



Effect of lithium ion addition on afterglow time of green-emitting Ce^{3+} and Pr^{3+} codoped CaS phosphor by black light irradiation

Yoshiyuki Kojima*, Kenichi Aoyagi, Tamotsu Yasue

Department of Materials and Applied Chemistry, Faculty of Science and Engineering, Nihon University, 1-8, Kanda-Surugadai, Chiyoda-ku, Tokyo 101-8308, Japan

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Abstract

This paper reports the effect of lithium ion addition on the afterglow time of green-emitting Ce^{3+} and Pr^{3+} codoped CaS phosphor by black light irradiation. $\text{CaS}:\text{Ce}^{3+}, \text{Pr}^{3+}$, irradiated with black light, emitted in the green region and showed afterglow. The afterglow time of $\text{CaS}:\text{Ce}^{3+}, \text{Pr}^{3+}$ was relatively short (about 10 min). When a Li^+ invades the free space in a CaS crystal lattice, new cation vacancy is formed for the charge compensation in the Ca^{2+} site. The afterglow intensity of $\text{CaS}:\text{Ce}^{3+}, \text{Pr}^{3+}$, with Li^+ incorporated in the host, increased to three times that of the original sample ($\text{CaS}:\text{Ce}^{3+}, \text{Pr}^{3+}$). The afterglow time of $\text{CaS}:\text{Ce}^{3+}, \text{Pr}^{3+}$, with Li^+ incorporated was extended to 40 min.
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Keywords: Li ion; Afterglow; Black light; Decay curve

1. Introduction

Calcium sulfide (CaS) is known as an afterglow phosphor with high luminescence efficiency and multiple luminescence centers. The CaS phosphor emits under irradiation at various wavelengths of light, including X-rays, ultraviolet- (UV) and

visible light. However, there has been limited research on CaS emission under black light (BL) irradiation. BL emits a band near the UV region at 300–400 nm, which is largely beyond the range of human vision and is also harmless to the human body. BL is thus considered an effective source of night lighting. Therefore, the synthesis of a phosphor that is a BL emitter will be of great value. We perform a series of syntheses of calcium carbonate phosphors by liquid phase reaction, and report that the calcium carbonate phosphor emits in the red, green and blue regions under BL

*Corresponding author. Tel.: +81 3 3259 0868;
fax: +81 3 3293 7572.

E-mail address: ykojima@chem.cst.nihon-u.ac.jp
(Y. Kojima).

irradiation [1–5]. However, under BL the calcium carbonate phosphor displayed no afterglow. Heavy metal ions such as Bi^{3+} and Eu^{2+} were also reported to be effectively doped into gypsum dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). We describe in detail the preparation of $\text{CaS}:\text{Bi}^{3+}$ by heating $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}:\text{Bi}^{3+}$ in a H_2S atmosphere at 900°C [6]. Under BL irradiation, $\text{CaS}:\text{Bi}^{3+}$ emitted in the blue region and afterglow emitted for several hours. In addition, the afterglow intensity of $\text{CaS}:\text{Bi}^{3+}$ increased by incorporating Na^+ . The intensity further increased with an increase in anion vacancies in the crystal lattice. It has been proposed that the anion vacancy is formed by the incorporation of Li^+ , which has a smaller ionic radius than Na^+ [7]. This paper reports the increased afterglow time under BL irradiation upon addition of Li^+ to the green-emitting $\text{CaS}:\text{Ce}^{3+}$, Pr^{3+} .

2. Experimental

The Ce^{3+} and Pr^{3+} codoped CaS was prepared by a reduction reaction of Ce^{3+} and Pr^{3+} with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in a H_2S atmosphere. The raw materials used were 95.0% CaCl_2 , 99.5% $(\text{NH}_4)_2\text{SO}_4$, 99.0% CeCl_3 , 99.95% PrCl_3 , and 99.0% Li_2CO_3 . $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}:\text{Ce}^{3+}, \text{Pr}^{3+}$ was synthesized by adding 0.2 mol/dm^3 $(\text{NH}_4)_2\text{SO}_4$ solution to 0.2 mol/dm^3 CaCl_2 solution supplemented with CeCl_3 and PrCl_3 . The initial Pr/Ca and Ce/Ca atomic ratio was 5×10^{-5} – 4×10^{-3} and 4×10^{-3} – 12×10^{-3} , respectively. A tablet was obtained by pressing at 250 kg/cm^2 after $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}:\text{Ce}^{3+}, \text{Pr}^{3+}$ was mixed with Li_2CO_3 . The initial Li/Ca atomic ratio was 0–0.10. The $\text{CaS}:\text{Ce}^{3+}$, Pr^{3+} incorporated Li^+ was prepared by heating the tablet under a H_2S atmosphere at 900°C for 3 h. The flow rate of H_2S was approximately $150 \text{ cm}^3/\text{min}$. $\text{CaS}:\text{Ce}^{3+}$ or $\text{CaS}:\text{Pr}^{3+}$ phosphor were synthesized similarly to $\text{CaS}:\text{Ce}^{3+}$, Pr^{3+} . The sample was characterized by X-ray diffraction, inductively coupled plasma spectrometry and atomic absorption analysis. The fluorescence of the sample was measured using a luminance meter and spectrophotometer. All measurements were carried out at room

temperature. The decay curve of afterglow was measured using a luminance meter, after the samples were irradiated by BL for 5 min. In this paper, 100% emission intensity relate to 422 nm emission intensity of calcium tungstate, which irradiated the UV of 254 nm. The calcium tungstate prepared by Nakaraitesuku Co., Ltd. (Japan).

3. Results and discussion

3.1. Emission and excitation spectra of Ce^{3+} doped CaS and Pr^{3+} doped CaS

Fig. 1. shows the relationship of additive/ Ca atomic ratio in CaS and lattice constant. The lattice constant of $\text{CaS}:\text{Ce}^{3+}$ was observed to increase linearly to 0.5708 nm because the ionic radius of Ce^{3+} is larger than that of Ca^{2+} . At atomic ratios larger than this, the lattice constant had a fixed value. The upper limit of incorporation of Ce^{3+} in a host was determined to be a Ce/Ca atomic ratio 1.34×10^{-3} . The lattice constant of $\text{CaS}:\text{Pr}^{3+}$, however, increased with the increase in the Pr/Ca atomic ratio because ionic radius the Pr^{3+} ion was larger than that of the Ca^{2+} ion. The upper limit of incorporation for Pr^{3+} in a host was not determined in this atomic ratio range.

The emission and excitation spectra of $\text{CaS}:\text{Ce}^{3+}$ are shown in Fig. 2. The excitation spectrum of Ce^{3+} shows three bands. One excita-

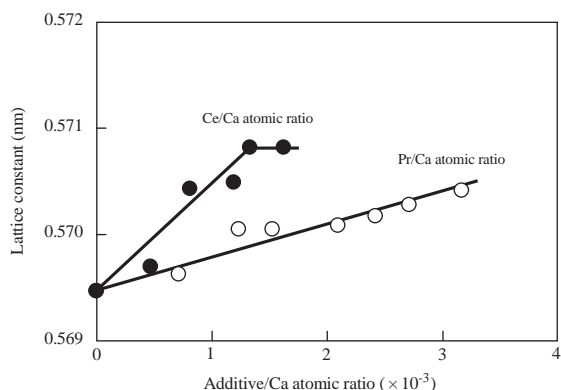


Fig. 1. Effect of additive on lattice constant of $\text{CaS}:\text{Ce}^{3+}$ and $\text{CaS}:\text{Pr}^{3+}$.

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