Large Enhancement of Electrical Conductivity in Magnesium Phosphate Glasses by Ion Implantation of Proton

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プロトンのイオン注入によるリン酸マグネシウムガラスの電気伝導度の顕著な増大

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Large enhancement of electrical conductivity has been observed in $\text{Mg}(\text{PO}_3)_2$ glasses by ion implantation of protons at 120 keV to a fluence of $1 \times 10^{18} \text{ cm}^{-2}$. Upon implantation d.c. conductivity at 300 K was drastically increased from $\sim 10^{-15} \text{ S} \cdot \text{cm}^{-1}$ to $5 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and the activation energy of the conduction was greatly reduced from $\sim 1.3 \text{ eV}$ to 0.18 eV . Observation of absorption current and the positive sign of Seebeck coefficient indicate that the primary charge carrier in H^+ -implanted $\text{Mg}(\text{PO}_3)_2$ glasses is a cation. The same conductivity enhancement was observed in D^+ -implanted $\text{Mg}(\text{PO}_3)_2$ glasses, but no significant change was seen in the He^+ -implanted glasses. These results strongly suggest that fast protonic conduction occurs in the H^+ -implanted $\text{Mg}(\text{PO}_3)_2$ glasses. No such a high conductivity was observed for H^+ -implanted SiO_2 glasses. It was found that implanted protons occur in the form of Si-OH and Si-H in SiO_2 but exist as POH groups and molecular water H_2O in $\text{Mg}(\text{PO}_3)_2$ glasses. A quantitative discussion on the proton conductivity led to a hypothesis that the coexistence of acidic groups such as POH and molecular water H_2O is a structural requirement for the emergence of fast proton transport in oxide glasses.

[Received March 14, 1996; Accepted May 15, 1996]

Key-words: Fast proton conductors, Ion implantation, Glasses, Phosphate glasses, Ion beam modification

1. Introduction

A large number of solid fast ion conductors have been discovered during the past two decades. However, few fast proton conducting solids,¹⁾⁻³⁾ which shows conductivity $> 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 300 K, have been reported so far. A typical example of a fast proton conductor is a heteropolyacid hydrates such as $\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$ and $\text{H}_3\text{W}_{12}\text{PO}_{40} \cdot 29\text{H}_2\text{O}$.⁴⁾ However, these materials are unstable to humidity and heat (decompose at $\sim 50^\circ\text{C}$), and they are not easily shaped into a thin film form.

Glasses are suitable materials for applications which require visible transparency and/or a thin film form. Protons in oxide glasses usually remain as X-OH groups ($X=\text{Si}, \text{P}$ or B) in a glass structure when glasses are prepared by melting raw materials in an ambient atmosphere.^{5),6)} Namikawa and Asahara⁷⁾ suggested a significant contribution of residual POH groups in phosphate glasses to the electrical conduction. We proved that protons are the main charge carrier in alkaline earth phosphate glasses by the experiments on deuterated glasses⁸⁾ and electrochromic cells⁹⁾ using glasses as an electrolyte, and subsequently clarified¹⁰⁾⁻¹²⁾ factors controlling proton conduction in oxide glasses. However, the maximum proton conductivity in the glasses prepared by a melt-quenching technique, to our knowledge, is $\sim 10^{-11} \text{ S} \cdot \text{cm}^{-1}$ at 300 K,¹¹⁾ which was obtained in $45\text{BaO} \cdot 55\text{P}_2\text{O}_5$ glasses containing H^+ of $\sim 1 \text{ mol} \cdot \text{L}^{-1}$. This conductivity is far below the level ($> 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 300 K) of fast ionic conduction. We consider that a material processing technique to introduce a large amount of mobile protons into glasses is required to realize fast pro-

tonic conduction in oxide glasses.

Here we report that a large enhancement of electrical conductivity, probably due to protons, has been obtained in $\text{Mg}(\text{PO}_3)_2$ glasses by ion implantation of protons and propose a hypothesis that the coexistence of acidic P-OH groups and molecular H_2O is a structural requirement for fast proton conduction in oxide glasses.

2. Experimental

Substrate glasses used for ion implantation were magnesium metaphosphate glasses, $\text{Mg}(\text{PO}_3)_2$, prepared by melt-quenching method using MgO and 85% H_3PO_4 liquid⁸⁾⁻¹²⁾ and synthetic water-free SiO_2 glasses (Suprasil W®).

Approximately 1 mm thick glass plates were implanted with 120 keV H^+ , 100 keV D^+ or 120 keV He^+ to fluences of 10^{16} to 10^{18} cm^{-2} at room temperature. The dose rate of each ion was $\sim 3 \mu\text{A} \cdot \text{cm}^{-2}$. The size of implanted area is $\sim 10 \text{ mm} \times 10 \text{ mm}$. The calculated range with the TRIM code¹³⁾ is $\sim 1 \mu\text{m}$ for 100 keV D^+ and 120 keV H^+ . The Al foil wrapping method¹⁴⁾ was used to reduce charging effects. The depth profiles of implanted D^+ ions was analyzed by detecting protons from the $\text{D}(^3\text{He}, ^4\text{He})\text{p}$ nuclear reaction of 1-2 MeV ^3He at normal incidence and a reaction angle of 160° .

D. C. electrical conductivities of the implanted glasses were measured in a 2-probe configuration using Pt electrodes sputter-deposited on the surface of implanted glasses. The measurements were carried out in the temperature range 450 K-160 K using a cryostat. On assumption that a H^+ -implanted layer in glasses may be regarded as a conduc-

tive thin film, electrical conductivities (σ) of the implanted layer were calculated by Eq. (1);

$$\sigma = \frac{1}{\rho} \frac{d}{t \cdot l} \quad (1)$$

where ρ is the resistance, d the separation between electrodes, l the length of the electrode, and t is the thickness of implanted layers. This assumption will be justified later by revealing that the implanted layers are extremely conductive than the unimplanted layers of the substrate glasses. Here, the full width of the half maximum (FWHM) of distribution of implanted deuterons, which can be measured directly by the nuclear reaction analysis described above, was used as the value of implanted layer thickness t .

Seebeck coefficients were measured at room temperature by attaching two pairs of Cu-constantan thermocouples to the implanted surfaces of glasses.

3. Results

Figure 1 shows infrared absorptions in $\text{Mg}(\text{PO}_3)_2$ and SiO_2 glasses induced by H^+ -implantation. In $\text{Mg}(\text{PO}_3)_2$ glasses, a broad absorption band peaking at $\sim 3200 \text{ cm}^{-1}$ is induced and its intensity increases with the fluence of protons. The shape of this band is almost the same as that in the substrate before implantation, and the band is due to POH groups forming a strong hydrogen bond with an oxygen attaching to the glass network.⁸⁾ In the substrate implanted to a fluence of $1 \times 10^{18} \text{ cm}^{-2}$, a new band peaking at $\sim 3400 \text{ cm}^{-1}$, marked by an arrow in the figure, becomes prominent besides the broad band peaking at $\sim 3200 \text{ cm}^{-1}$. This band is not seen for POH groups in the substrate before implantation and is attributed to be due to molecular water H_2O from the peak position.^{15),16)} Two absorption bands peaking at 3670 and 2230 cm^{-1} , are induced in SiO_2 glasses by proton implantation. The former and the latter

are due to Si-OH and Si-H groups, respectively. No formation of molecular water, H_2O , which should give the band at $\sim 3400 \text{ cm}^{-1}$,^{14),15)} was seen. The concentrations of created SiOH and SiH , estimated from the intensities using the molar extinction coefficients of $90 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for SiOH ¹⁷⁾ and of $40 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for SiH ,¹⁸⁾ were $5 \times 10^{17} \text{ cm}^{-2}$ and $4 \times 10^{17} \text{ cm}^{-2}$, and the sum of these two concentrations agreed with the concentrations ($1 \times 10^{18} \text{ cm}^{-2}$) of implanted protons within the uncertainty ($\sim \pm 10\%$) of fluence.

Figure 2 shows the temperature dependence of d.c. electrical conductivities of $\text{Mg}(\text{PO}_3)_2$ glasses implanted with H^+ or D^+ ions to a fluence of $1 \times 10^{18} \text{ cm}^{-2}$. Here, the thickness of conductive layers, which is required for calculation of conductivity by Eq. (1) was taken as $0.85 \mu\text{m}$ which corresponds to the FWHM of distribution (see the inset of Fig. 2) of implanted deuterons. The conductivity was reproducible in the temperature range $160\text{--}450 \text{ K}$ for repeated cycles of the measurement and the no significant difference in the conductivity between evacuated state ($\sim 10^{-3} \text{ Pa}$) and ambient atmosphere was perceived. Data on each specimen were well fitted to a straight line in the plot of $\log \sigma$ vs. reciprocal temperature. The conductivities of the H^+ -implanted substrate were almost the same as those of the D^+ -implanted substrate. The conductivity at 300 K and the activation energy of the conduction $6 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and 0.18 eV for the H^+ -implanted substrate or $4 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and 0.17 eV for the D^+ -implanted substrate, respectively.

The conductivities of all the implanted substrates except the above two ($\text{Mg}(\text{PO}_3)_2$ glasses implanted with H^+ and D^+ of $1 \times 10^{18} \text{ cm}^{-2}$) were below the low limit ($1 \times 10^{-7} \text{ S} \cdot \text{cm}^{-1}$, i.e., $\sim 10^{11} \text{ Ohm}$ for the present specimens with the conductive layer dimension of $10 \text{ mm} \times 10 \text{ mm} \times \sim 0.85 \mu\text{m}$ thick) of detection in the system used here.

No cracking was perceived for all the implanted surfaces. A distinct step was observed at boundary between the implanted and unimplanted areas on $\text{Mg}(\text{PO}_3)_2$ glass surfaces. The implanted region is higher than the unimplanted area, and the step-height was $\sim 20 \text{ nm}$ in the fluence range $1 \times 10^{16} \sim 3 \times 10^{17} \text{ cm}^{-2}$ and $\sim 40 \text{ nm}$ to $1 \times 10^{18} \text{ cm}^{-2}$.

Fig. 1. Proton implantation-induced infrared absorption. (A) $\text{Mg}(\text{PO}_3)_2$ glasses. Fluences of implanted 120 keV H^+ ions are described in the figure.

(B) SiO_2 glasses implanted with 120 keV H^+ of $1 \times 10^{18} \text{ cm}^{-2}$.

Fig. 2. D.C. electrical conductivities of $\text{Mg}(\text{PO}_3)_2$ glasses implanted with 120 keV H^+ or 100 keV D^+ to a fluence of $1 \times 10^{18} \text{ cm}^{-2}$ as a function of temperature. The dotted line denotes calculated conductivities using Eqs. (1)–(3) in the text on the assumption that all the implanted H^+ exist in the form of POH groups. The inset shows depth concentrations of implanted D^+ ions (100 keV , $1 \times 10^{18} \text{ cm}^{-2}$) in $\text{Mg}(\text{PO}_3)_2$ glass evaluated using the $\text{D}^{3\text{He}}$, ^4He nuclear reaction. N_D and N_P in the right ordinate denote concentrations of deuteron and phosphorus, respectively.

4. Discussion

The positive sign of Seebeck coefficients and observation of absorption current indicate that electrical conductivities in H^+ -implanted $Mg(PO_3)_2$ glasses are primarily controlled by positive ions. The conductivity in $Mg(PO_3)_2$ glasses implanted with 120 keV H^+ of $1 \times 10^{18} \text{ cm}^{-2}$ is close to that with 100 keV D^+ of $1 \times 10^{18} \text{ cm}^{-2}$, but the conductivity at 300 K was below the detection limit in $Mg(PO_3)_2$ glasses implanted with 120 keV He^+ of $1 \times 10^{18} \text{ cm}^{-2}$. These results strongly suggest that the charge carrier of high conductivity induced by H^+ -implantation is due to a proton (it was already proved in our previous papers^{8),9)} that proton is the primary charge carrier in $Mg(PO_3)_2$ glasses before proton-implantation). Here, the observed conductivity is compared with that for the case that all implanted protons occur as POH groups which make a hydrogen-bond similar to that in pre-existing POHs in $Mg(PO_3)_2$ glasses. The conductivity in the latter case may be calculated by the following relations:

$$\sigma_{417\text{K}} = A_H [H^+]^2 \quad (2)$$

$$\log A_H = -0.0097 \nu_{OH} + 17.1 \quad (3)$$

where $\sigma_{417\text{K}}$ is the conductivity at a reference temperature of 417 K and A_H is a constant depending on the glass composition, and is a measure of the mobility of proton and $[H^+]$ ($\text{mol} \cdot \text{L}^{-1}$) and $\nu_{OH} (\text{cm}^{-1})$ denotes the concentrations of proton and the peak wave number of OH-stretching vibration. These relations were obtained by Abe et al.¹¹⁾ through the analysis of experimental data for ~80 different types of oxide glasses containing residual X-OH groups (where X=Si, P and B). Substituting 3200 cm^{-1} as ν_{OH} and $17 \text{ mol} \cdot \text{L}^{-1}$ as $[H^+]$, we obtain $\sigma_{417\text{K}} = 4 \times 10^{-12} \text{ S} \cdot \text{cm}^{-1}$. The observed value of $\sigma_{417\text{K}}$ is $7 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, which is larger by ~8 orders of magnitude than the calculated value. The activation energy of proton conduction is also compared. We reported in the previous paper¹¹⁾ that the activation energy (E_a , in eV) of proton conduction in $Mg(PO_3)_2$ glasses containing only X-OH groups may be expressed as a function of the proton concentration by the following equation,

$$E_a = 1.14 - 0.124 \log_{10} [H^+] \quad (4)$$

Substituting $17 \text{ mol} \cdot \text{L}^{-1}$ as $[H^+]$ into Eq. (3), we obtain $E_a = 0.98 \text{ eV}$. The observed E_a (0.18 eV) is ~1/5 of the calculated value. These discrepancies indicate that a conduction mechanism which differs from that in the substrate glasses controls fast proton conduction observed in the H^+ -implanted glasses.

It is evident from the experiment that fast proton conduction was observed in the substrates in which both POH group and H_2O are present. The calculated conductivities due to protons in X-OH groups at 417 K in SiO_2 glasses is $\sim 10^{-16} \text{ S} \cdot \text{cm}^{-1}$. This value is far below the low limit (10^{-11} Ohm) of the present system. Therefore, the experimental results are consistent with an idea that fast proton conduction does not occur in glasses containing only X-OH groups. Since protons are transferred as H_3O^+ in acid solutions, we consider that the existence of acidic POH groups and H_2O resulted in easy formation of H_3O^+ and hence the mobility is greatly enhanced compared with system involving no molecular water. In fact, $H_3Mo_{12}PO_{40} \cdot 29H_2O$, $H_3Mo_{12}PO_4$ and $H_3W_{12}PO_{40} \cdot 29H_2O$, all of which are known as fast proton conductors at room temperature, commonly contain a large amount of both POH and H_2O . The activation energy of proton conduction in these materials is 0.14–0.16 eV, which is close to that (~0.18 eV) in $Mg(PO_3)_2$ glasses implanted with H^+ of $1 \times 10^{18} \text{ cm}^{-2}$. This similarity substantiates a hypothesis that the coexistence of POH and H_2O results in the emergence of fast proton conduction in oxide glasses.

It may be emphasized that no degradation was perceived

for H -implanted $Mg(PO_3)_2$ glasses after placing the implanted glasses in ambient atmosphere for 3 months. The formation mechanism of molecular water in $Mg(PO_3)_2$ glasses by proton implantation and the optimization of protonic conductivity by varying acceleration voltages are in progress.

5. Summary

(1) D.C. conductivity of $Mg(PO_3)_2$ glasses at room temperature was drastically enhanced from $\sim 10^{-15} \text{ S} \cdot \text{cm}^{-1}$ to $\sim 5 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and the activation energy of the conduction was greatly reduced from 1.1 eV to 0.18 eV upon implantation of 120 keV H^+ to a fluence of $1 \times 10^{18} \text{ cm}^{-2}$. Almost the same changes in conductivities and the activation energy were obtained for the glasses implanted with 100 keV D^+ (the calculated depth, ~1 μm , corresponds to that of 120 keV H^+) to the same fluence. No high proton conduction ($> 10^{-8} \text{ S} \cdot \text{cm}^{-1}$ at room temperature) was observed for SiO_2 glasses implanted with 120 keV H^+ to a fluence of $1 \times 10^{18} \text{ cm}^{-2}$.

(2) The observed conductivity in the H^+ ($1 \times 10^{18} \text{ cm}^{-2}$)-implanted $Mg(PO_3)_2$ glasses was higher by 8 orders of magnitude than the conductivity calculated using an empirical relation which was obtained for various oxides glasses containing residual X-OH groups (H_2O -free). The activation energy (~0.2 eV) of the conduction was close to that in fast proton conducting crystals of hydrated heteropolycids containing POH and H_2O such as $H_3Mo_{12}PO_4 \cdot 29H_2O$. These results indicate that coexistence of acidic X-OH such as P-OH and molecular water is a structural requirement for the emergence of fast proton conduction in oxide glasses.

Acknowledgments This work was supported in part by a Grant-in-aid for Scientific Research from the Japanese Ministry of Education, Science and Culture. One of the authors (HH) acknowledges the Ogasawara Foundation and the Sumitomo Foundation for a financial support.

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