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STRUCTURE AND PROPERTIES OF TiO$_2$-SiO$_2$ AND TiO$_2$-GeO$_2$ GLASSES

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Abstract. - The coordination of Ti$^{4+}$ ions in the low expansion TiO$_2$-SiO$_2$ glasses made from metal alkoxides by the sol-gel technique and TiO$_2$-GeO$_2$ glasses made by melting was investigated on the basis of the observation of crystallization behavior and the infrared spectroscopy. The α-cristobalite type SiO$_2$ and α-quartz type GeO$_2$ crystals containing 4-fold coordinated Ti$^{4+}$ ions precipitated in the TiO$_2$-SiO$_2$ and TiO$_2$-GeO$_2$ glasses. Infrared spectra of the glasses were very similar to the corresponding crystallized products. These facts suggest that the Ti$^{4+}$ ions in the TiO$_2$-SiO$_2$ glasses are 4-fold coordinated with oxygens as in the glasses made by the high temperature flame-spray technique, and that Ti$^{4+}$ ions in the TiO$_2$-GeO$_2$ glasses are also in 4-fold coordination.

1. Introduction.

The TiO$_2$-SiO$_2$ glasses made by the flame-spray technique show ultra-low thermal expansion coefficients$^{[1]}$. The present authors$^{[2,3]}$ have reported that the glasses of the same system made from metal alkoxides by the sol-gel technique also show low thermal expansion coefficients. The addition of TiO$_2$ to GeO$_2$ glass which is composed of three-dimensional networks of GeO$_4$ tetrahedra has been found to cause lowering of the thermal expansion$^{[4]}$.

In the present work, the coordination of Ti$^{4+}$ ions in the TiO$_2$-SiO$_2$ glasses made by the sol-gel technique and the TiO$_2$-GeO$_2$ glasses made by melting was investigated on the basis of crystallization behavior and infrared spectroscopy.

2. Experimental.

2.1 Glasses. - Silicon tetraethoxide Si(OC$_2$H$_5$)$_4$ and titanium tetra-isopropoxide Ti(O-i-iso-C$_3$H$_7$)$_4$ were used as raw materials for the TiO$_2$-SiO$_2$ glasses. Gels made by hydrolyzing the mixtures of these alkoxides were converted to glasses by heating to 900°C$^{[2,3]}$.

The mixtures of TiO$_2$ and GeO$_2$ powders were melted in platinum crucibles at 1500 - 1550°C for 2 or 3 hours. The clear TiO$_2$-GeO$_2$
glasses containing up to about 10 mol% TiO₂ resulted.

The compositions, thermal expansion coefficients and densities of those glasses are listed in Table 1.

Table 1. Compositions, thermal expansion coefficients α and densities of the TiO₂-SiO₂ and TiO₂-GeO₂ glasses

<table>
<thead>
<tr>
<th>TiO₂-SiO₂ TiO₂ (mol%)</th>
<th>α (10⁻⁷/°C)</th>
<th>density (g/cm³)</th>
<th>TiO₂-GeO₂ TiO₂ (mol%)</th>
<th>α (10⁻⁷/°C)</th>
<th>density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+ 5.4</td>
<td>2.20</td>
<td>0</td>
<td>74.8</td>
<td>3.670</td>
</tr>
<tr>
<td>2.3</td>
<td>+ 1.3</td>
<td>2.197</td>
<td>3.2</td>
<td>70.8</td>
<td>3.588</td>
</tr>
<tr>
<td>3.8</td>
<td>- 1.6</td>
<td>2.157</td>
<td>6.4</td>
<td>63.7</td>
<td>3.555</td>
</tr>
<tr>
<td>6.2</td>
<td>- 0.7</td>
<td>2.166</td>
<td>9.6</td>
<td>58.7</td>
<td>3.498</td>
</tr>
<tr>
<td>7.7</td>
<td>- 4.3</td>
<td></td>
<td>12.7</td>
<td>54.9</td>
<td>3.475</td>
</tr>
</tbody>
</table>

2.2 Crystallization. - The TiO₂-SiO₂ glasses were crystallized by heating in the air at 1450°C for 2 hours. The TiO₂-GeO₂ glasses were crystallized by heating at 1100°C for 15 hours. The lattice constants of the precipitated crystals were determined by X-ray diffraction.

2.3 Measurement of IR spectra. - Infrared spectra of the TiO₂-SiO₂ and TiO₂-GeO₂ glasses and crystallized products were measured using KBr pellets of those glasses and crystals.

3. Results.

3.1 Crystals precipitating in the glasses. - Only the tetragonal, α-cristobalite type SiO₂ crystal precipitated in the TiO₂-SiO₂ glasses containing up to 6.2 mol% TiO₂. In the glasses of the TiO₂ content larger than 7.7 mol%, small amounts of anatase precipitated along with the α-cristobalite type crystal. The lattice constants a₀ and c₀ of the crystal are shown in Fig.1 as a function of the TiO₂ content. The broken lines in Fig.1 show the results⁵) reported for the TiO₂-SiO₂ glasses made by the flame-spray technique. The deviation of the lattice constants from linearity at 7.7 mol% TiO₂ is ascribed to the coprecipitation of anatase crystal in the glass. The linear relation between the lattice constants and the TiO₂ content indicates that Ti⁴⁺ ions substitute for Si⁴⁺ ions of the cristobalite crystal, i.e., Ti⁴⁺ ions are 4-fold coordinated with oxygens.

The hexagonal, α-quartz type GeO₂ precipitated in the TiO₂-GeO₂ glasses containing up to 8 mol% TiO₂. In the glasses with larger TiO₂ contents a slight amount of rutile type GeO₂ coprecipitated with hexagonal GeO₂ crystal. The change of lattice constants a₀ and c₀ with the TiO₂ content is shown in Fig.2. The linear relation found for the glasses containing up to about 8 mol% TiO₂ indicates that Ti⁴⁺ ions substitute for Ge⁴⁺ ions in the α-quartz type GeO₂ and that Ti⁴⁺ ions are also in 4-fold coordination in that crystal. The coprecipitation of the rutile type GeO₂ at 9.6 mol% TiO₂ causes the deviation of lattice constants from the linearity.

3.2 Infrared spectra. - Infrared spectra of the TiO₂-SiO₂ glasses and corresponding crystals are shown in Fig.3. The TiO₂-containing SiO₂ glasses show an additional absorption peak around 950 cm⁻¹ in the SiO₂ crystals containing TiO₂. The broad absorption band around 650 cm⁻¹ of the crystal with 7.7 mol% TiO₂ is attributed to the coexisting anatase crystal.

The spectra of the TiO₂-GeO₂ glasses and crystals are shown in Fig.4. A small hump around 800 cm⁻¹ is observed in the glasses containing TiO₂, overlapping on the major peak of 875 cm⁻¹ assigned to Ge-O-Ge stretching vibration. The similar hump can be seen around 800 cm⁻¹ for the crystals containing TiO₂.
4. Discussion

Evans31 has shown that α-cristobalite in which some portion of Si⁴⁺ ions are replaced with 4-fold coordinated Ti⁴⁺ ions precipitates in the TiO₂-SiO₂ glasses made by flame-spray method, suggesting that Ti⁴⁺ ions are in 4-fold coordination even in the glass state. Sandstrom et al.6) have revealed by EXAFS technique that Ti⁴⁺ ions are in 4-fold coordination in those glasses.

The crystallization behavior and infrared spectra of the alkoxy-derived TiO₂-SiO₂ glasses agreed well with those5,7 of the glasses made by melting. Furthermore, infrared spectra of the glasses were very similar to those of the crystallized products which contained 4-fold coordinated Ti⁴⁺ ions. Then it is concluded that Ti⁴⁺ ions in the alkoxy-derived TiO₂-SiO₂ glasses are 4-fold coordinated with oxygens, constructing three-dimensional networks together with Si⁴⁺ ions. The infrared absorption peak around 950 cm⁻¹ is clearly associated with the 4-fold coordinated Ti⁴⁺ ions.

As already shown, the thermal expansion coefficient factor of TiO₂ in the TiO₂-GeO₂ glasses is identical with that in the TiO₂-SiO₂ glasses, implying that the coordination state of Ti⁴⁺ ions of the former glasses is the same as that of the latter glasses4). The precipitation of hexagonal GeO₂ crystal in which some portion of Ge⁴⁺ ions are replaced by 4-fold coordinated Ti⁴⁺ ions and the similarity of the infrared spectra of the TiO₂-GeO₂ glasses to those of precipitated crystals lead to the conclusion that Ti⁴⁺ ions in the TiO₂-GeO₂ glasses are 4-fold coordinated by oxygens.

The Ge⁴⁺ ions in GeO₂ glass changes coordination state from 4 to 6-fold when alkali oxides are added8). The infrared peak at 875 cm⁻¹ due to Ge-O-Ge bond has been shown to shift toward lower wavenumbers on addition of an alkali oxide at a rate of about 100 cm⁻¹ for 10 mol% alkali oxide. The peak at 875 cm⁻¹ remains unchanged upon addition of TiO₂ as can be seen in Fig.4, showing that the coordination state of Ge⁴⁺ ions would not change on addition of TiO₂.

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Fig. 3: Infrared spectra of the glasses (——) and precipitated crystals (-----) of the TiO$_2$-SiO$_2$ system.

Fig. 4: Infrared spectra of the glasses (——) and precipitated crystals (-----) of the TiO$_2$-GeO$_2$ system.

References
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