Hyperfine Interact
DOI 10.1007/s10751-011-0478-2

Effect of nanocrystallization on the electrical conduction of silver lithium phosphate glasses containing iron and vanadium

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Abstract $xLi_2O{\cdot}(20\text{-}x)Ag_2O{\cdot}20Fe_2O_3{\cdot}60P_2O_5$ glasses (x = 0, 5, 10, 15 and 20 mol%) and $5Ag_2O{\cdot}15Li_2O{\cdot}5V_2O_5{\cdot}15Fe_2O_3{\cdot}60P_2O_5$ glass were prepared by melt-quenching of the reagent mixture at 1000 °C. Glass transition temperature (T_g) and crystallization temperature (T_c) of these samples were determined by differential thermal analysis (DTA). It proved that T_g increased with Li_2O content. XRD of as-quenched glasses confirmed their amorphous nature. XRD of samples heat treated for one hour at temperature near their T_c, indicated nanocrystals precipitated in the glassy matrix with an average particle size of 35 nm. Mössbauer results revealed that the relative fraction of Fe^{2+} was decreased with an increasing Li_2O content. The isomer shift values of Fe^{3+} lie in a range of 0.38–0.45 mm s^{-1}, while those for Fe^{2+} were 1.10–1.31 mm s^{-1}. Heat-treated sample of $5Ag_2O{\cdot}15Li_2O{\cdot}5V_2O_5{\cdot}15Fe_2O_3{\cdot}60P_2O_5$ glass exhibit an enhancement of the electrical conductivity by three orders of magnitude due to the 3d-electron (polaron) hopping from V^{4+} to V^{5+} in the "vanadate glass" units.

Keywords Vanadate glass · ^{57}Fe-Mössbauer spectroscopy · Electrical conductivity · Nano-crystallization

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Published online: 29 November 2011

1 Introduction

The electrical conductivity of glass due to electronic conduction or mixed electronic–ionic conduction has been investigated extensively from the view points of their potential use as either electronic devices or electrolytes for rechargeable batteries [1]. Lithium or silver vanadate glasses containing other network-forming oxides (NWF) like P_2O_5 exhibit high mixed electronic–ionic conduction due to the transport of Li^+ or Ag^+ ions and the electronic conduction due to electron hopping between V^{4+} and V^{5+} [2]. Mixed electronic–ionic conduction can be utilized as a cathode material for secondary batteries [3, 4]. Improvement of the electrical conductivity of mixed electronic–ionic conducting amorphous materials after nanocrystallization has been observed in several glasses [3]. The main purpose of this work is to study the mixed ionic-electronic conduction of Ag_2O-LiO_2 phosphate glasses containing iron and vanadium, and also to study the effect of nanocrystallization on the enhancement of the conductivity.

2 Experimental

Reagent grade chemicals, Li_2CO_3, Ag_2O, V_2O_5, Fe_2O_3 and P_2O_5, were used for the sample preparation. After mixing a batch (10 g) in air, each mixture was melted at 1000°C for 30 min. By pressing the melt with copper blocks, bulk glass of 2 × 2 cm^2 size and 1 mm thickness was obtained with the composition of $x Li_2O \cdot (20-x) Ag_2O \cdot 20Fe_2O_3 \cdot 60P_2O_5$ and $5Ag_2O \cdot 15Li_2O \cdot 5V_2O_5 \cdot 15Fe_2O_3 \cdot 60P_2O_5$ (denoted by ALVFP). Heat treatment of glass was carried out by heating in air for one hour near their crystallization temperature (T_c), which was determined by differential thermal analysis (DTA) together with glass transition temperature (T_g), and melting temperature (T_m) with Shimadzu DTA50. The structure of nanocrystalline particles was determined by X-ray diffractometry with RINT-TTR3. Mössbauer spectra were measured in a standard transmission geometry, using a source of ^{57}Co diffused in rhodium matrix. The calibration was performed using a natural iron foil. The dc conductivity (σ) was measured at temperatures between 393 and 633 K. Electrodes were attached with silver paste on both faces of the polished samples. A multimeter type Keithely 760 was used to collect the *I-V* data at room temperature.

3 Results and discussion

The DTA curve of LAVFP and the glass composition dependence of T_g, T_c and T_m are shown in Fig. 1. From Fig. 1 it is clear that T_g, T_c and T_m increase with an increasing lithium content. Generally, T_g shows a distinct increase when the coordination number of the network former increases, while a construction of nonbridging oxygen (NBO) causes a decrease of T_g. The continuous increase in the T_g suggests a continuing decrease in the coordination number of Fe^{3+} and Fe^{2+} ions and destruction of NBO atoms [3]. This indicates that the glass structure becomes more closed as a result of Li^+ substitution for Ag^+ with a larger ionic radius. T_g/T_m values determined for all the compositions in the present system fall in a range of 0.78

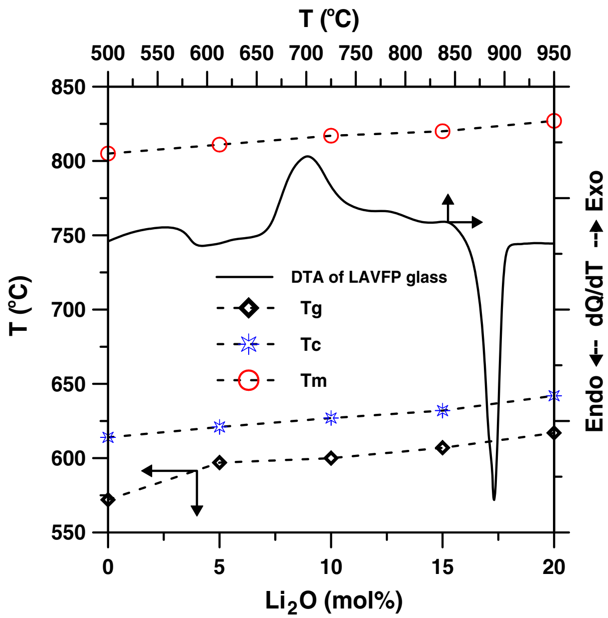

Fig. 1 DTA for LAFVP glass and composition dependence of glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m)

$\sim$ 0.80, indicating high thermal stability because the T_g/T_m value of ideally stable glass is reported to be 0.67 [3].

XRD for as-quenched glass and heat-treated samples were measured. In case of as-quenched samples, only one halo peak is observed with no indication of crystalline particles. In case of the samples heat treated at temperature near their T_c for one hour shows a lot of peaks corresponding to nanocrystalline particles, superimposed on the halo peak. The XRD study indicates that annealing near their T_c triggers the precipitation of nanocrystalline particles in the glass matrix [3]. This reminds us that we can design and control the amount of nanocrystalline particles formed in the glass matrix by changing temperature and duration of isothermal annealing, and that we can enhance its physical properties like electrical conductivity, magnetic moment, coercive force, etc. Application of the Scherrer formula, to linewidth of the diffraction peaks yielded a mean diameter of *ca.* 35 nm for the nanocrystalline particles.

Mössbauer spectra of ALVFP glass before and after the heat treatment are shown in Fig. 2. Before heat treatment, they are composed of two doublets representing tetrahedral Fe^{2+} and Fe^{3+} (Fig. 2A). The absorption area for Fe^{2+} seems to decrease as the Ag_2O content is decreased due to the reducing effect of Ag_2O; see Fig. 2A and B. However, the values of isomer shift (δ, 1.10 $\sim$ 1.31 mm s^{-1} for Fe^{2+} and 0.38 $\sim$ 0.45 mm s^{-1} for Fe^{3+}) and quadrupole splitting (Δ, 2.21 $\sim$ 2.56 mm s^{-1} for Fe^{2+} and 0.49 $\sim$ 0.72 mm s^{-1} for Fe^{3+}) were nearly identical in all samples. The spectra of the heat-treated samples showed two doublets (Fig. 2B) with different parameters for the Fe^{2+} doublet. One doublet in heated samples is ascribed to Fe^{2+} ions with δ ranging from 0.94 to 1.36 mm s^{-1}. Absorption area and Δ for Fe^{2+} decreased as the Li_2O content was increased. The decrease of Δ reflects that the local symmetry around the iron nucleus was increased [5].

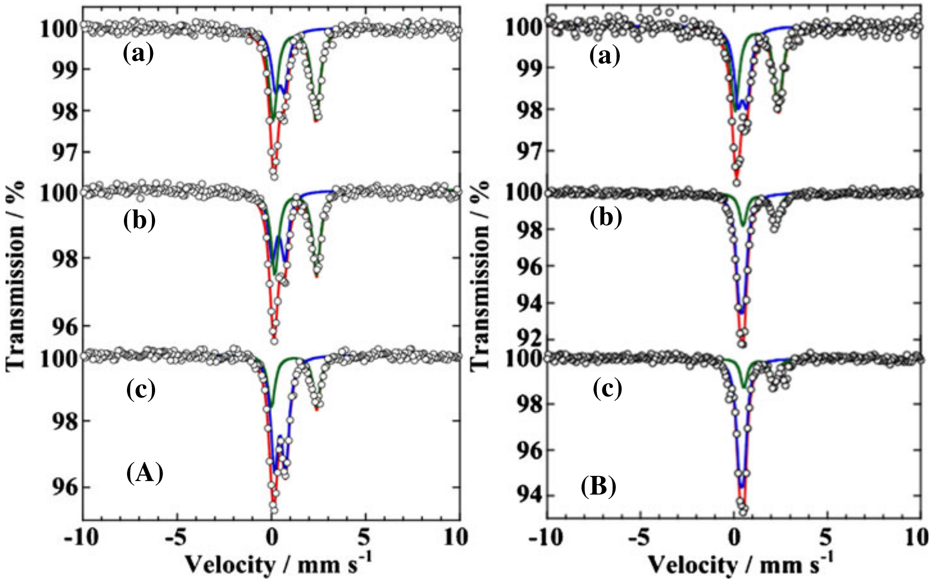

Fig. 2 Mössbauer spectra of LAVFP glasses with 'x' of (**a**) 0, (**b**) 5 and (**c**) 10 mol%; (**A**) before and (**B**) after annealing

Fig. 3 Temperature dependence of dc conductivity (σ) as a function of Li_2O content for glasses, ALVFP glass and their heat-treated glass

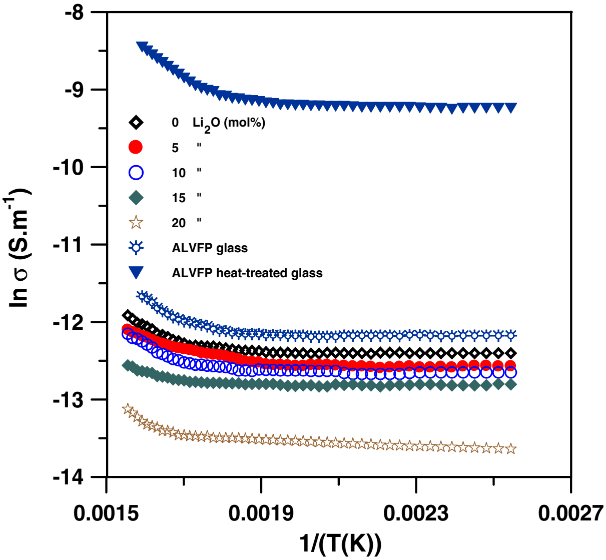

Figure 3 shows that dc conductivity, σ, for ALFVP glass and heat-treated samples is decreased with an increasing Li_2O content that was changed from 0 to 20 mol%. Arrhenius type change of conductivity is given by:

$$\sigma = \sigma_o \exp\left(-W/kT\right), \quad (1)$$

where σ_o is a pre-exponential factor and W the activation energy. These Arrhenius plots are curved in a high temperature region as shown in Fig. 3. The value of W was estimated from the slope of the curve in a higher temperature region; 0.10–0.20 eV for heat-treated samples and 0.25 eV for heat-treated ALFVP, while 0.12–0.23 eV for as-quenched glasses and 0.33 eV for ALFVP glass. This means that an increase of Fe^{2+} causes a decrease of, W, and an increase of σ. It is clear from Fig. 3 that ALFVP samples obtained after annealing at T_c exhibit an enhancement of σ by three orders of magnitude. Similar results were obtained in other heat-treated samples. This is ascribed to the structural relaxation of "vanadate glass" units, involved with an increased probability of polaron hopping, as observed earlier in barium vanadate glasses [4, 5]. More discussion will be made elsewhere on the mechanism of Li^+- ion and Ag^+-ion conduction combined with the polaron hopping of "vanadate glass" units. The enhancement of electrical conductivity of heat-treated glasses can be attributed to (i) an increase in the concentration of Fe^{2+}–Fe^{3+} and V^{4+}–V^{5+} pairs and (ii) formation of, well-conducting regions along the glass-crystallites interfaces [2, 3].

4 Conclusion

The structure and conductivity of $xLi_2O\cdot(20\text{-}x)Ag_2O\cdot 20Fe_2O_3\cdot 60P_2O_5$ glasses (x = 0, 5, 10, 15 and 20 mol%) and $5Ag_2O\cdot 15Li_2O\cdot 5V_2O_5\cdot 15Fe_2O_3\cdot 60P_2O_5$ glass were investigated before and after isothermal annealing at a temperature near their T_c. Nanocrystallization involved with an increase in the electrical conductivity was observed by DTA, XRD, Mössbauer and dc conductivity measurements. It is possible to optimize the condition of heat treatment in order to realize the desired conductivity. XRD study of $10Li_2O\cdot 10Ag_2O\cdot 20Fe_2O_3\cdot 60P_2O_5$ glass showed that heat treatment resulted in the precipitation of nanocrystals with an average particle size of 35 nm in the glassy matrix. Mössbauer results revealed that the fraction of Fe^{2+} decreased with an increasing Li_2O content. The isomer shift of Fe^{3+} lay in a range of 0.38–0.45 mm s^{-1}, while Fe^{2+} had an isomer shift of 1.10–1.31 mm s^{-1}. Heat-treated samples of $5Ag_2O\cdot 15Li_2O\cdot 5V_2O_5\cdot 15Fe_2O_3\cdot 60P_2O_5$ glass exhibited a marked enhancement of conductivity by three orders of magnitude due to the structural relaxation of "vanadate glass" units.

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