Selective crystallization of anatase and rutile by control of heat-treatment conditions and SiO₂ addition in TiO₂-crystallized glass

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In this study, we have investigated the effects of heat-treatment condition and SiO₂ addition on the crystallization behavior and chemical durability of TiO₂–ZnO–B₂O₃–Al₂O₃ (TZBA) glass. Systematic analysis indicated that not only the precipitated phases (rutile, anatase, and brookit) after crystallization but also the chemical durability of TZBA glass-ceramics were affected by heat-treatment condition and SiO₂ addition. In a specific glass composition, we have found that etching resulted in TiO₂ grains of several dozens nanometers and asperity of several hundred nanometers at the sample surface. The present method, in which the increase of specific surface area and formation of nanoparticles at the surface is achieved by chemical etching, will become an important technique for the fabrication of novel bulk photocatalysts with high catalytic activity.

Key-words : Glass-ceramics, Titanium dioxide, Chemical etching, Crystallization

1. Introduction

TiO₂ is one of the most important semiconducting oxides with interesting chemical, electrical, and optical properties. It is a good functional material in photonic devices, transparent conductive films, and dye-sensitized solar cells, among other applications. TiO₂ exists in three crystalline phases: rutile (most stable), anatase (metastable), and brookit (metastable). Among these phases, rutile and anatase are highly sought in industrial applications. Rutile is conventionally prepared by high-temperature and high-pressure synthesis or by the phase transition of anatase over 600°C depending on sample environment and impurity concentration. On the other hand, anatase is usually synthesized by sol–gel method or hydrothermal synthesis because of its low stability at high temperature.

Following the first report on the photocatalytic properties of TiO₂ by Fujishima and Honda in 1972, several researchers have analyzed and reported these properties. From the viewpoint of chemical reaction induced by photoexcited electrons and holes, band gap is one of the most important factors determining its performance. Since band gap of rutile and anatase is 3.0 and 3.2 eV, respectively, it seems that rutile can have high electron and hole concentrations, and hence, it is suggested that rutile can have a high catalytic activity.

In contrast to the conventional use of TiO₂ powders for photocatalytic applications, some researchers have reported the use of TiO₂-crystallized glass as a photocatalytic material. In our recent report, we have successfully demonstrated the fabrication of TiO₂-precipitated glass by using TiO₂–ZnO–B₂O₃–Al₂O₃ (TZBA) glass system. This glass system exhibits selective crystallization of rutile and anatase, which could be achieved by controlling the glass composition. Since the crystalline morphology of precipitated TiO₂ nanocrystallites also depends on the glass composition, it is suggested that chemical composition and glass network structure affect the precipitation of TiO₂ nanocrystallites.

Meanwhile, we have also reported microstructured ceramic materials as novel bulk materials with high specific surface area by using SrO–BaO–Nb₂O₅–B₂O₃–ZnO–SiO₂ glass system. The microstructured ceramic materials were fabricated by chemical etching after the crystallization of glass, with strontium barium niobate (SrₓBaₓNb₂O₆) existing at the surface of the etched sample. We have also observed the photocatalytic activity of the prepared microstructured sample under UV light irradiation. This activity was derived from SrₓBaₓNb₂O₆ phase, which is the first report on the activity of SrₓBaₓNb₂O₆ phase. It seems that the formation of micro/nanostructure at the surface is important to increase catalytic activity, and that the activity of bulk photocatalysts can be comparable to that of powder catalysts which is the case with micro/nanostructured ceramics.

2. Experimental procedure

In this study, TiO₂–ZnO–B₂O₃–Al₂O₃–SiO₂ (x = 0, 0.9, 4.5) glass-ceramics were prepared by conventional melt quenching method. The starting materials were TiO₂ (99.99%), ZnO (99.9%), B₂O₃ (99.9%), Al₂O₃ (99.99%), and SiO₂ (quartz, 99.9%). All chemicals were purchased from Kojundo Chemical Laboratory Co., Ltd. (Sakado, Japan). The starting materials were melted in a Pt crucible with a Pt cap at 1300°C for 40 min in an ambient atmosphere. The glass melt was quenched on a steel plate at 200°C. The obtained glass was then annealed at 10°C below the glass transition temperature Tg for 1 h. After annealing, the glass samples were cut into slides of size 8 mm ×
8 mm × 1 mm and mechanically polished to obtain a mirror surface.

Heat treatment was performed in ambient atmosphere in an electric furnace (KBF848N1; Koyo Thermo Systems, Tokyo, Japan) at a heating rate of 10°C/min from room temperature to 30°C below the heat-treatment temperature $T_h$. Then, the heating rate was reduced to 1°C/min from $T_h−30°C$ to $T_h$. After maintaining the temperature at $T_h$ for 3 h, the temperature of the furnace was cooled down without temperature control. Crystalized glasses were etched using 1 M HCl solution at room temperature for 120 min.

Furthermore, the glass transition temperature $T_g$, crystallization onset temperature $T_c$, and crystallization peak temperature $T_p$ of glasses were determined by differential thermal analysis (Thermo Plus 8120; Rigaku Co. Ltd., Tokyo, Japan) at a heating rate of 10°C/min. X-ray diffraction (XRD) analysis was performed at 40 kV and 40 mA using a New D8 ADVANCE (Bruker AXS Co. Ltd., Karlsruhe, Germany) X-ray diffractometer. The chemical durability of samples was determined by measuring the weight change by etching. Before measurement of weight, samples were washed with water, and then dried in an electric furnace at 100°C for 10 min. The surface morphology of the samples was analyzed by scanning electron microscopic (SEM) images taken using a JSM-6500F (JEOL, Tokyo, Japan) microscope. Similarly, transmission electron microscopic (TEM) images and electron diffraction (ED) patterns were taken using a HF-2000 (Hitachi Co. Ltd., Tokyo, Japan) microscope.

### Table 1. Thermal properties of 14TiO$_2$–23ZnO–45B$_2$O$_3$–18Al$_2$O$_3$–$x$SiO$_2$ glass-ceramics

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_g$</th>
<th>$T_c$</th>
<th>$T_p$</th>
<th>$\Delta T = T_p − T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>617</td>
<td>693</td>
<td>708</td>
<td>739</td>
</tr>
<tr>
<td>0.9</td>
<td>609</td>
<td>696</td>
<td>708</td>
<td>742</td>
</tr>
<tr>
<td>4.5</td>
<td>602</td>
<td>697</td>
<td>709</td>
<td>750</td>
</tr>
</tbody>
</table>

![Fig. 1. XRD patterns of the 14TiO$_2$–23ZnO–45B$_2$O$_3$–18Al$_2$O$_3$–0SiO$_2$ glass-ceramics heat treated at different temperatures. ICDD numbers of rutile and anatase are 071–6411 and 021–1272, respectively.](image1)

3. Results and discussion

#### 3.1 Selective crystallization of rutile and anatase

The obtained 14TiO$_2$–23ZnO–45B$_2$O$_3$–18Al$_2$O$_3$–$x$SiO$_2$ glass-ceramics were transparent and homogeneous. Table 1 shows the chemical composition and thermal properties of the prepared glasses. Although $T_g$ was found to decrease with the addition of SiO$_2$, no significant differences were observed in the values of $T_c$ and $T_p$. This indicates that the thermal stability of glass, $\Delta T (= T_p − T_g)$, increases with SiO$_2$ content.

Bulk XRD patterns of 14TiO$_2$–23ZnO–45B$_2$O$_3$–18Al$_2$O$_3$–$x$SiO$_2$ (ICDD No. 076–8290) is precipitated as a subcrystalline phase. Although both rutile and anatase were precipitated, it is found that the heat-treatment temperature affects the peak intensity ratio of rutile and anatase. It could be realized that anatase is the main phase upon heat treatment below 670°C, while rutile is the main phase upon heat treatment above 670°C. The observed difference in the crystalline phase after heat treatment is due to the phase transition of TiO$_2$. In other words, the metastable anatase phase, which is precipitated at lower temperatures, is transformed to the more stable rutile phase at higher temperatures. This phase transition temperature is almost equal to the reported temperature. These results imply that it is possible to selectively crystallize anatase and rutile by varying the temperature for heat treatment. Figure 2 shows the TEM image and ED pattern of the 14TiO$_2$–23ZnO–45B$_2$O$_3$–18Al$_2$O$_3$–0SiO$_2$ glass-ceramics heat treated at 667°C for 3 h. Upon heat treatment, nanocrystallites of size 20–50 nm were found to precipitate in the glass ceramics. Although the ED pattern indicates the formation of rutile, anatase, and Al$_2$B$_2$O$_6$ anatase is the main crystalline phase in the ED pattern of the glass-ceramic. This result is in agreement with our observation using XRD (Fig. 1).

Furthermore, Fig. 3 shows the bulk XRD patterns of the 14TiO$_2$–23ZnO–45B$_2$O$_3$–18Al$_2$O$_3$–$x$SiO$_2$ glass-ceramics heat treated at 50°C higher than each $T_p$ ($x = 0, 0.9, 4.5$). The XRD patterns signify the following two influences induced by SiO$_2$ addition. The first is the change of precipitated crystalline phase. Although the diffraction peak corresponding to Al$_2$B$_2$O$_6$ can be clearly observed when $x = 0$, it becomes weak with SiO$_2$ addition and disappears completely with further addition of SiO$_2$ when...
At the same time, the intensity of rutile peak weakens as we proceed from \( x = 0 \) to \( x = 4.5 \). This implies that the single-phase crystallization of anatase is achieved by further SiO\(_2\) addition. Second, FWHM of the main diffraction peak of anatase around 2\( \theta \) = 26° broadens with increase in SiO\(_2\) content. The precipitated grain size can be estimated by the Scherrer equation [Eq. (1)]

\[
d = \frac{k\lambda}{\beta\cos\theta},
\]

where \( d \), \( k \), \( \beta \), \( \lambda \), and \( \theta \) denote precipitated grain size, constant number, FWHM, wavelength of X-ray, and diffraction angle, respectively. It is inferred that the grain size decreases with the addition of SiO\(_2\). However, from the TEM images (Fig. 4), no significant difference in the size of the precipitated grain size or chemical composition was observed. It is notable that most precipitated crystallites are anatase when \( x = 4.5 \) and that Al\(_4\)B\(_2\)O\(_9\) is precipitated around TiO\(_2\) crystallites. Since the diffraction ring gets broader and obscure with the addition of SiO\(_2\), it is expected that the crystallinity of Al\(_4\)B\(_2\)O\(_9\) decreases with SiO\(_2\) addition.

Figure 5 shows bulk XRD patterns of the 14TiO\(_2\)–23ZnO–45B\(_2\)O\(_3\)–18Al\(_2\)O\(_3\)–xSiO\(_2\) glass-ceramics heat treated at 680°C. As evidenced from the XRD pattern, rutile is the main crystalline phase when \( x = 0 \), whereas anatase is the main phase in SiO\(_2\)-rich composition. This implies that the thermal stability of precipitated anatase has been improved by SiO\(_2\) addition. From the results mentioned above, it is obvious that the selective crystallization of rutile or anatase is possible by adept control of heat-treatment condition and SiO\(_2\) addition. This implies that the atomic mobility resulting from heat treatment or bonding with Si facilitates selective crystallization of anatase or rutile phase.

### 3.2 Examination of chemical durability

The time-dependent weight changes of the SiO\(_2\)-free TZBA glass-ceramics, which were obtained by heat treatment at different temperatures, followed by immersion in aqueous HCl, are shown in Fig. 6. In the case of the sample heat treated at 642°C (\( = T_g + 25^\circ\)C), no significant weight change was observed. The XRD pattern of this sample (Fig. 1) indicates weak crystallinity of this sample, signifying that a large fraction of the sample is amorphous and possesses high chemical durability. In other cases, the weight of the sample etched for 120 min is approximately 20 wt% of the initial weight. It is inferred that the residual phase after TiO\(_2\) crystallization, which is completely different from the as-prepared glass, has low acid durability. From the XRD patterns in Fig. 1, although heat treatment temperature has an influence on only phase transition of TiO\(_2\), the
residual glass is not affected by heat treatment temperature. So, weight difference among three heat treatment conditions after chemical etching was not observed.

Figure 7 shows the influence of SiO₂ addition on chemical durability. In this figure, the horizontal axis denotes the heat-treatment temperature, while the vertical axis represents the ratio of the weight obtained after etching to the initial weight. At the same heat-treatment temperature, SiO₂ addition is found to improve the acid durability of crystallized glass. In particular, when compared with glasses heat treated at approximately 660°C, although the weight after etching was 20 wt% in the composition without SiO₂ addition, no significant weight change before and after etching was observed in 4.5 mol% SiO₂-added sample. Therefore, it is considered that chemical durability after acid etching is controlled by heat-treatment condition or the addition of SiO₂. However, the results of glass transition temperature and chemical durability in this glass system seem incompatible with SiO₂ addition. Since it is possible that the role of intermediate oxides (glass network former and/or glass network modifier) is modified by glass composition, also in SiO₂ addition, it is very important to clarify the relationship between glass transition temperature and chemical durability. After heat-treatment at around glass transition temperature for 10 h, it was confirmed from XRD patterns in precipitation of anatase. However, diffraction peak intensity of anatase is very weak and decreases by SiO₂ addition. We think that this phenomenon is “crystallization of anatase” not “phase separation”. Phase separation in the amorphous state is not occurred in this glass system.

Figure 8 shows the surface SEM image of 4.5 mol% SiO₂-added sample heat treated at approximately 680°C before and after etching. SEM images indicate that the surface of crystallized glass is smooth without asperity, whereas grains of several dozen nanometers and asperity of a few hundred nanometers were observed on the etched samples. XRD patterns shown in Fig. 9 do not signify any difference before and after etching. This could be attributed to the precipitation of crystalline phases in the entire sample. The peaks at 2θ ≈ 21° and 24° (gray band) correspond to the utility wax, which is used for fixing the sample during XRD measurement. The order of the grain size calculated from the Scherrer equation [Eq. (1)] corresponded with that of particles in the SEM image (Fig. 8). These results imply that particles on glass surface after acid etching are anatase TiO₂. As mentioned above, chemical etching not only improves the specific surface area but also facilitates the formation of nanoparticles on the surface. This distinctive structure is very important for the fabrication of novel photocatalysts in the future.

4. Conclusion

In this study, we have examined the effects of heat-treatment condition and SiO₂ addition on the crystallization behavior and durability of the 14TiO₂–23ZnO–45B₂O₃–18Al₂O₃–4.5SiO₂ glass-ceramics. We have succeeded in the selective crystallization of TiO₂ by precisely controlling the precipitation ratio of rutile and anatase. Furthermore, the phase transition temperature from anatase to rutile was improved by SiO₂ addition. In addition, heat-treatment condition and SiO₂ addition seemed to effectively control the acid durability of the prepared samples. In particular, SiO₂ addition significant impacted the chemical durability. After etching, grains of several dozen nanometers and asperity of a few hundred nanometers were observed on the surface. From the XRD patterns and Scherrer equation, it is expected that the nanoparticles crystallized on the surface were TiO₂. We believe that the formation of nanoparticles on the surface, in addition to the improvement in specific surface area, will greatly improve the development of novel photocatalysts with high catalytic activity.

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References