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Influence of Sr and Mg on Luminescence of CaS Phosphor

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Abstract: *Sulfide based phosphors have been studied for more than 100 years. A simple method for preparing calcium sulfide phosphors useful for solid state lighting is described. Ce^{3+} and Eu^{2+} doped (Ca,Sr)S and (Ca,Mg)S have been synthesized by synthesis of sulfate by re-crystallization method followed by reduction. PL emission of Ce^{3+} and Eu^{2+} doped (Ca,Sr)S and (Ca, Mg)S phosphor was studied. The effect of different dopant concentration on the PL emission was also investigated. The maximum PL emission intensity was observed when (Ca, Mg)S was doped with 1 mole % of the Ce^{3+}. Intense green emission due to d-f transition of Ce^{3+} was observed for 450 nm excitation. Intense red emission due to d-f transition of Eu^{2+} was observed for 470 nm excitation in (Ca, Mg)S:Eu^{2+}. These phosphors will be used for solid state lighting.*

Keywords: *phosphors; sulfide; photoluminescence; Ce^{3+} and Eu^{2+} activator; solid state lighting.*

I. Introduction

In recent years, rare-earth doped alkaline earth sulfides have attracted the attention of many researchers and scientists due to their unique application in photoluminescence devices [1]. Energetically favorable defect structure within the photo physical environment of host lattice has captivated the materials engineering community and as a result, recently the researchers on doped CaS has gained a fresh impetus due to its possible afterglow features when co-doped with Eu and Ce impurities. The wide bandgap of this phosphor has been effectively utilized by Kojima et al to perturb the space charge neutrality condition by invasion of new ions leading to an increase in the persistent behavior with near UV and visible photon irradiability as an added advantage [2 & 3].

Alkaline earth sulfides have been known to be excellent and versatile phosphor host [4]. A large number of different activators produce phosphors having different emission colours ranging from the near ultraviolet to the deep red [5 to 9]. Calcium sulfide activated by trivalent cerium has been known as an excellent green emitting phosphor [2].

A serious objection to alkaline earth sulfide phosphors is their chemical instability against atmospheric carbon dioxide and water, which in most cases require spherical precaution during storage and use. This is doubtlessly the case for MgS, BaS and to a lesser degree SrS. CaS phosphors are comparatively stable when consisting of well grown particles, however they can freely be incorporated into various devices with only a minimum of precaution.

In this work Ce^{3+} and Eu2+ doped alkali-earth sulfides are studied. In this study recrystallization method was used to synthesize CaS:Ce^{3+}, (Ca,Mg)S:Ce^{3+}, (Ca,Sr)S:Eu^{2+}, (Ca,Sr)S:Ce^{3+} phosphors followed by reduction with different concentration of Ce^{3+} and their luminescence properties were investigated. In this paper the effect of Strontium and Magnesium on CaS based phosphors is being studied.

II. Experimental

Conventionally, host sulfides are prepared by method like carbo-thermal reduction. Doping is then done by solid state diffusion under inter/reducing atmosphere at temperature around 1000^{o} C. We attempted a different approach. In the first step $CaSO_4$ doped with the desired activators was prepared by Yamashita's method. This was then reduced to sulfide by double crucible method. CaS:Ce^{3+} sample was prepared using raw materials $CaCO_3$, H_2SO_4, $Ce_2(SO_4)_3$ [10]. Dopant compound $Ce_2(SO_4)_3$ and Eu_2O_3 were added with specified doping concentration for 1 mole % of Ce^{3+}. Sample was heated at 900^{o} C and kept for 1 hour in reducing environment. X-ray diffraction patterns were recorded on Philips PANalytical x'pert Pro-diffractometer. PL characteristics in the range of 200-700 nm at room temperature were studied using Hitachi F-4000 spectroflurimeter, with 1.5nm spectral slit width.

III. Result and Discussion

Fig.1 shows XRD pattern of CaS so prepared .It is seen that the pattern matches excellently with ICDD file No.75-0893. There are some weak lines present corresponding to $CaSO_3$(ICDD file No.36-529). PL spectra for Ce^{3+} activator in (Ca,Sr)S and (Ca,Mg)S are shown in fig.2. Intense green emission due to d-f transitions of Ce^{3+} was observed for 450 nm excitation. Maximum intensity was observed for Ce^{3+} concentration of 1 mole %

The relative energy position of the Ce^{3+} ground state with respect to E_g & T_{2g} levels can be found from the excitation and emission spectra. Thus relative positions of all the energy states of Ce^{3+} within the CaS host can be determined as shown in figure 2. The energy levels of $2F_{7/2}$ and $2F_{5/2,}$ T_{2g} and E_g of Ce^{3+} ion in CaS should be at 1.2 ,1.4 ,3.6 and 5.2 eV above the valance band respectively. This energy level diagram is consistent with the hypothesis that the T_{2g} and E_g levels are located below and above the conduction band edge respectively.

Emission and Excitation Spectra of Ce^{3+} doped CaS Phosphor:-

The broad band emission at 501 nm is due to the transition from 5d state of Ce^{3+} to the two 4f states , $2F_{7/2}$ and $2F_{5/2}$ respectively. The three broad excitation bands are found to be at 254 nm, 349 nm and 450 nm as shown in Fig 3. The excitation bands at 254 nm and 450 nm can be assigned to the E_g & T_{2g} 5d bands of Ce^{3+}. The 350 nm band is due to a charge transfer transition of Ce^{3+} from 4f to conduction band [10]. In CaS: Ce^{3+}, green emission is obtained at 501 nm.

Emission and Excitation Spectra of Ce^{3+} doped (Ca,Sr)S and (Ca,Mg)S Phosphor:-

The fig.4 shows the excitation and emission spectra of (Ca,Sr)S:Ce^{3+}. Two excitation peaks were observed at 270 nm and 440 nm. The broad band emission peaks were observed at 490 nm and 560 nm due to the transitions from 5d state to 4f state. Intense bluish green emission was observed. With addition of Sr emission spectra shift form 501 nm to 490 nm.

The fig.5 shows the excitation and emission spectra of (Ca,Mg)S:Ce^{3+}. Two excitation peaks were observed at 258 nm and 450 nm. The broad band emission peaks were observed at 505 nm and 565 nm due to the transitions from 5d state to 4f state.The PL emission at 505nm was assigned to the $2D(5d) \rightarrow 2F_{5/2}(4f)$ transition of Ce3+ ions and shoulder at 565 nm was due to $2D(5d) \rightarrow 2F_{7/2}(4f)$ transition.Intense bluish green emission was observed. Maximum intensity was observed for Ce^{3+} concentration of 1 mole %.

With addition of Mg, there is small shift in the emission maximum from 501 to 505 nm. Also, the shoulder around 565 nm became more distinct. Ratio of Green/Yellow emission changed from 4:1 for CaS:Ce to 2:1 (Ca,Mg)S:Ce. In the excitation spectrum, UV band around 254nm became prominent in (Ca,Mg)S:Ce.

Emission and Excitation Spectra of Eu^{2+} doped (Ca,Sr)S and (Ca,Mg)S Phosphor:-

The fig.6 shows the excitation and emission spectra of (Ca,Sr)S:Eu^{2+}. PL emission of (Ca,Sr)S:Eu^{2+} for 470 nm excitation located at 605 nm which is due to the typical 5d-4f transition emission of Eu^{2+}. The excitation spectra of the phosphor conclude two broad band at around 270 nm and 480 nm (400-600 nm). These phosphors have strong absorption from 400 nm to 600 nm, which were attributed to the 4f-5d transition of Eu^{2+}. These phosphors can be well excited by blue light (460 – 470 nm) from GaN LED chip [11].

Fig. 7 shows excitation and emission spectra of Eu^{2+} doped $(Ca_{0.8},Mg_{0.2})S$ phosphor. The compound $(Ca_{0.8},Mg_{0.2})S:Eu^{2+}$ having reddish body colour is promising for red phosphor. PL emission of $(Ca_{0.8},Mg_{0.2})S$ for 470 nm excitation located at 636 nm. CaS:Eu is an efficient deep red phosphor, the 5d-4f luminescent transition in Eu^{2+} peaks at about 655 nm but extent to the near infrared. As a result, the eye sensitivity for this type of light, expessed as LER (luminous efficacy of radiation, expressed in lumen/W), is quite low. The LER increases when the emission spectrum is shifted to lower wavelength, which is accomplished by slightly decreasing the crystal field on the Eu^{2+} sites. With addition of magnesium emission spectrum is shifted to lower wavelength from 655 nm to 636 nm.

While bandgap excitation is quite inefficient, the broad excitation band from about 400 nm to 550 nm corresponding to direct excitation of Eu^{2+} ions is very intense and makes this kind of phosphor material ideally suited for wavelength conversion of blue LEDs [12].

IV. Conclusion

$(Ca_{0.8},Mg_{0.2})S$ and $(Ca_{0.8},Sr_{0.2})S$ doped with Eu2+ and Ce3+ have been prepared by re-crystallization method followed by reduction. With addition of Mg and Sr in CaS:Eu^{2+} phosphor, emission spectrum is shifted to lower wavelength. For $(Ca_{0.8},Mg_{0.2})S:Eu^{2+}$ emission shift from 652 nm to 636 nm and for $(Ca_{0.8},Sr_{0.2})S:Eu^{2+}$emission shift from 652 nm to 605 nm. With addition of Mg in CaS:Ce^{3+} phosphor, emission spectrum shift from 501 nm to 505 nm and the shoulder around 565 nm became more distinct. The ration of green/yellow emission changed from 4:1 for CaS:Ce to 2:1for$(Ca_{0.8},Mg_{0.2})S:Ce^{3+}$. For $(Ca_{0.8},Sr_{0.2})S:Ce^{3+}$emission shift from 501 nm to 490 nm. It is thus seen that efficient (Ca,Mg)S and (Ca,Sr)S doped with Eu2+ and Ce3+ phosphor can be prepared by procedure described here. These phosphor can be useful for solid state lighting .

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Figure Caption

1. XRD for CaS
2. The energy level diagram of the 5d-states of Ce^{3+} and their position relative to the host band gap of CaS.
3. Photoluminescence emission and excitation spectra for CaS:Ce(0.1%,0.2%,0.5%)
4. Photoluminescence emission and excitation spectra for $(Ca_{0.8,}\ Sr_{0.2})S:Ce(0.5\%)$
5. Photoluminescence emission and excitation spectra for $(Ca_{0.8,}\ Mg_{0.2})S:Ce(0.2\%,1\%)$
6. Photoluminescence emission and excitation spectra for $(Ca_{0.8,}\ Sr_{0.2})S:Eu^{2+}(0.5\%)$
7. Photoluminescence emission and excitation spectra for $(Ca_{0.8}Mg_{0.2})S:Eu^{2+}(0.5\%)$

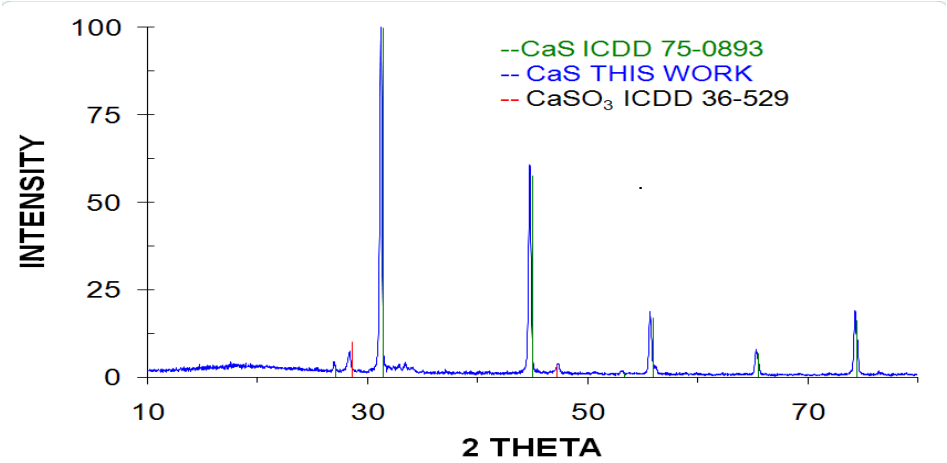

Figure 1: XRD for CaS

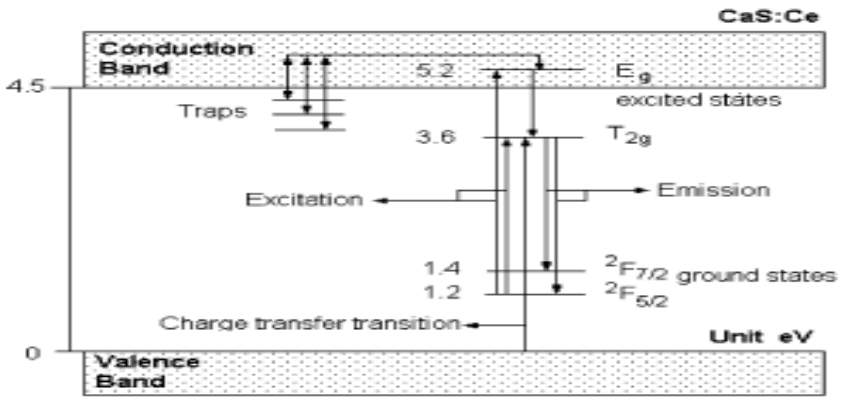

Figure 2: The energy level diagram of the 5d-states of Ce^{3+} and their position relative to the host band gap of CaS.

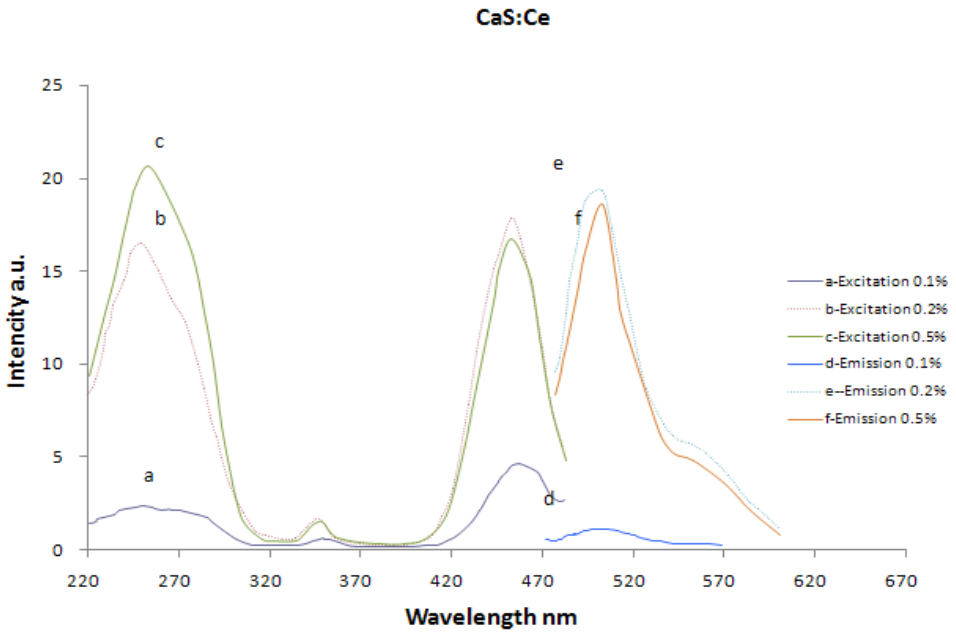

Figure 3: Photoluminescence emission and excitation spectra for CaS:Ce(0.1%,0.2%,0.5%)

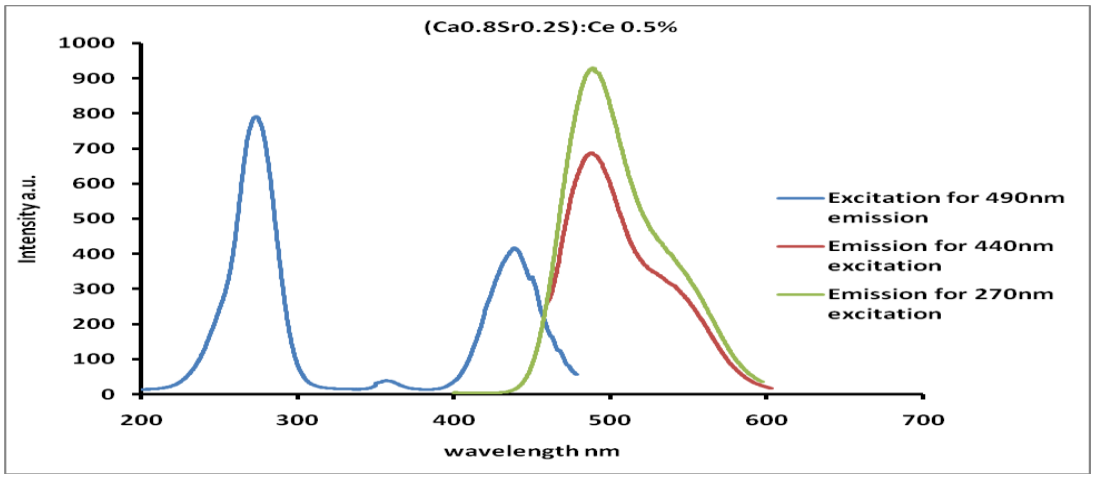

Figure 4: Photoluminescence emission and excitation spectra for ($Ca_{0.8,}$ $Sr_{0.2}$)S:Ce(0.5%)

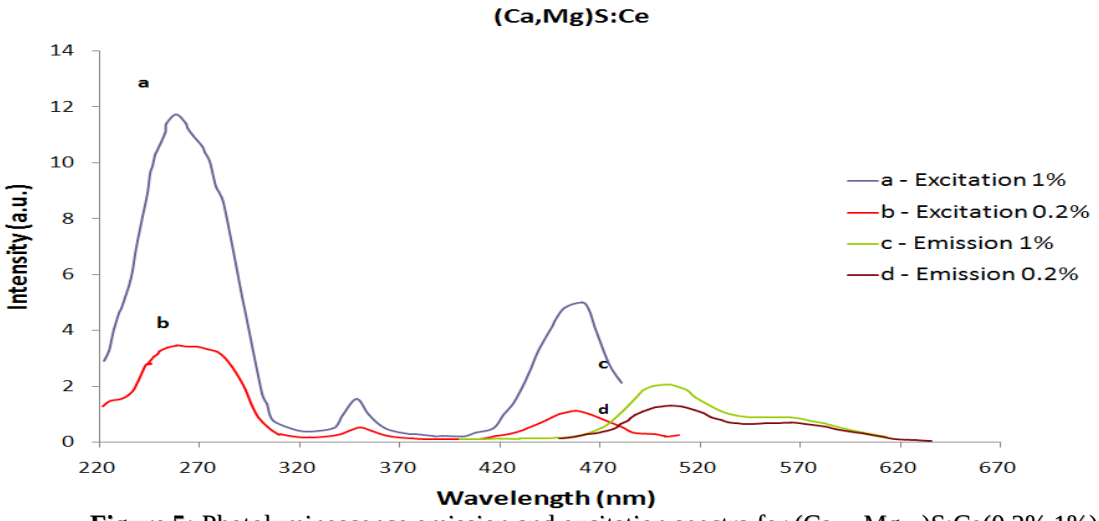

Figure 5: Photoluminescence emission and excitation spectra for ($Ca_{0.8,}$ $Mg_{0.2}$)S:Ce(0.2%,1%)

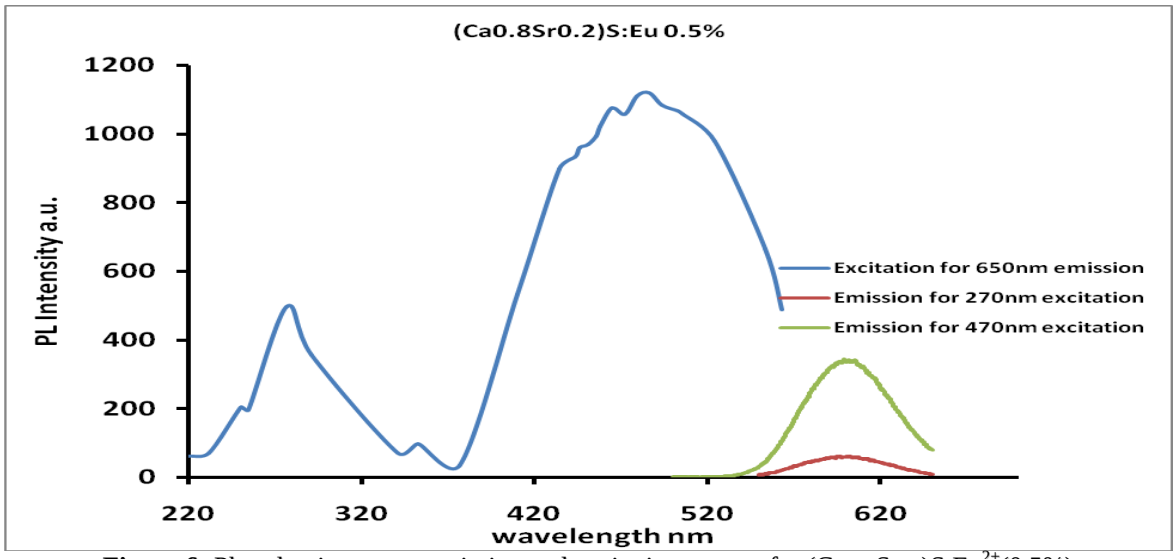

Figure 6: Photoluminescence emission and excitation spectra for $(Ca_{0.8,}\ Sr_{0.2})S:Eu^{2+}(0.5\%)$

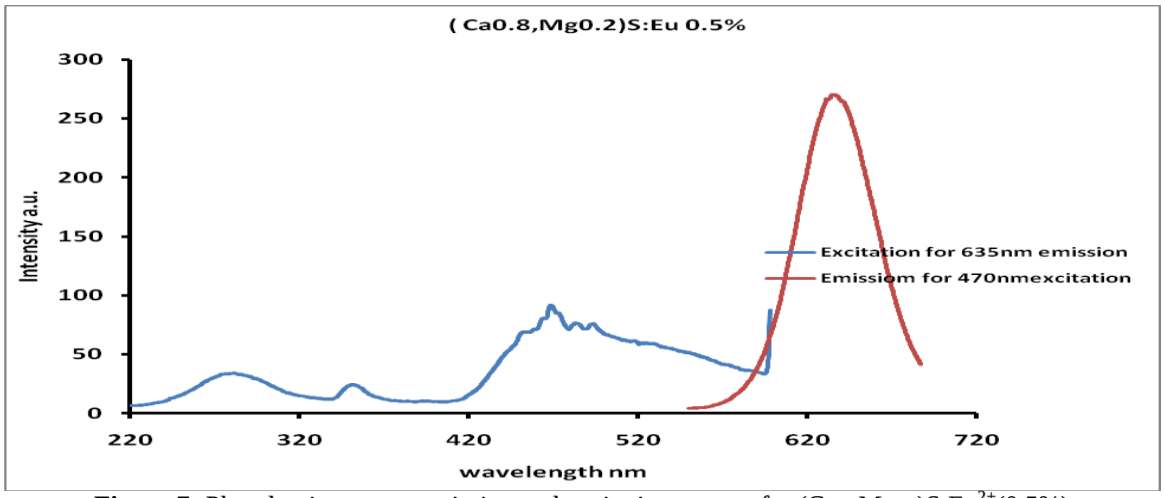

Figure 7: Photoluminescence emission and excitation spectra for $(Ca_{0.8}Mg_{0.2})S:Eu^{2+}(0.5\%)$