CHAPTER - 7

Summary and Conclusions

During the last decade, new vision in the materials research broadly defined as 'nano science and nanotechnology' have emerged. It is necessary to develop nano material with perfect economical and qualitative approach. $CdWO_4$ become a subject of renewed interest about years ago when its favorable characteristics as scintillation detector was reported. It has been also investigated for many applications, such as, industrial processing control and inspection, dosimetry, and nuclear weapons and waste monitoring. Now, it is need to improve scintillating and optical properties by changing various parameters like temperature variation, doping with appropriate dopants, different reaction media, different synthesis methods, etc.

We have synthesized undoped as well as rare earth (Ce, Nd, Eu and Er) doped $CdWO_4$ phosphor with various morphologies by low cost hydrothermal method at low temperature. To synthesis pure $CdWO_4$ phosphor with different dopant and reaction condition, we designed Stainless Steel Autoclave with Teflon vessel. It has 150 ml capacity to produce nano phosphor in one attempt.

In order to do systematic analysis, we have divided our experiment in to ***three parts***. In the first part, we synthesized undoped as well as doped $CdWO_4$ crystals with different dopants by Hydrothermal Method. In the second part of our experiment, we synthesized Cerium doped $CdWO_4$ by varying pH of reaction medium at constant temperature by same method. Effects of Europium on $CdWO_4$ with different pH of solution were synthesized in third part.

Cadmium Chloride ($CdCl_2$ .H2O), Sodium Tungstate (Na2WO_4.$2H_2O$) and Rare - earth Oxide are purchased from Alfa Aesar of A.R.(analytical reagent) grade and used without further purification. Distilled water was used as solvent to prepare all required solutions. Acetone and Ethanol were used to wash prepared samples. The pH value 4, 6, 8 and 10 of this solution was adjusted drop wise with CH_3COOH or NaOH solution .After that the samples were characterized by XRD, PL, TEM and FTIR.

XRD studies on the phosphors prepared using hydro thermal method revealed that all the phosphors are a pure monoclinic phase of $CdWO_4$ with a wolframite structure with space group P2/c (13) and the calculated crystallite size using Scherer's formula un-doped and undoped phosphors confirms the formation of nano crystallites.

Effect of dopants

The calculated crystallite size using XRD data suggest that the prepared RE doped $CdWO_4$ phosphors are in nano size.In doped $CdWO_4$, the PL emission at 468nm to 476nm was ascribed to the $^1A_1 \rightarrow {}^3T_1$ transition within the WO_6^{6-} complex. This is mainly due to the charge-transfer transitions between the O_2p orbital and the empty d orbital of the central W^{6+} of WO_6 octahedra or to the self-trapped exciton at a WO_6^{6-} oxyanion complex. It is concluded that the WO_6 octahedral structure in $CdWO_4$ is the luminescent center.

For $CdWO_4$: Eu phosphor, not only typical emission of WO_4^{2-} but also yields the characteristic emission of Eu^{3+} and the emission from the excited $^5D_0$ to ^7F_J (J = 0–3) of Eu^{3+} .The peak at 613 nm is predominant out of all these peaks, this feature may be due to the $^5D_0$-$^7F_2$electric dipole transitions of Eu^{3+}. This phenomenon indicates that Eu^{3+} ions have been occupied he non-symmetrysiteintheCdWO$_4$ host lattice the PL intensity of CdWO$_4$ is decreased. This allows us to conclude the energy transfer from WO_4^{2-} groups to Eu^{3+} suggests effective doping of Eu^{3+} in the CdWO$_4$ lattice.

In Er doped CdWO$_4$, different emissions are centered at 385nm, 405nm, 452nm, 476nm, 487nm, 518nm and 538nm are corresponding to the transitions $^4G_{11/2}\rightarrow{}^4I_{15/2}$, $^2H_{9/2}\rightarrow{}^4I_{15/2}$, $^4F_{5/2}\rightarrow{}^4I_{15/2}$, $^2K_{15/2}\rightarrow{}^4I_{13/2}$, $^4F_{7/2}\rightarrow{}^4I1_{15/2}$, $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$. In Nd doped CdWO$_4$, the characteristic peak of WO_4^{2-} group is weak intense compared to UV band edge peak.

The FTIR spectra recorded in the range of 1600-400 cm−1 of the Cerium doped CdWO4 particles. FTIR measurements were done using KBr method at room temperature. The intrinsic bending and stretching vibrations of Cd-O (517,560cm-1), W-O (~680 cm−1) and Cd-O-W (~824 cm−1) were observed in the all three samples. The FTIR spectrum of all samples exhibit broad band below 710 cm−1 which is due to the δ (Ce-O-C) mode.

Effect of pH on Ce doped CdWO$_4$

In the present study the Cerium doped CdWO$_4$ was successfully synthesized by hydrothermal process for 4, 6 and 8 pH. XRD patterns reveal that the cell parameters of as-synthesized products could continuously decrease and also crystallite size decreases as pH increases. From the XRD studies, it is concluded that as pH varied the cell volume and crystallite size reduced marginally.

PL emission studies shows broad intense peak at 469 nm and 476 nm wavelength at 270 nm excitation wavelength in violet - green region peaking in blue region due the formation of low dimensional particles in nano scale. It suggest that more radiative traps generate in basic preparative medium when compare to acidic solution and shifting of peak is attributed to basic medium due the formation of particles having least volume in nano scale.

TEM images infer that pH affect the morphology of cadmium tungstate in terms of its shape and size. As pH increases from 4 to 8, the PL intensity of characteristic peak increases more than 60 percentages. The increase in intensity is attributed to hollow nano tube which is confirmed by TEM studies. Since the hollow nano tubes are present when the phosphor is prepared with 8 pH, it reflects that the coloumbic repulsion are minimum which leads increase in intensity of characteristic peak of $CdWO_4$. The core shall model is established for the formation of hallo nano tubes. From TEM studies it is inferred that as pH increases 4 to 8, the phosphors change their shapes from spheres, rods and hollow tubes where in all are in pure nano scale. Therefore, it is emphasized and concluded that nano material by varying pH.

Effect of pH on Eu doped $CdWO_4$

Eu doped $CdWO_4$ phosphor has been synthesized successfully by varying pH (4 to 10) by using hydrothermal method. From XRD studies, it is concluded that as the pH is varies from 4 to 10, the cell volume marginally reduced. The average crystallite size calculated by using Scherrer formula found to be decrease as pH increase. It is interesting to conclude that at 10 pH the crystallite size hardly 11.6 nm which is approximately four times less to the phosphor prepared at pH 4.

At 4 pH, when the phosphor is excited at 295 nm the Eu emission $^5D_0$–$^7F_2$ having sharp peak at 615 nm with high intensity is observed. When phosphor is prepared at 6 pH, the overall PL emission is observed from 400nm to 625nm peaking at 471nm and 615nm. The band contained violet, blue, green and red emission as this phosphor can be used as white emitting phosphor. This statement also confirmed by CIE chromaticity coordinates.

The calculated color coordinates of $CdWO_4:Eu^{3+}$ phosphor for different pH suggests that in 4 pH were close to the values of standard chromaticity (x = 0.670and y = 0.33, color: red) excited by 295nm lesser the pH without changing the concentration of $Eu^{3+,}$ it emits more red color.

It is interesting to note that high intense violet, blue, green and red emission is found in Europium doped $CdWO_4$ prepared at 8 pH. It is concluded as pH varies from 4 to 10 the PL emission varies from red (4 pH) to white (6 pH) and white (6 pH) to violet-blue - green (8 and 10 pH). At 10 pH, the violet - blue - green emission reduced by approximately 3 times to phosphor prepared at 8 pH.

On comparison with PL emission and XRD studies, it is concluded that when the crystallite size is around 21nm (8 pH), maximum PL intensity is observed and when crystallite size is 11nm (10 pH), the PL intensity of violet - blue - green emission quenched by approximately two times. This allow to sure conclude that threshold crystallite size to get more luminescence output is around 21nm in Europium doped $CdWO_4$.

Suggestions for further studies:

The work presented in this study can be extended for finding new phosphors for solid state lighting and single host display applications. It is suggested further investigations to understand the photoluminescence of these phosphors may be taken up in future. Further investigation on the effect of the size, size distribution and the shape of a particle on the luminescence properties of phosphors may also be useful.

During the course of this work the some new and existing Oxide phosphors doped with Eu^{3+} and other co-doped rare earth elements has been studied. However, the structural characterization using XRD of these new phosphor materials can be under taken in future studies.

Cerium doped $CdWO_4$ can be used for blue-green emitting Lamp phosphor. The application of inorganic nano particles doped by lanthanides is thus an interesting alternative to the use of organic fluorophores and quantum dots for many application areas, e.g., in medical diagnostics, in biological sensors, and in fluorescence marking of biological probes for high throughput screening. Hollow Nano tubes of CdWO4 can be used or nano fluidic application in biomedical science

$CdWO_4$: Eu is very good phosphor. This can be extended by doping other RE elements and formation of nano crystallites in the size 100 nm and other XRD studies. Detailed investigation may be undertaken using various theoretical models to find out the

PL emissions and physics of this phosphor as well as detailed experimental analysis on $CdWO_4$: Eu phosphor.

Furthermore, it would be interesting to investigate the effect of the different host materials RE dopants and co-dopants as well as the different synthesis methods can be adopted for future studies.