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Low temperature synthesis and luminescence properties of re-dispersible Eu^{3+} doped $LaPO_4$ nanorods by ethylene glycol route

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ABSTRACT

Eu^{3+} doped $LaPO_4$ nanorods with monoclinic system have been prepared at relatively low temperature (150 °C) in ethylene glycol medium. Unit cell volume of $LaPO_4$ is found to decrease linearly with increasing Eu^{3+} concentration indicating the homogeneous substitution of La^{3+} ions in $LaPO_4$ by Eu^{3+} ions. Transmission electron microscopic images show that the particles are present in the form of nanorods having a length of 100 nm and diameter of about 20 nm. The photoluminescence study shows that the intensity of magnetic dipole transition ($^5D_0 \rightarrow {}^7F_1$) at 590 nm dominates over that of electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) at 617 nm. The optimum concentration of Eu^{3+} for the highest luminescence is found to be 7 at.%. Emission from the $^5D_0$ level of Eu^{3+} follows monoexponential decay which can be attributed to homogeneous substitution of La^{3+} sites in $LaPO_4$ by Eu^{3+} ions. As-prepared samples are found to be dispersible in methanol and water. This could be a potential candidate for various applications, i.e. incorporation of luminescent materials in polymer such as polyvinyl alcohol and in biological activity such as tracer.

1. Introduction

Study of luminescence properties of rare-earth doped nanoparticles has emerged as an interesting area in recent years due to its technological importance [1–10]. Particularly, lanthanide ions doped in inorganic host material has been extensively studied [11–20]. Lanthanide ions are well known for their fascinating optical properties such as solid state lighting, lasers, X-ray detectors and optical data storage [21–24]. Inorganic hosts such as lanthanide phosphate ($LaPO_4$) have got very high thermal stability and high refractive index which make them suitable candidate for the production of display lamps and sensors [25,11,26–28]. Recently, nanosized $LaPO_4$ based phosphors have been extensively investigated [11,26–29]. It has been found that phosphor material such as Y_2O_3:Eu^{3+} in the nanoparticles form have higher luminescence as compared to bulk counterpart under UV-excitation. This is due to increase in band gap with decreasing particle size and thereby increasing absorption cross-section for nanoparticles [30]. Further reduction of the particle size in a crystalline system can result in remarkable modification of properties compared to those of bulk due to high surface-to-volume ratio and the quantum confinement effect for nanomaterials [31–34].

Dexpert-Ghys et al. [11] prepared bulk polycrystalline $LaPO_4$ at high temperature 1300 °C. Meyssamy et al. [26] synthesized $LaPO_4$:Eu and $LaPO_4$:Tb nanocrystal for the first time. Various other methods such as sol–gel [35–39], hydrothermal [40–45] and co-precipitation technique [27,46] have been reported for preparation of lanthanide doped phosphate nanoparticles. However, preparation of lanthanide doped nanoparticles at high temperature results in clustering of optically active lanthanide ions. In general, agglomeration of particles is observed in chemical synthesis routes which reduce the luminescence intensity. As a result, there is disadvantage in the sense that bigger or agglomerated particles are difficult to disperse in water or organic solvents. Use of suitable capping agents is one of ways to reduce/avoid agglomeration of particles, and many authors have reported the preparation of nanoparticles using different capping agents. Lehmann et al. [27] synthesized Eu^{3+} doped $LaPO_4$ and $EuPO_4$ using tributyl phosphate (TBP), trihexylamine and dihexyl ether. Kömpe et al. [28] also prepared $CePO_4$:Tb core and $CePO_4$:Tb–$LaPO_4$ core–shell nanoparticles by co-precipitation method using the same coordinating ligands (TBP) at 200 °C. Wang et al. [47] prepared CeF_3 and CeF_3:Tb re-dispersible nanoparticles in diethylene glycol (DEG) medium at 200 °C.

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Although agglomeration is avoided by the use of capping agents, nanoparticles stabilized with long chain hydrocarbons have many disadvantages in luminescence applications because of high quenching effect from O–H, C=O, C=S and N–H functional groups. Moreover, these groups are difficult to remove when incorporated into polymer based films as well as moisture sensitive [48]. Such difficulties can be reduced/overcome using capping agents which have short chain hydrocarbons.

Ethylene glycol (EG) is a short chain hydrocarbon with chemical formula HO–CH_2–CH_2–OH and is liquid at room temperature. It is more viscous than water because of presence of more hydrogen bonding among molecules. Many reactions can be carried out below its boiling point of 197 °C. EG can act as capping agent as well as reaction medium [1–4,49]. EG is less expensive as compared to other capping agents such as oleic acid. Since it is biodegradable, polyethylene glycol (PEG) is used to functionalize surface of magnetic nanoparticles in drug delivery [50].

We have prepared $LaPO_4$ nanoparticles doped with Eu^{3+} up to 40 at.% in EG. Nanoparticles stabilized with short chain molecules have significant advantage in sense that organic part can be removed by heating at 500 °C [1–4,13]. The prepared nanoparticles can be re-dispersible in different solvents such as water, ethanol and methanol. The prepared samples were characterized for their structural and luminescence properties. We also carried out lifetime studies for $^5D_0$ level of Eu^{3+}as a function of increasing concentration of Eu^{3+} ions.

2. Experimental details

2.1. Sample preparation

Nanoparticles of $LaPO_4$ and $LaPO_4$ doped with Eu^{3+} (Eu^{3+} = 2, 5, 7, 10, 15, 20, 30 and 40 at.%) were prepared using ethylene glycol (EG) as both capping agent and reaction medium at 150 °C. Lanthanum oxide (La_2O_3, 99.99% Aldrich), europium oxide (Eu_2O_3, 99.99% Alfa Aesar), ammonium dihydrogen phosphate ($NH_4H_2PO_4$ 99.999% Aldrich) were used as sources of La^{3+}, Eu^{3+} and PO_4^{3-}, respectively. In a typical synthesis of 2 at.% Eu^{3+} doped $LaPO_4$ nanoparticles, 500 mg of La_2O_3, and 11 mg of Eu_2O_3 were dissolved together in dilute hydrochloric acid (HCl) in a 100 ml two neck round bottom flask. Excess HCl was removed by evaporating several times with double distilled water. To this reaction medium, 50 ml of EG and 360 mg of $NH_4H_2PO_4$ were added. The reflux was carried out at 150 °C for 3 h. The precipitate formed was separated with centrifugation at 10,000 rpm, washed several times with acetone and dried in ambient atmosphere. Same procedure was followed for preparation of all other doped samples by taking stoichiometric amounts.

2.2. Characterization

Structural studies of all the samples were carried out using Philips powder diffractometer (model PW 1071) with Cu Kα (1.5405 Å) radiation with Ni filter. The average crystallite size (d) was calculated using Debye–Scherrer relation, $d = 0.9\lambda/\beta\cos\theta$, where λ is wavelength of the X-ray and β is full width at half maximum (FWHM). Transmission electron microscopy (TEM) images were recorded using JEOL 2000 FX microscope. For the TEM measurement, the samples were ground and mixed together with EG and dispersed under ultrasonication for 30 min. A drop of dispersed sample was put over carbon coated copper grid and evaporated to dryness under a lamp.

FT-IR of the $LaPO_4$ samples were studied using Shimadzu (model 8400S). All the luminescence spectra of samples were recorded using Perkin–Elmer (LS-55). Lifetime of all the doped samples were measured using EDINBURGH instrument (model FLS920) equipped with μs flash lamp of 100 W xenon lamp. Samples were prepared by dispersing in methanol and coated over quartz slides and dried in ambient conditions.

3. Results and discussion

3.1. XRD study

Fig. 1 shows the XRD patterns of as-prepared samples of 2, 5 and 15 at.% Eu^{3+} doped $LaPO_4$ samples along with pure $LaPO_4$. XRD patterns of samples are in agreement with monoclinic system of pure $LaPO_4$ (JCPDS No. 73-0188). Similarly, all other samples show similar patterns (not shown here). The XRD patterns do not show any diffraction peak corresponding to the possible phases such as La_2O_3 or Eu_2O_3. Absence of such possible phases is an indication of homogeneous solid solution of $LaPO_4$ and Eu^{3+}, which further reveals incorporation of Eu^{3+} ions in the lattice sites of La^{3+} in $LaPO_4$. From the XRD patterns, crystallite sizes are calculated using Debye–Scherrer relation. Table 1 presents the detail values of lattice parameters, unit cell volumes and crystallite sizes of Eu^{3+} doped $LaPO_4$ samples. The unit cell volumes of pure and 40 at.% Eu^{3+} doped $LaPO_4$ samples are 305.7 and 294.8 $Å^3$, respectively. The reported values of lattice parameters for pure $LaPO_4$ are a = 8.25, b = 7.09, c = 6.47 Å and its unit cell volume is V = 305.55 $Å^3$ [JCPDP 73-0188]. The unit cell volume decreases linearly with increasing concentration of Eu^{3+} (Fig. 2), which is understandable as the ionic radii of La^{3+} and Eu^{3+} are 1.16 and 1.06 Å, respectively [51]. This linear decrease in unit cell volume clearly indicates the quantitative substitution of La^{3+} sites by Eu^{3+} in the $LaPO_4$ matrix. The crystallite sizes of pure and doped with 5 at.% Eu^{3+} in $LaPO_4$ are 10 and 12 nm, respectively.

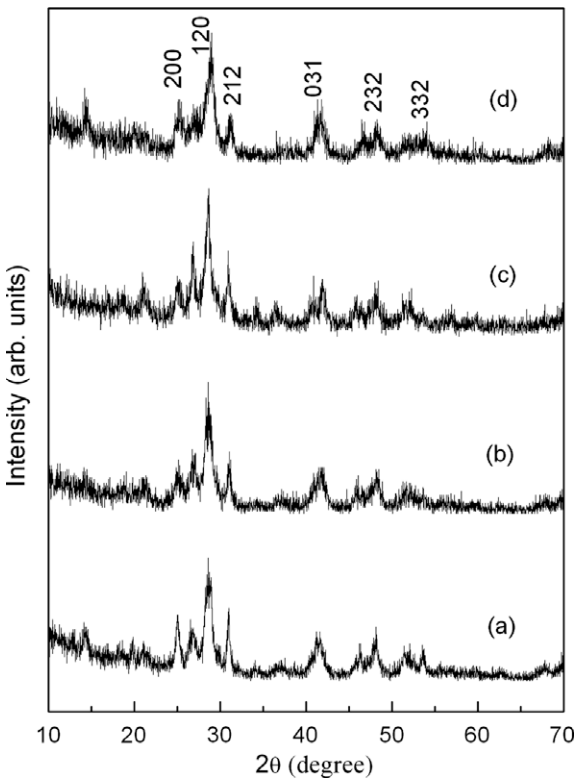

Fig. 1. XRD patterns of (a) 0, (b) 2, (c) 5 and (d) 15 at.% Eu^{3+} doped $LaPO_4$.