


 Cite this: *RSC Adv.*, 2023, **13**, 11002

Facile preparation and dielectric properties of BaTiO₃ with different particle sizes and morphologies

 Xinxiao Wu,^a Hengan Zhao,^a Weining Han,^a Zhimiao Wang,^a Fang Li,^{ab} Jing Li^{*c} and Wei Xue^{*ab}

BaTiO₃ nanoparticles were prepared by the hydrothermal method, and the effect of 1-(propyl-3-methoxysilyl)-3-methylimidazole chloride on the size of BaTiO₃ particles was investigated. The obtained BaTiO₃ was characterized by XRD, SEM, TEM, and Raman spectroscopy; and the dielectric properties of BaTiO₃ ceramic sheets were tested. The results indicate that the spherical BaTiO₃-N prepared without an ionic liquid was in a tetragonal phase with an average particle size of 129 nm. When an ionic liquid was added, the size of the BaTiO₃-IL decreased and the degree of agglomeration increased. In addition, with increasing quantity of ionic liquid, the tetragonal-phase content of BaTiO₃-IL gradually decreased until complete transformation into cubic phase. The dielectric constant of the BaTiO₃-N ceramics was the highest, and the dielectric constant decreased with decreasing BaTiO₃ particle size. Moreover, two types of BaTiO₃ nanoparticles (bowl- and sea urchin-shaped) were prepared by changing the hydrothermal conditions and additives. The average particle size of the former was 92 nm, the tetragonal-phase content was ca. 90%, and the dielectric constant was large; whereas the sea urchin-shaped BaTiO₃ consisted of small particles in the cubic phase, and the dielectric constant was small.

 Received 31st December 2022
 Accepted 2nd April 2023

DOI: 10.1039/d2ra08334e

rsc.li/rsc-advances

1. Introduction

Barium titanate (BaTiO₃) is a ferroelectric compound with excellent properties in the barium oxide–titanium dioxide (BaO–TiO₂) system,¹ which exhibits good dielectric as well as ferroelectric properties and is the basic material for electronic ceramic components.^{2,3} Barium titanate nanoparticles are widely used to make small, high-capacity microcapacitors and temperature-compensating components;^{4,5} as well as nonlinear components, dielectric amplifiers, memory components for electronic computers, ceramic sensitive components, microwave ceramics, and piezoelectric ceramics.^{6,7} In recent years, with the continuous development of the electronics industry, the demand for BaTiO₃-based ceramics has been increasing; and higher requirements for BaTiO₃ purity, particle size, crystal shape, and dispersion have been proposed.^{1,8} There is broad utility in preparing high-purity, ultrafine BaTiO₃ powder.^{9,10}

Currently, the main methods for synthesizing nano-BaTiO₃ include solid-phase synthesis, co-precipitation, sol-gel, and hydrothermal synthesis.^{11,12} Solid-phase synthesis requires

a high temperature of ca. 1100 °C, and the resulting barium titanate powder exhibits a large grain size as well as low powder purity.¹³ Co-precipitation requires high-temperature roasting, which is prone to impart agglomeration of and a nonuniform particle size to the synthesized powder.¹² Sol-gel method process conditions are not suitable for control and the organic solvent is highly toxic.^{14,15} In contrast, the hydrothermal method is excellent for preparing BaTiO₃ powder.¹ The resulting powder or nanocrystals are well-developed, with a composition close to stoichiometry as well as a uniform and controllable particle size distribution, and the average grain size of the resulting nano-BaTiO₃ is small (as little as tens or even several nanometers).^{16,17} At present, BaTiO₃ particles obtained by hydrothermal preparation with Ba(OH)₂·8H₂O and TiO₂ as raw materials are generally >100 nm in size and require high-temperature calcination to obtain smaller particles.^{17,18} Therefore, how to reduce the average size of nano-BaTiO₃ particles by hydrothermal synthesis under mild conditions is an active area of research.

Furthermore, the properties of nanomaterials are not only dependent on their size, but the influence of the microscopic morphology is also crucial, which has led to substantial interest in preparing barium titanate in various morphologies and sizes. Ma *et al.*¹⁹ used oleic acid and *tert*-butylamine as additives to synthesize BaTiO₃ nanocubes, with a smooth surface and an average size of 25 nm, by the hydrothermal method. Inada *et al.*²⁰ obtained tetragonal-phase barium titanate nanorods using BaCl₂ and TiCl₄ as raw materials, and ethylene glycol as

^aHebei Provincial Key Laboratory of Green Chemical Technology, High Efficient Energy Saving, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China. E-mail: weixue@hebut.edu.cn

^bTianjin Key Laboratory of Chemical Process Safety, Tianjin 300130, China

^cSchool of Civil and Transportation Engineering, Hebei University of Technology, Tianjin 300401, China



the solvent by the hydro/solvothermal method. Their mechanistic analysis suggests that ethylene glycol played an important role in the nucleation and anisotropic growth of tetragonal barium titanate. Li *et al.*²¹ prepared a nano-BaTiO₃ supercage structure—without organic additives—that exhibited excellent microwave absorption. Zhu *et al.*²² used a simple method to prepare cubic-phase BaTiO₃ nanotubes with an average diameter of 10 nm and a wall thickness of 3 nm. The material exhibited excellent high-frequency absorption and is a promising microwave-absorbing material. Surmenev *et al.*²³ prepared one-dimensional, nano/micron-sized, rod-shaped BaTiO₃ by the hydrothermal method and found that BaTiO₃ with various morphologies, sizes, and phase compositions could be prepared by adjusting the temperature, time, and alkalinity of the hydrothermal process.

Ionic liquids have many unique properties—such as wide electrochemical windows, low surface tension, and high thermal stability.^{26,27} In recent years, the advantages of ionic liquids in synthesizing inorganic nanomaterials have been gradually discovered and there are an increasing number of applications.^{24,25} Ionic liquids can act as reactants, solvents, and templates in preparing inorganic nanomaterials.^{29,30} The low surface tension of ionic liquids can lead to high nucleation rates and Ostwald ripening, and ultimately to small particles. Ionic liquids can also interact with the particle surface and thus play an important role in particle growth.²⁸ Zhou *et al.*³¹ used the ionic liquid [Bmim]BF₄ as an additive and prepared TiO₂ nanocrystals with an average size of only 2–3 nm under mild conditions. Cao *et al.*³² synthesized ultrafine amorphous metal hydroxide nanoparticles for efficient oxygen evolution by a one-step method with 1-aminopropyl-3-methylimidazolium tetrafluoroborate, resulting in particle sizes of 2–3 nm. Paszkiewicz *et al.*³³ prepared TiO₂ microspheres with ionic liquids as additives. The effect of the cation chain length of imidazole-based ionic liquids on the resulting TiO₂ morphology and photoactivity were systematically studied; both the electrostatic stability and coordination of imidazole cations facilitated growth of TiO₂ spheres. Kim *et al.*³⁴ prepared Ag nanostructures with various morphologies—including nanowires—with 1-butyl-3-methylimidazole-based ionic liquids as additives, and concluded that forming these morphologies was related to the stabilizing effect as well as self-organization of the ionic liquids.

As mentioned previously, ionic liquids play an important role in preparing inorganic nanomaterials. However, preparing BaTiO₃ with ionic liquids has not been reported to date. In the present paper, the 1-(propyl-3-methoxysilyl)-3-methylimidazole chloride ([Tmospmim]Cl) was used as an additive, and anatase TiO₂ as well as Ba(OH)₂·8H₂O were used as raw materials to prepare nano-BaTiO₃ by the hydrothermal method. The effects of the quantity of ionic liquid on the size, morphology, and tetragonal-phase content of BaTiO₃ were investigated; and the dielectric properties of BaTiO₃ were measured. In addition, hollow, bowl-shaped nano-BaTiO₃ with a small size and excellent dielectric properties was also prepared with polyvinylpyrrolidone (PVP) instead of an ionic liquid.

2. Experimental

2.1 Materials and reagents

Ba(OH)₂·8H₂O, TiO₂, Polyvinylpyrrolidone (PVP) and ammonia (NH₃·H₂O) were of analytical grade and used without further purification. 1-(Propyl-3-methoxysilyl)-3-methylimidazole chloride ([Tmospmim]Cl, 99%) was purchased from Shanghai Chengjie Chemical Co., Ltd Formic acid anhydrous (HCOOH, 98%) was purchased from Tianjin Comio Chemical Reagent Co., Ltd.

2.2 Hydrothermal synthesis of BaTiO₃

Hydrothermal synthesis of BaTiO₃ was conducted in a 100 mL PTFE-lined crystallization kettle. Firstly, Ba(OH)₂·8H₂O (14.2 g, 45 mmol), TiO₂ (1.4 g, 18 mmol), deionized water (30 mL) and [Tmospmim]Cl (1.0 g, 3.0 g or 5.0 g) were added to the kettle in turn and stirred well. Then, NH₃·H₂O (14 mL, 25%) was added to adjust the alkalinity of the system. The hydrothermal process was conducted at 200 °C for 48 h. When the reaction was finished, the crystallization kettle was cooled to room temperature and the solid was separated from the liquid. Afterwards, it was repeatedly washed with formic acid (1 mol L⁻¹) and water until the filtrate was neutral. The resulting solid was dried at 80 °C to a constant weight and designated as BaTiO₃-IL-*X* (*X* = 1, 3, or 5).

The preparation process without the addition of ionic liquid was the same as the above steps, and the resulting product was noted as BaTiO₃-N.

Urchin-like nano-BaTiO₃: Ba(OH)₂·8H₂O (4.7 g, 15 mmol), deionized water (30 mL), TiO₂ (0.48 g, 6 mmol) and [Tmospmim]Cl (5.0 g) were added to a 100 mL PTFE-lined crystallization kettle and stirred well. Then, NH₃·H₂O (25%, 14 mL) was added to adjust the alkalinity. The next reaction procedure was the same as BaTiO₃-IL. The prepared urchin-like nano-BaTiO₃ was denoted as BaTiO₃-U.

Hollow bowl-shaped of nano-BaTiO₃: the preparation process was similar to BaTiO₃-IL, except that polyvinylpyrrolidone (5.0 g, PVP) was used instead of ionic liquid and the resulting hollow bowl-shaped nano-BaTiO₃ was noted as BaTiO₃-B.

2.3 Characterization

X-ray diffraction (XRD) of samples were collected with a Bruker D8 Discover X-ray diffractometer using a graphite monochrome filter and Cu K α radiation. The tube voltage and the tube current were set at 40 kV and 40 mA, respectively. The samples were scanned in the 2θ range of 15–90°, scanning speed of 6° min⁻¹.

Transmission electron microscope (TEM) from FEI Talos F200S with a voltage of 200 kV and a resolution of 0.12 nm was used to observe the morphology and size of BaTiO₃ particles.

Scanning electron microscopy (SEM) from the FEI Nova Nano S450 was used to observe the morphology and particle size of the samples by collecting signals from secondary electrons and backscattered electrons for microscopic morphology analysis.



A LabRAM HR Evolution laser Raman spectrometer from HORIBA Jobin Yvon was used to perform the samples with a 532 nm Nd: YAG laser. The spectral range was 100–1000 cm^{-1} , and the spectral resolution was less than 1 cm^{-1} .

Bulk density was measured *via* Archimede's method.

2.4 Electrical performance test

A high frequency dielectric spectrometer, Agilent E4991A, was used to test the dielectric constants and dielectric losses of the ceramic samples at different temperatures at 1000 Hz and a DC voltage of 1 V. The dielectric constants of the BaTiO₃ ceramics were calculated according to eqn (1).

$$\varepsilon = C \cdot h / \varepsilon_0 S \quad (1)$$

where: ε_0 -vacuum dielectric constant, $\varepsilon_0 = 8.854 \times 10^{-12}$ F m⁻¹, C -type capacitance, F; h -thickness of ceramic sheet, m; S -electrode area, m².

The dielectric properties of nano-BaTiO₃ with different grain sizes were tested. Paraffin wax of 7% was mixed with 0.8 g nano-BaTiO₃ powder, and the wax was fried on a microwave induction oven to make the wax uniformly dispersed in the BaTiO₃ powder. The powder was passed through an 80 mesh sieve, sieved, and then pressed into shape under a pressure of 4 MPa to obtain raw flakes.

The raw BaTiO₃ ceramic flakes obtained after pressing were placed in a high-temperature sintering furnace for sintering. The sintering procedure is set at room temperature to 550 °C with a heating rate of 2.5 °C min⁻¹. After 550 °C, the binder is removed from the billets by holding them for 1 h. Afterwards, the temperature is rapidly increased to 1250 °C (8 °C min⁻¹) and held for 4 h. After the sintering is completed, the temperature is cooled down (3 °C min⁻¹) to room temperature. Finally, the BaTiO₃ ceramic sheets were coated with silver paste on both sides and tested for their dielectric properties after silver firing.

3. Results and discussion

3.1 Preparation of BaTiO₃ with various particle sizes

BaTiO₃ nanoparticles were prepared by the hydrothermal method with the ionic liquid [Tmospmim]Cl as an additive, and the effect of the quantity of ionic liquid was investigated. The obtained BaTiO₃ was characterized (Fig. 1–3).

Fig. 1 shows the XRD patterns of the BaTiO₃ samples. Based on the XRD pattern of BaTiO₃-N in Fig. 1A, diffraction peaks with 2θ of 22.26°, 31.56°, 38.91°, 45.08°, 45.38°, 51.08°, 56.25°, and 65.78° were evident; corresponding to the (100), (110), (111), (002), (200), (210), (211) and (220) crystal planes, respectively.³⁵ In particular, the diffraction peak near 45° was split into two peaks (Fig. 1B), which indicates that the prepared BaTiO₃-N was in the tetragonal phase (JCPDS NO. 05-0626).^{36,47} The calculated axial ratio c/a was 1.0086, which indicates that the content of tetragonal-phase BaTiO₃ was approximately 95%.³⁷ The XRD pattern of BaTiO₃-IL was similar to that of BaTiO₃-N after adding the ionic liquid [Tmospmim]Cl. However, the split two peaks at 45° gradually merged into a single peak with increasing ionic liquid dosage, indicating that the ionic liquid

facilitated formation of the cubic-phase BaTiO₃ (JCPDS NO. 31-0174).³⁸

Fig. 2 shows the Raman spectra of BaTiO₃-N and BaTiO₃-IL-5. The Raman peaks of tetragonal BaTiO₃ were evident at 185, 260, 307, 515, and 715 cm^{-1} in the spectrum of BaTiO₃-N. In contrast, the Raman spectrum of BaTiO₃-IL-5 exhibited no peaks, indicating that it exhibited no Raman activity and was all cubic-phase BaTiO₃, which is consistent with the XRD results. Adding an ionic liquid facilitated formation of cubic-phase BaTiO₃.

Fig. 3 shows SEM and TEM images of BaTiO₃ samples, as well as the particle size distributions. As evident from Fig. 3A1 and B1, the BaTiO₃-N particles were nearly spherical with uniform size and good dispersion. The diameter of the BaTiO₃-N particles was 129 nm. The BaTiO₃-IL-1 particles prepared with an ionic liquid were smaller: 86 nm (Fig. 3A2, B2, C2). With increasing quantity of ionic liquid, the particle size of BaTiO₃-IL-3 decreased substantially to only 46 nm. However, the dispersion deteriorated with obvious agglomeration. The average particle size of BaTiO₃-IL-5 was 34 nm and agglomeration of the particles was substantial. Adding an ionic liquid reduced the surface tension of the system and increased the nucleation rate of BaTiO₃, resulting in smaller particles.^{28,39} In addition, the viscosity of the reaction system increases with

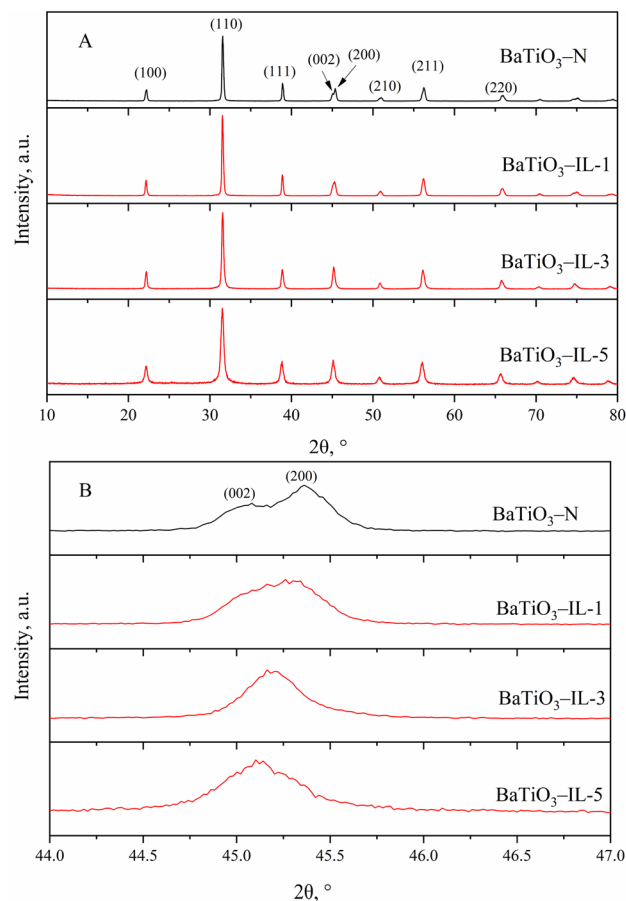


Fig. 1 XRD patterns of nano-BaTiO₃ ((A) full range; (B) in the 2θ range of 44.0–47.0°).



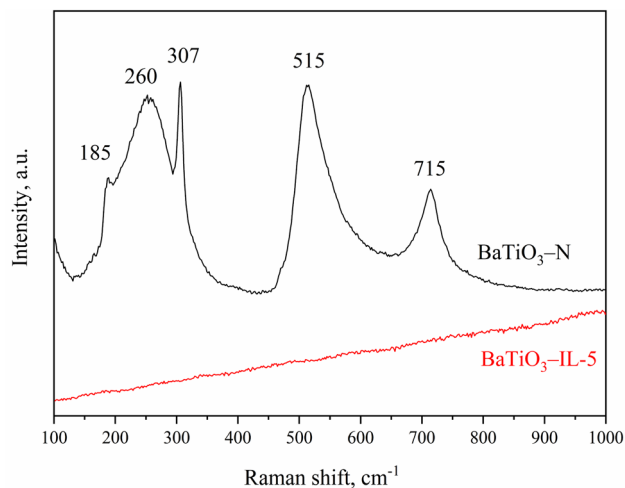


Fig. 2 Raman spectra of BaTiO₃-N and BaTiO₃-IL-5.

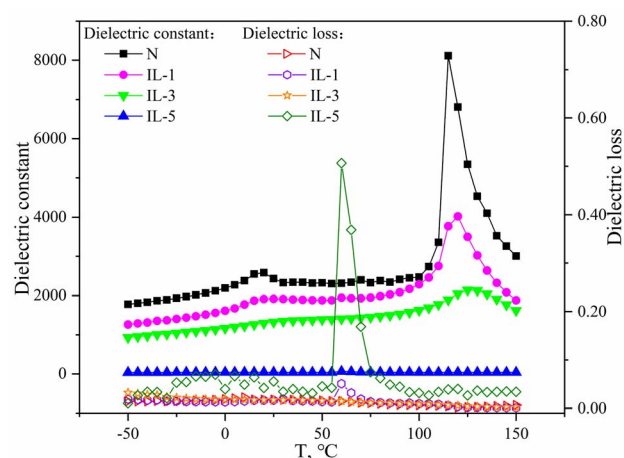


Fig. 4 Effect of ILs loadings on dielectric constant and dielectric loss of BaTiO₃ ceramics at different temperature.

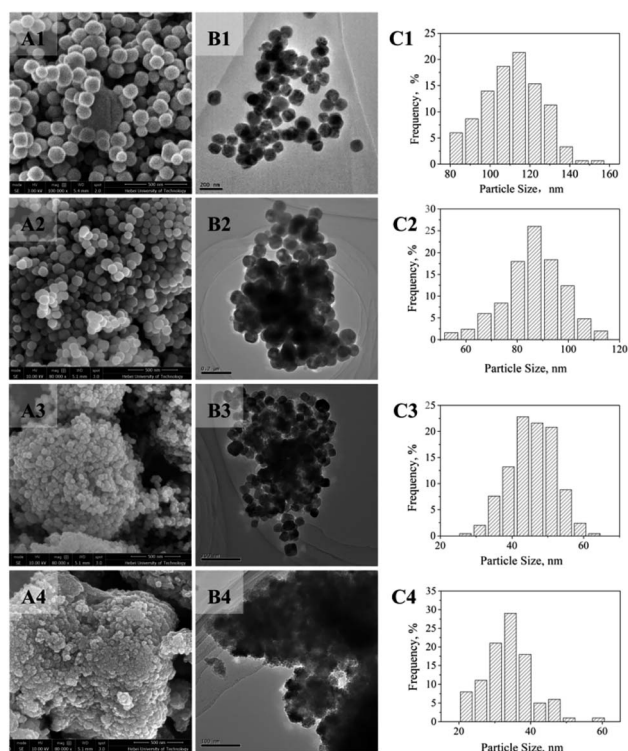


Fig. 3 SEM and TEM images, and particle size distributions, of nano-BaTiO₃. SEM: A1, BaTiO₃-N; A2, BaTiO₃-IL-1; A3, BaTiO₃-IL-3; A4, BaTiO₃-IL-5. TEM: B1, BaTiO₃-N; B2, BaTiO₃-IL-1; B3, BaTiO₃-IL-3; B4, BaTiO₃-IL-5. Size distributions: C1, BaTiO₃-N; C2, BaTiO₃-IL-1; C3, BaTiO₃-IL-3; C4, BaTiO₃-IL-5.

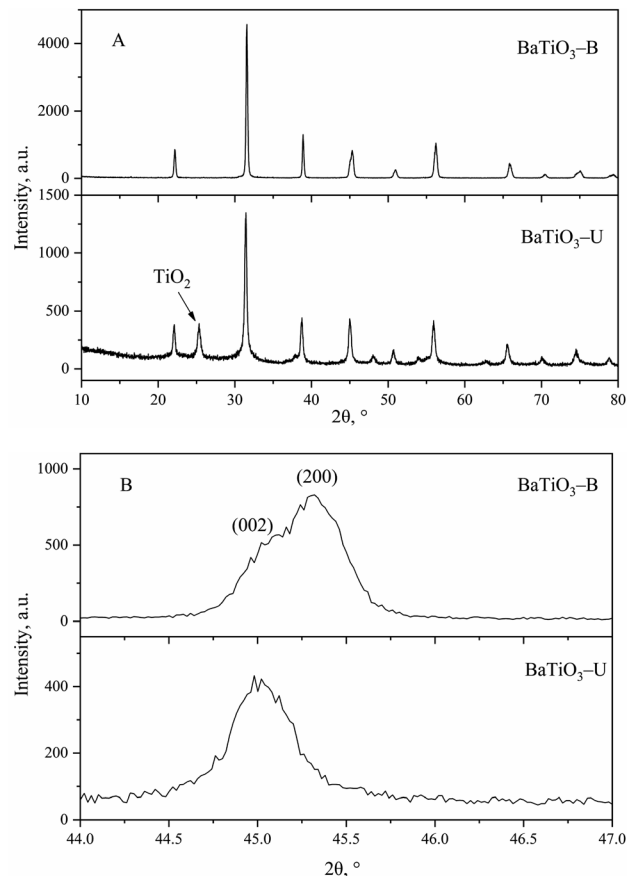


Fig. 5 XRD patterns of BaTiO₃-B and BaTiO₃-U ((A) full range; (B) in the 2θ range of 44.0–47.0°).

increasing quantity of ionic liquid,⁴⁰ which is not conducive to growth of BaTiO₃ microcrystals and thus also led to a gradual decrease in the particle size.

The dielectric properties of the aforementioned BaTiO₃ samples were evaluated at 1000 Hz after processing into ceramics; Fig. 4 shows the dielectric temperature curves. The dielectric constant of BaTiO₃-N with 95% tetragonal phase was

ca. 2500 at room temperature and 8100 at the Curie temperature, and the dielectric loss was very small over the entire temperature range. With the addition of ionic liquid and the increase in the amount of ionic liquid, the dielectric constant of BaTiO₃-IL samples gradually decreased. The dielectric peak at



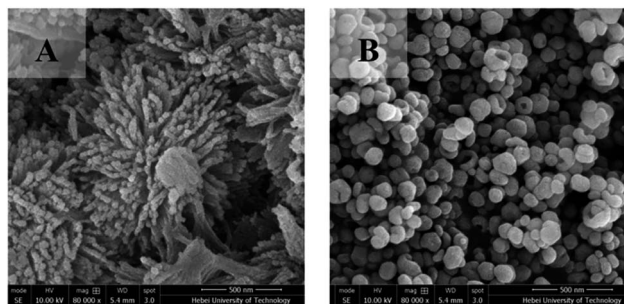


Fig. 6 SEM images of BaTiO₃-U (A) and BaTiO₃-B (B).

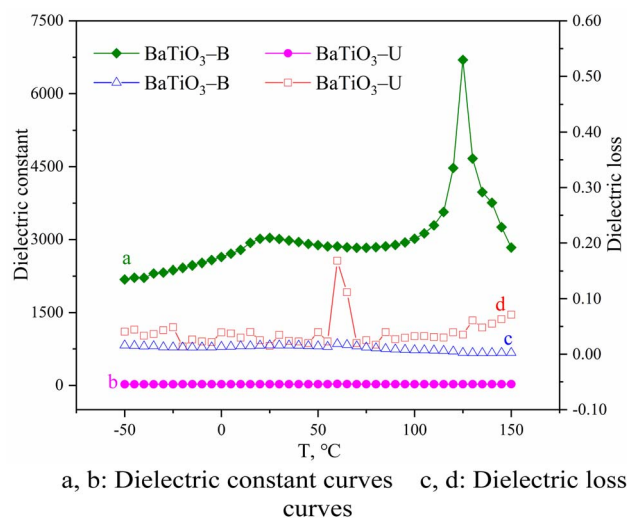


Fig. 7 Temperature-dependence of the dielectric constant and dielectric loss of BaTiO₃ ceramics with different morphologies.

Curie temperature gradually decreased and broadened, and the phenomenon of dielectric dispersion appeared, among which the dielectric loss of BaTiO₃-IL-1 and BaTiO₃-IL-3 did not change significantly compared with BaTiO₃-N samples. The dielectric constants of BaTiO₃-IL-1 and BaTiO₃-IL-3 at room temperature were 1900 and 1300, respectively, and at the Curie

temperature were 4000 and 2000, respectively. When the amount of ionic liquid was increased to 5 g, the dielectric constant of BaTiO₃-IL-5 ceramic sample was very low, only about 40, and remained unchanged with the change of temperature. Its dielectric loss increases significantly. In accordance with these characterization results, the dielectric constant of BaTiO₃ ceramics increased with increasing tetragonal-phase content.

The densities of BaTiO₃-N and BaTiO₃-IL-5 ceramic samples were determined by Archimedes' method, which were 5.78 and 4.9 g cm⁻³, respectively. According to the theoretical density of pure BaTiO₃ ceramics (6.08 g cm⁻³), the relative densities of the two are calculated to be 95.1% and 80.6%, respectively. The low relative density of BaTiO₃-IL-5 ceramic sample is due to the use of a large amount of ionic liquid in the preparation process. Due to the decomposition of ionic liquid in the roasting process, the BaTiO₃-IL-5 ceramic sample is relatively loose. This is also one of the reasons for its poor dielectric properties. Similar results were obtained by Ashokkumar *et al.*⁵² They prepared nano-sized BaTiO₃ with citric acid by hydrothermal method. The average grain size of BaTiO₃ ranges from 10–28 nm, and its dielectric constant is less than 50 when $T < 200$ °C, which increases with the increase of temperature.

Furthermore, the dielectric constants of the BaTiO₃ ceramics were also influenced by the particle size. BaTiO₃-IL-3 and BaTiO₃-IL-5 were both in the cubic phase, but the former exhibited a much larger dielectric constant than the latter because the particle size of BaTiO₃-IL-5 was only 34 nm. In accordance with Ruan *et al.*,⁴¹ with decreasing grain size of BaTiO₃, the volume of the surface layer increased, resulting in incomplete crystallization and thus a smaller dielectric constant. In addition, there is a critical size of BaTiO₃. Upon reducing the grain size to a certain value, BaTiO₃ changes from tetragonal phase to cubic phase. Mandal *et al.*³⁷ suggested that the tetragonal phase content of nano-BaTiO₃ is negatively correlated with the grain size. Li *et al.*⁴² reported that the critical size of BaTiO₃ was 56 nm, and the tetragonal phase was evident only when the grain size was >56 nm. Uchino *et al.*⁴³ obtained the critical size of BaTiO₃ to be *ca.* 44 nm by theoretical calculations. In the present study, the critical size could not be determined precisely because the grain size of the nano-BaTiO₃

Table 1 Comparison of BaTiO₃ prepared by different methods

| Entry | Ti source | Ba source | Preparation method | D_p^a (nm) | Dielectric constant | Ref. |
|-------|--|--|--|--------------|-------------------------------|-----------|
| 1 | TiO ₂ | Ba(OH) ₂ ·8H ₂ O | Hydrothermal | 129 | 8100 (1 kHz) | This work |
| 2 | TiO ₂ | Ba(OH) ₂ ·8H ₂ O | Hydrothermal | 86–34 | 4000–40 (1 kHz) | This work |
| 3 | TiO ₂ | Ba(OH) ₂ | Cold sintering | 122 | 2332 (1 kHz) | 49 |
| 4 | TiCl ₄ | BaCl ₂ ·2H ₂ O | Hydrothermal | 10–40 | 1106 (10 Hz) | 50 |
| 5 | Ti(OC ₄ H ₉) ₄ | Ba(NO ₃) ₂ | Oxalate co-precipitation assisted with microwave | 30–50 | 7823.5 (1 kHz) | 51 |
| 6 | Ti(i-OPr) ₄ | BaCl ₂ | Hydrothermal | 10–28 | <50 (50 Hz–5 MHz) | 52 |
| 7 | TiO ₂ | BaCO ₃ | Two-step calcination | 156 | ~12 800 (1 kHz) | 53 |
| 8 | Ti[OCH(CH ₃) ₂] ₄ | BaCl ₂ | Sol-gel | 120–280 | >120 | 54 |
| 9 | TiO ₂ | Ba(COOH) ₂ | Sol-gel | 287 | 117 (10 kHz, 25 °C) | 55 |
| 10 | TiO ₂ | BaCO ₃ | High energy ball milling | Submicron | 2180 (20 Hz, T _c) | 56 |

^a Particle size.



was not continuous, but the results indicate that BaTiO₃ with a grain size of <46 nm was cubic phase.

3.2 Preparation of BaTiO₃ with various morphologies

BaTiO₃-U was prepared by the hydrothermal method with [Tmospmim]Cl as an additive, and BaTiO₃-B was prepared with PVP as a morphology control agent. Both were characterized (Fig. 5 and 6).

Based on the XRD pattern of BaTiO₃-B (Fig. 5), there was a split peak near 45°, indicating that it contained tetragonal phase. The axial rate *c/a* was 1.0081 and the tetragonal-phase content was *ca.* 90%. In contrast, the XRD pattern of BaTiO₃-U exhibited a single peak near 45°, indicating a cubic-phase structure. In addition, a diffraction peak of TiO₂ was evident in the XRD pattern of BaTiO₃-U,⁴⁸ which is the result of an incomplete hydrothermal process, indicating that adding PVP was not conducive to the reaction between TiO₂ and Ba(OH)₂.

Fig. 6A shows an SEM image of BaTiO₃-U. BaTiO₃-U exhibited a three-dimensional structure; which was a sea urchin-like structure consisting of small, one-dimensional, rod-like grains. The crystal plane energies of (100), (110), and (111) of BaTiO₃ are different, among which the crystal plane energy of (111) is the largest and the growth rate in this direction is also the fastest.⁴⁴ When there was no ionic liquid in the system, the morphology of the product was approximately spherical. Adding an ionic liquid to the solution can inhibit irregular growth of the particles by chelation with one of the crystal surfaces, and control the morphology as well as size of the product. In the present study, the quantity of ionic liquid used for preparing BaTiO₃-U was much larger than that for preparing BaTiO₃-IL, and its effect was more obvious. During formation of BaTiO₃, the ionic liquid adsorbs onto the (100) and (110) crystal planes through chelation, which reduces the crystal energy and decreased the growth rate, thus facilitating growth of BaTiO₃-U along the (111) crystal plane direction and formation of a one-dimensional rod structure. Moreover, the alkyl chains of ionic liquids can assemble and form micelles in water, and the resulting rod-like BaTiO₃ aggregates onto the surface of IL micelles in a manner that forms a sea urchin-like, three-dimensional structure.

Fig. 6B shows an SEM image of BaTiO₃-B. These particles were hollow and bowl-shaped, with an average size of 92 nm. Formation of hollow particles is usually based on the Ostwald ripening mechanism or the Kirkendall effect.^{45,46} From a thermodynamic standpoint, during Ostwald maturation, larger particles are more stable than smaller particles, the latter of which exhibit a higher solubility and the ions that result from dissolution crystallize onto the surface of the larger particles, which further enlarges the particles. During diffusion of the ions, the smaller pores gradually increase and eventually form a hollow structure. The Kirkendall effect arises from the difference in ion diffusion rates at the interface. In a manner that compensates for the difference in diffusion rates during the internal diffusion of metal ions, there is vacancy diffusion, and the limited particle size and structural constraints lead to supersaturation of lattice vacancies, which initiates

a concentration of over-generated interstitial spaces and eventually formation of hollow structures within the particles.

The effect of the BaTiO₃ morphology on the dielectric constant and loss was investigated; Fig. 7 shows the dielectric temperature curves. The room-temperature dielectric constant of BaTiO₃-B ceramics was 3000 and the dielectric constant at the Curie-temperature was 6700.

The density of the BaTiO₃-B ceramic sample was 5.36 g cm⁻³ and the relative density was calculated to be 88.2%. Compared with BaTiO₃-N, which exhibited a large dielectric constant as previously mentioned, BaTiO₃-B exhibited a relatively large room-temperature dielectric constant and a small Curie-temperature dielectric constant. Moreover, the dielectric loss of BaTiO₃-B ceramics was very small, similar to that of BaTiO₃-N. However, the dielectric constant of BaTiO₃-U ceramics was only about 25 and almost not changes with temperature, and the dielectric loss was significantly greater than that of BaTiO₃-B ceramics. As previously mentioned, the magnitude of the dielectric constant of BaTiO₃ is related to the quantity of tetragonal-phase content in the particle; BaTiO₃ with a high tetragonal-phase content exhibited a stronger electric field response. Based on the characterization results, BaTiO₃-U formed by agglomeration of small grains of cubic BaTiO₃, which exhibits no ferroelectricity; thus, its dielectric constant was low with large dielectric loss. In contrast, the content of the tetragonal phase in BaTiO₃-B was *ca.* 90%; thus, it exhibited a large dielectric constant and a small dielectric loss.

Table 1 lists some literature related to the preparation of BaTiO₃ in recent years, and compares them with the results of this work, including preparation methods, raw materials, particle size of the product, dielectric constant, *etc.* Compared with the existing research, this study is that the ionic liquid was added as a template in the hydrothermal synthesis of BaTiO₃, and the smaller size nanoparticles were prepared, with higher dielectric constant and lower dielectric loss. In addition, various morphologies of barium titanate were also prepared by adding ionic liquids or PVP, and its dielectric constant and other properties were investigated.

4. Conclusions

BaTiO₃ nanoparticles were prepared by the hydrothermal method with Ba(OH)₂·8H₂O and anatase TiO₂ as raw materials, and the ionic liquid of 1-(propyl-3-methoxysilyl)-3-methylimidazole chloride ([Tmospmim]Cl) as an additive. BaTiO₃-N nanoparticles prepared without an ionic liquid were spherical, with an average particle size of 129 nm, and the tetragonal content was *ca.* 95%. After adding the ionic liquid, the size of the BaTiO₃-IL decreased and the content of the tetragonal phase gradually decreased until all of the particles changed into the cubic phase. The dielectric property test results indicate that the dielectric constant of BaTiO₃-N ceramics was the highest, decreased with decreasing BaTiO₃ particle size, and the tetragonal-phase content decreased. Cubic-phase BaTiO₃ particles with a sea urchin morphology were prepared by changing the reaction conditions and the dielectric constant was low. In addition, bowl-shaped BaTiO₃-B



particles with an average size of 92 nm and a tetragonal-phase content of 90% were prepared with PVP instead of an ionic liquid. The dielectric constant of the prepared ceramics was 3000 at room temperature and 6700 at the Curie temperature.

Author contributions

Xinxiao Wu: data curation, formal analysis, writing-original draft. Weining Han: data curation, formal analysis. Hegan Zhao: writing review & editing. Zhimiao Wang: writing review, editing. Fang Li: conceptualization, methodology, visualization. Jing Li: supervision, funding acquisition. Wei Xue: supervision, conceptualization, methodology, writing-review & editing.

Conflicts of interest

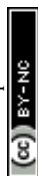
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. U21A20306, U20A20152), and Natural Science Foundation of Hebei Province (B2022202077). We thank Michael Scott Long, PhD, from Liwen Bianji (Edanz) (www.liwenbianji.cn) for editing the English text of a draft of this manuscript.

Notes and references

- H. Qi, L. Fang, W. Xie, H. Zhou, Y. Wang and C. Peng, *J. Mater. Sci.: Mater. Electron.*, 2015, **26**, 8555–8562.
- S. Y. Jun, S. H. Park, N. W. Baek, T. Y. Lee, S. Yoo, D. Jung and J. Y. Kim, *RSC Adv.*, 2022, **12**, 16412–16418.
- H. Meng, Z. Chen, Z. Lu, X. Wang and X. Fu, *Process. Appl. Ceram.*, 2021, **15**, 179–183.
- F. He, W. Ren, G. Liang, P. Shi, X. Wu and X. Chen, *Ceram. Int.*, 2013, **39**, S481–S485.
- P. R. Bhunia, S. Gupta, A. Garg and R. K. Gupta, *J. Polym. Sci.*, 2022, **60**, 961–967.
- G. L. Brennecke, J. F. Ihlefeld, J. P. Maria, B. A. Tuttle and P. G. Clem, *Int. J. Appl. Ceram. Technol.*, 2010, **93**, 3935–3954.
- K. G. Baiju, A. Nagarajan, A. Sadasivam, D. Rajan and D. Kumaresan, *Asia-Pac. J. Chem. Eng.*, 2020, **15**, e2550.
- D. H. Yoon and B. I. Lee, *J. Eur. Ceram. Soc.*, 2004, **24**, 739–752.
- N. Sareecha, W. A. Shah, M. Anis-Ur-Rehman, M. L. Mirza and M. S. Awan, *Solid State Ionics*, 2017, **303**, 16–23.
- C. Baek, J. E. Wang, S. Moon, C. H. Choi and D. K. Kim, *J. Am. Ceram. Soc.*, 2016, **99**, 3802–3808.
- B. B. Jiang, J. Iocozzia, L. Zhao, H. F. Zhang, Y. W. Harn, Y. H. Chen and Z. Q. Lin, *Chem. Soc. Rev.*, 2019, **48**, 1194–1228.
- L. R. Prado, N. S. D. Resende, R. S. Silva, S. M. S. Egues and G. R. Salazar-Banda, *Chem. Eng. Process.*, 2016, **103**, 12–20.
- F. He, *Appl. Chem. Ind.*, 2010, **39**, 1754–1757.
- M. Vijatović, J. Bobić and B. Stojanović, History and challenges of barium titanate: Part I, *Sci. Sintering*, 2008, **40**, 155–165.
- M. Vijatović, J. Bobić and B. Stojanović, *Sci. Sintering*, 2008, **40**, 235–244.
- N. J. Joshi, G. S. Grewal, V. Shrinet, A. Pratap and N. J. Buch, *Integr. Ferroelectr.*, 2010, **115**, 142–148.
- H. Chen and Y. Chen, *Ind. Eng. Chem. Res.*, 2003, **42**, 473–483.
- C. Liu, Y. Liu, C. An, H. Wang and X. Zhou, *Wujiyan Gongye*, 2012, **44**, 16–18.
- Q. Ma, K. Mimura and K. Kato, *J. Alloys Compd.*, 2016, **655**, 71–78.
- M. Inada, N. Enomoto, K. Hayashi, J. Hojo and S. Komarneni, *Ceram. Int.*, 2015, **41**, 5581–5587.
- J. Li, S. Hietala and X. Tian, *ACS Nano*, 2015, **9**, 496–502.
- Y. Zhu, L. Zhang, T. Natsuki, Y. Fu and Q. Ni, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2101–2106.
- R. A. Surmenev, R. V. Chernozem, A. G. Skirtach, A. S. Bekareva, L. A. Leonova, S. Mathur, Y. F. Ivanov and M. A. Surmeneva, *Ceram. Int.*, 2021, **47**, 8904–8914.
- Y. Marfavi, R. Aliakbari, E. Kowsari, B. Sadeghi and S. Ramakrishna, in *Ionic Liquid-Based Technologies for Environmental Sustainability*, Elsevier, Amsterdam, The Netherlands, 2022, pp. 155–166.
- J. Xia, Y. Ge, J. Di, L. Xu, S. Yin, Z. Chen, P. Liu and H. Li, *J. Colloid Interface Sci.*, 2016, **473**, 112–119.
- C. Cruz and A. Ciach, *Molecules*, 2021, **26**, 3668.
- Z. Chen, H. Ma, J. Xia, J. Zeng, J. Di, S. Yin, L. Xu and H. Li, *Ceram. Int.*, 2016, **42**, 8997–9003.
- K. A. Prokop, M. Guzik, Y. Guyot, G. Boulon, M. Wilk-Kozubek, M. Sobczyk, A. V. Mudring and J. Cybińska, *Mater. Sci. Eng., B*, 2022, **275**, 115503.
- J. Łuczak, M. Paszkiewicz, A. Krukowska, A. Malankowska and A. Zaleska-Medynska, *Adv. Colloid Interface Sci.*, 2016, **227**, 1–52.
- X. Liu, J. Ma and W. Zheng, *Rev. Adv. Mater. Sci.*, 2011, **27**, 43–51.
- Y. Zhou and M. Antonietti, *J. Am. Ceram. Soc.*, 2003, **125**, 14960–14961.
- Y. Cao, S. Guo, C. Yu, J. Zhang and G. Li, *J. Mater. Chem. A*, 2020, **8**, 15767–15773.
- M. Paszkiewicz, J. Łuczak, W. Lisowski, P. Patyk and A. Zaleska-Medynska, *Appl. Catal., B*, 2016, **184**, 223–237.
- T. Kim, W. Kim, S. Hong, J. Kim and K. Suh, *Angew. Chem. Int. Ed.*, 2009, **48**, 3806–3809.
- Z. Z. Lazarević, N. Romčević, M. Vijatović, N. Paunović, M. Romčević, B. Stojanović and Z. Dohčević-Mitrović, *Acta Phys. Pol. A*, 2009, **115**, 808–810.
- Y. Xie, Y. Shu, T. Hashimoto, Y. Tokano, A. Sasaki and T. Sato, *J. Eur. Ceram. Soc.*, 2010, **30**, 699–704.
- T. K. Mandal, *Mater. Lett.*, 2007, **61**, 850–854.
- S. R. K. Patel, P. Kumar, C. Prakash and D. K. Agrawal, *Ceram. Int.*, 2012, **38**, 1585–1589.
- X. Duan, J. Ma, J. Lian and W. Zheng, *CrystEngComm*, 2014, **16**, 2550–2559.



- 40 Y. Ding, Y. Cao, Y. Guo, T. Sun, Y. Sun, Q. Ye, J. Li and C. Peng, *J. Chem. Eng. Data*, 2022, **67**, 1350–1357.
- 41 S. P. Ruan, W. Dong, F. Q. Wu, Y. W. Wang, Y. Tu and Z. H. Peng, *J. Phys. Chem.*, 2003, **42**, 17–20.
- 42 X. Li and W. H. Shih, *J. Am. Ceram. Soc.*, 1997, **80**, 2844–2852.
- 43 K. Uchino, E. Sadanaga and T. Hirose, *J. Am. Ceram. Soc.*, 1989, **72**, 1555–1558.
- 44 S. Adireddy, C. Lin, B. Cao, W. Zhou and G. Caruntu, *Chem. Mater.*, 2010, **22**, 1946–1948.
- 45 J. S. Cho, J. S. Park and Y. C. Kang, *Nano Res.*, 2017, **10**, 897–907.
- 46 Y. Liu, Q. Li, S. Gao and J. K. Shang, *J. Am. Ceram. Soc.*, 2013, **96**, 1421–1427.
- 47 P. Yu, W. Liu, P. Gao, T. Shao, S. Zhao, Z. Han, X. Gu, J. Zhang and Y. Wang, *J. Mater. Sci.: Mater. Electron.*, 2022, **33**, 10828–10840.
- 48 E. Song, H. K. Dong, E. J. Jeong, M. Choi, Y. Kim, H. J. Jung and M. Y. Choi, *Environ. Res.*, 2021, **202**, 111668.
- 49 J. P. Ma, X. M. Chen, W. Q. Ouyang, J. Wang, H. li and J. L. Fang, *Ceram. Int.*, 2018, **44**, 4436–4441.
- 50 K. G. Baiju, A. Nagarajan, A. M. G. Sadasivam, D. D. S. Rajan and D. Kumaresan, *Asia-Pac. J. Chem. Eng.*, 2020, **15**, e2550.
- 51 Q. Zhang, J. Chen and M. C. Che, *Ferroelectrics*, 2020, **566**, 30–41.
- 52 R. Ashokkumar, S. Gnanam, K. Senthil Kannan, M. Shanmugaprasanth and S. Karthikeyan, *AIP Conference Proceedings*, AIP Publishing LLC, 2022, vol. 2446, p. 130006.
- 53 L. Zhang, J. Wen, Z. Zhang, J. Yang, H. Huang, Q. Hu, H. Zhuang and H. Yu, *Physica. B.*, 2019, **560**, 155–161.
- 54 W. Han, J. Kim and H. H. Park, *J. Korean Ceram. Soc.*, 2020, **57**, 213–219.
- 55 S. Islam, N. Khatun, M. S. Habib, S. F. U. Farhad, N. I. Tanvir, M. Aftab Ali Shaikh, S. Tabassum, D. Isiam, M. Sajjad Hossain and A. Siddika, *Heliyon*, 2022, **8**, e10529.
- 56 N. K. Verma, S. K. S. Patel, D. Kumar, C. B. Singh and A. K. Singh, *AIP Conference Proceedings*, AIP Publishing LLC, 2018, vol. 1953, p. 050075.

