

Visible light emission under UV and IR excitation of rare earth doped ZrO₂ nanophosphor

E. De la Rosa ^{a,*}, L.A. Diaz-Torres ^a, P. Salas ^b, R.A. Rodríguez ^c

^a Centro de Investigaciones en Óptica A.C., Lomas del Bosque 115, A.P. 1-948, León, Gto. 37150, Mexico

^b Instituto Mexicano del Petroleo, Eje Central Lázaro Cárdenas 152, D.F. 07730, Mexico

^c Universidad de Guadalajara en Lagos, Lagos de Moreno, Jal. 47460, Mexico

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Abstract

Strong visible emission under UV (320 nm) and IR (967 nm) excitation on ZrO₂:Sm³⁺ and ZrO₂:Er³⁺ nanophosphors were obtained and the concentration effect on the luminescence and crystalline structure is reported. Experimental results shows that phase composition depend on the ion concentration. The visible emission obtained under UV excitation is produced by the transitions $^4G_{5/2} \rightarrow ^6H_{5/2,7/2,9/2}$ of Sm³⁺ through a non-radiative energy transfer process from the host to the active ion. Energy transfer and quenching effect due to ion concentration was confirmed by measuring the fluorescence decay time. Green (545 nm) and red (680 nm) emissions bands were observed under IR excitation troughs an upconversion process. It was proved that visible emission for both nanophosphor could be tuned by controlling the ion concentration. The nature of this behavior is discussed taking into account the phase composition for ZrO₂:Sm³⁺ and two photon absorption and cross-relaxation process was considered for ZrO₂:Er³⁺ nanophosphor.

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1. Introduction

In the field of photonics materials, the demand for high performance systems is increasing everyday. For active applications such as bulk, fiber lasers and planar waveguides the fluorescence quantum efficiency is the key factor controlling the performance of the material. When the number of non-radiative pathways increases, the fluorescence quantum efficiency decreases considerably. One of the most important non-radiative processes that every material shows is the multiphonon relaxation by the vibration bands of the system. When the frequency of this vibration band increases the non-radia-

tive decay rate increases that in turn will reduce the quantum efficiency. The stretching frequency of ZrO₂ matrix is about 470 cm⁻¹ that is very small compared to that of other hosts. This low phonon energy opens up the possibility of higher efficient luminescence of active ions incorporated into ZrO₂ matrix. Furthermore, due to its superior hardness, high refractive index, optical transparency, chemical stability, photothermal stability, high thermal expansion coefficient, low thermal conductivity and high thermomechanical resistance, it can be used in a variety of photonics and industrial applications [1].

Considerable amount of work has been reported on the mechanical and other physical properties of ZrO₂, whereas only few research work have been done on the luminescence properties of this material. The reported results on the optical studies include the

* Corresponding author. Tel.: +52 477 773 1017; fax: +52 477 717 5000.

E-mail address: elder@cio.mx (E. De la Rosa).

photoluminescence of sol–gel derived amorphous and tetragonal crystalline phase thin films of $\text{ZrO}_2\text{:Eu}^{3+}$, Tb^{3+} , Sm^{3+} systems [2,3]. Bulk zirconium oxide has been grown by the Skull method and cubic doped samples have been characterized [4]. More recently, the interest in rare earth doped nanophosphor has been increased. Electrons confinement effect is not expected due the localization of electrons in atomic orbitals of active ions. However, excitation dynamics is influenced by the nanoscopic interaction and has been reported a dependence of the luminescence efficiency with particle size [5,6]. The interest on this new rare earth doped nanophosphor is to produce visible emission for application such as solid state lighting, displays and new generation television screen. In particular, the development of UV LED open up new possibility to obtain visible emission at any wavelength with the proper phosphor that must be developed [7]. Visible emission can also be obtained pumping the nanophosphor with an IR source by upconversion process [8]. This is an interesting approximation considering that IR source is a well developed technology. Using this approximation it is possible to obtain white light for solid state lighting but new nanophosphors with high upconversion efficiency and emission in the basic colors are required. The emission of this kind of nanophosphors is based in two photon absorption process and also finds application in biomedicine [9]. Recently, evidence of energy transfer from the host to the active ion for $\text{ZrO}_2\text{:Sm}^{3+}$ nanophosphor excited at 320 nm was reported [10]. It was also reported visible emission by upconversion process in $\text{ZrO}_2\text{:Er}^{3+}$ nanophosphor pumped at 967 nm [11,12]. In the present work, the concentration effect on the crystalline structure and luminescence properties by downconversion in $\text{ZrO}_2\text{:Sm}^{3+}$ and upconversion in $\text{ZrO}_2\text{:Er}^{3+}$ are reported.

2. Experimental

The samples were prepared by using the sol–gel method. All chemicals were reactive grade and supplied by Aldrich, Inc. Pure ZrO_2 was obtained by mixing zirconium *n*-propoxide (ZP) as precursor in a solution of ethanol (ETOH), nitric and hydrochloric acid at room temperature and vigorous stirring. Doped samples were prepared by adding different molar concentrations (0.2, 1, 1.5 and 2 mol%) and (0.16, 0.98 and 3.46 mol%) of Sm_2O_3 and Er_2O_3 , respectively. The obtained solution was stirred for 90 min, then CO_2 -free distilled water in a molar rate of 1/4 was added dropwise to manipulate the gel and oxolation processes. The samples were aged at room temperature, dried at 120 °C for 24 h and annealed at 1000 °C for 10 h.

The crystalline structure of the samples was investigated by X-ray diffraction (XRD), using a Siemens D-

500 equipment provided with a Cu tube with K_α radiation at 1.5405 Å. The X-ray spectra were obtained from 20° to 70° with increments of 0.2° and a swept time of 3 s. The optical absorption spectra were measured with a Perkin–Elmer UV–VIS–NIR Lambda 800 by using a 1.5 in. integrating sphere (Labsphere Co.). The fluorescence emission spectra for $\text{ZrO}_2\text{:Sm}^{3+}$ were obtained with a Perkin–Elmer fluorometer LS50. The upconversion emission of $\text{ZrO}_2\text{:Er}^{3+}$ was obtained pumping with a diode laser centered at 967 nm and a monochromator (Acton Research) with a resolution of 1 nm with a Hamamatsu Photonics R955 photomultiplier tube connected to a PC was used. All measurements were done at room temperature.

3. Results and discussion

3.1. Visible emission by downconversion in $\text{ZrO}_2\text{:Sm}^{3+}$

The concentration of the active ion determines the phase composition of the nanocrystals, see Fig. 1. The crystalline structure of $\text{ZrO}_2\text{:Sm}^{3+}$ nanophosphor annealed at 1000 °C is dominated by the monoclinic structure (98 wt.%) for low ion content (0.2 mol%) and is reduced to 27 wt.% for 2 mol% of active ion being dominant the tetragonal phase; the average crystallite size range from 36 nm to 14 nm for monoclinic and from 54 nm to 42 nm for tetragonal phase. The phase composition and average crystallite size for the crystalline structure was obtained by using the Ritveld method. A full analysis of the crystalline composition and lattice parameter as function of the samarium dopant concentration and annealing temperature has been reported recently [13].

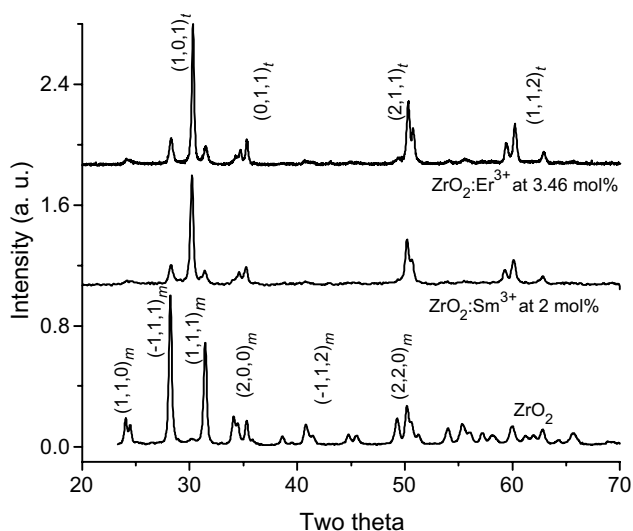


Fig. 1. XRD for undoped and Sm^{3+} and Er^{3+} doped nanocrystalline ZrO_2 phosphor annealed at 1000 °C.

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