Effect of Sulfur Addition on the Redox State of Iron in Iron Phosphate Glasses

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Abstract. Mössbauer, IR, and electrical conductivity were investigated in iron phosphate glasses, $40Fe_2O_3$–$60P_2O_5$ (in mol%), containing sulfur ranging from 0 to 2, 4, 6, and 8 mass%. Sulfur proved to act as a reducing agent for the redox reaction during the glass preparation. Mössbauer spectroscopy was used in order to determine the relative fraction of Fe^{2+}, i.e. Fe^{2+}/Fe(total), isomer shift (δ), and quadrupole splitting (Δ). Mössbauer results revealed that the relative fraction of Fe^{2+} increases with an increasing sulfur content. Electrical conductivity showed a similar composition dependency as the fraction of Fe^{2+}. These results indicate that higher electrical conductivity of sulfur-containing iron phosphate glasses is due to small polaron hopping (SPH) between iron atoms of different valance states, i.e., a step-by-step electron hopping from Fe^{2+} to Fe^{3+}. IR spectra of these glasses are very similar to those of sulfur-free iron phosphate glasses, proving that the structure of sulfur-containing iron phosphate glasses is essentially the same as that of sulfur-free phosphate glasses.

Key words: iron phosphate glasses, sulfur, Mössbauer, IR, dc conductivity.

1. Introduction

Iron phosphate glasses typically have a relatively poor chemical durability [1], which often limits their industrial applications. However several studies have shown that chemical durability of phosphate glasses can be improved by the addition of various oxides such as Al_2O_3 and Fe_2O_3 [2]. As result, iron phosphate glasses are now of interest for several technological and biological applications. Structural and physical properties of iron phosphate glasses have been investigated so far [1–3], but the effect of sulfur on the physical properties, structure, and redox state of iron phosphate glasses have rarely been reported to our knowledge.

Mössbauer spectroscopy is a useful technique for characterizing the coordination symmetry and redox states of iron in glasses. Mössbauer spectra of glasses generally have broader linewidth than those of crystalline materials, because of dis-

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ordered nature of the environment at around the absorbing atoms, such as different chemical bond lengths and bond angles. Reliable average hyperfine parameters, isomer shift (δ), and quadrupole splitting (Δ), can be obtained by fitting the Mössbauer spectra with a minimum number of broadened Lorentzians required to match the absorption envelope [4].

Electrical conductivity of iron phosphate glasses is originated from the electron hopping from an atom of lower valency state to that of higher valency state, e.g., from Fe^{2+} to Fe^{3+}. This is usually termed "small polaron hopping" (SPH) [5–10] and the electrical conductivity strongly depends upon the distance between two iron atoms [13]. In iron phosphate glasses, the electrical conductivity is related to the total concentration of iron atoms and to the ratio of Fe^{2+} to the total number of iron atoms: $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ [3]. In the present paper, Mössbauer, IR, and dc conductivity were investigated for iron phosphate glasses, $40Fe_2O_3-60P_2O_5$ (in mol%) containing additional amounts (x) of sulfur (S), where x is 0, 2, 4, 6, and 8 in mass%.

2. Experimental

Glass samples were prepared from analytical reagent grade chemicals according to the formula xS–$(40Fe_2O_3-60P_2O_5)$ (mol%), where $x = 0, 2, 4, 6$ and 8 (mass%). Batches were prepared by mixing reagent grade Fe_2O_3, P_2O_5 and S crystalline powders, which were melted in platinum crucibles in air at 1200°C for 1 hour with occasional stirring. Each melt was poured onto a polished copper block kept at room temperature and immediately pressed with another copper block. Amorphous nature of the glasses was ascertained from X-ray diffraction analysis. Density of the glasses was measured by the Archimedes method using toluene as the immersion liquid. Mössbauer measurements were performed at room temperature with a $^{57}Co(Rh)$ source of 925 MBq using Wissel spectrometer of a constant acceleration type. IR spectra of the glass samples were measured from 450 to 2000 cm^{-1} by a conventional KBr pellet method on a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer 1760 X). Each pellet was prepared by mixing about 4 mg of glass powder with 150 mg of anhydrous KBr. A background of the IR spectra was corrected with a spectrum of KBr. The dc conductivity (σ) of the as-quenched glass samples was measured at temperatures between 303 and 473 K. Silver paste electrodes were deposited on both faces of the polished samples. A satisfactory I–V characteristic was observed in these samples.

3. Results and discussion

3.1. MÖSSBAUER SPECTRA

Room-temperature (RT) Mössbauer spectra of the glass samples are similar to each other, as illustrated in Figure 1; a quadrupole doublet due to octahedral Fe^{3+} is observed with a weak peak due to octahedral Fe^{2+} in every case. Mössbauer

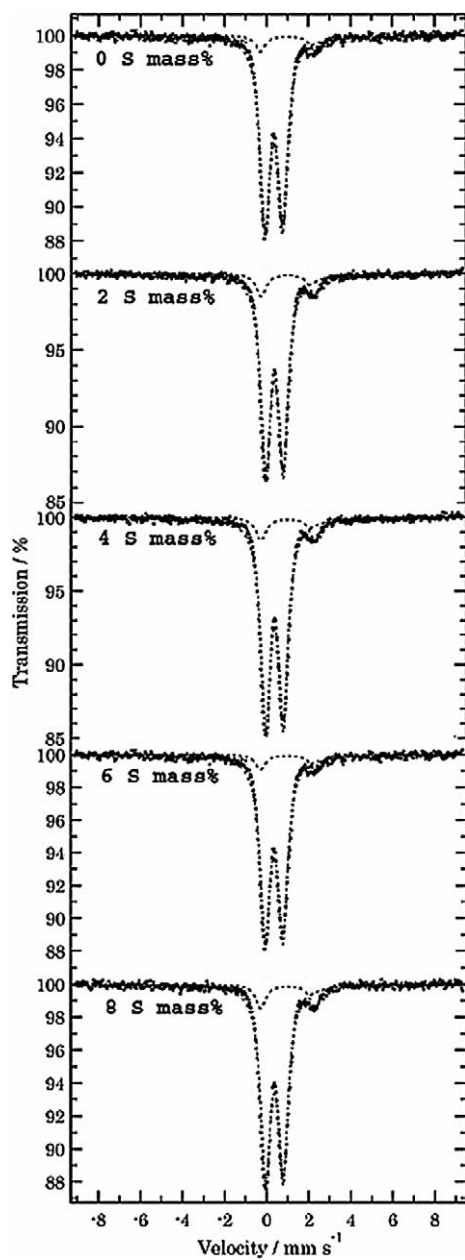*Figure 1.* Mössbauer spectra of glass samples with different sulfur content.

hyperfine parameters of each site show that Fe^{2+} has an isomer shift (δ) of 1.21 to 1.23 $\pm$ 0.005 mm s^{-1}, while a quadrupole splitting (Δ) decreases from 2.32 to 2.24 $\pm$ 0.01 mm s^{-1} along with a sulfur content. This means that the iron environment at this site becomes more symmetrical with an increasing sulfur content

ranging from 0 to 8 mass%. At the same time, the absorption area (A) increases from 10.2 to 13.4 $\pm$ 0.5% with an increasing sulfur content. The Fe^{3+} site has nearly constant δ values of 0.34 to 0.37 $\pm$ 0.005 mm s^{-1}, and an identical Δ value of 0.87 $\pm$ 0.01 mm s^{-1}. This means that the iron environment at a given site is independent of the Fe^{2+} content and the sulfur content. It should be noted that the reduction effect of sulfur is very small compared with our previous results for borate glass [11], basalt glass [12] and sodium phosphate glass containing iron [13].

3.2. IR SPECTRA

Typical IR spectra of sulfur iron phosphate glasses are shown in Figure 2. The IR spectra of these glasses show the most prominent bands at 515, 770, 918 and 1070 cm^{-1}.

The band between 1060 and 1080 cm^{-1} is attributed to a symmetric and an asymmetric vibration of PO_2^- and PO_3^{2-} terminal groups [8, 9]. A band between 915 and 930 cm^{-1} is due to an asymmetric vibration of P–O–P bridge [14, 15]. A band around 770 cm^{-1} is due to a symmetric stretching mode of the P–O–P bridge [18, 19] and a band at around 515 cm^{-1} may be due to an overlapping vibrations of iron–oxygen polyhedra and P_2O_7 groups [16]. The IR spectra of all the present samples have a shoulder peak at about 630 cm^{-1}; this may be due to vibration of some iron–oxygen bands [17]. IR spectra of these glasses are very similar to those of sulfur-free iron phosphate glasses, proving that the structure of sulfur-containing iron phosphate glasses is essentially the same as that of sulfur-free phosphate glasses.
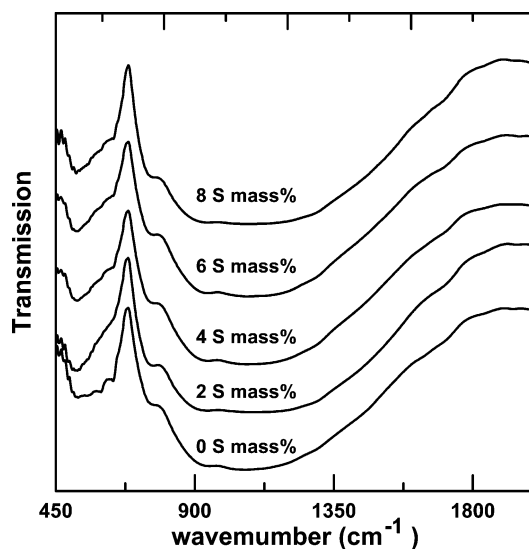

Figure 2. IR spectra for glass samples with different sulfur content.

3.3. DC CONDUCTIVITY AND ACTIVATION ENERGY

Figure 3 shows a relationship between dc conductivity, $\log \sigma$, for the glasses and reciprocal temperature. These glasses have σ values from 1.75×10^{-10} to 1×10^{-5} S m^{-1} at temperature from 303 to 473 K. Figure 3 shows a linear relationship between $\log(\sigma)$ and $1/T$. The slope of the curves gives an activation energy for the conduction, which increases at higher temperatures. The value of σ is apparently expressed as:

$$\sigma = \sigma_0 \exp(-W/kT), \tag{1}$$

where σ_0 is the pre-exponential factor, W the activation energy and k the Boltzmann constant. The activation energy (W) and the pre-exponential factor (σ_0) were obtained from a least-squares method for the experimental data above 335 K. The compositional dependence of the conductivity (σ) at 405 K and the activation energy are shown in Figure 4. A general trend observed in Figure 4 is that the magnitude of the conductivity at fixed (405 K) tends to be highest in those compositions having smallest activation energy. This result is consistent with the small polaron hopping (SPH) mechanism [8]. In Figure 3, dc conductivity varies linearly with $1/T$ in two temperature regions. Such phenomenon was found in mixed calcium and barium iron phosphate glasses [3] and sodium iron phosphate glasses [18]. This phenomenon is attributed to the change of the conduction mode from the SPH to an intermediate variable-range hopping (VRH) [8, 19]. We speculate that the change of the slope is caused by a transition from SPH to VRH, where the polaron binding energy is small and the static energy of the system plays a dominant role
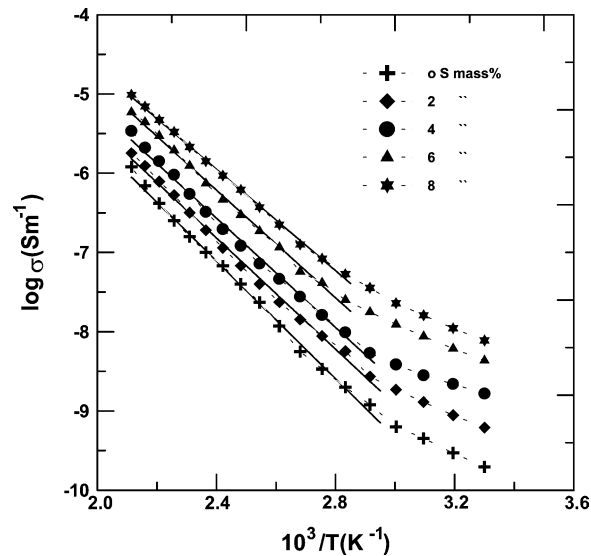

Figure 3. Temperature dependence of the dc conductivity (σ) for glass samples with different sulfur content. Solid lines are calculated by using a least-squares method.
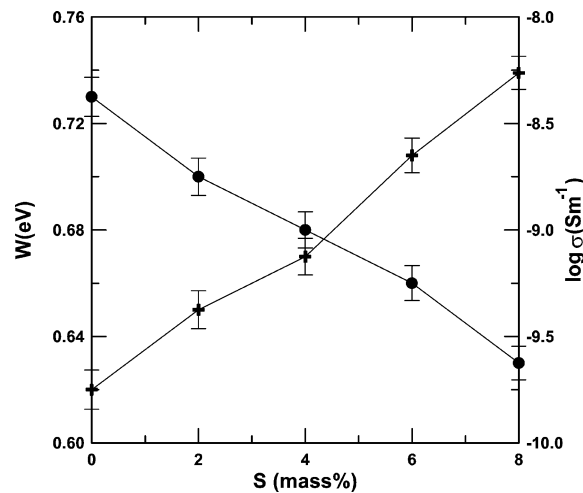
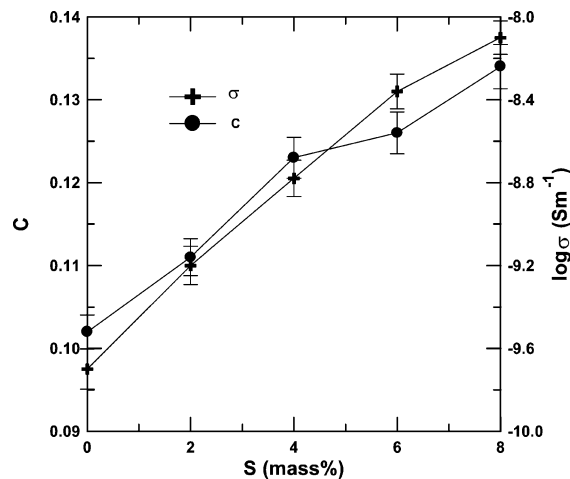*Figure 4.* Effect of sulfur (S) content on the dc conductivity (+) at $T = 405$ K on the activation energy (●).

Figure 5. The dc conductivity (σ) at 303 K and the TM ion ratio (C) for different sulfur content. Lines are drawn as a guide for the eyes.

in the conduction mechanism [3, 7]. Figure 5 shows the electrical conductivity (σ) and the fraction of reduced transition metal (TM) ion ($C = Fe^{2+}/Fe_{total}$) as a function of sulfur (S) content (in mass%) in the present glasses. Figure 5 shows the electrical conductivity (σ) of several glasses with different compositions. The σ values are within an order of magnitude of that of iron phosphate glasses [3, 18]. Since the electrical conduction in iron phosphate glasses [3] was assumed to be due to an electron hopping from Fe^{2+} to Fe^{3+} sites, it is reasonable to assume that the electron hopping also occurs in the sulfur-containing iron phosphate glasses. Also, it is clear that the C increases with an increasing S content (in mass%), as the

electrical conductivity increases in the same manner (see Figures 3 and 4). These results indicate that the electrical conductivity of sulfur-containing iron phosphate glasses can be understood by the SPH between iron ions of different valency states [8–10]. The small polaron and variable-range hopping parameters will be discussed in a forthcoming paper.

4. Conclusion

Semiconducting oxide glasses, S–Fe_2O_3–P_2O_5 system, are fabricated with S, Fe_2O_3 and P_2O_5 raw materials by a melt-quenching method. The IR spectra of the S-containing glass samples are similar to that of S-free iron phosphate glasses, indicating that the local structure of these glass samples is not affected by S-content. Sulfur seems to act as a reducing agent during glass synthesis and affects the electrical conductivity. Mössbauer spectra revealed that the Fe^{2+} ratio increases with an increasing sulfur content. The dc conductivity measurements leads to a conclusion that the electrical conductivity is dominated by the electron hopping between Fe^{2+} to Fe^{3+} sites which increases with an increasing sulfur content.

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