NEW CONDUCTIVE VANADATE GLASS WITH HIGH CHEMICAL DURABILITY

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Electrical conductivity (σ) of semiconducting $20BaO \cdot 10Fe_2O_3 \cdot 70V_2O_5$ glass can be changed from the order of 10^{-7} to 10^{0} S cm^{-1} by changing temperature and duration of isothermal annealing [1-3]. Mössbauer atoms incorporated into glass matrix play a role of probe for the local structural study. Mössbauer spectrum of vanadate glass shows a marked decrease in quadrupole splitting (Δ) after isothermal annealing at temperatures higher than glass transition temperature (T_g) or crystallization temperature (T_c) [1-3]. Quadrupole splitting is expressed by:

$$\Delta = eq \cdot eQ/2 \times (1 + \eta^2/3)^{1/2}, \qquad (1)$$

in which eq and Q are electric field gradient and nuclear quadrupole moment. The former is composed of eq_{val}, caused by valence electrons, and eq_{lat} caused by steric configuration of neighboring atoms. In case of high-spin Fe^{III}, eq_{val} becomes zero, since five 3d-orbitals are equivalently occupied by five valence electrons. Since glass has isotropic structure, it is considered that asymmetry parameter (η) is zero.

Decrease of Δ is ascribed to a decreased distortion of $Fe^{III}O_4$ tetrahedra or *structural relaxation* of 3D-network, since eq is equal to eq_{lat} and hence Δ is directly proportional to eq_{lat}. *Structural relaxation* of distorted $Fe^{III}O_4$ tetrahedra detected by Mössbauer measurement is also the case for distorted $V^{IV}O_4$ or $V^{V}O_4$ tetrahedra, since they share corner oxygen atoms with $Fe^{III}O_4$ in the 3D-network.

In this study, local structure of new conductive vanadate glasses, $20BaO \cdot 10Fe_2O_3 \cdot xWO_3 \cdot (70\text{-}x)V_2O_5$, was investigated by means of Mössbauer spectroscopy. Mössbauer spectra of new vanadate glass with "*x*" of 20, annealed at 500 °C for 240 min, resulted in a marked decrease of Δ from 0.82 to 0.76 mm·s^{-1}. This reflects a decreased distortion of $Fe^{III}O_4$, $V^{IV}O_4$ and $V^{V}O_4$ tetrahedra, as observed in $20BaO \cdot 10Fe_2O_3 \cdot 70V_2O_5$ [1-3] and $20BaO \cdot 10Fe_2O_3 \cdot xMnO_2 \cdot (70\text{-}x)V_2O_5$ glasses [4]. In case of vanadate glass with "*x*" of 35, an identical Δ value of 0.80 mm·s^{-1} was observed in the Mössbauer spectra, irrespective of the isothermal annealing.

Isothermal annealing of vanadate glass with "*x*" of 20 at 500 °C for 240 min resulted in a marked increase of σ from 3.9×10^{-6} to 2.1×10^{-3} S·cm^{-1}, while comparable σ values of 0.88×10^{-5} and 1.6×10^{-5} S·cm^{-1} were obtained when "*x*" was 35. These results indicate that the marked increase of σ observed when "*x*" was 20 is due to a decreased distortion of the 3D-network.

Plot of T_g against the Δ of Fe^{III} gives a straight line, depending on the site occupation of Fe^{III} atoms; slope of the straight line becomes 680 K·(mm·s^{-1})$^{-1}$ when they occupy tetrahedral network forming (NWF) sites [5], while it becomes 260 in octahedral NWF sites [6]. This experimental rule, "T_g-Δ rule" [5], is valid for several inorganic glasses, and hence we can know "site occupation" of Fe^{III} in several glasses. In the present study, slope of 680 was obtained for glasses with "*x*" of 0-50, indicating that Fe^{III} evidently occupied substitutional sites of $V^{IV}O_4$ or $V^{V}O_4$ tetrahedra, not of $W^{VI}O_6$ octahedra.

Leaching test with boiling water for 120 min indicated that dissolution of vanadium ion was depressed from 30 to 11 and 10 mg·l^{-1} when "*x*" was changed from 0 to 20 and 35, respectively. These results evidently prove that introduction of $W^{VI}O_4$ and $W^{VI}O_6$ units into 3D-network of vanadate glass is effective for the improvement of water-resistivity. Leaching test with 20%HCl solution at 25 °C for 72 h showed higher chemical durability of vanadate glass when "*x*" was equal to or more than 20. Hence, it is concluded that introduction of 20 mol% WO_3 is effective for the preparation of chemical durable conductive vanadate glass.

References

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