SYNTHESIS OF CRYSTALLINE AND PURE $BaTiO_3$ POWDERS AT 90°C

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Abstract

Sub-micron (150-200 nm), monosize and spherically-particulated powders of $BaTiO_3$ have been prepared by "hydrothermal synthesis" at 90°C in ordinary atmospheres. The slightly modified hydrothermal synthesis procedure adopted in this work did not necessitate the utilization of strict and expensive measures commonly required for the removal of free CO_2 present in the atmosphere. The produced powders were crystalline, pure, and did not contain $BaCO_3$ as an impurity phase. $BaTiO_3$ powders synthesized at 90°C did possess the cubic (space group: *Pm-3m*) crystal structure. Sample characterization is achieved by XRD, SEM, EDXS and Rietveld Analysis.

1. Introduction

The ceramic compositions (pure and doped) of $BaTiO_3$ have been one of the main constituents of the "type II" dielectric materials and of multilayer ceramic capacitors. It has been a widely acclaimed conception since the early 1960's that the dielectric properties of these ceramics are closely related to the grain size in their microstructures. $BaTiO_3$, depending on the synthesis procedure utilized and temperature, may exhibit four different polymorphic forms [1-4]. Among these four polymorphs of $BaTiO_3$, the cubic form (space group: *Pm-3m*) is "paraelectric," and the other three (tetragonal: *P4mm*, orthorhombic: *Pmm2*, and rhombohedral: *R3m*) are "ferroelectric."$BaTiO_3$ is of the tetragonal symmetry from room temperature upto its Curie temperature (T_c: ~ 128°C), and above T_c it adopts the cubic symmetry. When the ambient temperature is below T_c, $BaTiO_3$ is ferroelectric, and when the temperature is above T_c it becomes paraelectric [5-6]. The change observed in the crystal structure of barium titanate at its T_c could also be monitored by the significant change (from about 1000 to 11000) that simultaneously occurs in its dielectric constant. It has also been shown that the average grain size in the microstructure of $BaTiO_3$ turns out to be quite influential on its dielectric constant [7-8]. It is now a well-established fact that the decrease to be achieved in the average grain size (from 50 μm to ~ 1 μm) of the sintered ceramic microstructure of $BaTiO_3$ would show itself up in the form of an increase in its dielectric constant (RT) from 1000 to about 5000 [9-15]. To this reason, it has been an important concern in the synthesis of $BaTiO_3$ ceramics that any precautions which would be taken towards the precise control and consistency to be gained over the microstructural *particle* (pre-sintering) and *grain* (post-sintering) sizes will directly influence the electronic properties of the final product.

The preparation of monosized and crystalline $BaTiO_3$ powders by using hydrothermal synthesis has been known for a long time. This process uses the starting materials of water-soluble inorganic $Ba(OH)_2$ salts and insoluble TiO_2 powders to be mixed in an aqueous solution kept at a temperature near its boiling point for prolonged times. Hydrothermal synthesis involves the formation of crystalline materials from the starting materials in an

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2. Experimental Procedure

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Particle size and
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were, first, sputter coated wit
EDXS (Kevex, USA) analys
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runs were believed to be accu

3. Results and Discussion

The precipitates of Ba
for 72 hours were already
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$BaTiO_3$ powders did have a
XRD pattern (which has a
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[*] ***Patent pending***, Dr. A. Cüne

aqueous medium under strongly alkaline conditions. Thus accredited hydrothermal processing of $BaTiO_3$ powders has always been prescribed to utilize a certain quantity of excess barium hydroxide in the starting mixture to speed up the hydrothermal reactions [16-20]. Lencka and Riman [21] showed that successful preparation of $BaTiO_3$ by hydrothermal processing required a pH>12 in the aqueous solutions kept near the boiling point. They also stressed out the importance of eliminating CO_2 from the reaction vessel to avoid the formation of $BaCO_3$.

The present study focuses on the quest for finding an economical and alternative remedy to the problem of "$BaCO_3$-contamination" in hydrothermally synthesized (in habitual atmospheres) $BaTiO_3$ powders.

2. Experimental Procedure

Sub-micron, spherical $BaTiO_3$ powders were synthesized from the mixtures of *proprietary amounts*[*] of $Ba(OH)_2.8H_2O$ (*+99.9%, Riedel-de Haën AG, Germany*) and TiO_2 (*+99.9%, Riedel-de Haën AG*) placed in Teflon beakers together with a certain quantity of distilled water. Ordinary glass jars were used as "sealed" reaction vessels. The constant temperature of 90°C, required for prolonged times of aging, was maintained in a microprocessor-controlled (± 1°C) laboratory sterilizator. The aged precursors were washed several times with a *proprietary,*[*] extremely diluted acidic solution, and then filtered out from the supernatant liquor. The washed precipitates were then dried at 90°C overnight.

Powder X-ray diffraction spectra were obtained from the dried samples (at 90°C) for phase characterization purposes. A Rigaku DMax/B powder diffractometer was used with FeK_α radiation at the step size of 0.02° and a preset time of 1 second for the runs performed to accomplish phase characterization and to check the purity of the synthesized $BaTiO_3$ powders.

Particle size and morphology of the powders were monitored from the photomicrographs taken with a JEOL/ JSM6400 scanning electron microscope. The samples were, first, sputter coated with an approximately 25 nm-thick layer of gold-palladium alloy. EDXS (Kevex, USA) analysis were carried out on the samples to perform a semi-quantitative analysis for the determination of the elemental distribution in the powder samples. The EDXS runs were believed to be accurate to about ± 3 wt%.

3. Results and Discussion

The precipitates of $BaTiO_3$ aged (in a Teflon beaker placed in an ordinary jar) at 90°C for 72 hours were already crystalline and had the cubic (paraelectric) crystal structure displayed in Figure 1 below. The dodecahedra formed by the BaO_{12} groups describe the cubic perovskite structure. XRD analysis showed that the unit cell of the hydrothermally synthesized $BaTiO_3$ powders did have an isometric lattice parameter, a = 4.0186 Å. The experimental XRD pattern (which has a better refinement quality with ***M(13)*** = (639, 0.000049), and precision than the already present file-card, No: 31-174, for this phase in the JCPDS PDF database) generated from these samples is given in Table 1. This pattern will be submitted to the JCPDS PDF database for evaluation and for a possible replacement of the present

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[*] ***Patent pending***, Dr. A. Cüneyt Taş, Turkish Patent Institute, June 1996, File No: ***34295***

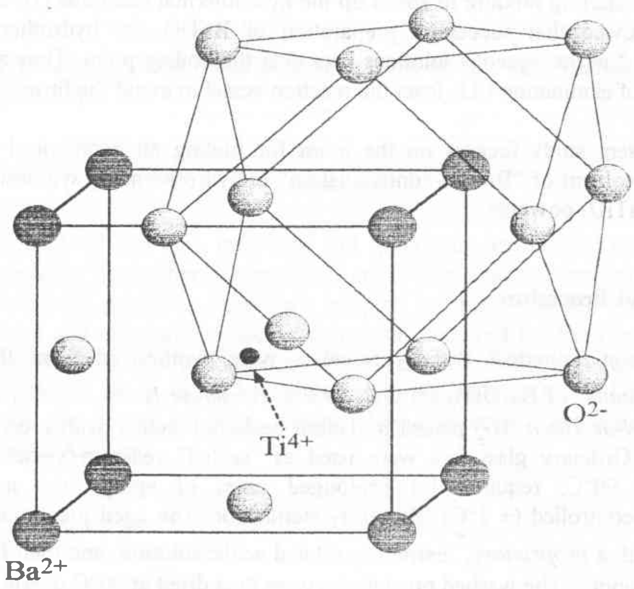

Figure 1. Crystal structure of hydrothermally synthesized (90°C) $BaTiO_3$ (*Cubic: Pm-3m*)

Table 1. The experimental XRD pattern of cubic $BaTiO_3$ (Pm-3m) hydrothermally synthesized at 90°C

hkl	d_{calc}	d_{obs}	I/I_0
100	4.0185	4.0200	21
110	2.8727	2.8420	100
111	2.3201	2.3205	22
200	2.0093	2.0099	28
210	1.7972	1.7973	7
211	1.6406	1.6406	24
220	1.4208	1.4209	12
300	1.3395	1.3395	4
310	1.2708	1.2708	9
311	1.2116	1.2116	5
222	1.1601	1.1600	5
320	1.1145	1.1145	2
321	1.0740	1.0740	11

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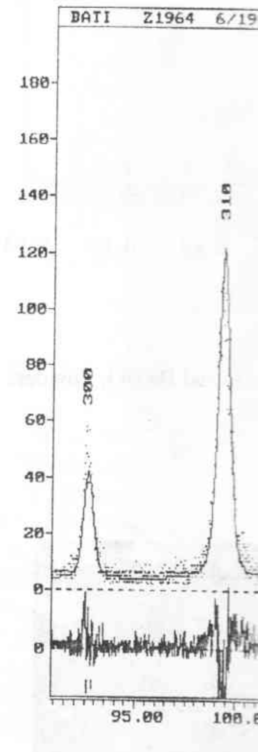

Figure 2. The Rietveld p

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file-card for cubic $BaTiO_3$. The powder samples of cubic $BaTiO_3$ synthesized (and then dried) at 90°C were checked for phase purity (and for the possible existence of its tetragonal polymorph in the powders) by Rietveld analysis [22-25]. XRD data to be used in these analysis were collected by using a step size of 0.02°, and a count time of 5 seconds. Pseudo-Voigt profile function was used, and the lattice parameters, as well as the preferred-orientation, asymmetry, temperature, scale, mixing, halfwidth and background parameters were refined to a final R_{wp} of 5.51%. A typical Rietveld plot obtained is depicted in Figure 2. It shows that the prepared $BaTiO_3$ powders are pure and does not contain the tetragonal phase. The FWHM values obtained from the Rietveld runs were utilized to determine the average crystallite size of the synthesized $BaTiO_3$ powders by using the Warren-Averbach method [26], and it was found to be around 11 Å as shown in Figure 3.

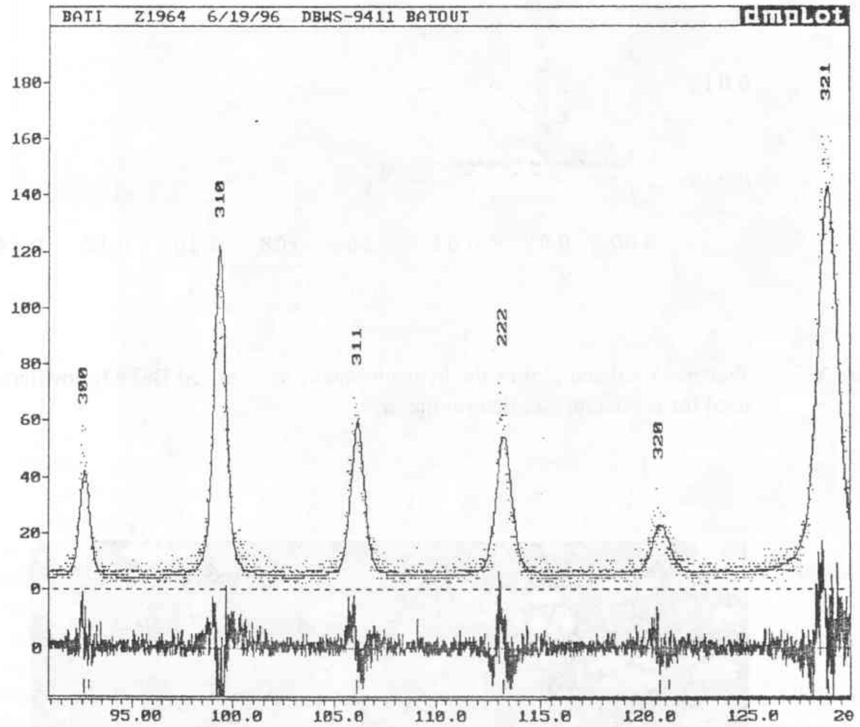

Figure 2. The Rietveld plot of hydrothermally synthesized $BaTiO_3$ powders

The morphological features of the hydrothermally synthesized powders of $BaTiO_3$ were examined by electron microscopy. Figure 4 displays a typical SEM micrograph of the 90°C spherical powders with an average particle size of 150 nm. A certain degree of agglomeration is present in the powder body and can be seen in Fig. 4. The extent of this

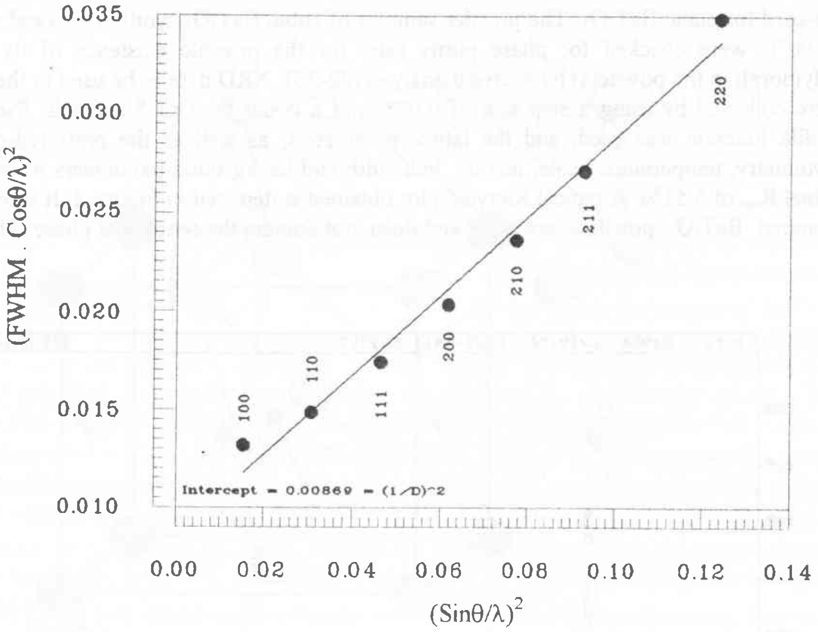

Figure 3. Warren-Averbach plot of the hydrothermally synthesized $BaTiO_3$ powders used for crystallite size determination

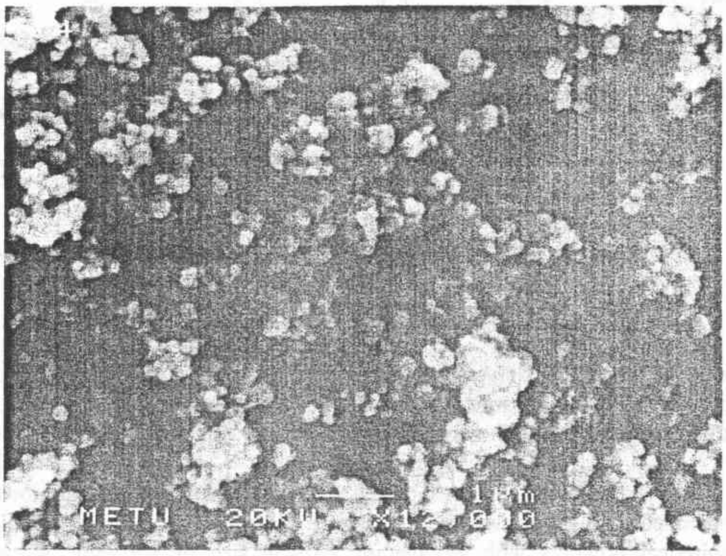

Figure 4. SEM micrograph of the hydrothermally synthesized (90°C) $BaTiO_3$ powders

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agglomeration of the spherical particles is believed to be influenced by the concentration of the cations in the reaction vessel and the time of aging.

The synthesized $BaTiO_3$ powders were cold and uniaxially pressed (at 50 MPa) in hardened steel dies into 1.2 cm diameter and 4 mm thick circular pellets for the study of their sintering behaviour. The produced pellets were heated at 1200°C, in a stagnant dry air atmosphere, for 6 hours. The fracture surfaces of the sintered pellets were then examined via SEM. Figure 5 shows a typical micrograph of those heated pellets, displaying an average sintered grain size of about 500 nm and about 15% residual porosity. The determination of the exact sintering characteristics of these powders does apparently warrant a further, detailed study, and thus, could not be contained within the context of the present work.

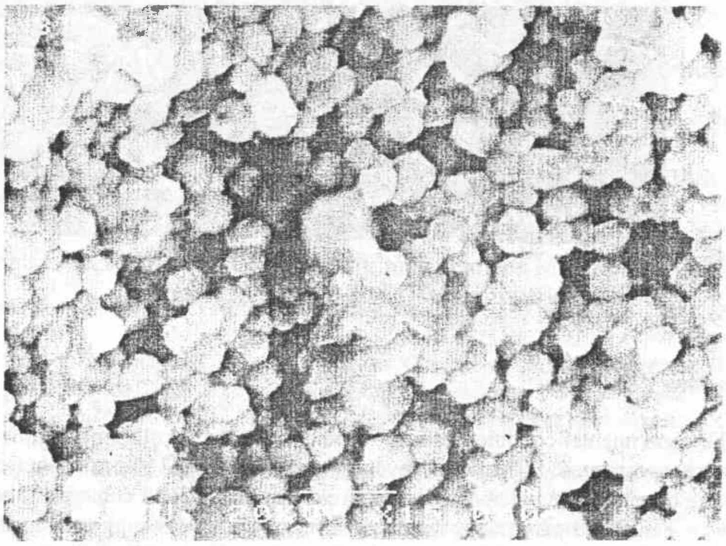

Figure 5. SEM micrograph of the typical fracture surface of pressed $BaTiO_3$ samples heated at 1200°C for 6 hours.

The effect of initial (*and intentional*) non-stoichiometry, in the starting materials ($Ba(OH)_2.8H_2O$ and TiO_2), on the as-sintered morphology has also been studied. Figure 6 shows a typical SEM micrograph taken from the fracture surfaces of pellets prepared from powders with about 2 mol% excess TiO_2 (in the pre-sintered, washed powders), after being heated at 1250°C for 17 hours. Even the slightest excess of TiO_2 in the initial mixture is already known [27] to cause *exaggerated* grain growth (with occasional grains of sizes in the range of 20 to 30 μm) in the sintered microstructures. The presence of excess TiO_2 is believed to induce the formation of a $BaTiO_3$-$Ba_6Ti_{17}O_{40}$ eutectic at high temperatures. The sligthest presence of such a eutectic liquid at the sintering temperatures promotes grain growth, especially at slow heating rates. The sample depicted in the SEM micrograph of Figure 5 possesses the *proprietary* stoichiometry referred to in the present study, and therefore, it does not have the above-mentioned excess TiO_2.

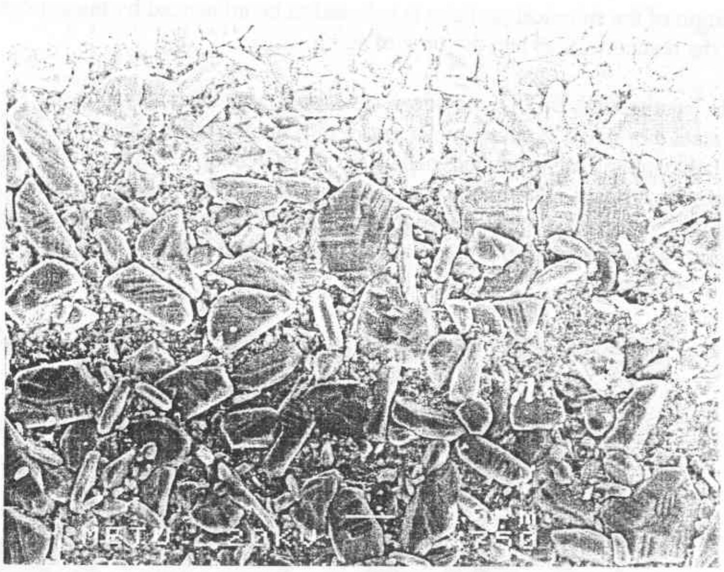

Figure 6. Typical SEM micrograph of sintered (1250°C, 17 h) $BaTiO_3$ samples with about 2 mol% excess of TiO_2 in the starting mixtures.

4. Conclusions

The experimental conditions and parameters of the hydrothermal synthesis of $BaTiO_3$ at 90°C were investigated. Sub-micron (average particle size of 150 nm), spherical particles of $BaTiO_3$ were obtained, the precipitates were already crystalline and cubic with the space group of *Pm-3m*. A new XRD pattern for the cubic form of $BaTiO_3$ is suggested in this study. The proprietary washing step included in the hydrothermal synthesis of $BaTiO_3$ eliminated the need for carrying out the aging and washing stages of the process in controlled atmospheres, free of CO_2. The Rietveld analysis performed on the XRD data of the synthesized powders revealed that the precipitates were free of the impurity phase, $BaCO_3$, and of the tetragonal form of $BaTiO_3$. The average grain size in the sintered (1200°C, 6 hours) samples of $BaTiO_3$ were in the vicinity of about 500 nm. The strong affect of the presence of shifts from the correct stoichiometry, in the starting mixtures, was confirmed, in the case of excess TiO_2, in the form of exaggerated grain growth to show up in the microstructures of the sintered samples.

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