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The effect of silver on obtaining pure phase of Eu^{3+}-doped Sr_2CeO_4 for white color emission using citrate as precursor

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ABSTRACT

This work focuses on Sr_2CeO_4 materials containing Ag^+ and Eu^{3+} that are obtained by a combustion method using citric acid as a precursor. The heat-treatment at 1100 °C was efficient and phase impurities are eliminated with presence of Ag^+, favoring the Sr_2CeO_4 formation, as confirmed by XRD. SEM analysis shows a proportional decrease in the organization of particles as a function of doping material, with a nanorods morphology. Diffuse reflectance shows that materials are transparent at visible region, with absorption at UV region. Exciting Sr_2CeO_4-based materials at 270 nm, photoluminescence analysis reveal a band at 470 nm, characteristic of this material and, incorporating Eu^{3+}, emission bands beyond 470 nm are observed characteristic of Eu^{3+}. Eu^{3+} photoluminescence makes the Sr_2CeO_4 materials present color coordinates at bluish green, green, white, yellowish pink and reddish orange regions of electromagnetic spectra. Decay lifetimes of Sr_2CeO_4 and Eu^{3+} were determined and are discussed. The results obtained demonstrate materials with a high potential for application in light emitting devices, and a methodology efficient at obtaining these materials.

1. Introduction

Photoluminescent materials have often been studied for photonics development [1]. These materials are vital for many technologies including telecommunications [2], energy conversion [3], illumination [4] and in devices such as optical amplifiers [5], lasers [6], among others.

To answer the demand for new photoluminescent materials, studies have focused on incorporating rare earth (RE^{3+}) ions into crystalline structures [7]. RE^{3+} present unique properties, primarily due to the ions containing occupied 4*f* orbitals, and the effects associated with shielding from 5*s*, 5*p* and 6*s* orbitals [1]. RE^{3+} demonstrate both magnetic and photoluminescent properties, but recently the photoluminescent properties have been highlighted for the development of light emitting devices [4].

Lighting accounts for approximately 20% of the total energy consumption in private households [8]. Worldwide power consumption can double in the next 3 decades [9]. The challenge to find alternative methods to reduce energy consumption and identify the most efficient lighting devices has begun.

The first white light emitting device using an UV alimentation source was developed in 1938, based on $MgWO_4$ (blue) and $(Zn_{1-x}Be_x)_2SiO_4:Mn^{2+}$ (red) [1]. After World War II, $Ca_5(PO_4)_3(F,Cl):Sb^{3+},Mn^{2+}$ halophosphates were also introduced as light emitters [10]. In 1970, the first system based on three colors containing RE^{3+} were presented by Philips, $YVO_4:Eu^{3+}$, the $Y_2O_3:Eu^{3+}$ or $Y_2O_2S:Eu^{3+}$ as red emitters, $Sr_3(PO_4)_2:Eu^{2+}$ as a blue emitter and Tb^{3+}-based materials as green emitting [11]. The main advantages of RE^{3+}-based materials are due their low toxicity, non-reactivity with Hg and thermal stability under UV radiation [12].

Since then, researchers have focused on more efficient phosphors for these systems, and improving the blue emitters has been the main challenge [13]. Among blue emitting materials containing RE^{3+}, $BaMgAl_{10}O_{17}:Eu^{2+}$, $CaMgSiO_6:Eu^{2+}$ and $Y(V,P)O_4$ are commercial blue phosphors [8]. Systems based on Ce^{3+} as $CaAl_2O_4:Eu^{2+},Nd^{3+}$ with wavelengths of 440 and 445 nm, $(Ba,Sr)Mg_2Al_{16}O_{27}:Ce^{3+}$ with an emission band centered at 441 nm and $MgSrAl_{10}O_{17}:Ce^{3+}$ with an emission band at 424 nm [13], highlight the potential of Ce^{3+}-based phosphors as blue emitting systems.

Studies have shown that Sr_2CeO_4, a stable blue phosphor, has an

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emission band located at 480 nm, attributed to charge transfer between metal-ligand [14]. Due to the ease of production and chemical and thermal stability, this material has had good results as a blue phosphor [15]. Despite easily producing Sr_2CeO_4, a frequent problem is the presence of secondary phases formed during heat treatment, for example, $SrCeO_3$ and $SrCO_3$, which directly influence the emission intensity of the material [16]. For polymorphic materials, an alternative method to control phase formations is metal ion addition. Ions such as Ag^+ have demonstrated positive results as phase catalysts [17].

This work aimed to obtain Sr_2CeO_4 via a combustion process from citric acid with heat treatment at 1100 °C. The presence of Ag^+ in the formation of Sr_2CeO_4 matrix was evaluated. The materials were doped with Eu^{3+} at 0.5; 0.7; 1.0; 1.3 and 1.5 mol%, and the structural and photoluminescent properties were studied.

2. Material and methods

The Sr_2CeO_4 was obtained by the combustion process using citric acid as a combustion agent. $SrCl_2.6H_2O$ (Dinâmica, 99%) and $CeCl_3·7H_2O$ (Vetec – 99%) were dissolved in deionized water to obtain the stock solutions containing Sr^{2+} and Ce^{3+}. $AgNO_3$ was used as a Ag^+ precursor (Sigma Aldrich – 99%). Initially the Sr_2CeO_4 photoluminescent material was obtained through the combustion method in which the solution contained Sr^{2+} and Ce^{3+} ions with proportions of 66% and 33%, respectively [15]. Samples were obtained under the same conditions, with the exception of containing 0.5 mol% of Ag^+ relative to the total molar concentration of Ce^{3+} and Sr^{2+}. The Eu^{3+}-containing samples were obtained adding Eu^{3+} aqueous solutions, obtaining concentrations of 0.5, 0.7, 1.0, 1.3, and 1.5 mol% in relation to the total molar concentration of Ce^{3+} and Sr^{2+}. The materials were obtained in two steps: (1) solutions containing all ions and citric acid (with mass corresponding twenties times of moles of Sr^{2+}, Ce^{3+} and Ag^+) were added to a beaker, and kept under stirring and heating for evaporation up to obtain the viscous solutions, and (2) the remaining material was heat-treated at 1100 °C for 8 h.

Thermal stability of the viscous solution from room temperature up to 1000 °C were analyzed operating Shimadzu Differential Thermal Analyzer (TGA/DTA DTG-60H) under synthetic air atmosphere, and heating rate of 10 °C/min. The materials obtained after heat-treatments were characterized by x-ray diffraction (XRD) using a Shimadzu diffractometer, with Cu K_α radiation (λ = 1.5418 Å), graphite monochromator and step of 0.02 degrees between 2θ = 10–80°. Scherrer's equation was used to calculate the crystallite sizes. Scanning electron microscopy (SEM) images were acquired through a Hitachi TM3000. Diffuse reflectance in the UV/Vis region was performed using Agilent Cary 5000 spectrometer between 200 and 800 nm. The experimental band-gap was determined using Kubelka-Munk methods. Photoluminescence spectra were collected at room temperature in a spectrofluorimeter Horiba-Jobin Yvon Fluorolog 3 and photomultiplier used as detector in visible range. Excitation spectra were recorded between 235 and 380 nm, with excitation and emission slit width of 3 nm and 2 nm, respectively, fixing the wavelength of emission at 610 nm. Emission spectra were collected exciting at 270 nm in the region between 350 and 750 nm, with excitation and emission slit width of 3 nm and 2 nm, respectively, using filter cut-off below 399 nm. Lifetime decay curves were obtained at room temperature using a pulsed lamp fixing excitation at 270 nm and emission fixed at 470 and 614 nm.

3. Results and discussion

Fig. 1 presents the TGA/DTA results of all viscous solutions used as precursor. A weight loss of approximately 97% is observed and assigned to the elimination of organic matter present in citrate mass used in the synthesis route (20 times in relation to the molar concentration of metals). The first loss is related to the elimination of water present in the viscous solutions. The second loss is due to the decomposition of anhydrous citrate and the third loss can be associated with the decomposition of many residues from the precursors used in the synthesis to form Sr_2CeO_4 photoluminescent material [18]. Thermograms allow the steps of the materials formation to be verified. Two endothermic peaks, around 68 and 185 °C, are related to the solvent evaporation and decomposition of organic matter, respectively. At approximately 350 °C there is an exothermic peak, related to combustion of citric acid and the thermo-oxidation of $Ce^{3+} \rightarrow Ce^{4+}$ [19]. The exothermic peak at region of 450 °C is assigned to organic species pyrolysis, during the rupture of the polymeric chain [20].

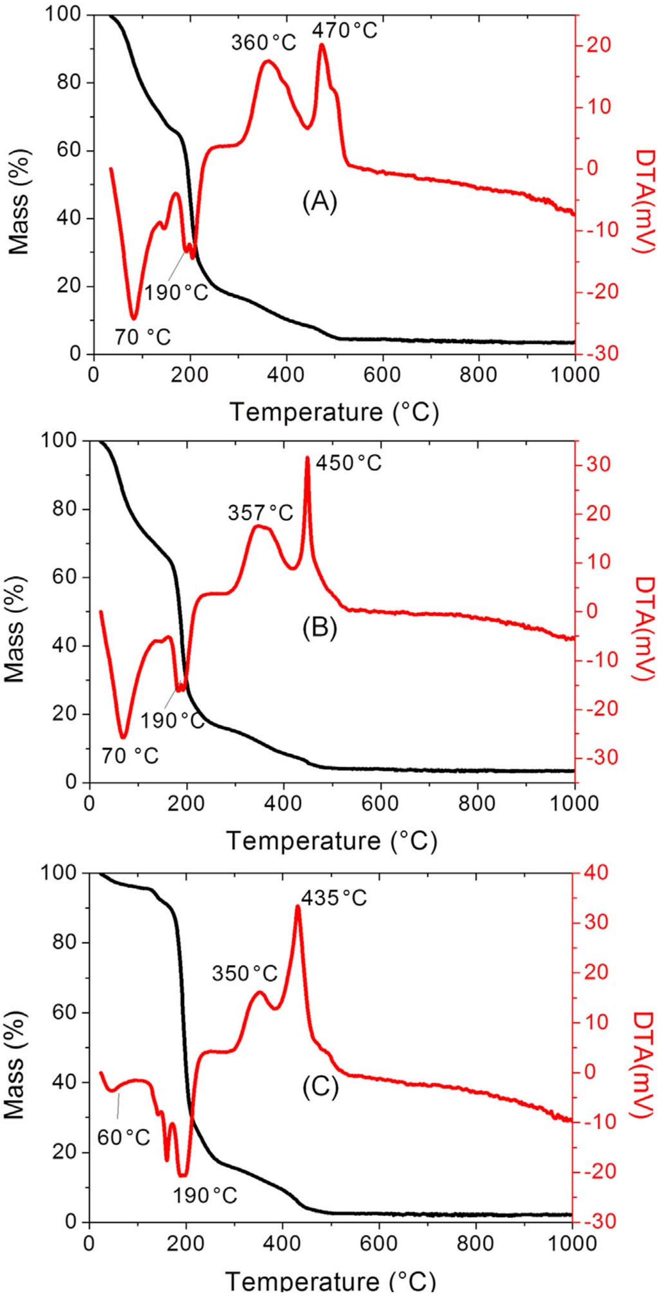

Fig. 1. TGA/DTA analysis performed for precursors obtained from solutions of (A) Sr^{2+} and Ce^{3+} (B) Sr^{2+}, Ce^{3+} and Ag^+ and (C) Sr^{2+}, Ce^{3+}, Ag^+ and Eu^{3+}.

Fig. 2 shows the XRD patterns of all materials obtained in the presence or absence of Ag^+. According the XRD patterns it is possible to observe the formation of Sr_2CeO_4 photoluminescence phase at 1100 °C without Ag^+ present, however the presence of secondary phases is found ($SrCeO_3$ and $SrCO_3$) [16]. In materials containing Ag^+, the presence of secondary phases are not observed, and all reflections are