Formation of spherulite and metastable phase in stoichiometric $\text{Ba}_2\text{Si}_3\text{O}_8$ glass

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We investigated the crystallization and resulting morphology of a stoichiometric barium-silicate glass $\text{Ba}_2\text{Si}_3\text{O}_8$ (B2S3) using TEM observation and Raman spectroscopy. Spherical crystal growth (i.e., spherulite) of stoichiometric B2S3 phase was observed in the heat-treated glass samples, and the size of the spherulites drastically increased as the temperature increased during the heat-treatment process. It was also found that an initial precipitating phase in the precursive stage of crystallization is neither the B2S3 phase nor other crystalline phases in the BaO-SiO_2 system. It was deduced that a metastable phase precipitates prior to the formation of spherulite and acts as nucleation site for the spherulite.

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1. Introduction

Silicate minerals are widely deposited in the Earth's crust, thereby making silicate glass easily available. Silicate glass and glass-ceramic composites have been investigated extensively, not only in terms of their practical use but also because of scientific interest in their properties. Recently, new glass-ceramic materials have been developed for applications such as advanced photonic-devices and solid-state lighting components.¹⁻³⁾ Another class of materials are the alkali/alkali-earth silicate system glasses, in particular stoichiometric glasses. These materials are significant for illustrating the amorphous structure and nucleation and crystallization processes in oxide glasses.⁴⁻⁷⁾

In the BaO-SiO_2 binary system, eight types of crystalline phases exist: BaSi_4O_9 , BaSi_2O_5 , $\text{Ba}_3\text{Si}_5\text{O}_{13}$, $\text{Ba}_5\text{Si}_8\text{O}_{21}$, $\text{Ba}_2\text{Si}_3\text{O}_8$, BaSiO_3 , Ba_2SiO_4 , and Ba_3SiO_5 . It has recently been reported that when combined with rare earth doping,⁸⁻¹⁰⁾ these crystals and glass-ceramics have demonstrated excellent photoluminescent properties suitable for LED applications. Furthermore, BaO-SiO_2 system glass, along with $\text{Li}_2\text{O-SiO}_2$ system glass, has been treated as a standard for examining crystallization. Nevertheless, detailed studies on the crystallizing phase and its resulting morphology of stoichiometric glass are limited to BaSi_2O_5 and $\text{Ba}_3\text{Si}_5\text{O}_{13}$ compositions.¹¹⁻¹⁴⁾ In this study, a stoichiometric glass with a richer Ba composition, $\text{Ba}_2\text{Si}_3\text{O}_8$, has been prepared and the crystallization and its morphology have been investigated. The relationship of glass structure with crystallizing phase is also discussed. Since Eu^{2+} -doped $\text{Ba}_2\text{Si}_3\text{O}_8$ crystal has been expected to be a green-emitting phosphor,^{10,15)} this study would contribute to fabrication of new glass-ceramic material for LED application as well.

2. Experimental

The 2BaO-3SiO_2 (B2S3) glass was synthesized using a conventional melt-quenching technique. Reagent grade BaCO_3 (99.95%) and SiO_2 (99.9%) were mixed and melted in a platinum crucible at 1500°C for 1 h. The glass-transition (T_g), crystallization on-set (T_x), and crystallization peak (T_p) temperatures of the as-quenched glass were determined by differential thermal analysis (DTA) at a heating rate of 20 K/min , and values of $T_g = 706^\circ\text{C}$, $T_x = 870^\circ\text{C}$, and $T_p = 897^\circ\text{C}$ were obtained. The as-quenched glass samples were subjected to isothermal heat treatment in a temperature range of $T_{\text{HT}} = 780\text{--}810^\circ\text{C}$ for 1 h to crystallize the glass samples. The heat-treated samples were studied using powder X-ray diffraction (XRD) analysis, transmission electron microscope (TEM), and electron diffraction analysis. Raman scattering observation of the as-quenched and crystallized samples was performed using an Ar^+ gas laser operating at 514.5 nm . Raman scattering spectrum on the Stokes side was detected using a system comprising a triple-grating monochromator and a liquid-nitrogen-cooled, charge-coupled device (HORIBA-Jobin Yvon, T64000). All measurements in this study were performed at room temperature.

3. Results and discussion

3.1 Crystallization behavior and morphology in B2S3 glass

Figure 1 shows powder XRD results of B2S3 glass samples heat-treated at different temperatures for 1 h. As the heat-treatment temperature (T_{HT}) increased, an increase in the diffraction intensities was observed, primarily around $2\theta = 23.8$, 27.1 , and 32.2° . According to the phase-diagram for BaO-SiO_2 systems,¹⁶⁾ formation of B2S3 phase was expected in the crystallized samples. Although the diffraction patterns of the crystallized samples were roughly identical to that of the ICDD card of $\text{Ba}_2\text{Si}_3\text{O}_8$ (No. 27-1035), the diffraction peaks were vague, preventing definite confirmation that a B2S3 phase had formed.

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Fig. 1. Powder XRD patterns in B2S3 glasses subjected to isothermal heat treatment at 780–810°C for 1 h. Crystallographic data of ICDD: 27-1035 ($\text{Ba}_2\text{Si}_3\text{O}_8$) is also included (gray bar).

Fig. 2. TEM images of B2S3 glasses heat-treated for 1 h at 790°C (a), 800°C (b), and 810°C (c, d). The corresponding electron diffraction patterns (inset) and their intensity profiles (e) are also included. Values correspond to d -spacing (Å) in the heat-treated samples.

Figure 2 shows the results of TEM observation and the electron diffraction (ED) intensity profiles in the crystallized samples. Although a halo pattern and no crystallites were confirmed in the sample treated at $T_{\text{HT}} = 780^\circ\text{C}$, the sample treated at $T_{\text{HT}} = 790^\circ\text{C}$ indicated evolution of a spherical structure about $5\ \mu\text{m}$ in diameter (Fig. 2(a)). Because a crystal-

Fig. 3. Raman spectra in B2S3 glasses heat-treated at different T_{HT} for 1 h (a) and crystal structure of $\text{Ba}_2\text{Si}_3\text{O}_8$ (b). Sphere and wire-frame corresponds to Ba ion and silicate linkage, respectively. Solid and dashed circles correspond to Q^2 - and Q^3 -units, respectively.

like ED profile could be observed from the aggregate, we confirmed that this was spherulite (spherical crystal). Number and size of the spherulite increased with the T_{HT} , indicating a tendency toward homogeneous nucleation, and eventually the spherulites impinged on each other (Figs. 2(a–c)). Apart from the spherulites with a $\sim 10\ \mu\text{m}$ diameter in the sample obtained at $T_{\text{HT}} = 810^\circ\text{C}$, crystallized parts with a fine or formless texture were also observed in the vicinity of the impinged region (Fig. 2(d)). This crystalline texture is possibly due to “secondary crystallization,” which is often seen in polymers with a tendency toward spherical crystallization. The secondary crystallization is the formation of crystallites (much smaller than spherulite by primary crystallization) that occurs in the residual glassy-phase region between the grown spherulites after impingement of each spherulite.¹⁷⁾ The secondary crystallization and resulting formless crystalline texture has also been reported by Freiman et al. in $\text{Ba}_3\text{Si}_5\text{O}_{13}$ glass showing spherical crystal growth.¹²⁾ Furthermore, comparing the intensity profiles (Fig. 2(e)) to the crystallographic data, the spherulite was finally identified as a $\text{Ba}_2\text{Si}_3\text{O}_8$ phase.

3.2 Glass structure and crystallizing phase

Raman spectra in the heat-treated B2S3 glass samples are shown in **Fig. 3**, together with the crystal structure of the B2S3 phase.¹⁸⁾ In the as-quenched sample, broad bands were observed at about 100, 600, 930, and $1060\ \text{cm}^{-1}$. These bands are attributed to the Boson peak,¹⁹⁾ n -membered ring consisting of SiO_4 tetrahedra ($n = 3, 4, 6$),²⁰⁾ a SiO_4 unit with two bridging oxygen atoms (i.e., Q^2), and a SiO_4 unit with three bridging oxygen atoms (Q^3), respectively.²¹⁾ As the T_{HT} increased in the heat-treated samples, sharpening of the Raman bands and shrinkage of the Boson peak were observed simultaneously, indicating the glass–crystal phase-transition, i.e., crystallization (Fig. 3(a)).

Trace of spectrum for as-quenched samples corresponded well to the Raman spectra of the crystallized samples and appeared as smoothed Raman spectra of these samples. In addition, the presence of Q^3 - and Q^2 -units strongly suggests that the silicate structure in B2S3 glass is sheet-like because the linkage of the Q^3 -units provides a silicate expanse and that of the Q^2 -units provides its edge (cf. Fig. 3(b)). Upon considering the experimental fact that the B2S3 crystalline phase is formed by the crystallization of glass (Figs. 1 and 2), it is reasonable to consider that there is a significant structural similarity between the stoichiometric glass and the B2S3 phase on the scale of short- and medium-range order, i.e., on the sheet-like (two-dimensional, 2D) silicate structure consisting of Q^2 and Q^3 units and the Ba-enriched/-cohesive region (cf. Fig. 4 of Ref. 19)). According to Takahashi et al., the layer structures of the crystallizing phase constitute a necessary or favorable condition for homogeneous nucleation, in addition to the local structural similarity.¹⁴⁾ Therefore, it is deduced that the structural similarity between the stoichiometric glass and the crystallizing-B2S3 phase provides the conditions for homogeneous nucleation and the subsequent spherical crystal growth.

3.3 Crystallization precursive stage

It has been demonstrated that the $Ba_5Si_8O_{21}$ phase initially precipitates in a nanometric inhomogeneous region of $BaSi_2O_5$ (BS2) glass, and this phase acts as the site for crystal growth of β -BS2 phase.^{14),19),22)} This leads us to consider that in the current B2S3 glass, a crystalline phase other than the B2S3 phase initially precipitates as a crystal nucleus during the crystallization precursive stage. Therefore, observation of structural change during the initial stage of crystallization was attempted.

Figure 4 shows the DTA and TEM results in the B2S3 glass heat-treated at 710°C ($\sim T_g$) for 30 h. The heat-treated sample (bulk form) exhibited a considerably lower T_p compared to that of the as-quenched sample ($\Delta T_p = 45^\circ\text{C}$) (Fig. 4(a)), indicating that a large number of nuclei developed during the isothermal

treatment period, i.e., there was a trend toward homogeneous nucleation.²³⁾ In addition, we also observed the crystalline aggregates with diameters of about 200 nm, which is much smaller than the spherulites of the B2S3 phase (Fig. 4(b)). Moreover, the ED profile of the aggregate was not identical to that of the spherulites obtained at $T_{HT} = 790\text{--}810^\circ\text{C}$, i.e., the B2S3 phase (Fig. 4(c)). Furthermore, the ED profile was not identical to other crystallographic data in the BaO–SiO₂ binary phase, implying that the aggregates formed at $T_{HT} = 710^\circ\text{C}$ represents a metastable phase. Taking the DTA result into account, it is deduced that the metastable phase in nano-size, which initially precipitates from the glassy phase around the T_g (or supercooled liquid, SCL) acts as the site for crystal growth of the B2S3 phase. In other words, the initial nucleating phase is different from the subsequent crystallizing phase in the B2S3 glass. These tendencies are also confirmed in other silicate and germinate glasses showing a trend toward homogeneous nucleation.^{14),24),25)} Although the origin of the metastable phase is still unclear, as far as crystallization of the BS2 glass is concerned we can suppose that the initial nucleating phase (or metastable phase) in the B2S3 glass is closely related to the presence of a nanometric inhomogeneous region in which Ba ions are enriched or cohesive.^{19),22)} To elucidate these issues, further study is now in progress.

4. Summary

TEM and Raman spectroscopic studies were conducted on the as-quenched and crystallized samples of a stoichiometric glass in BaO–SiO₂ system, i.e., $Ba_2Si_3O_8$ (B2S3) glass. In this study, the following results were obtained:

i) Spherical crystal growth (spherulite) of B2S3 phase was confirmed in the B2S3 glass samples that were subjected to isothermal heat treatment at $T_{HT} = 790\text{--}810^\circ\text{C}$. B2S3 glass exhibited a trend toward homogeneous nucleation, similar to other stoichiometric BaO–SiO₂ system glasses such as $BaSi_2O_5$ and $Ba_3Si_5O_{21}$. In particular, the size of the spherulites drastically increased as T_{HT} increased. This is possibly due to the structural similarity between the glass and the crystallizing phase, leading to a smooth progression of the SCL–crystal phase-transition.

ii) The B2S3 glass heat-treated in the proximity of T_g for 30 h showed a considerable shift of T_p to a lower temperature, and the crystalline aggregates with diameters of about 200 nm were also observed. The aggregates did not correspond to either the B2S3 phase or the other crystalline phases in the BaO–SiO₂ system, suggesting a metastable phase. It is deduced that the metastable phase initially precipitates in the crystallization precursive stage, and acts as a crystal nucleus in the B2S3 glass.

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Fig. 4. DTA patterns of as-quenched B2S3 glass and the sample heat-treated at 710°C for 30 h (a), TEM image of the sample heat-treated at 710°C (b), and its intensity profile of electron diffraction patterns (c).

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