

Sonochemical Hydrolysis of Ga³⁺ Ions: Synthesis of Scroll-like Cylindrical Nanoparticles of Gallium Oxide Hydroxide

S. Avivi,[†] Y. Mastai,[‡] G. Hodes,^{*,‡} and A. Gedanken^{*,†}

Contribution from the Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel, and Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

Received October 8, 1998

Abstract: The sonochemical reaction of an aqueous solution of GaCl₃ led to the formation of gallium oxide hydroxide rolled up in a scroll-like layered structure to give cylinders 80–120 nm in diameter and 500–600 nm in length. Small amounts of metallic Ga were incorporated with these tubes. A mechanism for this reaction has been suggested where the reaction takes place in a shell surrounding the collapsing bubble.

Introduction

The synthesis of metallic nanoparticles has been extensively studied, and various methods have been employed for this purpose. Rieke and co-workers have reduced salts of active metals in ethers or hydrocarbon solvents either heterogeneously with alkali metals or homogeneously with radical anions of aromatic compounds.^{1–3} Reductions using alkalides and electrides in aprotic solvents,^{4,5} reductions with alkali metal organoborohydride solutions, such as NaB(Et)₃H,⁶ and reductions with BH₄[−] for Co, Ni, Au, Ag, and Pt⁷ have all yielded metallic nanoparticles. Other methods include pyrolysis of various precursors,⁸ evaporation⁹ and sputtering¹⁰ of metals, and sol-gel processes.¹¹ Among the more recent methods are controlled chemical¹² and electrochemical¹³ reductions.

Sonochemical reactions arise from acoustic cavitation phenomena: the formation, growth, and collapse of bubbles in a liquid medium.¹⁴ The extremely high temperatures (>5000 K), pressures (>20 MPa), and cooling rates (>10¹⁰ K/s) attained during acoustic cavitation lead to many unique properties in the irradiated solution.¹⁵ Suslick and co-workers have prepared nanophase amorphous F,¹⁵ from the sonication of both pure Fe(CO)₅¹⁵ and Fe(CO)₅ solution in Decalin.^{15b} They also prepared

amorphous cobalt from Co(CO)₃NO¹⁶ and its solution in Decalin or decane. Our group has synthesized nanophase amorphous nickel by sonication of a Decalin solution of Ni(CO)₄.¹⁷ Other metallic nanoparticles that we have prepared using ultrasound radiation include copper¹⁸ and palladium.¹⁹ The ultrasound-initiated formation of metal particles in aqueous solution is reviewed by Grieser.²⁰ He reports in particular on the preparation of metallic colloids such as Ag, Au, Tl, Pt, and Pd.

Little effort appears to have been devoted to sonochemical formation of metallic gallium or to its oxide hydroxide in general and to nanoparticles of these compounds in particular. There have been, however, a few attempts to document the preparation of gallium nanoparticles. They include homogeneous reduction with alkalides and electrides,⁵ the use of inert gas condensation,²¹ and evaporation–condensation in ultrahigh vacuum.²² The major product in our sonochemical reaction is gallium oxide hydroxide, also known as gallium oxy hydrate or monohydrate. It has been prepared by heating either α-Ga₂O₃ or δ-Ga₂O₃ in a wet atmosphere.²³ It can also be prepared by heating gallium metal with water in an autoclave at 200 °C or by dehydration of gallium trihydroxide at 100 °C.²⁴ Gallium oxide hydroxide has an orthorhombic crystal structure (*Pbnm*).

In this study, we have sonicated an aqueous solution of GaCl₃ and have obtained rolled-up tubular particles consisting of gallium oxide hydroxide containing a small amount of metallic Ga. The formation of the rolled-cigar-shaped layers will be

[†] Bar-Ilan University.

[‡] Weizmann Institute of Science.

(1) Rieke, R. D. *Science* **1989**, *24116*, 1260.

(2) Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7178.

(3) Rieke, R. D.; Hudnall, P. M.; Uhm, S. *J. Chem. Soc., Chem. Commun.* **1973**, 269.

(4) Tsai, K.-L.; Dye, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 1650.

(5) Tsai, K.-L.; Dye, J. L. *Chem. Mater.* **1993**, *5*, 540.

(6) Bonnemann, H.; Brijoux, W.; Joussen, T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 273.

(7) Glavee, G. N.; Klabunde, K. J.; Sorenson, C. M.; Hadjipanayis, G. C. *Langmuir* **1992**, *8*, 771.

(8) Fox, P. G.; Ehretzman, J.; Brown, C. E. *J. Catal.* **1971**, *20*, 67.

(9) Phillips, W. B.; Desloge, E. A.; Skofronick, J. G. *J. Appl. Phys.* **1967**, *39*, 3210. Davis, S. C.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153. Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(10) Chow, G. M.; Chien, C. L.; Edelstein, A. S. *J. Mater. Res.* **1991**, *6*, 8.

(11) Jean, J. H.; Ring, T. A. *Langmuir* **1986**, *2*, 251.

(12) Pileni, M. P. *Langmuir* **1997**, *13*, 3266. Huang, H. H.; Yan, Y. Q.; Kek, Y. M.; Chew, C. H.; Xu, G. Q.; Ji, W.; Oh, P. S.; Tang, S. H. *Langmuir* **1997**, *13*, 172.

(13) Reetz, M. T.; Helbig, W. *J. Am. Chem. Soc.* **1994**, *116*, 7401. Bandyopadhyay, S.; Chakravorty, D. *J. Mater. Res.* **1997**, *12*, 2719.

(14) Suslick, K. S. *Ultrasound: Its Chemical, Physical and Biological Effects*; VCH: Weinheim, 1988.

(15) (a) Suslick, K. S.; Choe, S. B.; Cichowlas, A. A.; Grinstaff, M. W. *Nature* **1991**, *353*, 414. (b) Grinstaff, M. W.; Cichowlas, A. A.; Choe, S. B.; Suslick, K. S. *Ultrasonics* **1992**, *30*, 168.

(16) Suslick, K. S.; Fang, M.; Hyeon, T.; Cichowlas, A. A. In *Molecularly Designed Nanostructured Materials*; Gonsalves, K. E., Chow, G. M., Xiao, T. O., Cammarata, R. C., Eds.; MRS Symposium Proceedings 351; Materials Research Society: Pittsburgh, PA, 1994; pp 443–448.

(17) Koltypin, Yu.; Katabi, G.; Prozorov, R.; Gedanken, A. *J. Non. Cryst. Solids* **1996**, *201*, 159.

(18) Dahs, N. A.; Raj, C. P.; Gedanken, A. *Chem. Mater.* **1998**, *10*, 1446.

(19) Dhas, N. A.; Gedanken, A. *J. Mater. Chem.* **1998**, *8*, 445.

(20) Grieser, F. In *Semiconductor Nanoclusters*; Kamat, P. V., Meisel, D. Eds.; Elsevier Science: Amsterdam, The Netherlands, 1996; p 67.

(21) Laur, St.; Ehrhardt, H.; Zimmer, H. G.; Wolf, H.; Wichert, Th. *Mater. Sci. Forum* **1996**, *225*, 197.

(22) Nisoli, M.; Stagira, S.; De Silvestri, S.; Stella, A.; Tognini, P. Cheyssac, P.; Kofman, R. *Phys. Rev. Lett.* **1997**, *78*, 3575.

(23) Harms, G. J.; Gunsser, W. *Ber. Bunsen-Ges. Phys. Chem.* **1986**, *90*, 764.

(24) Downs, A. J. *Chemistry of Aluminium, Gallium, Indium and Thallium*; Blackie Academic & Professional: London, 1993; p 285.

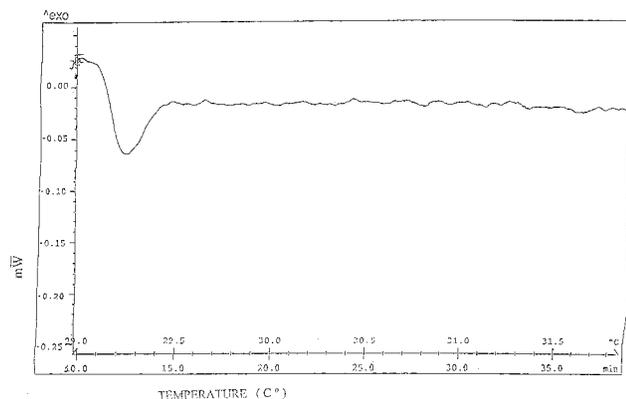


Figure 1. DSC spectrum of the sonication product. The heating rate was 0.5 °C/min.

explained as originating from the sonochemical reaction occurring on the circumference of the collapsing bubble.

Experimental Section

A solution of 1 g of GaCl₃ in 50 mL of distilled water (0.114 M) was exposed to high-intensity (100 W/cm²) 20-kHz ultrasound radiation for 6 h at room temperature by direct immersion of a titanium horn (Vibracell, horn diameter 1.13 cm) under argon at a pressure of 1.5 atm. The titanium horn was inserted to a depth of 1 cm in the solution. The resulting solid product was washed 4 times in distilled water and dried under vacuum.

Powder X-ray diffraction (XRD) was measured using a Rigaku diffractometer, model 2028. Differential scanning calorimetry (DSC) of the dried product was carried out using a Mettler DSC-30 instrument with a heating rate of 0.5 °C/min. The morphology of the product was determined by transmission electron microscopy (JEOL-TEM 100SX). The surface area was measured by the BET nitrogen gas adsorption method using a Micromeritics Gemini instrument.

Results

The DSC spectrum, shown in Figure 1, displays an endothermic peak at 29.2 °C. This is attributed to metallic gallium. Although the melting point of gallium is somewhat higher (29.75 °C), a depression of the melting point of this magnitude could occur if Ga is in the form of very small particles. The measured ΔH of fusion is 2.1 cal/g. Since the literature value for gallium is 191 cal/g, this indicates that only a small proportion (ca. 1%) of the material is metallic Ga. The amount of metallic gallium is dependent on the irradiation time: irradiating the starting solution for 90 min resulted in a metallic Ga DSC signal which was an order of magnitude smaller than that in Figure 1, which was obtained after 6 h of sonication.

All the peaks in the XRD pattern, shown in Figure 2, can be assigned to α -GaO(OH) (JCPDS card no. 6180). The GaO(OH) has an orthorhombic crystal structure (*Pbmn*) which is similar to that of diaspore, α -aluminum oxide hydroxide.²³

A TEM image of the powder is given in Figure 3. The particles are cylindrical, with a length of about 560 nm and a diameter of 120 nm. To determine whether the cylinder is solid or hollow, higher resolution TEM microscopy was carried out. In Figure 4 we present an HRTEM image of a particle whose center is defoliated from the layered structure. At least three exposed edges of three parallel inner layers are seen. The electron diffraction pattern of the sonication product is shown in the inset to Figure 4 and shows that the as-prepared material is crystalline.

The surface area of these cylindrical particles was measured by the BET method and was found to be 61 m²/g. Assuming a

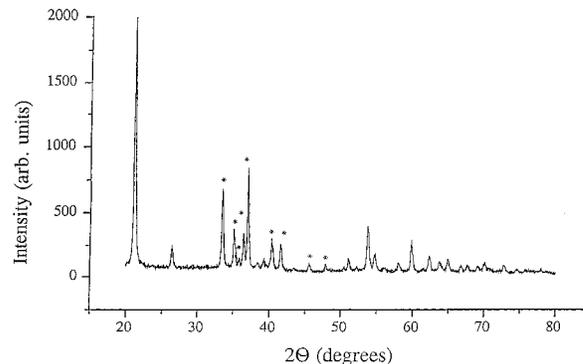


Figure 2. XRD patterns for the as-prepared material. The asterisks point to the diffractions of the metallic gallium.

material density of 5 g/cm³, the minimum surface area is calculated to be 12 m²/g. This leads to the conclusion that the layered structure enables molecules such as N₂ to penetrate into the structure. The actual density, measured from the weight and volume of a sample of the powder, was 0.5 g/cm³, an order of magnitude smaller than the literature value. Even allowing for increased volume due to packing geometry, it is clear that the tubes are substantially hollow.

In previous experiments, we demonstrated that we could control the particle size by varying the concentration of the precursor in the solvent, decane or Decalin. When the concentration was lowered, the particle size of the product became smaller.^{25,26} We have repeated this method for GaCl₃ and sonicated a solution which is 10 times more dilute, namely 0.1 g of GaCl₃ in 50 mL of water (0.011 M). Under these conditions, the nanoparticle diameter was reduced to 80 nm (from 120 nm) and the average length slightly reduced to 520 nm (from 560 nm).

As a control experiment, we heated a 1 M aqueous solution of GaCl₃ to 300 °C in a high-pressure cell, without sonication. No noticeable powder formation occurred after the solution was heated for 4 h.

Discussion

Unlike the sonication of carbonyls, which resulted in nanophase amorphous products,^{15–17} the sonication of GaCl₃ yields crystalline nanophase products. The difference between the two reactions can be understood on the basis of the existence of two regions of sonochemical reactivity, as postulated by Suslick et al.: the inside of the collapsing bubble and the interface between the bubble and the liquid.²⁷ In the sonication of the transition-metal carbonyls, the reaction takes place inside the collapsing bubble, and the amorphous product is a result of the high cooling rates ($>10^{10}$ K/s) obtained during this collapse. In addition to the reaction in the gas phase that takes place within the collapsing bubble, a reaction occurs in the thin liquid layer immediately surrounding the collapsing cavity.²⁷ The amount of GaCl₃ or any hydrolyzed Ga species will be very low inside the collapsing cavity because of their relatively low vapor pressure, and little product is expected to occur inside the bubbles. Similar ideas have been formulated by Henglein and co-workers²⁸ after studying the sonolysis of a nonvolatile solute,

(25) Cao, X.; Kolytyn, Yu.; Kataby, G.; Prozorov, R.; Gedanken, A. *J. Mater. Res.* **1995**, *10*, 2952.

(26) Cao, X.; Kolytyn, Yu.; Prozorov, R.; Kataby, G.; Gedanken, A. *J. Mater. Chem.* **1997**, *7*, 2447.

(27) Suslick, K. S.; Hammerton, D. A.; Cline, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 5641.

(28) Gutierrez, M.; Henglein, A.; Fischer, Ch.-H. *Int. J. Radiat. Biol.* **1986**, *50*, 313.

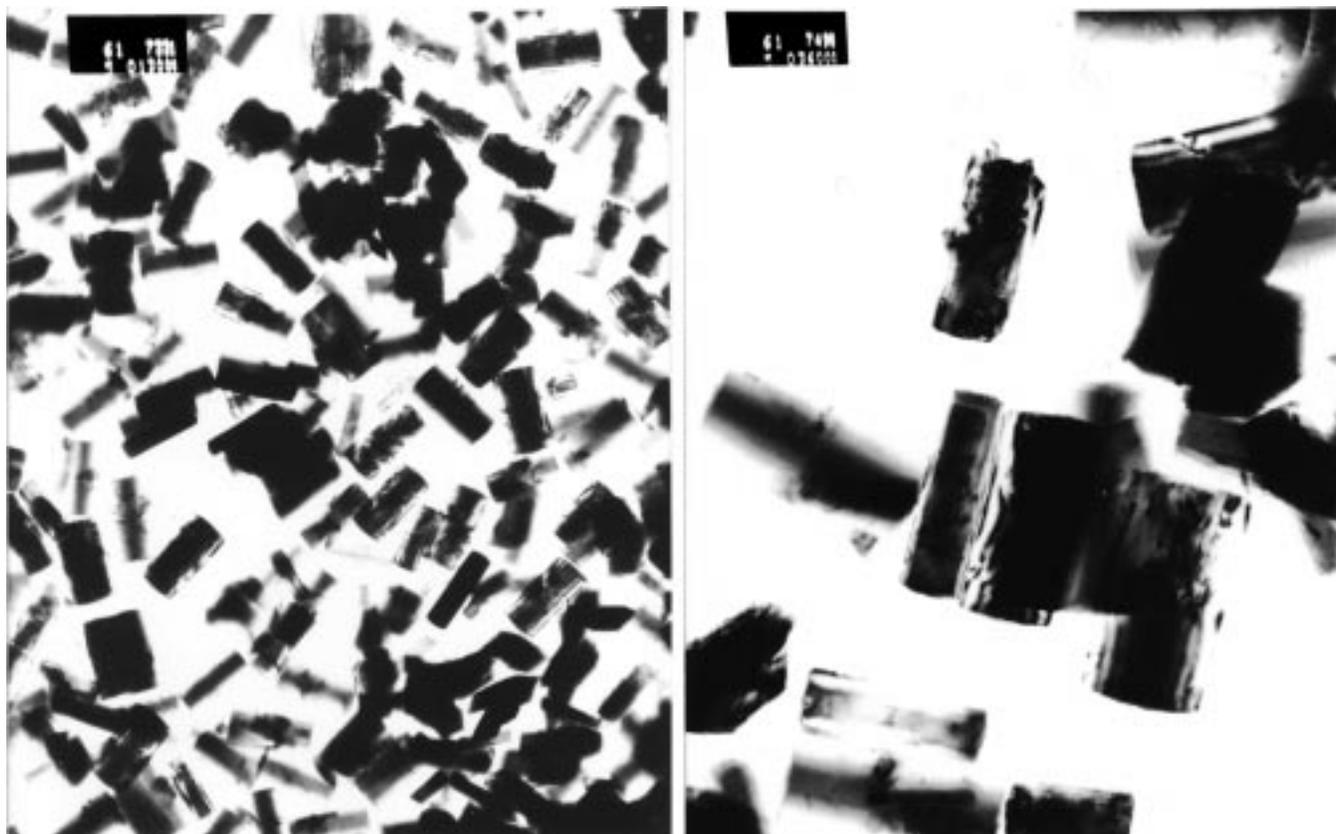


Figure 3. TEM image of the as-prepared material. (a, left) Magnification 13 000 \times , scale 1.04 cm = 800 nm. (b, right) Magnification 36 000 \times , scale 1.1 cm = 300 nm.

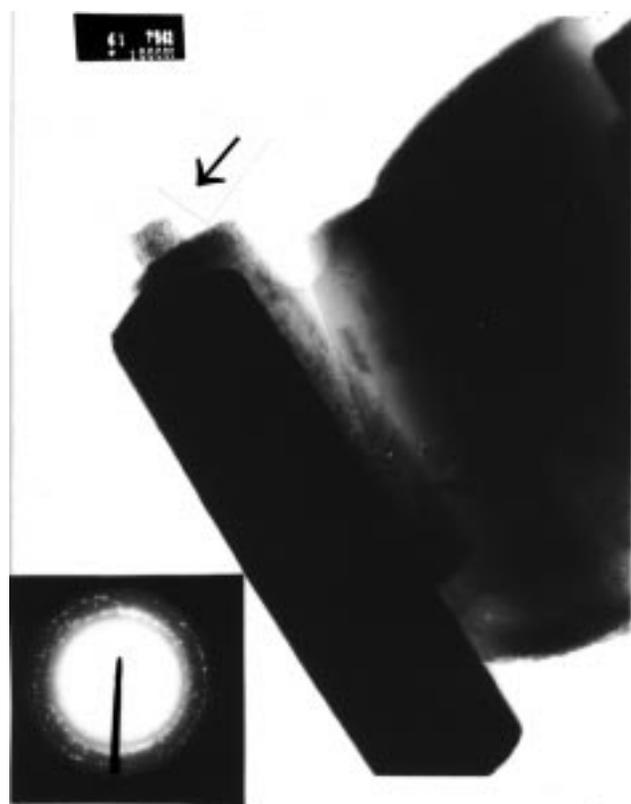
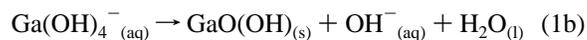
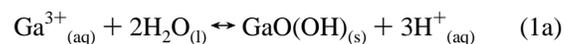


Figure 4. TEM image of the as-prepared material at a higher resolution than in Figure 3. Magnification 100 000 \times , scale 1 cm = 100 nm. Inset: Electron diffraction of the as-prepared material.

such as acetate anion. According to our proposed mechanism, the formation of the oxide hydroxide occurs at the solution–

bubble interface. The formation of GaO(OH) can occur by reaction 1a or 1b; both Ga species are present in solution.



The observation that the pH of the solution changes from 2.37 prior to the sonication to 1.61 at the end of the reaction implies that reaction 1a is the dominant pathway. This reaction is endothermic,²⁹ with an equilibrium constant at 50 °C of ca. 10^{-3} . The high local temperature in the shell surrounding the collapsing bubble constitutes the driving force for the formation of GaO(OH).

We cannot rule out the possibility that GaO(OH) is a product of reaction between H_2O_2 , a known product of the sonication of water,²⁰ and zero-valent Ga.



We now consider the mechanism by which the cigar-like layers are formed and rolled-up. While α -GaO(OH) is not the usual van der Waals layered compound encountered in nanotube formation, it does form a type of layered structure. Figure 5 shows a projection of the (001) plane of the diaspore structure, rotated somewhat to show three layers of this plane. The Ga atoms are situated at the centers of the tetrahedra with O atoms (in black) at the vertexes. (The H atoms are not shown for the sake of clarity.) From this figure, the most likely direction for bending to occur is for the top (100) plane (the plane with one side common to the top of the (001) plane in Figure 5 and lying perpendicular to the plane of the paper) to bend. Since the radius

(29) Craig, H. R.; Tyree, S. Y. *Inorg. Chem.* **1969**, *8*, 591.

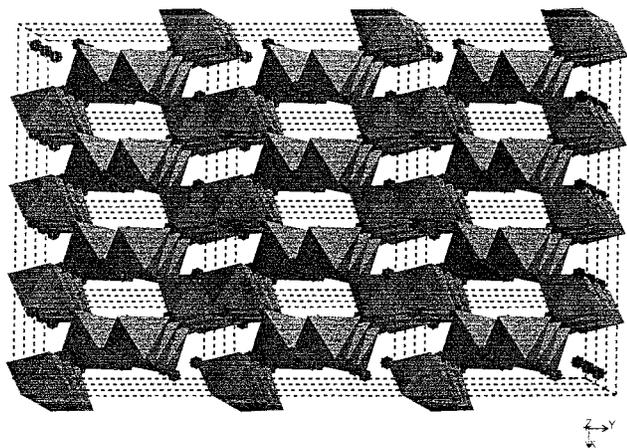


Figure 5. Projection of the (001) plane of the diaspore structure. The Ga is in the center of the tetrahedra, and the O atoms are at the vertices.

of curvature of the (external) surface is very large on the scale of a bond length, the strain inherent in this bending need not necessarily be very large. The [001] axis will then form the axial direction of the tubes seen in the TEM micrographs, and the main surface of the tubes will be formed by the (100) plane.

The formation of GaO(OH) is related to the collapse of the bubble, GaO(OH) and is formed as a layer surrounding the collapsing bubble. Suslick and Hammerton have calculated that the diameter of the bubble just before collapse is about 300 μm .³⁰ The liquid zone surrounding the cavity is estimated to extend to about 200 nm from the bubble. The temperature in the liquid zone has been measured to be 1900 K.²⁷ The GaO(OH) may then be formed around the collapsing bubble. In this

(30) Suslick, K. S.; Hammerton, D. A. *IEEE Trans. Sonics Ultrason.* **1986**, *SU-33*, 143.

case, a spherical structure might be expected. However, consideration of the crystal structure in Figure 5 leads to the conclusion that a spherical structure is not likely to form, in contrast to the observed tubular structure, which could do so as explained above. For either mechanism for more dilute solutions, there will be less GaCl₃ at the bubble–liquid interface, thereby explaining the smaller particles formed. *The sonohydrolyses of InCl₃, TlCl₃, and AlCl₃ have all led to cylindrical-shaped products similar to that observed for GaOOH.* This sonochemical technique, therefore, appears to be generally applicable for obtaining such cylindrical structures.

Conclusions

The sonication of an aqueous solution of GaCl₃ resulted in the formation of GaO(OH) with a small amount (about 1%) of metallic gallium enclosed inside GaO(OH). In the absence of the ultrasonic radiation, no reaction occurred. The formation of GaO(OH) has been attributed to the high local temperature in the neighborhood of the collapsing bubble. The products were formed as cigar-shaped particles having a diameter of about 100 nm. An explanation for the elongated layered structure of GaO(OH) based on cavitation collapse occurring at the solid–liquid boundary has been suggested. The particle size was found to decrease with decreasing concentration of GaCl₃ due to a reduced amount of reactant at the bubble–liquid interface.

Acknowledgment. We thank Abraham Herman for editorial assistance. This work was supported, in part, by the Israel Ministry of Science, Contract Nos. 5839-2-96 and 8461-1-98. This research was financially supported by a NEDO International Joint Research Grant.

JA9835584