



Synthesis and photoluminescence properties of a novel $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Mn}^{4+}$ red phosphor prepared with a B_2O_3 flux



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ABSTRACT

A novel Mn^{4+} -doped aluminate red phosphor $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Mn}^{4+}$ was synthesized by a solid-state reaction, and we investigated its photoluminescence properties. $\text{Sr}_2\text{Al}_6\text{O}_{11}$, which has a similar structure to $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, was formed as the main phase after heating alpha-alumina, strontium carbonate, manganese dioxide, and magnesium oxide with 2.5% B_2O_3 at 1000 °C for 12 h or more. The $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Mn}^{4+}$ phosphor exhibited red photoluminescence with peaks at around 652 and 665 nm, which arise from the spin-forbidden transition of the Mn^{4+} cation from the ${}^2\text{E}$ to the ${}^4\text{A}_2$ state. The phosphor can be excited by near ultraviolet or blue LED light because it had a broad excitation band from the near-ultraviolet to the blue light region. The emission intensity was increased by co-doping with Mg^{2+} cations, which act as charge compensators. The amount of Mg required for the most effective charge compensation was 10 times the optimum Mn concentration. From these results, we confirmed that $\text{Sr}_2\text{Al}_6\text{O}_{11}$ could act as the host structure for Mn^{4+} -doped phosphors.

1. Introduction

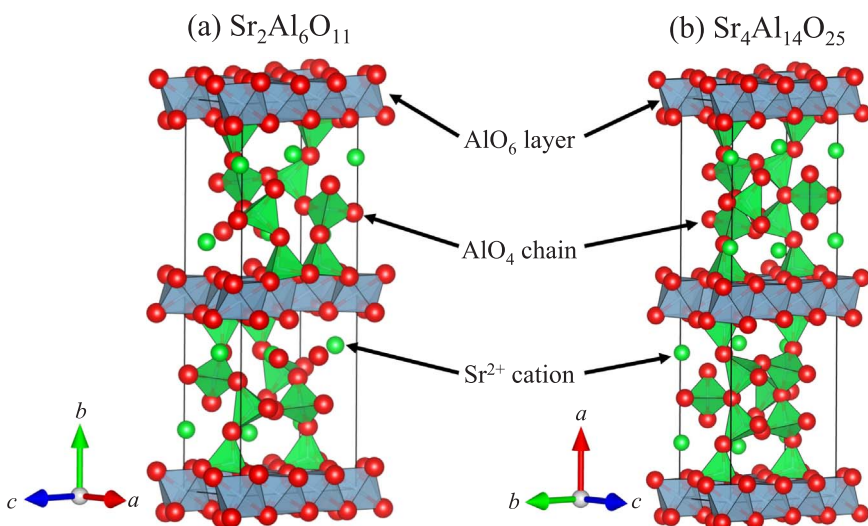
White light-emitting diodes (LEDs) are becoming more popular and replacing fluorescent lamps and incandescent bulbs as white light sources; this is primarily because of their long lifetimes, high efficiencies, and energy saving performance. In addition, they are mercury-free [1,2]. Commercially available white LEDs comprise a GaN-based blue LED and a yellow phosphor; typically, this phosphor is cerium-doped yttrium aluminum garnet (YAG:Ce). The combination of the blue light emitted by the blue LED and the yellow light emitted by the yellow phosphor excited by the blue LED produces a pseudo-white light. However, these LEDs have poor color rendering because of the lack of red light in their spectra. To improve the color rendering, white LEDs must contain the three primary colors: red, green, and blue. Some combinations of various LEDs and phosphors have been designed to produce high color rendering white LEDs, for example, a blue LED with red and green phosphors or a near-ultraviolet LED with red, green, and blue phosphors. Therefore, it is necessary to develop a red phosphor that is excitable by blue or near-ultraviolet LED for high color rendering white LEDs.

Tetravalent manganese-activated phosphors have attracted attention as rare-earth-free, transition metal-activated red phosphors for white LEDs. To date, many red phosphors, which are excited by the emission line spectrum (254 nm) of mercury [3–5], for fluorescent lamps have been reported. However, it can be difficult to excite these

phosphors using near-ultraviolet or blue LED light. Many (oxy)nitride phosphors have an excitation spectrum that matches the emission wavelength of near-ultraviolet or blue LED light, for example, $\text{CaAl}_2\text{SiN}_6:\text{Eu}^{2+}$ [6], $(\text{Ca},\text{Sr})_2\text{Si}_2\text{N}_5:\text{Eu}^{2+}$ [7], and α - or β - SiAlON [8,9]. However, these (oxy)nitride phosphors are synthesized at high temperatures and high nitrogen partial pressures. Furthermore, rare-earth elements, which are used as the activators in many existing phosphors, are expensive and unevenly distributed in the Earth's crust. Therefore, the development of a facile synthetic route to inexpensive phosphors is required. Mn^{4+} -activated oxide phosphors are expected to be rare-earth-free red phosphors for high color rendering white LEDs. These phosphors are excited by the spin-allowed transitions from the ${}^4\text{A}_2$ to the ${}^2\text{T}_1$ and ${}^2\text{T}_2$ states of Mn^{4+} and charge transfer transitions from O^{2-} to Mn^{4+} in the near ultraviolet to blue region. The phosphors emit red photoluminescence by the spin-forbidden transition from the ${}^2\text{E}$ to the ${}^4\text{A}_2$ state of Mn^{4+} . Hence, Mn^{4+} -doped phosphors can be excited by near ultraviolet or blue LEDs.

In this study, we focused on strontium aluminate ($\text{Sr}_2\text{Al}_6\text{O}_{11}$) as a host material for the Mn^{4+} -activated phosphors. Many aluminates have been reported as the host materials of Mn^{4+} -doped phosphors, for example, $\text{CaAl}_{12}\text{O}_{19}$ [10–15], $\text{SrAl}_{12}\text{O}_{19}$ [10,15], $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ [16–21], $\text{Ca}_2\text{Mg}_2\text{Al}_{28}\text{O}_{46}$ [22], $\text{CaMg}_2\text{Al}_{16}\text{O}_{27}$ [22], $\text{Sr}_2\text{MgAl}_{22}\text{O}_{36}$ [23,24], $\text{SrMgAl}_{10}\text{O}_{17}$ [25–27], and $\text{Ca}_{14}\text{Zn}_6\text{Al}_{10}\text{O}_{35}$ [28–30]. In particular, it has been reported that the integrated emission intensity of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Mn}^{4+}$ is greater than those of α - $\text{Al}_2\text{O}_3:\text{Mn}^{4+}$ and

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Fig. 1. Crystal structures of (a) $\text{Sr}_2\text{Al}_6\text{O}_{11}$ and (b) $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$.

$\text{SrAl}_{12}\text{O}_{19}:\text{Mn}^{4+}$ [16]. In addition, $\text{Sr}_2\text{Al}_6\text{O}_{11}$ has a similar structure to $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ [31]. The crystal structures of $\text{Sr}_2\text{Al}_6\text{O}_{11}$ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, drawn with the program VESTA [32], are shown in Fig. 1. These compounds consist of a layer of edge-sharing AlO_6 octahedra with corner-sharing tetrahedral AlO_4 chains between the AlO_6 layers. Whereas the AlO_4 chains of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ are linked in a symmetric fashion, the AlO_4 polyhedra of $\text{Sr}_2\text{Al}_6\text{O}_{11}$ are linked in zigzag chains. In the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Mn}^{4+}$ red phosphor, tetravalent manganese cations, which are the photoluminescence centers, are located in the octahedral AlO_6 layers. Therefore, we considered that $\text{Sr}_2\text{Al}_6\text{O}_{11}$, which has AlO_6 layers similar to those of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, is a candidate host material for Mn^{4+} -doped phosphors.

In this paper, we report the synthesis and photoluminescence properties of a $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Mn}^{4+}$ red phosphor and demonstrate that $\text{Sr}_2\text{Al}_6\text{O}_{11}$ is an excellent candidate as the host structure for Mn^{4+} -doped phosphors.

2. Experimental

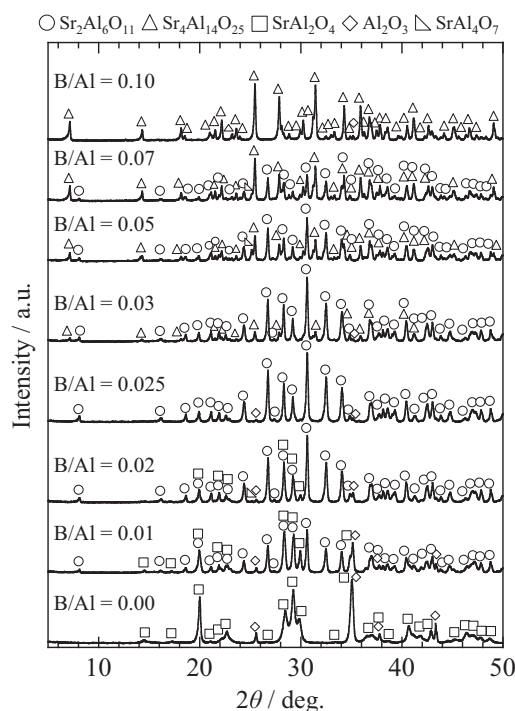
The $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{Mn}^{4+}$ red phosphor was prepared by a solid-state reaction. The raw materials were powdered SrCO_3 (99.9%, Kojundo Chem. Lab. Co., Ltd.), $\alpha\text{-Al}_2\text{O}_3$ (99.99%, ca. 1 μm , Kojundo Chem. Lab. Co., Ltd.), MnO_2 (99.99%, Kojundo Chem. Lab. Co., Ltd.), B_2O_3 (99.995%, Kojundo Chem. Lab. Co., Ltd.), and MgO (99.9%, 0.2 μm , Wako Pure Chem. Ind. Ltd.). The powders were weighed according to the formula $\text{Sr}_2(\text{Al}_{1-x-y}\text{Mn}_x\text{Mg}_y\text{B}_z)_6\text{O}_{11+9z}$, where z indicates the ratio of boron to aluminum. The powders, excluding B_2O_3 , were mixed with ethanol using an alumina pestle and mortar. After drying, the powder mixture was mixed again with the addition of B_2O_3 to avoid the segregation of B_2O_3 during drying because B_2O_3 is soluble in ethanol. Then, about 0.5 g of the powder mixture was pressed into a 10-mm diameter pellet at a pressure of 150 MPa. The pellet was placed on a platinum plate and heated at 1000 °C for 12 h in air using an electric furnace. For comparison with other host material of $\text{SrO-Al}_2\text{O}_3$ system, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Mn}^{4+}$ and $\text{SrAl}_{12}\text{O}_{19}:\text{Mn}^{4+}$ red phosphors were also prepared by a solid-state reaction. The raw powders for $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Mn}^{4+}$ and $\text{SrAl}_{12}\text{O}_{19}:\text{Mn}^{4+}$ were weighed and mixed according to $\text{SrCO}_3:\alpha\text{-Al}_2\text{O}_3:\text{B}_2\text{O}_3:\text{MnO}_2:\text{MgO}$ molar ratio of 2:2.9835:0.15:0.003:0.03 and $\text{SrCO}_3:\alpha\text{-Al}_2\text{O}_3:\text{MnO}_2:\text{MgO}$ molar ratio of 1:5.967:0.006:0.06, respectively. The pellets were formed by pressing, as described above, and placed on a platinum plate and heated at 1000 °C and 1600 °C for 12 h in air using an electric furnace, respectively. The heated pellets were ground using an alumina mortar and pestle before analysis.

The ground samples were characterized by powder X-ray diffraction (XRD) using a powder diffractometer (Rigaku Co., RINT-2200, $\text{Cu-K}\alpha$

radiation). The photoluminescence (PL) excitation and emission spectra of the specimens were measured at room temperature using a spectrofluorometer (JASCO Co., FP-6600) equipped with a Y-44 sharp-cut filter. The thermal quenching properties were measured by using a spectrofluorometer (JASCO Co., FP-6500). The quantum efficiency (QE) was determined using a quantum efficiency measurement system (Otsuka Electronics Co., Ltd., QE-1000). The particle morphology was observed by using a field-emission scanning electron microscope (FE-SEM, Hitachi High-Technologies Co., S4800).

3. Results and discussion

Fig. 2 shows the XRD patterns of $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{0.1\% Mn-Mg}$, $3z\text{B}_2\text{O}_3$ synthesized at 1000 °C for 12 h in air, where z represents the molar ratio of B to Al. The sample with $z = 0.0$ contained monoclinic SrAl_2O_4 and Al_2O_3 , but $\text{Sr}_2\text{Al}_6\text{O}_{11}$ was not formed without the addition of B_2O_3 .

Fig. 2. XRD patterns of $\text{Sr}_2\text{Al}_6\text{O}_{11}:\text{0.1\% Mn-Mg}$, $3z\text{B}_2\text{O}_3$ synthesized at 1000 °C for 12 h in air.

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