

Red emitting phosphors based on titanite with high thermal stability



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ABSTRACT

Red emitting phosphors based on titanite, $(\text{Ca}_{1-x-y}\text{Eu}_x\text{Na}_y)\text{TiSiO}_{5+\delta}$ ($x=0.05, 0.07, 0.10$; $y=0, 0.01, 0.03, 0.05$), were synthesized by the conventional solid state reaction method, and their photoluminescence properties were investigated. Among $(\text{Ca}_{1-x}\text{Eu}_x)\text{TiSiO}_{5+\delta}$ ($x=0.05, 0.07, 0.10$), $(\text{Ca}_{0.93}\text{Eu}_{0.07})\text{TiSiO}_{5+\delta}$ ($x=0.07$) showed the highest emission intensity of 14% in comparison with the commercial $(\text{Y}_{0.98}\text{Eu}_{0.02})_2\text{O}_2\text{S}$ phosphor. Introduction of monovalent Na^+ into the $(\text{Ca}_{0.93}\text{Eu}_{0.07})\text{TiSiO}_{5+\delta}$ lattice also enhanced the emission intensity by preventing the reduction of Ti^{4+} to Ti^{3+} . Consequently, the $(\text{Ca}_{0.90}\text{Eu}_{0.07}\text{Na}_{0.03})\text{TiSiO}_{5+\delta}$ phosphor enhanced the emission intensity up to 22%. From the thermal analysis results, it is revealed that the thermal stability of the present $(\text{Ca}_{0.90}\text{Eu}_{0.07}\text{Na}_{0.03})\text{TiSiO}_{5+\delta}$ phosphor was much higher than that of the commercial one.

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1. Introduction

White light-emitting diodes (WLEDs) are used for various applications such as solid state lighting sources and display devices, because of the high brightness, low energy consumption, and long lifetime [1]. Among several ways for fabricating the WLEDs, one that is composed of a near-ultraviolet (NUV) LED chip and red, green, and blue phosphors applied on the chip has been widely studied, because this type of WLED has high color-rendering index. Eu^{3+} -doped $\text{Y}_2\text{O}_2\text{S}$ oxysulfide is popularly used as a red phosphor for the WLEDs; however, its thermal stability is low. In addition, oxysulfide compounds are decomposed to oxides at high temperatures, accompanying with generation of toxic sulfur oxides. In contrast, oxide compounds are considered to be ideal materials for such phosphors from a practical perspective, because oxide compounds usually hold higher thermal stability than other compounds such as oxysulfide.

It is well known that the luminescent properties of phosphors significantly depend on the interaction between the activators in the host material. Generally, luminescent emission intensity enhances with increasing the concentration of the activator in the host lattice. However, redundant amount of the activator

would cause concentration quenching and lowering the luminescent emission intensity, because the decrease in the mean distance between the activators often induces non-radiative deactivation. Therefore, it is important to choose the crystal structure of the host material for designing a novel phosphor with high luminescent efficiency.

Among various candidates for new host materials, our research group has focused on several compounds with layered structure. In the layered structure, energy transfer between the excited luminescent ions across the anion groups was blocked by the long distance of rare earth ions of activators in the crystal structure. Therefore, such phosphors with the layered structure would be resistant to the concentration quenching, even if a large amount of activator was introduced into the host lattice. Considering this, our research group has successfully synthesized several novel phosphors with layered structure, and has revealed that these layered compounds are suitable for host materials of phosphors with high luminescent property [2–5].

In this study, we focused on a CaTiSiO_5 with a titanite structure (space group: $P2_1/c$), which is thermally stable (melting point: 1373°C [6]) and consists of abundant elements, such as Ca, Ti, Si, and O, as a host material for phosphor. In the titanite structure, chains of corner-shared TiO_6 units are cross-linked by SiO_4 units and compose rigid $[\text{TiOSiO}_4]^{2-}$ frameworks. These frameworks enclose the Ca^{2+} ions in 7-fold coordination [7]. Therefore, by introducing Eu^{3+} ion into the titanite structure, red emitting phosphors would be provided with heat-resistance property. Here, in the literature, Pr^{3+} doped titanite single crystals have been

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synthesized by Czochralski method, and partial reduction of Ti^{4+} to Ti^{3+} , which was induced by substitution of divalent Ca^{2+} ions with trivalent Pr^{3+} ions, was inhibited by codoping Na^+ [7]. It is well known that generation of Ti^{3+} may decrease the photoluminescence emission intensity, due to d–d transition of Ti^{3+} in red light region. From these concepts, in order to develop the red emitting phosphors with high thermal stability, the titanite $(Ca_{1-x-y}Eu_xNa_y)TiSiO_{5+\delta}$ powders were prepared by introducing Eu^{3+} and Na^+ into the $CaTiSiO_5$ with a conventional solid state reaction method. The photoluminescence properties of $(Ca_{1-x-y}Eu_xNa_y)TiSiO_{5+\delta}$ were then investigated.

2. Experimental

$(Ca_{1-x-y}Eu_xNa_y)TiSiO_{5+\delta}$ ($x=0, 0.05, 0.07, 0.10$; $y=0, 0.01, 0.03, 0.05$) solids were prepared by a conventional solid state reaction technique. Stoichiometric amounts of $CaCO_3$, TiO_2 (rutile), SiO_2 , Eu_2O_3 , and Na_2CO_3 powders were mixed in an agate mortar, followed by mechanical mixing using a planetary-type ball-milling apparatus (PULVERISETTE 7, Fritsch GmbH) at a rotation speed of 300 rpm for 3 h. The homogenous mixture was calcined at $1300^\circ C$ for 4 h under flowing the synthetic air ($N_2:O_2=79:21$). Before characterization, all samples were gently ground in an agate mortar.

The samples were characterized by X-ray powder diffraction (XRD; SmartLab, Rigaku) with Cu-K α radiation (40 kV and 30 mA). The lattice volumes of $(Ca_{1-x-y}Eu_xNa_y)TiSiO_{5+\delta}$ were calculated from the XRD peak angles, which were refined using $\alpha-Al_2O_3$ as a standard. X-ray photoelectron spectroscopy (XPS; PHI5000 VersaProbell, ULVAC-PHI) was performed at room temperature with Al-K α radiation (1486.6 eV). The charging effect on the binding energies was corrected with respect to the C 1s peak (284.6 eV). Particle morphologies were observed by a scanning electron microscopy (SEM; SS-550, Shimadzu). Photoluminescence excitation and emission spectra were measured at room temperature using a spectrofluorophotometer (RF-5300PC, Shimadzu) with a Xe lamp as light source. The emission spectra were obtained for excitation at 393 nm, and the excitation spectra were recorded for the emission at 614 nm. Relative emission intensities of the $(Ca_{1-x-y}Eu_xNa_y)TiSiO_{5+\delta}$ phosphors were evaluated by comparing the integrated area of the emission peak at 614 nm for Eu^{3+} with that of the emission peak at 626 nm for Eu^{3+} of a commercial $(Y_{0.98}Eu_{0.02})_2O_2S$ phosphor (for excitation at 333 nm). Internal quantum efficiencies of some phosphors were measured on a spectrofluorometer (FP-8500, Jasco) with a fluorescence integrate sphere unit (ILF-835, Jasco) using a Xe lamp as light source, and the data were corrected by deuterium and halogen lamps. Differential thermal analysis (DTA; DTA-60AH, Shimadzu) was carried out in the temperature range between 50 and $1000^\circ C$ at a heating rate of $10^\circ Cmin^{-1}$ in the synthetic air atmosphere, where a $\alpha-Al_2O_3$ powder in a platinum crucible was used as the counter reference material for the measurements. In addition, the prepared sample and the commercial $(Y_{0.98}Eu_{0.02})_2O_2S$ phosphor were heated at $1000^\circ C$ for 4 h under flowing synthetic air ($N_2:O_2=79:21$).

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(Ca_{1-x}Eu_x)TiSiO_{5+\delta}$ samples. The samples with $x \leq 0.07$ were indexed by a titanite single phase. On the other hand, for the sample with $x=0.10$, a $Eu_2Ti_2O_7$ was observed as an impurity phase in addition to the titanite phase. The lattice volume dependence on the Eu^{3+} content (x) of the $(Ca_{1-x}Eu_x)TiSiO_{5+\delta}$ samples is presented in Fig. 2. The lattice volume decreased with increasing amount of the Eu^{3+} content (x) in the composition range of $x \leq 0.07$, while it became approximately constant for the range of $0.07 \leq x \leq 0.10$. These results indicate that

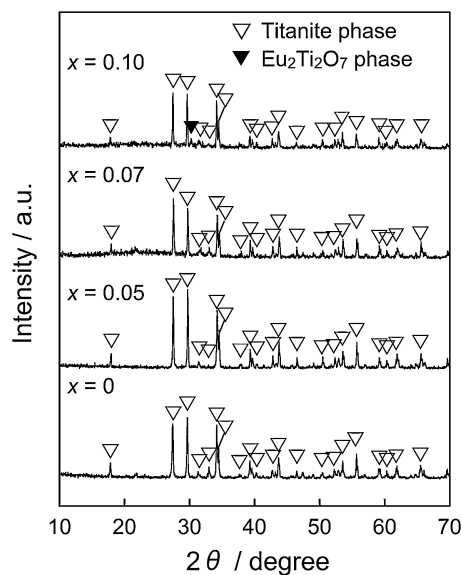


Fig. 1. XRD patterns of the $(Ca_{1-x}Eu_x)TiSiO_{5+\delta}$ samples.

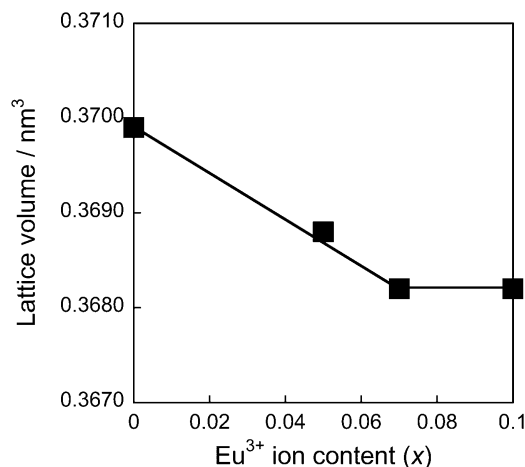


Fig. 2. Lattice volume dependence on Eu^{3+} content (x) of the $(Ca_{1-x}Eu_x)TiSiO_{5+\delta}$ samples.

a proportion of the Ca^{2+} ions in the $CaTiSiO_5$ lattice was substituted with Eu^{3+} , because ionic radius of Eu^{3+} (0.101 nm, 7-fold coordination) [8] is smaller than that of Ca^{2+} (0.106 nm, 7-fold coordination) [8].

Fig. 3 depicts the photoluminescence excitation (a) and emission (b) spectra of the samples ($x=0.05, 0.07, 0.10$). A weak broad band between 310 and 355 nm, and several sharp bands in wavelengths from 355 to 500 nm were recognized in the excitation spectra of all samples. The weak broad band corresponded to the charge transfer transition between Ti^{4+} and Eu^{3+} [9], and the sharp bands originated in f–f transitions of Eu^{3+} between ground state and excited levels of $4f^6$ configuration. In the emission spectra, all peaks originated in the transitions from the 5D_0 excited level to the 7F_J ($J=0, 1, 2, 3, \text{ and } 4$) ground levels of Eu^{3+} . The emission peak corresponding to the $^5D_0-^7F_2$ electric dipole transition at 614 nm was more dominant than those attributed to the $^5D_0-^7F_1$ magnetic dipole transitions at 592 and 598 nm, indicating that the Eu^{3+} ions occupied the Ca^{2+} site with no inversion symmetry. Relative emission intensities of the $(Ca_{1-x}Eu_x)TiSiO_{5+\delta}$ ($x=0.05, 0.07, 0.10$) phosphors are plotted in Fig. 4. The relative emission intensity increased with increasing the Eu^{3+} content (x) for the $(Ca_{1-x}Eu_x)TiSiO_{5+\delta}$ ($x=0.05$ and 0.07) samples, while that

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