

## Properties and Structural Features of Iron Doped BABAL Glasses

Signo Tadeu dos Reis<sup>a\*</sup>, Walter M. Pontuschka<sup>b</sup>, Jinbo B. Yang<sup>a</sup>, Dalva L.A. Faria<sup>c</sup>

<sup>a</sup>Graduate Center for Materials Research, 301 Strautmanis Hall,  
University of Missouri-Rolla, MO65409, U.S.A.

<sup>b</sup>Institute of Physics, University of São Paulo, C.P. 66318,  
053890-970 São Paulo - SP, Brazil

<sup>c</sup>Institute of Chemistry, University of São Paulo, C.P. 26077,  
05389-970 São Paulo - SP, Brazil

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The chemical durability, density and structure of the BABAL glasses with batch compositions  $(100-x)(0.30\text{BaO}\cdot 0.50\text{B}_2\text{O}_3\cdot 0.20\text{Al}_2\text{O}_3)\cdot x\text{Fe}_2\text{O}_3$  ( $1 \leq x \leq 10$  mol%), were investigated using Mössbauer spectroscopy, electron paramagnetic resonance (EPR), X-ray diffraction, Raman and differential thermal analysis (DTA). The chemical durability for the glass of composition  $27\text{BaO}\cdot 45\text{B}_2\text{O}_3\cdot 18\text{Al}_2\text{O}_3\cdot 10\text{Fe}_2\text{O}_3$  (mol%) at 90 °C in distilled water was 700 times lower than that of iron phosphate glass  $40\text{Fe}_2\text{O}_3\cdot 60\text{P}_2\text{O}_5$  (mol%). The Mössbauer spectra indicate the presence of iron (II) and iron (III) in tetrahedral or octahedral coordination. The results obtained from the  $g_{\text{ef}} = 4.3$  EPR line are typical of the occurrence of iron (III) occupying substitutional sites and the line  $g_{\text{ef}} = 2.0$  is related to the association of two or more Fe ions found in the interstices (or holes occupied by the glass modifier cations) of the glass network. The paths of X-ray diffraction are typical for glasses based in borate glasses. The Raman spectra showed that the boroxol ring disappears with the increase of iron content, concomitant with the appearance of  $\text{BO}_4$  and tetraborate structural units. At these conditions, an increase of dissolution rate and clustering of iron ions is observed.

**Keywords:** aluminoborate glass, structure, and chemical durability

### 1. Introduction

As long been known<sup>1</sup>, the considerable practical interest of borate glasses stems mainly from the complex influence of boron oxide on the physical properties<sup>2</sup>. Some appropriate values of constants such as low melting point, high thermal expansion coefficients and several optical data make these glasses potential candidates for many technological applications such as optical<sup>3</sup>, medical use<sup>4</sup>, and solid state electrolytes<sup>5</sup>.

The local structure of iron doped aluminoborate glasses has been studied using <sup>57</sup>Fe Mössbauer, Raman spectroscopy and electron paramagnetic resonance (EPR)<sup>6,7</sup>. The boroxol ring is the main structural group present in borate glasses and the addition of modifier oxide like CaO gradually converts three-coordinated boron into four-coordinated boron units, resulting in the formation of diborate, tetraborate and pentaborate glass network superstructural units<sup>7</sup>.

Iron is one of the most pervasive impurities in borate and phosphate glasses. Some specific features of the EPR line width and shape of  $\text{Fe}^{3+}$  ions in glass matrices depend on the glass composition and the concentration of paramagnetic ions<sup>8</sup>. The EPR spectra of most glasses containing iron exhibit the two well known resonances at the effective  $g$  values  $g_{\text{ef}} \approx 2$  and  $g_{\text{ef}} \approx 4.3$  that have been considered as a signature of the presence of  $\text{Fe}^{3+}$  ions in a glassy host<sup>9</sup>. The X-band EPR spectra ( $\sim 9$  GHz) of most oxide glasses with low  $\text{Fe}^{3+}$  concentrations show a  $g_{\text{ef}} = 4.3$  line, and in most cases the  $g_{\text{ef}} = 2$  line is also present. A low field feature ( $g_{\text{ef}} \sim 9.7$ ) is also observed in X-band EPR spectra of oxide glasses<sup>10</sup>. At low iron concentrations ( $< 1$  mol%), only a sharp  $g_{\text{ef}} \approx 4.3$  resonance is commonly observed<sup>9</sup>. As the concentration is increased, a broad line begins to grow at about  $g_{\text{ef}} \approx 2$ <sup>11</sup>. In many oxide glasses the intensity of the line with  $g = 2$  increases much faster than that of  $g = 4.3$  with increasing  $\text{Fe}^{3+}$  ions concentration above 5 mol%. This

\*e-mail: reis@umr.edu

result leads to the hypothesis of Fe<sup>3+</sup> clustering, which effectively contributes to the former broad line<sup>12</sup>. As the linewidth of the  $g_{\text{ef}} \sim 4.3$  resonance remains roughly constant, in practice the peak-to-peak amplitude of its derivative is proportional to the Fe concentration of the sample<sup>13</sup>, while the relative concentrations of the Fe<sup>2+</sup> and Fe<sup>3+</sup> ions are easily determined by Mössbauer spectroscopy.

Bogomolova and Henner<sup>14</sup> showed how the X-band the  $g_{\text{ef}} \approx 2$  line width can be explained by a clustering of Fe<sup>3+</sup> ions. Nevertheless, the Fe<sup>3+</sup> concentration determines not only the number of EPR lines and their positions, but the line shapes as well. The theory predicts an increase of line width with spin concentration due to the dipolar broadening. The exchange interaction appears at a sufficiently high concentration of paramagnetic ions (molar contents > 5 mol%)<sup>15</sup>, when neighboring spins become highly coupled<sup>14</sup>.

The aim of the present work is to investigate the conditions of the chemical durability of BABAL glasses. Evidence of the presence of diads and microclusters of iron ions and structural studies of the glass matrix were provided by EPR, X-ray diffraction and Mössbauer spectroscopy. The chemical durability of BABAL glasses was determined and compared with those of the iron phosphate glasses.

## 2. Experimental Procedure

Samples of BABAL glasses with compositions (100-x)(0.30BaO·0.50B<sub>2</sub>O<sub>3</sub>·0.20Al<sub>2</sub>O<sub>3</sub>)·xFe<sub>2</sub>O<sub>3</sub> where x = 0, 1, 2, 4, 8 and 10 mol% (see Table 1) were produced by melting the batches in dense alumina crucibles at 1200 °C for 1 h. The melt was quenched in air by pouring into 1 × 1 × 5 cm<sup>3</sup> steel mold. The samples were transferred to an annealing furnace and held at 350 °C for 3 h. The densities of the samples were measured by the Archimedes method using distilled water at room temperature. A portion of the glass samples was crystallized on heating at 750 °C for 8 h in air. Room temperature X-ray powder dif-

fraction (XRD) patterns for both glasses and crystalline counterparts were collected on a X-ray diffractometer (Scintag XDS2000). The chemical durability of the bulk glasses with approximate size of 1 × 1 × 1 cm<sup>3</sup> was evaluated by weight loss measurements from glasses exposed to deionized water at 90 °C for 2-8 days. Glasses were polished to 600 grit, finished with SiC paper, cleaned with acetone and suspended in glass flasks containing 100 ml of deionized water at 90 °C. Duplicated measurements were conducted for each glass and the average dissolution rate (DR), normalized to the glass surface area, and the corrosion time was calculated from the weight loss.

The Mössbauer spectra were obtained at room temperature on a spectrometer provided with a 50 mCi rhodium matrix cobalt-57 source. The amount of iron found at the sample holder was 4 mg/cm<sup>2</sup>. The velocity of the source was calibrated using a pure iron foil that was also used as a reference for the isomer shift value.

The Raman spectra of the glass samples were taken at room temperature using a Renishaw Raman system 3000, coupled to an Olympus metallurgical microscope. The spectra were excited at 6328 nm (He-Ne Spectra Physics mod. 127) and recorded in the 200-1800 cm<sup>-1</sup> range. EPR spectra of powdered samples were taken with a Bruker EMX 10/12 homodyne, X-band spectrometer.

## 3. Results

### 3.1 Chemical durability

The dissolution rates (DRs) of the BABAL glasses measured from the weight loss experiments conducted in distilled water at 90 °C are given in Table 1 and Fig. 1. Clearly DR varies with Fe<sub>2</sub>O<sub>3</sub> content: it decreases from 4.7 × 10<sup>-6</sup> g/cm<sup>2</sup>min for glasses containing 0 mol% Fe<sub>2</sub>O<sub>3</sub> containing glass to about 1.0 × 10<sup>-7</sup> g/cm<sup>2</sup>min for glasses containing about 4 mol% of Fe<sub>2</sub>O<sub>3</sub>. Even though the samples with Fe<sub>2</sub>O<sub>3</sub> content between 2 and 4 mol% had the low-

**Table 1.** Batch composition and measured of DR and density of the glasses studied.

Sample	Composition <sup>a</sup> (mol%)	Density <sup>b</sup> (g/cm <sup>3</sup> )	DR <sup>c</sup> (g/cm <sup>2</sup> min)
B0	30BaO·50B <sub>2</sub> O <sub>3</sub> ·20Al <sub>2</sub> O <sub>3</sub>	3.12	4.7 × 10 <sup>-6</sup>
B1	29.7BaO·49.5B <sub>2</sub> O <sub>3</sub> ·19.8Al <sub>2</sub> O <sub>3</sub> ·1.0Fe <sub>2</sub> O <sub>3</sub>	3.14	2.9 × 10 <sup>-6</sup>
B2	29.4BaO·49.0B <sub>2</sub> O <sub>3</sub> ·19.6Al <sub>2</sub> O <sub>3</sub> ·2.0Fe <sub>2</sub> O <sub>3</sub>	3.18	9.3 × 10 <sup>-7</sup>
B3	28.8BaO·48.0B <sub>2</sub> O <sub>3</sub> ·19.2Al <sub>2</sub> O <sub>3</sub> ·4.0Fe <sub>2</sub> O <sub>3</sub>	3.28	9.8 × 10 <sup>-7</sup>
B4	27.6BaO·46.0B <sub>2</sub> O <sub>3</sub> ·18.4Al <sub>2</sub> O <sub>3</sub> ·8.0Fe <sub>2</sub> O <sub>3</sub>	3.36	1.7 × 10 <sup>-6</sup>
B5	27.0BaO·45.0B <sub>2</sub> O <sub>3</sub> ·18.0Al <sub>2</sub> O <sub>3</sub> ·10.0Fe <sub>2</sub> O <sub>3</sub>	3.41	2.2 × 10 <sup>-6</sup>
Iron-phosphate <sup>d</sup>	40Fe <sub>2</sub> O <sub>3</sub> ·60P <sub>2</sub> O <sub>5</sub>	3.03	1.3 × 10 <sup>-9</sup>

<sup>a</sup> Raw materials used were BaCO<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

<sup>b</sup> The error is ± 0.01 g/cm<sup>3</sup>.

<sup>c</sup> Samples were immersed in 100 ml distilled water at 90 °C for 8 days.

<sup>d</sup> Ref. 14.

est chemical durability (see Table 1 and Fig. 1), there is an increase in DR for samples containing more than 4 mol%  $\text{Fe}_2\text{O}_3$ . As a comparison, the iron phosphate glass containing 40 mol%  $\text{Fe}_2\text{O}_3$ <sup>16</sup> had a dissolution rate 100 times less than the dissolution rate for window glass and 700 times less than the dissolution rate for the BABAL glass containing 10 mol% of  $\text{Fe}_2\text{O}_3$ , as shown in the Fig. 2.

The pH of the solution after the corrosion tests for a BABAL glass with 2 mol%  $\text{Fe}_2\text{O}_3$  is shown in Fig. 3. The reduction in the pH values for the iron phosphate glass during the first four days is consistent with the observed relatively higher DR values as a result of corrosion in these glasses to be correlated with the amount of phosphoric acid formed from the release of phosphorus from this glass. However for the BABAL glass the higher pH values indicates the formation of considerably higher amount of basic

compounds from the release of Ba and Al from interstitial (glass modifier) positions.

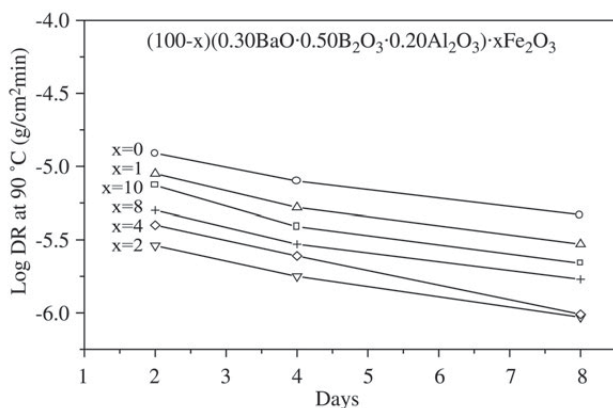
### 3.2 X-ray diffraction and density measurements

All of the compositions listed in Table 1 formed glasses, as no crystalline phases were detected by XRD. The XRD pattern of crystalline counterpart of a sample with  $x = 0$  mol% is given in Fig. 4 which indicates that the major crystalline phase in the crystallized sample is the  $\text{Ba}_2\text{Al}_2\text{B}_8\text{O}_{17}$ <sup>17</sup>.

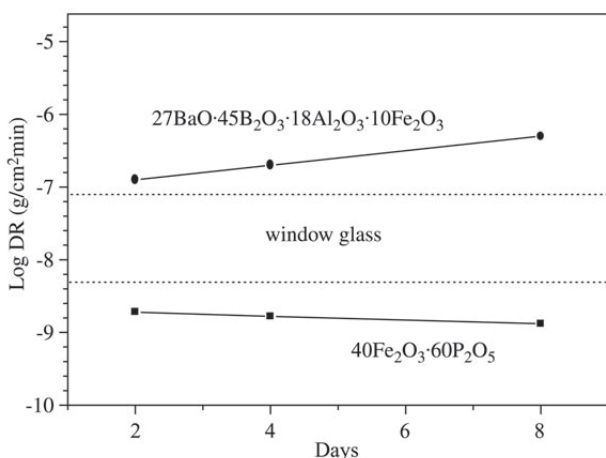
As shown in Fig. 5, the density of the BABAL glasses at room temperature increased linearly from 3.12 to 3.41  $\text{g}/\text{cm}^3$  with increasing  $\text{Fe}_2\text{O}_3$  content (see Table 1).

### 3.3 EPR

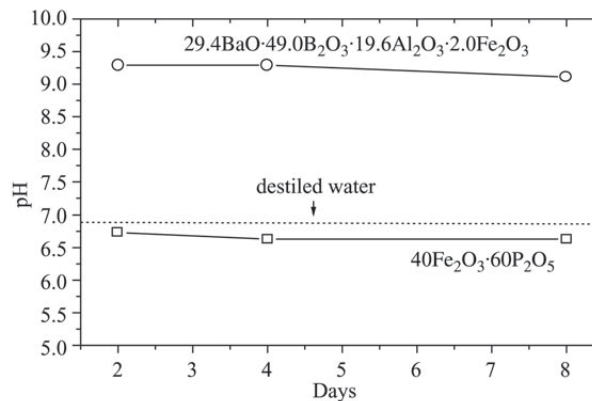
Figure 6 shows the X-band EPR spectra of BABAL glasses containing increasing amounts of 1 to 10 mol% of



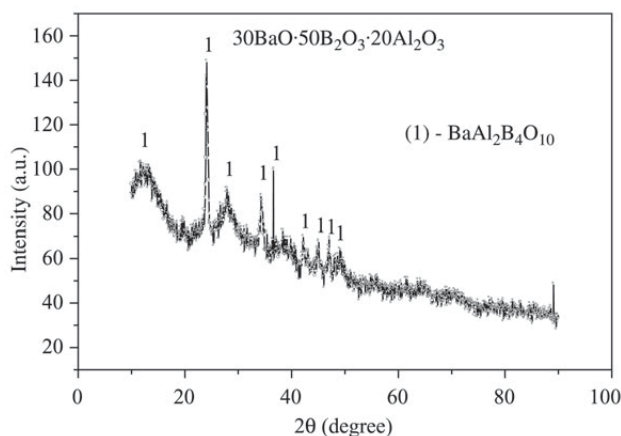
**Figure 1.** Variation of dissolution rates measured for 2, 4, and 8 days in distilled water at 90 °C with  $\text{Fe}_2\text{O}_3$  content.



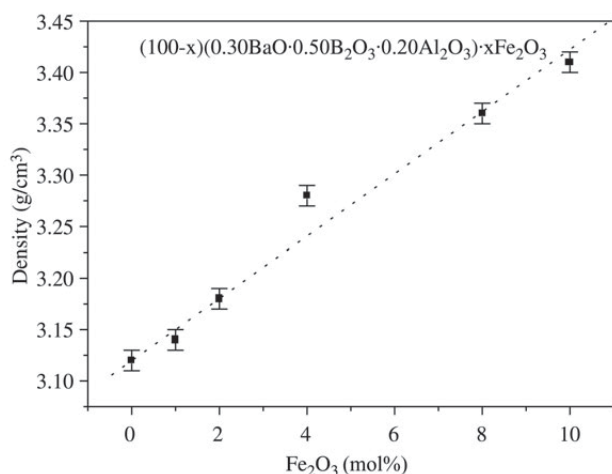
**Figure 2.** Dissolution rates of glass B5 and iron phosphate glass in distilled water at 90 °C for 2, 4, and 8 days.



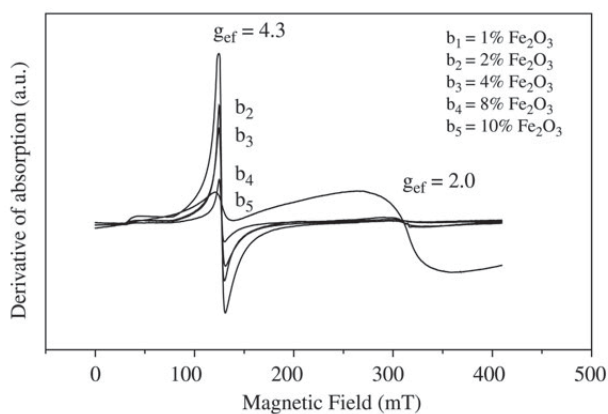
**Figure 3.** Variation of pHs with the iron content for BABAL and iron phosphate glasses.



**Figure 4.** X-ray diffraction pattern for crystalline counterparts of glass B5 after heat treatment of 750 °C for 24 h in air.



**Figure 5.** Variation of density values with the  $\text{Fe}_2\text{O}_3$  content. Line is drawn as guide for the eye.



**Figure 6.** The EPR spectra of BABAL glasses containing additional amounts of  $\text{Fe}_2\text{O}_3$  (1 to 10 mol%). The successive amplitudes were gradually reduced in order to show the relative evolution of the intensities and line shapes of the  $g = 4.3$  and  $g = 2.0$  resonance.

$\text{Fe}_2\text{O}_3$ . The intensities were progressively decreased in order to show the evolution of the relative line shapes and intensities at  $g = 4.3$  from a) isolated ions in local tetrahedral (and eventual octahedral) sites<sup>9</sup> and b) at  $g = 2.0$  from clusters of two or more  $\text{Fe}^{3+}$  ions which interact among themselves.

No significant changes were observed in the line width and shape of the  $g = 4.3$  EPR spectra, with the  $\text{Fe}_2\text{O}_3$  concentrations ranging from 1 to 8 mol%, indicating that the increase of Fe has occurred mainly by substitutions of  $\text{Fe}^{3+}$  ions at the sites of the  $\text{BO}_4$  tetrahedra of the glass forming network.

As the  $\text{Fe}_2\text{O}_3$  content reaches about 10 mol% there is observed a significant increase of the resonance at  $g = 2.0$  to-

gether with a strong line broadening which is also observed in the resonance at  $g = 4.3$  before it is going to be completely obscured by the former which becomes dominant.

A similar evolution has been observed by H.O. Hooper *et al.*<sup>18</sup> in the EPR spectra of iron containing sodium borate glasses, with the disappearance of the  $g = 4.3$  resonance at about the same relative amount of  $\text{Fe}_2\text{O}_3$  (8–0 mol%). Later on D.W. Moon *et al.*<sup>19</sup> have reported that in the glass system  $x\text{Fe}_2\text{O}_3 \cdot (100-x)[\text{BaO} \cdot 4\text{B}_2\text{O}_3]$  at concentrations greater than 3 mol%  $\text{Fe}_2\text{O}_3$ , iron ions associated in pairs (diads) and groups of three (triads) became predominant, in addition to the isolated  $\text{Fe}^{3+}$  ions. They assigned the shoulder at  $g = 6.0$  to weak crystal field terms and the  $g = 2.0$  resonance to clusters of more than one iron atom with antiferromagnetic interaction.

More recently, L. Cugunov *et al.*<sup>20</sup>, E.M. Yahiaoui<sup>11</sup>, and R. Berger *et al.*<sup>9,21</sup> carried out studies with computer simulations of the  $\text{Fe}^{3+}$  resonance in borate glass. The experimental EPR spectra were well described by assuming that the environment of  $\text{Fe}^{3+}$  ions are highly distorted and in addition to the orthorhombic distortion related to the  $g = 4.3$  feature, an important part of  $\text{Fe}^{3+}$  arises from axial or slightly rhombic distortions.

### 3.4 Raman

The Raman spectra for the lower concentration of  $\text{Fe}_2\text{O}_3$  are dominated by a narrow and intense band at  $806 \text{ cm}^{-1}$  (Fig. 7). The  $806 \text{ cm}^{-1}$  and  $540 \text{ cm}^{-1}$  line intensities decrease with the increasing concentration of  $\text{Fe}_2\text{O}_3$  and other bands centered at  $580$ ,  $780$  and  $920 \text{ cm}^{-1}$  appear. For higher concentration of  $\text{Fe}_2\text{O}_3$  the bands between  $580$ ,  $780$  and  $920 \text{ cm}^{-1}$  are predominating in the spectra.

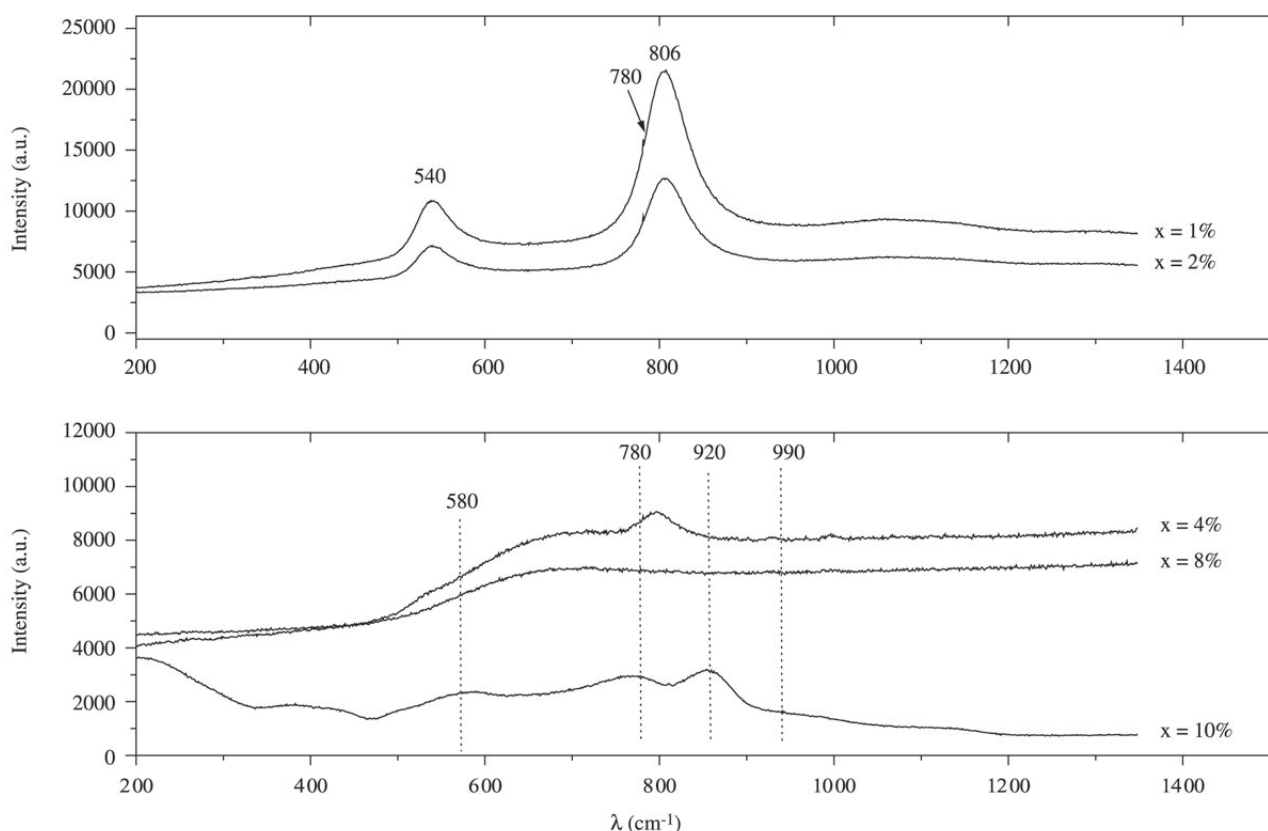
### 3.5 Mössbauer

The room temperature Mössbauer spectra of the BABAL glasses with iron content  $> 2$  mol% are shown in Fig. 8. The iron valence and hyperfine parameters, isomer shift  $\delta$  and quadrupole splitting  $\Delta E_Q$ , calculated from the Mössbauer spectra are given in Table 2. It is found that some of the  $\text{Fe(III)}$  ions in the starting batch are reduced to  $\text{Fe(II)}$  ions

**Table 2.** Room temperature Mössbauer hyperfine parameters and iron valence for BABAL glasses. The estimated error in these parameters is  $\pm 0.03 \text{ mm/s}$ .

Glass	$(\delta)^a$ (mm/s)		$(\Delta E_Q)$ (mm/s)		Fe(II) <sup>a</sup> fraction (%)
	Fe(II)	Fe(III)	Fe(II)	Fe(III)	
B3	1.23	0.36	2.31	1.12	2.9
B4	1.12	0.38	2.09	1.12	3.9
B5	0.97	0.37	1.84	1.15	5.1

<sup>a</sup>Fraction of Fe(II) calculated from the Mössbauer spectra.



**Figure 7.** The Raman spectra of BABAL glasses ( $1 < x < 10$ ).

as all of the glasses contain varying amounts of Fe(II) as determined from the Mössbauer spectra. The isomer shift values for Fe(III) and Fe(II) ions range between 0.39 mm/s and 1.08 mm/s while the quadrupole splitting values range between 1.10 mm/s and 2.09, respectively. These values of isomer shifts correspond to tetrahedral coordination for both Fe(II) and Fe(III) in these glasses.

#### 4. Discussion

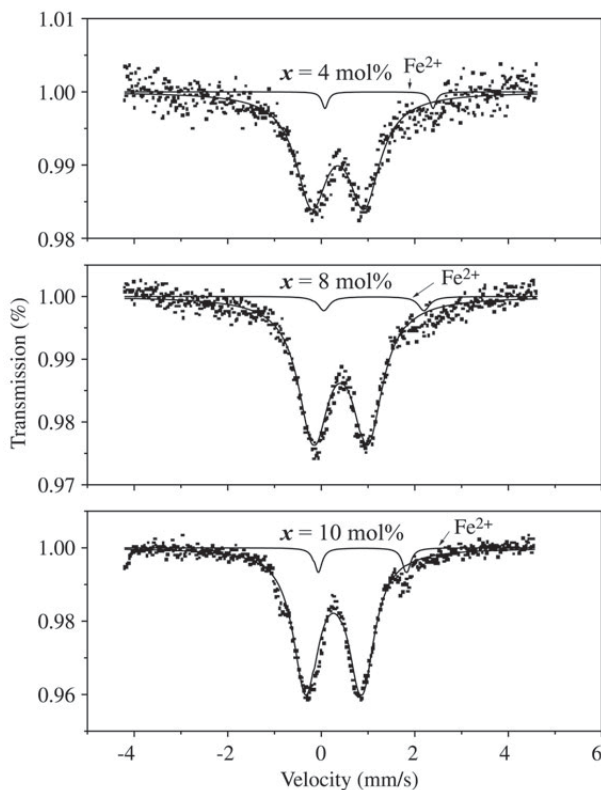
The chemical durability for the  $(100-x)(0.30\text{BaO}\cdot 0.50\text{B}_2\text{O}_3\cdot 0.20\text{Al}_2\text{O}_3)\cdot x\text{Fe}_2\text{O}_3$  glasses with iron content of 2 mol% is 700 times less than that iron phosphate glass containing 40 mol% of  $\text{Fe}_2\text{O}_3$ . In general the chemical durability for phosphate glasses improves with the increase in iron content<sup>16</sup>, however the decrease in the chemical durability of BABAL glasses for iron content  $> 4$  mol% could be attributed to the formation of microclusters in substitutional sites in the glass network<sup>22</sup>.

Figure 6 shows that the EPR lines  $g_{\text{eff}} \approx 2.0$  and  $g_{\text{eff}} \approx 4.3$  on the spectra these glasses are due to the diluted  $\text{Fe}^{3+}$  ions in tetrahedral or orthorhombic coordination<sup>9,23</sup> and small clusters

of exchange coupled  $\text{Fe}^{3+}$  ions in substitutional sites of the glass network. Figure 6 also shows a low field feature, as a shoulder, in the  $g \approx 10$  region. Moreover, this shoulder seems to disappear in the samples with the higher iron concentration.

The Raman band around  $806\text{ cm}^{-1}$  is attributed to boroxol rings, which is the main structural unit of the  $\text{B}_2\text{O}_3$  glasses<sup>6,7</sup>. The addition of  $\text{Fe}_2\text{O}_3$  converts three-coordinated boron into four-coordinated boron units (see Fig. 7), resulting in the formation of tetraborate groups ( $780\text{ cm}^{-1}$ ). The band in  $540\text{ cm}^{-1}$  is attributed to “loose”  $\text{BO}_4$  groups and “loose” diborate groups<sup>24</sup>, and the band in the  $920\text{ cm}^{-1}$  can be attributed to the formation of pentaborate groups<sup>25</sup>. These results are consistent with the investigation of Fe(II) and Fe(III) properties in calcium aluminoborate glasses<sup>7</sup>.

Mössbauer results indicate that even though there is no Fe(II) in the starting batch, the resulting glasses contain varying amounts of Fe(II) (ranging from 6 to 20%) which shows that some of the Fe(III) ions are reduced to Fe(II) ions during melting. The observed isomer shift values indicate that both Fe(II) and Fe(III) ions have oxygen neighbors in the tetrahedral coordination.



**Figure 8.** Mössbauer spectra obtained of glasses of  $(100-x)(0.30\text{BaO}\cdot 0.50\text{B}_2\text{O}_3\cdot 0.20\text{Al}_2\text{O}_3)_x\text{Fe}_2\text{O}_3$  measured at 295 K.

## 5. Conclusions

The BABAL glass corrosion rate in neutral environment is caused, respectively, by the increase in the pH of the solution (water) due to the attack of  $\text{OH}^-$  and by the reaction between  $\text{H}^+$  and metallic ions ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ). EPR lines  $g_{\text{ef}} \approx 2.0$  and  $g_{\text{ef}} \approx 4.3$  on the spectra of these glasses can be due to the diluted state of  $\text{Fe}^{3+}$  ions in tetrahedral or orthorhombic coordination and small clusters of exchange-coupled  $\text{Fe}^{3+}$  ions in substitutional sites of the glass network.

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