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Phase transition in barium titanate nanocrystals by chemical treatment

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Abstract

Effects of solvents on the cubic to tetragonal phase transition of barium titanate (BT) nanocrystals were investigated by solvothermal treatment. Different processing variables, such as temperature and time were taken into consideration for different solvents. There were no effects on the phase transition of BT below the boiling temperature of all the solvents. Above the boiling temperature, a nanocrystals of tetragonal barium titanate could be obtained from the commercial cubic phase BT powder (Cabot, BT-08). There were no significant changes of the particle size and morphology of the BT powders before and after the chemical treatment. There was small reduction of surface area and particle size observed in the chemically treated BT powders. The crystal structure, phase transition and morphology of the powders were analyzed by XRD, DLS, DSC, TGA and SEM.

Keywords: $BaTiO_3$; Tetragonality; Phase transformation

1. Introduction

Barium titanate powders ($BaTiO_3$; BT), due to its excellent dielectric properties, are extensively used in the preparation of multilayer ceramic capacitors (MLCCs). Effectively, powder characteristics such as purity, particle size and surface area mainly influence their behavior during sintering. BT-based dielectrics have dominated the ceramic capacitor industry since 1950s, representing 80–90% of the business.[1,2] Rapid reduction of the thickness of the dielectric layers in MLCCs to 1–2 μm dictates MLCC industry to acquire submicron BT powders. There has been considerable interest in developing new processes for $BaTiO_3$ powders synthesis allowing the formation of submicrometer homogeneous tetragonal phase particles.[2]

The phase transition of BT occurs at three temperatures in the vicinities of −90, 5 and 130 °C.[3,4] Above 130 °C BT has a stable cubic phase. In the temperature range of 5 and 130 °C, the crystal is spontaneously polarized along a ⟨1 0 0⟩ direction, accompanied with tetragonal symmetry. In the range of −90 and 5 °C, the crystal symmetry is orthorhombic and the direction of spontaneous polarization transfers to a pseudocubic ⟨1 1 0⟩, a face diagonal of the former cubic cell. Around −90 °C, a further transition to rhombohedral symmetry spontaneously polarized along a body diagonal takes place. These three transitions exhibit different electrical properties near the transition temperatures.

Size effects in nanostructured materials are of great importance from both fundamental considerations and practical applications. The properties and behavior of macroscopic ferroelectric systems are, in principle, well known. An area, which is poorly understood at best, is so-called size effect. Initial research on size effects in ferroelectrics has concentrated on $BaTiO_3$ with the desire to understand the governing mechanisms that control the performance of multilayer capacitors as a function of layer thickness. However, in ferroelectric fine particles, it was known that ferroelectricity decreases with decreasing particle and grain sizes, and disappears below a certain critical size.[5–11] The preferred tetragonal phase of BT may be unstable at room temperature for a crystallite size below a certain size and then the stable phase is cubic. Therefore, the size effect in ferroelectrics such as BT can be

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Table 1
Specification of BT powder[a] used in this study

Powder	Manufacturer	Diameter (nm)	Density (g/cc)	Specific surface; area (m^2/g)	Ba/Ti ratio
BT-8	Cabot Corp.	250	5.9	8.5	0.998

[a] Supplied by the manufacturer.

considered to be one of the most important phenomena for an interest to the industry as well as to the scientific community. The hydrothermal technique yields submicron size powders with a uniform geometry and narrow size distribution. Barium titanate ceramics are usually tetragonal pervoskites, with high dielectric constants, from approximately 0 °C up to 130 °C which is known as the Curie transition temperature. Single crystals of $BaTiO_3$ present a relative permittivity of 400 along the tetragonal c axis and of 4000 along the axes perpendicular to it.[12]

Wada et al.[13] established low temperature direct synthesis (LTDS) method to synthesis nanosize $BaTiO_3$ powders. However, since water is the general medium for the hydrothermal LTDS process, OH species are most likely incorporated into $BaTiO_3$ lattice as defects.[14] Hennings et al.[15–17] characterized hydrothermal $BaTiO_3$ powders and found OH groups were chemisorbed in the perovskite lattice, and showed similar "loose packed" structure of as prepared $BaTiO_3$ powders to the presence of large amount of water inside the particles. A defect chemical model was derived and the lattice defects were calculated from thermogravimetric analysis (TGA) data. Clark et al.[18] had the comparable observations. It is well known that such defects can lead to variation of stoichiometry, poor sintering density, inhomogeneous microstrucure of green tapes, quality and reproducibility and degradation of final products.[17] Thus, reducing such kind of defects are exigent for $BaTiO_3$ synthesis.

The recently developed solvorthermal technique, which involves use of organic solvent instead of water,[19–21] may provide an alternative to produce low defects $BaTiO_3$ nanoparticles. Cubic $BaTiO_3$ powders with small particle size of 20–60 nm and narrow particle size distribution were obtained by Chen and Jiao.[20] It was observed that solvothermal reaction was slower than hydrothermal, attributable to the low solubility of precursor gel in the alcohol medium. However, no defect analysis was reported in their paper. Bocquet et al.[21] synthesized $BaTiO_3$ powders by hydrolysis of the alkoxide in isopropanol under a high pressure (10 MPa) at temperatures between 100 and 200 °C in tubular flow reactor. Later, a thermal treatment of the formed solids was applied under the supercritical state of the solvent. They observed the particles size of the powders to be 10 nm with cubic phase and the dielectric properties of the as-synthesized $BaTiO_3$ powders are similar to those already reported in the literature.

Table 2
Physical properties[a] of the solvents used in this study

Sample	Solvent	Boiling; point (°C)	Dielectric; constant (K)
1	1-Propanol	97	20.33
2	Toluene	111	2.38
3	Dimethyl formamide	153	36.7

[a] CRC handbook.

In this study, we have examined the phase transformation in $BaTiO_3$ powders from metastable cubic to ferroelectric tetragonal phase using a solvothermal treatment. The strategy is to examine the phase change in as-received commercial cubic $BaTiO_3$ powders attributable to the effect of different solvents with different processing conditions. Assessment of the influence of different temperatures and different times have

Table 3
Experimental conditions BT powder samples chemically treated in autoclave

Sample	Solvent	Time (H)	Temperature (°C)	Phase change; cubic–tetragonal
1	1-Propanol	6	100	NA
2	1-Propanol	24	100	NA
3	1-Propanol	6	150	NA
4	1-Propanol	24	150	NA
5	1-Propanol	6	170	NA
6	1-Propanol	24	170	NA
7	Toluene	6	100	NA
8	Toluene	24	100	NA
9	Toluene	6	150	NA
10	Toluene	24	150	NA
11	Toluene	6	170	NA
12	Toluene	24	170	NA
15	Dimethyl formamide	6	100	NA
16	Dimethyl formamide	24	100	NA
17	Dimethyl formamide	6	150	NA
18	Dimethyl formamide	24	150	NA
19	Dimethyl formamide	6	170	Partially tetragonal
20	Dimethyl formamide	24	170	Fully tetragonal

shown that tetragonal phase BT can be formed from cubic phase under a solvothermal condition with respect to the solvent properties. Main characteristics of the chemically treated powders have been determined by X-ray diffraction, deferential scanning calorimeter, scanning electron microscopy and the results have been compared with as-received commercial powder.

2. Experimental procedure

All of the reagents and solvents used were of analytical grade and used without further purifications. Materials specification of highly pure commercial hydrothermal $BaTiO_3$ powder (Cabot, BT-08) is shown in Table 1 and three different solvents used are shown in Table 2. Two different times (6 and 24-h) and three different temperatures (100, 150 and 170 °C) were used for the treatment. At first, 2 g of BT powder were taken with 75 ml of the solvents in the autoclave. The reaction was carried out in a 100-ml Teflon-lined stainless steel autoclave (Parr Instrument Co.) without any agitation. The autoclave was heated up to different temperatures and times in an oven as shown in Table 3. After cooling down to room temperature in the oven, the resultant precipitate was centrifuged and washed with mixture of water/alcohol for several times, and finally dried at 80 °C for 24 h in a vacuum oven. Series of $BaTiO_3$ samples prepared are described in Table 3.

Room temperature X-ray diffraction (RTXRD, Scintag PAD V using CuK_α with $\lambda = 0.15406$ nm) was used for crystalline phase identification of the powder samples and determination of cubic to tetragonal phase transition were recorded with step scan mode: step 0.02°, 5 s per step, $2\theta = 20$–$80°$: 40 kV, 40 mA. The morphology of $BaTiO_3$ powders was an-

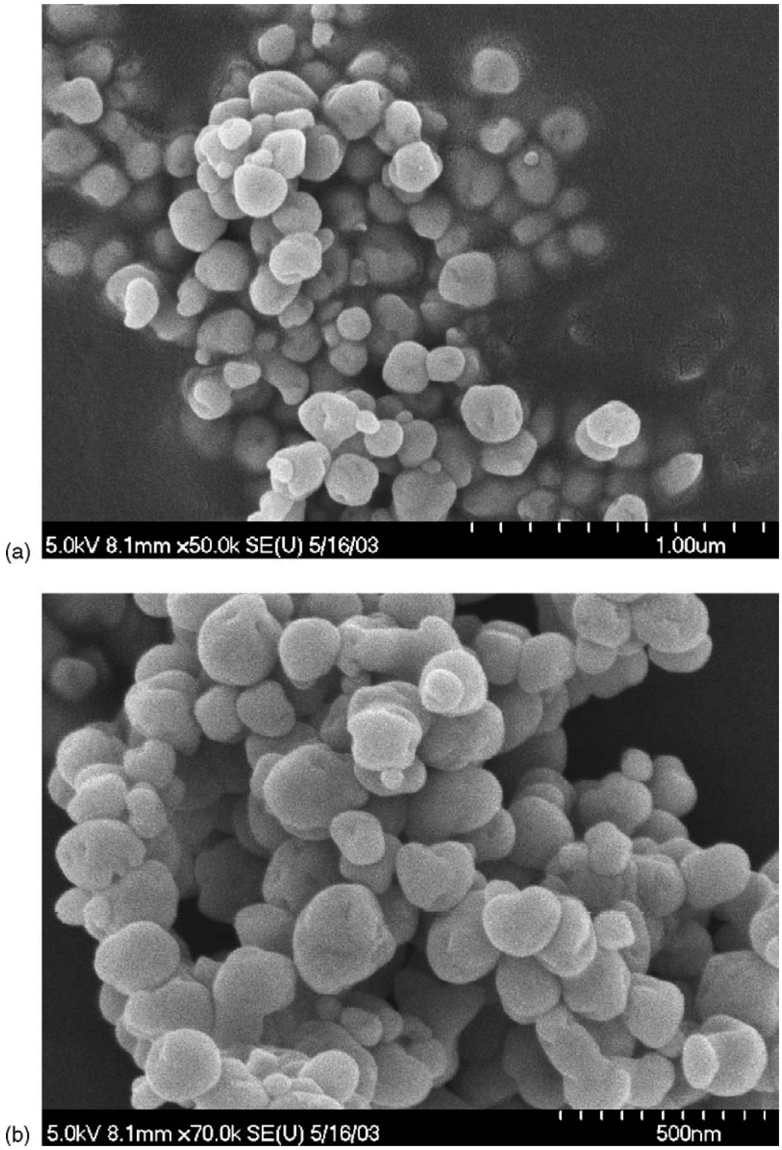

Fig. 1. (a) and (b) SEM micrographs of as-received $BaTiO_3$ particles at different magnifications.

alyzed by Hitachi FE SEM 4700. A small amount of $BaTiO_3$ powders were pressed on a carbon tape, which attached to the brass sample stub. Air spray was used to blow out the excess $BaTiO_3$ powders that were not adhered to the carbon tape. The $BaTiO_3$ powders were then coated with platinum via plasma sputtering to create a conductive surface layer that was necessary for SEM imaging. The particle size and particle size distribution of resulting $BaTiO_3$ powders were characterized using a Horiba LA-910 laser dynamic scattering particle size analyzer. The samples were diluted with deionized water and ultrasonicated for 20 min before analysis. DSC measurements were performed using a thermal analysis system (DSC-2920 Differential Scanning Calorimeter, TA-Instruments Inc., USA) at a heating rate of 10 °C/min under nitrogen gas flow from 50 °C up to 200 °C. TGA measurements were performed using a thermal analysis system (Hi-Res. TGA 2950 Thermogravimetric Analyzer-TA Instruments Inc., USA) connected to the TA5000 computer (also by TA instruments Inc. USA). About 20 mg of the different samples were heated at 20 °C/min under a nitrogen flow of 100 ml/min from 25 °C up to 900 °C. The specific surface area (S_{BET}) of powders was determined from nitrogen adsorption-desorption isotherms obtained at −196 °C using the Micromeritics ASAP 2020 instrument. All samples were outgassed at 100 °C overnight prior to each adsorption experiment. The BET and BJH methods were applied to the nitrogen adsorption–desorption isotherms to calculate the total surface area, total pore volume, pore size distribution and average pore size of BT samples.

3. Results and discussion

SEM micrographs of the starting BT nanocrystals are shown in Fig. 1: the average size of the BT powders is 250 nm. The specific surface area of the powder is 8.5 m^2/g

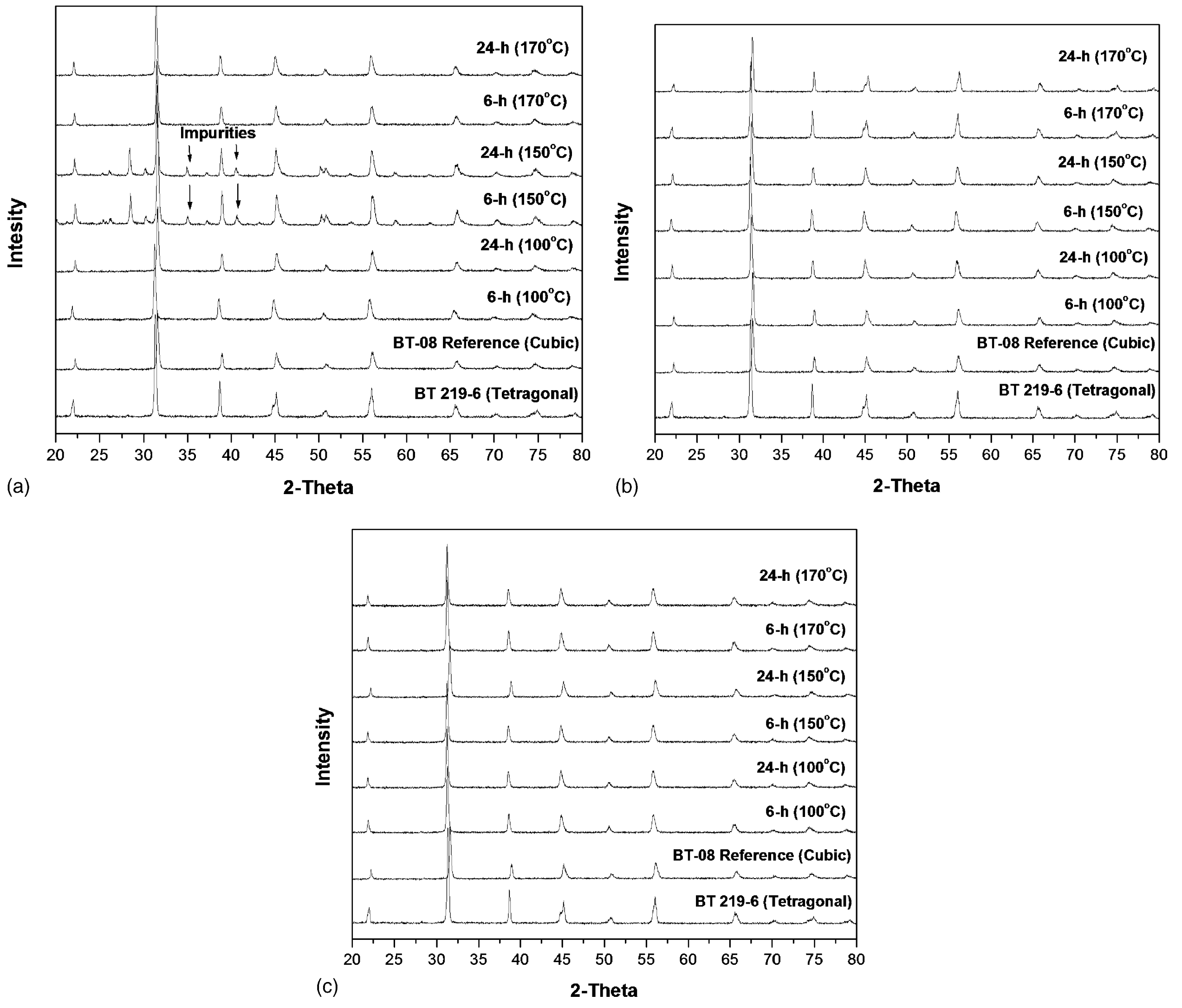

Fig. 2. (a)–(c) XRD patterns of $BaTiO_3$ powders chemically treated with 1-propanol, dimethyl formamide and toluene, respectively at 100, 150 and 170 °C for 6 and 24 h compared with commercial tetragonal $BaTiO_3$ powder.

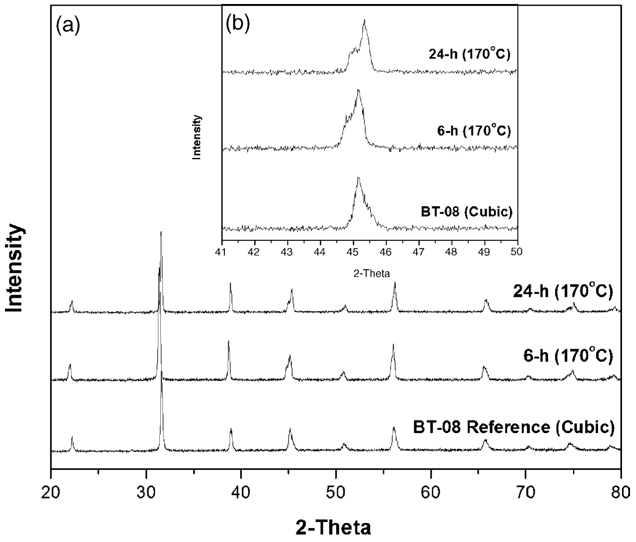

Fig. 3. (a) and (b) XRD patterns of $BaTiO_3$ powders chemically treated with dimethyl formamide at 170 °C for 6 and 24 h.

and the Ba/Ti ratio of the as received $BaTiO_3$ powder is 0.998. Fig. 2(a)–(c) shows XRD patterns of BT nanocrystals of chemically treated with 1-propanol, dimethyl formamide (DMF) and toluene at three different temperatures for 6 and 24 h. Different temperatures and different times were chosen with respect to the boiling point of each solvent. XRD patterns of the powders treated with 1-propanol and toluene show that there is no change in the phase transition after the chemical treatment. The XRD analysis indicates that the powders are pure cubic $BaTiO_3$ based on nonsplitting of the (2 0 0) and (0 0 2) peaks at 45° 2θ. There are varying degrees of split in the {2 0 0} peaks of the powder treated with DMF. There is a change in the phase from cubic to tetragonal when these powders treated with DMF 170 °C for 6 and 24 h as shown in Fig. 3(a). Fig. 3(b) expands the powder diffraction patterns in the 41–50° 2θ region, at room temperature for $BaTiO_3$. This region of the diffraction pattern is a characteristic of the tetragonal versus cubic form of $BaTiO_3$. There is a splitting of the {2 0 0} reflection in the tetragonal form, with the lower angle shoulder indexed at (0 0 2).[22] On the basis of this correlation, it is apparent from Fig. 3(a) and (b) that the $BaTiO_3$ treated with DMF is in the tetragonal form as compared to the cubic form in the starting of the process. Although the exact reason for this is still under investigation, it is believed that diminishing hydroxyl ions (OH^-) in the BT lattice results in the stabilization of the tetragonal form of $BaTiO_3$ at room temperature.[24] There are not many studies done on solvent based treatment of nanocrystalline $BaTiO_3$. It has been reported earlier that only cubic $BaTiO_3$ can be formed and tetragonal $BaTiO_3$ cannot be formed by solvothermal synthesis with the help of high pressure and temperature for a longer time.[20]

This is further demonstrated by the DSC data shown in Fig. 4. The $BaTiO_3$ powders chemically treated with DMF clearly shows an endothermic transition on heating at 124 °C compared to as received $BaTiO_3$. This corresponds to the tetragonal to cubic phase transition at the Currie point of $BaTiO_3$. The change in enthalpy corresponding to the transition is 550 and 663 mJ/g for 6 and 24 h chemically treated powder samples. In the literature, for a commercial tetragonal sample the change in enthalpy is given as ~650 mJ/g.[22] In the present work, the ΔH for the reaction is close to the fully tetragonal conversion of nanocrystalline $BaTiO_3$ as the reference. This shows chemical treatment gives the complete formation of tetragonal $BaTiO_3$. As mentioned earlier in this paper the extraction of the lattice hydroxyl ions (OH^-) helps in the phase transition of metastable cubic to tetragonal $BaTiO_3$. These results are also supported by TGA. The TGA curves of as-received $BaTiO_3$ powders lost ~1.5% weight while treated at 170 °C (6 and 24-h) lost almost no weight as

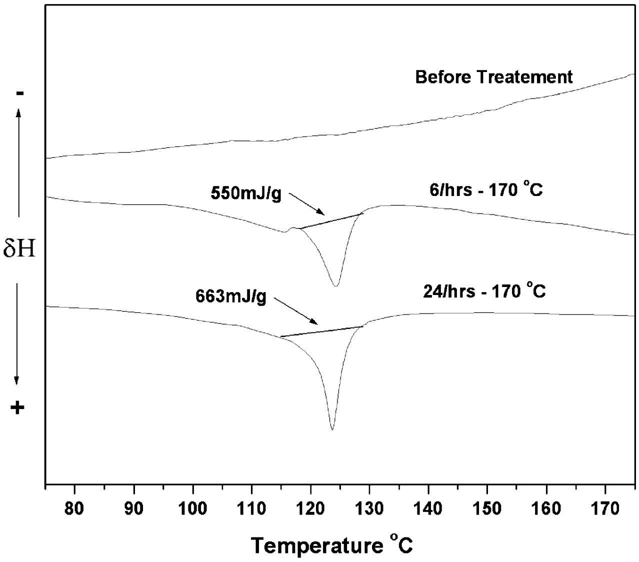

Fig. 4. Differential scanning calorimetry of $BaTiO_3$ powders chemically treated with dimethyl formamide at 170 °C for 6 and 24 h.

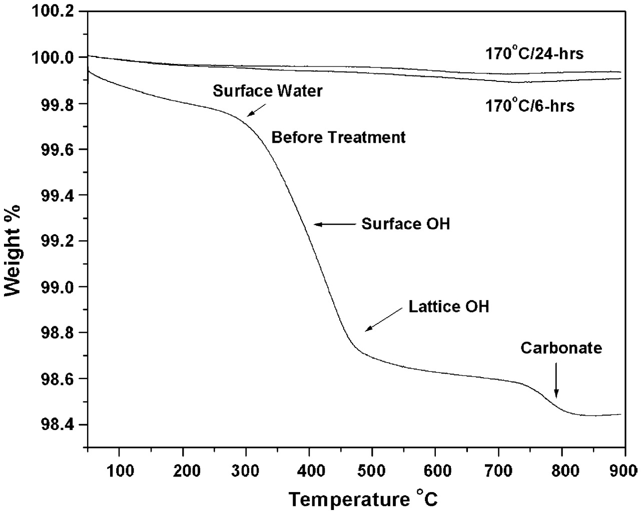

Fig. 5. Thermogravimetric analysis of $BaTiO_3$ powders chemically treated with dimethyl formamide at 170 °C for 6 and 24 h.

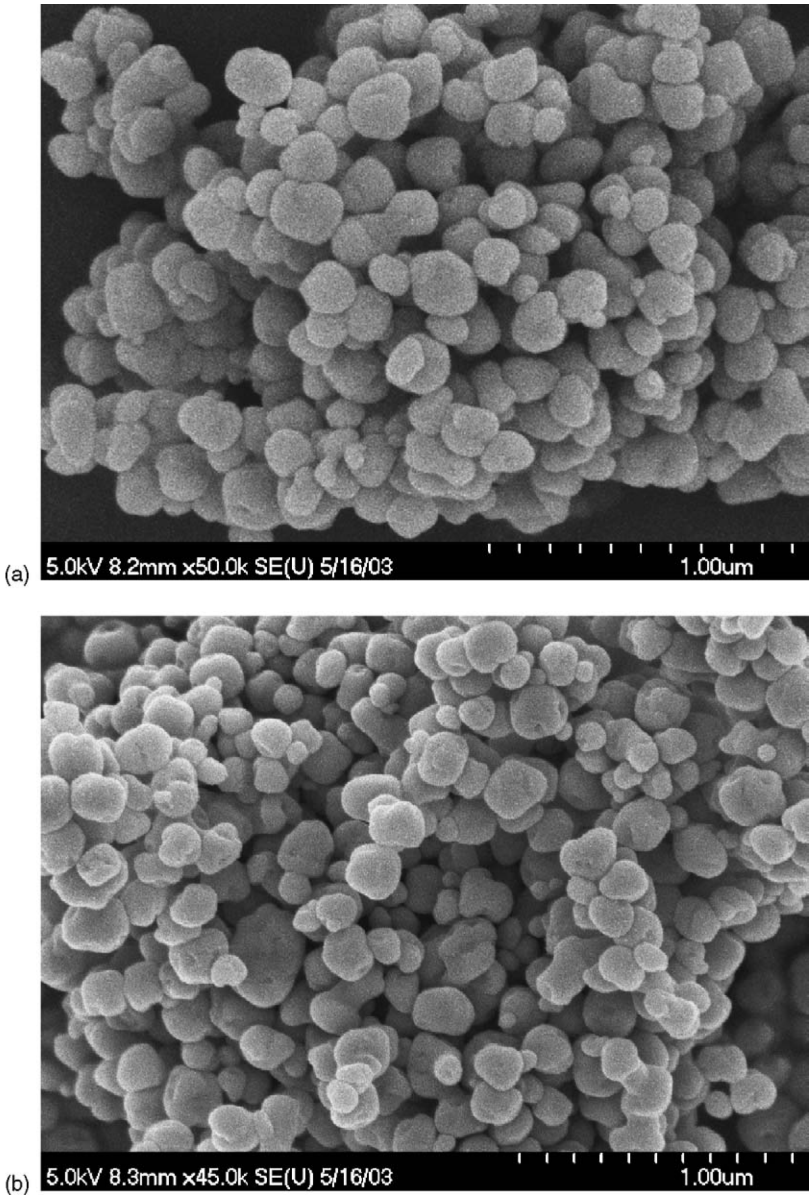

Fig. 6. (a) SEM micrograph of treated $BaTiO_3$ particles at 170 °C for 6-h. (b) SEM micrograph of treated $BaTiO_3$ particles at 170 °C for 24-h.

shown in Fig. 5. The chemically treated powder shows essentially no weight loss (surface water and lattice water) as well as the surface carbonate in comparison with the as-received $BaTiO_3$ powders.

SEM micrographs of the $BaTiO_3$ powders treated using DMF as solvent are shown in Fig. 6(a) and (b). Compared to the as-received $BaTiO_3$ powder (Fig. 1), the chemically treated powders give little change with respect to morphology and size of the particles. In order to realize the full potential of fine powders in terms of size distribution of particles, it is essential that the particles do not form agglomerates. The particle size, however, decreased slightly with the chemical treatment of the powders. The particles size analysis also proved this correlation between treated and untreated powders as shown in Fig. 7. The particle size decreased to some extent after the chemical treatment by DMF. It is clear from the various literature studies[22–25] that for the tetragonal form to be stabilized, the particle size has to be at least 100–300 nm ranges in order to alleviate the lattice strain. In this work, the particle size is practically in the same range of literature where the $BaTiO_3$ particles are in complete tetragonal form. The results of surface area measurements of $BaTiO_3$ particles in Fig. 8 show slight decrease in the surface area of the $BaTiO_3$ particles paralleling with the particle size reduction after the chemical treatment. The change in surface area is shown to correlate to the pore size which was initially present in as-received $BaTiO_3$ particles. Fig. 7 reveals decrease in particle size due to contraction of particles with the chemical treatment which leads to the reduction in pore size shown in Fig. 8 along with the surface area.

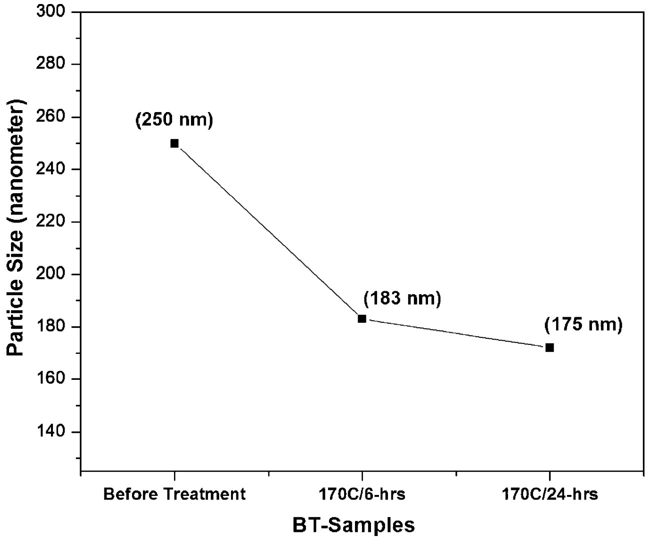

Fig. 7. Particles sizes of treated $BaTiO_3$ particles.

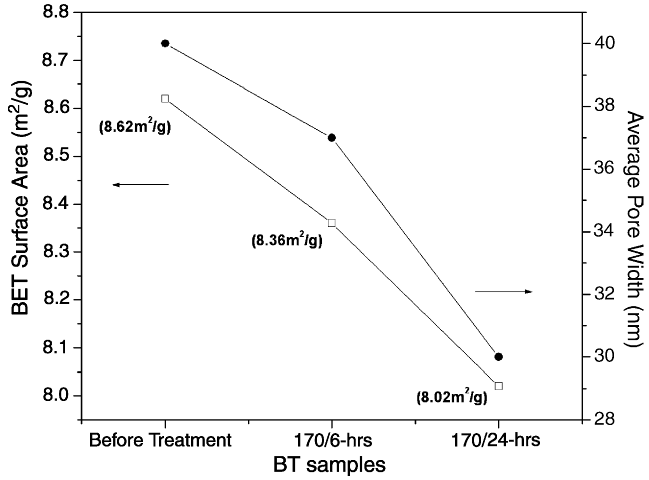

Fig. 8. Surface areas and pore size of treated $BaTiO_3$ particles.

4. Conclusions

Hydrothermal and solvothermal synthesis of $BaTiO_3$ resulting in the stabilization of the cubic form at room temperature has been reported earlier.[20,22] Previous studies have shown that ideally with the help of solvents tetragonal $BaTiO_3$ can not be formed or solvents do not help in the formation of tetragonal $BaTiO_3$.[20] In this work, after using three different types of solvents to determine the change in phase transition from cubic to tetragonal, we found that DMF is a suitable solvent. No other solvents imply change in crystal structure. The nature of the nanocrystals in the size range of ∼250 nm has been found to change with the treatment. The chemical treatment generates high pressure above the boiling point of the solvent and because of that phase change is achievable by using DMF as a solvent. This result indicates that pressure effect caused lattice parameter change that caused internal stress in the BT structure. Simultaneously, reduction in the hydroxyl group impurities provides the phase change in $BaTiO_3$ powders supported by DSC and TGA data. The optimum chemical treatment condition for the phase transition in $BaTiO_3$ particles was determined to be 24 h for 170 °C using DMF as an effective solvent. By increasing the temperature above the boiling point of the solvent and given more time, the tetragonality was increased. Extraction of the lattice OH relieves the lattice strain which in term transformed the cubic phase to tetragonal phase of BT.[16]

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