Ion-Exchange Treatment of Glass Surface in NaNO₃–TlNO₃ Molten Salt

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To make functional glasses, ion-exchange treatment of the glass surface was carried out in TlNO₃-NaNO₃ molten salt at 673 K and 723 K for various time periods, and then the Tl ions embedded in the glass were reduced to metallic Tl nanoparticles by hydrogen gas. The color of the glass containing metallic Tl nanoparticles changed to brown or black. The Tl nanoparticles were detected by a qualitative TEM analysis. The optical absorption spectra of these treated glasses showed a peak at about 370 nm. With increases in the temperature of the molten salt, the band intensity of the absorption is enhanced. The absorption increase may correspond to larger particle sizes and densities with the increase in temperature. The Tl nanoparticles with 10-150 nm diameter were observed at neighboring parts of the glass surface by TEM and FE-SEM.

Key Words : Thallium, Ion-exchange, Absorbance

1 Introduction

Introducing metallic nanoparticles such as gold, silver, and copper into glass has been used for coloring glasses and fabricating functionally useful glasses. A wide variety of functional glasses have been produced by three methods, such as ion implantation, sol-gel coatings, and ion-exchange treatment. The ion implantation forms a modified surface layer at high ion concentrations on glass. 1-3 Therefore, this method is effective to make functional glass with a very thin surface modification layer. The sol-gel coating is formed by hydrolysis and condensation of metal alkoxides, such as Si, Ti, Al, and Zr. 4-6 Optical filters have been produced by coating of sol-gel films containing noble metal nanoparticles, e.g., Au, Ag, and Cu, and their compounds on glasses. 7-9 A major advantage of this approach is its tailoring ability by appropriately choosing the non-hydrolyzable part, however the thickness of the film formed on the glass surface by one coating process is restricted to 0.1 to 0.2 μm. Repetition of the sol-gel processes is required for obtaining a thicker coated film. 10 Another traditional method for producing functional glasses is the ion-exchange treatment. In this method, a glass sheet is immersed in a molten salt at a relatively high temperature and alkaline metal ions are exchanged with metal ions in the molten salt at the surface layer. This treatment has been applied to chemical strengthening of glasses, flat waveguides, and gradient index lenses. 11 There are a few studies on introducing optical filters to glasses using this method. Pask et al. prepared glass including Tl by immersing in Thallium sulfate and found that the glasses exhibited non absorption and had surface layers with differential refraction indices. 12 Ishii et al. used sulfate molten salt with 10 mol% Tl₂SO₄–45% K₂SO₄–45% ZnSO₄ to produce brown–black glasses by ion-exchange in the molten salt followed by hydrogen reduction. They concluded that this coloration is due to the formation of 50-100 nm size Tl particles at the neighboring parts of the surface of the glass. 13

This paper reports the formation and characterization of Tl nanoparticles in glass by the ion-exchange treatment and subsequent hydrogen reduction. Especially, the paper focuses on the relation between the optical absorption properties of the glass, the condition of the ion-exchange, and the size of Tl nanoparticles as a basic study of developing the optical filter which selectively absorb the light of a particular wavelength.

2 Experimental

Glass samples for the ion-exchange were B270 super white from DESAG composed of (wt%): 68SiO₂, 9Na₂O, 8K₂O, 7CaO, 2BaO, 4ZnO, 1TiO₂, and 15B₂O₃ and cut into 20 mm × 20 mm × 2 mm. The glass samples were immersed in a molten salt bath formed by a mixture of 10 mol% TlNO₃ (Kanto chemicals, 99.5%) and 90 mol% NaNO₃ (Kanto chemicals, 99%) for 2, 4, 8, and 16 hours at temperatures of 673 K and 723 K. During immersion, the Tl ions of the molten salt bath diffuse into the glass replacing mainly the alkali metal ions. After the ion-exchange, samples were gradually cooled to room temperature with heating to prevent cracks and then washed with water to remove surface impurities. To reduce the Tl ions in the glass matrix to metallic Tl nanoparticles, the ion exchanged samples were treated in a hydrogen atmosphere for 1 hour at 803 K.

The transmittance of the glass samples thus treated was recorded using a UV/Vis/NIR spectrophotometer (JASCO Co. V570) at room temperature in the 300-1200 nm wavelength region. Cross-sections of the samples were observed using a transmission electron microscope (TEM, JEOL 2010F) and a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6500F). A qualitative analysis was demonstrated by Analytical electron microscopy.
3 Results

Without the ion-exchange process, the glass samples were colorless and had no measurable absorption in the recorded region. The degrees of coloration of the glasses which had been ion-exchanged under various conditions and reduced by hydrogen, are shown in Fig. 1. The samples without hydrogen reduction and the sample ion-exchanged at 673 K for 2 hours followed by hydrogen reduction are not colored. However, the color of the other glasses was changed from light brown to black with longer durations of immersion. The coloration was also changed with increases in the temperature for the immersion treatment.

To reveal the optical absorption property of the treated samples, transmittance spectra of the samples were recorded. The transmittance, \( T \), measured was converted to absorbance, \( A \), from the following

\[
A = -\log \left( \frac{T}{T_0} \right)
\]

where \( T_0 \) is the transmittance of the untreated glass.

The absorbance vs. wavelength is shown in Figs. 2 and 3 for the samples which were treated in the molten salt for various durations at 673 K (Fig. 2) and 723 K (Fig. 3). It is found that all the samples exhibit a spectral peak at approximately 370 nm wavelength. When glass samples are immersed in the molten salt at 673 K and 723 K for the longer durations, the absorbance band is larger and wider. A comparison of Figs. 2 and 3 show an increase in absorbance with higher temperature of molten salt for the same immersion duration.

The FE-SEM photographs of the cross-section of the

![Fig. 1](image1.png)  
Fig. 1 Glass coloration after ion-exchange for (a) 2 h, (b) 4 h, (c) 8 h, and (d) 16 h at 673 K; and (e)(h) for the same immersion durations at 723 K; all with subsequent hydrogen reduction for 1 hour at 803 K.

![Fig. 2](image2.png)  
Fig. 2 Absorbance of glass ion-exchanged at 673 K for various durations and subsequently reduced by hydrogen.

![Fig. 3](image3.png)  
Fig. 3 Absorbance of glass ion-exchanged at 723 K for various durations and subsequently reduced by hydrogen.

![Fig. 4](image4.png)  
Fig. 4 Cross-sectional FE-SEM images of glass ion-exchanged at 723 K for (a) 4 h, (b) 8 h, and (c) 16 h and subsequently reduced by hydrogen.
glass that was ion-exchanged at 723 K for various durations and reduced by hydrogen are shown in Fig. 4 (a)-(c). These photographs were taken at the point of around 10 μm below the surface with FE-SEM, here 20-150 nm Ti particles are observed as bright points in Fig. 4 (a) and (b). With longer immersion, there is a greater number of larger Ti nanoparticles. However, the average size of the Ti particles observed is about 30 nm in Fig. 4 (c) and they are uniformly embedded at the point in the glass. From Fig. 4, the density of Ti particle is calculated, (a) $1.6 \times 10^{13}$, (b) $4.2 \times 10^{13}$, and (c) $1.2 \times 10^{13}$ particles per cm$^2$. The Ti nanoparticles were also observed by TEM. From the TEM, smaller Ti particles can be seen in the samples treated in the same manner, as shown in Fig. 5. In the Ti particles, Ti atoms are regularly arranged. The particles were confirmed to consist of Ti atoms, by analytical TEM as shown in Fig. 6.

4 Discussion

The coloration of the treated glass is due to the reduced metallic Ti particles. As shown in Fig. 1, the glass color becomes darker under conditions where they are immersed in higher temperature baths and/or for longer durations. This tendency is due to the higher density of Ti particles. The number of metallic Ti particles is larger, when the temperature of the molten salt is higher and the immersion duration is longer, because the process of this ion-exchange is based on inter-diffusion of Ti ions from the molten salt to the glass and alkaline metal ions and vice versa. Since the coloration of the glass does not occur by ion-exchange at 673 K for 2 hours, it is suggested that 2 hours of immersion is not sufficient to diffuse the required amount of Ti ions into the glass for coloration. Prolonging the immersion duration and increasing the temperature of the molten salt, the absorption band becomes wider. This can be explained with the large variety of Ti nanoparticle sizes in the glass, since the peak wavelength optical absorption may correspond to the particle size. Generally, after the ion-exchange treatment, the Ti ions in the samples distribute from high concentrations at the surface to low concentrations at the inside. With increases in the diffusion rate as a function of the temperature, the Ti ion concentration is distributed in a wider region. Since the higher concentration of Ti ions may introduce the larger sizes of metallic Ti particles by the hydrogen reduction, the increased distribution of particle sizes may be expected for the higher temperature and longer immersion. Therefore, the glass ion-exchanged at higher temperatures for longer immersion durations is assumed to have a wider range of Ti particle sizes and an expanded optical absorption band. In addition, if the particle distribution is controllable, it will be possible to produce glass filters absorbing around the 370 nm wavelength which is shorter than the spectral peak of around 420 nm for Ag nanoparticle dispersed glass and glass filters which absorb longer wavelength could also be produced.

There are Ti nanoparticles of 20–150 nm size embedded in the glass as shown in Fig. 4 (a) and (b). This wide range of Ti particle sizes is due to the ion-exchange process as discussed. However, as shown in Fig. 4 (c), an average of about 30 nm Ti nanoparticles was observed in the glass. This can be explained by Ti ion diffusion in the glass matrix. During the ion-exchange treatment, Ti ions diffused from the molten salt move further into the glass to prevent locational bias of the Ti ion concentration. Comparably longer immersing durations, 16 hours, make Ti ions uniformly dispersed.

5 Conclusion

Ion-exchange treatment of glass and subsequent hydrogen reduction were carried out to successfully prepare glass containing Ti nanoparticles by immersion in TINO$_2$-NaNO$_3$ molten salt followed by hydrogen reduction, except for the sample ion-exchanged at 673 K for 2 hours and reduced by hydrogen at 803 K for 1 hour. The glass samples were colored by the ion-exchange in the nitrate molten salt bath containing Ti ions and the subsequent hydrogen reduction. The color varied from light brown to black with increasing ion-exchange duration and temperature. The spectral peak of the glass samples

![Fig. 5](image1.png)

**Fig. 5** TEM image of glass ion-exchanged at 723 K for 16 h and subsequently reduced by hydrogen.

![Fig. 6](image2.png)

**Fig. 6** Results of the Analytical electron microscopic analysis for Ti nanoparticles.
prepared under all the conditions was about 370 nm. The intensity of the absorbance due to the Tl nanoparticles formed in the glass was increased and the optical absorption band became wider when the immersion duration of the ion-exchange was longer and the ion-exchange temperature was higher. The average Tl nanoparticle size at the point of 10 μm below the glass surface was about 30 nm and the particles here were uniformly embedded on the condition with the ion-exchange temperature at 723 K and the immersion duration 16 hours.

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References
1) S. Sakka, GARASUKAGAKU NO KISO TO OYO, Uchida Rokakuho Publishing CO, LTD., Japan, p.73 (1997).
9) A. Ishii and K. Aikawa, Reports of the Research Laboratory, Asahi Glass, 15, 97 (1965).