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To cite this article: Lilian Syrbu *et al* 2007 *J. Opt. A: Pure Appl. Opt.* **9** 401

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# Red and green nanocomposite phosphors prepared from porous GaAs templates

Lilian Syrbu<sup>1</sup>, V V Ursaki<sup>2</sup>, I M Tiginyanu<sup>1,2</sup>, Ksenia Dolgaleva<sup>3</sup>  
and Robert W Boyd<sup>3</sup>

<sup>1</sup> National Center for Materials Study and Testing, Technical University of Moldova, MD-2004, Chisinau, Moldova

<sup>2</sup> Laboratory of Low-Dimensional Semiconductor Structures, Institute of Applied Physics, Academy of Sciences of Moldova, MD-2028, Chisinau, Moldova

<sup>3</sup> Institute of Optics, University of Rochester, Rochester, NY 14627, USA

Received 24 November 2006, accepted for publication 2 March 2007

Published 21 March 2007

Online at [stacks.iop.org/JOptA/9/401](http://stacks.iop.org/JOptA/9/401)

## Abstract

Rare-earth-containing oxide nanocomposites are prepared in a controlled fashion from porous GaAs templates. The initial porous GaAs network is replaced by a  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> one during annealing at temperatures from 500 to 900 °C. The impregnation of Eu and Er lanthanides from EuCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH and ErCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH solutions results in the formation of xenotime EuAsO<sub>4</sub> and ErAsO<sub>4</sub> microcrystals finely dispersed into the native oxide matrix. The 4f–4f intrashell transitions in Eu<sup>3+</sup> and Er<sup>3+</sup> ions ensure red and green emission from EuAsO<sub>4</sub> and ErAsO<sub>4</sub> nanophases. These nanocomposites may prove useful in future generations of optoelectronic and photonic devices.

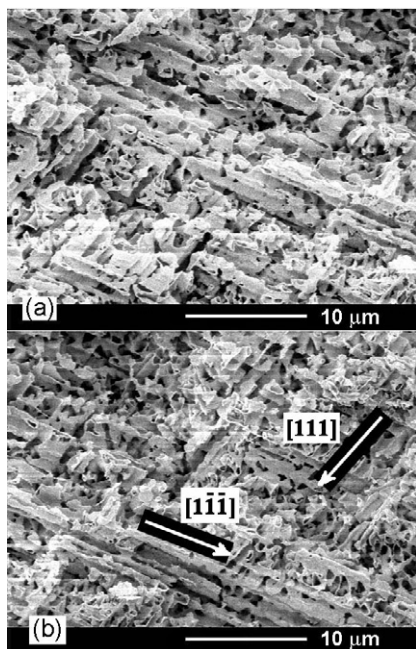
**Keywords:** porous materials, photoluminescence, x-ray diffraction

Over the last few years, there has been considerable interest in the understanding and control of materials including luminescent materials on a nanometre scale. The control of phosphor structure and morphology at a nanometre level allows one to tailor its macroscopic properties such as emission spectrum and luminous efficiency. Rare-earth-ion-doped nanocrystals dispersed in a transparent medium are of special interest as potential optoelectronic materials. This issue becomes especially important in connection with the growing interest in the development of random lasers (see, e.g., [1] and references therein). Porous semiconductor templates prepared by electrochemical treatment of bulk substrates are ideal matrices for the preparation of a variety of composites including those doped with rare-earth elements as well as media with controlled scattering properties for the development of random lasers. Recently, an attempt was undertaken to dope Eu ions into a porous GaP template [2]. It was supposed that the visible emission comes from the Eu<sup>3+</sup> ions incorporated into the porous GaP host. Apart from wide-bandgap semiconductors transparent to visible light, porous templates like GaAs and InP are of interest for doping with rare-earth ions exhibiting intrashell transitions in the IR spectral range, for instance, the 1500 nm transition in Er<sup>3+</sup> ions which is a popular choice in a wide variety of

telecommunication applications. Moreover, the easy oxidation of semiconductor templates results in nanostructured oxides which are the most commonly used materials in phosphor technologies. In this paper, we report on the development of technological methods for the preparation of nanocomposites on the basis of porous GaAs templates doped with Eu and Er lanthanides. We identify the nanophases and the electronic transitions responsible for the visible emission from these composites.

(100)-oriented n-GaAs:S wafers cut from Czochralski-grown ingots were used for the fabrication of porous GaAs layers. The free electron concentration in the as-grown substrates was  $0.3 \times 10^{18} \text{ cm}^{-3}$  at 300 K. The anodic etching was carried out in a double-chamber electrochemical cell. A four-electrode configuration was used: a Pt reference electrode in the electrolyte, a Pt electrode on the sample, a Pt counterelectrode, and a Pt working electrode. The electrodes were connected to a galvanostat/potentiostat. The anodization was carried out in 5% HCl aqueous electrolyte at a constant current density of  $100 \text{ mA cm}^{-2}$ . The temperature was kept constant at 23 °C. The area of the sample exposed to the electrolyte was  $0.2 \text{ cm}^2$ .

Eu<sup>3+</sup> and Er<sup>3+</sup> ions were incorporated into the por-GaAs layer from EuCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH and ErCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH solutions,



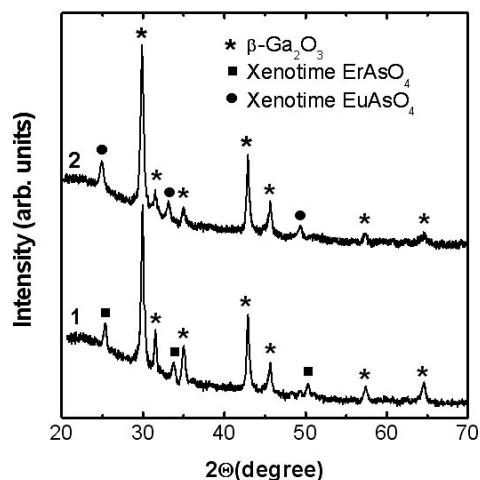
**Figure 1.** SEM images taken in cross section of an initially porous GaAs layer (a) and a sample annealed for 30 min at 600 °C (b).

respectively. Afterwards, the samples were annealed in a nitrogen flow containing less than 1% oxygen by using a halogen lamp heater during different periods of time ranging from several minutes to several hours at definite temperatures in the interval 400 to 1000 °C.

The morphology and the chemical composition microanalysis of etched samples were studied using a TESCAN scanning electron microscope (SEM) equipped with an Oxford Instruments INCA energy dispersive x-ray (EDX) system. The x-ray diffraction (XRD) analysis of the samples was performed with a Philips X-Pert MPD System PH 3710/1830 with Cu  $K\alpha_1$  radiation. The photoluminescence (PL) was excited by different lines of a SpectraPhysics Ar<sup>+</sup> ion laser and analysed in a quasi-backscattering geometry through a double spectrometer with 1200 grooves mm<sup>-1</sup> gratings producing a linear dispersion of 0.8 nm mm<sup>-1</sup> and equipped with a photomultiplier working in a photon counting mode. The spectral resolution was better than 0.5 meV.

The porous GaAs templates used in this work represent porous layers up to 100 μm thick with a three-dimensional structure containing crossing pores oriented along the  $\langle 111 \rangle_B$  crystallographic directions [3, 4], as illustrated in figure 1(a). The rare earth impurities introduced by impregnation into templates were found to be optically activated at annealing temperatures higher than 500 °C. In order to inhibit and easily control the oxidation of the porous template the annealing was performed in nitrogen flow containing less than 1% oxygen. Under these conditions, the oxidation of the skeleton walls starts at temperatures under 500 °C, and the porous template is totally oxidized at an annealing temperature of 500 °C after 30 min of annealing as demonstrated by the EDX and XRD analysis.

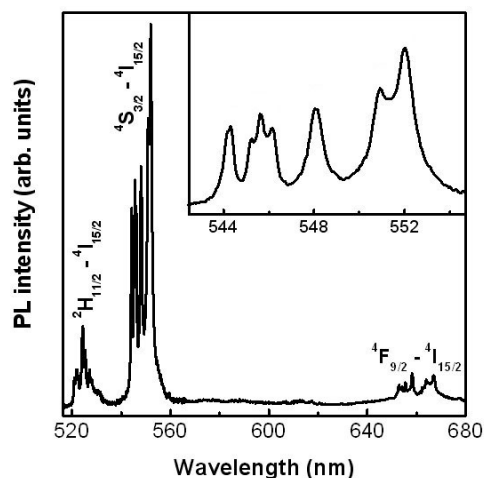
The EDX and XRD analyses of the oxide demonstrate the formation of a stoichiometric  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (monoclinic  $C2/m$ )



**Figure 2.** XRD analysis of composites prepared on GaAs templates infiltrated for 4 h with ErCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH (curve 1) and EuCl<sub>3</sub>:C<sub>2</sub>H<sub>5</sub>OH (curve 2) solutions with concentrations of 1 g/4 ml and annealed at 700 °C for 30 min.

phase (1997 JCPDS: 11-0370). Note that this is the most stable form of the Ga<sub>2</sub>O<sub>3</sub> oxide. The Ga atoms have two different environments in this structure, that is, half of the atoms are in tetrahedral sites and the other half in octahedral sites. It is well known that rare earth ions are rarely, if ever, found at the tetrahedrally coordinated sites of a III–V host because of their large ionic radii [5]. It was demonstrated that the presence of oxygen is imperative for achieving efficient emission from rare earth ions introduced into a III–V material [6, 7]. The oxygen co-doping leads to the formation of quasi-molecular centres at low impurity density [5–8] and to the segregation of an oxide phase at higher doping levels [9]. The theoretical study of the point defects in a monoclinic  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [10] showed that isovalent ions with a slightly larger ionic radius relative to Ga<sup>3+</sup> are likely to be stabilized at the octahedral gallium sites with a higher coordination index and a larger nearest-neighbour distance. However, the overly large rare earth ions prefer a coordination number higher than six, making their segregation into a separate oxide phase highly probable. In order to determine this issue and to identify the phases, we have prepared samples with a high density of the Eu or Er impurity. We found that the constitution of the composite is controlled by the conditions of infiltration and annealing. The density of the impurity can be controlled through the concentration of the infiltrated solution and the duration of time that the samples are held in the solution before the thermal treatment. Usually, the samples were held in the infiltrated solution for 4 h, and the content of Er or Eu in the obtained composite was found to increase linearly with their concentration in the solution reaching a value of 3 at.% at the concentration of 1 g ErCl<sub>3</sub> or EuCl<sub>3</sub> per 4 ml C<sub>2</sub>H<sub>5</sub>OH.

The composite represents ErAsO<sub>4</sub> (1997 JCPDS: 15-0751) or EuAsO<sub>4</sub> (1997 JCPDS: 15-0750) micro-crystallites incorporated into the porous Ga<sub>2</sub>O<sub>3</sub> native oxide structure at annealing temperatures above 500 °C for more than 30 min, as illustrated in figure 2. Annealing at temperatures lower than 500 °C for several minutes allows one to conserve a significant part of the zincblende GaAs skeleton. Interestingly,

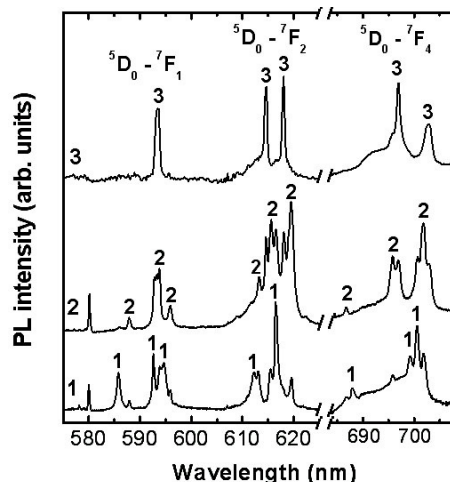


**Figure 3.** PL spectrum of a sample doped with Er measured at room temperature. Inset is the analysis of emission in the region of  $^4S_{3/2} \rightarrow ^4I_{15/2}$  transitions.

a morphology identical to that of the initial porous GaAs layer is preserved also after a lengthy annealing (30 min) at temperatures between 500 and 700 °C, as illustrated in figure 1(b), in spite of the fact that the skeleton is totally oxidized in these conditions. Moreover, the growing  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> oxide is well oriented since only several reflection peaks from this phase predominate the XRD spectrum (see figure 2). Only at annealing temperatures around 900 °C is the morphology of the sample changed and the XRD spectrum becomes identical to the one measured from  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> powder, indicating a totally disoriented oxide structure. As concerns the segregation of ErAsO<sub>4</sub> and EuAsO<sub>4</sub> phases, both of them belong to the xenotime (tetragonal  $I4_1/amd$ ) structure. It is known that the REAsO<sub>4</sub> oxides with a RE element having the atomic mass higher than Pm crystallize in a xenotime structure. Each RE ion in this structure is coordinated by eight oxygen atoms forming RO<sub>8</sub> dodecahedra. The point-group symmetry at the RE site is D<sub>2d</sub> ( $\bar{4}m2$ ). The sizes of ErAsO<sub>4</sub> and EuAsO<sub>4</sub> crystallites deduced from the XRD spectra according to the Debye–Scherrer formula vary from several nanometres to more than 100 nm, depending on the conditions of fabrication. The scanning EDX analysis with a resolution around 1  $\mu$ m shows a uniform distribution of ErAsO<sub>4</sub> and EuAsO<sub>4</sub> nanophases across the composite.

Analysis of the luminescence intensity under excitation by different laser lines shows that the highest luminescence intensity from samples doped with Er is observed under excitation by the 488.0 nm laser line, while in Eu doped samples this is achieved under the excitation by the 465.8 nm laser line. The fact that the photon energy of these lines corresponds exactly to the  $^4F_{7/2} \leftarrow ^4I_{15/2}$  and  $^5D_2 \leftarrow ^7F_0$  transitions in Er<sup>3+</sup> and Eu<sup>3+</sup> ions, respectively, suggests that the excitation occurs via respective transitions, followed by non-radiative relaxation to the lower energy states  $^2H_{11/2}$ ,  $^4S_{3/2}$  and  $^4F_{9/2}$  in Er<sup>3+</sup> ions and  $^5D_0$  in Eu<sup>3+</sup> ions. From these states, radiative transitions to the  $^4I_{15/2}$  ground state in Er and to the  $^7F_{1-4}$  states in Eu occur.

The PL spectrum of a sample doped with Er as illustrated in figure 3 proved to be independent of the annealing



**Figure 4.** PL spectra of samples doped with Eu and annealed for 30 min at 500 °C (curve 1), 700 °C (curve 2), and 900 °C (curve 3).  $T = 300$  K.

temperature, while the intensity of luminescence increases with increasing concentration of Er. The photoluminescence quantum efficiency of the best samples is estimated to be 5–10% using the integrated sphere. This observation suggests that emission comes from Er<sup>3+</sup> ions incorporated at true D<sub>2d</sub> sites of the xenotime ErAsO<sub>4</sub>, and the Er<sup>3+</sup> ions are well stabilized at these sites in the annealing temperature interval from 500 to 900 °C.

In contrast to Er-doped samples, Eu-doped materials exhibit a strong dependence of the emission spectrum upon the annealing temperature (see figure 4). One broad peak is observed at photon energies corresponding to  $^5D_0$ – $^7F_1$  transitions, two peaks are evidenced in the region of  $^5D_0$ – $^7F_2$  transitions and at least two peaks corresponding to  $^5D_0$ – $^7F_4$  transitions are found in the emission spectrum of samples annealed at 900 °C. This spectrum perfectly fits the one previously reported for xenotime EuAsO<sub>4</sub> [11] and is similar to the PL spectrum of an isostructural EuVO<sub>4</sub> compound [11–13]. The degeneracy of the  $^7F_n$  levels of Eu<sup>3+</sup> ions is only partially lifted by crystal fields at sites with D<sub>2d</sub> symmetry. Therefore, two energy levels (E and A<sub>2</sub>) are produced by crystal fields for the  $^7F_1$  level, and the  $^7F_2$  level is split also into two levels (E and B<sub>2</sub>). The very small splitting (5.4 cm<sup>-1</sup>) [11] of the E and A<sub>2</sub> levels corresponding to the  $^7F_1$  level is not resolved in the PL spectrum. However, the width of the peak around 593.6 nm indicates the overlap of bands related to the corresponding two transitions. The PL spectrum of samples annealed at 500 and 700 °C is more complicated, being dominated by two series of peaks labelled 1 and 2 for annealing temperatures 500 and 700 °C, respectively. This is clear evidence of the presence of other sites for the Eu<sup>3+</sup> ions in addition to the one with true D<sub>2d</sub> symmetry. The number of peaks corresponding to the  $^7F_1$  level (three) demonstrates that the symmetry of these sites is lower than that of the perfect crystal (D<sub>2d</sub>), therefore leading to complete lifting of the  $2J + 1$  degeneracy of the  $^7F_J$  levels. Note that the xenotime EuAsO<sub>4</sub> and the isomorphous EuVO<sub>4</sub> compounds were shown to be highly predisposed to the formation of crystallographically perturbed (defect) sites even

in high-quality single crystals [11, 12]. Our results demonstrate that the  $\text{Eu}^{3+}$  ions are stabilized in a crystallographic site of true  $D_{2d}$  symmetry only at an annealing temperature of  $900^\circ\text{C}$ , while at lower annealing temperatures different defect sites involving the  $\text{Eu}^{3+}$  ions are formed. The observation of lines around 580 nm in the PL spectrum of samples annealed at  $500$  and  $700^\circ\text{C}$  corresponding to the  ${}^5\text{D}_0$ - ${}^7\text{F}_0$  transition, which is strictly forbidden by the  $D_{2d}$  site symmetry, and their absence in samples annealed at  $900^\circ\text{C}$  corroborates this statement.

In conclusion, the results of this work demonstrate the controlled preparation of different rare-earth-doped oxide nanocomposites from porous GaAs templates impregnated with rare-earth ions and annealed at different temperatures. These composites are transparent for visible and UV light and may find applications as light emitters for integrated optoelectronic and photonic circuits. The composites prepared by annealing at temperatures lower than  $500^\circ\text{C}$  conserve partially the initial GaAs template skeleton and can be applied in devices which make use of rare-earth ion transitions in the IR spectral range, e.g. 1500 nm transition in  $\text{Er}^{3+}$  ions. The latter composites are also prospects for the design of multiphase random laser media in which the high-refractive index GaAs skeleton provides the strong light scattering necessary for the formation of laser micro-cavities, while the rare-earth-doped oxide nanophase plays the role of emitting and amplifying the electromagnetic radiation.

## Acknowledgments

This work was supported by US Civilian Research and Development Foundation under Grant Nos. MOR-1033-CH-03 and ME2-2527.

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