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Hydrothermal Synthesis of Pure and Dy:$BaTiO_3$ Powders at 90°C and Their Sintering Behavior

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ABSTRACT

Sub-micron (150-200 nm), monodisperse and spherical powders of pure and Dy-doped (0.8 at%) $BaTiO_3$ have been prepared by "hydrothermal synthesis" at 90°C in an air atmosphere. The powder preparation technique adopted in this work did not necessitate the utilization of strict and expensive measures which were commonly required for the removal of free CO_2 present in the atmosphere. The synthesized powders were crystalline, pure, and did not contain $BaCO_3$ as an impurity phase. Pure and Dy-doped $BaTiO_3$ powders synthesized at 90°C had the cubic (space group: *Pm-3m*) crystal structure. Grain growth characteristics of pure and Dy-doped $BaTiO_3$ pellets were investigated during sintering in air and compared with one another over the temperature range of 1200 to 1500°C. Sample characterization was achieved by XRD, SEM, EDXS, and Rietveld Analysis.

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. Yamaji, et al. [1-3] have demonstrated the strong effect of Dy in controlling and reducing the sintered grain size of $BaTiO_3$, however, they have used conventional solid-state reactive firing routes in their synthesis experiments. On the other hand, pure $BaTiO_3$, depending on synthesis procedure used and temperature, may exhibit four different polymorphic forms [4]. Among these four polymorphs of $BaTiO_3$, the cubic form (space group: *Pm-3m*) is "paraelectric," and the other three (tetragonal: P*4mm*, orthorhombic: P*mm2*, and rhombohedral: R*3m*) are "ferroelectric." $BaTiO_3$ is of the tetragonal symmetry from room temperature up to 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]. The change observed in the crystal

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structure of barium titanate at its T_c could also be observed by the significant change (from about 1000 to 11000) which 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 [1-3, 6]. It has now been 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 pure $BaTiO_3$ would show itself up in the form of an increase in its dielectric constant (RT) from 1000 to about 5000 [7], whereas for Dy-doped $BaTiO_3$ samples it would increase to about 10000 [1]. For 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 to be gained over the particle (pre-sintering) and grain (post-sintering) sizes would directly influence the electronic properties of the final product.

The preparation of monosize and crystalline $BaTiO_3$ powders by using hydrothermal synthesis has been known for a long time. This process commonly uses the starting materials of water-soluble inorganic $Ba(OH)_2.8H_2O$ salts and insoluble TiO_2 powders to be mixed in an aqueous solution kept at a temperature near to its boiling point for prolonged times. Hydrothermal synthesis involves the formation of crystalline materials from the starting materials in such aqueous media under strongly alkaline conditions. 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 [8-9]. Lencka and Riman [10] 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 underlined 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 solution to the problem of "$BaCO_3$-contamination" in hydrothermally synthesized (in air atmosphere) $BaTiO_3$ powders. The nominal addition of small amounts of a RE dopant (i.e., 0.8 at% Dy) has been achieved by incorporating prescribed amounts of Dy-nitrate solutions into the processing route of hydrothermal synthesis, in contrast to the addition of Dy_2O_3 into $BaTiO_3$ by mixing and milling [1-3] in the conventional schemes of synthesis.

EXPERIMENTAL PROCEDURE

Sub-micron, pure and Dy-doped $BaTiO_3$ 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). The preparation

conditions and parameters [11] of pure barium titanate powders were given in the flowchart of Fig. 1(a). Dy_2O_3 (+99.9%, Merck, Germany) powder was dissolved by reacting it with a stoichiometric amount of HNO_3 (99%, Merck, Germany) to form 0.1 M stock solutions of $Dy(NO_3)_3$. Similarly, the preparation conditions of Dy-doped (0.8 at%) barium titanate powders were given in the flowchart of Fig. 1(B). The constant temperature of 90°C, required for prolonged times (48 to 72 h) of aging (in a Teflon beaker placed in an ordinary closed glass jar), was maintained in a microprocessor-controlled (± 1°C) laboratory oven.

The pellets of pure and Dy-doped $BaTiO_3$ were heated in platinum crucibles for 6 hours at temperatures in the range of 1200 to 1500°C, in an air atmosphere. The pellets were heated to the peak sintering temperatures at the rate of 5°C/min, and cooled back to RT at the same rate. The effect of Dy-doping in $BaTiO_3$ powders on the sintered grain sizes and morphology was studied by scanning electron microscopy (SEM) (JEOL, JSM6400, Tokyo, Japan) micrographs taken directly from the surfaces of 0.5 cm-diameter pellets which were uniaxially pressed in hardened steel dies at a pressure of 200 MPa. The samples for SEM studies were, first, sputter coated with an approximately 25 nm-thick layer of gold-palladium alloy. Energy-dispersive X-ray spectroscopy (EDXS) (Kevex, Noran, CA, USA) analysis were performed on our samples to determine the elemental distribution in the powders.

Powder X-ray diffraction spectra were obtained from the 90°C-dried samples for phase characterization purposes. An X-ray powder diffractometer (Rigaku, D-Max/B, Tokyo, Japan) was used with FeK_α radiation at the step size of 0.02° and a preset time of 1 second to check the purity of $BaTiO_3$ powders. The possible presence of other polymorphs of $BaTiO_3$ in our hydrothermally synthesized powders were examined by Rietveld Analysis [12].

RESULTS AND DISCUSSION

The precipitates of $BaTiO_3$ aged at 90°C for 72 hours were already crystalline and had the cubic crystal structure. The small amounts of $BaCO_3$ present in these precipitates were easily removed by the dilute HCl-washing step included in the flowchart of Fig. 1(a). Figure 2 shows the comparative XRD charts of the "as-is" (trace-**A**, $BaCO_3$ present) and "HCl-washed" (trace-**B**, pure $BaTiO_3$) powders of pure $BaTiO_3$. XRD analysis showed that the cubic unit cell of pure $BaTiO_3$ powders had the lattice parameter, a = 4.0186 Å, with a cell volume of 64.89 $Å^3$. The experimental XRD pattern of Table I, generated from our HCl-washed samples displayed a better crystallographic quality [13] than the already present ICDD PDF (i.e., 31-174) for this phase.

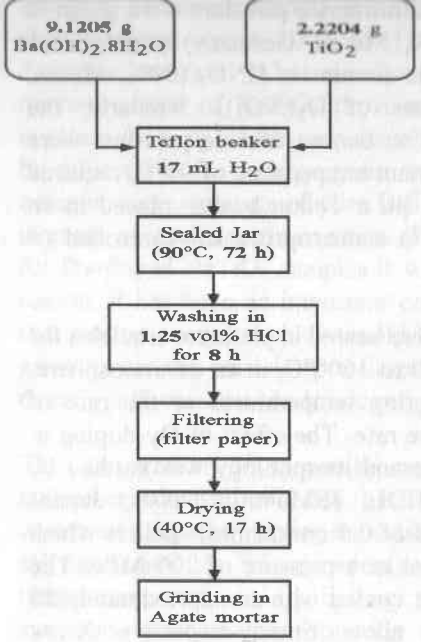

Fig. 1(a) Synthesis flowchart of pure $BaTiO_3$ Powders

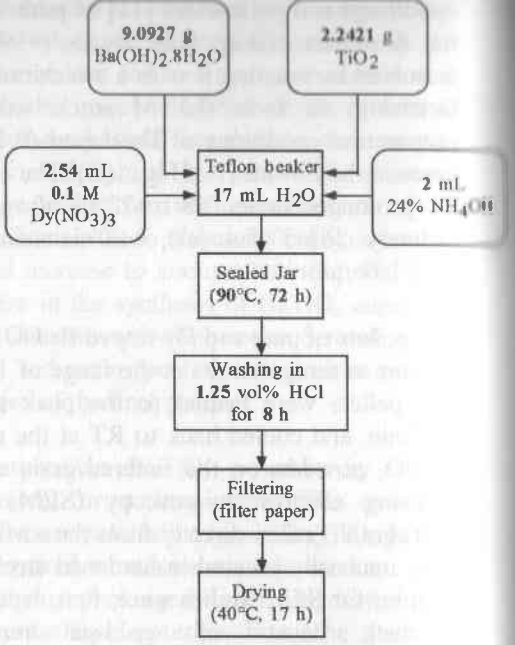

Fig. 1(b) Synthesis flowchart of Dy:$BaTiO_3$ Powders

Table I. Tentative XRD Pattern of $BaTiO_3$ Powders

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

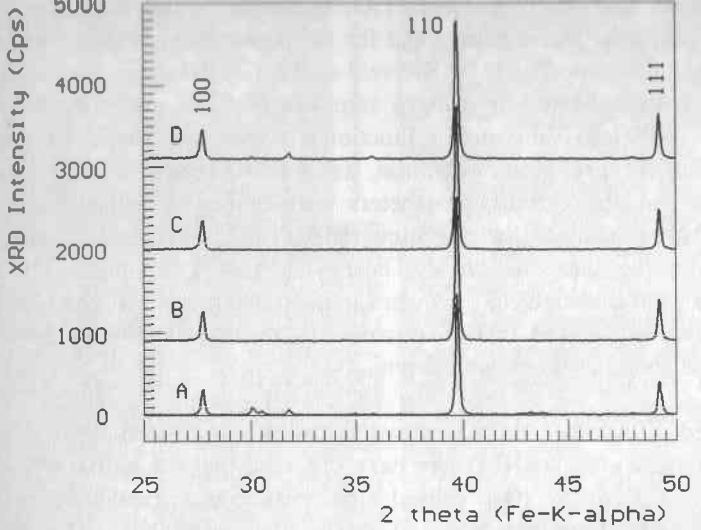

Fig. 2 XRD traces of pure and Dy:$BaTiO_3$ Powders

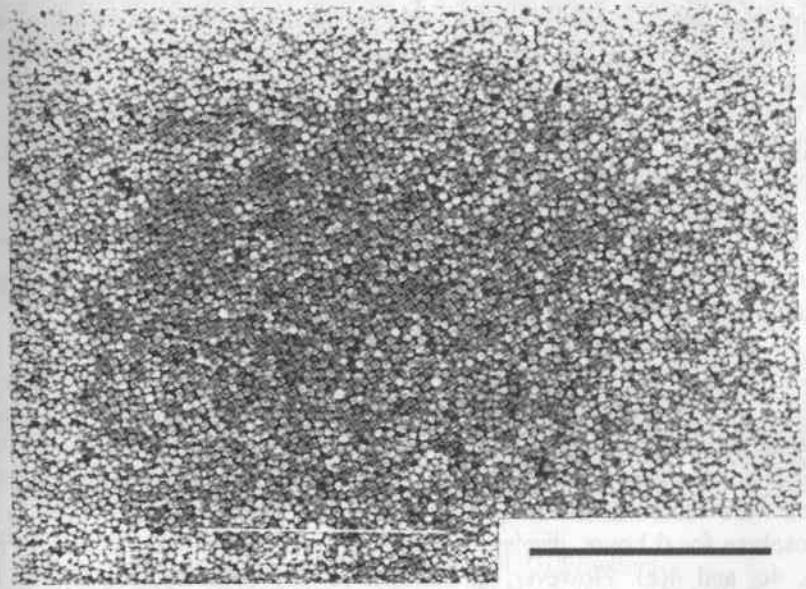

Fig. 3 Typical SEM micrograph of Dy:$BaTiO_3$ powders synthesized at 90°C (Bar = 10 μm)

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. 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. A Pseudo-Voigt profile function was used, and the lattice parameters, as well as the preferred-orientation, asymmetry, temperature, scale, mixing, half-width and background parameters were refined to a final R_{wp} of 5.51%. These analysis showed that the prepared $BaTiO_3$ powders were pure and did not contain the tetragonal phase. The FWHM values (for peaks 110 and 111) obtained from the Rietveld runs were used to determine the average crystallite size of the synthesized $BaTiO_3$ powders by using the Scherrer formula [14], and it was found to be around 28 nm.

Dy-doped (0.8 at%) $BaTiO_3$ powders were synthesized according to the flowchart given in Fig. 1(b). We have observed that the addition of the small volume of 0.1 M $Dy(NO_3)_3$ caused a decrease in the pH value (from 12.5 to 11.9) of the Ba-hydroxide and TiO_2 mixture heated to 90°C. This drop in the pH value of the precipitation suspensions also caused the poisoning of the resultant Dy:$BaTiO_3$ powders by a second phase of TiO_2. It was found that the addition of a 2 mL aliquot of 24% NH_4OH solution (after the addition of Dy-nitrate solution to the barium hydroxide and titania suspension in water) into the Teflon reaction beaker removed that second phase by increasing the pH to above 12.5. The influence of the initial NH_4OH addition on the phase purity of Dy:$BaTiO_3$ powders is depicted in the XRD spectra of Fig. 2 (trace-**D**: w/o NH_4OH (TiO_2 present), trace-**C**: w/ NH_4OH addition). The particle morphology of as-recovered Dy-doped $BaTiO_3$ powders (dispersed in isopropanol by an ultrasonic disrupter (Misonix, XL2015, USA) and then evaporated to dryness on a small piece of Al-foil) is shown in the SEM micrograph of Fig. 3. Dy-doped $BaTiO_3$ powders had monodisperse, spherical particles of about 200 nm average particle diameter.

The SEM micrographs given in Figs. 4(a) through 4(f) provide a chance of visual comparison to the strong role of dysprosium (Dy) added at the nominal level of 0.8 at% into the hydrothermally synthesized $BaTiO_3$ powders. Pure $BaTiO_3$ powders produced according to the processing flowchart of Fig. 1(a), which were heated at the temperatures of 1200, 1300, and 1400°C in an air atmosphere for 6 hours, displayed anomalous grain growth as shown in Figs. 4(a), 4c, and 4(e). However, in contrast to this behavior, the Dy:$BaTiO_3$ powders heated at the same temperatures, under exactly similar conditions, did not display exaggerated grain growth as given in the micrographs of Figs. 4(b), 4(d), and 4(f), respectively. On the other hand, Dy:$BaTiO_3$ pellets heated at 1500°C, for 6 h, had the typical microstructure given in Fig. 4(g).

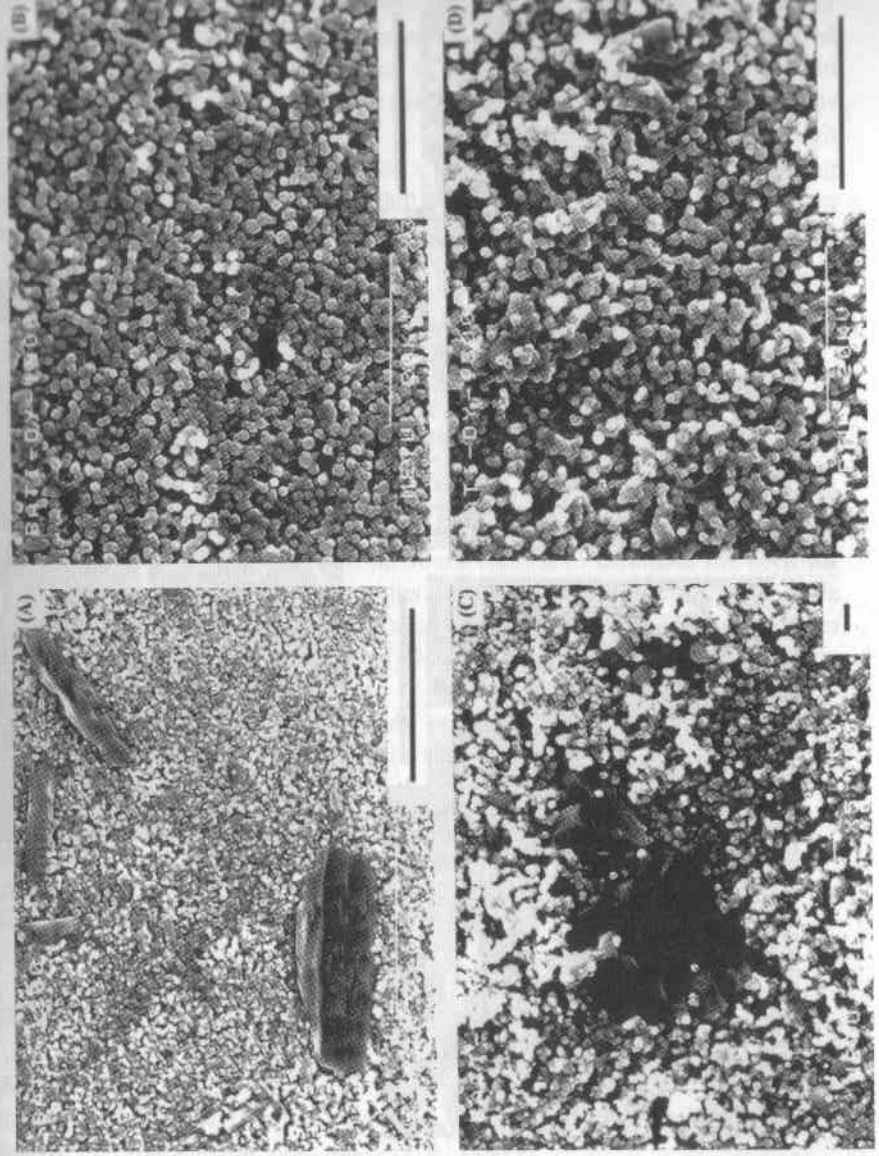

Fig. 4 SEM micrographs of Pure and Dy-doped $BaTiO_3$ Powders
(A) Pure $BaTiO_3$, 1200°C, Bar = 10 μm, (B) Dy:$BaTiO_3$, 1200°C, Bar = 10 μm,
(C) Pure $BaTiO_3$, 1300°C, Bar = 1 μm, (D) Dy:$BaTiO_3$, 1300°C, Bar = 10 μm

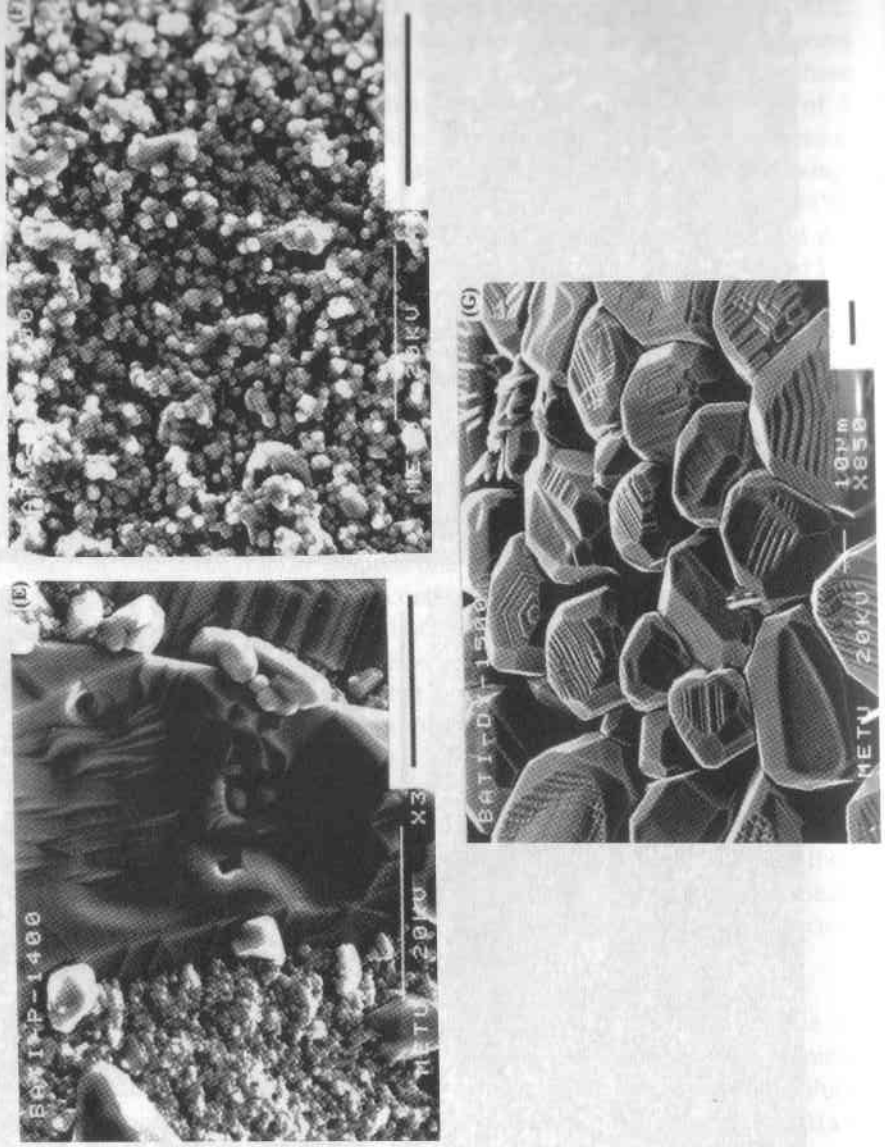

Fig. 4 SEM micrographs of Pure and Dy-doped $BaTiO_3$ Powders
(E) Pure $BaTiO_3$, 1400°C, Bar = 10 µm, (F) Dy:$BaTiO_3$, 1400°C, Bar = 10 µm,
(G) Dy:$BaTiO_3$, 1500°C, Bar = 10 µm

it was known [15] that even the slightest excess of TiO_2 in the initial, powder processing suspensions of barium hydroxide and titania to cause exaggerated grain growth (with occasional grains of sizes in the range of 20 to 40 µm) in the final, sintered microstructures. The presence of such an excess of TiO_2 was believed to induce the formation of a $BaTiO_3$-$Ba_6Ti_{17}O_{40}$ eutectic at high temperatures. The slightest presence of such a eutectic liquid at the sintering temperatures might then promote grain growth, especially at slow heating rates. Keeping the hydrothermal synthesis solutions in strongly alkaline conditions may also be helpful in the reduction of the amount of excess TiO_2 in the final powder bodies.

CONCLUSIONS

The experimental conditions and parameters of the hydrothermal synthesis of pure and 0.8 at% Dy-doped $BaTiO_3$ at 90°C, in an air atmosphere, were investigated. The dilute HCl-washing step included in the hydrothermal synthesis of pure and doped $BaTiO_3$ powders seemed to eliminate the need for carrying out the aging and washing stages of the process in controlled (i.e., free of CO_2) atmospheres. Sub-micron, monodisperse, spherical particles (with an average particle size of 150 nm) of $BaTiO_3$ were obtained.

The recovered precipitates were already crystalline and cubic with the space group of *Pm-3m*. A tentative XRD pattern (instead of the already present PDF 31-174 of the ICDD database) for the cubic form of pure $BaTiO_3$ was suggested in this study. 0.8 at% Dy-doping and the hydrothermal synthesis conditions of these powders were found to be quite effective in inhibiting the grain growth in $BaTiO_3$ samples heated over the temperature range of 1200 to 1400°C.

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Homogeneous Precipitation and Calcination

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ABSTRACT

Aqueous solutions of lead chloride ($PbCl_2$), zirconium oxychloride ($ZrOCl_2.8H_2O$) and titanium tetrachloride ($TiCl_4$), in appropriate volumetric amounts, were used as the starting materials in the synthesis of phase-pure $Pb(Zr_{0.52}Ti_{0.48})O_3$ powders. Preparation of the phase-pure PZT powders were achieved, in the presence of urea (CH_4N_2O), by the chemical powder synthesis route of homogeneous precipitation.

Calcination and phase evolution behaviors of PZT precursor powders were studied as a function of temperature by powder XRD (X-ray diffraction) in an air atmosphere, over the temperature range of 90 to 750°C. Morphological properties of the precipitated $Pb(Zr_{0.52}Ti_{0.48})O_3$ powders were investigated by the SEM (scanning electron microscopy) studies. Semi-quantitative chemical analysis of the samples were performed by EDXS (energy-dispersive X-ray spectroscopy).

INTRODUCTION

Lead zirconate titanate, $PbZr_xTi_{1-x}O_3$ (PZT), ceramics are of great technological interest due to their excellent piezoelectric and ferroelectric properties [1, 2]. PZT ceramics are extensively used as electromechanical transducer materials. The electromechanical response of these ceramics is maximum when x corresponds to the composition of the morphotrophic phase boundary (MPB) which separates the tetragonal (T) and rhombohedral (R) phases towards Ti-rich and Zr-rich sides, respectively. The precise determination of the MPB composition range, which is believed to be quite narrow, has, therefore, attracted immense interest.

Conventionally, the PZT phase is prepared by solid state reactive firing of the constituent oxides (PbO, ZrO_2 and TiO_2). However, due to intermediate reactions which lead to the formation of $PbTiO_3$ (PT) and $PbZrO_3$ (PZ), the PZT formed by this method is chemically heterogeneous, including compositional fluctuations, which modify several electrical properties [3, 4].

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