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Visible and infrared luminescence study of Er doped β -Ga₂O₃ and Er₃Ga₅O₁₂

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Abstract

The luminescence properties of Er doped β -Ga₂O₃ and of the erbium gallium garnet Er₃Ga₅O₁₂ (ErGG) have been investigated both in the visible and in the infrared (IR) ranges by means of photoluminescence (PL). Doping of the β -Ga₂O₃ was obtained in two different ways: erbium ion implantation into β -Ga₂O₃ and high temperature annealing of a mixture of Er₂O₃ and Ga₂O₃ powders. X-ray diffraction shows that the latter samples present both β -Ga₂O₃ and ErGG phases. The PL studies demonstrate that the β -Ga₂O₃ in these samples is doped with erbium. The differences in the luminescence emission and excitation peaks of the Er³⁺ ions in these two hosts are studied through selective PL measurements. Strong near IR emission and weak green emission from Er³⁺ in the β -Ga₂O₃ matrix is obtained. The opposite is obtained for Er³⁺ in ErGG when excited under the same conditions. Room temperature luminescence is observed from erbium in the two hosts.

1. Introduction

Gallium oxide has sparked a strong interest in the past years for several reasons, including its chemical and thermal stability, wide band gap (~ 5 eV) and conducting behaviour due to its intrinsic native donor band related to oxygen vacancies [1]. The optoelectronic applications are one of the main aims that lead the studies carried out on this material due to the high value of the band gap, which makes it very suitable to detect or emit light in the ultraviolet (UV), visible and infrared (IR) ranges [2–8]. Several studies have been carried out on the luminescence properties of rare earth (RE) doped β -Ga₂O₃ due to the sharp emission lines of these elements [2, 8–10]. It was shown by Favennec *et al* [11] that a wider band gap of the host implies lower thermal quenching of the luminescence of the RE, which points to β -Ga₂O₃ as a good host for room temperature efficient RE emission. Er has been widely studied in different hosts for luminescence purposes, mainly due to its green (⁴S_{3/2}–⁴I_{15/2}) [2, 8, 12–15] and IR (⁴I_{13/2}–⁴I_{15/2}) [16, 17] luminescence lines. The latter, centred at around 1.54 μ m, has a great importance in the telecommunications industry because of its coincidence with the wavelength at which the standard silica-based optical fibres present the lowest losses [16].

RE doped gallium garnets, mainly yttrium gallium garnet (YGG), are widely used as solid state lasers. Undoped RE gallium garnets (RGG) are also studied due to their magneto-optical and magnetic properties [18–20]. They are robust materials which, in some cases, show luminescence from the RE [20].

In this work, the Er³⁺ luminescence properties of gallium oxide samples doped with Er by ion implantation, as well as that of samples which contain both Er doped gallium oxide and erbium gallium garnet (ErGG), both in the visible and IR ranges, are reported. Comparison of the different samples allows the spectral characterization of at least two distinct Er³⁺ centres, one in ErGG and other in β -Ga₂O₃, of potential interest for visible or IR optoelectronic applications.

2. Experiment

A gallium oxide pellet of about 7 mm diameter and 2 mm thickness was prepared by compacting 99.999% purity Ga₂O₃ powder under compressive load. The pellet was then annealed at 1500 °C for 8 h and implanted with erbium ions at an energy of 150 keV to a dose of 1×10^{15} cm⁻². No RE luminescence was obtained from the as-implanted sample. Afterwards, it

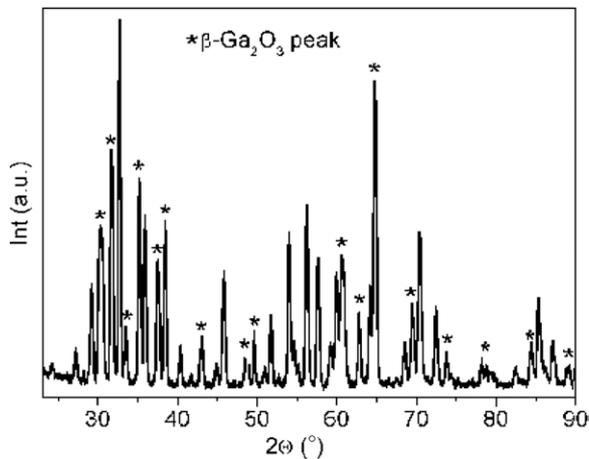


Figure 1. XRD spectra of sample GM. All the peaks correspond to ErGG or β -Ga₂O₃. The asterisks indicate the main peaks related to β -Ga₂O₃.

was annealed at 1000 °C for 1 h and 1300 °C for additional 1 h under Ar flow to remove the implantation induced defects so that the RE ions are optically activated. This sample is labelled GI. XRD spectra show that it is formed only by crystalline β -Ga₂O₃. Another sample was obtained from an Er₂O₃ and Ga₂O₃ powders mixture (5 at.% Er₂O₃) which was milled for 30 hours and subsequently annealed at 1500 °C for 5 h and 1350 °C for 5 h more under an Ar flow. It is labelled GM. The implanted sample was annealed at 1100 °C and 1300 °C in order to re-crystallize gallium oxide. Higher temperatures were avoided to prevent a strong loss of material from the surface what would include loss of implanted ions. The annealing of sample GM was performed at 1500 °C. The aim in that case was to obtain Er diffusion in gallium oxide, which needs very high temperatures.

Photoluminescence (PL) and PL excitation (PLE) spectra, as well as correlated excitation-emission (CEE) maps, were acquired with a 450 W Xe lamp attached to an Edinburgh Instruments CD900 spectrometer at 10 K using a closed cycle liquid He system. RT spectra were also obtained under excitation with the 366 nm line of a Hg lamp and a Spex 750 M monochromator. Measurements in the visible range were carried out with a photomultiplier while a nitrogen cooled Ge detector was used to record the IR spectra. Scanning electron microscopy (SEM) measurements were performed with a Leica Stereoscan 440 microscope. Energy dispersive x-ray (EDX) microanalysis was carried out in this SEM with a Bruker system working at 20 keV and 5 nA.

3. Results and discussion

The XRD spectrum shown in figure 1, obtained with the Cu K_{α1} line, presents peaks that correspond either to β -Ga₂O₃ (marked with asterisks) or Er₃Ga₅O₁₂ (ErGG). No peak corresponding to Er₂O₃ or other compounds was detected. Therefore, during annealing the Er₂O₃ reacted with the Ga₂O₃ to form ErGG.

SEM images of samples GI and GM are shown in figure 2. Sample GI shows crystal domains with dimensions of several micrometres, showing a surface step structure (figure 2(a)).

Sample GM presents a smaller average grain size and, besides, rounded grains, marked with arrows, are observed (figure 2(b)). They are not obtained in any pure or implanted β -Ga₂O₃ sample and, taking into account the XRD results, we attribute them to crystalline ErGG. Figures 2(c) and (d) show secondary electrons (SE) and EDX images of this sample, respectively. The rounded grains present much higher erbium content, which gives a further indication that they are formed by ErGG.

Figure 3 shows PL spectra of samples GI and GM in the green and IR ranges at 10 K. The green emission lines shown in this figure correspond to the ⁴S_{3/2}-⁴I_{15/2} Er³⁺ intraionic transition and the IR ones to ⁴I_{13/2}-⁴I_{15/2}, but the sets of peaks differ depending on the sample and/or the excitation wavelength. A set of peaks is observed in the green region, around 552 nm, and another one in the IR, around 1545 nm, in sample GI when exciting with photon energy equal to, or higher than, the β -Ga₂O₃ band gap (~5 eV, 250 nm) (figure 3(a)). This indicates that the emission of the Er³⁺ ions is obtained through excitation of electron-hole pairs in the oxide and subsequent energy transfer to the RE ions. This mechanism has been previously described for other semiconductor hosts [21]. From the XRD results, which indicate that only β -Ga₂O₃ is present in this sample, and the observation of erbium luminescence, which is excited through energy transfer after band to band excitation, we suggest that this green and IR couple of PL sets of peaks correspond to erbium ions embedded in the β -Ga₂O₃ host. It has been reported that the majority site for RE ions in this crystal is the octahedral Ga site, with O_h point symmetry [10].

The PL spectra of sample GM shown in figures 3(b) and (c) were obtained by excitation with two different wavelengths, 381.8 and 384.7 nm, resonant with the Er ⁴I_{15/2}-⁴G_{11/2} electronic transition. One couple of green and IR set of peaks are obtained with each excitation wavelength. It is well known that differences in the symmetry and strength of the crystal field result in changes of the splitting of the RE ion electronic levels, implying that both the emission and the excitation energies change for different centres [22]. This fact allows the selection of luminescence from a particular emitting centre, in a sample containing different kinds of centres, through the excitation photon energy [23]. We will assign one emission centre to each green-IR couple of sets of peaks. The couple which is emitted when exciting with 384.7 nm, which we will relate to a centre labelled Er₁, is coincident with the peaks obtained in sample GI. The other set of peaks, clearly different, will be assigned to a centre labelled Er₂.

Figure 4 shows the CEE map in the region between 379.3-386 nm excitation wavelength and 548-565 nm emission wavelength. The emission sets of peaks related to the two centres are clearly observed to have different excitation maxima. For Er₁, the maximum intensity is obtained at $\lambda_{exc} = 384.7$ nm, while for Er₂, the maximum is at 381.8 nm thus justifying the selection of these two excitation wavelengths for the PL spectra shown in figure 3. No other sets of peaks have been observed in the studied energy ranges.

The green-IR couple of sets of peaks related to the Er₁ centre in sample GM is assigned, by comparison with sample GI, to Er³⁺ embedded in the β -Ga₂O₃ host, in the

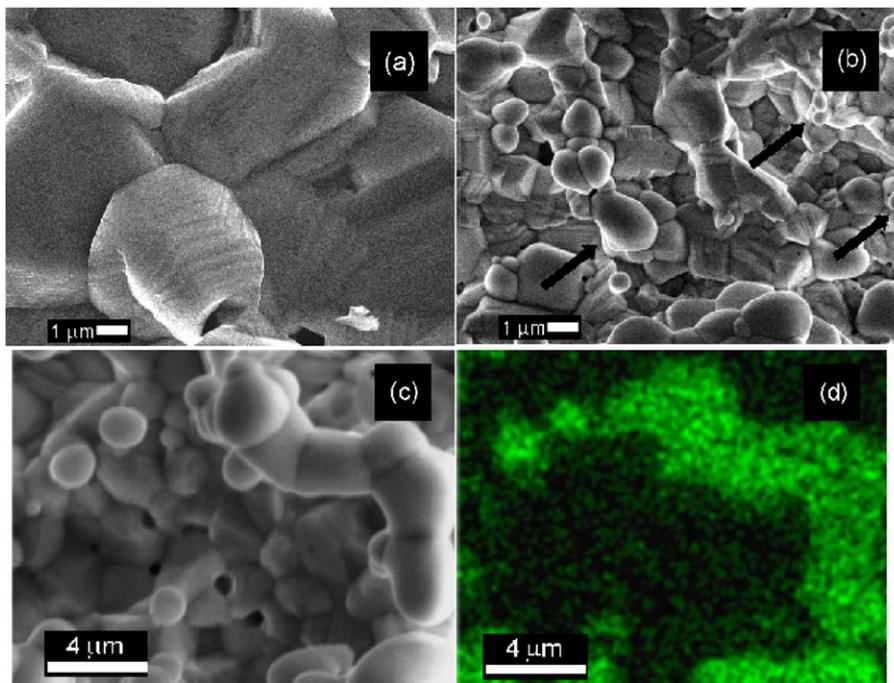


Figure 2. SEM images of sample (a) GI and (b) GM. (c) SE and (d) EDX erbium mapping of the corresponding area of sample GM. (This figure is in colour only in the electronic version)

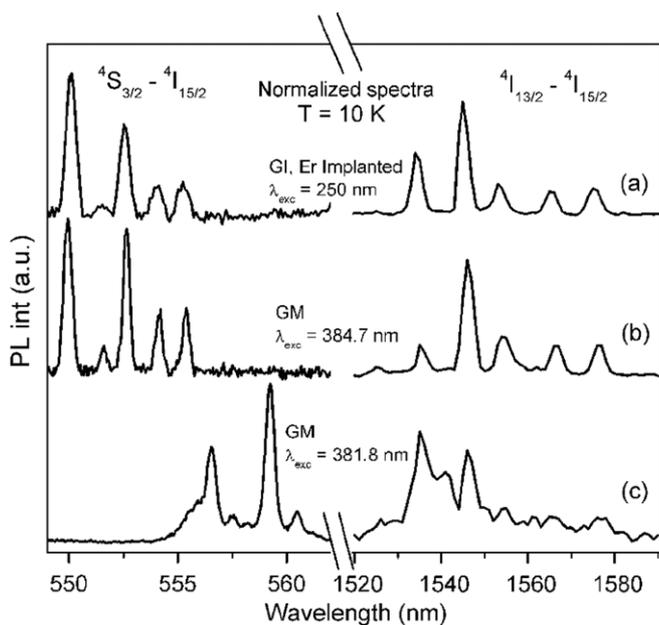


Figure 3. Normalized PL spectra of samples GI (a) and GM (b) and (c) in the visible and IR ranges. Different resonant excitation wavelengths have been chosen in sample GM in order to select the emitting centre. $\lambda_{exc} = 384.7$ nm corresponds to $^4I_{15/2} - ^4G_{11/2}$ intraionic transition for center Er_1 and $\lambda_{exc} = 381.8$ nm corresponds to $^4I_{15/2} - ^4G_{11/2}$ transition for Er_2 .

Ga sites with octahedral point symmetry. This demonstrates that there is erbium diffusion into the gallium oxide during annealing of the powder mixture. On the other hand, from the above described XRD results, it is concluded that the centre labelled Er_2 corresponds to Er^{3+} in ErGG matrix. The

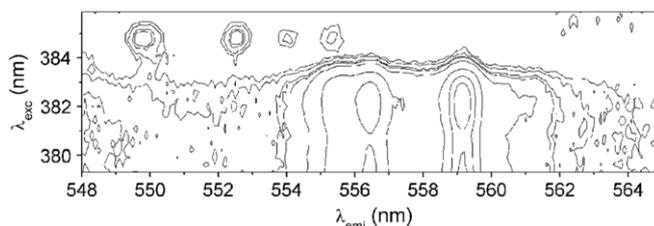


Figure 4. CEE of sample GM. Resonant excitation through $^4I_{15/2} - ^4G_{11/2}$ intraionic transition. Two sets of peaks can be observed, corresponding to Er_1 and Er_2 .

REs in RGG occupy dodecahedral sites with orthorhombic symmetry [20].

Figure 5 shows the PLE spectra at 10 K of the IR emission related to the 1545 nm line (Er_1 centre) in samples GI and GM, as well as that related to the 1535 nm line (Er_2 centre) in GM. It is clearly observed that the luminescence in sample GI is the strongest through band to band excitation. Resonant excitation of the erbium ions is also observed at around 380, 520 and 550 nm, when the spectrum is magnified by a factor 10 in the 325–570 range. The same peaks are obtained for Er_1 in sample GM, but resonant excitation is quite stronger than band to band. In this case, the range 220–280 nm has been magnified in the figure to show the weak 250 nm excitation band. A possible cause for the higher intensity of the resonant excitation compared with the band to band excitation could be a higher disorder in the crystals leading to recombination paths different than the energy transfer to the erbium ions. Resonant excitation is also dominant for Er_2 centre in this sample. Excitation peaks are in the same energy ranges for Er_1 and Er_2 , but relative intensities differ from one centre to the other. Relative intensities of the same lines change when

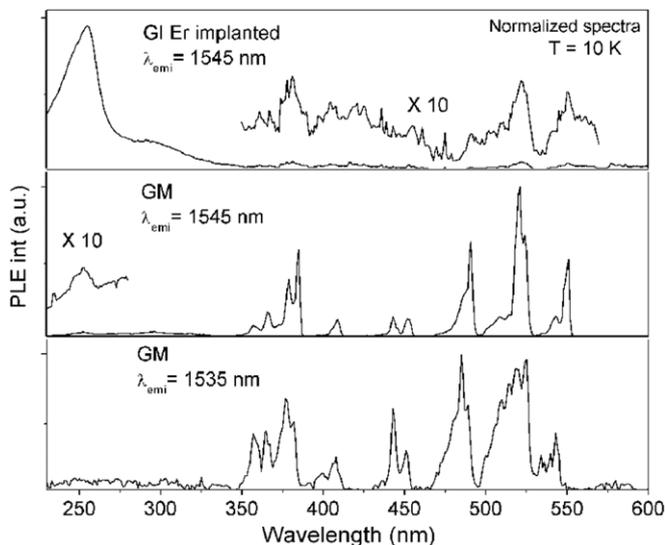


Figure 5. PLE spectra for IR emission corresponding to Er₁ in GI (above), Er₁ in GM (middle) and Er₂ in GM (below). Spectra were normalized.

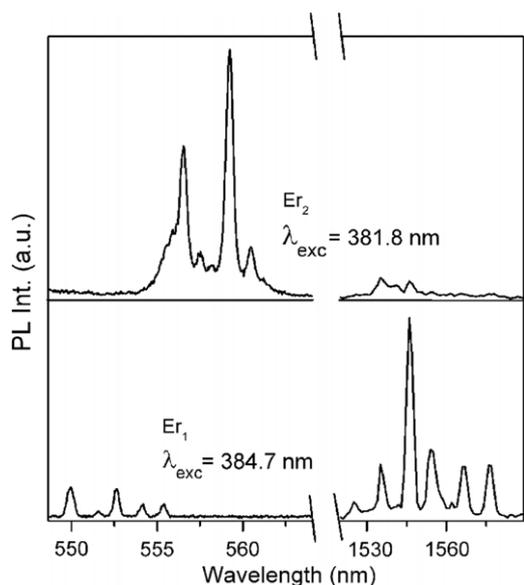


Figure 6. Comparison between the intensities of Er₁ and Er₂ centres in the visible and IR ranges through selective PL spectra of sample GM. $T = 10$ K.

the site symmetry changes, due to differences in the admixture of even and odd parity states, which changes the electric dipole component of the transitions [22].

A comparison of the luminescence intensity from the two erbium centres in the green and the IR ranges has also been carried out. For this comparison we take into account that sample GM which contains both centres so that we can selectively excite them. Figure 6 shows the selective PL spectra in the green and IR ranges of sample GM. The measurements were performed in the same conditions, so that we can compare quantitatively the relative intensities in the green range as well as those in the IR range. It is observed that green emission intensity is rather weak for $\lambda_{exc} = 384.7$ nm (Er₁ centre) compared with that for $\lambda_{exc} = 381.8$ nm (Er₂ centre), but the

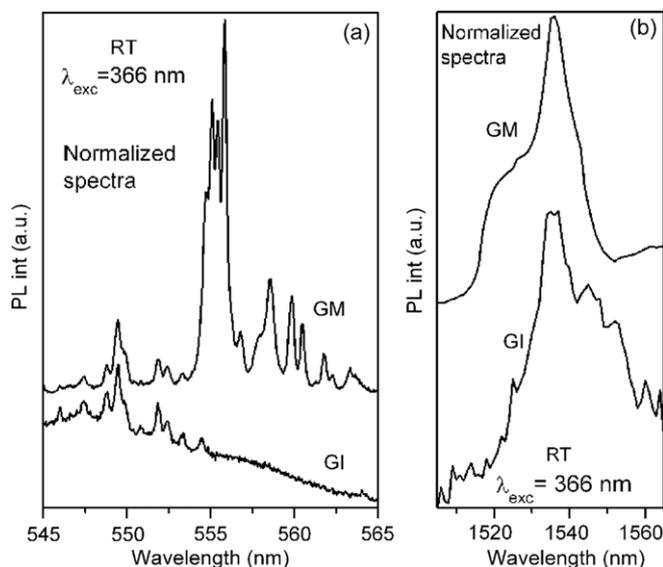


Figure 7. Room temperature PL spectra in (a) green range and (b) IR range of samples GM (upper spectra) and GI (lower spectra) excited with the 366 nm line of a Hg lamp. Spectra were normalized.

opposite is obtained in the IR range. This result indicates that the β -Ga₂O₃ host is not very suitable to obtain green emission from the Er³⁺ intraionic transitions. Weak green erbium related luminescence has been observed previously in this host [24], as well as in other important hosts, like ZnO [25]. On the other hand, a strong green emission from the Er₂ centre is observed in ErGG. The IR emission shows the opposite behaviour: it is more intense for Er₁ than for Er₂. We have concentrated on these excitation lines around 380 nm but we have also employed excitation wavelengths around 520 nm, corresponding to other Er PLE peaks (see figure 5), and obtained similar results. As an explanation for the marked differences between the intensities of the $^4S_{3/2} - ^4I_{15/2}$ and $^4I_{13/2} - ^4I_{15/2}$ transitions we suggest the strong dependence of the intraionic transition probability, determined by the Judd–Ofelt parameters, between two electronic levels at the centre, on the crystal field symmetry [22]. However, the exact emission dynamics will have to be studied to elucidate other possible influences, e.g. of defects, on the luminescence lifetimes of the different intraionic transitions from the two centres.

This result implies that the use of β -Ga₂O₃ as host for Er is more useful to obtain the RE IR emission than the green emission. On the other hand, the IR emission from ErGG is not so efficient, compared with the green one.

Room temperature PL is obtained both in the visible and IR ranges in samples GI and GM by excitation with the 366 nm line of a Hg lamp, as shown in figure 7. The incident photon wavelength excites both Er₁ and Er₂ centres, as can be deduced from the previous discussion and the comparison of the emission lines in the green range (figure 7(a)). The spectra in the IR range are quite similar for both samples, with the peak centred at around 1536 nm. From the above discussion we conclude that most of this emission arises from the Er₁ centres, erbium ions in β -Ga₂O₃ host, both in GI and GM samples. However, a shoulder in the low energy range of the

peak in sample GI is observed, indicating that there could be a certain contribution from centre Er₂. A shoulder centred around 1550 nm can be observed in sample GI.

4. Summary

Green and IR luminescence of Er doped β -Ga₂O₃ obtained by erbium ion implantation into β -Ga₂O₃ or by high temperature annealing of a Ga₂O₃/Er₂O₃ mixture have been studied. In the latter samples both Er doped β -Ga₂O₃ and erbium gallium garnet phases are obtained. Only one main erbium centre has been found in the implanted samples, which is mainly excited through band to band excitation followed by an energy transfer process, and assigned to Er³⁺ in octahedral Ga sites within the β -Ga₂O₃. On the other hand, two main centres have been found in the samples obtained from the mixture. One of those centres corresponds to Er³⁺ in octahedral Ga sites within the β -Ga₂O₃, while the other is suggested to be related to Er³⁺ in ErGG crystal. The former emits mainly in the IR range while the latter shows stronger luminescence in the green region. The RE luminescence is observed up to room temperature.

Acknowledgments

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