Preparation of functional glasses and glass ceramics using stable immiscibility

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High functionalization of materials by the combination of heterogeneous substances has become an important procedure for the development of high-performance materials. In various procedures for composite processes, the phase separation of glasses has a potential for use with combinations of the varieties of functional materials spontaneously in nanometer and micrometer scale. Moreover, because phase separation is applicable not only to glass–glass combinations but also to glass–crystal combinations which can control both crystalline phase and inside structure of the composite simultaneously, the utilization of phase separation becomes an interesting and effective technique to create novel high-performance composite materials. In this review, the phase separation of inorganic glasses and glass ceramics mainly caused by stable immiscibility phenomena in high-temperature melts and their applications to the preparation of the high-performance composites are summarized. The preparation procedures and the performances of the materials in silicate systems were described specifically, centering on the studies of the author’s group such as luminous, magnetic, and photocatalytic materials.

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1. Introduction

Immiscibility phenomenon or phase separation is common for various substances in gaseous, liquid, and solid states, and in their various conditions of temperature, pressure, and composition. The immiscibility phenomenon of substances has been studied and applied to various practical utilizations in the fields of metal alloy and organic polymer materials. Inorganic substances also showed immiscibility. Especially, immiscibility phenomena for oxide melts and glasses are designated as phase separation, and it exists in many compositions which consist of silicic acid, boric acid, alkaline metal oxides, alkaline earth metal ones, and oxides of transition elements.1–6 In glassy materials, although the phase separation becomes a cause of devitrification by light scattering between two separated phases, it is applicable to prepare various composite materials with high-performance characteristics. Actually, sodium borosilicate glasses showing phase separation have become typical and widely practical glass materials used as heat and chemical-resistant glasses, a high silica glass, and a porous silica glass. Those glasses are well known as Duran® (Schott AG), and Pyrex® and Vycor® (Corning Inc.).

However, the procedures for a complex of the structures of functional materials in nanometer and micrometer scale have been spreading widely and have become extremely important in the progress of materials research and their development. In various procedures for composite process, the phase separation of glasses presents the potential for the combination of the varieties of functional materials spontaneously in nanometer and micrometer scales. Moreover, because the phase separation is applicable not only to a glass–glass combination but also to a glass–crystal combination, with simultaneous control of the crystalline phase and inside structure of the composite, the utilization of phase separation becomes an extremely interesting and effective technique to create innovative high-performance composite materials.

This review summarizes the phase separation of inorganic glasses and glass ceramics caused by mainly stable immiscibility phenomena in high-temperature melts and their applications to the preparation of the high-performance materials. The preparation procedures and the performances of the materials in silicate systems were described specifically, centering on studies of the author’s group such as luminous, magnetic, and photocatalytic material composites.

2. Phase separation of glasses and melts

2.1 Mechanism and characteristic of phase separation

Because the phase separation of glasses and melts has been described in many reports in the literature as described above, its outline is presented here. In some multi-component systems of high-temperature melts, super-cooled liquids or glasses, the state which consists of two separated phases becomes a thermodynamically stable condition in their particular compositions and temperatures. In Fig. 1(a), the schematic phase diagram shows that the immiscibility region exists as the solid state, which is designated as a metastable immiscibility. The immiscibility region which exists above liquidus presented in Fig. 1(b) is designated as a stable immiscibility. In both immiscibility regions, the phase separation proceeds in two different mechanisms. One is a spinodal decomposition mechanism. The other is a nucleation-growth mechanism. When the homogeneous melt at high temperature (T1) is cooled and kept in the immiscibility region of a spinodal decomposition mechanism (shown as dotted area) at T2, the phase separation proceeds and the three-dimensional interconnected structure is formed, which consists of solid phases S1 and S2 in Fig. 1(a) or liquid ones, L1 and L2 in Fig. 1(b). In

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contrast, when those are kept in the region of a nucleation-growth mechanism, the discrete droplets or the flower shapes of minor phase are formed in the matrix of the major phase. The compositions of the major and minor phases are also $S_1$ and $S_2$, or $L_1$ and $L_2$, and the initial composition determines which phase-separated composition becomes the major or the minor phase by a lever rule.

In cases where the homogeneous high-temperature melt is quenched rapidly, the homogeneous glass can be formed. However, when such glass is heated and kept in the immiscibility region above the glass transition temperature for an appropriate time, the phase separation proceeds with time. The sodium borosilicate glasses in $\text{Na}_2\text{O} - \text{B}_2\text{O}_3 - \text{SiO}_2$ ternary system have a wide metastable immiscibility region. The phase separated glasses in this system have been used practically, as described already.

The phase separation phenomenon for the system having a stable immiscibility region is fundamentally the same as that of a metastable immiscibility. As an example, Fig. 2 shows the phase separation structures, observed using scanning electron microscopy (SEM), of the glasses in $\text{Fe}_3\text{O}_4 - \text{SiO}_2$, shown in (a) and (b), and $\text{CaO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$ systems, which have a stable immiscibility region at high temperatures, in (c). The latter are described later in section 3.2. The glass surfaces were chemically etched: the bright part shows the $\text{SiO}_2$ rich phase. The dark etched part shows the $\text{Fe}_3\text{O}_4$ (and $\text{CaO}$) rich phase. When the high-temperature melt ($2200^\circ\text{C}$) was maintained for 3 min and rapidly quenched, no phase separation structure was apparent, as shown in image (a). In contrast, when the melt was once kept in the immiscibility region ($1800^\circ\text{C}$) for 3 min and subsequently quenched, the glasses showed a droplet structure, as shown in image (b), that were formed by a nucleation-growth mechanism or the interconnected one in image (c) formed by a spinodal decomposition one. As described in the Introduction, the author’s group mainly investigated the preparation of high-performance materials using phase separation in the stable immiscibility regions of various systems. Consequently, phase separation in stable immiscibility is discussed in the following paragraphs and sections.

### 2.2 Stable immiscibility

Many silicate and borate systems have a stable immiscibility region in which high-temperature melt separates spontaneously into two liquid phases. In the stable immiscibility region, phase separation proceeds rapidly because of a high diffusion rate of substances in liquid phase. Typical composition systems having a stable immiscibility region are binary systems of alkaline earth metal oxide including magnesium oxide and silica ($\text{RO} - \text{SiO}_2$, $\text{R} = \text{Mg, Ca, Sr}$). The phase diagrams of $\text{MgO} - \text{SiO}_2$, $\text{CaO} - \text{SiO}_2$, and $\text{BaO} - \text{SiO}_2$ are presented schematically in Fig. 3(a). Among group 2 elements, the immiscibility region of the $\text{BaO} - \text{SiO}_2$ system exists below liquidus. It is defined as a metastable state. The difference of the tendency of phase separation was discussed by application of Debye–Hückel theory to alkaline metal and alkaline earth metal oxide and silica binary systems.

Various transition metals or heavy metal oxides and silica binary systems have a stable immiscibility region, such as $\text{TiO}_2$, $\text{Fe}_3\text{O}_4$, $\text{MnO}$, and $\text{Y}_2\text{O}_3$. The phase diagram of a $\text{TiO}_2 - \text{SiO}_2$ binary system is also presented schematically in Fig. 3(b) as an example. This system has a wide composition range of a stable immiscibility above liquidus temperature ($>1780^\circ\text{C}$). The multi-component systems mainly containing a composition that shows a stable immiscibility are apt to have an

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**Fig. 1.** Schematic phase diagram showing metastable and stable immiscibility regions with images of phase separation texture. The spinodal decomposition and nucleation growth mechanism are denoted, respectively, as “S” and “N”.

**Fig. 2.** SEM images of phase separation textures of the glasses in $\text{Fe}_3\text{O}_4 - \text{SiO}_2$, (a) and (b) and $\text{CaO} - \text{Fe}_3\text{O}_4 - \text{SiO}_2$, (c) after chemical etching.
immiscibility region. The silicate system and borate system have the same tendency: RO$_2$B$_2$O$_3$ (18, 19) and PbO$_2$B$_2$O$_3$.20, 21) Inoue et al. discussed phase separation phenomena under microgravity in a BaO–B$_2$O$_3$ system.22)

3. Control of phase separation texture

3.1 Size of the phase separation texture

When the phase-separated melt in the stable immiscibility region is quenched, glass having a phase separation structure is obtainable just as in a system having a metastable immiscibility region as presented in Fig. 2. The size of the phase separation texture can also be controlled using the composition, holding temperature, and the time in the immiscibility region. For example, the change of the phase separation texture of the glasses was examined in a CaO–SiO$_2$ system with the change of the Al$_2$O$_3$ content. The glass composition was changed on a base of the two end members of phase separation as 25SiO$_2$–75Al$_2$O$_3$ and 10CaO–90SiO$_2$ (mol%), as estimated from the phase diagram in the CaO–Al$_2$O$_3$–SiO$_2$ ternary system.23) Consequently, the sample composition is represented as $x$(25SiO$_2$–75Al$_2$O$_3$)–(100 – $x$)(10CaO–90SiO$_2$) (mol%, $x$ = 0–15). These glasses also contained 0.3 mol% of Eu$_2$O$_3$ for luminescence measurements, as described hereinafter. The melt-quenched glasses were prepared using an infrared image furnace. The sintered materials of the composition above were melted at 2000°C for 3 min first. The melts were then cooled and kept at 1800°C for 5 min. They were subsequently quenched rapidly. The temperatures of the melts were measured using an optical pyrometer system.24)

Figure 4 presents SEM images of the phase separation textures of the obtained glasses with schematic diagram of the composition. Images of all samples showed the interconnected texture, which indicates that the phase separation proceeded by the spinodal decomposition mechanism. As the amount of Al$_2$O$_3$ increased, the phase separation size became fine from micrometer to nanometer scale. This change was regarded as resulting from the increase of the mutual solution ability between CaO-rich and SiO$_2$-rich phases by the Al$_2$O$_3$ addition.

Our prepared glasses contained Eu$^{3+}$ ions. Therefore, they showed red photoluminescence (PL) under photoillumination of the appropriate wavelength. The change of the size of the phase separation texture affected their PL intensity considerably. Figure 5(a) shows the change of the transmitted PL intensity at 612 nm with Al$_2$O$_3$ content when the excitation light of 464 nm was irradiated from the bottom of the sample. The transmittance curves of the several samples in the UV–visible range are also presented in Fig. 5(b). The PL intensity once increased concomitantly with increased Al$_2$O$_3$ content and had a peak. Subsequently the PL intensity decreased steeply. On the other hand, the transmittance of the glass without Al$_2$O$_3$ contents were extremely low because of strong light scattering caused by the micrometer-scale phase separation texture, as portrayed in Fig. 4(a). However, the transmittance increased steeply with the increase of Al$_2$O$_3$ content, i.e., the size of the phase separation texture became small to sub-micrometer or less. That change is attributable to fact that the change of the transmittance curves from white (Mie) scattering in whole visible range to Rayleigh scattering has strong wave-
length dependence. These results indicate that the PL intensity was influenced strongly by light scattering (LS), which was induced by the phase separation texture. The strong transmitted PL intensity is regarded as obtained when the size of the phase separation texture is suitable for high LS of the excitation light (464 nm) and low LS of the emission light (612 nm). The glass at the peak PL intensity showed a phase separation texture of several hundred nanometers, which satisfied such an LS condition.

The results of scanning near field optical microscopy (SNOM) for the glass of 10CaO–90SiO2 (mol %) are depicted in Fig. 6. The one phase showed PL at 612 nm excited at 532 nm. This emitted phase was the CaO-rich phase because transition elements including rare earth ones are apt to concentrate in the SiO2-poor phase in the phase separated silicate glasses.3) This concentration of the emitted Eu3+ ions in the CaO-rich phase may affect the PL intensity because it also concerns the emission properties of the phase separated glass such as a concentration quenching and a waveguide effect. Therefore, control of the phase separation texture size is extremely important for optical properties. It is especially effective for the enhancement of emission properties.

3.2 Deformation of the phase-separation texture
Glasses and glass ceramics having deformed phase separation and crystallization texture can show anisotropy in dependence on a deformation shape. Effect of electric field on texture and crystallization behavior of phase separation was anticipated in some silicate glasses. The dynamic deformation of the phase separation texture was examined in PbO–B2O3 and borosilicate systems. In the case of the dynamic deformation, when a phase-separated melt in a stable immiscibility region is quenched with elongation as same as that in a metastable immiscibility region, the phase separation texture is expected to be deformed.

We specifically examined various multi-component glasses and glass ceramics based on Fe3O4–SiO2 system because those systems have a stable immiscibility region and the obtained materials have the potential to show magnetic and electric functions induced by the precipitated magnetic semiconductor materials such as a magnetite (Fe3O4). In the stable immiscibility region of binary 5Fe3O4–95SiO2 (mol %), which forms droplets of Fe3O4-rich phase in SiO2-rich matrix by a nucleation and growth mechanism as presented in Fig. 2(b), the phase separated melts were quenched as they were mechanically elongated. The droplets were deformed into a needle-like shape of which length was almost linearly increased with the elongation length. This result was similar to that reported in PbO–B2O3. However, the glasses did not precipitate magnetite or other magnetic crystalline phase. The CaO–Fe3O4–SiO2 ternary system also has a wide stable immiscibility region. Its phase-separation texture was expected to
be controlled by the composition. Furthermore, the glass in this system can precipitate magnetite or calcium ferrite, which are magnetic semiconductors having ferromagnetic and electric conductivity, by the appropriate subsequent heat treatment. As presented in Fig. 2(c), the melt-quenched glass of \(3.6\text{CaO} \cdot 4.8\text{Fe}_3\text{O}_4 \cdot 91.6\text{SiO}_2 \text{(mol%)}\), \([5\text{Fe}_3\text{O}_4 \cdot 95\text{SiO}_2 + 3.75\text{CaO} \text{(mol%)}]\) had an interconnected texture caused by a spinodal decomposition mechanism. When the phase-separated melt was quenched with the elongation, the texture also elongated into a needle-like form that was the same as the droplet type texture in the glass of binary \(5\text{Fe}_3\text{O}_4 \cdot 95\text{SiO}_2 \text{(mol%)}\). The SEM image of the etched surface of the elongated sample is portrayed in Fig. 7(a). After heat treatment at 700°C for 1 h, the sample showed ferromagnetism caused by the precipitation of magnetite (\(\text{Fe}_3\text{O}_4\)). Figure 7(b) shows magnetic torque curves of elongated and non-elongated samples. The magnetic torque curve of the elongated sample showed obvious periodic variation at every 180°. This result and other magnetic properties obtained from the magnetization curve indicated that the elongated sample had uniaxial magnetic anisotropy caused by the elongation of \(\text{Fe}_3\text{O}_4\)-rich phase.

Magnetic semiconductors such as magnetite are extremely important materials because of their ferromagnetic and electric conductive properties. Especially, oxide magnetic semiconductors have become candidates to achieve magnetic sensor devices used under severe conditions such as high temperatures and humidity, and are recently studied for application to the heat generation media under a high-frequency magnetic field for hyperthermia. The melt-quenched samples in the \(\text{CaO} \cdot 5\text{Fe}_3\text{O}_4 \cdot 95\text{SiO}_2 \text{ternary system showed precipitation of the magnetite as main crystalline phase accompanied with precipitations of fayalite (FeSiO}_4\), (Ca, Fe)SiO}_3 and wollastonite (CaSiO}_3\), depending on their composition. The changes of the electric conductivity of the elongated and non-elongated samples with \(5\text{CaO} \cdot 95\text{SiO}_2 + x\text{Fe}_3\text{O}_4 \text{(mol%)}\) composition are presented in Fig. 8(a). The electric conductivities of both the elongated and non-elongated samples steeply increased concomitantly with increased \(\text{Fe}_3\text{O}_4\) content of more than \(x = 10\). The existence of the threshold amount of \(\text{Fe}_3\text{O}_4\) suggests that the continuity of \(\text{Fe}_3\text{O}_4\)-rich phase and the mutual contact of magnetite particles in that phase are necessary. The magnetic semiconductor usually shows a magnetoresistive effect, which is a change of electric conductivity with the applied magnetic field. The change of the magneto resistance ratio, MR, of both the samples with the composition is presented in Fig. 8(b). The MR was defined as the ratio of the electric resistance under a magnetic field of 0.5 T, \(\rho_{0.5T}\), and no magnetic field, \(\rho_0\), that is MR = \((\rho_{0.5T} - \rho_0)/\rho_0\). The MR of the elongated sample was much larger than that of the non-elongated one in the composition, which contained a small amount of \(\text{Fe}_3\text{O}_4\) above the threshold. The elongated sample had elongated phase-separation texture containing \(\text{Fe}_3\text{O}_4\), which can induce the large internal magnetic field caused by uniaxial shape magnetic anisotropy, as portrayed in Fig. 7. However, the elongated sample containing...
larger amount of Fe₃O₄ than 15 mol% showed steep decrease of the MR value. In this composition area, the size of the Fe₃O₄ rich phase enlarged and might become a major phase. Moreover, the viscosity of the melt became low. This change of the character of the melt suppressed the deformation of phase separation texture by the elongation process, and consequently suppressed the induced internal magnetic field. Therefore, the MR value became close to that of the non-elongated sample.

These composite materials, which consist of magnetic semiconductor and glass matrix and which are prepared by phase separation phenomenon, have various potentials to show magnetic and electric functional properties, but the controls of the composition, the precipitated crystalline phase, and the size and shape of the texture are necessary. For application of the magneto-resistive effect and heat generation, various silicate systems have been investigated by the author’s group such as Fe₂O₃−TiO₂−SiO₂, Co₃O₄−TiO₂−SiO₂ and Fe₂O₃−MnO₂−SiO₂ systems.

4. Control of crystallization by phase separation

4.1 Size and phase control

As described in the previous section, precipitation of the appropriate crystals in the glassy materials is one beneficial point related to fabrication of the high-performance composite using phase separation. For such purposes, the control of crystallization behavior becomes extremely important. The TiO₂−SiO₂ binary system has a stable immiscibility region over a wide compositional range from 19 mass% TiO₂ to 93 mass% SiO₂, as depicted in Fig. 3(b). Another important point is that no compound forms exist between TiO₂ and SiO₂. Therefore, the TiO₂−SiO₂ binary system is applicable to fabricate the porous composite comprising discrete TiO₂ fine particles by way of the combination of the phase separation and the selective leaching technique, as illustrated schematically in Fig. 9. The sintered rod of xTiO₂−(100−x)SiO₂ (x = 30−60, mass%) was once melted at over 2000°C for 3 min, and was cooled at temperatures of 2000 to 1820°C. Subsequently, the phase-separated melt was quenched rapidly using a twin roller. The as-quenched samples were ground down to appropriate size. The silica-rich phase in the melt became close to that of the non-elongated sample.

These composite glasses were metastable anatase and stable rutile of TiO₂. The photocatalytic-active anatase increased with decreased TiO₂ content in the initial composition. The crystalline phase of TiO₂ in the as-quenched sample was also controllable by other experimental conditions such as the melting temperature and quenching rate. The lower melting temperature and the high quenching rate caused the increase of the ratio of anatase phase. Although this process was subjected to extremely high temperatures, the metastable phase of anatase was obtained using phase separation. The anatase phase was regarded as crystallized from TiO₂-rich phase in the phase separated melt. Therefore, the structure of TiO₂ cluster in the TiO₂ rich phase in the melt is expected to resemble that of metastable anatase phase. Moreover, the component of SiO₂ reportedly suppresses the phase transition from anatase to rutile. Consequently, SiO₂ contents in the TiO₂ rich phase can hinder the progress of the phase transition from anatase to rutile during quenching. The obtained porous TiO₂ showed much higher photocatalytic activity as hydrogen generation from ethanol aqueous solution under UV light irradiation compared with commercial anatase powders of which the.

476

Fig. 9. Porous composite comprising discrete TiO₂ fine particles by way of the combination of the phase separation and the selective leaching in TiO₂−SiO₂ stable immiscibility region.

(a) As quench  (b) After selective leaching

Fig. 10. (a) Photographic image of the as-quenched sample before grinding and leaching; (b) and (c) SEM images of the sample after grinding and selective leaching.
specific surface area was similar to that of the obtained powder. This high photocatalytic activity is regarded as attributable to the effect of the suppression of the recombination between photo-excited electrons and holes caused by the existence of SiO2 boundary among the TiO2 fine particles. This procedure can be combined with the elongation process. The wire-shaped composite was obtained. It can photocatalytically decompose the local area of the polyimide thin film39 and the self-assembled monolayer on the Si substrate.40}

4.2 Crystallization induced by phase separation texture

Phase separation is applicable to the fabrication of glass-ceramics because of the fine and bulk crystallization at the boundary of the two phases in the phase separation texture. This is a beneficial point of the crystallization in the phase-separated glasses because glasses generally tend to give rise to surface crystallization, which causes inhomogeneous structure and property. As described above, a CaO–Al2O3–SiO2 ternary system has a wide immiscibility region. Recently Eu2+ doped anorthite, CaAl2Si2O8:Eu2+, is a remarkable blue phosphor under vacuum UV light excitation because of its high durability against oxidation atmosphere and Xe ion bombardment.41 Therefore, homogeneous precipitation of Eu2+ doped anorthite occurs from a CaO–Al2O3 rich phase of the phase-separated glass in the immiscibility region of CaO–Al2O3–SiO2 ternary system. Moreover, dispersion of the micro crystals of Eu2+ doped anorthite in SiO2-rich matrix was expected to enhance their thermal and chemical durability.42,43 Consequently, the phase-separated glasses and glass ceramics with the composition of the immiscibility region of this system were prepared using conventional melt-quenching and subsequent heat treatment processing. The compositions of the glasses were (x − 1)SiO2−x(x + 30−60 mol %, x = 70, 76, 80, 90 and 0.3 mol % of Eu2O3. Metal Si powder (1 mol %) was added in the composition to enhance the reduction of Eu3+ to Eu2+. The melt-quenched glasses were heat-treated in two steps: a low-temperature heat treatment for promoting phase separation at 1050°C for 48 h and a high-temperature one for crystallization at 1150°C for various times to induce crystallization at the boundary of CaO−Al2O3 rich and SiO2-rich phases. The heat treatment temperatures were determined from the preceding DTA analysis.

All the melt-quenched glasses had a transparent yellow color due to the presence of the Eu2+ ions. Though the phase separation was anticipated to be formed by the stable immiscibility in this composition, the addition of alumina might suppress the phase separation in the melt as described in above section or the immiscibility region might change metastable condition below liquidus. The XRD patterns of the melt-quenched, phase-separated and crystallized glasses of x = 76, which showed remarkable enhancement of PL intensity, are presented in Fig. 12. The PL spectra of those samples excited at 350 nm for Eu2+ are also presented in Fig. 13. The melt-quenched glass was amorphous and showed blue emission caused by the 4f7→4f5d1 transition of Eu2+ ions. The glasses which were subjected to heat treatment showed precipitation of anorthite (CaAl2Si2O8) and cristobalite (SiO2). The amounts of both crystalline phases increased only with the second heat treatment time at 1150°C. The PL intensity also increased with time, which was much higher than that of the melt-quenched glass, but much longer heat treatment caused lower PL intensity such as the sample heat-treated for 12 and 24 h. The glass which was crystallized directly at 1150°C for 24 h showed large precipitations of anorthite and cristobalite. However, its PL intensity was much lower than that of the two-step heat-treated samples accompanied with the obvious blue shift of the peak wavelength. These results suggest that the PL intensity of the samples did not have relevance to the amount of anorthite.

This strong PL intensity of the two-step heat-treated sample occurred probably for two reasons. One is the change in the crystal field, which resulted from fluctuation of the glass composition with the progress of the phase separation because the blue emission from Eu2+ ions is affected strongly by the crystal field.
surrounding them. The change in the crystal field around Eu$^{2+}$ ions through the phase-separation and crystallization process was confirmed because the emission peak wavelength of the two-step heat-treated sample gradually blue-shifted with holding time at 1150°C from ca. 436 nm to ca. 428 nm, of which the wavelength was the same as that of the sample that was crystallized directly at 1150°C and that of the Eu$^{2+}$ doped anorthite prepared using a conventional solid-state reaction method.

Another reason is attributed to their crystallization behavior. To investigate the effect of phase separation on the crystallization, the micro texture of the two-step heat-treated samples was observed using SEM. Their SEM images are presented in Fig. 14. Here, the black region is attributed to a CaO–Al$_2$O$_3$ rich glassy phase or an anorthite precipitated phase. No phase-separation and/or crystallization texture was found in the sample heat-treated at 1150°C up to 6 h in Fig. 14(a). In contrast, the obvious interconnected structure was found in the samples that had been heat-treated for 12 h (b) and for 24 h (c). These results indicate that the glass of $x = 76$ was phase-separated by a spinodal decomposition mechanism. In addition, the size of the interconnected texture of the sample heat-treated for 24 h was much larger than that for 12 h.

It is inferred from the XRD and SEM results that the two-step heat-treated samples were crystallized on the nanoscale and/or the low crystallinity of anorthite in shorter holding time for crystallization. In general, micro-pulverization of phosphors to less than 1–2 μm engenders the degradation of their emission intensity caused by the increase in the population of their surface defects. In contrast, the crystallization process through the phase separation causes apparent homogeneous precipitation of anorthite nanocrystals in the glass matrix. This precipitation of nanocrystals in the glass matrix may suppress the formation of the defects. The emission intensity of the sample decreased with the growth of the phase separation texture to the sub-micrometer-scale, as presented in Figs. 14(b) and 14(c). The decrease of the intensity might be caused by the increase of the defects in the crystals or the light scattering due to the increase of the phase separation texture as discussed in above section. The mechanism of the PL enhancement must be investigated further. This procedure was applied to other phosphor materials. Those are the green-light-emitting phosphor, willemite (Zn$_2$SiO$_4$: Mn$^{2+}$) from ZnO–SiO$_2$ system$^{45}$ and the blue-light-emitting phosphor, fresnoite (Ba$_5$Ti$_2$Si$_2$O$_8$) from BaO–TiO$_2$–SiO$_2$ system$^{46,47}$ by the author’s group.

This bulk and homogeneous crystallization process of the glass using phase separation is applicable to the formation of the composite, which consists of functional crystalline phase and glass matrix. This procedure based on the concentration of the components of the functional crystalline phase and the heterogeneous crystallization at the two-phase boundary. Consequently, it can be applied widely to various systems.

5. Summary

The high functionalization of materials by a combination of heterogeneous substances has become a major procedure for the development of high-performance materials. This review presents various functional materials prepared using phase separation mainly in the stable immiscibility region. This process using phase separation resembles the fabrication of the structure from nanometer to micrometer scale, although this differs from the general build-up processes such as molecular beam epitaxy and a sol–gel process including atomic level control. However, this procedure is useful to fabricate large and bulk materials including nanometer-scale composite structures. Therefore, it can provide high performance, which is difficult to realize in a single material. The phase separation of the melts and glasses has been anticipated to enable various materials to have further superior and/or unique performance by reviewing phase separation phenomena from a new perspective.

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