Preparation and electric-field response of novel tetragonal barium titanate

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1. Introduction

Electrorheological (ER) materials as novel intelligent soft materials have precise and tunable response to an external electric field, which have wide applications in sensing [1,2], electronics [3], damper system [4,5], and vibration control [6]. ER elastomers (EREs), a family member of ER materials, have recently attracted considerable attention [7–10]. In EREs, ER particles (as dispersed phase) are dispersed into polymer network (as continuous phase). When an electric field applied, the polarized particles construct chain or column-like structures in the direction of the electric field. Therefore, the anisotropic microstructure and mechanical property (such as storage modulus) of EREs can be tuned by applying external electric field. So EREs exhibit ER effects which make EREs potentially important in numerous electromechanical devices, such as valves, dampers, clutches in automotive industries, and smart skins in bionic technology [11,12].

In the quest of excellent ER effect of ER materials, intense effort has been expended on preparing highly active ER particles [13–16]. Traditional ER particles, such as barium titanate (BaTiO3) and its analogs [17], have good chemical stability, high permittivity and low dielectric loss. According to literatures [18,19], the origin of ER effect is widely attributed to the polarization of dispersed particles in suspension under an electric field. Comparatively, tetragonal BaTiO3 has a spontaneous polarization trend along the c-axis at room temperature [20], so it is forecasted that tetragonal BaTiO3 particles might have stronger electric field response than cubic BaTiO3. Moreover, tetragonal BaTiO3 has excellent ferroelectric properties, regarded as the most important compound for the manufacture of multilayer ceramic capacitors (MLCC) [21,22]. However, in present, the electric-field response behavior of tetragonal BaTiO3 has rarely been investigated with respect to its’ morphologies.

It is difficult to synthesize expediently tetragonal BaTiO3 with high tetragonality. Up to now, tetragonal BaTiO3 nano-powders, such as nano-sphere [23], nano-torus [24], nano-dendrite arrays [25] and bowl-like nanoparticles [26], have been prepared, but the procedures are too complicated. In this communication, we report a surfactant-free preparation of two tetragonal barium titanate particles with novel morphologies by hydrothermal methods, and firstly report, to the best of our knowledge, electric-field response performance of tetragonal BaTiO3.
particles were synthesized via hydrothermal methods in the following description. Appropriate amounts of Ti(C₂H₃O₂)₄ were dissolved in water to form a Ti precursor solution. Subsequently, fresh Ti precursor and one equivalent amounts of Ba(NO₃)₂ solution were transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed, heated up to certain temperatures and held for 24 h, and then cooled naturally down to room temperature. The products were filtered, washed with diluted formic acid and water for several times, and then dried in a vacuum oven at 60 °C for 12 h. The concentration and adding time of mineralizer KOH, two different processes were adopted. One process was summarized in Fig. 1a through which sample 1 (S1) was synthesized, and another process was shown in Fig. 1b through which sample 2 (S2) was prepared.

2.2. Synthesis of BaTiO₃ particles by modified hydrothermal method

BaTiO₃ particles were synthesized via hydrothermal methods in the following description. Appropriate amounts of Ti(C₂H₃O₂)₄ were dissolved in water to form a Ti precursor solution. Subsequently, fresh Ti precursor and one equivalent amounts of Ba(NO₃)₂ solution were transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed, heated up to certain temperatures and held for 24 h, and then cooled naturally down to room temperature. The products were filtered, washed with diluted formic acid and water for several times, and then dried in a vacuum oven at 60 °C for 12 h. The concentration and adding time of mineralizer KOH, two different processes were adopted. One process was summarized in Fig. 1a through which sample 1 (S1) was synthesized, and another process was shown in Fig. 1b through which sample 2 (S2) was prepared.

2.3. Structure characterization of particles

The phase composition of as-prepared BaTiO₃ powders was identified with Raman spectroscopy (Raman, ALMEGA-TM, Therm Nicolet, America, using a 532 nm excitation of the Nd:YAG laser) and X-ray diffractometer (XRD, D/Max-3c, Rigaku, Kyoto, Japan, using Cu Kα radiation). The particle structures were investigated by scanning electron microscopy (SEM), with a Philips-FEI (Quanta 200) microscope.

2.4. Measurement of the dielectric property of particles

The relative dielectric property of particles was indicated indirectly by the dielectric constants of the suspensions of the particles dispersed in silicone oil. In preparation process of the suspensions, the dried particles with volume fraction of 6% were dispersed in silicone oil (η = 50 mPa s at 25 °C) by mechanical stirring and ultra-sonification. The dielectric spectra of the suspensions was measured by an impedance analyzer (HP 4284A) in the frequency range from 20 Hz to 10⁵ Hz using a measuring fixture (HP 16452A) for liquid [27,28]. 1 V of bias electrical potential was applied to the suspensions. It was so small that no chain formation within suspensions was induced, thus we could obtain the true behavior of interfacial polarization between particles and medium. Therefore, the dielectric properties of BaTiO₃ particles can be compared.

2.5. Measurement of the surface hydrophilic of particles

Hydrophilicity of particles’ surface was measured by an OCA 20 video-based optical contact angle (CA) measuring instrument and the infiltration situation is measured by sessile drop method. The test procedure is described as follows: Firstly, 2.0 wt% BaTiO₃ particles were dispersed into ethanol by ultrasonic wave for 30 min, and another process was shown in Fig. 1b through which sample 2 (S2) was prepared. Secondly, a clean glass substrate (74 mm diameter, and volume of the water drop was recorded and quantified. The values of CA of each particle in text were represented an average value of three separate drops at least.

2.6. Measurement of BaTiO₃ particles electric-field response in hydrorus elastomers

A certain amount of BaTiO₃ particles were ground with gelatin/glycerol/water mixture in the agate mortar which was bathed at 65 °C in an electric-heated thermostat water bath. After BaTiO₃ particles were dispersed evenly in a mixture of gelatin, glycerol and water, small amount of glutaraldehyde was added quickly as cross-linking agent. And then, the mixture was transferred to two plexiglass boxes (40 × 20 × 8 mm³) averagely and cured with or without an external dc electric field (1.2 kV/mm) [7,13] for 50 min from 65 °C to room temperature (remained 65 °C for 30 min, cooled down to room temperature for 20 min). The curing progress went on sequentially for 7 h at room temperature after removing the electric field. Finally, the BaTiO₃/gelatin/glycerin composite hydrous elastomers were prepared, called A-elastomers (cured without any electric field) and B-elastomers (cured with 1.2 kV/mm electric field), respectively [9,29]. In the curing process, dc voltage was applied by a high-voltage dc power supply (regulator range of 0–30 kV) which can deliver electric field strength up to 1.2 kV/mm. Storage modulus of A and B-elastomers were recorded by Q800DMA dynamic viscoelastic spectrometer in static-press multi-frequency mode within the range of frequency 1–10 Hz at room temperature. Each measurement was carried out and repeated at least three times. The difference in modulus (AG) of a pair of A and B-elastomers were explored and electric response of BaTiO₃ particles was investigated indirectly.

3. Results and discussion

3.1. Microstructure and morphology analysis

Based on repetitive experiments, we have found that the hydrothermal condition (≥ 200 °C, 24 h) is guarantee for the formation of tetragonal BaTiO₃ (verdict from XRD and Roman, not shown here). The concentration and adding time of mineralizer (KOH) played an important role in the morphology of BaTiO₃ [30]. The schemes of two processes are shown in Fig. 1.

According to path a in Fig. 1a (respectively 240 °C, 24 h), when mineralizer (KOH) of 0.1, 0.3, 0.7 and 1.0 mol/L was added, BaTiO₃ particles with different shapes were obtained (Fig. 2a–d). It can be found that with increasing of KOH concentrations, BaTiO₃ particles morphology change from amorphous to rods and sticks, and to homogeneous crystal druse, but then unexpectedly go back to unsightly shape (broke into irregular layer). As a result, the finer crystal druse (S1, Fig. 2c) was gained at KOH concentration of 0.7 mol/L. While KOH was added according to path b in Fig. 1b (respectively 220 °C, 24 h), new BaTiO₃ particles were prepared and a corresponding obvious morphology evolution from blocky shape to dendrite was observed (Fig. 2e–h). Similarly, when the concentration of KOH was increased to 0.7 mol/L, the samples (S2) are well dendrite as depicted in Fig. 2g. The preparation conditions of two samples (S1 and S2) are presented in Table 1.

3.2. Structure characterization

Fig. 3 shows the Raman spectra of as-synthesized BaTiO₃ samples (S1–S2) obtained at different temperatures. Four typical
Raman-active phonon modes of BaTiO$_3$ can be identified from S1 to S2 samples: $[A1(TO), E(LO)]$ at 260 cm$^{-1}$, $[B1, E(TO + LO)]$ at 307 cm$^{-1}$, $[A1(TO), E(TO)]$ at 515 cm$^{-1}$, and $[A1(LO), E(LO)]$ at 715 cm$^{-1}$. A weak peak at 185 cm$^{-1}$ contributed from $A1(LO)$ mode of BaTiO$_3$ is observed in the Raman spectrum of S1. Generally, the tetragonal phase of BaTiO$_3$ are identified by characteristic peaks at 307 cm$^{-1}$ [$B1, E(TO + LO)$] and 715 cm$^{-1}$ [$A1(LO), E(LO)$], and disappear when BaTiO$_3$ crystals change from tetragonal to cubic phase [31,32]. All Raman spectra of S1–S2 have peaks at 307 cm$^{-1}$ and 715 cm$^{-1}$, indicating that the as-synthesized crystallites contain tetragonal BaTiO$_3$.

Further evidence for the tetragonal phase in the sample could be found in XRD analysis. For a wide range of XRD measurement from 20$^\circ$ to 60$^\circ$, the scanning rate was 8$^\circ$/min. A slow scan rate of 0.02$^\circ$/min was used for a specific narrow range from 44$^\circ$ to 46$^\circ$. The MDI Jade 5.0 version program was used to determine the lattice parameters [33,34]. XRD patterns of the as-synthesized products (S1–S2) are shown in Fig. 4. All the indexes are in good agreement with tetragonal BaTiO$_3$ (JCPDS No. 5-0626).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morphologies</th>
<th>Temperature ($^\circ$C)</th>
<th>Time (h)</th>
<th>$C_{KOH}$ (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Crystal druse</td>
<td>240</td>
<td>24</td>
<td>0.7</td>
</tr>
<tr>
<td>S2</td>
<td>Dendrite</td>
<td>220</td>
<td>24</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Well-resolved diffraction peaks reveal that these products are tetragonal BaTiO$_3$ crystallites. Moreover, the tetragonal phase of BaTiO$_3$ crystallites can usually be identified from the splitting peaks at 2$\theta$ $\approx$ 45$^\circ$ of (200)/(002) reflections in XRD pattern, while the cubic phase only has one single diffraction peak at 2$\theta$ $\approx$ 45$^\circ$. 

Fig. 2. SEM images of the BaTiO$_3$ samples synthesized with of KOH (a and e) 0.1, (b and f) 0.3, (c and g) 0.7 and (d and h) 1.0 (mol/L), respectively; at (a-d) 240 °C or (e-h) 220 °C.

Fig. 3. Raman patterns of BaTiO$_3$ samples. a: S1, crystal druse and b: S2, dendrite.

Fig. 4. XRD patterns of BaTiO$_3$ samples. a: S1, crystal druse and b: S2, dendrite.

Fig. 5. Dielectric spectra of suspensions containing tetragonal BaTiO$_3$ particle. a: S1, crystal druse and b: S2, dendrite (6 vol.% $T = 25^\circ$C).
possess high tetragonality (c/a ratio) in crystal druse and dendrite particles in the elastomers. The interval of dendrite crystal druse (S1) is stronger than BaTiO3 affects their tetragonal-determines the dielectric property, and the corresponding particles in tetragonal crystal structure with crystal particles. The water contact angle of S1 and S2 are den-

Based on XRD analyses, the lattice parameters of S1 are a = b = 3.9958 Å & c = 4.0324 Å and corresponding value of S2 are a = b = 3.9945 Å & c = 4.0275 Å. Calculated through the indexes of XRD, their tetragonals (c/a ratio) are about 1.0092 and 1.0083, respectively. Therefore, it can be concluded that the as-obtained crystal druse and dendrite BaTiO3 possess high tetragonality (c/a ratio) increasing.

3.3. Dielectric property of tetragonal BaTiO3 particles

The dielectric spectra of suspensions were given in Fig. 5 which is not obviously affected by the frequency fluctuation at room temperature. The relative dielectric property of particles was presented indirectly. Higher dielectric constant of the suspension suggests a higher relative dielectric property of the corresponding dispersed particle. Comparing two BaTiO3 samples, the relative dielectric property of BaTiO3 crystal druse (S1) is stronger than BaTiO3 dendrite (S2), which suggests that the dielectric property increases with particle tetragonality (c/a ratio) increasing.

3.4. Hydropilicity of tetragonal BaTiO3 particles' surface

Fig. 6 shows the contact angles between water-drops and the BaTiO3 particles. The water contact angle of S1 and S2 are 17.8 ± 0.3° and 11.4 ± 0.3°, respectively. They are all less than 35°, which reveals that both S1 and S2 are super-hydrophilic and have a good dispersion property in aqueous medium and good compatibility with hydrosol [37]. Obviously, BaTiO3 dendrite possesses predominant surface hydrophilic capacity and better dispersion property in aqueous medium.

3.5. Electric-field response performance of tetragonal BaTiO3 particles

Fig. 7 shows the relationship between the storage modulus of A and B-elastomers via the frequency at a fixed strain of 1.0%. The curves a (a′)–b (b′) are corresponding to the A- and B-elastomers containing 1.0 wt% S1–S2 cured in absence or presence of an applied electric field, c (c′) presents the storage modulus of the gelatin/glycerin hydrous elastomers without BaTiO3 particles cured in absence or presence of an applied electric field. It is shown that the curves c (c′) almost coincide with each other, indicating that pure gelatin/glycerin hydrous elastomer have no obvious response to an electric field. Curves a (a′)–b (b′) are above c (c′), illustrating the filling role of BaTiO3 particles in the elastomers. The interval of the curves a (a′)–b (b′) are much larger than that of c (c′) forcefully, suggesting that particles S1–S2 dispersed in gelatin/glycerin elastomers have obvious response to the electric field. Comparing the difference in modulus (ΔG) between B- and A-elastomers dispersed with S1 and S2, respectively, ΔG of the elastomers dispersed with S1 is much larger than that dispersed with S2, showed in inset of Fig. 7. The results indicate that BaTiO3 crystal druses have stronger electric response obviously than the dendrites. As far as the tetragonality, dielectric property and surface hydrophilicity of the two BaTiO3 particles concerned, it can be concluded that the particle’s high tetragonality and high dielectric property are the driving force of enhancing the electric response in hydrous elastomers. The main reason may be that the higher tetragonality of S1 in crystal druse shape makes itself easily polarized and conduces to its higher dielectric property. The higher dielectric property of S1 facilitates the stronger “pearl chains" effect [7,9,38,39] and strengthen the modulus of the corresponding B-elastomer, and ΔG of the elastomers dispersed with S1 particles turn larger. Consequently, the response property of the BaTiO3 particles to electric field is in the order of crystal druse > dendrite.

4. Conclusions

The BaTiO3 particles in tetragonal crystal structure with crystal druse and dendrite were prepared and characterized. They are different in morphology, tetragonality and dielectric property. It has been found that the morphology of BaTiO3 affects their tetragonality and dielectric property. In conclusion, the tetragonality of BaTiO3 determines the dielectric property, and the corresponding particles with higher dielectric property show stronger electric field response.

References