Scientific Reviews & Chemical Communications

Sci. Revs. Chem. Commun.: 2(3), 2012, 305-307
ISSN 2277-2669

SYNTHESIS AND LUMINESCENT PROPERTIES OF EUROPIUM DOPED CALCIUM SULFIDE

D. N. GAME*, B. K. KATORE[a], N. B. INGALE[b], S. K. OMANWAR[c]

Govrnment Polytechnic, AMRAVATI (M.S.) INDIA
[a]Dr. Panjabrao Deshmukh Polytechnic, AMRAVATI (M.S.) INDIA
[b]Prof. Ram Meghe Institute of Technology and Research, Badnera, AMRAVATI (M.S.) INDIA
[c]Department of Physics, Sant Gadge Baba Amravati University, AMRAVATI (M.S.) INDIA

(*Received : 01.03.2012; Revised : 19.03.2012; Accepted : 25.03.2012*)

ABSTRACT

Sulfide based luminescent materials have attracted a lot of attention for a wide range of photo-, cathodo- and electroluminescecent applications. Upon doping with Ce^{3+} and Eu^{2+}, the luminescence can be varied over the entire visible region by appropriately choosing the composition of sulfide host. The red photoluminescent phosphor CaS : Eu^{2+} is widely used in lamp industry and display technology. In this article its synthesis by co-precipitation method and carbo-thermal reduction method is described. Its photoluminescent properties are studied. The PL intensity of the phosphor synthesized by carbo-thermal reduction method is nearly twice that of by co-precipitation method .The PL spectra shows the intense red emission at (λ_{em}) 631 nm for λ_{ex} = 254 nm. In both the cases sub-micron size fine red powder is obtained.

Key words: Phosphor, Sulfide, Rare Earth, Europium, Photoluminescence, Co-precipitation, Carbo-thermal

INTRODUCTION

Sulfide based luminescent materials have attracted a lot of attention for a wide range of photo-, cathodo- and electroluminescecent applications. Upon doping with Ce^{3+} and Eu^{2+}, the luminescence can be varied over the entire visible region by appropriately choosing the composition of sulfide host. The luminescence of impurity doped, alkaline earth sulfides like MgS, CaS, SrS and BaS has been extensively studied in the past century. For instance the rare earth ions (broad band d-f emitters like Eu^{2+} and Ce^{3+}) are all known to luminescence in one or more of the above mentioned hosts[1]. The emission wavelength strongly depends on the synthesis conditions, suggesting the presence of multiple optically active centers[2,3]. Luminescence of CaS doped with Eu^{2+} shows peak emission wavelength of 663 nm at room temperature[4]. Sulfide phosphors could be the phosphors in future for color conversion for white LEDs.

EXPERIMENTAL

Synthesis of CaS : Eu^{2+} by co-precipitation method

All the starting chemicals used were of analytical reagent grade. Ca $(NO_3)_2.4H_2O$ (10 g, Loba Chem)

Available online at www.sadgurupublications.com
*Author for correspondence; E-mail: deorao.game@gmail.com

and 0.7 mole% Eu $(NO_3)_3.6H_2O$ (0.1332 g, 99.99%, IRE) were dissolved in 100 mL of double distilled water and stirred thoroughly to get clear solution of mixed nitrates. $Na_2S.9H_2O$ (10.241 g, Loba Chem) was dissolved in 100 mL of double distilled water. The solution was stirred and filtered to get greenish solution of sodium sulfide. Then the solution of sodium sulfide was added drop-wise to the solution of calcium nitrate and europium nitrate. The white precipitate of europium doped calcium sulfide was obtained. The chemical reaction is-

$$0.993Ca\ (NO_3)_2.4H_2O + 0.007Eu\ (NO_3)_3.6H_2O + Na_2S.9H_2O \rightarrow Ca_{0.993}S : Eu^{2+}_{0.007}\downarrow + 2NaNO_3$$

The ppt. was filtered, washed and oven dried at 40°C. The dried ppt. was then fired in a slightly reducing atmosphere (in order to avoid the formation of sulfate) at 700°C for 2 h. The red color powder of CaS : Eu^{2+} phosphor was thus obtained.

Carbo-thermal reduction method

$CaSO_4$: Eu^{2+} was first synthesized by the co-precipitation method by reacting $Ca(NO_3)_2.4H_2O$ (10 gm, Loba Chem) and 0.7 mole% Eu $(NO_3)_3.6H_2O$ (0.1332 g, 99.99%, IRE) with dilute sulfuric acid. The chemical reactions are-

$$0.993Ca(NO_3)_2.4H_2O + 0.007\ Eu\ (NO_3)_3.6H_2O + H_2SO_4 \rightarrow Ca_{0.993}SO_4 : Eu^{2+}_{0.007}\downarrow + 5H_2O + 2NO_2\uparrow + O_2\uparrow$$

The precipitate was washed repeatedly by double distilled water and then dried slowly at 40°C. The dried $CaSO_4$: Eu^{2+} was heated in a closed assembly at 600°C for 2 h in reducing atmosphere in presence of charcoal and then allowed to cool slowly. The red color powder of CaS : Eu^{2+} phosphor was thus obtained.

$$Ca_{0.993}SO_4 : Eu^{2+}_{0.007} \rightarrow Ca_{0.993}S : Eu^{2+}_{0.007} + 2O_2\uparrow$$

RESULTS AND DISCUSSION

PL spectrum of CaS : Eu^{2+} is shown in figure. The curve (a) represents the PL excitation spectrum monitored at λ_{em} = 631 nm. The excitation spectrum of CaS : Eu^{2+} phosphor showed strong excitation bands centered at 318 nm, 458 nm, 507 nm and 534 nm. The band at 534 nm was sharp with highest intensity in the excitation spectrum. A very weak excitation band was also observed at 352 nm wavelength.

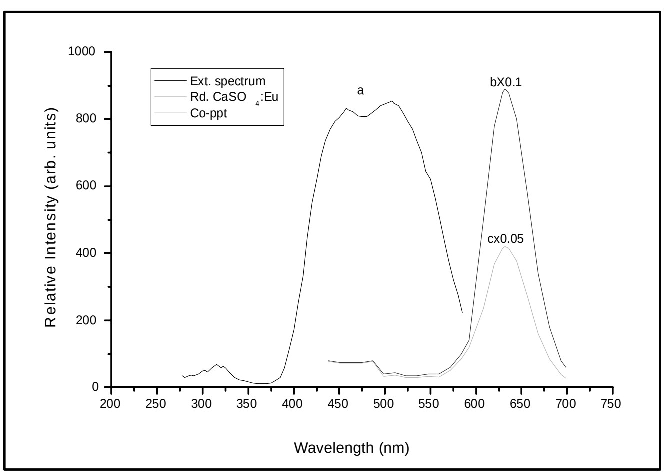

Fig. 1: PL spectrum of CaS : Eu^{2+} synthesized by two methods

(a) Excitation spectrum monitored at λ_{em} = 631 nm.

(b) Emission spectrum monitored at λ_{ex} = 254 nm.

The curve (b) represents the emission spectrum of CaS : Eu^{2+} phosphor monitored at λ_{ext} = 254 nm. An intense red emission corresponding to emission band peaking at 631 nm wavelength with FWHM of 55 nm was observed. Two very weak emission bands at 410 nm and 486 nm were also observed. The PL intensity for the sample prepared by carbo-thermal reduction method is much higher than in case of that one prepared by co-precipitation method.

CONCLUSION

The PL excitation and emission spectra of this CaS : Eu^{2+} phosphor prepared by co-precipitation method and carbo-thermal reduction method are in good agreement with those reported in the literature. From the above discussion the phosphor CaS : Eu^{2+} can be used in lamps industry and in the display technology.

ACKNOWLEDGEMENT

Author, DNG, is thankful to the Head of the Department of Physics, Sant Gadge Baba Amravati University, Amravati for providing all the research facilities and also to the Principal, Government Polytechnic, Amravati for constant encouragement and guidance.

REFERENCES

1. R. Pandey and S. Sivaraman, Spectroscopic Properties of Defects in Alkaline-Earth Sulfides, J. Phys. Chem. Solids, **52**, 211-225 (1991).
2. J. Rennie, K. Takeuchi, Y. Kaneko and T. Koda, Color Centers in Calcium Sulfide and Strontium Sulfide Single Crystals. J. Lumines., 48-49, 787-791 (1991).
3. A. N. Gruzintsev, V. T. Volkov and A. N. Pronin, Investigation of Lumiscence Centers of Unactivated CaS Films, J. Cryst. Growth, **117**, 975-978 (1992).
4. J. E. Van Haecke, P. F. Smet, K. De Keyser and D. Poelman, Single Crystal CaS : Eu and SrS : Eu luminescent Particles Obtained by Solvothermal Synthesis, J. Electrocem. Soc., **154**, J278-J282 (2007).