Applied Surface Science 258 (2012) 9157–9161

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Optical properties of LFZ grown β-Ga_2O_3:Eu^{3+} fibres

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ARTICLE INFO

Article history:
Available online 23 July 2011

Keywords:
LFZ
Ga_2O_3
Eu
PL
PLE

ABSTRACT

Due to their relevance for electronic and optoelectronic applications, transparent conductive oxides (TCO) have been extensively studied in the last decades. Among them, monoclinic β-Ga_2O_3 is well known by its large direct bandgap of ∼4.9 eV being considered a deep UV TCO suitable for operation in short wavelength optoelectronic devices. The wide bandgap of β-Ga_2O_3 is also appropriate for the incorporation of several electronic energy levels such as those associated with the intra-$4f^n$ configuration of rare earth ions. Among these, Eu^{3+} ions ($4f^6$) are widely used as a red emitting probes both in organic and inorganic compounds. In this work, undoped and Eu_2O_3 doped (0.1 and 3.0 mol%) Ga_2O_3 crystalline fibres were grown by the laser floating zone approach. All fibres were found to stabilize in the monoclinic β-Ga_2O_3 structure while for the heavily doped fibres the X-ray diffraction patterns show, in addition a cubic europium gallium garnet phase, $Eu_3Ga_5O_{12}$. The spectroscopic properties of the undoped and Eu doped fibres were analysed by Raman spectroscopy, low temperature photoluminescence (PL) and photoluminescence excitation (PLE). The Eu^{3+} luminescence is mainly originated in the garnet, from where different europium site locations can be inferred. The spectral analysis indicates that at least one of the centres corresponds to Eu^{3+} ions in dodecahedral site symmetry. For the lightly doped samples, the spectral shape and intensity ratio of the $^5D_0 \rightarrow {}^7F_J$ transitions is totally different from those on $Eu_3Ga_5O_{12}$, suggesting that the emitting ions are placed in low symmetry sites in the β-Ga_2O_3 host.

1. Introduction

β-Ga_2O_3 is a well known wide band gap semiconductor with reported band gap energy at room temperature (RT) near 4.9 eV [1–4]. The RT thermodynamically stable monoclinic crystal has cell dimensions a = 1.223 nm, b = 0.304 nm, c = 0.580 nm and β = 103.7° [3,4]. The material belongs to a $C_{2/m}$ space group and the Ga^{3+} ions may occupy tetrahedral or octahedral crystallographic sites [4,5]. The material exhibits isolator behaviour or n-type conductivity generally attributed to anion oxygen vacancies, the resistivity being strongly dependent on the atmosphere growth conditions [6]. However, this became controversial since recently theoretical studies [7] pointed that oxygen vacancies give rise to deep donors, with activation energies around 1.0 eV, and so cannot be responsible for the unintentional n-type conductivity observed in this oxide. Due to the above-mentioned electrical conductivity and high transparency, β-Ga_2O_3 has been frequently exploited for several electronic and optoelectronic applications including electrodes as a transparent conductive oxide (TCO) [3,4]. For such purposes, information about the optically active defects and their energy distribution inside the wide band gap host constitutes one important issue. Under above band gap excitation, ultraviolet, blue and green broad luminescence bands peaked near 3.4, 2.95 and 2.48 eV have been reported in undoped and doped β-Ga_2O_3 single crystals [8–10]. The ultraviolet emission has been found to be sample independent, while deep level recombination has been found to be dependent on the chemical nature of the impurities and their content [10]. Particularly, the ultraviolet recombination has been attributed to intrinsic luminescence and the blue band has been assigned to a donor–acceptor gallium–oxygen vacancy pair recombination [9,10].

Furthermore, the wide band gap of β-Ga_2O_3 makes this TCO a suitable host for phosphor applications [11–22]. As an example, high luminance was obtained in thin-film electroluminescent displays when gallium oxide is activated with europium ions [12]. However, due to poor crystallization of the gallium oxide films [13–15], the rare earth ion emission lines are very broad and little is known about the mechanisms behind the intraionic Eu^{3+} luminescence in the crystalline Ga_2O_3 environment. More recently, nanostructured β-Ga_2O_3 has been synthesized by different routes and intentionally activated with rare earth ions for nanophosphor applications [17–22]. As for the thin films [13–15], large full width at half maximum of the main $^5D_{0,1} \rightarrow {}^7F_J$ transitions of the Eu^{3+} ions in the nanopowders [18,20] contrast with the expected sharp lines

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doi:10.1016/j.apsusc.2011.07.069

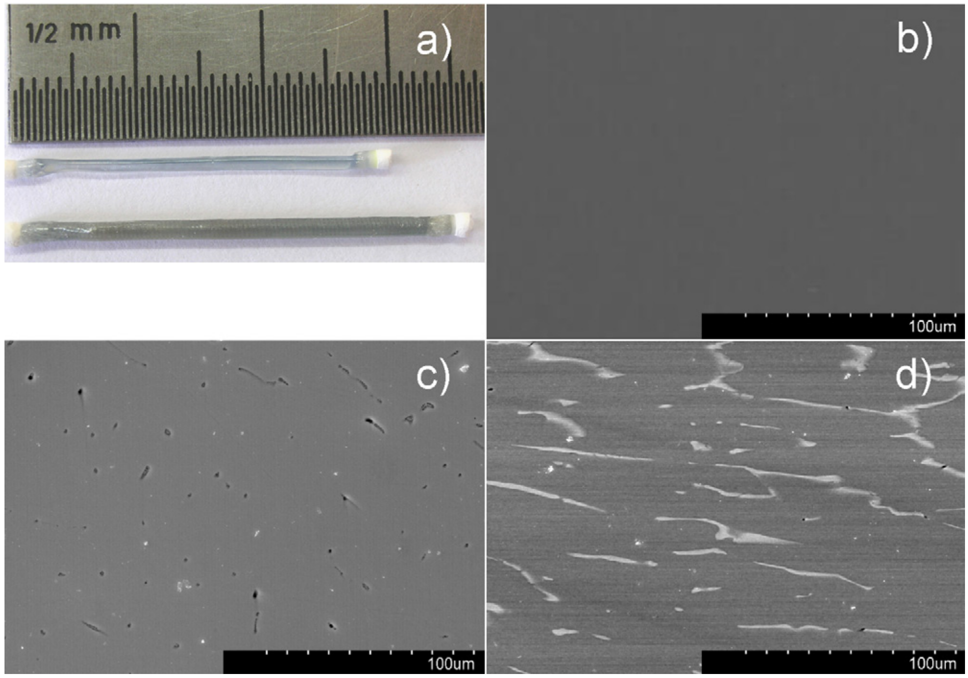

Fig. 1. Typical visual appearance of the (a) (top) undoped and (bottom) 0.1 mol % europium doped fibres grown at 30 mm h^{-1}. SEM micrographs of the (b) undoped fibre and europium doped fibres with (c) 0.1 mol % and (d) 3 mol % grown at 30 mm h^{-1}.

for the emitting ions in crystalline environments, from where the identification of the number of emitting Eu centres and site symmetry could be explored via the Stark level splitting due to the crystal field effect. Although the Eu^{3+} emission has been reported for thin films and nanopowders [11–22], information on the rare earth ion spectroscopic properties in bulk β-Ga_2O_3 remains scarce and constitutes an important issue to clarify the ion properties inside this TCO material.

In the present work, undoped and Eu doped β-Ga_2O_3 fibres were grown by laser floating zone (LFZ). The samples were characterized in what concerns their morphology and structure (SEM/EDS, PIXE, XRD, Raman spectroscopy), and their resulting low temperature optical properties (photoluminescence and photoluminescence excitation). The observed optical centres are discussed with respect to their possible phase origin and site symmetry.

2. Experimental details

The β-Ga_2O_3 crystalline fibres were grown by the *LFZ* technique, using rod precursors for both feed and seed materials prepared by cold extrusion. These rods were obtained by using gallium (III) oxide (Alfa Aesar) powders for the undoped samples and adding 0.1% and 3.0 mol% Eu_2O_3 (Aldrich) for the doped ones. The powders were mixed with polyvinyl alcohol (PVA 0.1 g/ml, Merck) in order to obtain a slurry that was further extruded into cylindrical rods with diameters of 1.75 mm.

The LFZ equipment comprises a 200 W CO_2 laser (Spectron) coupled to a reflective optical set-up producing a circular crown-shaped laser beam in order to obtain a floating zone configuration with a uniform radial heating. Crystalline fibres with diameters of 1–2 mm were grown at 10 and 30 mm h^{-1} in air at atmospheric pressure. Fibre microstructure and phase development were characterized by SEM (Hitachi S4100) with energy dispersive spectroscopy (SEM/EDS) on polished surfaces of longitudinal fibre sections. Additionally, in order to obtain information on the europium distribution in the fibres, particle-induced X-ray emission (PIXE) was performed using a 2.0 MeV ^1H micro beam and a 10-mm^2 Si (Li) detector with a resolution of 145 eV and a 5-mm Be window. The structural characterization was made by X-ray diffraction (XRD) experiments (PANalytical X'Pert PRO) and Raman spectroscopy. The latter were performed at room temperature (RT) in backscattering configuration with ultraviolet excitation by using the 325 nm line of a cw He–Cd laser (Kimmon IK Series) in a Horiba Jobin Yvon HR800 system and the 532 nm line from a Ventus-LP-50085 (Material Laser Quantum) laser in a Jobin Yvon T64000 instrument.

Steady state PL measurements were carried out at 14 K using a 1000 W Xe arc lamp coupled to a monochromator as excitation source. The luminescence was dispersed by a Spex 1704 monochromator (1 m, 1200 mm^{-1}) and detected by a cooled Hamamatsu R928 photomultiplier. For the PL excitation (PLE) measurements the emission monochromator was set at the Eu^{3+} emission lines, the excitation wavelength having been scanned up to 240 nm. The spectra were corrected to the lamp and optics.

3. Results and discussion

The visual appearance of the undoped and Eu doped gallium oxide fibres are shown in Fig. 1a. The undoped fibre was found to be transparent while the Eu doped samples exhibit a grey colour. The morphological analysis of the fibres longitudinal sections (Fig. 1b–d) reveals, for the undoped fibre, an uniform surface without grain boundaries or second phases (Fig. 1b) regardless the pulling rate (10 and 30 mm h^{-1}). In opposition, doping induces polycrystalline nature in both lightly (0.1 mol%) and heavily (3.0 mol%) doped samples. However, the heavily doped fibres show evidence of a second phase placed at the grain boundaries (light grey contrast), while the lightly doped fibres present polycrystalline morphology with good uniformity evidencing however dispersed precipitates. The SEM images of doped fibres (Fig. 1d) show evident grain boundary features aligned with the fibre axis as a result of directional solidification characteristic of the laser

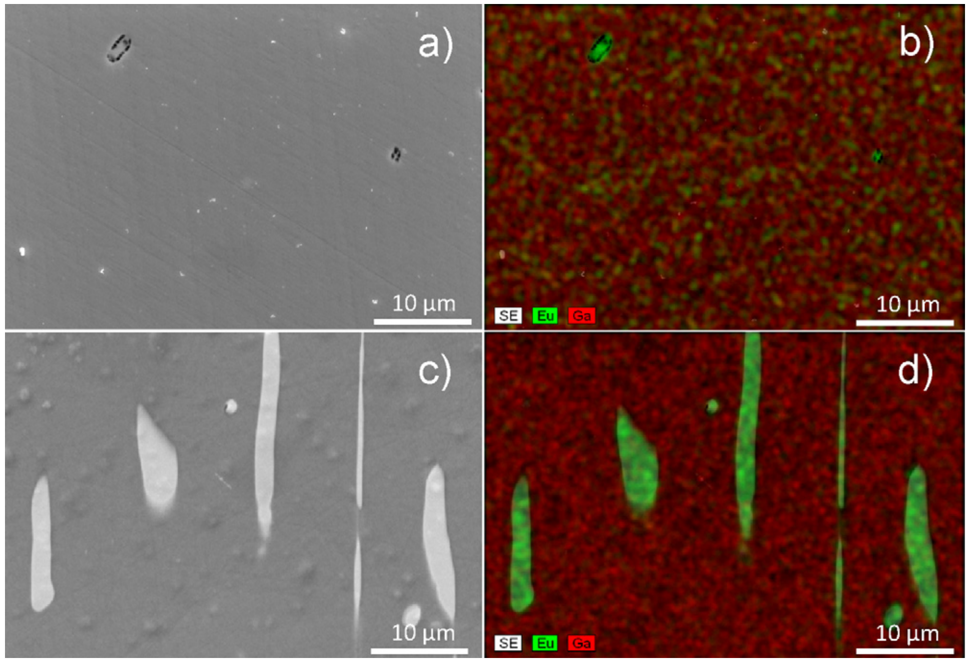

Fig. 2. SEM micrographs (a, c) and EDS maps (b, d) of the fibres grown at 30 mm h^{-1} lightly doped (a, b) and heavily doped (c, d).

floating zone growth technique. The additional contrasted regions in heavily doped fibres are due to local Eu richer crystalline phases as corroborated by PIXE (not shown), EDS (Fig. 2), XRD (Fig. 3) and Raman (Fig. 4) analysis. The peak positions of the XRD patterns of undoped and lightly doped fibres after milled into powders are in good agreement with the expected reflections from the monoclinic β-Ga_2O_3 crystalline structure. For the heavily doped fibres, besides the β-Ga_2O_3 crystalline structure, an additional crystalline phase was detected corresponding to the presence of europium gallium garnet, $Eu_3Ga_5O_{12}$. This additional crystalline phase corresponds to the clear regions in SEM with higher europium content. Since this phase could not be detected in the lightly doped samples, one can infer that the amount of Eu in these fibres is still scarce to promote the development of the garnet phase. Although europium rich precipitates were observed by SEM/EDS (Fig. 2a and b) most of the europium ions remain dispersed in the gallium oxide matrix.

The Raman active modes were observed for the LFZ fibres, either with visible (Fig. 4a and b) and ultraviolet (Fig. 4c) excitation. The measured vibrational frequencies indicated in Table 1 for both the undoped and lightly doped fibres, correspond well to the ones of the β-Ga_2O_3 host [23,24]. The observed Raman frequencies are classified in three groups of vibrations related with librations and translations (low frequency modes up to ~200 cm^{-1}) of tetrahedra–octahedra chains, vibrations of deformed Ga_2O_6 octahedra (mid frequency modes within 310–480 cm^{-1}) and stretching/bending of the Ga_2O_4 tethaedra (high frequency modes: 550–770 cm^{-1}) [23,24]. The Raman spectra of the undoped and lightly doped fibres are comparable as shown in spectra 1 and 2, respectively (Fig. 4a). For the heavily doped fibre (spectrum 3), additional modes at 261 cm^{-1} and 279 cm^{-1} were identified corresponding to the europium gallium garnet phase $Eu_3Ga_5O_{12}$, depicted in the expanded region obtained with visible excitation (Fig. 4b) [25]. The above information is summarized in Table 1. The visible Raman spectra were acquired with the samples oriented both parallely and normally to the polarization plane of the laser

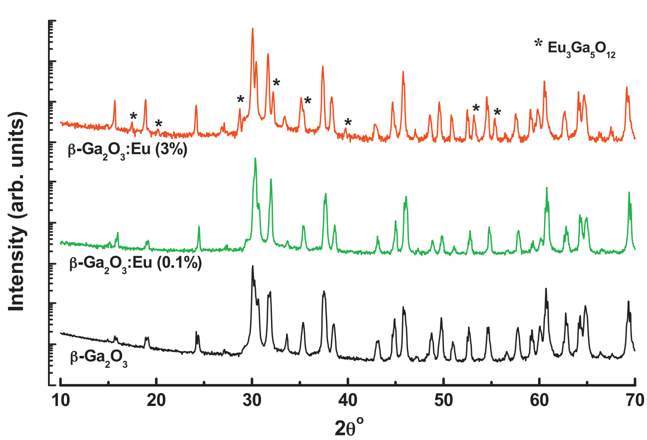

Fig. 3. XRD patterns for the undoped and doped (0.1 and 3 mol % Eu_2O_3) fibres grown at 30 mm h^{-1}.

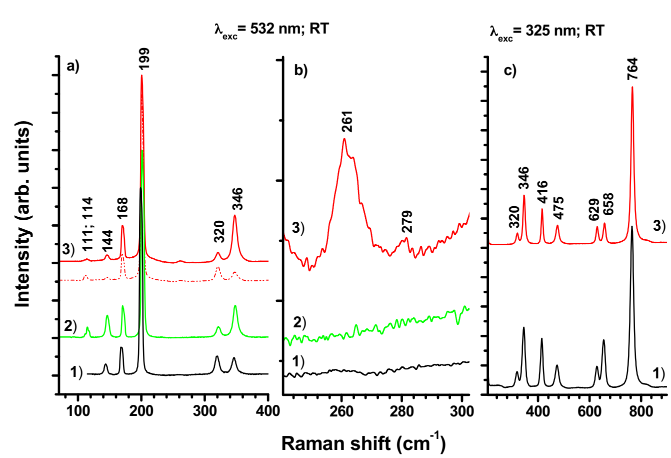

Fig. 4. (a) Raman spectra obtained with visible excitation (532 nm) for the undoped, lightly doped and heavily doped fibres, spectrum 1, 2 and 3, respectively. The dashed line in spectrum 3 corresponds to different sample orientation (parallel and normal to the plane of polarization). (b) Expanded region of the Raman spectra obtained with visible excitation. (c) UV (325 nm) Raman spectra for the same set of samples.

Table 1
Raman frequencies of undoped and Eu-doped β-Ga_2O_3 fibres. The additional modes detected for the Eu-doped fibres are identified by an asterisk (*).

Present work (cm^{-1})	Ga_2O_3			$Eu_3Ga_5O_{12}$	
	Dohy et al. [23] (cm^{-1})	Rao et al. [24] (cm^{-1})	Mode assignments [23]	Middleton et al. [25] (cm^{-1})	Mode assignments [25]
111	111		A_g		
114(*)	114		B_g	113	E_g
144	147	144	B_g	144	E_g
				159	T_{2g}
168	169	169	A_g	170	T_{2g}
				180	T_{2g}
199	199	200	A_g		
				233	T_{2g}
				239	T_{2g}
261(*)				262	E_g
279(*)				273	T_{2g}
				291	E_g
				309	T_{2g}
320	318	317	A_g		
346	346	344	A_g	346	A_{1g}
	353		B_g		
				367	T_{2g}
				407	T_{2g}
416	415	416	A_g	415	E_g
475	475	472	A_g, B_g		
				507	T_{2g}
				523	A_{1g}
				580	T_{2g}
				595	T_{2g}
629	628	629	A_g		
	651		B_g		
658	657	654	A_g		
				674	E_g
				736	A_{1g}
764	763	767	A_g		

incidence. The changes in the intensity ratios of the vibrational frequencies due to local polarization effects (dashed lined spectra 3) indicate a strong anisotropy, confirming the textured nature of the fibres [23].

Fig. 5 shows the low temperature luminescence spectra of the undoped and Eu doped fibres taken at 14 K. Exciting the undoped sample with photons of 260 nm (4.77 eV), the emission is dominated by a broad ultraviolet band peaked at 377 nm overlapped by minor luminescence bands near 438 nm and 526 nm (Fig. 5a). This luminescence spectrum is very similar to that previously reported by Zhang et al. [26] in β-Ga_2O_3 single crystals grown by the same LFZ technique. For Eu doped fibres (Fig. 5b) the characteristic orange/red luminescence due to the transitions between the $^5D_0$ and ^7F_J multiplets was detected. For heavily doped samples grown at 10 mm h^{-1} (spectrum 1) containing the two crystalline phases (β-Ga_2O_3 and $Eu_3Ga_5O_{12}$), well defined sharp lines (∼1 nm of full width at half maximum) are detected at 591 nm, 592 nm and 595 nm (spectrum 1) originated from the level of the $^5D_0$ state and terminating on the crystal field split states of the $^7F_1$ manifold. This magnetic dipole emission is the most intense one and for the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition only one line was found peaked at ∼610 nm. The heavily doped fibres grown at a faster pulling rate (30 mm h^{-1}) exhibit a distinct behaviour of the Eu^{3+} luminescence (spectrum 2). Here, the same lines previously detected are overlapped with the inhomogeneous broaden $^5D_0 \rightarrow {}^7F_{1,2}$ transitions likely due to Eu^{3+} ions in different environments. Additionally, the integrated intensity ratio between the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions increases, suggesting that the europium ions are placed in lower symmetry sites as also indicated by the presence of the $^5D_0 \rightarrow {}^7F_0$ line. The former spectrum well matches the one observed for the ions inside the cubic $Eu_3Ga_5O_{12}$ as reported by Van der Ziel and Van Uitert [27]. In this case, the splitting of the J = 1 state in three components and the absence of forbidden $^5D_0 \rightarrow {}^7F_0$ transition is in line with the expected results for the ions in dodecahedral sites with D_2 local symmetry [28,29]. Moreover, rare earth (RE) ions in $RE_3Ga_5O_{12}$ hosts are known to occupy multi-sites with the RE ions in non-regular sites due to distortions of local symmetry [27–30].

The similarity of the obtained spectra for the heavily doped LFZ grown samples either at 10 mm h^{-1} or 30 mm h^{-1} (spectra 1 and 2) with those obtained by Daldosso et al. [29] for nanocrystalline $Gd_3Ga_5O_{12}$ also doped with europium ions, suggest that the main emitting europium ions are located in the europium gallium garnet crystalline phase. On the other hand, for the lightly doped fibres, for which no $Eu_3Ga_5O_{12}$ crystalline phase was detected either by XRD and Raman spectroscopy, noticed spectral changes of the intraionic luminescence (spectrum 3) were identified, suggesting that the main emission is originated from Eu^{3+} ions in β-Ga_2O_3 host. The presence of the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions and their intensity ratios indicate that the europium ions are placed in lower symmetry sites. The inhomogeneous broadening of the lines observed for this lightly doped fibre, is consistent with the presence of the Eu^{3+} ions in low symmetry sites with an inhomogeneous environment, probably due to the fibre polycrystalline structure.

The identification of the different Eu^{3+} centres was further assessed by low temperature PLE and wavelength dependent PL measurements. PLE allows identifying the excitation population mechanisms which give rise to europium luminescence in doped fibres. The normalized PLE spectra monitored at the $^5D_0 \rightarrow {}^7F_2$ transition are shown in Fig. 5c. The spectra were normalized to the broad ultraviolet excitation band, from where all the Eu-centres are preferentially populated. Additionally, all the centres could be excited via the upper energetic levels of the Eu^{3+} ions which exhibit slight wavelength deviations as expected for different europium environments. Spectra 2 in Fig. 5b allow to the identification that distinct Eu centres could be preferentially excited with photons with different wavelengths.

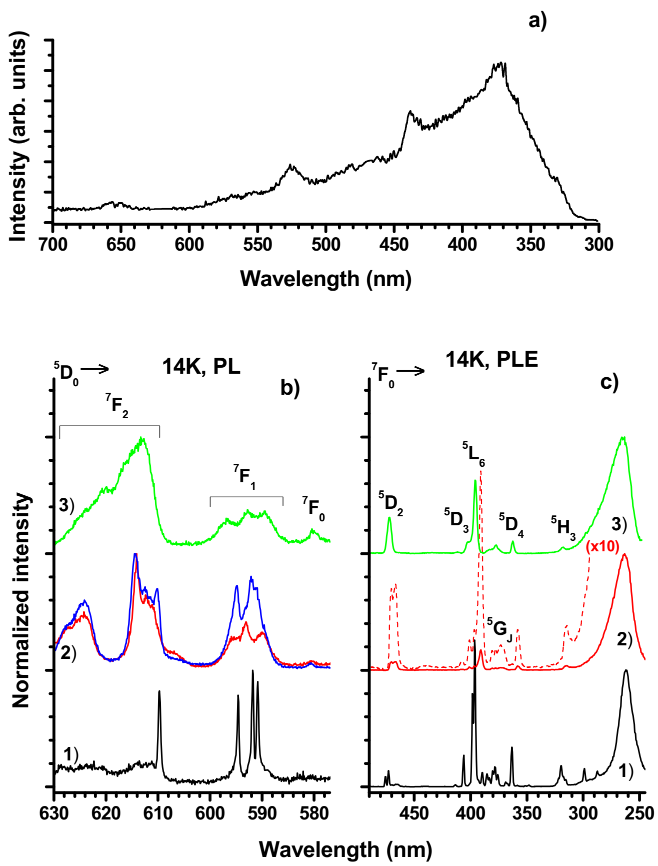

Fig. 5. 14 K PL spectra excited with 260 nm photons of the (a) undoped fibre grown at 30 mm h^{-1}, (b) heavily doped fibre grown at 10 mm h^{-1} (spectrum 1) and 30 mm h^{-1} (spectrum 2, red line). The blue line in spectrum 2 was obtained under resonant excitation at 390 nm, corresponding to a PLE maximum assigned to the $^7F_0 \rightarrow {}^5L_6$ transition. Spectrum 3 corresponds to the lightly doped fibre grown at 30 mm h^{-1}. (c) 14 K PLE spectra of the same fibres monitored on the $^5D_0 \rightarrow {}^7F_2$ transition.

4. Conclusions

Undoped β-Ga_2O_3 LFZ grown fibres and intentionally doped with 0.1 and 3 mol% of europium were produced at two different pulling rates (10 and 30 mm h^{-1}). The structural analysis using XRD and Raman measurements indicate that, regardless the pulling rate, only the β-Ga_2O_3 crystalline phase is present in the undoped and lightly doped samples. For heavily doped samples, an additional $Eu_3Ga_5O_{12}$ crystalline phase was identified. SEM/EDS and PIXE analysis show that europium rich regions are present in the latter fibres, corresponding to the europium gallium garnet phase. Low temperature PL measurements for the heavily doped samples evidence that most of the emitting europium ions are in the garnet structure in different local site symmetries and/or environments. Sharp Eu^{3+} lines were assigned to europium ions in dodecahedral symmetry and other two centres were visualized with the ions in lower site symmetry. On the other hand, for lightly doped samples, the intraionic lines are inhomogeneously broader with a spectral shape of the emitting ions different than those observed for the europium gallium garnet phase. The Eu^{3+} luminescence from the ions in β-Ga_2O_3 host is characterized by the presence of the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions, suggesting that the ions are placed in lower symmetry sites.

Acknowledgement

The authors acknowledge FCT for the financial funding from PTDC/CTM/66195/2006 project and PTDC/CTM/100756/2008 projects.

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