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Re-dispersible of $CdWO_4$:Ln (Ln = Sm^{3+}, Tb^{3+}) in Different Solvents

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$CdWO_4$:Ln (Ln = Sm^{3+}, Tb^{3+}) were prepared by the co-precipitation method followed by calcinations of the precipitated precursor at 500 °C for 2 h. The prepared samples were characterized by XRD, FTIR and photoluminescence. It shows the monoclinic phase with space group of P2/C without any impurity phase. The morphology of the prepared samples was characterized by scanning electron microscope and for elemental analysis by EDAX. Photoluminescence properties of re-dispersible of the prepared samples at different polar solvents were also investigated.

Keywords: $CdWO_4$:Ln (Ln = Sm^{3+}, Tb^{3+}), XRD, Photoluminescence, Re-dispersible.

INTRODUCTION

Tungstate and molybdate compounds are the two families which are largely studied as competitive host material. As a self-activating phosphors tungstate has some advantages because of it has high chemical stability, high average refractive index, high X-ray absorption co-efficient, high efficiency output, short decay time and low afterglow to luminescence [1]. Among the tungstate, $CdWO_4$ having wide band gap semiconductor has attracted because of its physical chemical and structural properties that endow to be widely used in various application like X-ray Scintillators [2] advanced medical X-ray detector in computerized tomography [3], phosphors [4]. Luminescence particles of nanometer size have attracted much attention owing to their wide application as luminescence probes in various biological detections and biotechnologies [5,6]. Large no of representative nanoparticles and quantum dots including dyes and semiconductor have been applied for biological detection. Some of them have strong luminescence properties and higher photo-stability. But some problems exist for them for the application of biological assays such as short lifetimes, photo bleaching and potential toxicity to life cells [7,8]. Therefore lanthanide doped nanoparticles are gaining much attention as the alternative way for the biological assays. Lanthanide doped nano particles have sharp absorption and emission lines, high quantum yield, long lifetime, *etc*. This is due to the shielding of 4*f* electron by the 5*s* and 5*p* electrons. Owing to this unique properties; lanthanide doped materials seem to be promising materials for biological applications [9].

In the present work, we prepared lanthanide doped $CdWO_4$ by the simple co-precipitation method followed by the annealing of the precipitate formed. The re-dispersible luminescence properties of the prepared samples at different polar solvents were investigated which may find its application in biological assays.

EXPERIMENTAL

Sample preparation: For the synthesis of $CdWO_4$:Ln (Ln = Sm^{3+}, Tb^{3+}); $Cd(NO_3)_2$ from Thomas Baker with analytical purity of 99 % and $NaWO_4$ from Himedia with the analytical purity of 98 % were the chemicals used in the preparation of $CdWO_4$ without any further purification for the source of Cd^{2+} and WO_4^{2-}. And for the dopant ion Sm^{3+} and Tb^{3+} we used $SmCl_3$ anhydrous and $TbCl_3{\cdot}xH_2O$ with the analytical purity of 99.9 % from the Alfa-Aesar. Double distilled water was used as the reaction medium for the synthetic process. In a typical synthesis, requisite amount of $Cd(NO_3)_2$ and $LnCl_3$ were dissolved in a 25 mL of double distilled water in a 100 mL conical flask and then $NaWO_4$ solution dissolved in 25 mL double distilled water in another beaker was added. The solution was magnetically stirred for 1 h. A white precipitate was obtained, which is centrifuged and washed with doubled distilled water for 4-5 times. Finally the precipitate was washed with acetone and dried in oven. After that the white precipitates was calcined at 500 °C for 2 h.

Characterization of the samples: The phase composition and crystal structure of the prepared samples were determined by the X-ray diffraction using the PANalytical powder diffractometer with CuK$_\alpha$ (1.5406 Å) radiation with Ni filter. FTIR spectra were measured at FTIR spectrometer Perkin Elmer UATR two. SEM and EDAX were taken at FEI quanta 250. The photoluminescence spectra were recorded using Perkin Elmer (LS-55) spectrometer in phosphorescence mode with Xenon discharge lamp as the excitation source having pulse width half height < 10 µs. The photoluminescence emission of the re-dispersible at different solvents was taken at Cary Eclipse fluorescence spectrophotometer in phosphorescence mode at University of Delhi. All the measurements were taken at room temperature.

RESULTS AND DISCUSSION

X-ray diffraction study: The phase purity and phase structure of the prepared samples were characterized by the X-ray diffraction using Ni filter. Fig. 1 shows XRD pattern of $CdWO_4$:Ln (Ln = Sm^{3+}, Tb^{3+}). The diffraction peaks in the patterns matched well with JCPDS card no. 14-0676, having monoclinic phase with a space group of P2/C. No possible additional phase like $Cd(NO_3)_2$ and $SmCl_3$ or impurities were detected which means the high purity of the samples and also Sm^{3+} have been successfully doped in the $CdWO_4$ matrix [10,11]. Strong and sharp peaks indicates good crystallinity of the synthesized product. The broadening of the peaks indicates the small size of the synthesized product. The average particle size of the samples can be calculated by using the Scheerer's equation [12].

$$D = \frac{K \times \lambda}{\beta \cos\theta}$$

where D = particle size, K = constant (shape factor, about 0.9), β = full width at half maximum, λ = wavelength of the X-ray used (0.15406 nm) and θ = angle of diffraction. The estimated average particle size calculated from the most intense peak in XRD spectrum (-111) for $CdWO_4$:Sm is 20.38 nm and (111) plane for $CdWO_4$:Tb is 8.1 nm.

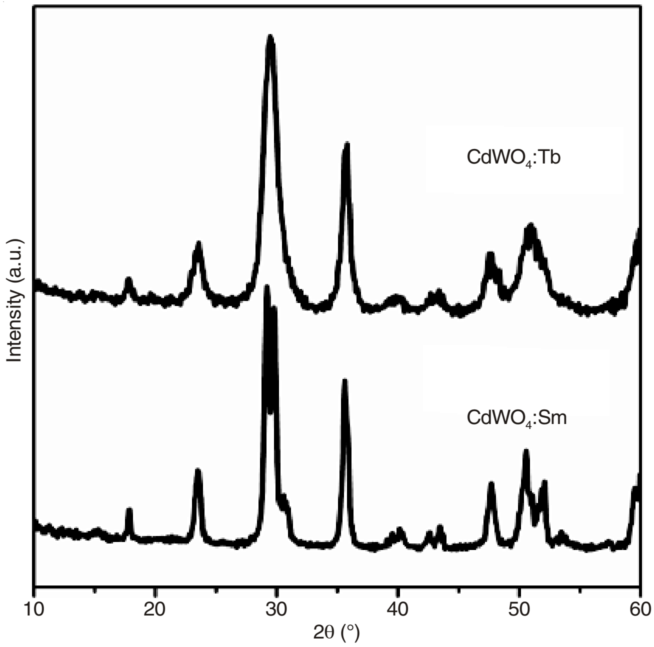

Fig. 1. XRD pattern of $CdWO_4$:Ln (Ln = Sm, Tb)

FTIR study: Fig. 2 shows the FTIR spectra of $CdWO_4$:Ln (Ln = Tb, Sm). In the synthesized sample, the stretching and bending vibrational mode of Cd-O-W are observed at 893 and 805 cm^{-1}, respectively. The band at 722 cm^{-1} and 556 cm^{-1} are due to the respective stretching and bending vibration of W-O. While the band at 453 and 412 cm^{-1} are due to the stretching and bending vibrational mode of Cd-O.

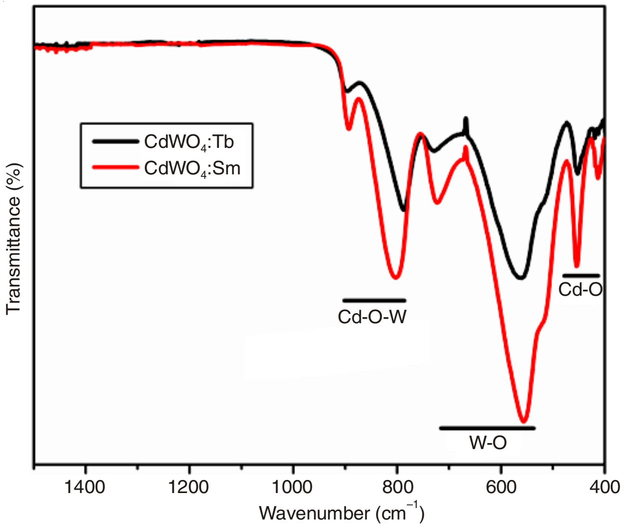

Fig. 2. FTIR spectra of $CdWO_4$:Ln (Ln = Sm, Tb)

SEM and EDAX study: Fig. 3 shows the SEM image of $CdWO_4$:Ln (Ln = Sm, Tb). It is observed that it is difficult to find out the size of the particles as it is having in agglomerated form. In the $CdWO_4$:Sm, the particles are forming irregular shape, some are like stick (rod) shape and some are in the form of flakes. While in the case of $CdWO_4$:Tb, we can observe regularity in morphology of the particles. It seems rod type shapes. EDAX spectra of the samples are shown in Fig. 4. It is confirmed from the analysis of the spectra the presence of required elements (Cd, O, W, Sm and Tb) in the prepared samples.

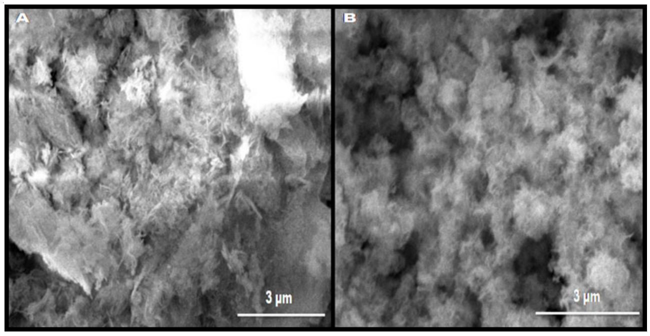

Fig. 3. SEM images of $CdWO_4$:Sm (A) $CdWO_4$:Tb (B)

Photoluminescence study: The photoluminescence excitation and emission of $CdWO_4$:Sm and $CdWO_4$:Tb are shown in Figs. 5 and 6, respectively. A broad band in between the 225-350 nm with the most intense at 279 nm is observed from the excitation spectra of $CdWO_4$:Sm monitoring emission at 610 nm. This is due to the charge transfer transition from the filled 2*p* orbital of oxygen to the empty *d*-orbital of W^{6+} [13]. Very less intense peak at the longer wavelength region

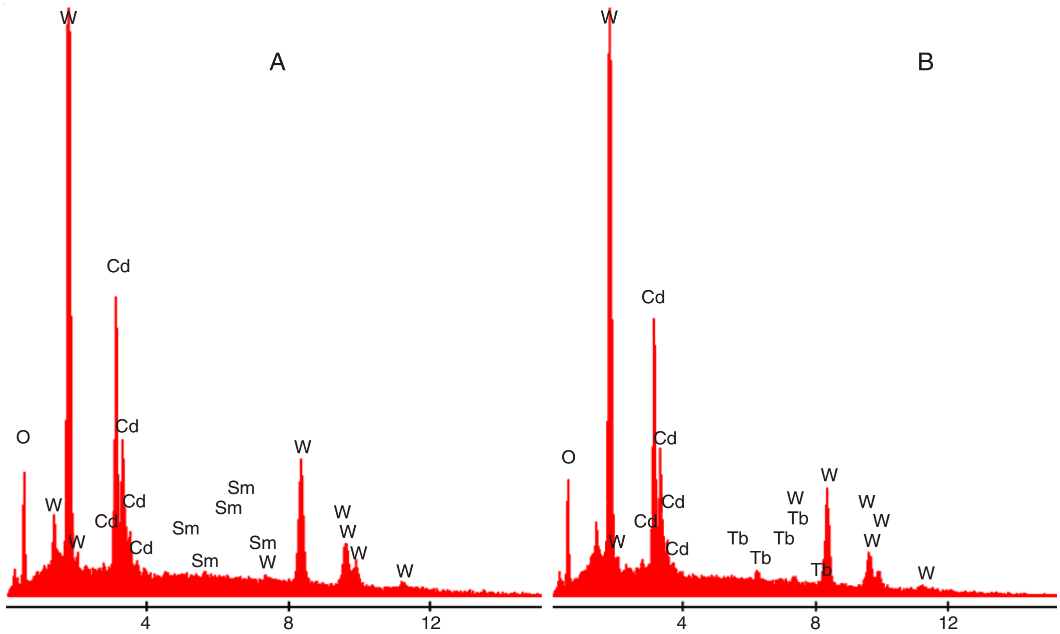

Fig. 4. EDAX spectra of $CdWO_4$:Sm (A) $CdWO_4$:Tb (B)

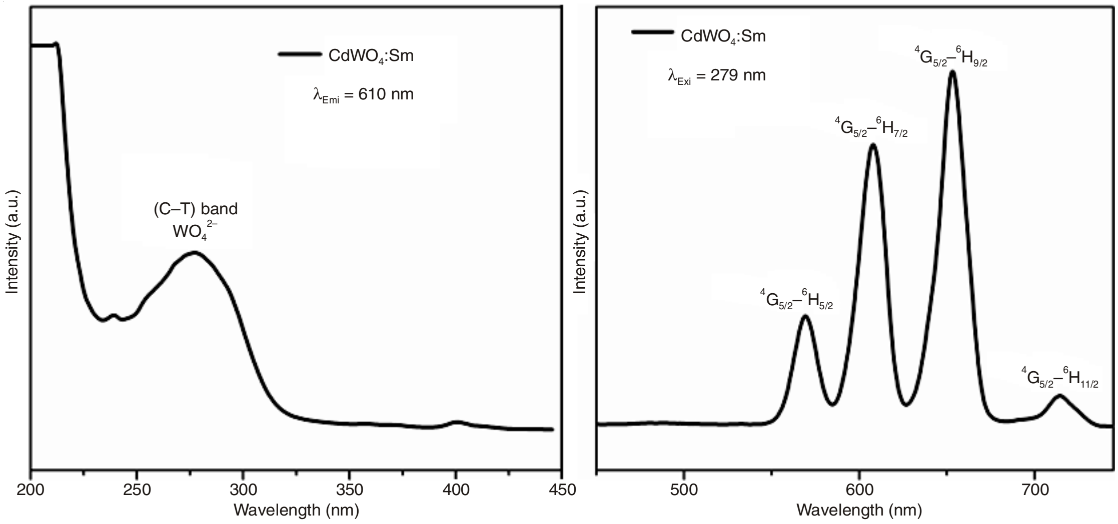

Fig. 5. Excitation and emission spectra of $CdWO_4$:Sm

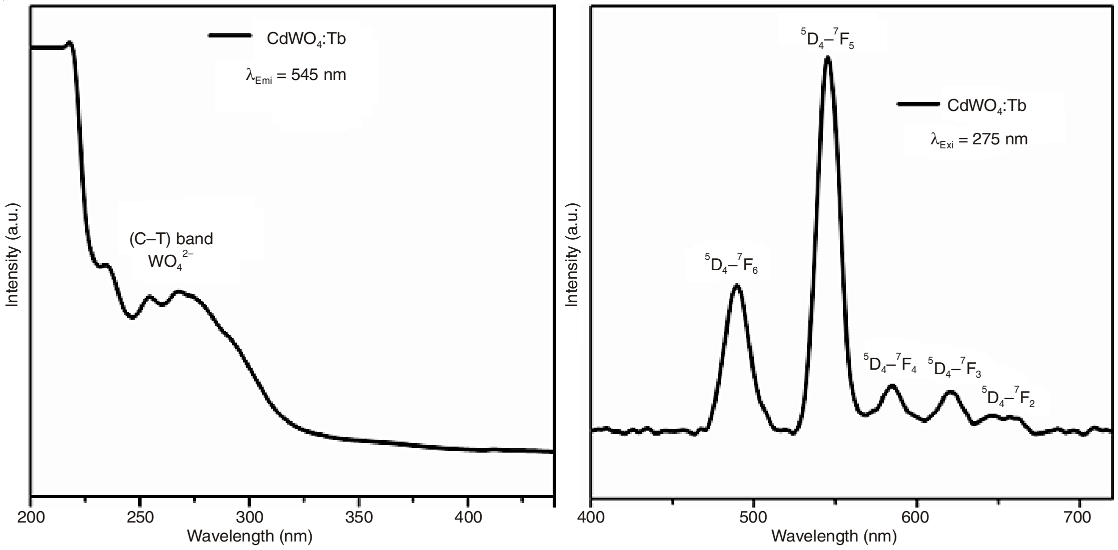

Fig. 6. Excitation and emission spectra of $CdWO_4$:Tb

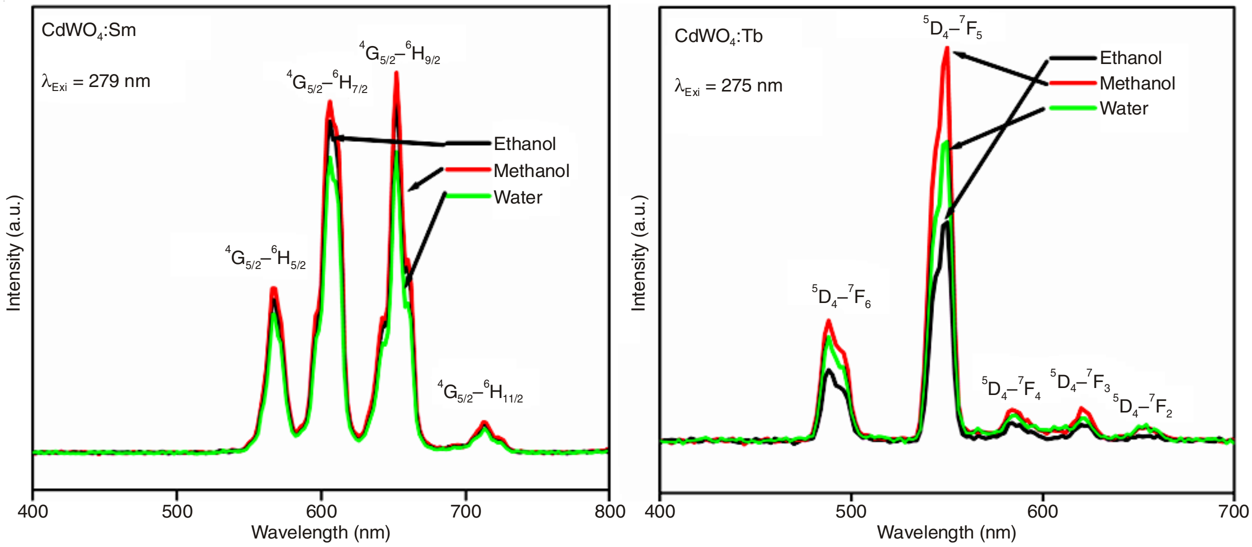

Fig. 7. Emission spectra of $CdWO_4$:Ln (Ln = Sm, Tb) disperse in different solvents

due to the forbidden *f-f* transition is observed. For the excitation spectra of Tb doped $CdWO_4$ monitoring emission at 545 nm; this charge transfer band is splitting and the most intense peak is slightly shifted to the lower wavelength and the intense peak is observed at 270-275 nm. The emission spectra showed the characteristic peaks of the related lanthanide ions. For the Sm doped sample, four peaks are obtained at 553 nm due to the ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), 609 nm ($^4G_{5/2}\rightarrow{}^6H_{7/2}$), 653 nm ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) and 713 nm ($^4G_{5/2}\rightarrow{}^6H_{11/2}$) [14]. Among this transitions, ($^4G_{5/2}\rightarrow{}^6H_{5/2}$) is due to the magnetic dipole transition and ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) is due to partly magnetic dipole and partly electric dipole transition, while ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) is refer to the purely electric dipole transition. Emission spectra of $CdWO_4$:Tb shows five peaks characteristic to the emission of Tb^{3+} ion at 489, 545, 584, 620 and 653 nm corresponds to $^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_5$, $^5D_4\rightarrow{}^7F_4$, $^5D_4\rightarrow{}^7F_3$ and $^5D_4\rightarrow{}^7F_2$, respectively. The green emission at 545 nm the more intense peak than the others which is due to the magnetic dipole transition with $\Delta J = 1$ [15].

The re-dispersion properties of the $CdWO_4$:Ln (Ln = Sm, Tb) were investigated by using polar solvents such as water, methanol and ethanol. Fig. 7 shows the emission spectra of $CdWO_4$:Ln (Ln = Sm, Tb) disperse in different polar solvents. Both the sample showed the characteristic emission of the dopant ion in all the solvents. Well and sharp peaks can be obtained when disperse in different solvents without any change in peak profile except the intensity of the peaks. The capability of the samples to disperse in different polar solvents may be applicable for incorporation of luminescence materials in a polymer matrix and it could be applicable in drug delivery and disease therapy as it can be easily identified, tracked and monitored by the luminescence [16,17].

Conclusion

Sm and Tb doped $CdWO_4$ were prepared by co-precipitation method followed by the calcinations of precipitated precursor. XRD study revealed the monoclinic phase to both the samples. Under UV excitation it gives the characteristic emission of the respective lanthanide ions. Study of the re-dispersible emission spectra of the prepared samples at different polar solvents gives well sharp emission spectra characteristic to lanthanide ions. These results show that the prepared samples may applicable to biological assays.

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