



ELSEVIER

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: [www.elsevier.com/locate/jlumin](http://www.elsevier.com/locate/jlumin)

# Enhancement of the luminescence intensity by co-doping $\text{Mn}^{2+}$ into $\text{Er}^{3+}$ -doped $\text{SrAl}_2\text{O}_4$



L.K.S. de Herval<sup>a</sup>, Y. Tuncer Arslanlar<sup>b</sup>, M. Ayvacikli<sup>b</sup>, F. Iikawa<sup>c</sup>, J.A. Nobrega<sup>a</sup>, P.S. Pizani<sup>a</sup>, Y. Galvão Gobato<sup>a</sup>, N. Can<sup>b,d</sup>, M. Henini<sup>e</sup>, M.P.F. de Godoy<sup>a,\*</sup>

<sup>a</sup> Departamento de Física, Universidade Federal de São Carlos (UFSCAR), 13560-905 São Carlos, SP, Brazil

<sup>b</sup> Celal Bayar University, Faculty of Arts and Sciences, Department of Physics, 45010 Muradiye-Manisa, Turkey

<sup>c</sup> Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), 13083-859 Campinas, SP, Brazil

<sup>d</sup> Physics Department, Jazan University, P.O. Box 114, 45142 Jazan, Kingdom of Saudi Arabia

<sup>e</sup> School of Physics and Astronomy, Nottingham Nanotechnology and Nanoscience Centre, University of Nottingham, Nottingham NG7 2RD, UK

## ARTICLE INFO

### Article history:

Received 14 November 2014

Received in revised form

9 February 2015

Accepted 17 February 2015

Available online 26 February 2015

### Keywords:

Luminescence

$\text{SrAl}_2\text{O}_4$

Rare-earths

Optical amplifier

## ABSTRACT

Structural and optical properties of erbium- and manganese-doped strontium aluminates ( $\text{SrAl}_2\text{O}_4$ ) phosphor materials synthesized by a solid state reaction were investigated. The samples presented the fundamental optical transitions due to  $\text{Er}^{3+}$  and  $\text{Mn}^{2+}$  which are typical features of the well-diluted doping process. A significant enhancement of the  $\text{Er}^{3+}$  optical emission band at 1530 nm was observed when the matrix is co-doped with Mn. Photoluminescence intensity under ultraviolet excitation was three times larger as compared to samples without Mn content. A model of energy transfer mechanism from  $\text{Mn}^{2+}$  to  $\text{Er}^{3+}$  ions due to optical energy matching is proposed to explain the experimental results. This result, presented first time, can be applied as useful tool for developments in optical communications.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

In optical fiber communications it is well known that minimum attenuation is observed in the near-infrared (IR) spectral range. Since the presence of hydroxyl ions causes an absorption peak at 1400 nm, the transmission range splits into two windows. One of these windows, denoted as C-band, has the great advantage to use optical fiber amplifiers using erbium-doped fiber amplifiers (EDFA) in the optical wavelength at 1530 nm which matches with Er ion optical transition between  $I_{13/2}$  and  $I_{15/2}$  levels. Therefore, studies of Er-doped materials and their related enhancement of the emission intensity are interesting issues for applied physics. Strontium aluminate ( $\text{SrAl}_2\text{O}_4$ ) is a promising system for Er ion doped matrix due to the transparency for Er optical emission and good chemical stability [1].  $\text{SrAl}_2\text{O}_4$  is a material with several technological applications in the visible optical range such as safety indication, emergency lighting, road signs and displays in dark environments based on its long lasting phosphorescence (LLP) characteristic [2–6]. To extent the applicability of strontium aluminates to infrared optical devices like optical amplifiers it is interesting to allow another channel of optical pumping beside the

characteristic 980 nm used in EDFA [7]. Furthermore, a proposal of co-doping can be used as an alternative to add new possibilities for pumping lines using the ultraviolet optical range provided by light sources as GaN diode lasers [8].

The co-doping process is usually employed to match optical emissions and absorptions between ions and enhance some other properties. Optical matching is a mechanism in which the emission of one element is in the same energy range of the absorption from a second element. The literature reports examples of this mechanism to enhance  $\text{Mn}^{2+}$  emissions [9] using  $\text{Nd}^{3+}$  in  $\text{SrAl}_2\text{O}_4:\text{Mn}^{2+}$  and  $\text{Ce}^{3+}$ ,  $\text{Eu}^{2+}$  and  $\text{Dy}^{3+}$  on emission of  $\text{Mn}^{2+}$ -doped phosphors [10]. Furthermore many lanthanides have been employed for up- and down-conversion in order to enhance spectral response in solar cells [11]. Recently the efficiency of energy transfer between  $\text{Eu}^{2+}$  and  $\text{Er}^{3+}$  has demonstrated the ability to design optical matching features and refine desired emissions [12].

We propose the use of a metal transition ion, such as manganese, to couple Er transitions in order to enhance the optical emission at 1530 nm. This work involves a systematic study using photoluminescence (PL) spectroscopy in the visible and near-infrared ranges considering Er and Mn as potential dopants with matching optical characteristics. A few reports explore in details this point, using indeed the up-conversion mechanism by exciting  $\text{Er}^{3+}$  at 1550 nm to enhance  $\text{Mn}^{2+}$  emission in  $\text{Y}_2\text{O}_2\text{S}$  [13]. Our samples consist of pure matrix, Er-doped, Mn-doped and Mn–Er-doped

\* Corresponding author. Tel.: +55 1633519727; fax: +55 1633614835.

E-mail address: [mgodoy@ufscar.br](mailto:mgodoy@ufscar.br) (M.P.F. de Godoy).

$\text{SrAl}_2\text{O}_4$  synthesized by solid state reaction. Under ultraviolet excitation the presence of  $\text{Mn}^{2+}$  increases the  $\text{Er}^{3+}$  luminescence in doped strontium aluminates as compared to the sample without Mn. The result is explained by the effect of the energy transfer mechanism from  $\text{Mn}^{2+}$  and  $\text{Er}^{3+}$ .

## 2. Experimental

We studied a set of four samples consisting of pure  $\text{SrAl}_2\text{O}_4$ ; Mn-doped  $\text{SrAl}_2\text{O}_4$ ; Er-doped  $\text{SrAl}_2\text{O}_4$  and Mn and Er doped  $\text{SrAl}_2\text{O}_4$ . We have labeled them pure, Mn, Er and MnEr, respectively. Structural phase identification was carried out using a Philips X'Pert Pro MPD diffractometer (XRD) with  $\text{Cu-K}\alpha$  radiation line ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature. We have performed photoluminescence (PL) measurements by using two excitation lines of a HeCd laser (the visible line at 442 nm and the ultraviolet (UV), at 325 nm) at 20 mW. The emissions were collected by a SPEX 0.5 m monochromator and a S20 photomultiplier in UV-visible optical range and a Triax 190 Jobin Yvon with a Ge detector in near-IR spectral range. Photoluminescence excitation spectroscopy (PLE) was carried out employing a Xe lamp as excitation source, dispersed in a 0.5 m SPEX 1870 monochromator and the emission at 1530 nm was collected by a 0.5 m Princeton monochromator and a Ge detector.

### 2.1. Samples

The samples were produced by bulk materials synthesis using the conventional solid state reaction method. Stoichiometric mixtures of high purity (typically 99.9–99.999%)  $\text{SrCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MnCO}_3$  and  $\text{Er}_2\text{O}_3$  were weighted out according to nominal composition. The starting compounds were mixed in the presence of an appropriate flux such as  $\text{H}_3\text{BO}_3$  (boric acid) and then heated in a furnace for two hours in a platinum crucible up to the required temperature (1400 °C) in a controlled atmosphere (Ar with 15% of  $\text{H}_2$ ). Finally, the prepared materials were cooled for about 24 h in the furnace. The nominal dopant concentration is 1.0% mole for singly Mn and Er-doped samples and 1.0% Mn and 0.8% Er for MnEr-doped sample [1,14,15].

## 3. Results and discussions

Typical X-ray diffraction patterns of the resultant  $\text{Er}^{3+}$ ,  $\text{Mn}^{2+}$  co-doped  $\text{SrAl}_2\text{O}_4$  are shown in Fig. 1. The Miller indices ( $hkl$ ) of most predominant diffraction peaks are (211), (220), (211), (002) and (031). The analysis of relative peaks intensities in the XRD allows the presence and identification of possible impurity phases with compositions different from  $\text{SrAl}_2\text{O}_4$ . The lattice parameters were extracted from the XRD data on the basis of the pattern  $\text{SrAl}_2\text{O}_4$ . The obtained lattice parameters agree with a monoclinic  $\text{SrAl}_2\text{O}_4$  phase ( $a \approx 8.440 \text{ \AA}$ ,  $b \approx 8.821 \text{ \AA}$ ,  $c \approx 5.157 \text{ \AA}$ ,  $\beta \approx 93.4$ ) with no measurable change in the cell volume. It is also noticed that the small amount of  $\text{Er}^{3+}$ , as well as  $\text{Mn}^{2+}$  co-doping play almost no effect on the basic crystal structure of  $\text{SrAl}_2\text{O}_4$ . In general, the substitution of  $\text{Mn}^{2+}$  difference of ionic radius between  $\text{Sr}^{2+}$  and  $\text{Mn}^{2+}$  is 40.0% and the electro negativity of  $\text{Mn}^{2+}$  (1.55) is larger than that of  $\text{Sr}^{2+}$  (0.95) this could make the excess Mn to form “ $\text{MnO}_2$ ” [16]. A systematic study of Mn doping levels on aluminates requires further investigation.

Fig. 2 shows the PL spectra at room temperature in infrared (a) and visible (b) optical ranges when the samples were excited by the Er-resonant 442 nm laser line. Several emission bands around 0.81 eV (1530 nm) were detected for Er-doped  $\text{SrAl}_2\text{O}_4$  and they are assigned to the transitions  $\text{S}_{3/2} \rightarrow \text{I}_{9/2}$  (0.775 eV),  $\text{I}_{13/2} \rightarrow \text{I}_{15/2}$  (0.81 eV) and  $\text{H}_{11/2} \rightarrow \text{I}_{9/2}$  (0.831 eV) [6]. Additional observed

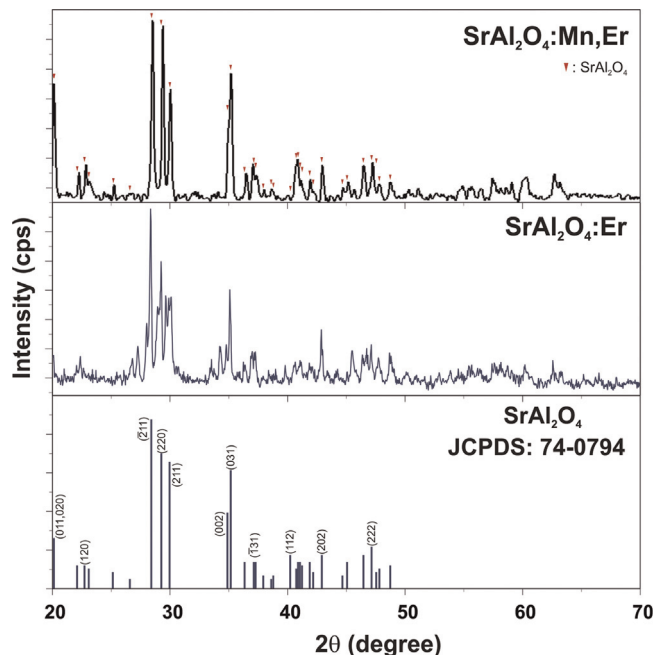


Fig. 1. Typical X-ray diffraction patterns of the  $\text{Er}^{3+}$ ,  $\text{Mn}^{2+}$  co-doped  $\text{SrAl}_2\text{O}_4$ .

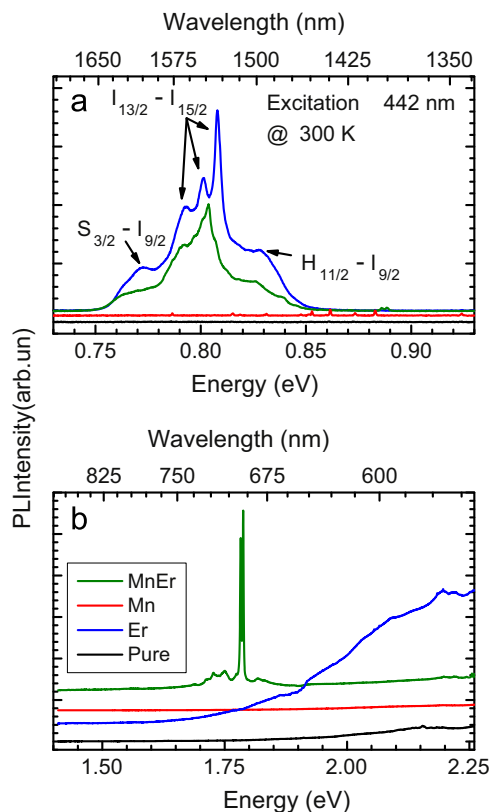


Fig. 2. PL spectra for excitation at  $\lambda_{\text{exc}} = 442 \text{ nm}$  in (a) infrared and (b) visible range. All samples were excited by same laser intensity.

peaks at 0.805 eV and 0.796 eV are attributed to the Stark splitting in  $\text{I}_{13/2} \rightarrow \text{I}_{15/2}$  transition induced by the matrix crystal field on Er ion [17]. For the same intensity excitation, Er-doped material presents higher PL intensity emission under the same intensity excitation probably due to its higher molar concentration. As expected, no luminescence in IR range is observed for pure and singly Mn-doped aluminates. For visible range two consecutive

Download English Version:

<https://daneshyari.com/en/article/5398832>

Download Persian Version:

<https://daneshyari.com/article/5398832>

[Daneshyari.com](https://daneshyari.com)