Nanostructured Barium Titanate Prepared in Microemulsions

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The present project studies the synthesis of well-defined nanometer sized BaTiO$_3$ particles by a microemulsion synthesis method. The overall project includes synthesis, processing, and sintering of a multilayer device. However, at this point only synthesis-related results will be presented.

1. INTRODUCTION
Nanostructured materials exhibit a tremendous potential for novel electronic applications and a few publications have addressed the formation of nanometer-sized barium titanate particles by various techniques.$^{1-4}$ One very interesting approach is the use of microemulsions. The latter synthesis technique allows for a very precise control of the particle size. By a particular choice of the surfactant/solvent combination even the chemical structure within the individual particles can be influenced. The particles are also extremely well dispersed, since the surfactant layer surrounds them. This latter fact is tremendously important in order to achieve high green densities. The layer acts as a steric repulsion between the particles and allows them to slide against each other. Particles then find their ideal position and higher green density results.

2. BACKGROUND
During the past decade substantial progress has been made in the area of microemulsions. A microemulsion system is essentially a water-oil-surfactant mixture. Depending on temperature and the concentration of each constituent various microstructures can be formed, e.g. micelles, reverse micelles, lamellar liquid crystal or hexagonal rod like structures. Fig. 1 shows a typical phase diagram for the H$_2$O / pentanol / sodium dodecyl sulfate (SDS) system. Numerous other surfactant

Fig. 1 Phase diagram water / pentanol / SDS$^5$
Microemulsions were prepared at room temperature by mixing the various chemical constituents in cleaned glass flasks or sample vials. All liquids and solutions were filtered through 0.45 µm Teflon filter cartridges beforehand. Two different methods were employed in the actual precipitation process. First, a dual microemulsion method was used, which had barium and titanium salts as precursors in one microemulsion and precipitation was introduced by adding a second microemulsion, which contained oxalate or carbonate ions. The second method, which utilized only one microemulsion, was applicable to barium or titanium alkoxides. Here an initial microemulsion was formed from water, oil and surfactant. A second solution of the alkoxides in the oil phase was then slowly added to the initial microemulsion and precipitation occurred within the water droplets by diffusion of the alkoxides towards the droplet interface. The alkoxides are extremely reactive and especially the barium alkoxide had to be handled and stored absolutely water-free in a glove-box environment. The particle size was confirmed by transmission electron microscopy and with a photo correlation spectroscopy instrument, Brookhaven 90 Plus.

3. EXPERIMENTAL PROCEDURES

Results of the concentrations of the various chemical constituents and the reaction temperature between 0°C and 50°C have been studied. The range within each phase diagram, which formed a reverse microemulsion changed at different temperatures and depending on the chosen reaction temperature different compositions had to be used. In general, lower temperatures favored a surfactant rich composition whereas a more oil-rich composition was needed at higher temperatures. The droplet size also changed with temperature and larger droplets formed at the higher temperatures. An increase of up to a factor of 2 was noticed in some of the systems. The barium or titanium salt concentrations also decreased the compositional range where a microemulsion formed due to the interaction of the ionic species with the polar head-group of the surfactant molecules.

In another approach truly nanosized titania particles were precipitated first and in a second step barium was precipitated onto the existing titania seeds. A major problem in this approach was the formation of aggregates during or prior to the coating step. Lower concentrations of all reactive species as well as a slow addition process of the barium precursor component were critical for a successful coating process.

In both processes barium titanate particles could be produced with typical particle sizes of 10 to 30 nm. The samples are well dispersed as could be seen in transmission electron micrographs. However, the chemical composition was not perfect. The barium precursor did not react completely and as a result slightly titanium rich materials resulted after calcination of the powders at 800°C. The effect will be corrected in the next couple of experiments either by increasing the concentration of the barium precursor or by an increase of the reaction efficiency either by longer reaction times or more drastic chemical conditions, e.g. higher pH or higher oxalate/carbonate concentrations.

Some of the systems showed crystallinity already after the precipitation at room temperature, whereas others needed an additional calcination step.

5. CONCLUSIONS

Nanosized barium titanate particles have been produced and in part the materials were already crystalline after the room temperature synthesis. However, a very critical step in terms of control of the overall chemical composition and/or the incorporation of dopants has to be further developed. The work is to be seen as an initial step and many further improvements have to be made within the reaction system. Including the development of a specific recycling process for all constituents. However, microemulsion synthesis provides the means to produce nanosized barium titanate in a very economic way. The second major advantage of this specific synthesis process is the agglomerate free dispersion state of the powder after the synthesis.

6. REFERENCES