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Tailoring size of $BaTiO_3$ nanocrystals via ambient conditions sol process

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As the miniaturization of electronic devices continues to demand smaller and uniform particle size of the powders, size control of the powder becomes critical. Under carefully controlled experimental conditions, nanocrystalline $BaTiO_3$ particles have been prepared by ambient condition sol process. Soluble precursors of barium and titanium in water have been used to produce a mixed metallic gel using KOH as the mineralizer. The gel was peptized and crystallized in water under refluxing condition. The effect of various experimental parameters such as the starting Ba/Ti ratio, temperature, time, and additives on the size of the crystallites have been investigated. A higher Ba/Ti ratio in the precursor solution led to smaller crystallite sizes of $BaTiO_3$ particles. A higher temperature of refluxing had a positive effect of producing smaller crystallites, as well as particle sizes of the resulting powder. Using a polymeric surface modifier during $BaTiO_3$ synthesis led to a smaller particle size and increased re-dispersibility of the particles in water. The duration of refluxing was determined to have a minimal effect on the resulting particle size. The powders have been characterized by X-ray diffractometry for phase purity, and by dynamic light scattering for particle size. Field emission scanning electron microscopy and transmission electron microscopy have been utilized to examine the morphology of the particles. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

The development of thinner dielectric layers for multilayer ceramic capacitors (MLCCs) for improved volume efficiency has tremendously increased the demand for smaller dielectric ceramic particles. Smaller particles in the nanometer range have a definite advantage compared to the particles in micrometer range, in reducing the thickness of the single ceramic layer to less than 2 μm [1, 2]. Nanocrystals of barium titanate ($BaTiO_3$) may facilitate the fabrication of MLCCs with more number of ceramic layers, without increase in the size of the device.

Most of the methods of $BaTiO_3$ powder preparation involve high temperatures and/or pressures. $BaTiO_3$ have been synthesized by various techniques such as solid state reaction at temperatures above 1000°C [3–6], hydrothermal method [1, 7–25], low temperature aqueous synthesis (LTAS) [26–28], sol-gel process [29–34], low temperature direct synthesis (LTDS) [35, 36], combustion synthesis [37], oxalate coprecipitation route [38, 39], microwave heating, and micro emulsion process [40]. Low temperature synthesis has provided an exciting possibility of high purity, ultrafine $BaTiO_3$ nanoparticles [41].

Lee *et al.* [42, 43] reported inferior microstructure of the MLCC $BaTiO_3$ tape with aqueous suspension when compared to the non-aqueous suspension. The fact that agglomerates are always present in the powders, especially with powders in the nanometer range, the problems of agglomeration and the difficulty of re-dispersibility becomes critical to deal with. For producing thin and homogeneous ceramic layer, better controlled starting materials having good re-dispersibility and smaller particle size are needed [1].

Considering all the factors such as temperature of synthesis, ambient pressure, cheaper sol medium, ambient condition sol (ACS) process has been considered in our laboratory. To produce finer particles with good

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re-dispersibility, we have studied the effect of various experimental parameters on the particle size, morphology, and dispersion.

Lu *et al.* [2] reported synthesis of $BaTiO_3$ by hydrothermal method in the presence of Tween80 as a surface modifier. $BaTiO_3$ nanoparticles (<100 nm) with narrow size distribution, and good re-dispersibility were obtained. Wada *et al.* [35, 36] for the first time, reported $BaTiO_3$ particles with crystallite size less than 10 nm. However the Ba/Ti ratio was found to be ~0.786, due to the formation of Ti rich phases as by-products such as $BaTi_2O_5$ or $Ba_6Ti_{17}O_{40}$ in the crystallites.

In our previous publications, Wang *et al.* [46, 47] reported the superior features of this ambient condition sol (ACS) process producing nanocrystalline $BaTiO_3$ powders. In this paper, we discuss the effect of experimental processing variables on the morphology and properties, to tailor the size of $BaTiO_3$ particles under the definition of an ambient condition as a near room temperature and pressure.

2. Experimental

$BaTiO_3$ particles have been prepared by ambient condition sol (ACS) process [46, 47]. An aqueous solution of barium and titanium was obtained by mixing barium chloride (99.6% $BaCl_2{\cdot}2H_2O$, Fisher Scientific), and titanium tetrachloride (99.6% $TiCl_4$, Alfa Aesar) in required stoichiometric amounts depending upon the desired Ba/Ti precursor ratio. The pH of the solution was adjusted to 14 by dropwise addition of 10 M potassium hydroxide (KOH), resulting in mixed metallic sol. After diluting the sol with deionized water to get a concentration of 0.1 M (Ti), the precursor gel was refluxed (at 102°C, 5 h unless specified otherwise). The product was then centrifuged and washed with dilute acetic acid and water, followed by drying in a vacuum oven at 80°C overnight as reported in our previous publications [46, 47].

To study the influence of experimental parameters on the properties of the final $BaTiO_3$ powder, a series of $BaTiO_3$ samples have been prepared. A set of experiments were conducted with varying parameters such as temperature, time of refluxing, Ba/Ti ratio, addition of polymeric surface modifier. All the samples are prepared with the gel pH of 14, with KOH as the mineralizer. The details of the powders produced and their processing conditions were given in Tables I and II. The morphology of the resulting powders has been examined by field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The powders, after drying and re-dispersion in ethanol, were deposited as a thin uniform layer of non-agglomerated particles on an aluminum stub and is kept under flowing air and allowed to dry. The $BaTiO_3$ powders were then coated with gold via plasma sputtering (Hammer 6.2 Sputtering System, Anatech). To prepare TEM samples, a tiny amount of powder was dispersed in iso-propanol by grinding in an agate mortar. A copper grid with a supported thin carbon film was dipped into the suspension, removed and dried on a filter paper. TEM examination was then done on the powders attached to the copper grid.

TABLE I Experimental parameters and the crystallite sizes for the samples prepared under varying temperature and times of refluxing

Sample ID	Ba/Ti	Temperature (°C)	pH	Reaction time (h)	Crystallite size (nm)
BT1(a)	1.5:1	70	14.0	5	63 ± 2
BT1(b)	1.5:1	70	14.0	10	61 ± 1
BT1(c)	1.5:1	70	14.0	15	64 ± 2
BT1(d)	1.5:1	70	14.0	20	63 ± 1
BT2(a)	1.5:1	80	14.0	5	59 ± 1
BT2(b)	1.5:1	80	14.0	10	57 ± 2
BT2(c)	1.5:1	80	14.0	15	57 ± 1
BT2(d)	1.5:1	80	14.0	20	58 ± 2
BT3(a)	1.5:1	102	14.0	5	53 ± 2
BT3(b)	1.5:1	102	14.0	10	53 ± 2
BT3(c)	1.5:1	102	14.0	15	52 ± 2
BT3(d)	1.5:1	102	14.0	20	54 ± 1

Ba/Ti ratio maintained is 1.5 in all the cases.

TABLE II Experimental parameters and the crystallite sizes for the samples prepared under varying Ba/Ti ratios

Sample ID	Ba/Ti	Temperature (°C)	pH	Reaction time (h)	Crystallite size (nm)
BT4	1:1	102	14.0	5	59 ± 2
BT5	1.25:1	102	14.0	5	57 ± 1
BT3(a)	1.5:1	102	14.0	5	53 ± 2
BT6	2:1	102	14.0	5	47 ± 2
BT7	3:1	102	14.0	5	42 ± 2

The elemental analysis was carried out by ICP-OES spectrometer, Intrepid by Thermoelectron Corporation. It is equipped with a CID detector for simultaneous acquisition of multiple lines. The analyses were carried out using standard quartz torch, nebuliser and cyclon.

Dynamic light scattering (DLS, Model BI-9000AT, Brookhaven Instruments Corp., Holtsville, NY) was applied to estimate the particle size and particle size distribution of resulting $BaTiO_3$ powders after ultrasonicating for 15 min. Phase purity of the $BaTiO_3$ was investigated by Room temperature X-ray diffraction (RTXRD, Scintag PAD *V* using CuK_α with $\lambda = 0.15406$ nm). The crystallite size was estimated from the broadening of (200) peak by the Scherrer equation:

$$d_x = \frac{0.94\lambda}{\beta \cos\theta} \quad (1)$$

where d_x is the crystallite size, λ is the X-ray wavelength, β is the full-width at half-maximum (FWHM), and θ is the diffraction angle. XRD peak broadening may be caused by the residual strain for the large surface area to volume ratio. The strain causing the contrast variation in backscattered TEM images has been reported in our previous work [2]. Nevertheless, the crystallite sizes by Equation 1 is acceptable within the experimental uncertainty based on the DLS particle size and TEM data. The measurement of the crystallite size for our powder by Scherrer peak broadening method is thus, believed to be acceptable.

3. Results and discussion

3.1. Effect of refluxing time and temperature

A series of samples with a Ba/Ti = 1.5 have been prepared in aqueous medium at temperatures 70, 80, and 90°C with the refluxing times varying from 5–20 h. The details of the samples preparation conditions are given in Table I. pH of all the samples was maintained at 14.0 for consistency of comparison. The RTXRD pattern in Fig. 1. reveals well crystallized cubic phase for the samples refluxed for 6 h and 20 h at 102°C. This crystallite size and the crystal structure data obtained was supported by XRD and particle size data published by Wang *et al.* [47].

Figure 2 shows the variation of crystallite size with time of refluxing. The crystallite size of the samples prepared at a particular temperature and varying refluxing times are statistically the same. DLS results indicate that the particle sizes of the powder produced with a Ba/Ti = 1.5 refluxed at 102°C for 5 h (112 ± 20 nm) and 20 h (126 ± 15 nm) are statistically similar and the extended refluxing has a very little or no effect on the particle size. This is in agreement with our previous study, as reported by Wang *et al.* [47] that the formation of $BaTiO_3$ nanoparticles followed an "*in-situ* transformation" mechanism and was a rapid process. Once the crystal particles are formed, extending the reaction time has little or no effect on the morphology, crystallite size, and crystallinity of $BaTiO_3$ particles. SEM results indicate similar morphology for samples prepared for extended periods of refluxing, other parameters being essentially the same.

The increase in the temperature of refluxing resulted in the formation of smaller crystallite sizes. This can also be verified in Fig. 2. The higher temperature of refluxing is believed to increase the kinetics of $BaTiO_3$ formation leading to faster nucleation with smaller crystallites. Higher temperature also increases the dispersion, which aids in breaking the agglomerates of crystallites leading to smaller particle sizes.

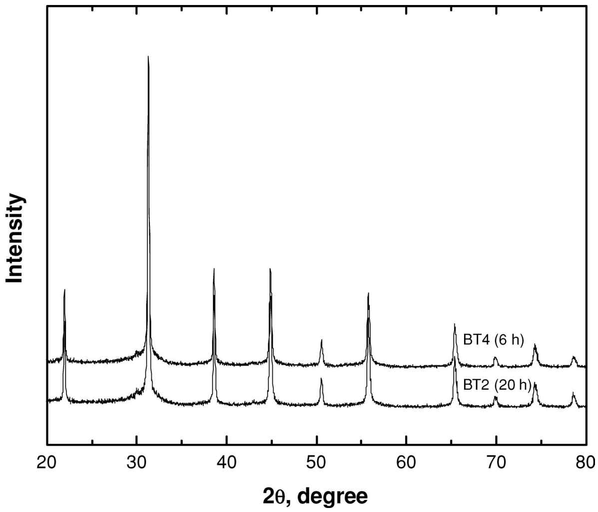

Figure 1 XRD patterns of the powder prepared at 102°C for different refluxing times.

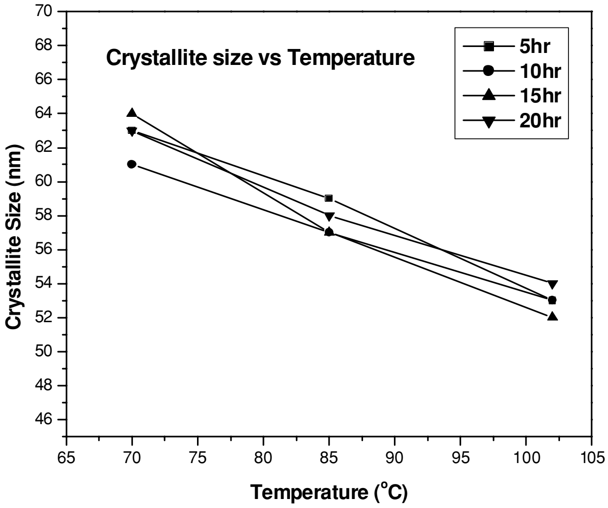

Figure 2 Variation of crystallite sizes of $BaTiO_3$ particles with the time of refluxing as a factor of temperature.

3.2. Effect of the initial Ba/Ti ratio (R)

To study the influence of Ba/Ti ratio (R) in the starting materials, powders were prepared with fixed pH(=14), refluxing temperature (102°C), and time (5 h) with R ranging 1 to 3. The crystallize sizes, determined by Equation 1 of these samples were given in Table II. Increase in R results in decrease in the crystallite size, and this can be observed in Fig. 3. No splitting of (200) peak at $2\theta = 44.95°$ is found in XRD pattern (Fig. 4), indicative of low tetragonality.

The Ti ions in the sol will initially be in the form of Ti-O-Ti long chains. Ba ions in the sol reacts with these chains and forms $BaTiO_3$. With the increase in the ratio

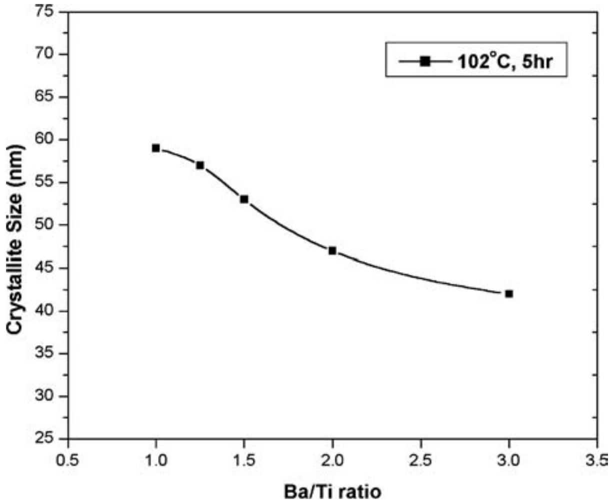

Figure 3 Crystallite size variation as a function of Ba/Ti ratio in the precursor.

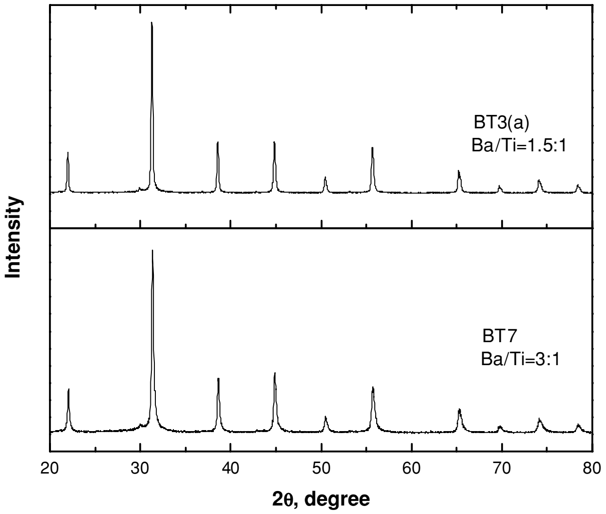

Figure 4 TGA XRD patterns of the $BaTiO_3$ samples prepared with different precursor Ba/Ti ratios at a temperature of 102°C for 6 h refluxing.

of Ba/Ti, the number of nucleation sites increases leading to smaller crystallite sizes. The higher temperature, i.e., 102°C also aids, in preventing the particle, as well as crystallite growth significantly. As shown in Fig. 5, the morphology of BT7 ($R = 3$) powders as compared with BT3(a) powders ($R = 1.5$), are noticeably smaller particles. One can also notice the increased degree of agglomeration of BT7 particles because of its smaller particle size. The DLS results show that the mean particle size of BT5 is 79 ± 10 nm. A similar observation was reported by Wada *et al.* [35] for $BaTiO_3$ powders prepared by LTDS method. At a fixed reaction temperature, increasing Ba/Ti ratio resulted in smaller crystallite size (37.0 nm when $R = 5$ and 12.9 nm when $R > 35$).

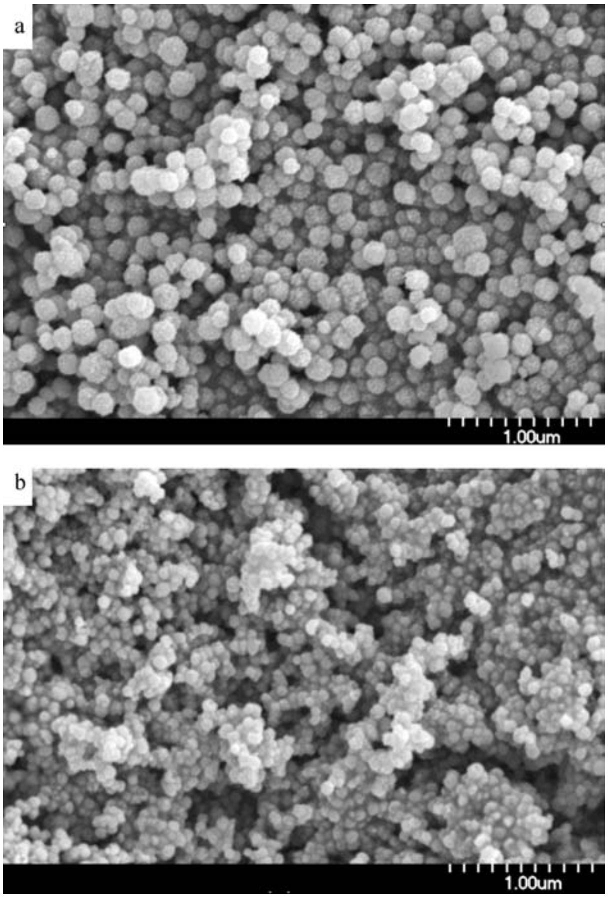

Figure 5 SEM micrographs of $BaTiO_3$ powders, (a) Ba/Ti = 1.5 (b) Ba/Ti = 3 (102°C, 6 h).

The chemical analysis by ICP spectrometry was carried out on the samples made with three precursor Ba/Ti ratios of 1, 1.5, and 2. To increase the precision of the analysis the calculations for the Ba and Ti were made referring all quantities to a standard $BaTiO_3$ powder made in the lab by solid state route. The Ba/Ti ratio in the product powder is always below the value used for synthesis and the ratio increases with the increase in the R of the precursor. The powder BT4, with a precursor Ba/Ti = 1 appears far from stoichiometry with a R = 0.89 in the powder while BT3(a) and BT6 are much closer with R values of.98 and 1.01. In order to confirm such results, the powders were heat treated at 1350°C for 2 h in air and analyzed the by XRD. At

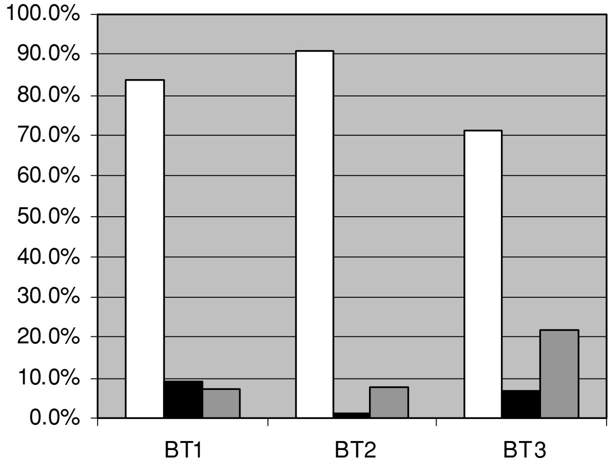

Figure 6 Histogram showing the amounts of $BaTiO_3$ (white), barium rich $Ba_2TiSi_2O_8$ (grey) and Ti rich $Ba_6Ti_{17}O_{40}$ (black).

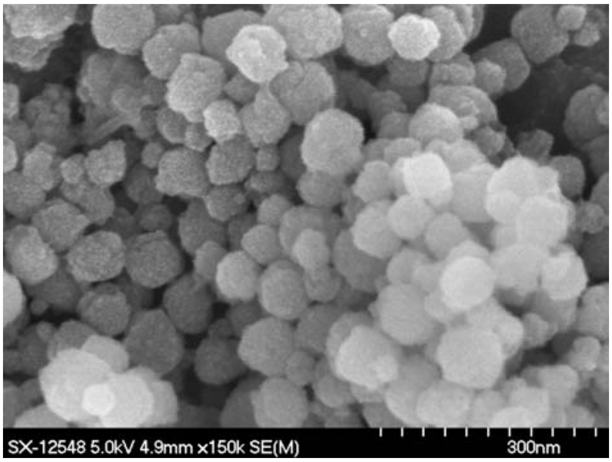

Figure 7 SEM image of $BaTiO_3$ powder prepared with APA as a polymeric surface modifier.

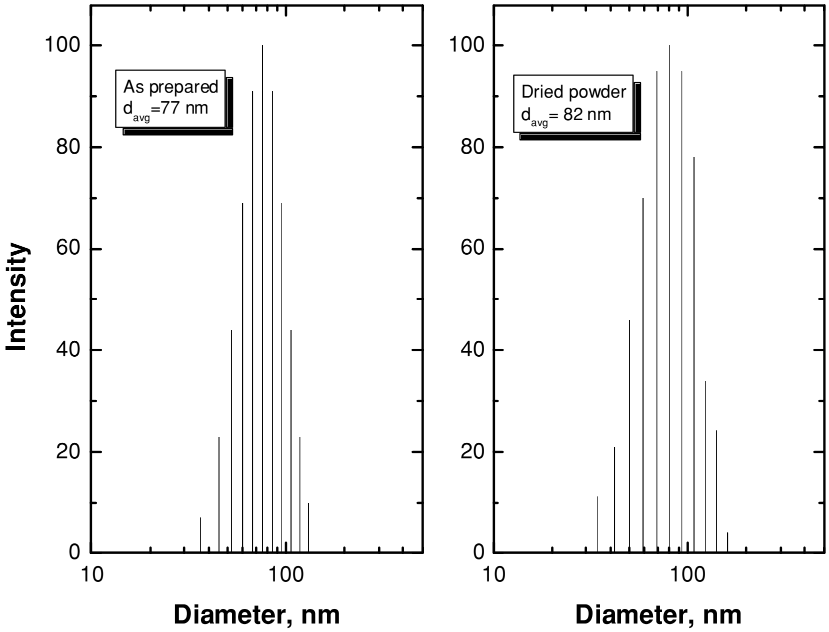

Figure 8 Particle size distribution of $BaTiO_3$ as prepared and re-dispersed (after drying) powders.

least two other phases, $Ba_2TiSi_2O_8$ and $Ba_6Ti_{17}O_{40}$ were visible. The results as quantified by XRD are shown in Fig. 6. There is a qualitative agreement between ICP and XRD for the Ba/Ti ratio. The powder having precursor R of 1.5 appeared better with minimum amounts of 2nd phases which are higher in the other powders. The powder with initial R of 1 (BT1) has the Ba deficient $Ba_6Ti_{17}O_{40}$ on the higher side and barium rich $Ba_2TiSi_2O_8$ non stoichiometric phase was observed for powder having intial R of 2 (BT3). The silicate phase present must have come from the borosilicate glass vessel used at high solution pH maintained for the ACS process. The process was modified to use Teflon vessel for refluxing.

3.3. Effect of polymeric surface modifier

$BaTiO_3$ nanocrystals were made in the presence of ammonium polyacrylate (APA, MW ∼ 6000 g/mol) as a polymeric surface modifier at 102°C, 5 h. Synthesis was carried out keeping Ba/Ti ratio of 1.5, and APA concentration at 0.002 g/mol. The crystallite size observed was 46.7 ± 1.4 nm and the particle size observed by dynamic light scattering was 82 ± 13 nm. The difference in size of the crystallite and particle sizes, which occur due to the agglomeration of the particles by growth of the crystallites, was minimized. Near spherical particles were observed in the SEM micrograph in Fig. 7. The particle distribution of the as prepared (wet, before drying) and the redispersed (after drying) powder given by DLS was shown in Fig. 8. The narrow particle size distribution of powder suggested that further growth and agglomeration of the nanocrystals has been hindered by the surface modifier by coating the crystals and eliminating the growth on the surface of the crystallites formed. The similar particle size distribution for the as prepared and the redispersed powders also indicates that introducing polymeric surface modifier also resists agglomeration that may result during the drying of the nanoparticles, and results in re-dispersible powders apart from narrowly distributed, small particle size.

4. Conclusions

Nanocrystals of cubic $BaTiO_3$ were prepared by the ACS process. Among the processing variables, higher initial Ba/Ti molar ratio and higher temperature of synthesis led to smaller crystallite size of $BaTiO_3$ powders. The optimum precursor Ba/Ti ratio was found to be ∼1.5. Even though its final R value is 0.98, it has highest percentage of stoichiometric $BaTiO_3$ with minimum amounts of second/non-stoichiometric phases in it (best in terms of phase purity) found to be minimal on the size of the crystallite. Addition of a polymer dispersant, such as APA, during $BaTiO_3$ synthesis led to a smaller particle size by inhibiting the particle/crystal growth and increased redispersibility of the particles in water.

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