Abstract of Dissertation

論文の内容の要旨

Mixed Conduction in Alkali Tungsten Phosphate Glass System

(アルカリタングステンリン酸塩ガラスの混合伝導)

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Phosphate glasses containing tungsten oxide are able to react with the hydrogen atmosphere even below the glass transition temperature and absorb the hydrogen into the glass. This absorption is accompanied by the generation of OH groups and the reduction of the transition metal. The following fast diffusion coefficient of these chemical species made us wonder if the mixed conduction was realized. Therefore, in order to gain insight into the carriers' contribution in the alkali niobium tungsten phosphate glass systems, the electrical conductivity analysis using the impedance measurement was applied changing the alkali ion and its content in the composition of the glass. This dissertation in composed of five chapters.

In **chapter 1**, a broad overview of the background and the theoretical framework in the tungsten phosphate glasses is provided. The basic theories behind the electrical conduction in the glasses depending on the charges carriers (ionic, electronic, protonic and mixed conduction) are also discussed. Finally, the objectives of this research are presented.

In **chapter 2**, the electrical conduction mechanism of the glass samples heat treated under oxidizing atmosphere is analyzed. The systems of alkali tungsten phosphate glasses are formulated with the following composition $45xMO_{1/2}$–$45(1\text{-}x)WO_3$–$30PO_{5/2}$–$25NbO_{5/2}$ (M = Na or K; $0.5 \leq x \leq 1.0$). The dependence of the alkali ions content on the electrical conductivity is observed by the impedance spectroscopy analysis.

In **chapter 3**, the electronic conduction mechanism of the glass samples with high content of transition metal oxide was analyzed. The glasses with the composition $45xKO_{1/2}$–$45(1\text{-}x)WO_3$–$30PO_{5/2}$–$25NbO_{5/2}$ ($0.5 \leq x \leq 0.7$) were prepared and heat treated under pure CO gas. The introduction of the electrons was observed by UV-visible absorption spectroscopy and electron paramagnetic resonance (EPR). In addition, the conduction mechanism is explained in terms of the Mott and Friedman Small Polaron Hopping theory.

In **chapter 4**, the mixed conduction in the alkali tungsten phosphate glass system $45xMO_{1/2}$–$45(1\text{-}x)WO_3$–$30PO_{5/2}$–$25NbO_{5/2}$ (M = Na and K, $0.5 \leq x \leq 1.0$) heat treated under hydrogen atmosphere was analyzed. The absorption of the hydrogen gas introduced protons and electrons were confirmed by Fourier transform infra-red spectroscopy (FTIR) and UV-visible absorption spectroscopy. Strong correlation between the increase in electrical conductivity due to heat treatment under H_2 atmosphere and the hydrogen absorption capacity of the glasses is observed. In addition, change in the conduction mechanism is generated by hydrogen absorption. The

composition dependence of the electrical conductivity of the treated glasses reached the minimum at the composition where the mixed conduction is realized.

In **chapter 5**, the author summarizes this research with a brief summary of the keys achievements.