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UV-Visible Excitable Luminescent Properties of $CaAl_2S_4:Eu^{2+}$ Phosphor

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Abstract— *The Photoluminescence (PL) emission and excitation study of the $CaAl_2S_4:Eu^{2+}$ (0.5mol%) powder phosphor is reported in detail. The phosphor was synthesized using the standard solid state reaction method. Photoluminescence excitation and emission spectra were taken to investigate the luminescence characteristics. Broadband UV – visible excited luminescence of the $CaAl_2S_4:Eu^{2+}$ was observed in the red region (λ_{max}= 635nm) due to transitions from $^4f_6\ ^5d_1 \rightarrow {}^4f_7$ configuration of the Eu^{2+} ion. Powder phosphor shows the highest photoluminescence under 467nm excitation wavelength. The results reveal that this phosphor has potential application in the display and in solid state lighting. Experimental J-O intensity parameters Ω_2 & Ω_4, radiative emission rate and quantum efficiency were calculated. Crystallinity and morphological investigations of the particles were made using XRD, SEM.*

Keywords— *Photoluminescence, Phosphor, Solid state reaction, Crystal, J-O parameters*

1. INTRODUCTION

In the year 1999, Miura introduced a ternary inorganic compound, $BaAl_2S_4$:Eu as a bright blue-emitting phosphor for full colour EL device [1]. Nevertheless, many lighting applications require green, red and blue-emitting phosphor materials. $BaAl_2S_4$:Eu as a blue-emitting phosphor, CaS:Eu as red-emitting phosphor. For the green-emission $CaAl_2S_4$:Eu is a promising material. The ternary compounds doped with rare earth ions have been studied for several years and were found to be very attractive for lighting and display applications, like FED [2], wavelength converters in pc-LEDs for solid state lighting [3]. Le Thi et al, [4] investigated different M-Al_2S_4 systems (M: Ca, Sr, Ba) and described some luminescence properties of Eu^{2+} as dopant.

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. Effective lighting devices can be realized by combining one or more phosphor materials with chips. Accordingly, it is very important that the architecture of phosphors be developed. Although numerous phosphors have been proposed in the past several years, the range of phosphors that are suitable for LEDs is limited. This work describes recent progress in our understanding of the prescription, morphology and spectrum [5-8].

The growing demand for phosphor converted LEDs has triggered targeted studies to find new phosphors [9]. The solid-state reaction process has been used intensively for phosphor synthesis. Phosphors of small particles are generally obtained by grinding the larger phosphor particles. Those processes easily introduce additional defects and greatly reduce luminescence efficiency [10]. It is well known that the valence state of the activator dictates the emission wavelength [11, 12]. Similarly the trivalent Eu^{3+} ions show red luminescence properties in highly stable lead-based heavy metal oxide glasses [13]. With the development of scientific technologies on materials, several chemical synthesis techniques, such as co-precipitation [14], sol-gel [15], microwave [16], Pechini [17], and combustion [18] synthesis methods, have been applied to prepare rare earth ions activation alkaline earth aluminate and/or its phosphors.

In this paper, we have studied the synthesis, the excitation and the emission spectrum of the Eu doped $CaAl_2S_4$ powder phosphor prepared by solid state reaction method. The influence of the excitation wavelength on the emission wavelength was investigated. Further the optimal excitation wavelength was determined. By comparing these results with the data available in literature was discussed. The prepared material was characterized by SEM and CIE techniques.

2. EXPERIMENTAL

Eu doped $CaAl_2S_4$ phosphor was synthesized by the conventional solid state reaction method. The Eu^{2+} ion dopant concentration in $CaAl_2S_4$ is 0.5mol%. To prepare $CaAl_2S_4$:Eu powder phosphor, stoichiometric amounts of commercially available $CaCO_3$ (Sigma-Aldrich Chemie, Inc, Germany 99.99%), Al_2O_3 (Sigma-Aldrich, 99.9%) and Sulfur (S) (National Chemicals, India, 99.5%) were used as starting materials for the host and Eu_2O_3 (National Chemicals, India, 99.5%) was used as activator. Mixture

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of these materials was thoroughly homogenized in an agate mortar and pestle for 1hr. The mixture was sintered in an alumina crucible under carbon reducing atmosphere. The powder was kept at 1200°C for 3 h with a heating rate of 5°C/min. Finally the sample was allowed to cool down to room temperature for about 20h. This preparation method is different from the reported by Le Thi et al, [19], J.E.V.Haeeke et al, [20] and Oh et al, [21]

The phosphor was characterized by the following techniques. 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 XRD analysis was carried out with a powder diffractometer (Scintag inc. USA, model ADS) using Cu Kα radiation. The shape and size of the phosphor particles were recorded using scanning electron microscopy (SEM, Carl Zeiss - Leo 1530VP). The colour co-ordinates are measured using Radiant Imaging colour calculator.

3. RESULTS AND DISCUSSIONS

3.1 Photoluminescence Characteristics- Excitation Spectrum

The excitation spectrum of $CaAl_2S_4$:Eu (0.5mol%) phosphor for the emission at 635nm is presented in Fig.1. The centre of the first excitation band is at about 270 nm (4.593eV). A second excitation band in the visible part of the spectrum is located at about 467 nm (2.655eV). The excitation recorded by monitoring emission at 635nm. Both bands are due to the 4f-5d transitions of Eu^{2+} ions. The second band is stronger than the first band. This is most fundamental requirement for LED applications. From the excitation spectrum we conclude that the prepared phosphor can be well excited by blue light i.e. 450-470nm from GaN LED chip which is available in the market.

In the $CaAl_2S_4$:Eu compound, part of the Ca^{2+} ions is substituted by Eu^{2+} ions. So the 5d orbitals of the Eu^{2+} ions are split in two levels. Transitions to the lowest Eu^{2+} levels give rise to the first and second excitation bands in $CaAl_2S_4$:Eu phosphor. By calculating the energy gap between these excitation bands as 4.593-2.655=1.938eV.

In the second excitation band, a characteristic 'staircase' structure of the Eu^{2+} absorption is present. This structure is due to spin–orbit coupling in the $4f^6$ configuration leading to the splitting of the ^7F level in seven levels: ^7F_J with J= 0–6. In the excitation spectrum (Fig.1), we observe 7 maxima at 450, 460, 464, 467, 475, 483 and 493 respectively. The energy differences between the maxima, which are not equidistant, are in good agreement with those of the ^7F_J levels derived from the $4f^6$ configuration of the free Eu^{3+} ion [22].

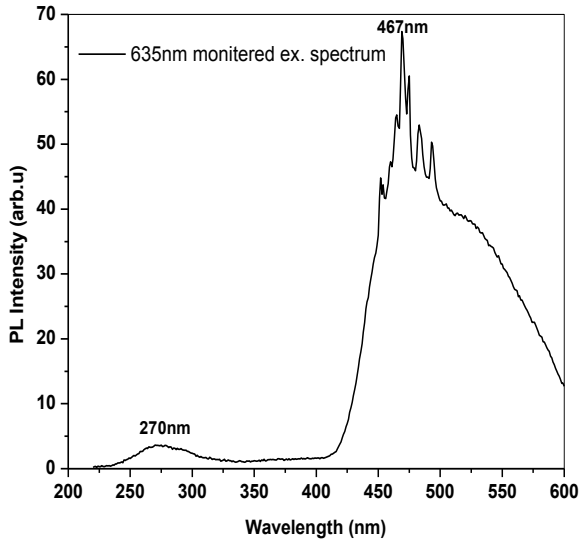

Fig. 1: Excitation spectrum of $CaAl_2S_4$:Eu (0.5%) monitored under 635nm wavelength

We can estimate the position of the lowest excited level of the $4f^6$ $5d^1$ state ($^7F_0$ level). As the emission spectrum peaks at 635 nm (1.952eV), we found from the absorption energy of 493 nm (2.51eV). This absorption energy E_{abs} of the f-d transition corresponds to the energy of the first step of the 'staircase' structure.

The energy between the lowest $4f^7$ ($^8S_{7/2}$) level and the first $4f^6(^7F_0)5d^1$ level is lowered from the free electron value when the Eu^{2+} ion is brought into a crystal environment. The effect of the host crystal on this energy difference is expressed by the red shift D and the Stokes shift ΔS. The energy of f -d absorption and of the d-f emission can be written respectively, as [24]

$E_{abs} - E_{free} = D$ and

$E_{em} = E_{free} - D - \Delta S$

E_{free} (Eu^{2+}) = 4.19eV [25] is the energy of the f –d transition for free (gaseous) Eu^{2+} ions. The emission spectrum of $CaAl_2S_4$:Eu powder provides the value of the emission energy, E_{em} = 1.952eV. We found absorption energy E_{abs} of 2.51eV. The Stokes shift can be calculated as $\Delta S = E_{abs} - E_{em} = 2.51 - 1.95 = 0.56$eV. Using the first equation, we determined the value of the red shift as D = 1.67 eV. When we compare this calculated value with the red shift of the Eu^{2+} emission with others such as $SrAl_2S_4$ (D = 1.58eV) and $BaAl_2S_4$ (D = 1.29eV). It tends to decrease with increasing size of the cation (Ca<Sr< Ba) [24]. The red shift is associated with two effects: the crystal field that splits the 5d levels and the nephelauxetic effect, which tends to lower the energy of the 5d levels.

3.2 Emission Spectrum

Fig.2 shows the emission spectrum of $CaAl_2S_4$:Eu (0.5%) phosphor under different excitation wavelengths recorded at room temperature. From the emission spectrum it is observed that the phosphor can be excited from 260-555nm range. Curves 1 to 8 shows the broad emission centered at 635nm (1.952eV) with a FWHM of 53nm, attributed to the $^5D_0 - {}^7F_2$, under 270, 450, 467, 483, 493, 520, 540 and 555nm wavelengths respectively. It is observed that the emission is increased as the excitation wavelength increases from 270 – 467 and then decreased. It is concluded that the phosphor shown high intensity under 467nm excitation which is well matched with the blue LED chip. Obviously this phosphor has potential application in the generation of white LEDs as red component.

Phosphor shows only one emission band. When the excitation wavelength was varied, no shift of the emission band and FWHM value was observed. This may be due to the Eu^{2+} ions substitute the Ca^{2+} ion site. This behavior has been observed in the CaS:Eu phosphor [8] as well. The emission spectrum confirms the absence of $CaAl_2S_4$:Eu^{2+} in the powder, as no emission peak is seen around 515nm (green).

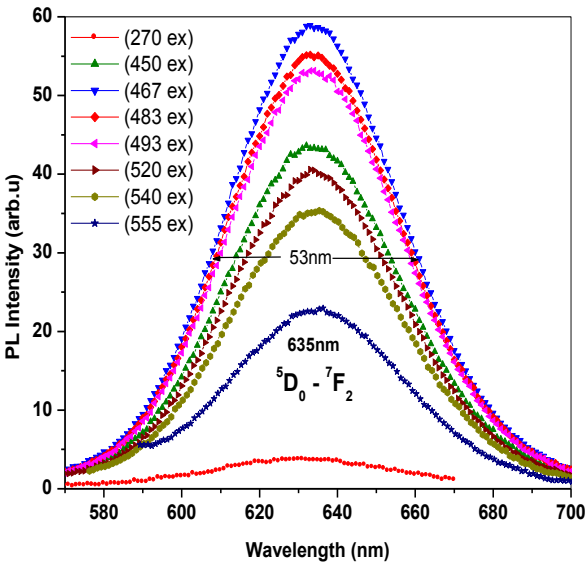

Fig. 2: 635nm emission spectrum of $CaAl_2S_4$:Eu (0.5%) under different excitation wavelengths

The presence of 635nm peak clearly indicates that CaS:Eu^{2+} emission but not $CaAl_2S_4$:Eu^{2+} phosphor. This emission is ascribed to the transition from the $^5D_0$ state to the $^7F_2$ ground state of the Eu^{2+} ions.

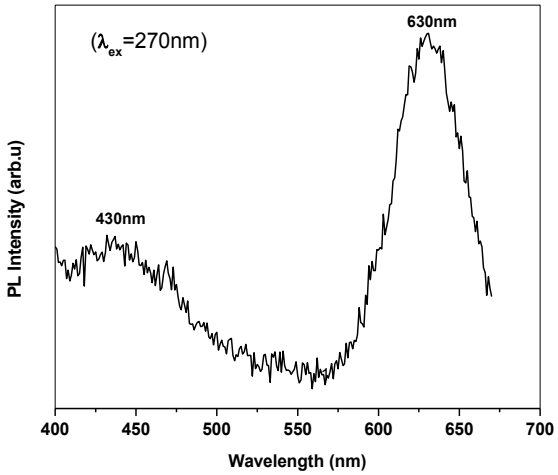

Fig. 2: (a) Emission spectrum of $CaAl_2S_4$:Eu (0.5%) under 270nm excitation wavelength

Fig.2a shows the emission spectrum of $CaAl_2S_4$:Eu^{2+} phosphor under 270nm excitation. The emission spectrum consists of two broad band's one peaked at 430nm (blue colour) and another peaked at 630nm (red colour). When this emission compared with other emissions under other excitation wavelengths the emission in blue region is absent.

The experimental J-O parameters Ω_2 & Ω_4, radiative emission rate and quantum efficiency were calculated and tabulated in table 1.

3.3 XRD Study

Calcium aluminum sulfide, $CaAl_2S_4$ doped with Eu^{2+} (0.5mol%) was prepared and investigated. Figure 3 shows the representative powder XRD pattern for the $CaAl_2S_4$:Eu^{2+}. As can be seen, orthorhombic phase diffraction peaks of parent $CaAl_2S_4$ are dominant in the XRD patterns, and are matching with the JCPDS data file (no. 77-1186). No other phase or un-reacted starting material was observed. This confirms the synthesized phosphor is in single phase. Small amount of doped rare earth active ions Eu^{2+} has almost no effect on $CaAl_2S_4$ basic crystal structure. Figure 3a shows the orthorhombic crystal structure of the phosphor

3.4 SEM Analysis

Scanning electron microscopy (SEM) study was carried out to investigate the surface morphology and crystallite sizes of the synthesized phosphor powder. The powder phosphors reduced at temperature 1200°C were taken for these experiments. Figure 3 show the representative SEM micrograph taken for $CaAl_2S_4$:Eu^{2+}(0.5mol%) phosphor.

It is clearly seen from this micrograph that the crystallites sizes are varying from few microns to several tens of microns. However, the crystallites are having sharp surface morphology of single crystalline grains.

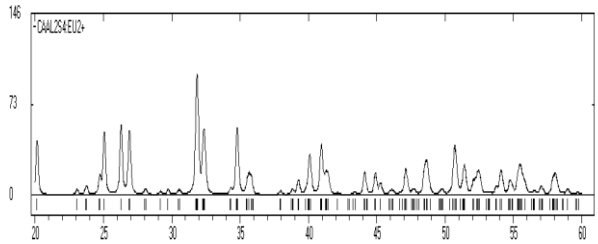

Fig. 3: XRD pattern of $CaAl_2S_4$:Eu (0.5%) phosphor

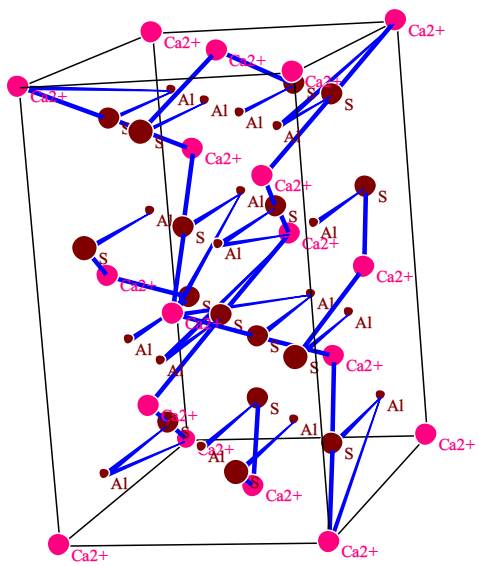

Fig. 3: (a) Structure of $CaAl_2S_4$:Eu (0.5%) phosphor

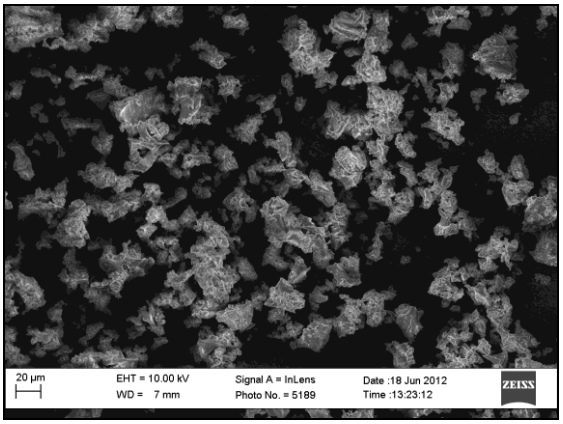

Fig. 3: SEM micrograph of $CaAl_2S_4$:Eu (0.5%) phosphor

Table 1

Parameter	*Value*
Excitation	UV - Visible
Emission	635nm (red) $^5D_0 - {}^7F_2$
FWHM	53nm
CIE co-ordinates	x= 0.661 and y = 0.335
Stokes shift ΔS	0.56eV
Red shift D	1.67eV
J-O parameter Ω_2	8.83 x10^{-20} cm^2
J-O parameter Ω_4	4.26x10^{-20} cm^2
Radiative emission rate	377.27 s^{-1}
Quantum efficiency	75.45%
Crystal structure	Orthorhombic (ICDD 77-1186)
Morphology	sharp surface with irregular morphology

3.5 CIE Analysis

The CIE co-ordinates of (chart -1931) were calculated by the Spectrophotometric method using the spectral energy distribution. Based on the emission spectra, it was possible to see the color of the emission of each sample in the CIE diagrams 1931. Fig.5 shows the CIE coordinates depicted on the 1931 chart of $CaAl_2S_4$:Eu (0.5%) phosphor. Point A indicates color co-ordinates x = 0.661 and y = 0.335 red colour under different excitations. Point B shows colour co-ordinates x = 0.396, 0.257 pink colour under 270nm excitation and this values are different from other reported papers.

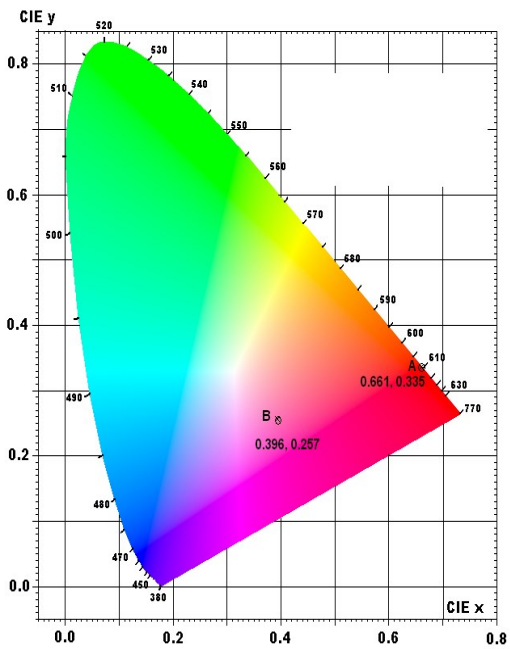

Fig. 5: CIE colour co-ordinates of $CaAl_2S_4$:Eu (0.5%) phosphor depicted on 1931 chart

4. CONCLUSIONS

$CaAl_2S_4:Eu^{2+}$ (0.5 mol%) phosphor was synthesized using solid-state reaction method. XRD analysis shows that the synthesized composition retains the mostly single phase with orthorhombic structure. SEM investigation confirms the large size irregular shaped particles. It was optimized that the highest PL intensity is for the 467nm excitation which is well matched with the blue LED chip. The experimental J-O parameter omega 2 has higher value than omega 4 which indicates the synthesized phosphor has more covalent nature. The CIE colour co-ordinates confirm the red emission. The immediate application of this phosphor is as red component in the generation of white light LEDs.

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