

Role of P_2O_5 on Protonic Conduction in Sol–Gel-Derived Binary Phosphosilicate Glasses

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二成分系リンケイ酸塩ゾル–ゲルガラスのプロトン伝導における P_2O_5 の役割

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Sol-gel derived P_2O_5 - SiO_2 glasses were studied and a remarkable improvement in protonic conduction was observed by increasing the P_2O_5 content. This was attributed to (1) the variation in glass structure including the reduction of the degree of cross-linking skeleton and the increase of specific surface area of glass due to the non-bridging oxygen (P=O) in P-O tetrahedron, (2) the formation of stronger hydrogen bond between hydroxyl group and P=O group as well as hydroxyl group and, (3) the p- π resonance effect in $O_{(3-t)}PO(OH)_t$ unit.

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1. Introduction

A number of studies on fast proton conductive glasses have been done by Abe et al. in the past two decades.^{1)–8)} According to their studies, some amorphous solids in MO- P_2O_5 system (M=Be, Mg, Ca, Sr, Ba, etc.) exhibit a high protonic conduction in comparison with silica glass,^{1)–3)} especially the zirconium phosphate glassy solid, its conductivity reaches as high as 10^{-2} S/cm at room temperature.¹⁾ Evidence that protons are the electric charge carriers in these alkali-free phosphate glasses has been demonstrated in some papers.^{2)–5)} However, from the viewpoint of feasibility in synthesis and application, selecting silicate-based glass with P_2O_5 constituent seems more attractive and realistic than a pure phosphate system glass. Recently, we made a study on protonic conduction of binary phosphosilicate glasses prepared by sol-gel processing.⁹⁾ Since both SiO_2 and P_2O_5 are glass network formers and no network modifier is incorporated, it is believed that protons in binary P_2O_5 - SiO_2 glasses play a role as the primary electric charge carriers, as in alkaline earth metaphosphate glasses. In this paper, we report the function of P_2O_5 on protonic conduction of these glasses and give a detail discussion. We suggest that the conductivity improvement with the P_2O_5 content is attributed to the reduction of the degree of cross-linking skeleton and the formation of strong hydrogen bonding due to the non-bridging oxygen in P=O group and the p- π resonance effect in tetrahedral $O_{(3-t)}PO(OH)_t$ unit ($0 < t \leq 3$). The reduction of the degree of cross-linking skeleton leads to an easy formation of micropore structure in glass, while the strong hydrogen bonding and resonance effect will make the protons more active. With the aid of hydrogen-bonded or free hydrogen-bonded molecular water, these mobile protons become easy to transfer in glass structure. As a result, a high protonic conduction can be achieved in P_2O_5 -containing glasses.

2. Experiment

2.1 Sample preparation

Glasses with a nominal composition (in mol%), $xP_2O_5 \cdot (100-x)SiO_2$ ($x=0, 5, 10, 15, 20$), were prepared by sol-gel processing, in which gels were obtained by the hydrolysis and condensation of the precursors of $Si(OC_2H_5)_4$ and $PO(OCH_3)_3$ in the presence of ethanol and water with a small amount of HCl (0.15 mol/l). In order to prevent the samples' cracking, the controlled drying and

heating procedures are necessary for glass preparation (with a heating rate not higher than $10^\circ\text{C}/\text{h}$). After a heat treatment at 500 – 800°C in air for 2 h, the related properties of glass were measured.

2.2 Measurement of alternating-current conductivity

AC complex impedance spectra were acquired with a Solartron SI 1260 Impedance Analyzer. The samples, on both sides of which gold was evaporated to form the circle electrodes with a 3 mm of diameter, were put in an Advantec AE-215 constant temperature-humidity chamber in order to alter the temperature and the relative humidity. During the measurement, the sweep frequency was selected at the range 1 Hz–7 MHz. The Cole-Cole plots consisted of a single semicircle, and the electrical conductivity was determined from the point of the semicircle intercepting with the real axis.

2.3 N_2 adsorption-desorption isotherms

The pore characteristics such as specific surface area and pore volume of 600°C -treated glasses, were obtained by a fully automated Quantachrome Corp. NOVA-1000 surface area analyzer. For the measurement, the samples were preheated at 250°C in a vacuum for 1 h to remove the residual adsorbed water (before measurements, the samples had been placed in vacuum at room temperature for at least 24 h). The data were interpreted according to the Brunauer-Emmett-Teller (B.E.T.) equation.

2.4 TG-DTA measurement

The thermogravimetric and differential thermal analysis were employed for the observation of the thermal history of gel. TG-DTA traces of the samples were recorded by a Seiko SSC/5200 TG/DTA 320 analyzer at the heating rate of $10^\circ\text{C}/\text{min}$ and the temperature in the range of 20 – 800°C .

In addition, the FT-IR spectra (4000 – 400 cm^{-1}) were obtained by using either a KBr pellet technique or a thin glass plate directly. The adsorbed water content was estimated by a difference in the sample weight at 0.21 atm of water vapor pressure (30°C , 30% of relative humidity) and that in vacuum, respectively.

3. Results and discussion

A typical DTA trace for $10P_2O_5 \cdot 90SiO_2$ gel is shown in Fig. 1. From the figure, it is evidenced that almost all organics in the sample has been removed at $\sim 500^\circ\text{C}$. Therefore, by heating the sample above 500°C , a transparent glass can be obtained. Moreover, the analyses

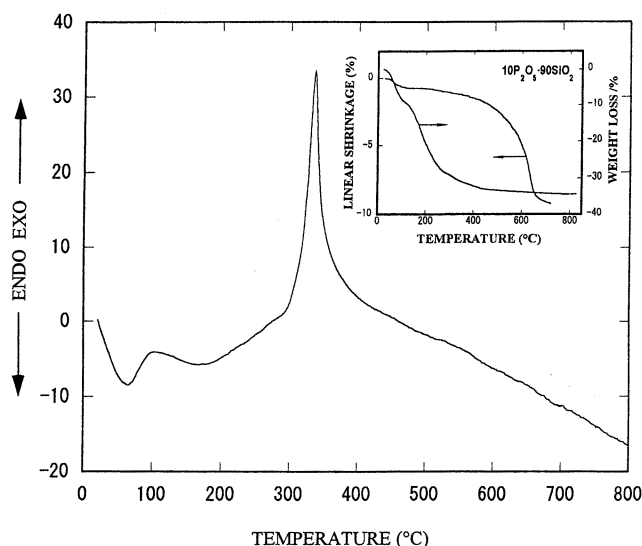


Fig. 1. A typical DTA trace for sol-gel derived 10P₂O₅·90SiO₂ sample in the range 20–800°C. The inset is the plot of thermal linear shrinkage and weight loss of 10P₂O₅·90SiO₂ sample versus temperature.

of thermal linear shrinkage and TG for the typical 10P₂O₅·90SiO₂ sample (inset in Fig. 1) indicate that an obvious shrinkage (>5%) associated with a little weight loss (<1%) in the temperature range of ca. 500–650°C. These studies imply that the viscous sintering results in the above temperature range. That means, at this temperature range, we can control the pore structure to acquire a high proton conductive glass.

Figure 2 shows the dependence of electrical conductivity on temperature for the binary P₂O₅–SiO₂ glasses, heat-treated at 600°C (measured at 50% of relative humidity). Obviously, the conductivity increases with the increase of P₂O₅ content, e.g., two orders higher in magnitude when 20 mol% P₂O₅ is incorporated. This enhancement should result from the different degree of cross-linking skeleton structures.

Phosphorus oxide, as a glass network former, it is generally accepted in the form of tetrahedral PO₄ unit in glass structure, which consists of three P–O single bonds and one P=O double bond. Clearly, the degree of cross-linking network weakens with the increase of P₂O₅ content due to the special non-bridging oxygen (in P=O group), which has no connection with any other tetrahedron. As a result, it will lead to an easy formation of an open structure or a micropore structure in glasses. The estimation of specific surface area and pore volume of the 600°C-treated glasses

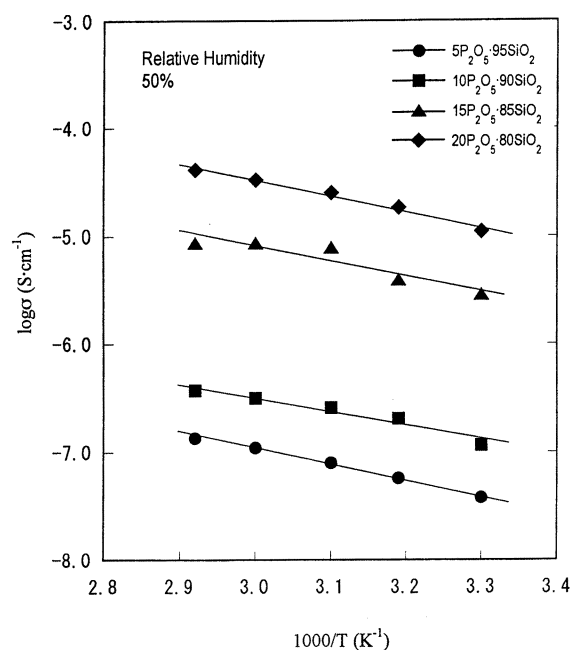


Fig. 2. Plot of AC electrical conductivity versus reciprocal temperature for the 600°C-treated x P₂O₅·(100– x)SiO₂ specimen ($x=5, 10, 15, 20$) (measured at 50% relative humidity).

by N₂ adsorption–desorption isotherms (summarized in Table 1, together with the adsorbed water content and calculated activation energy for conduction) supports the above statement. That is, the specific surface area or pore volume increases with increasing the P₂O₅ content because of the more and more P=O groups in glass structure (here the glasses are treated at 600°C).

Furthermore, the dependence of electrical conductivity on P₂O₅ content for the glasses with a similar specific surface area (ca. 50 m²/g, obtained by heating the samples at different temperatures or holding them for different course of time) is shown in Fig. 3. It indicates that the incorporation of P₂O₅ to silica glass can enhance the proton's mobility effectively. This can be attributed to the different proton environment between phosphosilicate glass and silica glass, besides the different degree of cross-linking network.

It was reported that the mobility of protons increases with the strength of the hydrogen bonding and the protonic conduction is controlled by the O–H bond-breaking step.^{2),3),7)} In the present binary P₂O₅–SiO₂ system glass, taking into consideration of polarization effects in tetrahedral O_(3– t)PO(OH) _{t} unit that displace electron density toward the more electronegative O, the double-bonded

Table 1. Specific Surface Area, Pore Volume, Activation Energy and the Adsorbed Water Content for the 600°C-Treated x P₂O₅·(100– x)SiO₂ Glass ($x=5, 10, 15, 20$)

Sample	5P ₂ O ₅ 95SiO ₂	10P ₂ O ₅ 90SiO ₂	15P ₂ O ₅ 85SiO ₂	20P ₂ O ₅ 80SiO ₂
Specific Surface Area (m ² /g)	1.4	2.6	50.8	61.4
Pore Volume (ml/g)	0.0026	0.0027	0.0318	0.0981
Activation Energy (kJ/mol)	31.2	29.7	27.1	30.7
Adsorbed Water Content (mass%)	1.7	2.1	2.7	3.3

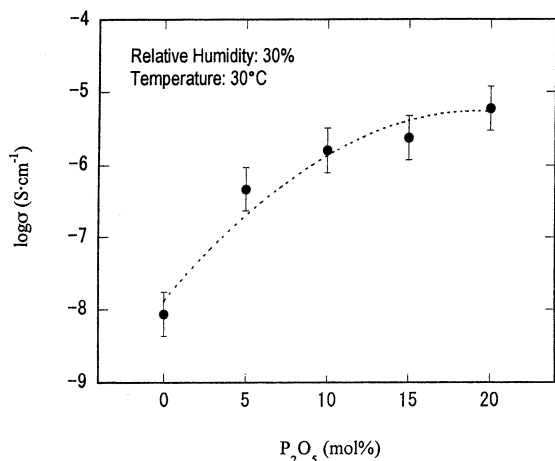


Fig. 3. Dependence of electrical conductivity on P₂O₅ content in binary P₂O₅-SiO₂ glasses (measured at 30°C and 30% relative humidity).

structure is more favorable for charge distribution.¹⁰⁾ In addition to this effect, the absence of steric hindrance for hydrogen bonding would make P=O group hydrogen bond with hydroxyl more easily than P-OH group. Although P-OH group is also very easy to form hydrogen bonding due to the high affinity of phosphorus (compared with that of silicon), a small steric hindrance from hydrogen in O-H bond will more or less weaken the hydrogen bonding. The analyses of DTA traces in low temperature region and the FT-IR spectra in high wavenumber range may help to understand the strong hydrogen bonding in P₂O₅-containing glass.

Figure 4 exhibits the DTA curves for $xP_2O_5 \cdot (100-x)SiO_2$ gels ($x=0, 10, 20$) in the range 20–250°C. Two endothermic peaks appear in the curves of P₂O₅-containing gels, one at ~80°C mainly due to the evaporation of alcohol and another at ~170°C to the desorption of strong hydrogen-bonded water (see curves (b) and (c) in Fig. 4),

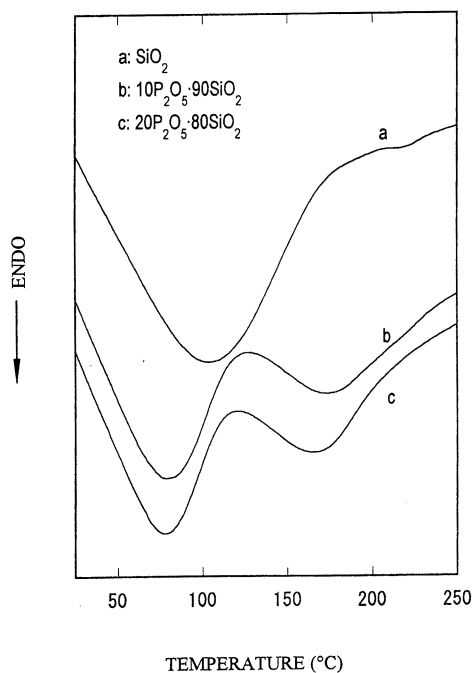


Fig. 4. DTA traces for sol-gel derived $xP_2O_5 \cdot (100-x)SiO_2$ specimen ($x=0, 10, 20$) in the range 20–250°C.

whereas only one peak in silica gel (at ~100°C, due to the desorption of physically adsorbed water, see curve (a) in Fig. 4). Strong hydrogen bonding leads to an evident retard for a desorption of molecular water. Apparently, the change in endothermic behavior results from the incorporation of P₂O₅.

In Fig. 5 shown is, the FT-IR spectra for 10P₂O₅ · 90SiO₂ and 20P₂O₅ · 80SiO₂ samples (~0.1 mm glass plate as a specimen). According to Scholze's studies on IR absorption spectra of OH group in oxide glasses,¹¹⁾ three kinds of OH stretching band can be observed in high-wavenumber side, which are characterized by band I (3640–3390 cm⁻¹), band II (3000–2600 cm⁻¹) and band III (2350 cm⁻¹) distinctly. Among them band I is due to the hydrogen bonding-free OH and band II and III are to the hydrogen bonded OH.^{11),12)} All these three OH stretching bands are noticed in Fig. 5. Moreover, the band at ~3280 cm⁻¹ due to the bound and free hydrogen-bonded water can also be observed.¹³⁾ The appearance of bands II and III verifies that the hydrogen bonding takes place more easily in binary phosphosilicate glass than in silica glass; in the latter case we could not observe these two bands. The strong absorption at 3280 cm⁻¹ also confirms that the P₂O₅-containing glass is much easier to allow molecular water remained in its structure even though the samples had been heated at 800°C.

On the other hand, since the P=O double bond is composed of one σ-bond and one π-bond, the p-π resonance effect occurs easily in tetrahedral O_(3-t)PO(OH)_t unit provided the hydroxyl exists in this unit, e.g., in O₂POOH unit ($t=1$). In sol-gel derived phosphosilicate glass, we believe, before its transformation into pore free glass, OH groups are always remained in glass structure. In this case, we may make an inference from close analogies, like organic chemists dealing with the carboxylic acids (e.g., CH₃COOH), the proton in O₂POOH unit should present its high activity due to the higher resonance stabilization of O₂POO⁻ unit than that of O₂POOH unit. For this reason, O₂POOH unit favors to react with H₂O to form a stable O₂POO⁻ unit and a free H₃O⁺ ion when H₂O molecule exists around the P-OH group. Here the O₂POOH unit donates the proton and the water accepts it. Consequently, when an electric field is applied to the glass, these protons transfer through the glass easily with the aid of the adsorbed molecular water. Another factor to consider is the elec-

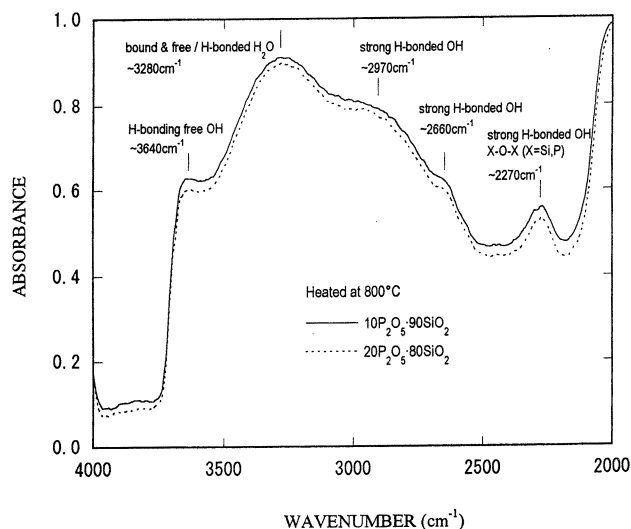


Fig. 5. FT-IR spectra of the thin plate specimens with a heat treatment at 800°C.

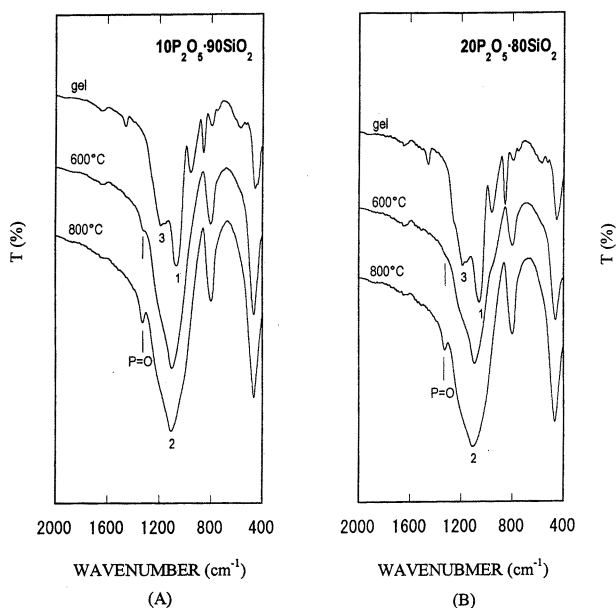


Fig. 6. FT-IR spectra of the samples with a heat treatment at different temperatures (A) 10P₂O₅·90SiO₂ (B) 20P₂O₅·80SiO₂ sample (using a KBr method).

tronegative character of the oxygen in P=O group, which leads to an attraction for electrons and also helps proton removal.

According to the above discussion, P=O and P-O groups are composed of a delocalized region in O₂POO unit due to the resonance effect. Thus it will weaken the P=O bond character. Our FT-IR results strongly support the existence of resonance effect in the present P₂O₅-SiO₂ glasses (see Fig. 6, using a KBr pellet technique). It is noted that the ~1320 cm⁻¹ absorption, which is identified as a stretching mode of P=O bond by Corl et al.,¹⁴ is very difficult to be detected in gel samples and only a weak shoulder observed in 600°C-treated samples. However, it becomes clear for 800°C-treated samples (Fig. 6). This phenomenon naturally is related to the reduction of the resonance effect with the temperature, which leads to an enhancement in P=O bond character. In addition, the broad absorption band around 1400-900 cm⁻¹, which mainly arises from three overlapping bands due to the three-center linkages, Si-O-Si at ~1060 cm⁻¹ (labeled by 1), P-O-Si at ~1100 cm⁻¹ (labeled by 2) and P-O-P at ~1180 cm⁻¹ (labeled by 3),^{15,16} indicates that these glasses are formed as homogeneous and chemical, rather than mechanical.

Based on the experimental result between electrical conductivity and temperature in our experiments, the experimental activation energy for productivity is estimated by the equation: $\sigma T = \sigma_0 \exp(-E/RT)$. The low activation energy of glass (ca. 29 kJ/mol, see Table 1) indicates that the protons in the present glasses (treated at 600°C) are very mobile. This result, together with the specific surface area, makes clear that a different amount of P₂O₅ incorporation has noticeable changes on pore characteristics and ad-

sorbed water content, despite a little variation in the activation energy (27.1 to 31.2 kJ/mol).

The sol-gel derived P₂O₅-SiO₂ glass provides very active protons and keeps a certain amount of molecular water in its structure. Consequently, two possible mechanisms for proton transfer may be proposed. One is the dissociated proton from an initial site to a neighboring site by the hydrogen-bonded water as a "bridge", which shortens the distance and lowers the activation energy for hopping.^{1,8} The other may involve the transfer of the dissociated proton from one H₂O molecule to another one by temporary formation of H₃O⁺, i.e., the dissociated proton moves in water directly which is remained in the pores or interstices due to the hydrogen bonding and physical adsorption. For this reason, the pore characteristic and the adsorbed water content becomes very sensitive to protonic conduction.

4. Conclusion

Incorporation of P₂O₅ to silica glass is found to be quite profitable to the protonic conduction of glass. This is attributed to a stronger hydrogen bonding, forming easily in P₂O₅-containing glasses due to the polarization effect of P=O and no steric hindrance for hydrogen bonding. The occurrence of p- π resonance effect in tetrahedral O₍₃₋₄₎PO(OH)_t unit is another important factor for the high mobility of proton in P-OH group. On the other hand, different amount of P₂O₅ causes variations in pore characteristics and adsorbed water content.

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