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Synthesis, structural and spectroscopic investigations of nanostructured samarium oxalate crystals



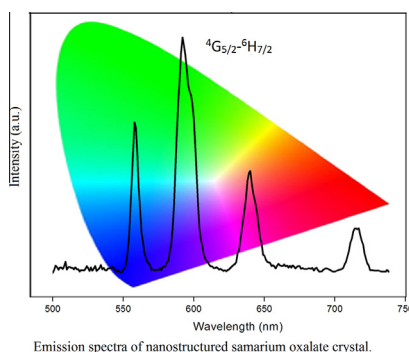
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HIGHLIGHTS

- First time report on nanostructured Samarium oxalate crystals.
- The mechanism of aggregation of nanocrystals as nanoplates is explained.
- Spectroscopic parameters are evaluated using Judd–Ofelt theory.
- Suitability of the materials as a phosphor was confirmed by fluorescence study.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured samarium oxalate crystals were prepared via microwave assisted co-precipitation method. The crystal structure and morphology of the sample were analyzed using X-ray powder diffraction, Scanning electron microscopy and Transmission electron microscopy. The presence of functional groups is ascertained by Fourier transform infrared spectroscopy. Samarium oxalate nanocrystals of average size 20 nm were aggregated together to form nano-plate structure in sub-microrange. Detailed spectroscopic investigation of the prepared phosphor material was carried out by Judd–Ofelt analysis based on the UV–Visible–NIR absorption spectra and photoluminescence emission spectra. The analysis reveals that the transition from energy level $^4G_{5/2}$ to $^6H_{7/2}$ of Sm^{3+} ion has maximum branching ratio and the corresponding orange emission can be used for display applications.

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Introduction

Nanostructured materials are the subject of extensive research in recent years due to their versatile applications in most of the fields of modern technology owing to their interesting physical properties which can be governed by optimizing the size, morphology and structure. Various synthesis methods are developed to prepare nanostructured materials with different pre-assigned morphologies such as nanowires, nanorods, and nanoplates with

tunable size [1,2]. In the nanometer regime the physical properties are highly altered by the presence of significant number of surface atoms, quantum confinement electronic states etc. which leads to the novel properties compared with their corresponding bulk phases. Rare earth based nanosystems gained considerable attention due to their potential applications in the fields of optical devices, solid oxide fuel cells, and high strength permanent magnets due to their unique optical, electric and magnetic properties respectively [3–5]. The distinctive properties of the rare earth compounds originate from the electronic transitions within the 4f shell of the rare earth ion which are shielded by 5s and 5p electrons but highly sensitive to the characteristics of the host lattice

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[6]. These dependences are usefully manipulated mainly in various fields of the optoelectronic industry where rare earth based nanomaterials find wide spread applications as luminescent devices, up conversion materials, optical fibers, bioimaging probes and scintillators etc. [7–9].

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 precursor for superconducting oxides [10–12]. Rare earth oxalates also found wide application in the field of miniature solid state lasers since it exhibits high active ion concentration. The coordinating ability of the oxalate ligand makes it superior among the rare earth compounds and also the subject of experimental and theoretical studies [13,14]. Single crystals of rare earth oxalates such as cerium oxalate, holmium oxalate and gadolinium samarium oxalate have been synthesized and studied in recent years [15–17]. The growth and detailed spectroscopic analysis of dysprosium praseodymium oxalate single crystals is also reported [18]. Studies on the up-conversion property and luminescent efficiency of neodymium oxalate and erbium oxalate have been carried out and confirmed their suitability as coating materials for display devices and solid state lasers [19,20]. However the synthesis and spectroscopic studies of nanostructured rare earth oxalates were seldom done. Samarium oxalate nanomaterials are expected to have potential applications because of the relatively high quantum efficiency of the $^4G_{5/2} - ^6H_{7/2}$ transition of Sm^{3+} ion. Hence the synthesis and detailed spectroscopic investigation of nanostructured samarium oxalate deserves special attention and importance.

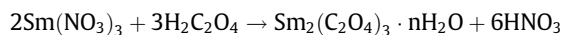
Here we describe the synthesis of nanostructured samarium oxalate crystals and its structural and spectroscopic studies. Samarium oxalate nanocrystals were synthesized via microwave assisted co-precipitation method. The structural characterization of the as prepared sample was carried out by using X-ray powder diffraction. Based on the scanning electron microscope (SEM) and transmission electron microscope (TEM) analysis, a possible mechanism involved in the formation of the platelet morphology was proposed. The spectroscopic properties such as radiative transition probability, and branching ratio of the nanocrystals were qualitatively analyzed and discussed using the absorption and fluorescence spectra.

Experimental

Synthesis of samarium oxalate nanocrystals

Analytical grade samarium nitrate hexahydrate (99.9%, Alfa Aesar), oxalic acid dehydrate (99%, Merck) and ethylene glycol (99%, Merck) were used for the synthesis. 12.5 ml aqueous solution of 0.1 M samarium nitrate solution was mixed with 25 ml of ethylene glycol and kept under vigorous stirring for an hour so as to form a homogenous solution. 12.5 ml of aqueous solution of 0.15 M oxalic acid was then poured onto the above solution with stirring. The pH of the solution was found to be in the range 1–2. The whole system was transferred to a domestic microwave oven (2.45 GHz, 700 W), immediately after the formation of a white colloidal solution indicating the nucleation of samarium oxalate crystals. The solution was subjected to a periodic irradiation for 20 s with a time interval of 10 s. The microwave irradiation helps to increase the rate of reaction and also avoid the temperature gradient in the system and therefore ensure the homogeneity of the products. After 10 cycles of irradiation, the precipitated solution was taken from the oven and washed many times in double distilled water and finally with the acetone. The samarium oxalate particles were then separated by centrifugation and dried.

The proposed chemical reaction is



Characterization

The structure of the crystal was identified by X-ray diffraction technique using X-ray diffractometer PANalytical X'pert Pro with a Cu K α radiation ($\lambda = 1.5460 \text{ \AA}$) operating at 30 mA, 40 kV. The intensity of the diffracted radiations against 2θ values were recorded in the range $10\text{--}40^\circ$. The FTIR absorption spectrum of the samarium oxalate was recorded using FTIR Spectrometer Shimadzu 8400S over the range of $400\text{--}4000 \text{ cm}^{-1}$. The morphology, purity and the crystalline size were examined with a scanning electron microscope JEOL JSM6390 with an accelerating voltage 30 kV attached with an EDS spectrometer and a transmission electron microscope JEOL JEM 2100. Optical absorption spectrum of the sample was measured on a UV-Visible-NIR spectrophotometer Varian Cary 5000 in the wavelength span of 250–2250 nm. Fluorescence spectra of the sample were recorded using spectrofluorophotometer Shimadzu RFPC 5301 in the range 500–730 nm.

Results and discussion

X-ray powder diffraction studies

X-ray diffraction pattern of the as prepared samarium oxalate nanocrystals is shown in Fig. 1 along with the ICDD (International Centre for Diffraction Data) of $Sm_2(C_2O_4)_3 \cdot 10H_2O$ (201021). The exact matching of the diffraction patterns confirms the formation of highly pure samarium oxalate nanocrystals and can be indexed to the monoclinic samarium oxalate decahydrate with lattice parameters $a = 11.10 \text{ \AA}$, $b = 9.21 \text{ \AA}$, $c = 10.155 \text{ \AA}$, $\beta = 114.30^\circ$ with space group $P2_1/c$.

The average crystallite size of the samarium oxalate nanocrystals was evaluated to be 20 nm, from 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 grain size, λ is the X-ray wavelength (1.5405 \AA), θ and β are the diffraction angle and full width at half-maximum (FWHM) of the peak respectively and K , the shape factor.

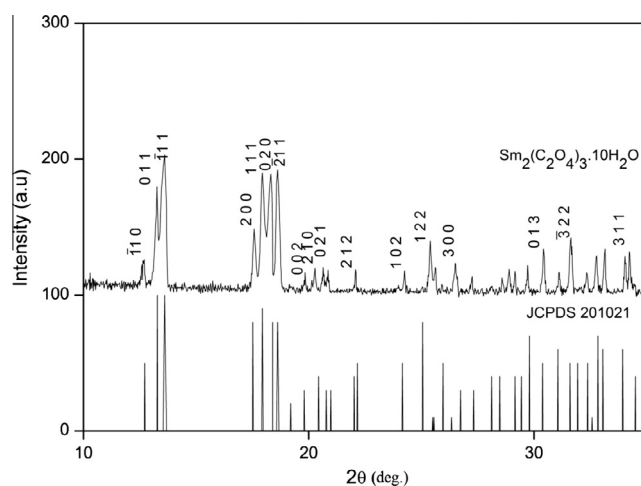


Fig. 1. X-ray diffraction pattern of samarium oxalate nanocrystals.

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