



Blue emitting Ce^{3+} doped SrS phosphor for solid state lighting

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Abstract - $\text{CaS}:\text{Ce}^{3+}$ is an efficient green emitting (535nm) phosphor, excitable with blue light (450-470nm) was synthesized via solid state reaction method heated under reducing atmosphere. The luminescent properties, PL excitation and emission, of phosphor were analyzed by spectrofluorophotometer. The excitation and emission peaks of $\text{CaS}:\text{Ce}^{3+}$ phosphor lies in the visible region which is good sign for LED application for the generation of white light. The Judd-oflet parameters were calculated. The result reveals that the emit green light upon blue illumination. The prepared phosphor has strong blue absorption at 470nm and broad green emission band range from 490-590nm peak at 537nm. The characteristics of $\text{CaS}:\text{Ce}^{3+}$ phosphor make them suitable for use as wavelength tunable green emitting phosphors for three band white LEDs pumped by a blue LED (470nm). The Commission International de l'Eclairage (CIE) co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution and (0.304, 0.526) confirm the green emission. The potential application of this phosphor is as pc-wLED.

Keywords: Photoluminescence, Phosphor, Solid state reaction method, pumped, cerium

1. INTRODUCTION

White Light emitting diode (W-LEDs) is one of the most efficient solid state lighting sources. Currently, for the generation of white light using LEDs can be achieved by different techniques. One is combining blue, green, and red LEDs, second one is by coating the three colour phosphors on a nUV LED chip and the third one is coating the green and red phosphors on a blue LED chip [1-3]. A blue LED (460 nm) in combination with Ce^{3+} doped yttrium aluminium garnet (YAG), a yellow emitting phosphor, is one of the best white light LED systems [4-7]. Light-emitting diodes (LEDs) are excellent candidates for general lighting because of their rapidly improving efficiency, durability, and reliability, their usability in products of various sizes and their environmentally friendly constituents. Although numerous phosphors have been proposed in the last decade, the range of phosphors that are suitable for LEDs are very much limited. Sulfide phosphors have attracted great attention recently because they are promising luminescent materials for phosphor-converted white light-emitting diodes (LEDs).

Sulfides have been used for a very long time as hosts in impurity-doped luminescent materials. The chemical stability of sulfides is rather limited; therefore, some precautions are needed when these

materials are used in practical applications. This disadvantage is often dwarfed by the huge advantages exhibited by this material class as a host for luminescent ions, especially rare earth ions. The wide spectrum of colors especially in the long wavelength range upon doping with divalent europium that can be obtained, the often broad range of preparation possibilities at relatively low temperature and cost and the high efficiency of some of these phosphors has resulted in there still being a lot of sulfide research being performed. Recently, protective coatings of luminescent particles were successfully applied to enhance the stability of these sulfide materials.

Alkali earth sulfide phosphors are good candidates for LED applications because all of them have strong absorption in the blue region that is suitable to blue LED pumping. During the last few decades many luminescence studies on alkaline earth sulfides doped with rare earth ions have been reported [8-11]. CaS, SrS, BaS and ZnS are wide-gap semiconductor materials and are commercially used as phosphors and also in thin film electroluminescent devices [12-16].

CaS has several applications when doped with Ce^{3+} . They form highly efficient green conversion material in LEDs due to their excitation and emission behavior, i.e. the emission spectrum of a

blue LED perfectly overlaps with the excitation to the lowest 5d state. The sulfide phosphors have the potential to be used in phosphor converted LED as a primary colour emitter in 3 band pc-LED phosphor converted white LED. However, synthesis of rare earth doped CaS particles using solid state method have received little attention and this research is mainly aimed at finding new phosphors, improving the efficiency of existing ones and using them for new applications.. It was therefore decided to synthesis the phosphor using the solid state reaction method.

In the present study, we investigated the optical properties of Ce doped CaS phosphor, synthesized by solid state reaction method heated at 950°C under reducing atmosphere, with focus on photoluminescence (PL) characteristics of phosphor converted coloured LEDs pumped by blue LEDs.

2. EXPERIMENTAL

2.1 Phosphors preparation: We have used solid state reaction method for synthesizing CaS:Ce³⁺. 3 gm of Calcium oxide (CaO) and 2 gm of Sulfur (S) were used as the starting materials for the host. Cerium oxide (CeO₂) was used as the activator and added with a specified doping concentration 0.125gm in CaS. Ammonium Fluoride (NH₄F) and added with a specified doping concentration 0.1 gm was used as a flux to decrease the calcination time and to enhance the luminescence intensity. The used chemicals were assay of 99.9%. The calculated quantities of ingredients were taken and mixed thoroughly with the help of an agate mortar and pestle. The powder was placed in a clean alumina crucible and a thin layer of carbon powder was spread over it. This crucible was covered with another similar crucible containing carbon. The carbon layer over the powder created a reducing environment. This whole arrangement was placed in a muffle furnace and the phosphors were heated to 950°C in 3h, and was kept at 950°C for 2h, then it was allowed to cool down to room temperature.

2.2 Characterisation Techniques: The phosphor was characterized by the photoluminescence excitation and emission spectra were measured at room temperature using a Spectrofluorophotometer (SHIMADZU, RF-5301 PC) with Xenon lamp as excitation source. The incident beam was perpendicular to the surface of the phosphor, and the observation angle was 45° relative to the excitation source. Emission and excitation spectra were recorded using a spectral slit width of 1.5nm. The Commission International de l'Eclairage (CIE) co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution.

3. RESULTS AND DISCUSSION

3.1 Physical properties

Fig.1 shows the photograph of the phosphor taken at room temperature under normal sunlight taken out from the furnace. The observed body colour is milky white and like a soft cake.



Figure 1 Photograph of the phosphor taken at room temperature under normal sunlight

3.2 Excitation study

The excitation spectrum of CaS:Ce³⁺ phosphor monitored under 537nm wavelength is shown in the fig.2. The excitation band at 470 nm is assigned to the 5d crystal field splitting levels, corresponding to T_{2g}. This 470nm excitation band is similar to the YAG:Ce³⁺ ⁴A₂ → ⁴T₂ excitation band. No further splitting of the T_{2g} peak was observed. This indicates that the site symmetry of Ce³⁺ in CaS remains close to O_h [2]. V.Kumar et. al. [8] observed two major absorption peaks at 225, 270 nm and a minor peak was observed at 460 nm. It is well known that the 5d excited configuration of the Ce³⁺ can be split by the crystal field into two five components namely E_g doublet and T_{2g} triplet, and the 4f ground configuration of Ce³⁺ can split into two levels (²F_{5/2} and ²F_{7/2}) due to spin-orbit coupling.

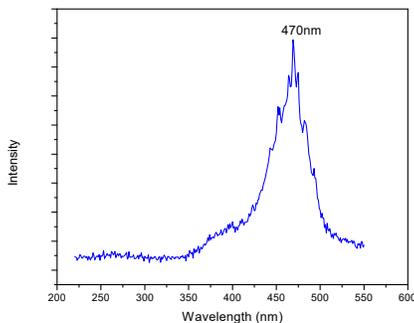


Figure 2 Excitation spectrum of CaS:Ce³⁺ phosphor

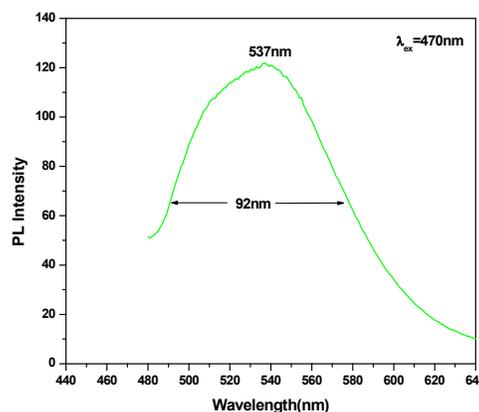


Figure 3 Emission spectrum of CaS:Ce³⁺ phosphor

3.3 Emission study

The emission spectra were taken by exciting the sample at 470 nm. Trivalent cerium produced single emission broad band in calcium sulfide peak at 537 nm. The broadness of the emission spectrum allows arriving at a decent color rendering using the combination of a blue pumping LED and a single phosphor. The excitation spectrum of Ce³⁺ consists of single excitation band (470nm) conforms the no splitting of the 5d state. Where as in the case of YAG:Ce³⁺ phosphor up to five often distinguishable excitation bands due to the crystal field splitting of the excited 5d state. For CaS:Ce³⁺, where Ce³⁺ experiences not much larger crystal field splitting than in most other oxide compounds. Therefore the emission spectrum of the pumping LED should be chosen such as to nicely match one of these excitation bands of CaS:Ce³⁺.

Only one emission broad peak was observed at 537 nm. This emission can be attributed to transition from the 5d state to the ²F_{5/2} components of the ground state. This emission peak is different from the peaks observed by Jia and Wang [10] from bulk CaS:Ce³⁺ at 515 and 570 nm. The quantum size induced blue-shifting of the Ce³⁺ emission peaks at 498 and 550 nm from CaS:Ce³⁺ was also reported by Singh et al [2]. This blue shifting of Ce³⁺ emission peaks in a cubic nanocrystal structure could be explained by the modified crystal field model proposed by Mhin et al.

3.4 CIE Study

The CIE co-ordinates from the below fig.4 clearly shows the emission color of the phosphor. **Figure 4** CIE co-ordinates depict on the 1931 chart indicates the emission colour of the four phosphors. The CIE coordinates and the appearance of green as the Ce³⁺ ion doped in CaS host. The Commission International de l'Eclairage (CIE) co-ordinates were calculated by the spectrophotometric method using the spectral energy distribution and (x=0.304, y=0.526) confirm the green emission with colour correlated temperature (CCT) 6101 K.

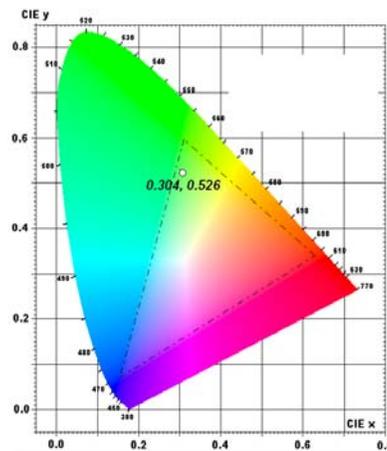


Table 1 Comparison of emission peaks with bulk and nano CaS:Ce³⁺

Sample	Particle size	Emission (Ce ³⁺ transition)	
		² D(5d)→ ² F _{5/2} (4f)	² D(5d)→ ² F _{7/2} (4f)



CaS:Ce bulk	--	515 nm	570 nm
CaS:Ce (prepared)	--	537 nm	--
CaS:Ce nano	20-30 nm	498 nm	560 nm
CaS:Ce nano	40-45 nm	507 nm	560 nm

- [14] F.Okamoto, K.Kato, J. Electrochem. Soc., 130, 432, (1983)
[15] P.J.Yadav, C.P.Joshi, S.V.Mohiril, J. of Luminescence, 136, 1-4, (2013)
[16] J.E.V.Haecke, P.F.Smet, D.Poelman, Spectrochem, Acta B 59, 1759, (2004)

CONCLUSIONS

CaS:Ce³⁺ phosphor has been synthesized by solid state reaction method successfully. The PL emission characteristics of CaS:Ce³⁺ phosphor has been investigated. Strong blue (400-500nm) absorption is observed in this phosphor. The powder phosphor doped with Ce³⁺ ion at the optimized concentration of 0.125 gm (substitution at Ca²⁺ site) was efficiently excited by blue light of wavelength 440-480 nm emit green at 537nm. The present results show that the white LEDs fabricated by coating the prepared phosphor on a blue LED chip have high luminescence and good colour properties.

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REFERENCES

- [1] G.Sharma, P.Chawla, S.P.Lochab, N.Singh, Radiat.Eff. Defects Solids, 164, 763, (2009)
[2] Vijay Singh, T.K.Gundu Rao, Jun-Jie Zhu, Manoj Tiwari, Materials Science and Engineering B 131, 195–199, (2006)
[3] De Mello Donegá C. Chem Soc Rev., 40:1512–46, (2011)
[4] P.K.Ghosh, B.Ray, Prog. Cryst. Growth Charact. 25, 1, (1992)
[5] K.Onisawa, Y.Abe, K.Tamura, Nakayama, T.M.Hanazono, T.A.Ono, J. Electrochem. Soc. 138, 599, (1991)
[6] C.Wang, K.Tang, C.An, B.Hai, G.Shen, Y.Qian, Chem. Phys. Lett. 351, 385, (2002)
[7] J.Zhang, Z.Zhang, Z.Tang, Y.Tao, X.Long, Chem. Mater. 14, 3005–3008, (2002)
[8] V.Kumar et al. Journal of Alloys and Compounds 492, L8–L12 L11, (2010)
[9] V.Kumar, N.Singh, R.Kumar, S.P.Lochab, J. Phys.: Condens. Matt. 18, 5029, (2006)
[10] D.Jia, X.Wang, Opt. Mater. 30, 375, (2007)
[11] N.Kodoma, Y.Tanii, M.Yamago, J. Lumin. 87–89, 1076, (2000)
[12] R.S.Crandall, Appl. Phys. Lett. 50, 551, (1987)
[13] W.Lehmann, F.M.Ryan, J. Electrochem. Soc. (U.S.A.), 119, 275, (1972)