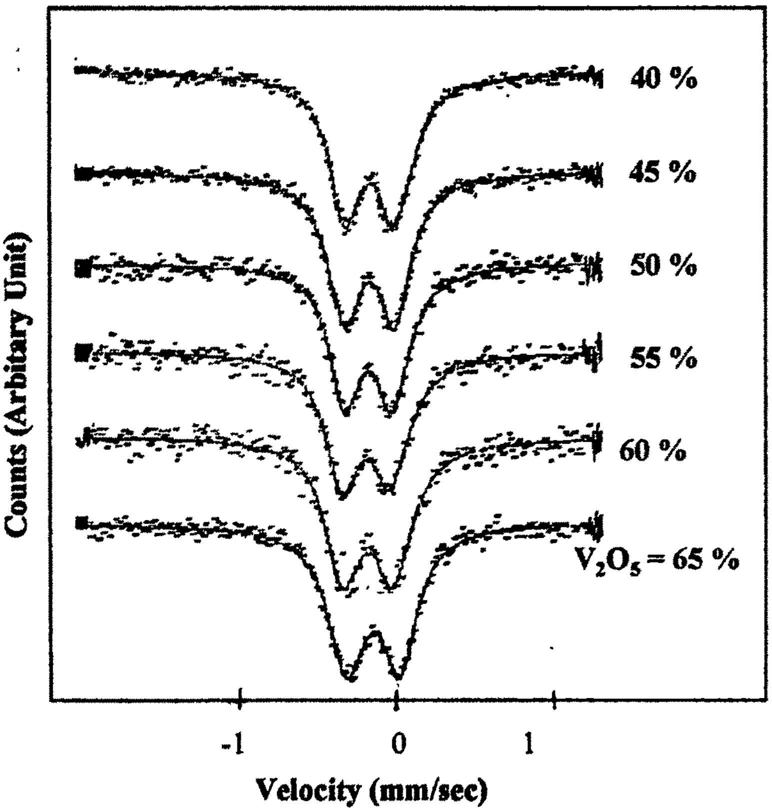
The Lorentzian doublet corresponding to Fe^{+3} tetrahedral or Fe^{+3} octahedral have line widths in the range of 0.561 to 0.873 for one peak and 0.812 to 0.466 for the other peak for all values of K_2O. An increase in width of one peak, whereas decrease in width of other peak is observed at the same time. The observed values of line width are large compared to that of the natural line width (≈0.20 mm/sec) and of the lines due to devitrified magnetic phase of Fe_2O_3 (≈0.23 mm/sec). In the disordered systems understudy, the surroundings of all the iron atoms are not the same but vary slightly from iron to iron. As a result of crystal field is slightly different at different sites. The signals corresponding to these different sites can not be seen distinctly and an average effect of all the signal is seen. This results in the broadening of lines. Clearly, such a broadening gives a measure of the non-uniformity of surroundings of the iron sites. Obviously, the change in peak width from K_2O =0 to 30 mole % indicates that the change in structure around iron must be taking place i.e., variation from more asymmetric to symmetric environment surround the iron ions is observed.

5.3 Studies of $20K_2O$: yV_2O_5: $(75-y)B_2O_3$: $5Fe_2O_3$ Glass Series:

Mössbauer spectra of the potassium boro-vanadate glasses of the second series are shown in Figure 5.31 which indicate the presence of only paramagnetic Fe^{+3} ions of high spin state [32]. It is understood clearly that the spectra of all glasses consist of asymmetric doublet. Each spectrum was analysed by computer fitting the data and using guess values in the program to converge the spectra in minimum number of iterations giving minimum chi square value. It is observed that all Mössbauer spectra could be converged into a single quadrupole doublet only. Mössbauer spectroscopy has also been utilized for the structural study of the vanadate glasses in which the coordination number of Fe^{+3} ions is reported to be only six in the case of BaO-V_2O_5 [20] glass and to be both six and four in the case of CaO-B_2O_3-V_2O_5 [33], BaO-B_2O_3-V_2O_5[34] and Na_2O-V_2O_5 [35] glasses.

Variation of Quadrupole Splitting:

All Mössbauer parameters for the present glasses series are summarized in Table 5.31 from which it can be seen that no systematic variation in isomershift values has been observed which vary between 0.398 mm/sec to 0.342 mm/sec and quadrupole splitting value vary from 0.626 mm/sec to 0.564 mm/sec. These values of quadrupole splitting indicate that Fe^{+3} ions occupy the octahedral environment at interstitial sites. It has been discussed in Section 5.21 that above 20 mole % of K_2O, Fe^{+3} ions occupy octahedral environment. Similarly, in the present glass series Fe^{+3} ions remain in octahedral environment in all glass samples as the amount of K_2O in the glass does not vary. The presence of iron ions in octahedral network modifying sites can be described on the lines similar to those discussed in series 1. Figure 5.32 shows the decrease of quadrupole splitting values with



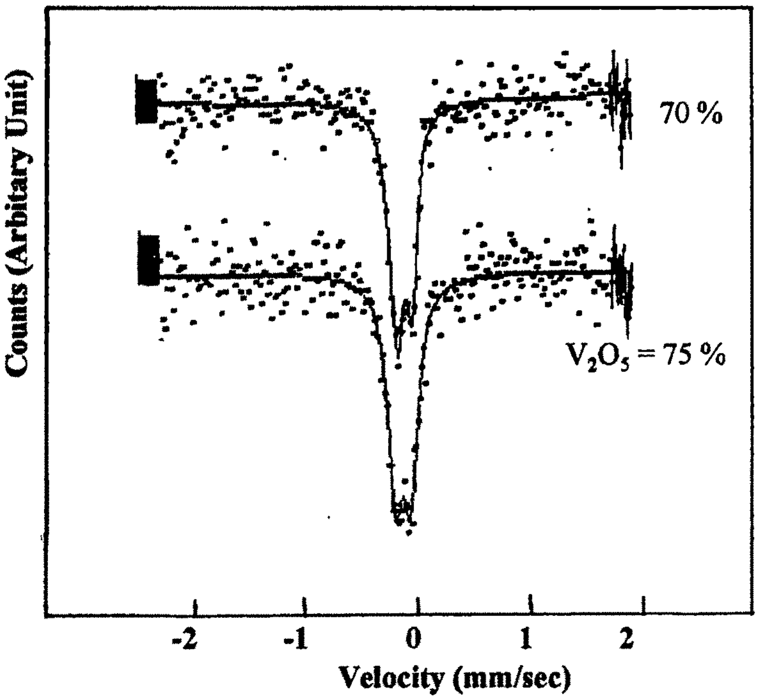


Figure 5.31: Mössbauer spectra of glasses of series 2.

Table : 5.31 Mössbauer Parameters of $20K_2O$: yV_2O_5 : $(75-y)B_2O_3$: $5Fe_2O_3$ Glass series.

V_2O_5 Mole %	**Fr. Int. Peak-1** ±3 %	**Fr.Int. Peak-2** ±3 %	**Width 1 mm/sec**	**Width 2 mm/sec**	**Isomershift (δ)mm/sec (± 3 %)**	**Quadrupole Splitting (ΔE) mm/sec (± 3 %)**
40	0.499	0.501	0.519	0.512	0.389	0.617
45	0.518	0.482	0.529	0.496	0.399	0.626
50	0.485	0.515	0.498	0.519	0.388	0.599
55	0.494	0.506	0.535	0.566	0.394	0.603
60	0.512	0.487	0.545	0.528	0.356	0.598
65	0.534	0.466	0.558	0.504	0.387	0.637
70	0.587	0.420	0.593	0.525	0.342	0.565
75	0.502	0.498	0.687	0.655	0.352	0.564

the increase of V_2O_5 amount. A similar decrease in quadrupole splitting was observed in the Mössbauer studies for the K_2O-B_2O_3-Fe_2O_3 [26], K_2O-V_2O_5 [24] and Na_2O-V_2O_5 [35] glasses in which the alkali content is higher than 20 mole %. The reasons for decrease in quadrupole splitting are ascribed as following;

(i) In the present series, the amount of glass modifier K_2O has been kept constant as 20 mole % and V_2O_5 is increasing at the expense of B_2O_3, keeping total amount of glass former as constant i.e., 75 mole %. As is evident from IR spectra, K_2O does not show any variation in borate structure, a change in only vanadate structure has been noticed (Section 4.23). It means K_2O, which is responsible for transforming VO_5 polyhedra to VO_4 along with the Fe_2O_3 in this series of glass samples, produces more number of groups of VO_4 culminating into a more symmetric environment around the Fe^{+3} ions which, of course, are in interstitial network-modifying sites. Therefore, the decrease of quadrupole splitting can be (Figure 5.32) ascribed to an increased symmetry around the iron nucleus, because the high spin Fe^{+3} ions have symmetric electron configuration of $3d^5$ in the outermost orbital and the electric field gradient caused by the neighbourhood atoms or ions i.e., oxygen atoms surrounding the iron nucleus in the present study should primarily affect the quadrupole splitting values.

(ii) As is discussed in series 1, at 20 mole % of K_2O, K^+ ions, not only interact with VO_5 polyhedra and convert VO_4 but also start converting BO_3 to BO_4 at this amount. To fulfil the requirement of oxygen for transformation of vanadium and boron polyhedras, Fe_2O_3 leaves and supplies its oxygen to the network and goes at interstitial sites. Therefore, all the glass samples show the presence of Fe^{+3} in octahedral position only.

(iii) It has also been also reported for BaO-B_2O_3- V_2O_5[19] glasses that introduction of B_2O_3 at the expense of V_2O_5 enhances the glass forming ability and hence the quadrupole splitting. In the present glass series, the amount of V_2O_5 is increasing at the expense of B_2O_3 which decreases the glass forming

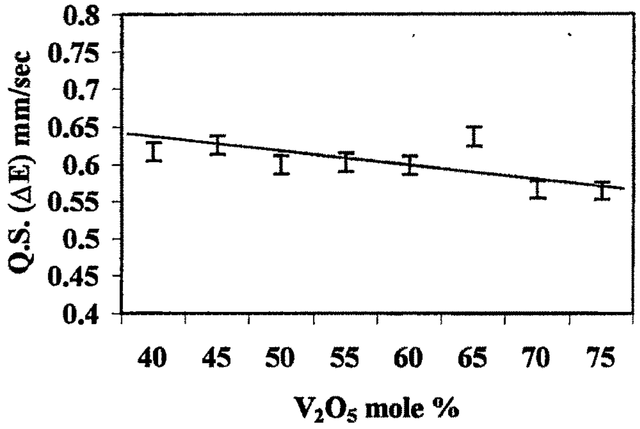


Figure 5.32 : Plot of Quadrupole Splitting versus V_2O_5 mole%.

ability and thereby increase the symmetry around the Fe^{+3} ions. Thus, with the increase of y, the symmetry surround the iron increases which thereby decreases the q_{latt} values means decrease of quadrupole splitting.

The Variation of Isomershift:

The isomershift of the present glass series, shown in Figure 5.33, does not show a systematic and appreciable change but a slight decrease in its values with the increase of y. Dimitriev et. al.[36] have pointed out that B_2O_3 and V_2O_5 do not have any chemical affinity for each other. Due to the presence of constant amount of K_2O and Fe_2O_3, the number of K^+ ions and Fe^{+3}, which are occupying only interstitial network modifying site, increase in vanadate chains than borate, because the vanadate polyhedra are increasing. The space created by K^+ ions rupturing the network structure of vanadate and borate, are larger than those created by Fe^{+3} ions because the ionic size of K^+ ion (1.33 Å) is larger than Fe^{+3} ions (0.8 Å). It means the distance between Fe^{+3} ions and oxygens of network glass former is less i.e., vanadate and borate polyhedra shrink around iron ions slightly as y increases, resulting into an increase in s-electron density at iron site and decrease in isomershift. At the same time, the presence of K^+ ions in the network at modifier tend to open the network more and larger in size which may result into decrease in distance between Fe^{+3} ions and oxygens of vanadium or boron polyhedra. This effect brings a decrease in s-electron density at iron site, which should increase the isomershift values. However, the net effect is slight decrease in isomershift values in the glass samples of the present series. The isomershift of Fe^{+3} ions is sensitive to the nearest neighbourhood only i.e., short range order around the iron nucleus is not affected much by change of network former or method of preparation. Thus s-electron density of Fe^{+3} ions does not change much which

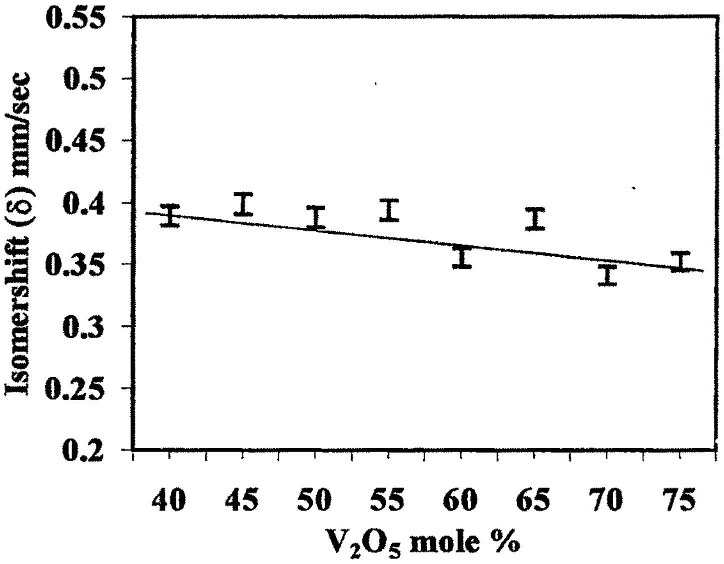


Figure 5.33: Plot of Isomershift versus V_2O_5 mole %.

gives rise to only a slight decrease in isomershift. A small decrease has also been observed in BaO-B_2O_3-V_2O_5 glass system[19,34].

Variation of Width and Fractional Intensity:

In the present glass system, a gradual increase in the width of the peak upto y=70 mole % and an abrupt increase in width in a sample with B_2O_3 = 0 mole % (Table 5.31). Nishida et. al.[25] had reported an increase of the width for P_2O_5-V_2O_5 glass system. This variation may be because of the increasing order of disorderness surrounding iron ions to give broadening in Mössbauer signals in all the samples even upon the variation in the amounts of glass formers, however, the total amount of V_2O_5+B_2O_3 remains 75 mole % in this series. The broadening starts increasing steeply at y=70 mole % due to small amount of B_2O_3 in the structure and a sudden increase in disorderness shows a larger width in the Mössbauer spectra at y=75 mole %.

The variation in fractional intensity with V_2O_5 under the peaks of Mössbauer spectra are shown in Figure 5.34 and their values are given in Table 5.31. Initially, the fractional intensities do not show any systematic change upto 50 mole % of V_2O_5. A decrease in fractional intensity of peak one while an increase in other peak of the Mössbauer spectra has been observed from y= 55 to 70 mole %. In the absence of B_2O_3 at y =75 mole %, the reverse effect has been observed. As is discussed that B_2O_3 and V_2O_5 do not mix and the added Fe_2O_3 finds the place in interstitial positions of borate as well as vanadate structures. Upto 50 mole % of V_2O_5, iron is uniformly distributed in both network structures . From y=55 mole % to 70 mole % large number of positions in interstitials are occupied by iron in vanadate structure than borate and a change is expected in the fractional intensities of both the peaks. At y= 75 mole %, the glass sample is devoids of borate structure and iron occupies positions only in vanadate structure which shows the reverse effect in the

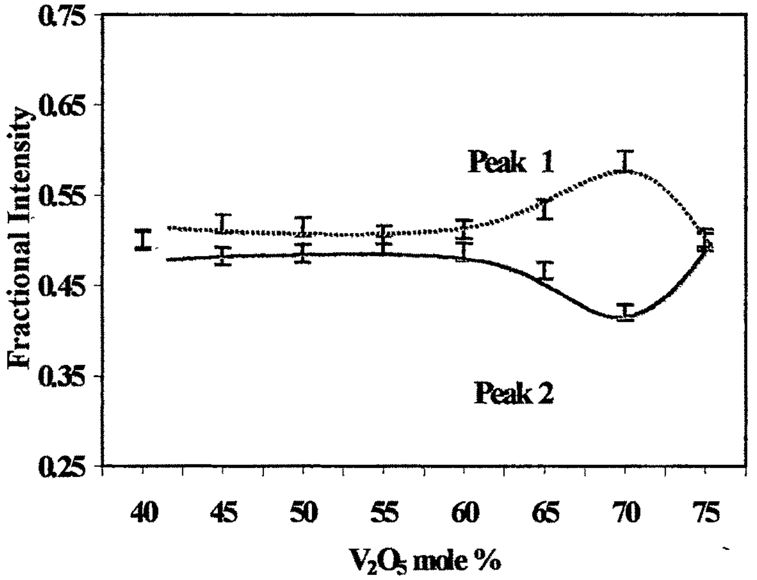


Figure 5.34 : Plot of Fractional Intensity versus V_2O_5 mole %.

values of fractional intensity of Mössbauer spectra and almost equal values for both the peaks are observed. It means it is not only the glass modifier which brings the change in width and intensity of the Mössbauer spectra due to the structural change in the glasses, but glass former too brings the structural changes due to their cation size and size of the network. In the present glass series, as the amount of K_2O, the glass modifier, and the amount of total glass former remain constant, one may not expect much changes in the structure close to iron ions, but an increase in intensity of one peak while decrease in other peak has been observed whereas increase in width for both peaks of the glasses are the main features in this series.

5.4 Studies of xK_2O: (100-x-y)[(1+n)V_2O_5: B_2O_3]: yFe_2O_3 Glass Series:

Figure 5.41 shows the Mössbauer spectra of a glass series for Fe_2O_3=5 to 15 mole %. All spectra show a broadened but approximately symmetric doublet only. As is done for the spectra of series 1 and 2, the broadened doublet, which is observed in all spectra, is resolved in to a single doublet. On the basis of quadrupole splitting considerations, Fe^{+3} ions are observed in the glass network at network-forming tetrahedral sites only. The fitted Mössbauer parameters are given in Table 5.41. The isomershift of Fe^{+3} ions lies in the range of 0.403 mm/sec to 0.375 mm/sec and quadrupole splitting lies in the range of 0.642 mm/sec to 0.693 mm/sec. In all glass samples, no hyperfine splitting is observed even for high iron contents (maximum 15 mole %). This is a consequence of very small dimension of these particles which are uniformly dissolved in a glass matrix. Bekrey et. al.,[3,37] reported that the alkali borate glasses above 20 mole % of Fe_2O_3, a complex hyperfine spectrum was obtained indicating crystallite formation. Sekhon et. al., [38] reported that in all cases, the crystallites were formed only above 20 mole % of Fe_2O_3. Earlier Mössbauer studies of several glasses revealed that Fe^{+3} ions are present at tetrahedral environments in borate and silicate glasses [1,24,39-40]. The values of isomershift and quadrupole splitting for K_2O =0 and Fe_2O_3=5 mole % in the first sample indicate that iron exist in octahedral environment. For the rest of the samples for K_2O=5 mole % to 20 mole % and Fe_2O_3=7.5 mole % to 15 mole % Fe^{+3} ions exist in tetrahedral environment in the chain. As discussed in Section 5.21, for zero amount of K_2O and in the first sample Fe^{+3} ions exist in octahedral environment due to its amphoteric nature and behaves as a network modifier in the absence of glass modifier K_2O. Now as the amount of K_2O and Fe_2O_3 are increased, K_2O starts modifying the structure by leaving it oxygen (as discussed in series 1) Fe_2O_3 starts behaving as a network glass

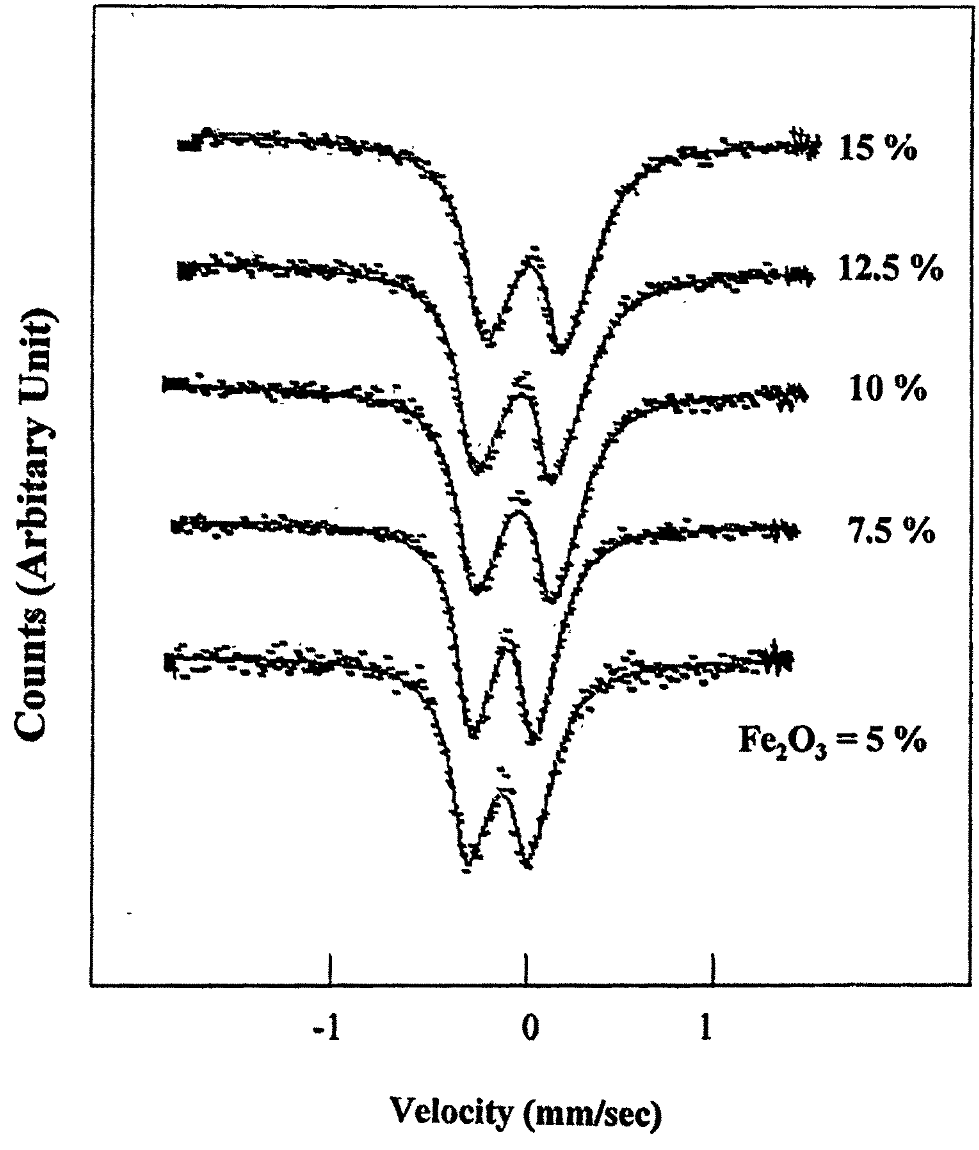


Figure 5.41: Mössbauer spectra of glasses of series 3.

Table : 5.41 Mössbauer Parameters of xK_2O: $(100\text{-}x\text{-}y)[(1+n)V_2O_5 : B_2O_3]$: $y Fe_2O_3$ Glass series.

Fe_2O_3 Mole %	**K_2O Mole %**	**Fr. Int. Peak-1 ±3 %**	**Fr.Int. Peak-2 ± 3 %**	**Width 1 mm/sec**	**Width 2 mm/sec**	**I.somershift (δ) mm/sec (± 3 %)**	**Quadrupole Splitting (ΔE) m/sec (± 3 %)**
5	0	0.512	0.488	0.507	0.493	0.393	0.642
7.5	5	0.511	0.489	0.495	0.449	0.403	0.665
10	10	0.511	0.489	0.494	0.458	0.383	0.681
12.5	15	0.512	0.488	0.506	0.471	0.378	0.686
15	20	0.517	0.483	0.535	0.477	0.375	0.693

former in the chains and iron remains in the chains and occupy tetrahedral environment. This may be due to the fact that with the addition of K_2O, K^+ ions leave their oxygen and go into the interstitial spaces of the network formers, rupture the chains, transform the vanadium and boron polyhedra and produce the non-bridging oxygens as discussed in Section 5.2 also. The need of oxygen to network formers in transforming from VO_5 to VO_4 and BO_3 to BO_4 is being fulfilled initially by K_2O. Further addition of K_2O decreases the total amount of glass formers in the glass. The requirement of oxygen to convert VO_5 to VO_4 and BO_3 to BO_4 is fulfilled by K_2O alone. The added Fe_2O_3 does not participate as modifier at all rather prefers to remain as glass network former in this system. Also, the ratio of K_2O/total amount of glass former is increasing sharply, the need of oxygen for transforming the vanadium and boron polyhedra is satisfied by K_2O alone and may be partially by Fe_2O_3, because of the fact that Fe^{+3} ions have higher electronegativity and do not leave oxygen easily. Consequently, added Fe_2O_3, even at higher amount of K_2O, goes only at substitutional network-forming sites only in this glass series.

Variation of Quadrupole Splitting:

Figure 5.42 shows the variation of quadrupole splitting with Fe_2O_3 amount. An increase in quadrupole splitting is observed with increase of Fe_2O_3 amounts. This is the result of the deformation of the V_2O_5 lattice, caused by the incorporation of an increasing number of iron ions. It has been also discussed in Section 5.2 that an introduction of K_2O causes the destruction of vanadate and borate structure, and a decrease of quadrupole splitting is observed with increase of K_2O amount whereas in the present glass series a reverse effect is observed for the increase of K_2O and Fe_2O_3. Burzo et. al., [15] had also discussed the effect of increase of Fe_2O_3 in V_2O_5-Fe_2O_3 and V_2O_5-

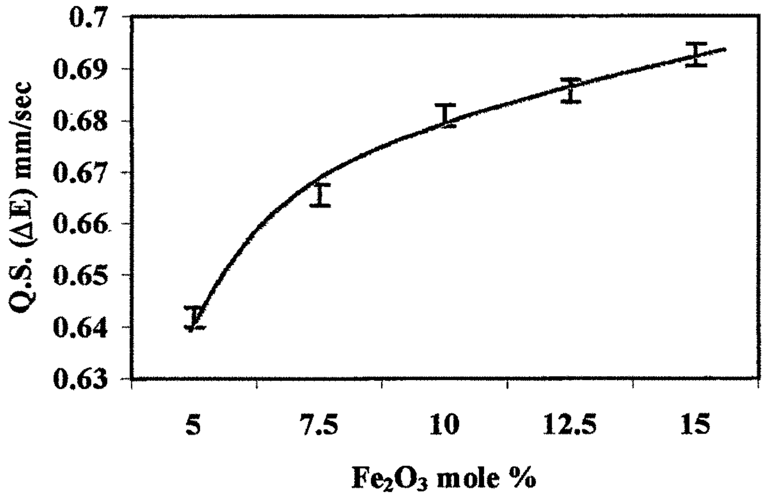


Figure 5.42 : Plot of Quadrupole Splitting versus Fe_2O_3 mole %.

Fe_2O_3-Li_2O glass systems, where the increase of iron results in a deformation of V_2O_5 lattice which further produces a VO_4 groups along with the formation of NBO at VO_4 polyhedra. It has been observed from IR spectra that an introduction of Fe_2O_3 amount into the borate and vanadate matrix brings changes in BO_3 and VO_5 polyhedras and causes destruction of these structure and forms BO_4 tetrahedra and VO_4 polyhedras along with the formation of other groups like BO_4^-, VO_4^-, V-O^- units. Thus, Fe^{+3} ion will be surrounded by different types of various group which create an asymmetry around the iron which exist in a substitutional position of tetrahedral environments. With the increase of Fe_2O_3 and K_2O amounts, more and more Fe^{+3} ions go to the substitutional position of tetrahedral sites and environment around Fe^{+3} ions become more asymmetric which increases the q_{latt} values and gives rise to the increase of quadrupole splitting. Burzo et. al. and Ardelean et. al.[41] reported the similar increase of quadrupole splitting with increase of Fe_2O_3 probably due to the gradual deformation of the environment by the increasing amount of iron dissolved in the matrix.

Thus, an overall effect of increase of quadrupcle splitting and iron at the substitutional position of tetrahedral sites has been observed with the increase of iron oxide in the glasses.

Variation of Isomershift :

Figure 5.43 shows the variation of isomershift with Fe_2O_3 contents. Decrease of isomershift is observed with the increase of Fe_2O_3 amounts. A similar decrease of isomershift of Fe^{+3} ions is observed in borate and borosilicate glasses [15,35,42-43], V_2O_5-Fe_2O_3 and V_2O_5-Fe_2O_3-Li_2O[15] glasses containing different amounts of Fe_2O_3. Nishida et. al.[42] also reported a decrease in isomershift values with the increase of alkali contents. A decrease of isomershift value has been ascribed to the formation of NBO atoms (-O^-) in

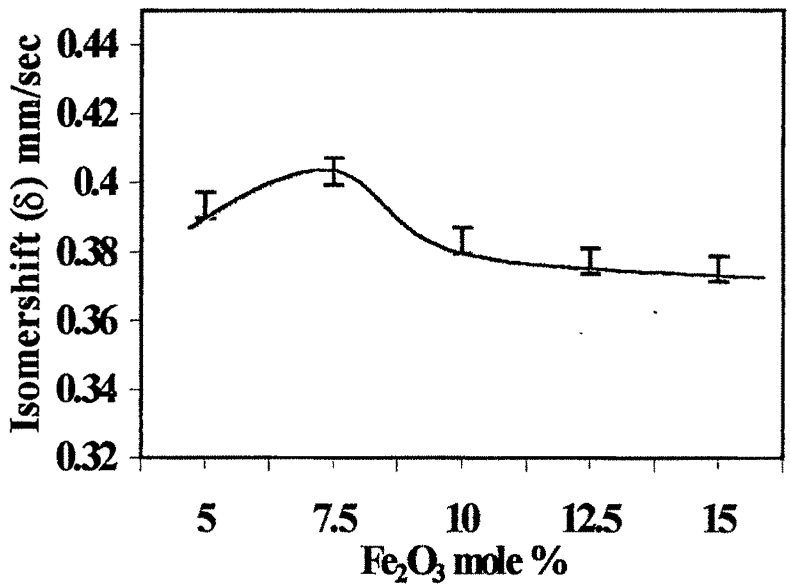


Figure 5.43 : Plot of Isomershift versus Fe_2O_3 mole %.

FeO_4, BO_4 and VO_4 tetrahedral units [25] because the formation of the NBO oxygen atoms results in decreased inter-atomic distance in the Fe-O. A similar composition dependency has been observed in the case of the potassium vanadate glasses [23], where the decrease in the isomershift was ascribed to the formation of NBO atoms in the VO_4 tetrahedra. The energy levels for the electrons of non-bridging oxygens are known to be higher than those of the bridging oxygen[44]. The chemical bond between boron and non-bridging oxygen is therefore, less rigid as compared to that between boron and bridging oxygen. Therefore, the coulombic interaction between non-bridging oxygen and iron is comparatively stronger than that between bridging oxygen and iron, which consequently, decreases the Fe-O distance[45]. It has been also confirmed from the density data (Chapter 4.4) that the calculated Fe-O distance decreases with the increase of Fe_2O_3 amount. A decrease in Fe-O distance gives rise to the overlapping of 3d orbital electrons of Fe^{+3} ion and therefore an increases the s-electron density at the iron nucleus and a decrease in isomershift.

Variation of Width and Fractional Intensity:

It can be also seen from the Table 5.41 that the fractional intensity of both the peaks of the doublet remains almost constant i.e., added iron is uniformly distributed in both peaks but amount of iron at peak 1 is more as compared to peak 2.(Figure 5.44) The Lorentzian doublets corresponding to Fe^{+3}(T) and Fe^{+3}(O) had a line width of about 0.5 ± 0.026 mm/sec for all values of x (Table 5.41). This value is large as compared to those of the natural line width (~ 0.20 mm/sec) of iron. In disordered system such as glass system, the surroundings of iron atom are not the same but vary slightly from point to point so that crystal field will be slightly different at different iron sites. The signal corresponding to these different sites can not be seen

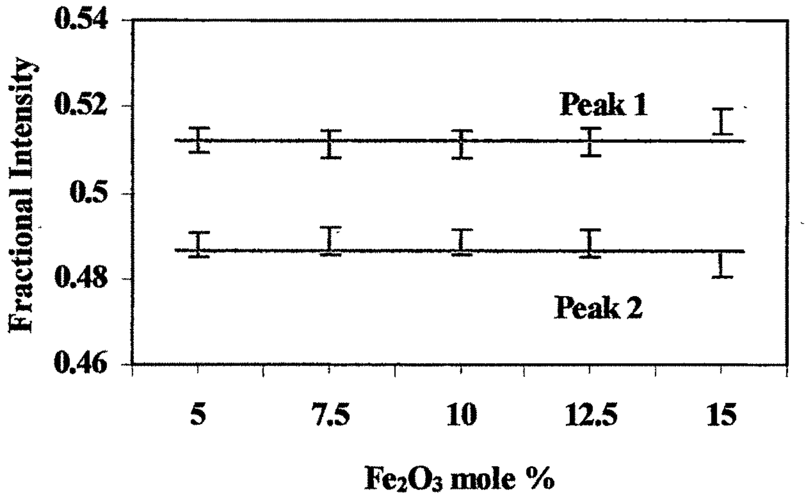


Figure 5.44: Plot of Fractional Intensity versus Fe_2O_3 mole %.

distinctly and an average effect of all the signal is seen. This results in the broadening of lines. Such a broadening gives a measure of the non-uniformity around iron sites. In the present glass system an unsystematic but constant width of the Mössbauer peaks have been observed with the increase of K_2O and Fe_2O_3 in the glasses and the preparation technique could not bring much disorderness in the glass system and a constant Mössbauer width for all the samples has been observed.

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