Lithium Carbonate Flux Effects on the Luminescence Properties of Europium-doped Lanthanum Oxycarbonate Phosphor

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Lithium carbonate flux was introduced in the preparation of $La_2O_2CO_3$: Eu^{3+} oxycarbonate phosphor particles to improve the photoluminescence intensities. The flux treatment brought increasing in the crystallinity of oxycarbonate phosphor accompanying the phase transition from the two-phase mixture of tetragonal and monoclinic forms to single hexagonal phase of rare earth oxycarbonate, resulting in the increase of the emission intensity.

Many kinds of rare earth activated materials have been studied owing to their application as phosphors. As a red emitting phosphor, yttrium oxide doped with Eu^{3+} (Y_2O_3: Eu^{3+}), which is commonly used in tricolor fluorescent lamps and field emission displays because of the efficient luminescence under ultraviolet and electron beam excitation,[1] was extensively investigated. As well as rare earth oxides, many rare earth compounds such as oxysulfides,[2] borates,[3] and phosphates[4] have been investigated as host crystalline phosphor materials.

Rare earth oxycarbonate ($R_2O_2CO_3$ (R: rare earths)) which possesses high durability against water and carbon dioxide,[5] was thought to be one of candidates of the host material similar to the case for above mentioned compounds. There are three different structural types in rare earth oxycarbonate, that is, tetragonal type I, monoclinic type Ia, and hexagonal type II.[6] The structure of phases I and Ia resembles the other rare earth oxysalts such as oxyhalide, oxysilicate, oxysulfate, oxymolybdate, etc.,[7] while phase II is similar to the conventional rare earth sesquioxides which are well known as good phosphors. Although spectroscopic properties of some Eu^{3+}-activated $R_2O_2CO_3$ have been reported,[7,8] the main phase of $R_2O_2CO_3$ investigated was Ia which is generally unstable with respect to phase II and the crystallinity of the type Ia was so low that the sample did not show an applicable enough luminescent intensity.[6,7]

In this letter, we selected lanthanum oxycarbonate as a host material because $La_2O_2CO_3$ has the highest thermal stability among the series of $R_2O_2CO_3$, and the stable phase II of $La_2O_2CO_3$: Eu^{3+} phosphor with high crystallinity was synthesized by using lithium carbonate as a flux.

A stoichiometric mixture of $La(NO_3)_3$ ($1.0\,mol{\cdot}dm^{-3}$) and $Eu(NO_3)_3$ ($0.2\,mol{\cdot}dm^{-3}$) aqueous solutions was dropped into a $0.5\,mol{\cdot}dm^{-3}$ oxalic acid aqueous solution. The hydrated oxalate was precipitated and aged at room temperature for 20 h. After filtering, the precipitate was dried at 353 K for 24 h and then calcined at 873 K for 6 h in air. The obtained $(La_{1-x}Eu_x)_2O_2CO_3$ was mixed with 10–30 mol % Li_2CO_3 and heated at 873 K for 12 h in a flow of 10% CO_2 diluted with N_2 gas. The samples with and without the flux treatment were characterized by X-ray powder diffraction (Rigaku, Multiflex) and X-ray fluorescence (Rigaku, ZSX100e) analyses, and the amount of Li in the sample was analyzed by the atomic absorption analysis (Shimadzu, AA-6500). Photoluminescence excitation and emission spectra of the samples were investigated at room temperature with a spectrofluorometer (Shimadzu, RF-5300PC). The emission spectra were recorded for excitation at 279 nm, and the excitation spectra were recorded by measuring the emission at 612 nm corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition.

The phase and crystallinity of the $La_2O_2CO_3$: Eu^{3+} particles prepared with and without Li_2CO_3 flux were investigated from the XRD patterns to identify the role of the Li_2CO_3 flux. As shown in Figure 1, the sample prepared without flux was composed of lanthanum oxycarbonate mixtures of phase I and Ia with a small amount of phase II (Figure 1a). On the other hand, $La_2O_2CO_3$: Eu^{3+} heated at 873 K with Li_2CO_3 (Figure 1b) consisted of a single phase of phase II and the crystallinity was appreciably improved in comparison with that of the sample prepared without Li_2CO_3 flux (Figure 1a). While the phase II of oxycarbonate was also produced without Li_2CO_3 flux by heating the phase I and Ia mixture at 1073 K in a flow of 10% CO_2 diluted with N_2, the sample was not a single phase but contained La_2O_3 as an impurity (Figure 1c) although the crystallinity became higher.

Table 1 tabulates the lattice constants of the oxycarbonate

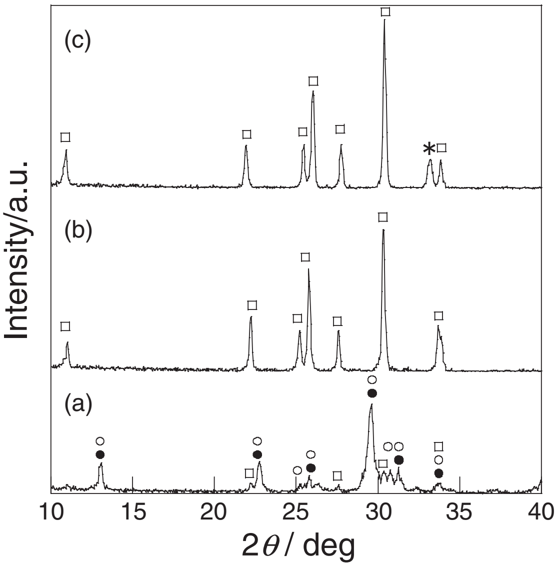

Figure 1. The X-ray powder diffraction patterns of the $(La_{0.94}Eu_{0.06})_2O_2CO_3$; (a) calcined at 873 K without Li_2CO_3, (b) calcined at 873 K with Li_2CO_3, and (c) calcined at 1073 K without Li_2CO_3. ●: phase I (tetragonal), ○: phase Ia (monoclinic), □: phase II (hexagonal), and ∗: La_2O_3.

Table 1. The lattice constants of the $(La_{1-x}Eu_x)_2O_2CO_3$ series

Eu amount, x	Lattice constants	
	a/nm	c/nm
0.00 (without Li_2CO_3 flux)[a]	4.078	15.973
0.00 (with 20 mol% Li_2CO_3 flux)	4.078	15.975
0.06 (with 20 mol% Li_2CO_3 flux)	4.072	15.948
0.10 (with 20 mol% Li_2CO_3 flux)	4.065	15.928
0.21 (with 20 mol% Li_2CO_3 flux)	4.047	15.873
0.32 (with 20 mol% Li_2CO_3 flux)	4.030	15.787

[a] The sample was heated at 1073 K and was a mixture of phase II oxycarbonate and La_2O_3.

series (phase II) after the flux treatment with 20 mol % Li_2CO_3 at 873 K with corresponding data for the sample heated at 1073 K without Li_2CO_3 flux, which is two phase mixture of phase II of oxycarbonate and La_2O_3. All the samples prepared with Li_2CO_3 flux were found to be a single phase of phase II rare earth oxycarbonate from the XRD results, and the lattice constants of both a and c linearly decreased with increasing the Eu amount, because the ionic size of Eu^{3+} (0.1087 nm[9]) is smaller than that of La^{3+} (0.1172 nm[9]). These results clearly indicate the formation of $(La_{1-x}Eu_x)_2O_2CO_3$ solid solutions. Atomic absorption analysis was carried out for the samples of $(1-y)$-$(La_{0.79}Eu_{0.21})_2O_2CO_3 - yLi_2CO_3$ (initial mixed amount of $y =$ 0.1 and 0.3) to identify the amount of Li in the samples and the analyzed y values were 0.0014 and 0.0039, respectively. As listed in Table 1, moreover, the lattice constants of $La_2O_2CO_3$ unchanged independently of the Li_2CO_3 flux treatment. These results suggest that Li_2CO_3 works only as a flux and almost all Li_2CO_3 vaporized during the calcination procedure.

Figure 2 shows the photoluminescence excitation and emission spectra of $(La_{0.94}Eu_{0.06})_2O_2CO_3$ phosphor particles prepared with and without Li_2CO_3 flux. The effect of flux on the photoluminescence spectra appeared in the sample fired with the flux. Intensities of the excitation spectra were quite different, although their profiles were similar. In the case of emission spectra, the samples as-prepared at 873 K had two main emission peaks at 615 and 620 nm, where the sample heated with the flux had peaks at 612 and 625 nm. Because all the spectra between 600 and 625 nm are assigned to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}, it is considered that the difference observed in the emission spectra was caused by the change of the symmetry around Eu^{3+} site in the host oxycarbonate lattice. These phenomena correspond to the structural change from phase Ia to phase II oxycarbonate. The relative emission intensities of $(La_{1-x}Eu_x)_2O_2CO_3$ calcined with and without flux are depicted in Figure 3. The $(La_{0.94}Eu_{0.06})_2O_2CO_3$ ($x = 0.06$) particles prepared with 20 mol% Li_2CO_3 flux had higher emission intensity which was 3.4 times as high as that of particles prepared without flux, while the intensity of the sample with Li_2CO_3 flux was still lower than that of commercial Y_2O_3: Eu^{3+} (ca. 26%). In addition, the emission intensity greatly enhanced by ca. 3.0 ($x = 0.10$) − 6.5 times ($x = 0.32$) after the flux treatment in all samples, while the concentration quenching was recognized at $x > 0.06$ irrespective of the Li_2CO_3 addition.

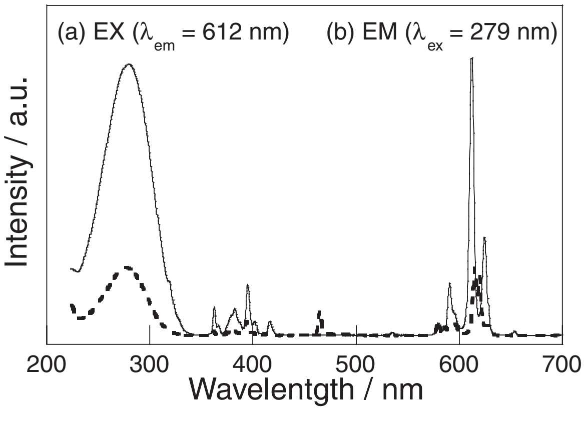

Figure 2. The excitation (a) and emission spectra (b) of the $(La_{0.94}Eu_{0.06})_2O_2CO_3$ prepared with (solid line) and without (dotted line) flux.

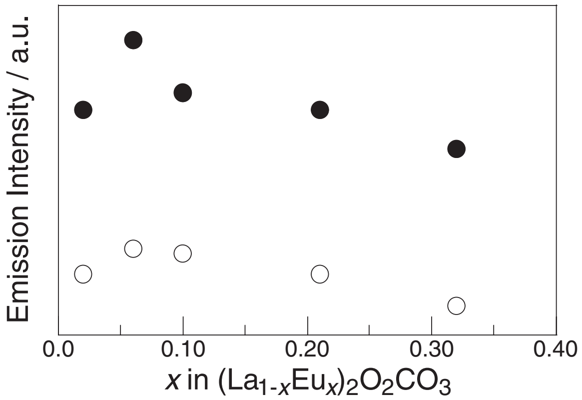

Figure 3. The compositional dependencies of emission intensities at 612 nm for $(La_{1-x}Eu_x)_2O_2CO_3$ with (●) and without 20 mol% Li_2CO_3 flux (○).

In conclusion, since the flux-treated samples promote the increase in crystallinity as well as the formation of more stable phase II oxycarbonate particles, the increase of the emission intensity was successfully achieved.

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