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Preparation of novel phosphor using intercalation of tobermorite

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ABSTRACT

The emission intensity of phosphors is often subject to concentration quenching after doping of the activator in the host crystal rises above a certain limit. This study describes the preparation of novel phosphors based on tobermorite that do not exhibit concentration quenching. In the preparation of phosphors, Eu^{3+} ions are exchanged with intercalated Ca^{2+} ions within the tobermorite by dipping in EuCl_3 solution. The emission intensity of the Eu^{3+} doped tobermorite increased with increasing Eu/Ca atomic ratio and attained a maximum value of 8.6% for a Eu/Ca atomic ratio of 0.22. Heating of the phosphor at 800 °C resulted in a three-fold improvement in emission intensity.

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1. Introduction

In recent years, white light-emitting diodes (LEDs) have been used as an alternative to fluorescent lamps. However, in these applications, the emission intensity of the red-emitting LED is weaker than that of the blue- or green-emitting LED [1,2]. One solution to this problem is to produce red light by capping the surface of a violet-emitting LED (emission at 395 nm) with a phosphor. In these applications, the Eu^{3+} ion is mainly used as the phosphor activator. The Eu^{3+} ion emits in the red for irradiation in the near-UV at 395 nm. A white color is obtained by mixing red-emitting phosphor with a yellow-emitting phosphor and a green- or blue-emitting phosphor having a strong emission intensity [3,4]. To obtain true white emission, the red-emitting phosphor must also have a strong emission intensity.

Generally, the activator used as a luminescence center, a rare earth ion, is incorporated with a positive ion in the host crystal. The emission intensity of this phosphor increases with increased doping of the activator. However, aggregates start to form in the host when the doping exceeds a certain amount and concentration quenching occurs upon further doping. The level of doping at which concentration quenching begins differs depending on the type of host crystal. For example, the doping limit before concentration quenching occurs is about 5% in calcium carbonate and 0.01% in calcium sulfide [5–8].

Tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) is a kind of calcium silicate hydrate bound together by intercalation. For one molecule of tobermorite there are five Ca^{2+} ions within the structure. Four of these Ca^{2+} ions form a polyhedral Ca–O layer in the crystal structure of the tobermorite [9]. The remaining Ca^{2+} ion exists in the interlayer. The distance of the interlayer of 1.1 nm is general in the tobermorite.

H_2O molecules and OH groups are also intercalated within the tobermorite structure. The Ca^{2+} ion intercalated within the tobermorite can be substituted by heavy metal ions such as Ni^{2+} , Co^{2+} and Cd^{2+} [10,11]. By this means, it is possible to introduce rare earth ions as activators within the interlayer structure. Phosphors that incorporate such activators in the structure are able to emit various colors under UV irradiation. If activator ions are included within the crystal structure, they are strongly paired with anions. However, if the activator ion is intercalated within the structure then it is weakly bound. The activator introduced into the host via intercalation does not exhibit concentration quenching, because it is retained within the host crystal by weak bonding.

This study investigated the relationship between doping of Eu^{3+} ions and the emission intensity using a novel synthetic phosphor that does not exhibit concentration quenching.

2. Experimental

The raw materials used for synthesis were 96% $\text{Ca}(\text{OH})_2$, 99.9% SiO_2 and 99.95% $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. All reagents were of high grade and obtained from Kanto Kagaku Co., Ltd. (Japan).

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For the synthesis, distilled water (200 cm³), Ca(OH)₂ and SiO₂ were added to a Teflon beaker. The synthetic conditions were set to give a CaO/SiO₂ molar ratio of 0.83 and a water/solid mass ratio of 40. The actual amounts of SiO₂ and Ca(OH)₂ added were 2.42 and 2.58 g, respectively. The beaker was set in an autoclave (Taiatsu Techno TEM-D type), and the suspension was stirred at 200 rpm. For the reaction, the autoclave was set at 180 °C for 3 h. The resulting product was washed thoroughly in distilled water and was dried to give tobermorite as a raw material for subsequent doping. The obtained tobermorite was dipped for 0.5–5 h in 0.05–0.030 mol/dm³ EuCl₃ solution, before thorough washing in distilled water to give the Eu³⁺ doped tobermorite phosphor. In addition, the Eu³⁺ doped tobermorite was heated to increase the emission intensity. The heating conditions were set to 700–1000 °C for 0.5–3 h.

The final sample was characterized by X-ray diffraction, scanning electron microscopy and inductively coupled plasma spectrometry. The fluorescence properties of the sample were measured using a Hitachi F-4500 spectrophotometer and a Topcon BM-50 luminance meter. All measurements were carried out at room temperature. In this paper, 100% emission intensity is relative to the 422 nm emission intensity of calcium tungstate, which was irradiated in the UV at 254 nm. The calcium tungstate reference was prepared by Nakaraitesuku Co., Ltd. (Japan). The emission intensity of calcium tungstate as phosphor of standard was measured, when emission intensity of the phosphor was measured. The measurement of emission intensity of the sample carried out at room temperature. The Eu³⁺ doped tobermorite was dissolved in the hydrochloric acid, and Eu/Ca atom ratio in the filtrate was measured using ICP.

3. Results and discussion

3.1. Ion exchange of Eu³⁺ ion and Ca²⁺ ion occurred in intercalation of tobermorite

Fig. 1 shows a scanning electron microphotograph of the tobermorite raw material. The primary particles were thin plate-like crystals of about 0.1 μm (thickness) × 3 μm (width) (Fig. 1(a)). The secondary particles were formed into approximate spheres of about 20 μm in size by aggregation of the thin plate-like crystals (Fig. 1(b)).

Ca²⁺ ions intercalated within the tobermorite were exchanged with Eu³⁺ ions by dipping in the EuCl₃ solution at different concentrations. Perfect exchange of all Ca²⁺ ions intercalated within the tobermorite with Eu³⁺ ions would yield a theoretical value of the Eu/Ca atomic ratio of 0.25. We have previously reported on a doping limit for Eu³⁺ doped calcium carbonate at a Eu/Ca atomic ratio of about 0.03. It is thus theoretically possible to incorporate six times this quantity of activator in the phosphor. To try to achieve this, experiments were carried out by dipping the tobermorite in the EuCl₃ solution.

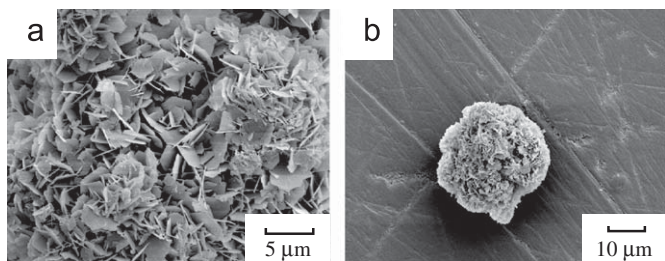


Fig. 1. Scanning electron microphotograph of tobermorite raw material.

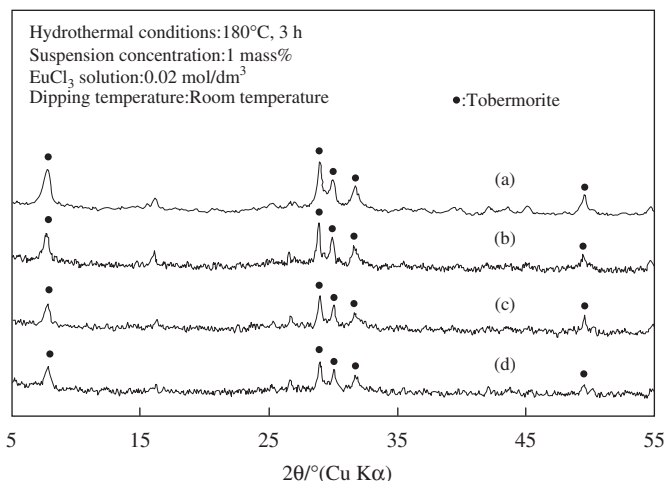


Fig. 2. X-ray diffraction patterns of tobermorite dipped for various times in EuCl₃ solution. Time : (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h.

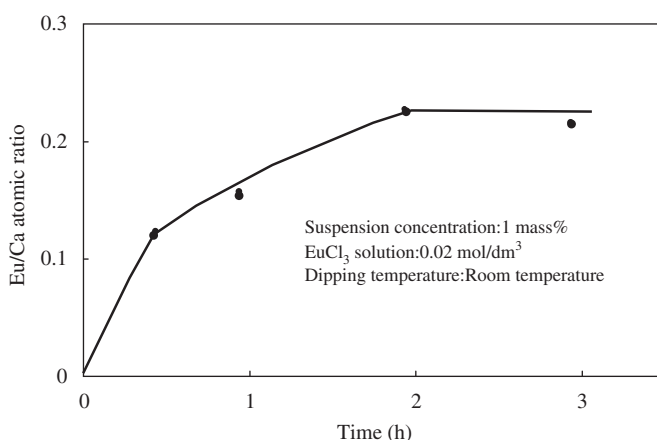


Fig. 3. Relationship between dipping time and Eu/Ca atomic ratio of tobermorite after dipping.

Fig. 2 shows X-ray diffraction patterns of tobermorite dipped in EuCl₃ solution for various times. The synthesized tobermorite was 1.1 nm in size as indicated by the diffraction peak assigned to intercalation observed at $2\theta = 7.8^\circ$. The crystallinity of the dipped tobermorite was reduced with increased dipping time. In addition, the diffraction peak at 7.8° shifted to the high-angle side after 2 h. However, it is difficult to observe this shift in this figure. The diffraction peaks of tobermorite at 7.8° , 29° and 32° were (0 0 2), (2 2 0) and (4 0 0) plane, respectively. The data of these planes was necessary, when the lattice constant is obtained.

Fig. 3 shows the relationship between dipping time and the Eu/Ca atomic ratio of tobermorite after dipping. The quantity of Eu³⁺ ions intercalated within the tobermorite increased with increasing dipping time. The Eu/Ca atom ratio achieved equilibrium at about 0.22 after about 2 h and hardly changed after 3 h, which was consistent with our expectations. Hence the Eu/Ca atomic ratio within the tobermorite could be controlled by changing the dipping time.

It was considered possible that the Eu³⁺ ions were replacing not only the intercalated Ca²⁺ ions but also the Ca²⁺ ions in the crystal structure. To verify this, the lattice constant of the tobermorite was examined after dipping. Since the ionic radius of the Eu³⁺ ion (0.095 nm) is smaller than that of the Ca²⁺ ion (0.099 nm), the lattice constant of the tobermorite would be contracted after exchange of Ca²⁺ with Eu³⁺. Fig. 4 shows the effect

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