Structural and photoluminescence behavior of thermally stable Eu^{3+} activated $CaWO_4$ nanophosphors via Li^+ incorporation

Sushri Sangita Nanda, P. V. Ramakrishna, T. Lakshmana Rao and S. Dash[1]

Dept. of Physics and Astronomy, National Institute of Technology, Rourkela, Odisha-769008

[1]Corresponding Author: dsuryanarayan@gmail.com

Lanthanide ion doped inorganic nanocrystals featured great attention due to their unique optical property and it can be employed to make optoelectronic devices. Metal tungstates and its derivatives are (RWO_4, R = Ca, Sr, Ba) excellent host materials in various optical application. In this work, we have studied the structural and photo physical analogue of Eu^{3+} activated CaWO4 nanophosphors via Lithium (Li^+ = 2, 5, 7 and 10 at.%) ion incorporation. As-prepared (APS) samples were annealed at 900 °C to eliminate unwanted organic moieties present in the sample and to improve crystallinity. The samples are characterized employing X-ray diffraction (XRD), Fourier transform IR spectroscopy (FTIR), UV-VIS spectroscopy, photoluminescence studies and lifetime decay studies. FTIR features an absorption band at ~832 cm^{-1}, which correspond to its antisymmetric vibrations into O-W-O band in the WO_4^{2-} tetrahedron. $CaWO_4$ having the scheelite type structure with C_{4h} point group and $I4_1/a$ space group. The surface morphology of the samples are studied with Scanning Electron Microscopy (SEM). Lithium Co-doped $CaWO_4$:Eu^{3+} nanoparticles show red luminescence because of strong host contribution and different energy transfer rates from host to Eu^{3+} ions under 266 nm excitations. Lithium ion enhances the crystallinity and radiative transition rate thus results in higher emissive property. Calculated CIE coordinates of these Li^+ doped 900 °C annealed samples under 266 nm excitation is x = 0.65 & y = 0.34, which are closer to the standard of NTSC (x = 0.67 & y = 0.33). This material may be potential candidates for white light emitting diodes.

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PRESENTED BY

SUSHRI SANGITA NANDA
Ph.D. Scholar

Supervisor
Dr. S. N. Dash
Dept. of Physics and Astronomy
NIT Rourkela, Odisha

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INTRODUCTION

Conventional incandescent

fluorescent light sources

White light emitting diodes

LEDs

- long operating lifetime
- higher luminous efficiency
- reliability and higher energy efficiency

- A phosphor with high quantum efficiency and excellent thermal stability is required to withstand high temperatures generated during the LED action without compromising the luminescence.

OBJECTIVE

Scheelite type $CaWO_4$ has attracted great attention:

- excellent thermal stability
- interesting luminescence behavior
- self-activated nature
- wide emission spectra in visible region and attractive structural properties which can be applied in optical fibers, laser host materials, photoluminescence, scintillation detectors and microwave applications.

The luminescence properties of $CaWO_4$ can be improved by doping various rare-earth ions that result in broad and intense absorption bands.

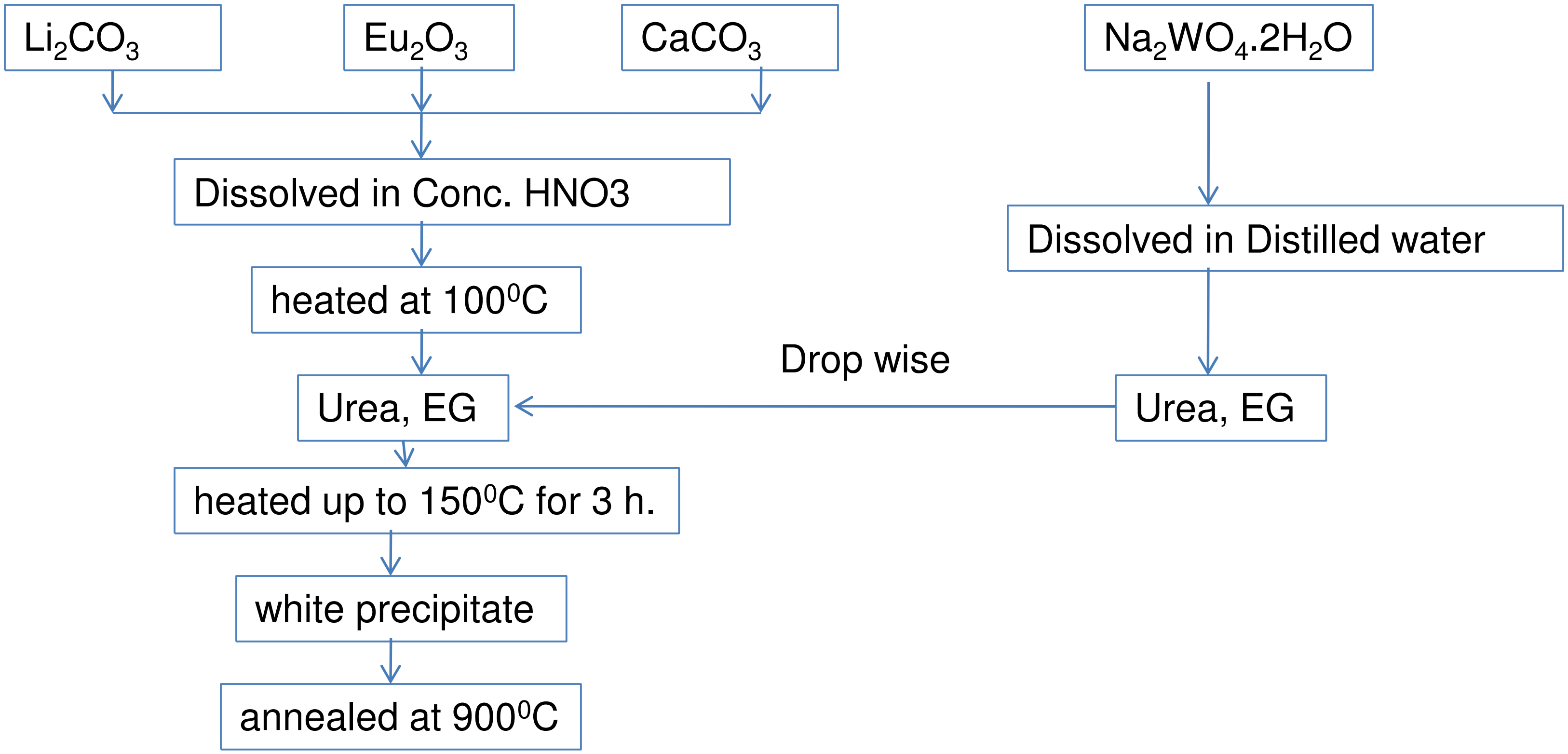
To improve the efficiency of nanomaterials, several approaches has been reported: such as host sensitization, energy transfer and incorporation of alkali metals ions (Li, Na, K)

In this work we have adopted the incorporation of Li in the materials

MATERIAL SYNTHESIS

We have prepared Nanophosphors using a polyol synthesis route, under urea hydrolysis

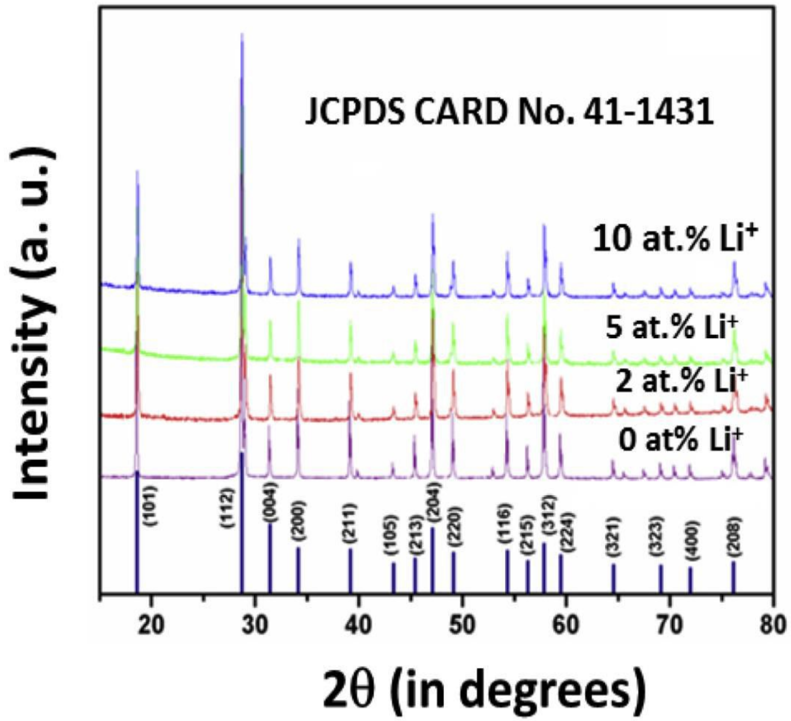
$CaWO_4$:3 at.% Eu^{3+} (concentration of Eu^{3+} was fixed) doped with Li^+ (Li^+ = 2, 5, 7 and 10 at.%)



Results and Discussions

XRD STUDY

XRD patterns of CaWO4:3 at.%Eu^{3+} with different at.% of Li^{+}

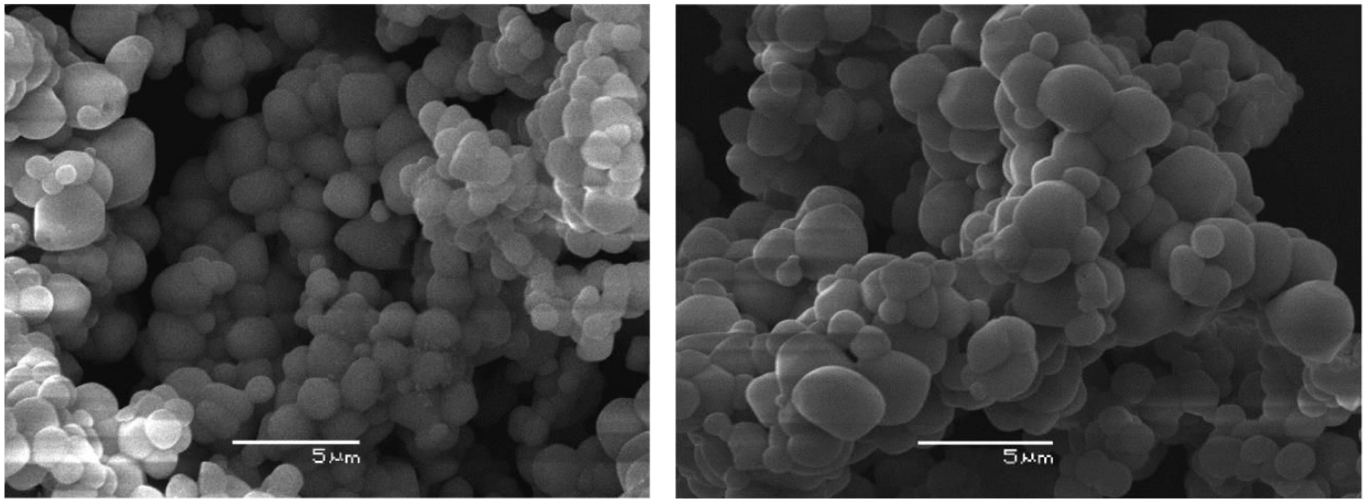


- It confirms the single phase formation.
- The unit cell parameters are a = 5.243 Å, b = 5.243 Å,c = 11.373 Å and V = 312.63 Å
- The size of nanocrystal was found to be 37 nm by using the Scherrer equation,

D =0.89λ/βCosɵ

SEM ANALYSIS

SEM micrographs of (a) Li^+ free and (b) 10 at. % Li^+ co-doped CaWO4:Eu.



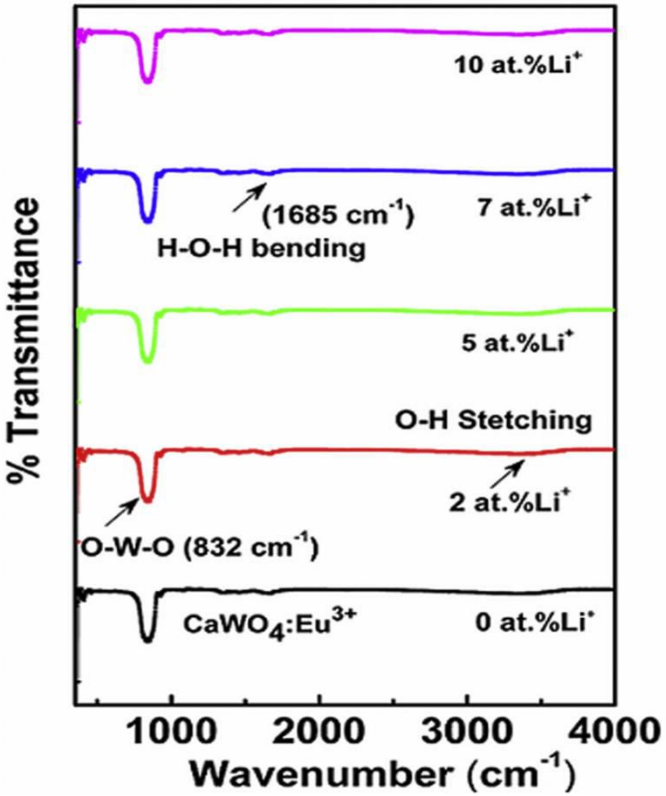
• lithium ion co-doping improves the density of nanoparticles and roughness of the surface. samples with lithium ion doping confirms its homogeneous behavior.

• Accommodation of Li^+ into lattice matrix does not affect the morphology of the CaWO4:3 at .% Eu.

• Almost nearly spherical nanoparticles are formed with and without lithium codoped samples.

FTIR STUDY

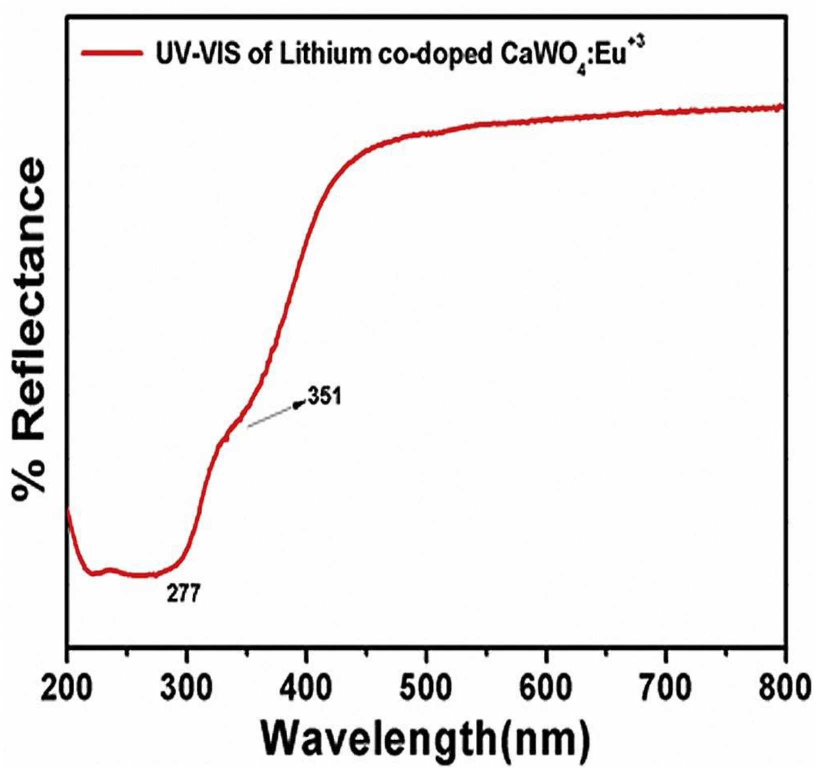
FTIR spectra of $CaWO_4$:3 at.%Eu^{3+} with different at. % of Li^{+}



- Peaks observed at 1685 and 3510 cm^{-1}implying H-O-H bending and O-H stretching vibrations, due to the presence of water molecules on the surface of nanoparticles.
- The strong absorption peak at 832 cm^{-1} is due to the O-W-O bond in $CaWO_4$ host matrix.
- It confirms the single-phase formation.

UV-VIS STUDY

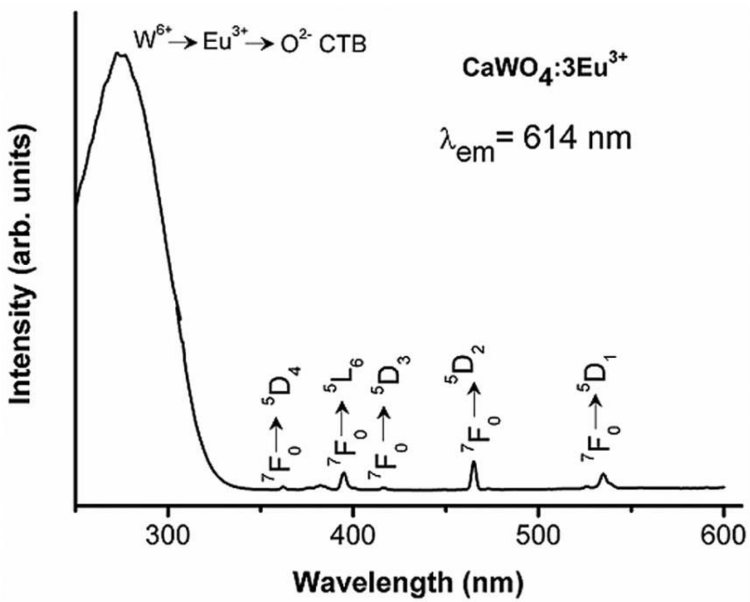
UV - VIS spectrum of 2 at.% Li^{+} co-doped $CaWO_4$:3 at%Eu^{3+}



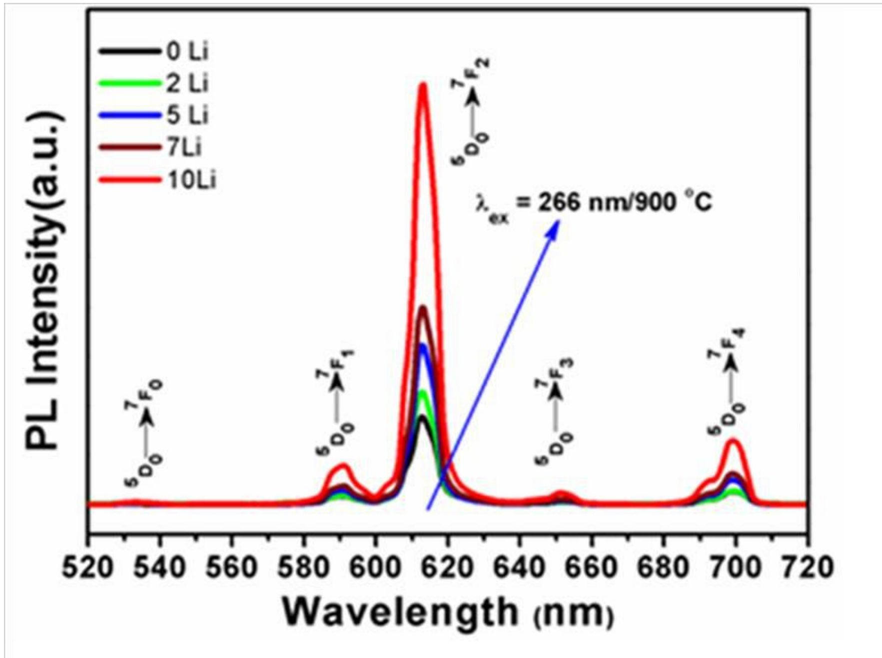
- The absorption band near 277 nm features the band formation of Eu^{3+} and/or W-O.
- Peak located near 351 nm confirms the characteristics of Eu^{3+} ion into $CaWO_4$ host matrix.

Photoluminescence study

Excitation spectrum of CaWO4:3 at.%Eu^{3+}



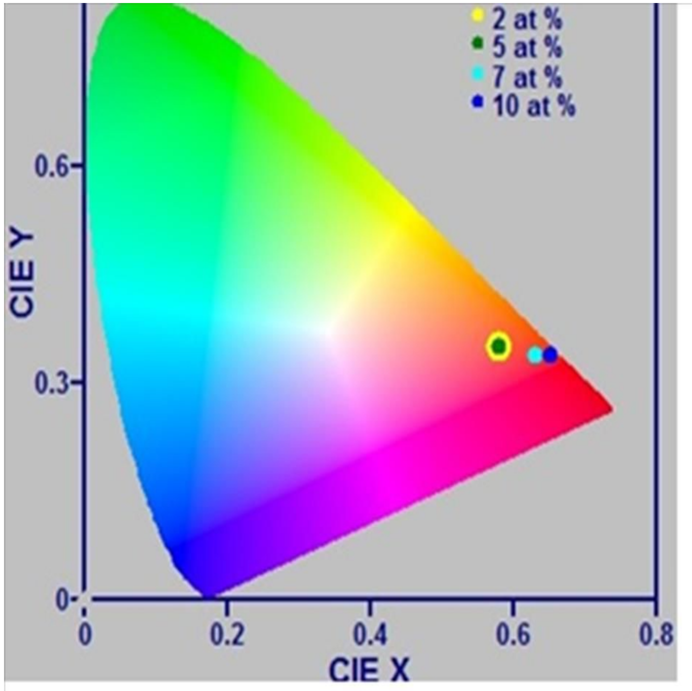
PL spectra of $CaWO_4$:3 at.% Eu^{3+}co-doped with Li^{+}(0, 2, 5, 7 and 10 at. %)



- The band at ~272 nm was mainly due to the combination of the ligand to metal charge transfer (O^{2-} -W^{6+}) and charge transfer band from the completely filled 2p orbitals of O_2 to the partially filled f-f orbitals of the Eu^{3+} ions(O^{2-} - Eu^{3+})
- In the emission spectra the strongest peak is visible at 614 nm and the samples show a predominant red emission of the characteristic Eu^{3+} ($^5D_0$ - $^7F_2$) transition when excited under 266 nm.

CIE STUDY

CIE diagrams for $CaWO_4$:3 at.%Eu^{3+} with Li^+ (2, 5, 7 and 10 at.%) doped samples



• The Li^+ (2, 5, 7 and 10 at. %) doped $CaWO_4$ show the CIE chromaticity coordinates around deep red regions. which is the characteristic region for emissions from Eu^{3+} .

CONCLUSION

- $CaWO_4$:3 at.%Eu^{3+} nano phosphor co-doped with Li^+(2, 5, 7and10 at %) were prepared using polyol synthesis route.
- XRD study confirms the tetragonal scheelite type structure.
- SEM study confirms the homogenous distribution of nanoparticles with nearly spherical morphology.
- Photoluminescence study confirms the reduction of nonradiative decay pathways and improves the host matrix crystallinity with incorporation of Li^+ ion into host matrices.
- These studies reveal that $CaWO_4$:Eu^{3+}nano-phosphors can be used as potential red emitting phosphors for the development of white LEDs.

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