Sonohydrolysis of In^{3+} Ions: Formation of Needlelike Particles of Indium Hydroxide

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Received June 9, 1999. Revised Manuscript Received September 29, 1999

This paper describes the formation and characterization of nanosize needle-shaped $In(OH)_3$ particles. The $In(OH)_3$ nanopowder was prepared via the sonication of an aqueous solution of $InCl_3$ at room temperature and at 0 °C. At these temperatures, nonsonicated hydrolysis does not occur. The role of the ultrasound radiation and the mechanism of the reaction is discussed. The proposed mechanism is based on the sonohydrolysis of In(III) ions in the outer ring, and the liquid shell, of the collapsing bubble.

Introduction

Matijevic and co-workers have recently reported[1−3] the preparation of micrometer-sized colloids of indium hydroxide. In one work,[1] forced hydrolysis of indium nitrate and chloride was employed, yielding cubic particles and prismatic crystals of $In(OH)_3$, respectively. The particles were of micrometer size and had a narrow size distribution. The hydrolysis was studied at 75 *o*r 85 °C.[1] When the hydrolysis was carried out in the presence of urea, rodlike particles of $In(OH)_3$ were obtained.[1] More recently, Matijevic et al.[2] have studied the high-temperature hydrolysis of $InCl_3$ in ethylene glycol to which an aqueous NaOH solution was added. The peptization of these micron-sized particles yielded nanosized $In(OH)_3$, without the addition of a surfactant.[2] The importance of indium, indium oxide, and indium hydroxide is related to the semiconducting and optical properties of these materials.[1−3] Prior to this work, other procedures[4,5] have been described, involving hydrolysis of an aqueous solution of In^{3+} at elevated temperatures, yielding uniform submicrometer $In(OH)_3$. The morphology of the as-prepared material was strongly dependent on many parameters, such as temperature, with platelets detected at 175 °C and rodlike particles at 150 °C. Recently, the preparation of $In(OH)_3$ thin films was reported by Ishida et al.[13] The conductivity of the films varied in the range of 10^{-7}−10^{-3} S/cm^2, depending on the experimental conditions. This range of conductivity values are typical for wide band gap semiconductors.

Sonochemical reactions arise from the acoustic cavitation phenomenon, which comprises the formation, growth, and collapse of bubbles in a liquid medium.[6] The extremely high temperatures (>5000 K), pressures (>20 MPa), and cooling rates (>10^{10} K/s) attained during acoustic cavitation collapse lead to many unique properties in the irradiated solution.[7] In a recent study,[8] we have reported on the sonohydrolysis of an aqueous solution of $GaCl_3$ that led to the formation of gallium oxide hydroxide. The product was formed in a unique cylindrical shape of 80−120 nm diameter and 500−600 nm in length. A close examination of the cylinder revealed that it had a scroll-like layered structure. We interpret this shape as being related to the reaction that takes place in a ring surrounding, but not in the center of, the collapsing bubble.

In this work, we present a new procedure for the preparation of nanosized rodlike $In(OH)_3$ particles, using sonohydrolysis of In^{3+} ions in an aqueous solution at room temperature.

Experimental Section

A solution of 6.4 g $InCl_3$ (Aldrich 99.999%, anhydrous**)** in 50 mL distilled water (0.68 M) was exposed to high-intensity (100 W/cm^2) 20 kHz ultrasound radiation for 1 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 sonication was carried out under a flow of argon. The solid products started to appear only after an induction time of approximately 30 min. The resulting solid product was washed four times in distilled water and dried under vacuum. Identical results were obtained when the sonication took place at 0 °C in a thermostated cooling bath. We have also carried out sonication in ethanol, using the same experimental conditions. To form a colloidal solution of the product, sonication was performed here in the presence of a surfactant. $InCl_3$ (6.4 g) was dissolved in a mixture of 15 mL Tween 80 (polyoxyethylene sorbitan monooleate) and 35 mL of distilled water. The solution was sonicated for 1 h under the same conditions as above.

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10.1021/cm9903677 CCC: $19.00
Published on Web 04/19/2000

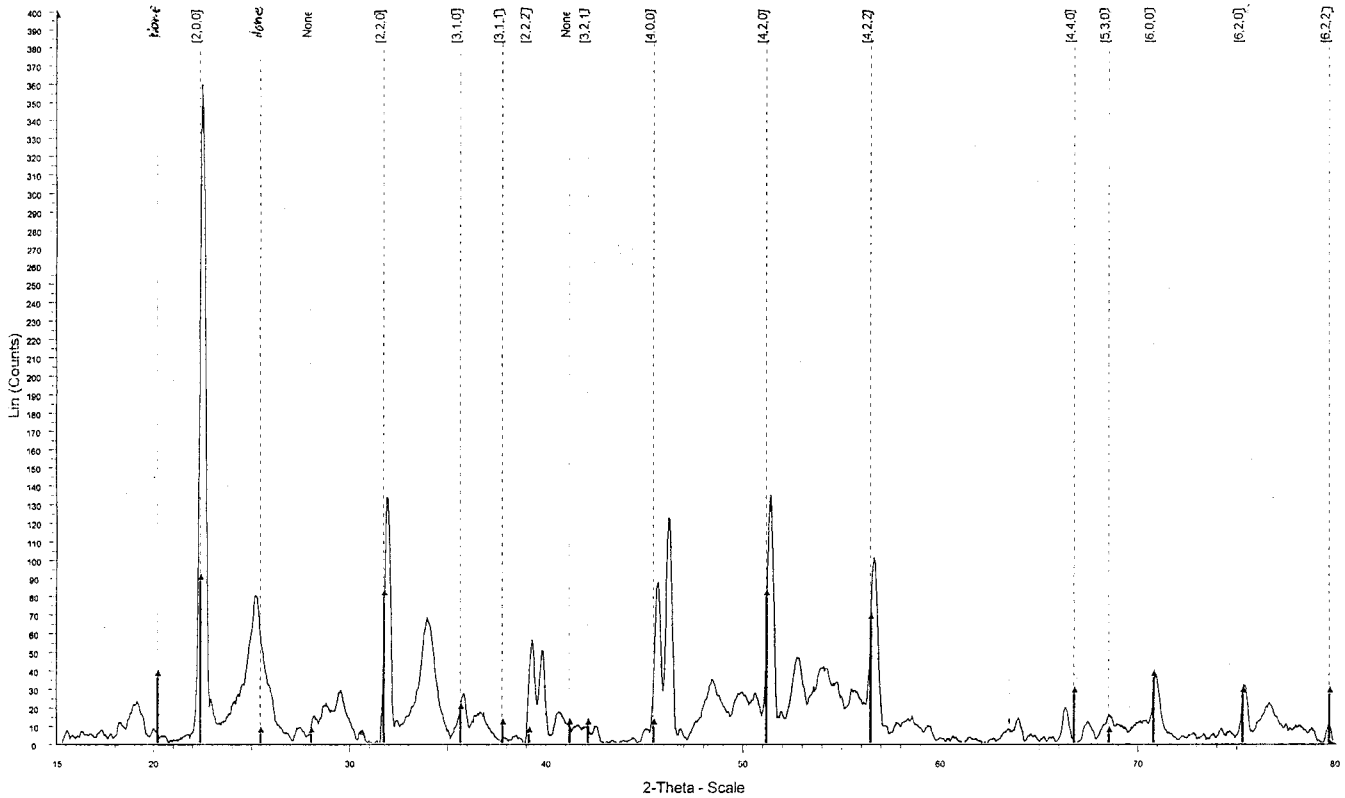

Figure 1. XRD diffraction pattern of the as-prepared material.

Powder X-ray diffraction (XRD) patterns were measured using a Bruker D8 advance. The instruments used for DSC (differential scanning calorimetry), TGA (thermogravimetric analysis), TEM (transmission electron microscopy), and BET (Brunauer−Emmett−Teller adsorbtion isotherm) measurements are described elsewhere.[14] DRS (diffused reflectance spectroscopy) measurements were carried out on a Jasco (V-570) spectrophotometer equipped with an integrating sphere. Spectra were recorded at room temperature, from 2000 to 220 nm with a scanning speed of 100 nm/min. $MgCO_3$ was used as a reference.

Results

In Figure 1, we present the XRD diffraction pattern of the as-prepared product. The spectrum is assigned to $In(OH)_3$, on the basis of its fitting to JCPDS card no. 16-161. The XRD pattern shows a well-defined peak at $2\theta = 22.26°$, corresponding to the (200) plane, and two peaks at $2\theta = 51.16°$ and 56.46° assigned to the (420) and (422) planes. This indicates a preferential growth of particles along the (200) plane, perpendicular to [001] direction, which result in a rodlike structure of the nanocrystals. The crystalline sizes, along the (200) and (422) planes, calculated from the fwhm using the Debye−Scherrer relationship, are 27 and 40 nm, respectively. The latter calculated size is more accurate, since two diffraction peaks might overlap at $2\theta = 22.26°$ (possible residues of $InCl_3$, JCPDS card no. 26-0767), while the diffraction peak at $2\theta = 56.47$ is associated only with $In(OH)_3$. The diffraction pattern is also very similar to that depicted by Matijevic et al.[1,2] for rodlike indium hydroxide. The XRD of the product obtained from the sonohydrolysis carried out in ethanol showed the same X-ray structure. Two features at $2\theta = 39.76$ and 46.24° are assigned to the platinum support of the measured sample. We cannot assign the three small diffraction peaks at $2\theta = 52.79$, 54.09, and 55.71°.

The TEM picture presented in Figure 2 shows bundles of rodlike structures approximately 10−15 nm wide and 60−150 nm long. The center of each bundle of rods is darker at the edges of the particle. This can be due either to a dense accumulation of shorter rods or to the deposition of amorphous $In(OH)_3$ on the surface. A high-resolution TEM micrograph of an individual rod is presented in Figure 3 and shows clearly the crystalline structure of a rod with an interplanar spacing of 3.95 ± 0.5 Å corresponding to the (200) plane. The same TEM pictures were obtained for the products of the sonication of $InCl_3$ in ethanol. The surface area measured for the as-prepared material is 70 m^2/g. For the sonohydrolysis of $GaCl_3$, similarly shaped particles were obtained, except that they were much thicker (120 nm) and longer (560 nm) than those observed in the current study.

The results of the sonication in the presence of Tween 80 were a stable colloidal solution. The TEM picture of the dried solution (Figure 4) presents monodispersed spherical particles having 5 nm diameters and some cylindrical particles with diameters of 15 nm. This is in accordance with Matijevic et al.'s previous reports,[1−3] which detected spherical and rodlike particles, depending on the preparation conditions.

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Figure 2. TEM image of the $In(OH)_3$ powder.

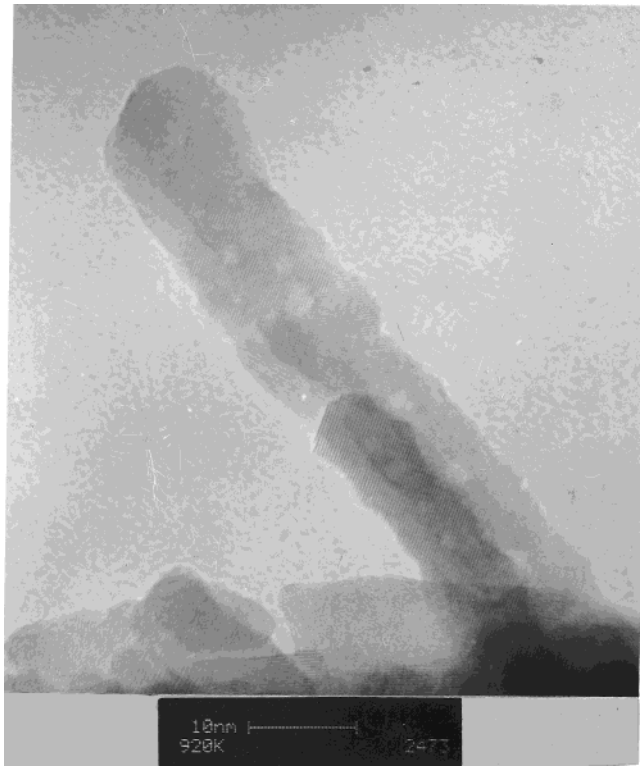

Figure 3. HRTEM of one individual $In(OH)_3$ rod.

The TGA spectrum of the as-prepared material is shown in Figure 5. It reveals a loss of weight of 18 ± 1%, having its inflection point at 269 °C. The calculated weight loss for the decomposition of the hydroxide into the In_2O_3 is 17%. Thus, our product differs from that obtained by Matijevic et al.,[2] which revealed a 40% weight loss at almost the same temperature. This is perhaps due to the hydrate, $In(OH)_3 \cdot xH_2O$, which is formed in the latter case, compared with the nonhydrated form obtained from the sonication. The nonhydrated hydroxide was not hygroscopic. The loss of water

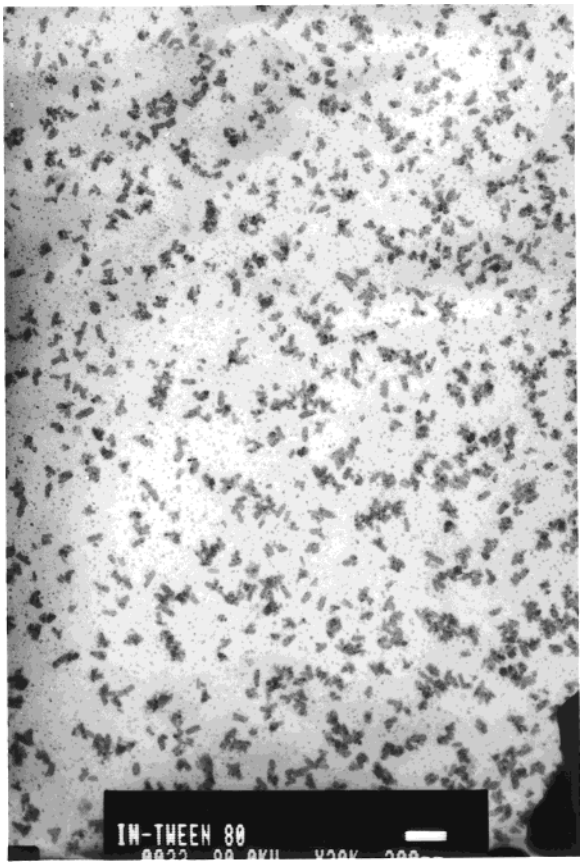

Figure 4. TEM picture of the as-prepared material synthesized in the presence of Tween 80.

in this reaction was also followed by a mass spectrometer coupled to the TGA instrument. A TPD (temperature-programmed desorption) spectrum reveals an 18 amu signal above the background in the 100−350 °C temperature range.

The DSC spectrum shows one endothermic band peaked at at 250 °C. This peak is related to the decomposition of the hydroxide to the indium oxide and appears at almost the same temperature as the deflection point in the TGA weight-loss spectrum. The ΔH of the decomposition is 44 kJ/mol $In(OH)_3$. Matijevic et al.[1] did not detect this peak since it was perhaps obscured by an exothermic peak assigned to the burning of the organic surfactant. The decomposition temperature of bulk $In(OH)_3$ into In_2O_3 is reported at higher temperatures.[9] Its appearance at lower temperatures is perhaps related to the nanometric scale of the products, whose large surface area makes them more reactive, with smaller activation energies. To support this claim, we have carried out a temperature-dependent X-ray diffraction measurement which is depicted in Figure 6. The figure shows the decrease of the diffraction peaks attributed to $In(OH)_3$ (2θ = 22.26 and 31.68°) and the simultaneous increase in the In_2O_3 diffraction peaks (2θ = 30.58°). The temperature increase in the XRD spectrum was carried out at a relatively high rate (30 °C/min). This is because we were interested only in the qualitative behavior of $In(OH)_3$, demonstrating its decomposition to In_2O_3. The exact temperature can be deduced more accurately from the TGA and DSC spectra.

As was noted in the Introduction, thin films of $In(OH)_3$ exhibit conductivity in the range of wide band gap

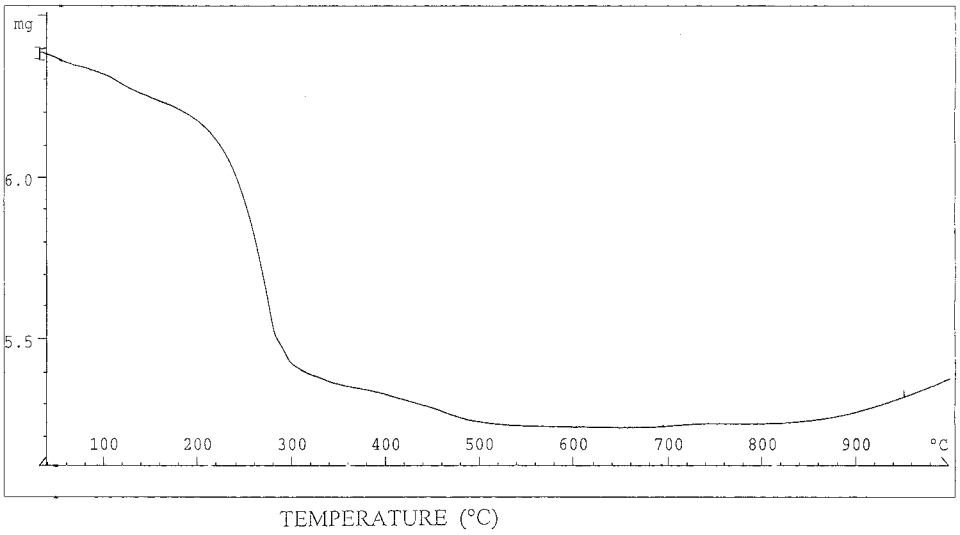

Figure 5. TGA spectrum of the as-prepared material. The heating rate is 2 °C/min, under a flow of N_2.

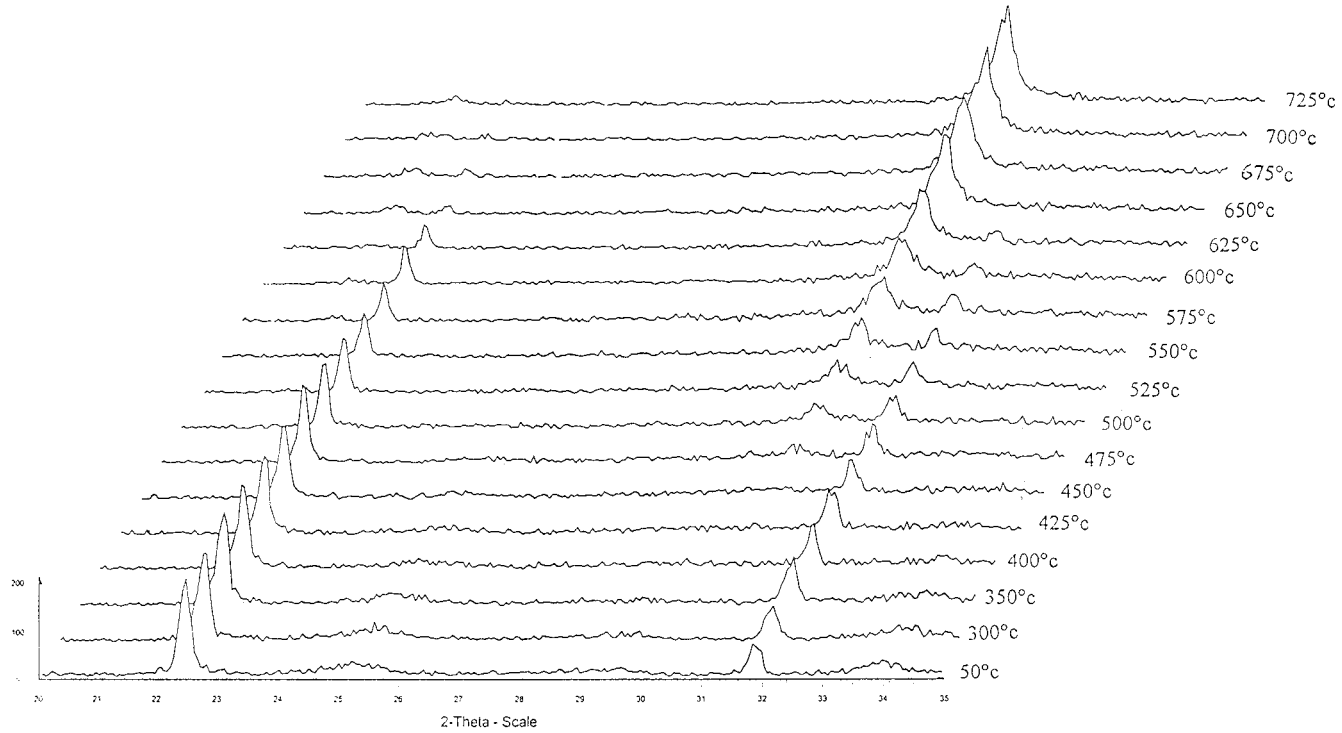

Figure 6. Temperature-dependent X-ray diffraction spectrum of the as-prepared material. The heating rate was 30°/minute, under a flow of N_2.

semiconductors. The electronic structure of $In(OH)_3$ is not reported in the literature; hence, it was important to determine its optical properties to measure the band gap of the material. Since our product is a powder, we employed DRS as a characterization tool (Figure 7a). Estimation of the optical band gap, E_g, from the as-measured DRS spectra and from Kubelka−Munk (KM) corrected spectra, is 5.15 eV. This is in accordance with the conductivity values obtained by Ishida and co-workers.[13]

Apart from the strong band gap absorption, two weak absorption transitions can be observed. This absorption bands can be clearly detected, as peaks at 4.24 and 4.78 eV, when the derivative spectra of the DRS is plotted (Figure 7b). We attribute these bands to Wannier excitons conversing to the bottom of the band gap.

Discussion

Although the hydrolysis of indium salts occurs at relatively low temperatures, it does not occur (without sonication) at temperatures lower than 75 °C. In this work, we report the sonohydrolysis of an aqueous solution of $InCl_3$ which is observed at 0 °C. This is related to the unique properties of sonochemistry. In the neighborhood of the collapsing bubble, there are three regions: the center of the collapsing bubble, where the temperature can reach 5000 K; the interface layer, estimated as a 200 nm width ring, where a lower temperature of about 2000 K is measured; and the bulk solution. For $InCl_3$, a nonvolatile compound, the reaction might happen in the bulk close to the interfacial ring, because, according to Matijevic et al.,[1] the hydrolysis

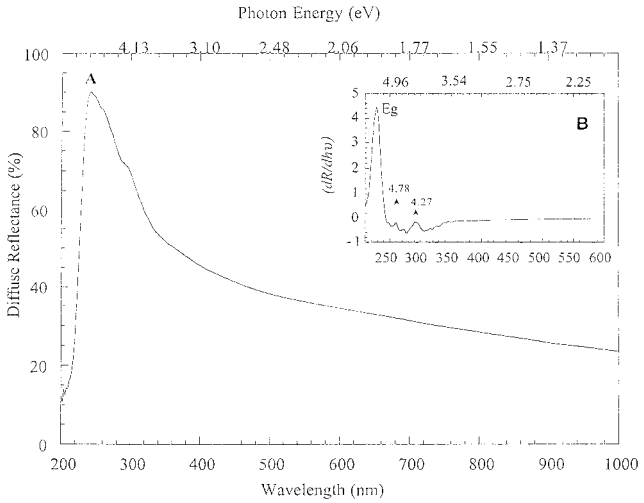

Figure 7. DRS of the as-prepared material.

occurs at 75 °C for 12 h, compared to1 h in this study, and given the fact that we have obtained products even at 0 °C, we conclude that the interfacial region is where the hydrolysis occurs. The crystalline structure of the product also provides indirect evidence for excluding the center of the collapsing bubble as the reaction site, since materials obtained from reactions that take place inside the bubble are amorphous.[7,10,11]

The reaction that takes place is

$$In^{3+}_{(aq)} + 3H_2O_{(l)} \xrightarrow{)))))} In(OH)_{3\,(s)} + 3H^{+}_{(aq)} \quad (1)$$

A decrease in pH from 2.76 to 1.22 substantiates this reaction. This reaction occurs in three steps. In each, a water molecule reacts, and the intermediates are $In(OH)^{+2}$ and $In(OH)_2^{+1}$. The first two equilibrium constants are $K_1 = 4.9 \times 10^{-5}$ and $K_2 = 0.95 \times 10^{-5}$ at 25 °C.[4] The third equilibrium constant, K_3, is unavailable, but it is estimated to be of same order of magnitude as K_1 and K_2. Products are obtained despite the small value of $K_1 \cdot K_2 \cdot K_3$ because of the high temperature obtained in the interfacial region during the bubble collapse.

Matijevic et al.[2,3] have demonstrated that the long rodlike micron particles are aggregates of nanosized precursors. It is possible that the same happens in our case as well; namely, the collapse of the bubble forms small (1−2 nm) particles that aggregate to form 60−150 nm needles by the microjets formed as a result of the collapsing bubble. The observation of the [200] peak in the XRD spectrum is also related to the observation of needlelike structures. This interpretation will not explain why the same shape $In(OH)_3$ is obtained under all various sonication conditions, namely, at 0 °C, at high temperatures, and in the presence of ethanol. These different conditions will lead to variations in the final temperature and the speed of the microjets. We are also puzzled by the fact that the sonohydrolysis of $GaCl_3$, $AlCl_3$, $InCl_3$, and $TlCl_3$ led in all cases to a variety of closed layered structures (fullerene-like structures for $TlCl_3$). Since the radius 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. It seems, therefore, that the sonication process is providing the energy to cross a minimal barrier leading to the bending of the chemical bonds. It is, therefore, that the lower energetics of the less favorable conditions, such as ethanol as a solvent, or a high sonication temperature suffice for the first step.

Experiments with the surfactant produced needlelike shapes, even for the small 15 nm particles. This is interpretated throughthe observation made by Suslick that,[12] "[i]n pure liquids the cavity remains spherical during collapse because its surroundings are uniform. Close to a solid boundary, however, cavity collapse is very asymmetrical and generates high speed jets of liquid." For this reason, we propose that the solid particles will have a needlelike shape, and, pushed by the microjets, they will aggregate to form a larger rod.

Acknowledgment. A.G. acknowledges the financial help of the NEDO International Joint Research Grant and the support of the German Ministry of Science through the Deutsche-Israeli Program (DIP). We thank Dr. Shifra Hochberg for editorial assistance.

CM9903677