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Roles of solvent, annealing and Bi^{3+} co-doping on crystal structure and luminescence properties of YPO_4:Eu^{3+} Nanoparticles

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R. S. Ningthoujam,* Anusha Sharma, K. S. Sharma, K. C. Barick, P. A. Hassan, R. K. Vatsa*

YPO_4:Eu^{3+} nanoparticles have been prepared in different solvents such as polyethylene glycol (PEG), PEG-diacid and water. These nanoparticles crystallize in mixture of tetragonal and hexagonal phases. Ratio of tetragonal to hexagonal phases in PEG and PEG-diacid mediums is much lower than that in water. Interestingly, luminescence intensity upon excitation at 260 and 395 nm for the sample prepared in water is higher than that for sample prepared in PEG or PEG-diacid. This is because of association of water molecules trapped inside the pores of hexagonal phase and this induces non-radiative rate. In order to study effect of Bi^{3+} co-doping on luminescence intensity, we have carried out detail crystal structure evolutions in different solvents. However, luminescence intensity decreases significantly upon Bi^{3+} co-doping because it enhances conversion of a mixture into hexagonal phase. Upon heating at 900 °C, luminescence intensity increases significantly because of conversion of hexagonal to tetragonal phase. Increase in lifetime value of Eu^{3+} as well as the red light enhancement has been observed in 900 °C heated samples by Bi co-doping.

Introduction

The lanthanide ion (Ln^{3+}) doped nanoparticles have been used in many applications such as laser, sensor, heat-resistant materials, field-effect transistors, solar cells and optoelectronic devices.[1-8] Among Ln^{3+} doped nanoparticles, YPO_4 is used as host because of the following characteristics: 1) All Ln^{3+} ions can substitute Y^{3+} sites due to similar ionic size as well as similar oxidation states, 2) precursors of Y^{3+} ions are very cheap as compared to other Ln^{3+} and thus, only small amount of Ln^{3+} activators (1-10 at.%) is sufficient, 3) host is chemically stable in acidic and alkaline mediums, 4) host is thermally stable at 1500 °C, 5) host is bio-compatible, 6) in nano-size particles, particle has many P-O-H groups and because of this they are dispersible in water and even can be extended by suitable molecules/ligands so that proper functionalization can be done, 7) they can be made hybrid with magnetic nanoparticles and thus multifunctional properties can be possessed by small size particle, 8) isotope substitution of ^{89}Y by ^{90}Y (β-emitter with $t_{1/2}$ = 64 h) or ^{31}P by ^{32}P (β-emitter with $t_{1/2}$ = 14 h) can produce short life time rays (β and/or γ) and thus this can be used in tracing of tumours and therapy in localized cells and even deep tissue can be mapped, 9) its P-O vibration lies at 1100 cm^{-1}, which do not much affect on luminescence of Ln^{3+} ions through multi-phonon relaxation and thus such particles show efficient luminescence, 10) large band gap (8.6 eV) and many intermediate bands can be created when particles is reduced to nano-size or by substitution, and 11) optically isotropic with a refractive index (~1.72).[2-6]

There are many reports on enhancement of luminescence of Eu^{3+} by energy transfer from Bi^{3+} on many hosts (YPO_4, $LnVO_4$, $CaWO_4$, $Na_3YSi_3O_9$, Y_2SiO_5).[9-14] Bi^{3+} absorbs light in 250-400 nm depending on host due to S-P transition and broad emission transition occurs in 350-800 nm. In this absorption band, Eu-O charge transfer band lies and also absorption peaks of Eu^{3+} at 395 and 460 nm coincide with broad emission transition of Bi^{3+}. In such situation, energy transfer from Bi^{3+} to Eu^{3+} occurs and thus, there is an enhancement of Eu^{3+} emission. Even Bi^{3+} was used as activator in many hosts.[15] However, there are not many reports on study of luminescence properties of Eu^{3+} by Bi^{3+} co-doping when there are quenchers near to Eu^{3+}.

In our previous study, decrease of luminescence in YPO_4:Eu, Bi was observed if there were quenchers in samples.[10] Sample was prepared in polyethylene glycol (PEG), which acts as solvent as well as capping agent. Even co-doping of Bi^{3+} can change crystal structure of YPO_4:Eu^{3+} from tetragonal to hexagonal phase. In many reports, crystal structure can be changed depending on solvent in which the preparation of rare-earth phosphates is performed. In preparation of YPO_4:Eu co-doped with Bi/Ce, hexagonal phase is favoured when solvent is polyethylene glycol (PEG, HO-(CH_2-CH_2-O)$_n$-H)/ethylene glycol (EG, HO-CH_2-CH_2-OH),[9,10] whereas, $LaPO_4$:Eu/Dy/Sm favours for formation of the monoclinic phase in EG solvent, but it forms hexagonal phase when medium of preparation is water.[16,17] In terms of luminescence intensity of Ln^{3+}, luminescence intensity of tetragonal phase is more than monoclinic phase and that of hexagonal phase is almost quenched. This has been explained in terms of water molecules trapped inside pores of hexagonal phase extended along z-axis and interestingly, such water molecules do not freeze at -50 °C.[17] The water molecules are nearer to Ln^{3+} and far from PO_4 group. When water is removed by heating above 600-800 °C,[8,9,10,16] luminescence intensity recovers and also, structure becomes tetragonal or monoclinic. In this direction, improvement in luminescence can be done by Bi^{3+} co-doping in case of tetragonal phase in $LnPO_4$ or even $LnVO_4$. In $LnVO_4$, tetragonal phase has more luminescence than monoclinic phase. Recent study suggests that even higher ratio of monoclinic to tetragonal phase has more luminescence if appropriate co-sensitizer (such as Bi^{3+}) is used.[11]

In this article, YPO_4 nanoparticles are heavily doped with Eu^{3+} (10 at.%), which means that it starts concentration quenching in luminescence above 5 at.% Eu^{3+} in many hosts.[7] Can we improve

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Chemistry Division, Bhabha Atomic Research Centre, Mumbai – 400085, India
Phone: + 91 22 25592321, Fax: + 91 22 25505151, E-mail: *rsn@barc.gov.in (RSN), rkvatsa@barc.gov.in (RKV)*

†Electronic Supplementary Information (ESI) available: XRD patterns, TEM images, excitation and emission spectra, CIE-coordinates, decay curves.

luminescence intensity? The samples are prepared in three different solvents such as polyethylene glycol (PEG), PEG-diacid ($HOOC-CH_2-O-(CH_2-CH_2-O)_n-CH_2-COOH$) and water. Here, PEG, PEG-diacid and water have different viscosities, refractive indexes, densities and dielectric constants.[18-22] These will change physical properties of material. Samples show variation of ratio of tetragonal to hexagonal phases (T/H) in different solvents. In such system, Bi^{3+} (10 and 20 at.%) are co-doped so that it will change h/t. The consequence of structure change by solvent or annealing on luminescence is studied.

Experimental

10 at. % Eu^{3+} doped YPO_4 was prepared by co-precipitation method. Initially, 0.5 g Y_2O_3 was dissolved in 3 ml of conc. HNO_3 at 80 °C and then 0.219 g $Eu(NO_3)_3.6H_2O$ was added. Excess HNO_3 was removed by evaporation at 100 °C. Before drying, 3 ml of double distilled water was added. This evaporation process was done. The similar process was repeated 4-5 times. About 30 ml of EG and 10 ml of PEG (10% = 10 g of PEG-6000 in 100 g of water) were added and homogenous solution was obtained. A solution of $(NH_4)H_2PO_4$ (1.08 g in 10 ml of distilled water) was added followed by heating at 160 °C for 2 h under refluxing conditions. The white precipitate was collected by centrifugation. Eu^{3+} (10 at.%) doped YPO_4 samples is written as YPO_4:Eu.

The same procedure was employed while preparing with different solvents (PEG-diacid and water). In case of preparation in aqueous medium, 40 ml of distilled water was added instead of adding EG and PEG and heating at 80 °C was performed. YPO_4:Eu prepared in solvents such as EG-PEG, PEG-diacid and water are named as YPO_4:Eu-PEG, YPO_4:Eu-PEG-diacid and YPO_4:Eu-water, respectively. It is to be noted that a lot of water molecules is available when solvent of EG-PEG or PEG-diacid is used below 100 °C. Above this temperature, free water molecules will vaporize and finally, a few co-ordinated H_2O molecules through hydrogen bonding with EG-PEG, PEG-diacid or even surface of YPO_4 particles will remain.

Bi^{3+} (10 and 20 at.%) is co-doped in YPO_4:Eu. Y_2O_3 (0.5 g) was dissolved in 2 ml of conc. HNO_3 by heating at ~80 °C until get a clear solution. Stoichiometric amount of $Eu(NO_3)_3.6H_2O$ (0.246 g for 10 at.% Eu) and $Bi(NO_3)_3.5H_2O$ (0.268 g for 10 at.% Bi) were dissolved in the above solution with addition of distilled water at least five times in order to remove the excess acid. To this reaction medium, 30 ml EG, 10 ml PEG and the required amount of $(NH_4)H_2PO_4$ were added. The reaction temperature is increased to 140-160 °C and maintained at that temperature for 2 h. The precipitate formed is separated by centrifugation, and washed several times with distilled water in order to get rid of the unreacted species. The same procedure was employed while preparing samples with different solvents (PEG-diacid and water).

EG-PEG/PEG-diacid molecules act as solvent as well as capping agent during the reaction for preparation of YPO_4 nanoparticles. When the nucleation starts, EG-PEG or PEG-diacid molecules present in the reaction medium cap smaller particles and thus, particle growth is slow, thereby hindering the agglomeration among the particles. Along with controlling the particle size, the capping agents also help in colloidal stability of the particles in aqueous media. Dielectric medium of reaction also helps in controlling particle size.

The 10 and 20 at.% Bi^{3+} co-doped in YPO_4:Eu are named as YPO_4:Eu-10Bi and YPO_4:Eu-20Bi, respectively. The suffix PEG, PEG-diacid and water are put in order to identify type of solvent used. YPO_4:Eu-10Bi prepared in EG-PEG, PEG-diacid and water are named as YPO_4:Eu-10Bi-PEG, YPO_4:Eu-10Bi-PEG-diacid and YPO_4:Eu-10Bi-water, respectively.

In order to compare annealing effect on physical properties, 0, 10 and 20 at.% Bi^{3+} co-doped YPO_4:Eu-PEG-diacid samples were heated at 900 °C for 4 h each.

Characterization

The crystal structure of the material was identified by Phillips PW1729 diffractometer with CuK_α radiation. All patterns were recorded over the angular range $10^o \leq 2\theta \leq 70^o$. The average crystallite size (t_c) is estimated from the X-ray line broadening using Scherrer formula: $t_c = 0.9\lambda/(\beta Cos\theta)$, where, λ is wavelength of CuK_α and β is full width at half maximum of the diffraction peak. Morphology of particles was characterized using Philips CM-200 transmission electron microscope (TEM). Fourier transform infrared (FTIR) Bomem spectrometer (Hartmann and Braun, MB-100 series) was used to study the interaction of PEG-diacid or EG-PEG with YPO_4. The photoluminescence (PL) spectra of these powder phosphors were recorded using an Edinburg instrument FLS920 equipped with 450 W Xenon lamp as a source at a spectral resolution of 3 nm. All the measurements were carried out at room temperature. PL decay (lifetime measurement) was carried out using μs flash lamp attached to Edinburgh Instruments – (model F920).

Results and discussion

Structural and morphology studies

Fig. 1(a) shows the XRD patterns of YPO_4:Eu and YPO_4:Eu-xBi-PEG (x = 10 and 20 at.%) samples. The presence of two phases, i.e. tetragonal (JCPDS card no. 11-0254) and hexagonal phases (JCPDS card no. 42-0082) is observed. At higher co-dopant concentration of Bi^{3+} (20 at. %), intensity of hexagonal peaks further increases and tetragonal phase has been almost completely converted to hexagonal phase. Thus, we observed that with increase in Bi^{3+} ion co-doping concentration, phase transformation takes place. Fig. S1 and S2 (ESI†) show the XRD patterns of YPO_4:Eu and YPO_4:Eu-xBi (x = 10 and 20 at.%) samples prepared in PEG-diacid and water, respectively. Similar trend is observed. The lattice parameters of YPO_4:Eu-water are found to be a = 6.820, c = 6.305 Å, V = 254.03 $Å^3$ for hexagonal phase, whereas those for tetragonal phase are a = 6.914, c = 6.038 Å, V = 288.62 $Å^3$. The tetragonal to hexagonal ratio of the prepared samples and their crystallite sizes are given in Table 1. To compare the peak intensities of tetragonal and hexagonal phases, (200) plane is considered for tetragonal phase, whereas (111) plane is considered for hexagonal phase. It can be seen that with increasing concentration of Bi^{3+}, this ratio is decreasing, i.e. hexagonal phase increases with respect to tetragonal phase. It was reported that Bi^{3+} ions can be incorporated to YPO_4:Eu (5 at.%) up to a maximum of 7 at. % and above which, it leads to the formation of a new phase of $BiPO_4$ (hexagonal) and also affects the luminescence intensity.[10] The crystallite size is found to decrease with Bi^{3+} co-doping. The significant reduction in crystallite size is observed on using PEG-diacid and water as solvent. Interestingly, without Bi-co-doping, tetragonal to hexagonal phase ratio is much higher in case of water solvent as compared to that of PEG or PEG-diacid. Even sample prepared in PEG-diacid has higher ratio than that in PEG. On other hand, hexagonal phase is stable only when water molecules occupy pores/interstitial sites. In this, tetragonal phase is more stable over hexagonal phase in water medium. In literature, it was suggested that dielectric constant (ε) of water decreases with addition of PEG due to reduction of co-ordinated hydrogen bonding present on water.[19] The viscosity of water increases significantly when PEG is added. This is suggested that there are roles of solvents on crystallite sizes.[20,21]

XRD patterns of 900 °C heated samples of 0 and 10 at.% Bi^{3+} co-doped YPO_4:Eu-PEG-diacid are shown in Fig. 1(b, c). Both crystallize in tetragonal phase. However, there are extra peaks of very lower intensity observed in Bi^{3+} co-doped sample and these are related to $BiPO_4$ (monoclinic), which are segregated. Some amounts of Bi^{3+} are substituted into Y^{3+} sites, which is reflected in lower shift of peak positions in XRD patterns. Also, an improved crystallinity is observed by Bi^{3+} co-doping. Lattice parameters of 0 and 10 at.% Bi^{3+} co-doped YPO_4:Eu are a = 6.888, c = 6.021 Å (V = 285.65 $Å^3$) and a = 6.899, c = 6.028 Å (V = 286.89 $Å^3$), respectively.

Fig. 1(d) shows the 3D schematic representation using the lattice parameters of hexagonal phase. In which, there are pores/interstitial sites with diameter of ~ 0.7 nm and water (H-O or H-H distance in H_2O will be less than 0.2 nm) molecules occupy pores/interstitial sites. In the previous study, it was reported that one molecule of YPO_4 can have 0.5-1.0 molecule of water.[9,17]

The FT-IR spectra of as-prepared YPO_4:Eu-PEG-diacid and 900 °C heated YPO_4:Eu-xBi (x = 0, 10 at.%). Peaks at 522, 623, 645, 1004, 1066, 1620 and 3430 cm^{-1} are observed in case of as-prepared sample (Fig. S3 ESI†). The 1st to 5th peaks are related to PO_4 unit of YPO_4.[7-10] and 1620 cm^{-1} is related to -COOH/-COO^- of PEG-diacid.[23] Since PEG-diacid has –COOH group, this group is used for capping over particle. Pure PEG-diacid has peak 1730 cm^{-1} (C=O of COOH) and shows peak at 1620 cm^{-1} after coating over particle.[23] The broad peak centered at 3430 cm^{-1} is related to H_2O/OH present in the system. Stretching vibrations of CH_2 could not be observed distinctly due to overlapping with broad peak of –COOH and -OH present on particle. Bending vibrations of CH_2 are also merged with those of PO_4 unit. Upon heating at 900 °C, the characteristic peaks of PO_4 unit are observed. The stretching and bending vibrations of water are also found at 3430 and 1647 cm^{-1} and these are related to water molecules present on surface of particle, but peak at 1647 cm^{-1} is different from that of as-prepared sample (1620 cm^{-1}). However, extra peak at 553 cm^{-1} is observed in Bi^{3+} co-doping sample.

Fig. S4 (ESI†) shows the TEM images of YPO_4:Eu prepared in PEG, PEG-Diacid and water mediums. The particles are of rice type (i. e., oval shape). Major and minor axes are ~ 100 and ~ 25 nm, respectively in all three cases. Upon heating as-prepared YPO_4:Eu PEG-Diacid at 900 °C, shapes of particles are found to be polyhedron with size 50 – 100 nm for 0 at.%Bi sample and highly agglomerated cuboids with size 0.5 – 1 μm for 10 at.%Bi sample (Fig. S5, ESI†). 0 at.% Bi gives nanoparticles, whereas single crystal nature is observed in case of 10 at.% Bi (Fig. S5, ESI†), which are supported by selected area electron diffraction (SAED) patterns.

Table 1. Intensity ratio of tetragonal (200 plane) to hexagonal (111 plane) phases of the samples (YPO_4:Eu-xBi) prepared in different solvents and crystallite size (t_c) of samples.

Sample prepared in solvents	Bi^{3+} (x at.%)	$I_{(200)}/I_{(111)}$ ratio	Crystallite Size (t_c, nm)
PEG	0	1.91	44
	10	0.45	33
	20	0.43	26
PEG-diacid	0	3.34	35
	10	0.56	31
	20	0.48	22
Water	0	6.70	34
	10	0.50	26
	20	0.56	22

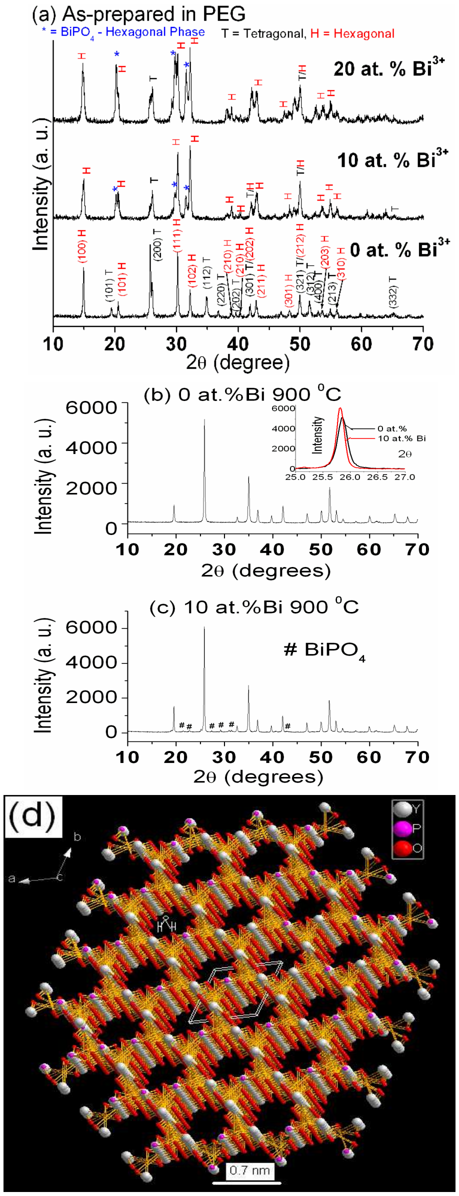


Fig. 1. (a) XRD patterns of as-prepared YPO_4:Eu-PEG co-doped with different concentrations of Bi^{3+} (0, 10 and 20 at. %). XRD patterns of 900 °C heated samples of YPO_4:Eu-PEG-diacid co-doped with different concentrations of Bi^{3+} ((b) 0 and (c) 10 at.%). (d) 3D schematic representation of hexagonal phase (YPO_4:xH_2O) in which water molecules can occupy pores/interstitial sites.

Luminescence study

Fig. S6 (ESI†) shows excitation spectra of as prepared samples of (YPO_4:Eu-xBi) prepared in different solvents (PEG, PEG-diacid, water). Excitation spectra are recorded by monitoring the emission wavelength at 612 nm. Excitation spectrum consists of strong absorption band between 230-280 nm with center at ~260 nm which can be assigned to the Eu-O charge transfer band (CTB).[7] This arises due to transition of 2p electrons of O^{2-} to the empty 4f orbitals of Eu^{3+} ions. Since Eu^{3+} has $4f^6$ configuration, therefore it needs to gain one more electron to achieve half-filled $4f^7$ configuration, i.e. relatively stable compared to partially filled configuration. CTB changes depending on particle size of host and environment of Eu^{3+}. In addition, peaks at 318, 361, 380 and 395 nm were also observed and correspond to $^7F_{0,1} \rightarrow {}^5H_{3,6}$, $^7F_{0,1} \rightarrow {}^5D_0$, $^7F_{0,1} \rightarrow {}^5L_7$ and $^7F_0 \rightarrow {}^5L_6$ transitions of Eu^{3+}, respectively.[7] It can be observed that the Eu-O CTB shows a red shift upon co-doping of Bi^{3+} in YPO_4:Eu.

The emission spectra of Bi^{3+} (x = 0, 10 and 20 at. %) co-doped YPO_4:Eu (prepared in three different solvents) have been recorded at two different excitation wavelengths: 260 and 395 nm (Fig. 2 and Fig. S7, S8, ESI†). We have used 375 nm cut off filter for recording emission spectra at 260 nm excitation and 455 nm cut off filter while exciting the sample at 395 nm. Emission spectrum of each sample exhibits a typical emission peak of Eu^{3+} at ~592 nm corresponding to the magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$) along with peaks at ~617 nm and ~695 nm which corresponds to the electric dipole transitions ($^5D_0 \rightarrow {}^7F_2$) and ($^5D_0 \rightarrow {}^7F_4$), respectively.[7] Apart from these, weak emission peak centered at ~650 nm corresponding to $^5D_0 \rightarrow {}^7F_3$ transition is also observed. The variation in intensity ratio of electric and magnetic dipole transitions are found with respect to excitation wavelength, solvent and Bi^{3+} concentration. In the emission spectra of YPO_4:Eu, the emission intensity in 400-500 nm with maximum at ~ 410 nm is observed when excited at λ = 260 nm. This emission peak comes from host or intermediate bands present in band gap of YPO_4.[4] An interesting feature has been observed in the emission spectra of these samples. Electric dipole transition peak at 695 nm is split into three peaks centred at 687, 695 and 702 nm. Theoretically, it should have 8 splitting (i.e. 2j + 1 = 9, but 0-0 transition is not allowed). Upon Bi^{3+} co-doping, we have observed the change in the ratio of peak intensities at 687 and 702 nm.

Full width at half maximum intensity (FWHM) is a valuable indicator for the change in luminescence. This FWHM is calculated for magnetic and electric dipole transitions ($^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$) using Gaussian distribution. The FWHM increases with co-doping of Bi^{3+}. The FWHM values of Bi^{3+} = 0, 10 and 20 at.% samples prepared in PEG are 8.2, 10.3 and 11.0 nm, respectively, for $^5D_0 \rightarrow {}^7F_1$ transition and 9.2, 11.3 and 12.0 nm, respectively, for $^5D_0 \rightarrow {}^7F_2$ transition. Increase in FWHM value indicates decrease in luminescence intensity.

The asymmetric environment of europium ion (Eu^{3+}) in host lattice can be calculated by intensity ratio of the electric ($^5D_0 \rightarrow {}^7F_2$) to magnetic ($^5D_0 \rightarrow {}^7F_1$) dipole transitions.[7] This is called asymmetric ratio (A_{21}). Here, subscript '2' and '1' refer to the transitions of $^5D_0$ to ^7F_j, j = 2 and 1, respectively. A_{21} values for as-prepared samples at two different excitation wavelengths (260 and 395 nm) are given in Table 2. In case of 0 at. % Bi^{3+}, A_{21} values for excitation at 260 and 395 nm are less than 1.0 for the samples prepared in PEG. A_{21} values for samples prepared in PEG-diacid and water are more than 1.0. In general, A_{21} values are less than 1.0 upon co-doping of Bi^{3+}. It is suggested that Eu^{3+} environment in tetragonal phase is more asymmetric as compared to that in hexagonal phase.

Emission intensities of (YPO_4:Eu-xBi) samples prepared in different solvents (PEG, PEG-diacid, water) after excitation at two different wavelengths (260 and 395 nm) are compared for electric and magnetic dipole transitions centered at 592 nm and 615 nm, respectively (Fig. 3, 4). All the fittings were carried out in 550-750 nm after removal of background and the integrated area under the curve is calculated for magnetic and electric dipole transitions. When PEG and PEG-diacid are used for preparation, the emission intensity is more when excited at wavelength 260 nm (Eu-O CTB) as compared to that at 395 nm. This suggests strong energy transfer from Eu-O to Eu^{3+}. However, this observation is opposite in case when water is used.

In case of samples prepared in PEG and PEG-diacid, ratio of hexagonal to tetragonal phases is high, thus water can occupy the pores along c-axis. When excitation wavelength is 395 nm (which is direct excitation of Eu^{3+}), fraction of light is lost due to transfer its energy to nearby water molecules (surrounding of the Eu^{3+} ions). Thus radiative rate decreases as compared to the non-radiative rate which leads to weak luminescence intensity. In case of samples prepared in water, ratio of tetragonal to hexagonal phase is high, thus low amount of water molecules is trapped in the pores leading to high radiative rate.

Variation in intensities of these two dipole transitions at different excitation wavelengths may be related to the interaction of incoming excitation light with Eu^{3+} (nearest environment (O) and

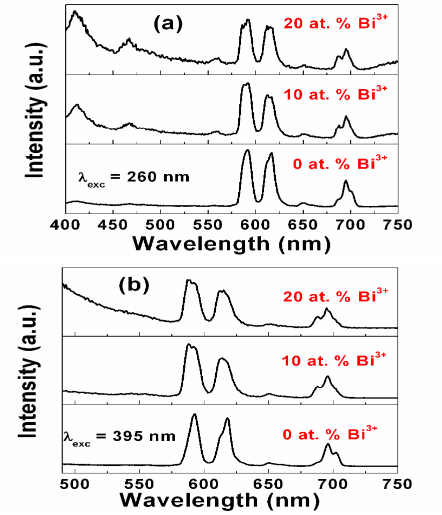


Fig. 2. Emission spectra of Bi^{3+} co-doped YPO_4:Eu prepared in PEG solvent after excitation at (a) 260 and (b) 395 nm.

Table 2. Asymmetric ratio (A_{21}) of the samples (YPO_4:Eu-xBi) prepared in different solvents at two different excitation wavelengths.

Sample prepared in solvents	Bi^{3+} (x at.%)	A_{21} at excitation wavelength	
		260 nm	395 nm
PEG	0	0.96	0.93
	10	0.85	0.77
	20	0.90	0.84
PEG-diacid	0	1.24	1.14
	10	0.89	0.81
	20	0.85	0.81
Water	0	1.15	1.10
	10	0.91	0.76
	20	0.92	0.76

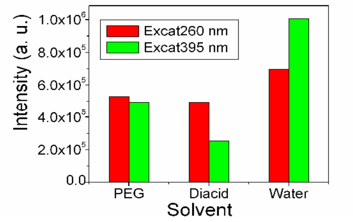


Fig. 3. Comparison of integrated emission intensities (range = 550-750 nm) of YPO_4:Eu prepared in three different solvents (PEG, PEG-diacid, water) after excitation at 260 and 395 nm.

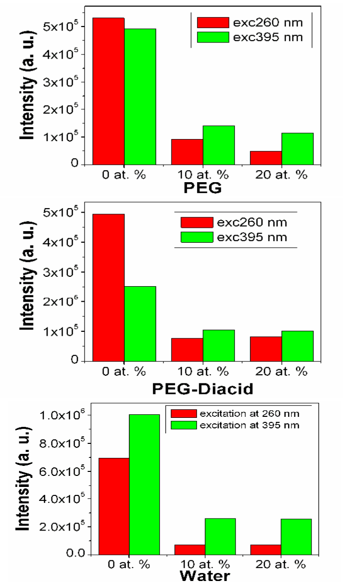


Fig. 4. Comparison of integrated emission intensity (range = 550-750 nm) of YPO_4:Eu with Bi^{3+} co-doping (prepared in PEG, PEG-diacid, water) at wavelength 260 and 395 nm.

second nearest environment (PO_4).[24,25] The electric dipole transition is hypersensitive transition (hypersensitive to its local symmetry/ environment around Eu^{3+} ion). It is allowed only when Eu^{3+} ion occupies a site without an inversion center. In cases where magnetic dipole transition intensity is dominant over the electric dipole transition, it implies a higher occupancy of Eu^{3+} in a symmetric environment.[7]

Crystal symmetry of YO_8 or EuO_8, does not have an inversion symmetry element, and thus environment of Y^{3+} or Eu^{3+} is asymmetric.[7] According to Judd-Ofelt theory, intensity associated with electric dipole transition should be more than the magnetic dipole transition in such an asymmetric environment.[7,8] This has not happened in YPO_4:Eu-xBi. However, existence of variation in intensities of magnetic and electric dipole transitions, with incoming excitation wavelength was explained in our previous work.[26]

Also, the variation of magnetic and electric dipole transitions depends on the intensity of the incoming light at the same wavelength. It is observed that luminescence intensity of Eu^{3+} decreases with increase of the Bi^{3+} co-dopant concentrations. The decrease in luminescence intensity is mainly due the presence of H_2O, which is an efficient luminescence quencher through multiphonon relaxation.[9,10,17] Presence of water molecules on the surface of particles is unavoidable, as samples are exposed to ambient atmosphere. However, greater quenching of luminescent signal is observed in case of Bi^{3+} co-doping due to presence of water in the pores of hexagonal structure.[10] Such confined water molecules can remain stable upto 800 °C.[10] The hexagonal structure has the zeolite like configuration, in which pores are available along c-axis, thus forming a channel.[17] The rate of non-radiative transition, R_0, is expressed as[9]

$$R_0 = A \exp[-(\Delta E - 2h\nu_{max})B]$$

where, A and B are constants. ΔE is the energy difference between the excited and ground states of Eu^{3+} ion. ν_{max} denotes the highest available vibrational mode of the host or molecule which surrounds rare-earth ion (Eu^{3+}). In Eu^{3+}, ΔE is about 10,000 – 15,000 cm^{-1}, this value is comparable with the third/fourth overtone vibration of the O-H group (3450 cm^{-1}). The O-H functional group arises from H_2O molecules which are absorbed or confined within hexagonal structure. Thus, the value of R_0 becomes large (because $\Delta E \approx 2h\nu_{max}$), and as a result of which, there is significant extent of non-radiative transfer of energy from the Eu^{3+} ion excited state to the different vibrational modes of O-H species. This leads to significant reduction in the luminescence intensity, as charge carriers combine without release of photon; instead phonons of H_2O molecules are excited. This phenomenon is termed as multiphonon relaxation which can be defined as non-radiative transfer of energy from excited state of Eu^{3+} ion to the surrounding phonons of O-H species.[17]

It can be easily seen that for each solvent, the emission intensity of Eu^{3+} decreases upon increasing the Bi^{3+} concentration which is being attributed to the phase transformation from tetragonal to hexagonal. In the absence of Bi (x = 0 at.%), emission intensity for 260 nm excitation is more than that for 394 nm when solvent is PEG or PEG-diacid. These have T/H ratio (T = Tetrgonal phase and H = Hexagonal phase) of 2-3. In case of water as solvent, T/H ratio is 6.7. Luminescence intensity is more in case of sample prepared in water as compared to that prepared in PEG or PEG-diacid. In presence of Bi (x = 10, 20 at.%), there is higher luminescence intensity for 395 nm excitation than that for 260 nm excitation irrespective of solvent used during preparation of sample and those have T/H ratio < 0.6.

Fig. 5(a-c) shows emission spectra of 900 °C annealed samples of (a) 0, (b) 10 and (c) 20 at.% Bi co-doped YPO_4:Eu-PEG-diacid. Here, two excitation wavelengths are used (250 or 270 and 395 nm). Characteristic emission peaks of Eu^{3+} are observed. Luminescence intensity at 250 nm excitation (Eu-O CTB) is higher than that at 395 nm excitation (direct Eu^{3+}) for 0 at.% Bi co-dopant. The opposite happens in case of 20 at.% Bi co-dopant. For comparison, Fig. 6(d) shows emission spectra of 0 at.% Bi as-prepared and 900 °C annealed samples of 0, 10 and 20 at.% Bi co-doped YPO_4:Eu-PEG-diacid and excitation wavelength is fixed at 395 nm. Luminescence intensity is improved by annealing samples as well as Bi-co-doping. The 0, 10 and 20 at.% Bi co-doped 900 °C heated samples have 9, 18 and 38 times increase in luminescence intensity as compared to that of as-prepared 0 at.% Bi co-doped sample. 900 °C heated samples crystallize in tetragonal phase, in which there are no confined water molecules, whereas as-prepared sample crystallizes in hexagonal phase (with a small fraction of tetragonal phase), in which there are confined water molecules. Significant increase in luminescence intensity for 900 °C heated sample is due to removal of confined water molecules, which act as quencher in luminescence. In addition, improved crystallinity as well as removal of organic moiety (such as PEG or PEG-diacid) gives rise to enhance luminescence after heat-treatment at 900 °C. Interestingly, luminescence intensity is significantly improved by Bi-co-doping in 900 °C heated samples, which is opposite in case of as-prepared samples. It means that Bi induces an improvement in luminescence if there are no confined water molecules. Bi acts as sensitizer as well as increases absorption cross-section. Extra impurity of $BiPO_4$ does not have much effect on luminescence because luminescence intensity of host (YPO_4:Eu,Bi, tetragonal phase) is more than that of $BiPO_4$ (monoclinic phase).

The luminescence decay curves of the level $^5D_0$ (612 nm) have been measured for as-prepared YPO_4:Eu-xBi-PEG-diacid (Fig. 6(a)). The excitation wavelength is fixed at 395 nm. The decay curves are not well fitted by the mono-exponential equation ($I = I_0 \exp(-t/\tau)$, where I and I_0 are the intensity at time t and 0 s, respectively and τ is the lifetime).[4]

All the decay data are fitted using multi-exponential decay equation, which is expressed as following:[4]

$$I = \Sigma I_i \exp(-t/\tau_i)$$

where I_i is the intensity at different time interval and τ_i is its corresponding lifetime. The average lifetime can be calculated using the equation.[4]

$$\tau_{av} = \Sigma I_i \tau_i / \Sigma I_i$$

The fitting parameters obtained after the bi-exponential decay equations are given in Table 3. The bi-exponential decay suggests the availability of Eu^{3+} ions on surface (τ_1) and core (τ_2) of particles. Average lifetime decreases from 1.0 to 0.7 ms with increase of the Bi co-dopant concentration. The luminescence decay curves for YPO_4: Eu-xBi samples prepared in PEG and water mediums are shown in Fig. S9 (ESI†) and their parameters after fitting data with bi-exponential equation are given in Table 3. Similarly, the average lifetime decreases with Bi co-dopant.

The luminescence decay curves of the level $^5D_0$ (612 nm) have been measured for 900 °C heated YPO_4:Eu-xBi-PEG-diacis (x = 0, 20 at.%) are shown in Fig. 6(b, c). For x = 10 at.%, this is shown in Fig. S9 (ESI†). The excitation and emission wavelengths are fixed at 395 nm and 617 nm, respectively. Decay data are fitted with tri-exponential equation and parameters obtained after fitting are given in Table 4. Data range is 0-50 ms. The average lifetime (τ_{av}) increases with increasing doping levels of Bi^{3+} and τ_{av} values are 2.05, 2.18 and 2.52 ms for 0, 10 and 20 at.% Bi co-dopants, respectively and these values are more than those of corresponding as-prepared samples.

When excitation and emission wavelengths are fixed at 250 nm (x = 0 at.% Bi) or 270 nm (x = 10, 20 at.% Bi) and 617 nm, respectively, luminescence decay follows non-exponential equation because at initial stage, energy transfer from Eu-O or Bi^{3+} to the excited states of Eu^{3+} occurs and then decays from $^5D_0$ level. The non-exponential equation is given below:

$$I = I_1 \exp(-t/\tau_1 - Dt^{0.5}) + \Sigma I_{i=2,3---} \exp(-t/\tau_i)$$

Where D is duffusion rate. Luminescence decay curves of the level $^5D_0$ (612 nm) have been measured for 900 °C heated YPO_4:Eu-xBi samples prepared in PEG-diacid are shown in Fig. 6(d) by fixing excitation at 250 or 270 nm. Decay data are fitted with non-exponential equation and parameters obtained are given in Table 5. The lifetime value of longer component is found to increase from 3.72 to 48.85 ms when 20 at.% Bi are doped in YPO_4:5Eu. The value of 48.85 ms is exceptionally longer. Even emission intensity remains after 1 s (i.e., still decay counts remain). The reported values of lifetimes in $Bi_{1-x}PO_4$:Eu_x, $Ce_{1-x}PO_4$:Eu_x and $Bi_{1-x}PO_4$:Eu_x are 2-4 ms,[27] 1.4 ms[9] and 5.1 ms,[10] respectively. This means that our prepared sample will be better host than the recent report on $Bi_{1-x}PO_4$:Eu_x. The possible reason is that in those reported values,[9,10,25] they used 395 nm as the excitation wavelength (direct excitation). In this work, we have used two excitation wavelengths (395 nm and 270 nm through Eu-O/Bi^{3+} absorption). Delay luminescence (1s or more) is observed after indirect excitation through Eu-O/Bi^{3+}, which will be the first report on such system to the best of authors' knowledge. Upon excitation at 270 nm, excited energy is migrated among Bi^{3+} ions (or defects/traps) and part of energy from excited Bi^{3+} is transferred to excited states of Eu^{3+} non-radiavely followed by

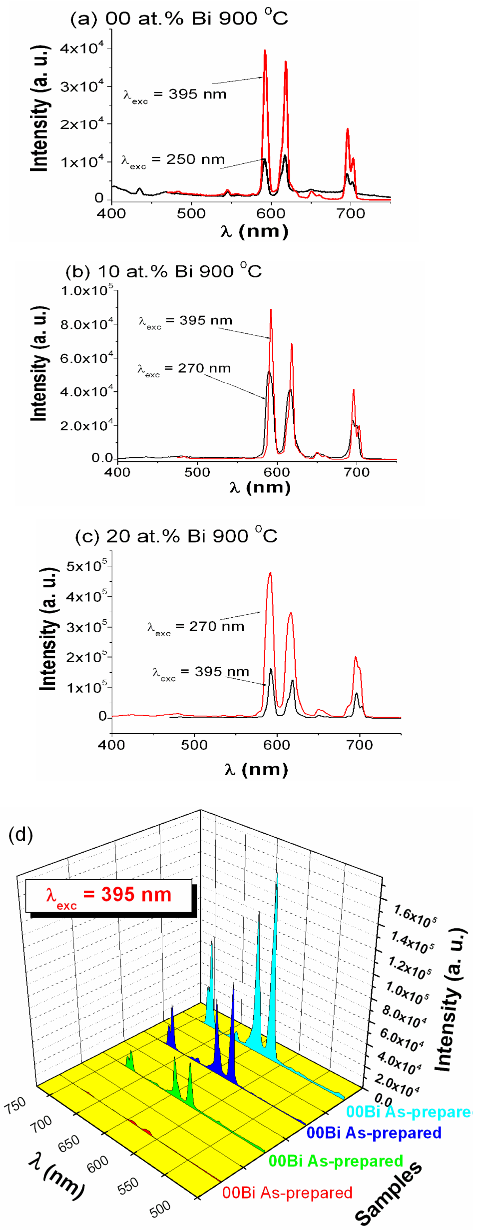
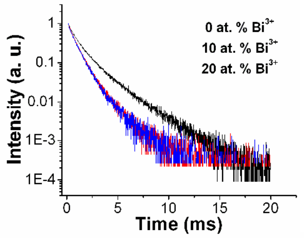


Fig. 5. Emission spectra of 900 °C annealed samples of (a) 0, (b) 10 and (c) 20 at.% Bi co-doped YPO_4:Eu^{3+}-PEG-diacid. Here, two excitation wavelengths are used (250 or 270 and 395 nm). (d) Emission spectra of 0 at.% Bi as-prepared and 900 °C annealed samples of 0, 10 and 20 at.% Bi-PEG-diacid (λ_{exc} = 395 nm).

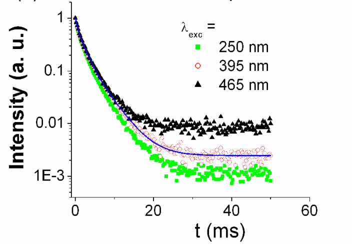
emission of Eu^{3+}. However, we could not be able to see grow process at the initial stage. It may be due to the insufficient excitation light or very fast energy transfer (in nanoseconds).

Fig. S10 (ESI†) shows the CIE Coordinates of YPO_4:Eu-xBi samples prepared in different solvents (PEG, PEG-diacid, water) at 260 nm excitation. The CIE coordinates for x = 0 (absence of Bi) for samples prepared in three different solvents are x = 0.54 - 0.56, y = 0.33 – 0.35, which lies in red region. In case of Bi co-doping (10 and 20 at.%), the CIE coordinates are x = 0.33 - 0.40, y = 0.25 – 0.28, which lie in pink region. In case of 900 °C heated samples prepared in PEG-diacid, CIE coordinates (Fig. S11, ESI†) shift from red to deep red colour.

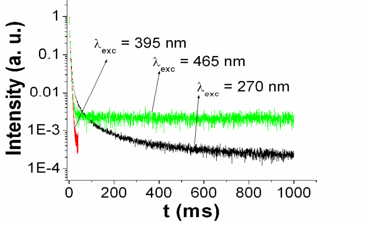
(a) PEG-Diacid



(b) 0 at.%Bi 900 °C sample



(c) 20 at.% Bi 900 °C sample



(d) 0, 10, 20 at.% Bi 900 °C samples

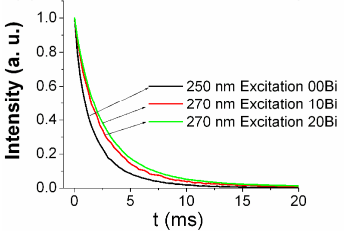


Fig. 6. Decay curves of $^5D_0$ (612 nm) level of Eu^{3+} in Bi-doped YPO_4:Eu-PEG-diacid: as-prepared sample (a) after excitation at 395 nm and 900 °C annealed samples (0 at.% (b) and 20 at.% Bi (c)) after excitations at 250 or 270, 395 and 465 nm. For comparison, decay curves for 900 °C annealed samples (0, 10, 20 at.% Bi) after excitation at 250 nm (0 at.% Bi) and 270 nm (10, 20 at.% Bi) are shown as (d) and notably, decay counts at 20 ms decreases for samples from 20 to 10 at.% Bi and become zero for 0 at.% Bi.

Table 3. Parameters obtained after bi-exponential decay fit to data of the samples (YPO_4:Eu-xBi) prepared in different solvents. Excitation and emission wavelengths are fixed at 395 nm and 612 nm, respectively.

Sample prepared in solvents	Bi^{3+} (x at.%)	I_1 (%)	τ_1 (ms)	I_2 (%)	τ_2 (ms)	τ_{avg} (ms)
PEG	0	70	0.63	30	1.19	1.02
	10	66	0.55	34	1.17	0.76
	20	61	0.49	39	1.16	0.75
PEG-diacid	0	68	0.76	32	2.12	1.19
	10	59	0.49	41	1.12	0.75
	20	68	0.56	32	1.21	0.77
Water	0	60	0.58	40	1.80	1.07
	10	73	0.56	27	1.27	0.75
	20	77	0.56	23	1.25	0.71

Table 4. Parameters obtained after tri-exponential decay fit to data of the 900 °C heated samples (YPO_4: Eu-xBi-PEG-diacid). Excitation and emission wavelengths are fixed at 395 nm and 617 nm, respectively. Data range is 0-50 ms.

Sample Prepared in solvents	Bi^{3+} (x at.%)	τ_1 (%) (ms)	τ_2 (%) (ms)	τ_3 (%) (ms)	τ_{avg} (ms)
PEG-diacid (900 °C)	0	0.39 (21%)	1.55 (48%)	3.96 (31%)	2.05
	10	1.47 (52%)	2.85 (15%)	3.02 (33%)	2.18
	20	0.30 (07%)	1.68 (36%)	3.33 (57%)	2.52

Table 5. Parameters obtained after non-exponential decay fit to data of the 900 °C heated samples (YPO_4:Eu-xBi) prepared in PEG-diacid solvent. Excitation and emission wavelengths are fixed at 250 nm (x = 0 at.% Bi) or 270 nm (x = 10, 20 at.% Bi) and 617 nm, respectively.

Sample Prepared in solvents	Bi^{3+} (x at.%)	D ($ms^{-0.5}$)	τ_1 (%) (ms)	τ_2 (%) (ms)	τ_3 (%) ms)
PEG-diacid (900 °C)	0	0.20	0.45 (22%)	1.46 (53%)	3.72 (25%)
	10	0.16	1.31 (32%)	2.95 (66%)	15.95 (2%)
	20	0.10	2.34 (75%)	5.39 (23%)	48.85 (2%)

Conclusions

YPO_4 nanoparticles co-doped with Eu^{3+} and Bi^{3+} have been synthesized three different solvents. After co-doping of Bi^{3+}, the crystal structure changes from tetragonal to hexagonal and also there is a significant decrease in Eu^{3+} luminescence intensity due to the presence of water molecules in the pores of hexagonal structure of YPO_4 along z-axis. The luminescence intensity can be manipulated by changing the solvent. Upon heating at 900 °C, luminescence and lifetime improves significantly due to conversion of a mixture of tetragonal and hexagonal phases to tetragonal phase. Luminescence up to 1 s could be observed. Color enhancement in red region is observed by Bi^{3+} co-doping.

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Graphical Abstract/TOC

There are roles of solvent, annealing and Bi^{3+} co-doping on crystal structure and luminescence properties of YPO_4: Eu^{3+} nanoparticles