The Electrical Properties of Phosphate Glass Thin Films with Increasing Proton Concentration

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Solid proton conductors of phosphate glasses have attracted much attention due to low glass transition temperature, low melting point and high ionic conductivity in the electrochemical devises such as fuel cells, batteries, sensors and electrolyte, etc [1,2]. Especially, protons in phosphate glasses have much higher mobility than those in silica glasses. In contrast with silica glasses, O-H bonding in phosphate glasses is generally weak owing to the formation of hydrogen bonding [3]. The proton conductivity of phosphate glasses is known to be affected by content of water molecule, proton concentration, mobility and contents of P_2O_5. The residual water is incorporated into a glass network in the form of P-OH groups and works as a catalyst through lowering the activation energy for proton transport. In addition, non-bridging oxygen (NBO) is reported to increase proton conductivity because NBO of the glasses gives rise to strong hydrogen bonding [4]. In summary, protons of the phosphate glasses are very mobile and also have very high proton conductivity. It is noteworthy that the conductivity increases with the content of the phosphorus in the phosphate glasses even at high temperature range over 100°C in which vehicle conduction is ignored [5]. As a result, phosphate glasses are expected to keep the high proton conductivity at intermediate temperature (200~400℃). Although a large amount of P_2O_5 improves proton conductivity, it also drastically reduces chemical durability and induces severe volatilization of P_2O_5 during heat treatment.

In this study, phosphate glass thin films of ZrO_2-P_2O_5, BaO-P_2O_5 and BaO-La_2O_3-Al_2O_3-P_2O_5 were fabricated using water-based precursor solution and electrical properties were investigated. To prevent volatilization of phosphorus from the thin films during heat treatment, we intentionally changed the starting materials and investigated the resultant properties. The observed properties were compared with the reported properties of the bulk glasses. Especially, the concentration of non-bridging oxygen (NBO) of the fabricated glass films is measured and its effect on the obtained proton conductivity was analyzed.

The Fabricated phosphate thin films are non-crystalline, and also are homogeneous and transparent. Fig.1 shows relation between proton concentration and conductivity analyzed using Eq. 1 [3].

$$\sigma_{417} = A_0[H^+]^2 \qquad \text{(Eq. 1)}$$

The proton mobility increases with a decrease of $\upsilon_{OH,}$ which varies with the ion species in the glasses. The proton mobility of BaO-Al_2O_3-La_2O_3-P_2O_5 and BaO-P_2O_5 thin films are higher than those of ZrO_2-P_2O_5 thin film. Relatively high proton conductivity at intermediate temperature over 100℃ were observed in the fabricated glass thin films.

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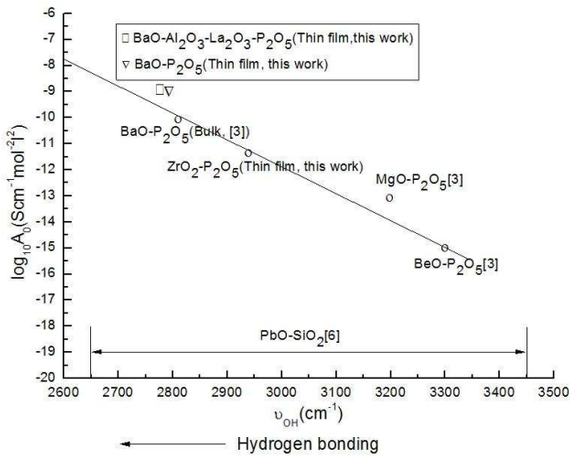

Fig. 1 Relation between proton mobility [A_0] and peak wave number [υ_{OH}]