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Effect of initial Eu/Ca atomic ratio on the afterglow properties of red-emitting CaS:Eu²⁺, Pr³⁺ phosphors

Kentarou Mori, Yoshiyuki Kojima* and Nobuyuki Nishimiya

Department of Materials and Applied Chemistry, Faculty of Science and Technology, Nihon University, Tokyo 101-8308, Japan

The afterglow time of typical red-emitting phosphors is much shorter than those of green- or blue-emitting phosphors which afterglow time were longer than 1000 min. This study reports on the effect of initial Eu/Ca atomic ratio on the afterglow properties of a red-emitting CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor. The resulting phosphor exhibited red-emission at 645 nm originating from Eu^{2+} ions upon visible light irradiation, and gave some afterglow after visible light irradiation. The afterglow time was affected by initial Eu/Ca atomic ratio. Trap depth of TL peak was calculated from Hoogenstraaten method. The afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor was changed by the 1st trap depth change due to initial Eu/Ca atomic ratio.

Key words : Red afterglow, Calcium sulfide, Visible light, Thermoluminescence, Trap depth.

Introduction

Fluorescence implies light emission during excitation, while light emission that persists after the cessation of excitation is called afterglow. In addition, some materials can emit light upon heating, in a process called thermoluminescence. in this process, energy stored in socalled 'deep traps' or 'trapping centers'. after previous light irradiation of a material is reemitted upon heating due to the recombination of electron and holes thermally reactivated from the deep traps.

Blue- and green-emitting long-afterglow phosphors have been synthesized by addition of ions such as Eu²⁺ and Dy^{3+} to strontium aluminate [1-3] and calcium aluminate [4, 5]. It is possible to produce multiple luminescent colors by mixing phosphors that emit in the red, green, and blue. However, the afterglow time of red-emitting phosphors is extremely short as compared with that of green- or blue-emitting phosphors. CaS has often been studied as a host material for afterglow phosphors because trapping centers can be easily created in the host by doping with an activator, and the resulting phosphors exhibit a long afterglow. For example, for CaS:Bi3+ prepared at 900 °C [6], a long afterglow is observed after irradiation with visible light. In addition, the red-emitting CaS:Eu²⁺,Pr³⁺ phosphor, when prepared with incorporated Li⁺ ions, has been found to exhibit desirable afterglow and thermoluminescence (TL) properties upon visible light irradiation [7].

This paper reports about the effect of initial Eu/Ca atomic ratio on the afterglow properties of a redemitting CaS:Eu²⁺,Pr³⁺ phosphor with Li⁺ incorporated after visible light irradiation.

Experimental procedure

The material used for the synthesis were 95% CaCl₂, 99.5% $(NH_4)_2SO_4$, 99.95% EuCl₃ · 6H₂O and 99.95% PrCl₃ · 7H₂O. All the regents were obtained from Kanto Kagaku Co., Ltd. (Japan) and were high grade.

Appropriate quantities of EuCl₃ and PrCl₃ solutions were added to a 0.2 mol/dm³ CaCl₂ solution to obtain initial Eu/Ca and Pr/Ca atomic ratios of $0-8.0 \times 10^{-4}$ and 1.2×10^{-2} , respectively. The mixed solution was stirred for 30 min. $(NH_4)_2SO_4$ was then added with the same concentration as CaCl₂ (0.2 mol/dm³) and the mixed solution was stirred for 1 h. The final Eu³⁺, Pr³⁺ codoped gypsum dehydrate was obtained by filtering the resulting suspension, and the Eu³⁺,Pr³⁺ codoped calcium sulfate anhydrite was obtained by dehydration at 400 °C for 2 h. For the experiments involving the addition of Li^+ ions, the product was mixed with lithium carbonate to yield II-anhydride with Li/Ca atomic ratio of 0.04. The materials obtained were pressurized at 60 MPa for a few minutes to form a compact and the Eu²⁺, Pr³⁺ codoped CaS phosphor was formed by heating the tablet in H₂S atmosphere at 1050 °C for 0.5 h and in Ar-H₂ atmosphere at 1050 °C for 1.5 h.

The final sample was characterized by X-ray diffraction. The fluorescence properties of the sample were measured using a Hitachi F-4500 spectrophotometer and a Topcon BM-50 luminance meter. The afterglow time is defined as the time for the luminance to reach 0.32 mcd/m^2 which human eyes can see the lowest luminance after cessation of the visible light irradiation for 5 min. All measurements were performed at room temperature. TL measurements of the phosphor with luminance

^{*}Corresponding author:

Tel:+81-3-3259-0868

Fax: +81-3-3293-7572

E-mail: cskt10001@g.nihon-u.ac.jp



Fig. 1. X-ray diffraction patterns of the CaS:Li⁺,Eu²⁺,Pr³⁺ phosphors with changed initial Eu/Ca atomic ratio.



Fig. 2. Effect of initial Eu/Ca atomic ratio on excitation and emission spectra of the CaS: Li^+ , Eu^{2+} , Pr^{3+} phosphor.

meter were carried out by placing it in a tubular furnace. A heating rate of 15-35 °C/min was used and the TL was measured up to 400 °C.

Results and discussion

Fig. 1 shows X-ray diffraction patterns of the CaS:Li⁺,Eu²⁺,Pr³⁺ phosphors with changed initial Eu/Ca atomic ratio. The monophase of CaS was prepared by reducing CaSO₄ under H₂S atmosphere at 1050 °C for 0.5 h followed by Ar-H₂ reducing atmosphere at 1050 °C for 1.5 h. The lattice constant of CaS was hardly changed by initial Eu/Ca atomic ratio increasing (not shown). This result observations imply that crystal structural of CaS was hardly affected by Eu²⁺ ion into matrix crystal.

Fig. 2 shows effect of initial Eu/Ca atomic ratio on excitation and emission spectra of the CaS:Li⁺,Eu²⁺, Pr³⁺ phosphor. The excitation spectra were obtained by monitoring the emission at 645 nm. Excitation spectra were broad bands in the visible light region of 400-600 nm on all samples. Upon visible light irradiation, red emission of 645 nm originating from the 4f⁶5d¹ \rightarrow 4f⁷ transition of the Eu²⁺ ion was observed on all samples. Therefore, Eu²⁺ ion took a part of emission center in the CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor. And the emission intensity increased with the increase of initial



Fig. 3. Effect of Eu/Ca atomic ratio on the afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor and the photograph of red afterglow of the phosphor in the dark room after visible light irradiation.



Fig. 4. Effect of initial Eu/Ca atomic ratio on the TL glow curve of $CaS:Li^+$, Eu^{2+} , Pr^{3+} phosphor.

Eu/Ca atomic ratio. This result indicates that fluorescence properties were affected by initial Eu/Ca atomic ratio.

Fig. 3 shows effect of Eu/Ca atomic ratio on the afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor and the photograph of red afterglow in the dark room after visible light irradiation. A red afterglow was observed in all phosphors after visible light irradiation, like photograph. The afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor was over 60 min under less than the initial Eu/Ca atomic ratio of 5×10^{-4} . But the afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor shortened with the increase initial Eu/Ca atomic ratio. This result indicates that the afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor shortened with the increase initial Eu/Ca atomic ratio. This result indicates that the afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor was affected by initial Eu/Ca atomic ratio. Therefore, it was indicated that the trap of which the afterglow phenomenon was caused by present in phosphors was affected by initial Eu/Ca atomic ratio.

Fig. 4 shows effect of initial Eu/Ca atomic ratio on the TL glow curve of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor. A peak at about 140 °C and a shoulder at about 240 °C were observed from the TL glow curve. However, the TL luminance decreased on initial Eu/Ca atomic ratio more than 2×10^{-4} . This result indicated that the trap of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor was affected by a little change of initial Eu/Ca atomic ratio.

Fig. 5 shows effect of heating ratio on the TL curve of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor. The TL luminance of



Fig. 5. Effect of heating ratio on the TL glow curve of $CaS:Li^+,Eu^{2+},Pr^{3+}$ phosphor.



Fig. 6. Effect of initial Eu/Ca atomic ratio on the 1st and 2nd trap depth CaS:Li⁺, Eu^{2+} , Pr^{3+} phosphor.



Fig. 7. Effect of the 1st trap depth of peak on the afterglow time of $CaS:Li^+, Eu^{2+}, Pr^{3+}$ phosphor.

the phosphor increased with the increase heating ratio. And, the temperature of the peak increased. The trap depth was measured by the Hoogenstraaten method, which relates the TL peak temperature and heating rate [8]. The trap depth was determined using the following equation:

$$\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{\varepsilon}{k \cdot T_m} + \ln\left(\frac{s \cdot k}{\varepsilon}\right) \tag{1}$$

where β is the heating ratio, T_m is the temperature of the peak, ε is trap depth, k is the Bóltzmann constant, and s is a frequency factor.

And, trap of a peak at about 140 °C and a shoulder at

about 240 °C were named 1st trap and 2nd trap, respectively.

Fig. 6 shows effect of initial Eu/Ca atomic ratio on the 1st and 2nd trap depth of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor. The 1st trap depth which was considered to involve in afterglow time was showed. The 1st trap depth became deep with the increase initial Eu/Ca atomic ratio. But the 2nd trap depth was not linearly with the increase initial Eu/Ca atomic ratio. This result was indicated that the 1st trap depth was involved in afterglow time.

Fig. 7 shows effect of the 1st trap depth on the afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor. The afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor shortened with the 1st trap depth. This result was indicated that the afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor was longer, under shallower the 1st trap depth.

Conclusions

In the present work, to lengthen the afterglow time of the red-emitting CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor, we investigated the effect of initial Eu/Ca atomic ratio on the afterglow properties of resulting phosphor. Various phosphors were prepared by reduction under H₂S and Ar-H₂ (5%) atmosphere from CaSO₄:Li⁺,Eu²⁺,Pr³⁺.

The following results were obtained:

• Eu^{2+} ion took a part of emission center in the CaS:Li⁺, Eu^{2+} , Pr^{3+} phosphor. And emission intensity was increased with the increase of Eu/Ca atomic ratio.

• Red afterglow was observed in the phosphor after visible light irradiation. And less than 5×10^{-4} initial Eu/Ca atomic ratio, afterglow time was about 60 min.

• Trap depth of TL peak calculated from the Hoogenstraaten method was affected by initial Eu/Ca atomic ratio. And the 1st trap depth of TL peak was involved in the afterglow time of CaS:Li⁺,Eu²⁺,Pr³⁺ phosphor.

• The afterglow time of CaS: Li^+ , Eu^{2+} , Pr^{3+} phosphor was changed by the 1st trap depth change due to initial Eu/Ca atomic ratio.

References

- T. Katsuyama, K. Sasajima, T. Komuro, and T. Morikawa, J. Am. Ceram. Soc. 81 [2] (1998) 413-416.
- 2. I.C. Chen, and T.M. Chen, J. Mater. Res. 16 (2001) 644-651.
- M. Ohta, M. Maruyama, Y. Hayakawa, and T. Saijo, J. Ceram. Soc. Japan 108 (2000) 284.
- 4. Y. Lin, Z. Tang, Z. Zhang, and C. Nam, J. Eur. Ceram. Soc. 23 [1] (2003) 175-178.
- T. Aitasalo, J. Hoelsae, M. Lastusaari, and J. Niittykoski, J. Alloys. Compounds 380 (2004) 4-8.
- Y. Kojima, K. Kawagishi, and T. Yasue, J. Soc. Inorg. Mater. Japan 9 (2002) 30-37.
- 7. Y. Kojima, K. Aoyagi, and T. Yasue, J. Lumin. 126 (2007) 319-322.
- Y. Kojima, K. Aoyagi, and T. Yasue, J. Soc. Inorg. Mater. Japan 13 (2006) 228-233.