Formation and photoluminescence of zirconia dendrites in borosilicate glass-ceramics

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We prepared a borosilicate glass, in which the ZrO_2 phase is singly crystallizable, i.e., $15\text{Na}_2\text{O}-15\text{ZrO}_2-30\text{B}_2\text{O}_3-40\text{SiO}_2$ glass, and investigated the texture and morphology of the resulting glass-ceramics. ZrO_2 dendrites with a tetragonal system (high-temperature phase) were developed as initial phase, and the tetragonal phase was transformed to the monoclinic phase (low-temperature phase) by elongation of the heat-treatment time, and finally the needle-/rod-like crystals on a scale of few hundred nanometers were obtained. The glass-ceramics with monoclinic ZrO_2 showed photoluminescence around 480 nm by excitation in the ultraviolet region. The effect of TiO_2 -addition on the photoluminescent property was also considered.

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1. Introduction

A promising way to create the nanostructured materials is glass-ceramic (GC) processing, i.e., structural ordering in glass evolved by thermal stimulation. Glass structures possess a disordered random-network, resulting in flexibility and formability, and a great deal of effort has gone into creation of functional materials based on GC processing so far.^{1)–4)} The GCs consisting of an emissive phase with rare-earth (RE)-dopant has also been fabricated for applications as photoluminescent (PL) materials, e.g., white-LED, long-lasting phosphor, and optical thermometer.^{5)–7)} PL phenomena have a great potential, not only for emissive-/photovoltaic-device components, but also for bio-imaging applications^{8),9)} that contribute to our cultural, sustainable, and healthy lives. For instance, in vivo observation of temperature in tissue using PL material has absorbed much attentions recently,¹⁰⁾ and is considered to be helpful for a medical treatment, in which temperature-monitoring is a key to improving the quality of the treatment.¹¹⁾

Zirconia (ZrO_2) is a wide-bandgap dielectrics, and is also utilized to synthesize an engineering ceramics and artificial teeth because of its high chemical durability and harmless. In addition, blue PL phenomena have been studied in ZrO_2 in 1960's: Sarver reported the broad PL band with peak at ~ 480 nm by ultraviolet (UV) excitation in pure and Ti-doped ZrO_2 ,¹²⁾ and an afterglow PL by X-ray excitation was also reported by Bettinali et al.¹³⁾ Recently, it is of particular interest to elucidate the PL phenomena and to improve their performance because of the emissive phase free from any RE-dopants. At first, origin of the blue PL is considered to be the presence of Ti as an impurity.¹²⁾ On the

other hand, Emeline et al. attribute an oxygen-vacancy to a luminescent center.¹⁴⁾ Although the origin of luminescence center is thus still controversial,^{15)–20)} ZrO_2 has attracted much attention because of being a great candidate for RE-free phosphor. In this study for the purpose of fabricating ZrO_2 -crystallized GCs, we therefore studied the crystallization behavior of glass, in which ZrO_2 is included as a main constituent, and observed the texture and morphology in obtained GC samples. The PL properties of the samples also examined.

2. Experimental

2.1 Preparation of precursor glass and glass-ceramics

Although there are many literatures concerning crystallization in glass with ZrO_2 so far, the ZrO_2 is added as a nuclear agent so that its amount is limited up to a few or less than ~ 10 mol %. On the other hand, Maschio and Scardi reported single crystallization of a ZrO_2 phase in $10\text{Na}_2\text{O}-10\text{ZrO}_2-20\text{B}_2\text{O}_3-60\text{SiO}_2$ glass.²¹⁾ As pre-examination for this study, we attempted to prepare glass with the same composition and checked the precipitated phase after crystallization. However, the glass crystallized the ZrO_2 and cristobalite (SiO_2) phases. For single crystallization of the ZrO_2 phase, we also checked several glass compositions, in which the SiO_2 content was less than the previous glass. As a result, we successfully prepared $15\text{Na}_2\text{O}-15\text{ZrO}_2-30\text{B}_2\text{O}_3-40\text{SiO}_2$ glass, in which only the ZrO_2 phase is crystallizable. Therefore, this glass was employed as the base precursor thereafter. In addition, a base precursor substituting a small amount of TiO_2 for ZrO_2 , i.e., $15\text{Na}_2\text{O}-(15-x)\text{ZrO}_2-x\text{TiO}_2-30\text{B}_2\text{O}_3-40\text{SiO}_2$ glass ($x = 0.01, 0.03, 0.05$) was also prepared in order to examine the Ti-additive effect on the PL properties in the resulting GCs.

The precursor glasses were prepared by a conventional melt-quenching method. The chemical reagents of Na_2CO_3 , ZrO_2 , TiO_2 , B_2O_3 , and SiO_2 powders were mixed with an alumina mortar, and the mixtures were melted in a platinum crucible with

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a lid at 1450°C for 1 h in air atmosphere. The as-quenched precursor showed a halo pattern in the X-ray diffraction (XRD) pattern, indicating that the precursor was in glassy state. The thermal parameters of the base precursor were determined by means of a differential thermal analysis at a heating rate of 10 K/min, and the glass-transition, crystallization-onset, and crystallization-peak temperatures were estimated to be $T_g = 561^\circ\text{C}$, $T_x = 755^\circ\text{C}$, and $T_p = 779^\circ\text{C}$, respectively. The precursor glass was subjected to isothermal heat-treatment at $T_p - 50^\circ\text{C}$ (729°C) for different time periods in air to crystallize the ZrO_2 phase in the glass. Although it may be better to crystallize the precursor glass at T_p in order to examine the resulting GCs, the GCs obtained at T_p showed a considerable deformation, which is not suitable for evaluation. Therefore, we attempted to prepare the GCs below the T_p . As a result, the condition at $T_p - 50^\circ\text{C}$ provided a less deformed sample so that the $T_p - 50^\circ\text{C}$ was chosen as the treatment temperature.

2.2 Characterizations of glass-ceramics

The GC samples were characterized by XRD analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDX). In terms of optical measurements, the PL and PL excitation (PLE) spectra were studied using a spectrofluorometer with a xenon lamp as an excitation source. Internal quantum-yield (QY) of the PL in the ZrO_2 samples was estimated by a PL spectrometer with an integrating sphere (Hamamatsu Photonics: Absolute PL Quantum Yield Measurement System C9920-20). All of the measurements were performed at room temperature.

3. Results

3.1 Phase formation in glass-ceramics

In Fig. 1, we show the XRD patterns in precursor glasses (bulk state) subjected to heat-treatment for different time periods. In the glasses treated for short times (1 and 4 h), diffraction peaks appeared mainly at $2\theta \sim 30^\circ$ and $\sim 50^\circ$, and the series of peaks were determined to be tetragonal ZrO_2 by comparison of ICDD with the diffraction pattern. In the glass treated for 9 h, the additional peaks, e.g., at $2\theta \sim 28^\circ$ and $\sim 31^\circ$, appeared and were

attributed to formation of monoclinic ZrO_2 , meaning the coexistence of tetragonal and monoclinic phases. Further increase in the treatment time provided the formation of major monoclinic phase with a minor tetragonal phase (24 h), and the crystallized phase was eventually converted to a monoclinic (48 h). The XRD analysis predicts that precipitation of ZrO_2 crystals is almost completed at 1 h, and is subsequently converted gradually into the monoclinic phase by prolongation of treating time. Thus, the precursor glasses crystallized ZrO_2 crystals only by means of proper heat-treatment, indicating that ZrO_2 -crystallized GCs were successfully fabricated.

3.2 Texture and morphology observation

In Fig. 2, we show the crystallized textures in GC samples in this study. The SEM and TEM observations revealed that micrometer-sized dendrites with a crystal width of ca. 50 nm were

Fig. 1. XRD patterns in as-quenched precursor glass and glasses heat-treated at $T_p - 50^\circ\text{C}$ (729°C) for 1–48 h. The samples were measured in bulk form. ICDD of monoclinic (#36-0420; red bars) and tetragonal ZrO_2 (#50-1089; blue bars) are also included.

Fig. 2. SEM images for ZrO_2 -crystallized glass-ceramics obtained by heat-treatment for 1, 4, and 24 h (a–c) and the corresponding TEM images (1, 4, and 24 h; d–f).

homogeneously distributed in the sample for 1 h [Figs. 2(a) and 2(d)]. Elongation of the treatment time provided no significant increase in the number of dendrites, implying that crystallization of ZrO_2 dendrites was already finished in the early stage of heat-treatment. Interestingly, the elongation also gave the dendrites to be small; $\sim 3.5 \mu\text{m}$ for 1 h and $\sim 2.0 \mu\text{m}$ for 4 h [Figs. 2(b) and 2(e)]. Eventually needle-/rod-like crystals on a few hundred nanometer-scale were formed with a treatment time of 24 h [Figs. 2(c) and 2(f)]. Basically, the size of crystallized phase in glass tends to increase with the heat-treatment duration. However, the result obtained in this study was the opposite.

To investigate the crystallized texture in detail, we performed an electron diffraction (ED) analysis. In Fig. 3, we show the TEM images and corresponding selected area electron diffraction (SAED) patterns in GC samples for 1, 4, and 24 h. In all the samples, the dendrites indicated a spot-like ED pattern, suggesting that the ZrO_2 phases are single domain. In the GC sample for 1 h, the SAED pattern was assigned to the tetragonal phase with a trace of monoclinic phases [Fig. 3(a)]. The SAED patterns in the GC samples for 4 and 24 h were assigned to the monoclinic phase [Figs. 3(b) and 3(c)]. Although the XRD result (Fig. 1) indicates total formation of the tetragonal phase in the GC samples for 1 and 4 h, the SAED patterns in their samples strongly suggest that a nano-sized/small-amount of monoclinic phase, which is hardly observable by means of XRD, is developed. Thus, the series of SAED patterns probably show the transition state from tetragonal to the monoclinic phase.

The EDX analysis was also carried out to determine the element-distribution after the dendrite-formation. In Fig. 4, we show the results of element mapping by means of TEM-EDX analysis in a GC sample for 1 h. One can see that the Zr element is condensed in the dark regions, corresponding to the dendrites, and is hardly observed in the surrounding region. The other elements are evenly distributed. This strongly suggests that the ZrO_2 is almost consumed to form the dendrites during heat-treatment for 1 h. The results of EDX analysis also supports the prediction based on the XRD analysis.

Fig. 3. TEM images (left) and SAED patterns (right) in glass-ceramics obtained by heat-treatment for 1, 4, and 24 h (a–c). The green circles correspond to the observed area.

Fig. 4. EDX mapping results for glass-ceramics obtained by heat-treatment for 1 h.

Fig. 5. PL and PLE spectra for the precursor glass and glass-ceramics obtained by the heat-treatment for 1–48 h. Note that the plots of sample for 1 h is almost superimposed on that of sample for 4 h.

3.3 Spectroscopic study of glass-ceramics with ZrO_2 dendrites

In Fig. 5, we show the results of spectroscopic measurements of the ZrO_2 -crystallized GC samples. PL and PLE bands were hardly detected in the samples obtained for 1 and 4 h, which crystallize only the tetragonal phase, as well as the precursor glass. On the other hand, the samples for 9–24 h, which consist of monoclinic phase, obvious spectral structures, i.e., a broad PL band at ~ 480 nm in the blue region and PLE band at ~ 280 nm, could be observed. The PL intensity was increased with the treatment time, which is responsible for conversion of the tetragonal phase to the monoclinic phase. The internal QY concerning the blue PL was evaluated to be about 6% in the GC samples obtained for 48 h, consisting of solely monoclinic ZrO_2 .

The PL properties of monoclinic ZrO_2 are affected by the presence of impurities, and the addition of TiO_2 , in particular, improves the PL intensity.¹²⁾ Therefore, we also examined the PL properties of GCs made from the Ti-bearing precursors, i.e., $15\text{Na}_2\text{O}-(15-x)\text{ZrO}_2-x\text{TiO}_2-30\text{B}_2\text{O}_3-40\text{SiO}_2$ glass. The glasses were heat-treated at T_p-50 K for 48 h, and crystallized only the monoclinic phase, as confirmed by XRD analysis. In Fig. 6, we show the optical features of Ti-bearing GC samples. When the pieces of GCs were exposed to UV light at 254 nm, we could visually confirm the brighter blue emission of Ti-bearing GCs than that of base GCs ($x = 0$) [Fig. 5(a)]. In addition, the Ti-bearing GCs possess the PL and PLE bands at ~ 480 and ~ 280 nm, respectively. The spectra of a sample with $x = 0.01$ is shown as a representative in the inset. The spectral feature of Ti-bearing GC samples were identical to those of base GCs. On the other hand, the internal QY increased compared to the base GCs and the values were maximized at $x = 0.01$, i.e., about 10% [Fig. 6(b)].

4. Discussion

4.1 Phase and morphological variations of ZrO_2 dendrites

ZrO_2 crystals possess polymorphism and related phase-transitions: Monoclinic–tetragonal (~ 1100 – 1200°C) and tetragonal–cubic phase-transitions ($>2300^\circ\text{C}$). If the tetragonal phase is stabilized below the transition temperature, Y_2O_3 is introduced into the ZrO_2 phase, the so-called yttria-stabilized zirconia. However, in this study the tetragonal phase was initially crystallized at a temperature much lower than the temperature at which monoclinic–tetragonal phase-transition occurs. Because it is thermodynamically a non-equilibrium, the glass/supercooled-

Fig. 6. (a) Photo of glass-ceramics obtained by crystallization of base ($x = 0$) and Ti-bearing precursors. UV-light with a 254 nm-wavelength was irradiated; (b) the spectra of Ti-bearing glass-ceramics with $x = 0.01$ (inset) and the values for the internal quantum yield (QY) as a function of TiO_2 -content, x .

liquid (SCL) phase is in a higher energy state than the corresponding crystal phase. If potential curve of a metastable state exists between the SCL and stable-phase potential curves, the metastable phase is able to crystallize prior to the stable phase.²²⁾ Indeed, crystallization of the metastable phase is empirically confirmed in several glasses.^{23),24)} It is considered that tetragonal ZrO_2 is free-energetically higher than monoclinic ZrO_2 below the transition temperature. Consequently, the initial crystallization of the tetragonal (high-temperature type) phase and its subsequent formation of the monoclinic (low-temperature type) phase could be interpreted in the same manner.

The formation of ZrO_2 dendrites is possibly due to crystal-growth based on diffusion-control in GCs, and such dendritic growth is often confirmed by crystallization of glass/SCL in multicomponent systems.²⁵⁾ The Zr element, a component of precursor glass, could migrate/diffuse in viscoelastic SCL during heat-treatment (above T_g), and then be captured competitively in the nearest growth-front of ZrO_2 crystals, providing a dendritic structure. In addition, the transformation of ZrO_2 -dendrites into needle-/rod-like crystals occurred with the elongation of heat-treatment (Fig. 2). Taking the XRD results into account, it is suggested that the morphology of the crystallized ZrO_2 is changed simultaneously during the transformation. Monoclinic ZrO_2 is martensitically transformed into the tetragonal phase, resulting in a large volume change of $\sim 3\%$ (shrinkage),²⁶⁾ and ZrO_2 ceramics therefore involve a strain energy, which is able to induce the ceramic body to destruction. Therefore, the needle-/rod-like crystals in the sample for 24 h (Figs. 2 and 3) are supposed to be produced by the destruction of dendrites due to internal strain caused by the volume change based on the phase-transition.

4.2 Photoluminescent properties of glass-ceramics

Until now, ZrO_2 micro-/nano-powder has been prepared in order to study the physical properties, and tetragonal ZrO_2 has been synthesized especially via the sol–gel and aqueous-solution routes.^{27),28)} This study demonstrates that emissive ZrO_2 crystals

can also be synthesized using the GC technique, and selective crystallization between monoclinic–tetragonal phases can be achieved by changing the heat-treatment time. Spectroscopic study revealed that increases in the heat-treatment time promote the development of a blue PL band and phase-transformation into monoclinic phase in the GCs with ZrO₂-dendrites, suggesting that the tetragonal phase is non-emissive.

The maximum internal QY was obtained at $x = 0.01$ in the Ti-bearing GCs [Fig. 5(b)], and the concentration of Ti in ~ 0.07 mol % against the ZrO₂ content. Meanwhile, the brightness of blue PL in Ti:ZrO₂ powder reaches a maximum when the Ti-concentration is 0.08 mol %.¹²⁾ The closeness of these values implies that the TiO₂ added to the precursor glass is fully incorporated into the crystallized ZrO₂ dendrites. In addition, the decrease in QY values above $x = 0.01$ is probably explained by so-called concentration quenching, and such decreases are also confirmed in other Ti-bearing phosphors.²⁹⁾ According to Cong et al., the improvement of PL property in ZrO₂ by TiO₂-addition is attributed to formation of oxygen-defects caused by Ti³⁺, which occupies the Zr⁴⁺ site, for charge-compensation.¹⁶⁾ Assuming this mechanism, we can strongly expect that the formation of Ti³⁺ into a ZrO₂-crystallizing precursor provides an improvement in the PL performance in the ZrO₂-dendrites. Indeed, it is possible to form Ti³⁺ and introduce it to the crystallizing phase by introducing a reducing agent into the precursor glass: Yoshida et al. have succeeded in fabrication of GCs consisting of Ti³⁺-doped anatase-type TiO₂, and demonstrated the enhancement of photocatalytic properties based on the Ti³⁺-doping effect.³⁰⁾

5. Summary

For the purpose of fabricating GCs consisting of RE-free phosphor, ZrO₂, we prepared ZrO₂-containing borosilicate glass, in which ZrO₂ is singly crystallizable, and examined the crystallization behavior. The precursor glass precipitated tetragonal ZrO₂ with a dendritic structure as the initial phase, and the tetragonal phase was gradually transformed into a monoclinic phase as the heat-treatment time increased. The phase-transformation caused segmentation of the dendrites, resulting in needle-/rod-like ZrO₂ crystals on a few hundred nanometer-scale, and also providing an increase in blue PL intensity and its internal QY. Furthermore, the introduction of TiO₂ into precursor glass provided further improvement of the PL properties.

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