Surface Functionalization of Barium Titanate Nanoparticles

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Abstract:

Barium titanate nanoparticles were synthesized using an aqueous coprecipitation reaction with barium hydroxide and titanium n-propoxide at a temperature of 90°C. A surfactant was added to cap the particles in order to inhibit particle growth and agglomeration. A variety of surfactants were used: anionic, cationic, and non-ionic. The samples were then analyzed using a series of techniques including x-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), scanning electron microscopy (SEM), dielectric measurements, and secondary harmonic generation. Based on XRD, the particles were cubic in nature with average size varying from 25-50 nm. FT-IR spectroscopy was used to measure the effectiveness of the capping agents. The influence of these capping agents on size, structure, and dielectric properties of the $BaTiO_3$ powder is discussed.

Introduction:

High dielectric nanoparticles have caught the attention of researchers due to their higher efficiency and other unique properties that could be obtained at this size scale. Ferroelectric materials exhibit very high dielectric constants, due to their noncentrosymmetric unit cells. However, there seems to exist a critical size below which the particles take on a cubic system [1]. Despite the lack of ferroelectric properties, the materials still retain high permittivity. This project focuses on the creation of $BaTiO_3$ nanoparticles. $BaTiO_3$ was chosen because it is a well studied ferroelectric material in bulk form.

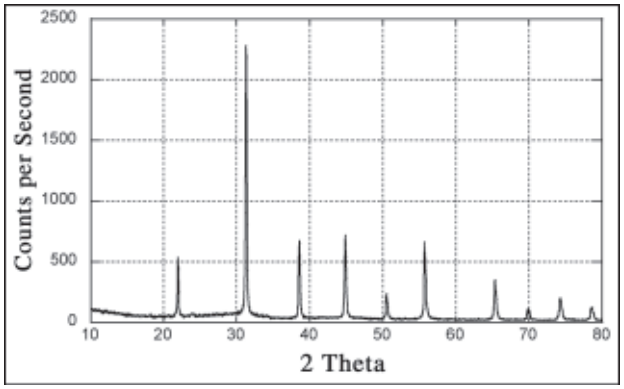

Figure 1: θ–θ x-ray scan of $BaTiO_3$ sample. All peaks coincide with $BaTiO_3$ except small peak located at 23.9°.

Procedure:

$BaTiO_3$ was synthesized using an aqueous coprecipitation reaction based on the LaMer method [2], using Barium Hydroxide and Titanium n-propoxide as the reactants Nitrogen gas was bubbled through the solution in order to hinder the formation of $BaCO_3$, an unwanted impurity. The pH of the solution is controlled using NaOH. A basic solution is required for both the formation of $BaTiO_3$, and to increase the effectiveness of the surfactant. The reaction occurs over 24 hours at 90°C. After this time the surfactant is added. The suspended powder is rinsed and dried in a vacuum for 12 hours.

Results and Conclusions:

Each sample yielded a white powder, which was then analyzed using the theta-theta technique for powder x-ray diffraction. As can be seen in Figure 1, the scans conclusively showed that the samples were cubic $BaTiO_3$, and that there were traces of $BaCO_3$. The $BaCO_3$ forms in rod-shaped particles [3], unlike $BaTiO_3$ which forms sphere-like particles. This was supported with the SEM images which showed rod-shaped particles amongst the $BaTiO_3$ particles.

Average particle size measurements were obtained from the x-ray data using Scherrer's formula [4]. The full width half max of the largest peak was measured using a Reitveld refinement technique. This calculation gave particle sizes in the range of 30 to 50 nm, with no significant difference between the types of surfactants used.

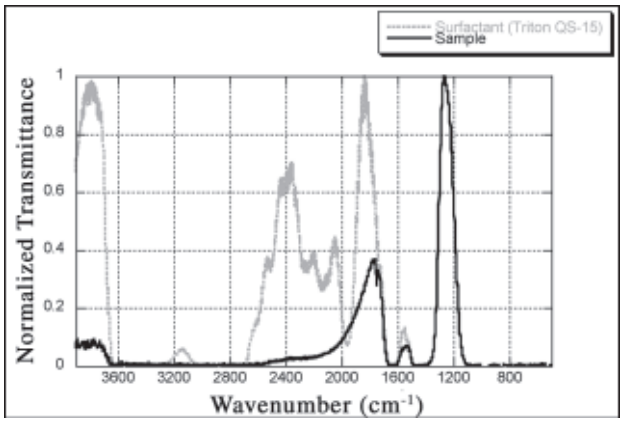

Figure 2: FT-IR comparison of a sample and surfactant. The scans were normalized to one.

Fourier Transform Infrared Spectroscopy (FT-IR) was used in order to determine if the surfactant remained on the particles. These scans were used to compare the sample absorption spectra to pure surfactant absorption spectra to qualitatively determine if the capping agent remained on the sample. An example of the data comparison can be seen in Figure 2. There is a large amount of matching in the range from 1900 cm^{-1} to 1400 cm^{-1}, which implies that the surfactant is present in the end sample.

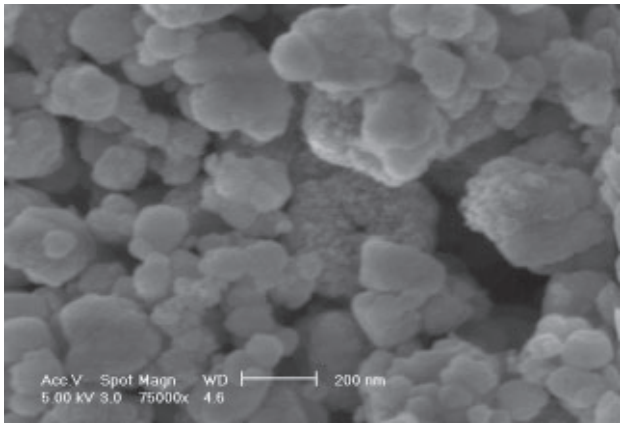

Figure 3: SEM scan of $BaTiO_3$ sample. Notice the different particle sizes and agglomeration.

To get a closer look at the particles SEM and TEM were performed. The SEM pictures, as seen in Figure 3, show particles of different sizes and possible agglomerations. Some of the particles appear to be much larger than originally thought by the x-ray scans. This observation is probably due to the upper limit of Scherrer's formula, about 100 nm [4]. In order to determine if the particles agglomerate post growth, or grew in the raspberry-like formations, TEM was used. The TEM scans showed that they were most likely agglomerations. Also, the scans showed that the samples were not 100% crystalline. Once again the type of surfactant used showed no difference in the electron microscopy scans.

Dielectric measurements of the samples were taken using pellets of various densities with a dielectric test fixture on an Agielent Impedance analyzer. The experimental dielectric constants ranged from 20 to 50. These numbers are much lower than the theoretical value of 80. A comparison of dielectric constant to density was plotted along with a simple model based on the rule of mixtures using $BaTiO_3$ and air for the components. These plots, Figure 4, do coincide, which implies that density, not surfactant type, accounts for most of change from theoretical values.

Overall no significant differences were seen in the types of surfactants used. This could be due to the fact that all, or none, of the surfactants partially bonded to the surface. Another reason could be the interference of the alcohol groups associated with the Ti n-propoxide. The particles did show small particle size, though perhaps not in the nanometer range. Furthermore, based on the FT-IR scans some type of surfactant was present on the samples.

Future Work:

Work that needs to be completed on this project in the future includes further FT-IR scans, dielectric scans at lower frequencies, and quantitative analysis of the substance remaining on the particles. FT-IR scans can be used to help quantify the material left on the particles. Lower frequency dielectric scans would be better suited for these particles, and allow more data to be collected.

Acknowledgements:

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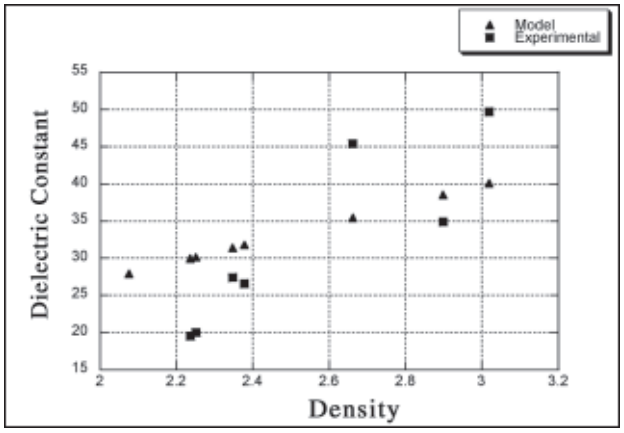

Figure 4: Comparison of experimental dielectric constants & a model based on a mixture of $BaTiO_3$ & air.