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Nano Red Emitting LED Phosphor RE doped $CaWO_4$

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Abstract

Very few reports available on rare-earth doped calcium tungstate nanophosphors and study of their optical properties. Extensive studies are required for the complete understanding of the luminescent properties including energy transfer mechanism and morphology of nano tungstates. The present paper reports the synthesis of 1% Europium doped $CaWO_4$ phosphor Via Hydrothermal method and reheated at 900ºC for two hours. The photoluminescence study is done at different excitations to understand the luminescent characteristics, XRD; for the phase, crystallite size and structural characteristics and FTIR; study is for the formation of metal oxide legands, were done on the prepared sample. The structure of the crystal was drawn and the Crystallite size was calculated using Scherrer's formula with XRD data. The photoluminescence emission spectra for different excitation wavelengths confirms that it was in orange red and Red ranges with good intensities when excited with 466 is presented in fig.1.

Key words: PL, XRD, SEM, FTIR, Crystallite Size, Transitions, Excitation and Emission Spectra.

Introduction:

The goal of the preset research is to improve the internal quantum efficiency of the materials. LED phosphors, such as YAG:Ce, (Ca,Sr)S:Eu, or (Ca,Sr)2Si5N8:Eu, are already available as far as the internal quantum efficiency is concerned. Even though, the final goal is to produce LED light sources with a color quality close to that of a black-body radiator at a temperature of 2500 to 6000 K. This means that upcoming LEDs have to match the spectrum of incandescent and halogen lamps more closely. Many novel Eu^{2+} and Ce^{3+} doped nitride and oxy nitride host lattices are presently under development, since the spectra of Eu^{2+} and Ce^{3+} can easily tunable by the host lattice, and many of the luminescent materials activated by these ions exhibit high efficiency, strong absorption, short decay time, and broad emission bands. The success of white pcLEDs operating on the basis of blue InGaN dies, the conversion of near-UV LEDs (370–420 nm) is another approach of broad interest since long. In particular, Eu^{3+} doped phosphors are of strong interest for the application in near-UV LEDs, since they exhibit a high lumen equivalent, quantum efficiency and photo stability at the same time. Moreover, from a practical point of view a fluorescent light source comprising a red line emitter emitting at 610–615nm is the best compromise between luminous efficacy and color rendering. A drawback is, however, the weak absorption of Eu^{3+} in the blue and even in the near UV. A recent idea is to convert near-UV or blue light via the 4f-4f transitions of Eu^{3+} located at 394 ($^7F_0$–$^5D_6$) and 465nm ($^7F_0$–$^5D_2$), which are rather intense in tungstates and molybdates. Following the excitation process, Eu^{3+} relaxes nonradiatively to the $^5D_0$ state, which is the emitting energy level. These results feed the hope that an Eu^{3+} phosphor, which is sufficiently strongly luminescent under 394- and/or 465-nm excitation, can be found in the future. The higher lumen equivalent of Eu^{3+} (260–300 lmW/1) compared to Eu^{2+} phosphors will contribute to a further enhancement of the luminous efficacy of pcLEDs.

1. Synthesis:

The present paper reports the Synthesis and Photoluminescence study of $CaWO_4$ phosphor doped with Eu ions. Calcium Carbonate ($CaCO_3$) and Tungsten oxide (WO_3) were taken as starting compounds in a stoichiometry of 1:1 to prepare $CaWO_4$. The starting compounds along with 1% of Europium oxide were taken and diluted with 25ml distilled water and taken in to an autoclave and it is sealed properly and cover with glass wool and heated to 300^0C and stirred for about 7hours. It was allowed to cool until room temperature and then washed with ethanol and dried in an oven at 100^0C for 6 hours. The obtained powder was taken into a alumina crucible and heated in a muffle furnace in open atmosphere, at a calcinating temperature of 900°C for two hours. Photoluminescence spectra were recorded at room temperature using Spectrofluorophotometer having Xenon lamp as excitation source.

2. Characterization:

The prepared phosphor samples were characterized for Photoluminescence spectra using Spectro-fluorophotometer RF-5301 PC of SHIMADZU make at M.S.U, Baroda. The Photo-luminescence spectra were recorded at room temperature. The source used in this is a xenon lamp. The slit width for the emission and excitation was kept at 1.5nm for all the measurements. A Quartz filter was used to remove the second order peak of the excitation light in the PL measurements. X-ray diffraction (XRD) using RIGAKU D'MAX III Diffractometer having Cu Kα radiation (lambda=1.5418nm). The scan range was kept from 5 degrees to 80 degrees at the scan speed of 0.05 degree per second. SEM of the samples were taken using JEOL make JSM – 5610 LV for studying the morphology of the compound at RRCAT, Indore. FTIR spectrum was obtained using Varian 1000 FTIR Spectrometer.

2.1 Photoluminescence study:

2.1.1 Photoluminescence of $CaWO_4$:

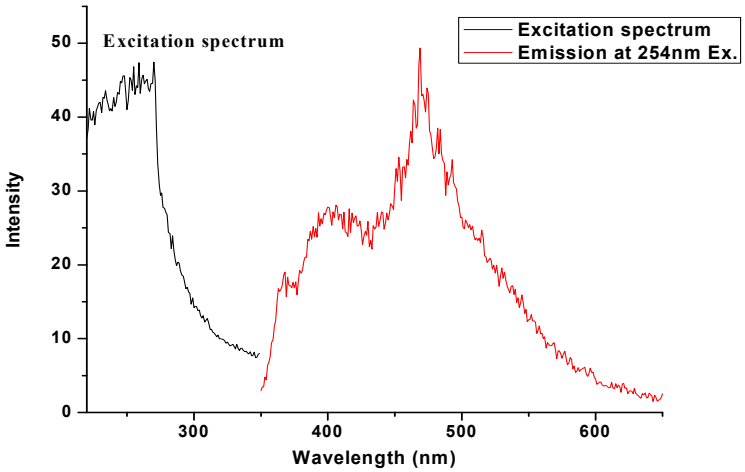

Fig.1: Excitation and Emission spectra of $CaWO_4$ (As recieved)

Fig.1 shows the Excitation and emission spectra of the base $CaWO_4$ Phosphor. The excitation spectrum speeds from 220nm to 280nm with many spiky peaks. A broad emission spectrum starts from 350nm to 600nm having many spiky peaks were observed with three humps around 360nm, 400nm and 470nm. The

hump at 380nm may be due the crystal field of the lattice and the hump around 400nm and the blue region 470nm are the basic emissions of $CaWO_4$ and arise due to Ca-WO_4.

2.1.2 Photoluminescence of $CaWO_4$:Eu1%: The received phosphor powder from the hydrothermal cell is subjected to heating at 900ºC for two hours. Fig.2 is the excitation spectrum of the Phosphor when monitored at 420nm. When the phosphor under study is monitored at 420nm, the excitation band is a broad one from 220nm to 280nm peaking at 254nm.

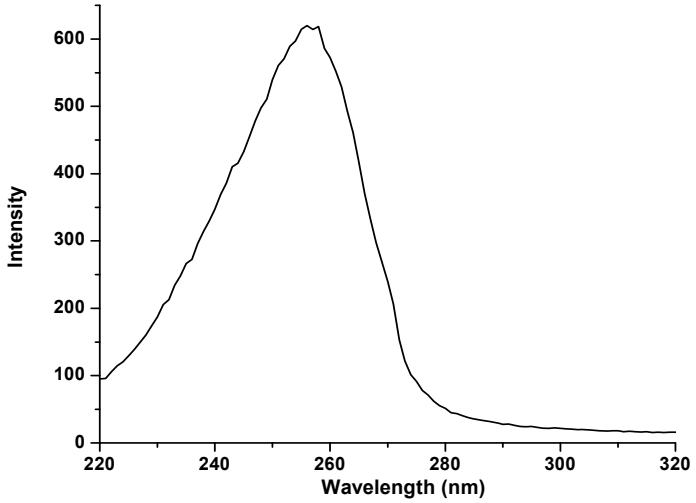

Fig.2: Excitation spectrum of $CaWO_4$: Eu1% monitered at 420nm

Fig.3 is the emission spectrum of 900ºC annealed $CaWO_4$ phosphor. From the figure, it is found that there are two emission bands. One is from 350 to 550nm peaking at 420nm, which is from near UV to Green colour with highest intensity. Another band is from 610nm to 620nm with peaking at 616nm with 400 units as intensity, which is in red region. The emission band peaking at 420nm arises due to Ca-WO_4 primary emission with 650 units as intensity. The minor emission at 593nm and the red emission at 616nm with 400 units of intensity are due to the basic emissions from Eu^{3+}, which are the allowed transitions of Eu^{3+} are due to **4f-5d.**

Fig.4 is the excitation spectrum of 900ºC heated $CaWO_4$: Eu1% phosphor, when monitored at 616nm. From the figure, exciting results are found; which are observation of many absorption bands from 220 to 600nm. However, for PL measurements, we considered the following peaks: 395nm, 466nm, 527nm and 536nm due to highest absorption intensities.

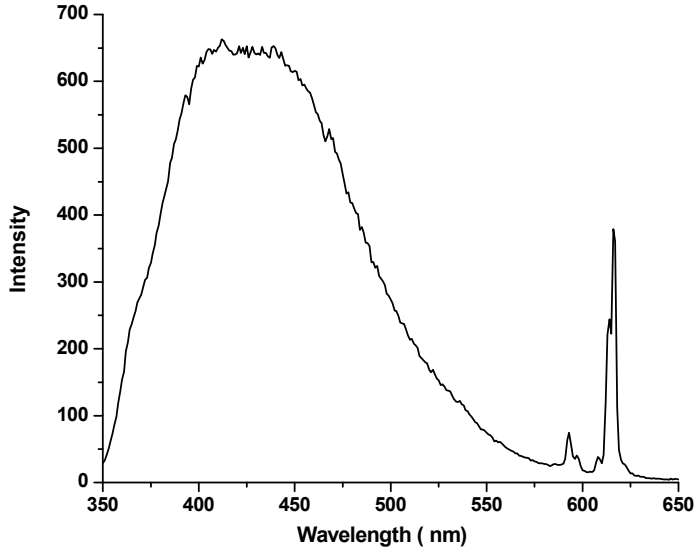

Fig.3: Emission spectrum of $CaWO_4$:Eu1% at 254nm Ex.

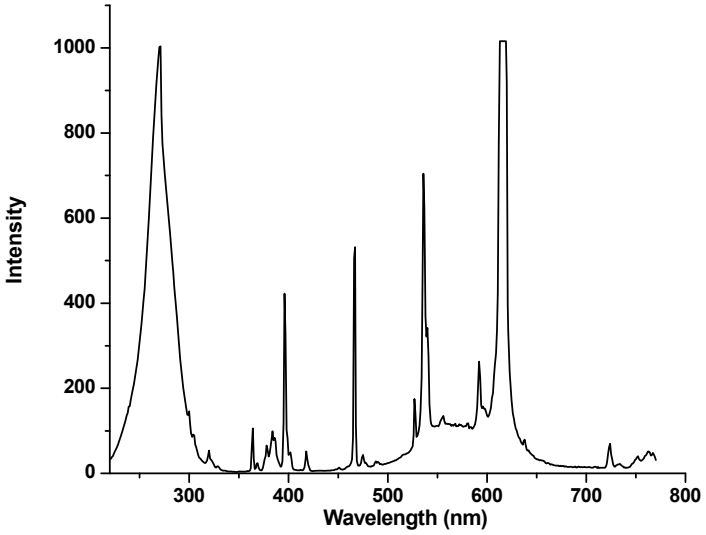

Fig.4: Excitation spectrum of $CaWO_4$: Eu1% monitored at 610nm.

Fig.5 shows the emission spectra of $CaWO_4$: Eu1% phosphor at different excitations; 395nm, 466nm, 527nm and 536nm respectively. Europium as a dopant, at these excitation wavelengths succeeded to suppress efficiently the domination of basic broad emission at the blue region due to Ca-WO_4. At the other hand, emit the prominent peaks around orange red and red regions. Whereas, emission around orange red is low and very good emission at red regions was observed. The respective intensities for the missions at different excitation wavelengths were tabulated in table-1, for the better understanding. The emission at 593nm, 608nm and 616nm with a sibbling at 614nm was observed. Out of which the intensity of the orange range peaks at 593nm and 608nm are low and the intensity of the red peak at 616nm is very high and prominent. The intensity of the 616nm peak is high around 630 units for 460nm excitation,

around two third for 316nm excitation, around one third for 591nm excitation and is around one fourth for 527nm excitation. 616nm emitted peak is due to $^5D_0 \rightarrow {}^7F_2$ transition of Europium and is due to sensitive electric dipole with energy 2.015 eV. 608nm emitted peak is due to $^5D_0 \rightarrow {}^7F_2$ transition of Europium and is due to sensitive electric dipole with energy 2.015 eV. 593nm emitted peak is due to $^5D_0 \rightarrow {}^7F_1$ transition of Europium and is due to magnetic dipole with energy 2.118 eV.

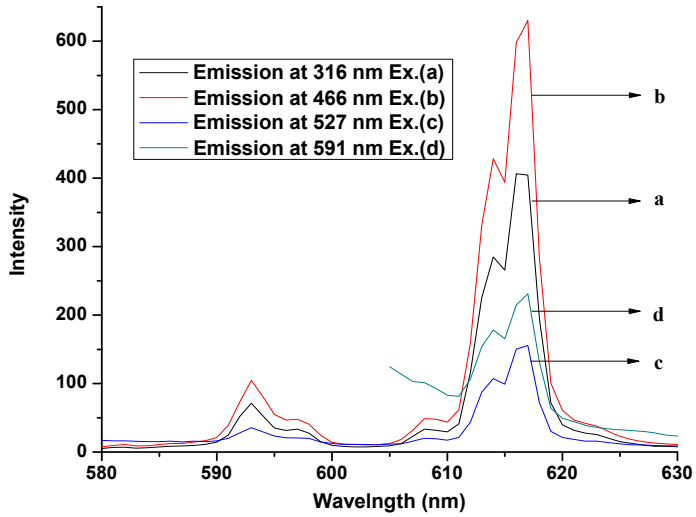

Fig.5: Emission spectra of $CaWO_4$: Eu1% at different Excitations

S.No.	Excitation Wavelength(nm)	Emission wavelengths(nm)	Respective Intensities
01.	316	593, 608, 614, 616	71, 33, 285, 406
02.	466	593, 608, 614, 616	105, 50, 429, 630
03.	527	593, 608, 614, 616	35, 20, 107, 156
04.	591	593, 608, 614, 616	--, 101, 178, 231

Table- 1 Intensities of emissions for different excitations

2.2 X- Ray Diffraction:

Fig.6 is XRD of $CaWO_4$:Eu1%. The calculated crystallite size for the highest intensity peak, using Scherer's formula, $d = K\lambda / \beta \cos\theta$, where 'K' is the Scherer's constant (0.94), 'λ' the wavelength of the X-ray (1.5418 Å), 'β' the full-width at half maxima (FWHM) (0.3936), 'θ' the Bragg angle of the highest peak is 23. 4355°, $\cos\theta$ = 0.9175, is around **22.98nm**. Average value of crystallite size calculated by considering all the peaks is **24.78nm.** Further from the JCPDS data the crystal structure is found to be tetragonal. The depicted peaks in the XRD spectrum are well matched with the JCPDS data (with card no.85-0443).

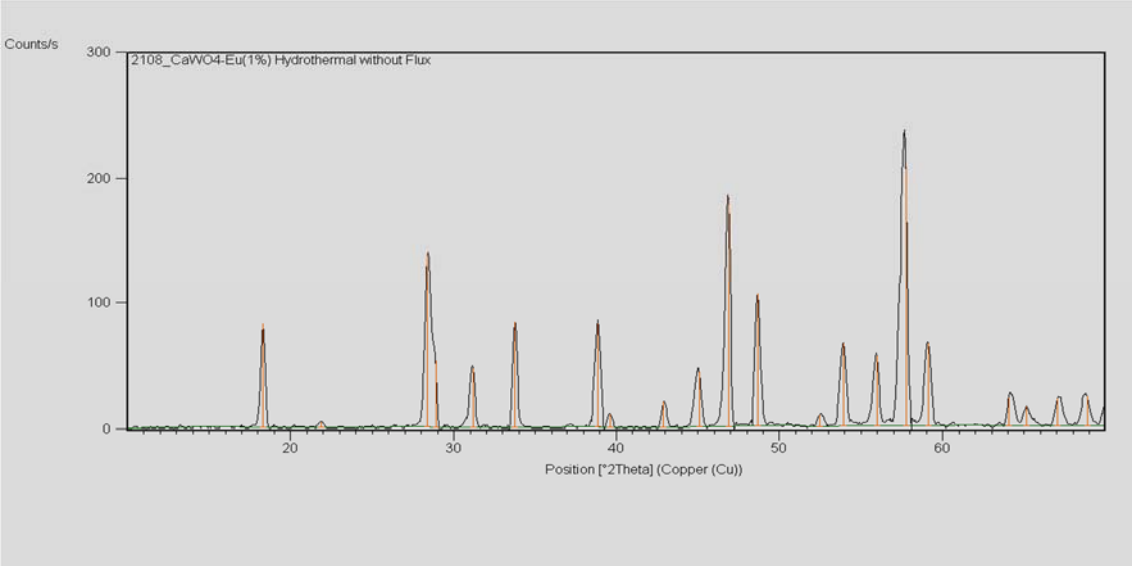

Fig.6: XRD of $CaWO_4$:Eu1%

2.3 HRSEM:

Fig.7: High Resolution SEM OF $CaWO_4$:Eu(1%)

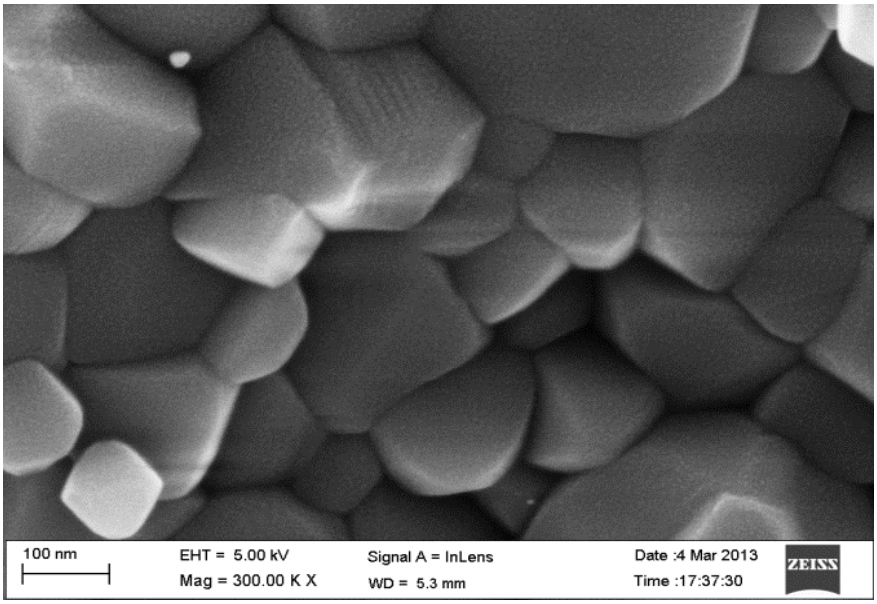

Fig.7 is the High Resolution Scanning electron micrograph (HRSEM) of CaWO4:Eu (1%) hydrothermally prepared and heated at 900°C with magnification of 300K. From the Scanning Electron Micrograph of $CaWO_4$: Eu (1%) it is found that, the particles are mostly pentagon in shapes with various sizes from 80-200nm. From the SEM micrograph the calculated average basal diameter is 90nm.

2.4 FTIR Spectrum:

Fig.8 shows FTIR spectrum at the wave number range of 400-4000 cm^{-1} of the $CaWO_4$ and Europium (1%) doped $CaWO_4$. FTIR measurements were done using KBr method at room temperature. The bending and stretching vibrations of Ca-O (542cm^{-1}), W-O (681 cm^{-1}) and Ca-O-W (823 cm^{-1}) were observed in the undoped as well as doped $CaWO_4$. The FTIR spectrum of sample exhibits broad band below 700 cm^{-1} which is due to the δ (Ca -O-C) mode. The absorption peaks exhibit bands around 1626 and 3448 cm^{-1} may be attributed to O-H stretching mode of water. Residual water - hydroxy groups may be due to absorption of water molecules from atmosphere.

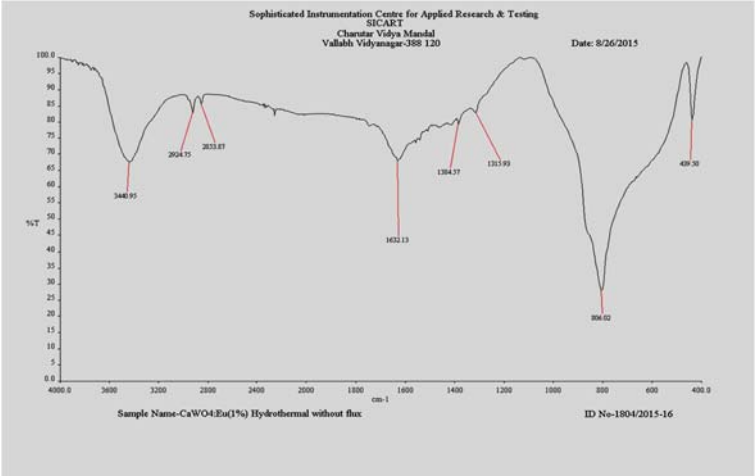

Fig.8: FTIR spectrum of $CaWO_4$:Eu1%

3. CONCLUSIONS:

1. Eu $^{3+}$ is successfully doped in to a $CaWO_4$ system.

2. The XRD pattern of $CaWO_4$: Eu, sintered at 900^oC shows the formation of majority single-phase compound. The average crystallite size is **24.78nm.** Further from the JCPDS data the crystal structure is found to be tetragonal. The depicted peaks in the XRD spectrum are well matched with the JCPDS data (with card no.85-0443).

3. From the Scanning Electron Micrograph of $CaWO_4$: Eu (1%) it is found that, the particles are mostly pentagon in shapes with various sizes from 80-200nm. From the SEM micrograph the calculated average basal diameter is 90nm.

4. From the different stretching of the FTIR spectrum confirms the presence of $CaWO_4$. The peak at 1626 and 3448 cm^{-1} may be assigned to H_2O. The specimen might have absorbed moisture from the atmosphere. Since the sample was sent to characterization after six months of the preparation of the phosphor.

5. XRD and HRSEM reveal that the Phosphor is nano in size.

6. $CaWO_4$: Eu (1%) Phosphor is a good candidate for LED applications for solid state LED of 395 and 467nm excitation.

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