CHAPTER - 6

Study of Europium doped Cadmium Tungstate at different pH

6.1. Introduction

It has been investigated that the luminescence properties of $CdWO_4$ can be improved by doping different active cations (Co^{2+}, Bi^{3+}, Mn^{2+}, Cr^{3+}, etc),according to their ionic electro negativities [1,2]. For example, Co^{2+} doping could increase its fluorescence intensity at 778nm [3], while Bi^{3+} doping could reduce its fluorescence intensity at 1078nm [4].

Eu^{3+} ions doped tungstates emit blue-green lights under ultraviolet UV excitation. At the same time, tungstates may also effectively transfer energy to Eu^{3+} ions, producing excellent red emissions [5-10]. Eu^{3+} ions doped tungstates also become vital in white-light phosphors. The studies on luminescence properties of phosphors are attracting current interests; because it is significant not only for applications but also for essential understanding on effective reaction medium. Among them, few rare earth doped nanophosphors have attracted particular attention [11-13], because the corresponding bulk materials have large practical applications in lighting and display intensity [14,15] etc. In addition, some rare earth ions such as Eu^{3+} and Sm^{3+} may act as common activators to detect local environments due to their supersensitive *f-f* transitions [16]. Recently, M.You et al. demonstrated that $CdWO_4$: Eu^{+3} is a promising red phosphor for blue based LEDs [8]. In recent years, there were quite a few papers about tungstate; however, among them very few papers were about the pH variation in tungstate.

Q.Dai et al. investigated the variation of pH values has significant effect on the structure, type and number of surface defects. Therefore, it has great influence on the

photoluminescence. They explained two types of tungstates, the normal and the perturbed, exist in nano crystalline $CdWO_4$: Eu powders. The ratio of the perturbed structure to the normal structure decreases with increasing pH values at different annealing temperatures [7]. In our study, we discussed optical and structural properties of $CdWO_4$: Eu phosphors obtained by the hydrothermal method under different pH values (4, 6, 8 and 10) at constant temperatures without changing concentration of Europium.

6.2. Sample Preparation

Cadmium Chloride ($CdCl_2$ .H_2O), Sodium Tungstate ($Na_2WO_4.2H_2O$) and Europium Oxide (Eu_2O_3) analytical grade was used as received without any further purification purchased from Alfa Aesar to prepare the phosphors. Distilled water was used as a solvent to prepare all required solutions used in the present investigations. Initially 40 ml solution of 0.1M concentration of $CdCl_2.H_2O$ was prepared by continuous stirring and also 40 ml solution of 0.1M concentration of $Na_2WO_4.2H_2O$ was added into it drop wise subsequently 40 ml solution of 0.01M concentration of Eu_2O_3 was added. The pH value 4, 6, 8 and 10 of this solution was adjusted drop wise with CH_3COOH for pH 4, 6 and NaOH for pH 8, 10 solutions. These precursor solutions were transferred to Teflon-lined stainless-steel autoclave having 150 ml capacity filled with reaction media up to 80% one by one. The autoclave was maintained at a temperature of 150^oC for 12 h and allowed to cool to room temperature. The prepared samples were washed several times with distilled water and lastly washed with absolute ethanol. Finally, a white powder was obtained after drying in vacuum at 80^oC for 2 hours. Figure 6.1 shows the flow chart of Europium doped $CdWO_4$ using the hydrothermal method.

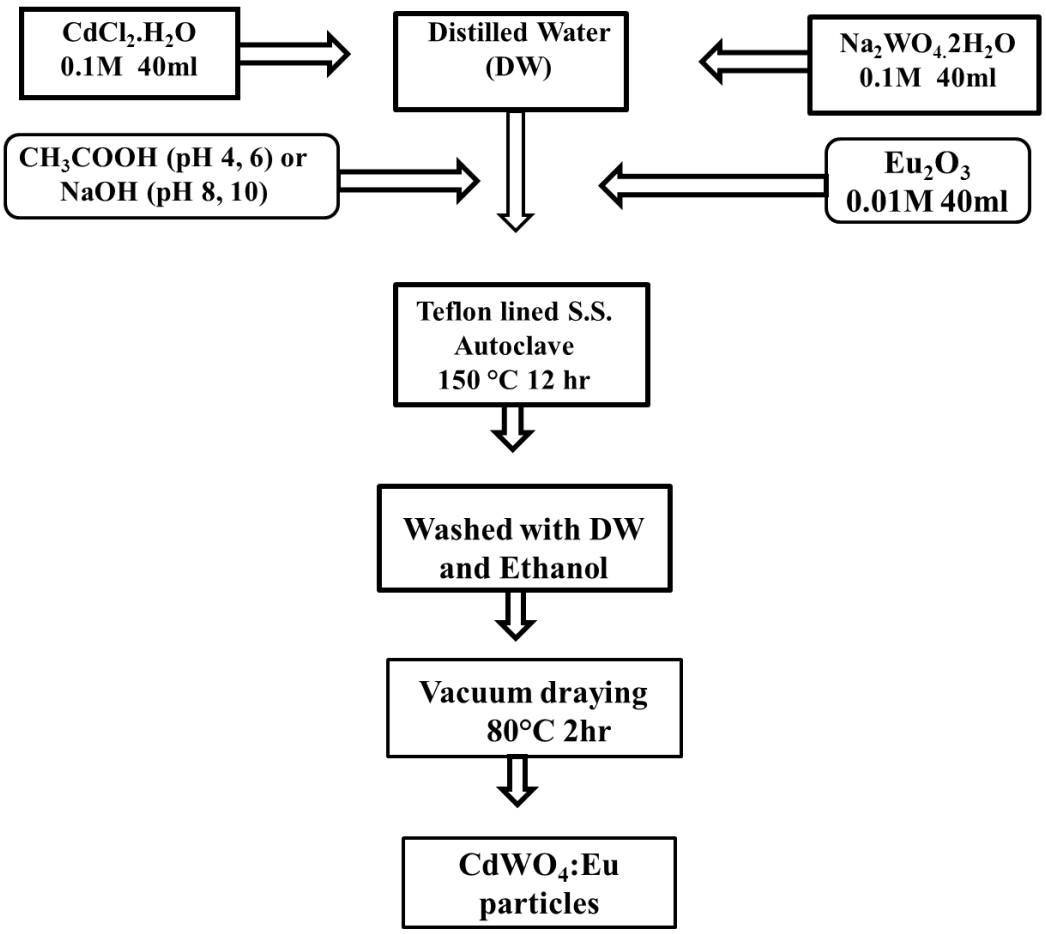

Figure 6.1 Flow chart of Europium doped $CdWO_4$ synthesized at pH (4, 6, 8, 10) .

6.3 Characterization

The prepared samples are characterized by photoluminescence analysis (PL) and X-ray diffraction (XRD).The PL of the samples was investigated on a Shimadzu spectrofluorophotometer at room temperature with a xenon lamp as excitation source.

The XRD measurements were carried out with Japan Rigaku D/max X-ray diffractometer, using Ni-filtered Cu Kα radiation. A scan rate of 0.05°/s was applied to record the patterns in the 2θ range 10-70°.

6.4 X-Ray Diffraction (XRD) – Structural Study

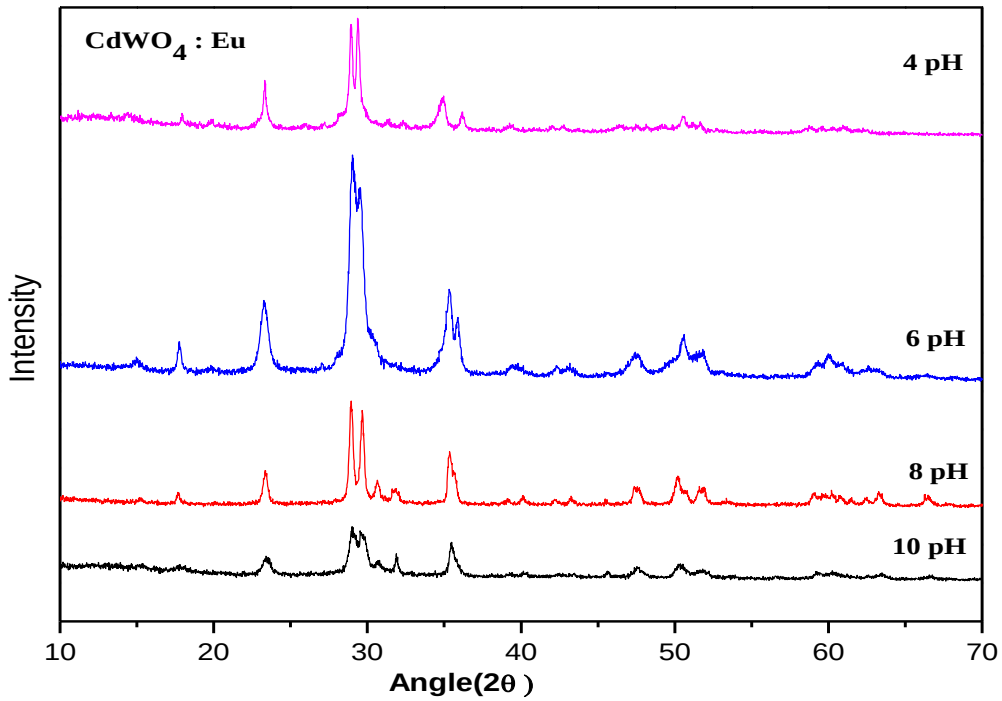

Figure 6.2 XRD patterns of Europium doped $CdWO_4$ synthesized at pH (4, 6, 8, 10)

Figure 6.2 shows the XRD patterns of $CdWO_4$:Eu powders prepared at different pH (4, 6, 8 and 10).XRD patterns revealed that the $CdWO_4$ can be indexed to a pure monoclinic phase of $CdWO_4$ with a wolframite structure with space group P2/c (13) ; in agreement with JCPDS (Joint Committee on Powder Diffraction Standards) card No. 14-0676. It can be seen that the crystal structures of all the samples belong to the pure monoclinic phase. However, on comparing the curves of the four products, it is observed that the relative intensity of the peaks varied considerably, which indicates different crystallinity. The samples prepared at pH 4 and 6 show better crystallization than the made at pH 8 and 10.

The broadening of the peaks indicates that the crystallite size is small. These XRD patterns indicate that well-crystallized $CdWO_4$ crystals were observed in the present synthetic process.

Phosphor	**pH**	**a (Å)**	**b (Å)**	**c (Å)**	**Volume(Å^3)**	**Avg. crystallite size(nm)**
$CdWO_4$:Eu	4	5.057	5.865	5.078	150.49	44.24
	6	5.056	5.867	5.073	150.42	24.60
	8	5.052	5.876	5.09	150.07	20.90
	10	5.053	5.865	5.073	149.67	11.60

Table 6.1 XRD analysis of Europium doped $CdWO_4$ synthesized at pH (4, 6, 8, 10)

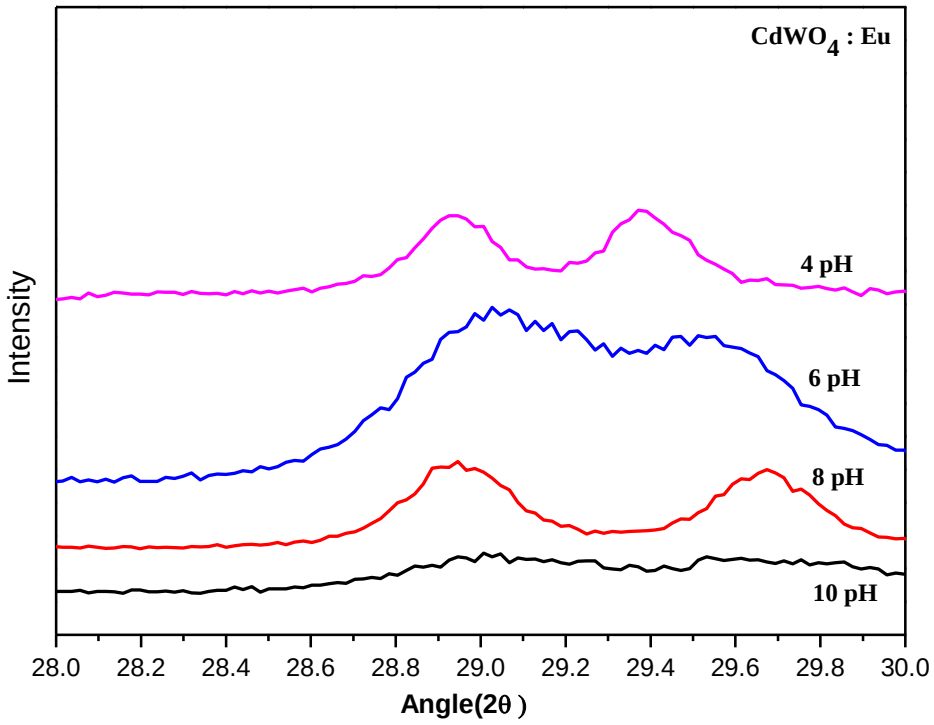

Figure 6.3 Shift of reflection peak of Europium doped CdWO4 synthesized at pH (4, 6, 8, 10).

Shift in the main reflection peak of Europium doped $CdWO_4$ is compared and presented in Figure 6.3. It can be seen from the figure that when sample prepared at 4 pH the peak shows lowest angle and that for sample prepared at 8 pH is at highest angle. According to the Bragg equation, the shift toward higher angle of reflection suggests that the cell parameters of as-synthesized products could continuously decrease and also crystallite size decreases.

6.5 Photoluminescence (PL) Studies

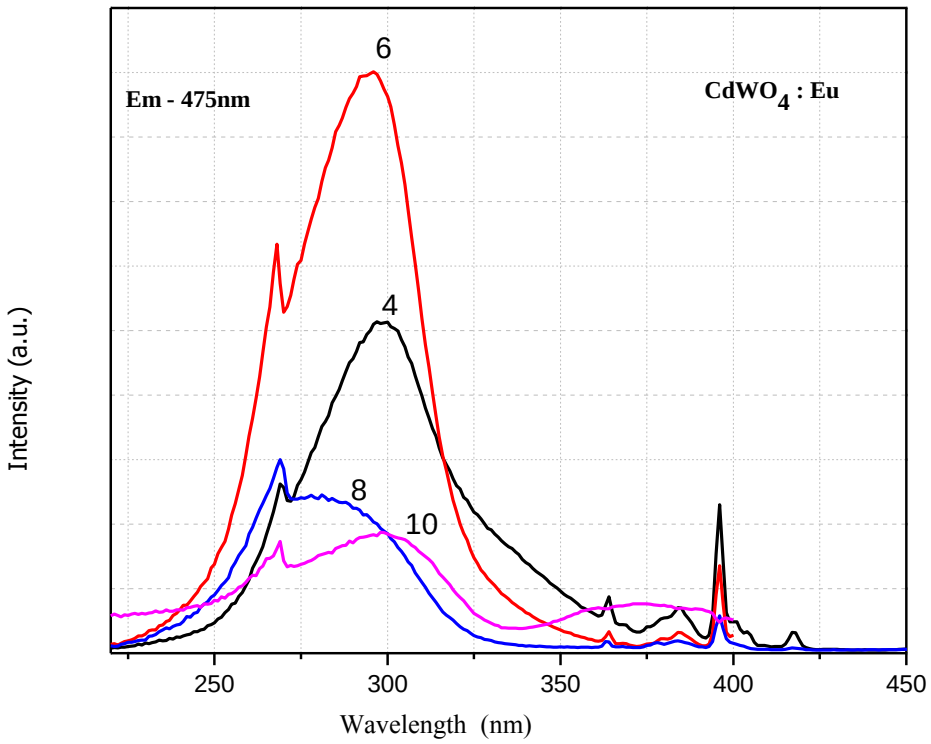

Figure 6.4 Excitation spectra of Europium doped $CdWO_4$synthesized at pH(4, 6, 8,10).

Figure 6.4 exhibited the photoluminescence excitation (PLE) spectra of $CdWO_4$: Eu phosphors with different reaction medium monitored at 475nm. The intensity is increased when compared basic to acidic reaction medium. As can be observed from the spectra, a smooth peak at 295 nm and certain sharp lines at wavelengths of 364, 384, 396, 404 and 417 were observed, which were assigned to the $^7F_0 - {}^5D_4$, $^7F_0 - {}^5G_J$, $^7F_0 - {}^5L_7$, $^7F_0 - {}^5L_6$,

$^7F_0 - {}^5D_3$ transitions of Eu^{3+}, respectively [117]. The broad band centered at 295nm was originated from charge transfer between the O_{2p} orbitals and the empty d orbitals of the central W ion. Moreover, the PLE intensities at 295nm and 396nm were much higher than that of other bands, which indicated that, the UV and near UV regions are suitable to excite $CdWO_4:Eu^{3+}$ phosphors.

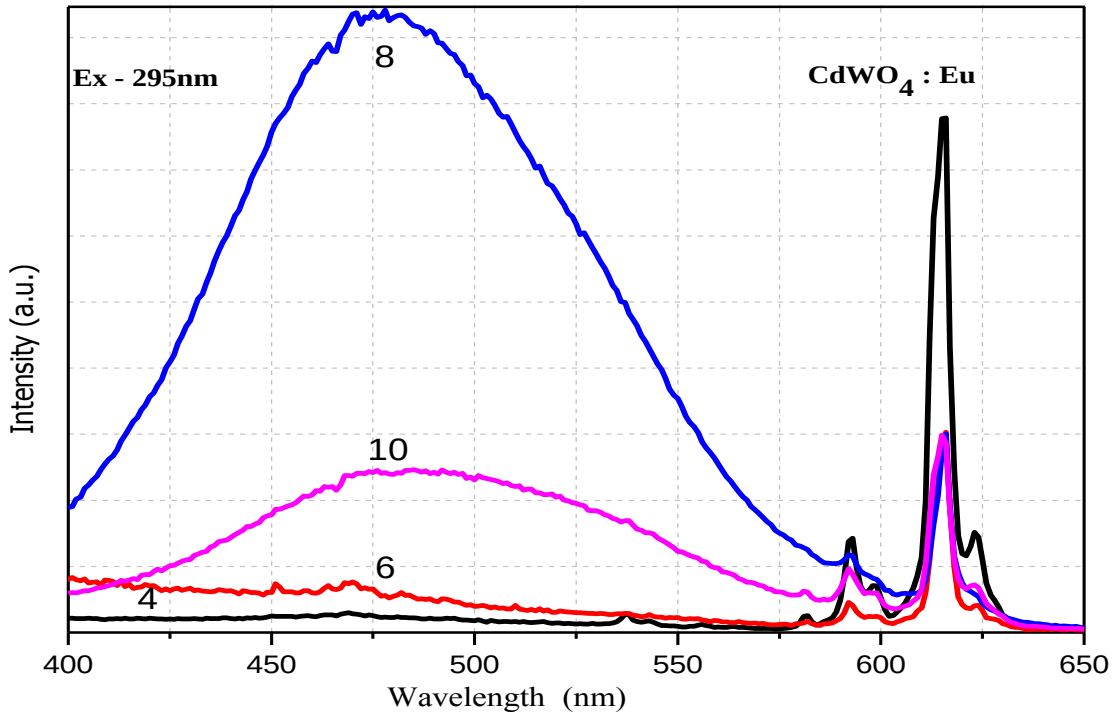

Figure 6.5 Emission spectra of Europium doped $CdWO_4$ synthesized at pH (4, 6, 8, 10).

The PL emission spectra of the Europium doped $CdWO_4$ synthesized at different pH are shown in Fig. 6.5. It is clearly seen that, the PL emission band (400-575 nm) with intense emission (477nm) are identical in all spectra of basic reaction medium , the characteristic band of tungstate is disappeared in acidic medium. That is why the $CdWO_4$ doped with Eu^{3+} may be used as red phosphor. This type of LED phosphors is rare in tungstate group.

In all four samples, emissions at 582nm, 593nm, 599nm, 615nm and 624 nm were observed, which could be ascribed to $^5D_0$–^7F_J (J¼0–3) transitions of Eu^{3+} ions [18]. The peak at 613 nm was the strongest in all of these peaks, which was due to the $^5D_0$–$^7F_2$ electric dipole transitions of Eu^{3+}. This phenomenon indicated that Eu^{3+} ions have occupied the non-symmetry site in the $CdWO_4$ host lattice [19]. The results indicate that PL spectra exhibit violet - green emission band peaking in blue region only in basic reaction medium. The emission bands were ascribed to the $^1A_1 \rightarrow {}^3T_1$ transition within the WO_6^{6-} complex [20]. This is mainly due to the charge-transfer transitions between the O_{2p} orbital and the empty d orbital of the centralW^{6+} of WO_6 octahedra or to the self-trapped exciton at a WO_6^{6-} oxyanion complex [21, 22]. The change in PL intensity can be attributed to change in dimensional confinement of Eu ions which is due to the preparation of the material through effective approach of pH. Moreover, the Fig.6.3 showed that when the pH of reaction medium is decreased, the PL intensity at 477nm decreased and the PL intensity at 615nm increased with same europium concentration, which indicated that there was energy transfer from WO_4^{2-} groups to Eu^{3+}. It exhibited potent approach of pH into the $CdWO_4$ lattice. Based on the emission spectra, it is concluded that at 4 pH the rate of energy transfer from tungstate group to Eu increases and luminescent center of Eu^{3+} will become dominant.

Phosphor	pH	Excitation wavelength (nm)	Excitation energy (eV)	Peak position (nm)	Peak position (eV)	Peak Intensity (a.u.)
$CdWO_4$:Eu	4	295	4.02	470	2.637	21
	6			471	2.632	55
	8			476	2.604	697
	10			481	2.582	181

Table 6.2 Emission spectra analysis of Europium doped $CdWO_4$ synthesized at pH (4, 6, 8, 10).

Phosphor	pH	Excitation wavelength (nm)	Excitation energy (eV)	Eu Peak position (nm)	Eu Peak energy (eV)	Eu Peak Intensity (a.u.)
$CdWO_4$:Eu	4	295	4.02	593	2.09	107
	6			593	2.09	30
	8			593	2.09	87
	10			593	2.09	74

Table 6.3 Eu peak (593nm) analysis of Europium doped $CdWO_4$ synthesized at pH (4, 6, 8, 10).

Phosphor	pH	Excitation wavelength (nm)	Excitation energy (eV)	Eu Peak position (nm)	Eu Peak energy (eV)	Eu Peak Intensity (a.u.)
$CdWO_4$:Eu	4	295	4.02	615	2.01	583
	6			615	2.01	224
	8			615	2.01	224
	10			615	2.01	224

Table 6.4 Eu peak (615nm) analysis of Europium doped $CdWO_4$ synthesized at pH (4, 6, 8, 10).

Emission peak analysis of Europium doped $CdWO_4$ with various pH concentrations excited at 295nm are mentioned in table 6.3, 6.4 and 6.5. From the figure 6.5, table 6.4 and table 6.5 two peaks of Europium are observed: one at 593nm which is due to magnetic dipole component of crystal and other at 615nm which originates from hyper sensitive electric dipole component of the phosphor. It is also found that the intensity of 615nm peak at 4 pH is 583 units which very high. As pH increases from 4 to 10 , the peak intensity of 615nm is nearly same around 224 units. However, at 593nm the peak intensity varied marginally.

6.6 CIE chromaticity coordinates of $CdWO_4:Eu^{3+}$ phosphor

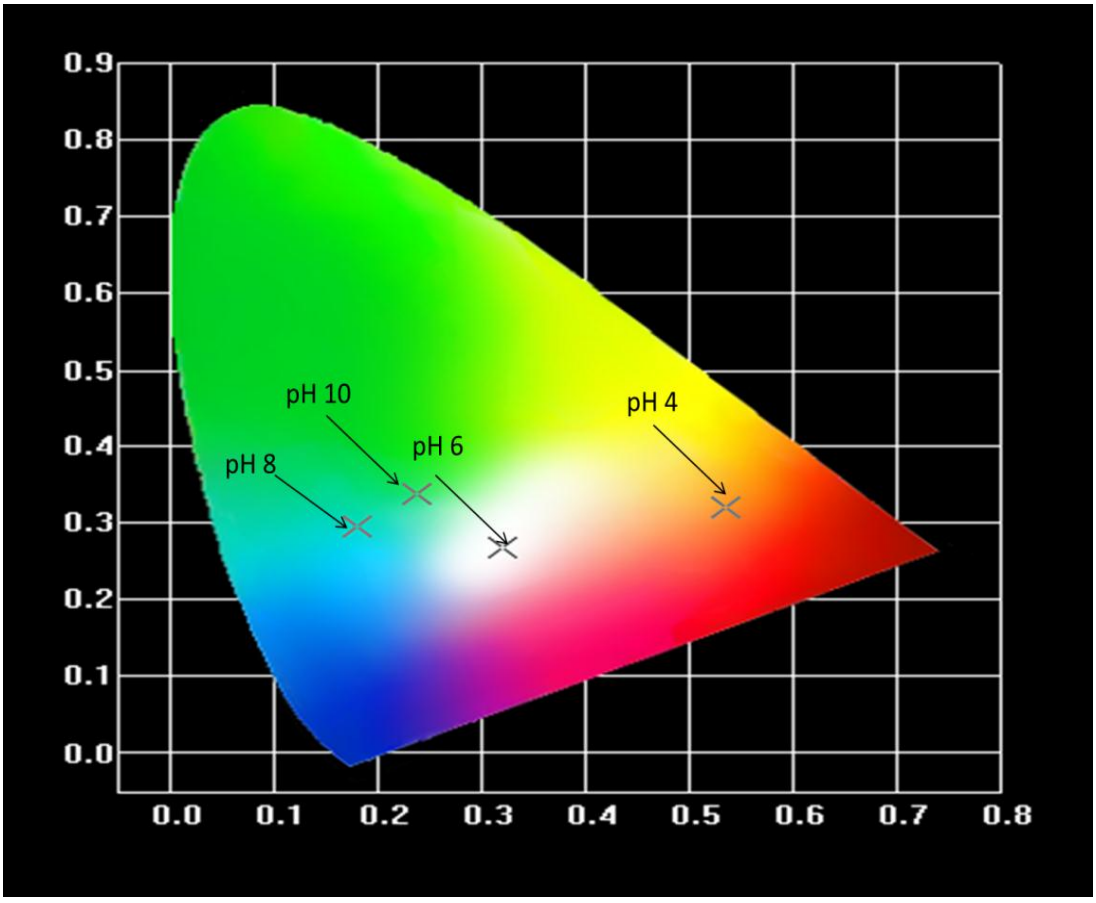

Figure 6.6 CIE chromaticity diagram with points indicating coordinates for Europium doped $CdWO_4$ synthesized at different pH (4, 6, 8,10) recorded with 295 nm excitation wavelength.

pH	X	Y
4	0.534	0.321
6	0.321	0.268
8	0.181	0.294
10	0.238	0.338

Table 6.5 X and Y coordinates for Europium doped $CdWO_4$ synthesized at different pH (4, 6, 8,10) recorded with 295 nm excitation wavelength.

The color coordinates of $CdWO_4:Eu^{3+}$ phosphor was portrayed in Fig.6.6. The CIE chromaticity coordinates of the $CdWO_4:Eu^{3+}$ phosphors with different pH are given in table 6.5. The phosphor prepared in 4 pH were close to the values of standard chromaticity (x=0.670and y=0.33, color: red) as per the National Television Standards Committee (NTSC) system. This result demonstrated that $CdWO_4:Eu^{3+}$ in acidic reaction medium could be an excellent red-light-emitting phosphor in illuminating and display devices excited by 295nm. It is also suggested that to reduce the pH without changing the concentration of $Eu^{3+,}$ it emits red color.

The following conclusions are drawn from this chapter are given as below:

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.

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 $CdWO_4$.

References

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