Synthesis of a new green-emitting phosphor based on lanthanum oxycarbonate (La$_2$O$_2$CO$_3$-II)

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It has been known that rare earth oxycarbonates $Ln_2O_2CO_3$ (Ln = rare earths) exist in three different types of crystal structures, that is, tetragonal type I, monoclinic type Ia, and hexagonal type II [1, 2]. Among these three structures, the type II phase is the most stable one and has a high durability against water and carbon dioxide [3]. The phase II has a hexagonal structure similar to the conventional rare earth sesquioxides which are well-known as host materials of good phosphors, and the crystal structure of La$_2$O$_2$CO$_3$-II and Nd$_2$O$_2$CO$_3$-II have recently been investigated in details by means of high-resolution powder neutron and synchrotron X-ray diffraction combined with selected area electron diffraction [4]. However, luminescent properties of the phosphors based on rare earth oxycarbonates have received little attention and only a few references have been reported [5–7]. Furthermore, the materials investigated mainly were Eu^{3+}-activated $Ln_2O_2CO_3$ phosphors which exhibit red emission, and there is no report on the rare earth oxycarbonate phosphors for other color emission.

In this letter, we describe the results of our investigation on the preparation and the luminescent properties of Tb^{3+}-doped La$_2$O$_2$CO$_3$ which is a new green emitting phosphor based on the type II rare earth oxycarbonate. The reason for choosing lanthanum oxycarbonate as a host material is that it has the highest thermal stability among the series of $Ln_2O_2CO_3$ [8, 9] and the stable II phase of high crystallinity can be easily synthesized by a simple method we have established using alkaline metal carbonate as a flux [7].

A stoichiometric mixture of La(NO$_3$)$_3$ (1 mol·dm^{-3}) and Tb(NO$_3$)$_3$ (0.1 mol·dm^{-3}) aqueous solutions was dropped into a 0.5 mol·dm^{-3} oxalic acid aqueous solution. The hydrated oxalate was precipitated and was aged overnight with stirring at room temperature. The amount of Tb^{3+} ion was adjusted between 2.20 and 21.2 at.% in the precipitate. After filtering, the precipitate was dried at 353 K for 24 hr and then calcined at 873 K for 6 hr in air. The oxycarbonate obtained was mixed with a 0.476Li$_2$CO$_3$–0.270Na$_2$CO$_3$–0.254K$_2$CO$_3$ mixture in a ratio of 50 mol%, which has the eutectic melting point of 663 K in the series of alkaline metal carbonate systems, and was heated at 873 K for 12 hr in a flow of 10% CO$_2$–90% N$_2$ gas. In our previous paper [7], lithium carbonate was used as the flux to obtain hexagonal type II oxycarbonate in a single phase. In contract,

the eutectic mixture is employed in the present study in order to obtain the flux effect more efficiently even at rather moderate heating conditions, because the melting point of the eutectic mixture (663 K) was appreciably lower than that of lithium carbonate (999 K), that is, the former is completely molten at 873 K while the latter is not. After the flux treatment, the sample was rinsed with distilled water and then ethanol, and dried at room temperature.

The phosphors were characterized with a scanning electron microscope (SEM, Hitachi S-4300SD) and with an X-ray powder diffractmeter (XRD, Rigaku Multiflex) using Cu-Kα radiation. The mean size and the size distribution were estimated by measuring the diameters of 100 particles on the SEM photographs. The sample composition was determined by X-ray fluorescence analysis (Rigaku, ZSX100e) and by atomic absorption spectroscopic analysis (Shimadzu, AA-6500). Photoluminescence excitation and emission spectra were recorded at room temperature with a fluorescence spectrophotometer (Shimadzu, RF-5300PC). Excitation spectra were recorded by measuring the emission at 543 nm corresponding to the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+}. Emission spectra were recorded for excitation at 254 nm, and the relative emission intensity was evaluated by comparing the integrated area of the emission peak at 543 nm with that of a commercial LaPO$_4$:Ce,Tb phosphor.

The X-ray powder diffraction (XRD) patterns for La$_2$O$_2$CO$_3$:xTb-II with x = 4.5, 10.9, 16.8 and 21.2 at.% are shown in Fig. 1. It was found that the XRD patterns of all the samples are in agreement with a single phase of the La$_2$O$_2$CO$_3$-II compound [10, 11]. Although there was no diffraction peak corresponding to any impurities in the XRD patterns, a nominal amount of potassium was detected by the X-ray fluorescence analysis. Neither lithium nor sodium remained in the samples. As expected, obvious shifting of peaks to higher diffraction angle was observed when x increases, because the La site (ionic radius: 0.116 nm for 8 coordination) [12] in the hexagonal La$_2$O$_2$CO$_3$-II was partially substituted with the smaller Tb^{3+} cation (ionic radius: 0.104 nm for 8 coordination) [12]. The inset in the figure depicts the Tb^{3+}content dependence of the La$_2$O$_2$CO$_3$:xTb-II lattice volume, which decreases monotonically with the La^{3+} site replacement for Tb^{3+} ion.

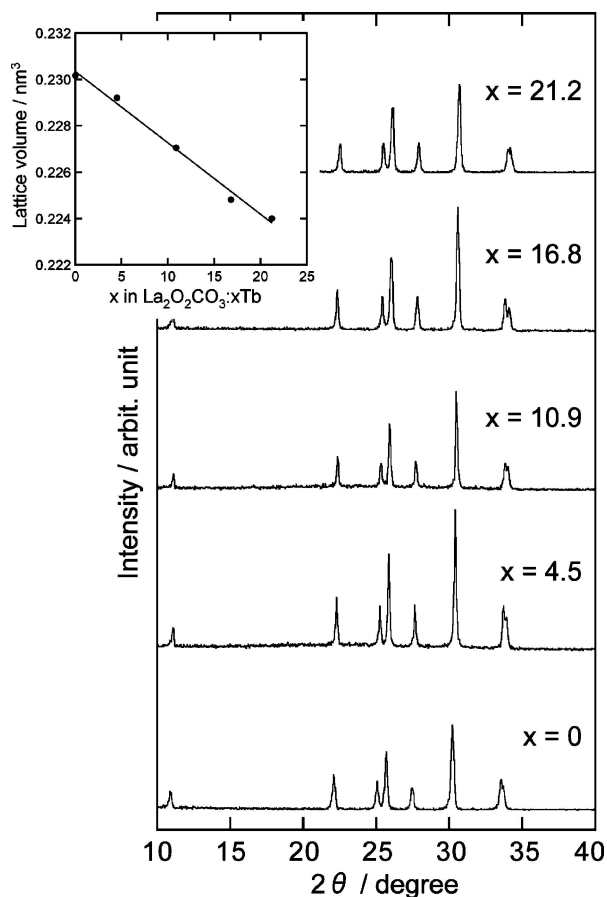*Author to whom all correspondence should be addressed.

Figure 1 X-ray powder diffraction patterns for $La_2O_2CO_3$:xTb phases with $x = 0$, 4.5, 10.9, 16.8 and 21.2 at.%. The inset shows the Tb^{3+} content dependence of the lattice volume of $La_2O_2CO_3$:xTb.
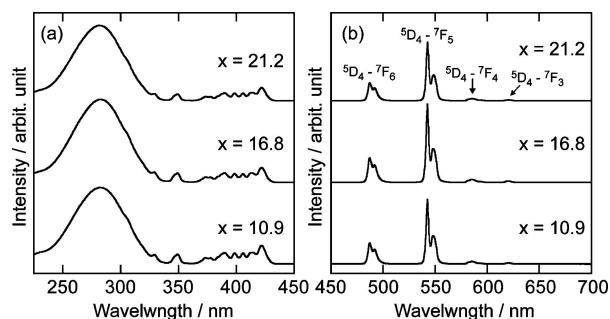

Figure 2 Photoluminescence excitation (a) and emission (b) spectra for $La_2O_2CO_3$:xTb phosphors with $x = 10.9$, 16.8 and 21.2 at.%.

The photoluminescent excitation and emission spectra of the $La_2O_2CO_3$:xTb ($x = 10.9$, 16.8 and 21.2 at.%) phosphors are depicted in Fig. 2. These phosphors exhibited a well-known characteristic Tb^{3+} emission and no self-activated emission was observed in the undoped $La_2O_2CO_3$ sample. The excitation spectra of the $La_2O_2CO_3$:xTb samples 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 Tb^{3+} [13]. The emission peaks at 487 (492sh), 543 (548sh), 585, and 620 nm correspond to the transition from $^5D_4$ to $^7F_6$, $^7F_5$, $^7F_4$, and $^7F_3$ ground states of Tb^{3+}, respectively. The photoluminescent properties of these three phosphors do not differ essentially from one another, but the only difference is observed in the emission intensity.
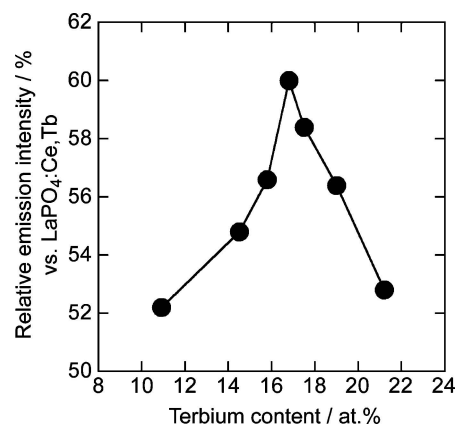

Figure 3 Fluorescence intensity change of the $La_2O_2CO_3$:xTb phosphors as a function of terbium content.

The emissions in the green spectral region in Fig. 2 remarkably depend on the sample composition. In order to examine the terbium concentration dependence on the photoluminescent emission intensity, several samples with different terbium content varying from 10.9 to 21.2 at.% were synthesized. Fig. 3 presents the relationship between the luminescent intensity of the $La_2O_2CO_3$:xTb phosphors and the atomic concentration of the activator (Tb^{3+}). The activator concentration dependence of the emission intensity can be well recognized and it is obvious that the green emission intensity shows maximum at $x = 16.8$ at.%. This behavior of photoluminescent emission intensity with increasing activator concentration can be accounted for by the well-established theory of concentration quenching [14].

Generally, it is advantageous that the phosphor particle size is as small as possible, because this potentially leads to higher screen resolution in displays and lower loading in lamps. However, typically, there is a substantial decrease in luminescence efficiency as particles become smaller than about 3 μm [15, 16]. In some cases, for example, the relative intensity becomes about one-third by the reduction of the particle size [17, 18]. Although the emission intensity of the $La_2O_2CO_3$:16.8 at.%Tb was 60.0% of the commercial $LaPO_4$:Ce,Tb phosphor, this material is expected to be applicable for some optical devices by further research, because the intensity is relatively high by the consideration of its smaller size (0.69 μm) than that of the commercial one (2.84 μm), as seen in their SEM images (Fig. 4).

In summary, a new green emitting phosphor, $La_2O_2CO_3$:xTb, was synthesized for the first time by a simple flux method using the 0.476Li_2
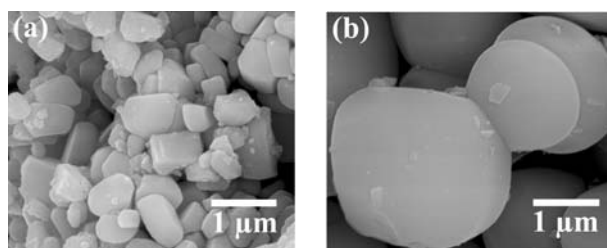

Figure 4 SEM images of (a) the $La_2O_2CO_3$:16.8 at.%Tb and (b) the commercial $LaPO_4$:Ce,Tb phosphors.

CO_3–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture. The samples developed in the present study have stable hexagonal type II structure in a single phase with a high crystallinity. The photoluminescent emission spectra showed emissions from $^5D_4$ excited state to ^7F_J ground states of Tb^{3+} and the luminescent intensity became maximum at the composition of $La_2O_2CO_3$: 16.8 at.%Tb. Although the particle size of this phosphor is in sub-micrometer scale, the emission intensity is relatively high, which suggests potential possibility of this phosphor to be applicable for some optical devices, because small phosphors are advantageous for higher screen resolution in displays and lower loading in lamps.

References

1. R. P. TURCOTTE, J. O. SAWYER and L. EYRING, *Inorg. Chem.* **8** (1969) 238.
2. J. O. SAWYER, P. CARO and L. EYRING, *Montash. Chem.* **102** (1971) 333.
3. N. IMANAKA, M. KAMIKAWA and G. ADACHI, *Anal. Chem.* **74** (2002) 4800.
4. A. OLAFSEN, A.-K. LARSSON, H. FJELLVÅG and B.C. HAUBACK, *J. Solid State Chem.* **158** (2001) 14.
5. O.-K. MOUNE-MINN and P. CARO, *J. Crystallogr. Res.* **12** (1982) 157.
6. J. HÖLSÄ and T. TURKKI, *Thermochim. Acta* **190** (1991) 335.
7. S. TAMURA, K. KOYABU, T. MASUI and N. IMANAKA, *Chem. Lett.* **33** (2004) 58.
8. V. V. SUBBA RAO, R. V. G. RAO and A. B. BISWAS, *J. Inorg. Nucl. Chem.* **27** (1965) 2525.
9. R. L. N. SASTRY, S. R. YOGANARASIMHAN, P. N. MEHROTRA and C. N. R. RAO, *ibid.* **28** (1966) 1165.
10. A. N. CHRISTENSEN, *Acta Chem. Scand.* **24** (1970) 2440.
11. J. P. ATTFIELD and G. FÉREY, *J. Solid State Chem.* **82** (1989) 132.
12. R. D. SHANNON, *Acta Cryst.* **A32** (1976) 751.
13. G. BLASSE and B. C. GRABMAIER, in "Luminescent Materials" (Springer Verlag, Berlin, 1994) p. 28.
14. *Idem.*, *ibid.*, p. 91.
15. T. HASE, T. KANO, E. NAKAZAWA and H. YAMAMOTO, *Adv. Electron. Phys.* **79** (1990) 271.
16. H. YAMAMOTO, *J. Soc. Inform. Disp.* **4** (1996) 165.
17. C.-H. LU, H.-C. HONG and R. JAGANNATHAN, *J. Mater. Chem.* **12** (2002) 2525.
18. J. DHANARAJ, R. JAGANNATHAN and D. C. TRIVEDI, *ibid.* **13** (2003) 1778.