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A new method to synthesize long afterglow red phosphor

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Abstract

Long afterglow phosphor Y_2O_2S:Gd,Eu,Ti,Mg was synthesized by a gas absorption method and the effect of Ti^{4+} and Mg^{2+} ions doping on the luminescent properties was also investigated. Single phase Y_2O_2S can be obtained by calcining the oxide mixture in a graphite crucible absorbed with sulfur. Ti^{4+} and Mg^{2+} ions decrease the luminescent intensity of the phosphor, but either Ti^{4+} or Mg^{2+} ion doping results in red long afterglow. A strong thermoluminescence peak appears when codoping Ti^{4+} and Mg^{2+} ions in the phosphor.

Keywords: A. Calcination; C. Optical properties; E. Functional applications; Phosphor

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1. Introduction

In recent years, the wide application in safety indication, emergency lighting, automobile instrument, luminous paint and optical data storage of long afterglow phosphors resulted in increased research in the field. Although efficient green and blue long afterglow phosphors have been investigated in detail, the progress on red phosphor is very slow [1–4].

The long afterglow red phosphor based on sulfide is very efficient and has about 180 min afterglow; nevertheless it is extremely sensitive to moisture and thus chemically unstable [5]. $CaTiO_3:Pr^{3+}$, $BaTiO_3:Pr^{3+}$ and $BaTiO_3:Cr^{3+}$ are very stable, but have only a few minutes afterglow [6]. $MO:Eu^{3+}$(M = Ca, Sr, Ba) phosphors with a afterglow of 120 min are not an ideal choice, because alkaline earth oxide is not very stable [7]. Yttrium oxysulfide doped with europium ($Y_2O_2S:Eu^{3+}$) red phosphor is a highly efficient material that is used extensively in display devices [8,9]. Recently, the long afterglow phenomenon found in $Y_2O_2S:Gd^{3+}$,Eu^{3+} doped with Ti^{4+} an Mg^{2+} ions has attracted attention on this material [10].

The fabrication of $Y_2O_2S:Eu^{3+}$ is not an easy task. In all the synthesis methods, there exits a common disadvantage: escape of harmful gas and polluting of the vessel [11,12].

In this paper, a new method of synthesizing Y_2O_2S:Gd,Eu,Ti,Mg phosphor which is called the gas absorption method was presented. Single phase Y_2O_2S was obtained without any output of polluting products. The effect of Ti^{4+} and Mg^{2+} ions doping on the luminescent properties was also investigated.

2. Experimental

Y_2O_2S:Eu,Gd,Ti,Mg phosphor was prepared by a gas absorption method. Firstly, sulfur was calcined in a graphite crucible sealed up with graphite powder to make the crucible absorb sulfur until no remains were left. Then starting materials of Y_2O_3, Eu_2O_3, Gd_2O_3, TiO_2 and MgO were intimately ground to a homogeneous mixture by a ball mill, and the mixture was calcined in the same graphite crucible that had absorbed sulfur to obtain long afterglow red phosphor, using H_3BO_3 as a flux. The so-obtained phosphor powder was washed with water to remove the residual flux.

RigakuD/MaxIIIB XRD diffraction meter was employed to check the crystal structure of the phosphor

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powder using CuK_α radiation. Excitation and emission spectra at room temperature were recorded with a Hitachi 850 fluorescence spectrometer, and the spectra were corrected using sodium salicylate. The decay curve of the afterglow was measured by the ST-86LA brightness meter connected with the data collection system. After the initial luminescence had been relaxed, the thermoluminescence glow curve was obtained by recording the decay curve as the phosphor was heated in a furnace from room temperature to 130 °C.

3. Results and discussion

After sulfur was calcined in the graphite crucible at 1300 °C for about 3 h, there were no remains left, indicating that all the sulfur was absorbed by the graphite crucible. Then the mixture of the oxide powder was calcined in the same crucible, and a white phosphor powder was obtained. The XRD patterns of the phosphor obtained by calcining the starting materials at 1300 °C for 3 h are revealed in Fig. 1, showing all the prominent lines corresponding to Y_2O_2S. No secondary phases or impurities were found when the dopants concentration changed. When another batch of starting material was calcined in the same crucible, single phase Y_2O_2S can also be obtained and the same crucible can be used for a few times before needing to absorb sulfur again.

The overall reaction for the forming process of Y_2O_2S:Gd,Eu,Ti,Mg can be presented as two-step reactions.

Firstly, sulfur was absorbed by the graphite curable:

$$C + S \rightarrow CS_2 \tag{1}$$

Then the oxide powder was sulfurated when calcined in the same curable:

$$Y_2O_3 + Gd_2O_3 + Eu_2O_3 + TiO_2 + MgO + CS_2 \rightarrow Y_2O_2S : Gd, Eu, Ti, Mg + CO_2 \tag{2}$$

In the preparation process, no polluting gas escaped. This new gas absorption method as a clean and energy-saving means has potential to be used in synthesizing efficient phosphors based on oxysulfide.

The excitation and emission spectra of Y_2O_2S:Gd,Eu doping with Ti^{4+} or Mg^{2+} ion and codoping with Ti^{4+} and Mg^{2+} ions are indicated in Figs. 2 and 3. For all three, the excitation spectrum is a wide band with two peaks at about 263 and 310 nm attributing to CTS (charge transfer state) transition. The one at 263 nm corresponds to Eu-O CTS, and that at 310 nm to Eu-S CTS. The emission spectrum under Eu-O CTS or Eu-S CTS excitation indicates typical emission of Eu^{3+} ion. The strong red-emission lines at 626 and 614 nm due to transition from $^5D_0$ to $^7F_2$ level of Eu^{3+} ion result in red emission. Either Ti^{4+} or Mg^{2+} ion does not change the shape of excitation and emission spectra dramatically, but both of them decrease the luminescent intensity more or less.

When excitation lights are cut off, the Y_2O_2S:Gd,Eu phosphor prepared by this method shows no long afterglow, but those doped with either Ti^{4+} or Mg^{2+} ion show very bright red afterglow and the longest can last for more than 2 h. Figs. 4 and 5 illustrate the effect of Ti^{4+} and Mg^{2+} ions doping on the afterglow of the phosphor. From the decay curves, it can be seen that doping both Ti^{4+} and Mg^{2+} ions can result in long afterglow of the Y_2O_2S:Gd,Eu phosphor. When the concentration of Ti^{4+} ion is fixed, the initial brightness and afterglow increase with the increase of Mg^{2+} ion concentration. If the concentration of Mg^{2+} ion is fixed, small amount of Ti^{4+} ion can increase the initial

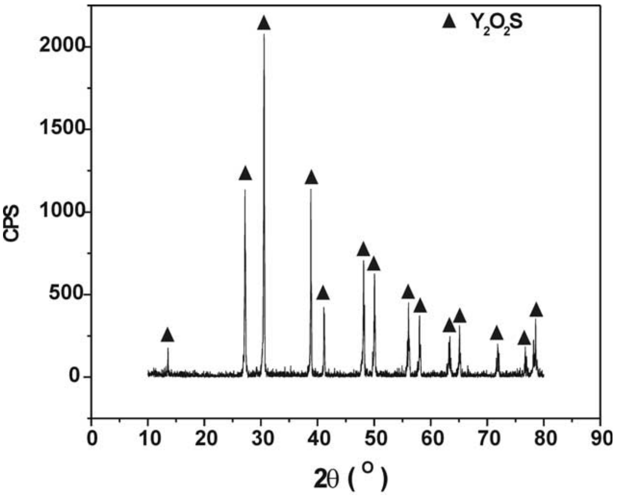

Fig. 1. XRD patterns of Y_2O_2S:Eu,Gd,Ti,Mg phosphors.

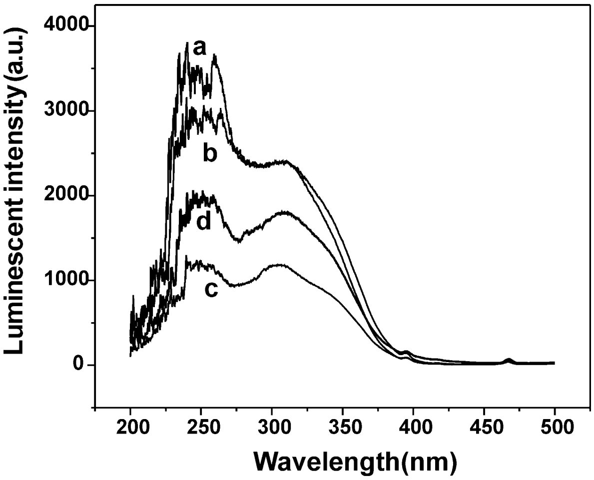

Fig. 2. Excitation spectra of phosphors by monitoring 627 nm emission: (a) Y_2O_2S:Eu,Gd, (b) Y_2O_2S:Eu,Gd,Mg, (c) Y_2O_2S:Eu,Gd,Ti, (d) Y_2O_2S:Eu,Gd,Ti,Mg.

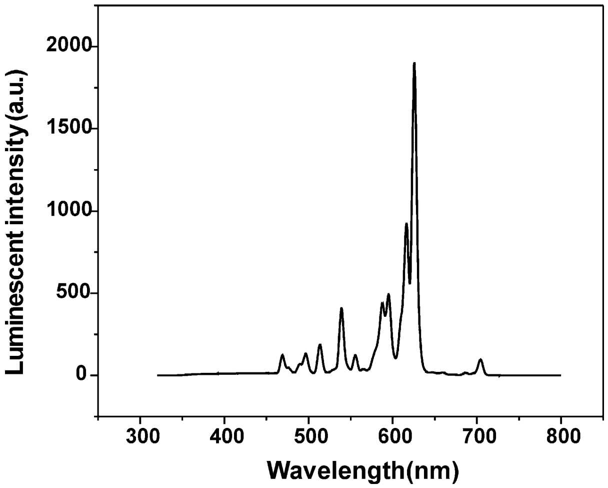

Fig. 3. Emission spectrum of Y_2O_2S:Eu,Gd,Ti,Mg phosphor.

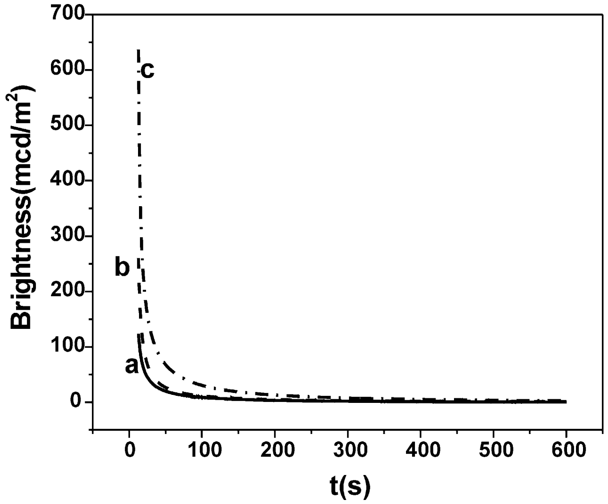

Fig. 4. Decay curves of the phosphors doped with different Mg^{2+} concentration: (a) $Y_2O_2S:Eu_{0.05},Gd_{0.2},Ti_{0.02}$, (b) $Y_2O_2S:Eu_{0.05},Gd_{0.2},Ti_{0.02},Mg_{0.02}$, (C) $Y_2O_2S:Eu_{0.05},Gd_{0.2},Ti_{0.02},Mg_{0.1}$.

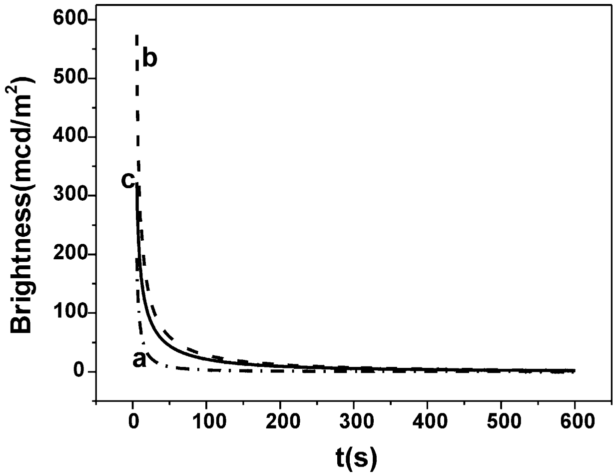

Fig. 5. Decay curves of the phosphors doped with different Ti^{4+} concentration. (a) $Y_2O_2S:Eu_{0.05},Gd_{0.2},Mg_{0.09}$, (b) $Y_2O_2S:Eu_{0.05},Gd_{0.2},Ti_{0.01},Mg_{0.09}$, (c) $Y_2O_2S:Eu_{0.05},Gd_{0.2},Ti_{0.04},Mg_{0.09}$.

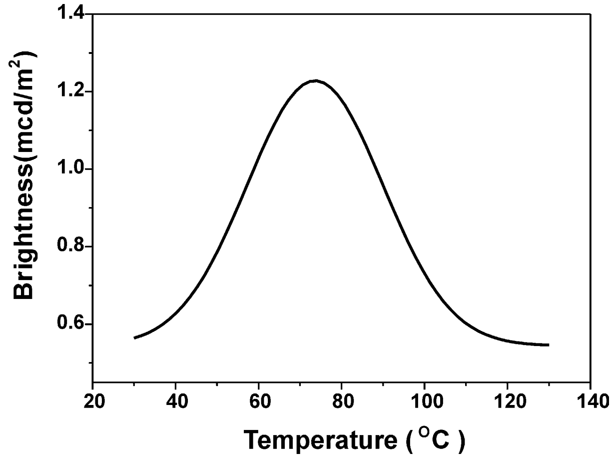

Fig. 6. Thermoluminescence curve of $Y_2O_2S:Eu_{0.05},Gd_{0.2},Ti_{0.02},Mg_{0.02}$ phosphor.

brightness and afterglow, and a maximum is reached at a Ti^{4+} ion concentration of 0.01. Too large amount of Ti^{4+} ion results in the decrease of the initial brightness and afterglow.

In order to investigate the mechanism of long afterglow phosphor, the thermoluminescence glow curve is often measured. In the experimental process, we found that, when either Ti^{4+} or Mg^{2+} ion was doped in the phosphor, weak thermoluminescence can be observed. Whereas, when codoping with Ti^{4+} and Mg^{2+} ions, a wide strong glow peak was found between 40 and 100 °C, with the maximum at 73.6 °C as indicated in Fig. 6. The existence of thermoluminescence indicates that when codoping Ti^{4+} and Mg^{2+} ion, electron or hole traps form in the phosphor. The depth of the traps was calculated as 0.47 eV. The trapping level of the traps is at a suitable depth, so that long afterglow appears.

4. Conclusion

Efficient long after glow red phosphor Y_2O_2S:Gd, Eu,Ti,Mg can be synthesized by a nonpolluting gas absorption method. The phosphor gives emission of Eu^{3+} ion, while doping Ti^{4+} or Mg^{2+} ion forms the long red afterglow. Thermoluminescence glow curve indicates that codoping Ti^{4+} and Mg^{2+} ions in the phosphor forms a trapping level at suitable depth.

Acknowledgements

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References

[1] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, New long phosphorescent phosphor with high brightness $SrAl_2O_4$: Eu^{2+}, Dy^{3+}, Journal of the Electrochemical Society 143 (1996) 2670–2673.

[2] M. Kamada, J. Murakami, N. Ohno, Excitation spectra of a long-persistent phosphor $SrAl_2O_4$:Eu, Dy in vacuum ultraviolet region, Journal of Luminescence 87–89 (2000) 1042–1044.

[3] Y.H. Lin, Z.T. Zhang, F. Zhang, Z.L. Tang, Preparation of the ultrafine $SrAl_2O_4$:Eu,Dy needle-like phosphor and its optical properties, Materials Chemistry and Physics 65 (2000) 103–106.

[4] W. Zhou, H.Y. Do, B. Gao, A.P. Wu, J.Y. Sun, Progress on study of non-radiative red long afterglow phosphor, Journal of Beijing Technology and Business University 19 (3) (2001) 5–8.

[5] D.D. Jia, L.H. Jiang, Y.L. Liu, A study on $Ca_xSr_{1\text{-}x}S$:Bi,Tm,Cu and CaS:Eu long persistence materials, Chinese Journal of Luminescence 4 (1998) 308–312.

[6] L.M. Liu, L.H. Zeng, S.X. Lian, J.H. Zhang, X.H. Mao, Synthesis and luminescence characteristics of $CaTiO_3$:Pr^{3+} phosphors, Hunan Nonferrous Metals 14 (5) (1998) 45–47.

[7] F. Jie, Orange and red emitting long-lasting phosphors MO:Eu^{3+} (M = Ca, Sr, Ba), Electrochemical and Solid-State Letters 3 (7) (2000) 350–351.

[8] Y.H. Tseng, B.S. Chiou, C.C. Peng, L. Ozawa, Spectral properties of Eu^{3+}-activated yttrium oxysulfide red phosphor, Thin Solids Films 330 (1998) 173–177.

[9] C.H. Lo, J.G. Duh, B.S. Chiou, C.C. Peng, L. Ozawa, Synthesis of Eu^{3+}-activated yttrium oxysulfide red phosphor by flux fusion method, Materials Chemistry and Physics 71 (2001) 179–189.

[10] China Patent 1308664.

[11] M. Koskenlinna, M. Leskela, L. Niinisto, Synthesis and luminescence properties of europium-activated yttrium oxysulfide phosphors, Journal of the Electrochemical Society 123 (1) (1976) 75–78.

[12] M. Pham-Thi, A. Morell, Process optimization and characterization of the red no-mill phosphor Y_2O_2S:Eu, Journal of the Electrochemical Society 138 (4) (1991) 1100–1103.