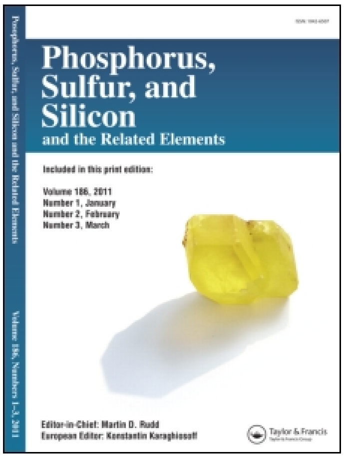

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Protonic Conduction and O-H Bonding State in Phosphate Glasses

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PROTONIC CONDUCTION AND O-H BONDING STATE IN PHOSPHATE GLASSES

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Abstract: Protons in alkaline-earth phosphate glasses give much higher mobility than those in silicate glasses. This is caused by the difference in O-H bonding state. Protons in P-OH form a strong hydrogen bonding with oxygen anion, resulting in formation of weak O-H bond.

The electrical conductivity of the glasses is proportional to the square of the proton concentration. The activation energy for the conduction is related to ν_{OH}, peak wavenumber of infrared absorption band (around~3000 cm^{-1}), due to fundamental O-H stretching vibration. The mobility of protons increases with decreasing ν_{OH}, which depends on the species of ions included in the phosphate glasses.

Protonic conduction in glasses has attracted much attention as the search for developing fast proton conductive glasses which are applicable to a solid electrolyte for H_2-O_2 fuel cell and for a H_2 gas sensor. In most oxide glasses, electric charge carriers are mobile alkali ions or electrons, but not protons.

Glasses, in most cases, contain a small amount of protons as hydroxyl groups(-OH), which was first studied extensively by Scholze[1] for silicate glasses. Some phosphate glasses exhibit characteristic unique behaviors in the crystallization[2]. The protonic conduction is one of the characteristic properties of phosphate glasses. Since the O-H bonding in phosphate glasses is generally weak owing to the formation of hydrogen bonding, protons in this case are mobile.

Experimental

Glasses were prepared by melting a given mixture of reagents,such as H_3PO_4 and alkaline-earth carbonates, in a platinum crucible at 1200 to 1300°C for various times. The proton concentration in the glasses was controlled by the melting duration times[3]. Direct current conductivity measurments were made with a vibrating reed electrometer (impedance 10^{16}) over a temperature range from 80°C to 200°C.

Proton content in the glasses was determined by infrared sprectroscopy, where the molar absorption coefficient is assumed to depend on ε_{H_2O} as shown in Fig.1.

Results and Discussion

Protons in glass form -OH groups. Fig.2 shows an example of IR spectrum of glass plate specimen for $Ca(PO_3)_2$ glasses. Scholze[1] established that there are three main absorption bands due to OH or "water" in glass, i.e.,Band 1 in the range 3640-3390 cm^{-1}, Band 2(3000-2600 cm^{-1}), and Band 3(2350 cm^{-1}). However, Band 3 was excluded from the present discussion because the existence of Band 3 is not certain yet and various absorption bands due to network formers(i.e.,P-O-P etc) are overlapped. Silica glass has only Band 1, but Na_2O-CaO-SiO_2 glasses have all three bands. In alkaline-earth phosphate glasses, Band 1 exists but is not clealy observed owing to the overlapping with Band 2 ; the deconvolution result shows clealy the existence of Band 1, although the Band 1 is smaller than the Band 2. Band 1 is due to hydrogen bonding-free OH and Band 2 is to hydrogen bonded OH. It was found that protons in Band 2 are much more mobile than those in Band 1. The electrical conductivity in alkaline-earth phosphate glasses was found to increase with the square of protron concentration in Band 2 as expressed by equation (1)[4],

$$\sigma_{417} = A_0 [H^+]^2 \quad \text{--------------------} \quad (1)$$

where σ_{417} is the conductivity(S/cm) at 417K(10^3/T=2.4), $[H^+]$ is proton concentration(mol/l), and A_0 is a constant which is a measure of mobility. The value of A_0 was found to vary to a great extent with ν_{OH} as shown in Fig.3.

$$\log A_0 = -0.00937\nu_{OH} + 17.1 \quad \text{------------} \quad (2)$$

The experimental activation energy for the electrical conduction E was assumed to be expressed by equation (3),

$$E = E_0 + E_1 \quad \text{------------------------} \quad (3)$$

where, E_0 is an activation energy at a unit concentration of the proton ($[H^+]$=1) and E_1 depends on the proton concentration.

It is found that E_0 increases linealy with increasing ν_{OH} and E_1 is propotional to log$[H^+]$. The major portion of E is determined by E_0 ($E_0 \gg E_1$); E is estimated to be decreased to 9/10 times when $[H^+]$ increases by ten times the initial concentration. Thus, E is mainly determined by ν_{OH}. The O-H bonding strength decreases with increasing hydrogen bonding, i.e.,with decreasing ν_{OH}. Generally,in phosphate glasses proton concentration is considerably higher and hydrogen bonding is stronger than in silicate glasses. This is the reason why phosphate glasses exhibit protonic conduction.

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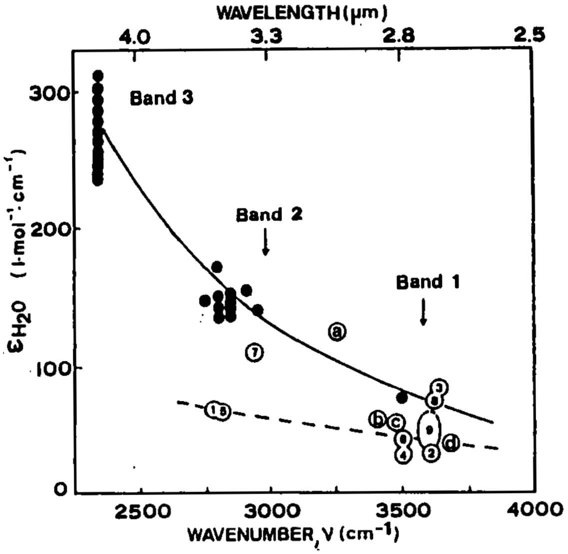

Fig.1, Relation between ε_{H_2O} and ν_{OH}.

(plotted from the data in references so far obtained. The solid line should be used for the separate determination of the Bands.)

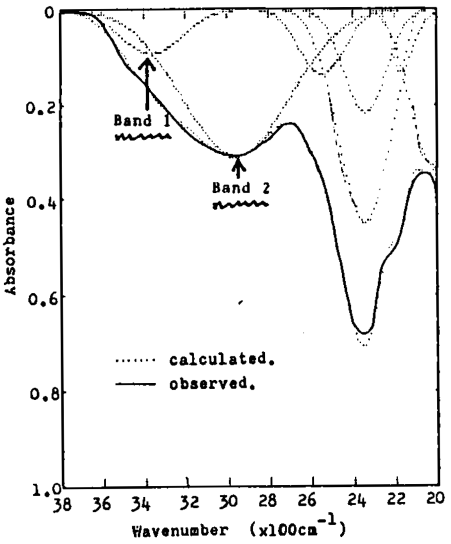

Fig.2, Example of deconvolution of IR spectrum for $Ca(PO_3)_2$ glass.

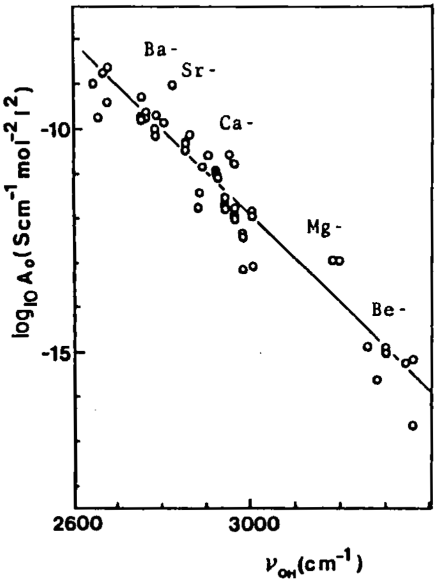

Fig.3, $\log A_0$ vs ν_{OH} plot
The position of respective alkaline-earth metaphosphate glasses are indicated.