



Synthesis and Photoluminescence analysis of Eu^{3+} activated Calcium Tungstate Phosphor

P.B.L Prasanna¹, K. R. Sayana¹, B S Rao² K. V. R. Murthy³ & J Lakshmi Kumari⁴

^{1,2}Department of Physics, QIS College of Engineering and Technology, A.P, Ongole, India

²VSR and NVR College, Tenali, AP

³Display Materials Laboratory, Applied Physics Department, Faculty of Technology & Engineering, M.S University of Baroda, Baroda-390001, India

⁴Department of Physics, GVSM Government Degree College, Ulavapadu, AP

Email: iprasanna931@gmail.com

Abstract

In this work we report the synthesis of CaWO_4 pure and doped by various concentrations of Eu^{3+} by advanced solid state reaction method. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence analysis. The crystal structure and luminescence properties were investigated by X-ray diffraction patterns, photoluminescence excitation and emission spectra. The results indicate that $\text{CaWO}_4:\text{xEu}^{3+}$ phosphors can be excited by ultraviolet wavelengths 254 nm and a strong orange red emission located at 611, 616 nm ($^5\text{D}_0\text{-}^7\text{F}_2$) corresponding to the characteristic emission of Eu^{3+} ions was observed in all the samples. Scanning electron microscopy (SEM) images revealed that the replacement of Ca^{2+} by Eu^{3+} ions changed the particles' shapes, resulting in different morphologies of the micro crystals. The $\text{CaWO}_4:\text{Eu}^{3+}$ phosphor shows great potential for applications in white light-emitting diodes and field-emission displays as an excellent red-emitting phosphor.

Keywords: Photoluminescence [PL], Rare Earth ions [RE ions], X-ray diffraction [XRD], Solid State Reaction [SSR].

Introduction

Research to improve the luminescence properties of phosphor material became very important, because of its wide applicability in modern technologies such as lighting (fluorescent lamp, LED, displays (PDP, FED), scintillator, communication (optical fiber), for the sake of growing problem of energy crisis. A phosphor with efficient absorption in near UV or blue spectral region and emission in visible region could be potential material for the application in solid state lighting (LED) (an effective and eco-friendlier replacement of fluorescent lamp) [1–4]. The scientific community around the world is continuously exploring the luminescence properties of rare earth ions activated by various host materials [5,6], for finding the efficient phosphors with stable optical properties. Tungstate is one of the interesting host materials that have attracted a great deal of interest owing to self-activation, good stability for physical conditions (chemical and thermal) and wider applicability in various fields such as scintillation, solid state laser, electro-optic, catalytic. Tungstate based phosphors show broad excitation and emission bands due to the ligand to metal charge transfer (CT) transition of $(\text{WO}_4)^{2-}$ and $(\text{WO}_6)^{6-}$ oxyanion complex. Partially filled deep-lying 4f shells of the rare earth ions cause interesting optical properties which make them favorite activators for doping in various hosts. However, the sharp excitation lines of rare earth are less effective and this higher concentration in host lattice leads to quenching of emission. Thus the host sensitization of rare earth ions in tungstate materials is actively studied since last decades [7].

Calcium tungstate has been extensively investigated because its wide applicability in various areas such as X-

ray phosphors, scintillators, solid-state optoelectronic devices, lasers and optical fibers components and a distinguishing property of self activated blue emission related to tetrahedral WO_4^{2-} groups. Also CaWO_4 is a naturally occurring phosphor, which makes it more attractive to the researcher among other alkaline earth metals. Tungstate with scheelite structure, owes its good thermal and chemical stability to tetrahedral symmetry of W^{6+} coordinated with four Oxygen atoms. Tungstate has broad and intense emission bands due to charge transfer (CT) from oxygen to metal in the blue region. Doping of various rare earth ions is used to improve optical property of CaWO_4 . Specially Eu^{3+} has special importance because this rare earth doped in various host materials has application in various fields where intelligent nanomaterials are required and also due to the well established fact that there is efficient energy transfer WO_4^{2-} to Eu^{3+} [8]. Kang et al has studied the luminescent properties of Eu^{3+} in MWO_4 ($\text{M} = \text{Ca, Sr, Ba}$) matrix which shows characteristic red emission of Eu^{3+} with long afterglow upon excitation of 254nm, In the present work synthesis of calcium tungstate activated with Eu^{3+} rare earth ion, photoluminescence (PL) properties of $\text{CaWO}_4:\text{xEu}^{3+}$ synthesized by modified solid state synthesis are reported. Phase purity and formation of synthesized phosphors were confirmed by XRD technique, whereas surface structure was analyzed by using SEM micrograph.

Experimental Details

Chemicals and apparatus

All the chemical reagents were analytically pure and used without further purification. For synthesis of CaWO_4

phosphor pure and doped with varying concentrations of Eu (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mol %) rare-earth ions prepared using solid state reaction method. Stoichiometric proportions of raw materials namely, calcium carbonate (CaCO_3), Tungsten Oxide (WO_3) and Europium Oxide (Eu_2O_3) of 99.9% purity were used as starting materials, alumina crucibles, agate mortar pestle and high temperature muffle furnace were used to synthesize these phosphors and as synthesized materials were characterized by X-ray diffractometer (XRD) (PANalytical X'Pert Pro) with Cu $K\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$), scanning electron microscope (SEM) (JEOL, JSM-6380), Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using 150 Watt Xenon lamp as excitation source.

Synthesis and Physical Characterization

The stoichiometric proportions are weighed and ground into a fine power using agate mortar and pestle for 1 hour, the ground samples were placed in an alumina crucible and heated at 1200°C for 4 hours in muffle furnace with a heating rate of $5^\circ\text{C}/\text{min}$. The samples are allowed to cool to room temperature in the same furnace for about 20 hours. The prepared samples were again ground in to powder for taking the characteristic measurements. All the synthesized phosphor samples were characterized by X-ray diffraction (Synchrotron Beam Indus -II) to identify the crystallinity and phase purity of the phosphor. The Photoluminescence (PL) emission and excitation spectra were measured by Spectrofluorophotometer (SHIMADZU, RF-5301 PC) using 150 Watt Xenon lamp as the excitation source. The emission and excitation slit were kept at 1.5 nm, and recorded at room temperature. The particle morphology of the prepared solid nano powders was characterized by SEM.

Results and discussion

The XRD patterns of the resulting base and Eu^{3+} ions doped CaWO_4 powder samples are shown in Fig.1, all the diffraction peaks of $\text{CaWO}_4\cdot x\text{Eu}^{3+}$ phosphors can be indexed by the standard power diffraction file card of JCPDS:85-0443 and it is seen that all acquired diffraction peaks and calculated cell parameter are $a = b = 5.26 \text{ \AA}$, $c = 11.42 \text{ \AA}$ are in good agreement with standard data of scheelite structure (see Fig. 2) of CaWO_4 with tetragonal crystal system and I41/a space group.

From the figure it is found that majority of phosphor is in single phase. It clearly indicates that the heat treatment temperature and time were sufficient to form single phase [9]. The crystallite sizes of pure CaWO_4 and Eu^{3+} doped CaWO_4 are calculated 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 (1.54060 \AA), ' β ' the full-width at half maxima (FWHM), ' θ ' the Bragg angle of the XRD big peak, and found to be 4.88nm and 9.47nm. Synthesized phosphor samples are said to be phase pure

because no additional diffraction peaks are observed that could be attributed to the impurities because the Eu^{3+} ions were diffused into CaWO_4 host lattices.

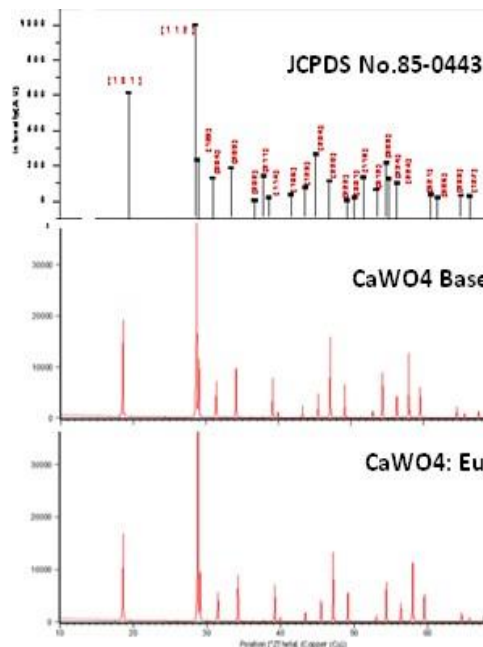


Figure.1. XRD pattern of CaWO_4 phosphor

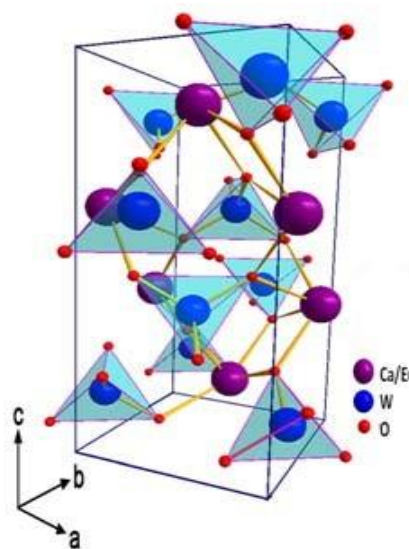


Figure.2. Crystal structure of CaWO_4 (Scheelite structured tungstate) with one unit cell

Fig.3 shows the excitation and emission spectrum of resulting base CaWO_4 phosphor monitored at 450 nm, excitation spectrum shows broad band corresponding to ligands to metal charge transfer (LMCT) WO_4^{2-} group of CaWO_4 [10,11]. It can be seen clearly that the excitation

spectrum mainly consists of a broad band with maximum at 260nm which arises due to electric dipole (ED) allowed transitions ($^1A_1 \rightarrow ^1T_1, ^1T_2$) of WO_4^{2-} group of host lattices ($CaWO_4$). Curve 2 shows the PLE spectra of the $CaWO_4$ base phosphors with 254nm excitation. The PLE spectra (monitored at 450 nm) exhibited a wide band ranging from 350 to 600 nm with a center wavelength at about 450 nm which is a charge transfer (CT) band corresponding to the $O^{2-} \rightarrow W^{6+}$ transitions [12,13].

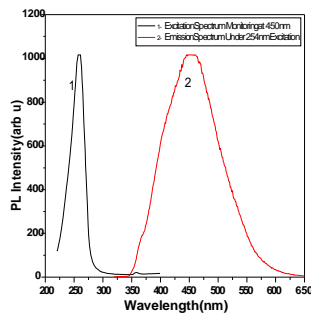


Figure.3. PL Excitation and Emission Spectrum of $CaWO_4$ Base Phosphor

Fig.4 and 5 show PL Emission spectra of Eu^{3+} doped $CaWO_4$ phosphors with different Eu^{3+} ion concentrations. Figure 2 shows the PL emission spectrum of the $CaWO_4:xEu^{3+}$ phosphor excited at 254 nm, the broad emission band centered at about 433 nm is assigned to the CT transition of WO_4^{2-} group, while the other four narrow peaks located at 580, 592, 611 and 616 nm are attributed to $f-f$ transition within the $Eu^{3+} 4f^6$ electron configuration. The spectra show prominent peaks at 580, 592 and 611, 616 nm corresponding to magnetic dipole transition ($^5D_0 - ^7F_1$) and electric dipole transition ($^5D_0 - ^7F_2$) respectively. With the excitation of CT band, the existence of emission peaks of Eu^{3+} ions suggests that the ET from WO_4^{2-} group to Eu^{3+} ions occurs, which is in good agreement with the result from the PL emission spectrum.

It is well known that the activator concentration greatly influences the emission intensity. Figure.4 shows the variation of Eu^{3+} narrow PL emission peaks with Eu^{3+} concentration from 0.5 to 3.0 mol%. It is obvious that increase the emission intensity one has to increase activator concentration without getting quenching due to concentration attributed to non radiative energy transfer (ET) processes from WO_4^{2-} to Eu^{3+} . In order to find the optimum concentration of Eu^{3+} the intensity of ED transition ($^3D_0 \rightarrow ^7F_2$) is observed for different concentration of Eu^{3+} and is shown in Fig. 5 (Inset) the intensity of MD and ED transition is maximum for 2.5 mol % concentration of Eu^{3+} in host matrix and beyond that it starts decreasing because of dissipation of energy through nonradiative

transitions which might arise due to the defect structures caused by Eu^{3+} doping. Doping of Eu^{3+} causes to increase the defects in host lattices which is due to the difference in ionic radius and charge compensation effects.

The emission spectrum of Eu^{3+} ion is dominated by the hypersensitive red emission $^5D_0 - ^7F_2$ transition of Eu^{3+} ion at 611 and 616 nm. This indicates that Eu^{3+} ions are located at sites without inversion centres in $CaWO_4$ [14], which is in agreement with the crystal structure of $CaWO_4$. $CaWO_4$ has tetragonal scheelite structure and space group C_{4h} , in which the Ca^{2+} ion is coordinated by eight oxygen atoms and has an S_4 point symmetry (without an inversion centre)[15]. The doped Eu^{3+} ion will substitute for the Ca^{2+} ion in the host lattice i.e. $CaWO_4$ due to their close ionic radii ($Eu^{3+}=0.107nm$; $Ca^{2+}=0.112 nm$ for eight coordination respectively)[16-18]. As a result, the Eu^{3+} ion should hold a local site symmetry of S_4 in the $CaWO_4$ host lattice. If the Eu^{3+} ions occupy host sites with inversion symmetry, optical transitions inside the $4f^n$ configurations are strictly forbidden as electric dipole transition. So it can be concluded that the Eu^{3+} ion is not located at the site with inversion symmetry for the phosphor.

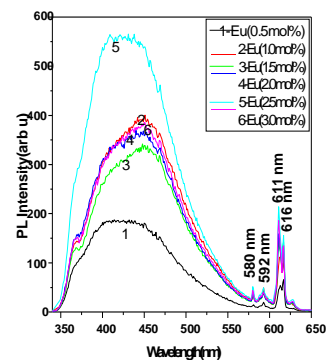


Figure.4. PL Emission Spectrum of $CaWO_4:xEu^{3+}$ ($x=0.5-3.0$ mol %) phosphor under 254nm Excitation

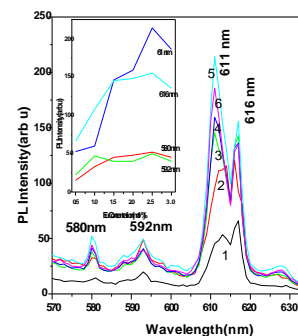


Figure.5. PL Emission Spectrum of $\text{CaWO}_4:\text{xEu}^{3+}$ ($\text{x}=0.5\text{-}3.0$ mol %) phosphor under 254nm excitation. Inset shows intensity variation of emission peaks with Eu^{3+} concentration

In comparison, electrons are first excited to conduction band from valance band when excited at 254 nm, and then the energy is partly transferred to the Eu^{3+} ions (see Fig. 6). In this ET process, the excessive energy can be dissipated by the vibration of the lattice. Eventually, the characteristic emissions of Eu^{3+} ions from ${}^5\text{D}_0$ to ${}^7\text{F}_j$ ($\text{j}=1,2$) transitions were observed.

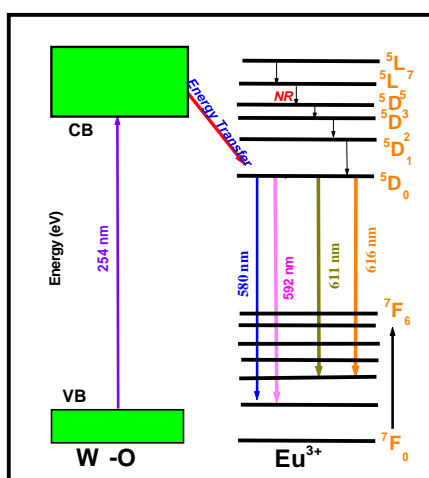


Figure.6. Schematic representation of the energy level diagram with the corresponding energy transfer processes for Eu^{3+} ions doped CaWO_4 phosphors

The typical SEM micrographs of the phosphor powders are depicted in Figure. 7. The morphology of resulting sample which reveals the formation of polycrystalline material with grain size shape distribution is irregular and average grain size is in sub-micrometer range due to agglomeration of smaller grains which forms due to thorough crushing and high temperature processing of the samples. This proves the solid state synthesis method is favorable for synthesis macro structured samples of reported phosphor. The particle sizes are in the size range of 2–8 μm . From SEM images, it has been noted that the agglomeration of synthesized powder phosphors has been increased with the change in Eu content, owing to the density variation [19-21].

Conclusion

In the present work CaWO_4 and Eu^{3+} doped CaWO_4 phosphors were successfully synthesized by conventional solid state reaction method and its photoluminescence studies were investigated in detail. A Scheelite tungstate based blue [450nm] and orange red emitting phosphor, tested by X-ray diffraction pattern and SEM micrographs show the formation of microcrystalline sample. The

photoluminescence studies of synthesized Eu^{3+} doped CaWO_4 phosphor material shows intense orange red emissions at 580nm & 592nm and 611nm & 616nm corresponding to characteristic transitions corresponding to MD (${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$) and ED (${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$) of Eu^{3+} ion under the excitation wavelength of UV 254 nm respectively. The XRD and PL results indicate the tetragonal system and quantitative substitution of Eu^{3+} ion in the lattice sites of Ca^{2+} in CaWO_4 . The developed red phosphors could be potential candidates for applications in phosphor converted white light emitting diodes. These phosphors with tunable emissions may find potential applications in the fields of miniature color displays in the near future.

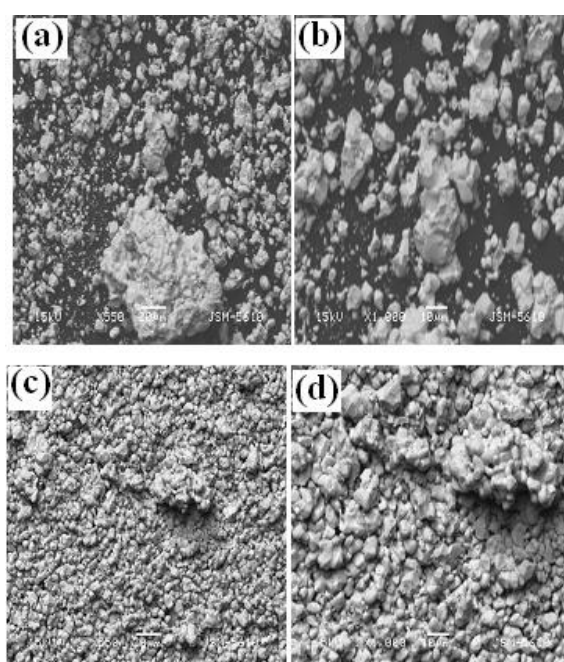


Figure.7 Typical SEM images of $\text{CaWO}_4:\text{xEu}^{3+}$ (base and mol %) powders with different magnification (base (a) X550, (b) X1000 and Eu doped (c) X550, (d) X1000) and different positions.

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