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Europium doped gallium oxide nanostructures for room temperature luminescent photonic devices

E Nogales¹, B Méndez¹, J Piqueras¹ and J A García²

¹ Departamento de Física de Materiales, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Madrid 28040, Spain

² Departamento de Física Aplicada II, Apartado 644, Universidad del País Vasco, 48080, Spain

E-mail: emilio.nogales@fis.ucm.es

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Abstract

Cathodoluminescence and photoluminescence techniques have been used to investigate room temperature light emission from β -Ga₂O₃:Eu nanostructures, which were obtained by two methods. In one of them, a mixture of Ga₂O₃/Eu₂O₃ powders was used as precursor material and annealed under an argon flow. In the other one, undoped β -Ga₂O₃ nanostructures were first obtained by thermal oxidation of metallic gallium and europium was subsequently incorporated by a diffusion process. Room temperature luminescence at 610 nm due to Eu³⁺ intraionic transitions from β -Ga₂O₃:Eu has been observed. Waveguiding of this red emitted light through the structures was shown.

(Some figures in this article are in colour only in the electronic version)

Semiconductor nanowires and nanobelts exhibit particular physical properties, very interesting for novel photonic nanodevices. These nanostructures may play different roles, such as light emitters [1, 2], waveguides [3, 4] or light detectors [5, 6]. In the last years, an intense activity has been carried out on nanostructures based on binary oxide semiconductors, such as ZnO or SnO₂ among others [7]. In particular, monoclinic β -Ga₂O₃ is a promising material for optoelectronic applications and the physical properties of thin films of this material have been the subject of study by several groups [8–12]. The main reasons for the strong interest on this material are its high thermal and chemical stability as well as its wide band gap, around 5 eV, while preserves n-type conductivity attributed in most of the cases to native oxygen vacancies [9, 13]. In fact, gallium oxide is the transparent conductive oxide with widest transparency range and its fairly high refractive index, around 2 in the visible–UV range, makes this oxide of interest for waveguiding applications. Its wide band gap enables to modify the luminescence properties by the incorporation of suitable ions in the Ga₂O₃ lattice. In particular, doping of Ga₂O₃ with optically active ions, such as rare earth (RE) ions, allows the fabrication of devices based on this material which can emit light in different wavelengths

spanning from the UV, all the way through the visible to the IR ranges. Although the intraionic emissions of the RE ions are usually stable and almost independent on the matrix, there are problems in rare earth doping of bulk semiconductors due to the difficulty to achieve effective concentrations or the need of further thermal treatments to activate the RE ion luminescence [14]. Some of these problems can be overcome in the case of nanostructures during the fabrication process.

There is a number of works related to undoped gallium oxide nanostructures with different shapes, e.g. nanowires, nanorods and nanobelts, obtained following different routes [7] and, in particular, thermal treatments involving vapor–solid (VS) or vapor–liquid–solid (VLS) mechanisms have been used for the growth of these nanostructures [11, 15]. Several works on light emitting doped gallium oxide have appeared during the last years. Eu³⁺ [16] and Cr³⁺ [8] ions were introduced in bulk gallium oxide, while Er³⁺ and Cr³⁺ ions have been introduced into gallium oxide nanostructures [4, 17, 18]. Waveguiding behavior of β -Ga₂O₃ nanowires doped with optically active ions, Cr³⁺ or Er³⁺, has been reported [4].

In this paper, we demonstrate the growth of Eu doped gallium oxide nanowires by two synthesis routes, which enable to grow the nanostructures and to activate the europium ions.

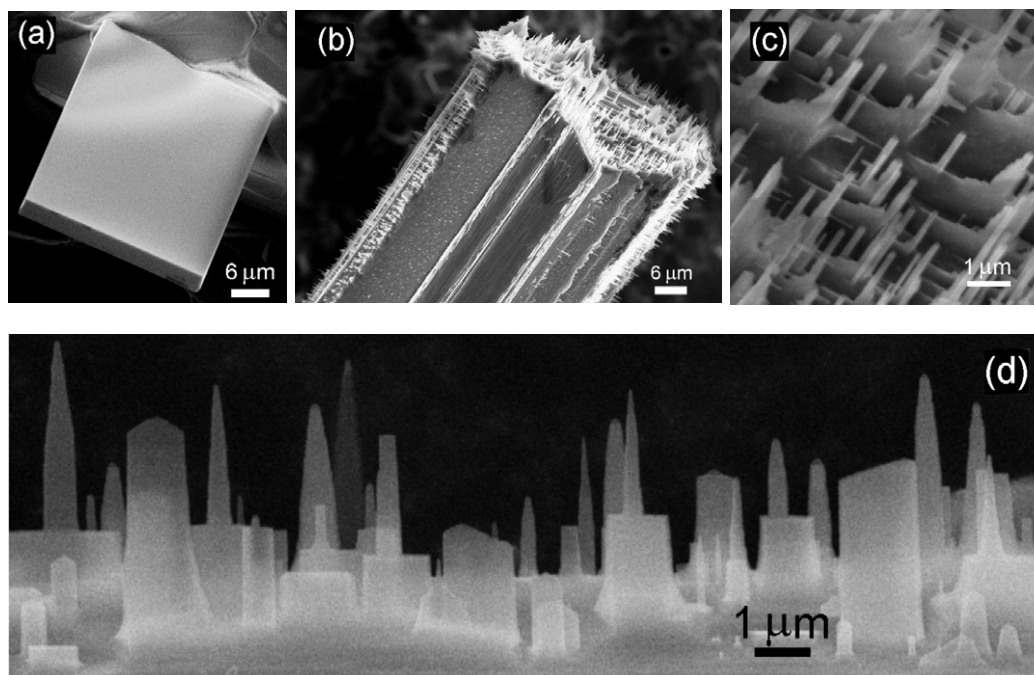


Figure 1. SEM images of Eu doped β -Ga₂O₃ structures in samples (a) M1 and (b)–(d) M2.

The effective incorporation of Eu³⁺ is demonstrated by cathodoluminescence (CL) and photoluminescence (PL) measurements. We characterize the red luminescence band related to the characteristic intraionic transition of the rare earth ion and assess the waveguiding of such luminescence.

Two different procedures were used to grow the nanostructures. In one of them a mixture of high purity 90 wt% Ga₂O₃ and 10 wt% Eu₂O₃ powders was milled for 30 h, pressed into a pellet and subsequently annealed under an argon flow at high temperatures either in a single treatment at 1500 °C for 15 h (sample M1) or a double treatment, at 1500 °C for 10 h and 1350 °C for 5 h (sample M2). A similar process was used in [18] to obtain erbium doped gallium oxide micro and nanostructures. A two steps procedure starting from a different precursor has also been used: first, nanowires and nanobelts have been grown, as will be shown in figure 2, by thermal oxidation of metallic Ga on a Ga₂O₃ pellet under an Ar flow at 1150 °C; in the second step, the sample with nanostructures was annealed at 1500 °C in the presence of Eu₂O₃ in order to achieve Eu doping by diffusion (sample D). All samples M1, M2 and D presented micro and nanostructures doped with luminescent europium ions. For comparison, we have obtained a reference β -Ga₂O₃:Eu sample by annealing a Ga₂O₃ pellet at 1500 °C in the presence of Eu₂O₃ powder to obtain diffusion of the rare earth into its surface (sample R). No micro or nanostructures were obtained in this sample due to differences in the argon flow. The crystal properties of the samples were studied by x-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution-TEM (HRTEM) and selected area electron diffraction (SAED). The morphology of the structures was characterized by scanning electron microscopy (SEM) in a Leica 440 Stereoscan microscope. A Bruker energy

dispersive x-ray microanalysis (EDX) system was used for the compositional studies. The luminescence measurements were performed with a cathodoluminescence (CL) system in a SEM, working at 15–20 keV and 1–5 nA, or a micro-photoluminescence (μ -PL) system included in an Olympus optical microscope with a Hg lamp.

SEM secondary electron images of the structures obtained by the first procedure are shown in figure 1(a), sample M1, and in figures 1(b)–(d), sample M2. The growth of nanostructures on certain faces of the microstructures occurs after the second thermal treatment, at lower temperature, in sample M2. In particular, nanowires with lateral dimensions ranging from tens to hundreds of nanometers are obtained in this way. A similar result was observed in erbium doped β -Ga₂O₃ [18].

Figure 2 shows SEM images of the micro and nanostructures obtained from metallic gallium by annealing at different temperatures and Ar flow. Structures such as nanoribbons (figure 2(a)), nanorings (figure 2(b)), nanoneedles (figure 2(c)) and nanorods are observed. The subsequent annealing at 1500 °C in the presence of Eu₂O₃ does not significantly change the morphology of the structures, as figure 2(d) of sample D shows. TEM images, figures 2(e) and (f), demonstrate the high crystal quality of the nanostructures grown in this way. Figure 2(e) shows a nanowire grown in the (001) direction with a lateral grown nanosheet.

Figure 3 shows the EDX spectrum of the nanostructures obtained by annealing the powder mixture (sample M1). Similar results are obtained in samples M2, D and R. Quantitative microanalysis yields a Eu concentration of around 1 at.%. A similar quantitative value was obtained in the doped nanostructures from sample D.

XRD measurements performed on samples M1 and M2 reveal the presence of Eu₃Ga₅O₁₂, europium gallium garnet

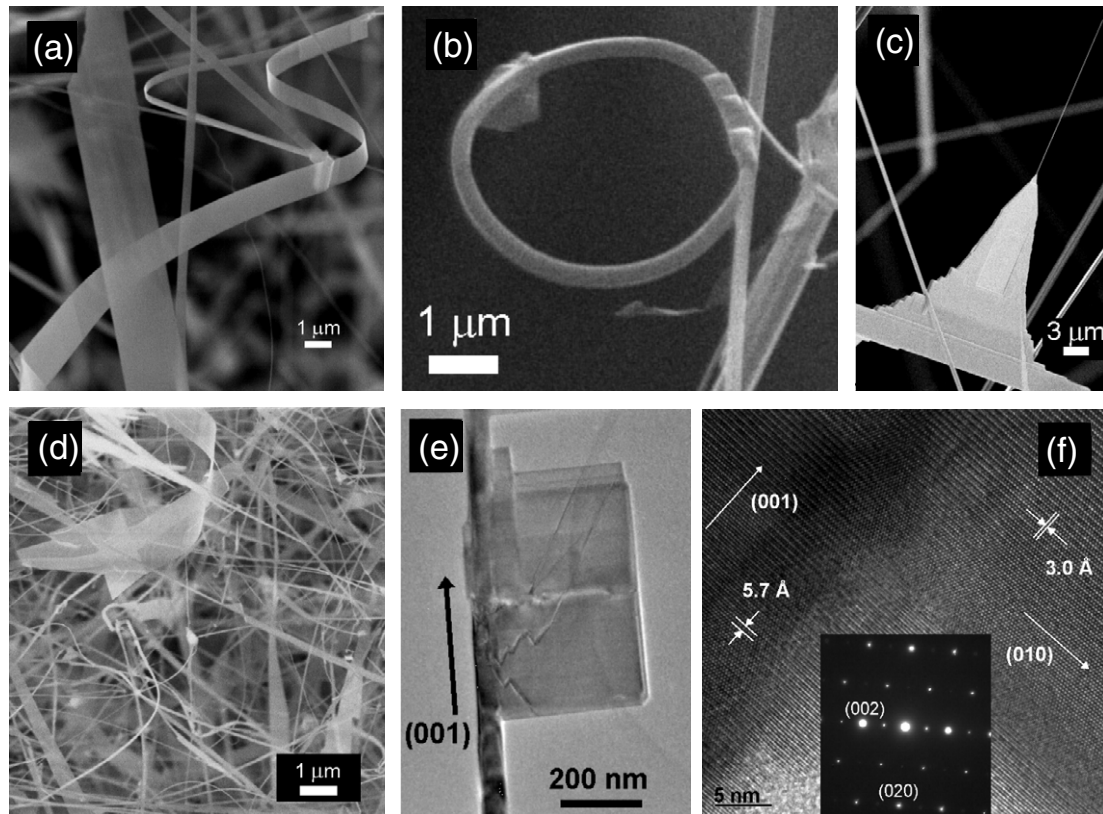


Figure 2. SEM images of (a)–(c) undoped nanowires obtained from metallic gallium and (d) Eu doped β -Ga₂O₃, sample D. The morphology of the structures is not significantly affected by the 1500 °C annealing for Eu doping. (e) TEM and (f) HRTEM (inset: SAED) showing that the nanowires of sample D are single crystalline.

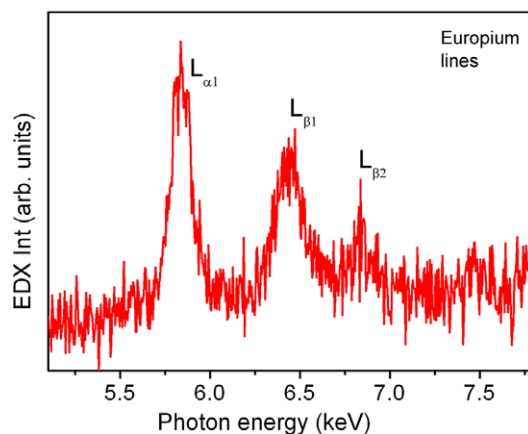


Figure 3. EDX spectrum from nanostructures grown in sample M1.

(EuGG, JCPDS 00-014-0128) in addition to β -Ga₂O₃. A similar result was previously found in erbium doped gallium oxide starting from a powder mixture [18] in which erbium gallium garnet was detected after the thermal treatment. XRD spectra from samples D and R show that only β -Ga₂O₃ is formed.

Figure 4 shows the normalized CL spectra from pure Eu₂O₃ (dashed black), β -Ga₂O₃:Eu in sample R (solid red) and Eu₃Ga₅O₁₂ in sample M1 (dotted blue). A red main peak centered at around 610 nm, which corresponds to the

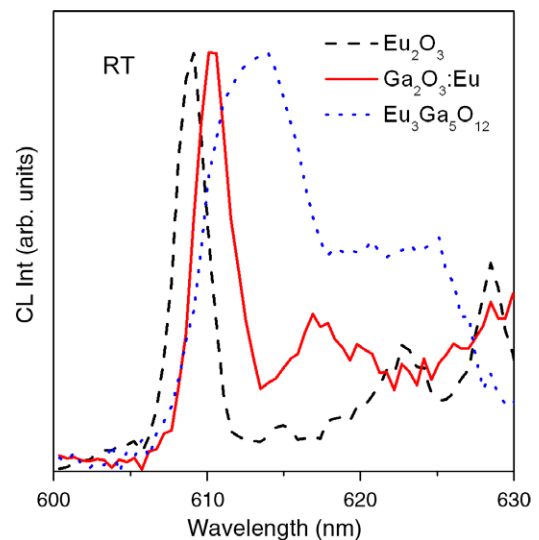


Figure 4. Room temperature CL due to Eu³⁺ included in three different hosts: Eu₂O₃ (dashed black), β -Ga₂O₃ (solid red) and Eu₃Ga₅O₁₂ (dotted blue). The spectra have been normalized.

Eu³⁺ related 5D_0 – 7F_2 intraionic transition, is observed in all of them. However, shifts in the position of the main peak can be observed depending on the host: for Eu³⁺ in Eu₂O₃ is 609 nm, in β -Ga₂O₃ is 610 nm and in EuGG is 613 nm. Additionally, to

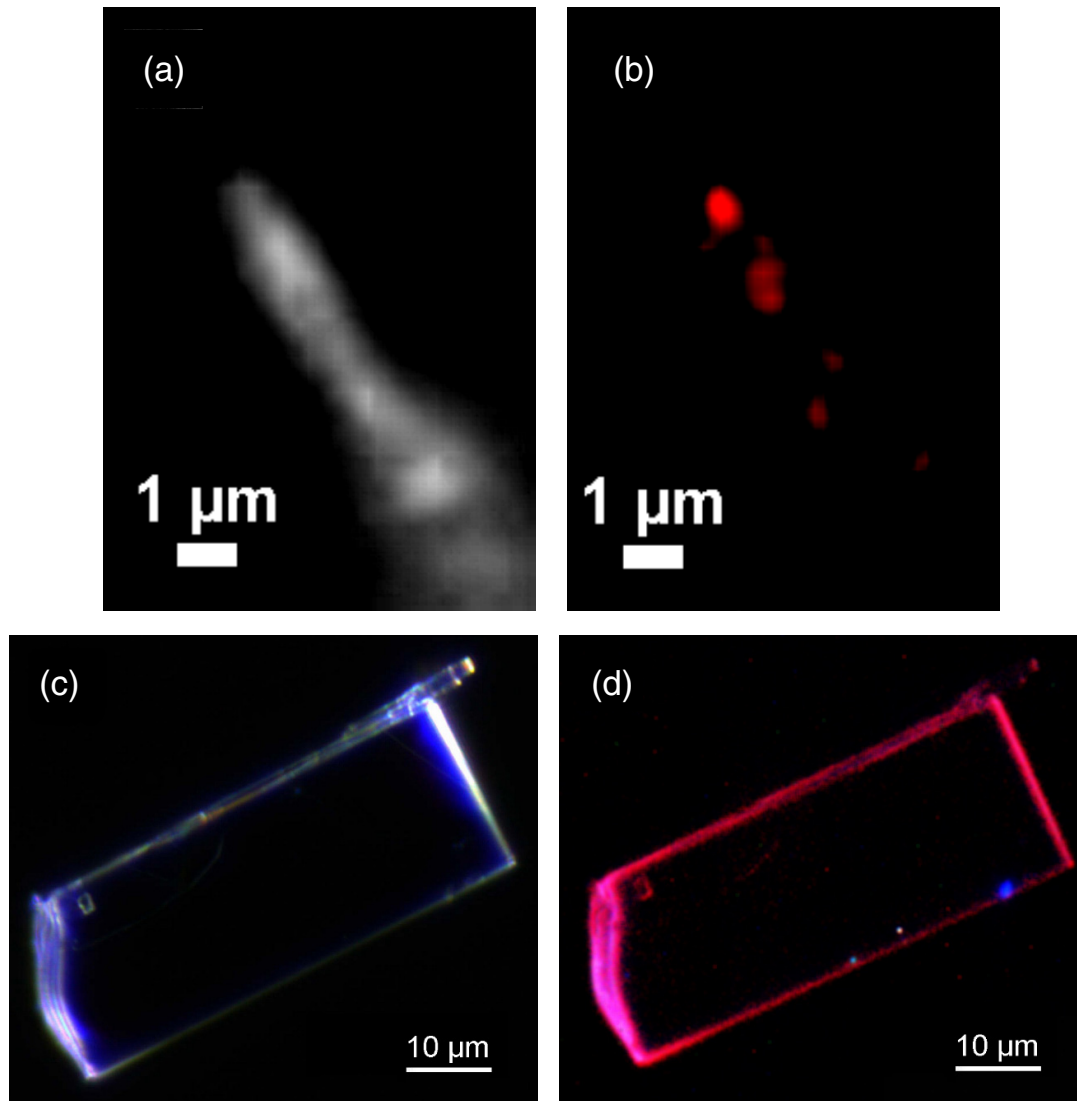


Figure 5. (a), (c) Dark-field optical microscopy and (b), (d) corresponding room temperature μ -PL images of Eu doped structures in sample M1. The μ -PL spectrum in figure 6 was obtained from the structure shown in (d). $\lambda_{\text{exc}} = 366$ nm.

further differentiate Eu in β -Ga₂O₃ and in Eu₂O₃, we observe that a peak at around 618 nm is present in the former, while this second peak is centered at 623 nm in the latter. Luminescence results from sample M2 are similar to those obtained from sample M1.

It is well known that differences in the crystal field surrounding the rare earth ions result in slight shifts of their luminescence peaks and differences in their relative intensities [19, 20]. Eu³⁺ in β -Ga₂O₃ is substituting Ga in octahedral position while in Eu₃Ga₅O₁₂ is within a dodecahedral site with lower symmetry [19]. By comparison of the spectra from different hosts, we can deduce the origin of the luminescence observed in the nanostructures.

The waveguiding behavior of the β -Ga₂O₃ nanostructures makes them very interesting for potential photonic nanodevices [4]. The nanostructures can guide external light and light emitted by the nanostructures themselves in a photoluminescence process. Figure 5 shows this effect in two different structures obtained in sample M1. The images show the dark-

field optical image and the room temperature μ -PL image of two structures. One of them is a nanowire of some hundreds of nanometers diameter, figures 5(a) and (b). The other one, shown in figures 5(c) and (d), is a thin plate as that shown in figure 1(a). Light guiding in both structures leads to the intense light signal observed in their edges or ends. A rough calculation yields a level of confinement of the emitted light of around 80% by total internal reflection in the microplate. This effect has been used very recently for solar concentrators [21].

Figure 6 shows the room temperature (RT) CL spectra from nanowires in sample D (dotted blue) and from structures in sample M1 (dashed red). The RT μ -PL spectrum obtained from a structure in sample M1 is also plotted (solid black). The spectra show a main peak centered at 610 nm which, by comparison with figure 4, is associated to Eu³⁺ in β -Ga₂O₃. However, there is a difference between the CL spectra from the structures in D and M1. A broad shoulder at longer wavelengths can be observed in the latter. A contribution from Eu³⁺ in Eu₃Ga₅O₁₂ clusters formed within the structure could

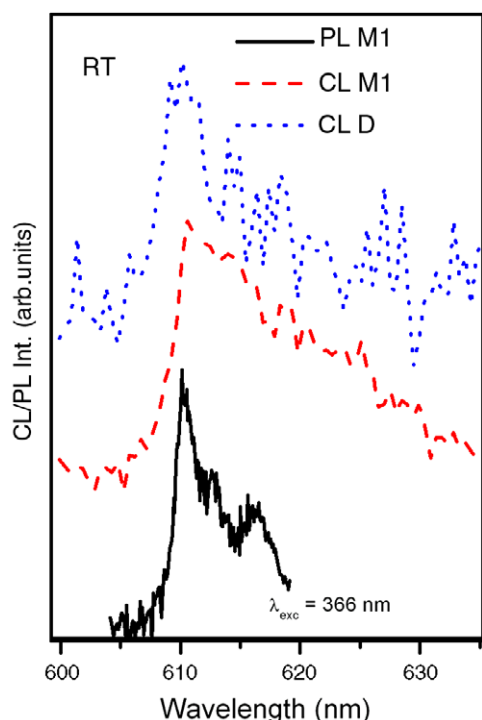


Figure 6. Room temperature CL from samples M1 (dashed red) and D (dotted blue). Room temperature μ -PL from a microstructure from sample M1 (solid black). The optical and μ -PL images are shown in figures 5(c) and (d). The spectra have been normalized and vertically shifted for the sake of clarity.

explain this result. However, the main peak centered at 610 nm shows that most of the luminescence is due to Eu^{3+} in $\beta\text{-Ga}_2\text{O}_3$. The μ -PL spectrum corresponding to the structure from M1 presents peaks which are associated only to Eu^{3+} in $\beta\text{-Ga}_2\text{O}_3$, which shows that the luminescence from these structures is due to europium doped gallium oxide.

In summary, Eu doped $\beta\text{-Ga}_2\text{O}_3$ nanowires have been obtained either from a mixture of $\text{Ga}_2\text{O}_3\text{:Eu}_2\text{O}_3$ powders or by Eu diffusion into previously obtained nanostructures by high temperature annealing in the presence of Eu_2O_3 . The morphology of the structures is varied depending on the growth procedure. In particular, a higher number of long, doped nanowires and nanoribbons is obtained by the second method. Europium ions, with a concentration of around 1 at.% for both growth procedures, have been successfully incorporated into the $\beta\text{-Ga}_2\text{O}_3$ lattice and behave as optically active centers. Room temperature red luminescence related to the

Eu^{3+} intraionic transitions has been demonstrated by spatially resolved cathodoluminescence and photoluminescence of the grown structures. Furthermore, μ -PL measurements show that the Eu emitted light is guided through the doped nanowires and nanoplates.

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