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Coloration and Decoloration of Tungsten Phosphate Glasses by Heat Treatments at the Temperature Far below T_g under a Controlled Ambient

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Reversible coloration−decoloration of tungsten phosphate glasses was observed by heat treatments at temperatures between 300 and 500 °C which were far below the T_g (570 °C) under the ambient with controlled partial pressure of hydrogen and/or water. The color center responsible for the coloration was found to be an electron-trapped W^{5+}. The assignment was done by detecting an anisotropic ESR singlet of $g = 1.7$ and broad optical absorption bands extending from the visible to the near-infrared region. The charge compensator of W^{5+} was found to be H^+. Mechanisms of the coloration by heat treatments under an ambient with the hydrogen-bearing species were proposed to be (1) decomposition of molecular water or hydrogen at the surface of the glasses, (2) selective dissolution of the generated hydrogen atom by the reaction with W^{6+} ions to form the W^{5+}/H^+ redox pair in the glasses, and (3) diffusion of the charge-compensating H^+ into the glass. The decoloration process was expressed by the reverse reactions. The rate of the coloration−decoloration was found to be determined by the diffusion of the atomic hydrogen. The diffusion constant of the atomic hydrogen at 500 °C in the glass was found to be as large as 1.5×10^{-6} cm²/s.

1. Introduction

Valence state and redox reactions of cationic species in glass-forming oxide melts have been one of important issues in glass technology. Optical absorption characteristics of transition metal cations with a particular valence state are used in preparing band-pass glass filters. Photoluminescence of Nd^{3+} and Er^{3+} are, respectively, a key function of the glass laser for nuclear fusion and an amplifier in optical communication networks. The temperature dependence of redox reactions of As and Sb has been utilized in the refining process of glass melts. Generally, the redox equilibrium of the cationic species in oxide melts under air ambient tends to go to higher oxidation state with decreasing temperature.[1] Under the refining process the oxygen molecule in a fine bubble in the melts is consumed in the oxidation reaction of As^{3+} and Sb^{3+}, which formed in the preceding melting process at a higher temperature.[2]

Recent applications of a charge-coupled device for a digital color camera stimulated development of a low-cost precision press-molded process for aspherical lenses with high refractive index.[3] Although lead was used exclusively for producing a series of lenses with high refractive index and high dispersion,[4] its use is prohibited to suppress the contamination of the environment.[5] Tungsten phosphate glasses with low melting temperature, high refractive index, and high dispersion are one of the possible alternatives for the mold lenses. We have observed that the as-prepared phosphate glasses with relatively high WO_3 concentration are colored dark blue, and decoloration of the glasses occurred by annealing in air ambient below the glass transition temperature (T_g). Although tungsten ion (W^{6+}) in oxide melts can be reduced under reducing atmosphere and by addition of reducing reagent,[6] there has been no report on the thermal decoloration of the glasses at temperatures far below T_g, as far as we are aware.

In the present paper the reversible coloration−decoloration reaction of the tungsten phosphate glasses under an ambient of hydrogen-bearing species such as water vapor and hydrogen at temperatures below T_g is reported. The reaction mechanism of the coloration is proposed to be the reduction

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of W^{6+} by a hydrogen atom,

$$W^{6+}{}_{G} + H \rightarrow W^{5+}{}_{G} + H^{+}{}_{G} \qquad (1)$$

where $W^{6+}{}_{G}$, $W^{5+}{}_{G}$, and $H^{+}{}_{G}$ are the species dissolved in the glass and H is the hydrogen atom formed at the surface of the glass and diffused into the glass. It is shown that the diffusion constant of the hydrogen in the solid glass is extraordinarily high. Decoloration is expressed by the reverse reaction of eq 1. It is proposed that there is dissociation equilibrium of the water vapor on the glass surface at temperatures below T_g,

$$H_2O(g) \leftrightarrow 2H_S + {}^{1}\!/_{2}O_2(g) \qquad (2)$$

where H_S means the hydrogen atom adsorbed on the glass surface. H_S is used in the coloration reaction of eq 1. The equilibrium goes to the right-hand side at higher temperatures. It is tentatively proposed that eqs 1 and 2 can be applied to the melts at higher temperature, although the effect must be taken into consideration of the translational motion or diffusion of the structural units in the melts.

2. Experimental Section

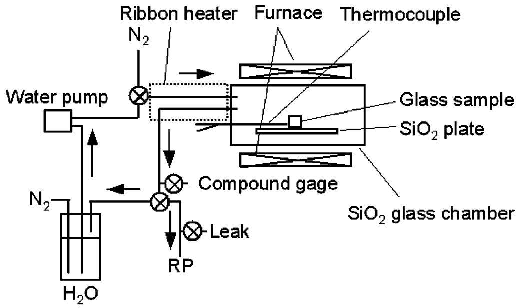
2.1. Glass Preparation. The chemical composition of the glass samples used in the present experiments was $30PO_{5/2}\cdot10WO_3\cdot25NbO_{5/2}\cdot10BaO\cdot25NaO_{1/2}$ in mol. A stoichiometric mixture of Na_2CO_3, $NaPO_3$, $Ba(PO_3)_2$, WO_3, and Nb_2O_5 was melted with a platinum crucible in air. The batch weight was 100 g. The melt was poured into a mold and was placed in a furnace preheated at 570 °C, which is the T_g of the glass determined by using differential thermal analysis (ThermoPlus TG8120, Rigaku). The glasses obtained were cut and mirror-polished, and the optical absorption spectra were measured by using a UV−vis−NIR spectrometer (UV3100PC, Shimadzu) and FT-IR spectrometer (FTIR-8200PC, Shimadzu). The color centers responsible for the coloration were identified by ESR measurements at room temperature (EMX, Bruker).

2.2. Decoloration of Colored Glasses. Mirror-polished and colored glass plates 15 mm × 15 mm × 5 mm in size were heat-treated at temperatures below T_g for different times in dry air. The optical absorption spectra of the heat-treated samples with gradient coloration were measured for the center area (1 mm × 5 mm) to evaluate the diffusion constant of the coloring species.

2.3. Reaction with Water Vapor. Bleached glass plates (details are mentioned in section 3.2) were heat-treated at temperatures below T_g in water vapor ambient (∼1 atm) by using the equipment illustrated in Scheme 1. The gas fed into the SiO_2 chamber was initially N_2 and was changed to water vapor at 200 °C in the course of the heating process. The plate samples were 15 mm × 15 mm × 3.5 mm in size, and their opposite surfaces were ground with a sand paper in order to enhance the reaction with water vapor. The water vapor-treated samples were mirror-polished before optical absorption and ESR measurements. The same experiment was also performed in N_2 atmosphere for comparison.

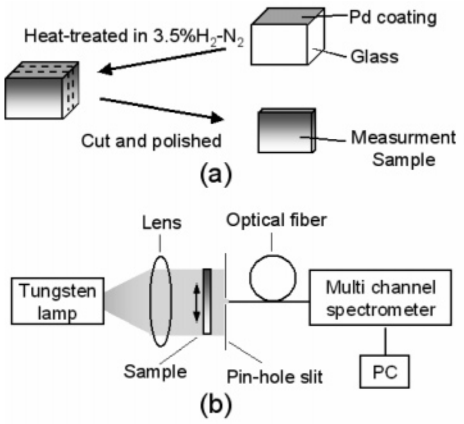
2.4. Reaction of the Glasses with Hydrogen. A thin layer of Pd was deposited by sputtering (E-1030, Hitachi) on the opposite surfaces of the bleached glass plates (10 mm × 10 mm × 1 mm in size), and the glass plates were heat-treated at temperatures below T_g in 3.5% H_2–96.5% N_2. After the Pd coating was removed by polishing, optical absorption and ESR measurements were performed. The absolute spin concentration of the color centers was estimated by comparing the intensities for the glasses with that of $CuSO_4\cdot5H_2O$ reference. To evaluate the diffusion constant of the coloring species, the glass samples with gradient coloration (20 mm × 20 mm × 10 mm in size) were also prepared by heat-treating the bleached glasses with Pd coating on a single surface at 500 °C in the same atmosphere. The heat-treated samples were cut and mirror-polished, and visible absorption spectra at different positions were continuously measured by moving the sample on the X-stage, as shown in Scheme 2. The incident light from the tungsten lamp was adjusted by the optical lens to pass the pinhole slit with a diameter of 100 μm. The transmitted light was introduced to the multichannel spectrometer (USB2000, Ocean Optics) through the optical fiber with a core diameter of 600 μm. The thickness of the samples was approximately 0.8 mm.

Scheme 1. Experimental Setup of the Water Vapor Heat Treatment[a]



[a] Water vapor was introduced to the preheated SiO_2 glass chamber.

Scheme 2. (a) Preparation of the Sample for Small Area Visible Absorption Measurement and (b) Experimental Setup of Small Area Visible Absorption Measurement System[a]



[a] Absorption spectra at different positions were continuously measured by moving the sample on an X-stage.

3. Results and Discussion

3.1. Coloration of As-Melted Glasses. In this section we describe the coloration characteristics of the as-melted glasses. It was reported[7] that the optical absorption intensity of tungsten phosphate glasses depends on melting conditions, time, temperature, and atmosphere.

Preliminary experiments were carried out to reduce the effects of variation in the melting conditions on the coloration. The partial pressure of water vapor in the ambient for

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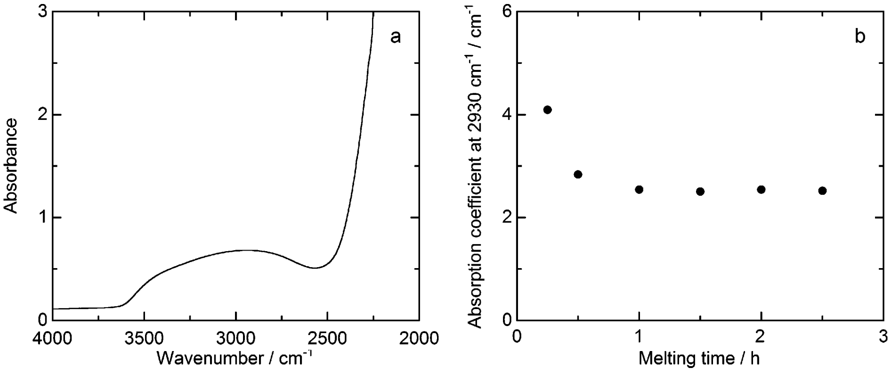

Figure 1. (a) Infrared absorption spectrum of the glass melted at 1400 °C for 15 min. The absorption band due to OH groups peaking at 2930 cm^{-1} was observed. (b) Melting time dependence of the OH absorption intensities at 2930 cm^{-1}. The melting temperature was fixed to 1400 °C. OH groups decreased rapidly in the initial stage of the melting and became almost constant for melting times longer than 1 h.

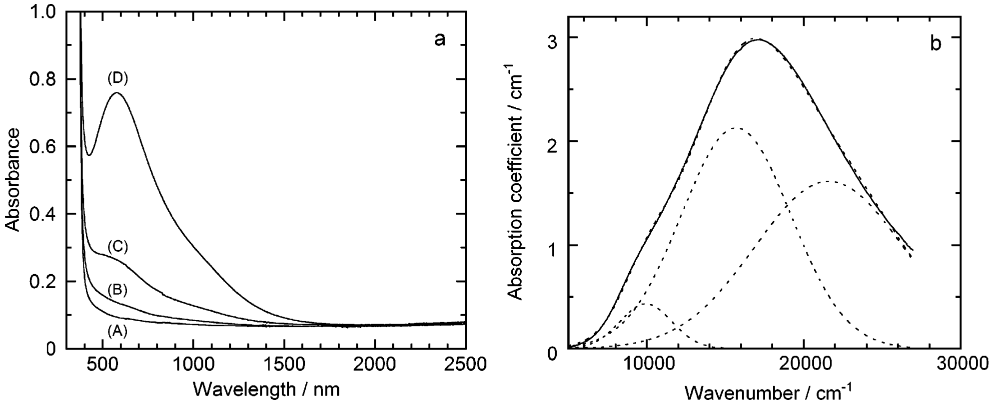

Figure 2. (a) Optical absorption spectra of the as-melted glasses. The melting temperatures are (A) 1100 °C, (B) 1200 °C, (C) 1300 °C, and (D) 1400 °C. A broad optical absorption band was discernible in the glasses melted above 1200 °C. (b) Gaussian deconvolution of the optical absorption band induced in the glass melted at 1400 °C. The absorption band assigned as W^{5+} was decomposed into three Gaussian components as illustrated with broken lines.

the melts should be an important factor of the coloration, but it is not easy to control the pressure effectively for the phosphate glasses. The raw materials contain a large amount of adsorbed water as an impurity. The water dissolved in the melts as P−OH is very stable and cannot be removed completely from the phosphate melts. Then we monitored the intensity of infrared absorption band due to OH as a measure of the equivalent pressure of water in the melts.

Figure 1a shows the infrared absorption spectrum of the glass melted at 1400 °C for 15 min. The absorption band peaking at 2930 cm^{-1} is due to OH groups in the glass. The strong absorption observed below 2500 cm^{-1} is the second harmonics of the intrinsic absorption of the glass. The change in the OH absorption intensity with increasing melting time is shown in Figure 1b. The melting temperature was kept at 1400 °C. The intensity decreased rapidly in the initial melting and became almost constant for the melting times longer than 1 h. The quasi-equilibrium concentration of OH was estimated to be 1.2×10^{19} cm^{-3}.[8,9]

To investigate effects of melting temperature on the coloration, the melts were first quasi-equilibrated by melting at 1400 °C for 1 h, and they were further melted at a temperature between 1100 and 1400 °C for 1 h. The glasses were then quenched without annealing to prevent decoloration (details are explained in section 3.2). The color of the glasses varied from pale yellow to dark blue with increasing melting temperature. Figure 2a shows optical absorption spectra of the as-melted glasses obtained by the different melting temperatures. A broad optical absorption band peaking at 585 nm was discernible in the glass melted at temperatures higher than 1200 °C. The absorption was thought to be due to two strong intraionic excitations and a weak intervalence excitation of W^{5+} (Figure 2b).[10,11] Simultaneously with the appearance of the optical absorption, a broad singlet signal assignable to W^{5+} ($g = 1.7$)[11] was also observed as a major paramagnetic species in the ESR spectrum of the glass melted at 1400 °C as shown in Figure 3. It will be stated in section 3.4 that the optical absorption intensity was proportional to the absolute spin concentration of the ESR absorption with $g = 1.7$. Therefore, the center responsible for the coloration was concluded to be W^{5+}. By using the estimated cross section of the visible absorption (section 3.4), the concentration of W^{5+} in the glass melted at 1400 °C was calculated as 2.0×10^{17} cm^{-3}, which is considerably lower than that of the OH bond.

The fact that the optical absorption intensity of the as-melted glasses becomes higher with increasing melting temperature suggests that reduction of W^{6+} to W^{5+} in the melt advances at higher temperature. The tendency seems apparently to be consistent with the oxidation−reduction

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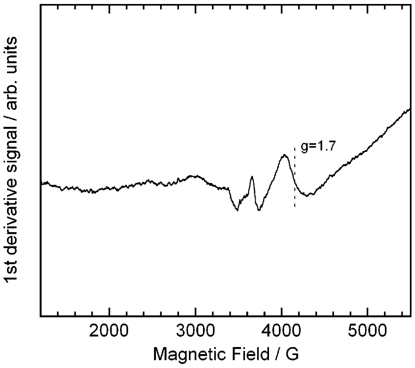

Figure 3. ESR spectrum of the glass melted at 1400 °C. A broad singlet signal ($g = 1.7$) was assigned to W^{5+}, and it was a major paramagnetic species.

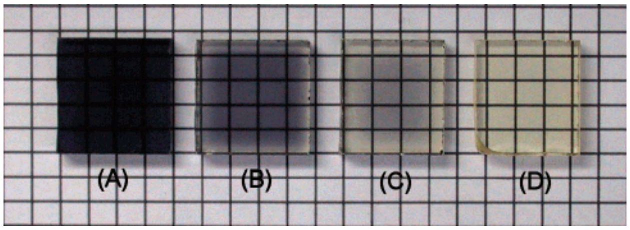

Figure 4. Photographs of the glasses heat-treated at 500 °C for different times in dry air. The heat-treatment times are (A) 0 h, (B) 1 h, (C) 4 h, and (D) 16 h. The colored glasses melted at 1400 °C were bleached from the surface during the heat treatments.

equilibrium of transition metal cations and p-block ions observed in glass-forming oxide melts. Here, however, an alternative redox reaction of W ions in the glass will be proposed, that is, dissociation of water vapor at the surface of the glass, selective dissolution, and diffusion of the hydrogen atom into the glass, and the reaction of the hydrogen with W ions in the glass.

3.2. Discoloration of the Colored Glass by Annealing at Temperatures below T_g. As-melted and colored glasses prepared in section 3.1 were bleached by the heat treatment in air at temperatures far below T_g. In this experiment, the glasses melted at 1400 °C for 2 h were used. Figure 4 shows photographs of the glasses before and after the heat treatments at 500 °C for different times in dry air. The color of the as-melted glass was uniformly dark blue, and the glass was bleached from the surface during the heat treatment. A gradient of coloration intensity was discernible in the glasses after the heat treatment for 1 and 4 h. This is thought to be an indication that the decoloration reaction, oxidation of W^{5+} to W^{6+}, is diffusion limited. The glass after the heat treatment for 16 h was completely bleached, and the color changed to pale yellow, which was the same color with that of the glass melted at 1100 °C.

On the basis of this observation, we assume that the oxidation of W^{5+} is diffusion limited, although the diffusing species remains unidentified at the present stage. The diffusion constant of the coloring species, which played as a reducing species or an electron donor for W^{6+}, was determined by the following method. Assuming the rate of the decoloration process is limited by one-dimensional diffusion of the coloring species with zero surface concentration, the total number (optical absorption intensity) of the coloring species within a unit cross section along the optical pass ($M(t)$) in the glass is given by the following equation as a function of heat-treatment time (t),[12]

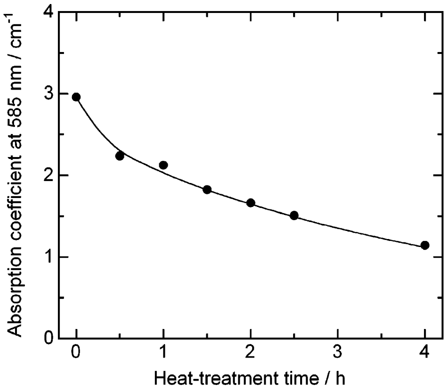

Figure 5. Changes in the optical absorption intensities of the glasses are plotted as a function of heat-treatment time. The colored glasses melted at 1400 °C were heat-treated at 500 °C for different times in air. The symbol (●) shows the experimentally observed intensities, and the solid line denotes the result calculated using eq 3.

$$M(t) = M_0 \sum_{n=0}^{\infty} \left\{ \frac{8}{(2n+1)^2 \pi^2} \right\} \exp \left\{ \frac{-D(2n+1)^2 \pi^2 t}{4l^2} \right\} \quad (3)$$

where M_0, D, and l denote the initial total number (initial optical absorption intensity) of the coloring species within a unit cross section along the optical pass, the diffusion constant of the coloring species, and the half-thickness of the glass, respectively. Figure 5 shows changes in the optical absorption intensities of the glasses as a function of heat-treatment time. The symbol (●) shows the experimentally observed intensities and the solid line denotes the result calculated using eq 3. An excellent fit was obtained between the measured intensities and the theoretical estimation. The diffusion constant of the coloring species in the glass at 500 °C was found to be 1.4×10^{-6} cm^2/s from the simulation. The diffusion constant was comparable to that of hydrogen in silica glass,[15] which is the known highest transport of gas species in oxide glasses except for rare gases. The similar decoloration was also observed at temperature as low as 300 °C, which is 270 °C lower than T_g. Decoloration is assumed to originate from the oxidation of W^{5+} to W^{6+}. However, it is incredible that the extraordinarily fast diffusion of oxygen from air to the glass occurs at the low temperature far below T_g.[13,14]

Here, we tentatively propose that the diffusing species is the hydrogen atom, and the decoloration reaction would be expressed by the following reaction,

$$W^{5+}{}_{G} + H^{+}{}_{G} \rightarrow W^{6+}{}_{G} + {}^{1}/{}_{2}H_2(g) \quad (4)$$

where the evolved hydrogen gas may react with oxygen to form a water molecule in the case of heat treatment under air.

The electron released from the hydrogen atom does not always reside on a single W ion but migrates on neighboring

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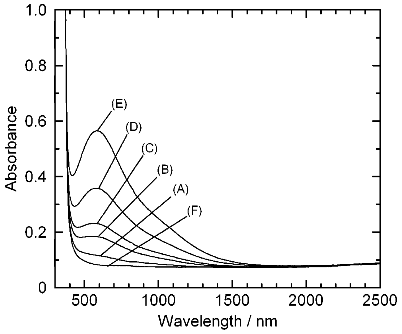

Figure 6. Optical absorption spectra of the glasses heat-treated at different temperatures for 3 h in water vapor. The bleached glass was used for the heat treatments. The heat-treatment temperatures are (A) 300 °C, (B) 350 °C, (C) 400 °C, (D) 450 °C, and (E) 500 °C. Glass F was obtained by heat-treating glass E at 500 °C for 24 h in dry air.

W^{6+} ions such as in tungsten hydrogen bronze.[16,17] The degree of the localization depends mostly on concentration of W^{6+} in the glass, that is, the average distance between two neighboring W^{6+} ions. A proton is thought to be located around a nearby W^{5+} ion for charge compensation. The charge-compensating pair of H^+_G and W^{5+}_G is hereafter abbreviated as $(W^{5+}/H^+)_G$.

In eq 4, H^+_G is supposed to originate from water, because the glasses are prepared under ambient air by using the raw materials which contained adsorbed water, as mentioned in section 3.1. The present view will be confirmed in the following section.

3.3. Coloration under Water Vapor Annealing and Decoloration of the Water-Colored Glass under Dry Air Annealing below T_g. In the present experiments the bleached glass plates explained in section 3.2 were used as a starting sample. The opposite surfaces were ground slightly to enhance the reactions of the glass with ambient gaseous species. Optical absorption spectra of the glasses heat-treated under water vapor at 300−500 °C for 3 h are shown in Figure 6. It is clearly seen that exactly the same optical absorption was induced for the glasses heat-treated at a temperature as low as 300 °C. Heat treatment in N_2 induced no change in the optical absorption. The induced optical absorption of the water vapor-annealed glass was bleached by the heat treatment at 500 °C under dry air for 24 h (F in Figure 6), this being the similar observation with the decoloration of the as-melted glasses mentioned in section 3.2.

In parallel with the formation of the optical absorption band the ESR singlet due to W^{5+} was seen for the water vapor-treated glasses. The average absolute spin concentration of W^{5+} in the glass heat-treated at 500 °C was calculated as 2.0×10^{17} cm^{-3} from the estimated absorption cross section given in section 3.4. No significant change was detected in intensities of the infrared absorption due to OH groups for the colored glasses. This would result from the fact that the concentration of induced W^{5+} was 2 orders of magnitude lower than that of the OH (1.2×10^{19} cm^{-3}) impurity and/or that the charge-compensating H^+_G did not exist as OH groups. We tried to detect the dissolved and charge-compensating hydrogen by using IR absorption and MAS NMR measurements,[18,19] but this was unsuccessful. The difficulty seems to originate from the very low concentration of the dissolved hydrogen, in the order of 10^{17} cm^{-3}.

Although the charge-compensating species remains unidentified yet, it is thought to be appropriate that the proposed reaction mechanisms for the coloration−decoloration of the tungsten phosphate glasses heated below T_g are shown in the following reactions. In the coloration process, ambient water vapor is decomposed by the glass at the surface following eq 2.The generated hydrogen atoms are selectivity dissolved in the glass by the following reaction with W^{6+}, while the oxygen molecule remains in air

$$H_S + W^{6+}{}_G \rightarrow (W^{5+}/H^+)_G \qquad (5)$$

The charge-compensating pair $(W^{5+}/H^+)_G$ is responsible for the optical absorption. The decoloration mechanism is the reverse of eqs 2 and 5, and the total reaction is expressed by

$$\text{(decolored) } W^{6+}{}_G + {}^1/_2H_2O(g) \leftrightarrow (W^{5+}/H^+)_G + {}^1/_4O_2(g) \text{ (colored)} \qquad (6)$$

The rate of the coloration−decoloration is determined by the diffusion of the dissolved atomic hydrogen.

3.4. Coloration of the Bleached Glass by the Reaction with Hydrogen Diffused through Pd Coating at Temperatures below T_g. In the previous section it was strongly suggested that the hydrogen extracted from water vapor is a candidate of the reducing species for the W^{6+} in the glasses. To further confirm the reaction models proposed in section 3.3 another coloration experiment was carried out by restricting the chemical species migrating to the reacting surface of the glasses to be hydrogen atom exclusively. As is well-known, Pd dissociates the H_2 molecule at the surface and dissolves the hydrogen atom. A thin layer of Pd was deposited on a single surface of the bleached glass, and the glass is heat-treated at 400 °C for 1 h in 3.5% H_2–96.5% N_2. Under this condition the Pd-coated glass surface feels the equivalent pressure of atomic hydrogen determined from the absorption−desorption equilibrium of Pd with the partial pressure of hydrogen in the ambient.

As shown in Figure 7 the strong optical absorption band peaking at 600 nm was induced for the Pd-coated glass. The slight red shift of the peak wavelength is thought to be due to the larger contribution of the intervalence excitation. For comparison, the spectrum for the glass without a Pd coating and similarly heat-treated is also shown in the figure. Very weak but the same optical absorption was observed in the naked glass. This observation indicates that the glass has a function of decomposing molecular hydrogen in addition to dissociating molecular water. The intensity of coloration was found to decrease by the additional heat treatment at 400 °C for 1 h under the ambient with lower partial pressure of

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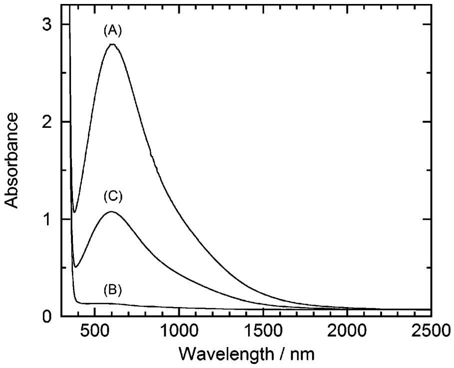

Figure 7. Optical absorption spectra of the (A) Pd-coated and (B) naked glasses heat-treated at 400 °C for 1 h in 3.5% H_2–96.5% N_2. Glass C was obtained by heat-treating glass A at 400 °C for 1 h in N_2.

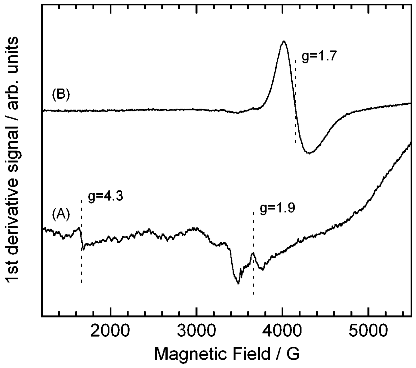

Figure 8. ESR spectra of the bleached and Pd-coated glass (A) before and (B) after the heat treatment at 400 °C for 1 h in 3.5% H_2–96.5% N_2. A broad signal ($g = 1.7$) assigned as W^{5+} was clearly discernible in glass B.

molecular hydrogen such as dry N_2 (C in Figure 7). The decoloration can be explained by the reaction expressed by eq 4.

Figure 8 shows the ESR spectra of the Pd-coated glass before and after the heat treatment. A large anisotropic singlet ($g = 1.7$) assigned as W^{5+} was induced in the glass after the heat treatment under the forming gas, but small signals of Fe^{3+} ($g = 4.3$),[20] Mo^{5+} ($g = 1.9$),[21] and VO^{2+}($g = 1.9$)[22] were detected in the glass before the coloration. These ions were thought to be due to impurities derived from the raw materials,[20,21] and the concentrations were found to be in the order of 10^{16} cm^{-3}. The results are reasonable because Fe^{3+} and V^{4+} are thought to be species that are more easily reduced than W^{6+} and the redox equilibrium of Mo^{6+} is almost comparable with that of W^{6+}.[23,24] It should be noted that no signal assigned as Nb^{4+} was detected in both spectra.[25]

To determine the cross section of the optical absorption band of W^{5+}, several glasses with the different concentrations

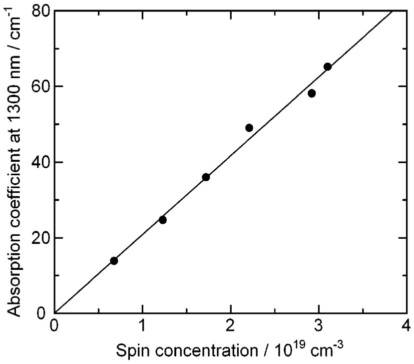

Figure 9. Relationship between the optical absorption intensity at 1300 nm and the absolute spin concentration of ESR absorption with $g = 1.7$. The optical absorption cross section at 1300 nm was found to be 2.1×10^{-18} cm^2/W^{5+} from the slope of the line.

of W^{5+} were prepared by the same method. Since the optical absorption intensities at peak wavelength were too strong to be directly measured, those at 1300 nm were used for the evaluation. The relationship between the optical absorption intensities at 1300 nm and the absolute spin concentrations of the ESR absorption with $g = 1.7$ is displayed in Figure 9. The straight line through the origin was obtained, and the optical absorption cross section at 1300 nm was found to be 2.1×10^{-18} cm^2/W^{5+} from the slope of the line.

The cross section at around 600 nm was estimated in the following way. The peak wavelength of all colored glasses used for the evaluation should be around 600 nm, because the total line shape of the optical absorption bands was found to be exactly the same in the measurable range. Therefore, the optical absorption cross section at around 600 nm can be obtained from the known ratio of the absorption intensities at 600 and 1300 nm, and the value was estimated as 1.5×10^{-17} cm^2/W^{5+}.

It is convenient, here, to use the Pd-coated glass for evaluation of the diffusion constant of atomic hydrogen in the glasses because of their strong optical absorption. Assuming the coloration process is a one-dimensional diffusion of the atomic hydrogen with constant surface concentration (C_0), the concentration of the hydrogen ($C(x)$) in the form of $(W^{5+}/H^+)_G$ as a function of distance (x) from the surface is given by the following equation,[26]

$$C(x) = C_0\left(1 - \mathrm{erf}\frac{x}{2\sqrt{Dt}}\right) \tag{7}$$

where D and t denote diffusion constant and heat-treatment time, respectively. The optical absorption intensity at 600 nm as a function of distance from the surface is shown in Figure 10. The symbol (●) shows the experimentally observed intensity profile and the solid line is the result calculated from eq 7. A surprisingly beautiful fit was obtained between the observed and calculated. The diffusion constant of the hydrogen atom at 500 °C was thus calculated to be 1.3×10^{-6} cm^2/s. This value is almost the same as that obtained in section 2.2.

From the results obtained in sections 3.3 and 3.4 it is inferred that the reaction model proposed in section 3.3 is

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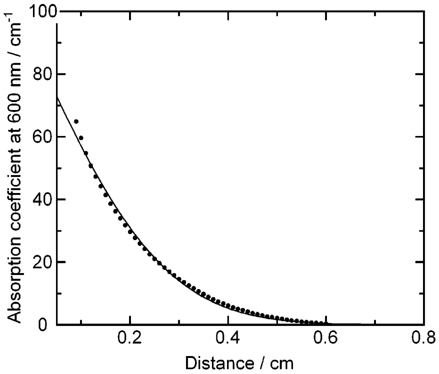

Figure 10. The depth profiles of the optical absorption intensities estimated at 600 nm. The symbol (●) shows the experimentally observed intensity profile, and the solid line denotes the result calculated using eq 7.

reliable at least in the temperature region below T_g, that is, W^{6+} at the surface of the glasses works for dissociating molecular water and for dissolving the generated atomic hydrogen by extracting an electron from the hydrogen.

3.5. Some Additional Remarks on the Coloration. *3.5.1. Niobium in the Glass.* No Nb^{4+} was discernible in the ESR measurements, and therefore niobium in the glass is not the coloring species. However, it was preliminary found that Nb in the glass affected the diffusion constant of atomic hydrogen.[27] The diffusion constant monotonically decreased with substituting W for Nb, and the value for the Nb free glass was 2.8×10^{-7} cm^2/s at 500 °C.

3.5.2. Coloration−Decoloration Model. This model seems to be applicable up to the melting temperature (above the T_g), but the redox reaction associated with oxygen simultaneously occurs in the melts. Therefore, we must take into consideration the competition between the reaction proposed in the present paper and redox reactions relating to oxygen.

3.5.3. Charge-Compensating H^+_G. Trials for determining the chemical state of the charge-compensating H^+_G were unsuccessful. This is the most important problem for determining the reaction mechanisms of the coloration−decoloration of the glasses. It is strongly requested to increase the concentration of H^+_G by several orders of magnitude or to devise an experimental technique which can detect hydrogen of such low concentration.

4. Conclusion

It was found that reversible coloration−decoloration of tungsten phosphate glasses at temperatures far below T_g was induced by controlling the partial pressures of water in the ambient. In the coloration a water molecule is dissociated at the surface of the glasses, and the hydrogen atom is dissolved in the glass by reacting with W^{6+} generating the color center in the form of $(W^{5+}/H^+)_G$. Decoloration in the annealing under air is expressed by the reverse reactions of the coloration. The rate of the coloration−decoloration depends on the diffusion constant of the atomic hydrogen in the glass.

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