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Pressure-assisted combustion synthesis of red-emitting $SrIn_2O_4$: Eu^{3+} phosphor powders for applications in solid state white lamps

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Red-emitting phosphor powders of $SrIn_2O_4$ activated with Eu^{3+} ions were synthesized by a high pressure assisted combustion method. X-ray diffraction analysis of the crystalline properties of these powders revealed single phase SrIn2O4 for Eu concentrations up to 4 atomic % of Eu. The photo and cathodoluminescence emission spectra of $SrIn_2O_4$: Eu^{3+} powder shows bright red emission mainly caused by the $^5D_0 \rightarrow {}^7F_2$ intra-shell transition of Eu^{3+}. Furthermore, photoluminescence excitation (PLE) spectroscopy revealed that an efficient energy transfer from the $SrIn_2O_4$ host lattice onto the Eu ions is accomplished in addition to the excitation band peaked at $\lambda = 396$ nm that directly excites the Eu ions, making this material an excellent candidate for applications in solid state white-emitting lamps.

Key words: Rare Earth, Luminescence, Solid state lamps.

Introduction

The most popular approach to fabricate white-light emitting diodes (W-LEDs) is that attained by covering a blue emitting InGaN LED die with a yellow emitting phosphor powder. Yttrium aluminum garnet doped with cerium (YAG : Ce) is commonly used as phosphor for this purpose. However, white light emitting devices fabricated in this way deliver bi-chromatic white light with a poor color quality (CRI~70) [1] due to the low intensity of the red component emission of YAG:Ce. Research is being made to find new phosphors to supply intense emission in the red region. Oxides are promising phosphor materials thanks to their wide band gap, low absorbance in the visible region, and their chemical and thermal stabilities [2]. Among the oxides, the red emitting material $SrIn_2O_4$: Eu^{3+} is very suitable for white LED applications, because, in addition to the advantage of an oxide, it has a strong absorption band at 396 nm, which matches perfectly with the emission spectrum of InGaN LEDs.

Rare earth doped $SrIn_2O_4$ has been typically synthesized by the solid state reaction method, which is known to be very slow [3-6], and recently by the Pechini method [7]. Here we report on the synthesis and characterization of red emitting $SrIn_2O_4$: Eu^{3+} powders by a pressure assisted combustion method. This method has been used for other rare earth (RE) activated oxide phosphors and it has been observed that it promotes a better integration of the RE ions into the host lattice, which enhances the luminescent properties of materials [8].

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Experimental

Microcrystalline powders of $SrIn_2O_4$ and $SrIn_2O_4$: Eu^{3+} were synthesized by combustion synthesis using indium nitrate [$In(NO_3)_3 \cdot xH_2O$ Puratronic 99.99%] and strontium nitrate [$Sr(NO_3)_3 \cdot H_2O$ Puratronic 99.9965%], europium nitrate [$Eu(NO_3)_3 \cdot 6H_2O$ REacton 99.9%] as precursors and hydrazine [N_2H_4] as reductive non-carbonaceous fuel. The concentration of Eu^{3+} in $SrIn_2O_4$: Eu^{3+} was 0.04 in molar weight. The precursors were weighed in the appropriate stoichiometric ratio and dissolved in de-ionized water in a quartz beaker. The resulting mixture was homogeneous and had a gelatinous consistency. The beaker with the mixture was introduced in to a high pressure reactor. The first step was to flush the reactor with argon for ~15 minutes to create an inert atmosphere, then the reactor was closed. Secondly, the temperature was raised to 100 ºC and the argon flow was started again for about 10 minutes to remove the water vapor. The third step was to close the reactor exhaust and open the argon inlet to pressurize it up to ~2.75 MPa. The fourth step was to gradually increase the reactor temperature up to 340 ºC and hold this for 15 minutes to let the exothermic reaction occur in a pressurized environment. Once the reaction has finished, the exhaust valve was carefully opened to release the pressure and to flush the reactor with argon to evacuate any residual gas. Finally, the powders were removed from the high pressure reactor and heat treated at 1,100 ºC for 4 h in a muffle furnace with a static air atmosphere.

All the powders were characterized by X-ray diffraction (XRD) in a Philips X'pert diffractometer with CuK_α radiation ($\lambda = 0.15406$ nm). The powder morphology was analyzed by scanning electron microscopy (SEM) in a JEOL JSM-5300 SEM microscope. Photoluminescence (PL) spectra were collected with a fluorescence spectrophotometer (Hitachi FL-4500). Cathodoluminescence (CL) was measured with a spectrometer consisting of a 0.25 m monochromator (Oriel MS260i) and a thermoelectrically cooled CCD (InstaspecIV). The spectrometer was coupled with a quartz optic fiber to an ultra high vacuum (UHV) CL chamber equipped with a 10 keV electron gun (Kimball Physics). All the measurements were made at room temperature.

Results and Discussion

$SrIn_2O_4$ has an orthorhombic crystal structure with a space group of *Pnam*(62) and lattice parameter values $a = 9.83$ Å, $b = 11.5$ Å and $c = 3.27$ Å. Figure 1 shows the XRD profiles of $SrIn_2O_4$: Eu (4 at%) and pure $SrIn_2O_4$, in both samples, it was found that the predominant reflections correspond to the $SrIn_2O_4$ phase (JCPDS card file No. 33-1336). Some small residues of other two phases, SrO and In_2O_3, indexed with Greeks α and β, respectively, are also present demonstrating that the conversion of crystalline phases to $SrIn_2O_4$, is almost complete during the treatment at 1,100 ºC. It is important to note that in these phosphor samples the europium oxide is absent. This is a clear indication of the excellent rare earth ion incorporation into the $SrIn_2O_4$ host achieved by the high pressure combustion synthesis method [8-10].

A representative SEM image of $SrIn_2O_4$: Eu^{3+} powders is shown in Fig. 2. It can be observed that elongated grains with a uniform size distribution and average lengths of ~2 μm are formed showing that coalescence is promoted during the thermal treatment at 1,100 ºC.

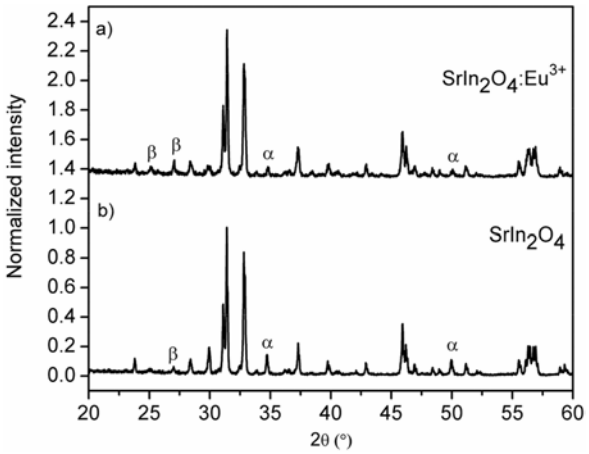

Fig. 1. X-ray powder diffraction patterns of: a) pure $SrIn_2O_4$ and b) 4 at% Eu doped $SrIn_2O_4$. All non labeled reflections correspond to the $SrIn_2O_4$ phase, α and β labels indicate SrO and In_2O_3, respectively.

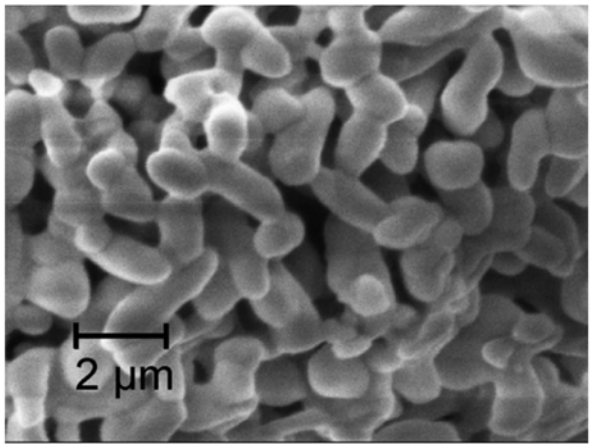

Fig. 2. SEM image of $SrIn_2O_4$: Eu^{3+} microcrystalline powders, operating at 10 kV.

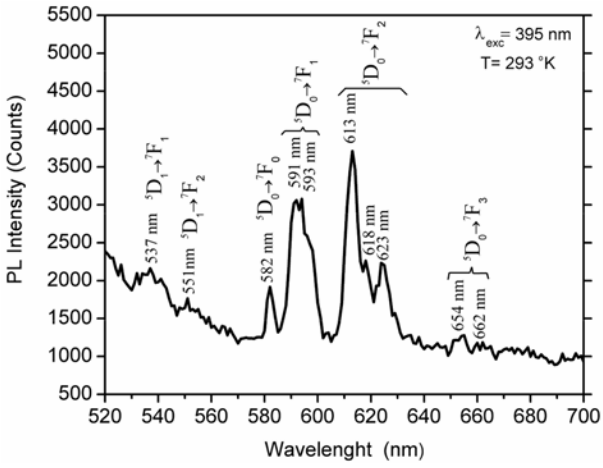

Fig. 3. PL emission spectra of $SrIn_2O_4$: Eu^{3+} powders (4 at%), with $\lambda_{exc} = 395$ nm.

The $SrIn_2O_4$: Eu^{3+} (4 at%) powder shows intense red emissions under long UV excitation. The strongest contributions to the red emission come from the Eu^{3+} ions, mainly from hypersensitive $^5D_0\rightarrow{}^7F_2$ transition forced by an electric dipole mechanism, and the doublet peak located at 591 nm and 593 nm due to the $^5D_0\rightarrow{}^7F_1$ magnetic dipole. Figure 3 shows the PL emission spectrum of $SrIn_2O_4$: Eu^{3+} (4 at%) powder acquired under 395 nm excitation wavelength. The main features of this spectrum are the sharp emission lines originated from within the intra-shell transitions from the $^5D_{0,1,2,3}$, excited levels to the ^7F_J ground states of Eu^{3+}, the identification of each

Table 1. Eu^{3+} ion transitions in a $SrIn_2O_4$ host lattice

Transition	Wavelength (nm)
$^5D_1\rightarrow{}^7F_1$	537
$^5D_1\rightarrow{}^7F_2$	557
$^5D_0\rightarrow{}^7F_0$	582
$^5D_0\rightarrow{}^7F_1$	591, 593
$^5D_0\rightarrow{}^7F_2$	613, 618, 623
$^5D_0\rightarrow{}^7F_3$	**654, 662**

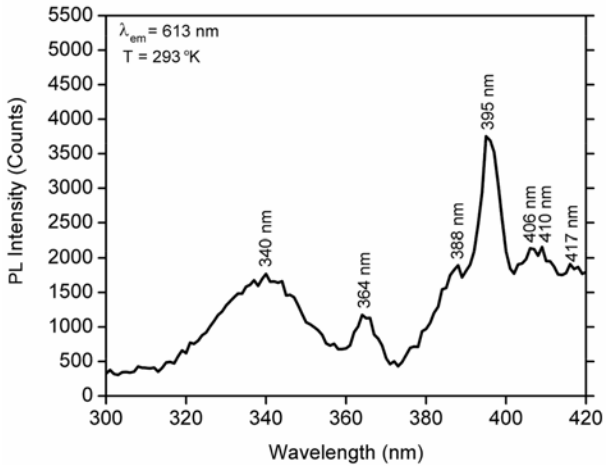

Fig. 4. PL excitation spectra of 4 at% Eu doped $SrIn_2O_4^+$ powders, with $\lambda_{em} = 613$ nm.

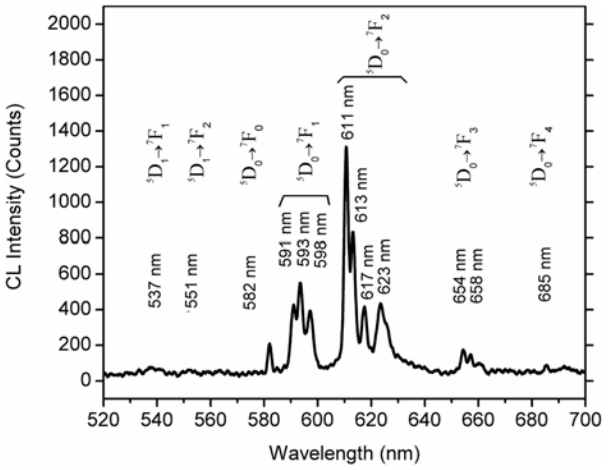

Fig. 5. CL spectra of $SrIn_2O_4$: Eu^{3+} powders (4 at%), electron energy was 4 keV at 80 mA.

peak is in Table 1.

An efficient energy transfer from the $SrIn_2O_4$ host lattice to the Eu^{3+} activator ions is confirmed by the PL excitation spectra shown in Fig. 4. This spectrum was acquired with fixed emission at $\lambda = 613$ nm. A broad excitation band centered $\lambda = 340$ nm can be observed and is attributed to the band gap of the $SrIn_2O_4$ host lattice. The spectrum shows narrow excitation lines at longer wavelengths corresponding to the characteristic f→f transitions of Eu^{3+}, these lines are assigned as follows: $^7F_0 \rightarrow {}^5D_4$ ($\lambda = 364$ nm), $^7F_0 \rightarrow {}^5G_4$ ($\lambda = 388$ nm) and the main excitation $^7F_0 \rightarrow {}^5L_6$ ($\lambda = 395$ nm).

Bright red emission is also observed under electron excitation, the CL spectrum in Fig. 5. confirms that the red luminescence of this material is obtained due to Eu^{3+} doping. The higher resolution of the CL spectrometer (0.2 nm), in comparison with the PL spectrometer (1 nm), allows the detection that the $^5D_0 \rightarrow {}^7F_2$ transition is a doublet formed by a peak at $\lambda = 611$ nm and another at $\lambda = 613$ nm.

Conclusions

Luminescent powders of $SrIn_2O_4$: Eu^{3+} were successfully fabricated by combustion method in a high pressure environment (~2.75 MPa), which promoted the integration of the Eu^{3+} ions into the $SrIn_2O_4$ lattice as confirmed by X-ray diffraction measurements. After thermal treatment at 1,100 °C for 4 hours the powder consists of uniformly distributed grains of ~2 μm. Photoluminescence and cathodoluminescence emission spectra showed strong emission lines owed to the Eu^{3+} ions. Finally, photoluminescence excitation measurements confirmed that an efficient energy transfer from the $SrIn_2O_4$ host lattice onto the Eu ions is promoted in addition to the excitation band peaked at $\lambda = 396$ nm that directly excites the Eu ions, making this material an excellent candidate for applications in solid state white-emitting lamps. The quantum yield efficiency of $SrIn_2O_4$: Eu^{3+} phosphor powders prepared by high pressure combustion synthesis is ~40% and could be increased by optimizing experimental parameters. Based on its photoluminescent properties (emission and photoexcitation characteristics) this oxide is an excellent candidate as a red emitter in white light-emitting solid state lamps.

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