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Phase development of barium titanate from chemically modified-amorphous titanium (hydrous) oxide precursor

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Abstract

A synthesis procedure for barium titanate involving a chemically modified titanium precursor has been developed. Using a titanium isopropoxide precursor modified with acetylacetone and barium acetate, coprecipitated gels were obtained by addition to a KOH solution. Direct precipitation of cubic $BaTiO_3$ from such precursor suspensions was obtained under hydrothermal conditions. The pH value was found to be a critical reaction parameter such that production of phase pure $BaTiO_3$ required high pH (> 13.0), a finding consistent with thermodynamic predictions of the Ba–Ti–H_2O stability system and prior hydrothermal syntheses. It was determined that phase-pure barium titanate can be synthesized at temperatures as low as 50 °C and that higher reaction temperatures accelerate the crystallization process. The particle size of the synthesized powder ranged from 50 to 350 nm for the synthesis conditions explored in the current work.. It was demonstrated that particle size can be controlled by proper selection of the hydrothermal synthesis conditions such as reaction concentration, temperature, and time. The chemically modified synthesis produces barium titanate more rapidly at lower reaction temperatures than previously reported for similar syntheses. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: $BaTiO_3$; Hydrothermal methods; Powders-chemical preparation; Precursors-organic

1. Introduction

The outstanding dielectric and ferroelectric properties of barium titanate make it the desirable primary material for a variety of applications including multilayer capacitors, thermistors, and electrooptic devices.[1,2] It is well-known that the properties of barium titanate for electronic applications depend significantly on the microstructure of the sintered body. Sintered barium titanate having a dense and fine grained microstructure shows superior performance.[3] Therefore, special attention has been focused on the control of powder synthesis which produces well-crystallized barium titanate particles with suitable particle size, size distribution, and morphology.[4]

Barium titanate is conventionally produced by solid-state reactions between $BaCO_3$ and TiO_2 at high temperature (700–1200 °C).[5] However, the conventional method suffers from interparticle sintering and contamination problems in the calcination and required milling steps, respectively. Several approaches have been developed to overcome the limitations of the traditional solid state reaction process in preparing high-purity, ultrafine barium titanate powder with good chemical homogeneity at lower temperatures. These methods include the thermal decomposition of coprecipitated barium titanyl oxalate[6] or the citrate modification,[7] molten salt methods,[8] sol-gel,[9] and hydrothermal synthesis.[10–15] Hydrothermal synthesis, which can be defined as the treatment of aqueous solutions or precursors at elevated temperatures in pressurized vessels, is particularly promising due to its attractive processing features such as single-step processing and high-yield of the anhydrous product.[12,16,43]

Extensive research has been directed towards the hydrothermal synthesis of barium titanate. Phase of the resulting product is usually a metastable cubic perovskite, unless larger particles (greater than 1.0 μm) are produced under the special conditions of higher reaction temperature and longer time.[17] In earlier studies, both

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anhydrous titanium oxide and the amorphous titanium (hydrous) oxide have been used as titanium sources.[10–14] Recently, Bagwell et al. investigated the synthesis of $BaTiO_3$ from anatase and barium hydroxide octahydrate in water at 90 °C in the presence of polyacrylic and polyethylene oxide-block-polymethacrylic acids.[18] The polymers affected the morphological evolution of the forming powder by adsorbing preferentially on specific planes. The polymeric species also slowed the formation of barium titanate. Moreover, it has been reported that the crystallization rate of $BaTiO_3$ from crystalline precursors is retarded by the overgrowth of $BaTiO_3$ on the crystalline TiO_2 precursor particle surface.[12–14] Eckert et al. in particular, showed that overgrowth on a crystalline TiO_2 is the rate-limiting step.[12] On the other hand, the amorphous Ti (hydrous) oxide precursors result in more rapid $BaTiO_3$ nucleation kinetics.[11,15] Metal alkoxide decomposition is often used to prepare the amorphous precursor.[19–22] However, high reactivity of the unmodified alkoxides towards moisture tends to result in undesirable, uncontrolled hydrolysis and condensation reactions and eventually may cause chemical inhomogeneity in the final ceramic product.[23] To overcome this problem, glacial acetic acid or acetylacetone as chelating agents have been used to increase the stability of the metal alkoxide.[24] Glacial acetic acid has been used in barium titanate syntheses earlier.[25–28] Moreover, recently, we have determined that the introduction of the modified titanium isopropoxide by addition of acetylacetone in the hydrothermal synthesis leads to production of well-defined lead titanate powders at lower reaction temperatures than previously reported.[29] However, there have been no previous studies on barium titanate hydrothermal synthesis involving the modified metal alkoxide precursor by addition of acetylacetone.

Consequently, the research objectives of this study were: (I) to determine the feasibility of the modified titanium isopropoxide by addition of acetylacetone for hydrothermal synthesis of $BaTiO_3$ and (II) to evaluate synthesis parameter effects including solution pH, reactant concentration in the initial solution, time and temperature on $BaTiO_3$ phase development and particle size.

2. Experimental procedure

Barium acetate and modified Ti-isopropoxide were used as Ba and Ti sources to synthesize $BaTiO_3$ particles. Barium acetate (Fisher Scientific, Pittsburgh, PA) was dissolved in CO_2-free deionized water with the solution filtered through 0.22 μm filter paper (MSI, Westboro, MA). The modification of titanium (IV) isopropoxide (Aldrich Chemical Co., Milwaukee, WI) was achieved by adding acetylacetone (denoted as acacH, Aldrich Chemical Co., Milwaukee, WI) in a ratio of Ti:acacH = 1:1. The modified alkoxide was diluted with ethanol to obtain a stable sol solution through an alcohol interchange reaction between the ethoxy and propoxy groups. Each standard solution was prepared by mixing the Ba-acetate and the modified Ti-isopropoxide solutions to obtain a 1:1 Ba:Ti ratio. Metal hydrous oxide precursors were coprecipitated by addition of the yellow homogeneous sol solution into KOH solution while stirring under an inert N_2 atmosphere to minimize barium carbonate formation. The pH of the precursor suspension was controlled by changing the concentration of KOH solution from 0.1 M to 1.0 M. After the coprecipitation, the suspension pH was recorded. The feedstock concentration ranged from 0.025 to 0.1 M. The precursor powder for additional analyses was collected by centrifugation followed by freeze drying. The physical characteristics of the coprecipitated gels were determined by XRD and transmission electron microscopy (TEM, Jeol 200CX, Boston, MA).

Hydrothermal reactions were performed at temperatures from 40 to 150 °C in either a 23 ml Teflon lined acid digestion bomb (Model 4744, Parr Instrument Company, Moline, IL) or 600 ml-capacity autoclave with a magnetically driven stirrer (Model 4560, Parr Instrument Company, Moline, IL). Except for a high degree of agglomeration in the unstirred reaction vessels, the size and shape of the resulting $BaTiO_3$ particles after hydrothermal treatment was the same. The resulting hydrothermally treated powders were repeatedly washed by centrifugation and decantation with pH adjusted deionized water (pH 9.5–9.6) to avoid incongruent dissolution of the Ba^{+2} from the $BaTiO_3$.[11] The washed powders were dried in a vacuum oven for 24 h at 120 °C. The phase composition of the recovered products was determined by X-ray diffractometry (XRD, Philips APD 3720, Mahwah, NJ) over a 2θ range from 20 to 60° at a scan rate of 2.4°/min. Morphology of the particles was determined using a scanning electron microscope (SEM, JEOL JSM 6400, Boston, MA). Particle size analysis was performed by a centrifugal sedimentation technique (Horiba CAPA-700, Irvine, CA).

3. Results and discussion

3.1. Low temperature barium titanate synthesis from the chemically modified-precursor

The obtained coprecipitated gels were dried at 100 °C for 18 h prior to analysis. Phase of the as-precipitated Ba–Ti precursor gel was determined to be amorphous under both X-ray and electron beam conditions based on the observation of a broad scattering peak and diffuse ring structures, respectively. The precursor had a nanometer-scale structure with typical gel morphology (Fig. 1) similar to that described by other researchers in previous works.[25,30]

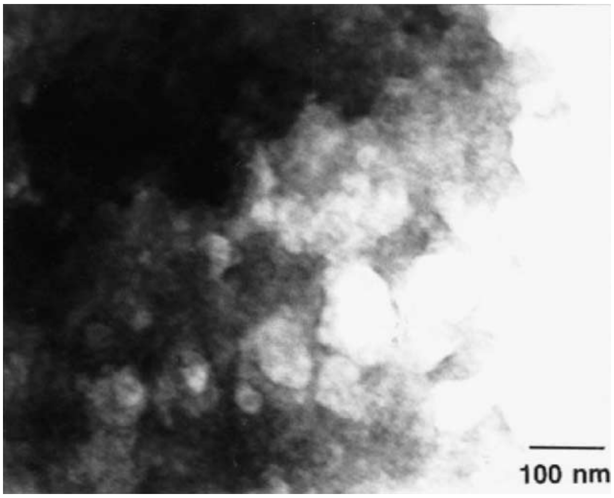

Fig. 1. TEM micrograph of the coprecipitated Ba–Ti gel.

In their patented process, Klee and Brand were able to form stoichiometric $BaTiO_3$ from the reaction of amorphous titanium oxide with excess barium hydroxide in water at 60 °C < T < 95 °C.[4] However, it was reported that this process requires relatively long times (e.g. ~91 h). To determine the lowest $BaTiO_3$ synthesis temperature in the chemically modified Ti-precursor containing system, the feedstock suspensions with pH > 13.5 were aged at room temperature and placed in an oven at temperatures of 40, 50, and 60 °C using the 23 ml acid digestion bombs for 12 h. As shown in Fig. 2a and b, the phase of the sample aged at room temperature was amorphous with a small amount of barium titanate formed for the sample treated at 40 °C although the majority was barium carbonate, respectively. At 50 °C, phase pure $BaTiO_3$ was synthesized (Fig. 2c), but it was mixed with unreacted amorphous precursor whereas

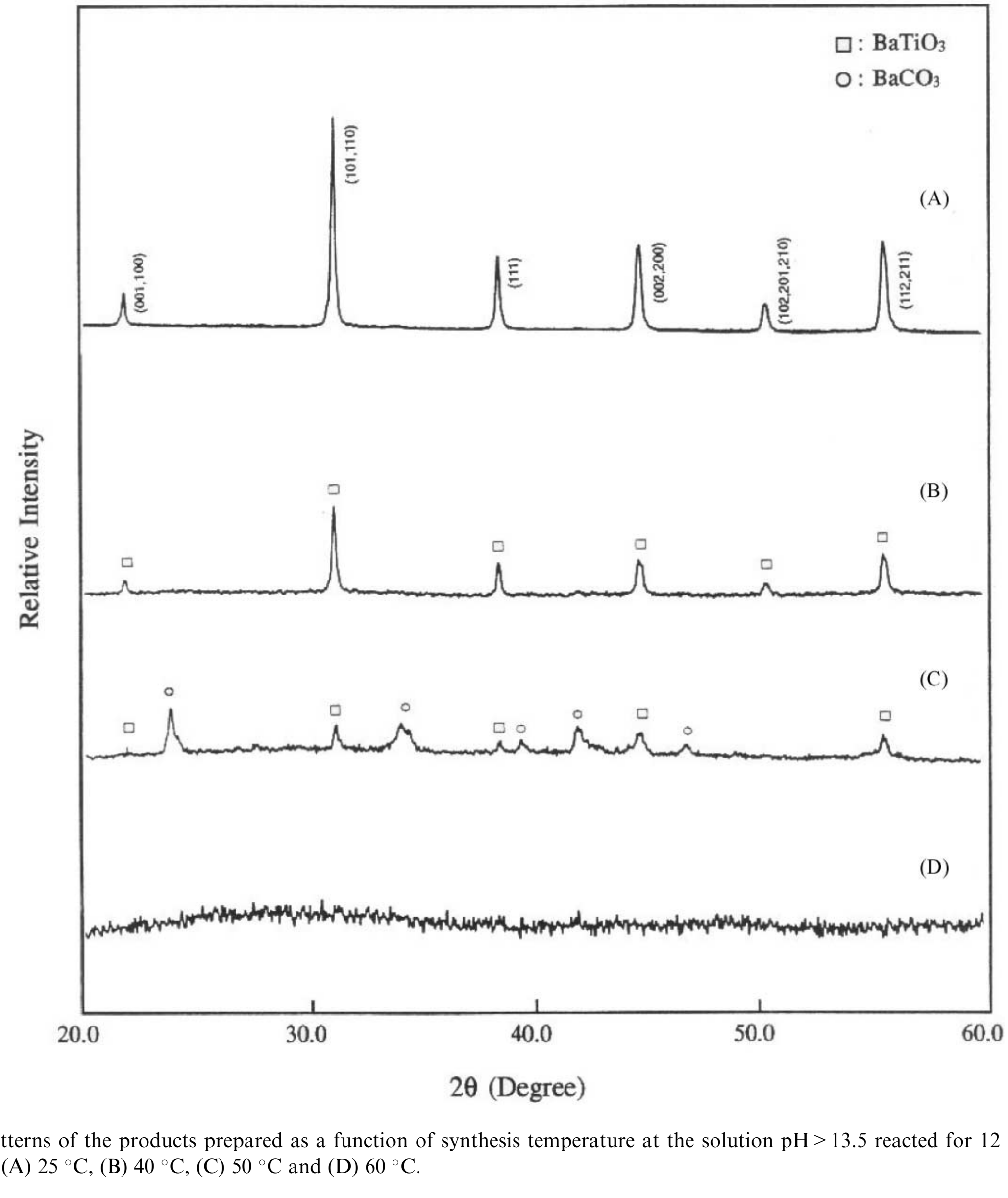

Fig. 2. XRD patterns of the products prepared as a function of synthesis temperature at the solution pH > 13.5 reacted for 12 h in the unstirred reaction vessels: (A) 25 °C, (B) 40 °C, (C) 50 °C and (D) 60 °C.

well-crystallized $BaTiO_3$ was obtained at 60 °C within the 12 h reaction time (Fig. 2d). Transformation of amorphous Ba–Ti gel into the crystalline $BaTiO_3$ involves breakage of the Ti–O–Ti bonds and incorporation of Ba^{2+} in the perovskite lattice structure regardless of formation mechanism.[31] For such a transformation, the energy barrier, which is closely related to the nature of the rate controlling step in the dominant formation process, must be overcome. In the current material system, the transformation temperature from amorphous gel to crystalline barium titanate is taken to be around 50 °C, but more rapid conversion requires greater thermal energy to overcome the energy barrier for crystallization.

The ability to synthesize $BaTiO_3$ powders at low temperatures can be related to the unique molecular structure of the current precursor system. Acetylacetone (acacH) reacts with titanium (IV) isopropoxide as a chelating agent. For a stoichiometric reaction of Ti/acacH = 1, the nucleophilic reaction of acacH leads to formation of a new monomeric Ti precursor as follows:

$$Ti(OPr^i)_4 + acacH \rightarrow Ti(OPr^i)_3(acac) + Pr^iOH$$

Leaustic et al. investigated the molecular structure of titanium isopropoxide during chemical modification using X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption Fourier spectroscopy (EXAFS).[32,33] It was shown that the coordination number of titanium increases from four [$Ti(OPri)_4$] to five [$Ti(OPri)_3acac$] by the modification with acetylacetone, then to six [$Ti(OH)_x(OEt)_{3-x}acac$] with oligomeric species formed during the dilution with ethanol. Chemical modification significantly increases the stability of the titanium alkoxide against moisture, leading to a water-soluble titanium precursor instead of forming an extensively polymerized Ti gel.[25] As a consequence, such modified Ti alkoxide is hydrolyzed and condensed in a relatively controlled manner so that stable colloidal titania forms in a wide range of pH from 2 to 10. It was determined that the colloidal TiO_2 has an anatase-like structure and its particle size ranges from 3 to 6 nm.[33]

In the current synthesis procedure, the use of this modified titanium isopropoxide allows homogeneous solution mixing without forming heterogeneous precipitates when the aqueous barium solution is introduced. Prior studies by Phule and co-workers [25–27] on barium titanate gels have shown that the subsequent addition of such clear precursor solution into KOH solution results in a stoichiometric coprecipitated hydrous gel (i.e. [$BaTi(OH)_xO_y(acac)_z$]) in which Ba and Ti species are intimately incorporated at the nanometer scale instead of forming individual regions of titanium hydrous oxide gel and barium acetate gel. It is expected that the barium ions are absorbed on the surface of the amorphous Ti gel without incorporation in the network structure of Ti gel. In this gel structure, however, the acetate group may still exist in the form of $Ba(CH_3COO)^+$ due to strong complexing ability of acetate with barium. It is also likely that the acetylacetonate group is still attached to the Ti. During hydrothermal treatment of the current coprecipitated metal hydrous gel, it is believed that barium species have a shorter diffusion distance for reaction with the Ti gel. In addition, the strong complexing ability of acetylacetone towards Ti increases the solubility of the hydrous Ti gel at elevated temperature and pressure.[34] Therefore, this combined effect significantly reduces the hydrothermal synthesis temperature.

Low temperature synthesis in the current study implies that the reaction can be performed in a continuous manner under atmospheric condition below 100 °C without employing expensive autoclave equipment. Furthermore, the ability to synthesize $BaTiO_3$ at low temperatures makes it easier to study crystallization kinetics and formation mechanism of barium titanate under hydrothermal conditions. The results of the kinetic analysis, including a microstructural investigation of the particles as a function of reaction time is provided elsewhere.[35]

3.2. Influence of solution pH on the phase development

The precursor suspensions with six different pH values (from 9 to 14) were hydrothermally treated at 150 °C for 18 h. It is generally well known that phase pure $BaTiO_3$ can only be synthesized above ~pH 13.[36,37] However, the influence of pH over this wide range was conducted because of uncertainties in phase stability in the presence of chemical modifier, acacH. Detailed reaction conditions are summarized in Table 1. Below a pH value of 13, the products were amorphous except for minor barium carbonate phase, as determined by XRD. However, barium titanate began to form above pH 13 and well-crystallized phase-pure $BaTiO_3$ was synthesized in solutions above pH 14. The presence of other titanates such as Ba_2TiO_4 or $BaTi_2O_5$ was not detected. These results verify that the solution pH has a profound effect on crystallization of $BaTiO_3$ and the production of phase-pure $BaTiO_3$ requires highly alkaline conditions (pH > 13) regardless of the feedstock precursor. The thermodynamically calculated stability diagram of the Ba–Ti–H_2O system predicts that barium titanate can be precipitated in a wide pH range from 9 to 14 at appropriately selected synthesis conditions, such as Ba^{2+} concentration and CO_2 environment.[36,38,39] However, in the current material system, a highly alkaline condition (pH > 13) is necessary to promote $BaTiO_3$ formation within a reasonable reaction time. In addition, as the solution pH increases, the peak intensity increases. The differences in the X-ray intensities imply that the solution pH (i.e. the concentration of OH^-) plays an important role in barium titanate formation kinetics.

Table 1
Influence of pH of hydrothermal reaction medium on the phase composition

Sample ID	BAT-1	BAT-2	BAT-3	BAT-4	BAT-5	BAT-6
Molar ratio (Ba:Ti:acacH[a])	1:1:1	1:1:1	1:1:1	1:1:1	1:1:1	1:1:1
Concentration	0.1 M	0.1 M	0.1 M	0.1 M	0.1 M	0.1 MH
Hydrothermal reaction conditions	150 °C, 18 h	150 °C, 18 h	150 °C, 18 h	150 °C, 18 h	150 °C, 18 h	150 °C, 18 h
Initial pH	9.23	10.12	11.02	12.01	13.05	14.20
Final pH	5.88	8.30	10.78	11.80	12.90	14.19
Primary phase	AM[b]	AM	AM	AM	BT[d]	BT
Minor phases		BC[c]	BC	BC		

[a] acacH, acetylacetone.
[b] AM, amorphous phase.
[c] BC, $BaCO_3$.
[d] BT, cubic $BaTiO_3$.

3.3. Influence of reaction conditions on the particle size

SEM micrographs of the hydrothermally derived $BaTiO_3$ at different reaction conditions are shown in Fig. 3. Barium titanate has a relatively equiaxed shape with particle size ranging from 0.05 to 0.35 μm, as estimated by SEM. It was determined that the average particle size was controlled by reaction conditions including reaction concentration, temperature, and time. An increase in particle size was observed as a function of reaction time at low temperature while there is no such tendency at high temperature. At the feedstock concentration of 0.1 M, for example, the particle size of $BaTiO_3$ synthesized at 75 °C for 30 min was

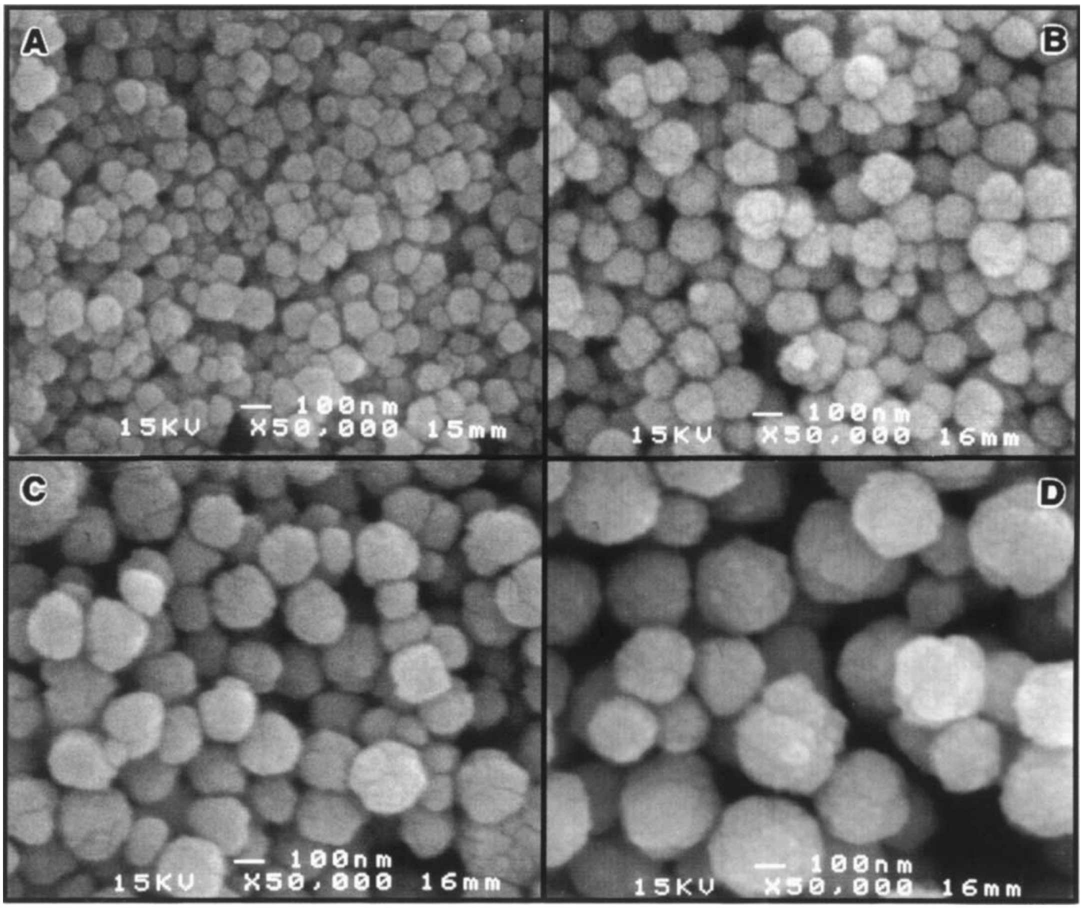

Fig. 3. SEM micrographs of the prepared $BaTiO_3$ powders as a function of reaction parameters such as reaction concentration, temperature, and time, respectively [(A) 0.1 M—75 °C—4 h; (B) 0.1 M—150 °C—1 h; (C) 0.05 M—150 °C—1 h; and (D) 0.025 M—150 °C—1 h] in the stirred reaction vessels.

approximately 0.05 μm, which increased to 0.09 μm after 4 h of further reaction (Fig. 3a). However, the product particle size (~0.15 μm) prepared at 150 °C for 1 h (Fig. 3b) remained nearly constant relative to a hydrothermal treatment at 150 °C for 4 h. This is because particle nucleation and growth are very fast at high reaction temperatures and the reaction is virtually complete within 1 h. Barium titanate obtained from 0.1 M feedstock concentration at 150 °C for 4 h was selected to determine the particle size distribution. The particles were suspended in methanol prior to analysis. The barium titanate particles had a measured median diameter of 0.23 μm and standard deviation of 0.13.

Reactant concentrations in the initial solution also influence the particle size. The barium titanate particle size obtained from 0.05 M feedstock concentration at 150 °C for 1 h was approximately 0.20 μm (Fig. 3c) while that from 0.025 M at 150 °C for 1 hour was 0.35 μm (Fig. 3d). These results show that the particle size can be tailored in the current system by tailoring the nucleation frequency and the growth via controlling the reactant concentration in the initial solution, reaction temperature and time. Consequently, the current hydrothermally derived $BaTiO_3$ can be an ideal system in which a wide range of synthesizable particle sizes can allow systematic study of the particle size effect on the crystal structure and related dielectric properties which has been a subject of several investigations in the ferroelectric literature.[40–43]

4. Conclusions

The use of stable modified titanium alkoxide with acetylacetone and barium acetate leads to an amorphous Ba–Ti hydrous gel in which the reacting species are homogeneously mixed and react more rapidly at lower reaction temperatures than prior studies. From these precursors, barium titanate with a cubic perovskite structure has been synthesized under hydrothermal conditions. In the chemically modified precursor, $BaTiO_3$ can be obtained at temperatures as low as 50 °C within 12 h. For the formation of phase-pure $BaTiO_3$ from the chemically modified precursor, the critical conditions are that the pH of initial reaction medium be above pH 13 and CO_2 content within the atmosphere be minimized. The resulting particles have the average particle sizes ranging from 0.05 to 0.35 μm depending upon reaction parameters such as reaction concentration, temperature and time.

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