Gel Nitridation Preparation and Luminescence Property of Eu-doped $RE_2O_2CN_2$ (RE = La and Gd) Phosphors

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$RE_2O_2CN_2$ (RE = La, Eu, and Gd) and Eu-doped $RE_2O_2CN_2$ (RE = La and Gd) phosphors were prepared by nitridation of oxide precursors through rare earth citrate gel. This preparation method increased the doping limit to 20 atom % in $La_2O_2CN_2$. The value was considerably wider than 7 atom % of solid-state synthesis through rare earth oxide. Eu-doped $Gd_2O_2CN_2$ was firstly synthesized by this method. The shape of luminescence spectra and luminescence intensity were different between these oxycyanamides reflecting the difference in their crystal structure and crystallinity.

Recently, inorganic compounds containing several kinds of anions have been paid much attention in optical materials, e.g., oxynitride phosphor in LED by UV excitation[1–3] and photocatalyst by UV–vis excitation.[4] Nitrogen introduction to oxide changed the band gap of phosphor and catalyst to absorb effectively the incident light. Containing different kinds of anions can make structure, physical and chemical properties unique and multiple. Rare earth oxysulfide, RE_2O_2S, has been widely used as phosphor for CRT and X-ray scintillator.[5,6] There is a series of oxy compounds RE_2O_2X, where X is divalent anion such as S^{2-}, Se^{2-}, Te^{2-}, $CO_3{}^{2-}$, $CN_2{}^{2-}$, and $SO_4{}^{2-}$. Crystal structure of the oxy compounds consists of $RE_2O_2{}^{2+}$ layers and their interleaving anion. Reversible uptake of oxygen in $RE_2O_2SO_4$ by a reaction of $SO_4{}^{2-} \rightleftharpoons S^{2-} + 2O_2$ has been studied as a new efficient oxygen storage material.[7] A wide variety of function is anticipated by changing interlayer anions between $RE_2O_2{}^{2+}$ layers.

There are two structural types in oxycyanamide $RE_2O_2CN_2$. The linear anion $(N–C–N)^{2-}$ lies in parallel to the $La_2O_2{}^{2+}$ layers in type-I structure because of the large ionic size of La^{3+}. The La^{3+} ions are coordinated with 4 oxygen and 4 nitrogen atoms in tetragonal lattice. The $(N–C–N)^{2-}$ anions are in type-II $RE_2O_2CN_2$ perpendicular with the smaller RE where RE = Ce, Nd, Sm, Eu, and Gd. The RE^{3+} cations are coordinated with 4 oxygen and 3 nitrogen atoms in trigonal lattice.[8,9] The distance between $RE_2O_2{}^{2+}$ interlayer rare earth ions is larger in type-II structure (≈0.57 nm) than in type-I structure (≈0.37 nm). The distance between $RE_2O_2{}^{2+}$ intralayer rare earth ions is nearly same (≈0.37 nm). Two-dimensional character in type-II structure may suppress the concentration quenching and lower the symmetry of luminescence center. The longer interlayer distance in $Gd_2O_2CN_2$ can lead to higher luminescence intensity.

Luminescence property of rare earth oxycyanamides has been reported only for $La_2O_2CN_2$ doped with Pr, Sm, Eu, and Tb.[10–12] They were prepared by nitriding a mixture of rare earth oxide in ammonia flowing at 950 °C. There has been no report on doped $Gd_2O_2CN_2$ because of the difficulty in synthesis of pure $Gd_2O_2CN_2$.[9] Sol–gel method may make the preparation much easier because the low temperature in synthesis and the uniform mixing of the constituents. The doping range in $La_2O_2CN_2$ may also be expanded by sol–gel method.

In the present study, $RE_2O_2CN_2$ (RE = La, Eu, and Gd) and Eu-doped $RE_2O_2CN_2$ (RE = La and Gd) were prepared by nitridation of rare earth citrate gel in contrast to solid-state reaction. Luminescence property in the doped products was studied in relation to their crystal structure and crystallinity.

Rare earth (La, Ce, Eu, Gd, and Y) nitrates (Wako Pure Chemicals Co., GR) were dissolved in distilled water with the equal molar ratio of glycine (Wako Pure Chemicals Co., GR) to nitrate. For Eu doping, Eu nitrate was mixed in a molar ratio of RE:Eu $= (1 - x):x$ (x = 0–0.4) against La and Gd. They were heated on a hot plate, and the obtained gel was fired in a muffle furnace at 350 °C. After crushing and mixing with a mortar and pestle, it was fired again in ammonia flowing at 750–850 °C for 10 h. X-ray diffraction (XRD) patterns were recorded with a diffractometer with monochromatized Cu Kα radiation (PANalytical, X'pert-MPD). Photoluminescence (PL) spectra were measured with a spectrofluorometer (JASCO, FP6200).

The fired products in ammonia at 750 °C were either oxycyanamide or oxide depending on the kinds of rare earth as shown in Figure 1. The oxycyanamides were obtained as tetragonal $La_2O_2CN_2$ in type-I and trigonal $RE_2O_2CN_2$ (RE = Eu and Gd) in type-II. The crystallinity lowered in the order of La, Eu, and Gd oxycyanamides. The synthesis temperature was lower by 200 °C than that of solid-state synthesis. La_2O_3 coexisted with $La_2O_2CN_2$ in the nitrided product at 850 °C. The oxycyanamide had already decomposed into the oxide at 850 °C. Products were not oxycyanamides but only oxides in Ce and Y. For Ce, tetravalent Ce^{4+} is stable and low crystalline CeO_2 was already ob-

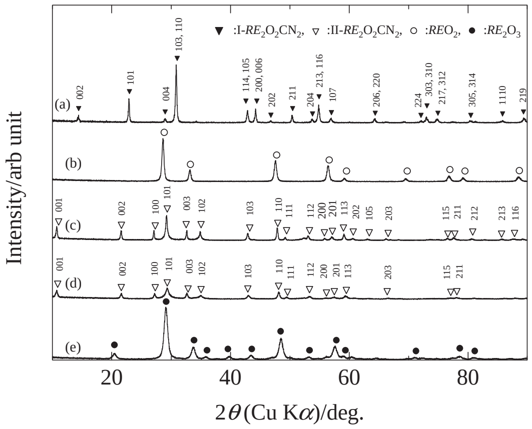

Figure 1. XRD patterns of the nitrided products of rare earth citrate gel at 750 °C with various kinds of RE(III), where RE = (a) La, (b) Ce, (c) Eu, (d) Gd, and (e) Y.

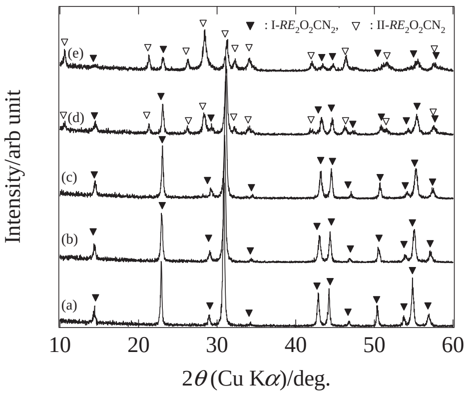

Figure 2. XRD patterns of the nitirded products by mixed La–Eu citrate gel at 750 °C. Their Eu contents are (a) 0, (b) 10, (c) 20, (d) 30, and (e) 40 atom %, respectively.

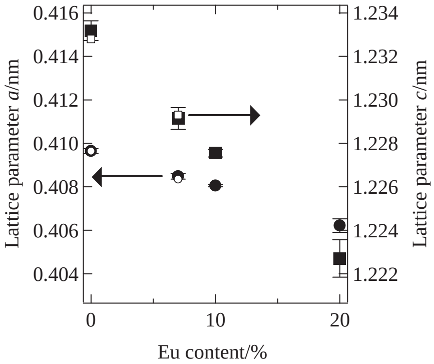

Figure 3. Lattice parameters a and c versus Eu-doping content in $(La_{1-x}Eu_x)_2O_2CN_2$. Valuses reported by solid-state reaction are shown as references in open marks.[12]

served even in the prefired product at 350 °C. It remained after the nitridation. For Y, the ionic size (Y^{3+}(VIII) $= 0.1015$ nm) might be too small to stabilize the oxycyanamide in type-II structure. Gd (Gd^{3+}(VIII) $= 0.106$ nm) was the smallest rare earth ion to form oxycyanamide both in solid-state[9] and in sol–gel syntheses.

Eu-doped products were prepared for La and Gd oxycyanamides at 750 °C. Only $(La_{1-x}Eu_x)_2O_2CN_2$ in type-I was observed in the range $0 < x \leq 0.2$, and the lattice parameters a and c decreased linearly with the amount of doped Eu as shown in Figures 2 and 3. The product in type-II structure appeared above 30 atom %, and its fraction increased with the Eu content as represented in Figure 2. The limit of doping increased to 20 from 7 atom % previously reported in solid-state synthesis.[12] Eu doping was possible up to 4 atom % in $Gd_2O_2CN_2$, and Gd_2O_3 and $Gd_2O_2CO_3$ impurities were observed above 7 atom %.

Luminescence spectra were observed on both $(La_{0.97}Eu_{0.03})_2O_2CN_2$ and $(Gd_{0.96}Eu_{0.04})_2O_2CN_2$ under excitation at 289 and 280 nm as shown in Figures 4a and 4b, respectively. They showed line spectra corresponding to $^5D_0 \rightarrow {}^7F_1$ (≈590 nm) and $^5D_0 \rightarrow {}^7F_2$ (610–620 nm) transitions characteristic for Eu^{3+}, and their shape were different each other. This is due to the different coordination environments around Eu^{3+}; 4 oxygen and 4 nitrogen atoms coordinate in $La_2O_2CN_2$, and 4 oxygen and 3 nitrogen atoms coordinate in $Gd_2O_2CN_2$. The intensity was higher in $La_2O_2CN_2$ than in $Gd_2O_2CN_2$ probably because the crystallinity of the latter was lower than the former as depicted in Figure 1. The luminescence intensity of $(La_{1-x}Eu_x)_2O_2CN_2$ had a maximum at $x = 3$ atom %. This is due to the concentration quenching. The concentration agreed with the value observed in the solid-state reaction.[12] In $(Gd_{1-x}Eu_x)_2O_2CN_2$, the suppression of concentration quenching was not recognized because of the presence of impurities in high Eu-doping content. The luminescence enhancement anticipated by two dimensionality in crystal structure was not achieved in this study.

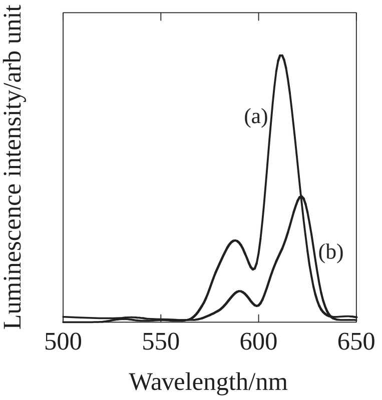

Figure 4. Luminescence spectra of (a) $(La_{0.97}Eu_{0.03})_2O_2CN_2$ ($\lambda_{ex} = 289$ nm) and (b) $(Gd_{0.96}Eu_{0.04})_2O_2CN_2$ ($\lambda_{ex} = 280$ nm).

In conclusion, the nitridation of rare earth citrate gel was applied to prepare Eu-doped $RE_2O_2CN_2$ ($RE =$ La and Gd). Eu-doping range considerably increased compared to solid-state synthesis in $La_2O_2CN_2$. The Eu-doped $Gd_2O_2CN_2$ was synthesized for the first time. The luminescence intensity was weak owing to its low crystallinity.

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