SYNTHESIS OF GALLIUM OXIDE HYDROXIDE CRYSTALS IN AQUEOUS SOLUTIONS WITH OR WITHOUT UREA AND THEIR CALCINATION BEHAVIOR

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ABSTRACT

Gallium oxide hydroxide ($GaOOH{\cdot}xH_2O$) single crystals were synthesized in aqueous solutions by using two different precipitation techniques; homogeneous decomposition of urea and forced hydrolysis in pure water. Precipitation of crystals started at exactly the same pH value (i.e., 2.05 at 85°C) in both cases. The morphology of crystals turned out to be quite different (zeppelin-like with urea, rod-like without urea) in each of the above methods. Calcination of these gallium oxide hydroxide crystals in air at temperatures ≥500°C transformed them into Ga_2O_3. Characterization of the samples were performed by x-ray diffraction, scanning electron microscopy, thermal analyses, infrared spectroscopy, and carbon and nitrogen analyses.

INTRODUCTION

Gallium (named after the region Gallia of France[1]) is an element, which is more abundant in the earth's crust as compared to some of the technologically important elements, such as B, Pb, Bi, Nb, Mo, W, Hg, or Sn[2]. Gallium oxide, like other oxides of Group III metals, is widely used for the preparation of phosphors and catalysts. Ga_2O_3 is normally an insulator, with a forbidden energy gap of ~4.9 eV[3]. However, calcination of Ga_2O_3 in reducing atmospheres turns it into an n-type semiconductor, due to the creation of oxygen vacancies[4]. The high-temperature structure of Ga_2O_3 (β form) is monoclinic (space group C2/*m*), and this is only one of five well known forms[5] of gallium oxide: α-, χ-, δ-, and ε-Ga_2O_3, and all of these polymorphs are converted to β-Ga_2O_3 at T>870°C[6]. Manufacture of *n*-type semiconducting Ga_2O_3 thin films on electrically insulating substrates have been studied by Meixner, *et al.*[7], which are considered and developed for the detection of reducing gases. It was also reported that different gas sensitivities can be chosen by the appropriate setting of the operating temperature, and at temperatures in excess of 900°C, the sensors may even be operated as O_2 sensors[8]. On the other hand, Haneda, *et al.* reported[9] that the Ga_2O_3-Al_2O_3

ceramic catalysts prepared by using the sol-gel method showed superior activity (as compared to those of either pure Al_2O_3 or Ga_2O_3) for the selective reduction of NO with propene in the presence of H_2O and SO_2.

Gallium oxide has recently been used in the synthesis of solid electrolytes of superior (as compared to stabilized zirconia's) ionic conductivity, i.e., $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$ (LSGM)[10], also beyond its significance for the semiconductor, optoelectronic, and catalysis technologies. We have encountered the fortuitous formation of GaO(OH) in aqueous solutions throughout the course of our recent studies, which were mainly focused on the wet-chemical synthesis of doped $LaGaO_3$ fuel cell ceramics[11, 12].

Laubengayer, *et al.*[13] synthesized α-GaO(OH) from a gel obtained *via* hydrolysis of gallium nitrate (or gallium chloride) at temperatures between 110° and 300°C. They found that $Ga(OH)_3$ transformed slowly into α-GaO(OH) in the aqueous solution. Precipitation of GaO(OH) from $GaCl_3$ solutions, upon the addition of various alkalis (such as NaOH and KOH), has also been studied by Sato, *et al.*[14], and they reported that the freshly precipitated (at pH values varying between 6 and 10) precursors were all X-ray amorphous and converted to crystalline α-GaO(OH), with an orthorhombic crystal structure similar to that of diaspore (α-AlO(OH))[15], only after about 1 day of aging in their mother liquors. α-GaO(OH) is a structural analogue of other oxidic hydrates, such as α-MnO(OH)[16] and Goethite: α-FeO(OH)[17]. Avivi, *et al.*[18] produced tubular particles of α-GaO(OH), after inserting an ultrasonic finger into 0.114 M aqueous solutions of $GaCl_3$ for 6 h. They claimed that the sonochemical reaction provided by the ultrasonic finger caused the hydrolyses of Ga-chloride solutions.

In this study, we used the precipitation methods of (a) the homogeneous decomposition of urea[19-21], and (b) forced hydrolysis (without urea, at 90°C) of dilute gallium nitrate solutions to form the GaO(OH) crystals. We believe that this study will help the upcoming researchers who would work on the wet-chemical synthesis of Ga-containing ceramics, which may have numerous applications.

EXPERIMENTAL

$Ga(NO_3)_3 \cdot 4.06H_2O$ (99.999%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) was used as the gallium source. A 0.37 M stock solution was first prepared by dissolving an appropriate amount of gallium nitrate in de-ionized water. Urea used was also reagent-grade (>99.5%, Merck GmbH, Darmstadt, Germany). Synthesis experiments were performed by two different precipitation techniques. For the homogeneous precipitation experiments, a 6.7 mL aliquot of the Ga-stock solution was mixed with 90 mL of de-ionized water, and 1.756 g of urea was then added. The resultant solution was heated

on an hot-plate to 90°C in about 45 minutes. For the forced hydrolysis experiments, again a 6.7 mL aliquot of the Ga-stock solution was mixed with 90 mL of de-ionized water, followed by heating it on an hot-plate to 90°C in about 45 minutes. Precipitates (in each of the above-described procedures), after 95 minutes of aging at the constant temperature of 90°C, were finally separated from their mother liquors by centrifugal filtration, followed by washing 4X with 2-propanol (>99%, Merck). Washed precipitates were dried in an oven at 90°C, overnight. The dried powders were first finely ground by using an agate mortar/pestle, and then calcined for 6 h (with a heating and cooling rate of 5°C/min), as loose powders, in alumina boats in air at various temperatures in the range of 250° to 1200°C.

Phase constitution of the powders was investigated by a powder X-ray diffractometer (D-5000, Siemens GmbH, Karlsruhe, Germany) using CuK_α radiation (40kV, 30 mA, step size: 0.016°, count time: 1 s). Pyrolysis of the accurately-weighed 224.8 mg portions of powders was monitored by simultaneous differential thermal and thermogravimetric analysis (STA501, Bähr GmbH, Bremen, Germany) in air with a scan rate of 5°C/min. Powder samples (1 wt% in KBr) were also characterized by FTIR (IFS 66, Bruker GmbH, Karlsruhe, Germany). C and N contents of samples were determined by the combustion-IR absorption method (CS-800, Eltra GmbH, Neuss, Germany). Powder samples were also investigated by field-emission scanning electron microscopy (FESEM: DSM 982 Gemini, Zeiss GmbH, Oberkochen, Germany).

RESULTS AND DISCUSSION

Both techniques used in this study produced well defined, monodisperse crystals of $GaO(OH) \cdot xH_2O$. Variation of pH, with time, during the precipitation runs (for both routes) has been continuously monitored and a

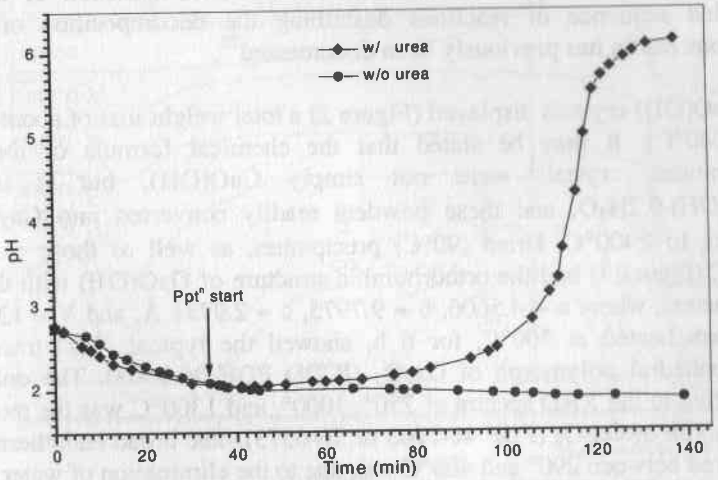

Figure 1 pH-time variation during precipitation runs typical plot is given in Figure 1. Thermal analysis of the precipitates of both

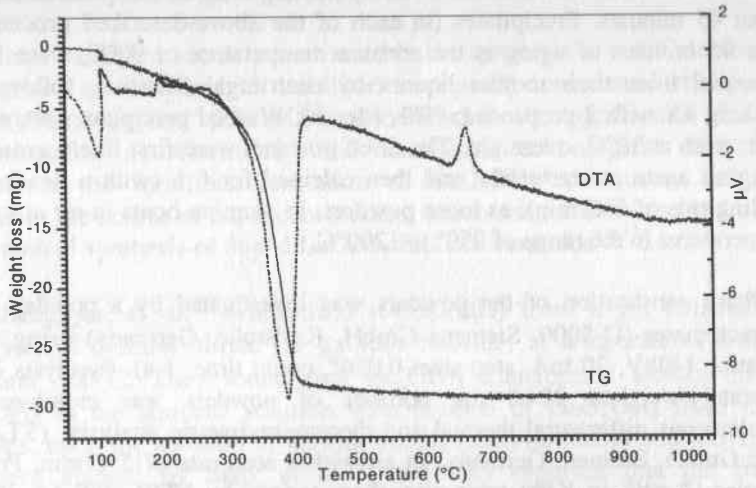

Figure 2 TG/DTA traces of GaO(OH) crystals formed

routes produced the same TG/DTA data and they are given in Figure 2. Precipitation started (seen by the onset of turbidity in the solutions) when the temperature reached 85°-86°C, regardless of the presence of urea in the solutions. The initial pH value of the 0.026 M Ga^{3+} solutions (with or without urea) was in the vicinity of 2.80 at 23°C, and precipitation started in both kinds of solutions when pH dropped down exactly to 2.05.

On the other hand, the steep rise in pH (when t > 80 min) observed in urea-containing solutions is characteristic for the decomposition of urea. The detailed sequence of reactions describing the decomposition of urea in aqueous media has previously been documented[22].

GaO(OH) crystals displayed (Figure 2) a total weight loss of about 13% (up to 1040°C). It may be stated that the chemical formula of the freshly precipitated crystals were not simply GaO(OH), but it is rather $GaO(OH)\cdot0.2H_2O$, and these powders readily converted into Ga_2O_3 upon heating to ≥400°C. Dried (90°C) precipitates, as well as those calcined at 250°C (Figure 3) had the orthorhombic structure of GaO(OH) with the lattice parameters, where a = 4.5606, b = 9.7975, c = 2.9731 Å, and V = 132.85 $Å^3$. Powders heated at 500°C, for 6 h, showed the typical XRD trace of the rhombohedral polymorph of Ga_2O_3 (ICDD PDF 06-0503). The only phase identified in the XRD spectra of 750°, 1000°, and 1300°C was the monoclinic polymorph of Ga_2O_3 (PDF 41-1103 or 76-0573). The broad endothermic peak appeared between 290° and 400°C was due to the elimination of water from

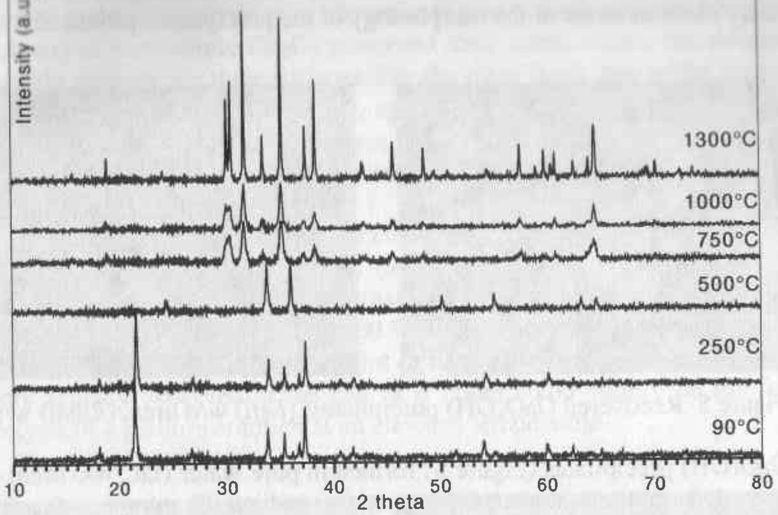

Figure 3 XRD traces of GaO(OH) crystals as a function of temperature

constitutional OH groups (Figure 2). The exothermic peak detected in the DTA trace of the powders, at around 670°C, corresponded to the polymorphic phase transformation in Ga_2O_3, from rhombohedral to monoclinic. The FTIR spectra (Figure 4) of the 90°C and 250°C-samples also showed (in agreement with the XRD data) the bands at 2036 and 1942, together with the bands at 1026 and 952 cm^{-1}, and these were assigned to be the constitutional Ga-OH bending bands, and their overtones, respectively, as reported by Sato, *et al.*[14].

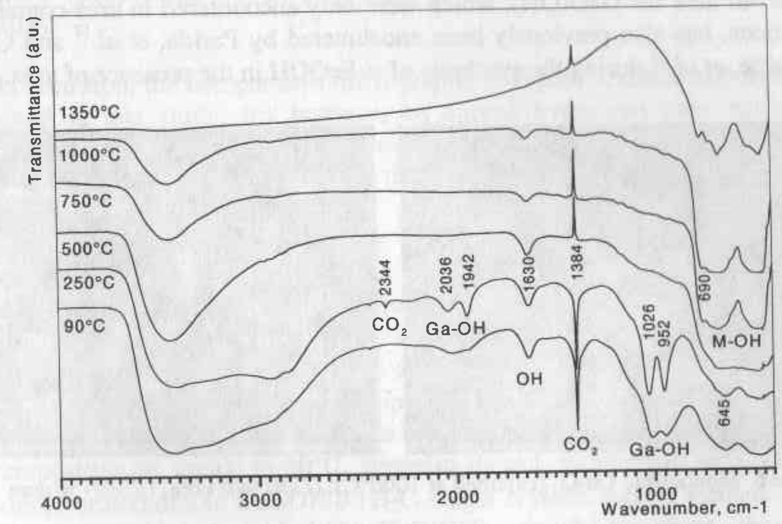

Figure 4 FTIR spectra of GaO(OH) crystals as a function of temperature

The main difference between the two synthesis techniques of this study actually came in terms of the morphology of the precipitates produced.

Figure 5 Recovered GaO(OH) precipitates; (*Left*) w/o urea, (*Right*) w/urea

GaO(OH) precipitates (Figure 5) formed in pure water (i.e., w/o urea) were recovered from their mother liquors at the end of 95 minutes of aging at 90±1°C and at the final pH value of 1.87. These single crystals possessed a unique rod-like morphology as shown above, with an average rod length of about 3 μm. However, the precipitates formed just at the precipitation-start point (i.e., pH=2.05, T=86°C) in urea-containing solutions consisted of little (200 to 500 nm-long) crystalline "zeppelins." Precipitates recovered from the same solution (w/urea) after 95 minutes of aging (at 90±1°C, final pH=6.10) in the mother liquor still had the unique zeppelin morphology, but their lengths increased to about 1 to 2 μm. Bigger zeppelins were also crystalline and had the same orthorhombic unit cell as given above. This unique morphology (zeppelins or elongated acicular or epitaxial-twinned crystals) observed here for GaO(OH), which were only encountered in urea-containing solutions, has also previously been encountered by Parida, *et al.*[17] and Goni-Elizalde, *et al.*[23] during the synthesis of α-FeOOH in the presence of urea.

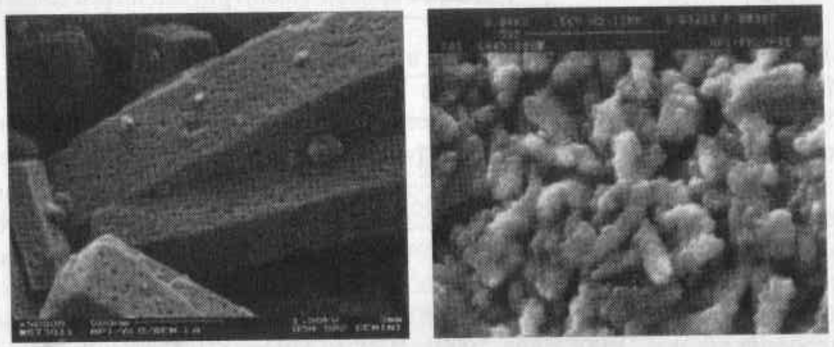

Figure 6 Monoclinic Ga_2O_3 (calcined at 1000°C); (*Left*) w/o urea, (*Right*) w/urea

Calcination of the powders at 1000°C in air, for 6 h, also produced a difference in their morphology as shown in Figure 6. Rods (obtained by forced hydrolysis) of monoclinic Ga_2O_3 preserved their initial shape, but developed nano-scale porosity on their surfaces. On the other hand, the initial zeppelin-like morphology totally disappeared, upon heating the powders obtained via homogeneous decomposition of urea at 1000°C, although they had the characteristic XRD pattern for monoclinic Ga_2O_3.

Avivi, *et al.*[18] reported the strong necessity of "ultrasonic hydrolysis for the sonochemical formation" of scroll-like cylindrical or tubular GaO(OH) particles. It should be remembered that the insertion of an ultrasonic finger into a solution, and operating it (@100 W/cm^2) in that solution for a long time like 6 hours would certainly cause a lot of heating of that solution. What these authors actually observed at the end of 6 hours could simply be the forced hydrolysis of a gallium solution at an elevated temperature.

Figure 7 Monoclinic Ga_2O_3 (*L*) w/o urea, 1000°C, (*R*) commercial Ga_2O_3 powders

As seen from the comparative micrographs of Figure 7, GaO(OH) powders obtained in this study, for instance, by forced hydrolysis may easily be converted to monoclinic Ga_2O_3 after heating at 1000°C, and they possess more uniform morphology as compared to those of Sigma-Aldrich Ga_2O_3 powders (Lot. No. 33281-110).

CONCLUSIONS

Upon heating a dilute (0.026 M) aqueous solution of Ga-nitrate at 90°C for 95 minutes (i.e., forced hydrolysis), rod-like, monodispersed, 1-3 μm-long orthorhombic $GaOOH{\cdot}0.2H_2O$ single crystals can be formed (starting at the pH value of 2.05 at 85°C), whereas upon heating a dilute (0.026 M) solution of Ga-nitrate, which also contains 0.304 M urea (i.e., homogeneous decomposition of urea), to 90°C, zeppelin-shaped, monodispersed, 200-500 nm-long, orthorhombic $GaOOH{\cdot}0.1H_2O$ single crystals can be formed, again at the exact pH value of 2.05. GaO(OH) crystals transform first into rhombohedral and then monoclinic polymorphs of Ga_2O_3, upon calcination in an air atmosphere for 6 h at temperatures ≥500°C. Carbon and nitrogen analyses, as well as the FTIR results, showed that the formed crystals (following drying at 90°C) did not contain any structural CO_3^{2-} and NO_3^- ions.

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