Synthesis of New Green-emitting $Gd_2O_2CO_3$:Tb^{3+} Fine Particles with High Luminescence Intensities

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(Received May 17, 2005; CL-050653)

New green-emitting $Gd_2O_2CO_3$:$x$$Tb^{3+}$ fine particles were synthesized by a flux method using the 0.476Li_2CO_3–0.270Na_2CO_3–0.254K_2CO_3 eutectic mixture. The emission intensity of the $Gd_2O_2CO_3$:16.9 atom %Tb^{3+} phosphor was equivalent to that of the commercial $LaPO_4$:Ce^{3+},Tb^{3+}, in spite that the size was apparently smaller (ca. 1/10) than the commercial one.

Synthesis of high-efficiency crystalline phosphor particles with submicron size is a key for advanced technology and commercial applications to realize high resolution in large flat display panels and low loading with high packing density in fluorescent lamps. In these applications, quality of the phosphor materials is significantly important. However, the luminescence efficiency decreases when the particle size becomes smaller than a critical value, especially less than 1 μm in diameter, because of the increase of surface defects that induce luminescence quenching,[1] and hence the particle size of the commercial products is adjusted around 3–5 μm. Therefore, it is significant to find new phosphor materials which are suitable for the morphology of fine particle in order to realize higher resolution, lower powder weight, and higher packing density in many optical devices.

Although there are many candidates for new luminescent materials, we have paid attention to rare earth oxycarbonates which have three different structures, i.e., tetragonal (type I), monoclinic (type Ia), and hexagonal (type II) $RE_2O_2CO_3$ (RE: rare earths). Among the three structures, the hexagonal (type II) oxycarbonate has a potential to be a suitable material for phosphors,[2] because it has high thermal stability and durability against water and carbon dioxide.[3]

In the series of rare earth elements, gadolinium oxycarbonate (II)-$Gd_2O_2CO_3$ with hexagonal structure was selected as a host material and terbium ion was chosen as an activator in this study. The gadolinium ion (Gd^{3+}) has a half-filled 4f shell which gives a very stable $^8S_{7/2}$ ground state, and also shows energy transfer from the excited $^6P_{7/2}$ level to most rare earth ions except Pr^{3+} and Tm^{3+}, which is well known energy migration in concentrated Gd compounds.[4] On the other hand, Tb^{3+} is a popular activator which shows transitions of the green emission.

It is difficult to synthesize hexagonal $RE_2O_2CO_3$ in a single phase by the conventional synthesis from oxalates, carbonates, acetates, and oxides.[5] In the case of $Gd_2O_2CO_3$, it is necessary to heat gadolinium carbonate monohydrate at 773 K for a week under humid CO_2 to obtain II-type oxycarbonate, but the long-time heating in this method results in grain growth of the particles. On the contrary, we have used a wet chemical process followed by our original flux treatment using lithium carbonate or a eutectic mixture of alkali carbonates[2] to synthesize $Gd_2O_2CO_3$:Tb^{3+} fine particles. This method makes it possible to obtain the type II oxycarbonate in a single phase without difficulty only 12-h heating at 823 K in a flow of 10% CO_2 diluted with N_2 gas, and can produce fine particles in submicron scale effectively. Moreover, the flux treatment brings about the smooth surface of the particles without growth. The luminescence properties of the prepared particles have been compared with those of the commercially available $CePO_4$:Ce^{3+},Tb^{3+} bulk material (2.7 μm particle size).

A stoichiometric mixture of $Gd(CH_3COO)_3 \cdot 4H_2O$ and $Tb(CH_3COO)_3 \cdot 4H_2O$ was dissolved in deionized water. The amount of Tb^{3+} ion was adjusted between 14.7 and 21.2 atom % of the total acetate. The solvent was evaporated at 333 K, and the solid residue was dried at 353 K for 12 h. After calcination at 873 K for 6 h in air atmosphere, the sample was mixed with the 0.476Li_2CO_3–0.270Na_2CO_3–0.254K_2CO_3 eutectic mixture in a ratio of 50 mol %, where the eutectic melting point is 663 K. The mixture was heated at 823 K for 12 h in a flow of 10% CO_2 diluted with N_2 gas. The sample was dried at room temperature after washing with deionized water for three times and subsequently once with ethanol.

X-ray powder diffraction (XRD) patterns of all samples were in good agreement with a single phase of the hexagonal type II rare earth oxycarbonate. These oxycarbonates are stable up to 823 K. The photoluminescence excitation and emission spectra of the $Gd_2O_2CO_3$:16.9 atom %Tb^{3+} phosphor are shown in Figure 1. This phosphor exhibited well-known characteristic Tb^{3+} emission and no self-activated emission was observed in the undoped $Gd_2O_2CO_3$ sample. The excitation spectrum of the $Gd_2O_2CO_3$:$x$$Tb^{3+}$ sample consists of a broad band with the maximum at 260 nm, corresponding to the energy transition from the $4f^8$ to $4f^75d$ configuration of Tb^{3+}, and an additional peak observed at 312 nm is assigned to the $^8S_{7/2}$–$^6P_{7/2}$ transition of Gd^{3+}.[6] 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, where the symbol “sh” represents a shoulder peak.

The photoluminescence intensities of the $Gd_2O_2CO_3$:$x$$Tb^{3+}$ phosphors depended on the Tb^{3+} content. Figure 2 presents terbium concentration dependence of the luminescence intensity for the $Gd_2O_2CO_3$:$x$$Tb^{3+}$ phosphors with different terbium content varying from 14.7 to 17.7 atom %. The activator concentration dependence of the emission intensity is recognized and the green emission intensity shows the maximum at $x = 16.9$ atom %. It is notable that the relative intensity becomes 101% of the commercial $LaPO_4$:Ce^{3+},Tb^{3+} phosphor at this composition, where the comparison was carried out by using the integrated energy intensities of the emission spectra. The decrease in the photoluminescence emission intensity with increasing activator

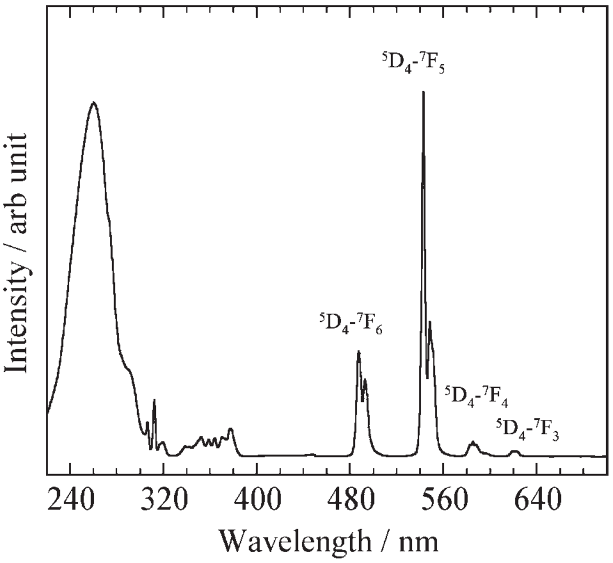

Figure 1. Photoluminescence excitation (left) and emission (right) spectra of the $Gd_2O_2CO_3$:16.9 atom %Tb^{3+} phosphor.

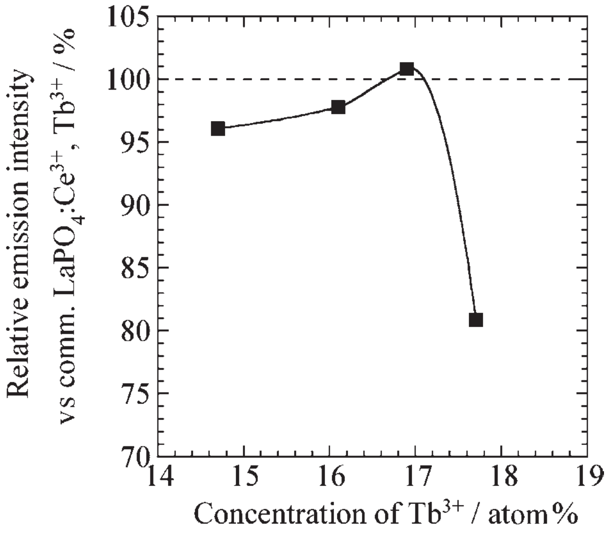

Figure 2. Fluorescence intensity change of the $Gd_2O_2CO_3$: $x$$Tb^{3+}$ phosphors as a function of terbium content.

concentration beyond $x = 16.9$ atom % can be accounted by the concentration quenching theory.[4]

The morphology of the phosphors synthesized in this study was also observed as shown in the SEM micrographs in Figure 3 with the commercial $LaPO_4$:Ce^{3+},Tb^{3+} phosphor. The average particle size obtained by measuring the diameters of 100 particles on the SEM photographs was 0.26 μm for the $Gd_2O_2CO_3$: 16.9 atom %Tb^{3+}, while that of the $LaPO_4$:Ce^{3+},Tb^{3+} was 2.7 μm. Generally, it is advantageous that the phosphor particle is as small as possible, because this potentially leads to high resolution in displays and lower powder weight in lamps. However, decreasing the particle size usually results in a decrease in the emission efficiency, which is attributed to the increase in surface defects.[7] On the contrary, the oxycarbonate $Gd_2O_2CO_3$:16.9 atom %Tb^{3+} phosphor exhibits excellent photoluminescence characteristics under excitation at 254 nm in spite of 1/10 size of the commercial phosphor, suggesting that they are expected to be applicable for various optical devices.

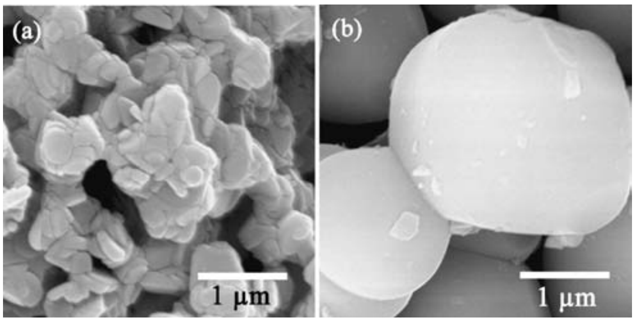

Figure 3. SEM images of (a) the $Gd_2O_2CO_3$:16.9 atom %Tb^{3+} and (b) the commercial $LaPO_4$:Ce^{3+},Tb^{3+} phosphors.

In summary, a new green-emitting phosphor, $Gd_2O_2CO_3$: $x$$Tb^{3+}$, was synthesized for the first time by the flux method using the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture. The samples obtained in the present study have stable hexagonal type II structure in a single phase with high crystallinity. The photoluminescence emission spectra show emissions from $^5D_4$ excited state to ^7F_J ground states of Tb^{3+}, and the luminescence intensity became maximum at the composition of $Gd_2O_2CO_3$:16.9 atom %Tb^{3+}. The emission intensity of this phosphor is equivalent to that given by the commercial $LaPO_4$:Ce^{3+},Tb^{3+}, although the particle size is in submicron scale which is about 1/10 of the commercial one.

This work was supported by the Industrial Technology Research Grant Program in ’02 (project ID: 02A27004c) from the New Energy and Industrial Technology Development Organization (NEDO) based on funds provided by the Ministry of Economy, Trade and Industry, Japan (METI).

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