



<http://www.e-journals.net>



ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2010, 7(3), 894-898

Template-Assisted Sol-Gel Synthesis of Nanocrystalline BaTiO₃

T.V. ANURADHA

Department of Materials Engineering,
Indian Institute of Science, Bangalore – 560 012, India.

anu_guhan@yahoo.co.in

Received 28 October 2009; Accepted 20 December 2009

Abstract: Nanocrystalline perovskite barium titanate with an average particle size less than ~10 nm is produced using sol-gel route involving ligand-assisted templating. BaTiO₃ is obtained by the controlled hydrolysis and condensation reaction of barium acetate (Ba(CH₃COO)₂) with titanium tetra chloride (TiCl₄) in the reverse micelles of dodecylamine (DDA) which is used as the template. Our attempts to produce mesoporous BaTiO₃ have resulted in the formation of nanocrystalline BaTiO₃. The synthesis of nanostructured BaTiO₃ is carried out using the ligand-assisted templating approach which proceeds through the sol-gel route. Dodecylamine is used as the template. The sol-gel process in general presents inherent advantages because the nanostructure of the desired materials can be controlled together with their porous structure. Ligand-assisted templating approach involves the formation of covalent bond between the inorganic analogue and the template. Ba(CH₃COO)₂ and TiCl₄ are used as barium-source and titanium-source respectively. The reaction between Ba(CH₃COO)₂ and TiCl₄ is found to take place deliberately on the pre-assembled species which acts as the template or occurring with in them which in turn will lead to the generation of the desired nanoscale structure (nanopores or nanoparticles).

Keywords: Ligand-assisted templating; Ba(CH₃COO)₂, TiCl₄, Dodecylamine; XRD, TEM.

Introduction

Barium titanate (BaTiO₃) is well-known for its high dielectric constant. The dielectric properties are controlled by purity and microstructure which in turn are dependent on the method of preparation¹. Recent advances in nanotechnology such as: Multilayer capacitor, Micro Electro Mechanical Systems and Dynamic Random Access Memories have resulted in the miniaturization of devices². These require nanosize BaTiO₃. Various chemical routes like coprecipitation³, sol-gel⁴, hydrothermal⁵⁻⁶ and solution combustion⁷ are known to yield

nanoparticle products. Applying meso-scale design strategies to perovskite compounds is a very interesting topic and may bring new exciting discoveries in these widely utilized materials, especially when considering the current and future needs for functionalized materials to perform smart functions. The synthesis of mesoporous BaTiO₃ by template-assisted sol-gel process is earlier reported where tetradecylamine is used as template⁸. There is also a report on the synthesis of mesoporous BaTiO₃ using cationic surfactants like cetyltrimethyl ammonium chloride⁹ as template. But the synthesis of mesoporous BaTiO₃ using dodecylamine as the template is attempted here which indeed resulted in the formation of nanocrystalline BaTiO₃. The synthesis of nanocrystalline BaTiO₃ through templating approach is first of its kind.

Experimental

To 1 g of dodecylamine (DDA) in 5 mL of isopropanol, 1 mL of TiCl₄ in 2 mL of isopropanol was added in liquid N₂ atmosphere. It was followed by the addition of 1 g of barium acetate (Ba(CH₃COO)₂) in 3 mL of isopropanol and 2 mL of distilled water to form a sol. The sol was then transferred to the polypropylene bottle and kept in the hot air oven at 100 °C for 3 h to form a white colored barium titanate gel. Then it was filtered, washed and dried at 100 °C for 3 h. The 1:1 solution of ethanol and HCl was used as the solvent during washing to extract dodecylamine. It was then followed by the heat treatment at 750 °C for 1h so as to extract the template completely.

Results and Discussion

Figure 1 gives the x-ray diffraction pattern of BaTiO₃ obtained finally after heat treatment at 750 °C for 1h. XRD studies indicated the complete extraction of the template resulting in the formation of perovskite BaTiO₃ with cubic structure (JCPDS no. 75-0212) and the studies have also revealed the nanocrystalline nature of barium titanate with the average crystallite size ~20 nm.

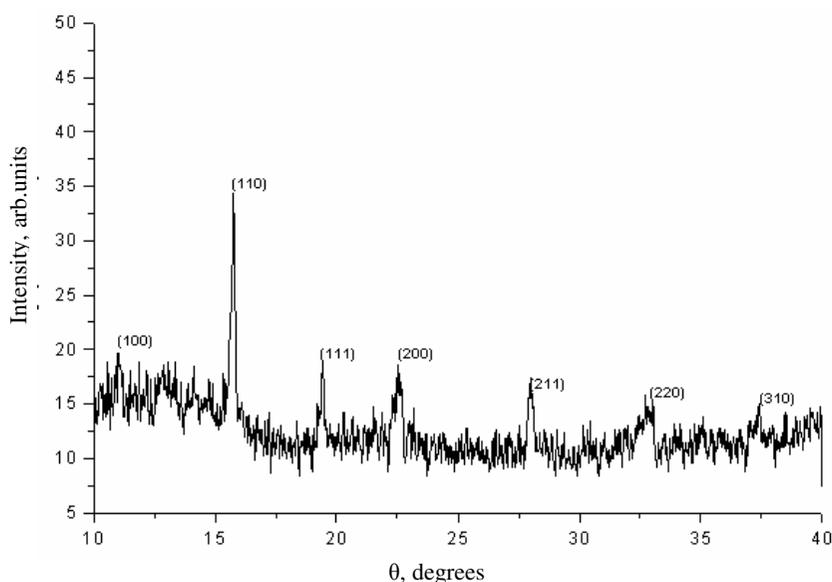


Figure 1. XRD pattern of BaTiO₃ obtained after subsequent heat treatment at 750 °C for 1 h.

Figure 2 gives the scanning electron microscopic (SEM) image of barium titanate obtained here. SEM studies confirmed the porous nature of the product and the particles are found to be nearly spherical. The formation of agglomerates is evident from the SEM studies which has the cauli-flower like morphology.

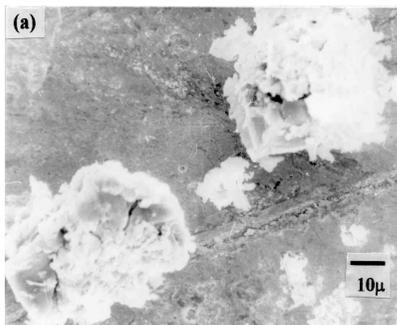


Figure 2. SEM micrograph of BaTiO₃ obtained after heat treatment at 750 °C.

Figure 3 gives the bright field transmission electron microscopic (TEM) image of barium titanate powder with its corresponding selected area electron diffraction (SAED) pattern and Figure 4 gives its corresponding dark field TEM image. TEM studies indicated the average particle size to be less than 10 nm.

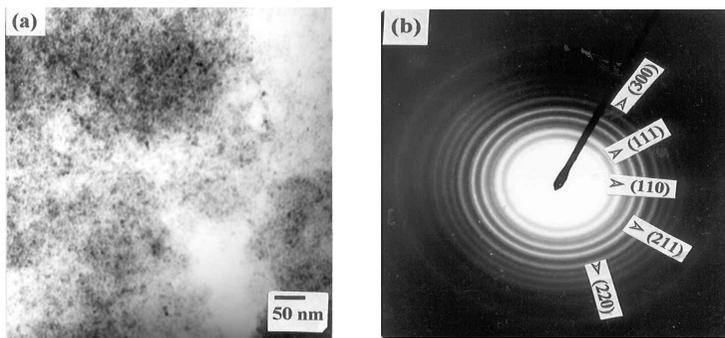


Figure 3. The bright field TEM image of BaTiO₃ obtained after heat treatment at 750 °C and (b) its corresponding selected area diffraction pattern.

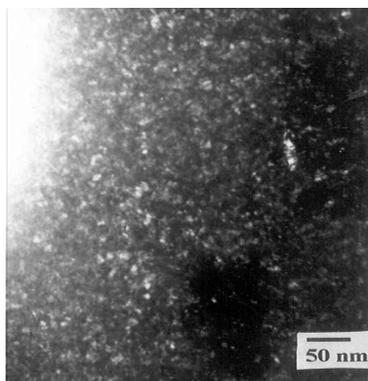


Figure 4. The dark field image of BaTiO₃ produced.

The surfactant molecule which is used as the template forms molecular self-assemblies called micelles with spherical shape in aqueous solutions at a particular concentration called, first critical micellar concentration (cmc1) and if the concentration exceeds cmc1 and reaches the second critical micellar concentration (cmc2), the spherical micelle transforms to the rod-like micelles which then organizes to form liquid-crystalline phases with various structures as shown in the Figure 5. The spherical micelles can be either normal (with all the hydrophilic head groups projecting out) or reverse (with all the hydrophilic head groups projecting in). Formation of mesoporous material involves the normal micellar rods forming the liquid crystalline mesophase as the template. On the other hand, the reverse micelles result in the formation of reverse liquid crystalline mesophase which fails to form mesoporous material through templating, but aids in the formation of nanocrystalline material by a way of providing the core of the micellar rod containing water as a 'nano reactor' within which the reaction of the precursors take place. Thus it is believed that the reverse micellar rods of dodecylamine is formed in these experiments with the controlled hydrolysis and condensation of the precursors namely Ba(CH₃COO)₂ and TiCl₄ taking place in its aqueous core which acts as the 'nano reactor'.

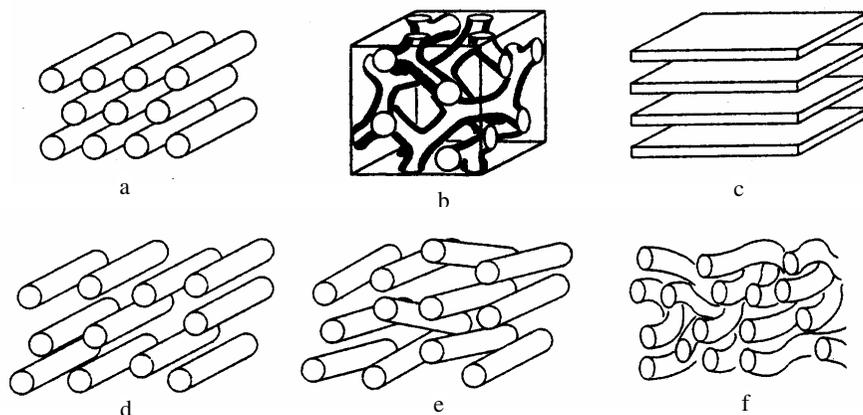


Figure 5. Structures of mesostructured phases. The top row shows structures with long-range order: a) hexagonal phase, b) cubic phase, c) lamellar phase. The bottom row shows possible disordered structures, as they may occur in some of the mesoporous metal oxides: d) disordered arrangement of parallel cylindrical pores, e) disordered packing of cylindrical pores, f) worm-shaped pores.

Conclusions

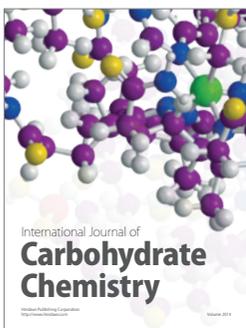
Nanocrystalline cubic BaTiO₃ with the average particle sizes less than ~10 nm is formed by the condensation and controlled hydrolysis of Ba(CH₃COO)₂ and TiCl₄ in the reverse micelles of dodecylamine of the reverse hexagonal liquid crystalline phase (mesostructure). It is evident from the TEM studies that the particle size distribution of sol-gel derived BaTiO₃ is very narrow. Electron microscopic studies indicated that the particle morphology of BaTiO₃ derived by the sol-gel method to be spherical.

Acknowledgments

The author acknowledges the financial support from CSIR (India) through senior research fellowship. The author is also thankful to Prof. S. Ranganathan (Department of Materials Engineering, IISc, Bangalore, India) for his guidance in this research.

References

1. Subbarao E C, Prasad V C S and Veerbhadra Rao K, Preparation and characterization of Materials; Honig J M and Rao C N R, Academic Press, New York, 1981, 217.
2. Setter N and Waser R, *Acta Mater.*, 2000, **48**, 151.
3. Lee S K, Park T J, Choi G J, Koo K K and Kim S W, *Materials Chem Phys.*, 2003, **82**, 742.
4. Lemoine C, Gilbert B, Michaux B, Pirard J P and Lecloux A J, *J Non-crystalline Solids*, 1994, **175**, 1.
5. Zhu X, Zhu J, Zhou S, Liu Z, Ming N and Hesse D, *J Crystal Growth.*, 2005, **283**, 553.
6. Guo L, Luo H, Gao J, Guo L and Yang J, *Mater Lett.*, 2006, **60**, 3011.
7. Anuradha T V, Ranganathan S, Mimani T and Patil K C, *Scripta Materialia* 2001, **44**, 2237.
8. Wang H W, Kuo C H, Liao T H, Lin R J and Cheng S Y, *J Mater Res.*, 2006, **21**, 941.
9. Huo R Z, Ferreira P and Vilarinho P M *Microporous & Mesoporous Mater.*, 2008, **110**, 392.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

