

# SURFACTANT-ASSISTED SYNTHESIS OF BaTiO<sub>3</sub> NANOPARTICLES BY MICRO-EMULSION METHOD

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Preliminary Note – Prethodno priopćenje

Barium titanate (BaTiO<sub>3</sub>) nanoparticles were successfully synthesized by using a surfactant-assisted method. The various processing parameters, namely, the species of surfactant, reaction temperature and micro-emulsion concentration had been varied, and the effects on the micrographs and crystal structure of BaTiO<sub>3</sub> particles had been analyzed by scanning electron microscope (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). XRD analyses confirming the tetragonal structure of the BaTiO<sub>3</sub> nanoparticles using hexadecyl trimethyl ammonium Bromide (CTAB) or nonylphenol polyoxyethylene ether (NP-10) as surfactant. The SEM analysis showed that by changing the species of surfactant, grains with different dimensions could be synthesized. TEM analyses indicate that BaTiO<sub>3</sub> nanoparticles with 15–20 nm in diameter were successfully synthesized.

*Key words:* barium titanate; nanoparticles; surfactant; micro-emulsion

## INTRODUCTION

Barium titanate (BaTiO<sub>3</sub>) possesses an exceptional position in the electronics industry due to their attractive combination of ferroelectric, dielectric, piezoelectric and pyroelectric properties [1]. Progress in the development of thinner multiplayer ceramic chip capacitors has tremendously increased the demand for smaller size dielectric ceramic powders and leads to the study of BaTiO<sub>3</sub> nano-powders [2].

Various approaches including sol-gel [3], high-temperature solid-state reaction [4], hydrothermal [5] and microwave synthesis methods [6,7] have been used to synthesize micro- and nano-scale BaTiO<sub>3</sub>. In order to synthesize nano-BaTiO<sub>3</sub>, a low calcinations temperature and a short isothermal holding are both critical. Compared with these processes, hydrothermal synthesis method carried out at lower temperatures is considered as the conventional routine. However, hydrothermal processing carried out at lower temperatures always yields cubic or pseudocubic BaTiO<sub>3</sub>. To convert it to the tetragonal form, a further heating at temperatures in excess of 1 000 °C is required, which always leads to grain growth and particle agglomeration [8,9].

Micro-emulsion method has several advantages including the use of low cost raw materials, a simplified process and the ability to obtain fine particles, which is one of the promising method to prepare the ultra-fine ceramic powder of narrow grain size distribution [10].

Herein, it had made an attempt to synthesize BaTiO<sub>3</sub> nanoparticles by using a surfactant-assisted micro-emulsion method. Here, alcohol polyoxyethylene ether (APE),

nonylphenol polyoxyethylene ether (NP-10) and hexadecyl trimethyl ammonium Bromide (CTAB) were used as the surfactant, respectively. Titanium tetrachloride was used as titanium source and barium chloride was used as barium source for the crystallization of BaTiO<sub>3</sub> particles. In this study, we had investigated the conditions required for the crystallization of BaTiO<sub>3</sub>. The structure and morphology of the BaTiO<sub>3</sub> particles were also studied.

## EXPERIMENTAL

The surfactant, APE, NP-10 and CTAB were purchased from Xinxi Chemical Co.(China). Other chemicals including titanium tetrachloride, barium chloride, n-butyl alcohol and n-hexane provided by Sinopharm Chemical Reagent Shenyang Co., Ltd, China (Chemical grade).

20 ml of TiCl<sub>4</sub> (0,4 M) was mixed with 20 ml of aqueous BaCl<sub>2</sub> (0,33 M), to form a binary precursor solution (BPS). Micro-emulsion emulsion (MES) was prepared by mixing equimolar amount of n-butyl alcohol and n-hexane with the surfactant (100 g/L). BPS was added to MES under vigorous constant 3 h stirring at constant temperature.

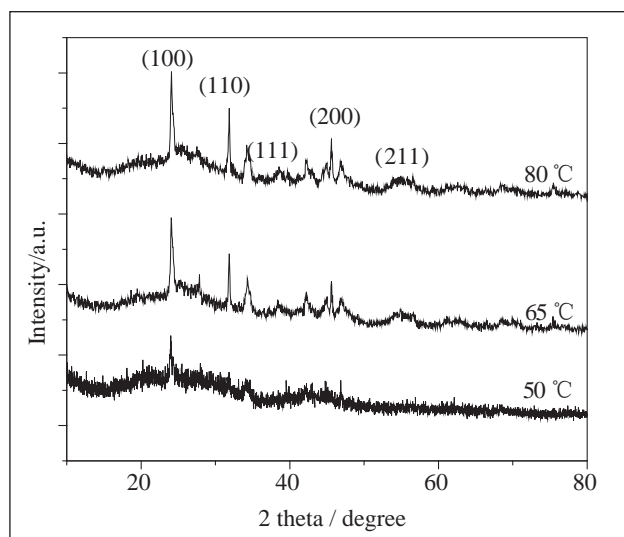
After completion of the reaction, the BaTiO<sub>3</sub> particles were separated out by centrifugation. The centrifuged precipitate was further washed repeatedly using water and ethanol to obtain high-purity BaTiO<sub>3</sub> particles. The as-obtained BaTiO<sub>3</sub> particles were white in color. Finally, the BaTiO<sub>3</sub> particles were dried in a vacuum oven at 60 °C for 6 hours. In this study, the different processing parameters including reaction temperature, volume ratio of BPS to ES, and the species of surfactant were varied.

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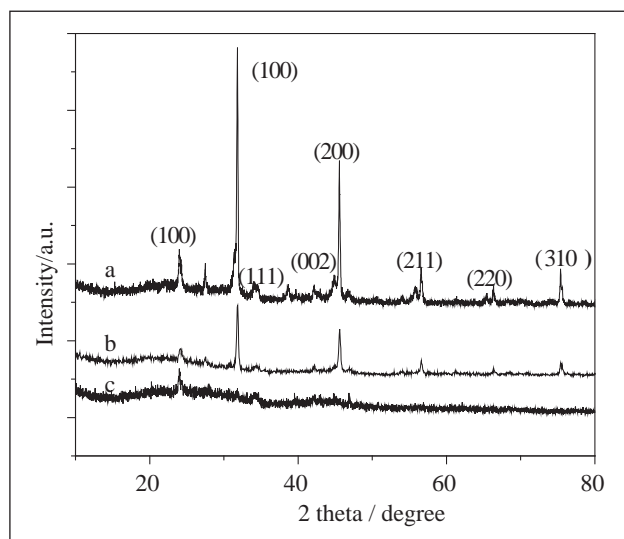
Morphology of the as-prepared samples was analyzed by using scanning electron microscopy (SEM, Philip XL-20) and transmission electron microscopy (TEM, Hitachi H800). The crystalline structure of the samples was determined by a X-ray diffraction (XRD, Rigaku D/max-RB) with Cu K-radiation.

## RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the product without surfactant at 50 °C, 65 °C and 80 °C, respectively. The XRD patterns indicated that the peak of the low reaction temperature of 50 °C was not recognized with crystal characteristics. When the temperature rose to 65 °C or 80 °C, most of the diffraction peaks assigned to BaTiO<sub>3</sub> appeared, the crystal system was tetragonal for the two powders. but there were still some weak diffraction peaks of impurities. As suggested by the typical diffraction peaks at (100), (110), (111), (200), (211). Therefore, considering the cost, reaction temperature



**Figure 1** XRD patterns for the particles prepared at different temperature



**Figure 2** XRD patterns for the particles prepared with different volume ratio of BPS to ES (a) 0,5:1 (b) 1:1 (c) 3:1

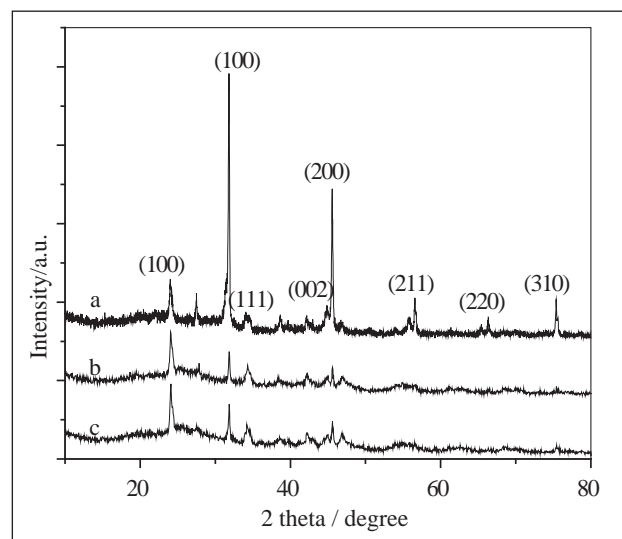
65 °C was considered to be the optimum temperature necessary for the formation of BaTiO<sub>3</sub> particles.

Figure 2 shows XRD patterns of the samples prepared using CTAB as surfactant at 65 °C. Ratio of BPS:MES used in this progress was 0,5:1, 1:1 and 3:1, respectively. Lower micro-emulsion content showed relatively higher broadening of the characteristic peak corresponding to the (200) plane than that of higher micro-emulsion content, which indicates the tetragonal form content is higher. The extent of tetragonality in BaTiO<sub>3</sub> is an important factor which directly influences its dielectric behavior. Higher the extent of tetragonality; greater will be its dielectric properties; thereby; increasing its effectiveness in the ceramic capacitor applications [11].

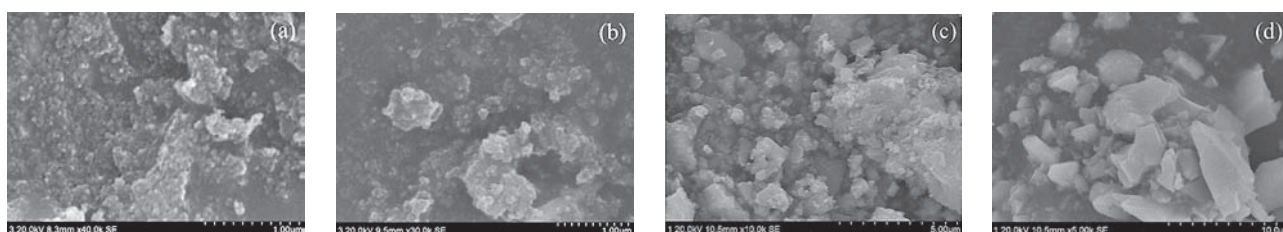
The XRD patterns of the different samples shown in Figure 3 indicate the dependence of the crystal structure of BaTiO<sub>3</sub> particles on the species of surfactant. All the BaTiO<sub>3</sub> particles were prepared with 0,5:1 ratio of BPS to MES at 65 °C. The presence of peaks related to BaTiO<sub>3</sub> could be noted. Crystalline BaTiO<sub>3</sub> can be synthesized when the micro-emulsion contained (a) CTAB, (b) NP-10 or (c) APE. An asymmetric splitting of the (200) reflection at a lower angle signal indexed as (002) is an indication of tetragonal form of BaTiO<sub>3</sub> [12-14]. In cubic form, this peak is not split [12,14]. Moreover, the profiles of the (220) and (310) peak appeared when CTAN or NP-10 was used as surfactant, which confirmed the tetragonal form of BaTiO<sub>3</sub>.

It could be obviously seen that the intensities of diffraction peaks associated with BaTiO<sub>3</sub> particles increased and half-peak-width became wider when CTAN was used as surfactant, which indicated crystallinity of BaTiO<sub>3</sub> particles increased and the crystallite sizes were smaller than those of NP-10 or APE.

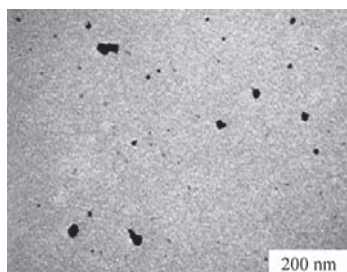
The micrographs obtained for BaTiO<sub>3</sub> nanoparticles are illustrated by the SEM micrographs in Figure 4(a – d) for various surfactants or without surfactant, respectively. SEM micrographs revealed an abnormal and



**Figure 3** XRD patterns for the particles prepared with different surfactant (a) CTAB, (b) NP-10, (c) APE



**Figure 4** SEM micrographs of the (a)CTAB, (b)NP-10 ,(c) APE, (d)without surfactant



**Figure 5** TEM micrographs of the BaTiO<sub>3</sub> nanoparticles

even more than 10  $\mu\text{m}$  particles size without surfactant (Figure 4d), which phenomenon could be contributed to the following reasons. (1) the existence of second phase precipitates or impurities, (2) materials in high chemical in equilibrium. In micro-emulsion without surfactant derived BaTiO<sub>3</sub> which crystallizes in a tetragonal structure it can be assumed that the abnormal grain growth comes from the existence of two-phase structure[15]. However, a spherical morphology for all the synthesized nanoparticles were observed when the micro-emulsion contained (a)CTAB, (b)NP-10 or(c) APE. Surfactant CTAB led to a uniform morphology that consisted of small grains. On the other hand, the samples treated by APE consisted of big grains isolated and embedded in a matrix of small grains. The most serious agglomeration could also be seen. The agglomeration process was attributed to Van der Waals forces. To reduce the surface energy, the primary particles have a tendency to form nearly spherical agglomerates, in a minimum surface to volume ratio and hence reducing surface free energy [15-17].

Figure 5 supports the nanometric nature of BaTiO<sub>3</sub> particles obtained using CTAB as surfactant and 1:3 proportion of BPS to MES at 65 °C. It was difficult to estimate the average particle size by using TEM because of agglomeration. However, some particles of 15 – 20 nm regions in images can be observed in Figure 5 as dark-grey regions in images, along with one agglomerate of about 50 nm as dark regions .

## CONCLUSIONS

Employing the micro-emulsion method and optimizing the surfactant composition, nano-crystalline BaTiO<sub>3</sub> particles was obtained. The reaction temperature required for the crystallization of BaTiO<sub>3</sub> nanoparticles BaTiO<sub>3</sub> was 65 °C. The ratio of BPS to MES required for the crystallization of BaTiO<sub>3</sub> nanoparticles was 3:1.

XRD analyses confirming the tetragonal structure of the BaTiO<sub>3</sub> nanoparticles using CTAB or NP-10 as surfactant. The SEM analysis showed that by changing the species of surfactant, grains with different dimensions could be synthesized. TEM analyses indicate that BaTiO<sub>3</sub> nanoparticles with 15 – 20 nm in diameter were successfully synthesized. Surfactant-assisted micro-emulsion method is interesting not only for the low temperature used, but also for short treatment time and structural properties. Therefore, this method is undeniably a genuine technique for low temperatures and short times.

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**Note:** The responsible translator for English language is K. Bei - Hangzhou Qihang translation Co.LTD, China