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Enhancement of the luminescence intensity by co-doping Mn^{2+} into Er^{3+}-doped $SrAl_2O_4$

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ABSTRACT

Structural and optical properties of erbium- and manganese-doped strontium aluminates ($SrAl_2O_4$) phosphor materials synthesized by a solid state reaction were investigated. The samples presented the fundamental optical transitions due to Er^{3+} and Mn^{2+} which are typical features of the well-diluted doping process. A significant enhancement of the 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 Mn^{2+} to 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.

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 ($SrAl_2O_4$) is a promising system for Er ion doped matrix due to the transparency for Er optical emission and good chemical stability [1]. $SrAl_2O_4$ 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 Mn^{2+} emissions [9] using Nd^{3+} in $SrAl_2O_4$:Mn^{2+} and Ce^{3+}, Eu^{2+} and Dy^{3+} on emission of 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 Eu^{2+} and 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 Er^{3+} at 1550 nm to enhance Mn^{2+} emission in Y_2O_2S [13]. Our samples consist of pure matrix, Er-doped, Mn-doped and Mn–Er-doped

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$SrAl_2O_4$ synthetized by solid state reaction. Under ultraviolet excitation the presence of Mn^{2+} increases the 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 Mn^{2+} and Er^{3+}.

2. Experimental

We studied a set of four samples consisting of pure $SrAl_2O_4$; Mn-doped $SrAl_2O_4$; Er-doped $SrAl_2O_4$ and Mn and Er doped $SrAl_2O_4$. 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 Cu-K_α radiation line ($\lambda = 1.5418$ Å) 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%) $SrCO_3$, Al_2O_3, $MnCO_3$ and Er_2O_3 were weighted out according to nominal composition. The starting compounds were mixed in the presence of an appropriate flux such as H_3BO_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 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 Er^{3+}, Mn^{2+} co-doped $SrAl_2O_4$ are shown in Fig. 1. The Miller indices (*h k l*) 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 $SrAl_2O_4$. The lattice parameters were extracted from the XRD data on the basis of the pattern $SrAl_2O_4$. The obtained lattice parameters agree with a monoclinic $SrAl_2O_4$ phase ($a \approx 8.440$ Å, $b \approx 8.821$ Å, $c \approx 5.157$ Å, $\beta \approx 93.4$) with no measurable change in the cell volume. It is also noticed that the small amount of Er^{3+} , as well as Mn^{2+} co-doping play almost no effect on the basic crystal structure of $SrAl_2O_4$. In general, the substitution of Mn^{2+} difference of ionic radius between Sr^{2+} and Mn^{2+} is 40.0% and the electro negativity of Mn^{2+} (1.55) is larger than that of Sr^{2+} (0.95) this could make the excess Mn to form "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 $SrAl_2O_4$ and they are assigned to the transitions $S_{3/2} \rightarrow I_{9/2}$ (0.775 eV), $I_{13/2} \rightarrow I_{15/2}$ (0.81 eV) and $H_{11/2} \rightarrow I_{9/2}$ (0.831 eV) [6]. Additional observed peaks at 0.805 eV and 0.796 eV are attributed to the Stark splitting in $I_{13/2} \rightarrow I_{15/2}$ 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

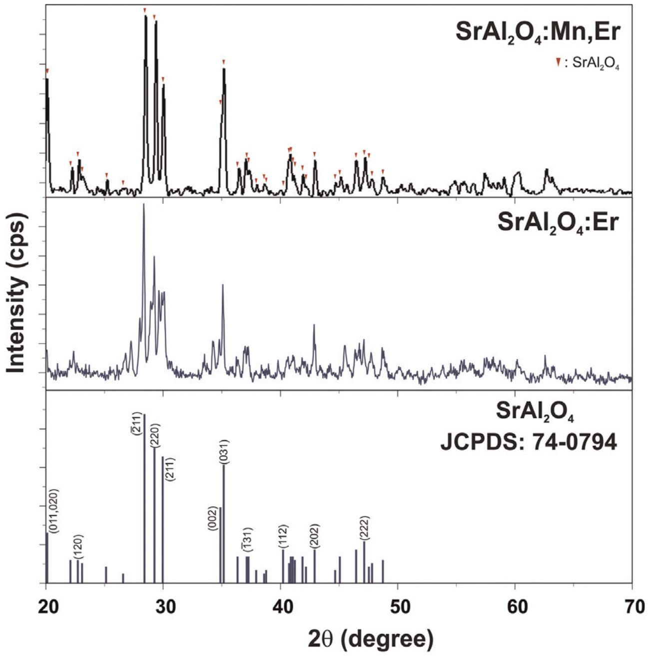

Fig. 1. Typical X-ray diffraction patterns of the Er^{3+}, Mn^{2+} co-doped $SrAl_2O_4$.

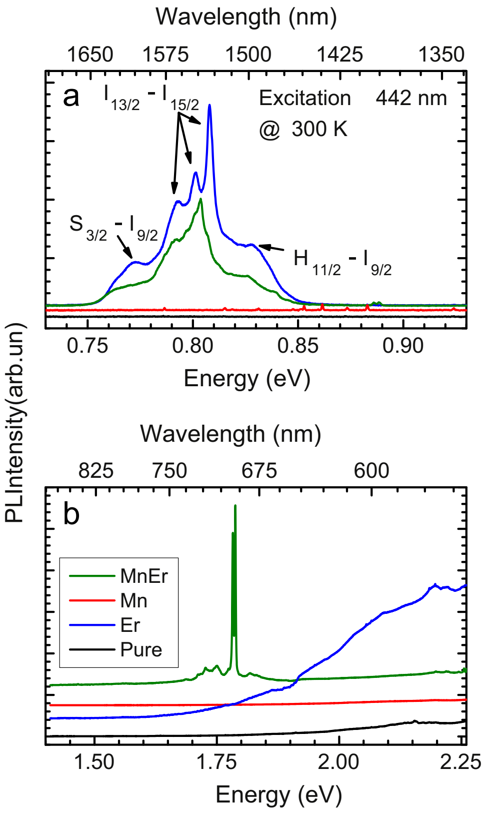

Fig. 2. PL spectra for excitation at $\lambda_{exc} = 442$ nm in (a) infrared and (b) visible range. All samples were excited by same laser intensity.

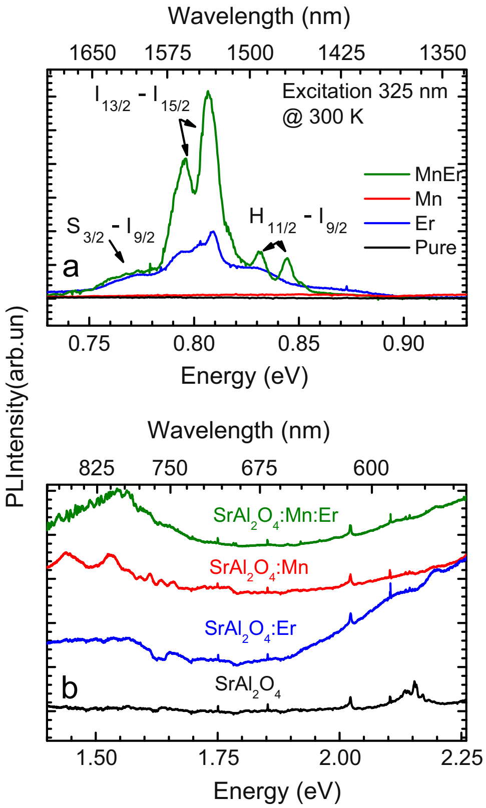

Fig. 3. PL spectra for excitation at λ_{exc}=325 nm in (a) infrared and (b) visible range. There is an enhancement about 300% for 0.81 eV (1530 nm) emission for MnEr-doped aluminate as compared to singly Er-doped. Emissions around 1.5 eV are attributed to Mn^{2+} ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

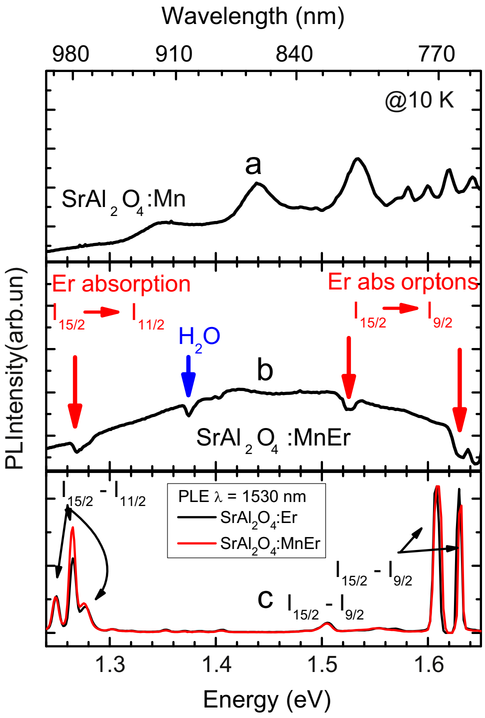

Fig. 4. PL spectra at 12 K for Mn^{2+} intra-atomic emission in (a) $SrAl_2O_4$:Mn sample. (b) $SrAl_2O_4$:Er^{3+}, Mn^{2+}. For MnEr doped the band emission is broader and exhibits Er absorption lines as indicated by red arrows. The blue arrow indicates water dimer absorption. (c) PLE spectrum at 1530 nm for Er and MnEr doped samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

peaks around 1.78 eV (1.787 eV and 1.792 eV) are detected just for the sample containing Mn and Er. These peaks may be related to Cr^{3+} impurities in the precursor Al_2O_3 [18]. The broad band above 2 eV is associated to the glue used to fix samples in the holder.

PL spectra at room temperature for the whole set of samples shown in Fig. 3 employed higher photon energy λ_{exc}=325 nm laser line. The Er-related peaks around 0.8 eV are presented in Fig. 3(a), where the transitions $S_{3/2}\rightarrow I_{9/2}$, $I_{13/2}\rightarrow I_{15/2}$ and $H_{11/2}\rightarrow I_{9/2}$ are evidenced. In contrast to the results shown in Fig. 2, these peaks present higher intensity for Mn-co-doped sample than for singly Er-doped sample. The PL intensity is increased by 3 times under the same experimental conditions. We remark that both excitation energies are roughly in the resonance with the excited states of the Er ion. However, only the 325 nm line is close to the resonance with the Mn ion optical transition. This means that for the Mn-co-doped sample there is an extra absorption.

For Mn and MnEr-doped samples we observed an additional band around 1.5 eV associated to Mn-ions transition as shown in Fig. 3(b). For singly Mn-doped sample this optical transition is well resolved in two peaks at 1.441 eV and 1.535 eV. This red-color transition is usually associated with the crystal field splitting of d-orbitals into the T_{2g} and E_g orbitals of Mn in octahedral coordination environment in the host matrix [13,19,20].

Interesting features are present in PL spectra for both Mn doped samples at low temperatures for excitation at 325 nm (Fig. 4). Mn-doped (Fig. 4a) and MnEr-doped (b) samples show two lines and a broad band, respectively, where both transitions are associated to Mn ions. However, for the latter some dips appear which can be related to the Er absorptions. In order to address this point, we performed photoluminescence excitation measurements detected at the 1530 nm Er emission as shown in Fig. 4c. The observed absorption lines around 1.265 eV are associated to the transitions between $I_{15/2}\rightarrow I_{11/2}$ levels. Absorptions around 1.5 eV and 1.6 eV are related to the transitions between $I_{15/2}\rightarrow I_{9/2}$ split levels due to crystal field. The absorption line at 1.375 eV is attributed to the water dimer absorption in atmosphere laboratory [21]. Except for the peak at 1.375 eV the positions of the absorption lines coincide with the dips observed in the broad emission band from MnEr-doped sample.

The energy level diagram presented in Fig. 5 is used to explain the different PL features when we use these different laser lines for excitation. The energy level diagrams of Er and Mn show the respective allowed transitions. In fact, the position of the dips (red arrows in Fig. 5) coincides with the Er transitions shown by red arrows on the PL spectrum in Fig. 4b. The excitation at 442 nm (2.805 eV) is resonant to the erbium states ($I_{15/2}$–$F_{3/2}$) [13] and the excited electron follows the decay processes indicated by red light line in Fig. 5. The radiative emissions were assigned as transitions $S_{3/2}\rightarrow I_{9/2}$, $I_{13/2}\rightarrow I_{15/2}$, and $H_{11/2}\rightarrow I_{9/2}$ observed in Fig. 1. However, the line at 442 nm cannot excite Mn ions, because there is no allowed transition for this photon energy.

For UV excitation, the λ_{exc}=325 nm (3.815 eV) is close to both the $P_{3/2}$ level of Er^{3+} and also $D_{1/2}$ level of Mn^{2+} and both ions can be excited simultaneously. For singly Mn doped and Er doped samples the electrons relax (dark red line in Fig. 5) emitting a photon around 1.5 eV and 0.81 eV, respectively. In the case of MnEr-doped sample, both atoms may absorb incident photons. The photons emitted by Mn at 1.5 eV present a broad band due to interaction with distorted lattice neighborhood at different sites. Therefore, they are eventually absorbed by Er ions through the transition between $I_{15/2}$ and $I_{9/2}$ levels (1.525 eV) and other indicated dips. Consequently a consistent transfer of energy between Mn and Er ions seems to occur, which contributes to the enhancement of the $I_{13/2}\rightarrow I_{15/2}$ (0.81 eV) Er emission intensity.

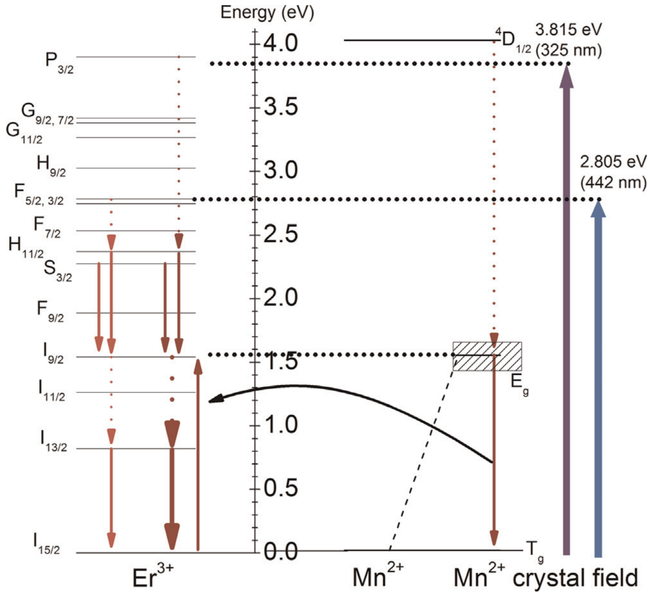

Fig. 5. Energy levels diagrams [11] for Er^{3+} and Mn^{2+} with the schematic of energy transfer mechanism from Mn to Er ions. The light and dark red arrows indicate the decay processes when the sample is excited by 442 nm or 325 nm laser lines, respectively (dashed lines: non-radiative transitions and solid lines: radiative transitions). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

Our experimental data strongly evidence that the introduction of Mn in Er-doped $SrAl_2O_4$ leads to an enhancement of the photoluminescence emission intensity in the near infrared range by ultraviolet optical excitation. This result is associated to an energy transfer mechanism from Mn^{2+} to Er^{3+}. Although being a two-step process, the observations are consistent with an improvement in infrared emission efficiency. The fundamental emission from Mn^{2+} matches well to Er^{3+} levels and it contributes considerably to the increase of the luminescence intensity at 0.8 eV (1530 nm) by a factor of 300% as compared to non-Mn content sample. We suggest that this effect can play an important role for applications related to optical amplifiers in infrared range.

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