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Application of sol–gel method in the synthesis of gallium(III)-oxide

M. Ristić[a,*], S. Popović[b], S. Musić[a]

[a]Division of Materials Chemistry, Ruđer Bošković Institute, P. O. Box 180, HR-10002 Zagreb, Croatia
[b]Department of Physics, Faculty of Science, University of Zagreb, P. O. Box 331, HR-10002 Zagreb, Croatia

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Abstract

Precipitations by hydrolysis of gallium(III)-isopropoxide and from aqueous $GaCl_3$ solution by addition of aqueous tetramethylammonium hydroxide (TMAH) solution were utilized to obtain gallium(III)-oxide precursors. The precursors thus formed and the samples obtained upon heating these precursors at high temperatures were analysed by XRD, FT-IR and TEM. Amorphous phase (dominant) and nanosized α-GaOOH particles (several nanometers in size) were obtained by addition of hot water and TMAH solution to the solution of gallium(III)-isopropoxide dissolved in 2-propanol. A completely amorphous precipitate was obtained by hydrolysis of gallium(III)-isopropoxide with pure water at room temperature, and upon heating this precipitate at 500 °C the nanosized β-Ga_2O_3 particles (size ~10 to 20 nm) were obtained. On the other hand, α-GaOOH particles, as a single phase, were obtained by precipitation from aqueous $GaCl_3$ solution with addition of aqueous TMAH solution. These α-GaOOH particles transformed at 500 °C to α-Ga_2O_3 as a single phase. Upon heating at 900 °C, in all cases only β-Ga_2O_3 was detected. The size and morphology of the particles in the samples investigated depended on the starting chemicals and the conditions of the experiment. Differences in the mechanism of the precipitation by hydrolysis of gallium(III)-isopropoxide or the precipitation from aqueous solution of $GaCl_3$ by addition of strong organic alkali (TMAH) were suggested.

Keywords: Sol–gel; α-GaOOH; α-Ga_2O_3; β-Ga_2O_3; XRD; FT-IR; TEM

1. Introduction

Gallium(III)-oxyhydroxide or amorphous gallium(III)-(hydrous)oxide are suitable precursors in the synthesis of crystalline gallium(III)-oxide. The chemical, microstructural and physical properties of Ga_2O_3 depend on the properties of its precursor, and this means that it is possible to control the properties of Ga_2O_3 by varying the precipitation chemistry of the corresponding precursor.

The precipitation chemistry of gallium(III)-(hydrous)oxide has not been extensively investigated in relation to other metal oxides, and specifically in comparison with aluminium which is chemically similar to gallium. Gimblett [1] monitored hydrolysis of $Ga(ClO_4)_3$ solutions and formation of the solid phase at 50 °C using turbidimetric and pH measurements. The crystalline phase was identified as gallium(III)-oxyhydroxide. Hamada et al. [2] monitored hydrolysis of Ga(III)-salt solutions at 98 °C. Additions of H_2SO_4 or mixture of acids, H_2SO_4+HNO_3, influenced the size and shape of the precipitated particles. Yada et al. [3] investigated the precipitation process induced by heating the aqueous system: $GaCl_3$+urea+SDS (SDS=sodium dodecyl sulfate). In specific cases, dodecyl alcohol was added to that system. The formation of a templated mesophase with hexagonal and lamellar structures was noticed. Tas et al. [4] reported the formation of GaOOH particles by forced hydrolysis of Ga^{3+} ions in pure water or in the presence of decomposing urea. Two different morphologies of GaOOH particles (rod-like without urea and zeppelin-like with urea) were obtained.

Cheng and Samulski [5] prepared Ga_2O_3 nanotubes by immersing alumina membrane in amorphous $Ga_2O_3 \cdot nH_2O$ sol, followed by drying, then heating at 500 °C. Amorphous $Ga_2O_3 \cdot nH_2O$ gel was precipitated from ethanolic solution

* Corresponding author. Tel.: +385 1 4680 107; fax: +385 1 4680 098.
E-mail address: mira.ristic@irb.hr (M. Ristić).

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of $Ga(NO_3)_3$ using ammonia solution, then the precipitate was thermally treated to obtain γ-Ga_2O_3 [6] or β-Ga_2O_3 [7].

Recently, researchers also focused on the synthesis of nanostructured Ga_2O_3 using high-temperature reactions. For example, Ga_2O_3 nanowires were obtained by evaporation of gallium nitride in the argon/oxygen flow [8], arc-discharge method [9] or laser ablation [10]. Additional nanostructures such as nanoribbons and nanosheets were obtained by high-temperature reaction of Ga° with water [11] or by evaporation of gallium nitride at high temperature in the presence of oxygen [12].

Ga_2O_3 is a material of technological importance, for example, in preparation of mixed Ga_2O_3–Al_2O_3 catalysts [13–16]. Thin Ga_2O_3 films are of commercial interest, as gas sensitive material [17–19]. Ga_2O_3 based glasses are among the best optical materials used in advanced glass technologies [20].

In the present work, we have focused on the application of sol–gel method in the synthesis of gallium(III)-oxide using gallium(III)-isopropoxide as the starting chemical. For comparison, the precipitation from $GaCl_3$ aqueous solution is also reported. The aim of this research has been to obtain more data on the influence of experimental procedure on the synthesis and properties of gallium(III)-oxide.

2. Experimental

2.1. Chemicals

Gallium(III)-isopropoxide [$Ga(OC_3H_7)_3$], gallium(III)-chloride and TMAH [tetramethylammonium hydroxide; 25% w/w electronic grade (99.9999%) aqueous solution] were supplied by Alfa Aeser®. Water-free 2-propanol and absolute ethanol of analytical grade by Kemika were used. Twice distilled water was prepared in authors' laboratory.

2.2. Preparation of samples

Sample G1 was prepared by dissolving 2.704 g of $Ga(OC_3H_7)_3$ into 200 ml of water-free 2-propanol under strong mixing. The resulting solution was clear. 200 ml of hot (90–100 °C) twice distilled water was then abruptly added into the solution, followed by addition of 2 ml of 25% w/w TMAH solution, also under strong mixing. The precipitate obtained was separated from mother liquor using an ultra-speed centrifuge, Sorvall RC2-B, with an operational range up to 20,000 r.p.m. The precipitate was subsequently washed with absolute ethanol and twice distilled water, then dried.

Sample G2 was prepared by abrupt adding 50 ml of twice distilled water (~20 °C) to 1.796 g $Ga(OC_3H_7)_3$. The closed flask with the colloidal suspension was treated ultrasonically for 1 h. Then, the suspension was transferred into Petri dish and the liquid phase was evaporated at 70 °C over 24 h.

Sample GC1 was prepared by adding 175 ml of twice distilled water (~20 °C) to 25 ml of 0.284 M $GaCl_3$ aqueous solution, then the precipitation was performed with 25% w/w aqueous solution of TMAH up to pH 7.82. After 2 h of aging at room temperature the precipitate was isolated by centrifugation, then subsequently washed with twice distilled water and dried.

Samples G1, G2 and GC1 were heated in contact with air in a standard laboratory furnace at 500 °C for 4 h, and then at 900 °C for 2 h.

2.3. Instrumentation

All samples were characterized with XRD, FT-IR and TEM. X-ray powder diffraction patterns were taken at RT using a Philips diffractometer (model MPD 1880, proportional counter, graphite monochromator, radiation Cu$K\alpha$). A small amount of each sample was spread on a very thin layer on a microscopic glass in order to minimize parasitic scattering of X-rays. Fourier transform infrared (FT-IR) spectra were recorded at RT using a Perkin-Elmer spectrometer, model 2000. The IR Data Manager (IRDM) program supplied by Perkin-Elmer was used to process the recorded spectra. The specimens were pressed into small discs using a KBr matrix, spectroscopically pure obtained from Merck. TEM observation of the samples was performed using a Philips transmission electron microscope, model Morgagni 268.

3. Results and discussion

Characteristic parts of XRD patterns of precipitates G1, G2 and GC1 are shown in Figs. 1–3 together with the patterns of samples obtained by heating these precipitates at 500 and 900 °C. XRD data obtained for all the samples are given in Table 1.

The crystalline phases in the investigated samples were identified according to the data contained in the ICDD Powder Diffraction File [21]: Card No. 06-0180 for α-GaOOH [space group *Pbnm* (62), unit-cell parameters a=4.58, b=9.80, c=2.97 Å, isostructural with α-FeOOH, goethite]; Card Nos. 43-1013 and 74-1610 for α-Ga_2O_3 [space group $R\bar{3}c$(167), unit-cell parameters a=4.982, c=13.433 Å, isostructural with α-Fe_2O_3, hematite]; Card Nos. 43-1012, 76-0573 and 87-1901 for β-Ga_2O_3 [space group $C2/m$ (12), unit-cell parameters a=12.21, b=3.037, c=5.798 Å, β=103.83°].

XRD pattern of sample G1 (Fig. 1) showed dominantly amorphous fraction and small fraction of a crystalline phase identified as α-GaOOH. When heated at 500 °C, it remained dominantly amorphous, but showed faint diffraction lines of α-Ga_2O_3 and β-Ga_2O_3. The same sample, upon heating at 900 °C, was β-Ga_2O_3 with broadened diffraction lines. XRD pattern of sample G2 (Fig. 2) showed completely amorphous nature of this sample. β-Ga_2O_3 was obtained