Available online at www.sciencedirect.com
ScienceDirect
Materials Letters 61 (2007) 850–854
materials letters
www.elsevier.com/locate/matlet

Characterization of tetragonal $BaTiO_3$ nanopowders prepared with a new soft chemistry route

T.K. Mandal

ICFAI Institute of Science and Technology, Woodland House, Subhas Nagar Chowk, Mohabewala, Dehradun, 248002, India

Received 21 February 2006; accepted 2 June 2006
Available online 5 July 2006

Abstract

Preparation of $BaTiO_3$ nanopowders (37–42 nm) is carried out by a controlled reconstructive thermal decomposition and crystallization from an amorphous polymeric precursor with polyvinyl alcohol (PVA) and sucrose at 400–600 °C in air. The Rietveld refinement of the XRD profile, processed at 600 °C in 2 h, infers the P4mm tetragonal crystal structure (95% of tetragonality) of the as prepared $BaTiO_3$ nanopowders, with $a=0.3994$ nm and $c=0.4024$ nm. A cubic symmetry (Pm3m) of 5% in amount with $a=4.0057$ is also detected in addition with tetragonal symmetry. The characteristic tetragonal splitting of 002/200 XRD peaks also supports the tetragonal symmetry ($c/a=1.0075$) of the as prepared $BaTiO_3$ nanopowders. The average particle size (D) of the $BaTiO_3$ powders, estimated with the help of the specific surface area, measured by BET method, is 39.91 nm. Average D value, calculated by $\Delta 2\theta_{1/2}$ in the XRD peaks with the Debye Scherrer relation is ~40 nm. TEM study measures the particle size of the $BaTiO_3$ powders with an average diameter of 37 to 42 nm.

Keywords: Chemical synthesis; $BaTiO_3$ nanopowders; Tetragonal phase; PVA-sucrose; Ferroelectrics

1. Introduction

Barium titanate ($BaTiO_3$), with a perovskite structure, finds extensive applications in making electronic devices such as multilayer ceramic capacitors (MLCCs), self-controlled heaters, communication filters and piezoelectric sensors [1–5]. The present advancement in microelectronics and communications is gradually leading to the miniaturization of ferroelectric components and of MLCCs. The quality of ceramic capacitors can be improved through smaller-sized components and larger capacitance values. In order to achieve high capacitance in a small volume, the dielectric layer thickness has to be reduced while increasing the total number of layers. Thus, the interest in high-quality $BaTiO_3$ nanopowders with narrow particle size distribution is continuously increasing. For $BaTiO_3$, the best dielectric properties are obtained with tetragonal phase [6].

The physical properties of $BaTiO_3$ powders are critically affected by their size [4,7–12]. The transformation from tetragonal to cubic symmetry of $BaTiO_3$ powders at a critical particle size of 0.12 μm at room temperature has been discussed in terms of surface tension by Uchino et al. [7]. Begg et al. [11] reported that powders over 0.27 μm in size are of the tetragonal phase, while powders under 0.19 μm in size are of the cubic phase at room temperature. On the contrary, it is also investigated that in polycrystalline $BaTiO_3$ ceramics, the tetragonal–cubic transition temperature remains relatively constant even when the grain size changes, although a significant size effect on the dielectric constant has been observed [8,13]. However, Li and Shih [12] reported that $BaTiO_3$ powders over 80 nm have the tetragonal phase; powders 56–80 nm in size have a mixed state of tetragonal and cubic phases, and powders under 56 nm only have the cubic phase. They explained this observation by the clustering behavior of small particles. Recently, Park et al. [4] observed that the nanograined $BaTiO_3$ ceramics prepared from the noncoated $BaTiO_3$ nanopowders showed a mixed state of cubic and tetragonal phases; on the other hand, nanograined $BaTiO_3$ ceramics prepared from $BaTiO_3$ nanopowders coated with Mn exhibited only the tetragonal phase. They examined that the dielectric constant of the latter is about 10 times larger than that of the former. Thus, the literature indicates a possible conflict between the nanometer particle size and the tetragonal phase. Therefore, a low temperature synthesis procedure that

E-mail address: tapanm@yahoo.com.

0167-577X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2006.06.006

directly results in the formation of $BaTiO_3$ nanopowders of tetragonal phase is of extreme interest.

Traditionally, $BaTiO_3$ is prepared by solid-state reactions between the constituent oxides or oxides and carbonates at temperatures above 1000 °C. $BaTiO_3$ prepared at high temperatures produces relatively coarse, impure and agglomerated particles not suitable for the processing of MLCCs with thin dielectric layers. Several recent methods, such as alkoxide–hydroxide route [14], solvothermal process [15], hydrothermal method [11,16–18], hot-press sintering $BaTiO_3$ nanopowders coated with Mn [4], have been developed in order to synthesize $BaTiO_3$ in controlled dimension in fine powders. Nevertheless, most of these methods are unsuccessful in preparing $BaTiO_3$ in nanopowders with tetragonal phase. Kajiyoshi et al. [16] and Dutta et al. [17,18] have prepared tetragonal BT. Unfortunately powders reported in these studies have submicrometer-sized. Chaput et al. [14] synthesized $BaTiO_3$ powders at very low temperatures. But, powders prepared by them are also in the submicrometer range. The formation of nanopwders (20–60 nm) of $BaTiO_3$ was successful by Chen and Jiao [15]. But, the powders reported by them are cubic. However, the development of soft-chemistry routes are a promising alternative for the synthesis of perovskite materials, because they can be better controlled from the molecular precursor to the final material to give highly pure and homogeneous materials and allow low reaction temperatures to be used, the size and morphology of the particles to be controlled [19–23].

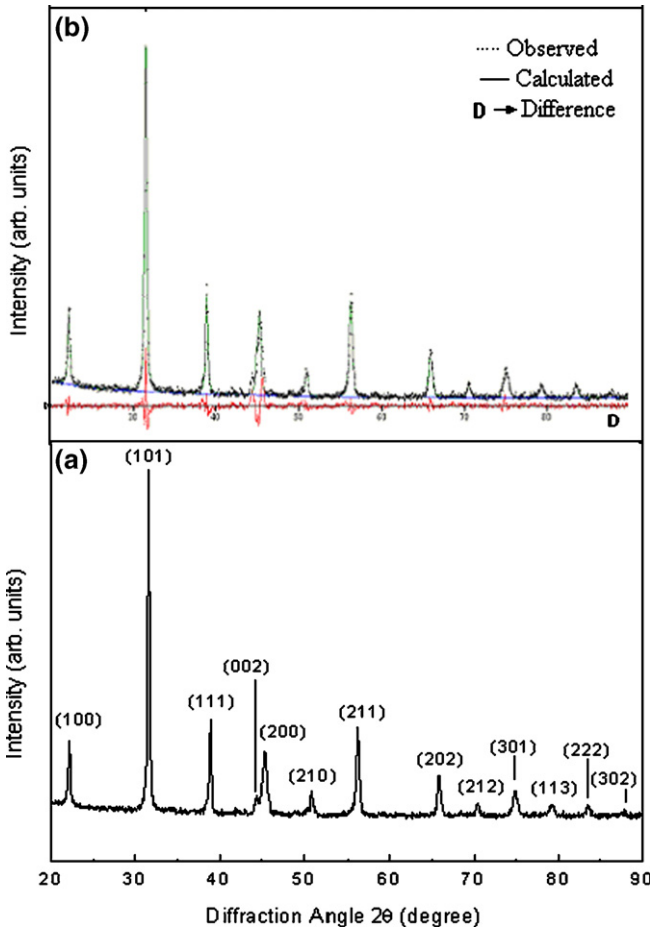

Fig. 1. (a) X-ray diffractogram of $BaTiO_3$ nanopowders synthesized by heating polymeric precursor at 600 °C for 2 h and (b) Rietveld refinement of (a).

Table 1
Interplanar spacing (d_{hkl}) and relative intensities (I_p) in X-ray powder diffraction peaks in $BaTiO_3$ nanopowders derived through a polymeric precursor

d_{hkl} (nm)		I_P	h	k	l
Observed	Calculated				
0.3996	0.3996	21	1	0	0
0.2834	0.2840	100	1	0	1
0.2311	0.2318	33	1	1	1
0.2018	0.2015	11	0	0	2
0.2001	0.2000	26	2	0	0
0.1780	0.1788	14	2	1	0
0.1634	0.1635	31	2	1	1
0.1420	0.1419	17	2	0	2
0.1336	0.1338	08	2	1	2
0.1267	0.1266	14	3	0	1
0.1212	0.1214	09	1	1	3
0.1157	0.1159	08	2	2	2
0.1111	0.1112	05	3	0	2

The sample has been calcined at 600 °C for 2 h.

The present paper deals with the preparation of $BaTiO_3$ nanopowders by a chemical method, which is a modified approach of the usual sol–gel method. This method is explored with a reactive polymer matrix of PVA and sucrose polymer molecules and applied it to synthesize $BaTiO_3$ nanoparticles. It involves a reconstructive molecular decomposition of the polymeric-precursor followed by a self-controlled recrystallization in the ceramic nanoparticles at 400 to 600 °C temperatures. The as prepared $BaTiO_3$ powders are of tetragonal (with 5% of cubic symmetry) with uniformely distributed, nanometer sized particles, as characterized by XRD and TEM studies.

2. Experimental details

2.1. Synthesis

The synthesis of $BaTiO_3$ nanopowders is carried out with the raw materials of titanium (IV) isopropoxide, barium acetate, ethyl alcohol, acetic acid, polyvinyl alcohol (molecular weight = 80,000) and sucrose. All of these materials were supplied by the Aldrich chemicals in 99.99% purity. A solution (1 M) of titanium (IV) isopropoxide in a mixture (1:1) of ethyl alcohol and acetic acid was prepared with costant stirring. An aqueous solution (1 M) of barium acetate was prepared in another container. These two solutions were mixed homogeniously with constant stirring for 2 h with a magnetic stirrer. To this solution a polymeric solution of PVA (5 wt%) and sucrose (10 wt%) mixture was added slowly with a glass rod. This mixed solution was again strirred with a magnetic stirrer for 4 h in order to get a clear gel. This gel was dried at a temperature of 50–70 °C to get a dry precursor mass. This amorphous precursor mass on calcination (400–600 °C) produced nanopowders of $BaTiO_3$.

2.2. Characterization of $BaTiO_3$ nanopowders

Phase analysis of the samples calcined at various temperatures is carried out with X-ray powder diffraction. The diffractograms