

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

**jmr&t**  
Journal of Materials Research and Technology  
[www.jmrt.com.br](http://www.jmrt.com.br)



## Original Article

# Growth and characterization of Sm<sup>3+</sup> doped cerium oxalate single crystals



Minu Mary C<sup>a</sup>, Vimal G<sup>a</sup>, Kamal P. Mani<sup>a</sup>, Gijo Jose<sup>b</sup>, Biju P.R.<sup>a</sup>, Cyriac Joseph<sup>a,\*</sup>,  
Unnikrishnan N.V.<sup>a</sup>, Ittyachen M.A.<sup>a</sup>

<sup>a</sup> School of Pure and Applied Physics, Mahatma Gandhi University, Kottayam, India

<sup>b</sup> Department of Physics, S B College, Changanassery, India

## ARTICLE INFO

## Article history:

Received 25 February 2015

Accepted 27 January 2016

Available online 9 March 2016

## Keywords:

Single crystal growth

Rare earth compounds

Oxalates

Phosphors

Microhardness

## ABSTRACT

Single crystals of Sm<sup>3+</sup> doped cerium oxalate decahydrate were synthesized using single diffusion gel technique and the conditions influencing the size, morphology, nucleation density and quality of the crystals were optimized. Highly transparent single crystals of average size 3 mm × 2 mm × 1 mm with well-defined hexagonal morphology were grown during a time period of two weeks. X-ray powder diffraction analysis revealed that the grown crystals crystallize in the monoclinic system with space group P2<sub>1</sub>/c as identical with the pure cerium oxalate. The various functional groups of the oxalate ligand and the water of crystallization were identified by Fourier transform infrared spectroscopy. The photoluminescence spectrum of the Sm<sup>3+</sup> doped cerium oxalate indicated that the Sm<sup>3+</sup> ions are optically active in the cerium oxalate matrix. The crystal has a strong and efficient orange red emission with a wavelength peak at 595 nm and hence can be effectively used for optical amplification. Microhardness measurements of the crystal revealed that they belong to the soft material category.

© 2016 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda.

## 1. Introduction

High quality, defect free single crystals have always evoked great attention due to their wide applications in the field of optoelectronics, solid state lasers, remote sensing and medical diagnostics [1–3]. Particular attention can be given to single crystals of trivalent lanthanide compounds owing to their smart optical and spectroscopic properties, which led to potential applications in optoelectronics, lasers, optical

amplifiers and in telecommunications [4–6]. The distinctive properties originate from the electronic transitions within the 4f shell of the rare earth ion that is well shielded by 5s and 5p electrons but highly sensitive to the characteristics of the host lattice. Among the rare earth compounds, rare earth oxalates are of special importance because of their interesting luminescent, magnetic and electrical properties [7–10]. Recent investigations on the fluorescence of some rare earth oxalates suggest their potentiality for optical applications [7,11]. Oxalates are also utilized as a precursor for many

\* Corresponding author.

E-mail: [cyriacmgu@gmail.com](mailto:cyriacmgu@gmail.com) (C. Joseph).

<http://dx.doi.org/10.1016/j.jmrt.2016.01.001>

2238-7854/© 2016 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda.

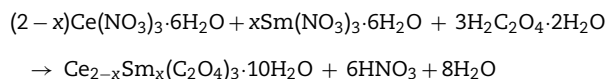
of the technologically important ferroelectric, magnetic and superconducting materials such as BaTiO<sub>3</sub>, Ni–Co–Zn ferrites and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7–x</sub>. [12–14]. Significant attention has been paid to rare earth ion doped crystals, since the dopants play a vital role in enhancing their physical properties. Of the various rare earth ions, Sm<sup>3+</sup> ions have gained particular attention and are widely investigated in a variety of systems such as bulk crystals, nanocrystals and glasses, due to their high fluorescence quantum yield [5]. Hence, Sm<sup>3+</sup> ion doped rare earth oxalates deserve special attention and importance.

Here we describe the growth of samarium doped cerium oxalate decahydrate single crystals. Gel method is the only viable method to grow these crystals since oxalates are sparingly soluble in water and decompose before melting, which impose constraints on the use of other conventional techniques. In addition, gel method also allows ease optimization of physical parameters influencing the growth of high quality single crystals. The present work mainly aims to investigate the growth parameters and the effect of Sm<sup>3+</sup> doping on the optical properties of the cerium oxalate single crystal. The structural and mechanical properties of the crystal are also studied in detail.

## 2. Experimental

### 2.1. Crystal growth

Cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99.9%, CDH), Samarium nitrate hexahydrate (Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99.9%, CDH), oxalic acid dihydrate (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, 99%, Merck) and sodium meta silicate nonahydrate (Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O, CDH) were used as the starting materials. Sodium meta silicate solution of density 1.03 g/cc was mixed with 1M oxalic acid to obtain hydrosilica gel of pH 6. The solution was transferred to a test tube of dimension 15 mm in diameter and 150 mm in length to fill half of its volume and then kept undisturbed for 24 h for proper gelation. 0.5 M aqueous solutions of cerium nitrate and samarium nitrate were mixed in stoichiometric proportions and poured gently on the top of the gel column. The reactants slowly diffuse through the gel and react with the oxalic acid already incorporated in the medium. The chemical reaction involved is



where  $x$  is taken as 0 and 0.1 for getting pure and 5% Sm doped cerium oxalate decahydrate, respectively. It is observed that whatever be the pH and density of the gel, it cracked as soon as the rare earth solutions were added over the set gel. The concentration of the feed solution was then varied but the observations were the same. To overcome these difficulties neutral gel and double diffusion systems were also undertaken. But the result was not as expected.

Finally, the single diffusion technique was again tried with the feed solution acidified with dilute nitric acid in various proportions. The observation revealed that the presence of nitric acid in the feed solution plays an important role in defining the nature of the precipitation. The density of the

precipitation front lowers as the amount of HNO<sub>3</sub> in the feed solution increases. When concentrated HNO<sub>3</sub> was used to acidify the feed solution, there was no precipitation but spherulitic crystals are formed. As the volume of concentrated HNO<sub>3</sub> was further increased, tiny well faceted crystals were obtained. Hence, the acidification of the feed solution was found to be a necessary step in the growth of these groups of crystals.

Morphological changes are exhibited by the crystals due to the variation of the microenvironments like density of the gel, pH of gel, acidity of feed solution and degree of supersaturation. It is observed that crystals taken from different regions of the gel medium show changes in morphology. Fig. 1(a) and (b) shows growth system of Sm<sup>3+</sup> doped cerium oxalate crystals in silica gel. It is observed that the transparent crystals formed at the bottom of the gel column are thin and have most developed hexagonal prism face while the crystals found at the top of the gel column are of thick rhombic prism morphology. Good quality crystals are found at the bottom of gel column since the availability of the ions is just sufficient for the growth of crystals. Distance of crystallization zone from the gel interface is also different with the acidity of the feed solution. With lower concentration of acid, the heavy nucleation resulted especially at the gel–solution interface as shown in Fig. 1(a). As the acid concentration is increased, nucleation density is decreased and crystallization occurred in a region below gel solution interface, resulting the formation of transparent hexagonal crystals as shown in Fig. 1(b). High concentration of the reactants at the interface of the feed solution and gel surface leads to spontaneous multinucleation resulting to the formation of clustered crystals as shown in Fig. 1(c) and (d). Fig. 1(e) shows the well-developed hexagonal crystal of average size 4 mm × 2 mm × 1 mm grown in the system. Clustered crystal of Sm<sup>3+</sup> doped cerium oxalate is given in Fig. 1(f) and reveals that these type of crystals are formed by the intergrowth of two or more individual crystals in such a way that they grow together with only part of their similar faces visible.

The effects of the various growth parameters such as density of SMS (sodium meta silicate) solution, pH of the gel, concentration of the reactant and acidity of the feed solution on growth process are manipulated to optimize the conditions of growing good quality crystals. For getting maximum sized, good quality crystals, the optimized conditions are:

- Density of the SMS solution – 1.03 g/cc
- pH of the gel – 6
- Aging of the gel– 24 h
- Concentration of inner reactant – 1 M
- Concentration of the feed solution – 0.5 M
- Acidity of the feed solution – 50% by volume, pH < 2

### 2.2. Characterization

The structure of the grown crystals was identified by X-ray powder diffraction analysis in the range 10–40° using PANalytical X'Pert Pro X-ray diffractometer with Cu-K $\alpha$  radiation operating at 30 mA, 40 kV. FTIR absorption spectrum of the crystal was recorded using Shimadzu 8400S FTIR spectrometer in the range 400–4000 cm<sup>-1</sup>. The absorption and emission spectra of the crystals were recorded using Shimadzu UV Probe

Download English Version:

<https://daneshyari.com/en/article/1479820>

Download Persian Version:

<https://daneshyari.com/article/1479820>

[Daneshyari.com](https://daneshyari.com)