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Letter

Indium hydroxide nanocubes and microcubes obtained by microwave-assisted hydrothermal method

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ABSTRACT

Single crystalline indium hydroxide ($\text{In}(\text{OH})_3$) architectures were prepared by a rapid and efficient microwave-assisted hydrothermal (MAH) method using indium chloride as the precursor. Nanostructures were obtained at a low temperature (140°C with a time of 1 min). $\text{In}(\text{OH})_3$ samples were prepared at the same temperature for 8 with a time of 64 min. Using this method, $\text{In}(\text{OH})_3$ samples were obtained at milder conditions of temperature and time compared to the conventional hydrothermal method. Field emission scanning electron microscopy images confirm that these samples are composed of 3D nanocubic, microcubic and irregular structures of about 70 nm to $5\ \mu\text{m}$ in size. Fourier transform Raman spectroscopy and photoluminescence (PL) measurements were used to characterize the products.

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1. Introduction

The indium hydroxide ($\text{In}(\text{OH})_3$) semiconductor with a wide band gap (E_g) estimated to be 5.15 eV is attractive due to its electronic and optical properties [1]. In recent years, $\text{In}(\text{OH})_3$ nanostructures with different morphologies such as cubes [2,3], flowers [4], truncated polyhedral microcrystals [5], spheres [6], etc., have been synthesized by several synthesis methods. The physical and chemical properties of these nano- or micron-sized powders can be influenced by shape, size and size distribution of the particles which depend on the synthesis method. The hydrothermal synthesis has been used to obtain nanostructures and the microstructure of indium hydroxide using a method which is simple, practical and environmental friendly [6].

The use of microwave radiation in the hydrothermal system introduced by Komarneni et al. [7] promotes the development of a new technique offering reaction kinetic enhancement, formation of materials with different morphologies, low synthesis temperature and reduced processing times. Recently, the MAH method has been successfully employed to obtain materials, such as ZnO [8], BaTiO_3 [9], CuO [10] and CeO_2 [11].

In this paper, we report the rapid synthesis of $\text{In}(\text{OH})_3$ single crystalline nanostructures using MAH method at a low temperature

at (140°C) and a short synthesis time (1 min) as compared to the conventional hydrothermal method. $\text{In}(\text{OH})_3$ samples prepared at 140°C with times of 8 and 64 min were also obtained. The structure, morphology and photoluminescence properties of these samples were studied.

2. Experimental

$\text{In}(\text{OH})_3$ powders were obtained by microwave-assisted hydrothermal (MAH) method. The typical experimental procedure is described as follows: 3.6 mmol indium (III) chloride (99% purity, Aldrich) was dissolved in 80 mL of deionized water under constant stirring for 30 min. The pH of the solution was adjusted to 10 by adding NH_4OH . The reaction system was heated at 140°C for 1, 8 and 64 min. The heating rate in this system was fixed at $25^\circ\text{C}/\text{min}$ and the pressure into the autoclave was stabilized at 294 kPa. The MAH (Brazilian patent 2008-PI0801233-4) one hole was drilled into the wall of a domestic oven (2.45 GHz/800 W) for a polytetrafluoroethylene (PTFE) vessel in the oven top. The magnetron was monitored to a very efficient proportional-integral-derivative (PID) external controller. Intuitive software enables the user to control everything from process conditions (temperature, time and heating rate). The user simply defines the desired temperature–time profile, and the MAH will automatically carry out the programmed cycle [9,10]. After MAH treatment, the white precipitate was washed with distilled water and dried at room temperature. The powders were characterized by X-ray diffraction (XRD) using a Rigaku diffract meter (Model D/max-2500/PC) with $\text{Cu K}\alpha$ radiation. Raman spectra were obtained using RFS/100/S Bruker FT-Raman equipment (scan range of $100\text{--}1400\ \text{cm}^{-1}$) using the 1064 nm exciting wavelength of a Nd:YAG laser. The $\text{In}(\text{OH})_3$ morphology and size were observed by field emission scanning electron microscopy (FE-SEM; Jeol JSM 6330F) images. UV–vis reflectance spectra of $\text{In}(\text{OH})_3$ powders were taken using Cary 5G equipment. PL spectra were measured using a Thermal Jarrel-Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier. The 350.7 nm line of a krypton ion laser (Coherent Innova 90K) was used as the excitation source with out-

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Table 1
In(OH)₃ structures obtained by the hydrothermal method using InCl₃ as a precursor.

Reagent	Synthesis method Temperature/time	Phase(JCPDS no.)	Morphology	Ref.
InCl ₃ + NaOH InCl ₃ + NH ₃ ·H ₂ O	Conventional hydrothermal 200 °C/1200 min	Cubic (76-1463)	Cubes-like	[2]
InCl ₃ ·4H ₂ O	Conventional hydrothermal 160 °C/720 min	Cubic (85-1338)	Spheres-like	[6]
InCl ₃ ·4H ₂ O + urea	Microwave-assisted hydrothermal uncontrolled temperature/3 min	Cubic (85-1338)	Cubes-like	[14]
InCl ₃ ·4H ₂ O + ethyleneamine	Conventional hydrothermal 210 °C/960 min	Cubic (85-1338)	Cubes-like and spheres-like	[15]
InCl ₃ ·4H ₂ O + urea	Conventional hydrothermal 120 °C/720 min	Cubic (85-1338)	Flower-like	[16]
InCl ₃ + NaOH	Conventional hydrothermal 150 °C/1200 min	Cubic (76-1463)	Cubes-like	[17]
InCl ₃ + NaOH	Conventional hydrothermal 160 °C/1200 min	Cubic (85-1338)	Rectangular shape	[18]
InCl ₃ + NH ₄ OH	Microwave-assisted hydrothermal 140 °C/1 min, 8 min and 64 min	Cubic (85-1338)	Cubes-like, rectangular-like and irregular-shaped	This work

put power of the lasers kept at 200 mW. All measurements were taken at room temperature.

3. Results and discussion

X-ray patterns and Raman spectra of the In(OH)₃ powders synthesized at different times (1, 8 and 64 min) are presented in Fig. 1(a) and (b), respectively. All the diffraction peaks could be indexed to the cubic lattice [space group *Im*₃(204)]. The lattice parameters were calculated using the least square refinement from the UnitCell-97 program [12], with *a* = 7.9558(4) Å (1 min), 7.9541(4) Å (8 min) and 7.9632(4) Å (64 min) are in good agreement with standard data from a JCPDS card 85-1338 (*a* = 7.979 Å), indicating that crystalline single structures were obtained.

Fig. 1(b) shows three sharp scattering peaks in the ranges 309, 358 and 392 cm⁻¹ referent to In(OH)₃ Raman modes. According to crystallography data, the globally cubic matrix of indium hydroxide and Raman spectrum exhibited characteristic modes. Raman spectroscopy is a feasible method due to its sensitivity to the short-range order such as clusters where the degree of local order is such that structurally inequivalent sites can be distinguished because of their different types of electronic transitions and are linked to a specific structural arrangement [13].

Many researchers have reported In(OH)₃ powders with different morphologies obtained by conventional hydrothermal synthesis using different routes. Table 1 shows In(OH)₃ structures obtained from an InCl₃ precursor using a conventional hydrothermal method and the MAH method reported in this work. Koga and Kimizu [14] reported the synthesis of In(OH)₃ particles using MAH method for 3 min (short treatment time), however the temperature in this system and the pressure in the autoclave are not controlled. In the present method, the rapid heating colloidal suspension by microwave radiation led to the growth and enhance crystal growth of In(OH)₃ under conditions controlled of low temperatures, short reaction times and pressure. Furthermore, rapid heating under hydrothermal conditions offers higher mobility of dissolved ions and accelerates solid particles to high velocities, increasing the collision rate and effective fusion at the collision point [8,9].

Fig. 2(a) and (b) depicts FE-SEM images of the In(OH)₃ shows cubic and irregular structures (obtained at 140 °C/1 and 8 min). According XRD results the In(OH)₃ phase is formed with 1 and 8 min however these times of treated hydrothermal shows that the morphology presented is less defined than 64 min of treated. Microcubes and rectangular-shaped structures with a smooth and uniform surface where the angle between the adjacent edges is relatively close to 90° (Fig. 2(c)) as observed [3]. The edge length of the In(OH)₃ structures ranging from 70 nm to 5 μm are observed.

The increase in the particle size can be attributed to hydrothermal conditions [3].

Optical diffuse reflectance measurements have been carried out on In(OH)₃ particles obtained under MAH conditions. An estimation of the optical band gap “E_g” was obtained using the Wood and Tauc method [19] (see Fig. 3, inset (b)–(d)), the calculated values of E_g

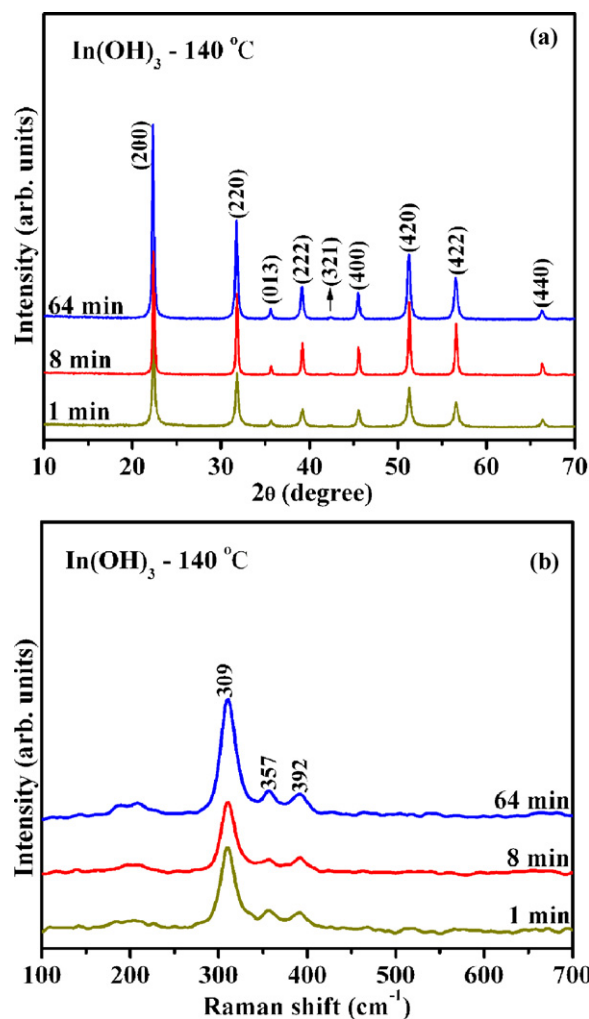


Fig. 1. In(OH)₃ powders obtained by the MAH method at 140 °C for 1 min, 8 min, and 64 min. (a) XRD patterns and (b) Raman spectra.

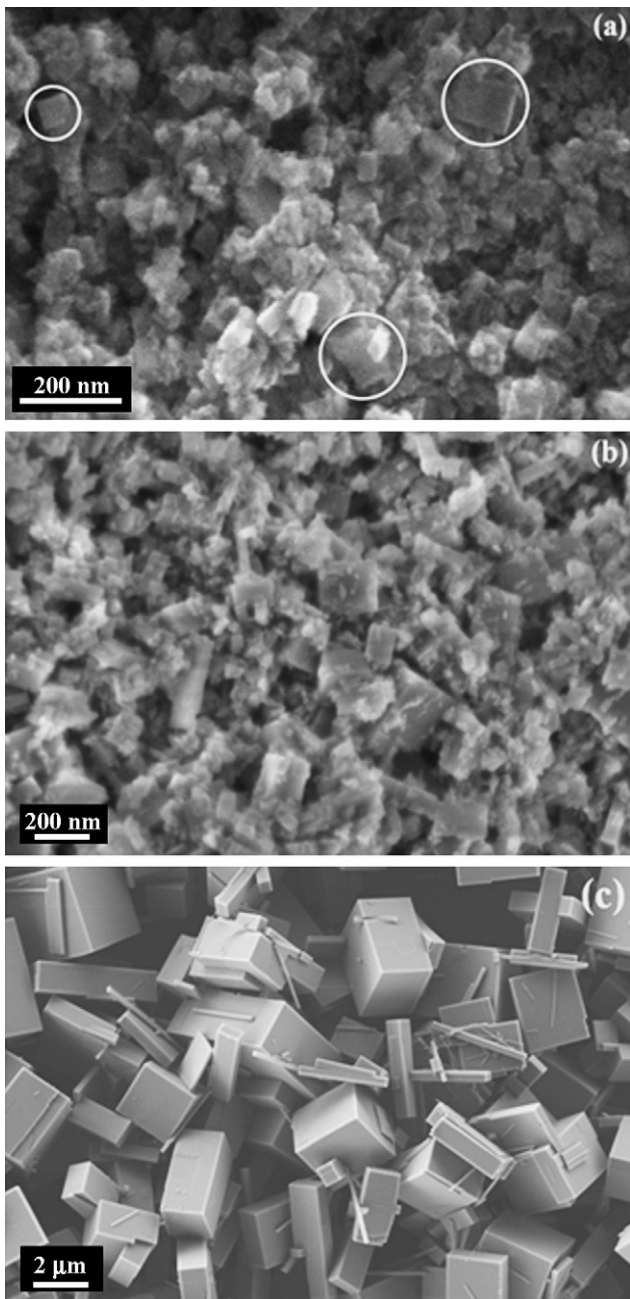


Fig. 2. FE-SEM images of $\text{In}(\text{OH})_3$ structures obtained by the MAH method at 140°C for (a) 1 min, (b) 8 min and (c) 64 min.

were 4.95, 5.11 and 5.40 eV for the samples treated at 140°C for 1, 8 and 64 min, respectively.

PL spectra of $\text{In}(\text{OH})_3$ samples synthesized at different treatment times are shown in Fig. 3(a). The broad and intense band emission covering a large part of the visible spectra (from 400 to 750 nm) can be observed for $\text{In}(\text{OH})_3$ particles. The profile of the emission band is typical of a multiphonon and multilevel process, i.e., a system in which relaxation occurs by several paths involving the participation of numerous states within the band gap of the material [20]. Using the Gaussian method, PL curves of the sample heated at 140°C were decomposed into five components, referring to the region in the visible spectrum where its maximum peak intensity appears (Fig. 3(b)–(d)). The PL curves for all samples are composed of five PL components: a violet (maximum in 435 nm), a blue (maximum in 474 nm), a green (maximum in 526 nm), a yellow

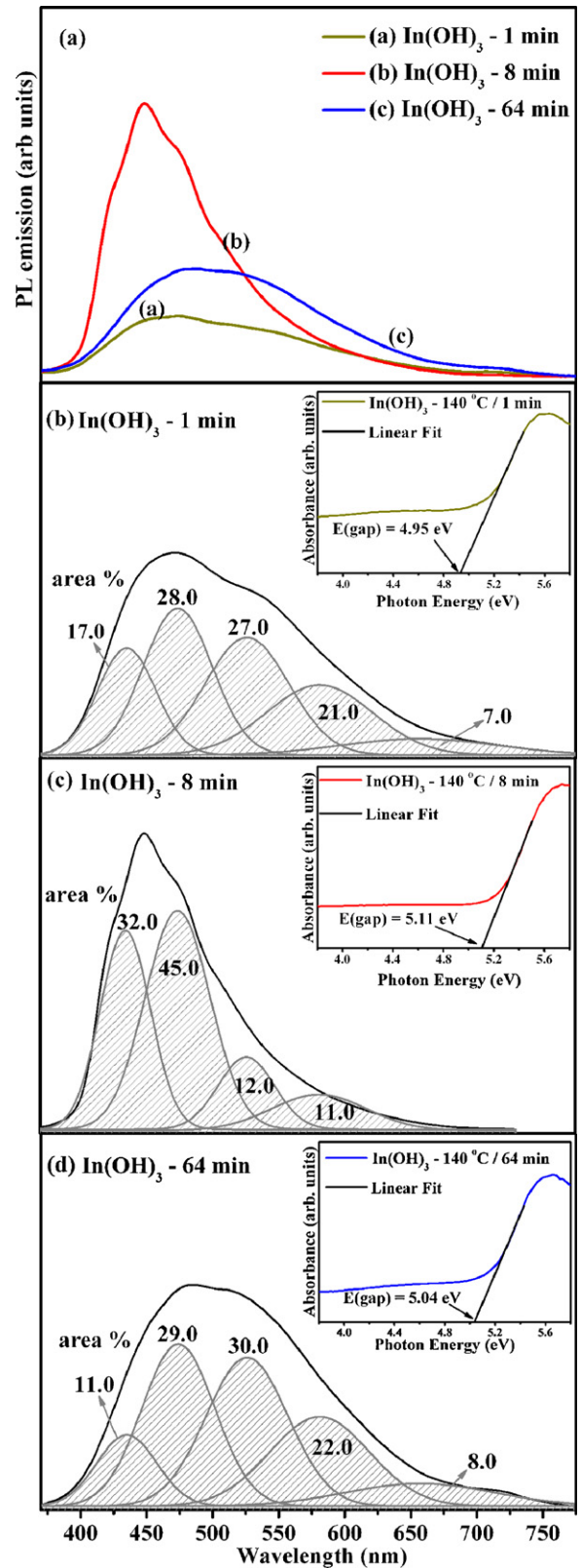


Fig. 3. (a) PL spectra of $\text{In}(\text{OH})_3$ structures obtained at 140°C at different reaction times and (b)–(d) PL deconvolution curves of samples obtained after 1 min, 8 min and 64 min, respectively. (UV-vis reflectance spectra are shown in inset (b)–(d).)

low (maximum in 581 nm) and a red (maximum in 657 nm). Each color represents a different types of electronic transition and can be linked to a specific structural arrangement. PL curves were analyzed using the PeakFit deconvolution program [21]. Violet and blue maximum percentage areas were observed for the sample treated for 8 min. Recently, Shi et al. [5] reported $\text{In}(\text{OH})_3$ truncated polyhedral microcrystal formation via hydrothermal treatment at 180°C for 16 and 18 h that showed two emission peaks at 496.6 and 419.2 nm. Yan et al. [22] showed a broad PL blue-green emission at 480 nm of $\text{In}(\text{OH})_3$ nanocubes. This high PL intensity seems to indicate that this material presents an optimum structural order–disorder degree resulting in photoluminescence which can be associated with different $\text{In}(\text{OH})_3$ defects generated during the synthesis process [23]. Crystalline $\text{In}(\text{OH})_3$ belongs to n-type semi-conductors where oxygen vacancies can induce the formation of new energy levels in the band gap. Thus, during the MAH process, the displacement of oxygen related to the In modulates different species of trapped holes (V_o^+ , V_o^x and V_o^{2+} species) around $[\text{InO}_5V_o^x]$ clusters and gives rise to complex cluster vacancies [4,8,22,23]. The differences observed in the position of the maximum PL emission in $\text{In}(\text{OH})_3$ probably can be associated with the structural organization levels, preparation method and thermal treatment conditions. These factors can be responsible for generating visible color centers in the $\text{In}(\text{OH})_3$ lattice and contribute to the PL emission.

4. Conclusion

In summary, cubes-like, rectangular-like and irregular-shaped $\text{In}(\text{OH})_3$ was prepared by the MAH method. The single phase was obtained at a low temperature and a short synthesis time. The $\text{In}(\text{OH})_3$ obtained exhibits a strong violet–blue PL emission which allows it to be considered as a promising material for electronic and optical properties.

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References

- [1] S. Avivi, Y. Mastai, A. Gedanken, *Chem. Mater.* 12 (2000) 1229.
- [2] H.L. Zhu, Y. Wang, N.Y. Wang, Y. Li, J. Yang, *Mater. Lett.* 58 (2004) 2631.
- [3] X.H. Liu, L.B. Zhou, R. Yi, N. Zhang, R.R. Shi, G.H. Gao, G.Z. Qiu, *J. Phys. Chem. C* 112 (2008) 18426.
- [4] H. Zhu, X.L. Wang, Z.J. Wang, C. Yang, F. Yang, X.R. Yang, *J. Phys. Chem. C* 112 (2008) 15285.
- [5] Z. Shi, W. Wang, Z.K. Zhang, *Mater. Lett.* 62 (2008) 4293.
- [6] B.X. Li, Y. Xie, M. Jing, G.X. Rong, Y.C. Tang, G.Z. Zhang, *Langmuir* 22 (2006) 9380.
- [7] S. Komarneni, R. Roy, Q.H. Li, *Mater. Res. Bull.* 27 (1992) 1393.
- [8] R.C. Lima, L.R. Macario, J.W.M. Espinosa, V.M. Longo, R. Erlo, N.L. Marana, J.R. Sambrano, M.L. de Santos, A.P. Moura, P.S. Pizani, J. Andrés, E. Longo, J.A. Varela, *J. Phys. Chem. A* 112 (2008) 8970.
- [9] M.L. Moreira, G.P. Mambrini, D.P. Volanti, E.R. Leite, M.O. Orlandi, P.S. Pizani, V.R. Mastelaro, C.O. Paiva-Santos, E. Longo, J.A. Varela, *Chem. Mater.* 20 (2008) 5381.
- [10] D.P. Volanti, D. Keyson, L.S. Cavalcante, A.Z. Simoes, M.R. Joya, E. Longo, J.A. Varela, P.S. Pizani, A.G. Souza, *J. Alloys Compd.* 459 (2008) 537.
- [11] C.S. Riccardi, R.C. Lima, M.L. Dos Santos, P.R. Bueno, J.A. Varela, E. Longo, *Solid State Ionics* 180 (2009) 288.
- [12] T.J.B. Holland, S.A.T. Redfem, *Miner. Mag.* 61 (1997) 65.
- [13] T.Y. Kim, H.M. Jang, S.M. Cho, *Solid State Ionics* 119 (2001) 527.
- [14] N. Koga, T. Kimizu, *J. Am. Ceram. Soc.* 91 (2008) 4052.
- [15] L.Y. Chen, Y.G. Zhang, W.Z. Wang, Z.D. Zhang, *Eur. J. Inorg. Chem.* (2008) 1445.
- [16] H. Zhu, X.L. Wang, L. Qian, F. Yang, X.R. Yang, *J. Phys. Chem. C* 112 (2008) 4486.
- [17] H.L. Zhu, N.Y. Wang, L. Wang, K.H. Yao, X.F. Shen, *Inorg. Mater.* 41 (2005) 609.
- [18] S.Y. Chen, M.C. Wu, C.S. Lee, M. Lin, *J. Mater. Sci.* 44 (2009) 794.
- [19] D.L. Wood, J.S. Tauc, *Phys. Rev. B* 5 (1972) 3144.
- [20] F.V. Motta, A.T. de Figueiredo, V.M. Longo, V.R. Mastelaro, A.Z. Freitas, et al., *J. Lumin.* 129 (2009) 686.
- [21] T. Ding, W.T. Zheng, H.W. Tian, J.F. Zang, Z.D. Zhao, et al., *Solid State Commun.* 132 (2004) 815.
- [22] T.J. Yan, X.X. Wang, J.L. Long, P. Liu, X.L. Fu, G.Y. Zhang, et al., *J. Colloid. Interface Sci.* 325 (2008) 425.
- [23] J.C. Sczancoski, L.S. Cavalcante, M.R. Joya, J.A. Varela, P.S. Pizani, E. Longo, *Chem. Eng. J.* 140 (2008) 632.