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

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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 $\beta = 103.7^\circ$ [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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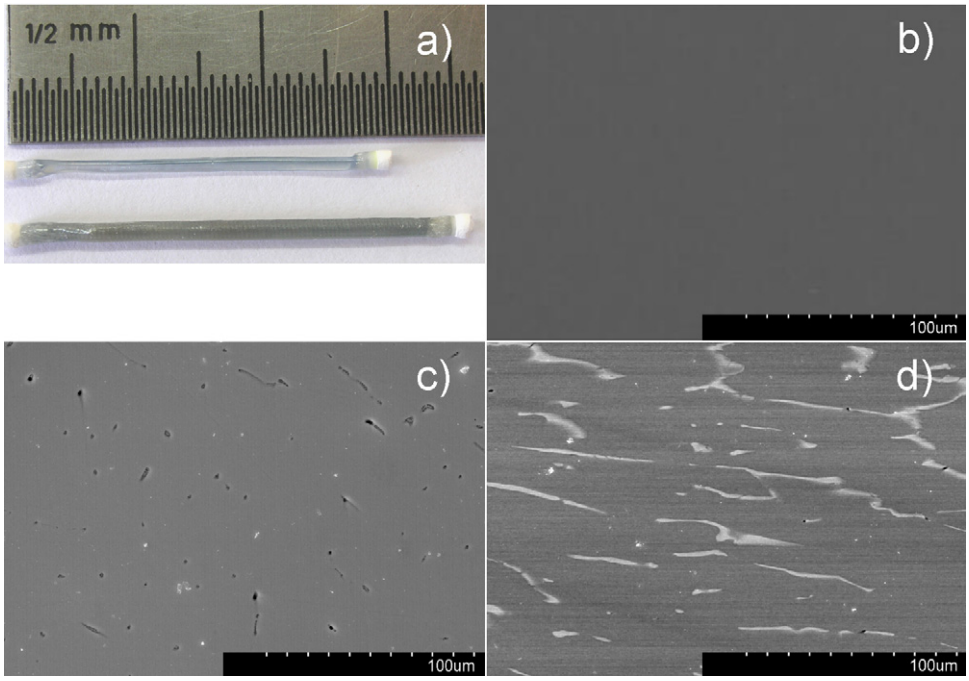

Fig. 1. Typical visual appearance of the (a) (top) undoped and (bottom) 0.1 mol % europium doped fibres grown at 30 mm h^{-1}. SEM micrographs of the (b) undoped fibre and europium doped fibres with (c) 0.1 mol % and (d) 3 mol % grown at 30 mm h^{-1}.

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