International Journal of Electronic Engineering Research
ISSN 0975 - 6450 Volume 2 Number 4 (2010) pp. 581-588

https://dx.doi.org/10.37622/IJEER/2.4.2010.581-588

Synthesis and Characterization of $BaTiO_3$ by Thermal Decomposition of Metal Oxalate Precursors

Arunkumar Lagashetty[1], A.M Bhavikatti[2], B. Mahadevi[3] and Subhash Kulkarni[4]

[1]*Appa Institute of Engineering & Technology, Gulbarga, Karnataka, India*

[2]*Rural Engineering. College, Bhalki, Bidar, Karnataka, India*

[3]*PDA College of Engineering, Gulbarga, Karnataka, India*

[4]*Jaya Prakash Narayan College of Engineering, Mahabubnagar, AP, India*

Abstract

Synthesis of nanosized polycrystalline binary oxide materials integrates the modern synthetic nanotechnology. Intensive efforts for the synthesis of various mixed materials through different methods are reported in the literature. Out of these, combustion method could be an interesting because of its simplicity and it needs simple equipments. Barium titanate is one of the important polycrystalline oxide materials used as semiconductor, catalytic and dielectric materials. Combustion route is adopted for the synthesis of nanosized $BaTiO_3$ through barium and titanium oxalate precursors using polymer as a fuel. In search of a suitable economic fuel, our use of poly (ethylene glycol) has given promising results in the conversion of metal oxalates precursors in to $BaTiO_3$ nanoparticles. The feasibility of the conversion of the precursors to its $BaTiO_3$ through combustion route is reported Barium oxalate and titanium oxalate precursors was prepared by dissolving stiochiometric quantities of barium chloride and titanium chloride with solvent. These two oxalates were grinded with polyethylene glycol as a fuel in a pestel and mortar and ignited to barium titanate nanoparticles. The structure of the prepared nano titanate particles is studied by X-ray diffraction (XRD) technique. This study shows the formation of polycrystalline structure. Morphology of the barium titanate is viewed by Scanning electron micrograph (SEM) . This SEM image shows irregular shaped particles with compact and globular arrangement. Infrared (IR) spectroscopic technique is used to know the bonding in the prepared oxide sample. Metal-Oxygen (Ba-O & Ti-O) and metal-metal (Ba-Ti) bonding is observed in the spectrum.

Key words: Polycrystalline, precursor, nanoparticles, structure, morphology, bonding.

Introduction

There have been the major advances in materials and solid state chemistry in the last decade, further, the subject is growing rapidly with the understanding of synthesis and development of new materials when the materials are miniaturized to nanoscale, many interesting properties and tailored applications are obtained [1-3].

Intensive research on materials synthesis has lead to a large interdisciplinary field in materials science [4]. New routes for materials synthesis at nano dimension integrate the synthetic technology [5-6]. Recently, development of techniques such as sol-gel and other soft chemical methods have led to the preparation of engineering materials [7]. Development of synthetic efforts has been focused on preparation of metal oxide materials owing to their markedly physical and chemical properties with respect to bulk materials. The rapidity of the reactions offers excellent conditions for meta stable phases.

Advanced ceramics found applications in many areas, such as electro-optic devices, multilayer capacitors and others [8]. The growing demand for such ceramics with nanometer dimensions has accelerated the development of new powder synthetic methods. Performance of binary oxide materials which are determined by morphology of the nanoparticles could have profound influences on their properties [9].

The synthesis of ferrite's through a self-propagation route employing a precursor gel is an integral part of synthetic technology. This synthetic route can be considered interesting for its simplicity, reproducibility and easy scale-up. It produces a homogenous precursor with a controlled stoichometry and also does not require expensive chemicals. It is a low-energy reaction and can be carried out in a china dish in an open atmosphere. In this self-propagation combustion reaction, a suitable oxidant/fuel for our study was found to be polyethylene glycol. In our earlier studies we have successfully used this oxidant/fuel for the synthesis of ultrafine gamma ferric oxide particles from different precursors [10-11].

Current investigation is a new combustion synthetic route using metal oxalate precursors for synthesis of $BaTiO_3$. In search of a suitable economic fuel, our use of poly (ethylene glycol) has given promising results in the conversion of barium oxalate and titanium oxalate precursors in to $BaTiO_3$. The feasibility of the conversion of the precursors to its $BaTiO_3$ through combustion route is reported. The characterization study of as prepared $BaTiO_3$ was undertaken by employing XRD, SEM and IR techniques.

Experimental

Materials and methods

All the chemicals used were AR grade. Poly (ethylene glycol) of molecular weight 4000 was obtained commercially. Cold distilled water is used in the present work. Self-Propagating combustion synthetic route was adopted for the synthesis of $BaTiO_3$

particles. In this method thermal decomposition of metal oxalate precursors takes place. The polyethylene glycol is used as a fuel for the combustion reaction.

Preparation of barium oxalate and titanium oxalate precursors

These precursors were prepared by dissolving equimolar quantities of barium chloride and titanium chloride with oxalic acid and were stirred well in separate beakers. The precipitates of these two metal oxalates obtained was filtered through sintered glass crucible and was washed with cold distilled water till free from chloride ions and oxalic acid, finally with dry acetone and was then dried under vacuum.

Synthesis of nano-sized $BaTiO_3$

The barium oxalate, titanium oxalate and poly (ethylene glycol) was mixed in weight ratio 1:1:5 [12] and ground well in a pestle and mortar. Resultant solid was placed in a crucible and heated in air. It was observed that initially poly (ethylene glycol) melted, then frothed and finally ignited at 1400^0C for eight hours to form $BaTiO_3$. On cooling to room temperature no trace of carbon impurities was observed in the final residue of $BaTiO_3$. The possible theoretical reactions taking place in the synthetic process are given below.

$$TiCl_4 + (COOH)_2 \longrightarrow (COO)_2Ti + 2HCl + Cl_2$$

$$BaCl_2 + (COOH)_2 \longrightarrow (COO)_2Ba + 2HCl$$

$$(COO)_2Ti + (COO)_2Ba + 3/2O_2 \xrightarrow{\text{(fuel) } 1400^0\text{C}} BaTiO_3 + 4CO_2$$

Characterization

The X-ray diffraction patterns were obtained employing a Geol JDX-8p spectrometer using CuK_α radiation. The X-ray generator was operated at 30kV and 20mA. The scanning range, $2\theta/\theta$ were selected. The scanning speed $=1^0$ min^{-1} were employed for precise lattice parameter determination. High purity silicon powder was used as an internal standard. The shape, size and distribution of the powder, as prepared tin oxide sample, microstructure of the sample have been examined using a Leica-440 Cambridge Stereoscan, scanning electron microscope image. The SEM was operated at 20kV. The samples were made conducting by the sputtering of gold using a Poloron DC "sputtering unit" operated at 1.4kV and 18-20mA. The infrared spectra were recorded on a Perkin-Elmer FTIR spectrophotometer [Model 1000] in the range 300 cm^{-1} to 4000cm^{-1}.

Density measurement

Density evaluation from X-ray data

The X-ray density of the samples have been computed from the values of lattice Parameters using the formula [13-14].

$d=8\ M / Na^3$ - ---------- (1)

Where 8 represents the number of molecules in a unit cell of a spinel lattice

M = Molecular weight of the sample
N = Avogardo's number =6.023 x 10^{23} atoms / mole
a = Lattice parameter of the sample
The lattice constant for the cubic was calculated using the equation

$$d = a / (h^2 + k^2 + l^2)^{½} \quad \text{---------- (2)}$$

Tap density

The as prepared $BaTiO_3$ was crushed in agate mortar using a pestle and mortar. A known amount of this powder was filled into a graduated cylinder of 25ml capacity. The cylinder was tapped until the powder level remains unchanged. The volume occupied by the powder was noted. The ratio between the weight of the substance and the volume gave tap density [15].

Powder density

The powder densities were measured using Archimedes principle [20] with a pycnometer and xylene as a liquid medium. The pycnometer of volume 25ml was used. The following weights were taken and used in the density calculation.

Weight of the bottle = W_1g,
Weight of the bottle + Substance = W_2g
Weight of the bottle + Substance + Xylene = W_3g
Weight of the bottle + Xylene = W_4g,
Density of Xylene = ρ_{sol}
Density of sample = ρ_{sample}

$$\rho_{sample} = \frac{(w_2 - w_1)\,\rho_{sol}}{(w_4 - w_3) + (w_2 - w_1)} \quad \text{---------- (3)}$$

Crystallite size

Detailed knowledge of crystallite size, shape and strain in a finely divided powder often helps to correlate many physical properties of a system undergoing transformation in a solid-state reaction. X-ray line broadening analysis provides a method of finding bulk average size of coherently diffracting domains and r.m.s strain. The average crystallite size (D) from X-ray line broadening has been calculated using the Scherrer equation [16-17]. The instrumental broadening was corrected using quartz as a internal standard.

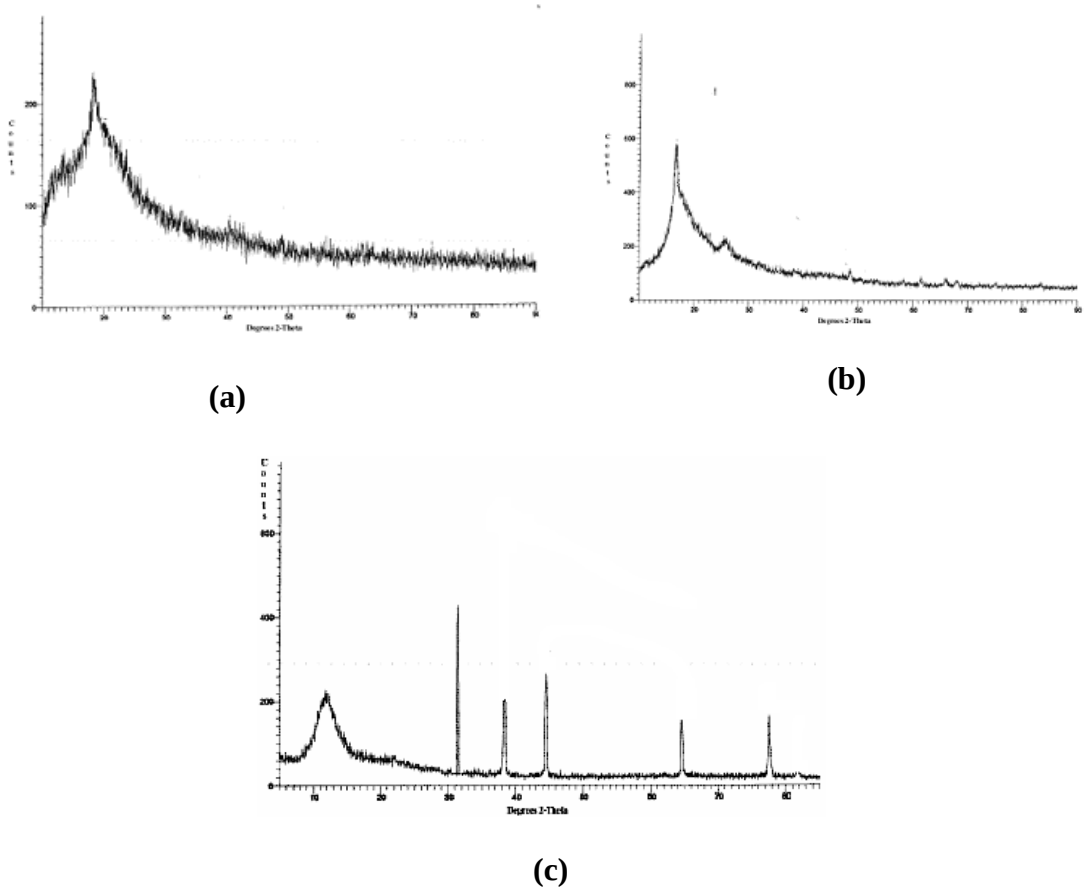
$$D = 0.9\lambda / \beta_{1/2}\text{Cos}\theta \quad \text{---------- (4)}$$

Where λ is the wavelength of the X-ray beam, $\beta_{1/2}$ is the angular width at the half-maximum intensity and θ is the Braggs angle

Results and Discussion

X-ray diffraction study

Figure 1(a) presents XRD patterns of metal oxalates with fuel heated at 500^0C. The absence of Bragg's reflection in the pattern represents the amorphous nature of the product. The same sample was heated up to 800^0C and its XRD pattern is given in figure 1(b). This pattern reveals the development of crystallinity in the sample and the heat treatment may be continued till the expected sample is obtained ..Partial crystalline solid is heated at 1400^0C for eight hours which turns the perfectly crystalline product. Bragg's reflections of this product are in agreement with literature data (JCPDS 31-174). It reveals a good crystalline cubic structured $BaTiO_3$ nanoparticles and its XRD pattern is given in figure 1(c).



(a) **(b)**

(c)

Figure 1: XRD pattern (a) Barium and titanium oxalate with fuel Heated (a) at 500^0C (b) at 800^0C and (c) at 1400^0C.

Scanning Electron Micrograph Study

The surface morphology of the as synthesized barium titanate is studied by scanning electron micrograph. Figure 2 Shows SEM image of as synthesized barium titanate. The image shows irregular shaped particles formed in globular arrangement and some particles are found as agglomerates.

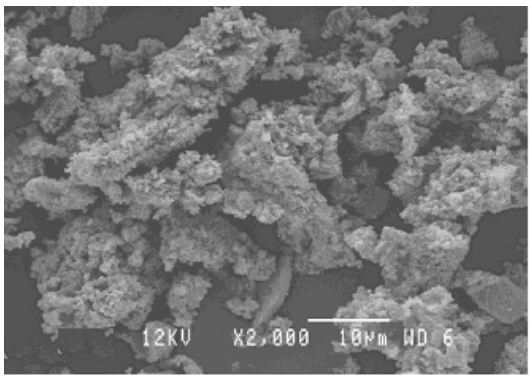


Figure 2: SEM image of as prepared Barium titanate.

Infrared study

The infrared study was performed aiming to ascertain the metal-oxygen and metal-metal bond in the prepared product. Table-1 gives the vibrational frequencies of as synthesized $BaTiO_3$. The $BaTiO_3$ sample shows the absorption in the region 3100, 1060, 505, 455, 425, 410, 250 and 210 cm^{-1}. The peak at 3150 cm^{-1} corresponds to water of adsorption and the peak at1060cm^{-1} is due to the presence of some overtones. The peaks at 505, 455, 425 and 410cm^{-1} correspond to the metal-oxygen (Ba-O and Ti-O) vibrational modes of the spinal compound [18]. The peaks at around 250 and 210cm^{-1} is observed due to metal-metal (Ba-Ti) vibration frequency range. This confirms the formation of $BaTiO_3$.

Table 1: Vibrational Frequencies of $BaTiO_3$ sample.

Peak No	Vibrational Frequencies(cm^{-1})
1	3100
2	1060
3	505
4	455
5	425
6	410
7	250
8	210

Density measurement and Crystallite size

Density evaluation from X-ray data, Tap density and Bulk density of as synthesized Barium titanate is 4990, 5040 and 4890 respectively. The density values evaluated from different methods are approximately same. The calculated crystallite size of the as synthesized Barium titanate is 30.5 nm.

Acknowledgement

Authors are grateful to Prof. Venkateraman, Department of Materials Science, Gulbarga University, Gulbarga for XRD analysis. One of the authors Arunkumar Lagashetty acknowledges the kind support of Dr. Sharanabasavappa Appa, President, Appa Institute of Engineering & Technology, Gulbarga for providing laboratory facilities. One of the authors, A.M.Bhavikatti would like to express his sincere thanks to the principal Dr.B.B.Lal and the Hon'ble Sri.Ishwar.khandre, President SVES Bhalki, for their constant support.

References

[1] C N R Rao, G U Kulkarni, P John Thomas, Ved Agarwal, Ujjal K Gautam and M Ghosh Curr.Sci., **85**(2003)1041

[2] C N R Rao, G U Kulkarni, P J Thomas and P P Edwards Chem. Eur. J., 8(2002)29

[3] A T Ngo and M P Pileni J. Phys. Chem., 105 (2001) 53.

[4] J. Gopalakrishnan, Chem. Mater. **7** (1995) 1265.

[5] Arunkumar Lagashetty, Vijayanand Havanoor, S Basavaraj, S D Balaji and A Venkataraman. Sci. & Tech of Adv. Mater., 8(2008)484-493

[6] Basavaraja S, S. D. Balaji Arunkumar Lagashetty, S. Rajasab and A. Venkataraman. Mater. Res. Bull. 41(2008)1162-1170.

[7] Arunkumar Lagashetty, Vijayanand Havanoor, S Basavaraj and A Venkataraman Ind. J Chem. Tech. Ind. J Chem. Tech. 15(2008)41-42.

[8] D Hennings, M Klee and R waster, Adv. Mater., 1991, 3, 334.

[9] A. M. Bhavikatti, Subhash Kulkarni and Arunkumar Lagashetty J. Mater. Sci. Res. Ind. 4(2)(2007)456-463.

[10] N. N Mallikarjuna, B Govindraj, Arunkumar Lagashetty and A Venkataraman J. Therm. Anal. & Cal. 71(2003) 915.

[11] Arunkumar Lagashetty and A Venkataraman Bull. Mat. Sci. 27(6)(2004)419.

[12] A.Venkataraman, Vijay. A. Hiremath, S. K. Date and S. D. Kulkarni, Bull. Mater. Sci. 24(6)(2001) 101.

[13] Venkataraman, V. A. Hiremath, S. K. Date, S. M. Kulkarni, *Bull.Mater.Sci.*, **2001**, *24(6)*, 101.

[14] J. Smith, H.P.T Wijn, N.N.Phillips, Gloeilampenjabricken, Eindnoven" *Ferrites*", Holland, **1959**, p.144.A.

[15] S. Kinsman *" Systematic Materials Analysis"* Vol. 4, (eds.), T.H.Richardson and R V Peterson Academic, Newyork ,**1978**, p.200.

[16] J. Smith, H.P.T. Wijn, N.N.Philips, Gloeilampen jabriken Eindnoven, Ferrites, Holland, 1959.

[17] S. Kinsman, in: T.H. Richardson, R.V. Peterson (Eds), Systematic Materials Analysis, Academic, New York, 1978, p. 200.

[18] C. N. R. Rao, "Chemical Approaches to Synthesis of Inorganic Materials", Wiley Eastern, Ltd., New Delhi, 1994

Biographies of authors

A M Bhavikatti received a degree in Electronics & communication in 1985, has completed ME in power electronics in 1991 and is a research scholar in Electronic materials .Till date, he has more than 25 publications in International and National journals and Conferences .Presently he is a Professor and Head of Electronics and Communication Engineering Dept at Rural Engineering College, Bhalki, Karnataka state.

Dr.Arunkumar.Lagashetty completed M.Sc in 2000 and M.phil in 2001 from Gulbarga University, Gulbarga. He was awarded PhD from Gulbarga University in 2004 in the area of Physical chemistry .He was a Junior Research fellow for an UGC Project. Till date he has more than 28 publications in International and National journals and more than 30 publications in conferences. Presently, he is working as a Head of department of Chemistry at Appa Institute of Engineering and Technology, Gulbarga, Karnataka state.

Smt. Mahadevi.B. Completed degree in Electrical and electronics engineering in 1986 and M.E in power electronics 1995 from Gulbarga University, Gulbarga.. Till date she has more than 6 publications in International and National conferences.. Presently, she is working as a selection grade lecturer at PDA College of Engineering, Gulbarga, Karnataka state.

Dr. Subhash S. Kulkarni completed BE in Electronics and Communication Engg in 1988 and Masters program in Electronic Design & Technology from Indian Institute of Science, Bangalore in 1995.He was awarded PhD from IIT, Kharagpur in 2002 in the area Geometric Deformable Models for Image Segmentation .Presently he is working as Principal in Jayaprakash Narayan College of Engineering, Mahabubnagar, Andhra Pradesh. Till date he has more than 30 publications in International & National journals and Conferences and is guiding 8 research scholars.