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Re-dispersible $CaWO_4:Tb^{3+}$ nanoparticles: Synthesis, characterization and photoluminescence studies

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Nanoparticles of $CaWO_4$ doped with Tb^{3+} were synthesized in ethylene glycol, DMSO, water and mixed solvents at a very low temperature. XRD patterns showed that the nanoparticles prepared in all these solvents have a scheelite-type tetragonal structure without the presence of deleterious phases. The photoluminescence (PL) spectra of Tb^{3+} doped $CaWO_4$ (EG) nanoparticles doped with different Tb^{3+} concentrations under 243 nm excitation show the characteristic green emission (545 nm) of Tb^{3+} corresponding to $^5D_4 \rightarrow {}^7F_5$ transition due to efficient charge transfer from WO_4^{2-} to Tb^{3+}. Other emissions can be observed due to $^5D_4 \rightarrow {}^7F_{6,4,3}$ transitions. The optimum concentration of Tb^{3+} for the highest luminescence was found to be 10 at%. The luminescence intensity of the samples prepared in EG:water (1:1) is more than that in EG, DMSO and other mixed solvents. As-prepared samples are well dispersed in polar solvents like methanol, ethanol and water and will be useful in biological applications.

1. Introduction

Recently, nanoparticles of inorganic compounds activated by rare earth ions have received much attention due to their broad applicability and high technological promise. These fluorescent nanomaterials have intriguing optical properties, which are expected to outdo their bulk counterparts. They have been used in luminescent devices such as fluorescent lamps [1,2], cathode ray tubes [3], components of telecommunications [4] etc. An ardent quest for highly luminescent materials has made inorganic host compounds an interesting field for research. Such applications are highly dependent on the host matrix and the rare earth ion employed. Calcium tungstate ($CaWO_4$) scheelite crystal is an important optical material which has been used for decades in scintillators, optoelectronic devices, drug release [5–7] etc. Various preparation methods have been employed to prepare $CaWO_4$ nanoparticles and single crystals in the recent years, e.g. solid-state reaction [8], polymeric precursor [9], Czochralski method to prepare single crystal [10], Pechini [11], microemulsion-mediated hydrothermal [12], molten salt [13], co-precipitation [14], solvothermal [15], combustion reactions [16] etc. The luminescence properties of this inorganic host are further enhanced by introducing lanthanide ions (Ln^{3+}) [17]. Phosphors such as $CaWO_4:Tb^{3+}$ modifies the luminescence spectrum of the host due to the creation of emission centers that generates the specific green light when excited by UV wavelength light. Therefore Ln^{3+} doped $CaWO_4$ powder samples might be promising candidates as phosphors for visual display and solid-state lighting [18]. Special attention has been given for the synthesis of Tb^{3+}doped phosphors in the recent years since the corresponding green emission is a key component of the tricolor luminescence and hence it is necessary to look for novel Tb^{3+} doped green phosphors. Usually such potential phosphors are synthesized at high temperatures or by post-annealing at high temperatures. Such synthetic method leads to agglomerated nanoparticles. This may cause decrease in luminescence intensity due to cross relaxation among Ln^{3+} ions. Such agglomerated particles may become deprived of organic–inorganic groups on the surface thereby making them poor dispersants in solvents. This limits its application in biological systems. Therefore, in recent years, efforts have been made to synthesize efficient phosphors with high luminescence intensity and dispersible properties employing low temperature synthesis. There have been reports about the hydrothermal synthesis and combustion reaction for the synthesis of Tb^{3+}-doped $CaWO_4$ powders [19,20]. Appropriate organic–inorganic ligands can be used to tune the size and shape of the nanoparticles but long chain organic ligands cause quenching of luminescence due to high energy vibrations of the ligands. Ligands and coordinated solvent molecules usually contain C–H and O–H bonds that can cause vibrational quenching of electronically excited lanthanide ion. The long-lived excited state of the lanthanide ions is quenched very effectively by the high-energy vibrations of closely spaced organic groups. Therefore

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organic ligands having a short chain like ethylene glycol becomes an important solvent for low temperature synthesis. In our previous work, $CaWO_4:Eu^{3+}$ nanoparticles were prepared successfully by ethylene glycol route at a very low temperature [21] and in continuation of the previous work, we have synthesized Tb^{3+} doped $CaWO_4$ nanoparticles following the same procedure.

To the best of our knowledge, synthesis of $CaWO_4:Tb^{3+}$ phosphor powders by ethylene glycol route has not been reported so far in the literature. In this report, $CaWO_4:Tb^{3+}$ phosphors with different Tb^{3+} ion concentrations were synthesized via ethylene glycol (EG) route. Here EG acts as the reaction medium as well as the capping agent. We have prepared $CaWO_4:Tb^{3+}$ samples up to 20 at% Tb^{3+}. In addition, the same concentrations of $CaWO_4:Tb^{3+}$are also prepared in water, DMSO and the mixed solvent medium to see the effect of solvents on their photoluminescence behavior. The re-dispersion properties of the prepared samples in methanol, ethanol and water are also investigated. The prepared samples were characterized for their structural and luminescence properties.

2. Experimental

2.1. Preparation

All chemical reagents were used as received.

Nanoparticles of $CaWO_4$ and $CaWO_4$ doped with Tb^{3+} ($Tb^{3+}=2$, 5, 7, 10, 15 and 20 at%) were prepared using ethylene glycol (EG) as both capping agent and reaction medium at 130 °C. Calcium nitrate tetrahydrate ($Ca(NO_3)_2\cdot 4H_2O$, AR), terbium nitrate hexahydrate ($Tb(NO_3)_3\cdot 6H_2O$, 99.99%, Aldrich) and sodium tungstate dihydrate ($Na_2WO_4\cdot 2H_2O$, AR) were used as sources of Ca^{2+}, Tb^{3+} and WO_4^{2-}, respectively. In a typical synthesis procedure of 5 at% Tb^{3+} doped $CaWO_4$ nanoparticles, 250 mg of $Ca(NO_3)_2\cdot 4H_2O$ and 25 mg of $Tb(NO_3)_3\cdot 6H_2O$ were dissolved together in conc. HNO_3 and excess acid was removed by evaporation with water. To this solution, 367 mg of $Na_2WO_4\cdot 2H_2O$ was added followed by 25 ml of EG. The pH of the solution was adjusted to 9–9.5 using NaOH solution. The resulting solution was refluxed for 3 h at 130 °C for the samples prepared in EG and DMSO and 100 °C for that prepared in water. The resulting white precipitate was collected by centrifugation at 10,000 rpm for 10 min, washed several times with acetone and finally dried under ambient atmosphere. The dried sample was used for characterization.

2.2. Characterization

X-ray powder diffraction (XRD) data for all the samples were examined using PANalytical powder diffractometer (X Pert PRO) with CuKα (1.5405 Å) radiation with Ni filter. Transmission electron microscopy (TEM) was recorded using CM-200 TEM. For TEM measurement the samples were ground and dispersed in methanol. A drop of the dispersed particles was placed over the carbon coated copper grid and evaporated to dryness at room temperature. Infrared spectra were recorded on a Fourier transform infrared (FTIR) spectrophotometer of Shimadzu (model 8400S) using thin pellets of KBr. All the photoluminescence spectra and lifetime measurements of the samples were recorded using Perkin Elmer (LS-55) luminescence spectrometer in phosphorescence mode with xenon discharge lamp as the excitation source having pulse width at half height <10 μs. For the lifetime measurements gate time was fixed at 0.05 ms and the delay time was varied starting from 0.1 ms. All the measurements were taken at room temperature.

3. Results and discussion

3.1. X-ray diffraction (XRD) study

The XRD patterns of $CaWO_4:Tb^{3+}$ synthesized via EG route are shown in Fig. 1(a). As can be observed the X-ray diffraction patterns of samples are in good compatibility with the standard JCPDS card of $CaWO_4$ (no. 01-077-2234) [16] having tetragonal phase with a scheelite structure. It shows that doping little amount of rare earth ions has approximately no effects on the $CaWO_4$ crystalline structure. The XRD patterns do not show any diffraction peak corresponding to the possible phases such as $Ca(NO_3)_2\cdot 4H_2O$ or $Tb(NO_3)\cdot 6H_2O$. Absence of such possible phases means that the rare earth has been successfully doped in $CaWO_4$ lattice sites. The particle size is about 23.03 nm as calculated by Debye–Scherrer formula. The particle sizes estimated using the same formula for those prepared in DMSO and water are 16 nm and 19 nm respectively.

Fig. 1(b) shows the XRD patterns for 5 at% Tb^{3+} doped in $CaWO_4$ prepared in DMSO, water, and water mixed solvents namely EG+water (1:1), DMSO+water (1:1). The XRD peaks reveal that the nanoparticles prepared in DMSO, water and water mixed solvents are completely consistent with the previous JCPDS

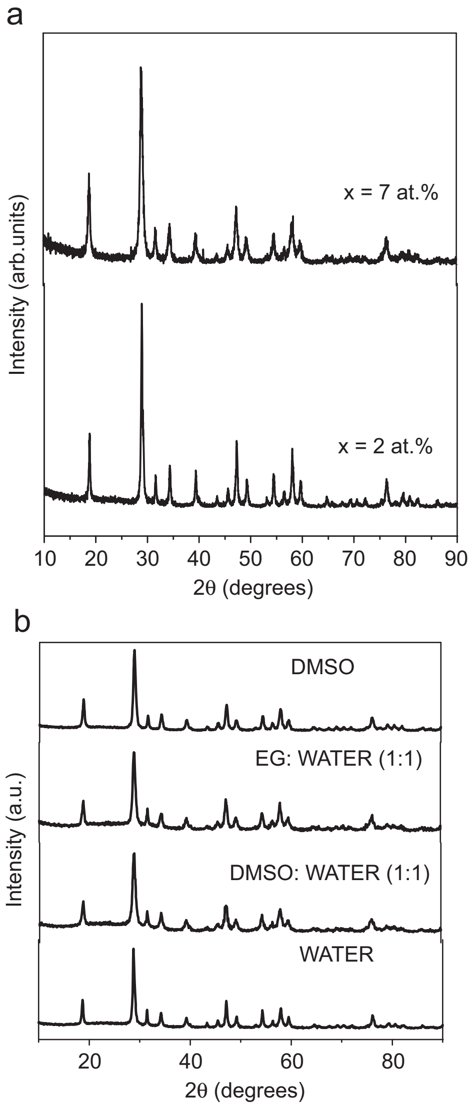

Fig.1. (a) X-ray diffraction patterns of as-prepared $CaWO_4$ doped with x at% Tb^{3+} and (b) 5 at% $CaWO_4:Tb^{3+}$.