

Simple and Efficient Approach for the Synthesis of Nanocrystalline Boehmite *via* Hydrothermal Assisted Sol-gel Processing

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Boehmite (AlOOH) nanoparticle have been prepared from aluminum 2-butoxide by hydrothermal assisted sol-gel processing. The development of boehmite phase at various temperatures has been investigated by X-ray diffraction and Fourier transform infrared. X-ray diffraction of boehmite prepared at 50 °C poorly crystallized and pseudoboehmite develops at 100 °C and well crystallized boehmite forms at 200 °C. The intensities of O-H stretching vibrations in infrared spectra and corresponding bending vibrations, boehmite characteristic peaks, increased with increasing hydrothermal treatment temperature. Thermal analysis showed that the intensity of endothermic peak at 450-500 °C in the DSC curves depends on degree of crystallization of boehmite. The BET specific surface area decreased with increasing hydrothermal treatment temperature and transmission electron microscopy showed plate-like morphology for the boehmite processed at 150 °C and fibrils for the one processed at 100 °C.

Key Words: Boehmite, Nanocrystalline hydrothermal, Sol-gel, Aluminum butoxide.

INTRODUCTION

In recent years, preparation of ceramic powders by hydrothermal method has attracted a considerable amount of interest¹⁻⁵. Part of this interest is due to having good grip in control of morphology, particle size, pore distribution and surface area⁶. In addition, hydrothermal method provides an easy and simple route for the preparation of crystalline single-phase oxides. Among hydrothermal methods for the preparation ceramics, alumina and boehmite (AlOOH) have received the most attention of extensive application⁷⁻⁹. Apparently, textural properties of boehmite depend on preparatory methods and experimental conditions. Various precursors have been used for the preparation of alumina or boehmite by hydrothermal

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method, including aluminum hydroxide precipitated from aluminum nitrate and alkaline solution¹⁰, basic aluminum chloride solution^{11,12}, alkoxide-derived gel or alcogel^{13,14} and aluminum nitrate and urea¹⁵. In all of the hydrothermal methods, which employed for the preparation of alumina and boehmite from aluminum alkoxides, aluminum alkoxide hydrolyzed in various conditions, *e.g.*, changing temperature, solvent and then alkoxide-derived gel was introduced into autoclave. By this method alumina and boehmite with various physical characters and textures have been prepared¹⁶. For instance fibrils boehmite from hydrothermal treatment of a basic aluminum chloride solution at 155-220 °C¹¹, mesoporous boehmite from hydrolysis of aluminum *sec*-butoxide and subsequent prolong heating at 20-45 °C in a sealed glass jar¹⁷, rods and plates by hydrothermal treatment of the precipitates obtained¹⁰ from aluminum nitrate and sodium hydroxide at 160 °C and fine agglomerated particles from hydrothermal treatment of alcogel, obtained from hydrolysis of ethyl acetoacetate aluminum di-*iso*-propylate, at 170-270 °C¹⁸. In majorities of routes in the preparation of boehmite, hydrothermal treatment of aluminum hydroxide precipitate, obtained from reaction of aluminum salts with sodium or ammonium hydroxide between 25 and 240 °C¹⁹, or prolong hydrothermal treatment of gel derived from aluminum tri-*sec*-butoxide is required¹⁶. Furthermore, large amount of carbon in the precursor gel derived from aluminum alkoxides, as shown by thermal analysis²⁰, prevents from complete crystallization of alumina at low temperature. In the present study, we have used a novel approach for the hydrolysis of aluminum alkoxide and report preparation of nanosize boehmite in mild condition in short period of time without using chelating agent for control hydrolysis.

EXPERIMENTAL

Aluminum 2-butoxide was synthesized from aluminum and 2-butanol according to the general preparation procedure of aluminum alkoxide [R]. The prepared aluminum alkoxide was vacuum distilled twice to obtain high quality aluminum alkoxide precursor. The purity of aluminum alkoxide was confirmed by nuclear magnetic resonance spectroscopy and aluminum analysis. Aluminum analysis calculated for C₁₂H₂₇O₃Al: Al, 10.95 %. Found: 10.81 %.

For hydrothermal assisted hydrolysis, aluminum 2-butoxide was diluted with 2-butanol to 50 % and then was loaded into a glass container and transferred into a 300 mL stainless autoclave chamber. Dilution of aluminum alkoxide was carried out in Schlenk line and transfer of that into autoclave was performed in moisture free atmosphere in order to prevent aluminum alkoxide from hydrolysis prior of introducing into hydrothermal chamber. The gap between autoclave chamber and glass container was

filled with 50 mL of distilled water and then autoclave was heated at 50, 100, 150 and 200 °C and aluminum alkoxide was hydrothermally hydrolyzed. After 24 h, autoclave was cooled and dry powder was removed and characterized without further heat treatment. The purity of boehmite (99 %) was measured by aluminum analysis. Aluminum analysis calculated for AlO_2H (boehmite): Al, 44.97 %. Found: 44.52 %.

Characterization techniques: X-ray diffraction pattern of powders were collected on a Phillips PW-1730 diffractometer with CuK_α radiation. Thermal analysis was carried out in a rheometric scientific STA-1500 with heating rate of 10 °C/min in air. The crystal morphology was investigated using a Phillips XL-30 scanning electron microscope (SEM) or a Zeiss 120-KeV Libra transmission electron microscope (TEM). For observation of morphology by SEM powders were coated with gold/palladium. Infrared spectra were recorded (KBr pellets) on a Bomem MB-Series FT-IR spectrophotometer working at a resolution of 4 cm^{-1} . Specific surface areas were measured using BET method on a quantachrome surface area analyzer at 77 K by nitrogen absorption (SBET). Samples degassed at 150 °C for several hours prior to analysis.

RESULTS AND DISCUSSION

Experimental conditions for the hydrothermal hydrolysis of aluminum 2-butoxide along with the crystal size and specific surface areas of the resulted boehmites are given in Table-1.

TABLE-1
EXPERIMENTAL CONDITIONS FOR THE HYDROTHERMAL
ASSISTED SOL-GEL PROCESSING OF BOEHMITE ALONG WITH
CRYSTALLITE SIZE AND SURFACE AREAS

Sample	Processing temp. (°C)	Crystallite size from diffraction line (D nm)		SBET (m^2/g)
		020	120	
HS1	50	–	–	ND
HS2	100	5.6	7.9	326
HS3	150	13.6	24.0	124
HS4	200	18.1	31.0	81

ND = Not detected.

The X-ray diffraction patterns of boehmites prepared at various temperatures are shown in Fig. 1. The sample prepared at 50 °C does not have diffraction peaks, but infrared spectroscopy clearly demonstrate formation of boehmite phase. Therefore, one can concluded atomic clusters for the boehmite rather than amorphous phase. By increasing hydrothermal

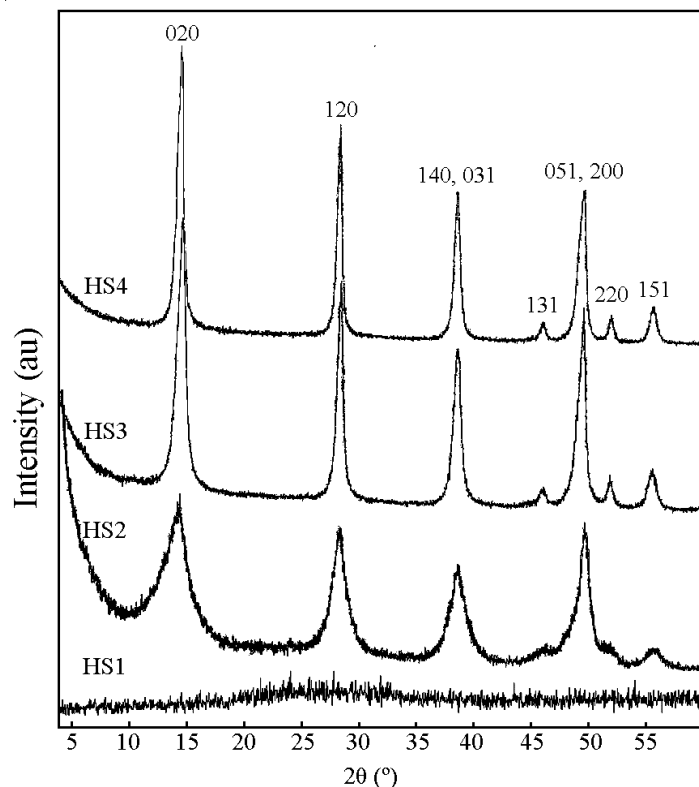


Fig. 1. XRD patterns of HS2, HS3 and HS4 samples

temperature, degree of crystallization gradually increased and at 200 °C well-crystallized single-phase boehmite is formed²¹. The diffraction peaks of boehmite, whose crystalline structure has orthorhombic unit cell, have been indexed using the space group of C₂m. Similar to the previous report in the preparation of boehmite from aluminum nitrate and urea by hydrothermal method¹⁵, reflection of pseudoboehmite with the I/I_0 of 100 % is appeared at 2θ ca. 9.6° and for the well-crystallized boehmite at 14°. It seems that the low temperature processed sample is resulted to the formation of pseudoboehmite and the well-crystallized boehmite only develops at higher temperature. However, it has been shown that pseudo-boehmite actually is non-crystallized boehmite¹⁹. Furthermore, diffraction peaks for the sample processed at 100 °C are broad and by increasing processing temperature the line broadening decreased. The line broadening of (020) reflection for the fibrils boehmite has previously been attributed to the presence of water in the (010) interlayers between octahedral layers¹¹. It is worth to mention that bayerite, α -Al(OH)₃, was the major phase in the preparation of boehmite from precipitated precursor from aluminum

nitrate and sodium hydroxide under hydrothermal conditions at 120 °C and pure boehmite forms only in prolonged heating time¹⁰ at 160 °C. Interestingly, present study showed no bayerite phase forms in the processing temperatures range of 50-200 °C. This clearly revealed the significant role of processing strategy or precursor in the preparation of boehmite under hydrothermal conditions. The crystalline sizes of boehmite for the various samples were calculated from the broadening of the diffraction lines according to Scherrer equation and results are given in Table-1. As previously noticed, the peaks broadening of various diffraction lines of boehmite that prepared under hydrothermal conditions are different¹⁰. This can be attributed to the thin platelets morphology of boehmite and its anisotropic behaviour. In other word, direct comparison of the crystallite sizes from Scherrer estimation less meaningful, by taking to consideration the difference in particle dimensions.

Fig. 2 shows the TGA and DSC data for a boehmite samples that prepared under hydrothermal condition at, 50, 100 and 150 °C. The results are similar to those reported for the fibrillar boehmite¹¹. The TGA curve for the sample processed at 150 °C shows 2 % losses in the temperature range of 75-100 °C. This weight loss was accompanied by an endothermic peak centered at 70 °C in the DSC curve, suggesting that the weight loss is due to the elimination of physically adsorbed water. For the sample processed at 100 °C, HS-2, the weight loss and intensity of endothermic peak around 70 °C is higher. Interestingly, the center of this endothermic peak is shifted to higher temperature from HS-3 sample to HS-1 and for the HS-1 the peak is extended to 200 °C and weight losses is reached to 13 %. The present results are in good agreement with the thermal analysis of boehmite prepared from aluminum chloride by conventional hydrothermal process²². The amount of desorbed water molecules on boehmite surface increased with decrease of crystallite size, in accordance with the pervious report²³ and clearly demonstrates the effect of processing temperature on properties of boehmite. Among samples studied by thermal analyzed, only sample processed at 50 °C, HS-1, shows couple percent of organic residue. Preparation of boehmite without using organic additives is advantage of hydrothermal assistance sol-gel processing in comparison with conventionally processing in presence of additives²⁰. The distinct endothermic peak in the temperature range of 400 to 550 °C in the DSC curve with significant weight loss in the TGA curve is associated with the dehydration and transformation of boehmite into γ -alumina. In contrast to the water desorption peak, the intensity of boehmite transformation peak increased and became sharper at higher processing temperatures. The weight loss in the temperature range of 400-550 °C in the TGA curve of boehmite prepared at 150 °C is 15 wt. %, which is corresponds to loss of 1 mol of

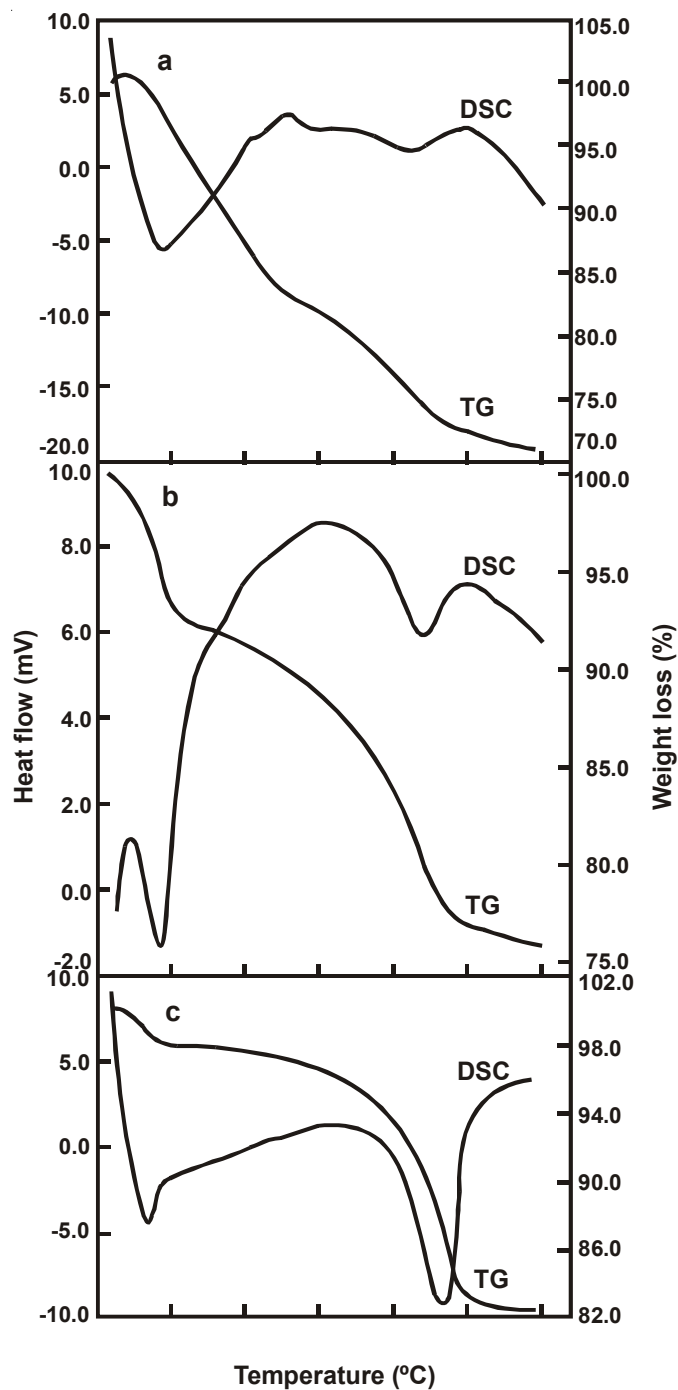


Fig. 2. DSC and TGA curves of sample HS1 (a), HS2 (b) and HS3 (c), obtained from hydrothermal treatment of aluminum 2-butoxide

water from 2 mol of boehmite and transformation to 1 mol of alumina. For the boehmite, was prepared by conventional hydrothermal process of the gel obtained from hydrolysis of aluminum chloride, previously noticed that the transformation temperature decrease with decreasing crystalline size¹⁷. This is in good agreement with the XRD result, which shows boehmite phase well developed at 150 °C. Furthermore, the XRD analysis indicates that the boehmite powder calcined at 500 °C is γ -alumina, the well-known process for the preparation of fine alumina from boehmite²⁴.

Typical bands for the well-crystallized boehmite²⁵, 3075 and 3280 cm^{-1} , O-H stretching vibrations; 1075, 1150 cm^{-1} , O-H bending vibrations; 740 cm^{-1} , Al-O stretching vibration; and strong band at 480 cm^{-1} , Al-O bending vibration, are visible in the spectra. The intensities of above mentioned bands increases from sample HS-1 to HS-4. It is in good agreement with the crystallites sizes calculated from XRD peak widths. Results indicate that the size of crystallites increases by increasing processing temperature. From intensity of IR peak at 1075 cm^{-1} a particle size less than 5 nm can be estimated for the sample processed at 50 °C, HS-1. Interestingly, the broad hydroxyl and water band at *ca.* 3500 cm^{-1} , for the sample processed at 50 °C, splits to two bands at higher processing temperature and exhibits develop of well crystallize boehmite phase. It seems that in lower processing temperature the rate of hydrolysis is very slow and water mostly traps in powder that resulted from partial hydrolysis of aluminum alkoxide. This argument is consistent with the TGA data, which indicate that the sample processed at higher temperature contains lesser amount of water. Therefore, one may concluded that in the hydrothermal processing of boehmite, processing temperature is more critical than other parameters. This could be a reason for the formation of none-boehmite phase in conventional hydrolysis of aluminum alkoxides, which provides a large amount of water to system during hydrolysis at room temperature²⁶. Apparently, mechanism of hydrolysis of aluminum alkoxide in the hydrothermal assisted sol-gel processing differs from conventional one. The infrared spectra similar to the XRD results show no formation of bayerite phase, which is typical phase in the low temperature conventional hydrothermal processing of boehmite¹⁰.

Specific surface areas of samples that prepared by hydrothermal assisted sol-gel processing at 100, 150 and 200 °C in 2-buthanol are given in Table-1. The specific surface areas decrease with increasing hydrothermal treatment temperature. Those data are consistent with the XRD data, which shows that the degree of crystallites increase with increasing processing temperature and consequently causes a significant drop in surface areas. The 326 m^2/g surface area of the sample processed at 100 °C is close to the recently reported value, 322 m^2/g , for the mesoporous boehmite that

obtained by hydrolysis of aluminum 2-butoxide in mixture of ethanol and water at ambient temperature¹⁷ for 20 h.

Boehmite morphology depends on hydrothermal treatment condition and formation of rods, fibrils and thin microfoils has been reported^{10,11}. Attempt has been made to observe the morphology of prepared boehmite by scanning electron microscopy and micrograph for the boehmite prepared at 200 °C is shown in Fig. 3. Even with 25000X magnification, the primary particles and details, due to the agglomeration and nanometer size of boehmite particles are not clear. For the elucidation of boehmite morphology and effect of processing temperature on particle size, samples were analyzed by transmission electron microscopy (TEM). Fig. 4a and 4b show TEM images of boehmite that process at 100 and 150 °C. As can be seen the boehmite crystals processed at 150 °C are plate-like, while the one processed at 100 °C looks fibrils. It seems that the crystal morphology can be tailored to some extent by processing temperature. It is also noticed that the particle sizes obtained from TEM study slightly are larger than that of from XRD. This indicates that the plate-like boehmite particles are composed of much smaller crystallites.

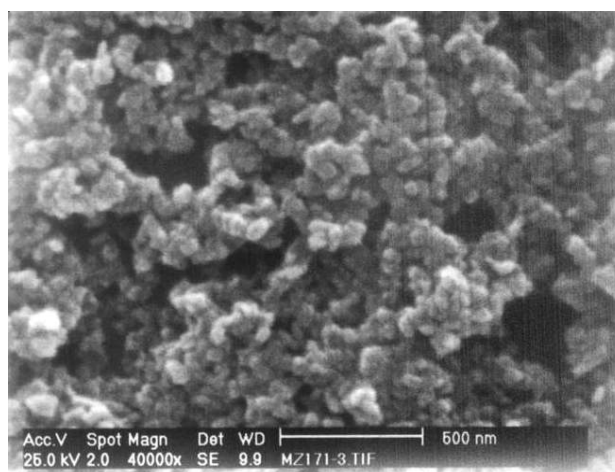


Fig. 3. SEM micrograph of HS4 sample

The exact assembly mechanism of boehmite formation in the present work is not known. However, it seems likely that the nanoparticle assembly instate of supramolecular assembly mechanisms, which previously reported for the formation of boehmite and other oxides is the operating mechanism^{17,27}. The broad pore size distribution of the sample processed at 100 °C is consistent with the suggested mechanism¹⁷.

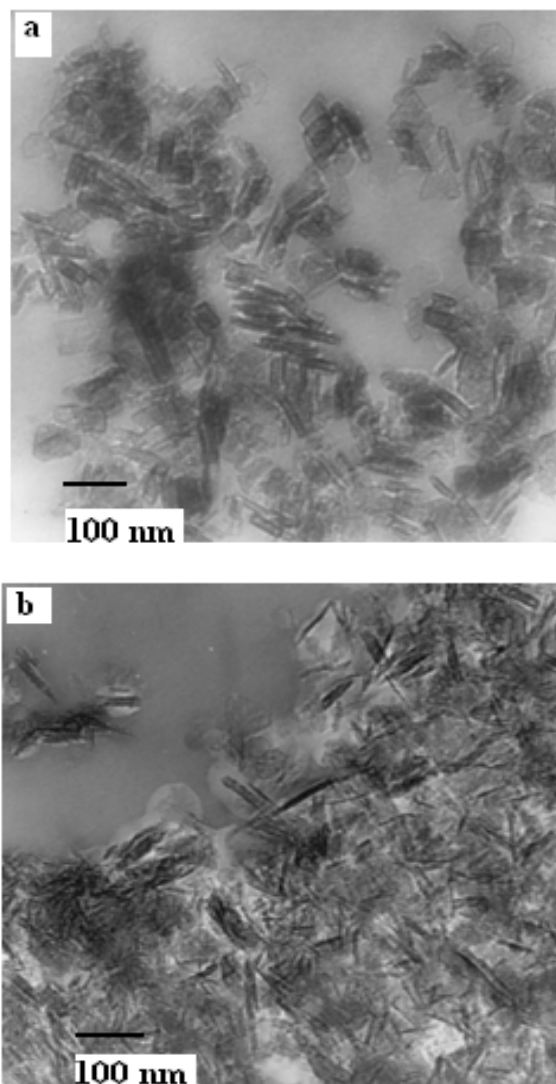


Fig. 4. TEM images of the boehmite (a) for sample HS3 and (b) for sample HS2

Conclusion

In the present study, we have prepared pure nanosize boehmite, AlOOH , powder by hydrothermal assisted sol-gel processing of aluminum 2-butoxide in 2-buthanol. The interesting morphology, particle size and phase of alumina, which arose from hydrothermal hydrolysis of aluminum 2-butoxide can be attributed to the slow and static conditions of hydrothermal hydrolysis of aluminum 2-butoxide.

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REFERENCES

1. M. Wu, G. Lin, D. Chen, G. Wang, D. He, S. Feng and R. Xu, *Chem. Mater.*, **14**, 1974 (2002).
2. Y. Li, X. Duan, H. Liao and Y. Qian, *Chem. Mater.*, **10**, 17 (1998).
3. K. Yanagisawa, J.C. Rendon-Angeles, H. Kanai and Y. Yamashita, *J. Mater. Sci.*, **35**, 3011 (2000).
4. D. Chen, X. Jiao and M. Zhang, *J. Eur. Ceram. Soc.*, **20**, 1261 (2000).
5. Q. Yang, Y. Li, Q. Yin, P. Wang and Yi-B. Cheng, *Mater. Lett.*, **55**, 46 (2002).
6. M. Rozman and M. Drogenik, *J. Am. Ceram. Soc.*, **78**, 2449 (1995).
7. J. Sanchez-Valente, X. Bokhimi and J.A. Toledo, *Appl. Catal. A*, **264**, 175 (2004).
8. Z.R. Ismagilov, R.A. Shkrabina and N.A. Koryabkina, *Catal. Today*, **47**, 51 (1999).
9. M. Thiruchitrambalam, V.R. Palkar and V. Gopinathan, *Mater. Lett.*, **58**, 3063 (2004).
10. S. Music, D. Dragcevic, S. Popovic and N. Vdovic, *Mater. Sci. Eng.*, **B52**, 145 (1998).
11. P.A. Buining, C. Pathmamanoharan, M. Bosboom, J.B.H. Jansen and H.N.W. Lekkerkerker, *J. Am. Ceram. Soc.*, **73**, 2385 (1990).
12. D. Kuang, Y. Fang, H. Liu, C. Frommen and D. Fenske, *J. Mater. Chem.*, **13**, 660 (2003).
13. J. Sanchez-Valente, X. Bokhimi and F. Hernandez, *Langmuir*, **19**, 3583 (2003).
14. T. Fukui and M. Hori, *J. Mater. Sci.*, **31**, 3245 (1996).
15. D. Mishra, S. Anand, R.K. Panda and R.P. Das, *Mater. Lett.*, **42**, 38 (2000).
16. X. Bokhimi, J. Sanchez-Valente and F. Pedraza, *J. Solid State Chem.*, **166**, 182 (2002).
17. R.W. Hicks and T.J. Pinnavaia, *Chem. Mater.*, **15**, 78 (2003).
18. T. Fukui and M. Hori, *J. Mater. Sci.*, **30**, 1794 (1995).
19. X. Bokhimi, J.A. Toledo-Antonio, M.L. Guzman-Castillo and F. Hernandez-Beltran, *J. Solid State Chem.*, **159**, 32 (2000).
20. J.A. Wang, X. Bokhimi, A. Morales and O. Novaro, *J. Phys. Chem. B*, **103**, 299 (1999).
21. Powder Diffraction File, Card Nos. 10-425 and 21-1307, Joint Committee on Powder Diffraction Standard, Swarthmore, PA.
22. X. Bokhimi, J.A. Toledo-Antonio, M.L. Guzman-Castillo, B. Mar-Mar, F. Hernandez-Beltran and J. Navarrete, *J. Solid State Chem.*, **161**, 319 (2001).
23. T. Tsukada, H. Segawa, A. Yasumori and K. Okada, *J. Mater. Chem.*, **9**, 549 (1999).
24. C. Misra, Industrial Alumina Chemicals, ACS Monograph 184, American Chemical Society, Washington DC (1986).
25. J. Hobert, A.K. Vasudevan, A.D. Damodaran and K.G.K. Warriar, *J. Solid State Chem.*, **131**, 181 (1997).
26. A. Alipour, H. Jazayeri, A. Nemati and M.M. Amini, *Mater. Lett.*, **48**, 15 (2001).
27. G. Pacheco, E. Zhao, A. Garcia, A. Sklyarov and J. Fripiat, *J. Mater. Chem.*, **8**, 21 (1998).