Detection of Infrared Silent Proton in Hydrogen-Reduced Tungsten Phosphate Glasses by Thermal Desorption

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Tungsten phosphate glasses show unique chemical reactions with hydrogen gas and water vapor in ambient atmosphere.[1,2] W^{6+} ions in the glasses are reduced to W^{5+} by annealing at temperatures below the glass-transition temperature (T_g), and the color of the glass changes to dark blue. In our reaction model for this reaction, a proton must be sitting near the W^{5+} ion as a counterion. Spectroscopic techniques for detecting the charge-compensating proton such as infrared absorption, ^1H NMR, and pulsed ENDOR between the W^{5+} and ^1H or ^2D have been utilized but unsuccessful to date. In addition, the colored glass was found to show significant ionic and electronic conductivities on the order of 1×10^{-3} S cm^{-1} at ca. 500 °C.[3] These observations suggest that the proton is not in the well-defined chemical entity such as hydroxyls. In this sense, the proton is reasonably called an unidentified proton. The proton may be similar with those called free or quasi-free proton in solid proton conductors by Colomban and Tomkinson[4] and Fillaux.[5] The free or quasi-free protons were proposed to be existing mainly in mixed conductors and detectable as a continuum in incoherent inelastic neutron scattering spectra.

In the present paper, we report that the charge-compensating protons exist in two different chemical entities in the tungsten phosphate glasses. One is a proton with a smaller diffusion constant, constituting strongly hydrogen-bonded OH−O. The other is infrared silent proton (ISP), with a larger constant. Existence of the ISP is evidenced by detection of hydrogen gas thermally desorbed from the dark-blue-colored glass.

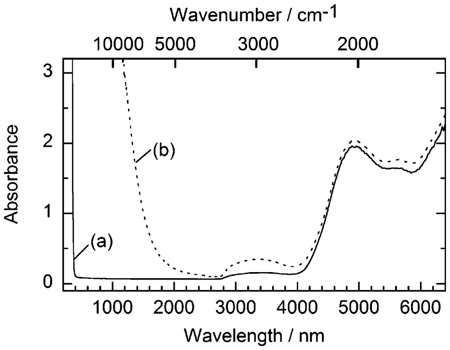

Figure 1. Optical absorption spectra of (a) the bleached glass and (b) the glass heat-treated at 500 °C for 24 h in 3.5% H_2−96.5% N_2. Absorption bands due to W^{5+} and OH were induced by dissolution of hydrogen.

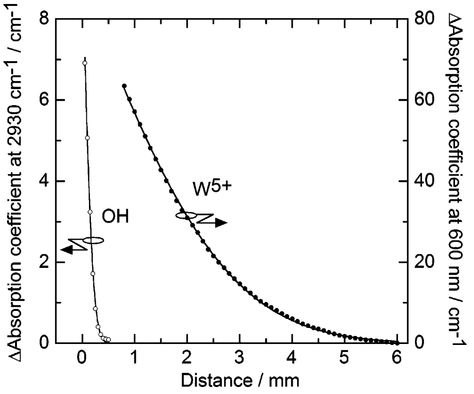

Figure 2. Depth profiles of OH and W^{5+} induced in the glass heat-treated at 500 °C for 5 h in 3.5% H_2−96.5% N_2. The symbols show the measured OH (○) and W^{5+} (●) intensities and the solid lines denote the calculated traces assuming one-dimensional diffusion from the surface with infinite area.[1]

Chemical composition of the glass samples used in the present experiments was $30PO_{5/2}\cdot 10WO_3\cdot 25NbO_{5/2}\cdot 10BaO\cdot 25NaO_{1/2}$ in moles (T_g=570 °C). The as-quenched glasses were thermally annealed to bleach the purple color due to W^{5+} ions.[1] Thin layers of Pd were deposited on the polished surfaces of the bleached glass plates (10 mm × 10 mm × 1 mm), and they were heated at 500 °C for 24 h in 3.5% H_2−96.5% N_2. Figure 1 shows changes in optical absorptions induced by the hydrogen annealing. No absorption band of W^{5+} was observed in the bleached glass (a). The absorption band peaking at 2930 cm^{-1} is assigned to strongly hydrogen-bonded OH groups.[6] In the H_2-annealed glass (b), strong and broad absorptions due to W^{5+} ions appeared in the visible−near-infrared region, and the intensity of OH absorption was increased. These apparently parallel induced optical changes imply that the charge-compensating proton generated in the glass by dissolution of hydrogen is present in the form of a OH group.

However, this idea was found to be invalid by comparison in the depth concentration between the induced optical band due to W^{5+} and the infrared absorption band due to OH;

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(1) Tawarayama, H.; Utsuno, F.; Inoue, H.; Hosono, H.; Kawazoe, H. *Chem. Mater.* **2006**, *18*, 2810−2816.

(2) Tawarayama, H.; Utsuno, F.; Inoue, H.; Kawazoe, H. *J. Power Sources* **2006**, *161*, 129−132.

(3) Fujitsu, S.; Komori S.; Tawarayama, H.; Kawazoe, H. *Abstract Book*, The 44th Symposium on Basic Science of Ceramics, Kochi, Japan, Jan 19−20, 2006; Ceramic Society of Japan: Tokyo, Japan, 2006; 2E-11, p 412.

(4) Colomban, Ph.; Tomkinson, J. *Solid State Ionics* **1997**, *97*, 123−134.

(5) Fillaux, F. *Solid State Ionics* **1999**, *125*, 69−79.

(6) Abe, Y.; Hosono, H.; Ohta, Y.; Hench, L. L. *Phys. Rev. B* **1988**, *38*, 10166−10169.

10.1021/cm701917k CCC: $37.00

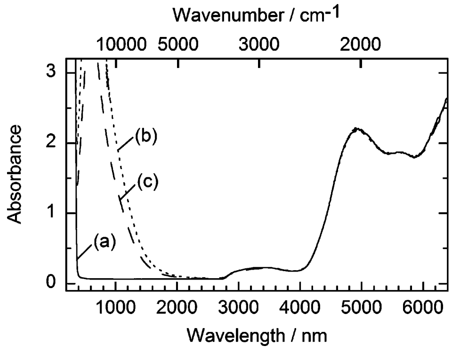

Figure 3. Optical absorption spectra of (a) the bleached glass and the glass containing the ISP (b) before and (c) after thermal desorption measurement. The glass containing the ISP was prepared by heat-treating in H_2-containing ambient atmosphere and removing the increased OH layers. Absorption intensity due to W^{5+} decreased after desorption of hydrogen.

Figure 2 shows the depth concentrations of the induced concentrations of OH groups estimated from the OH band and of W^{5+} (the method was the same as in ref 1). It is evident that the depth profiles or concentrations (OH, 4×10^{19} cm^{-3}; W^{5+}, 6×10^{18} cm^{-3})[1,7,8] are quite different from each other. The result indicates that the charge-compensating proton in the glasses does not exist primarily in the form of OH but in a different chemical state. The estimated diffusion constant of the charge compensating proton moving faster was 1.3×10^{-6} cm^2 s^{-1}, which is larger than 6.5×10^{-9} cm^2 s^{-1} by 3 orders of magnitude for the slower proton in the form of OH bonding.

Here, we assumed that dissolution of hydrogen in the glass is expressed by two different reactions

$$-O-W(VI)-O-X- + H \rightarrow -O-W(V) + HO-X- \quad (1)$$

$$-O-W(VI)-O-X- + H \rightarrow -O-[W(V)/H^{+}]-O-X- \quad (2)$$

where X is a cation constituting the network structure of the glass such as P, Nb, and W. In eq 1, W(VI)−O bonding is broken by reaction with hydrogen, and the charge-compensating proton forms X−OH. On the other hand, the O−[W(V)/H^+]−O structure in eq 2 is formed without destruction of the W(VI)−O bond. The charge-compensating proton is tentatively assigned to be the ISP.

Existence of the ISP in the glass was confirmed by detecting hydrogen released from the following samples. The bleached and Pd-coated glass (20 mm × 10 mm × 3 mm) was heat-treated at 500 °C for 5 h in 3.5% H_2−96.5% N_2. The increased OH layers were removed from the obtained glass, and a mirror-polished sample (15 mm × 7 mm × 1 mm) was prepared for thermal desorption measurements. As shown in Figure 3, the surface-removed sample before the thermal desorption treatment (b) showed induced absorption of W^{5+} and the exactly same intensity of OH band as that of the bleached glass (a). Therefore, the surface OH layer was effectively removed and the sample had only the ISP for the charge compensation of W^{5+}.

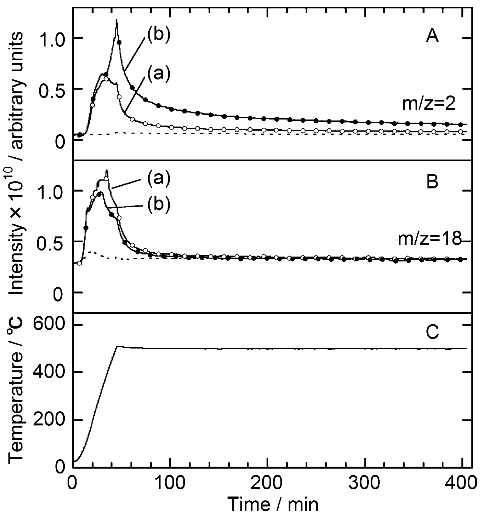

Figure 4. Thermal desorption spectra of the glasses (a) before and (b) after H_2 treatment. Gas species monitored were (A) H_2 and (B) H_2O. (C) The samples were heated up to 500 °C from room temperature following a temperature program. The dotted line denotes the background intensity of each gas species.

The sample coated with thin layer of Pt was placed in a silica tube connected with a vacuum system, and released gases from the sample were monitored using a quadrupole mass spectrometer (Q-mass). Pd coating was inappropriate for the measurement because of reaction with water adsorbed on the sample surface. Figure 4 shows changes in the intensities of H_2 and H_2O gas species from the samples. The intensities peaked at around 300 °C and recovered to the background level (because of adsorbed water) at around 120 min. Although the profile of H_2O desorption is similar between them, a clear difference is seen for the H_2 desorption. An additional sharp maximum is seen at 45 min, and the desorption level continuing from the peak to the end is distinctly higher in (b) than in (a). The difference in H_2 concentration desorbed between samples (b) and (a) estimated using a standard gas leak was 4.6×10^{-8} mol of H.[2] This concentration is close to that of the decreased W^{5+} ion, which was evaluated from the change in the optical absorption (plots b and c in Figure 3). This agreement is experimental evidence for a hydrogenous species, except OH groups are present as a counter cation of W^{5+} ion, suggesting the ISP as the primary counter cation.

In conclusion, two types of protons with different diffusion constants are found to be generated for charge compensation of W^{5+} in the tungsten phosphate glasses by dissolution of hydrogen. It is inferred that the reactions are expressed in eqs 1 and 2 and the primary charge compensating protonic species in eq 2 is the ISP.

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(7) Day, D. E.; Stevls, J. M. *J. Non-Cryst. Solids* **1973**, *11*, 459−470.
(8) Abe, Y.; Clark, E. C. *J. Mater. Sci. Lett.* **1990**, *9*, 244−245.