Impact of Nd-doping on crystallization and phase separation in glassy ferroelectric LaBSi⁸Ge₉O₅ (x = 0, 0.4)

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Since stillwellite-type ferroelectric LaBGeO₅ shows the intriguing physical properties by the doping/substituting-modification, the stillwellite-type glass-ceramics has been studied extensively from viewpoint of material engineering. In this study, we examined how the Nd-doping affects the glassy ferroelectric LaBGeO₅ and its modified sample, LaBSi⁸Ge₉O₅. We experimentally demonstrated that small amount of the doping gives a significant effect on the crystallization and phase-separation trends.

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1. Introduction

Basically, there are two ways to provide a glass with optical functionality; i) doping with rare-earth (RE) ion, and ii) formation of optically-active phase by crystallization (glass-ceramics processing). Combination of i) and ii) has been also attempted to produce new class of phosphor.

A lanthanum borogermanate, LaBGeO₅, is ferroelectrics with a hexagonal stillwellite (CebSiO₃)-type structure. This phase is known to be an excellent nonlinear-optical crystal, and to be a novel phosphor with RE-doping (RE=Eu, Tb, and Tm).

13) For instance, formation of LaBGeO₅-crystalline dots has been succeeded in Nd-doped glassy LaBGeO₅ by means of a laser processing. However, the silicogermanate system, i.e., glassy La(Si,Ge)O₅, has not been reported so far. Therefore, it is of particular interest in fabricating the glassy La(B(Si,Ge)O₅). Replacement of the minor metal (Ge) with a common element (Si) is important from the viewpoint of resource conservation.

A small amount of RE-doping to glass affects its micro/nanostructure, e.g., clustering, phase separation, and formation of the non-bridging oxygen. This implies that the thermal properties of the doped glass, e.g., crystallization and phase-separation, is largely different from that of the base (non-doped) glass. Therefore, to prepare the RE-doped glass-ceramics, it is of particular interest in fabricating the glassy LaB(Si,Ge)O₅.

2. Experimental

The glass compositions in present study were stoichiometric LaBGeO₅ and LaBSi₉Ge₉O₅ (denoted by LBG and LBSG, respectively) and the compositions, which are substitutionally-doped with Nd⁴⁺, i.e., La₉₈Nd₂B₉Ge₅O₅ and La₉₈Nd₂BSi₉Ge₅O₅ (Nd-LBG and Nd-LBSG, respectively). The glassy samples were prepared by a melt-quenching method. Polycrystalline samples (Batch weight: ~20 g) of the corresponding stillwellite phases, which were synthesized via a conventional solid-state reaction, were melted in a platinum crucible with a lid at 1350–1400°C for 20 min in an electric furnace. In the synthesis, commercial powders of reagent grade La₂O₃, Nd₂O₃, B₂O₃, SiO₂, and GeO₂ were used. The melts were poured onto an iron plate heated at ~200°C and pressed to a thickness of about 1.5 mm. As-quenched glassy samples (powdered and bulk states) were investigated by a differential thermal analysis (DTA) at a heating rate of 10 K/min to determine the thermal parameters, i.e., glass-transition (Tg), crystallization-onset (Tc) and crystallization-peak (Tp) temperatures. The crystalline phases present in the heat-treated samples were checked by X-ray diffraction (XRD) analysis using Cu-Kα radiation, in addition to the lattice constants. The heat-treated sample was studied by field emission scanning electron microscope (FE-SEM) with an energy-dispersive X-ray (EDX) fluorescence spectrometer (JEOL, JSM-6500F).

3. Results and discussion

The reason for the selection of glassy LBSG (LaBSi₉Ge₉O₅) as a representative in the silicogermanate system is that in preliminary study, we have confirmed a milky-white region attributed to immiscibility in the as-quenched LaBSi₉Ge₉O₅ sample. Therefore, the LBG and LBSG are considered to lie within the miscible range (or 1-liquid phase). Indeed, the as-quenched samples were visually-transparent, and were confirmed to be amorphous by means of the XRD analysis: Fig. 1 shows the DTA results for studied glasses with powder and bulk states. The values of Tg, Tc, and Tp determined by the analyses are also included. The glasses were heat-treated on the basis of the thermal parameters to obtain the crystallized samples. The reasons for the selection of glassy LBSG (LaBSi₉Ge₉O₅) as a representative in the silicogermanate system is that in preliminary study, we have confirmed a milky-white region attributed to immiscibility in the as-quenched LaBSi₉Ge₉O₅ sample. Therefore, the LBG and LBSG are considered to lie within the miscible range (or 1-liquid phase). Indeed, the as-quenched samples were visually-transparent, and were confirmed to be amorphous by means of the XRD analysis: Fig. 1 shows the DTA results for studied glasses with powder and bulk states. The values of Tg, Tc, and Tp determined by the analyses are also included. The glasses were heat-treated on the basis of the thermal parameters to obtain the crystallized samples. Figure 2 shows the powder XRD patterns in the non-doped glassy samples subjected to isothermal heat-treatment at Tp for 1 h. The Tp for glassy LBG and LBSG were measured in bulk state, and were estimated to be 883 and 914°C, respectively. Crystallization of the stillwellite phase could be confirmed in the heat-treated samples. Although the stillwellite phase singly formed in the LBG sample, the LBSG sample...
indicated a trace of diffraction peak at 2θ~28° attributed to formation of a secondary phase. Lattice constants of the stillwellite phase for the crystallized LBG sample were estimated to be \( a = 6.993 \) and \( c = 6.862 \), which well correspond to the values in a previous study (\( a = 6.989 \) and \( c = 6.860 \)). The constants for the crystallized LBSG sample were \( a = 6.925 \) and \( c = 6.819 \), which are smaller than the constants for the crystallized LBG sample, suggesting the incorporation of smaller Si\(^{4+}\) into the Ge\(^{4+}\) site in stillwellite structure.

Surface crystallization (or inhomogeneous nucleation) frequently leads to crystal-orientation of the crystallized phase to its preferential-growth direction based on geometrical selection. Because glassy LBG has a strong tendency of surface crystallization, we performed the DTA measurement using the powdered samples, and then obtained \( T_g = 753\)°C and \( T_x = 784\)°C for LBG and LBSG samples, respectively. Fig. 3 shows the XRD patterns on the surface region of glassy LBG and LBSG heat-treated at \( T_x \) for 3 h (The samples were subjected to mirror-polishing before the heat-treatment). The heat-treated LBG and LBSG samples indicated good transparency, meaning that no phase-separation occurs (pictures of the samples; inset). In the as-treated samples (indicated by dashed lines), relative diffraction-peak intensity of (110) plane is larger than that of JCPDS data, i.e., preferential growth of (110) plane at the initial surface. Eliminating the surface (depth of ~40–50 μm from the initial surface), we observed the strong (102)-peak, and weak (003) and (014)-peaks, i.e., preferential growth to [102]-direction instead of the (110)-peak (indicated by red and blue patterns). These crystallization features have been also confirmed in previous study.

We also examine the Nd-doped samples, i.e., Nd-LBG and Nd-LBSG, in accordance with the protocol of the non-doped samples above-mentioned. Although glassy La\(_{0.8}\)Tb\(_{0.1}\)Yb\(_{0.1}\)BGeO\(_5\) has been prepared in order to examine the emission property by Liu et al., the RE amount of our samples is much smaller than that of their sample. We visually confirmed a pale blue coloration in the as-quenched Nd-doped samples, which is due to specific optical absorption of the Nd\(^{3+}\). The crystallized Nd-doped samples were prepared by the isothermal heat-treatment at \( T_p \) for 1 h. The \( T_p \) for Nd-LBG and Nd-LBSG samples (bulk state) were estimated to be 897 and 915°C, respectively. The powder XRD analysis revealed that phase-formation tendency of the crystallized Nd-doped samples is similar to that of the crystallized non-doped ones, i.e., single crystallization of stillwellite phase in the Nd-LBG sample, and appearance of small peak due to the impurity phase in the Nd-LBSG sample: Fig. 4 shows the XRD patterns on the surface region of glassy Nd-LBG sample heat-
treated at $T_x$ for 3 h. The $T_x$ was estimated to be 767°C (powdered sample). In the as-treated sample, the initial surface already indicated the strong orientation to [102]-direction (dashed line). After eliminating the surface, the diffraction peak of (003) plane was mainly observed (depth of 48 μm), and the stillwellite phase was more oriented in the interior (depth of 92 μm). Thus, we demonstrated the polar $c$-orientation by the Nd-doping in the surface-crystallized glass-ceramics.

In the glassy Nd-LBSG, we found the sample heat-treated at $T_x$ for 3 h to be opalescent [The $T_x$ was estimated to be 785°C; cf. Fig. 4(a)] despite that the non-doped LBG sample kept transparency after the heat-treatment (Fig. 3). In order to elucidate the reason for the opalescence, we conducted the microstructure observation: Fig. 5 shows the SEM and EDX results in cross-section of the as-treated Nd-LBSG sample. The backscattered electron (BS) mode revealed numerous fingered-particles with approximately 1 μm, in which the mean atomic number should be small [Fig. 5(a)]. As a result of EDX mapping, the constituent of the particles is considerably Si-richer than that of surrounding matrix [Fig. 4(b)]. This is also supported by result from the point analysis. The Si-rich region is suggested to develop on the basis of a phase-separation process. Thus, the opalescence in Nd-LBSG sample is attributed to a light scattering due to the development of the fingered particles. Although the phase-separation morphology found in the heat-treated sample is quite different from spinodal- and binodal-types, the similar morphology, in which Si-element is enriched, has been reported in phase-separated ZnO-B$_2$O$_3$-SiO$_2$ and MgO-SiO$_2$-Si$_3$N$_4$ system glasses.20) Unfortunately, the reason for the strange morphology (like a virus) has been unclear, but Taylor has supposed by analogy of dendritic crystal-growth that such structure is developed on the basis of diffusion controlled condition.21)

4. Summary

We examined the Nd-doping effect on crystallization and phase-separation in glassy ferroelectric LaB$_x$Ge$_{1-x}$O$_5$ and LaBSi$_{0.4}$Ge$_{0.6}$O$_5$. Whereas the non-doped samples indicated surface crystallization with strong orientation to [102] direction, the Nd-doping led the crystallized stillwellite-phase to the polar $c$-orientation. Furthermore, the heat-treated LaBSi$_{0.4}$Ge$_{0.6}$O$_5$ samples were visually transparent, its Nd-doped sample, i.e., La$_{0.96}$Nd$_{0.04}$Si$_{0.4}$Ge$_{0.6}$O$_5$, became opalescent after the heat-treatment due to phase separation. These results strongly suggest that the doping even with small amount of RE ($\approx$ a few %) governs the crystallization and phase-separation trends in glass. Our study also suggests that RE-doping enables us to control the crystal growth and orientation in glass-ceramics.

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