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Synthesis of a new phosphor based on rare earth oxycarbonate

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Abstract

A new synthesis route to easily obtain the II-type lanthanum oxycarbonate in a single phase has been developed by using a simple flux method, and photoluminescence properties of Eu^{3+}- or Tb^{3+}-doped $La_2O_2CO_3$ were characterized. These new phosphors, the II-type $La_2O_2CO_3$:Eu^{3+} and $La_2O_2CO_3$:Tb^{3+}, were synthesized by the calcination with a flux in a flow of 10%CO_2–90%N_2 gas, where lithium carbonate or a 0.476Li_2CO_3–0.270Na_2CO_3–0.254K_2CO_3 eutectic mixture was employed as the flux. The higher emission intensity was observed by employing the Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic system, which has a considerably lower melting point (663 K) than that of Li_2CO_3 (999 K). The red and green emission intensities became maximum at the composition of $La_2O_2CO_3$:6at.%Eu^{3+} and $La_2O_2CO_3$:17at.%Tb^{3+}, and the relative emission intensities compared with the commercial Y_2O_3:Eu^{3+} and $LaPO_4$:Ce^{3+},Tb^{3+} phosphors were 22.5 and 60.0%, respectively.

Keywords: Rare earth oxycarbonate; Phosphor; Flux method; Eutectic compound

1. Introduction

It is well known that trivalent rare earth ions have sharp line emission spectra because the 4f-elecrons are well shielded from the surroundings by the filled 5s and 5p orbitals. Therefore, rare-earth-doped phosphors have been widely studied for application to luminescent materials. As host crystalline phosphor materials, rare earth oxides such as Y_2O_3, which is commonly used as a host material of red phosphor in the tricolor fluorescent lump and color displays, was vigorously investigated. As well as rare earth oxides, various rare earth compounds such as borates, phosphates, and aluminates have been also extensively investigated as host lattices [1].

It is known that rare earth oxycarbonates have three different structures such as tetragonal (I-), monoclinic (Ia-), and hexagonal (II)-$RE_2O_2CO_3$ (RE: rare earths). The structure of the phases I and Ia bears very close resemblance to the rare earth oxysalts such as oxyhalides, oxysilicates, oxysulfates, and oxymolybdates, while the phase II is similar to the conventional A-type rare earth sesquioxides which are well known as good hosts of phosphors [2]. Among these structures, the II-type is the most suitable for the host material of phosphors because it has the highest thermal stability and durability against water and carbon dioxide. However, luminescent properties of Eu^{3+}-activated $RE_2O_2CO_3$ have been reported only for the Ia-type material [3].

In the series of rare earth oxycarbonates, lanthanum oxycarbonate ($La_2O_2CO_3$) is the most appropriate compound as a host material, because it has the highest thermal stability among the several rare earth oxycarbonates, and two methods have been reported for the preparation of $La_2O_2CO_3$ [2]. One is the thermal decomposition of lanthanum compounds containing both carbon and oxygen such as oxalates and acetates, and the other is the reaction of lanthanum oxide with CO_2. However, it is difficult to obtain the II-$La_2O_2CO_3$ in a single phase by the conventional methods described above, because the I- or Ia-type oxycarbonates are produced by the thermal decomposition of oxalates and acetates or it is necessary to heat lanthanum oxide at 773 K for a week under humid CO_2 to obtain type II oxycarbonate [2,3].

In our previous work, on the contrary, we have found a new synthesis route to easily obtain the high crys-

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talline II-type lanthanum oxycarbonate in a single phase by using lithium carbonate as a flux, and photoluminescence properties of the Eu^{3+}-doped $La_2O_2CO_3$ were characterized [4]. In the present study, we have successfully synthesized the II-type Tb^{3+}-doped $La_2O_2CO_3$ in a single phase by the flux method. Furthermore, we have succeeded in increasing the emission intensities of the II-type $La_2O_2CO_3$:Eu^{3+} and $La_2O_2CO_3$:Tb^{3+} by employing the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic system as the flux.

2. Experimental

An aqueous solution of stoichiometric mixture of 1.0 mol L^{-1} $La(NO_3)_3$ and 0.2 mol L^{-1} $Eu(NO_3)_3$ or 0.1 mol L^{-1} $Tb(NO_3)_3$ was dropped into 0.5 mol L^{-1} oxalic acid aqueous solution. The amount of Eu^{3+} or Tb^{3+} was adjusted between 2 and 21 at.%. The precipitate was filtered and washed for three times with distilled water. After drying at 353 K, the sample was calcined at 873 K for 6 h in air. The calcined sample was mixed with 10 mol% Li_2CO_3 or 50 mol% $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ (these ratios were optimized to give the highest emission intensities) and heated at 873 K for 12 h in a flow of 10% CO_2 diluted with N_2 gas. Then, the sample was washed again for three times with distilled water and once with ethanol, and dried at room temperature. The crystal structure of samples was identified by X-ray powder diffraction (XRD, Rigaku Multiflex) analysis and the sample composition was determined by X-ray fluorescence (Rigaku ZSX100e) analysis. Morphology of the particles was characterized by means of scanning electron microscopy (SEM, Hitachi S-4300SD). Photoluminescence excitation and emission spectra of samples were measured at room temperature with a spectrofluorometer (Shimadzu RF-5300PC). The emission spectra were recorded for excitation at 254 nm, and the excitation spectra were recorded by measuring the emission at 612 nm for Eu^{3+} or at 543 nm for Tb^{3+}. The relative emission intensities of the $La_2O_2CO_3$:Eu^{3+} and the $La_2O_2CO_3$:Tb^{3+} phosphors were estimated by comparing the integrated areas of the emission peaks at 612 nm ($^5D_0$-$^7F_2$ transition of Eu^{3+}) and 543 nm ($^5D_4$-$^7F_5$ transition of Tb^{3+}) with those of the commercial Y_2O_3:Eu^{3+} and $LaPO_4$:Ce^{3+}, Tb^{3+} phosphors, respectively.

3. Results and discussion

Representative XRD patterns of $La_2O_2CO_3$:6at.%Eu^{3+} and $La_2O_2CO_3$:17at.%Tb^{3+} prepared with the flux of Li_2CO_3 or Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic system are shown in Fig. 1. All samples were identical to a single phase of II-type $La_2O_2CO_3$ and any impurity peaks were not observed. This result shows that the Eu^{3+} and Tb^{3+} ions substituted the La^{3+} site whose symmetry was C_{3v} [2]. A small amount of Na and K remained ($\leq$1 mol%) was identified in the samples prepared using the Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic system from the X-ray fluorescence analysis. In our previous work, however, it has been elucidated that a small amount of flux species remained in the sample did not affect the luminescence properties [4].

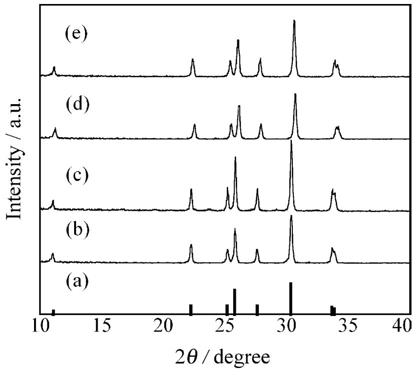

Fig. 1. X-ray powder diffraction patterns of standard II-type $La_2O_2CO_3$ (a), $La_2O_2CO_3$:6at.%Eu^{3+} prepared with Li_2CO_3 (b) or Li_2CO_3–Na_2CO_3–K_2CO_3 (c), and $La_2O_2CO_3$:17at.%Tb^{3+} prepared with Li_2CO_3 (d) or Li_2CO_3–Na_2CO_3–K_2CO_3 (e).

SEM images of the samples prepared with Li_2CO_3 and Li_2CO_3–Na_2CO_3–K_2CO_3 are depicted in Fig. 2 with commercially available Y_2O_3:Eu^{3+} and $LaPO_4$:Ce^{3+},Tb^{3+} phosphors. The average particle sizes estimated by measuring the diameters of 100 particles on the SEM photographs were 3.1 and 2.7 μm for the Y_2O_3:Eu^{3+} and $LaPO_4$:Ce^{3+},Tb^{3+}, respectively, whereas those of the $La_2O_2CO_3$:6at.%Eu^{3+} and $La_2O_2CO_3$:17at.%Tb^{3+} prepared with the Li_2CO_3 flux were 1.03 and 0.77 μm, respectively. In addition, the particle became smaller and more homogenous by the flux treatment with the Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic mixture. The mean particle sizes were 0.58 μm for $La_2O_2CO_3$:6at.%Eu^{3+} and 0.65 μm for $La_2O_2CO_3$:17at.%Tb^{3+}, which were less than a quarter of that of the commercial phosphor.

Fig. 3 represents the relationship between the luminescent intensity of the $La_2O_2CO_3$:M^{3+} (M = Eu or Tb) particles and the atomic concentration of the activator (Eu^{3+} or Tb^{3+}). The maximum red and green emission intensities were obtained at the compositions of $La_2O_2CO_3$:6at.%Eu^{3+} and $La_2O_2CO_3$:17at.%Tb^{3+}, and the relative emission intensities compared with the commercial Y_2O_3:Eu^{3+} and $LaPO_4$:Ce^{3+},Tb^{3+} phosphors were 22.5 and 60.0%, respectively. The excitation at 254 nm causes charge transfer from O^{2-} to Eu^{3+} in the case of $La_2O_2CO_3$:Eu^{3+} and transition between $4f^8$ and $4f^7$ 5d states of Tb^{3+} in $La_2O_2CO_3$:Tb^{3+}. This might be one of the possible reasons for the considerable difference between the relative emission intensity of $La_2O_2CO_3$:Eu^{3+} and that of $La_2O_2CO_3$:Tb^{3+}.

Fig. 4 illustrates the excitation spectra of Eu^{3+} and Tb^{3+} emission in $La_2O_2CO_3$ prepared with Li_2CO_3 and Li_2CO_3–Na_2CO_3–K_2CO_3. The excitation spectra of $La_2O_2CO_3$:6at.%Eu^{3+} consists of a strong broad peak with a maximum at 280 nm, corresponding to charge transfer

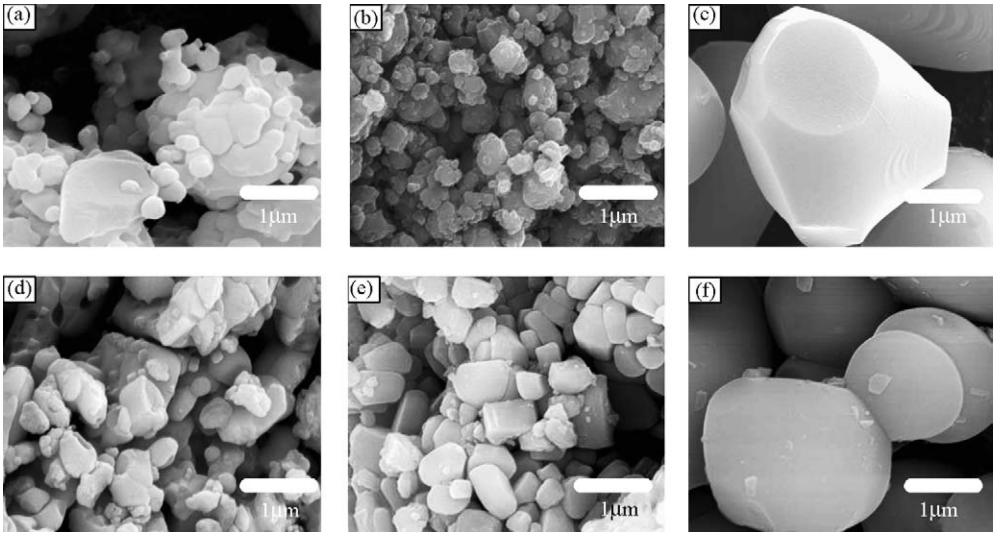

Fig. 2. SEM photographs of the samples: $La_2O_2CO_3$:6at.%Eu^{3+} prepared with (a) Li_2CO_3 and (b) Li_2CO_3–Na_2CO_3–K_2CO_3; (c) commercial $Y_2O_3:Eu^{3+}$; $La_2O_2CO_3:Tb^{3+}$ prepared with (d) Li_2CO_3 and (e) Li_2CO_3–Na_2CO_3–K_2CO_3; (f) commercial $LaPO_4:Ce^{3+},Tb^{3+}$.

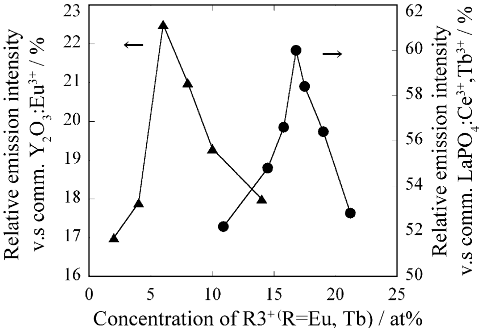

Fig. 3. Luminescent intensity variation of the $La_2O_2CO_3:Eu^{3+}$ (▲) and $La_2O_2CO_3:Tb^{3+}$ (●) particles prepared with the Li_2CO_3–Na_2CO_3–K_2CO_3 flux as a function of the atomic concentration of europium and terbium ion.

state (CTS) of Eu^{3+} and some weak peaks in the region of 350–400 nm. The peaks result from transitions between the ground state and the excited levels of $4f^6$ configuration [5,6], and these peaks shifted to shorter wavelength by using eutectic mixture as the flux. The excitation spectra of the $La_2O_2CO_3$:17at.%Tb^{3+} also consist of a broad band with a maximum at 260 nm, corresponding to the energy transition from the $4f^8$ to $4f^75d$ configuration of the Tb^{3+} [6]. The small peaks in the range of 310–390 nm are assigned to transitions between the energy levels of the $4f^8$ configuration. In both samples, excitation peak intensity is increased by applying the Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic mixture instead of Li_2CO_3.

Fig. 5 shows the emission spectra of $La_2O_2CO_3$:6at.%Eu^{3+} and $La_2O_2CO_3$:17at.%Tb^{3+} prepared using Li_2CO_3 or Li_2CO_3–Na_2CO_3–K_2CO_3. Characteristic luminescence corresponding to the $^5D_0 \rightarrow {}^7F_J$ transition of Eu^{3+} and the $^5D_4 \rightarrow {}^7F_J$ transition of Tb^{3+} are observed. Similar to the results of the excitation spectra described in Fig. 4, the emission intensity increased by using the Li_2CO_3–Na_2CO_3–K_2CO_3 flux, although the particle size becomes smaller than that of the samples prepared with Li_2CO_3. These differences can be clearly explained from the melting point of these two fluxes. The melting points of

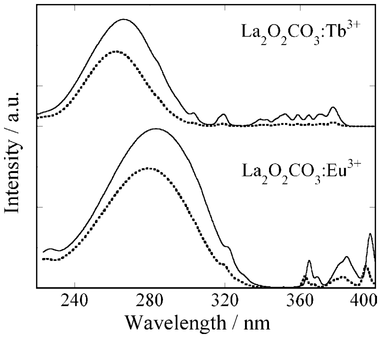

Fig. 4. Excitation spectra of the $La_2O_2CO_3:M^{3+}$ (M = 6at.%Eu or 17at.%Tb) samples prepared with Li_2CO_3 (broken line) and with Li_2CO_3–Na_2CO_3–K_2CO_3 (solid line).

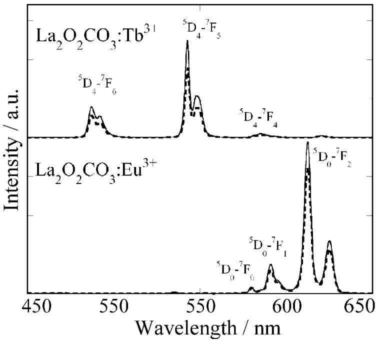

Fig. 5. Emission spectra of the $La_2O_2CO_3:M^{3+}$ (M = 6at.%Eu or 17at.%Tb) phosphors prepared with Li_2CO_3 (dotted line) and with Li_2CO_3–Na_2CO_3–K_2CO_3 (solid line).

Li_2CO_3 and the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic system are 999 K [7] and 663 K [8], respectively. When the flux treatment is carried out at 873 K, the former is still in a solid state but the latter completely melts to be the molten state. The surface of the oxycarbonate covered with the eutectic molten salt partly dissolves into this liquid phase, diffuses to the particle-particle contact points, and precipitates there again. As a result, the surface defects are eliminated effectively by the liquid flux treatment and higher emission intensity is observed by using the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ flux.

4. Conclusions

New red and green phosphors, II-type $La_2O_2CO_3:Eu^{3+}$ and $La_2O_2CO_3:Tb^{3+}$ were synthesized as a single phase by the flux method using Li_2CO_3 and $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$. The emission intensity of these phosphors was increased by employing Li_2CO_3–Na_2CO_3–K_2CO_3 rather than Li_2CO_3, even if the particle size became smaller. The maximum emission was obtained at the compositions of $La_2O_2CO_3$:6at.%Eu^{3+} and $La_2O_2CO_3$:17at.%Tb^{3+}, and the relative intensities compared with the commercial $Y_2O_3:Eu^{3+}$ and $LaPO_4:Ce^{3+}$, Tb^{3+} phosphors were 22.5 and 60.0%, respectively.

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