

Single-Step Solid-State Synthesis of $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}$ Phosphor

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The green-emitting $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}$ (CMAT) phosphor has been prepared at 1200 °C by the simple solid-state reaction using AlF_3 as a self-flux. This preparation temperature is much lower than those (1500-1700 °C) for conventional solid-state reaction and spray pyrolysis method. In particular, the complete process to produce high-quality phosphor particles was carried out through the single-step heat treatment of the mixture of corresponding oxide-type metal sources. An addition of AlF_3 as a self-flux significantly decreased the crystallization temperature of CMAT with plate-like shape. The particle morphology could be controlled from plate-like to spherical by using H_3BO_3 as an additional flux. Thus, an optimal morphology and luminescence characteristics of CMAT were achieved when both AlF_3 and H_3BO_3 fluxes were simultaneously used. Compared with conventional solid-state process, which is accompanied by the calcination step(s), and other alternative liquid solution techniques such as sol-gel method and spray pyrolysis, no use of active precursors and liquid media that are harmful to the environment is a distinctive advantage for the industrial purpose.

Key Words : CMAT, Phosphor, Aluminate, Single-step, Self-flux

Introduction

With the blue-emitting $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ (BAM) and the red-emitting $\text{Y}_2\text{O}_3:\text{Eu}$ oxides, the green-emitting $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}$ (CMAT) has been one of the commercialized popular oxide phosphors. Fluorescent lamps (FL) employing these oxide phosphors offered equivalent luminous output to that of the lamps employing the common calcium halophosphate phosphor.¹ Accordingly, CMAT with the magnetoplumbite structure has been widely used as the green-emitting component of three-band lamps and has also been investigated for plasma display panel (PDP) applications.^{2,3} Because of the high durability against intense UV radiation, CMAT is applied particularly for very high-loading and long life-time fluorescent lamps. The preparation of CMAT using conventional solid-state reaction is generally carried out under a reducing atmosphere as high as 1500-1700 °C and resulting products show poor morphology and size distribution.^{1,4} Because high preparation temperature imposes high-cost and energy requirements on the production process, several kinds of fluxes have been used to reduce the reaction temperature and control the particle size of the phosphor.

The synthesis of CMAT by a sol-gel process using organic precursors has been reported.⁵ Such a technique has an advantage for the phosphor film deposition.⁶ As in typical sol-gel method, however, this process is composed of several steps and requires large amount of solvents and thermal decomposition of the active complexes. Spray pyrolysis was also proposed as an alternative technique to induce high homogeneity in size and composition and spherical shape of CMAT.⁷⁻¹⁰ This process improves multi component oxide phosphor particles or films.^{11,12} A route to spherical shape, fine size, narrow size distribution, and non-aggregation characteristics of phosphor particles is provided

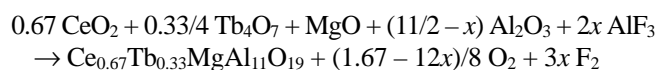
by the spray pyrolysis technique. Despite such advantages, unfortunately, resulting hollow particles have low brightness and poor long-term stability. Moreover, the performance of product is quite dependent on the solubility of precursors, spray solution concentrations, spray rates, droplet sizes, and evaporation rates, which is impractical for industrial purpose.

If we sufficiently reduce the crystallization temperature of CMAT, conventional solid-state reaction method, which is simple and produces much less environmental wastes compared with liquid solution methods including the sol-gel method and the spray pyrolysis, would be one of the most desirable synthetic processes. Recently, we developed the thermal-shock assisted solid-state process for the production of high-quality BAM phosphor powder.¹³ Because the formation of stable intermediate phases could be avoided or bypassed by the rapid heating, the single-phased BAM phosphor was obtained at much lower temperature than those of typical solid-state reactions. In the present study, we explored an environment-friendly process to produce another aluminate phosphor, CMAT. Here we report that the preparation temperature of CMAT phosphor can be effectively decreased if we use a small amount of AlF_3 as a self-flux. In particular, high-quality CMAT particles could be obtained through the single-step heat treatment by using oxide-type metal sources. It is also proposed that an additional flux H_3BO_3 is quite efficient for the improvement of the particle morphology in this process.

Experimental

CMAT phosphor of a composition, $\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$, was explored in this study. Stoichiometric amounts of CeO_2 , Tb_4O_7 , MgO , 98-90 wt% of Al_2O_3 , and 2-10 wt% of AlF_3

were thoroughly mixed in agate mortar. The total amount of Al_2O_3 and AlF_3 was adjusted to achieve the nominal composition of $\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$ according to the equation;



The single-step preparation of CMAT was performed by heating these mixtures directly to 1200 °C with the heating rate higher than 3 °C/min. Well crystallized single phase product was obtained after subsequent holding at 1200 °C for 6-10 h followed by cooling in the furnace. To induce a spherical shape of CMAT particles, 2-10 wt % of H_3BO_3 was added as an additional flux to the mixture of oxide precursors. Heating and cooling processes were carried out under a $\text{H}_2(4\%) + \text{Ar}(96\%)$ mixed gas flowing condition.

The powder X-ray diffraction (XRD) patterns were recorded on a rotating anode installed diffractometer (18 kW). The Cu K_α radiation used was monochromated by a curved-crystal graphite. Field emission scanning electron microscopy (FE-SEM) was carried out with a Zeiss LEO SUPRA 55 electron microscope operating at 10 kV. Energy-dispersive X-ray (EDX) analysis was also used to characterize the samples imaged by FE-SEM. Specimens for electron microscope were coated with Pt for 200 s under vacuum. The photoluminescence (PL) intensities of phosphors were measured at room temperature using a Hitachi F-4500 spectrophotometer with a Xenon flash lamp. The sample loaded on a powder holder provided by Hitachi was mounted about 45° to the excitation source for PL measurement. All samples were analyzed with the same weight using the same slits of spectrophotometer to measure the excitation and emission spectra. The emission spectra were recorded using 254 nm excitation wavelength.

Results and Discussion

The Ce^{3+} ion plays a role of the sensitizer for Tb^{3+} luminescence in $\text{CeMgAl}_{11}\text{O}_{19}$ host.¹⁴ Thus, the energy absorbed by the Ce^{3+} ion through the f-d transition is transferred efficiently to Tb^{3+} .¹⁵ It is known that the Ce^{3+} emission band disappears when the molar ratio of $\text{Ce}^{3+}:\text{Tb}^{3+}$ approaches 2:1.¹⁶ Therefore, the composition of $\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$ (CMAT) has been considered for the optimal luminescence characteristics in the literatures and industrial processes.

An attempt to synthesize CMAT using 2-10 wt% excess AlF_3 as an additional flux was unsuccessful at 1200 °C in this work. Instead a large amount of CeAlO_3 , MgAl_2O_4 , and Al_2O_3 were observed after reaction. The general obstacle to a low temperature synthesis of the aluminate phosphors applying typical solid-state method is that the stable intermediates are formed and large amount of Al_2O_3 remains unreacted at the firing temperature lower than 1200 °C. Rapid heating process is quite efficient to avoid the formation of highly stable intermediate phases during heat treatment of starting materials. For instance, an application of thermal-shock for the production of aluminate phosphor, BAM ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$), considerably lowered the prepa-

ration temperature as well as highly improved the particle morphology.¹³ Similar solid-state process assisted by a thermal-shock at 1200 °C resulted also in pure CMAT phase with no impurities such as CeAlO_3 , MgAl_2O_4 , $\text{Tb}_4\text{Al}_2\text{O}_9$, and/or Al_2O_3 in the present work. However, this process must be carefully carried out with high quality alumina tube and container for safety and requires a separated reduction step. In an attempt to improve the process for safe, easy, and large scale production, the influence of heating rate on the formation temperature was first investigated. In particular, only oxide-type precursors except small amount of AlF_3 were used to perform the whole process by one-step without any calcination process under reducing gas flow condition. Unfortunately, the single-phased CMAT was not obtained when we added excess amount of AlF_3 as a flux. The Al_2O_3 impurity was always observed in the final products after heating the mixtures of oxide precursors to 1200 °C with a variety of heating rates. To complete the reaction and determine the optimal heating rate, several attempts were made with different ratios of Al_2O_3 and AlF_3 , the total amounts of which were adjusted to achieve the nominal composition of $\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$. As a result, it was found that the heating rate higher than 3 °C/min is sufficient for the single-step synthesis of CMAT at 1200 °C.

Figure 1 compares the powder X-ray diffraction (XRD)

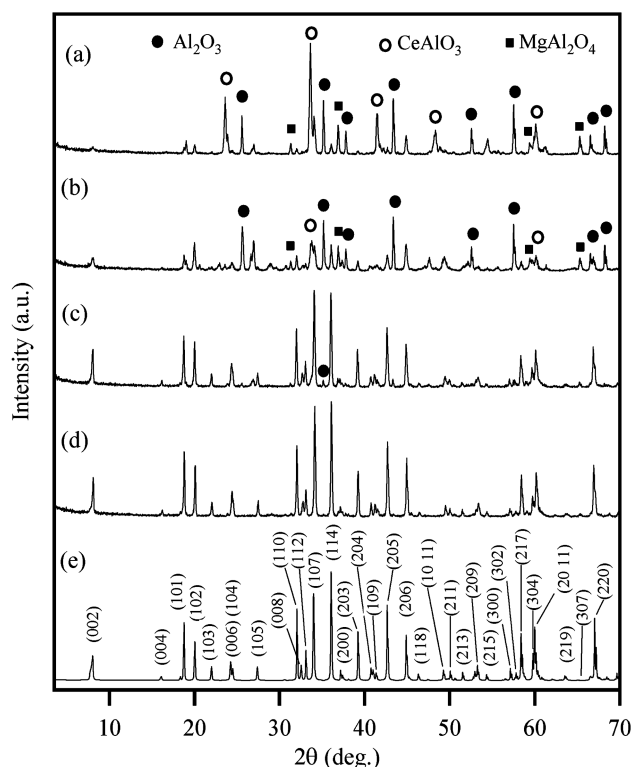


Figure 1. X-ray powder diffraction patterns of $\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$ prepared at 1200 °C using (a) Al_2O_3 only and (b) 98 wt% $\text{Al}_2\text{O}_3 + 2$ wt% AlF_3 , (c) 95 wt% $\text{Al}_2\text{O}_3 + 5$ wt% AlF_3 , and (d) 90 wt% $\text{Al}_2\text{O}_3 + 10$ wt% AlF_3 as the Al sources. (e) The simulated X-ray powder diffraction patterns of $\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$ (space group $P6_3/mmc$, Wyckoff positions in magnetoplumbite structure: (Ce,Tb); 2d, (Al,Mg)1; 2a, (Al,Mg)2; 2b, (Al,Mg)3; 4f, (Al,Mg)4; 12k, (Al,Mg)5; 4f, O1; 4e, O2; 4f, O3; 6h, O4; 12k, O5; 12k)

patterns of the samples obtained after heating the mixtures of starting materials with different ratio of Al_2O_3 and AlF_3 to $1200\text{ }^\circ\text{C}$ with the rate of $3\text{ }^\circ\text{C}/\text{min}$. When the preparation is performed with Al_2O_3 only as an Al source, the impurity phases such as $CeAlO_3$ and $MgAl_2O_4$ and a large amount of unreacted Al_2O_3 are observed (Figure 1a). In contrast, the partial replacement of Al_2O_3 by AlF_3 facilitated the rapid crystallization of CMAT. As shown in Figure 1b, the amount of $CeAlO_3$ impurity is largely reduced if the synthesis is carried out with 98 wt% Al_2O_3 and 2 wt% AlF_3 as the Al sources. When we increased the replacement amount of AlF_3 to higher than 5 wt%, no impurity was observed in the XRD pattern of the sample after heat treatment at $1200\text{ }^\circ\text{C}$. This result suggests that AlF_3 plays a role of a reactant as well as a self-flux. An optimal morphology and luminescent property of phosphor were achieved when 90 wt% Al_2O_3 and 10 wt% AlF_3 was added as the Al sources (Figure 1d). The simulated XRD pattern of $Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19}$ (Figure 1e), which is based on the structural data of the magnetoplumbite,¹⁷ is in good agreement with that of prepared CMAT phosphor. Considering that the sintering and the post-heat treatment at higher than $1500\text{ }^\circ\text{C}$ are required for typical solid-state and spray pyrolysis techniques, respectively, it is interesting that the reaction is completed at $1200\text{ }^\circ\text{C}$ by normally heating ($3\text{ }^\circ\text{C}/\text{min}$) the mixture of oxide-type precursors for CMAT. In particular, it is noted that the complete process to produce high-quality phosphor particles was carried out through the single-step without liquid media.

The H_3BO_3 flux has been widely used to improve the morphology and photoluminescence characteristics of the oxide phosphors.^{10,13} When the stoichiometric amount of Al_2O_3 without AlF_3 was used in the synthetic process, the addition of H_3BO_3 as a flux material gave no effect on the crystallization behavior and the single-phased CMAT was not obtained even after the solid-state process assisted by a thermal-shock at $1200\text{ }^\circ\text{C}$. Many impurity phases were observed in the XRD patterns of products regardless of the amount of added H_3BO_3 (2-10 wt%). This result is similar to that obtained when the same process is performed without any flux at the same temperature. Thus, overall behaviors are not different from those reported in a conventional solid-state, sol-gel, or spray pyrolysis reactions when performed at lower than $1200\text{ }^\circ\text{C}$. In contrast, it was observed that the addition of H_3BO_3 to the mixture of reactants results in a change of particle morphology in shape and size. The variation of the quantity of added H_3BO_3 gave an insight into the effect of flux on particle shape and size in the single-step process. The aspect ratio of plate-like particles was highly improved when a small amount of H_3BO_3 was added and the spherical particles became dominant with increasing the amount of such a flux. As pointed out above, however, pure CMAT was not obtained with the use of H_3BO_3 alone below $1200\text{ }^\circ\text{C}$. Accordingly, we investigated the synthetic conditions to induce an optimal characteristic of CMAT in particle morphology and luminescence by simultaneously using both AlF_3 and H_3BO_3 . Based on the XRD patterns, CMATs prepared using 90 wt% Al_2O_3 and 10 wt% AlF_3 as the Al

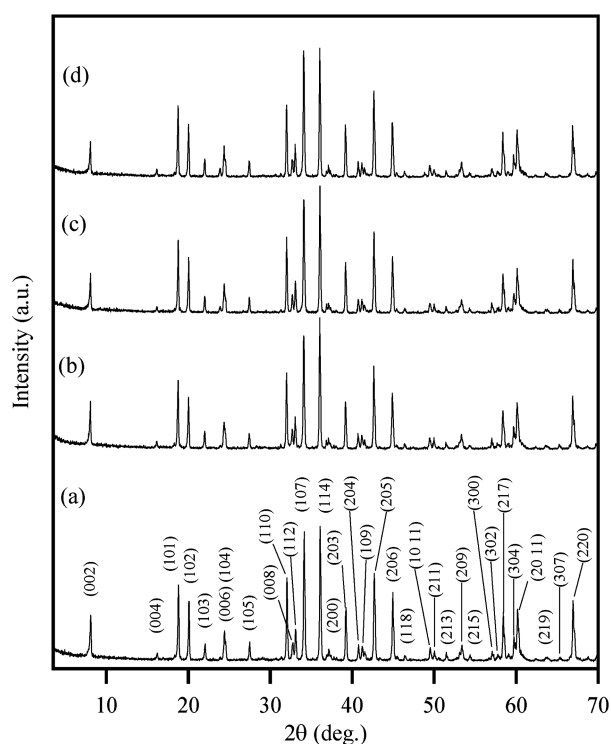


Figure 2. X-ray powder diffraction patterns of $Ce_{0.67}Tb_{0.33}MgAl_{11}O_{19}$ prepared at $1200\text{ }^\circ\text{C}$ using 90 wt% Al_2O_3 + 10 wt% AlF_3 (a) before and after addition of (b) 2 wt%, (c) 5 wt%, and (d) 10 wt% H_3BO_3 .

sources were consistently single phased at $1200\text{ }^\circ\text{C}$. As shown in Figure 2, such a behavior was independent of the amount of added H_3BO_3 . Nevertheless, H_3BO_3 flux was required for the control of particle morphology in the present work.

Field emission scanning electron microscopy (FE-SEM) photographs of CMATs prepared using 90 wt% Al_2O_3 and 10 wt% AlF_3 and different amounts of H_3BO_3 at $1200\text{ }^\circ\text{C}$ are compared in Figure 3. The particle shape of CMAT phosphor prepared without H_3BO_3 flux tends to be hexagonal as observed in the magnetoplumbite structure (Figure 3a). In part strong agglomeration is also observed in the image. Hence, it could be suggested that the AlF_3 partially replaced for Al_2O_3 plays an important role to decrease the preparation temperature but gives no significant influence on the shape of CMAT particles in this single-step process. The plate-like morphology of phosphor particles is not desirable because the high light scattering and low packing density decrease the screen brightness and resolution. The single-step process in the presence of H_3BO_3 as an additional flux yielded the phosphor particles with highly improved morphology (less plate-like, less aggregation, and narrower size and shape distributions) at $1200\text{ }^\circ\text{C}$. When only 2 wt% H_3BO_3 was added, the particle shape changes from plate-like to spherical and the agglomeration of particles was much improved (Figure 3b). It is seen in Figures 3c and 3d that the morphology of particles becomes more spherical and the particles grow with increasing the amount of H_3BO_3 to 10 wt%. These results indicate the necessity of two-flux combi-

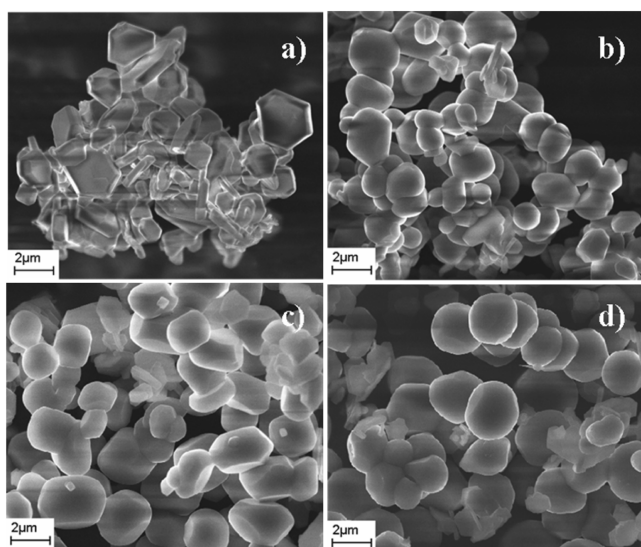


Figure 3. SEM photographs of $\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$ prepared at 1200 °C using 90 wt% Al_2O_3 + 10 wt% AlF_3 (a) before and after addition of (b) 2 wt%, (c) 5 wt%, and (d) 10 wt% H_3BO_3 .

nation for the single-step synthesis at lowered temperature as well as for the production of high-quality CMAT phosphor powder. Although a large amount of H_3BO_3 (20 wt%) is used as a flux, a spherical and dense morphology of CMAT is obtained at 1600 °C by the spray pyrolysis.¹⁰ It is consequently a distinctive advantage of the present method that no liquid medium is used and the formation of spherical particles is completed at 1200 °C.

In Figure 4, the photoluminescence (PL) emission spectra of CMAT phosphors excited at 254 nm are compared in the function of the amount of added H_3BO_3 flux when 90 wt% Al_2O_3 and 10 wt% AlF_3 were used as the Al sources. The intense emission observed at around 545 nm is associated with the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition of the Tb^{3+} ion.¹⁴ High emission intensity of CMAT comparable to that of a commercial green-emitting phosphor could be obtained by the single-step synthesis at 1200 °C. It is apparent in this figure that the relative emission intensity is enhanced with increasing the amount of H_3BO_3 . The maximum enhancement in intensity is close to ~15% when 5 wt% of H_3BO_3 was added as a flux. Correlating only particle shape and size (Figure 3) to PL behavior (Figure 4), the emission intensity of CMAT increases when the particle shape is spherical and the size becomes larger. Despite more spherical morphology and larger average size of phosphor particles, however, the PL emission intensity of CMAT prepared using 10 wt% of H_3BO_3 decreases as shown in Figure 4d. The residual H_3BO_3 flux after reaction would be responsible for such a decrease in intensity because of relatively low reaction temperature. Actually, the phosphor prepared using 10 wt% of H_3BO_3 showed the relative PL intensity comparable with that prepared using 5 wt% of H_3BO_3 after washing with water. Further addition of H_3BO_3 resulted in a significant decrease in emission intensity of CMAT and an additional washing step was required to enhance the observed emission intensity.

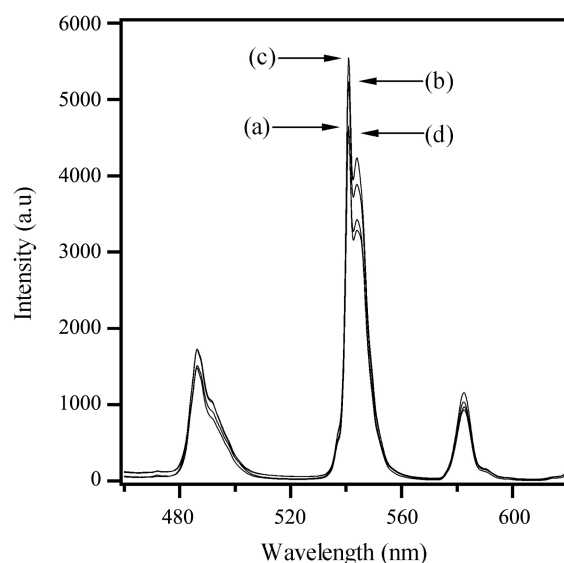


Figure 4. PL emission spectra ($\lambda_{\text{ex}} = 254$ nm) of $\text{Ce}_{0.67}\text{Tb}_{0.33}\text{MgAl}_{11}\text{O}_{19}$ prepared at 1200 °C using 90 wt% Al_2O_3 + 10 wt% AlF_3 (a) before and after addition of (b) 2 wt%, (c) 5 wt%, and (d) 10 wt% H_3BO_3 .

Conclusion

The green-emitting $\text{CeMgAl}_{11}\text{O}_{19}:\text{Tb}$ (CMAT) phosphor was successfully prepared at 1200 °C by a simple one-step solid-state process using corresponding oxide-type metal sources. The partial replacement of Al_2O_3 by AlF_3 for an Al source effectively reduces the crystallization temperature of CMAT. The addition of 2-10 wt% of H_3BO_3 as an additional flux to the mixture of oxide precursors induces a spherical shape of CMAT particles. Alternative liquid solution techniques including sol-gel method, combustion technique, and spray pyrolysis, could be selected for the production of CMAT. In those techniques, the active precursors make easy to control the composition and homogeneity. However, most of the liquid media are volatile and harmful to the environment. The distinctive advantage of the present method is that any active precursor or liquid solvent is not required. In this respect, the single-step solid-state process appears to be and very promising for the low-cost industrial production of high performance CMAT phosphor.

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