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Electrical conductivity and local structure of lithium tin iron vanadate glass

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Abstract A relationship between electrical conductivity (σ) and local structure of $15Li_2O{\cdot}10Fe_2O_3 \cdot x SnO_2{\cdot}(70–x)V_2O_5{\cdot}5P_2O_5$ glass (x = 0–20 mol%), abbreviated as xLFSVP glass, was investigated by ^{57}Fe- and ^{119}Sn-Mössbauer spectroscopies, differential thermal analysis (DTA) and dc-four probe method. A small increase in quadrupole splitting (Δ) for Fe^{III} was observed from 0.70 to $0.74_{\pm 0.02}$ mm s^{-1} with an increase of "x", whereas isomer shift (δ) values of $0.40_{\pm 0.01}$ mm s^{-1} were independent of "x". This result suggests that local distortion of $Fe^{III}O_4$ tetrahedra was slightly increased in SnO_2-containing vanadate glasses, which was reflected as an increase in glass transition temperature (T_g) from 266 to $285_{\pm 5}$ °C. A slope of 675 K / (mm s^{-1}) obtained in 'T_g vs. Δ plot' proved that Fe^{III} occupied the site of network former (NWF). An isothermal annealing of 10LFSVP glass at 500 °C for 100 min resulted in a marked decrease of Δ from 0.72 to $0.56_{\pm 0.02}$ mm s^{-1}, indicating that local distortion of FeO_4 tetrahedra was reduced by the structural relaxation of 3D-network. In contrast, identical δ and Δ values of $0.07_{\pm 0.01}$ and $0.53_{\pm 0.02}$ mms^{-1}, respectively, were observed in ^{119}Sn-Mössbauer spectra of 10LFSVP glass before and after the annealing. These results indicate that $Sn^{IV}O_6$ octahedra are loosely bound in the glass matrix as a network modifier (NWM). A marked increase in σ from 7.4×10^{-7} to 9.1×10^{-3} S cm^{-1} was observed in 20LFSVP glass after the

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isothermal annealing, indicating that structural relaxation of 3D-network evidently causes a marked increase in σ.

Keywords Lithium iron tin vanadate glass · ^{57}Fe-Mössbauer spectroscopy · ^{119}Sn-Mössbauer spectroscopy · Electrical conductivity · Structural relaxation

1 Introduction

Vanadate glass is generally known as a semiconductor with an electrical conductivity (σ) of $10^{-7}-10^{-5}$ S cm^{-1} caused by 3*d* electron (polaron) hopping from V^{VI} and V^{III} to V^{V} [1]. A drastic increase in σ was discovered after annealing of barium iron vanadate glass, $BaO\text{-}Fe_2O_3\text{-}V_2O_5$ [2], at temperatures higher than glass transition temperature (T_g). Manganese- and tungsten-substituted vanadate glasses also show a marked increase in σ after isothermal annealing at temperatures higher than T_g or crystallization temperature (T_c) [3, 4]. It is expected that vanadate glass would be an excellent candidate for the host material of solar battery, cathode active material for lithium-ion battery (LIB), *etc*. For example, $LiFeVPO_x$ glass shows satisfactorily charge-discharge behaviour when applied as a cathode active material for LIB [5]. Mössbauer spectra of LIB in which $LiFeVPO_x$ glass was used as a cathode active material showed a reduction and an oxidation of Fe^{III} as a result of interaction (during discharge) and deintercalation of Li^+ ions (during charge), respectively [5]. Introduction of tin oxide into vanadate glass seems to be very interesting, since it is an excellent carrier as has been applied in transparent film of indium tin oxide (ITO). In this study, a relationship between local structure and physical properties was investigated in SnO_2-containing lithium iron vanadate glasses by means of ^{57}Fe- and ^{119}Sn-Mössbauer spectroscopies, differential thermal analysis (DTA) and dc four-probe method.

2 Experimental

A new vanadate glass with a composition of $15Li_2O{\cdot}10Fe_2O_3 x{\cdot}SnO_2{\cdot}(70-x)V_2O_5{\cdot}5P_2O_5$, $x = 0$–20 in mol%, abbreviated as *x*LFSVP, was prepared by a conventional melt-quenching method. Weighed amounts of Li_2CO_3, Fe_2O_3, SnO, V_2O_5 and $NH_4H_2PO_4$ of reagent grade were thoroughly mixed in an agate mortar, and were heated at 1200 °C for 1 h in air in an electric muffle furnace.

Glass samples with dark brown colour could be prepared when "*x*" was equal to or less than 20. Homogeneous *x*LFSVP glass was not obtained when SnO_2 was used as a starting material. Enriched isotope of $^{57}Fe_2O_3$ (^{57}Fe = 95.54 %) was used for sample preparation. Isothermal annealing was carried out in air at 500 °C for 100 min. ^{57}Fe- and ^{119}Sn- Mössbauer measurements were carried out in a constant acceleration mode with a source of ^{57}Co(Rh) and $Ca^{119m}SnO_3$, respectively. DTA was conducted from RT to 600 °C at a heating rate of 10 °C min^{-1}. Electrical conductivity (σ) was measured at room temperature by dc-four probe method, in which the electrical current was changed from −10.0 to 10.0 mA.

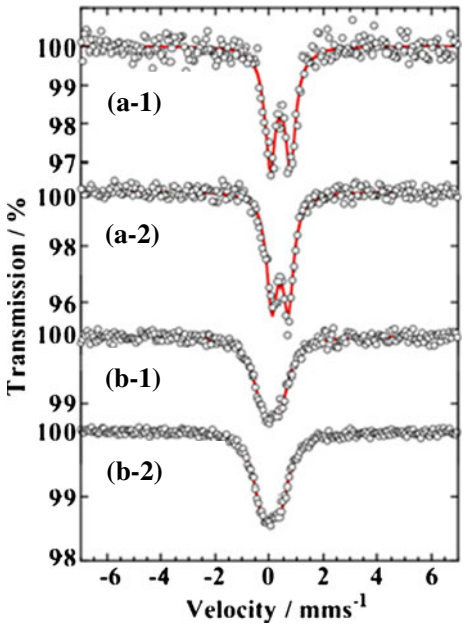

Fig. 1 **a** ^{57}Fe- and **b** ^{119}Sn-Mössbauer spectra of 10LFSVP glass (1) before and (2) after isothermal annealing at 500 °C for 100 min

3 Results and discussion

Mössbauer spectra of 10LFSVP glass measured before and after annealing at 500 °C for 100 min are shown in Fig. 1. Each ^{57}Fe-Mössbauer spectrum consists of a paramagnetic doublet due to distorted $Fe^{III}O_4$ tetrahedra with identical isomer shift (δ) values of 0.41 and $0.40_{\pm 0.01}$ mm s^{-1}. In contrast, a marked decrease in quadrupole splitting (Δ) from 0.72 to $0.56_{\pm 0.02}$ mm s^{-1} was observed after annealing, indicating that the local distortion of $Fe^{III}O_4$ tetrahedra was decreased. On the other hand, ^{119}Sn-Mössbauer spectra of 10LFSVP glass showed a broad doublet with δ of $0.07_{\pm 0.01}$ and Δ of $0.53_{\pm 0.02}$ mm s^{-1}, irrespective of the annealing. This result indicates that tin oxide (SnO) incorporated into 10LFSVP glass was oxidized to SnO_2, and that its local structure is not affected by the isothermal annealing at 500 °C, since Sn^{IV} atoms occupy interstitial sites as a network modifier (NWM). Similar changes in Mössbauer parameters were also observed for 20LFSVP glass before and after the annealing ; a constant δ of $0.41_{\pm 0.01}$ mm s^{-1} and decreasing Δ from 0.74 to $0.56_{\pm 0.01}$ mm s^{-1} were confirmed from ^{57}Fe-Mössbauer spectra, while stable δ and Δ values of $0.07_{\pm 0.01}$ and $0.52_{\pm 0.02}$ mm s^{-1} were confirmed from ^{119}Sn-Mössbauer spectra.

DTA curves of xLFSVP glass with "x"s of 0, 10 and 20 are shown in Fig. 2. Values of T_g, and T_c respectively increased from 266 to 272 and $285_{\pm 5}$ °C and from 341 to 340 and $344_{\pm 2}$ °C with an increasing amount of SnO_2. It is noted that both T_g, and T_c are lower than those of $20BaO{\cdot}70V_2O_5{\cdot}10Fe_2O_3$ glass ($T_g = 307$ °C, $T_c = 375$ °C [6]), which indicates that heat resistivity was lowered when Li_2O, $SnO_2$and P_2O_5 were incorporated into barium iron vanadate glass. A linear relationship discovered between T_g and Δ termed as T_g-Δ rule [7], is given by

$$T_g = a\Delta + b. \quad (1)$$

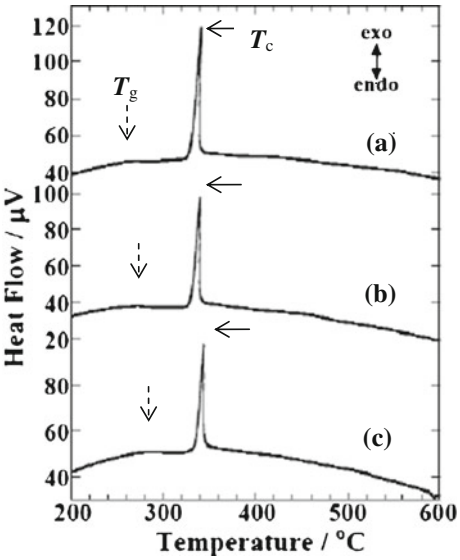

Fig. 2 DTA charts for *x*LFSVP glass with "*x*"s of **a** 0, **b** 10 and **c** 20, measured under a heating rate of 10°C min^{-1}

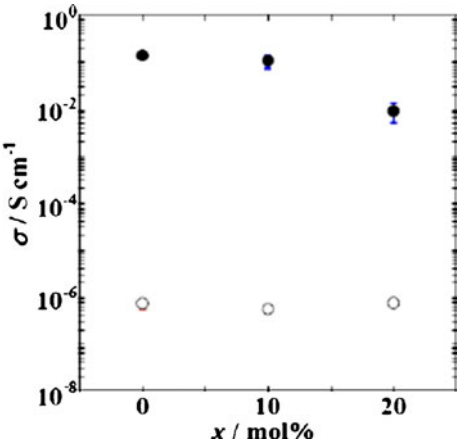

Fig. 3 Electrical conductivity of *x*LFSVP glass measured before (*open circle*) and after isothermal annealing at 500 °C for 100 min (*solid circle*)

A large slope "*a*" of 680 K/(mm s^{-1}) is generally yielded when Fe^{III} atoms occupy the sites of network former (NWF), whereas it becomes only 35 K/(mm s^{-1}) when they occupy the sites of NWM. In this study, Δ values of 0.70 mm s^{-1} ($x = 0$), 0.72 mm s^{-1} ($x = 10$) and $0.74_{\pm 0.02}$mm s^{-1} ($x = 20$) were obtained. T_g vs. Δ plot yielded a straight line with a slope of 675 K/(mm s^{-1}), evidently indicating that Fe^{III} atoms occupied the sites of NWF, as recently observed in tungsten-substituted $20BaO{\cdot}10Fe_2O_3 \cdot xWO_3{\cdot}(70\text{-}x)V_2O_5$ glasses [8]. Increase in T_g from 266 to 272 and 285 $_{\pm 5}$°C described above is ascribed to increased distortion of 3D-network, as deduced from the increase in Δ of Fe^{III} from 0.70 to 0.74 mm s^{-1}. It is concluded that Sn^{IV} atoms being present at NWM sites causes a slight increase in the distortion of FeO_4 tetrahedra constituting the 3D-network.

Conductivity (σ) of 7.3×10^{-7}, 5.5×10^{-7} and 7.4×10^{-7} S cm^{-1} were obtained for xLFSVP glasses with "x"s of 0, 10 and 20, respectively. They were increased to 1.4×10^{-1}, 1.1×10^{-1} and 9.1×10^{-3} S cm^{-1} after isothermal annealing at 500 °C for 100 min, as shown in Fig. 3. It is noted that σ of 1.4×10^{-1} and 1.1×10^{-1} S cm^{-1} obtained for LFSVP glasses ($x = 0$ and 10) are comparable to that of $20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$ glass [6]. In contrast, smaller σ values of 1.4×10^{-2} and 3.0×10^{-8} S cm^{-1} were obtained after isothermal annealing of manganese-substituted $20BaO{\cdot}10Fe_2O_3 \cdot x MnO_2{\cdot}(70\text{-}x)V_2O_5$ glasses ($x = 10$, 20) [3]. These results indicate that an increase in σ, caused by structural relaxation of the glass network, is intrinsic of vanadate glass [8]. The present study revealed that introduction of Li_2O, SnO_2 and P_2O_5 into vanadate glass is effective in achieving higher conductivity caused by structural relaxation of the glass network. It is speculated that ionic conductivity due to Li^+ is advantageous for the performance of higher conductivity in vanadate glass.

4 Summary

Mössbauer study of $15Li_2O{\cdot}10Fe_2O_3 \cdot x SnO_2{\cdot}(70\text{-}x)V_2O_5{\cdot}5P_2O_5$ glass ($x = 0$–20 mol%) revealed that the Fe^{III} and Sn^{IV} occupied sites of network former (NWF) and network modifier (NWM), respectively. A marked increase in σ, observed after isothermal annealing when "x" was 0 and 10, suggests that introduction of Li_2O, SnO_2 and P_2O_5 into vanadate glass is effective in achieving higher electrical conductivity caused by the structural relaxation of 3D-network.

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