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Interplay between chromium content and lattice disorder on persistent luminescence of $ZnGa_2O_4:Cr^{3+}$ for in vivo imaging

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ABSTRACT

In the quest of bright and long persistent far-red/near-infrared phosphors for in vivo optical imaging, the interest in the family of $ZnGa_2O_4$ spinel compounds doped with Cr^{3+} has been aroused in the most recent years. We show that the dopant concentration plays an important role in the total persistent luminescence output of the material. $ZnGa_2O_4$ doped with 0.25%, 0.50% and 0.75% Cr relative to (Ga+Cr) was prepared by solid state synthesis. 0.50% Cr was found optimal to obtain the most intense persistent luminescence after matrix excitation with X-rays or localized excitation in Cr^{3+} absorption band with 550 nm wavelength. Up to 0.5% Cr content, persistent luminescence increases as a consequence of an increased number of Cr^{3+} luminescent centers and associated defects. With 0.75% Cr content, a too large number of defects locally concentrated around Cr^{3+} ions are detrimental to the long-term persistent luminescence intensity. We supplement long lasting phosphorescence investigation with laser excited photoluminescence and thermally stimulated luminescence results.

1. Introduction

$ZnGa_2O_4$ (ZGO) is a large band gap (4.5 eV) semiconductor with normal spinel structure [1,2]. In the 1990s it was reported for applications in vacuum fluorescent displays and field emission displays as the material was shown to present a broad blue emission band at 470 nm with excellent cathodoluminescence characteristics at low voltage and a perfect thermal stability [3,4]. It also drew attention as a novel UV transparent electronic conductor and as one of the most interesting substrates for GaN deposition to make thin films electroluminescent devices [5,6]. Doped with transition metal ions such as Mn^{2+} or Cr^{3+} the material turns into a phosphor emitting a bright green or red luminescence, respectively [7–9]. As a red phosphor emitting in the range 660–720 nm, Cr^{3+}-doped $ZnGa_2O_4$ (ZGO:Cr) aroused interest in bio-imaging application. Furthermore ZGO:Cr was recently discovered to exhibit an intense persistent luminescence – also called long-lasting phosphorescence (LLP) – i.e. to continue emitting light for hours after the end of an excitation [10]. Therefore we showed that ZGO:Cr nanoparticles presented ideal properties to play the role of persistent luminescence bio-markers and realize in vivo imaging of small animals using a cost-effective and harmless technique [11]. Indeed mammal tissues present a maximum transparency to light in the 650–1100 nm wavelength range [12]. Compared to first generation LLP bio-markers such as $Ca_{0.2}Zn_{0.9}Mg_{0.9}Si_2O_6:Eu^{2+}$, Mn^{2+}, Dy^{3+} [13] and $CaMgSi_2O_6:Eu^{2+}$, Mn^{2+}, Pr^{3+} [14] used for the proof of concept, ZGO:Cr family presents outstanding persistent luminescence properties after UV and visible light excitation [10,15–17]. The latter was shown to enhance the imaging capabilities of LLP phosphors since ZGO:Cr nanoparticles could be excited in vivo several times by orange excitation and enable long-term imaging necessary to the detection of carcinogenic tumors [16].

Considering the remarkable properties of this far-red/near infrared (NIR) persistent phosphor, the interest in ZGO:Cr has been aroused further in the most recent months. On the one hand, ZGO:Cr has become a compound of choice to investigate persistent luminescence mechanism [17,18] and on the other hand some interesting attempts to further enhance efficiency have been proposed. The following procedures have been reported as successful ways to improve LLP light yield/decay time duration: (i) a 1% ZnO deficiency in the reactants medium [10,18], (ii) a gallium substitution by tin or germanium [15,19], (iii) a co-doping by bismuth [20], and (iv) Cr^{3+}/Pr^{3+} codoping in gallogermanates [21]. It is interesting to note that all these materials were doped with chromium ions. However, we believe that the Cr content should also be checked for optimization of persistent luminescence which is not reported so far to best of our knowledge.

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The object of the present work is to investigate the influence of the chromium content in ZGO:Cr. The study will establish the interplay between the chromium concentration for most intense persistent luminescence and the presence of quenching structural defects.

2. Materials and methods

Four ZGO:Cr samples were prepared by a solid state method. A nominal 1% Zn deficiency relative to stoichiometry was introduced in the reactants ratio (Zn/(Ga+Cr)=0.495) as this was shown to yield enhanced LLP and to manage the structural disorder [10,18]. One un-doped and three doped samples with 0.25, 0.50 and 0.75 at% Cr relative to (Ga+Cr) were prepared. Appropriate amounts of zinc oxide (ZnO), gallium oxide (Ga_2O_3) and chromium trioxide (CrO_3) were mixed and ground in an agate mortar with isopropan-2-ol to obtain 1 g final product. The mixtures were dried at 60 °C to evaporate excess alcohol. 1 cm-diameter pellets were pressed before annealing in air at 1300 °C for 6 h. The samples were carefully ground before any measurement. It is important to note that the oxidation state of Cr in the starting doping CrO_3 is 6+. However, CrO_3 decomposes above 197 °C liberating oxygen and gives Cr_2O_3 following the reaction: $4\ CrO_3 \rightarrow 2\ Cr_2O_3 + 3\ O_2$ [22]. As our samples were annealed at much higher temperature, an obvious decomposition is expected. The lack of Cr in 4+, 5+ and 6+ valence states was checked by reflectance, photoluminescence and EPR, as discussed in later sections.

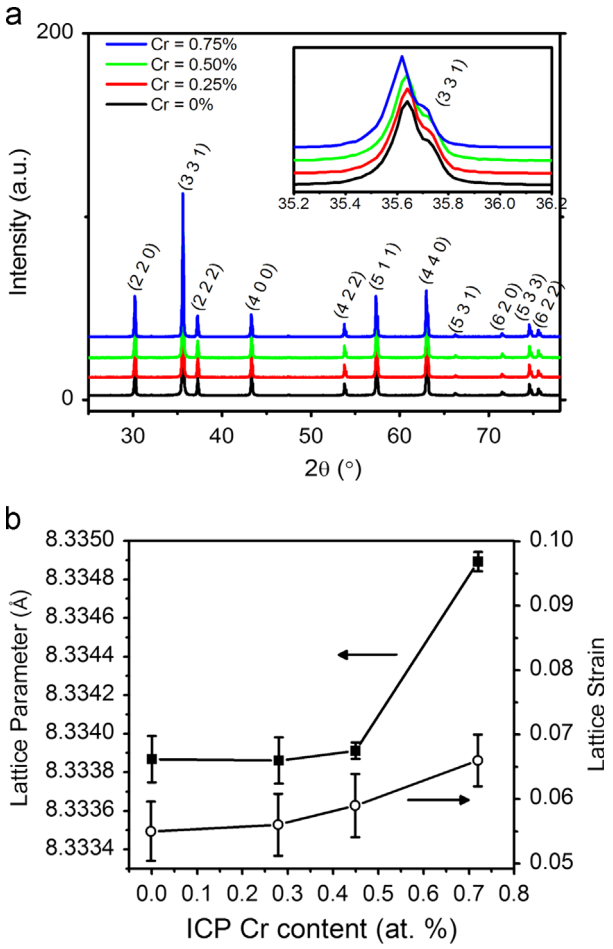

Fig. 1. (a) X-ray diffraction pattern of undoped and chromium-doped $ZnGa_2O_4$. The inset shows an expanded view of the (331) diffraction peak. (b) Variation of lattice parameter and lattice strain with chromium concentration measured by ICP-AES.

X-ray diffraction (XRD) patterns were recorded with a Rigaku X-ray diffractometer working with CuKα radiation (λ=1.5406 Å) and equipped with a horizontal goniometer. The diffractograms were recorded at a scan speed of 2°/min and a step size of 0.02° over a wide 2θ range (20–80°). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on iCAP 6000 series emission spectrometer with charge injection device (CID) detector RACID86. Prior to ICP-AES measurement, overnight refluxing at 120 °C was performed to dissolve 10 mg powder sample into 10 ml 51% HNO_3 aqueous solution. Standard Cr solution from SCP Science (number S110505001) was used to prepare solutions for calibration curve. Diffuse reflectance was measured by a Varian Cary UV–vis–NIR spectrophotometer 6000i. The light from a halogen lamp for visible range (> 360 nm) and deuterium lamp for UV range (< 360 nm) is passed through a monochromator before it reaches an integrating sphere containing the sample and a barium sulfate standard (for baseline correction). The powders were firmly packed into a 1.5 cm diameter sample holder and mounted on the sample port of the integrating sphere. Pulsed laser excited photoluminescence (PL) was run on 6 mm-diameter pellets (50 mg powder) silver glued on the cold finger of a cryogenic system and maintained at 20 K. The emitted light was collected by an optical fiber and transmitted to a Scientific Pixis 100i CCD camera cooled at −20 °C and coupled to a monochromator with 1200 groves/mm grating. The pellets were excited by an optical parametric oscillator (OPO) pumped by the tripled excitation of a YAG:Nd laser. The PL spectra were measured with 10 ms gate width and 26 ns gate delay. X-band (~9.45 GHz frequency) and Q-band (~35 GHz) electron paramagnetic resonance (EPR) measurements were performed at room temperature on weight normalized samples using a Bruker Elexsys E500 continuous wave EPR spectrometer. Simulations of EPR spectra were performed using X-Sophe software tool from Bruker. LLP was measured at room temperature (295 K) on 180 mg powder samples packed into a 1 cm-diameter sample holder. Emitted light was collected via an optical fiber with a Scientific Pixis 100 CCD camera cooled at −65 °C coupled with an Acton SpectraPro 2150i spectrometer for spectral analysis. Two types of excitation, X-rays (Mo-tube, 20 mA – 50 kV, λ=0.66729 ± 0.0463 Å) and green laser light from the OPO (λ=550 nm, 10 mJ, pulse width 4 ± 1 ns) were used to excite LLP. Excitation and luminescence were performed at 45° angle from the sample surface thereby making a total 90° angle between excitation and detection. All the samples were bleached at 250 °C for 20 min and kept in the dark prior to any LLP measurement.

3. Results and discussion

The XRD patterns of the four samples are shown in Fig. 1(a). They all present the expected diffraction peaks of ZGO spinel with the Fd3m cubic space group. The un-doped and all doped samples exhibit no impurity phases. The position and width of the peaks are identical for the 0%, 0.25% and 0.50% Cr-doped samples, evidencing no structural change or disorder with the introduction of up to 0.50% Cr in ZGO structure. The XRD peaks of the 0.75% Cr-doped sample are slightly shifted towards small angles (see the inset of Fig. 1(a)). The lattice parameters calculated using Rietveld refinement and the lattice strain evaluated using the Williamson–Hall method are reported in Fig. 1(b). The abscissa of Fig. 1 (b) displays the samples chromium content measured by ICP-AES. The latter for the nominal 0.25% Cr-doped sample was found to be 0.28 ± 0.01%, i.e. slightly higher than the nominal value. For the two other Cr-doped samples, the value measured by ICP-AES is