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Luminescent properties of a new long afterglow Eu^{2+} and Dy^{3+} activated $Ca_3MgSi_2O_8$ phosphor

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Abstract

Long afterglow $Ca_3MgSi_2O_8$:Eu,Dy phosphor with high brightness and long afterglow was firstly prepared at high temperature and weak reductive atmosphere. The excitation and emission spectra of this phosphor showed that both of them are broad band, and the main emission peaking at 475.5 nm is due to 4f–5d transitions of Eu^{2+}, which is in good agreement with the calculated value 467.7 nm with the relation $E=Q[1-(V/4)^{1/V}10^{-(n.ea.r)/8}]$, and implied that luminescent centers Eu^{2+} occupied the octa-coordinated Ca^{2+} sites in the $Ca_3MgSi_2O_8$ host. The decay graph indicated that this phosphor also contains fast-decay and slow-decay process, which can last over 5 h in the limit of the light perception of the dark-adapted human eye (0.32 mcd/m^2). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Afterglow; $Ca_3MgSi_2O_8$; Luminescence; Phosphor

1. Introduction

It is generally agreed that the phosphorescence of Eu^{2+} in most of hosts is believed to be caused by the 4f–5d transitions, and the peak positions in the emission spectra depend strongly on the nature of the Eu^{2+} surroundings in host lattices. Alkaline earth silicates are useful luminescent hosts with stable crystal structure and high physical and chemical stability,[1,2] and, therefore, a great deal of work has been done on rare earth ion activation of these hosts. Barry prepared $Ca_3MgSi_2O_8$:Eu phosphor by prefiring at 600°C in air employed NH_4Cl as a flux, and then firing at 1200°C for 4 h in an atmosphere of four parts nitrogen to one part hydrogen, and found that the main emission peaks at room temperature were located at 475 nm.[3] Huang et al. prepared $Ca_3MgSi_2O_8$:Ce phosphor, and found that two kinds of emission centers existed in the host.[4] However, the long afterglow was not observed in these phosphors.

In this study, a new blue-emitting long afterglow $Ca_3MgSi_2O_8$:Eu,Dy (CMS-ED) phosphor was firstly synthesized, which is different from the long afterglow aluminate-based phosphor. The preparation conditions and the effect of Dy/Eu (molar ratio) on the luminescence properties of CMS-ED phosphor have been investigated.

2. Experimental procedure

$CaCO_3$, $4MgCO_3.Mg(OH)_2.5H_2O$, SiO_2, Eu_2O_3, Dy_2O_3 were employed as the raw materials (these materials are all analytical grade). Small quantities of H_3BO_3 (about 5 m/o per mol of one silicate) were added as a flux. The raw materials were mixed homogeneously by the ball mill for 6 h, and a new long afterglow blue-emitting CMS-ED photoluminescent phosphor was prepared at 1200°C for 3 h and weak reductive atmosphere of flowing 5%H_2–95%N_2 gas, and its phase composition and optical properties were fully characterized.

The prepared phosphor powders were analyzed by X-ray Diffraction (XRD) using CuK_α radiation at 40 kV and

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100 mA to analyze the phases of the crystalline products. A Hitachi 850 Fluorescence Spectrophotometer was utilized to detect the excitation and emission spectra of products. The decay curve of afterglow was measured by the ST-86LA brightness meter, and the powder samples were irradiated by the 1000LX D_{65} standard lamp for 5 min. All measurements were carried out at room temperature, and the relative data were collected on a PC using a program written by ourselves.

3. Results and discussion

The typical XRD pattern of CMS-ED sample sintered at 1200°C for 3 h and weak reductive atmosphere is shown in Fig. 1, which indicates that the co-doped Eu and Dy ions have little influence on the structure of luminescent materials, and all of the peaks are assigned to the phase of $Ca_3MgSi_2O_8$.

The doped Eu^{2+} ions in CMS host give rise to a blue emission under UV excitation. Fig. 2 shows the excitation and emission spectra of CMS-ED at room temperature. The results illustrate that two broad excitation bands centered at 364 and 391 nm are observed. The main emission peaking at 475.5 nm is viewed as the typical emission of Eu^{2+} ascribed to the 4f–5 d transitions. However, no special emission peaks of Eu^{3+} are observed in the spectra, which proved that Eu^{3+} in the matrix crystals have been reduced as Eu^{2+} completely. The special Dy^{3+} emission peak is also not present, which may be ascribed to the function of hole or electron traps and energy transporting for Dy^{3+} and not as the luminescent centers in the CMS-ED host crystal lattice.

As previously reported,[5] the position in energy for the lower d-band edge for Eu^{2+} or Ce^{3+} in various compounds can be calculated as the following empirical relation:

$$E = Q[1 - (V/4)^{1/V} 10^{-(n.ea.r)/8}] \tag{1}$$

which can provide a good fit to the emission peak and/or excitation edge data for Eu^{2+}. Where Q is the position in energy for the lower d-band edge for the free ion, here Q is 34 000 cm^{-1} for Eu^{2+}. V is the valence of the active cation, here V is 2. n is the number of anions in the immediate shell about this ion, and ea is the electron affinity of the atoms that form anions — here ea is 2.5 ev. r is the radius of the host cation replaced by the active cation in host crystal. In CMS crystal structure, there are two kinds of coordination number for Ca^{2+} (8 and 9), and so the corresponding r is 0.112 nm ($n=8$) and 0.118 nm ($n=9$), respectively. And r is 0.065 nm for Mg^{2+} with the coordination number 6.[6]

Using the above-mentioned Eq. (1), the calculated values of position in energy of the lower d-band edge for Eu^{2+} occupying different crystallographic sites are given in Table 1. As can be seen, when the coordination number of Ca^{2+} is 8, the calculated emission peak is 467.7 nm and good accord with the observed value 475.5 nm. The calculated emission peaks at 438.5 and 631.3 nm are not observed in the emission spectra, which demonstrates that the Eu^{2+} ions probably occupy the octa-coordinated Ca^{2+} sites in the CMS host.

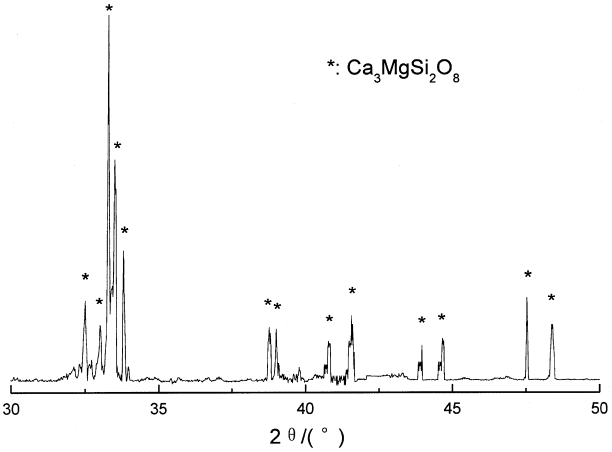

Fig. 1. The XRD patterns of CMS-ED phosphor.

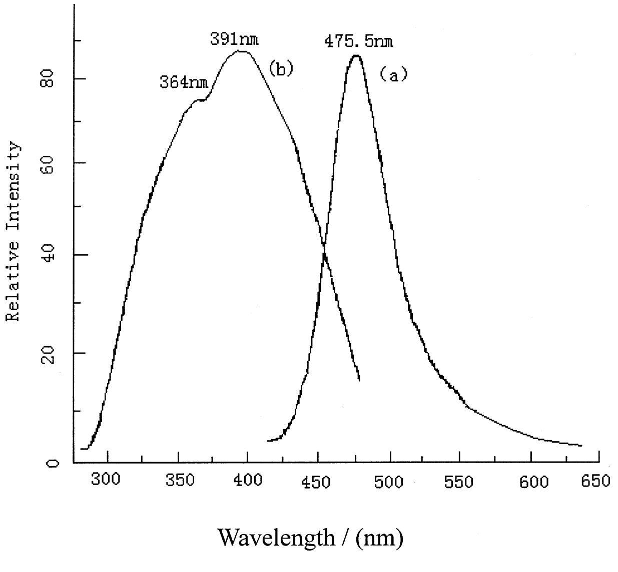

Fig. 2. The excitation and emission spectra of CMS-ED phosphor: (a) emission spectra; (b) excitation spectra.

Table 1
The calculated values of position in energy of the lower d-band edge for Eu^{2+} occupying different crystallographic sites

n	r (nm)	Energy (cm^{-1})	Emitting wavelength (nm)
6	0.065	15 841.3	631.3
8	0.112	21 382.9	467.7
9	0.118	22 803.4	438.5

In addition, according to the crystal structure of CMS, because the radius of Eu^{2+} is 0.112 nm and equal to that of Ca^{2+}($n = 8$), the Eu^{2+} may be preferably occupied the Ca^{2+} sites ($n = 8$), but not the Mg^{2+} sites.

The luminescent decay curves of different phosphors co-doped with various amount of Dy^{3+} under excitated by the 1000LX D_{65} standard lamp for 5 min at room temperature shown in Fig. 3 imply that all of them show a rapid decay and then a long-lasting phosphorescence. The intensity of Eu^{2+} emission at 475.5 nm increase with increasing Dy^{3+} content slightly at fixed Eu^{2+} content (0.05 mol) in CMS-ED phosphor. But when the value of Dy/Eu is over 3/1, the luminescent intensity decreases slowly, which may be ascribed to concentration quenching and decrease the luminescence effect. The initial intensity of nominal composition of $Ca_3MgSi_2O_8:Eu_{0.05},Dy_{0.15}$ phosphor powder reaches about 1200 mcd/m^2, and its afterglow intensity is 1.07 mcd/m^2 after removed of the excitation source about 5 h as shown in Fig. 4, and, therefore, the duration can reach over 5 h in the limit of the light perception of the dark-adapted human eye (0.32 mcd/m^2).

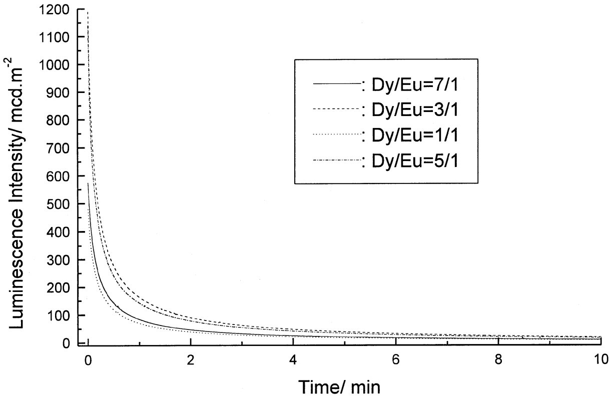

Fig. 3. The decay curves of phosphors co-doped at various Dy/Eu ratios in CMS host.

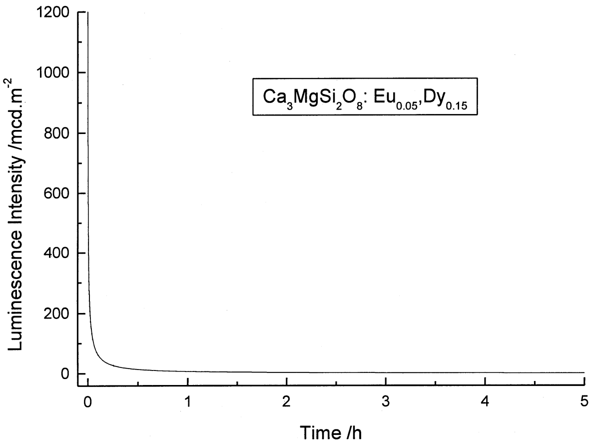

Fig. 4. The typical decay curve of $Ca_3MgSi_2O_8:Eu_{0.05},Dy_{0.15}$ phosphor.

As for the mechanism of the long afterglow of CMS-ED phosphor, the co-doped Dy^{3+} may be played an important role in prolonging the duration. In the previous reports about strontium aluminate phosphors (e.g. $SrAl_2O_4$:Eu,Dy),[7] researchers thought that the co-doped Dy^{3+} are worked as the hole trap levels and prolonged the afterglow, and, thus, in the CMS-ED host, we think the Dy^{3+} may be also acted as the role of trap levels, which captured the free holes, released the trapped holes and recombined with electrons accompanying with the luminescence, and the relative work is processing.

4. Conclusions

A new blue-emitting long afterglow $Ca_3MgSi_2O_8$:Eu,Dy photoluminescent phosphor was prepared by firstly heating at 1200°C for 3 h in a weak reductive atmosphere of flowing 5%H_2–95%N_2 gas. This made a phosphor whose initial intensity reaches about 1200 mcd/m^2, and the afterglow time can last over 5 h in the limit of the light perception of the dark-adapted human eye. The emission spectra and the calculated value of position in energy of the lower d-band edge for Eu^{2+} indicate that there is only one kind of Eu^{2+} emission center occupied in the octa-coordinated Ca^{2+} crystallographic sites in the $Ca_3MgSi_2O_8$ host.

Acknowledgements

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