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Luminescence properties of long-persistence silicate phosphors

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Abstract

Tb^{3+}-doped and (Ce^{3+}, Tb^{3+})-codoped $Ca_{0.5}Sr_{1.5}Al_2SiO_7$ were prepared using a solid-state reaction at 1273 K for 3 h in air and 1623 K for 6 h in a weakly reductive atmosphere of 5% H_2–95% N_2 gas. The resultant (Ce^{3+}, Tb^{3+})-codoped $Ca_{0.5}Sr_{1.5}Al_2SiO_7$ phosphor shows four main emission peaks: one at 386 nm for Ce^{3+} and three at 483, 542 and 591 nm for Tb^{3+}. Emission intensity of Tb^{3+} in the (Ce^{3+}, Tb^{3+})-codoped phosphor was five times greater than that of the Tb^{3+} single-doped phosphor because of the energy transfer from Ce^{3+} to Tb^{3+}. The codoped phosphor showed long-persistence white phosphorescence.

Keywords: Ce^{3+}; Tb^{3+}; Long-persistent phosphor; White phosphorescence; Silicate phosphor

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1. Introduction

Recently, long-persistence phosphors, alkali earth aluminates ($SrAl_2O_4:Eu^{2+}$, Dy^{3+}), which phosphoresce without excitation by a radioisotope, have attracted attention because they show persistence properties that are far superior to those of conventional zinc sulfide phosphors (e.g. ZnS:Cu) [1]. Although these phosphors show high intensity emission, their luminescence spectra have remained restricted within a narrow greenish range. Green emission has been utilized in luminous paints because of its high visibility in darkness. Nevertheless, that narrow greenish range prevents its application for other uses. If multicolor emission long-persistent phosphors are synthesized, their application could be extended to the color escape signboards without energy supplement, which may be helpful for earthquakes and fire disasters.

Long-persistence phosphorescence in Ce^{3+} doped $Ca_2Al_2SiO_7$ with a melilite structure has been reported recently by Kodama et al. [2,3]. Ce^{3+} functions as a high-efficiency emission center because 4f–5d transitions in Ce^{3+} allow parity. Sensitization by energy transfer from Ce^{3+} to Tb^{3+} is usually very effective for obtaining bright luminescence of Tb^{3+} because of the highly efficient emission of Ce^{3+} [4]. In this study, we report long-persistence white luminescence emitted from a single-phase phosphor of (Ce^{3+}, Tb^{3+})-codoped $Ca_{0.5}Sr_{1.5}Al_2SiO_7$.

2. Experimental

Starting materials were $CaCO_3$ (4N; Kanto Chemical Co., Inc.), $SrCO_3$ (3N; Kanto Chemical Co., Inc.), SiO_2 (3N; Kanto Chemical Co., Inc.), Al_2O_3 (4N; Kojundo Chemical Laboratory Co., Ltd.), Tb_4O_7 (3N5; Kanto Chemical Co., Inc.) and CeO_2 (4N; Kanto Chemical Co., Inc.); B_2O_3 (3N; Kanto Chemical Co., Inc.) was added by 5 mol% as a flux. The starting powders were suspended in ethanol and mixed in an agate mortar for 15 min. The mixture was fired in an alumina boat at 1273 K for 3 h in air. The samples obtained after firing were ground and pressed into 15 mm diameter disk-shaped pellets with about 1 mm in thickness under a pressure of 30 MPa for 10 min. Then, the pellets were fired in the alumina boat at 1623 K for 6 h in a weak reductive atmosphere of 5% H_2–95% N_2 gas.

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The synthesised phosphors were ground to obtain fine powder.

Powder neutron diffraction patterns were recorded using the HERMES (T1-3) diffractometer installed at JRR-3M Guide Hall in the Japan Atomic Energy Research Institute (JAERI) [5]. An incident neutron wavelength of λ = 0.182035 nm was obtained from a Ge(3 1 1) monochromator. Data were collected on thoroughly ground powders using a multi-scanning mode in the 2θ range from 5° to 155° with a step width of 0.1° and a 16 min monitoring time. Powder patterns obtained were analyzed using the RIETAN2000 profile refinement program [6]. Excitation and emission spectra were measured for the powder sample using a JASCO FP-6500/6600 spectrofluorometer and the CIE chromaticity coordinates were measured on a powder sample using a Hamamatsu Photonics PMA-11 photo multichannel analyzer equipped with an 11 W Hg lamp.

3. Results and discussion

3.1. Crystal structure of $(Ca/Sr)_2Al_2SiO_7$

The crystal structure of the compound, $Ca_{0.44}Sr_{1.5}Ce_{0.06}Al_2SiO_7$, was determined using Rietveld refinement of neutron diffraction data, based on a tetragonal system with space group $P\bar{4}2_1m$ (No. 113). The Ce^{3+} ion was assumed to substitute the site for Ca/Sr [7]. The resultant pattern fitting is shown in Fig. 1. Calculated and observed patterns are shown, respectively, on the top as a solid line and a dotted line. Vertical marks in the middle show the position of calculated Bragg reflections. Traces at the bottom show a plot of the difference between calculated and observed intensities. In addition, Table 1 lists crystallographic data as finally refined by the Rietveld refinement. All peaks of the powder neutron diffraction patterns were indexed on the tetragonal cell with $a = 0.78050(2)$ nm and $c = 0.52262(2)$ nm. A satisfactorily good fit was achieved and the final R_{wp} factor was 4.38%. Fig. 2 shows the crystal structure of the $(Ca/Sr)_2Al_2SiO_7$.

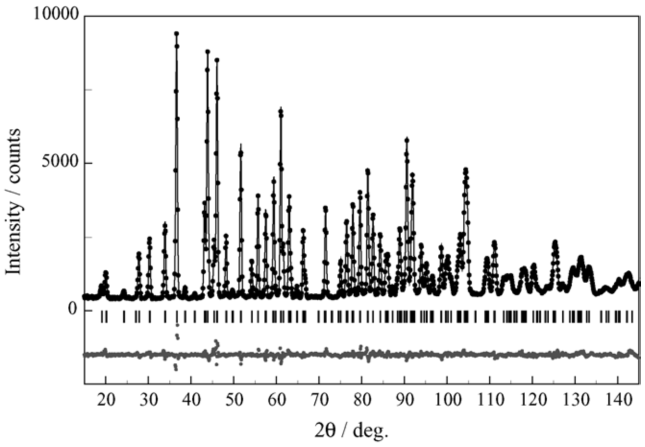

Fig. 1. Neutron Rietveld refinement patterns of $Ca_{0.44}Sr_{1.5}Ce_{0.06}Al_2SiO_7$.

Table 1
Neutron Rietveld refinement results of $Ca_{0.44}Sr_{1.5}Ce_{0.06}Al_2SiO_7$

Atom	Site	g	x	y	z	$10^2 \times B$ (nm^2)
X	4e	1.0	0.3373(2)	0.1616(2)	0.5095(3)	1.02(3)
Al	2a	1.0	0	0	0	0.57(9)
Al	4e	0.5	0.1416(4)	0.3568(3)	0.9619(5)	0.52(7)
Si	4e	0.5	0.1416(4)	0.3568(3)	0.9619(5)	0.52(7)
O(1)	2c	1.0	0.5	0	0.1652(6)	1.08(5)
O(2)	4e	1.0	0.1426(2)	0.3567(2)	0.27987(3)	1.02(4)
O(3)	8f	1.0	0.0843(1)	0.1695(1)	0.8175(3)	1.04(3)

$P\bar{4}2_1m$ (no.113), $a = 0.78050(2)$ nm, $c = 0.52262(2)$ nm, $R_{wp} = 4.38\%$, $R_P = 3.26\%$, $R_e = 2.93\%$, $R_I = 1.46\%$, $R_F = 1.37\%$, $S = 1.4978$.

This compound is crystallized in a melilite-type structure. The emission Ce^{3+} ions may be distributed on the site of Ca/Sr, located in a two-dimensional arrangement.

3.2. Luminescence properties

Fig. 3 shows excitation and emission spectra obtained for $Ca_{0.42}Sr_{1.5}Tb_{0.08}Al_2SiO_7$ and $Ca_{0.4}Sr_{1.5}Ce_{0.02}Tb_{0.08}Al_2SiO_7$ at room temperature. The emission spectrum of the single doping of Tb^{3+} (a) shows three sharp peaks corresponding to $^5D_4 \rightarrow {}^7F_j$ ($j = 6, 5, 4$). These are caused by the cross relaxation from $^5D_3$ to $^5D_4$. Enhancement of cross relaxation is achieved in the case of the high concentration of dopant, engendering a strong emission of $^5D_4 \rightarrow {}^7F_j$ transition. The emission spectrum of the double doping of Tb^{3+} and Ce^{3+} (b) shows several sharp peaks corresponding to the $^5D_4 \rightarrow {}^7F_j$ ($j = 6, 5, 4$) of Tb^{3+} and a broad peak (400 nm) corresponding to $^2D_{3/2}$ $(5d^1) \rightarrow {}^2F_j$ ($j = 7/2, 5/2$)

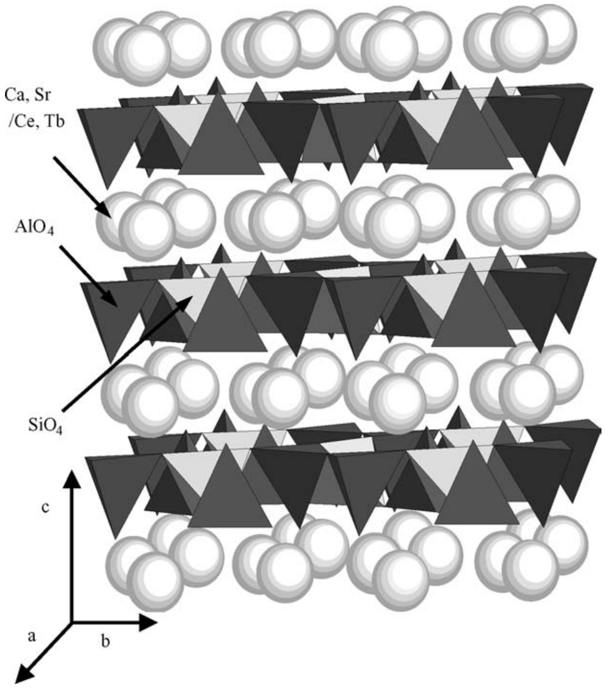

Fig. 2. Crystal structure of $(Ca/Sr)_2Al_2SiO_7$.

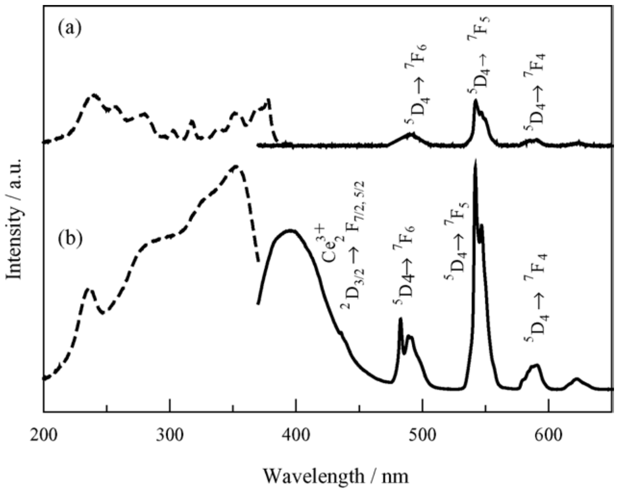

Fig. 3. Excitation and emission spectra of $Ca_{0.42}Sr_{1.5}Tb_{0.08}Al_2SiO_7$ (a) and $Ca_{0.4}Sr_{1.5}Ce_{0.02}Tb_{0.08}Al_2SiO_7$ (b).

of Ce^{3+}. The emission intensity of Tb^{3+} in the codoped phosphor is five times higher than that of the Tb^{3+} single-doped phosphor. This remarkable intensity is caused by the energy transfer from Ce^{3+} to Tb^{3+}. The decay curve of $Ca_{0.4}Sr_{1.5}Ce_{0.02}Tb_{0.08}Al_2SiO_7$ is shown in Fig. 4. The decay curve of the double-doped phosphor monitored at 386 nm corresponding to the $^2D_{3/2}$ $(5d^1) \to {}^2F_j$ ($j = 7/2, 5/2$) of Ce^{3+} (a) and monitored at 542 nm corresponding to the $^5D_4 \to {}^7F_5$ of Tb^{3+} (b) after irradiation by the Xe lamp at 352 nm for 5 min. The decay time was calculated using following equation:

$$I_{(t)} = I_0 \exp\left(\frac{-t}{\tau}\right), \qquad (1)$$

where $I_{(t)}$ is the phosphorescence intensity after t (s), I_0 the phosphorescence intensity at the initial stage, t the time and τ is the decay rate constant, respectively. The calculated decay rate constant was 6.3 s for the Tb^{3+} emission and 6.5 s for the Ce^{3+} emission, respectively. These results indicate that the phosphorescence color at the initial stage is almost pure white. However, the phosphorescence color shifted to bluish white in a short time because of the slight difference in the decay rate constants for Tb^{3+} and Ce^{3+}. The chromaticity diagram of $Ca_{0.4}Sr_{1.5}Ce_{0.02}Tb_{0.08}Al_2SiO_7$ is shown in Fig. 5. As described above (a) and (b) are almost white and (c) is bluish white.

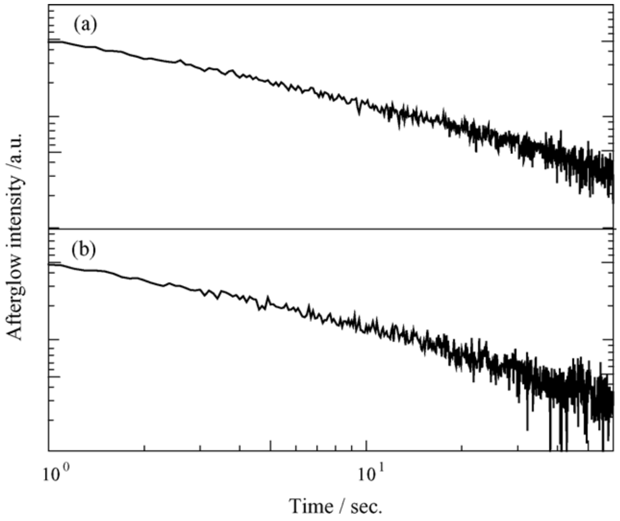

Fig. 4. Intensity decay of phosphorescence in $Ca_{0.4}Sr_{1.5}Ce_{0.02}Tb_{0.08}$ Al_2SiO_7 monitored at 386 nm (a) and 542 nm (b). The sample was illuminated for 5 min with 352 nm light from a Xe lamp.

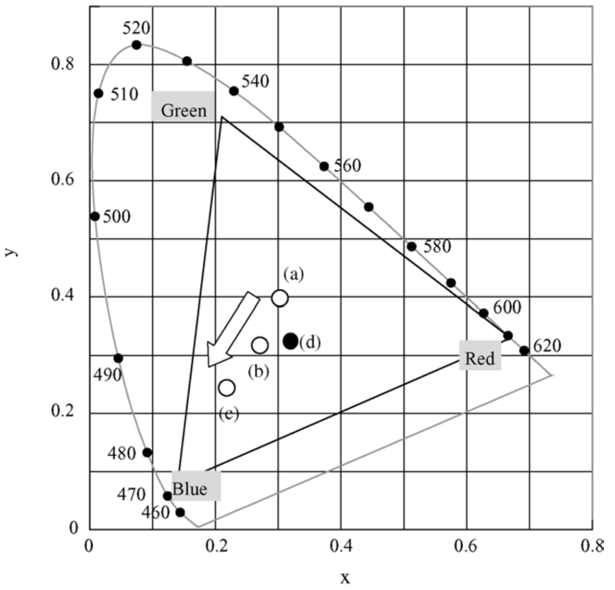

Fig. 5. Chromaticity coordinates of photo-luminescence (a), afterglow at the initial stage (b), afterglow after 60 s from the first stage in $Ca_{0.4}Sr_{1.5}Ce_{0.02}Tb_{0.08}Al_2SiO_7$ (c) and CIE day light (d).

3.3. Percolation theory

High luminance is a necessary property for phosphors. The increased concentration of emission ions is usually effective to obtain high brightness. However, the emission is often quenched when the concentration is greater than a critical concentration. This phenomenon results from migration of excitation energy among the emission ions and closely dependent on the crystal structure [8,9]. Avoiding concentration quenching in the region of a high concentration of emission ions, it is desirable that the emission ions exist in the low-dimensionally arrayed sites such as one-dimensionally or two-dimensionally arrayed sites. For that reason, the low-dimensional array has less direction though which excitation energy can migrate. Therefore, high concentration doping of emission ions for matrix is possible for such a case [10–12]. The Ce^{3+} and Tb^{3+} substituted for Ca/Sr sites in $(Ca/Sr)_2Al_2SiO_7$ are located in the two-dimensional site with a fairly low concentration. In the case of $Ca_{0.4}Sr_{1.5}Ce_{0.02}Tb_{0.08}Al_2SiO_7$, the energy transfer from Ce^{3+} to Tb^{3+} may hardly occur even though the dopants are placed in the two-dimensional array because the dopant concentrations are very low. This situation may give multicolored

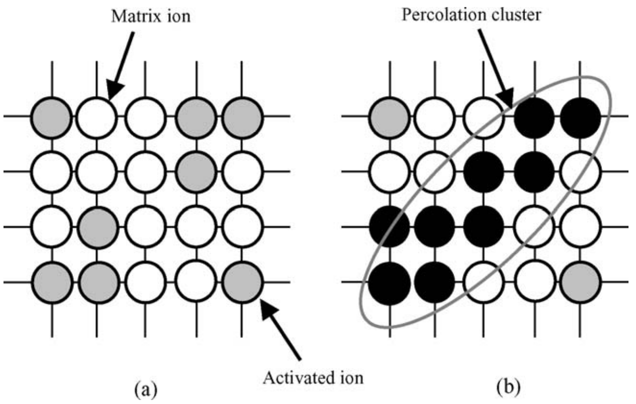

Fig. 6. Percolation models greater than the critical concentration (a) and less than the critical concentration (b).

emissions from both Ce^{3+} and Tb^{3+}. The percolation model concept is shown in Fig. 6. Percolation clusters of the Tb^{3+} ion are formed at high concentrations of Tb^{3+} ions. Such a cluster has a good chance of meeting the codoped Ce^{3+} ion, engendering sensitization of the Tb^{3+} by Ce^{3+} emission. The critical concentration of the percolation cluster depends on the dimensionality and the number of neighboring sites. The value can be calculated using the following equation [13,14],

$$P_c = \frac{d}{z(d-1)}, \qquad (2)$$

where P_c is the critical concentration, d the site dimension and z is the number of neighboring sites. In the present case, the calculated critical concentrations are 0.40 for the two-dimensional structure and 0.217 for the three-dimensional structure. The high critical concentration obtained in the former case suggests that the energy transfers from Ce^{3+} to Tb^{3+} are fairly low in the case of the low dopant concentration. Because only those percolation clusters with large size of Tb^{3+} can encounter the sensitizing Ce^{3+} ions, each Ce^{3+} and Tb^{3+} ion emits independently occurring emissions, thereby creating a multicolored luminescent.

4. Conclusion

Long afterglow phosphors of $Ca_{0.5}Sr_{1.5}Al_2SiO_7$ doped with Tb^{3+} and Ce^{3+} were prepared using a solid-state reaction. The neutron diffraction study indicated that the activation Ce^{3+} ions substituted for the Ca/Sr site in $Ca_{0.5}Sr_{1.5}Al_2SiO_7$. This compound crystallized in the melilite-type structure. The $Ca_{0.4}Sr_{1.5}Ce_{0.02}Tb_{0.08}Al_2SiO_7$ phosphor showed four main emission peaks at 386 nm caused by Ce^{3+} and at 483, 542, 591 nm caused by Tb^{3+}, creating a white luminescence. The PL emission intensity of Tb^{3+} in the codoped phosphor was five times higher than that of the Ce^{3+} single-doped phosphor. This results from an energy transfer from Ce^{3+} to Tb^{3+}. The codoped phosphor exhibited white long-persistence luminescence. This is the first report describing the development of a white long-persistence luminescence emitted from a single-phase phosphor.

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