Persistent luminescence of inorganic nanophosphors prepared by wet-chemical synthesis

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A B S T R A C T

The synthesis of efficient nanosized persistent luminescence materials remains a challenge for the community. Paradoxically, due to the dependence of the point lattice defects and the persistent luminescence efficiency, the control of the defect formation, favorable when the materials are prepared at high temperatures, normally leads to particle growth and sintering. In this work, efficient nanosized rare earth doped disilicates $Sr_2MgSi_2O_7:Eu^{2+},Dy^{3+}$ were synthesized via three different wet-chemical methods taking advantages of the microwave-assisted reduction process as a support step to produce high-quality polycrystalline materials. The crystallite size of the sample showed to be smaller when the decomposition temperature of the precursors is higher and close to the phase formation energy. The excitation VUV spectroscopy indicated that despite being nanocrystalline, the materials optical band gap has just a small difference compared one to another. The reduction of Eu^{3+} to Eu^{2+} was successfully obtained, since the f-d interconfigurational transitions of Eu^{2+} $4f^65d^1{\rightarrow}4f^7$ emission were observed in the blue region of the spectra. The persistent luminescence efficiency measured through its lasting decay time was close to the commercial materials references and with the advantage of having size control during the synthesis method that can lead to the size dependent applications of photonic materials.

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1. Introduction

Persistent luminescence is a class of luminescent phenomena comprehending the emission of electromagnetic radiation in a visible or NIR wavelength range for a prolonged period (from a couple seconds to many hours) after the stoppage of irradiation. Due to the imperfections that exist in any crystal structure, the charge carriers coming from the irradiation process play an important role in trapping-detrapping processes, increasing by this way the duration of the persistent luminescence [1–3].

This particular case of thermostimulated luminescence phenomenon has been observed over the past millennium and has been extensively studied since Vincenzo Cascariolo's discovery of the barite ($BaSO_4$), a sulfate mineral which exhibit persistent

luminescence after its reduction process to BaS (named Bologna stone) [4,5]. In this case, the emission came from the impurities of Cu^+, which was both the activator and the defect generator for the energy storage [5]. Through the history of the phosphors, some compounds, spotted due their persistent luminescence efficiency, including the Eu^{2+}-doped aluminates MAl_2O_4 (M = Ca, Sr, Ba) [6–9], which have been investigated since its discovery in 1996, and the Eu-doped Rare Earth (RE)-codoped disilicates $M_2MgSi_2O_7$ [1,7,10–13], known for their very long persistent emission. Recently, a few compounds such as the gallates, stannates, oxysulfides, etc., have been developed to achieve a long-wavelength emission/excitation (VIS-NIR) persistence [14–16]. These compounds are widely applied as the materials for safety/emergency signs, road luminescent paints, displays and theranostic applications supported by *in-vivo* biomarkers [5,17–20].

The synthesis methods of inorganic compounds play an important role in determining fundamental characteristics of particles, such as particle morphology, porosity, crystallite size,

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homogeneity of composition, defects distribution, etc. Since the solid-state reactions (i.e. ceramic method) are the easiest way to prepare oxide materials, a huge amount of materials has been prepared by heating the mixture of powdered raw precursors. However, these methods require a long heat treatment at high temperatures to form the desired product. This method normally creates large particle agglomerates with irregular morphology and heterogeneity, bringing disadvantages to photonic materials, once the luminescent properties are strongly dependent on these parameters [1,18,19]. In the meanwhile, wet-chemical methods such as sol-gel [20–23], combustion [1,24–26], hydrothermal [27–29], co-precipitation [30–32], modified-Pechini [33–36] and so on, show great potential to prepare nanoparticles with reasonable control of parameters [18,37].

Particularly, the strontium magnesium disilicate $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+} has been widely studied due its chemical stability [38] and very long persistent luminescence showing the Eu^{2+} broad emission band centered around 460 nm (the blue region of the spectrum) [39,40]. The luminescence mechanism of Eu^{2+} doped $Sr_2MgSi_2O_7$ involves primarily the photoexcitation by UV–Vis radiation, promoting the electronic transitions $4f^7(^8S_{7/2}) \rightarrow 4f^65d^1$ where the $4f^65d^1$ excited state is partially overlapped with the conduction band (CB) of matrix. Thus, charge carriers, i.e. the excited electrons, can be delocalized to the conduction band and trapped by lattice defects into the host crystal. Finally, these electrons are thermally detrapped as a function of k_bT recombining to the emitting ion [1,37,38].

The aim of this study is to understand the influence of different wet-chemical methods on the efficiency of disilicate $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+} nanoparticles. We have chosen the well-known modified-Pechini method, the complexation method using citric acid and oxalic acid with two different routes and the condensation method to prepare the material. Besides, we propose a microwave-assisted reduction process to speed up and enhance the conversion of Eu^{3+} to Eu^{2+}. In order to obtain the necessary data to explain crystallographic, morphologic, chemical and spectroscopic properties, these materials were investigated by thermogravimetric analysis (TG), X-ray powder diffraction (XPD), nanoparticle tracking analysis (NTA), instrumental neutron activation analysis (INAA) and VUV-UV-visible luminescence spectroscopy.

2. Experimental

2.1. Materials synthesis

Persistent luminescence nanoparticles of $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+} were prepared by three different wet-chemical routes: 1) modified-Pechini method; 2) complexation method and 3) condensation method, starting from the tetraethoxysilane ($SiC_8H_{20}O_4$ - TEOS), magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), strontium nitrate ($Sr(NO_3)_2$) and rare earth nitrates ($R(NO_3)_3 \cdot 6H_2O$, R = Eu^{3+} and Dy^{3+}). For these three methods, the ethanolic silica-based precursor solution was stirred along with the alkaline and rare earth nitrate aqueous solutions at 90 °C for 2 h, nitric acid and ammonium hydroxide were used to adjust the pH of the mixture to around 4. After a clear and translucent liquid was obtained, the solution was maintained in stirring at 70 °C for 15 h until a complete sol-gel reaction occurred. The Condensation method samples corresponds to this initial solution without any other reagent. For the Pechini method, samples were prepared by a mixing the proportion of 60:40 of citric acid ($C_6H_8O_7$ - 99.5%, Sigma-Aldrich) and ethylene glycol ($C_2H_6O_2$ - 99.8%, Sigma-Aldrich) into the initial solution described above. The metal ions and citric acid ratio varied as (1:1), (2:3) and (1:2). Finally, for the Complexation method, samples were prepared by a

mixture of either citric acid or oxalic acid ($C_2H_2O_4$ - 99%, Merck) with the initial solution using (1:2) of metal ions-complexation agent ratio. For all the methods, after the mixing, all solutions were stirred once again for another 2 h at 90 °C until the viscous gel became homogeneous. Then, the product was heat-treated at 300 °C for 2 h in a resistive furnace. The powder precursors were ground with a ceramic mortar and then calcined in alumina crucibles at different conditions, from 700 to 1200 °C for 1 and 5 h in air. Finally, the $Sr_2MgSi_2O_7$:Eu^{3+},Dy^{3+} powders were reduced in a domestic microwave oven (Electrolux MEF41, 1000 W) using granular coal as the susceptor/reducing agent, at 700 W for 15 min. The scheme of the microwave-assisted reduction process used in this work is shown in Supplementary Fig. S1 and was previous well described by Pedroso et al.(2016) [19].

2.2. Characterization

Powder precursors of each synthesis method, before the calcination process, were studied via thermogravimetric analysis [41]. Thermal decomposition behavior, expressed by the mass losses as a function of the temperature, was carried out using a TGA-51H (Shimadzu) equipment. The raw precursors were heated using a platinum crucible, from 25 up to 1100 °C with a 10 °C.min^{-1} rate, and a static air environment was used to simulate the furnace conditions during calcination process.

X-ray powder diffraction (XPD) [42] was carried out in a Rigaku Miniflex II diffractometer using a graphite monochromator with Kα Cu radiation source (λ = 1.5418 Å). The polycrystalline sample patterns were scanned continuously in 2θ between 15 and 60° with a step of 0.02° and 1 s of integration time per point. The samples were prepared on a glass sample holder and measured at room temperature for all heat-treatment, calcination and reduction conditions, indicating the effect of the phase transition through the thermal processes of the material. The mean crystallite size of the samples after calcination and reduction processes were determined via mathematical correlation of the most intense (121) peak profile of the main Sr-åkermanite phase (well-adjusted by a Pseudo-Voigt function) into the Scherrer equation. The instrumental broadening corrections were made using the (222) peak of Y_2O_3 as the standard reference [43].

The nanoparticle tracking analysis (NTA) [44] was carried out with a NanoSight NS300 (Malvern) equipment using a 532 nm (green) laser source and a sCMOS sensor to detect the Brownian motion of the particles. The samples were dispersed in water at room temperature, sonicated during 1 min and collected using a syringe pump in a continuous flow into the sample holder of the optical system. The measurements were record with 25 FPS (frames per second), totalizing 5 videos of 1 min each one for each sample.

Elemental distribution within the particles were analyzed by Energy Dispersive X-Ray (EDX) under Scanning Transmission Electron Microscopy (STEM) using a FEI -Titan microscope operating at 300 kV. High-Angle Annular Dark Field (HAADF) images were captured by a Fischione Model 3000 ADF detector. EDX spectra were collected by using a FEI SuperX quad windowless detector based on silicon drift technology with a solid angle of 0.7 steradian for about 15 min.

The concentration of rare earth elements present into the $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+} powders was obtained via Instrumental Neutron Activation Analysis (INAA) [45–47] carried out at the IEA-R1 Nuclear Research Reactor (located on the Research Reactor Center at IPEN-CNEN/SP). The samples were irradiated with a thermal neutron flux of 10^{13} cm^{-2} s^{-1} during 8 h, then a Canberra HPGe detector model GC2018 coupled to the Canberra DSA 1000 digital spectral analyzer was used to identify and quantify ^{153}Eu and ^{164}Dy radionuclides through the correspondent gamma ray decay.