



## Synthesis and microstructural properties of mixed iron–gallium oxides



Stjepko Krehula<sup>a,\*</sup>, Mira Ristić<sup>a</sup>, Shiro Kubuki<sup>b</sup>, Yusuke Iida<sup>b</sup>, Marija Perović<sup>c</sup>, Martin Fabián<sup>d</sup>, Svetozar Musić<sup>a</sup>

<sup>a</sup> Division of Materials Chemistry, Ruđer Bošković Institute, P.O. Box 180, HR-10002 Zagreb, Croatia

<sup>b</sup> Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Minami-Osawa 1-1, Hachi-Oji, Tokyo 192-0397, Japan

<sup>c</sup> Institute of Nuclear Sciences Vinca, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia

<sup>d</sup> Institute of Geotechnics, Slovak Academy of Sciences, 043 53 Košice, Slovakia

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### ABSTRACT

Various mixed Fe–Ga oxides were prepared by the calcination of mixed Fe–Ga oxyhydroxide precursors ( $\alpha$ -Fe<sub>1-x</sub>Ga<sub>x</sub>OOH solid solutions,  $0 \leq x \leq 1$ ) at 500 or 1000 °C. Isostructural corundum-type oxides  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, as well as their solid solutions  $\alpha$ -Fe<sub>2-x</sub>Ga<sub>x</sub>O<sub>3</sub> in the entire concentration range ( $x = 0, 0.4, 1, 1.6$  and  $2$ ) were prepared by calcination at 500 °C. An increase in the Ga content in  $\alpha$ -Fe<sub>2-x</sub>Ga<sub>x</sub>O<sub>3</sub> resulted in a reduction of the unit cell size, a weakened hyperfine magnetic field, a disappearance of the Morin transition, an increase of magnetization at low temperatures, a shift in the position of IR bands to higher wavenumbers, and a lower intensity of absorption bands in the UV–Vis–NIR spectra. The calcination of Fe–Ga oxyhydroxides at 1000 °C resulted in the formation of a rhombohedral  $\alpha$ -Fe<sub>2-x</sub>Ga<sub>x</sub>O<sub>3</sub> phase for  $x = 0$  and  $0.4$ . An orthorhombic GaFeO<sub>3</sub> phase with Fe<sup>3+</sup> cations located in 3 different octahedral sites was obtained by the calcination at 1000 °C of mixed Fe–Ga oxyhydroxide with the Fe:Ga ratio of 1:1. A monoclinic phase  $\beta$ -Fe<sub>2-x</sub>Ga<sub>x</sub>O<sub>3</sub> ( $x = 1.6$  and  $2$ ) was obtained by the calcination at 1000 °C of Fe–Ga oxyhydroxides with 80 and 100 mol% Ga. The monoclinic  $\beta$ -Ga<sub>1.6</sub>Fe<sub>0.4</sub>O<sub>3</sub> showed two strong luminescence peaks in the blue region of the PL spectrum.

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### 1. Introduction

Iron and gallium oxides have been intensively investigated over the past decade due to their suitable properties for a number of advanced applications (magnetic materials, catalysts, photocatalysts, photoanodes, gas sensors, luminescent materials, etc.) [1–7]. The properties of these oxides can be improved or tuned by modifying the morphology [1–4], as well as by incorporating foreign cations into their structure [1,4]. Due to the same charge and similar ionic radii, Fe<sup>3+</sup> and Ga<sup>3+</sup> have a high potential for mutual substitution in the structure of the corresponding iron or gallium oxide, respectively [8,9]. However, fairly different electron configurations of these two cations cause a strong dependence of the properties of mixed iron–gallium oxides on their relative content.

Mixed iron–gallium oxides have been the subject of scientific interest for years. Orthorhombic gallium–iron oxide Ga<sub>2-x</sub>Fe<sub>x</sub>O<sub>3</sub> ( $0.7 \leq x \leq 1.4$ ) [10,11], which is isostructural with AlFeO<sub>3</sub> [12] and  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> [13,14], has been largely investigated for its multiferric (ferromagnetic and ferroelectric) properties [10,15–19]. The

magnetic properties of orthorhombic Ga<sub>2-x</sub>Fe<sub>x</sub>O<sub>3</sub> are strongly dependent on the Ga and Fe content (parameter  $x$ ) [16,19–21] and on the distribution of these cations in four different cationic sites which can be varied by modifying the preparation method [16,18,22,23].

Corundum-type rhombohedral  $\alpha$ -(Ga<sub>x</sub>Fe<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> solid solutions (in the range  $0.01 \leq x \leq 0.90$ ) were prepared by the thermal treatment of mixed Fe–Ga hydroxides at 600 °C, while their properties were studied using XRD and Mössbauer spectroscopy [8]. Mixed gallium–iron oxides obtained by the calcination of mixed gallium–iron oxyhydroxides [24] at 400, 800 or 1000 °C were studied by XRD, FT-IR and UV–Vis spectroscopy [9]. The structural and magnetic properties of  $\alpha$ -Fe<sub>2-x</sub>Ga<sub>x</sub>O<sub>3</sub> samples ( $x = 0.28$ – $0.6$ ) prepared by the vacuum annealing of Fe–Ga hydroxides were also studied [25]. Ga-doped hematite ( $\alpha$ -Fe<sub>2-x</sub>Ga<sub>x</sub>O<sub>3</sub>,  $x = 0.6$  and  $1$ ) has been successfully tested as a photocatalyst in the visible-light photodecomposition of H<sub>2</sub>S [26]. Kaneko et al. [27] prepared thin  $\alpha$ -(Ga<sub>1-x</sub>Fe<sub>x</sub>)<sub>2</sub>O<sub>3</sub> films with optical band gaps tuned to values between those of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> (2.2 and 5.3 eV, respectively) by changing the Fe and Ga content ( $x$ ).  $\alpha$ -(Ga<sub>0.42</sub>Fe<sub>0.58</sub>)<sub>2</sub>O<sub>3</sub> thin film, with a Curie temperature above 300 K, showed a higher magnetization and coercivity than  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin film [28]. Ga-doped hematite  $\alpha$ -Fe<sub>1.4</sub>Ga<sub>0.6</sub>O<sub>3</sub> with specific magnetic, dielectric and

\* Corresponding author. Tel.: +385 1 4561 094; fax: +385 1 4680 098.

E-mail address: [krehul@irb.hr](mailto:krehul@irb.hr) (S. Krehula).

photo-absorption properties was synthesized by the mechanical alloying of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> powders and subsequent heating at 800 °C in vacuum [29]. The onset potential of photoelectrochemical water oxidation on hematite photoanode can be enhanced by the deposition of an isostructural  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> overlayer [30].

Ohkoshi et al. investigated Ga-substituted  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles ( $\epsilon$ -Ga<sub>x</sub>Fe<sub>2-x</sub>O<sub>3</sub>,  $0 < x \leq 0.67$ ) and observed an increase in saturation magnetization (up to  $x = 0.47$ ) and a decrease in Curie temperature upon Ga-substitution [31,32]. Having shown ferromagnetic resonance in the millimeter wave range with a frequency depending on the Ga content, this material has a potential application as an absorber of electromagnetic radiation in the millimeter wave spectral region [31]. Enhanced magnetism in Ga-doped iron oxide was also observed for magnetite nanoparticles doped with Ga<sup>3+</sup> ions in tetrahedral positions [33,34]. A decrease in the Curie temperature of magnetite through Ga-doping was observed using Mössbauer spectroscopy [35].

In our previous work [36] we investigated the properties of mixed Fe–Ga oxyhydroxide samples ( $\alpha$ -Fe<sub>1-x</sub>Ga<sub>x</sub>OOH solid solutions,  $0 \leq x \leq 1$ ) synthesized by precipitation in a weakly alkaline medium using an organic alkali tetramethylammonium hydroxide (TMAH) for pH adjustment. A strong influence of the Ga and Fe content on the unit cell size, particle size and shape, hyperfine magnetic field, thermal, infrared and UV–Vis properties was observed. In order to elucidate the influence of the Ga and Fe content on the properties of mixed Fe–Ga oxides, thus formed  $\alpha$ -Fe<sub>1-x</sub>Ga<sub>x</sub>OOH solid solutions were used for the preparation of different Fe–Ga mixed oxides by their calcination at two different temperatures (500 or 1000 °C).

## 2. Experimental

### 2.1. Sample preparation

Mixed Fe–Ga oxide samples were prepared by the calcination of mixed Fe–Ga oxyhydroxide samples,  $\alpha$ -Fe<sub>1-x</sub>Ga<sub>x</sub>OOH where  $x = 0$  (sample Ga0),  $x = 0.2$  (Ga20),  $x = 0.5$  (Ga50),  $x = 0.8$  (Ga80) or  $x = 1$  (Ga100), synthesized within an earlier work [36]. The thermal analysis of Fe–Ga oxyhydroxide samples (Fig. 1) showed a weight loss in the TGA curve and peaks in the DTG and DTA curves varying in the range from 250 to 400 °C (in dependence on the Ga and Fe content). These features were induced by the thermal dehydroxylation of  $\alpha$ -Fe<sub>1-x</sub>Ga<sub>x</sub>OOH followed by the formation of  $\alpha$ -Fe<sub>2-x</sub>Ga<sub>x</sub>O<sub>3</sub> ( $x = 0, 0.4, 1, 1.6$  or  $2$ ).  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is the most stable iron oxide at high temperatures in air atmosphere [37], whereas  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> transforms at high temperatures into the most stable gallium oxide  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [38,39]. For this reason, mixed Fe–Ga oxide samples were prepared by the calcination of corresponding Fe–Ga oxyhydroxides at two different temperatures, 500 or 1000 °C.

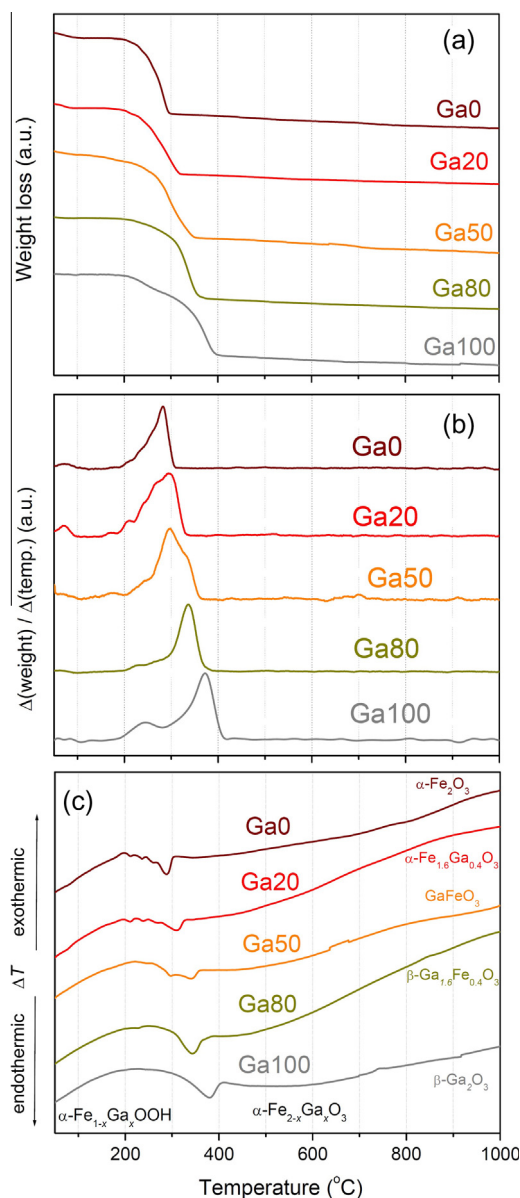
Oxyhydroxide samples were calcined in a furnace at 500 °C for 2 h or at 1000 °C for 6 h, respectively. The temperature in the furnace was raised to the corresponding value at a rate of 5 °C/min. The calcined samples were cooled down to room temperature naturally within the furnace. Obtained powder samples (Fig. 2) were characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and Fourier transform infrared (FT-IR) spectroscopy. Samples containing iron were analyzed by <sup>57</sup>Fe Mössbauer spectroscopy. Selected samples were additionally analyzed by SQUID magnetometry, diffuse reflectance UV–Vis–NIR spectroscopy and photoluminescence (PL) spectroscopy.

### 2.2. Instrumentation

Thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG) and differential thermal analysis (DTA) of Fe–Ga oxyhydroxide samples (5 mg) were carried out by Rigaku Thermo Plus TG8120 between RT and 1000 °C at a heating rate of 10 °C min<sup>-1</sup> in air atmosphere using the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> standard.

X-ray powder diffractometer APD 2000 (Cu K $\alpha$  radiation, graphite monochromator, NaI-Tl detector) manufactured by ItalStructures (G.N.R. s.r.l., Novara, Italy) was used. Potassium bromide (Sigma–Aldrich,  $\geq 99\%$  trace metals basis) was used as an internal standard. The Rietveld refinements of XRD data were performed using the MAUD program [40].

A JEOL thermal field emission scanning electron microscope (FE-SEM, model JSM-7000F) was used for the observation of particle morphology. FE-SEM was connected to the Oxford Instruments EDS/INCA 350 energy dispersive X-ray analyzer for elemental analysis. The specimens were not coated with an electrically conductive surface layer.



**Fig. 1.** Thermal analysis of prepared  $\alpha$ -Fe<sub>1-x</sub>Ga<sub>x</sub>OOH samples: (a) thermogravimetric analysis (TGA), (b) differential thermogravimetric analysis (DTG), and (c) differential thermal analysis (DTA).

<sup>57</sup>Fe Mössbauer spectra were recorded at 20 °C (293 K) in the transmission mode using a standard WissEl (Starnberg, Germany) instrumental configuration. A <sup>57</sup>Co/Rh Mössbauer source was used. The velocity scale and all data refer to the metallic  $\alpha$ -Fe absorber at 20 °C. A quantitative analysis of the recorded spectra was made using the MossWinn program [41].

Magnetic measurements were carried out on a superconducting quantum interference device magnetometer (Quantum Design MPMS XL-5). The temperature dependences of magnetization (field cooling, FC, and zero field cooling, ZFC) were measured in the temperature range 2–300 K and in the applied field of 1000 Oe. The isothermal dependence of magnetization on an external magnetic field was measured at 5 and 300 K in the field range –5 to 5 T.

Fourier transform infrared (FT-IR) spectra were recorded at RT using a Perkin-Elmer spectrometer (model 2000). The FT-IR spectrometer was connected to a PC with the installed IRDM (IR data manager) program to process the recorded spectra. The specimens were pressed into small disks using a spectroscopically pure KBr matrix.

Diffuse reflectance UV–Vis–NIR spectra were obtained at 20 °C using a Shimadzu UV–Vis–NIR spectrometer (model UV-3600) equipped with an integrated sphere. Barium sulfate was used as reference.

PL spectra were recorded using PC1 (ISS, USA) spectrofluorimeter using a 300 W Xe lamp. Approximately  $2.5 \times 10^{-5}$  mol dm<sup>-3</sup> solid in an ethanol dispersion of investigated sample was prepared by ultrasonification. The dispersion was measured under 90° scattering geometry with an excitation wavelength of 254 nm.

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