Luminescence Property and Phase-Separation Texture of Phase-Separated Glasses and Glass-Ceramics in Mn-Doped ZnO–SiO₂ System

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In order to achieve fine phosphor materials with high efficiency, phase-separated glasses and glass-ceramics in Mn-doped ZnO–SiO₂ system, of which composition was $x\text{ZnO}-(100-x)\text{SiO}_2$ mol% ($x=10, 20, 30$) in the immiscibility region, were prepared by melting and subsequent heat-treatment process. All the melt-quenched glasses were phase-separated into two phases, i.e. a ZnO-rich phase and a SiO₂-rich one. The SiO₂-rich particles were formed into the ZnO-rich phase in the composition of $x=20$ and $x=30$, while the ZnO-rich particles were formed in the SiO₂-rich phase in the composition of $x=10$. The melt-quenched glass showed the orange-emission at around 625 nm of its peak wavelength. After the heat-treatment on the melt-quenched glasses, the Zn₂SiO₄ (willemite) phase were precipitated, and the glass-ceramics gave strong green-emission at around 525 nm. The intensity of the green-emission of the glass-ceramics in the composition of $x=10$ was higher than those in the composition of $x=20$ and $x=30$ in spite of the same amount of precipitated Zn₂SiO₄ phase.

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1. Introduction

The development of fine fluorescent materials with high and stable luminescence efficiency is demanded in order to achieve much higher emission and finer resolution in technical innovation of a display. Zn₂SiO₄:Mn²⁺ has been used as an effective green emitting phosphor in fluorescent lamps and plasma display panels (PDPs). Commercially available Zn₂SiO₄:Mn²⁺ particles have been synthesized by conventional solid-state reaction, and they were ground or milled to obtain the fine particles. However, it is difficult to obtain the fine particles with high efficiency because microparticulation of phosphors less than 1–2 μm leads to their degradation of the emission intensity, because of the increase in the population of their surface defects.¹⁾

Phase-separation and crystallization are very popular phenomena in melt-quenched glasses. The particular texture of phase-separation has been utilized for the applications of various functional glasses such as chemically durable glasses and porous glasses.^{2),3)} Also, they are applied to fabrications of some functional and practical materials of glass-ceramics due to particular phase separation texture and fine crystallization at the boundary of two phases in the materials. The phase diagram of a ZnO–SiO₂ system was reported by Bunting in 1930,⁴⁾ and they mentioned that the ZnO–SiO₂ system has an immiscibility region above its liquidus temperature. Applying a heat-treatment process to the Mn-doped ZnO–SiO₂ system glass with phase-separation, the precipitation of texture-controlled Zn₂SiO₄:Mn²⁺ nanocrystals from the phase-boundary of ZnO-rich phase and SiO₂-rich one is expected. However, their phase-separation and crystallization phenomena in the immiscibility region are not clear.

The precipitation of Zn₂SiO₄:Mn²⁺ phosphors through phase-separation and crystallization process have some advantages, such as the precipitation of Zn₂SiO₄:Mn²⁺ fine particles and their thermostability caused by SiO₂-rich glass phase around them. As for the improvement of thermostability of phosphors, several studies have been made on coating of phosphor surface with SiO₂,^{5),6)} Al₂O₃,⁷⁾ and MgO,⁸⁾ and the degradation of fluorescence intensity could be suppressed. Moreover, the high efficient luminous property due to the effective excitation is expected for the glass-ceramics prepared

by the phase-separation and the crystallization process, because the difference of refraction index between the two phases induces the incident excitation-light scattering at the phase-boundary more than once, which is called multiple-light-scattering effect, and resulted in the efficient excitation of phosphors in the glass-ceramics.

In this study, Mn-doped two-liquid immiscible melts in a ZnO–SiO₂ system were melt-quenched and heat-treated in order to precipitate Zn₂SiO₄:Mn²⁺ crystals into the SiO₂-based glass-ceramics, and their phase-separation texture, crystallization behavior and luminous property were examined.

2. Experiments

The schematic illustration of the phase diagram of a ZnO–SiO₂ system⁴⁾ is shown in Fig. 1. The phase-separated glass and glass-ceramics in the composition of stable immiscibility region of this system were prepared by a melt-quenching and a following heat-treatment process. Reagent grade α-quartz (SiO₂), zinc oxide (ZnO) and manganese oxide (MnO₂) in the compositions of $x\text{ZnO}-(100-x)\text{SiO}_2-0.01x\text{MnO}_2$ mol%

Fig. 1. Phase diagram in ZnO–SiO₂ system (mol%).

Fig. 2. SEM images of the melt-quenched glasses, (a) $x=10$, (b) $x=20$, and (c) $x=30$.

($x=10, 20, 30$) were mixed. The mixed powder was shaped into rods using a cold isostatic press. The formed rods were melted using an infrared arc imaging furnace (ULVAC, PRC MR-H500) above 1700°C for 10 min. The obtained melt-quenched glasses were heat-treated at 800–1400°C for 12 h.

The crystallization temperatures of the melt-quenched glasses with each composition were determined from the exothermic peak on the differential thermal analysis (DTA, DTA-50, SHIMADZU) curves. The obtained glasses and glass-ceramics were characterized by an X-ray diffraction (XRD, XRD-6100 Lab X, Shimadzu) method and a scanning electron microscope (SEM, JSM-5800, JEOL). The photoluminescence (PL) spectra of the powdered samples, which were prepared by grinding of the melt-quenched glasses and glass-ceramics up to the size of about 5 μm in an alumina mortar, were measured using a fluorescence spectrophotometer (RF-5000, Shimadzu) at room temperature. The excitation wavelength for Mn²⁺ ions was fixed at 254 nm.

3. Results and discussion

All melt-quenched glasses were tinged with white because of Rayleigh and Mie scattering by phase-separated texture. In order to investigate the phase-separation texture, the cross sectional morphologies of these melt-quenched glasses were observed by SEM. The SEM images of the melt-quenched glasses were shown in Fig. 2. In the SEM observations, the melt-quenched glasses were just cut and polished and any etching process was not carried out. Therefore, the white and black regions are attributed to a ZnO-rich glassy phase and a SiO₂-rich one, respectively. As shown in this figure, the phase-separation textures were observed in all the melt-quenched glasses. Many roundish patterns were formed in the all melt-quenched glasses, indicating that these patterns are formed by nucleation-growth process. The melt-quenched glasses in the composition of $x=10$ was composed of the ZnO-rich particles and the SiO₂-rich matrix, and the size of ZnO-rich particles was about 300 nm. To the contrary, the melt-quenched glasses in the composition of $x=20$ and $x=30$ had the similar phase-separation texture which composed of the SiO₂-rich particles and the ZnO-rich matrix. The ratio of the ZnO-rich matrix to the SiO₂-rich particles and the particle size of SiO₂-rich phase increased with increasing the value of x in the composition of melt-quenched glass. In this study, the phase-separation texture formed by spinodal decomposition was not observed of which texture consisted of the interconnected structure of the ZnO-rich phase and the SiO₂-rich one, however the texture of spinodal decomposition seems to be formed near the composition of $x=15$ in a ZnO-SiO₂ system. It is quite likely that the phase-separation texture of the sample $x=20$ (Fig. 2(b)) is developed from an interconnected texture due to spinodal

Fig. 3. DTA curves of ZnO-SiO₂ phase-separated glasses. The broken line indicates the exothermic peaks of crystallization.

decomposition.

Figure 3 shows the DTA curves of the melt-quenched glasses, which were measured in order to determine the heat-treatment temperature for crystallization of the phase-separated glasses. The exothermic peaks of the DTA curve of the melt-quenched glasses in the composition of $x=20$ and $x=30$ appeared at around 800°C, so that the heat-treatment temperature at 800°C and higher was selected for crystallization of all samples.

The XRD patterns of the melt-quenched glass, glass-ceramics heat-treated at 800°C and that of 1400°C were shown in Fig. 4 for $x=10$ sample. The melt-quenched glass showed only amorphous halo pattern, and weak Zn₂SiO₄ peaks were found in XRD pattern at 800°C for 12 h. The peak intensity of Zn₂SiO₄ gradually increased with increasing the heat-treated temperature. However, no obvious changes in their full-width at half-maximum and peak position of diffraction peaks were observed. Therefore, the amount of crystalline Zn₂SiO₄ phase is proportional to the integrated intensity of their diffraction peaks. The crystallite size of the Zn₂SiO₄ crystals in our crystallization process estimated from Scherrer's equation were about 35–45 nm in diameter and were independent of the heat-treatment process. On the other hand, crystalline SiO₂ peaks were observed in glass-ceramics heat-treated at 1100°C and higher. Therefore, the exothermic peaks of the DTA curve at around 800°C shown in Fig. 3 were attributed to the crystallization peaks of Zn₂SiO₄ phase. The change of XRD patterns of the samples $x=20$ and 30 with heat-treatment were

Fig. 4. XRD patterns of the samples in the composition of $x=10$, (a) melt-quenched glass, (b) the glass-ceramics heat-treated at 800°C, and (c) that heat-treated at 1400°C.

Fig. 5. PL spectra of the samples in the composition of $x=30$, (a) the melt-quenched glass, (b) the glass-ceramics heat-treated at 800°C, and (c) the glass-ceramics heat-treated at 1000°C.

almost similar to that of the sample $x=10$.

Figure 5 shows the PL spectra of the melt-quenched glass and the glass-ceramics in the composition of $x=30$. Broad orange-emission at 600 nm was observed in the melt-quenched glasses, and the orange-emission peak wavelength was blue-shifted from 600 nm to 525 nm with increasing the heat-treatment temperature up to 900°C. The intensity of green-emission was increased with increasing the heat-treatment temperature without peak shift, and saturated up to 1400°C. The same emission property was observed in the glass-ceramics of $x=10$ and 20. These results could be interpreted by taking the crystal field of the melt-quenched glass and the glass-ceramics into consideration. These orange- and green-emission are attributed to the ${}^4T_1-{}^6A_1$ transition of Mn^{2+} ions. The emission wavelength of Mn^{2+} ions strongly depend on the crystal field surrounding them because the excited electron state of 3d is outer shell electron.⁹⁾ In general, the coordination number of Mn^{2+} ions in silicate-glass matrix is six and the Mn^{2+} ions in the glass matrix shows the red-emission.¹⁰⁾ As for the Mn^{2+}

Fig. 6. Relationship between the PL intensity and the XRD intensity of the heat-treated glass-ceramics. The PL intensity and the XRD intensity were integrated intensity of emission peaks and integrated intensity of (113) peak of Zn_2SiO_4 phase, respectively.

ions in the Zn_2SiO_4 crystals, the coordination number is four and they emit green-emission at 525 nm.⁹⁾ Therefore, it is reasonable that the peak shift of Mn^{2+} emission was due to the change of the crystal field, involving the change of the coordination number of Mn^{2+} ions, caused by the crystallization of Zn_2SiO_4 phase in the phase-separated glass. Indeed, the emission peak shift with the heat-treatment was accompanied by the precipitation of crystalline Zn_2SiO_4 phase, and the green-emission at 525 nm was consistent with the many previous studies in $Zn_2SiO_4:Mn^{2+}$ phosphor.^{11),12)} Furthermore, Qiu et al.¹³⁾ reported the change in luminescence wavelength from 590 nm to 535 nm in the Mn-doped $GeO_2-B_2O_3-ZnO$ system glasses and their crystallized glass-ceramics containing the Zn_2GeO_4 crystals by means of the heat-treatment process. Thus, the $Zn_2SiO_4:Mn^{2+}$ phosphor with green-emission was considered to precipitate through the phase-separation and crystallization process in Mn-doped $ZnO-SiO_2$ glasses. In addition, some of the samples showed the partly difference of emission intensity; the green emission intensity from the surface of the samples was larger than that from their inside. Therefore, it is considered that the crystallization of the $ZnO-SiO_2$ glasses tends to take place from a heterogeneous nucleation at the surface and the interface.

The relationship between the PL intensity of the heat-treated glass-ceramics and the XRD intensity of Zn_2SiO_4 (113), which was corresponding to the amount of the precipitated Zn_2SiO_4 phase, was shown in **Fig. 6**. The PL intensity was proportional to the amount of Zn_2SiO_4 crystalline phase, and the slopes of the XRD intensity versus PL intensity in each composition were nearly same, that is, independent of the composition of the melt-quenched glasses. The most noteworthy point is the composition dependency of the PL intensity in the same amount of precipitated Zn_2SiO_4 crystalline phase. The PL intensity of the glass-ceramics in the composition of $x=10$ was higher than those of $x=20$ and 30 despite their same amount of Zn_2SiO_4 crystalline phase (XRD intensity = 40–80 in Fig. 6). As mentioned above, the crystallite size and crystallinity of the heat-treated glass-ceramics were independent of the heat-treatment temperature, while the amount of precipitated Zn_2SiO_4 phase increased with increasing the heat-treatment temperature. On the other hand, the green-emission from the glass-ceramics increased with increasing the heat-

treatment temperature in the temperature range of 900–1400°C without peak shift. Therefore, the crystal field surrounding Mn²⁺ ions in Zn₂SiO₄ phase was almost same in the samples heat-treated above 900°C, because the excited electron state of 3d attributed to the green-emission in Mn²⁺ ion is outer shell electron. In deed, the orange emissions from Mn²⁺ ions were only observed in the melt-quenched glasses and glass-ceramics heat-treated at relatively low temperature of 800°C or less. We concluded that the Mn²⁺ ions were incorporated into the Zn₂SiO₄ phase, and the crystal field of surrounding Mn²⁺ ion was not changed by heat-treatment processes higher than 900°C. In addition, the ratio of Mn to Zn₂SiO₄ in our research composition was constant and the value was 0.01, which was about one-fifth of commercially available Zn₂SiO₄: Mn²⁺ phosphor. Therefore, concentration quenching of Mn²⁺ ions is not expected in this study.

This result indicates that the incident excitation-light were efficiently exited the Mn²⁺ ions in the Zn₂SiO₄ phase, and/or the green-emission from the excited Mn²⁺ ions were efficiently radiated outward. This emission enhancement seemed to have relation to the phase-separation texture of these glass-ceramics. In deed, the phase-separation texture in the sample of $x=10$ were different from those of $x=20$ and 30 as shown in Fig. 2. The phase-separation texture in the sample of $x=10$ composed of the ZnO-rich particles and the SiO₂-rich matrix, while those of $x=20$ and $x=30$ were composed of the SiO₂-rich particles and the ZnO-rich matrix. Moreover, the particle size of phase-separation texture increased with increasing the value of x , that is the amount of ZnO. After the heat-treatment process, the crystallized Zn₂SiO₄:Mn²⁺ phase were formed at the interface between the ZnO-rich phase and the SiO₂-rich one. In consequence, the powdered glass-ceramics of which particle size was about 5 μm had the different structure in spite of the same amount of Zn₂SiO₄, and the each phase-separation texture resulted in the change of light-scattering of their interface.

The reason for the luminescence enhancement of the melt-quenched glasses in the composition of $x=10$ has not been clarified. At the present stage of research, we speculate that this luminescence enhancement implies the multiple-light-scattering effect in the heat-treated glass-ceramics. Similar emission enhancement caused by phase-separation and crystallization process were reported in rare-earth doped borosilicate-glasses, and their mechanism were interpreted from the viewpoint of light scattering of their interface.^{14),15)} However, Jung et al.⁶⁾ reported the fluorescence enhancement of BaMgAl₁₀O₁₇:Eu²⁺ by means of the coating with SiO₂. They showed that the emission intensity increased in comparison with the non-coated one, and they concluded the increase of the emission intensity was due to the increase of the excitation-light transmitted into the phosphor. Thus, the mechanism of the luminescence enhancement concerned with phase-separation texture is still open for discussion. Further

research will be made in this system.

4. Summary

Mn-doped two-liquid immiscible melts in ZnO-SiO₂ system, were quenched and heat-treated in order to precipitate the Zn₂SiO₄:Mn²⁺ crystals as green color phosphor. All the melt-quenched glasses phase-separated into the ZnO-rich phase and the SiO₂-rich phase formed by nucleation-growth process. The broad orange-emission owing to the Mn²⁺ ions was observed in the melt-quenched glasses and the emission turned into the strong green-one after the heat-treatment process. This change of emission was caused by the different crystal field subjected to the Mn²⁺ ions in the glass and Zn₂SiO₄ crystal. In spite of the same amount of the precipitated Zn₂SiO₄ phase, the intensity of the green-emission of the crystallized glass-ceramics in the composition of $x=10$ were higher than that of $x=20$ and $x=30$. This emission enhancement seemed to be in relation to the multiple-light-scattering due to the phase-separation texture, but further investigation is necessary.

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References

- 1) Tanaka, M. and Masumoto, Y., *Chem. Phys. Lett.*, Vol. 324, pp. 249–254 (2000).
- 2) Doremus, R. H. and Turkalo, A. M., *Science*, Vol. 164, pp. 418–419 (1969).
- 3) Morimoto, S., *Key Eng. Mater.*, Vol. 115, pp. 147–158 (1996).
- 4) Bunting, E. N., *J. Am. Ceram. Soc.*, Vol. 13, pp. 5–10 (1930).
- 5) Lee, R. Y. and Kim, S. W., *J. Lumin.*, Vol. 93, pp. 93–100 (2001).
- 6) Jung, I. Y., Cho, Y., Lee, S. G., Sohn, S. H., Kim, D. K., Lee, D. K. and Kweon, Y. M., *Appl. Phys. Lett.*, Vol. 87, 191908 (2005).
- 7) Do, Y. R., Park, D.-H. and Kim, Y.-S., *J. Electrochem. Soc.*, Vol. 151, pp. H210–212 (2004).
- 8) Jüstel, T. and Nikol, H., *Adv. Mater.*, Vol. 12, pp. 527–530 (2000).
- 9) Nakazawa, E., "Phosphor Handbook," Ed. by Shionoya, S. and Yen, W. M., CRC, Boca Raton (1998) pp. 169–173 (ISBN 0849375606).
- 10) Song, C. F., Lu, M. K., Yang, P., Gu, F., Xu, D. and Yuan, D. R., *J. Sol-Gel Sci. Technol.*, Vol. 28, pp. 193–197 (2003).
- 11) Wan, J. X., Wang, Z. H., Chen, X. Y., Mu, L., Yu, W. C. and Qian, Y. T., *J. Lumin.*, Vol. 121, pp. 32–38 (2006).
- 12) Kwon, M. S., Kim, C. J., Park, H. L., Kim, T. W. and Lee, H. S., *J. Mater. Sci.*, Vol. 40, pp. 4089–4091 (2005).
- 13) Qiu, J., Igarashi, H. and Makishima, A., *Sci. Technol. Adv. Mater.*, Vol. 6, pp. 431–434 (2005).
- 14) Yao, Z., Ding, Y., Nanba, T. and Miura, Y., *Mater. Sci. Res. Int.*, Vol. 4, pp. 141–147 (1998).
- 15) Yao, Z., Ding, Y., Nanba, T. and Miura, Y., *Mater. Sci. Res. Int.*, Vol. 4, pp. 244–248 (1998).