JOURNAL OF MATERIALS SCIENCE 18 (1983) 3137–3142

Preparation of titania–silica glasses by the gel method

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A series of bulk glasses in the TiO_2–SiO_2 system have been prepared by hydrolysing the mixture solution of $Ti(OC_3H_7)_4$ and $Si(OC_2H_5)_4$ with water and hydrochloric acid, and slowly heating the resultant gels up to 800° C. The conversion of gels to glasses was examined by the measurements of Vickers' hardness, IR and TGA. The properties of TiO_2–SiO_2 glasses in the less than 12.9 wt % TiO_2 range obtained by the gel method were very similar to those of oxide glasses made by the flame hydrolysis process. These glasses showed ultra-low thermal expansion, but the precipitation of anatase remarkably increased the thermal expansion. In the less than 10.4 wt % TiO_2 range, the glasses obtained by heating up to 800° C were not crystallized at 1000° C or higher, while in the more than 20 wt % TiO_2 range anatase was precipitated at 900° C. It was found that glasses obtained by the gel method were a true solid solution at least up to 7.4 wt % TiO_2 composition.

1. Introduction

The TiO_2–SiO_2 glasses containing TiO_2 up to about 10 wt % are known to show ultra-low thermal expansion. A series of glasses in the TiO_2–SiO_2 system has been prepared by the flame hydrolysis process [1]. Clear glasses containing TiO_2 up to about 16.5 wt % were obtained, but more TiO_2 caused opacity due to phase separation and anatase/rutile crystallization during glass formation. As very high melting temperature (about 1750° C) and specially designed apparatus are required for making these glasses by the flame hydrolysis process, the use of these glasses, in spite of their extreme desirability, is not widespread. Therefore, the formation of glasses in the TiO_2–SiO_2 system from titanium and silicon alkoxides has been investigated by Kamiya and Sakka [2, 3], Yoldas [4] and Yamane *et al.* [5]. But the conditions to make monolithic glasses and the characterization of the glasses has not been sufficiently established yet. As the hydrolysis rate of silicon alkoxide is very slow, compared with that of titanium alkoxide, a differential precipitation of titanium hydroxide occurs during hydrolysis by the rapid addition of water. Therefore, the amount of water and its adding speed must be strictly controlled to obtain homogeneous gels.

The purpose of this investigation was to prepare TiO_2–SiO_2 monolithic glasses and to characterize the glasses obtained by the gel method.

2. Experimental procedures

2.1. Preparation and heat treatment of gels

Titanium tetraisopropoxide, $Ti(O^iPr)_4$, and silicon tetraethoxide, $Si(OEt)_4$, were used as raw materials. The compositions of the glasses in the binary system are shown in Fig. 1. The desired amounts of $Ti(O^iPr)$ (0.01 to 0.05 mol) and $Si(OEt)_4$ (0.20 to 0.25 mol) were mixed in 150 cm^3 of ethanol at room temperature. The mixture of water and the catalyst, hydrochloric acid, diluted with 30 cm^3 of ethanol, was added very slowly under vigorous stirring to the alkoxides mixture for hydrolysis. The molar ratios of water and hydrochloric acid to alkoxides were 2:50 and 0.01:0.5, respectively. The resulting clear solution was transferred to teflon beakers and covered with thin plastic films having several pin-holes to con-

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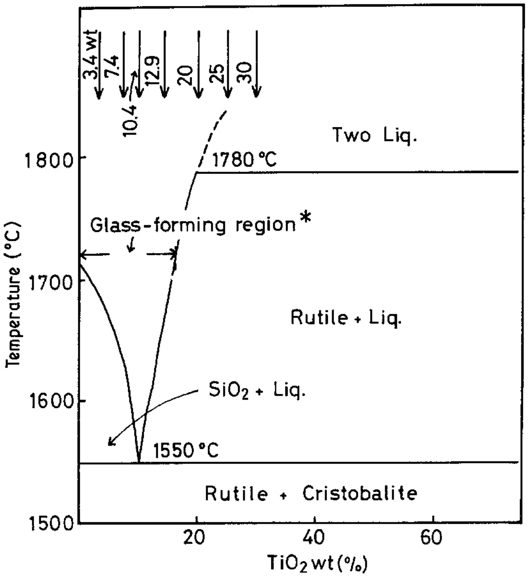

Figure 1 Phase diagram of TiO_2–SiO_2 system showing the positions of the compositions investigated. * = Anatase-precipitated samples [1]. (Flame hydrolysis method.)

trol the evaporation of water and alcohol. The solutions gelled into jelly-like transparent solids in 1 to 10 days, depending on the hydrolysis conditions. The bulk gels were kept standing in open system for about 3 months for drying.

The gels were heated slowly up to 100° C, kept there for 1 day and then heated up to 800° C with a heating rate of 10° C h^{-1}.

2.2. Measurements of the properties of gels and glasses

Vickers' hardness, infrared (IR) spectroscopy and shrinkage were measured on the samples of gels heated at the various temperatures for 6 h in order to examine the conversion process of gels to glasses. Vickers' hardness was measured by applying a load of 100 g to the samples for 15 sec. Density, refractive index and thermal expansion coefficients, $\alpha_{25-600° C}$, of the glasses obtained by heating gels up to 800° C were measured. The density was measured by Archimedes' method, and the refractive index by the oil immersion technique.

3. Results

3.1. Preparation of gels

Since $Ti(O^iPr)_4$ is extremely fast to hydrolyse, compared to $Si(OEt)_4$, the hydrolysis of a mixture of these two alkoxides with rapid addition of large amounts of water caused differential hydrolysis of titanium alkoxide and segregation, and the solution became turbid. A clear solution was obtained, only when limited amounts of water and HCl diluted with ethanol were added very slowly to the alkoxides solution in order to avoid the preferential precipitation the titanium hydroxide. This may be because partially hydrolysed $Ti(O^iPr)_{4-x}(OH)_x$ is soluble in acidic aqueous solution and reacts with $Si(OEt)_4$ to form the soluble species having Si–O–Ti bonds.

The smaller the amount of water added, the clearer the gels formed, but the greater the tendency to crack into several pieces while drying at room temperature. In the case of the addition of large amounts of water, the gels tend to become easily translucent or opaque. The optimum conditions to make transparent gels are as follows: H_2O/alkoxides = 16 (molar ratio), HCl/alkoxides = 0.03 (molar ratio).

The gelation time varied depending on the hydrolysis conditions, e.g. the amount of the added water, the pH of the mixture solution and the concentration of $Ti(O^iPr)_4$. As the concentration of $Ti(O^iPr)_4$ in the alkoxides mixture solution increased, the gelation time was shortened.

This is assumed to be due to the catalytic action of the hydroxyl ions in the partially hydrolysed $Ti(O^iPr)_{4-x}(OH)_x$ content [6] or the dehydration reaction of $Ti(O^iPr)_{4-x}(OH)_x$ with $Si(OEt)_4$.

3.2. Heat treatment of gels

The change in IR spectra of gels with heating is shown in Fig. 2. The absorption band around 1100 cm^{-1}, attributed to the Si–O vibration in the SiO_4 tetrahedron, shifted slightly to lower frequencies as the temperature increased to around 300° C, whereas it shifted to higher frequencies as the temperature was raised above 400° C, suggesting that the Si–O bonds in tetrahedra were strengthened.

Next, the change in micro-Vickers' hardness with heating is shown in Fig. 3. The hardness of the gels increased gradually with the temperature up to about 500° C and increased suddenly between 500 and 700° C. The hardness of the products heated to 700° C decreased as the amounts of water added for hydrolysis increased. This result is attributed to micropores which still exist at 700° C, because the indentation hardness is determined from the area of the specimen directly supporting an applied load. The hardness of the

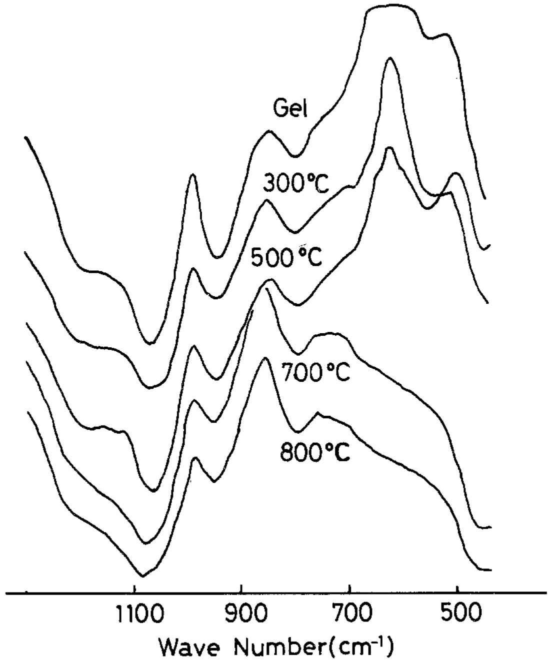

Figure 2 Infrared absorption spectra of the specimens obtained by heating the gels containing 12.9 wt% TiO_2 at various temperatures.

products heated to 900° C reached a value (700 kg mm^{-2}), which is comparable to that of fused silica.

Typical differential thermal analysis (DTA), thermogravimetric analysis (TGA) and linear shrinkage for gel containing 7.4 wt% TiO_2 in the case of H_2O/alkoxides of 16 molar ratio are shown in Fig. 4. An endothermic peak, which is probably due to the evaporation of the adsorbed water and solvent, was observed around 150° C. But a weight loss was observed in the range of room temperature to 700° C because of the evaporation of the water liberated by the polycondensation of the silanol groups in addition to the adsorbed water and solvent. The shrinkage also occurred until about 700° C. But, when large amounts of water were added, e.g. in the case of H_2O/alkoxides of 50 molar ratio, the gels continued to shrink until about 1000° C. The difference in these results may be explained by the difference of gel structures which are substantially determined by the rate of the hydrolysis and the dehydration polymerization. That is, the larger the amounts of water added, the more porous tne gels produced which have a relatively low bulk density.

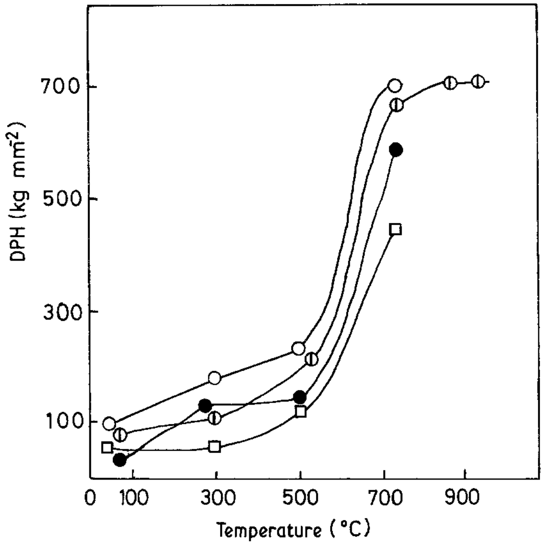

Figure 3 Vickers hardness of the specimens obtained by heating the gels at various temperatures. ○: 12.9 wt%, no addition of water; ⦶: 12.9 wt%, H_2O/alkoxides = 2 (molar ratio); •: 12.9 wt%, H_2O/alkoxides = 16 (molar ratio); □: 7.4 wt%, H_2O/alkoxides = 16 (molar ratio).

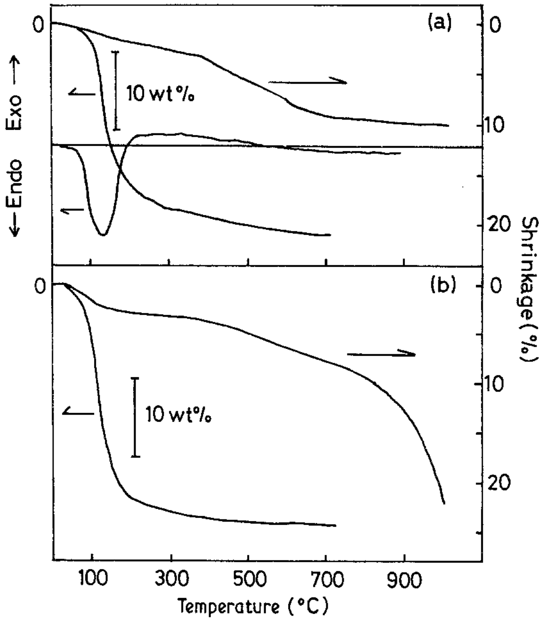

Figure 4 DTA, TGA and shrinkage curves of the gels containing 7.4 wt% TiO_2: (a) H_2O/alkoxides = 16 (molar ratio); and (b) H_2O/alkoxides = 50 (molar ratio).

3.3. Properties of resulting oxide glasses

The photographs of glasses obtained by heat treatment up to 800° C are shown in Fig. 5. X-ray diffraction pattern showed no crystalline phase and no appreciable small-angle scattering, indicating that the products are oxide glasses.

When the amount of water added was large, the gels did not crack under heat treatment up to 800° C and the initial disc shape was still main-

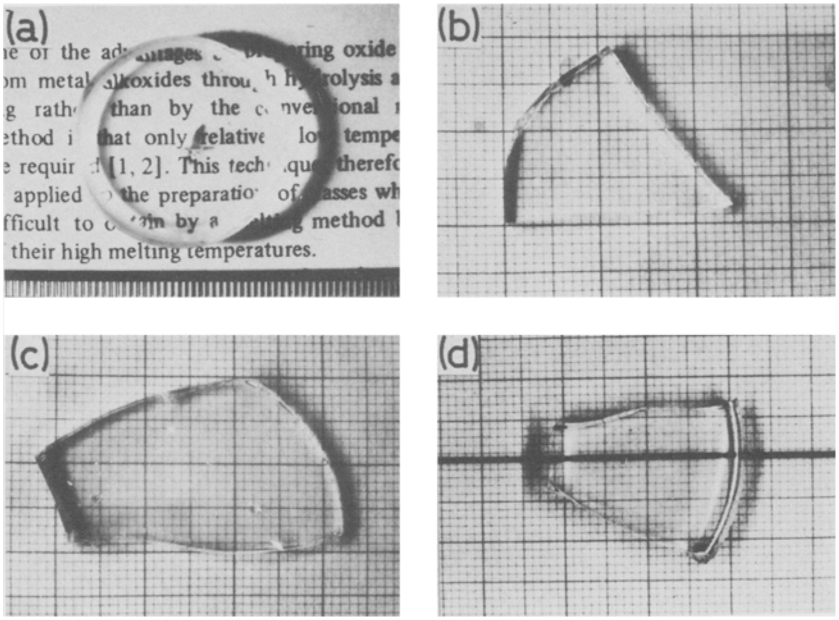

Figure 5 Photographs of the glasses with various compositions obtained by heating up to 800° C. (a) TiO_2 3.4 wt %; (b) 7.4 wt %; (c) 12.9 wt %; and (d) 20 wt %.

tained, but anatase was easily precipitated from the gels at the relatively low temperatures of 500 to 700° C. When the amount of water added was less, the gels cracked more extensively into smaller particles 2 to 5 mm in diameter. But, in the case of H_2O/alkoxides of 16 molar ratio, the gels cracked into larger pieces by the heat treatment up to 800° C, as shown in Fig. 5.

The densities, refractive indices and thermal expansion coefficients of the glasses obtained in the present study are shown in Figs. 6 and 7,

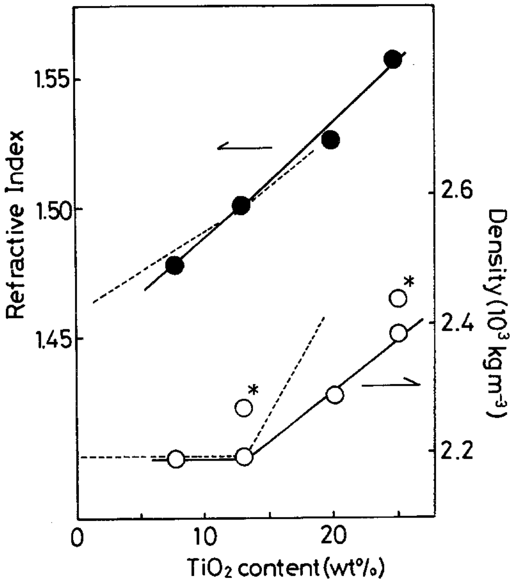

Figure 6 Refractive index and density of the glasses obtained from alkoxides by the heat treatment up to 800° C. Dotted line: the data obtained by the flame hydrolysis method [1].

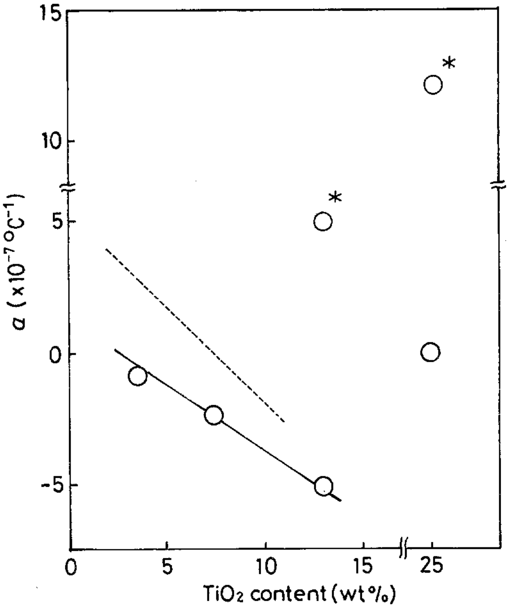

Figure 7 Thermal expansion coefficient of the glasses obtained from alkoxides by heat treatment up to 800° C. Dotted line: flame hydrolysis method [1]. * = Anatase-precipitated samples.

together with those obtained by flame hydrolysis. The refractive indices are comparable with those obtained by flame hydrolysis in the more than 13 wt % TiO_2 range, indicating that many pores may exist in the bulk glasses. In addition, the densities of the anatase-precipitating samples were higher than those of the anatase-nonprecipitating samples.

The thermal expansion coefficients of the glasses containing less than 12.9 wt % TiO_2 were as low as those prepared by flame hydrolysis, but those of anatase-precipitating samples were higher than those of glasses, as shown in Fig. 7. The thermal expansion coefficients of the glasses containing 25 wt % TiO_2 were very high, compared with those obtained by flame hydrolysis. This may be attributed to the presence of the six-fold-coordinated titanium ion–high positive expansion form (e.g. six-fold rutile has average $\alpha = 80$ to $90 \times 10^{-7}\,°C^{-1}$).

3.4. Infrared spectra of glasses

To diminish the overlapping of the absorption peaks of Si–O and Ti–O bonds, a difference infrared spectral technique was used [7]. The difference spectra were obtained by placing titanium-containing glass in a sample beam and vitreous silica in the reference beam, as shown in Fig. 8. A band, which is probably the asymmetric Ti–O stretching mode for a tetrahedrally structured titanium-containing group, was observed at about 735 cm^{-1}.

4. Discussion

The conversion of gels to glasses occurred continuously with the heat treatment and a considerable change in the structure of the gels due to the disappearance of small pores was observed in the range of 500 to 700° C by the measurements of Vickers' hardness, IR and TGA. The glassy noncrystalline solids were obtained only through heat treatment of clear gels, while the heating of opaque gels resulted in the precipitation of TiO_2. In the present work, glassy noncrystalline solids in the 3.4 to 25 wt % TiO_2 range were obtained by the gel method. The densities and refractive indices of the glassy noncrystalline solid in the less than 12.9 wt % TiO_2 range were reasonably consistent with those of glasses obtained by flame hydrolysis, but the densities in 20 and 25 wt % TiO_2 were very low, compared to the expected values from glasses obtained by flame hydrolysis.

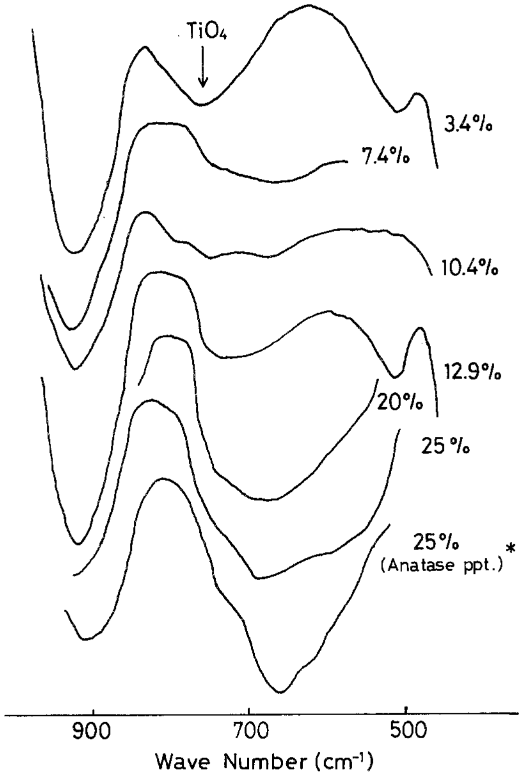

Figure 8 Difference infrared spectra of the glasses obtained by heat treatment up to 800° C. * = Anatase-precipitated samples.

It was found that glasses similar to oxide glasses made by flame hydrolysis could be obtained only in the less than 12.9 wt % TiO_2 range by the gel method.

It is well known that the TiO_2–SiO_2 glasses containing 5 to 11 wt % TiO_2 have the thermal expansion coefficients smaller than that of vitreous silica. This ultra-low thermal expansion is assumed to be due to the results that TiO_2 can act as a network former [8] and exist in a silicon-equivalent four-fold coordinated site in the SiO_2 network. Thus, the anomalous behaviour of densities and thermal expansion coefficients in the more than 20 wt % TiO_2 range can be explained by the presence of the six-fold coordinated titanium ion.

Next, the glasses obtained by heat treatment up to 800° C were further heated to 1100° C and the results of the X-ray diffraction are shown in Fig. 9. In the less than 10.4 wt % TiO_2 range, the products heated up to 1000° C or higher were still amorphous and transparent, while in the 20 wt % TiO_2 range, anatase was precipitated at 900° C.

It has been reported by Evans [9] that the true solution of TiO_2 in SiO_2 glass existed and produced

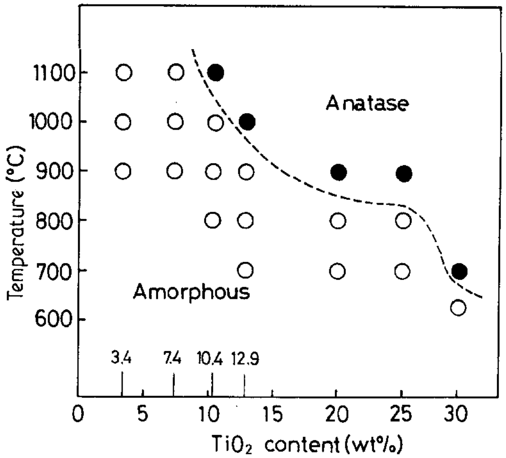

Figure 9 X-ray diffraction of samples after heating at various temperatures for 15 h in air. ○: Amorphous; and ●: Anatase.

only an α-cristobalite solid solution family of phase between 0 and 10.8 wt% TiO_2 by heat treatment at 1450° C, indicating the presence of the four-fold coordinated titanium ion. Thus, in order to consider the configurations of the titanium ion in the glasses obtained in the present work, they were heated at 1450° C for 1 h and examined by X-ray diffraction. The precipitated phases and X-ray diffraction patterns are shown in Table I and Fig. 10. In the less than 7.4 wt% TiO_2 range, the diffraction lines of α-cristobalite solid solution crystallized from the glasses were shifted toward a lower angle with increasing TiO_2 content, but in the more than 10 wt% TiO_2 range, the line was shifted toward a higher angle with increasing TiO_2 content, contrary to expectation. This is probably due to the precipitation of rutile. In the 7.4 wt% TiO_2 content, the diffraction lines of α-cristobalite solid solution were shifted toward a low angle by prolonged heating (138 h) of the sample because of the decomposition of the solid solution, i.e. the precipitation of rutile. From the results above, it was found that in the less than 7.4 wt% TiO_2 range, the complete solution of TiO_2 in SiO_2 glass occurred and the homogeneity of the glasses obtained was very high, while in the more than 10 wt% TiO_2 range, anatase and rutile were precipitated. The precipitation of anatase is presumably associated with the presence of the six-fold coordinated titanium ion rich heterogeneous phase, which was formed in the hydrolysis and gelation processes of the metal alkoxides.

TABLE I The precipitated phases from glassy noncrystalline solids by heat treatment at 1450° C for 1 h

TiO_2 (wt %)	Precipitated phase
0	α-Cristobalite
3.4	α-Cristobalite solid solution
7.4	α-Cristobalite solid solution
10.4	α-Cristobalite solid solution anatase, (rutile)
12.9	α-Cristobalite solid solution anatase, (rutile)
20	α-Cristobalite solid solution anatase, (rutile)
25	α-Cristobalite solid solution anatase, rutile

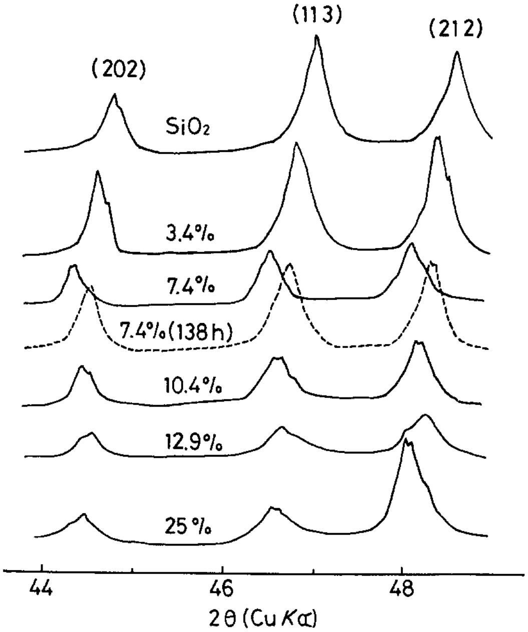

Figure 10 X-ray diffraction patterns of samples after heating at 1450° C for 1 h. Dotted line: samples heated at 1450° C for 138 h.

In summary, the monolithic TiO_2–SiO_2 glasses of high homogeneity were obtained only in the 7.4 wt% TiO_2 range by the gel method.

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Received 21 January
and accepted 24 February 1983