

Synthesis and luminescence properties of new long persistent phosphors.

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Long persistent phosphors are materials which can absorb visible light energy to show afterglow. Previously, alkaline earth metal sulfides and zinc sulfides doped radioactive materials were used for the long persistent phosphors. However, sulfides tend to deteriorate upon exposure of moisture in air. On the other hand, though the radio luminous phosphors give long afterglows, radioactive materials have serious influence on environment. The highly stable and highly luminescent long persistent phosphors without radioactive materials are desired.

In this study, silicate families were chosen as hosts because of their excellent physical and chemical stability. The $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{Al}_2\text{SiO}_7: \text{Ce}^{3+}, \text{Tb}^{3+}$ phosphor showed the fluorescence of 5 times as high radiation intensity as the Ce^{3+} single-doped phosphor. The cause is energy migration from Ce^{3+} to Tb^{3+} . The co-doped phosphor showed white long-persistent phosphorescence. The non-stoichiometric $\text{BaMg}_2\text{Si}_2\text{O}_7: \text{Eu}^{2+}, \text{Mn}^{2+}$ phosphors with a Ba-deficient component exhibiting a long persistent phosphorescence with reddish color with two emission peaks of 400 nm and 660 nm. The cause is energy migration from Eu^{2+} to Mn^{2+} . The afterglows of these long persistent phosphors are occurred by sensitization between co-doped ions.

Key words: Long-persistent phosphor, Silicate phosphor, White phosphorescence, Red phosphorescence

1. INTRODUCTION

Recently the attention has been focusing on long-persistent phosphor, alkali earth aluminates ($\text{SrAl}_2\text{O}_4: \text{Eu}^{2+}, \text{Dy}^{3+}$), without radioisotope, because this shows the long-persistent properties better than the conventional zinc sulphide phosphor (e. g. ZnS: Cu) [1].

These long persistent phosphors show high intensity and high visibility of emission. The long persistent phosphors emitting only green luminescence are, however, applicable only to narrow application fields. These long persistent phosphors show high intensity and high visibility of emission. The long persistent phosphors emitting only green luminescence are, however, applicable only to narrow application fields. Developments of long persistent multicolored phosphors are very important because they can provide expanded application fields. Alkaline earth silicates show remarkably properties as phosphors hosts with various crystal structures and high chemical stability.

In this research, we reported co-doped long persistent luminescence phosphors, $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{Al}_2\text{SiO}_7: \text{Ce}^{3+}, \text{Tb}^{3+}$ with white color afterglow and $\text{BaMg}_2\text{Si}_2\text{O}_7: \text{Eu}^{2+}, \text{Mn}^{2+}$ red color afterglow [4,5].

2. Experimental

Starting materials for $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{Al}_2\text{SiO}_7: \text{Ce}^{3+}, \text{Tb}^{3+}$ were CaCO_3 (Kanto Chemical, Co., Inc, 4N), SrCO_3 (Kanto Chemical, Co., Inc, 3N), SiO_2 (Kanto Chemical, Co., Inc, 3N), Al_2O_3 (Kojundo Chemical Laboratory Co., Ltd., 4N), Tb_4O_7 (Kanto Chemical, Co., Inc, 3N5) and CeO_2 (Kanto Chemical, Co., Inc, 4N). 5 mol% B_2O_3 (Kanto Chemical, Co., Inc, 3N) was added as a flux. The starting powders were suspended in ethanol and mixed in an agate mortar for 15 min. The mixture was

fired in alumina boat at 1273 K for 3 h in air, and then the samples were refired in the alumina boat at 1623 K for 6 h in a weak reductive atmosphere of 5 % H_2 -95 % N_2 gas.

Starting materials for $\text{BaMg}_2\text{Si}_2\text{O}_7: \text{Eu}^{2+}, \text{Mn}^{2+}$ were BaCO_3 (Kanto Chemical, Co., Inc, 3N), MgO (Kanto Chemical, Co., Inc, 4N), SiO_2 (Kanto Chemical, Co., Inc, 3N), Eu_2O_3 (Shinetsu Chemical Co., Inc., 4N), and MnCO_3 (Kojundo Chemical Laboratory Co., Ltd., 3N). 10 mol% B_2O_3 (Kanto Chemical, Co., Inc, 3N) was added as a flux. The starting powders were suspended in ethanol, and mixed in an agate mortar. The mixture was dried and fired in an alumina boat at 1173 K for 3 h in air. After firing, the powder samples were fired in an alumina boat at 1473 K for 6 h in a weak reductive atmosphere of 5% H_2 -95%Ar gas.

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 $\lambda = 0.182035$ nm was obtained from a Ge(311) monochromator. The data were collected on thoroughly ground powders by a multi-scanning mode in the 2θ range from 5 to 155° with a step width of 0.1° and a monitoring time of 16 min. The powder patterns obtained were analyzed using the RIETAN2000 profile refinement program [6]. The excitation and the emission spectra were measured on a powder sample using a JASCO FP-6500/6600 spectrofluorometer. The CIE chromaticity coordinates were measured on a powder sample using a HAMAMATSU PMA-11 equipped with a 11 W Hg lamp.

3. Results and discussion

3-1 $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{Al}_2\text{SiO}_7: \text{Ce}^{3+}, \text{Tb}^{3+}$

The crystal structure of $\text{Ca}_{0.44}\text{Sr}_{1.5}\text{Ce}_{0.06}\text{Al}_2\text{SiO}_7$ was determined by the Rietveld refinement of neutron diffraction data, assuming the space group $P\bar{4}_{21}m$ (No.113) and Ce^{3+} substituted for Ca / Sr site [7]. Figure 1 shows the result of pattern fitting. In addition, the crystallographic data is listed in Table 1. All the peaks of the powder neutron diffraction patterns were indexed on a tetragonal space group of $P\bar{4}_{21}m$ cell with $a = 0.7805(2)$ nm, $c = 0.5226(2)$ nm. This compound takes the melilite-type structure. The emission ion site replaced by the Ca/Sr is distributed to two-dimensional arrangement. The high critical concentration in the two-dimensional structure is explained by the percolation theory [9]. Since Ce^{3+} and Tb^{3+} are doped at low concentration, it is hard to occur the energy sensitization. Consequently, Ce^{3+} and Tb^{3+} ions emit multicolor in the single component phosphor simultaneously. Figure 2 shows the excitation and emission spectra of $\text{Ca}_{0.42}\text{Sr}_{1.5}\text{Tb}_{0.08}\text{Al}_2\text{SiO}_7$ and $\text{Ca}_{0.4}\text{Sr}_{1.5}\text{Ce}_{0.02}\text{Tb}_{0.08}\text{Al}_2\text{SiO}_7$ at room temperature. Tb^{3+} has seven emission transition $^5\text{D}_3 \rightarrow ^7\text{F}_6, ^7\text{F}_5, ^7\text{F}_4, ^7\text{F}_0$ and $^5\text{D}_4 \rightarrow ^7\text{F}_6, ^7\text{F}_5, ^7\text{F}_4$. The emission spectrum (a) shows three sharp peaks corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$). This is due to the cross relaxation from the $^5\text{D}_3$ to the $^5\text{D}_4$ energy levels. The enhancement of the

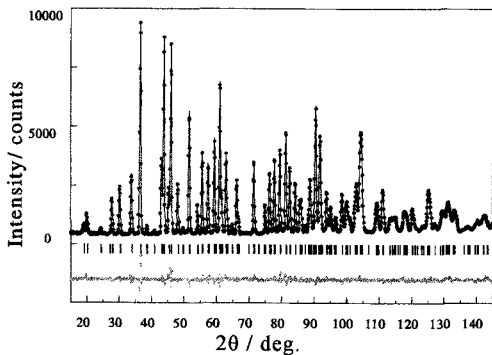


Figure 1 Neutron Rietveld refinement patterns of $\text{Ca}_{0.44}\text{Sr}_{1.5}\text{Ce}_{0.06}\text{Al}_2\text{SiO}_7$.

The vertical marks and middle show the position calculated Bragg reflections. The trace on the bottom us a plot of the difference between calculated and observed intensities.

Table 1 Neutron Rietveld refinement results of $\text{Ca}_{0.44}\text{Sr}_{1.5}\text{Ce}_{0.06}\text{Al}_2\text{SiO}_7$.

Atom	Site	g	x	y	z	B / nm ⁻²
X	4e	1.0	0.3373(2)	0.1616(2)	0.5095(3)	0.010(3)
Al	2a	1.0	0	0	0	0.006(9)
Al	4e	0.5	0.1416(4)	0.3568(3)	0.9619(5)	0.005(7)
Si	4e	0.5	0.1416(4)	0.3568(3)	0.9619(5)	0.005(7)
O(1)	2c	1.0	0.5	0	0.1652(6)	0.011(5)
O(2)	4c	1.0	0.1426(2)	0.3567(2)	0.2799(3)	0.010(4)
O(3)	8f	1.0	0.0843(1)	0.1695(1)	0.8175(3)	0.010(3)

$P\bar{4}_{21}m$ (no.113), $a = 0.7805(2)$ nm, $b = 0.7875(2)$ nm, $c = 0.5226(2)$ nm, $R_w = 4.38\%$, $R_p = 3.26\%$, $R_e = 2.93\%$, $R_I = 1.46\%$, $R_F = 1.37\%$, $S = 1.4978$.

cross relaxation is due to the high ion concentration leading to a strong emission of $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transition. The emission spectrum (b) shows several sharp peaks by Tb^{3+} corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j = 6, 5, 4$) and a broad peak by Ce^{3+} corresponding to the $^2\text{D}_{3/2}(5d^1) \rightarrow ^2\text{F}_{7/2}, ^2\text{F}_{5/2}$. The emission intensity of Tb^{3+} in the co-doped phosphor exhibited five times higher than that of the Ce^{3+} single-doped phosphor. This is due to an energy migration from Ce^{3+} to Tb^{3+} . Figure 3 shows the decay curve of $\text{Ca}_{0.4}\text{Sr}_{1.5}\text{Ce}_{0.02}\text{Tb}_{0.08}\text{Al}_2\text{SiO}_7$. The decay curve of (a) was observed in 386nm corresponding to $^2\text{D}_{3/2}(5d^1) \rightarrow ^2\text{F}_{7/2}, ^2\text{F}_{5/2}$ of Ce^{3+} and (b) was observed in 542 nm corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ of Tb^{3+} after irradiation by a Xe lamp at 352 nm for 5 min respectively. The decay time were calculated by using following equation

$$I(t) = I_0 \exp(-t/\tau) \dots (2)$$
where $I(t)$ is the phosphorescence intensity after t s; I_0 is the phosphorescence intensity at the first stage; t is the time; τ is the decay rate constant, respectively. The calculated decay rate was $\tau = 6.3$ s for the Tb^{3+} and $\tau = 6.5$ s for the Ce^{3+} . These results show that the phosphorescence color at the first stage is white. However the phosphorescence color shifted to blue white as time progresses because of the difference of the decay rate constant of Tb^{3+} and Ce^{3+} . The color of photo-luminescence and afterglow at the first stage are almost white, the afterglow after 60 s from the first stage is bluely white in $\text{Ca}_{0.4}\text{Sr}_{1.5}\text{Ce}_{0.02}\text{Tb}_{0.08}\text{Al}_2\text{SiO}_7$ respectively. It is desirable that the emission ions exist in

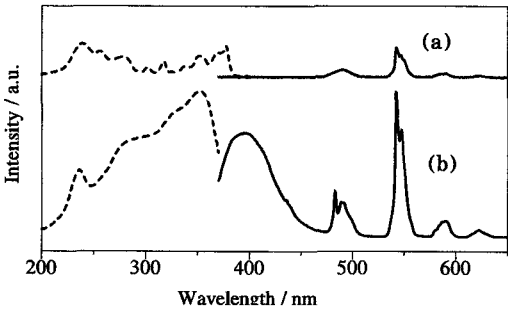


Figure 2 Excitation and emission spectra of $\text{Ca}_{0.42}\text{Sr}_{1.5}\text{Tb}_{0.08}\text{Al}_2\text{SiO}_7$ (a) and $\text{Ca}_{0.4}\text{Sr}_{1.5}\text{Ce}_{0.02}\text{Tb}_{0.08}\text{Al}_2\text{SiO}_7$ (b).

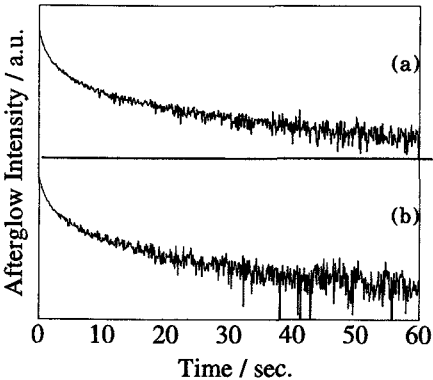


Figure 3 Intensity decay of phosphorescence in $\text{Ca}_{0.4}\text{Sr}_{1.5}\text{Ce}_{0.02}\text{Tb}_{0.08}\text{Al}_2\text{SiO}_7$ monitored at the 386 nm (a) and 542 nm (b). Sample was illuminated for 5 minutes with 352 nm light from Xe lamp.

the low dimensional array sites such as one- or two-dimensional sites in the case of the emission ions are arranged in the host lattice. The low dimensional structures inhibit the excitation energy transfer and the decrease of emission intensity. Therefore, high concentration doping of the activated ion for matrix is possible [10-12]. The critical concentration of the percolation cluster depends on the dimension and the number of neighboring site [13, 14]. The Ce³⁺ and Tb³⁺ emitted respectively in substituting two-dimensional Ca/Sr sites of (Ca/Sr)₂Al₂SiO₇. Sensitization takes place by energy transfer of the near co-doped Ce³⁺ ions to the percolation cluster of Tb³⁺. Therefore, afterglow colors are changed by concentration of Tb³⁺. Afterglow color of low Tb³⁺ concentration phosphor exhibits blue as emission color of Ce³⁺ with low sensitization. On the other hand, afterglow color of high Tb³⁺ concentration phosphor shows green as emission color of Tb³⁺ with high sensitization. The white afterglow is exhibited in suitable Tb³⁺ concentration.

High critical concentration means that the possibility of the energy transfer from Ce³⁺ to Tb³⁺ decrease. Since only the percolation cluster (large cluster) of Tb³⁺ encounter the sensitizer Ce³⁺ ions, the Ce³⁺ and Tb³⁺ ions simultaneously emit multicolor.

3-2 BaMg₂Si₂O₇: Eu²⁺, Mn²⁺

The structure of Ba_{0.99}Eu_{0.01}Mg_{1.8}Mn_{0.2}Si₂O₇ was refined by the Rietveld analysis for the neutron diffraction data using structural parameters of BaCo₂Si₂O₇ [8]. Figure 4 shows the result of pattern fitting. The refined atomic parameters are listed in Table 2. The structure belongs to a monoclinic space group C2/c and the lattice constants refined were a = 0.72529(2) nm, b = 1.27345(5) nm, c = 1.37846(5) nm, and β=90.213(3)°. A structural model where manganese atoms were assigned to the three magnesium sites with an equimolar ratio as a mixed species gave the most reasonable refinement. The structure of BaMg₂Si₂O₇: Eu²⁺, Mn²⁺ is shown in Figure 5. Figure 6 shows the excitation and emission spectra of Eu²⁺ or Mn²⁺ single-doped phosphors Ba_{0.99}Eu_{0.01}Mg₂Si₂O₇ (a), BaMg_{1.8}Mn_{0.2}Si₂O₇ (b) and Eu²⁺ and Mn²⁺ co-doped phosphor Ba_{0.99}Eu_{0.01}Mg_{1.8}Mn_{0.2}Si₂O₇ (c). The Eu²⁺ single-doped phosphors emitted a 400 nm violet light, and those only with Mn²⁺ emitted dim red light. The violet light and the red light are attributed to the 4f-5d transition of Eu²⁺ and the ⁴T₁→⁶A₁ transition of Mn²⁺ [10], respectively. On the other hand, in the Eu²⁺ and Mn²⁺ co-doped phosphor, reddish luminescence with two emission peaks of 400 nm and 660 nm was observed by the naked eyes. Comparison of Eu²⁺ and Mn²⁺ co-doped phosphor Ba_{0.99}Eu_{0.01}Mg_{1.8}Mn_{0.2}Si₂O₇ and single-doped phosphor BaMg_{1.8}Mn_{0.2}Si₂O₇, the red emission peak of 660 nm is similar to emission of Mn²⁺. The emission intensity of (c) is seven times higher than that of (b). These facts suggest that the energy transfer from Eu²⁺ to Mn²⁺ is cause of such a higher emission intensity of Ba_{0.99}Eu_{0.01}Mg_{1.8}Mn_{0.2}Si₂O₇.

Furthermore, the Eu²⁺ single-doped phosphor Ba_{0.99}Eu_{0.01}Mg₂Si₂O₇ with showed a low intensity but certain amount of afterglow. However, the afterglow intensity and the decay time decreased remarkably as the quantity of doped Mn²⁺ ion increased. Since the doping

concentration of Mg²⁺ is over 10 mol%, the afterglow became invisible. This fact means that the phosphors co-doped Eu²⁺ and Mn²⁺ show a red afterglow because Mn²⁺ receives energy from Eu²⁺ continuously. By the way, in the long persistent phosphors the co-doped dopants sensitize to increase the afterglow intensity [11]. These rare earth ions are considered to create oxygen defects or cation defects. According to Ohta et al., a Sr (Ca) defect works as an electron hole trap which is stabilized by Dy³⁺ (Nd³⁺), providing a

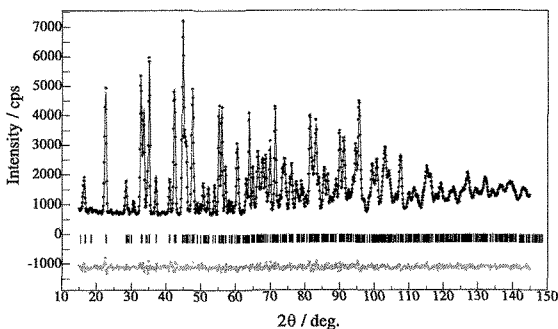


Figure 4 Rietveld refinement profile of neutron diffraction data for Ba_{0.99}Eu_{0.01}Mg_{1.8}Mn_{0.2}Si₂O₇. The dot line is observed, and the solid line represents the calculated pattern. The vertical marks in the middle show the positions calculated for Bragg reflections. The trace on the bottom is plot of the differences between the calculated and observed intensities.

Table 2 Refined atomic parameters of Ba_{0.99}Eu_{0.01}Mg_{1.8}Mn_{0.2}Si₂O₇.

Atom	Site	g	x	y	z	B / nm ²
Ba1	8f	1.0	0.2017(7)	0.0177(2)	0.1186(7)	0.0061(4)
X1	4e	1.0	0.5	0.2677(3)	0.25	0.0029(8)
X2	4e	1.0	0.5	0.7342(7)	0.25	0.0029(8)
X3	8f	1.0	0.0383(1)	0.2343(8)	0.5088(2)	0.0029(8)
Si1	8f	1.0	0.2889(9)	0.8759(4)	0.3650(5)	0.0083(7)
Si2	8f	1.0	0.3263(4)	0.1042(2)	0.3804(8)	0.0036(3)
O1	8f	1.0	0.4287(5)	0.7772(3)	0.3842(3)	0.0071(1)
O2	8f	1.0	0.1722(3)	0.1159(8)	0.2955(8)	0.0072(1)
O3	8f	1.0	0.248(6)	0.138(5)	0.4875(7)	0.0066(2)
O4	8f	1.0	0.5029(1)	0.1795(4)	0.3650(4)	0.0063(1)
O5	8f	1.0	0.410(4)	0.984(5)	0.3811(6)	0.0078(7)
O6	8f	1.0	0.220(4)	0.8594(4)	0.254(9)	0.0141(3)
O7	8f	1.0	0.1158(2)	0.883(6)	0.440(2)	0.0096(1)

R_{wp}=3.46%, R_p=2.68%, R_F=0.50%, and S=1.396.
X means a mixed species
with a ratio of Mg : Mn = 0.9 : 0.1

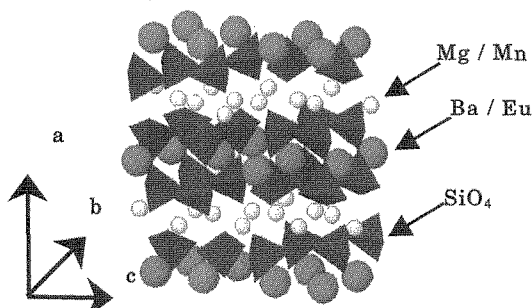


Figure 5 Crystal structure of BaMg₂Si₂O₇: Eu²⁺, Mn²⁺.

remarkable increase in afterglow intensity [12,13]. Consequently, the non-stoichiometric composition samples have expected the improvement of the afterglow properties. The afterglow intensity of initial stages became higher in the samples with Ba content a little deficient from stoichiometry (Ba-poor samples), although the luminescence intensity decreased. Ba-poor samples were considered that Ba cation defects or oxygen defects as a trap for holes or electrons were produced. Figure 7 shows the decay curves for the stoichiometric sample of $\text{Ba}_{0.99}\text{Mg}_{1.8}\text{Eu}_{0.01}\text{Mn}_{0.2}\text{Si}_2\text{O}_7$ (d) and the non-stoichiometric Ba-poor sample (e). The

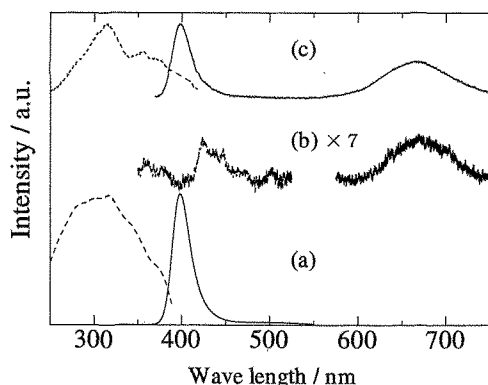


Figure 6 Excitation and emission spectra of $\text{Ba}_{0.99}\text{Eu}_{0.01}\text{Mg}_2\text{Si}_2\text{O}_7$ (a), $\text{BaMg}_{1.8}\text{Mn}_{0.2}\text{Si}_2\text{O}_7$ (b) and $\text{Ba}_{0.99}\text{Eu}_{0.01}\text{Mg}_{1.8}\text{Mn}_{0.2}\text{Si}_2\text{O}_7$ (c).

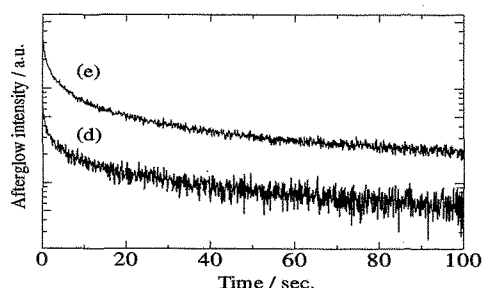


Figure 7 Afterglow decay curves for stoichiometric sample of $\text{Ba}_{0.99}\text{Eu}_{0.01}\text{Mg}_{1.8}\text{Mn}_{0.2}\text{Si}_2\text{O}_7$ (d) and non-stoichiometric Ba-poor (20%) sample (e). The decay curve was monitored at around 660 nm after excitation by a Xe lamp for 3 minutes.

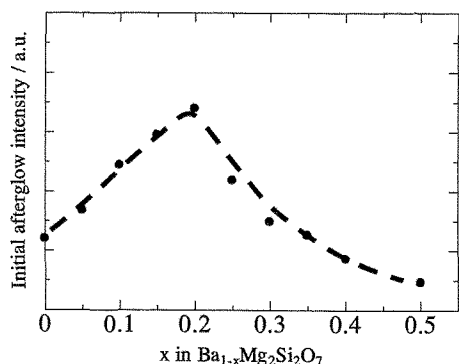


Figure 8 Dependence of initial afterglow intensity on the Ba deficiency in $\text{Ba}_{1-x}\text{Mg}_2\text{Si}_2\text{O}_7$.

dependence of the initial afterglow intensity on the Ba deficiency is shown in Figure 8. According to this result, it is considered that Ba ion defects or oxygen defects cause the increase of initial afterglow intensity.

4. Conclusion

The co-doped long-persistent phosphors based on two kinds of silicate hosts were reported.

The neutron diffraction study of $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{Al}_2\text{SiO}_7$: Ce^{3+} phosphor was indicated that the activation ion Ce^{3+} substituted for Ca / Sr in $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{Al}_2\text{SiO}_7$. This compound crystallized in the melilite-type structure. The $\text{Ca}_{0.4}\text{Sr}_{1.5}\text{Ce}_{0.02}\text{Tb}_{0.08}\text{Al}_2\text{SiO}_7$ phosphor shows four main emission peaks at 386 nm by Ce^{3+} and at 483, 542, 591 nm by Tb^{3+} and emitted white color. The emission intensity of Tb^{3+} in the co-doped phosphor was five times higher than that of the Ce^{3+} single-doped phosphor because of an energy transfer from Ce^{3+} to Tb^{3+} . The phosphorescence color shifted to bluely white due to a difference of decay rate between Ce^{3+} and Tb^{3+} .

$\text{BaMg}_2\text{Si}_2\text{O}_7$: Eu^{2+} , Mn^{2+} phosphors showed a reddish luminescence with seven times higher comparison with that of doped only with Mn^{2+} . It is due to an energy transfer from Eu^{2+} to Mn^{2+} . The increase of doped Mn^{2+} concentration causes a decrease in afterglow intensity and decay time. However, a non-stoichiometric co-doped phosphor with a deficiency in Ba component showed higher initial afterglow intensity. It is suggested that the defects of Ba cations or oxygen vacancies introduced by the deficiency of Ba component is strongly correlated with the afterglow.

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