

## Synthesis of Green-emitting $\text{La}_2\text{O}_2\text{S}:\text{Tb}^{3+}$ Phosphors by Two-step Flux Method

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Hexagonal rare earth oxysulfides,  $\text{Ln}_2\text{O}_2\text{S}$  (Ln = rare earth), have been widely investigated as a host material for phosphors, because it has high thermal durability and chemical stability against water.<sup>1,2)</sup> Furthermore, rare earth oxysulfides have a suitable layer structure to as a host materials for phosphors.<sup>3)</sup> Therefore, the phosphors based on rare earth oxysulfides have been applied in color monitor tubes, high-resolution cathode ray tubes color television screens and field emission display due to their optical properties. The rare earth oxysulfid phosphors was commonly synthesized by solid-state reaction method, such as reduction of rare earth sulfate by  $\text{H}_2$  or  $\text{CO}$ , sulfuration of rare earth oxied by  $\text{H}_2\text{S}$  or  $\text{CS}_2$ , and reaction between an rare earth oxide and a sulfide.<sup>4,5)</sup> However, these methods are difficult to synthesize the rare earth oxysulfide as a single phase form with high crystallinity and  $\text{H}_2\text{S}$  and  $\text{CS}_2$  gas is an extremely harmful gas for humans.

In this study, we have used two-step flux method to synthesize the green-emitting  $\text{La}_2\text{O}_2\text{S}:\text{Tb}^{3+}$  phosphor as a single phase of highly crystalline hexagonal rare earth oxysulfid without  $\text{H}_2\text{S}$  and  $\text{CS}_2$  gas. This method involves a first oxidation step leading to the lanthanum oxysulfate  $\text{La}_2\text{O}_2\text{SO}_4$ , which is subsequently reduced to the lanthanum oxysulfide  $\text{La}_2\text{O}_2\text{S}$  by switching to the reduction atmosphere. Furthermore, in order to further enhance the emission intensity of the  $\text{La}_2\text{O}_2\text{S}:\text{Tb}^{3+}$  phosphor, the  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  eutectic mixture was employed as flux in the preparation process.

Figure 1 shows the XRD patterns of the  $\text{La}_2\text{O}_2\text{S}:\text{Tb}^{3+}$  phosphors prepared in the absence and in the presence of the  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  eutectic mixture. The sample prepared without flux obtained a two-phase mixture of hexagonal rare earth oxysulfide and LaS phase. In contrast, for the sample prepared in the presence of the  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  eutectic mixture, a single phase corresponding to the hexagonal rare earth oxysulfide,  $\text{La}_2\text{O}_2\text{S}$  (Ln = rare earth) structure was obtained.

Figure 2 depicts the excitation and emission spectra of the  $\text{La}_2\text{O}_2\text{S}:\text{5mol}\%\text{Tb}^{3+}$  phosphor prepared in the absence and in the presence of the  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  eutectic mixture. The excitation spectra of these samples consist of a strong broad band from 200 to 350 nm, which corresponds to the absorption of host material and the energy transition from the  $4f^8$  to  $4f^75d^1$  configuration of  $\text{Tb}^{3+}$ . some small peaks between 350 and 400 nm correspond to the  $4f\text{-}4f$  transition of  $\text{Tb}^{3+}$ . Application of the  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  eutectic mixture as the flux in the preparation process was effective to enhance the intensity of the excitation peak. In addition, the excitation peak wavelength based on the  $4f\text{-}5d$  transition shifted to the longer wavelength (lower energy) direction by employing the flux in the preparation process. This is considered to be due to the exchange of the environment around the  $\text{Tb}^{3+}$  ion in the host lattice by the flux treatment.<sup>6)</sup> In contrast, the emission peak wavelength and

the peak shape of all samples were identical, with no spectral shift due to employing the  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  eutectic mixture in the preparation process due to shielding of the  $4f$  orbital electrons by the outer  $5s$  and  $5p$  orbitals.<sup>7)</sup> However, the emission peak intensity was also successfully enhanced by employing the flux. Optimization of the  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  eutectic mixture content resulted in the maximum emission peak intensity being obtained for the sample with 30 mol% flux, where the relative emission intensity was 98% compared to that of the commercial green-emitting  $\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$  phosphor.

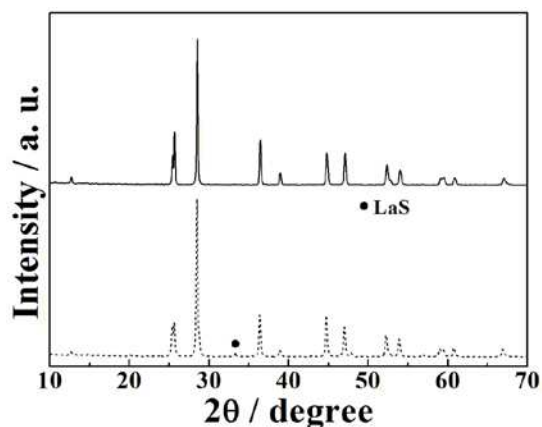


Fig. 1. XRD patterns of the  $\text{La}_2\text{O}_2\text{S}:\text{5}\%\text{Tb}^{3+}$  phosphor prepared in the absence of a flux (broken line) and in the presence of  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  (solid line).

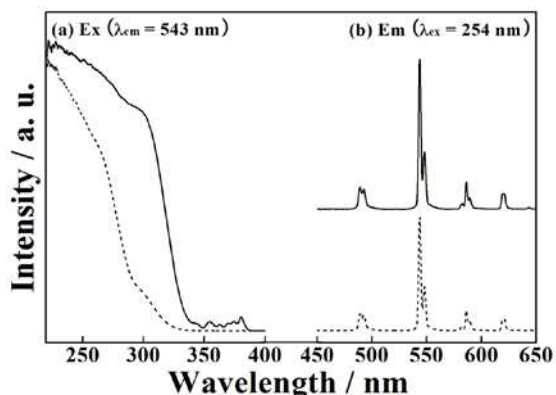


Fig. 2. The excitation (a) and emission (b) spectra of  $\text{La}_2\text{O}_2\text{S}:\text{5}\%\text{Tb}^{3+}$  phosphor prepared in the absence of a flux (broken line) and in the presence of  $0.6\text{Li}_2\text{SO}_4\text{-}0.4\text{Na}_2\text{SO}_4$  (solid line).

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