Hexagonal GdF₃:Tm³⁺, which is thermodynamically unstable at room temperature, was successfully crystallized in borosilicate glass using a phase separation technique. The crystal structure of GdF₃ was controlled by the addition of alkaline earth metals to the glass composition. Increasing the amount of SrF₂ added to the glass composition to 1.65 mol % increased the amount of precipitation of hexagonal GdF₃:Tm³⁺ crystals and the luminescence intensity. Lanthanide trifluoride phosphors were restrictively obtained in the borate phase as a result, and the emission of Tm³⁺ at 458 nm was observed. Furthermore, the luminescence intensity of GdF₃:Tm³⁺ in the phase separation glass upon SrF₂-doping was about three times larger than that without doping.

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Key-words : Borosilicate glass, Phase separation, Lanthanide fluoride, Luminescence intensity

Table 1. Crystal structure, space group, coordination number, and lattice volume of orthorhombic and hexagonal GdF₃. Gray and green spheres indicate Gd³⁺ and F⁻ in the illustration of GdF₃, respectively

| Crystal structure | Space group | Coordination number | Lattice volume/Å³ |
|-------------------|-------------|---------------------|-------------------|
| Orthorhombic      | Pnma        | 9                   | 200.73            |
| Hexagonal         | p3-c1       | 6                   | 289.35            |

1. Introduction

It is widely known that several lanthanide fluoride host materials yield increased luminescence intensity upon rare earth doping, when compared to the lanthanide oxide hosts. GdF₃, which shows promise as an MRI contrast agent and in gadolinium neutron capture therapy (GdNCT) for selectively attacking tumor tissue, is an attractive agent and in gadolinium neutron capture therapy (GdNCT) hosts. When compared to the lanthanide oxide materials, lanthanide trifluoride phosphors were restrictively obtained in the borate phase as a result, and the emission of Tm³⁺ at 458 nm was observed. Furthermore, the luminescence intensity of GdF₃:Tm³⁺ in the phase separation glass upon SrF₂-doping was about three times larger than that without doping.

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In this study, we investigate the synthesis of the lanthanide fluoride phosphor Gd\(\text{F}_3\):Tm\(^{3+}\) in the borate phase of phase separation glass, as well as the control of its crystal structure by co-doping with alkali earth metals. We also report the influence of the crystal structure and amount of precipitation in phase separation glass on its luminescent characteristics.

2. Material and methods

\(\text{SiO}_2\), \(\text{Na}_2\text{CO}_3\), \(\text{Al}_2\text{O}_3\), and \(\text{B}_2\text{O}_3\) were purchased from Kishida Chemical Co., Ltd., \(\text{H}_3\text{BO}_3\) from Kanto Chemical Co., Ltd., and \(\text{NaF}, \text{GdF}_3, \text{MgF}_2, \text{CaF}_2, \text{SrF}_2,\) and \(\text{BaF}_2\) from Kojundo Chemical Laboratory Co., Ltd., and used without further purification. The compositions of the glass investigated were 54.6\% \text{SiO}_2, 18.5\% \text{Al}_2\text{O}_3, \text{N}_2\text{CO}_3, 11.1\% \text{MgO}, 5.5\% \text{CaO}, 1.0\% \text{SrO}, and 1.0\% \text{BaO} (in molar percent). Stoichiometric amounts of the chemicals corresponding to the various compositions were mixed and loaded in an alumina crucible. The crucible was heated in an electric furnace (Motoyama Rh-2025D, SUPER-BURN) at a heating rate of 500 °C/h, and maintained at a temperature of 1350 °C for 1 h, until the mixture was completely molten. After the melting process, the molten glass was poured into a graphite mold (dimensions 1.5 cm \(\times\) 2.0 cm \(\times\) 2.0 cm). Thereafter, the glass sample was cooled gradually from 600 to 250 °C in a desktop muffle furnace (DENKEN Co., Ltd., KDF P90). The resulting glass sample was cut to a thickness of 2.65 mm with a diamond cutter (Refine Tec Co., RCA-005). It was then embedded in a fine powder of alumina (Kanto Chemical Co., alpha-type, 99\%) in an alumina crucible, and heated at 800 °C for 48 h in a small desktop furnace (Nitto Kagaku, NHK1-170) at a heating rate of 200 °C/h for phase separation of the glass and crystallization of the phosphor.

Identification of the crystalline phases was conducted by X-ray diffraction (XRD, Rigaku Ltd., Ultima IV) using Cu K\(\alpha 1\) radiation (\(\lambda = 1.541\) Å). The bulk sample was used and the measurements were carried out at a tube voltage of 40 kV, tube current of 40 mA, and scanning rate of 2 °/min in the 2\(\theta\) range 10–80°.

The surface of the obtained sample was polished with a SiC waterproof abrasive paper (IMT Co., Ltd., S31SR-2232000-DN), and its luminescence spectra were measured with a spectrophotometer (HITACHI, Ltd., F-2500) using a 150-W Xe lamp as the light source. The excitation wavelength employed was 355 nm and the measurement was carried out in the range of 420–480 nm.

From the XRD data, the scattering region derived from the amorphous and crystalline materials was separated using Jade 7 ver. 7.5.13 XRD analysis software. As shown in Eq. (1), we obtained the crystallinity \(X\)%), from the ratio of the crystalline scattering intensity to total scattered intensity:

\[
X = \frac{I_c}{I_a + I_c} \times 100
\]

where \(I_a\) and \(I_c\) are the integrated intensities derived from the amorphous and crystalline phases, respectively.

3. Results and discussion

The XRD profiles of \(\text{GdF}_3\) doped with Mg\(^{2+}\), Ca\(^{2+}\), Sr\(^{2+}\), and Ba\(^{2+}\) (Fig. 1) revealed the successful formation of hexagonal \(\text{GdF}_3\), with the highest peak intensities for the Sr-doped crystal. However, both the hexagonal and orthorhombic phases were observed in the Mg-doped sample. It is apparent from the ionic radii of the alkaline earth metals (Table 2) that the hexagonal phase was obtained when the dopant metal possessed a larger ionic radius than Gd\(^{3+}\), indicating that it expanded the crystal lattice and decreased the repulsion between F\(^-\) ions.

The luminescence spectra for all the doped \(\text{GdF}_3\):Tm\(^{3+}\) samples (Fig. 2) showed the emission peak of Tm\(^{3+}\) at 450 nm, corresponding to the \(1\text{D}_2 \rightarrow 3\text{H}_4\) transition. Of these, the Sr-doped sample displayed the highest fluorescence intensity, followed by the Ba-doped sample. This is because Sr and Ba possessed larger ionic radii than Gd, and the major phase obtained was hexagonal. The Mg- and Ca-doped samples, which contained the orthorhombic and hexagonal phases, exhibited lower luminescence intensity. It is clear from these results that the luminescent characteristics of \(\text{GdF}_3\) are susceptible to the crystal structure, and that Sr\(^{2+}\) is a suitable dopant for obtaining the hexagonal phase.

XRD profiles of \(\text{GdF}_3\) doped with differing amounts of Sr\(^{2+}\) (0–0.5 mol \%) are shown in Fig. 3. At 0.3 mol \% of Sr\(^{2+}\), the hexagonal diffraction peaks showed maximum intensity when compared to the other dopants. Peaks corresponding to the orthorhombic phase appeared, however, different dopants for the glass composition at \(x = 0.3\) and \(y = 1.0\), respectively.

| Table 2: Ionic radii of selected atoms |
|--------------------------------------|
| Ions           | Gd\(^{3+}\) | Mg\(^{2+}\) | Ca\(^{2+}\) | Sr\(^{2+}\) | Ba\(^{2+}\) |
| Ionic radius/Å | 0.94       | 0.72       | 1.00       | 1.18       | 1.35       |

Fig. 1. XRD patterns of glass ceramics with different dopants for the glass composition at \(x = 0.3\) and \(y = 1.0\), respectively.
upon increasing the amount of Sr$^{2+}$. The GdF$_3$ sample with no dopant was found to be orthorhombic.

XRD profiles of glass are shown for different levels of Sr-doping in the $2\theta$ range 27–31° (Fig. 4). With increases in the amount of doping, the diffraction peak assigned to (0,0,2) shifted to a lower angle. This shows that the doped Sr$^{2+}$ was solid-dissolved in GdF$_3$, extending the lattice distance. The GdF$_3$ crystal underwent a phase transition from orthorhombic to hexagonal during phase separation, moreover, as a result of F$^-$ defects created to electrically compensate the Sr$^{2+}$ substitution in the Gd$^{3+}$ site.

The luminescence spectra at an excitation wavelength of 355 nm (Fig. 5) revealed an emission peak at 458 nm for every sample. The luminescence intensity of the crystal doped with 0.3 mol% of Sr$^{2+}$ was the highest among them and more than twice as large as the undoped phosphor. Thus, the change in the crystal structure with increases in Sr-doping greatly influenced the luminescent intensity.

The relationship of the values of the emission peak at 458 nm and the diffraction peaks of orthorhombic GdF$_3$ ($2\theta = 27.5$ and 28.6°) with the amount of Sr$^{2+}$ doped into the glass system is shown in Figs. 6 and 7, respectively. Since the luminescence intensity increased with the amount of the hexagonal GdF$_3$, it appears that there is a strong correlation between the crystal structure of the lanthanide fluorides and their luminescence properties.
According to Zhang et al., the distances between Gd atoms in the crystal structure models, determined by VESTA ver. 1.4.4 software, are 0.393 and 0.385 nm for the orthorhombic and hexagonal structures, respectively. Generally, in the case of dipole–dipole transition, the probability of energy transfer between the donor and acceptor is given by Eq. (2).

\[
P_{\text{AB}} = \frac{3c^4h^4}{16\pi^6R^6} \frac{\sigma A}{\tau A} \int \frac{f_D(E)F_A(E)}{E^4} dE \quad (2)
\]

where \(c\) is the velocity of light, \(h\) is defined as \(h/2\pi\) (Planck constant), \(n\) is the refractive index, \(R\) is the distance between the donor and acceptor (the distance between gadolinium ions), \(s\) is the absorption cross-section, \(t\) is the radiative decay time, \(f_D(E)\) is the area under the absorption band of the donor, and \(F_A(E)\) is the area under the emission band of the acceptor. Equation (2) shows that the probability of energy transfer is inversely proportional to \(R^6\). Thus, the enhancement of luminescence intensity in the hexagonal structure was attributed to the increase in probability of energy transfer due to the shortness of the Gd–Gd distances in composition to those of the orthorhombic structure.

Peak fitting of the diffraction data obtained in Fig. 8 was performed by the Jade 7 XRD analysis software. The crystallinity in relation to the doping amount of SrF\(_2\) in the glass composition, calculated using Eq. (1), is shown in Fig. 9. The ideal value of crystallinity obtained from the calculations was 16.13\% for the glass composition at \(y = 1.0\), but the actual values of the crystallinity obtained in the prepared glasses were lower. The value gradually increased with an increase in the amount of SrF\(_2\) added to the glass composition, however, and the crystallinity at 11 mol\% SrF\(_2\) (\(y = 2.0\)) was twice as large as the value at 5.5 mol\% SrF\(_2\) (\(y = 1.0\)).

The luminescence spectra of GdF\(_3\):Tm\(^{3+}\) for \(x = 0.3\) and \(y = 1.0, 1.5\) and 2.0, in the glass composition 54.6SiO\(_2\)-11.1B\(_2\)O\(_3\)-15.8NaF-18.5Al\(_2\)O\(_3\)-5.5xSrF\(_2\)-5.5yGdF\(_3\)-0.4TmF\(_3\) are shown in Fig. 10. The luminescence intensity was found to increase with increases in the...
The amount of SrF₂-doping, and the intensity of the phosphor doped with 11 mol% of SrF₂ (y = 2.0) was three times larger than that of the phosphor with 5.5 mol% doping (y = 1.0). This increase was attributable to the increasing crystallinity of GdF₃ in the glass (Fig. 9). Increasing the amount of GdF₃ crystals the scattered excitation light was repeatedly at the interface between the crystals, and the probability of excitation of Tm³⁺ increased. The crystallinity, which revealed a maximum value at y = 2.0 in the glass composition, was therefore considered to exhibit a high fluorescence intensity. In addition, increasing the amount of Tm³⁺ substitution in GdF₃ also increased the luminescence intensity. The lattice constants of the orthorhombic and hexagonal structures calculated from the XRD patterns are summarized in Table 3, and the lattice volumes calculated from the amounts of GdF₃ and the lattice constants are indicated in Fig. 11. The lattice volume of orthorhombic [Fig. 11(A)] and hexagonal GdF₃ [Fig. 11(B)] decreased with increases in the amount of GdF₃ deposition in the glass. Increasing the precipitate amount of GdF₃ in the glass leads to an increase in the number of substitution sites and the probability of Tm³⁺ substitution in the crystal. The ionic radii of Gd³⁺ and Tm³⁺ are 0.94 and 0.88 Å, respectively. The smaller Tm³⁺ displaced the Gd³⁺, therefore, decreasing the lattice volume of the host crystal.

4. Conclusions

In this study, the luminescence characteristics of GdF₃:Tm³⁺ were examined by changing the crystal structure and the precipitation amount in the phase separation glass. We arrived at the following conclusions:

1. Precipitation of fine crystals of hexagonal GdF₃ in the phase separation glass was successfully achieved by the addition of alkaline earth metals (Mg, Ca, Sr, and Ba) to the glass composition. Higher luminescence intensities could be obtained when the ionic radii of the alkaline earth metal dopants was larger than that of Gd³⁺.

2. The proportion of hexagonal GdF₃ crystals increased with increases in the amount of Sr-doping up to 1.65 mol%. The orthorhombic phase began to precipitate, however, when the amount of the dopant was more than 5.5 mol%. Upon increasing the amount of Sr²⁺, the GdF₃ peak contribution to (0,0,2) shifted to a lower angle. This is because the Sr²⁺ was solid-solved in GdF₃ and the crystal lattice was extended. Hence, the hexagonal phase was easily formed with a smaller amount of Sr²⁺, because the repulsion among F⁻ ions in the crystal decreased.

3. Higher luminescence intensities could be obtained when the distance between Gd atoms in the crystal was lower.

4. Increasing the crystallinity of GdF₃ by the addition of alkaline earth metals and the substitution amount of Tm³⁺ to Gd³⁺ site in the crystal increased the luminescence intensity of GdF₃:Tm³⁺ to approximately three times its original value.

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