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The effects of cooling rate on the structure and luminescent properties of undoped and doped $SrAl_2O_4$ phosphors

Claudiane dos S. Bezerra [a, *], Adriano B. Andrade [a], Paulo J.R. Montes [b], Marcos V.dos S. Rezende [c], Mário E.G. Valerio [a]

[a] Laboratory of Materials Preparation and Characterization, Physics Department, Federal University of Sergipe, 49100-000, São Cristóvão, SE, Brazil
[b] Federal Institute of Sergipe-IFS, 49400-000, Lagarto, SE, Brazil
[c] Functional Nanomaterials Group, Physics Department, Federal University of Sergipe, 49500-000, Itabaiana, SE, Brazil

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ABSTRACT

Undoped and doped $SrAl_2O_4$ were synthesized by the Proteic sol-gel method using different cooling rates. The structural properties were investigated using X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The concentration of monoclinic and hexagonal phases in each sample calcined at the same temperature but with different cooling rates was determined via XRD Rietveld refinement. The effect of different cooling rates on the radioluminescence (RL) properties of undoped and doped $SrAl_2O_4$ phosphor also was investigated and the results suggest that the $Eu^{3+} \rightarrow Eu^{2+}$ reduction process depend on the relative concentration of monoclinic and hexagonal phases in the sample.

1. Introduction

Eu-doped $SrAl_2O_4$ phosphor have been extensively applied due to its excellent persistent luminescent properties when co-doped with Dy^{3+} ions [1,2]. Due to this property, $SrAl_2O_4$ phosphors is applied in a variety of applications, such as luminescent pigments, fluorescent lamps, colour display, plasma display panels (PDP), radiation dosimetry and X-ray imaging [3–6]. $SrAl_2O_4$ phosphors can be prepared using different routes such as solid-state reaction [7], sol–gel method [8], combustion process [9] and Pechini method [10]. Particle sizes, i.e, average particle size and size distribution width, morphology and relative concentration of polymorph are normally influenced by the synthesis processes used in the $SrAl_2O_4$ phosphors production. Other parameters in the synthesis processes such as calcining temperature, calcining time (plateau time duration at the maximum calcination temperature), heating rate and cooling rate can also influence in the structure and luminescence properties of $SrAl_2O_4$ phosphors.

$SrAl_2O_4$ can be found in two polymorphic phases with a reversible phase transition at 650 °C [11,12]. At lower temperature, the $SrAl_2O_4$ exhibits monoclinic phase (space group $P2_1$) and at high temperature exhibits a hexagonal phase (space group $P6_3$) [13]. The phase transition from hexagonal phase to monoclinic phase gradually occurs around 650 °C [14]. The monoclinic structure is formed by three dimensional networks of corner-sharing AlO_4 tetrahedral and two different nine-fold coordinated Sr^{2+} sites.

Some works report that luminescent properties of doped $SrAl_2O_4$ could be influenced by the relative concentration of the monoclinic and the hexagonal phases in the samples [15]. Therefore, the characterization of the phase content in a sample is of great importance. Wu et al. [16] report that for different calcining temperature can be change the relative concentration of $SrAl_2O_4$ produced by the Sol–gel-microwave synthesis, keeping constant the calcining time, heating rate and cooling rate. Therefore, in the present work, the effect of cooling rate in the synthesis of undoped and doped $SrAl_2O_4$ prepared by proteic sol-gel route were done. Structural phases present in the samples and the luminescence emission were investigated by powder XRD, SEM and Radioluminescence measurements.

* Corresponding author.
E-mail address: cdsantos20@gmail.com (C.S. Bezerra).

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2. Experimental

Undoped and doped $SrAl_2O_4$ were prepared by the Proteic sol-gel method [17] using coconut water as starting solvent. The coconut water is used as polymerizing agent, and has the advantage of being cheap and readily available. It is composed based of sugar, vitamins, minerals, amino acids and phytohormones [18]. The great advantage of the use of coconut water is that it has large protein chains which can easily anchor the metallic ions. The mixed micelles obtained from the coconut water, are responsible for the synthesis of the nanosize powders and for the control of their morphology. Strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$), Aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$), Europium Nitrate hexahydrate ($Eu(NO_3)_3$) and Dysprosium Nitrate pentahydrate ($Dy(NO_3)_3 \cdot 5H_2O$) were used as starting sources for the metal ions. The reagents were mixed in the coconut water forming the sol. A sol is defined as a colloidal suspension of solid particles in liquid [19].The concentration of Eu and Dy dopants were 3 mol %. The concentrations of the metal salts were chosen to obtain in the samples with nominal composition of $SrAl_2O_4$: Eu^{3+} and $SrAl_2O_4$: Dy^{3+}. For each sample, the transparent sol was heated at 100 °C for 24 h transforming into a xerogel. The obtained xerogel samples was calcined following a heating program composed by a first step of heating rate of 10 °C/min from room temperature to 1100 °C (plateau temperature). The samples were kept at this temperature for 4 h and subsequently cooled down to room temperature following different cooling rates.

The Crystalline phase of samples was checked by means powder XRD measurements done in a Rigaku Rint 2000/PC diffractometer in the Bragg-Brentano geometry operating at 40 kV/40 mA using Cu Kα radiation. The measurements were performed in step-scan mode, in the 2θ range from 10° to 70° with steps of 0.02° and counting time of 5 s. A quantitative analysis of crystalline phases was done using the PowderCell program [20]. The influence of the cooling rates in the morphology of the particles was investigated by scanning electron microscopy (SEM) using a JEOL JSM-6510LV (CMNano/UFS) with powder samples deposited through isopropanol suspension in conductive substrate. Radioluminescence (RL) measurements were performed by exciting the samples with Cu Kα X-ray from the X-ray source of the Rigaku RINT 2000/PC diffractometer and the RL spectra were recorded using an Ocean Optics HR2000 spectrometer.

3. Results and discussion

Figs. 1–3 shows the XRD patterns of undoped, Eu-doped and Dy-doped $SrAl_2O_4$ samples calcined at different cooling rates. The diffraction peaks are compared with the JCPDS standard pattern of the monoclinic [21] and hexagonal [22] $SrAl_2O_4$ phases. In all doped samples the XRD powder patterns did not show any other crystalline phases than these two ones meaning that the little amount of Eu or Dy ions have almost no effect on the $SrAl_2O_4$ phase composition. The relative concentrations of monoclinic and hexagonal phases for each sample (undoped and doped ones) calcined at different cooling rates obtained from Rietveld refinement of the XRD data and the results are shown in Table 1. It is also shown the samples that were produced with a natural cooling, i.e. without any control of the cooling step. The preparation method and on the conditions used for the thermal treatment can lead to a hexagonal and monoclinic $SrAl_2O_4$ phase mixture. Recently Rojas-Hernandez et al. observed the hexagonal phase of $SrAl_2O_4$ [23] and the mixture of monoclinic and hexagonal $SrAl_2O_4$ phase produced by molten salt assisted process, using salt/$SrAl_2O_4$ molar ratio [24]. From results showed in Table 1, it can be seen that the cooling rate is an important synthesis condition that should be taken into account

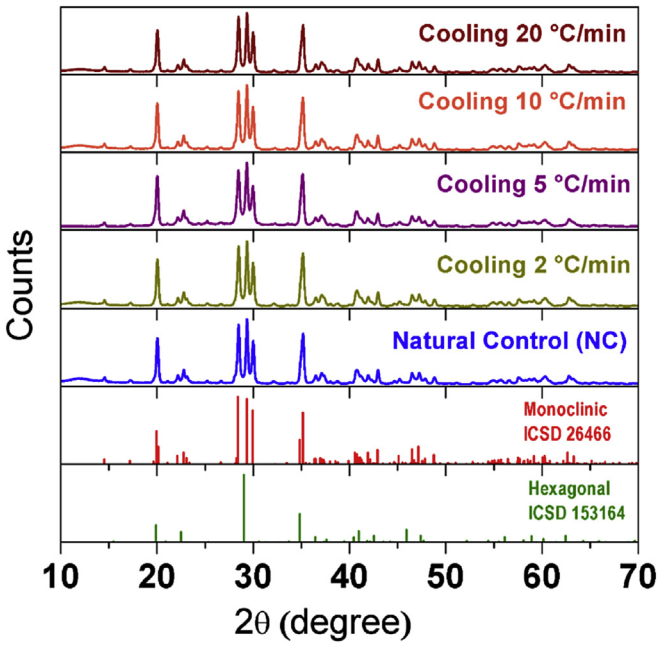

Fig. 1. XRD patterns of undoped $SrAl_2O_4$ calcined at 1100 °C for 4 h at different cooling rates.

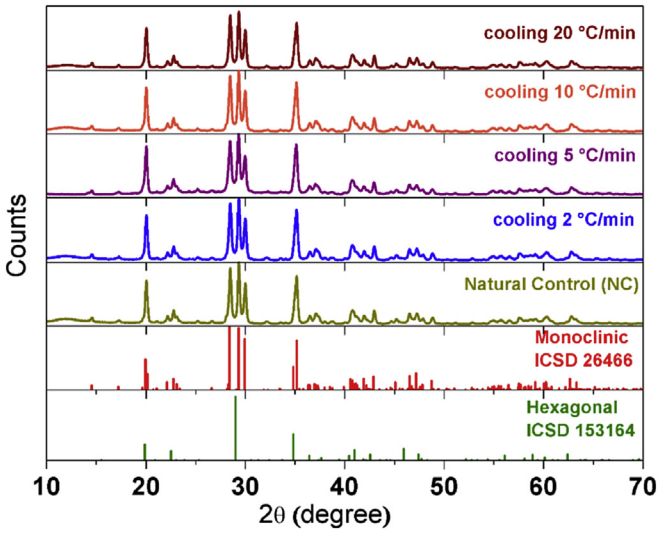

Fig. 2. XRD patterns of the Eu-doped $SrAl_2O_4$ calcined at 1100 °C for 4 h at different cooling rates.

in order to control the proportions of the $SrAl_2O_4$ polymorphs. Additionally, the results showed that, besides the influence of the cooling rate on the monoclinic and hexagonal phase mixture, the relative phase concentrations also depend on the doping.

In general, for application purposes as persistent phosphors, monoclinic $SrAl_2O_4$ phase is preferred due a best performances in terms of light yield [25]. The results showed that a cooling rate of 10 °C/min is the better condition to produce undoped and Dy-doped $SrAl_2O_4$ with a higher concentration of the monoclinic phase. On the order hand, higher concentrations of the monoclinic phase for Eu-doped samples were obtained using a cooling rate of 2 or 5 °C/min.

The samples can be grouped in two groups, the ones that were cooled slower (2 and 5 °C/min) and the faster ones (10 and 20 °C/