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Synthesis and photoluminescence properties of a novel aluminosilicate $Sr_3Al_{10}SiO_{20}$:Mn^{4+} red phosphor

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ABSTRACT

A novel aluminosilicate red phosphor $Sr_3Al_{10}SiO_{20}$:Mn^{4+}, which has some octahedral sites, was synthesized by a solid-state reaction, and we investigated its photoluminescence properties. $Sr_3Al_{10}SiO_{20}$ doped with tetravalent manganese showed a red photoluminescence transition from ^2E to $^4A_2$ after excitation in the near ultraviolet region to the blue region in the visible spectrum. The $Sr_3Al_{10}SiO_{20}$:Mn^{4+} synthesized at 1500 °C for 6 h exhibited maximum emission intensity. From these results, it was confirmed that aluminosilicates could be the host structure for Mn^{4+}-doped phosphors.

1. Introduction

Tetravalent manganese-activated phosphors show red photoluminescence by excitation in the near-ultraviolet region to the blue region [1] and have attracted attention as rare-earth-free, transition metal-activated red phosphors [1–7]. Therefore, Mn^{4+}-doped phosphors can potentially be applied to devices such as white LEDs, LEDs for plant growth, and wavelength-converting materials for solar cells.

Various compounds such as oxides [8,9], nitrides [10], sulfides [11], halides [2,12], and mixed-anion compounds [13–15] are used for the host structure of phosphors. However, the reported Mn^{4+}-doped phosphors still have low emission intensities, and emission wavelength of them is limited to a narrow range. Therefore, various emission wavelengths are needed for the above uses; it is required to develop novel host materials for Mn^{4+}-activated phosphors. Various oxide host materials have been reported for Mn^{4+}-activated phosphors. Among them, many aluminates [1,4,6,16,17], germanates [3,18–23], and titanates [5,7,24] have been reported as host structures for Mn^{4+}-doped oxide phosphors. In addition, host materials such as gallate [6], stannate [25,26], niobate [27,28], tungstate [29], and molybdate [30] have also recently been reported. On the other hand, silicate, which is applied to various phosphors, has not been reported as a host material for Mn^{4+}-activated phosphor. For Mn^{4+} to emit photoluminescence as a luminescent center, the tetravalent Mn cation must be located in an octahedral site. However, many silicates with the exception of high pressure phase having SiO_6 polyhedron are composed of tetrahedral SiO_4 polyhedral networks. Therefore, Mn^{4+} does not emit photoluminescence in the silicates because it is not octahedrally coordinated.

In this study, we focused on an aluminosilicate matrix structure for Mn^{4+}-activated phosphors. It has been reported that aluminosilicates composed of tetrahedral SiO_4 and tetrahedral AlO_4 and/or octahedral AlO_6 polyhedra are host structures for various phosphors [31,32]. Therefore, aluminosilicates with octahedral sites expected to be candidates for Mn^{4+}-activated phosphors. In particular, $Sr_3Al_{10}SiO_{20}$ has tetrahedral (Al,Si)O_4 and octahedral AlO_6 polyhedra and is also a host material for Eu^{2+}-activated phosphors [31]. Thus, we chose $Sr_3Al_{10}SiO_{20}$ as a candidate for the aluminosilicate host structure with octahedral AlO_6 polyhedra for the Mn^{4+}-doped phosphor.

In this paper, we report the synthesis and photoluminescence properties of a novel aluminosilicate $Sr_3Al_{10}SiO_{20}$:Mn^{4+} red phosphor and confirmed that the aluminosilicate could become the host structure for Mn^{4+}-doped phosphor.

2. Experimental

Mn^{4+}-doped $Sr_3Al_{10}SiO_{20}$ red phosphor was synthesized by a solid-state reaction. The raw materials were powders of $SrCO_3$ (99.9%, Kojundo Chem. Lab. Co., Ltd.), Al_2O_3 (99.99%, ca. 1 μm, Kojundo Chem. Lab. Co., Ltd.), SiO_2 (99.9%, ca. 0.8 μm, Kojundo Chem. Lab. Co., Ltd.), and MnO_2 (99.99%, Kojundo Chem. Lab. Co., Ltd.). The powders were weighed according to the desired molar ratio, $SrCO_3$:Al_2O_3:SiO_2:MnO_2 = 3:5(1-x):1:10x, and mixed with ethanol using an alumina mortar and pestle. After drying, about 0.5 g of the powder mixture was pressed into a pellet, 10 mm in diameter, at a pressure of 150 MPa. The pellet was placed on an alumina plate and heated at 1200–1600 °C for 3–18 h in air using an electric furnace. The heated pellets were ground using an alumina mortar and pestle before analysis.

The ground samples were characterized by powder X-ray diffraction

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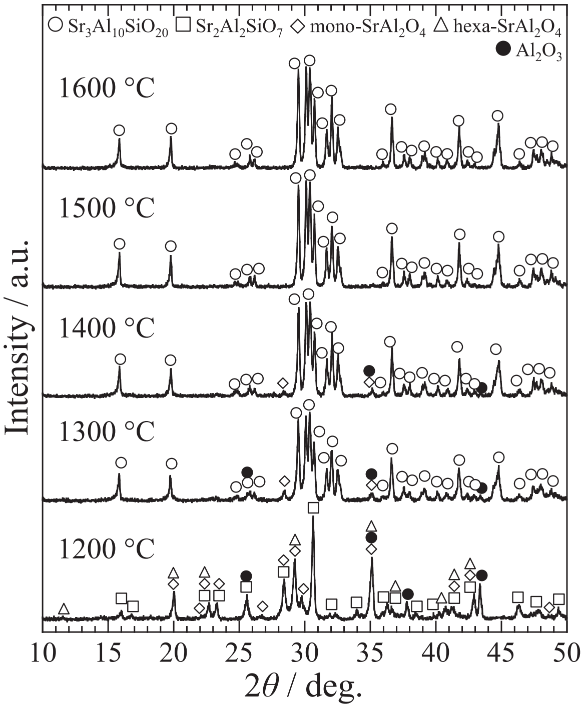

Fig. 1. XRD patterns of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn synthesized at 1200–1600 °C for 12 h.

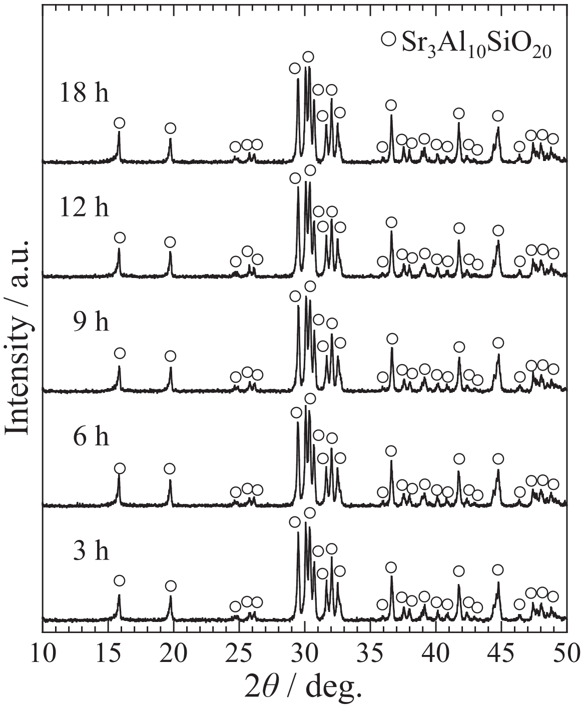

Fig. 2. XRD patterns of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn synthesized at 1500 °C for 3–18 h.

(XRD) using a powder diffractometer (Rigaku Co., RINT-2200, Cu-K_α radiation). The crystal structure parameters were refined by Rietveld analysis using the RIETAN-FP program [33]. The particle size and morphology of the sample were observed using a scanning electron microscope (SEM, Hitachi High-Technologies Co., TM3000). The photoluminescence (PL) excitation and emission spectra of the specimens were measured at room temperature using a spectrofluorometer (JASCO Co., FP-6600) equipped with an O-58 sharp cut filter.

3. Results and discussion

3.1. Synthesis and crystal structure refinement

Fig. 1 shows the XRD patterns of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn synthesized at 1200–1600 °C for 12 h. At 1200 °C, $Sr_2Al_2SiO_7$, monoclinic $SrAl_2O_4$, hexagonal $SrAl_2O_4$, and Al_2O_3 were produced without the desired product, $Sr_3Al_{10}SiO_{20}$. The samples prepared at 1300 and 1400 °C contained the main phase of $Sr_3Al_{10}SiO_{20}$ and trace amounts of monoclinic $SrAl_2O_4$ and Al_2O_3. Above 1500 °C, the sample contained a single phase of $Sr_3Al_{10}SiO_{20}$ without any impurity phases. Fig. 2 shows the XRD patterns of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn synthesized at 1500 °C for 3–18 h. The product contained a single phase of $Sr_3Al_{10}SiO_{20}$ with no dependence on synthesis time.

To investigate the coordination environment of the octahedral sites that accommodated the activator Mn^{4+}, the crystal structure was refined by Rietveld analysis using the single crystal structural data reported by Rief and Kubel [34] as the model structure. The profile-fit and the difference patterns of the Rietveld method are shown in Fig. 3. It was confirmed that the calculated and observed diffraction profiles were similar in terms of peak position and relative peak intensity. Table 1 summarizes the results of the structure refinement of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn. Reliability indices of the Rietveld analysis resulted in $R_{wp}=10.40\%$, $R_p=10.40\%$, $R_B=2.89\%$, $R_F=1.66\%$, and goodness-of-fit $S=1.326$. The atomic coordinates, occupancies, and isotropic atomic displacement parameters of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn are listed in Table 2. Fig. 4 shows the crystal structure of $Sr_3Al_{10}SiO_{20}$ drawn with the program VESTA [35]. These refinement results were almost the same powder refinement results reported by Kubota et al. [36]. Considering the ionic radii, the manganese cation occupies an aluminum site. Although there are two octahedral sites and two tetrahedral sites in $Sr_3Al_{10}SiO_{20}$, it is inferred that the tetravalent manganese cation—playing the role of a luminescence center—occupies the octahedral Al3(4*h*) and Al4(2*a*) sites. However, as doped Mn is at a trace level, it was not clear from the Rietveld analysis as to which site was occupied by the Mn cation.

Fig. 5 shows the SEM image of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn synthesized at 1300–1600 °C for 12 h. The particle size of the ground sample prepared at 1300–1500 °C was ~3 µm. However, the particle size of a ground sample formed at 1600 °C was about 30 µm, which was larger than the sample synthesized below 1500 °C.

3.2. Photoluminescence properties

Fig. 6(a) shows the photoluminescence (PL) excitation and emission spectra of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn prepared at 1200–1600 °C for 12 h. The samples synthesized above 1300 °C, where $Sr_3Al_{10}SiO_{20}$ was obtained as the main phase or as a single phase, showed similar photoluminescence spectra. Therefore, it can be inferred that these PL spectra show the photoluminescence of Mn^{4+} in the $Sr_3Al_{10}SiO_{20}$ host structure. On the other hand, the PL spectra of the specimen prepared at 1200 °C were different from those of the samples synthesized above 1300 °C. Considering the XRD results, the photoluminescence of the sample synthesized at 1200 °C is assumed to be due to Al_2O_3: Mn^{4+}. The excitation spectra of $Sr_3Al_{10}SiO_{20}$:Mn^{4+} exhibited a broad band with three peaks at around 305, 390, and 490 nm. These peaks were attributed to the charge transfer transition from O^{2-} to Mn^{4+} and the spin-allowed transition of Mn^{4+} from $^4A_2$ to $^4T_1$ and $^4T_2$, respectively. The emission spectra of $Sr_3Al_{10}SiO_{20}$:Mn^{4+} obtained using near-ultraviolet radiation displayed a narrow band peaking at 662 nm and was assigned to the spin-forbidden transition of Mn^{4+} from ^2E to $^4A_2$. The dependence of the PL emission intensity of $Sr_3Al_{10}SiO_{20}$: 0.1% Mn on synthesis temperature is shown in Fig. 6(b). The emission intensity increased with increasing synthesis temperature up to 1500 °C because of the improvement in crystallinity, and decreased above 1500 °C. The causes of the decrease in emission intensity seem to be the formation of