Hydrothermal Synthesis of Ferroelectric Materials

by

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Introduction

Since the late 1950s, material scientists and engineers have sought alternative methods for preparation of ferroelectric ceramic materials. One method which has shown promise is called hydrothermal synthesis. Its advantages include the ability to synthesize a wide range of ferroelectric compositions at low temperature, while producing powders or slurries exhibiting excellent homogeneity and crystallinity, and very fine and uniform particle size. Barium titanate has been the most studied material due to its relatively large commercial potential. However, since the 1970s, hydrothermal synthesis has also been investigated for production of piezoelectric and electrooptic materials, as well as those useful for sensors. This paper reviews significant recent developments in hydrothermal synthesis research and practice, and suggests some ideas for new applications.

Hydrothermal Synthesis

Hydrothermal synthesis entails the precipitation of inorganic materials (primarily oxides) from an aqueous solution raised to a temperature near or above its boiling point. The driving force for the precipitation is due to the thermodynamic stability of the precipitated solute in relation to the water soluble metal species and other possible solute phases. Thermodynamic modeling has been used successfully to predict the formation and dissolution of solid phases from solutions under hydrothermal conditions. Hydrothermal synthesis experiments are performed in vessels which can withstand the vapor pressure of the aqueous solution at temperatures above boiling plus any reactive or inert gas phase which is added to or generated in the reactor. For screening studies, small static vessels have been used to identify hydrothermal phase diagrams (typically these include the identity and physical characteristics of the precipitated as a function of precipitation temperature versus pH, gas pressure, or other significant process variables). However, to remove the inherent mass and heat transfer limitations of these vessels, mixed or continuous flow autoclaves are more effective process development tools. In a well stirred vessel, hydrothermal reaction times can be less than 10 minutes, once the optimum temperature is reached. This feature of the process makes it very attractive for large scale commercial applications.

Barium Titanate Manufacture

In the area of advanced electronic ceramic materials, barium titanate was the first to be synthesized by hydrothermal methods. Processes for synthesis are also at the most advanced stage, with many modifications having reached at least the commercial demonstration stage. Cabot Corporation, in the U.S., is now in the process of scaling up...
its process to a commercially viable scale. Sakai Chemical Ind. Co. and Fuji Titanium, both in Japan, have also scaled up hydrothermal processes to at least a scale suitable for production of tens of kilogram of powder. Independently, several investigators are looking at the barium titanate reaction to learn more about the fundamental chemistry of hydrothermal synthesis.

The primary challenges for hydrothermal production of commercial barium titanate, each of which will be discussed in more detail, are listed below:

- Reproducible control of stoichiometry, particularly the compositional relationship between A and B site cations which dictates the firing and electrical properties of the final product. Control of the A:B ratio should be no worse than $\pm 0.001$ which also presents a challenge for analytical measurement and quality control.

- Incorporation of dopants for formulated powders. Adding dopants by conventional methods degrades the final powder properties and loses the advantages offered by hydrothermal synthesis.

- Optimizing ceramic processing methods specifically designed for fine scale powders with surface area in the range of 8 to 12. These powders have been shown to interact with some of the standard binders used for commercial powder manufacture.

- Design of a continuous production system which will allow for reproducible batch or continuous flow reaction, while minimizing capital and operating costs.

The growth of barium titanate grains during the sintering process has been shown to be affected by the stoichiometry of the starting powder. This interaction is particularly acute for fine, more reactive, barium titanate powders. Because hydrothermal synthesis occurs at low temperatures (in the range of 100 to 250 C), the precipitate can have a range of molar A:B stoichiometries on either side of the stoichiometric ratio of 1.000 for BaTiO$_3$. Hence, several methods have been devised for control of stoichiometry.

The Cabot process (see Figure 1) involves two major steps. First a hydrous mixed oxide gel is formed by neutralization of a titanium chloride solution. This gel is washed to remove salt and is dried for storage and characterization. Based on the titanium and dopant concentrations, a slurry of the dried gel is made with purified water which is subsequently mixed with a barium hydroxide (plus other A-site hydroxides) solution to give the desired stoichiometry. The slurry is then reacted in an autoclave at a specified temperature and time to produce a precipitated barium titanate powder.

A modification of this process was developed by Battelle Memorial Institute. In this process, pH and temperature control during the hydrous oxide precipitation and hydrothermal reaction steps was shown to allow for careful control of stoichiometry and particle size. The need for pH control arises from the limited solubility of hydrothermal barium titanate under hydrothermal synthesis conditions. A feed slurry with an A:B
stoichiometry of 1.000 can result in production of a product with less than unity due to incongruent solubility of A-site dopants.

\[ \text{INITIAL HYDROLYSIS} \]

\[ \text{TiCl}_4 + \text{ZrOCl}_2 (\text{or Sn}^{2+}, \text{Hf}^{4+}, \text{etc.}) \]

\[ \rightarrow \text{H}_2\text{O} \]

\[ \text{Titanium, Zirconium Hydrous Oxide} \]

\[ \text{(Ti,Zr)_OH}_2 \text{O} \]

\[ \text{Collect, Wash, and Dry} \]

\[ \text{Add Water, Send Slurry to Reaction Vessel} \]

\[ \text{HYDROTHERMAL REACTION} \]

\[ \text{Ba(OH)}_2 \]

\[ \times \text{MA(OH)}_x (\text{aq}) \]

\[ \rightarrow \text{Mix (Ti,Zr)_OH}_2 \text{O} (\text{aq}) \]

Where MA = Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, Pb\textsuperscript{2+}, etc.

\[ \rightarrow \text{BaMA}_x (\text{OH})_{2x+2} (\text{aq}) \]

\[ \text{Hold Specified Time at Temperature} \]

\[ \text{Collect, Wash, Dry} \]

\[ \text{Package and Store} \]

**FIGURE 1. PROCESS FOR FORMULATED BARIUM TITANATE (CABOT)**

A further modification of the Battelle process involves a post production step. Prior to spray drying the A:B ratio can be enhanced by addition of a barium hydroxide surface layer, or reduced by acid removal of a portion of the barium content. This post-treatment has been shown to have profound effect on sintering behavior (see Figure 2). In a modification by Sakai Chemical, the barium content of the powder was adjusted by precipitation of barium carbonate on the surface of the powder. While this is a good method for stoichiometry control, many studies have shown that carbonate is an undesirable impurity and should be avoided.

**FIGURE 2. SINTERED DENSITY VS. TEMPERATURE AND Ba:Ti FOR (A) LEACHED, AND (B) ENRICHED BaTiO\textsubscript{3}**
Incorporation of dopants directly during the hydrothermal reaction process is possibly the key element for success of the approach. Pure barium titanate is rarely used for commercial applications because of the large temperature dependence of the dielectric constant. This relationship is shown in Figure 3 for some of Cabot's hydrothermal powders. Dopants are added to the A and B-sites to modify this temperature dependence. Often these modifications are made, using conventional ball-mill technology, by powder end users. However, this approach is like using a pipe-wrench to adjust the volume on your stereo. The dopants must be chemically incorporated in order to maintain the homogeneity built into hydrothermal powders. An example of the properties of a doped hydrothermal powder is shown in the Figure 4. Note the very fine and uniform grain size of this ceramic, as well as the relatively flat dielectric constant-temperature curve.

Figure 3. Dielectric Constant vs. Temperature for Hydrothermal BaTiO$_3$

Figure 4. Dielectric Properties and Grain Structure for Formulated BaTiO$_3$
Optimization of ceramic processing techniques, specifically designed for the finer and more reactive powders, is a key to application of hydrothermally synthesized powders. Studies have shown that selection of the correct binder, and optimization of the binder dispersion to minimize binder use are keys to success. For example a reduction in mean ceramic grain size from 1.92 to 0.77 microns was detected when substituting a KD-2/isopropanol binder system for PVB/acetone. Exaggerated grain growth was prevalent when using the latter binder system, even at only very slight deviations from optimum A:B stoichiometry.

Recently, many innovations have been made on design of commercially practical hydrothermal systems. One system which uses a semi-continuous production scheme has been designed by Chemical Engineering Company CEC (Switzerland). This system, depicted in Figure 5, has been scaled up to a vessel size of 6,000 liters. Its primary design features are efficient heat transfer during the heating, control of pressure let-down to eliminate erosion-related contamination and mechanical stress on the crystalline product, and reproducible production cycle. In another development, Battelle Memorial Institute scaled up a continuous pipe reactor which is capable of production of 5-kg per hour at a total hydrothermal reaction time of only 10 minutes.

![Semi-Continuous Production System (CEC Switzerland)](image)

**FIGURE 5. SEMI-CONTINUOUS PRODUCTION SYSTEM (CEC SWITZERLAND)**

Advantages of commercial powders include the ability to tailor the physical properties and to introduce dopants in a chemically homogeneous manner, and the reduction of sintering temperature to 1175 to 1200 C. According to Cabot, the process can be price competitive with current premium barium titanate powders.
Manufacture of PZT and Related Products

Conventional preparation of PZT ceramics is done using the ball-mill and calcination process. The disadvantages of the conventional process are many. Ball-milling operation require several days, making the process best suited to batch operation. The calcination reaction occurs above a temperature where appreciable lead volatilization occurs, thereby requiring the use of extensive scrubbing operations. Because several wet operations are required, drying costs are high. The waste in the process is relatively high due to loss of dust in the scrubber and slurry losses in the ball mills. In addition rejection rates in the process are high due to inhomogeneities in the finished ceramic parts, and to difficulty in control of lead oxide stoichiometry.

Hydrothermal synthesis shows good promise for production of PZT for the following reasons:

- The reaction temperature is relatively low (300 °C), well below that where lead oxide volatilization is a problem;
- Much greater chemical homogeneity is possible because of the ability to control combination of Pb, Zr, Ti, and dopants at a molecular level through control of the chemical synthesis process;
- Control of particle size is much better and finer particles can be produced which result in better reactivity of the green body, higher densities in the finished part and greater mechanical reliability.

In 1988, Morgan Matroc and Battelle initiated a program to determine whether these potential advantages could indeed be realized. The program has now gone through a preliminary scale-up stage and is ready for commercialization. The process is described in detail in a recent patent (U.S. 5,112,433).

Operating conditions and process steps have been optimized using a stirred one-gallon autoclave (Autoclave Engineers). Each laboratory run produced between 100 and 300 grams of PZT powder. Characterization of product by X-ray diffraction showed a single crystal material displaying a lattice parameter which can be calculated based on the contents of Ti and Zr in the crystal structure. Particle size can be controlled over the range of less than 0.01 microns to 1 micron. Particle size distribution is very uniform. An SEM photomicrograph of a typical powder is shown in Figure 6. Estimation of crystallite size by XRD line broadening yields an estimate of roughly one-fourth the particle size estimated by SEM. Therefore, the particles are assumed to be made up of a few crystallites. The shape of the particles mimics that of the cubic crystal structure as is typified by the perovskite structure. Purity of the product powder was greater than 99.8%, the primary impurities coming from the raw materials and corrosion by-products from the 316 stainless steel reactor.

A useful feature of the hydrothermal PZT process is the ability to control particle size. This is probably the key distinguishing feature of the method compared to other processes, e.g., sol-gel and coprecipitation, for preparation of high performance ceramic powders. Laboratory development work on PZT revealed a novel method for control of particle size. The coprecipitation step involves the neutralization of the mixed zirconium and titanium...
acid solution with an inorganic base (sodium, potassium and ammonium hydroxide were used). The pH at the conclusion of this step can be controlled within the range of 5 to 11.8, while still achieving complete conversion of metal chlorides to a mixed metal hydroxide oxide. The pH endpoint has been shown to impact the particle size and shape and the composition of the precipitated oxide formed in the hydrothermal reaction. It has been postulated that variations in pH affect the structure of the hydrous oxide gel, as well as the level of trapped salts, acids, and bases. These changes can result in a nearly threefold change in particle size from 0.40 microns to over 1.00 micron.

In a scale-up program, batches of PZT powder were prepared in a 20-gallon capacity Autoclave Engineers stirred vessel. The vessel was equipped with an internal thermocouple, agitator, and containment liner constructed of a corrosion resistant material. Conditions for peripheral process steps were fixed at the optimum conditions determined from laboratory batch work. Results of the larger scale tests showed that electrical properties, physical characteristics, control of composition were all matched, and purity was improved compared to the original batch scale tests. Particle morphology was nearly identical and the size distribution was very tight. A histogram showing particle size distribution for a one-micron product is given in Figure 6. The average spherical equivalent particle diameter was 1.03 microns, with ninety percent of the particles having a diameter of between 0.77 and 1.29 microns. Electrical properties of ceramics for conventional and hydrothermal powders are compared in Table 1 (Near, 1993). Ceramics made with pilot hydrothermal powder demonstrate a greater than 30 percent increase in coupling factor. This was despite the fact that the purity of ceramics were equal.

FIGURE 6. PARTICLE MORPHOLOGY AND SIZE DISTRIBUTION FOR HYDROTHERMAL PZT
TABLE 1. SELECTED PROPERTIES OF CONVENTIONAL AND HYDROTHERMAL PZT-4 CERAMICS (MORGAN MATROC)

<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>DoD 1376 TYPE I</th>
<th>Conventional Average</th>
<th>Conventional Best</th>
<th>Hydrothermal</th>
</tr>
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<tr>
<td>$K_{33}^T$</td>
<td>1275</td>
<td>1354</td>
<td>1369</td>
<td>1461</td>
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<tr>
<td>$d_{33}$</td>
<td>290</td>
<td>304</td>
<td>334</td>
<td>362</td>
</tr>
<tr>
<td>$k_p$</td>
<td>0.58</td>
<td>0.561</td>
<td>0.577</td>
<td>0.601</td>
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<tr>
<td>$Q_M$</td>
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<td>709</td>
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<tr>
<td>density</td>
<td>&gt;7.45</td>
<td>7.71</td>
<td>7.72</td>
<td>7.66</td>
</tr>
</tbody>
</table>

Other Ferroelectric Materials

Hydrothermal synthesis is particularly well suited to production of most important electronic ceramics in the perovskite family. These include compositions based on barium titanate, barium strontium titanate, lead zirconate titanate, lead titanate, lead lanthanum zirconate titanate. A notable exception are the relaxor compositions in the lead magnesium niobate family. These compounds tend to form in the pyrochlore crystalline modification, also a common problem in conventional manufacture.

Conclusions

Hydrothermal synthesis remains an important tool for production of improved ferroelectric raw materials. Efforts toward commercialization of this technology continue in the U.S., Europe and Japan. It is anticipated that hydrothermally derived powders and ceramic products will be commercially available in the very near future. Commercial prospects are brightest for fine scale dielectric and piezoelectric devices, and those requiring improved physical and electrical properties for special applications.