Photoluminescence Behaviours of CePO4: Tb3+, M (M = Li+, Ba2+, Bi3+) Nanoparticles Synthesized in Different Reaction Medium

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Abstract-Highly luminescent Tb³⁺ doped CePO₄ nanoparticles (NPs) co-doped with some metal ions (Li⁺, Ba²⁺, Bi³⁺) are prepared using different solvents. The prepared samples show changes in phase and luminescent properties with the solvent used. Samples prepared in EG shows maximum luminescence intensity compared to other solvents. Highly green luminescence properties of the prepared NPs are due to the emission peak at 544 nm corresponding to ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition of Tb³⁺. The hexagonal phase of the samples prepared in water and water mixed solvent transformed to monoclinic phase after heating at 900°C. The luminescence intensity further enhanced with co-doping of Li⁺ ions while co-doping of Ba²⁺ and Bi³⁺ ions reduces the intensity. These NPs can be incorporated in polymer films such as polyvinyl alcohol (PVA). Thus the prepared phosphors can be used as green emitting material in the field of illuminations and display devices.

Keywords- Rare Earth; Enhanced Luminescence; Phase Change; Nanoparticles; Re-dispersible

I. INTRODUCTION

In recent years, great effort has been devoted to the controllable synthesis of rare earth-doped nanoparticles (NPs) driven primarily by the fact that doped nanocrystalline phosphors yielded high luminescence efficiencies ^[11]. With rapidly shrinking size, nanomaterials display novel shape and size-dependent properties for their extremely small size and relatively large specific surface areas ^[2-6]. Based on these unique and fascinating properties, rare earth doped nanocrystalline materials may play an outstanding role in display devices, optical telecommunication, solid-state lasers, and so on ^[7]. Therefore, the development of a facile synthetic method toward high quality rare earth nanocrystals with uniform size and shape appears to be of key importance for the exploration of new research and application fields.

It is well known that Ce^{3+} and Tb^{3+} doped materials (for eg. LaPO₄:Ce, Tb; CePO₄:Tb) serve as efficient green emitting phosphors due to high efficiency of energy transfer from Ce^{3+} to Tb^{3+} [^{8,9]}. They are extensively applied as fluorescent lamps, cathode ray tubes and plasma display panels as green emitting components ^[10,11]. Due to the high absorption of ultraviolet light radiation, Tb^{3+} activated YPO₄ has been emerging as a new type of efficient phosphor in PDPs ^[12]. Thus, Tb^{3+} doped phosphate nanocrystals have aroused great interest among researches. In addition, if incorporated in a suitable polymer matrix, nanoparticles of such rare earth phosphates can be used in a variety of applications ranging from biological to optoelectronics. The

introduction of inorganic NPs into a polymer matrix has proved to be an effective method to improve the performance of polymer materials and bring about novel properties in them ^[13,14].

Here, we report a facile one pot synthesis of redispersible CePO₄ doped with Tb^{3+} in different solvents like EG (ethylene glycol), water, DMF (N,N'-dimethyl formamide) and their mixed media at a relatively low temperature of 140°C in the absence of any surfactant, catalyst or template during the synthesis. The influence of addition of various metal ions in the luminescence properties of CePO₄:Tb³⁺ have been studied. The as-prepared samples were characterized by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) for their structural properties. Photoluminescence properties for all the samples were also characterized and studied.

II. EXPERIMENTAL DETAILS

A. Sample Preparation

Cerium nitrate hexahydrate (Ce(NO₃)₃. 6H₂O, CDH), terbium nitrate (Tb(NO₃)₃.6H₂O, 99.99%, Aldrich) and ammonium dihydrogen phosphate (NH₄H₂PO₄, 99.999%, Aldrich) were used as starting materials. Solvents used were ethylene glycol (EG), water and N,N'-dimethylformamide (DMF). All the reagents were of analytical grade and used without further purification.

In a typical synthesis of 5 at.% Tb^{3+} doped CePO₄, 0.5000 g of Ce(NO₃)₃ and 0.0274 g of Tb(NO₃)₃ were dissolved in minimum amount of conc. HCl in a 100 mL round bottom flask. The excess acid was removed by evaporation with double distilled water. To this solution, 0.1394 g of NH₄H₂PO₄ and 50 mL of EG were added. The solution was refluxed for 3 hrs at a relatively low temperature of 140°C and at 100°C for samples prepared in water. The precipitates formed were separated by centrifugation for 10 mins. at 15,000 rpm. It was washed several times with acetone and finally dried under ambient atmosphere. The dried sample was used for characterization. The same procedure was followed for the preparation of all the other doped samples by taking stoichiometric amounts.

B. Characterization

The structural characteristics and purity of the final products were inspected using PANalytical powder

diffractometer (X'Pert PRO) with Cu-Ka radiation $(\lambda = 1.5405 \text{ Å})$ with Ni filter in the 2θ ranges from 10° to 80° for 45 mins. The size distribution and morphology of the samples were elucidated by Transmission Electron Microscopy (TEM) observation on a Philips make CM-200 transmission electron microscope operating at an accelerating voltage of 200 kV. For this, the samples were ground and mixed together with EG and dispersed under ultrasonic vibration for 30 mins. A drop of the dispersed particles was put over the carbon coated copper grid and evaporated to dryness in ambient atmosphere. FT-IR of the CePO₄ samples was studied using SHIMADZU (model 8400 S) spectrometer by making thin pellets with KBr. UV/Vis absorption spectrum was measured on Shimadzu (model 2450) spectrophotometer. All the photoluminescence spectra and lifetime measurements of the samples were recorded using Perkin Elmer (LS-55) luminescence spectrometer in phosphorescence mode equipped with xenon discharge lamp as the excitation source. Pulse width at half height is $< 10 \ \mu s$. The emission spectra were recorded using maximum excitation wavelength. For the lifetime measurements gate time was fixed at 0.05 ms and the delay time was varied starting from 0.1 ms. All excitation and emission spectra were measured at room temperature with the same instrumental parameters.

III. RESULTS AND DISCUSSIONS

A. XRD Study

The typical XRD pattern of as-prepared 5 at.% Tb^{3+} doped CePO₄ prepared in EG, DMF and that co-doped with metal ions (Li⁺, Ba²⁺ and Bi³⁺) prepared in EG (Fig.1) are found to be in good accord with monoclinic system of pure CePO₄ (JCPDS card no. 73-0478). However, the samples

prepared in water and water mixed solvents (1:1 EG+water and 1:1 DMF+water) shows hexagonal phase (JCPDF 04-0632) which transforms to monoclinic phase after heating at 900°C for 3 hrs (Fig. 2). The XRD patterns do not reveal any diffraction peaks from the starting materials indicating homogeneous incorporation of Tb³⁺ ions in the lattice sites of Ce³⁺ in CePO₄ matrix. The unit cell volume determined by calculating the cell parameters from the XRD pattern goes on decreasing with increase in the concentration of the dopant ions. This is accountable to the larger ionic radius of Ce^{3+} (1.150 Å) than that of Tb^{3+} (1.040 Å). Crystallite sizes are calculated using Scherrer equation, $d=0.9\lambda/\beta \cos\theta$, where d is the average grain size, 0.9 is Scherrer constant, λ is the X-ray wavelength, θ is the diffraction angle and β is full width at half maximum. Table I presents the detailed values of lattice parameters, unit cell volume and crystallite sizes of Tb³⁺ doped CePO₄ samples. Phase transformation for the samples prepared in water, 1:1 EG+water and 1:1 DMF+water from hexagonal to monoclinic phase after heating upto 900°C may be attributed to the presence of sufficient water molecules to surround Ln^{3+} in $[Ln(H_2O)]^{3+}$. Coulombic attraction occurs when PO₄³⁻ ion from $NH_4H_2PO_4$ approaches Ln^{3+} ion, resulting in the formation of LnPO₄. But still, there are sufficient water molecules available in the medium. Moreover, hexagonal structure can have many pores along the c-axis like a channel (zeolite configuration) ^[15-17], easily occupied by water molecules. Thermodynamically, hexagonal phase will be more favourable in water medium because such pores along the caxis will not be possible in tetragonal or monoclinic phases. In pure EG or DMF, the water molecules, if present, will not be able to surround the Ln³⁺ ions resulting in the formation of other possible phases.



Fig. 1 XRD patterns of CePO4:Tb3+ (5 at.%) prepared in EG, DMF and that co-doped with metal ions (Li+, Ba2+ and Bi3+) prepared in EG.



Fig. 2 XRD patterns of CePO4:Tb3+ (5 at.%) prepared in water, 1:1 EG+water and 1:1 DMF+water and that heated at 900oC.

TABLE I. LATTICE PARAMETERS, UNIT CELL VOLUME AND CRYSTALLITE SIZES OF TB3+ DOPED CEPO4 SAMPLES

Tb ³⁺ conc.(at.%)	Lattice parameters			Unit cell	Crystallite
	a(Å)	b(Å)	c(Å)	volume (Å ³)	size(nm)
2	7.220	7.146	6.369	316.38	29
5	6.791	7.018	6.451	297.90	17
7	6.852	6.946	6.383	297.07	14
10	6.746	7.021	6.445	296.57	13
15	6.770	6.986	6.439	296.05	11
20	6.746	7.009	6.441	296.04	11

B. TEM Study

Fig. 3 represents the TEM image along with corresponding selected area electron diffraction (SAED) patterns of 5 at.% Tb^{3+} doped CePO₄ samples prepared in EG. It clearly indicates that the synthesized NPs has an average diameter of 4-6 nm, length of 11-14 nm for Tb^{3+} doped CePO₄ samples prepared in EG. The crystallinity of the samples has been confirmed from the circular patterns observed in the SAED image.



Fig. 3. TEM image for CePO4:Tb $^{3+}$ (5 at.%) prepared in EG; along with the corresponding SAED patterns.

C. FT-IR Study

The FT-IR spectrum of 5 at.% Tb³⁺ doped CePO₄ NPs prepared in EG, water and DMF is shown in Fig. 4. Bands appearing at 535-639 cm⁻¹, considered as the v_4 region, correspond to the bending vibrations of $PO_4^{3^-}$ and it overlap with those of O=C-N stretching mode for samples prepared in DMF whereas the stretching vibrations of $PO_4^{3^-}$, which are referred to as v_3 region, are observed at 960-1130 cm⁻¹. In this region, peak corresponding to CH₃ rocking mode of DMF is merged with those of $PO_4^{3^{-3}}$ group ^[18-21]. The wagging vibration at 1266 cm⁻¹, twisting vibration at 1155 cm⁻¹ and rocking vibration at 899 cm⁻¹ due to presence of CH_2 are merged with bands of $PO_4^{3^-}$. The peaks at 2888 and 2950 cm⁻¹ are assigned to the stretching vibrations of CH₂ group of ethylene glycol molecule whereas its bending vibration (scissoring) can be seen at 1404 and 1455 cm⁻¹ ^[20,22-24]. Peaks appearing at1632 and 3345 cm⁻¹ correspond to bending and stretching vibrations for O-H group respectively of ethylene glycol molecule, which is used as capping agent for the nanoparticles ^[20,22-24]. N-C-H bending vibration of DMF can be seen in the region 1380 cm^{-1 [21]}. All these indicate the presence of EG molecules as stabilizers on the surface of the NPs. When the samples are heated at 900°C, peaks corresponding to the solvents/organic molecules are removed (Supplementary Fig. S1).



Fig. 4 IR spectra of CePO4:Tb3+ (5 at.%) prepared in different solvents.



Fig. S1 IR spectra of CePO4:Tb3+ (5 at.%) prepared in different solvents when heated at 900oC.

D. Luminescence Study

The UV-visible absorption spectrum of as-prepared 5 at.% Tb³⁺ doped CePO₄ sample shows strong absorption band at 275 nm (Supplementary Fig. S2). The band is ascribed to charge transfer band (CTB) and is found to be in good accord with the excitation wavelength (274 nm) of Tb³⁺ doped CePO₄. The excitation spectra for as-prepared samples of Tb³⁺ doped CePO₄ are shown in Fig. 5. In crystalline monoclinic CePO₄, each Ce³⁺ ion can have only C₁ symmetry, as it is coordinated to nine oxygen atoms forming an irregular polyhedron ^[25]. This leads to the splitting of 5*d* levels into five non-degenerate levels.



Fig. 5 Excitation spectra of CePO4:Tb3+ (5 at.%) prepared in EG.

The emission spectra of CePO₄:Tb³⁺ excited at different wavelengths at 225, 243, 274 and 305 nm (Supplementary Fig. S3) show strong Tb³⁺ emission along with Ce³⁺ emission. The presence of both Ce³⁺ and Tb³⁺ emission suggests that the energy transfer between the host CePO₄ and Tb^{3+} is incomplete. This is understandable, as the energy transfer takes place through dipole-dipole interaction, Ce³⁺ ions which are near to the Tb³⁺ ions, can only transfer the excited energy to Tb³⁺ ions. However, with increase in excitation wavelength, there occurs a decrease in Ce³⁺ emission. The intensity of the emission peak is found to be maximum for 274 nm excitation wavelength. The spectrum exhibit the characteristic emission of Tb³⁺ at 489, 544, 585 and 621 nm which arises from the excited ${}^{5}D_{4}$ to the ground state ${}^{7}F_{J}$ (J = 6,5,4,3) transitions respectively. The green emission transition $({}^{5}D_{4} \rightarrow {}^{7}F_{5})$ at 544 nm, which is a magnetic dipole transition with $\Delta J = 0, \pm 1$, is more intense than the electric dipole transition $({}^{5}D_{4} \rightarrow {}^{7}F_{6})$ at 489 nm with $\Delta J = \pm 2$ ^[26]. On the basis of Judd-Ofelt theory ^[27,28], the

magnetic dipole transition is allowed while electric dipole transition is allowed except on the condition that the activators occupy sites without inversion centre. This means that Tb^{3+} ions occupy high symmetric sites. But it is opposite to the actual crystal symmetry site of CePO₄ (i.e. asymmetry). This may be accounted to the polarization effect which arises from the surrounding PO₄³⁻ ions ^[19]. The emission intensity gradually decreases with increase in dopant concentration which is attributed to the concentration quenching effect. It is a typical property of lanthanide-doped systems when the distance between the neighbouring dopant ions decreases. This leads to cross-relaxation among the lanthanide ions when the mean distance between them is less than a critical value and hence the probability of radiative transition is reduced.



Fig. S3 Emission spectra of as-prepared CePO4:Tb3+ (5 at.%) prepared in EG when excited at different wavelengths.

The emission spectra of as-prepared samples of 5 at.% Tb³⁺ doped CePO₄ samples prepared in different solvents (EG, water, DMF and their mixtures) are shown in Fig. 6. It was found that the emission intensity is higher for the samples prepared in EG than that prepared in water, DMF or their mixed solvents. As revealed by the XRD study, the samples prepared in EG and DMF exhibit monoclinic phase while the samples prepared in water and water mixed solvents exhibit hexagonal phase. In hexagonal phase, water molecules can occupy the voids along the c-axis like zeolite structure. When water molecules are present near the Ln³⁺ ions, there is a chance of quencher in luminescence [29]. Therefore, samples having monoclinic phase show higher luminescence intensity than that exhibiting hexagonal phase. The reason that can be given is that after a suitable excitation wavelength, the energy of the excited state is utilized in both radiative and non-radiative processes. Nonradiative process is dependent on the surrounding environment of the Ln³⁺ ions. If the surrounding environment has a high vibrational energy, non-radiative rate is high, resulting in weak luminescence intensity. As is well-known, OH vibration frequency occurs in the broad range of 2700-3700 cm⁻¹ ^[30,31] which is much higher than other vibration such as PO_4^{3-} . As a result, only few phonons are required for non-radiative de-excitation. OH⁻ ions, thus, seem to be efficient quenchers for luminescence through multiphonon relaxation. Hence, samples prepared in water and water mixed media show weaker luminescence intensity. Moreover, samples prepared in DMF show stronger quenching effect than that prepared in EG. This could be due to the presence of N-H group ^[32] from DMF, which acts as quencher in luminescence.



Fig. 6 Emission spectra of CePO₄:Tb³⁺ (5 at.%) prepared in different solvents (EG, water, DMF and their mixtures).

Fig. 7 shows the emission spectra of 5 at.% Tb^{3+} doped CePO₄ NPs annealed at 900°C prepared in water and DMF and that mixed with EG or DMF along with the spectra of as-prepared samples for comparison. It can be seen that the emission intensity is highly enhanced for the annealed samples than the as-prepared ones. This can be attributed to the removal of water molecules that can act as efficient quenchers, surface dangling bonds over the NPs and organic molecules from the environment of the NPs.



Fig. 7 Emission spectra of CePO4:Tb3+ (5 at.%) as-prepared and annealed at 900oC prepared in water and DMF mixed with EG or DMF.

With a view to increase the luminescence efficiency of CePO₄:Tb³⁺ NPs, univalent (Li⁺), divalent (Ba²⁺) and trivalent (Bi³⁺) ions were introduced. Fig. 8 (a) represents the enhanced photoluminescence intensity of ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ and ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transitions of as-synthesized CePO₄:Tb³⁺ (5 at.%), Li⁺ NPs as a function of Li⁺ concentration. The luminescence is most optimum for 0.5 at.% of Li⁺ and then decreases. It is speculated that low fraction of Li⁺ substitution (0.5 at.%) in the host lattice induced fast energy transfer from the host to the dopant ions and a decreased in interstitial oxygen and hence conducing an increase in the hole concentration leading to a decrease in competitive absorption and produced a higher quantum yield ^[33,34]. Also, the incorporation of Li⁺ ions create oxygen vacancies, which might act as sensitizer for the energy transfer to the rare earth ions due to the strong mixing of charge transfer states resulting in highly enhanced luminescence ^[35]. With the gradual increase in Li⁺ content, the oxygen vacancies of host lattice greatly increase which will destroy the crystallinity and lead to luminescence quenching. However, the introduction of Ba^{2+} and Bi^{3+} ions in 5 at.% Tb^{3+} doped CePO₄ NPs does not lead to luminescence enhancement (Fig. 8 (b)). This phenomenon is complicated to explain but one possible reason that may be given is that for Tb³⁺ transitions to be quenched in any particular Tb^{3+} ion, it requires that at least two neighbouring ions are excited to a specific energy state. Any luminescence quenching in Tb³⁺ then occurs via excitation transfer to non-radiative sinks like defects or impurities. This may occur as a result of either direct energy transfer to acceptor states or by migration of the excitation among Tb³⁺ ions until it arrives in the vicinity of a suitable sink [36].







Fig. 8 Emission spectra of CePO4:Tb3+ (5 at.%) co-doped with (a) Li+ and (b) Ba2+ and Bi3+.

The integrated intensity area under the curve is determined by fitting with Gaussian distribution function, given by

$$I = I_{B} + \sum_{i=1}^{n} \frac{A_{1}}{W_{i} \sqrt{\frac{\pi}{2}}} e^{-2 \frac{(\lambda - \lambda_{ci})^{2}}{W_{i}^{2}}}$$
(1)

where *I* is the intensity, I_B is the background intensity, w_i is the width at half-maximum intensity of the curve and A_i is the area under the curve. λ is the wavelength and λ_{ci} is the mean wavelength value corresponding to the transition. All the fittings were carried out in the range 520-560 nm and 470-510 nm for the transitions ${}^5D_4 \rightarrow {}^7F_5$ and ${}^5D_4 \rightarrow {}^7F_6$ respectively (Fig. 9). It is observed that the emission intensity increases up to 5 at.% Tb³⁺ (optimum concentration) and decreases with further increase in Tb³⁺ concentration due to concentration quenching effect.



Fig. 9 Integrated area under the curve against Tb3+ concentration for two emission peaks at 544 nm for 5D4→7F5 and at 489 nm for 5D4→7F6 (Inset: Decay curves for 5D4→7F5 of Tb3+ (5 at.%) doped CePO4 samples prepared in EG).

In order to investigate the luminescence dynamics of the samples, the photoluminescence decay curves have been measured by fixing the excitation and emission wavelengths at 274 nm and 544 nm respectively. The curves are fitted with both monoexponential and biexponential decay equations to the decay data. The goodness of fits of parameters for 5 at.% Tb³⁺ doped CePO₄ with mono- and biexponential equations were found to be 0.95980 and 0.99926 respectively. Thus the curves follow biexponential decay (inset of Fig. 9). This behaviour can be explained by the presence of structural water, which acts as non-radiative transition channels ^[37,38]. The biexponential fitting was carried out using Equation (2)

$$\boldsymbol{I}_{t} = \boldsymbol{I}_{1}\boldsymbol{\varrho}^{-\frac{t}{\tau_{1}}} + \boldsymbol{I}_{2}\boldsymbol{\varrho}^{-\frac{t}{\tau_{2}}}$$
(2)

where I_1 and I_2 are the intensities at different times and τ_1 and τ_2 are their corresponding lifetimes. The average lifetime was calculated by the equation,:

$$\tau_{av} = \frac{I_1 \tau_1 + I_2 \tau_2}{I_1 + I_2}$$
(3)

The biexponential decay behaviour is found to be dependent on the number of different luminescent centres, energy transfer, defects and the presence of impurities in the host ^[39]. The average lifetime value for the most intense transition, 5 at.% Tb³⁺ doped sample was determined to be 2.06 ms. In addition, the calculated average lifetime for Li⁺ (0.5 at.%) co-doped CePO₄:Tb³⁺ (5 at.%) comes out to be 3.54 ms which means that the non-radiative decays are less and these NPs will have better photoluminescence properties. Whereas the average lifetime for Ba²⁺ and Bi³⁺ co-doped CePO₄:Tb³⁺ (5 at.%) samples were found to be 0.96 ms and 1.42 ms respectively. The lifetime value of 5 at.% Tb³⁺ doped sample was reported to be 4.23 ms [40]. As the concentration of Tb^{3+} in Tb^{3+} doped CePO₄ increases above 5 at.%, the lifetime decreases. This is attributed to strong quenching as the distance between the $Tb^{3+}-Tb^{3+}$ decreases. Moreover, cross-relaxation among the Tb³⁺ ions is dominant over the non-radiative relaxation, which arises from the surface or near the surface for higher-doped samples.

E. Dispersion of Nanoparticles in Polar Solvents and PVA Film

Stock solutions of 5% PVA (polyvinyl alcohol) and 0.1 M borax (cross linker) were prepared in double distilled water. 5 mL of PVA stock solution was mixed with 10 mg of CePO₄:Tb³⁺ (5 at.%) and the mixture was subjected to ultra-sonication for 1 hr to get homogeneous dispersion. After sonication, 1.5 mL of borax solution was added to the mixture and stirred gently using a glass rod avoiding bubble formation. The polymer gel formed is then transferred to a glass slide. A uniform film is formed after keeping for 5

days at ambient atmosphere. Here, the PVA molecules are cross-linked by borax. Also, PO_4^{3-} of $CePO_4:Tb^{3+}$ can interact with the OH group of the PVA.

Fig. 10 shows the emission spectra of $CePO_4$:Tb³⁺ (5 at.%) dispersed in methanol and that incorporated in PVA film excited at 274 nm along with the photographic image, after irradiation under UV light. The characteristic emission peaks of Tb³⁺ are well observed and the image shows bright green (Tb³⁺) light. The presence of EG on the surface of the NPs accounts for their re-dispersibility in polar solvents like water, ethanol, methanol, etc. Good dispersibility is an important criterion that aids ease of fabrication and also facilitates the use of NPs for biological assays. Such dispersed NPs could prove to be potential phosphors for biological fluorescence labelling, biological imaging and other diagnostic applications.



Fig. 10 Emission spectra of CePO4:Tb3+ (5 at.%) dispersed in methanol and that incorporated in PVA film excited at 274 nm along with photographic images after UV irradiation in (a) methanol and (b) PVA film.

IV. CONCLUSIONS

Monoclinic and hexagonal phases of Tb³⁺ and Dy³⁺ doped CePO₄ nanoparticles have been prepared successfully at 140°C in different solvents (EG, DMF, water and their mixed media) by a simple route. TEM image reveals rod like morphology of Tb³⁺ doped CePO₄ prepared in EG. The luminescence intensity of the samples prepared in EG with monoclinic phase are found to be most prominent than those prepared in other solvents. Hexagonal phase is obtained for the samples prepared in water and water mixed solvents. This hexagonal phase transformed to monoclinic phase after heating the sample at 900 °C. The luminescence emission intensity of the as-prepared samples increases significantly after introduction of Li⁺ ions and heat treatment. The asprepared samples are dispersible in polar solvents and can be incorporated in polymer films of PVA. These nanomaterials may find industrial applications due to their properties, simplicity of process, low cost and availability of raw materials.

V. ACKNOWLEDGEMENTS

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VI. SUPPLEMENTARY INFORMATIONS

IR spectra of CePO₄:Tb³⁺ (5 at.%) prepared in different solvents when heated at 900 °C, UV-visible absorption spectrum of as-prepared CePO₄:Tb³⁺ (5 at.%) NPs and emission spectra of as-prepared CePO₄:Tb³⁺ (5 at.%) prepared in EG when excited at different wavelengths.

REFERENCES

- R. Bhargava, D. Gallaghar, X. Hong, A. Nurmikko, "Optical Properties of Manganese-Doped Nanocrystals of ZnS", Phys. Rev. Lett., vol.72, pp. 416–419, 1994.
- [2] J. Boyer, F. Vetrone, L. Cuccia, J. Capobianco, "Synthesis of Colloidal Upconverting NaYF4 Nanocrystals Doped with Er3+, Yb3+ and Tm3+, Yb3+ via Thermal Decomposition of Lanthanide Trifluoroacetate Precursors", J. Am. Chem. Soc., vol. 128, pp. 7444–7445, 2006.
- [3] O. Lehmann, K. Kompe, M. Haase, "Synthesis of Eu3+-Doped Core and Core/Shell Nanoparticles and Direct Spectroscopic Identification of Dopant Sites at the Surface and in the Interior of the Particles", J. Am. Chem. Soc., vol. 126, pp. 14935–14942, 2004.
- [4] S. Heer, K. Kompe, H. Gudel, M. Haase, "Highly Efficient Multicolour Upconversion Emission in Transparent Colloids of Lanthnide-Doped NaYF4 Nanocrystals", Adv. Mater., vol. 16, pp. 23–24, 2004.
- [5] H. Mai, Y. Zhang, Z. Yan, L. Sun, L. You, C. Yan, "High-Quality Sodium Rare-Earth Fluoride Nanocrytals: Controlled Synthesis and Optical Properties", J. Am. Chem. Soc., vol. 128, pp. 6426–6436, 2006.
- [6] F. Wang, X. Liu, "Recent Advances in the Chemistry of Lanthanide-Doped Upconversion Nanocrystals", Chem. Soc. Rev., vol. 38, pp. 976–989, 2009.
- [7] G. Qin, W. Qin, C. Wu, S. Huang, J. Zhang, S. Lu, D. Zhao, H. Liu, "Enhancement of Ultraviolet Upconversion in Yb3+ and Tm3+ Codoped Amorphous Fluoride Film Prepared by Pulsed Laser Deposition", J. Appl. Phys., vol. 93, pp. 4328–4330, 2003.
- [8] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer, Berlin, 1994.
- [9] O.A. Serra, E.J. Nassar, G. Zapparolli, I.L.V. Rosa, "Photophysical properties of Ce3+:Tb3+ supported on silicas and zeolites", J. Alloys compd., vol. 225, pp. 63-65, 1995.
- [10] J. Dexpert-Ghys, R. Mauricot, M.D. Faucher, "Spectroscopy of Eu3+ ions in monazite type lanthanide orthophosphates LnPO4, Ln = La or Eu", J. Lumin., vol. 69, pp. 203-215, 1996.
- [11] B. Monie, G.Bizarri, "Rare-earth doped phosphors: oldies or goldies?", Mater. Sci. Eng. B, vol. 105, pp. 2-7, 2003.
- [12] W. Di, X. Wang, B. Chen, H. Lai and X. Zhao, "Preparation, characterization and VUV luminescence property of YPO4:Tb phosphor for a PDP", Opt. Mater., vol. 27, pp. 1386-1390, 2005.
- [13] M. Okamoto, S. Morita, Y.H. Kim, T. Kotaka, H. Taeyama, "Synthesis and structure of smectic clay/poly(methyl methacrylate) and clay/polystyrene nanocomposites via in situ

intercalative polymerization", Polymer, vol.41, pp. 3887-3890, 2000.

- [14] M. Avella, M.E. Errico, E. Martuscelli, "Novel PMMA/CaCO3 Nanocomposites Abrasion Resistant Prepared by an in Situ Polymerization Process", Nano Lett., vol. 1, pp. 213-217, 2001.
- [15] M. Ferhi, K. Horchani-Naifer, M. Ferid, "Hydrothermal synthesis and photoluminescence of the monophosphate LaPO4:Eu(5%)", J. Lumin., vol. 128, pp. 1777-1782, 2008.
- [16] X. Xiao, Bing Yan, "Reproducible Solvent–Thermal Synthesis, Controlled Microstructure, and Photoluminescence of REPO4:Eu3+, Tb3+ (RE=Y, La, and Gd) Nanophosphors", J. Am. Ceram. Soc., vol. 93, pp. 2195-2201, 2010.
- [17] C. Zollfrank, H. Scheel, S. Brungs, P. Greil, "Europium(III) Orthophosphates: Synthesis, Characterization, and Optical Properties", Cryst. Growth Des., 8, pp. 766-770, 2008.
- [18] M. Ferhi, K. Horchani-Naifer, M. Ferid, "Combustion synthesis and luminescence properties of LaPO4: Eu (5%)", J. Rare Earths, vol. 27, pp. 182-186, 2009.
- [19] G. Phaomei, R.S. Ningthoujam, W. R. Singh, N. S. Singh, M. N. Luwang, R. Tewari, R.K. Vatsa, "Low temperature synthesis and luminescence properties of re-dispersible Eu3+ doped LaPO4 nanorods by ethylene glycol route", Opt. Mater., vol. 32, pp. 616-622, 2010.
- [20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, USA, 1986.
- [21] M.M.E. Jacob, A.K. Arof, "FTIR studies of DMF plasticized polyvinyledene fluoride based polymer electrolytes", Electrochimica Acta, vol. 45, pp. 1701-1706, 2000.
- [22] R.S. Ningthoujam, N.S. Gajbhiye, A. Ahmed, S. S. Umre, S.J. Sharma, "Re-Dispersible Li+ and Eu3+ Co-Doped Nanocrystalline ZnO: Luminescence and EPR Studies", J. Nanosci. Nanotechnol., vol. 8, pp. 3059-3062, 2008.
- [23] N.S. Gajbhiye, R.S. Ningthoujam, A. Ahmed, D.K. Panda, S.S. Umre, S.J. Sharma, "Re-dispersible Li+ and Eu3+ co-doped CdS nanoparticles: Luminescence studies", Pramana, vol. 70, pp. 313-321, 2008.
- [24] W. Kemp, Organic Spectroscopy, Macmillan, Hampshire, 1975.
- [25] Y. Ni, J.M. Hughes, A.N. Mariano, "Crystal chemistry of the monazite and xenotime structures", Am. Mineral, vol. 80, pp. 21-26, 1995.
- [26] S.D. Cheng, C.H. Kam, S. Buddhudu, "Enhancement of green emission from Tb3+:GdOBr phosphors with Ce3+ ion codoping", Mater. Res. Bull., vol. 36, pp. 1131-1137, 2001.
- [27] B.R. Judd, "Optical absorption intensities of rare-earth ions", Phys. Rev., vol. 127, pp. 750-761, 1962.
- [28] G.S. Ofelt, "Intensities of crystal spectra of rare-earth ions", J. Chem. Phys., vol. 37, pp. 511-520, 1962
- [29] A. Huignard, V. Buissette, A.C. Franville, T. Gacoin, J.P. Boilot, "Emission Processes in YVO4:Eu Nanoparticles", J. Phys. Chem. B, vol. 107, pp. 6754-6759, 2003.
- [30] D.E. Day, J.M. Stevels, "Internal friction of NaPO3 glasses containing water", J. Non-Cryst. Solids, vol. 11, pp. 459-470, 1973.
- [31] L. Zhang, H. Hu, "The effect of OH- on IR emission of Nd3+, Yb3+ and Er3+ doped tetraphosphate glasses", J. Phys. Chem. Solids, vol. 63, pp. 575-579, 2002.
- [32] R. Okram, N.R. Singh, Ak.M. Singh, "Simple preparation of Eu3+-doped LaVO4 by ethylene glycol route: a luminescence study", Micro & Nano Letters, vol. 6, pp. 165–169, 2011.

- [33] S.S. Yi, J.S. Bae, K.S. Shim, J.H. Jeong, J.C. Park, P.H. Holloway, "Enhanced luminescence of Gd2O3:Eu3+ thin-film phosphors by Li doping", Appl. Phys. Lett., vol. 84, pp. 353-355, 2004.
- [34] J.K. Park, J.M. Kim, K.N. Kim, C.H. Kim, H.D. Park, "Effect of Li+ on the Luminescence Properties of Gd2O3: Eu Phosphor", Electrochem. Solid State Lett., vol. 7, pp. H39, 2005.
- [35] O.A. Lopez, J. McKittrick, L.E. Shea, "Fluorescence properties of polycrystalline Tm3+-activated Y3Al5O12 and Tm3+-Li+ co-activated Y3Al5O12 in the visible and near IR ranges", J. Lumin., vol. 71, pp. 1-11, 1997.
- [36] M.J. Weber, "Luminescence Decay by Energy Migration and Transfer: Observation of Diffusion-Limited Relaxation", Phys. Rev. B, vol. 4, pp. 2932-2939, 1971.
- [37] W.H. Di, X.J. Wang, P.F. Zhu, B.J. Chen, "Energy transfer and heat-treatment effect of photoluminescence in Eu3+-

doped TbPO4 nanowires", J. Solid State Chem., vol. 180, pp. 467-473, 2007.

- [38] L.X. Yu, H.W. Song, Z.X. Liu, L.M. Yang, S.Z. Lu, Z.H. Zheng, "Electronic Transition and Energy Transfer Processes in LaPO4-Ce3+/Tb3+ Nanowires", J. Phys. Chem. B, vol. 109, pp. 11450-11455, 2005.
- [39] G. Jia, Y. Song, M. Yang, Y. Huang, L. Zhang, H. You, "Uniform YVO4:Ln3+ (Ln = Eu, Dy, and Sm) nanocrystals: Solvothermal synthesis and luminescence properties", Opt. Mater., vol. 31, pp. 1032-1037, 2009.
- [40] G. Phaomei, R. S. Ningthoujam, W. R. Singh, R. S. Loitongbam, N. S. Singh, A. Rath, R. R. Juluri, R. K. Vatsa, "Synthesis of re-dispersible Ce3+ co-doped LaPO4:Tb3+ nanorods and effects of concentrations of Ce3+ or Tb3+ and reaction medium on luminescence properties: luminescence switching behavior through redox reaction and polymer films", Dalton. Trans., vol. 40, pp. 1–10, 2011.