A modified Clabaugh method has been used to produce a well-dispersed barium titanyl oxalate tetrahydrate (BTO) powder with a particle size of less than 0.2 μm. Production of the BTO powder is based on a double injection system, with reagents rapidly mixed using pressurized gas. The mixture resulting from the double injection of the reactants was subsequently quenched into a solution containing polyethyleneimine as a dispersant. The resulting dispersed BTO powder forms a suspension that is stable against coarsening or aggregation for greater than 1400 h. The dispersed BTO powder was also shown to produce BaTiO₃ with a particle size of 0.25 μm or less after calcination.

I. Introduction

The ability to achieve high-purity BaTiO₃ from the precipitation of barium titanyl oxalate tetrahydrate (BTO) and subsequent heat treatment of this BTO was first reported by Clabaugh et al. in 1956.¹ The synthesis and thermal decomposition of BTO to the formation of BaTiO₃ has been studied by prior investigations.²–⁶ This topic is of importance since the particle size and morphology of BaTiO₃ produced from the Clabaugh process is directly linked to the particle size and morphology of the precipitated BTO. The primary use of BaTiO₃ is in devices such as capacitors. As the miniaturization of capacitors continues, control of the particle size of BaTiO₃, particularly in the submicrometer regime, is becoming of greater importance.⁷ The goal of the present study was to produce BaTiO₃ by a coprecipitation process with particle sizes comparable to that of BaTiO₃ produced by hydrothermal methods.⁷–⁹ Particle sizes of BaTiO₃ in the range from 60 to 300 nm in diameter are routinely produced in hydrothermal systems.⁷

In preliminary experiments, the traditional Clabaugh process was investigated to determine the feasibility of producing BTO particles on the order of 0.2 μm. A number of issues were defined including variation in particle properties during the course of reactant mixing, agglomeration, and coarsening. It was determined that this size requirement could be reached only by increasing the mole concentrations on the order of 1.05:1.0:2.2M for BaCl₂, TiCl₄, and H₂C₂O₄, respectively. However, preliminary analyses of the product and solution showed considerable deviations as a function of mixing time, leading to wide particle size distributions in the resulting powders. Observation using SEM also showed significant agglomeration of the final product with agglomerate sizes up to tens of micrometers. Within the agglomerates, primary particles were observed on the order of the desired size, 0.2 μm. In addition to agglomeration, the BTO particles also exhibited coarsening over time. The rate of coarsening increased particle size by as much as 100% within a 24 h period. Therefore, a modified process was required to obtain well-dispersed BTO particles with the desired submicrometer particle size.

A modification of the Clabaugh process was used to precipitate BTO from which BaTiO₃ was obtained after subsequent heat treatment. A double injection system was used in which a mixture of barium chloride and titanium tetrachloride are combined at high shear rate with oxalic acid to minimize mixing effects. From this high shear rate mixing, a BTO gel was produced that with additional mechanical agitation and chemical dispersion produced a BTO particle size of about 0.2 μm. Subsequent study of this gel led to the development of a dilution and dispersion scheme with little or no coarsening of particles due to aging effects. Preliminary calcination studies indicate this modification is a possible production alternative for BaTiO₃ produced by hydrothermal methods.

II. Materials and Methods

A double injection system consisting of two holding chambers pressurized by nitrogen gas, shown in Fig. 1, was used in the present study to produce high-shear mixing. The reactants held in these chambers are released and combined at a high shear rate, producing the final product. BaCl₂·2H₂O (ACS grade, Alfa Chemical, Wardhill, MA), TiCl₄ (minimum 99% pure, Alfa Chemical), and H₂C₂O₄·2H₂O (ACS grade, Alfa Chemical) solutions were mixed with various mole ratios. The TiCl₄ solution was prepared by the addition of chilled water to TiCl₄(l) at an initial rate of 10 mL/min while stirring, as described by Clabaugh et al.¹ The TiCl₄ solution was kept refrigerated, which prevented hydrolysis before

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![Fig. 1. Schematic of double injection system. The BaCl₂/TiCl₄ solution and the oxalic acid solution are placed in holding chambers (1) and (2), respectively. The solutions are released from the holding chambers and mixed in (3), where the diameter of the channels in the mixing chamber (X) are 2 mm. The final product is collected in (4).](image-url)
use. The BaCl₂·2H₂O and H₂C₂O₄·2H₂O solutions were prepared by dissolution of BaCl₂·2H₂O(s) and H₂C₂O₄·2H₂O(s), respectively, in water. Calibration of the flow from the two holding chambers was performed to ensure approximately equal flow rates. The mixture of TiCl₄ and BaCl₂ solutions was placed in one chamber, while the oxalic acid solution, preheated to 80°C, was placed directly into the second chamber. The two chambers were then pressurized to ~30 psi. The release valves were simultaneously opened with the resulting product collected in a beaker. In some instances, the final product was delivered directly into a previously prepared solution to provide proper dilution and dispersion. Otherwise, dilution and dispersion were performed after the entire final product had been collected. Dilution and dispersion were accomplished by the addition of DI water and a cationic polyelectrolyte, polyethyleneimine (PEI) (avg MW ~25 000, Aldrich, Milwaukee, WI). Sample BTO1A was freeze-dried for sample preservation (Flexi-Dry Freeze Drier, FTS Systems, Inc., Stone Ridge, NY). A summary of the synthesis conditions is provided in Table I.

Before calcination, sample BTO6 was washed six times to remove chloride. Washing treatments were performed by centrifugation (Marathon 22K Centrifuge, Fisher Scientific, Pittsburgh, PA) in a 10⁻²⁰M HNO₃ (ACS Grade, J. T. Baker, Phillipsburg, NJ) solution. The presence of chloride was tested for by the dropwise addition of a 1M AgNO₃ (ACS Grade, Alfa Chemical) solution to the recovered washing solution, which allowed for detection of chloride concentrations greater than about 10⁻¹⁴ M Cl⁻.

X-ray diffraction (X2 theta-theta powder diffractometer, Scin-tag, Inc., Cupertino, CA) was used to determine crystal structure of the as-precipitated and calcined BTO. A light scattering technique was used to determine particle size distributions and zeta potential of the precipitated BTO particles (Brookhaven Quasi-elastic Light Scattering System, Zeta-PALS Instrument, Brookhaven Instruments Co., Holtsville, NY). Particle size and morphology were

### Table I. Summary of the Experiments Performed Using the Double Injection System

<table>
<thead>
<tr>
<th>Sample ID (concentration)</th>
<th>Preparation conditions</th>
<th>As-precipitated D₅₀ (μm)</th>
<th>Calcined D₅₀ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTO1 (1M)</td>
<td>As precipitated</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Diluted 5:1 DIH₂O:BTO</td>
<td>0.22</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Diluted + 3 wt% PEI</td>
<td>0.22</td>
<td>0.25</td>
</tr>
<tr>
<td>BTO3 (1M)</td>
<td>Dispersed in EtOH</td>
<td>0.37</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Dispersed in oxalic acid</td>
<td>0.37</td>
<td>N/A</td>
</tr>
<tr>
<td>BTO5 (0.25M)</td>
<td>As precipitated</td>
<td>2.0</td>
<td>N/A</td>
</tr>
<tr>
<td>BTO8 (1M)</td>
<td>5:1 DIH₂O:BTO + 3 wt% PEI</td>
<td>0.23</td>
<td>0.25</td>
</tr>
<tr>
<td>BTO9 (1M)</td>
<td>Dispersed in NH₄OH, pH 9</td>
<td>9.9</td>
<td>N/A</td>
</tr>
<tr>
<td>BTO91109a (1M)</td>
<td>5:1 DIH₂O:BTO + 3 wt% PEI</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>BTO91109b (1M)</td>
<td>5:1 DIH₂O:BTO, no dispersant</td>
<td>1.1</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Fig. 2. (A) and (B) are SEM photomicrographs of BTO produced in preliminary experiments. (A) shows an agglomerated BTO powder with a wide distribution in particle size, while (B) shows that submicrometer particles are possible. (C) and (D) are FESEM photomicrographs of BTO6 produced from the double injection system and the resulting BaTiO₃ powder from calcined BTO6, respectively (the grainy texture seen is the Au/Pd sputter coating).
further characterized by FESEM (JSM6300FV field emission scanning electron microscope, Jeol, Inc., Tokyo, Japan) and SEM (S-3500N scanning electron microscope, Hitachi Scientific Instruments, San Jose, CA).

III. Results and Discussion

In the preliminary experiments using the conventional Clabaugh process, primary particle sizes were found within the agglomerates in the range of the desired 0.2 μm. Figures 2(A) and (B) show SEM photomicrographs of selected particles. It was decided that reactant concentrations of 1.05:1.0:2.2M for BaCl₂, TiCl₄, and H₂C₂O₄, respectively, used in the preliminary experiments were sufficient to obtain the desired particle size. Using these concentrations, BTO was precipitated using the double injection system, with a summary of the various synthesis and processing conditions given in Table I. The reaction product from the first run, BTO1A, produced a gel. The gel was diluted by an equal volume of water, centrifuged, and freeze-dried. This sample, designated BTO1A, initially exhibited a particle size of ~0.2 μm. However, the particles exhibited coarsening as a function of aging. A typical change in the particle size distribution with time is given in Fig. 3 for the BTO2B samples. Measurements by DSC/TGA were made on the dried gel from BTO1A and were similar to published data. The XRD results on the unwashed BTO1A powder showed that after calcination at 800°C for 2 h, BaTiO₃ and BaTi₂O₅ phases were present. Observation by SEM showed the BTO1A powder to be agglomerated. Zeta potential measurements gave a negative value (~6.5 mV) for the BTO1A particles in DI water. In future work, zeta potential as a function of pH, [oxalate], and [Ba²⁺] will be determined to provide a more complete view of the solid-solution interface. Nonetheless, given the net negative charge, dispersion treatments were performed on BTO1A, as well as the other indicated samples in Table I using the cationic polyelectrolyte dispersant. PEI. Use of the cationic PEI ensures adsorption of the positively charged dispersant on the negatively charged surface of BTO particles. This adsorption provides efficient electrostatic dispersion of the suspension. Aging experiments showed the dispersion treatments to be stable in excess of 1400 h (~2 months). Median particle sizes as a function of time for the aging experiments are shown in Fig. 4. A portion of the BTO1A powder which had been freeze-dried was dispersible by this treatment as well. When a 0.25M BTO synthesis was attempted, sample BTO3, the particle size was larger than desired (~2 μm). Samples of BTO1B, BTO4, and BTO6 that were calcined to produce BaTiO₃ had little or no increase in particle size from their respective starting BTO powders. The results of the calcination experiments are also summarized in Table I.

In an attempt to make the synthesis process continuous, BTO4 was produced and delivered directly into a solution of water and dispersant. The final product had a median particle size, D₅₀, of 190 nm. This suspension was also found to be stable for greater than 1400 h as indicated in Fig. 4. Similar dispersions were attempted with BTO5 at an alkaline pH of 9, created by the addition of ammonia to water, and with BTO2A in ethanol. Neither of these attempts yielded a stable dispersion, as coarsening of the particles was promoted both under alkaline conditions and by dilution in ethanol. The continuous process was also used to make samples BTO6 and BTO7. The dispersed sample, BTO6, yielded a D₅₀ of 0.15 μm and exhibited the same suspension stability as BTO4. Field emission SEM photomicrographs of sample BTO6 are shown in Figs. 2(C) and (D) for the as-precipitated particles and after calcination to BaTiO₃, respectively. The BaTiO₃ particles obtained after calcination maintain size ranges from 100 to 200 nm.

IV. Conclusion

A modified Clabaugh method, based on a double injection system and dispersion scheme, is reported to precipitate a dispersed BTO with a particle size of less than 0.2 μm. This double injection synthesis method and dispersion scheme precipitated a BTO suspension that was stable for greater than 1400 h. The resulting BTO was shown to produce BaTiO₃, with a particle size of 0.25 μm or less, after further heat treatment.

References


Fig. 3. Particle size distribution changes observed in typical coarsening of BTO powder without dispersant treatment (psd measured in oxalic acid).