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Electrical conductivity and local structure of barium manganese iron vanadate glass

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Abstract Local structure and electrical conductivity of semiconducting $20BaO{\cdot}10Fe_2O_3 \cdot x\,MnO_2 \cdot (70-x)V_2O_5$ glass ($x = 0-30$), abbreviated as xBFMV, were investigated by means of ^{57}Fe-Mössbauer spectroscopy, differential thermal analysis (DTA) and DC four-probe method. Mössbauer spectrum of these vanadate glasses consists of a doublet with an identical isomer shift (δ) of 0.38±0.01 mm s^{-1}, indicating that distorted FeO_4 tetrahedra constitute the structural units with distorted VO_4 tetrahedra and VO_5 pyramids. Quadrupole splitting (Δ) gradually increases from 0.70±0.02 to 0.87±0.02 mm s^{-1} with an increase in the MnO_2 content, indicating an increased local distortion of $Fe^{III}O_4$ tetrahedra. DTA study of these glasses showed a gradual increase of glass transition temperature (T_g) from 329±5 to 411±5°C, showing an improved thermal durability. 'T_g vs. Δ plot' yielded a straight line with a large slope of 707°C(K)/mm s^{-1}, proving that Fe^{III} played a role of network former (NWF). An isothermal annealing of 10BFMV glass at 500°C for 1000 min resulted in a marked increase in the electrical conductivity (σ) from (4.5±3.9) × 10^{-7} to (1.4±0.3) × 10^{-2} S cm^{-1} and a decrease in the activation energy for the electrical conduction (E_a) from 0.33 ± 0.07 to 0.11±0.01 eV, while Δ of Fe^{III} decreased from 0.76±0.02 to 0.49±0.02 mm s^{-1}. These results suggest that decrease

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in the distortion of $Fe^{III}O_4$ tetrahedra involved with the structural relaxation causes an increase in the probability of electron hopping from V^{IV} or V^{III} to V^{V}.

Keywords Barium manganese iron vanadate glass · ^{57}Fe-Mössbauer spectroscopy · Electrical conductivity · Structural relaxation

1 Introduction

Vanadate glass is known to be a semiconductor with an electrical conductivity (σ) of 10^{-7}–10^{-5} S cm^{-1}. The electrical conduction is known to be caused by polaron hopping from V^{IV} or V^{III} to V^{V} [1]. A drastic increase in σ was discovered in annealed barium iron vanadate glass [2] having a registered trademark of '*NTA glass*™' in Japan. Nishida reported a large charge-discharge capacity of 150 mAh g^{-1} in lithium-ion battery (LIB) in which cathode active material of annealed vanadate glass, Li_2O-Fe_2O_3-V_2O_5-P_2O_5, was used successfully [3]. This result indicates that vanadate glass could be a good candidate for the cathode active material of LIB. In the present study, substitution of manganese for vanadium was investigated in barium iron vanadate glass, BaO-Fe_2O_3-V_2O_5, in order to investigate the relationship between the local structure and the conductivity.

2 Experimental

Vanadate glasses with a composition of $20BaO{\cdot}10Fe_2O_3 \cdot x MnO_2{\cdot}(70\text{-}x)V_2O_5$, abbreviated as *x*BFMV, were prepared by a conventional melt-quenching method. Weighed amounts of $BaCO_3$, Fe_2O_3, MnO_2 and V_2O_5 of reagent grade were well mixed in a mortar and melted at 1200°C for 1 h in an electric muffle furnace. Homogeneous dark brown glass samples could be prepared when '*x*' was equal to or less than 30. Enriched isotope of $^{57}Fe_2O_3$ (^{57}Fe = 95.54 %) was used for some sample preparation. Isothermal annealing was carried out at 500°C for 1000 min. Mössbauer measurement was performed by a constant acceleration method with a source of ^{57}Co(Rh) and a reference of α-Fe foil for isomer shift (δ). DTA was conducted from RT to 500°C under a heating rate of 10°C min^{-1} by using 10 mg of finely pulverized glass sample. α-Al_2O_3 was used as a reference of the temperature. Values of σ were measured at temperatures ranging from 30 to 125°C by dc-four probe method under the electric current from −1.0 to 1.0 mA.

3 Results and discussion

Mössbauer spectra of 10BFMV glass measured before and after isothermal annealing at 500°C for 1000 min, are shown in Fig. 1. When '*x*' was increased from 0 to10, 20 and 30, consistent δ value of 0.38±0.01 mm s^{-1} were observed, while quadrupole splitting (Δ) increased from 0.70 to 0.76, 0.79 and 0.87±0.02 mm s^{-1}. These results indicate that Fe^{III} atoms form distorted $Fe^{III}O_4$ tetrahedra, and that they became more distorted when MnO_2 was substituted for V_2O_5. In annealed samples, a marked decrease in Δ was observed like 0.52 ($x = 0$), 0.49 ($x = 10$) and 0.43±0.02 mm s^{-1} ($x = 20$), showing a largely decreased local distortion of FeO_4

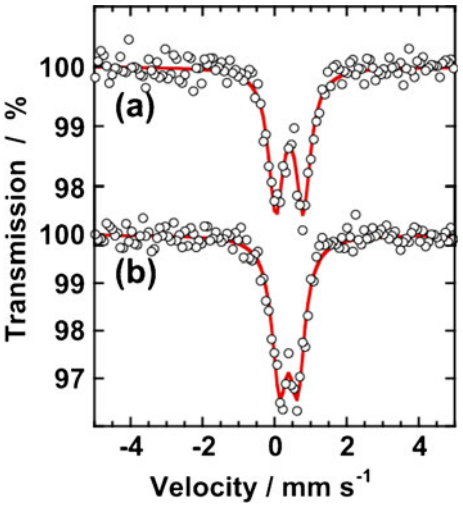

Fig. 1 Mössbauer spectra of $20BaO{\cdot}10Fe_2O_3{\cdot}10\,MnO_2{\cdot}60\,V_2O_5$ glass of (**a**) before and (**b**) after isothermal annealing conducted at 500°C for 1000 min

tetrahedra involved in the structural relaxation. In case of annealed sample with x of 30, Δ of 0.54±0.02 mm s^{-1} was observed, which is slightly larger than other annealed samples. This can be explained by the difference in the ionic radius of Mn^{IV} (39 pm) that is much smaller than that of V^{IV} (53 pm) [4]. It is considered that oxygen atoms constituting the network will be intensively attracted to Mn^{IV} in both as-quenched glass and annealed samples. Large Δ of 0.87±0.02 mm s^{-1} obtained for as-quenched glass sample supports this idea. We can describe that chemical property of "vanadate glass" is predominantly observed when MnO_2 content is equal to or less than 20 mol%.

DTA curves of xBFMV glass are depicted in Fig. 2. A gradual increase in glass transition temperature (T_g) was observed from 329 to 347, 372 and 411±5°C, while that in crystallization temperature (T_c) from 378 to 400, 429 and 465±5°C. A linear relationship found between T_g and Δ of Fe^{III} was termed 'T_g-Δ rule' [5], *i.e.*:

$$T_g = a\Delta + b \tag{1}$$

where a and b are slope and intercept of the straight line, respectively. According to the 'T_g-Δ rule' [5], large 'a' value of 680°C(K)/mm s^{-1} is generally obtained when Fe^{III} is located at tetrahedral site as network former (NWF), whereas 'a' becomes only 35°C(K)/mm s^{-1} when Fe^{III} is located at octahedral site as network modifier (NWM). In the present study, a large 'a' of 707°C(K)/mm s^{-1} was obtained, indicating that Fe^{III} atoms occupy tetrahedral site as NWF.

A slight decrease in σ value from (2.5±1.2) × 10^{-6} to (4.7±3.8) × 10^{-7}, (4.2±0.3) × 10^{-7} and (2.3±1.0) × 10^{-7} S cm^{-1} was observed when the 'x' value of xBFMV glass increased from 0 to 10, 20, and 30. These results will be due to decrease in number of carriers (V^{IV}or V^{III}) when MnO_2 was substituted for V_2O_5. In the case of 10BFMV glass, a marked increase in σ was observed from (4.7±3.8) × 10^{-7} to (1.4±0.3) × 10^{-2} S cm^{-1} after the annealing. According to the small polaron hopping theory [1], temperature dependence of σ is expressed by:

$$\sigma T = \sigma_0 \exp(-E_a/kT), \tag{2}$$

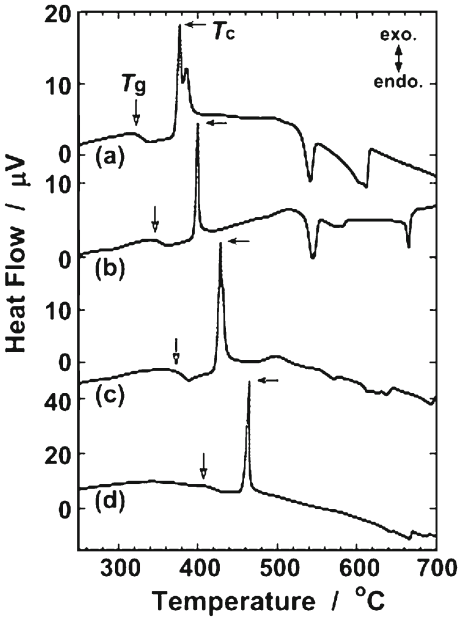

Fig. 2 DTA curves of $20BaO{\cdot}10Fe_2O_3 \cdot xMnO_2 \cdot (70-x)V_2O_5$ glasses with 'x' of (**a**) 0, (**b**) 10, (**c**) 20 and (**d**) 30, recorded at a heating rate of 10°C/min

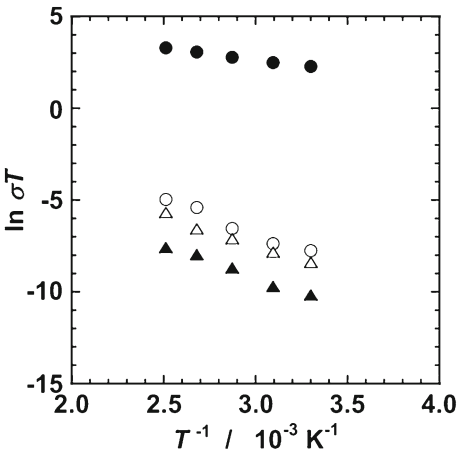

Fig. 3 $\ln \sigma T$ *vs.* $1/T$ plot of $20BaO{\cdot}10Fe_2O_3 \cdot xMnO_2 \cdot (70-x)V_2O_5$ glasses with x of 10 (circle) and 30 (triangle) measured before annealing (open symbols) and after isothermal annealing conducted at 500°C for 1000 min(closed symbols)

where E_a and k are activation energy for electric conduction and Boltzmann constant, respectively. As shown in Fig. 3, a drastic decrease in the E_a from 0.33±0.07 to 0.11±0.01 eV was observed after the annealing of 10BFMV glass. On the other hand, a constant E_a value of 0.29±0.06 eV was obtained in the case of 30BFMV glass. It is interesting that the decrease in the local distortion of $Fe^{III}O_4$ tetrahedra and a marked increase in the conductivity are clearly observed when 'x' is 10 or less, *i.e.*, the distortion of network involved with an increase in σ is intrinsic the vanadate glass.

4 Summary

Structure of *x*BFMV glass with *x* of 0, 10, 20 and 30 was investigated by means of ^{57}Fe-Mössbauer and DTA. Fe^{III} atoms are incorporated in the glass matrix to form distorted FeO_4 tetrahedra, and play a role of NWF at the substitutional sites of VO_4 tetrahedra by sharing corner oxygen atoms with each other. Electrical conductivity of 10BFMV glass increased from 4.7×10^{-7} to 1.4×10^{-2} S cm^{-1} after isothermal annealing conducted at 500°C for 1000 min. Increase in the conductivity is ascribed to a decrease in the distortion of VO_4 and FeO_4 units constituting the glass network, accompanied by a decrease in the activation energy for the electron hopping (E_a) from 0.33 to 0.11 eV, and an increased probability of polaron (3d-electron) hopping from V^{IV} or V^{III} to V^{IV}.

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