Preparation, microstructure and crystal structure studies of Li\textsuperscript{+} co-doped YPO\textsubscript{4}:Eu\textsuperscript{3+}†

A. K. Parchur\textsuperscript{a} and R. S. Ningthoujam\textsuperscript{a,b}

Received 25th April 2012, Accepted 9th September 2012
DOI: 10.1039/c2ra20763j

Rod-like shape particles of tetragonal phase Li\textsuperscript{+} co-doped YPO\textsubscript{4}:Eu samples are prepared by using a polyol method at low temperature (\textasciitilde 100–120 °C for 1 h). Li\textsuperscript{+} co-doping enhances the crystalline nature of the sample and reduces the agglomeration among the particles. The shift in the reflection peaks of the tetragonal phase to the lower 2θ angle in the X-ray diffraction pattern indicates the occupancy of Li\textsuperscript{+} ions in the interstitial sites of the host lattice. The point group symmetry of Y\textsuperscript{3+}/Eu\textsuperscript{3+} in YPO\textsubscript{4} is demonstrated in simple representation.

1 Introduction

The luminescence properties of rare earth ion-doped nanomaterials (Ln\textsuperscript{3+}) have been attractive because their properties differ from the bulk and have been adopted extensively in optoelectronic device fabrications.\textsuperscript{1–6} In recent years, the emission intensity of Ln\textsuperscript{3+} doped nanoparticles have been significantly enhanced by introducing Li\textsuperscript{+}, Ag\textsuperscript{+} and core-shell formations, etc.\textsuperscript{2,7} Due to the small size of a Li\textsuperscript{+} ion incorporated in an inorganic host, it will change the shape and size of particles and crystalline nature of the samples. However, the intensities of electric and magnetic dipole transitions of the Eu\textsuperscript{3+} ion also depend on Li\textsuperscript{+} ion concentration/defects created in the host which is discussed elsewhere.\textsuperscript{4} Moreover the structural changes that happen in the YPO\textsubscript{4}:Eu host due to the incorporation of the Li\textsuperscript{+} ion have not been studied much in literature. Recently, Ocana and his co-workers\textsuperscript{8} prepared Eu, Ce, Tb and Ce–Tb-doped YPO\textsubscript{4} nanoparticles in ethylene glycol (EG) solution. They showed high quantum yield (QY). The QY is found to be 60% for Eu\textsuperscript{3+}-doped YPO\textsubscript{4} and 80% for Tb\textsuperscript{3+}-doped YPO\textsubscript{4} samples. Due to high stability, both chemically and thermally, high QY and low toxicity, the YPO\textsubscript{4} host can be used in a variety of technological and biomedical applications.

In this article, we have discussed the preparation of Li\textsuperscript{+} co-doped YPO\textsubscript{4}:Eu nanoparticles (Li\textsuperscript{+} = 0, 3, 5, 7 and 10 at.%) using a polyol method, followed by annealing at 900 °C in order to increase the crystallinity. Its structural properties are studied using a Rietveld refinement on the X-ray diffraction (XRD) pattern, FTIR (Fourier transform infrared) spectroscopy and TEM (transmission electron microscopy) techniques. Also, the point group symmetry of YPO\textsubscript{4} is explained in a very simple representation of symmetry operations/elements. The particles prepared from the polyol method are highly crystalline and non-agglomerated. Here EG (ethylene glycol) is used as both the capping agent as well as the reaction medium.

2 Experimental section

2.1 Reagents and materials

Yttrium oxide (Y\textsubscript{2}O\textsubscript{3}, 99.99%, Sigma Aldrich), ammonium dihydrogen phosphate (NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, 99.999%, Sigma Aldrich), europium oxide (Eu\textsubscript{2}O\textsubscript{3}, 99.99%, Sigma Aldrich), lithium hydroxide (LiOH, 99.99%, Sigma Aldrich), nitric acid, ethanol and ethylene glycol (EG) from SD Fine Chemicals Limited were used as received without further purification. Double distilled water was used in the experiment.

2.2 Synthesis

The samples of Eu\textsuperscript{3+} (5 at.%) doped YPO\textsubscript{4} (i.e., YPO\textsubscript{4}:Eu) and Li\textsuperscript{+} (Li\textsuperscript{+} = 3, 5, 7 and 10 at.%) co-doped YPO\textsubscript{4}:Eu were prepared using a polyol route at low temperature (\textasciitilde 100–120 °C for 1 h). In typical synthesis procedure of 5 at.% Li\textsuperscript{+} co-doped YPO\textsubscript{4}:Eu, 1 g of Y\textsubscript{2}O\textsubscript{3}, 0.086 g of Eu\textsubscript{2}O\textsubscript{3} and 0.012 g of LiOH were dissolved together in concentrated nitric acid (HNO\textsubscript{3}) and were heated at 80 °C with the addition of double distilled water in order to remove the excess acid. To this 1.13 g of NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4} dissolved in 10 ml of distilled double water and 100 ml of EG were added. The solution was stirred for 2 h and followed by 1 h sonication for uniform mixing. The reaction mixture was heated at 100–120 °C for 1 h under refluxing conditions until the white precipitation was completed. EG molecules act as a solvent as well as capping agent during the preparation of the YPO\textsubscript{4} nanoparticles. When the nucleation starts, the surrounding EG molecules cap smaller particles and thus, particle growth is hindered. The agglomeration among the particles is hindered.

\textsuperscript{a}Department of Physics, Banaras Hindu University, Varanasi-221005, India
\textsuperscript{b}Chemistry Division, Bhabha Atomic Research Centre, Mumbai-400085, India. E-mail: vaqsha锰an@yahoo.co.in (R. S. Ningthoujam); ranj@barc.gov.in (R. S. Ningthoujam); Fax: +91-22-25505151; Tel: +91-22-2559321
† This paper is dedicated to Professor N. S. Gajbhiye on the occasion of his 60th birthday.
The precipitate so obtained was washed two times by centrifugation in ethanol to remove the excess of EG, and then dried at ambient atmosphere and room temperature for four days. Finally, the as-prepared sample was annealed at 900 °C in ambient atmosphere at a rate of 2 °C min⁻¹ for 4 h in order to remove the dangling bonds on the surface of nanoparticles. 900 °C annealed samples are studied here because they have high crystallinity.

2.3 Characterization

The crystal phase of the samples was identified by an X-ray diffractometer (XRD) using PW 1071 Philips powder with Ni filtered Cu-Kα (1.5405 Å) radiation having tube voltage ~30 kV and current ~20 mA. XRD patterns recorded in the angular range 10° ≤ 2θ ≤ 70° with a step size of Δ2θ = 0.02°. The average crystallite size (D) was calculated from Scherrer relation:

\[ D = \frac{0.89\lambda}{\beta_{hkl} \cos \theta} \]  

where λ is the wavelength of the X-ray and β_{hkl} is the full width at half maximum (FWHM) of the peak of the XRD pattern. Moreover, XRD data was recorded on a PANalytical diffractometer using Cu-Kα radiation (40 kV voltage and 30 mA current with a step size 0.02° and 1.8 s per step) for Rietveld analysis. The X-ray data was analyzed using Fullprof software. Structure representation is generated from Diamond Software Program (version 3.0a).

The samples were examined by a transmission electron microscope (TEM, JEOL) and 200 kV acceleration voltage was used for the experiment. The high resolution TEM (HRTEM) images are recorded at 300 kV using FEI Titan Microscopy. For TEM measurement the samples were ground using a mortar and dispersed in ethylene glycol followed by ultrasonication for 1 h. A drop of the dispersed particles was put over the carbon coated copper grid and evaporated to dryness in the ambient atmosphere. The Fourier transform infrared (FTIR) spectrum was measured with a FTIR spectrometer (Bomem MB 102) with a resolution of 1 cm⁻¹ using the KBr pellet technique.

3 Results and discussion

3.1 Structural study

Fig. 1(a) shows the XRD patterns of 0 and 10 at.% Li⁺ co-doped YPO₄:Eu. It clearly shows the increase in crystallinity due to the addition of Li⁺ ion in YPO₄:Eu. Tetragonal phase is formed and
planes are assigned to pattern. Fig. 1(b) shows the expanded region of (hkl = 200) peak of all samples (Li⁺ = 0, 3, 5, 7 and 10 at.%). The data in the range 25 to 27° in 2θ are collected on the same day (5 min duration of each sample within a 1 h period) to minimize error from temperature and instrumental factor. The (200) peak position is shifted to lower 2θ from 25.88 to 25.77° and the full width at half maximum (FWHM) decreases from 0.47° to 0.13° when the Li⁺ ion concentration increases up to 10 at.% (shown as inset of Fig. 1(b)). Similarly, other peaks shift to lower 2θ on Li⁺ co-doping. The crystallite sizes corresponding to Li⁺ = 0, 3, 5, 7 and 10 at.% co-doped YPO₄:Eu are found to be ~20, 23, 36, 42 and 60 nm indicating an increase of crystallite size on Li⁺ co-doping. The unit cell parameters and volume for 0 and 10 at.% doped Li⁺ doped YPO₄:Eu are found to be $a = 6.879$ Å, $c = 6.010$ Å and $V = 284.4$ Å³ and $a = 6.891$ Å, $c = 6.030$ Å and $V = 286.4$ Å³, respectively. These values are comparable with JCPDS card no: 11-0254, $a = 6.904$ Å, $c = 6.035$ Å and $V = 287.66$ Å³. When we see the ionic radii of $Y^{3+}$/Eu³⁺ ion (~0.9–1.0 Å) and Li⁺ ion (~0.76 Å), it is expected to decrease in unit cell volume. In this study, the addition of Li⁺ ion concentration enhances the unit cell volume significantly (i.e. unit cell expansion). This will be related to the occupancy of Li⁺ ions in the interstitial sites rather than $Y^{3+}$ ion sites. However, we could not observe any extra impurity peaks up to 10 at.% Li⁺ co-doping.

The XRD pattern of 5 at.% Li⁺ co-doped YPO₄:Eu is recorded using PANalytical XRD diffractometer and used as input data for Rietveld analysis using Fullprof software. The structural parameters were refined with the Rietveld method using WinPLOTR (April 2010) program. We used a 6 coefficient polynomial function for the background and a

Fig. 3 (a) Crystal structure of YPO₄ (tetragonal). (b) Polyhedral representations of PO₄ (tetrahedron) and YO₈ (dodecahedron) linkage along the a-axis.

Fig. 4 Symmetry elements ($C_3(Z)$)-principal axis, $C_1(X)$, $C_2'(Y)$, $\sigma_{13}$ and $\sigma_{24}$ of point group $D_{2d}$ in YPO₄ tetragonal structure.

This journal is © The Royal Society of Chemistry 2012
pseudo-Voigt function for peak profile fitting. Isotropic atomic displacement parameters ($B$) are used for all atoms. Fig. 2 shows Rietveld-XRD plot of 5 at.% Li$^+$ co-doped YPO$_4$:Eu sample. In the tetragonal structure of YPO$_4$ (Fig. 3a), Y is surrounded by 8O with two different bond lengths (4(Y–O1 = 2.3025 Å) and 4(Y–O2 = 2.3667 Å)) and P is surrounded by 4O with equal bond lengths (P–O = 1.5504 Å). Positions of atoms: Y (0, 0.750, 0.125), P (0, 0.25, 0.375) and O (0, 0.072, 0.213). Bragg R-factor = 14.5, R$_f$-factor = 12.4, $\chi^2 = 7.67$. Between YO$_8$ and PO$_4$ units, 2O are corner-sharing (Fig. 3b). PO$_4$ (tetrahedron) has $S_4$ symmetry whereas YO$_8$ (dodecahedron) has $D_{2d}$ symmetry.

The symmetry elements/operations present in YO$_8$ are shown in Fig. 4. The principal axis is $C_2$ along the $z$-axis (i.e. $C_2(z)$, which means 360°/2 = 180° rotation) and another $2C_2$ operations along the x and y-axes (i.e. $C_2(x)$ and $C_2(y)$). This becomes $D_2$. Is there horizontal plane along the $xy$-axes? No, there is no horizontal plane along the $xy$-axes. The possibility of $D_{2h}$ is ruled out. Along the $x$- and $y$-axes, there are no possibilities of vertical planes. Thus, $D_{2h}$ is ruled out. Interestingly, there are two planes between $x$ and $y$-axes and these are known as the dihedral planes (i.e. diagonal of cube or rectangle). The symmetry point group is $D_{2d}$. Here point refers common point (i.e. Y), which is not shifted by any of the symmetry operations. In addition, there is another symmetry operation called $S_4$ (90° rotation followed by a reflection plane perpendicular to the rotation axis or vice versa, i.e. they are commutable) and this is shown in Fig. 5.

### 3.2 FTIR study

Fig. 6 shows the FTIR spectrum of 5 at.% Li$^+$ co-doped YPO$_4$:Eu in the 4000–400 cm$^{-1}$ range. The peaks at 531 and 644 cm$^{-1}$ correspond to the bending vibration of PO$_4^{3-}$ (termed as the $v_4$ region). The band centered at 1071 cm$^{-1}$ along with humps at 1040 and 1099 cm$^{-1}$ correspond to the stretching vibration of PO$_4^{3-}$ (termed as the $v_3$ region) and these peak positions are comparable with reported values. The vibration intensity of the $v_3$ region is found to be 2.2 times stronger than the $v_4$ region. We do not find any extra phosphorus-containing groups such as P$_2$O$_7^{4-}$ which is generally observed at 1265 cm$^{-1}$. The peaks corresponding to bending and stretching vibrations of O–H/H$_2$O are assigned at 1624 and 3433 cm$^{-1}$, respectively and these are due to adsorption over the surface of the particles.

### 3.3 TEM study

Fig. 7 (a) shows the TEM image of 3 at.% Li$^+$ co-doped YPO$_4$:Eu in bright field condition. The shape of the particle is found to be a rod 38 nm in length and 12 nm in width. Inset shows its selected area electron diffraction (SAED) pattern. Its high resolution TEM (HRTEM) image is shown in Fig. 7 (b). The lattice spacing is found to be 3.458 Å which matches with the $(hkl) = (200)$ plane of the tetragonal phase.

### 4 Conclusions

Structural properties of Li$^+$ co-doped YPO$_4$:Eu are discussed in this article. Shifting of the (200) XRD peak to lower angles with
the addition of Li+ indicates that Li+ ions occupy interstitial sites rather than Y3+/Eu3+ sites. Li+ co-doping significantly improves the crystallinity. The crystallite sizes corresponding to Li+ = 0, 3, 5, 7 and 10 at.% co-doped YPO₄:Eu are found to be ~ 20, 23, 36, 42 and 60 nm, respectively. Fullprof software is used to refine the structural parameters of samples. It is shown that samples have tetragonal structure and Eu3+/Y3+ ion has D2d symmetry.

HRTEM image shows that particles are grown along the (200) plane having a d-space of 3.458 Å.

Acknowledgements

This work has been sponsored by the University Grants Commission (UGC) under the D. S. Kothari Postdoctoral Fellowship Scheme (No.F.4-2/2006(BSR)/13-309/2008(BSR)) to Dr A. K. Parchur. Authors thank Dr T. Mukherjee, Chemistry Group and Dr D. Das, Dr R. K. Vatsa and Mr. R. Shukla, Chemistry Division, BARC for their support and encouragement during this work.

References


