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# $Sr_2CeO_4$: Electronic and structural properties

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## ABSTRACT

This work presents on the preparation and photoluminescent properties of $Sr_2CeO_4$ obtained from the heat treatment of Ce(III)-doped strontium oxalate (10, 25 and 33 mol%). The oxalate precursors were heat treated at 1100 °C for 12 h. The structure of this photoluminescent material was evaluated by the Rietveld method. The route used in this work to prepare the materials showed to be viable when compared to other synthesis reported in the literature. The $Sr_2CeO_4$ material showed a broad and intense band emission with a maximum around 485 nm. The quantitative phase analysis showed that the $Sr_2CeO_4$ photoluminescent phase is the majority one compared to the impurity phases of $SrCeO_3$ and $SrCO_3$. From all results it was possible to verify a complete elimination of the $CeO_2$ phase for the sample obtained from the heat treatment of oxalate precursor containing 33 mol% of cerium(III). The material showed excellent properties for possible candidate as scintillator materials, and in the improvement of efficiency of solar cells when excited in the UV–vis region. The CIE chromaticity diagram it is also reported in this work.

## 1. Introduction

In the last several decades, research has been focused on oxide-based photoluminescent materials due to their commercial applications in color television, fluorescent tube, X-ray phosphors, and scintillators [1–3]. To avoid degradation when exposed under high energy radiation, theses oxide systems need to show adequate mechanical resistance and chemical stability. Among the different phosphors that have the above-cited properties and also exhibit blue emission, only a few are available as blue photoluminescent materials for devices.

In the 90s, a new rare-earth-based photoluminescent material with chemical formula $Sr_2CeO_4$ showing an emission peak around 485 nm was reported by Danielson et al. [4]. The authors synthesized this material by a combinatorial chemical procedure, and successfully identified the structure through structural analysis by X-ray diffraction (XRD) and the Rietveld method [5] for refinement of the structure. Since then, many studies have been reported in the literature describing its importance and contribution as a blue photoluminescent material [6–9]. In parallel, some authors have published information on the application of $Sr_2CeO_4$ as a host of other rare earths yielding excellent optical features [10] in different regions of the electromagnetic spectrum.

In accordance with many papers reported in the literature, the photoluminescence of $Sr_2CeO_4$ is a consequence of the energy transfer between $O^{2-}$ and Ce(IV) localized in one-dimensional chains of the edge-sharing $CeO_6$ octahedron [11–15]. Also, it has been proven that the photoluminescence depends directly on the size and shape of particles [16–18]. Among the several methods to prepare the photoluminescent $Sr_2CeO_4$, the thermal decomposition of acetates, oxalates or carbonates, microwave calcinations, pulsed laser deposition and Pechini method are examples mostly cited in the literature [11,19–25]. However, the presence of secondary phases, such as $SrCeO_3$, $SrCO_3$ and $CeO_2$ [26], along with the photoluminescent $Sr_2CeO_4$ are observed regardless of the preparation route. In this sense, systematic studies considering the amounts of phases present together with the phosphor after

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its synthesis should be evaluated in order to facilitate the understanding of the mechanisms to obtain the $Sr_2CeO_4$ phase with optimized photoluminescent properties. Therefore, the aim of this work is to report on the preparation of the photoluminescent material $Sr_2CeO_4$ starting from 10, 25 to 33 mol% of Ce(III)-doped strontium oxalate. The synthetic route chosen in this work was previously reported as an alternative way for obtaining the photoluminescent material with properties suitable for various applications. Moreover, the methodology used here is one of the most common for bulk materials production because it is simple, low cost, low temperature, and also allows the control of the solution homogeneity [25,27]. In addition, the spectroscopy properties of the $Sr_2CeO_4$ samples prepared from the oxalate precursors were investigated and correlated with the structural refinement that was made based on the Rietveld method [5].

## 2. Material and methods

The synthesis used here has been described in prior work [27]. However, the percentage of Ce(III) in strontium oxalate used as precursor were 10, 25, and 33 mol%. The precursors were prepared from the mixture of the metal chloride solutions, $SrCl_2{\cdot}6H_2O$ (VETEC, 99.99% purity), and $CeCl_3{\cdot}7H_2O$ (ALDRICH, 99.999% purity), with $(NH_4)_2C_2O_4{\cdot}H_2O$ (REAGEM, 99% purity) solution, and heated at 80 °C (pH≅1). The Ce(III) concentrations reported in this work were used to obtain material with a greater quantity of $Sr_2CeO_4$ luminescent phase. After the adjustment of the pH to ~4, the temperature was increased to 80 °C, and the solution was kept under ultrasonic stirring for 1 h. Then, it was left to rest for 4 h prior to posterior filtration and dried under reduced pressure in a desiccator with silica gel and calcium chloride. These precursors were heat treated at 1100 °C in a horizontal oven with heating rate of 20 °C/min, for 12 h in a static air atmosphere to obtain the final product. All products of thermal decomposition of the precursors were analyzed by X-ray diffraction (XRD) using a D5000 SIEMENS® diffractometer, using Cu Kα radiation ($\lambda_{K\alpha1}$ = 1.5405 Å, $\lambda_{K\alpha2}$ = 1.5443 Å), in the $2\theta$ range between 14° and 70°, step of 0.02 ($2\theta$) with 1.0 s per point. The product of thermal decomposition of the precursor with 33 mol% of $Ce^{3+}$ was also analyzed by XRD, using a Rigaku® RINT2000 diffractometer (42 kV × 120 mA) using Cu Kα radiation ($\lambda_{K\alpha1}$ = 1.5405 Å, $\lambda_{K\alpha2}$ = 1.5443 Å, $I_{K\alpha1}/I_{K\alpha2}$ = 0.5), in the $2\theta$ range between 15° and 120°, step 0.02° ($2\theta$) with 2.0 s/step, using a divergence slit = 0.5 mm, and receiving slit = 0.3 mm. The Rietveld refinements [5] were calculated using the program package General Structure Analysis System (GSAS) program of Larson & Von Dreele [28], and graphical user interface EXPGUI [29]. Peak profile functions were modeled using a convolution of the Thompson–Cox–Hastings pseudo-Voigt function [30] with the asymmetry function described by Finger et al. [31], which accounts for the asymmetry due to axial divergence. Based on the results of Rietveld refinement structure we performed a semi empirical Sparkle/PM7 solid state calculation in order to obtain the band gap energy through the HOMO/LUMO energy difference. The calculation was carried out using the MOPAC2012 computational package. Diffuse reflectance spectrum was employed to the S33 material for calculation of the experimental band gap using the Kubelka–Munk was submitted. All products displayed emission under UV excitation ($\lambda_{exc}$ = 275 nm), and were investigated by photoluminescence spectroscopy in the visible region (in the range between 375 and 700 nm) using a Fluorolog SPEX F212I fluorescence spectrofluorimeter equipped with an R928 Hammamatsu photomultiplier and a 450 W Xe lamp). The emission spectrum of the material showing the more intense emission was used to build the CIE chromaticity diagram 1931. It is important to report that the precursor used to obtain better intensity of photoluminescence of the final product, was that containing 33 mol% of Ce(III). In order to obtain scintillation properties, the X-ray excited optical luminescence (XEOL) spectra were obtained in a homemade system [32]. The powders were excited with radiation of copper X-ray tube (operating at 35 kV and 20 mA) and the luminescence signal was collected in front-face mode by optical fiber coupled to Shamrock SR-303i spectrometer and detected in a CCD camera Newton USB DU940-BV with 2048 × 512 pixels, both from Andor Technology.

## 3. Results and discussion

In order to facilitate the presentation of the results, the samples obtained from the heat treatment of the precursor containing 10, 25 and 33 mol% of Ce(III) were labeled as S10, S25 and S33, respectively. In previous works reported by Moosath et al. [33] and Ferrari et al. [25], the Ce(III) ions undergo a thermal oxidation during the thermal treatment of the oxalate precursor at around 343 °C resulting in Ce(IV) ions. Consequently, after the thermal oxidation during the reaction, the reagents available led to the formation of the photoluminescent $Sr_2CeO_4$ phase.

The emission spectra ($\lambda_{exc}$ = 275 nm) recorded for the photoluminescent samples are depicted in Fig. 1, where a large emission band centered at 480 nm is observed, independent from the precursor used in the preparation of the samples. In accordance with Lu et al. [11], the emission band is assigned to a metal-to-ligand transition between Ce(IV) → $O^{2-}$, in the case of the photoluminescent $Sr_2CeO_4$, where two different $O^{2-}$ positions exist in the structure of the material (equatorial and terminal positions).

In order to obtain more detail about the nature of the emission, each emission spectrum was deconvoluted in two bands that are assigned to each Ce(IV) → $O^{2-}$ charge transfer transition [17]

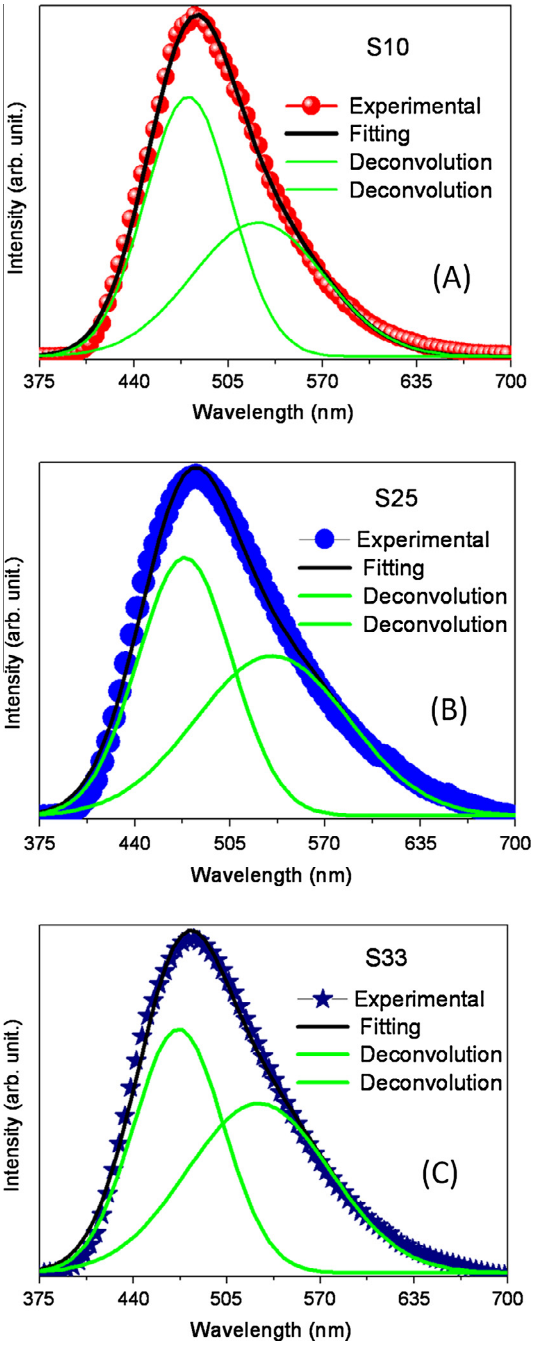

**Fig. 1.** Emission photoluminescence spectra deconvoluted of the (A) S10, (B) S25 and (C) S33 samples.