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Effects of nanostructuring on luminescence properties of SrS:Ce,Sm phosphor: An experimental and phenomenological study

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ABSTRACT

In this work, we employ various experimental techniques to illustrate the effects of nanostructuring on improvement of the luminescence properties of the polycrystalline SrS co-activated by cerium and samarium dopants (*SrS*:*Ce*,*Sm*). The nano and microstructure *SrS*:*Ce*,*Sm* powders were synthesized by the co-precipitation and solid state diffusion methods, respectively, followed by the spark plasma sintering (SPS) process to densify powders into pellet shape. It is observed that the photo-luminescence (PL), radio-luminescence (RL), and optically stimulated luminescence (OSL) emission intensity of the nanostructure samples are significantly improved with respect to the microstructure samples. Moreover, by using an accurate photomultiplier tube, we measured the CW-OSL decay curves of the samples to demonstrate much higher and faster sensitivity of the nanostructure *SrS*:*Ce*,*Sm* for in-flight and online OSL radiation dosimetry. The obtained absorption and emission spectra are used for phenomenology of the electronic band structure of the *SrS*:*Ce*,*Sm* micro and nano-phosphors inside the band gap. The proposed phenomenological electronic structures are then used to clarify the role of Ce^{3+} and Sm^{3+} localized energy levels in the luminescence properties of the nano and microstructure samples. It is argued that electronic transitions from the $^2T_{2g}$ state of Ce^{3+} and the $^4G_{5/2}$ state of Sm^{3+} have strong contribution to the PL and RL emission spectra, while in the OSL mechanism, the Sm^{3+} $^4G_{5/2}$ state is mainly responsible for electrons trapping.

1. Introduction

Thermo-Luminescence (TL) and Optically Stimulated Luminescence (OSL) are two well-known radiation dosimetry techniques based on the luminescence phenomenon. In the OSL technique, a crystalline insulator or semiconductor is exposed to ionizing radiation (X, gamma, or beta rays) for a specific period of time and then is stimulated by an optical source with a proper wavelength to exhibit luminescence [1–3]. Synthesis and development of various OSL materials have extended applications of this technique to personal [4,5], space [6–9], security [1,10] and medical [5,11–13] dosimetry. The alkaline earth sulfides (AESs) co-activated by cerium and samarium dopants (i.e. *SrS*:*Ce*,*Sm*) were found to be appropriate OSL materials in real-time radiation monitoring sensors [1,14]. These sensors are suitable to measure dose or dose-rate in harsh radiation environments where the immediate readout and indeed the prompt luminescence of sensors are required [15,16]. They have been significantly used for pulsed dose-rate facilities [9], medical accelerator (radiation therapy) [17,18], space radiation dosimetry [7,19–21] and also for the high energy physics experiments at the CERN LHC accelerator [22]. Moreover, rare earth doped AESs are excellent phosphor materials for X-ray radiation imaging plates, IR sensors, and optical storage memories [5,23,24]. The rare earth dopants create localized electronic states in the band gap of host material which are responsible for electron trapping and electron-hole recombination. Therefore, it is well established that rare earth dopants have significant roles in controlling the luminescence properties of nano and bulk materials [5,25–28].

It is found that nano-phosphors exhibit enhanced luminescence properties, relative to micro-phosphors, due to increased surface to

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volume ratio and quantum size effect [29–35]. Thermoluminescence response of SrS:Ce and SrS:Bi nanostructures exposed to UV and gamma rays have been investigated by Vij et al. [23,36] and Chawla et al. [37]. Mishra et al. [38,39] have recently studied the optical and TL properties of SrS:Ce nano-phosphor. The study and comparison of OSL nanostructure materials with their microstructure samples have been reported for Al_2O_3:C [40], $SrSO_4$:Eu [30], $K_2Ca_2(SO_4)_3$:Cu [32] and $Y_3Al_5O_{12}$:Er, Yb [41,42]. While the bulk (microstructure) phase of SrS:Ce,Sm material is widely investigated in real-time and online OSL dosimetry [9,14,22,43,44], the nanostructure phase of this OSL material has not yet been investigated.

Hence, our specific aim in this work is to investigate effects of nanostructure on improvement of luminescence properties of SrS:Ce,Sm material. In addition, to phenomenology of luminescence mechanisms, the role of localized energy levels associated to Ce^{3+} and Sm^{3+} in PL, RL and OSL emission spectra were evaluated. The nano and micro structures of Ce and Sm co-doped SrS powder have been synthesized by co-precipitation and solid state diffusion methods, respectively. The prepared polycrystalline micro and nano powders have been sintered by spark plasma sintering (SPS) method in pellet shape with identical diameter and mass. The SPS method is a process for sintering and consolidation of powders using simultaneously electrical current (pulsed DC) and pressure. This method is specially used to densify a nanostructure pellet and preserve nanoparticles size by minimization Ostwald ripening [45]. Heating rate and holding time in this process are higher and shorter than the other conventional press-sinter methods respectively. Both of these characteristics are advantages of this method in sintering of nano-powders with slight growth of grains [45,46]. The structural analysis, morphology, and elemental composition were verified by X-ray diffraction (XRD), scanning electron microscopy (SEM), and electron dispersive X-ray spectroscopy (EDS) techniques, respectively. The UV–Vis absorption spectra, Photo-Luminescence (PL), Radio-Luminescence (RL) and Optically Stimulated Luminescence (OSL) of SrS:Ce,Sm nano-phosphor are investigated and compared to their corresponding microstructure material. The Continuous-Wave OSL (CW-OSL) decay curves of nano and microstructures SrS:Ce,Sm pellets irradiated by X-rays have been investigated and compared to the commercial α-Al_2O_3:C result.

2. Experimental procedures

2.1. Materials and synthesis methods

The SrS:Ce,Sm micro- and nano-phosphors were prepared using two different methods. The solid state diffusion method was adopted to prepare micro-phosphors while nano-phosphors were synthesized by the co-precipitation technique. The starting materials for micro powders production were $SrSO_4$ (99.0%), $Na_2S_2O_3\cdot 5H_2O$ (98.5%), activated charcoal (96.0%), $Ce(NO_3)_3\cdot 6H_2O$ (99.9%), $Sm(NO_3)_3\cdot 6H_2O$ (99.9%) and ethanol (98.0%). The stoichiometric mixtures of raw materials were weighted and thoroughly ground by an agate mortar. The amounts of cerium and samarium were 0.02 and 0.01 mol%, respectively. The cerium nitrate and samarium nitrate were separately dissolved in ethanol, to achieve a homogeneous dispersion of dopants within the powder mix. After mixing, the mixed powder was taken into an alumina crucible and this crucible was placed in a larger porcelain crucible filled with carbon and closed with a lid and then was fired in a muffle furnace at 1000 °C for 2 h in a strong reducing atmosphere. After heating, the crucibles were removed and placed in atmosphere to cool. After cooling, the material was pulverized using agate pestle and mortar to get fine powder.

The synthesis of nano-phosphors was started from $SrCl_2\cdot 6H_2O$ (99.9%), $Na_2S_2O_3\cdot 5H_2O$ (98.5%), EDTA (ethylene diamine tetra-acetic acid) (98.0%), $Ce(NO_3)_3\cdot 6H_2O$ (99.9%), $Sm(NO_3)_3\cdot 6H_2O$ (99.9%), 1-thioglycerol (99.9%) and deionized water. A 0.20M EDTA solution was prepared by dissolving a suitable quantity of EDTA in 50 ml of the deionized water. 25 ml of $0.1994MSrCl_2\cdot 6H_2O$ solution was added as a source of the Sr^{2+} ion. A 0.001 M $Ce(NO_3)_3\cdot 6H_2O$ and a 0.0005 M $Sm(NO_3)_3\cdot 6H_2O$ solutions were then added to the solution as dopants. 100 ml of 1.00 M $Na_2S_2O_3\cdot 5H_2O$ solution was also added as a source of the S^{2-} ion. A 10 ml of 0.05 M capping agent (1-thioglycerol) was mixed drop-wise with the solution to control the particles size. The solution was heated at 80°C for 90 min and then dried in an oven at 100°C for 24 h. The solid portions were collected by centrifugation and washed with the deionized water twice and three times with ethanol. The final precipitation was placed in an alumina crucible and annealed in a muffle furnace at 600°C for 3 h in a carbon reducing atmosphere to recrystallize to NaCl phase of SrS.

Finally, the synthesized polycrystalline SrS:Ce,Sm (0.02 and 0.01 %mol) powders in the micro and nano structures were sintered by the Spark Plasma Sintering (SPS) method for 5 min under a pressure of 50 MPa and a temperature of 1600°C in a graphite die with 8 mm diameter and samples were prepared in pellet form as indicated in Fig. 1.

2.2. Methodology and instrumentations

The structural characterizations (phase purity and average crystallite sizes) of the powder and pellet samples (in micro and nano structures) were carried out using a PANalytical X'Pert Pro MPD X-ray diffractometer (Cu K$_\alpha$, 40 kV, 30 mA). The surface morphology and elemental composition were determined by Scanning Electron Microscopy (SEM) and Electron Dispersive X-ray Spectroscopy (EDS) analyses using the TESCAN SEM system.

UV–Visible absorbance spectra of nano and microstructure samples have been recorded using Perkin Elmer Lambda 1050 model UV–Vis spectrometer in the spectral range of 200–500 nm at room temperature as aqueous colloidal suspensions.

The PL excitation spectra were recorded with a Perkin Elmer LS-55 Fluorescence Spectrometer, but the PL emission spectrum measurement was carried out using a Cadmium-Mercury lamp (excitation wavelength 320 nm) as an excitation source and the high resolution spectrometer (HR4000CG-UV-NIR, Ocean Optics, Inc.) for recording the emitted luminescence in the spectral range between 200 and 1100 nm. A Hoya U-340 filter was used in front of the lamp to prevent wavelengths other than 320 nm.

The OSL decay curves were measured using an in-house OSL reader system. A 100 mW diode laser at 980 nm wavelength and a solid-state Nd:YAG laser at 532 nm wavelength were used for stimulation of SrS:Ce,Sm and commercial α-Al_2O_3:C (TLD-500) samples respectively. The luminescence emission was collected by

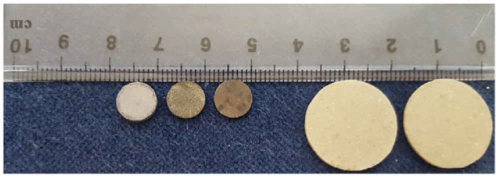

Fig. 1. SrS:Ce,Sm pellet samples prepared by sintering of the synthesized powders using the SPS method.