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Adiabatic small polaron hopping in K_2O–WO_3–Nb_2O_5–P_2O_5 glasses

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ABSTRACT

The electrical conductivity of $45xKO_{1/2}$–$45(1-x)WO_3$–$25NbO_{5/2}$–$30PO_{5/2}$ ($x = 0.5$, 0.6, and 0.7) glasses was investigated. Heat treatment of the sample under a CO atmosphere at temperatures below the glass-transition temperature introduced electrons into the glass as carriers, following which W^{6+} was reduced to W^{5+}. The electrical conductivity increased by four orders of magnitude for the $x = 0.5$ glass and by two orders of magnitude for the $x = 0.6$ glass, whereas it only doubled for the $x = 0.7$ glass. The results suggested that the increase in the electrical conductivity of the glasses for which $x = 0.5$ and 0.6 was caused by hopping of small polarons, which were generated by nearby W^{5+}, in an adiabatic process. However, the adiabatic small polaron theory could not be applied to the $x = 0.7$ glass, which we attributed to the change in the K^+-ion conductivity in the case of the $x = 0.7$ glass, where the K^+ ions contributed substantially to the electrical conductivity even before the heat treatment under a CO atmosphere.

1. Introduction

Oxide glasses that contain transition-metal ions often exhibit electronic conductivity when the transition-metal ions are present in more than one valence state [1]. The electronic conduction is fundamentally caused by electron transfer between the transition-metal ions in different valence states [2,3]. In the case of phosphate glasses, a portion of the transition-metal ions are often reduced, which results in transition-metal ions with different valence states. However, the relative number of reduced ions is typically small unless the glasses are prepared under controlled conditions, such as the introduction of reducing agents into the melt or the use of a strongly reducing atmosphere [4–6].

In 2006, Tawarayama et al. reported that when $30NaO_{1/2}$–$10BaO$–$10WO_3$–$20NbO_{5/2}$–$30PO_{5/2}$ glass was heat-treated under a hydrogen atmosphere or under water vapor pressure, W^{6+} ions were reduced to W^{5+} [7–9]. The authors also confirmed that all of the W^{5+} ions could be completely oxidized under an oxidizing atmosphere. The reduction and oxidation reactions occurred from the surface to the inside of the glass, even at temperatures below the glass-transition temperature. The occurrence of similar phenomena below the glass-transition temperature has been observed in $45xRO_{1/2}$–$45(1-x)WO_3$–$25NbO_{5/2}$–$30PO_{5/2}$ (R = Na or K, $x = 0.5$–1.0) glasses [10]. In these glasses, the electric conductivity was reported to be greatly enhanced by the generation of W^{5+} ions, and the concentration of OH groups was reported to have increased after heat treatment under a hydrogen atmosphere [10,11]. The OH groups are considered as a source of protons. Accordingly, the authors suggested that in addition to alkali ions existing in the glasses, electrons and protons are generated as mobile carriers in the glasses. Furthermore, the increase in the conductivity was greater in glass compositions with lower alkali content. In these compositional regions, glasses that contained K^+ ions showed increases in electric conductivity of almost four orders of magnitude, whereas the conductivity of glasses that contained Na^+ ions increased only by two orders of magnitude. These results indicate that the electrical conductivity was affected by the amount of electrons, protons, and alkali ions—in addition to the type of alkali ions. As a result, the details of the electrical conduction mechanism of these glasses have not yet been elucidated. To investigate the increased electrical conductivity more simply, the types of charge carriers should be decreased from three to two or one.

When the glasses were annealed under hydrogen, protons were generated. If a CO atmosphere is used instead of a hydrogen atmosphere, the following reduction without the introduction of a proton in the glass is expected:

$$O^{2-} + CO \rightarrow CO_2 + 2e^-. \quad (1)$$

Electrons generated at the surface will reduce the valence state of transition-metal ions and function as charge carriers. In this study, we investigate the electrical conductivity of $45xKO_{1/2}$–$45(1-x)WO_3$–$25NbO_{5/2}$–$30PO_{5/2}$ ($x = 0.5$, 0.6, and 0.7) glasses heat-treated under a CO atmosphere to exclude the effect of protons. The electrical conductivity is analyzed on the basis of small polaron theory.

2. Experimental

Glasses having composition of $45xKO_{1/2}$–$45(1-x)WO_3$–$30PO_{5/2}$–$25NbO_{5/2}$ ($x = 0.5$, 0.6, and 0.7) were prepared by a conventional melt-quenching method. K_2CO_3, $NH_4H_2PO_4$, WO_3, and Nb_2O_5 were

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used as raw materials. The mixed raw materials were preheated at 723 K for 2 h to remove volatile products. The mixtures were melted in a platinum crucible at 1573–1723 K for 1 h in air. The melts were stirred every 15 min to improve their homogeneity and were subsequently poured into a preheated graphite mold. The glasses were cut and polished to form plates with parallel surfaces with dimensions of $10 \times 10 \times 2$ mm^3. The as-melted glasses exhibited a blue color owing to the presence of reduced transition-metal ions. The amount of reduced ions and OH groups in these glasses depends on the conditions used in the glass-making process. Therefore, the as-melted glasses were heat-treated in air for 100 h at 773 K to fully oxidize the transition-metal ions. This state is referred to as the initial state. To reduce the valence state of the transition-metal ions, the glasses were heat-treated under a CO atmosphere (99.9% of purity) for 96 h. The color of the glasses changed to dark blue after the heat treatment.

Ultraviolet–visible spectroscopy (UV–VIS) transmissions of the glasses were measured with a Shimadzu UV3100PC UV–VIS–NIR scanning spectrophotometer at room temperature to detect the reduction of the transition-metal ions. Fourier-transform infrared (FT-IR) absorption spectra were collected using a Shimadzu FT-IR/8200PC at room temperature to detect the OH groups in the glasses. Using the molar absorption coefficient of the OH vibration reported by Abe and Clark [12], the OH concentrations in the glasses were estimated from the peak intensities in their FT-IR spectra.

The temperature dependence of the electrical conductivity of the glasses in their initial state and after heat treatment under a CO atmosphere was measured by a standard AC impedance method using a Hewlett Packard HP 4192 impedance analyzer. Gold electrodes were deposited onto opposite sides of the samples. The frequency range ranged from 100 Hz to 10 MHz, and the temperature range of the measurement was 573–773 K. Atmospheres used for measurements were air for the initial-state glasses and N_2 for the heat-treated samples.

3. Results

Fig. 1 shows the UV–VIS absorption spectra of the $x = 0.5$ and 0.7 initial-state glasses and those of the samples heat-treated under a CO atmosphere. No absorption at wavelengths longer than 400 nm was observed in the case of the initial-state glasses, which indicates a fully oxidized state of the transition-metal ions. After heat treatment under a CO atmosphere, broad absorption bands with peaks at approximately 700 nm were observed. The absorption peak for the $x = 0.7$ glass was sharper and was shifted to shorter wavelengths compared to that of the $x = 0.5$ glass. The Nb^{5+} ions may have been reduced. However, evidence for the reduction of Nb^{5+} or any other reduced state of the tungsten ion was not observed by electron paramagnetic resonance (EPR). Only a broad singlet signal at g value 1.73 which is assignable to the W^{5+} [7]. Therefore, the optical absorption bands were only attributed to W^{5+} [13,14].

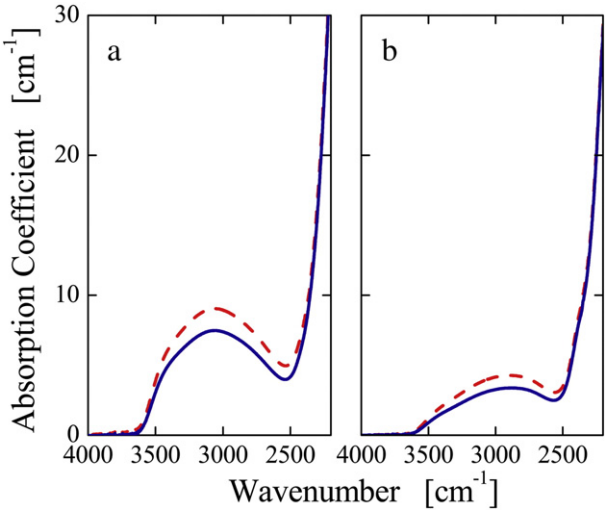

Fig. 2. FT-IR spectra of $45x KO_{1/2}$–$45(1-x)WO_3$–$25NbO_{5/2}$–$30PO_{5/2}$ glasses ((a) $x = 0.5$ and (b) $x = 0.7$) in their initial state (dashed line) and after the samples were heat-treated under a CO atmosphere (solid line).

The FT-IR spectra contained broad asymmetric bands at 2600–3300 cm^{-1} owing to the OH stretching vibration (Fig. 2). The absorption intensities decreased slightly after heat treatment under a CO atmosphere. Using the estimated molar absorption coefficient of the OH groups, we estimated the concentrations in the initial state for $x = 0.5$ and 0.7 to be 2.62×10^{18} cm^{-3} and 3.04×10^{18} cm^{-3}, respectively. Furthermore, the concentrations of the OH groups after the heat treatment for $x = 0.5$ and 0.7 were 2.5×10^{18} cm^{-3} and 2.73×10^{18} cm^{-3}, respectively. Accordingly, the amount of possible mobile protons was small.

Fig. 3 shows the composition dependence of the electrical conductivities at 773 K of the initial state and after the heat treatment under a CO atmosphere. The electrical conductivities of the initial state decreased as the potassium-ion content was decreased, whereas the conductivities showed a drastic increase after the heat treatment.

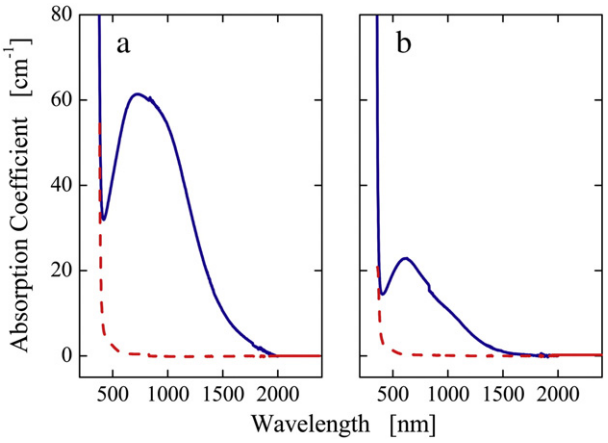

Fig. 1. Optical absorption coefficient as a function of x in $45x KO_{1/2}$–$45(1-x)WO_3$–$25NbO_{5/2}$–$30PO_{5/2}$ glasses ((a) $x = 0.5$ and (b) $x = 0.7$) in their initial state (dashed line) and after the samples were heat-treated under a CO atmosphere (solid line).

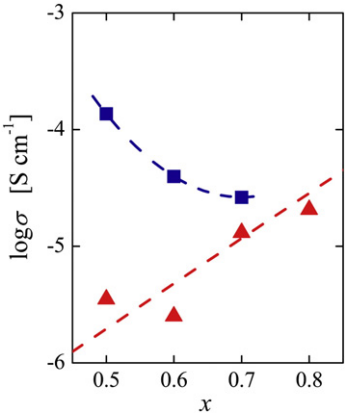

Fig. 3. Composition dependence of the electrical conductivities at 500 °C of $45x KO_{1/2}$–$45(1-x)WO_3$–$25NbO_{5/2}$–$30PO_{5/2}$ glasses in their initial states (triangles) and after they were heat-treated under a CO atmosphere (squares).