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# Solvothermal synthesis and Curie temperature of monodispersed barium titanate nanoparticles

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ABSTRACT

Barium titanate ($BaTiO_3$) nanoparticles with various particle sizes were prepared by a solvothermal method. X-ray powder diffraction (XRPD) patterns show that the as-prepared powders are of pure perovskite $BaTiO_3$. Scanning electron microscopy (SEM) reveals that all the particles of $BaTiO_3$ with different sizes are dispersed homogenously and have uniform size. The room temperature and in situ high temperature XRD analyses indicate that both the proportion of the tetragonal phase and the Curie temperature of $BaTiO_3$ increase with increasing particles size. The effects of the reaction parameters, such as the concentration of reactants, the polarity of solvent, the reaction temperature and the amount of surfactant, on the size, morphology and uniformity of $BaTiO_3$ nanoparticles are studied in detail.



## 1. Introduction

Lead-free barium titanate ($BaTiO_3$) has been extensively studied for its environment friendly feature and numerous industrial applications. As a typical ferroelectric material, $BaTiO_3$ has been used in sensors, switches, receivers [1–6], etc. As a microwave dielectric ceramics, $BaTiO_3$ is commonly used in dielectric resonators, microwave integrated circuit substrates, dielectric waveguides, dielectric antenna, attenuator, phase adjustment devices [7–14] and multi-layer ceramic capacitors [15,16]. As the electronic devices continue to be down-sized and integrated with the development of nanotechnology, more and more attention has been focused on the "size effect" which seems to limit the applications of ferroelectric nanoparticles. Therefore, the synthesis and the understanding of the ferroelectricity in $BaTiO_3$ nanoparticles have thus become an urgent task [17]. In general, the ferroelectricity decreases significantly with decreasing grain size, which is the so called "size effect". The ferroelectricity of $BaTiO_3$ nanoparticles disappears when the grain size decreases to about 44 nm according to the calculation by Zhong et al. [18–22]. The grain size effect of $BaTiO_3$ ceramics has been extensively studied since it was first reported in 1954 [23–26]. However, it is difficult to study the size effect of $BaTiO_3$ on nanoscale in the samples prepared by traditional solid state reaction and ceramic processing because the grains generally grow up during sintering.

In order to study the size effect in $BaTiO_3$, nanoparticles with various sizes are needed. As a commonly used solution technique, hydrothermal synthesis provides a special physical and chemical environment for the reaction and crystallization of precursors. Compared to other preparation methods, the particles synthesized by the hydrothermal method are usually integral, uniform and well dispersed. Taking advantage of these merits, in this work $BaTiO_3$ nanoparticles with various sizes from 25 to 500 nm have been prepared by an improved hydrothermal or solvothermal method and characterized by X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM). The reaction parameters and conditions that affect the synthetic results are discussed.

### 2. Experimental

$BaTiO_3$ nanoparticles of various sizes from 25 to 500 nm were prepared by a solvothermal method at 180–200 °C and the molar ratio of barium ion to titanium ion was maintained 1:1 throughout the synthetic process. The following five different preparation processes were used to synthesize the particles of various sizes. The reactants were sealed in a Teflon-lined stainless steel autoclave and placed in an electric furnace (DHG-9036A, Rongfeng Scientific Instrument Co., Ltd. Shanghai) in each preparation process.

(1) The $BaTiO_3$ nanoparticles of 25 nm size were prepared by reacting 2 mmol barium hydroxide octahydrate (98%, Alfa Aesar) and 0.680 ml titanium (IV) n-butoxide (VERTEC®TNBT, 98 + %, Alfa Aesar) in 15 ml methanol at 180 °C for 24 h. In this process, the barium hydroxide octahydrate was first ground, and then mixed with the titanium (IV) n-butoxide–methanol solution. The mixture was stirred for 10 min before being sealed in the Teflon-lined stainless steel autoclave.

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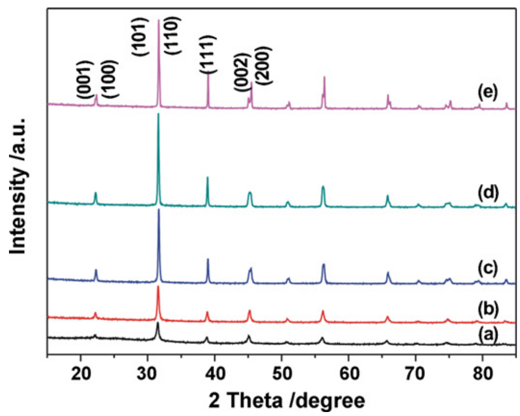


**Fig. 1.** XRPD patterns of $BaTiO_3$ powders with five typical particle sizes: (a) 25 nm, (b) 50 nm, (c) 80 nm, (d) 150 nm and (e) 500 nm.

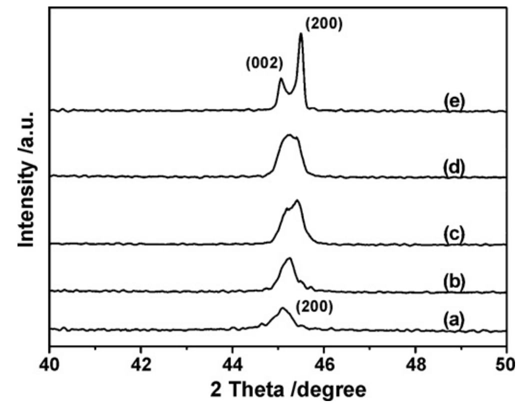


**Fig. 2.** $(2\,0\,0)_{cub}$ reflection of $BaTiO_3$ powders with various particle sizes: (a) 25 nm, (b) 50 nm, (c) 80 nm, (d) 150 nm and (e) 500 nm.

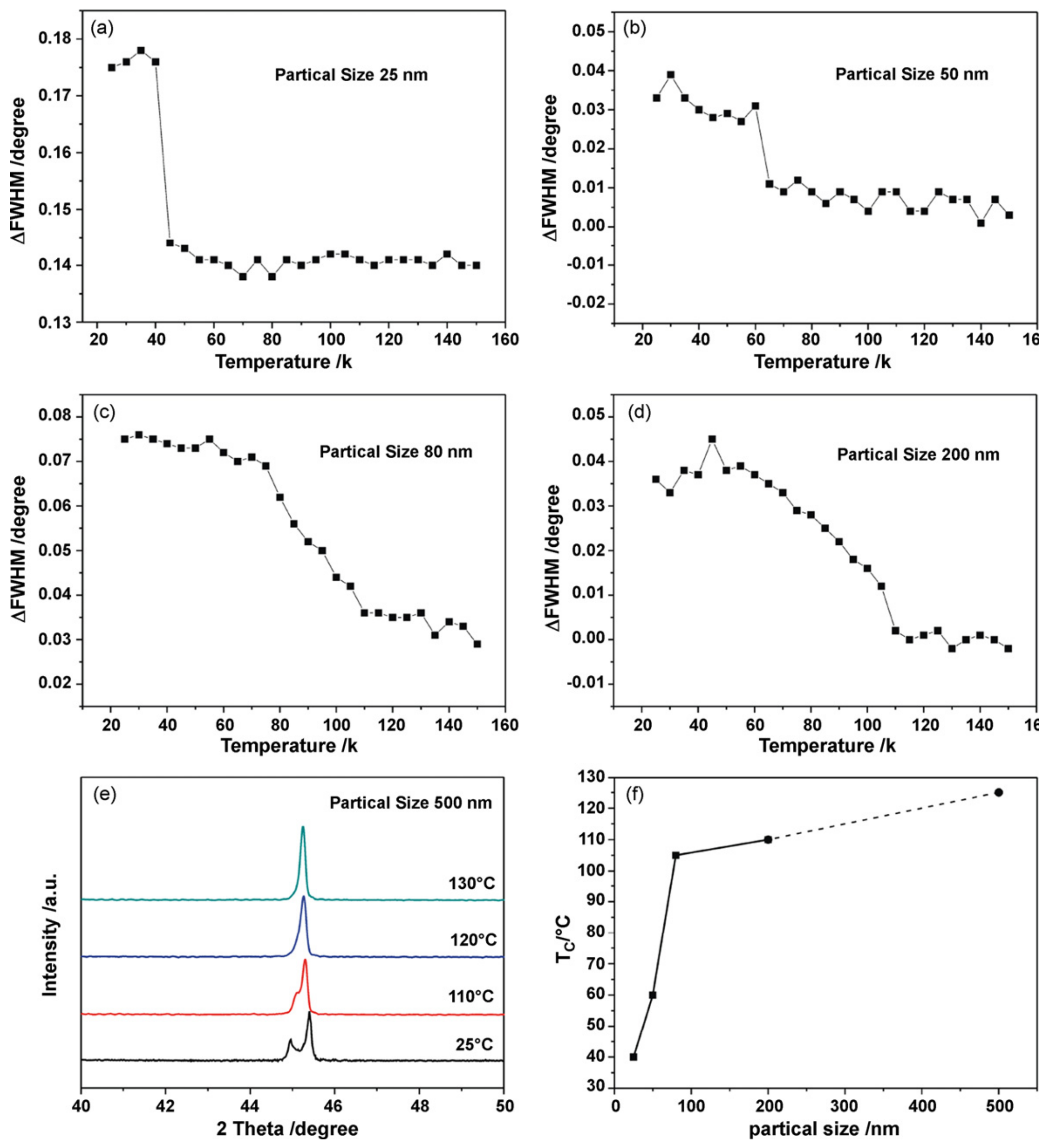


**Fig. 3.** In situ high temperature XRPD patterns of $BaTiO_3$ samples with various particles sizes: (a) 25 nm, (b) 50 nm, (c) 80 nm, (d) 200 nm and (e) 500 nm. (f) Curie temperature ($T_C$) as a function of the size of the $BaTiO_3$ nanoparticles.