

Synthesis and spectroscopic investigation of nanostructured europium oxalate: A potential red emitting phosphor



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ABSTRACT

Nanostructured europium oxalate was successfully synthesized for the first time by microwave assisted co-precipitation method. Structure and nanocrystalline nature of the synthesized europium oxalate was analyzed using X-ray diffraction and the results were confirmed by transmission electron microscopy. Fourier transform infrared spectroscopy was employed to identify the different functional groups present in the nanostructured europium oxalate. Detailed spectroscopic investigations were carried out using Judd–Ofelt theory to find out the spectroscopic parameters of europium oxalate. Nature of the metal–ligand bond and symmetry of the environment around Eu^{3+} ions, which strongly influences the luminescence characteristics of the material, were analyzed. Photoluminescence emission spectrum of the material confirmed the strong red emission predicted by the JO theoretical analysis which is further ascertained by CIE chromaticity diagram. Further analysis on the luminescence parameters such as life time, quantum efficiency and color purity of nanostructured europium oxalate revealed the suitability of this material as a potential phosphor for red emission.

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1. Introduction

Rare earth based luminescent materials have gained much attention in recent years owing to their potential technological applications in the field of display devices, X-ray imaging, solid state lasers and optical amplifiers [1,2]. Rare earth based nanophosphors are widely considered to be the most promising candidate for optical applications due to their excellent luminescence characteristics such as sharp emissions, high quantum efficiency, color purity and long radiative life time [3,4]. The attractive spectroscopic properties of rare earth ions are due to the well-shielding of their 4f orbitals by 6s, 5p and 5d orbitals, which weakens the coupling between the 4f orbitals and surrounding ligands. Rare earth based nanophosphors have also gained much attention because of the quantum confinement effect which leads to novel optical properties [5]. Of the various rare earth compounds, rare earth oxalates are of particular importance because of their wide applicability in the fields of molecular based magnetic materials, luminescent materials and also as a precursor for superconducting oxides [6–8]. Due to the efficient luminescence in moderate

temperature regions, rare earth oxalates also found application in the field of optoelectronic devices [7]. The thermal decomposition of rare earth oxalates leads to the formation of fine oxide nanocrystals which is considered to be an effective and simple method for synthesizing rare earth oxide nanocrystals [9]. This aroused a great deal of attention in recent years on the synthesis of rare earth oxalate single crystals and investigations on its micro and nano structures [10–15].

Trivalent europium ion has been recognized as an excellent activator in many red phosphors [16,17] in which the intense red emission is achieved by the hypersensitive ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ transition of Eu^{3+} occurring at 610–612 nm for cubic and 618–620 nm for monoclinic systems. As an effective red phosphor, Eu^{3+} doped materials were widely investigated in recent years in a variety of systems such as single crystals, glasses, thin films, nano materials etc [18–21]. In most of the systems emission quenching is observed at higher concentrations of Eu^{3+} which limits the doping concentration and thereby the luminous intensity [22,23]. However no concentration quenching is observed in some fully concentrated systems like, $\text{NaEu}(\text{MoO}_4)_2$, $\text{EuP}_5\text{O}_{14}$ and $\text{K}_5\text{Eu}(\text{MoO}_4)$ etc. and they exhibit remarkable optical properties [24–26]. Among them europium oxalate is an important candidate which can produce strong red emission without exhibiting any concentration quenching, but less investigated other than that on the micro

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structured europium oxalate [27,28]. To the best of our knowledge, there is no report on the synthesis of nanostructured europium oxalate and its spectroscopic investigations. Since the emission properties are sensitive to the local environment of Eu^{3+} ions, the influence of ligand – metal interactions and local symmetry are also to be considered to optimize the emission characteristics of the material. Hence, a comprehensive spectroscopic investigation of europium oxalate is very essential to confirm the applicability of this material as an effective red phosphor.

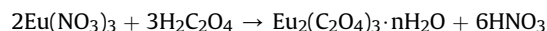
In the present study, we report a simple and successful method to synthesize nanostructured europium oxalate employing microwave assisted co-precipitation method and analysis of its structural and spectroscopic properties. Different characterization techniques are adopted to find the structure and size of the nanocrystals. Detailed spectroscopic investigations are carried out with the help of Judd–Ofelt analysis and photoluminescence spectrum. Since the ${}^5\text{D}_0$ – ${}^7\text{F}_2$ transition is hypersensitive, particular attention is paid to discuss the nature of environment around Eu^{3+} ion and the nephelauxetic effects due to the ligands. Different spectroscopic parameters are calculated to confirm the suitability of this material as an efficient red phosphor.

2. Experimental methods

2.1. Synthesis of nanostructured $\text{Eu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$

Analytical grade europium nitrate hexahydrate (99.9%, Alfa Aieser), oxalic acid dehydrate (99%, Merck) and ethylene glycol (99%, Merck) were used for the synthesis of nanostructured europium oxalate. Aqueous solution of 0.1 M europium nitrate was mixed with equal volume of ethylene glycol and kept under stirring to form a homogenous solution. Stoichiometric amount of aqueous solution of 0.15 M oxalic acid was prepared and mixed with equal volume of ethylene glycol and then poured in to the above solution with constant stirring. The white colloidal solution thus obtained was subjected to a periodic microwave irradiation (2.45 GHz, 700 W) for 20 s with a time interval of 10 s. The precipitate obtained after 10 such cycles of irradiation were separated by centrifugation, washed many times in acetone and finally with double distilled water, and then dried at 60 °C.

The proposed chemical reaction is



2.2. Characterization

The structure and crystalline size of the synthesized europium oxalate was identified by powder X-ray diffraction analysis (XRD) using PANalytical X'pert Pro diffractometer with a $\text{Cu K}\alpha$ radiation ($\lambda = 1.5460 \text{ \AA}$) operating at 30 mA, 40 kV from 10 to 35°. For profile fitting slow scan data is taken over the range 8 to 35° with a step size of 0.02 and a step time of 3 s for each step. Fourier transform infrared spectrum (FTIR) was recorded using Perkin Elmer Spectrum 400 Spectrometer over the range of 400–4000 cm^{-1} . The crystalline size was confirmed by transmission electron microscope (TEM) JEOL JEM 2100. U–V Visible–NIR absorption spectrum of the sample was measured on a UV–Visible–NIR spectrophotometer Varian Cary 5000 in the wavelength span of 250–2250 nm. Photoluminescence spectra of the nanostructured europium oxalate were recorded with Horiba Jobin flouromax4 spectrofluorometer over the wavelength range 420–750 nm. Luminescence decay was measured by using PerkinElmer LS 50 spectrometer.

3. Results and discussion

3.1. Structural characterization

X-ray powder diffractogram of the as synthesized europium oxalate is given in Fig. 1 along with the standard data of $\text{Eu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (ICDD 200400). The position and intensity of the diffraction peaks of the sample matches well with the standard data. Profile fit of the diffraction data is carried out by using Match 2 software with the PDF 2 database and is given in Fig. 1(b). Profile fitting shows a close agreement with the standard data (ICDD 200400) reported by Ollenderoff et al. for monoclinic structured europium oxalate decahydrate [29]. The figure of merit of the fitting is 0.945 which proved the goodness of the fit and confirms the monoclinic structure of synthesized europium oxalate. Hence the diffraction peaks of europium oxalate are indexed to pure monoclinic phase of $\text{Eu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ with space group $\text{P}2_1/c$ and the lattice parameters are calculated to be $a = 10.98$, $b = 9.59$, $c = 10.05 \text{ \AA}$ and $\beta = 114.18^\circ$. Sheng hua et al [30] have reported a detailed structural studies of $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ and proposed that the structure is composed of two-dimensional networks of edge sharing 1:5:3 coordination polyhedra matching the (020) set of planes. Each lanthanum atom is being surrounded by three chelating oxalate groups and three aqua ligands. The intervening space is filled by lattice water molecules disordered over seven major sites. Since the lattice parameters of the europium oxalate is identical with that of $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, it is quite reasonable to propose an identical crystal structure to $\text{Eu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. A schematic lattice model of the crystal structure of europium oxalate decahydrate is given in Fig. 1(c)

Average crystalline size of the $\text{Eu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ is calculated to be 24 nm from the X-ray line-broadening of the major diffraction peak using the Debye–Scherrer equation

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where D is the average crystalline size, λ is the X-ray wavelength (1.5405 Å), θ and β are the diffraction angle and full width at half-maximum (FWHM) of the peak respectively and K is the shape factor.

Different functional groups present in nanostructured europium oxalate are identified by FTIR spectrum and is given in Fig. 2. Strong absorption bands in the spectrum are mainly due to the different symmetric and asymmetric stretching vibrations of functional groups associated with the oxalate ligand. Broad absorption in the region 3000–3600 cm^{-1} is due to the stretching vibrations of OH groups and confirms the presence of water molecules in the compound. Very strong peak observed at 1617 cm^{-1} is due to the combined effect of asymmetric stretching of C=O in oxalate ligand and the bending vibrations of the OH group [31]. The small peak observed at 1362 cm^{-1} and the strong peak at 1318 cm^{-1} , evidences symmetric stretching vibrations of CO_2 and absorption at 610 cm^{-1} is attributed to CO_2 wagging modes. Bonding of oxalate ligand and europium ions is confirmed by the presence of M–O bond vibrations at 796 and 491 cm^{-1} [32]. Absorption at 491 cm^{-1} can be also related to the ring deformation and bending of δ (O–C=O). Thus, the FTIR spectroscopic analysis of nanostructured europium oxalate confirmed the presence of oxalate ligand, M–O bond and water molecules.

TEM image of the as synthesized europium oxalate is given in Fig. 3(a) and implies that the average size of the nanocrystals is in the range of 20–30 nm which is in agreement with the crystalline size calculated by Debye Scherrer equation. TEM image also reveals that these nanocrystals are of uniform size and are aggregated to form large structures as in the case of nanostructured samarium

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