



Role of Sulfur as a Reducing Agent for the Transition Metals Incorporated into Lithium Silicate Glass

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Abstract: $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ glass was prepared with and without 5 wt % sulfur (S) while melting the mixture of the starting materials at 1350 °C for 1 h in air. A part of the as-prepared glass was heat treated for 1 h near its crystallization temperature (T_c) as determined from differential thermal analysis. Each glass was also investigated by means of Mössbauer spectroscopy, X-ray diffraction, FTIR, and DC conductivity. The Mössbauer spectra showed ionic Fe^{2+} and Fe^{3+} species in the glass as well as in the precipitated phase obtained after heat treatment. XRD patterns demonstrated the glassy phase formation in the as-quenched samples irrespective of the presence of sulfur. The heat treated samples showed different precipitated phases containing iron particles of nanometer size. The electric conductivity measurements showed that sulfur-doped samples had high values of (σ) probably because of small polaron hopping between Fe^{2+} and Fe^{3+} .

Keywords: Mössbauer spectroscopy, electrical conductivity, sulfur, heat treatment.

INTRODUCTION

LITHIUM silicate glass and related ceramic have important applications such as heat-resistant glasses, glass fiber, optical glass, bioglass and bioglass-ceramic.^[1–2] Glass-ceramics are produced by controlled heat treatment of glass at temperatures near its T_c . If the heat treatment time is short (e.g., less than 1 h), the size of crystalline particles is expected to be of nanometer size, and provides interesting physical properties.^[3–4] Transition metal (TM) ions introduced in the glass matrix improve the physicochemical properties of glass and glass-ceramics. These ions improve the electrical conduction due to electron hopping from the lower valence state to the higher state (e.g. from Fe^{2+} to Fe^{3+}).^[5]

Recently, much attention has been paid to the development of fast-ion conductors of glass and glass-ceramics. Li-ion batteries (LIB) are the most popular source

for different modern portable electronic devices.^[6–8] Lithium silicate glass was found to be usable as fast-ionic conductor even at low temperatures, because of its high mechanical strength and chemical stability.^[9] It could be used for ceramic-metal sealing and for dental restoration.^[10–11]

In the present study, we investigated the dc conductivity of $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ glass and its glass-ceramics, in addition to Mössbauer, DTA, IR, density and XRD measurements. Since sulfur is a reducing agent, we added it to the reagent mixture to control the ionic states of Ni and Fe to facilitate the electronic conduction beside the ionic one in the glass and glass-ceramic samples.

EXPERIMENTAL

Glass samples of the composition $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ (in mol %) with and without 5 wt % of sulfur (S) were prepared by melt-quenching method in a platinum crucible

at 1350 °C for 1 h in air using an electric furnace. The melt was quenched on a copper plate and yielded a glass plate of 1 mm thickness. Heat treatment was conducted for 1 h at 550 °C, being close to its crystallization temperature (T_c) as obtained from DTA (Shimadzu). The bulk densities were measured at room temperature using Archimedes method with carbon tetrachloride as the immersing liquid ($r = 1.593 \text{ g cm}^{-3}$). XRD measurements of glass and heat-treated samples were conducted using [Rigaku RINT 2100] with $\text{CuK}\alpha$ (0.1541 nm) radiation. The maximum current and voltage were 300 mA and 50 kV, respectively. FT-IR spectra were recorded at room temperature by standard KBr pellet method using computerized FT-IR spectrophotometer [JASCO FT-IR-300E] in the range (400–4000 cm^{-1}).

The DC electrical conductivity for glass and glass-ceramics were measured by means of two-probe method, which is appropriate for high resistance materials. Polished surface of each sample was coated with silver paste, and two polished cleaned copper electrodes was attached to the coated area. A Pico-ammeter 760 was used to collect the DC data over the temperature range of 300–550 K. The sample temperature was measured by a chromel–alumel type thermocouple which was placed at a position to the sample as close as possible. The Mössbauer spectra were recorded at room temperature by a constant acceleration method with Wissel MDU-1200, connected to a digital function generator (Wissel DFG-1000). A source of $^{57}\text{Co}(\text{Rh})$ of 925 MBq and $\alpha\text{-Fe}$ foil were used as a source and a reference, respectively. Mössbauer spectra were analyzed assuming a Lorentzian peak shape using the fitting program *Mösswinn 3.0i XP*.

RESULTS AND DISCUSSION

DTA

DTA was used to determine the characteristic temperatures of materials. Fig. 1 shows the DTA curve of the as-quenched glass with a composition of $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ containing 5 wt % of sulfur. Glass formation was confirmed from the glass transition temperature (T_g) observed at 458 °C, and successive three exothermic peaks corresponding to crystallization temperatures (T_{c1} , T_{c2} , T_{c3}) observed at 597, 664 and 736 °C, respectively, followed by endothermic effect due to melting (T_m) at 1015 °C.

Density

Densities of the as-quenched glass sample with and without 5 wt % sulfur are listed in Table 1, together with those for HT samples. Table 1 show that the density of S-free sample is greater than that of S-doped sample. The decrease in the density after sulfur addition indicates the reduced rigidity

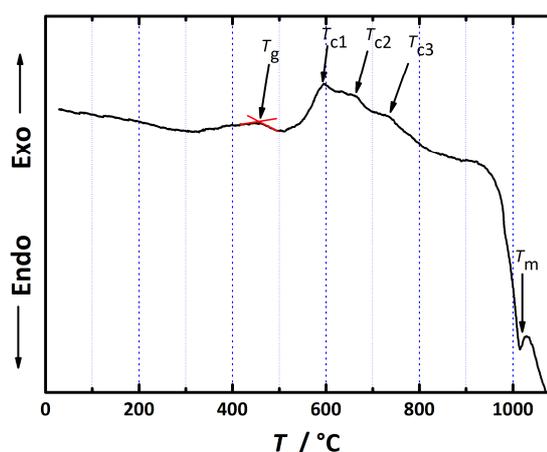


Figure 1. DTA curve of as-quenched glass with a composition $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ plus 5 wt % sulfur.

of the glass matrix; there is a weakening of the structure, which will be favorable for the higher mobility of cations and consequently higher electrical conductivity (see section “Electrical Conductivity”). On the other hand, density of HT samples was greater than that of corresponding as-quenched glasses. The increase in the density of HT samples may be due to the rearrangement of ions causing structural changes to form glass-ceramics, *i.e.* the ions closely packed than in glass.^[4]

X-ray Diffraction (XRD)

XRD of the glass samples and its HT samples was measured using $\text{CuK}\alpha$ radiation at room temperature to examine their amorphous and/or crystalline nature. Fig. 2 shows XRD pattern of $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ glass with 5 wt % sulfur (bottom), and those of HT samples with and without sulfur. In the case of as-quenched glasses, as shown in Fig. 2 (bottom), a representative halo was observed at around $2\theta = 20\text{--}35$ degrees with no diffraction peaks, confirming the glass formation. In the case HT-samples, some sharp peaks were observed being ascribed to $\text{LiFeSi}_2\text{O}_6$ (JCPDS card 71–1064) with a structure close to monoclinic, $\text{Fe}_{21.32}\text{O}_{34}$ (JCPDS card 80–2186) with a structure close to tetragonal and Fe_2O_3 (JCPDS card 89–0596) with a structure close to rhombohedral.

Table 1. Densities of $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ glasses with and without sulfur (S) and those of corresponding HT samples.

Samples with S / wt %	Density of glass samples / g cm^{-3}	Density of HT samples / g cm^{-3}
0	2.86	2.89
5	2.76	2.81

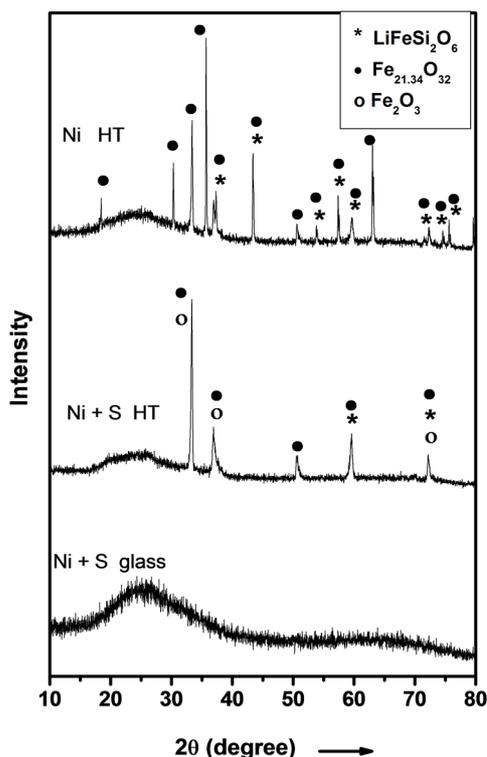


Figure 2. XRD patterns of $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ glasses with 5 wt % sulfur (S) and HT samples with and without S.

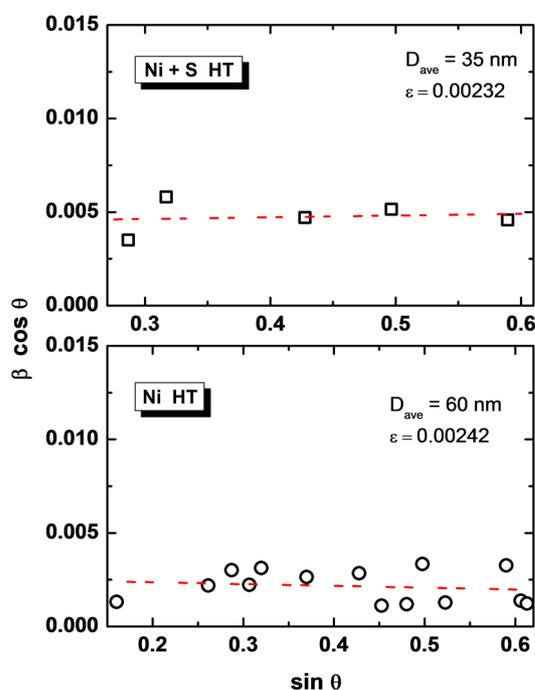


Figure 3. W-H plot for $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ samples (HT) with and without 5 wt % sulfur (S).

Using XRD data, the average crystallite size was calculated from Williamson–Hall (W-H) plot between $\beta\cos\vartheta$ and $\sin\vartheta$, as given in Fig. 3.^[4,12] The Williamson-Hall equation is

$$\beta\cos\vartheta = \frac{c\lambda}{D_{ave}} + 4\varepsilon\sin\vartheta, \quad (1)$$

where β is the fullwidth at half maximum (FWHM), ϑ is the Bragg angle, c the correction factor ($c \approx 1$), D_{ave} the average crystallite size, λ the wavelength of X-ray, ε the lattice strain. It is observed that the average crystallite size of S-free sample is greater than that of S-doped one.

Fourier-Transform Infrared Spectroscopy

FTIR spectroscopy is an important tool for the characterization of glass sample. Figure 4 shows FTIR absorption spectra of HT samples of S-doped and S-free glasses. In the case of S-free glass, the broad band observed at $\sim 485\text{ cm}^{-1}$ was assigned to Si-O-Si bending vibration of SiO_4 tetrahedra.^[13–15] After HT, this broad band slightly shifted to a high wavenumber region of 493 cm^{-1} . In the case of S-doped glass, the broad band observed at $\sim 478\text{ cm}^{-1}$ was assigned to Si–O–Si bending vibration in SiO_4 tetrahedra. This broad band shifted to 485 cm^{-1} after HT.

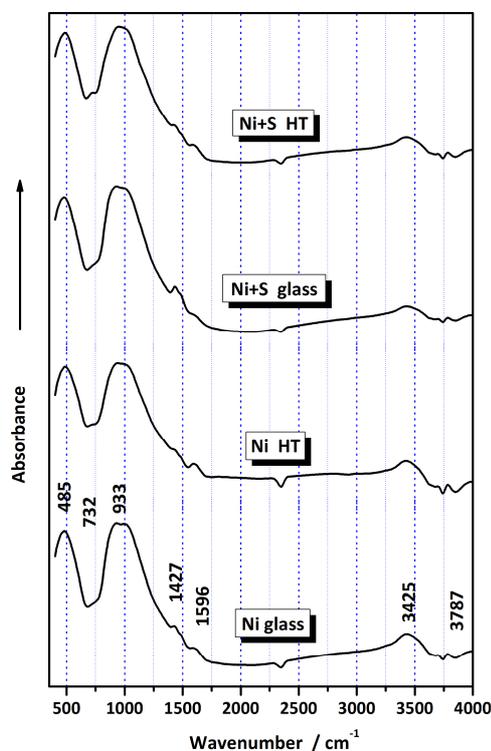


Figure 4. FTIR absorption spectra of $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ glasses with and without 5 wt % sulfur (S), together with the spectrum of HT sample (S-free).

In the case of S-free glass, a weak shoulder at 732 cm^{-1} , attributed to the symmetric stretching vibration of Si–O–Si bridging bonds, was observed at the same position after HT.^[16] After the sulfur addition, this shoulder was observed at almost the same position. The bands appearing in the region of $933\text{--}995\text{ cm}^{-1}$ were attributed to the asymmetric stretching vibrations of Si–O–Si bridging bonds.^[16] The band observed at 1427 cm^{-1} was assigned to the deformation vibration of H–O–H groups in the structure of glass or surface adsorbed water.^[17] The band appearing at 1596 cm^{-1} will be due to the deformation vibration mode of the H_2O .^[4,18] The band observed at around 3425 cm^{-1} is ascribed to the stretching vibration of OH group.^[4,18]

Mössbauer Spectroscopy

Figure 5 shows Mössbauer spectra measured at room temperature. In the case of S-free samples, Mössbauer spectra exhibited one doublet of Fe^{3+} tetrahedral (T_d) in both the as-quenched and HT samples. In case of S-doped glass, the above doublet appeared with another weak doublet due to Fe^{2+} (O_h). In the sample doped sulfur, peaks due to Fe_2O_3 precipitated observed as a result of heat treatment, as was confirmed the XRD study. Mössbauer parameters are summarized in Table 2.

Electrical Conductivity

Figure 6 shows a semiconducting temperature dependence of the electrical conductivity $\sigma(T)$, for S-free and S-doped glasses and that for HT samples, which are described by Mott equation (2).^[5,19]

$$\sigma T = \sigma_0 \exp(-W / kT) \quad (2)$$

where σ_0 is a pre-exponential factor as discussed below. The activation energy (W) and pre-exponential factor (σ_0) were obtained from the least square fits of the data. The straight line nature of the Mott-type plot indicates that the conduction is thermally activated, as often found in several semiconductors. Value of W reflecting the thermal energy required to promote the polaron hopping from one site to another was calculated to be $0.51\text{--}0.59\text{ eV}$. Values of σ and W obtained at 408 K are listed in Table 3.

Table 2. RT-Mössbauer parameters of $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ glasses with and without 5 wt % sulfur (S) and those for HT samples.

Samples	$\text{Fe}^{3+}(T_d)$				$\text{Fe}^{2+}(O_h)$			
	IS / mm s^{-1}	QS / mm s^{-1}	LW / mm s^{-1}	A / %	IS / mm s^{-1}	QS / mm s^{-1}	LW / mm s^{-1}	A / %
S-free Glass	0.30	0.97	0.56	100	–	–	–	–
S-free Glass (HT)	0.31	0.96	0.59	100	–	–	–	–
5 wt % S- Glass	0.30	0.96	0.56	85.7	1.08	2.066	0.42	14.3
5 wt % S-Glass (HT)	0.28	1.01	0.56	86.0	1.10	2.20	0.42	14.0

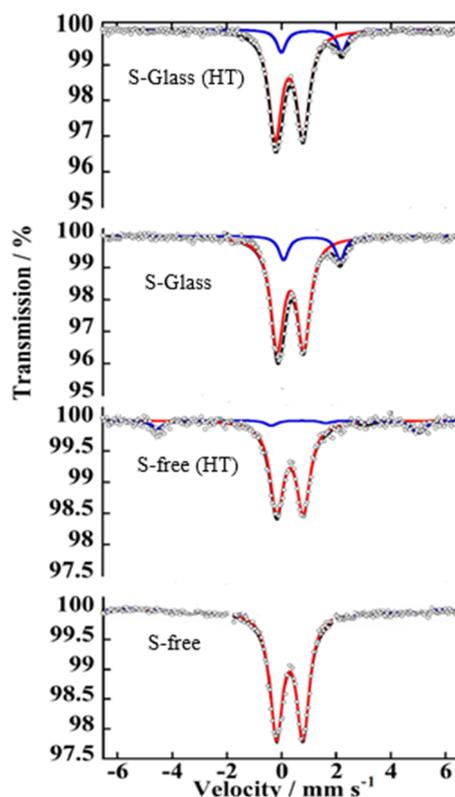


Figure 5. RT Mössbauer spectra of $\text{Li}_2\text{O}\cdot 0.25\text{Fe}_2\text{O}_3\cdot 0.25\text{NiO}\cdot 1.5\text{SiO}_2$ glasses with and without 5 wt % sulfur (S), and those of HT samples.

In Fig. 6 and Table 3 are shown dc conductivities of S-doped and S-free glasses, together with those for HT samples measured at a fixed temperature (408 K). They indicate that the conductivity of S-doped glass samples is higher than that of S-free glass. This may be due to the presence of Fe^{2+} ions in S-doped glass and its HT sample, as confirmed by the Mössbauer study. It is considered that sulfur atoms acted as a reducing agent in S-doped glass, which caused the reduction of Fe^{3+} to Fe^{2+} ions.^[20] When the glass was heat treated at 550 °C for 1 h, randomly dispersed nanocrystals were formed in the glass matrix. As a result, the electrical conductivity was one order of

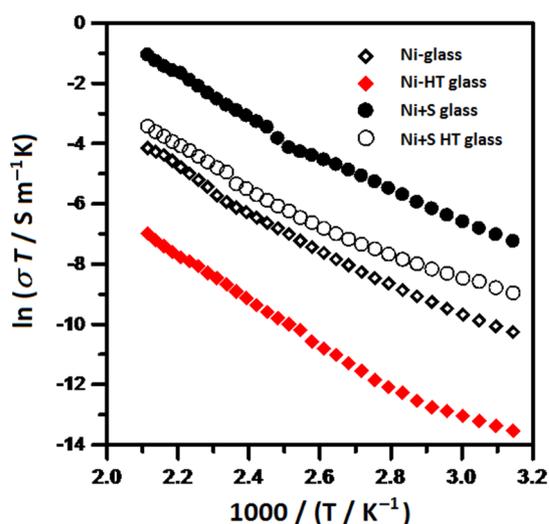


Figure 6. Temperature dependence of dc conductivity (σT) for the glasses with and without S and their (HT) samples.

magnitude smaller than that of as-quenched glass. It is speculated that nanocrystals produce ion-blocking effect imposed in the lithium ions in the glass matrix. This blocking effect was discussed for the oxygen-conducting nanomaterials.^[21] In our samples, the blocking effect on the oxygen ions might be caused by grain boundaries or pores that formed in the samples after heat treatment.

The concentration of iron ions N (cm^{-3}) may be evaluated using the density by the relation:

$$N = dpN_A / A_w \quad (3)$$

where d is the density of the sample, as evaluated above and presented in Table 1, p is the weight percentage of atoms, N_A is the Avogadro's number and A_w the molecular weight. While the relationship between N and the mean distance R between iron ions is generally described as:

$$R = (1 / N)^{1/3} \quad (4)$$

The calculated values of R and N are summarized in Table 3.

Table 3. Physical properties for the glasses with and without S and also for heat-treated samples, measured at 408 K.

Samples	$\ln(\sigma T / \text{S m}^{-1} \text{K})$	W / eV	$10^{22} N / \text{cm}^{-3}$	R / nm
S-free glass	-6.63	0.52	0.88	0.484
S-free glass (HT)	-9.59	0.59	0.90	0.480
S-doped glass	-3.45	0.51	0.85	0.489
S-doped glass (HT)	-5.87	0.53	0.87	0.486

In the range of measurements (Table 3), W depends on the site-to-site distance R . These results show that there is a correlation between W and R between iron ions. The effect dependence of σ on the present samples can be explained by the changes of the distance between the iron ions, R . It is concluded, therefore, that the conduction between iron ions depends strongly on R which is important to the conduction mechanism of our samples. This agrees with the results obtained recently by El-Desoky.^[22]

CONCLUSION

XRD patterns confirmed the glassy and precipitated nature of as-quenched glass samples before and after heat treatment, respectively. Particle size of the precipitated nanocrystals was estimated after the HT process. Density of sulfur-free glass sample was higher than that of sulfur-doped sample. Decrease of the density in the sulfur-containing glass sample was consistent with the reduced rigidity. Mössbauer spectra of S-free samples showed one doublet due to tetrahedral Fe^{3+} in both the as-quenched and HT samples. In S-doped samples, a weak doublet due to Fe^{2+} appeared along with the doublet of Fe^{3+} proving that sulfur acted as a reducing agent for Fe^{3+} . Glass sample doped with 5 wt % sulfur exhibited higher conductivity and smaller activation energy than S-free samples. This is due to the presence of Fe^{2+} ions in addition to Fe^{3+} ions. HT-samples showed lower conductivity due to the blocking effect.

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