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Usage of Optoelectronic devices in Photoluminescence studies of $CaWO_4$: Ce Phosphor

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Abstract: ***At present, there are very few reports available on rare-earth doped calcium tungstate($CaWO_4$) nanophosphors synthesized using hydrothermal method and study of their optical properties. An extensive spectroscopic study is required to completely understand the luminescent properties, including energy transfer mechanism and morphology of nano tungstates. This completes solid state reaction. The phosphor$CaWO_4$: Ce(0.5 – 3.0 mol%) is Excited with 254nm the PL emission is found around 450nm.The tungstate doped with rare-earth nanophosphors have attracted special attention due to the corresponding bulk materials have large practical applications in solid state lighting and displays. It was also discovered that doping of calcium tungstate ($CaWO_4$) with trivalent ions or mono valent ions is particularly effective in improving radiation sensitivity of the scintillate material.***

Key words: - Photoluminescence, X-ray diffraction [XRD], Scanning Electron Microscopy [SEM], Energy Dispersion Spectrum [EDS], Particle size Analysis, Solid State Reaction technique

I. INTRODUCTION

From literature survey it is observed that nano sized inorganic low-dimensional systems exhibit a wide range of unique optical properties. Luminescent materials in the form of nanobelt, nanoparticles, nanorods, nanowires, nanotubes are of interest not only for basic research, but also for fascinating applications .Divalent metal ion tungstates are of interest for their luminescent properties and metal tungstate have good application prospects in scintillators, optical fibers, microwave applications, humidity sensors, photoluminescence materials, and catalysts, etc. Most of the tungstates have scheelite structure or wolframite mainly depending on their cationic radii. Small radii which are in favour of forming wolframite structure and large radii which are in favour scheelite structure. In wolframite structured tungstates the intrinsic luminescence is occurred from the annihilation of self - trapped excitation, and thereby forms excited $[WO_6]^{6-}$ complex that can be either excited in the absorption band or in the recombination process.

Even rare-earth ions Ce^{3+} acts as common activators such that it will detect local environments due to their super-sensitive f–f transitions in some hosts. Photoluminescence study of Ce^{3+} doped host materials have been studied widely, strong emission of Ce^{3+} is first observed in LaF_3. In particular a host Ce^{3+} showed a very intense emission and in tungstates emission was quenched by Ce^{3+} doping. Recently, M.You et al. demonstrated that $CaWO_4$:Eu^{+3} is a promising red phosphor for blue based LEDs.

II. MATERIALS AND EXPERIMENTAL METHODS

We present the rare earth Ce doped $CaWO_4$ by solid state reaction method heated at 1200 ^{0}C temperature. The effects of do pant on the crystallization, optical properties and size of particles were presented. The received powder after grinding is transferred into Aluminum crucibles, these crucibles contains mixer covered with lids are transferred into furnace. This crucibles contained mixer is heated at 1200^{0}C for 2 hours and allowed to cool to room temperature by switching off the furnace. After 18 hours of cooling the sintered material which is a ceramic phosphor is collected from the crucible and grinded thoroughly to get uniform size of phosphor grounded using motor and pestle for 30 minutes of each phosphor. All the phosphor samples were characterized by X-ray diffraction using (Synchrotron Beam Indus -II). The Photoluminescence (PL) emission and excitation spectra were measured by Spectro fluoro photometer (SHIMADZU, RF-5301 PC) using Xenon lamp as excitation source at display research Lab, Department of Applied Physics, Faculty of Technology and Engg., M.S. University, Baroda. The emission and excitation slit were kept at 1.5 nm, recorded at room temperature.

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III. RESULTS AND DISCUSSIONS

A. Photoluminescence Studies of $CaWO_4:Ce^{3+}$ phosphors

Fig.1 Is the PL excitation and emission spectra of Ce doped $CaWO_4$ phosphor. Curves 1-6 are various concentrations of Ce in $CaWO_4$. Interestingly, the luminescence intensity increases when the cerium concentration increases in $CaWO_4$ as shown in figure 1. The luminescence observed in $CaWO_4$ is due to the intrinsic defects sites which are responsible and also due to self-trapped holes (STH) and radiative recombination. Table 1 is the dopant concentration vs PL emission peak intensity.

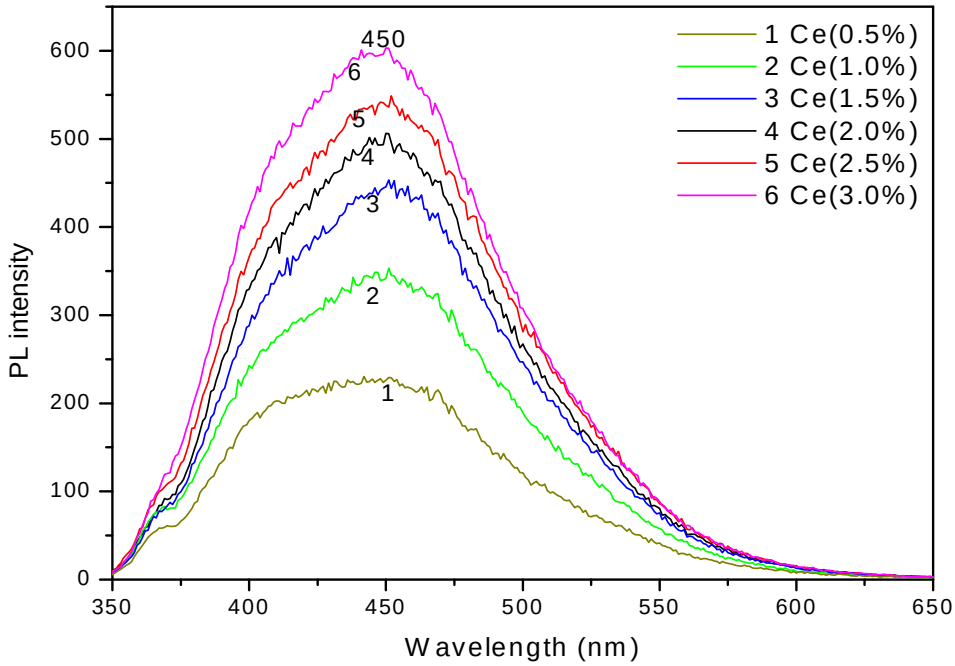

Fig.1 PL excitation and emission spectra of Ce (0.5 – 3.0 mol%) doped $CaWO_4$ phosphor

Table 1

S.No	Sample	Dopant concentration	Emission Peak Intensity
1	$CaWO_4$: Ce (0.5% - 3.0%)	0.5%	237
2		1.0%	353
3		1.5%	455
4		2.0%	511
5		2.5%	549
6		3.0%	606

It is found from table with dopant Ce concentration the emission peak intensity also increased. However Ce (0.5%) doped $CaWO_4$ the intensity of 450nm peak is just 237units. The suppression of intensity is due to the non radiative 5d–4f transition of the excited Ce ion. Therefore, Ce ions could serve as non radiative traps in $CaWO_4$ crystal lattice. However, as the Ce ions concentration increases the non radiative traps in $CaWO_4$ crystal lattice is enhancing the PL out of 450nm peak.

B. XRD Pattern of $CaWO_4$:Ce (3.0%)Phosphors

From the XRD pattern it can be observed both the phosphors looks mostly in single phase. The crystallite size is calculated using Scherrer'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 Å), 'β' the full-width at half maxima (FWHM),'θ' the Bragg angle of the XRD big peak. Using the Schrieffer's formula the crystallite size.

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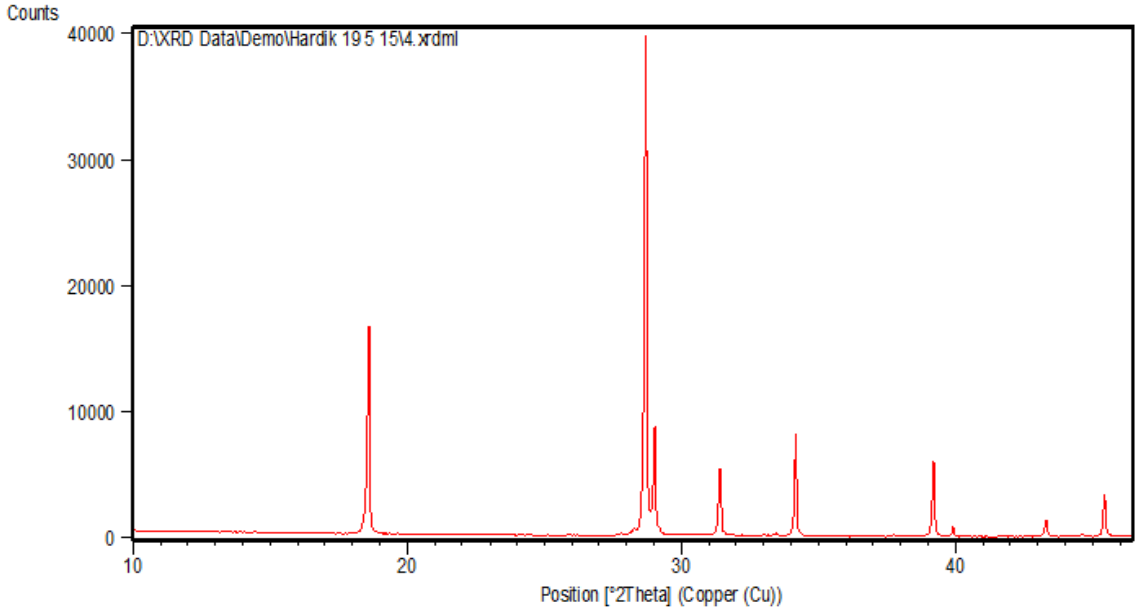

Fig.2 XRD pattern of Ce (3.0 mol%) doped $CaWO_4$ phosphor

The calculated crystallite size for the base $CaWO_4$:Ce (3.0%) phosphor is 9.47nm. From overall XRD study the phosphor under study the addition of do pants to the host material did not change their crystallite size significantly.

C. SEM diagram of $CaWO_4$:Ce (3.0%)Phosphor:

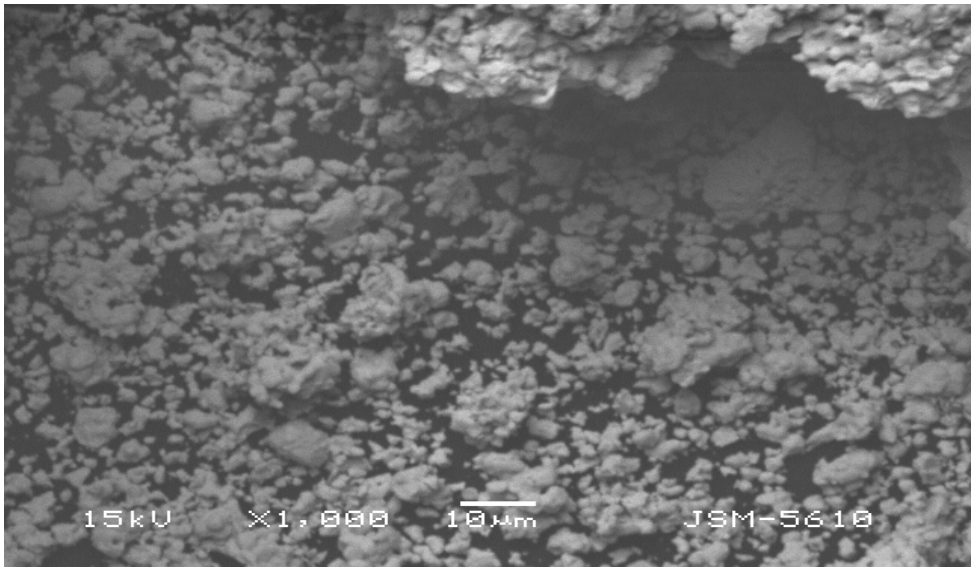

Fig. 3 SEM image of Ce (3.0%) doped $CaWO_4$ phosphor

Fig 3is the SEM micrograph of Ce(3.0%) doped in $CaWO_4$. From the micro graphs it is found that particles are irregular shape and agglomerated of various sizes from micron to 50 microns.

D. EDS Spectrum of $CaWO_4$:Ce (3.0%)Phosphor:

EDS is recorded in the SEM machine where in SEM micrographs are recorded. Here Fig. 4is the EDS spectra of the phosphor mentioned. In EDS spectrums mostly elements of base materials are seen. However in the few of the EDS spectrum strontium is

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seen which are adjacent elements of the host elements and their contribution to PL is negligible. There fore in general it is normally concluded that the phosphors Under EDS study are pure without any impurities.

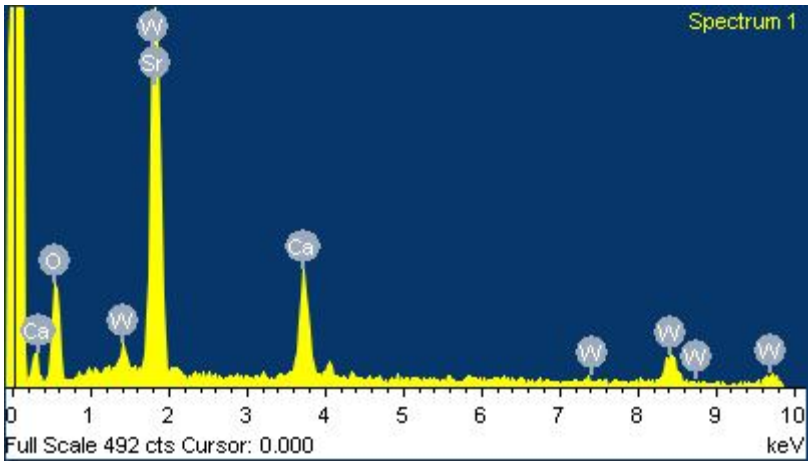

Fig.4 EDS of Ce (3.0%) doped $CaWO_4$ phosphor

E. Particle size analysis

The particle size histogram of cerium doped $CaWO_4$ whose specific surface area is 0.8162sqm/gm. From Fig.5 it is found majority of particles are around 65micro meter range. To get uniform particle size high power ball milling is required.

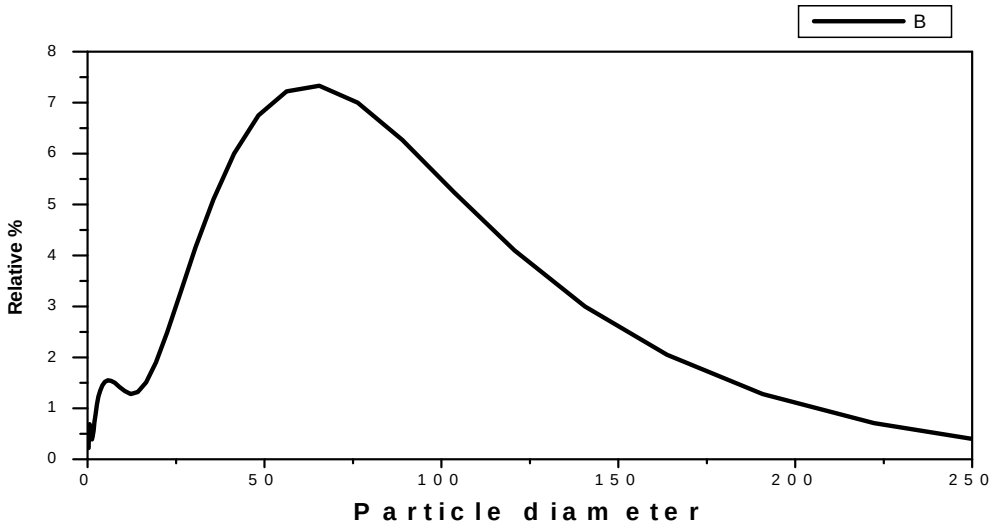

Fig. 5 particle size histogram of $CaWO_4$:Ce(3.0%) phosphor

IV. CONCLUSIONS

A. The PL characteristics of $CaWO_4$:Ce phosphor can be used as white light and can be used in back light producing for liquid display and other optoelectronic devices.

B. It can be also used in CFL's since the results obtained are comparable with the commercially available phosphors.

C. The photoluminescence study shows that the emissions from electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) is less over that of magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$).

D. From the fig 1 it is observed as the excitation Wavelength increases the PL emission Increases linearly up to 265nm and this decreases marginally.

E. XRD study the calculated crystallite size for the $CaWO_4$:Ce(3.0%) phosphor is 9.47nm.

F. EDS study it is normally concluded that the phosphors are pure without any impurities.

G. The particle size histogram of cerium doped $CaWO_4$ whose specific surface area is 0.8162sqm/gm.

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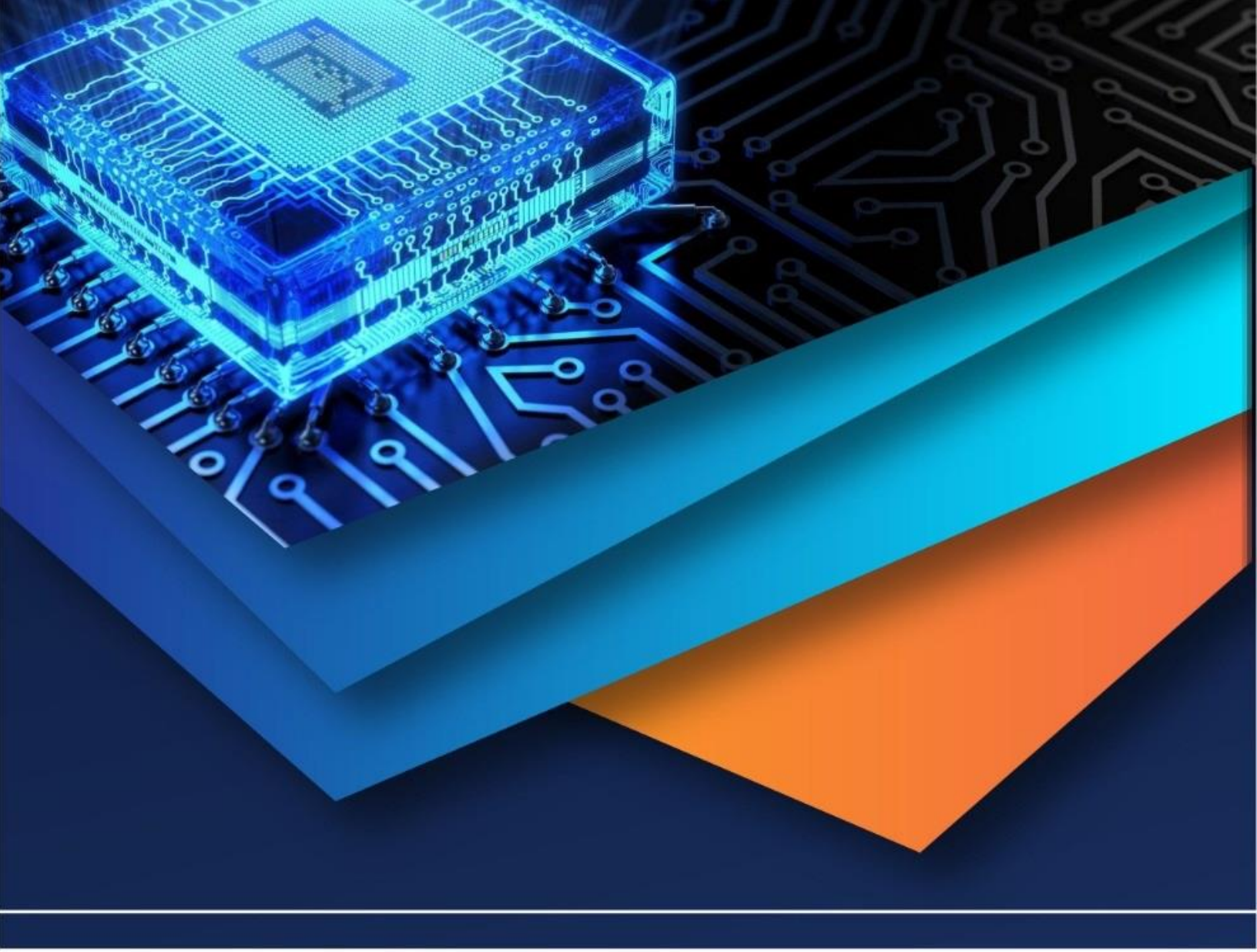

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