Hydrothermal Synthesis of Dy-Doped $BaTiO_3$ Powders

ERSIN E. OREN and A. CUNEYT TAS

Submicron-sized (~200 nm), monodisperse, and spherical powders of pure and dysprosium (Dy)–doped (0.8 at. pct) $BaTiO_3$ have been prepared by "hydrothermal synthesis" at 90 °C in an air atmosphere. The powder preparation procedure developed in this work did not necessitate the use of strict and expensive processes, which were commonly required for the removal of free CO_2 present in the atmosphere. The prepared powders were found to be crystalline, pure, and contained no $BaCO_3$ as an impurity phase. Pure and Dy-doped $BaTiO_3$ powders synthesized at 90 °C had the pseudocubic (space group: *Pm*-3*m*) crystal structure. Grain growth characteristics of pure and Dy-doped $BaTiO_3$ pellets were compared during sintering in air over the temperature range from 1200 °C to 1500 °C. The Dy doping was found to be significantly effective in inhibiting the anomalous grain growth in $BaTiO_3$ samples heated at or above 1200 °C.

I. INTRODUCTION

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 1960s that the dielectric properties of these ceramics are closely related to the grain size in their microstructures. Yamaji and co-workers[1,2,3] have demonstrated the strong effect of dysprosium (Dy) in reducing the sintered grain size of $BaTiO_3$; however, they used conventional solid-state reactive firing routes in their synthesis experiments.

On the other hand, pure $BaTiO_3$, depending on the synthesis method used and temperature, may exhibit four different polymorphic forms.[4] Among these four polymorphs of $BaTiO_3$, the pseudocubic form (space group: *Pm*-3*m*) is "paraelectric," and the other three (tetragonal: *P*4*mm*, orthorhombic: *Pmm*2, and rhombohedral: *R*3*m*) 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 structure of barium titanate at its T_C could also be observed by the significant change (from about 1000 to 11,000) 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 is now a well-established fact that the decrease to be achieved in the average grain size (from 50 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 (room temperature) from 1000 to about 5000,[7] whereas, for Dy-doped $BaTiO_3$ samples, it would increase to about 10,000.[1] For this reason, it has been an important concern in the synthesis of $BaTiO_3$ ceramics that any precautions which would be exercised toward the precise control to be gained over the particle (presintering) and grain (postsintering) 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 $Ba(OH)_2 \cdot 8H_2O$ 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 such aqueous media, under strongly alkaline conditions. Hydrothermal processing of $BaTiO_3$ powders has always required the use of 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 an RE (rare earth) dopant (*i.e.*, 0.8 at. pct 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,[1,2,3] as in the conventional schemes of synthesis.

II. EXPERIMENTAL PROCEDURES

Submicron-sized pure and Dy-doped $BaTiO_3$ powders were synthesized from the mixtures of proprietary amounts of $Ba(OH)_2 \cdot 8H_2O$ (+99.9 pct, Riedel-de Haen AG, Seelze, Germany) and TiO_2 (+99.9 pct, Riedel-de Haen AG). The preparation conditions and parameters[11] of pure barium titanate powders are given in the flow chart of Figure 1(a). Dy_2O_3 (+99.9 pct, Merck, Darmstadt, Germany) powder was dissolved by reacting it with a stoichiometric amount of HNO_3 (99 pct, Merck) to form 0.1 M stock solutions of $Dy(NO_3)_3$. Similarly, the preparation conditions of Dy-doped

ERSIN E. OREN, Research Assistant, is with the Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara 06531, Turkey. A. CUNEYT TAS, Associate Professor, formerly with the Department of Metallurgical and Materials Engineering, Middle East Technical University, is with the Max-Planck-Institute, Stuttgart, Germany D-70569.

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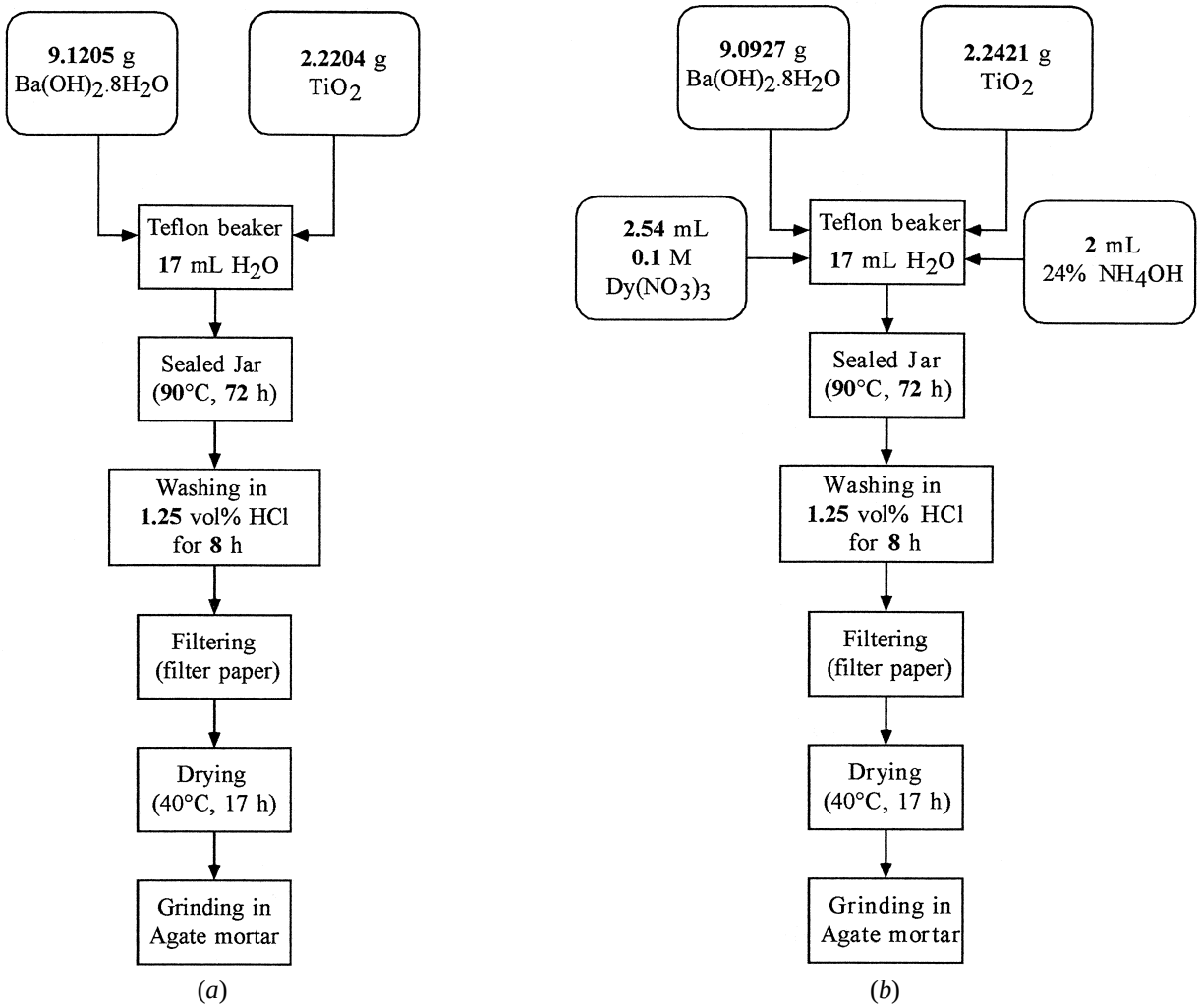

Fig. 1—(*a*) Synthesis flow chart of pure $BaTiO_3$ powders. (*b*) Synthesis flow chart of Dy:$BaTiO_3$ powders.

(0.8 at. pct) barium titanate powders are given in the flow chart of Figure 1(b). The constant temperature of 90 °C, required for prolonged times (48 to 72 hours) of aging (ina TEFLON* beaker placed in an ordinary closed glass jar), was maintained in a microprocessor-controlled (±1 °C) laboratory oven.

*TEFLON is a trademark of E.I. DuPont de Nemours, Wilmington, DE.

The pellets of pure and Dy-doped $BaTiO_3$ were heated in platinum crucibles for 6 hours at temperatures ranging from 1200 °C to 1500 °C, in an air atmosphere. The pellets were heated to the peak sintering temperatures at the rate of 5 °C/min and were cooled back to room temperature 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) 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 (Kevex, Noran, CA) analysis was performed on our samples to determine the elemental distribution in the powders.

*JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

Powder X-ray diffraction (XRD) spectra were obtained from the samples dried at 90 °C for phase characterization purposes. An X-ray powder diffractometer (Rigaku, D-Max/B, Tokyo) was used with Fe K_α radiation, at the step size of 0.02 deg 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 was assessed by Rietveld analysis.[12]

III. 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 flow chart of Figure 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 $BaTiO_3$. The XRD analysis showed that the cubic unit cell of pure $BaTiO_3$ powders

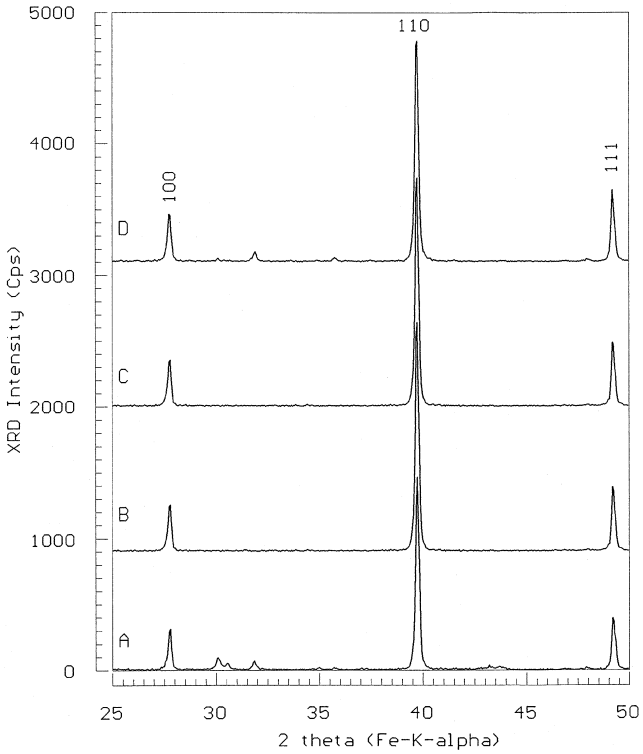

Fig. 2—Powder XRD traces of pure and Dy:$BaTiO_3$ powders.

Table I. Experimental XRD Pattern of $BaTiO_3$ (P*m*-3*m*) 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

had the lattice parameter of $a = 4.0186$ 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.

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. The XRD data to be used in these analyses were collected using a step size of 0.02 deg 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} value of 5.51 pct. This analysis showed that the prepared $BaTiO_3$ powders were pure and did not contain the tetragonal phase. The FWHM values (0.162 and 0.191, for peaks 110 and 111, respectively) 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.

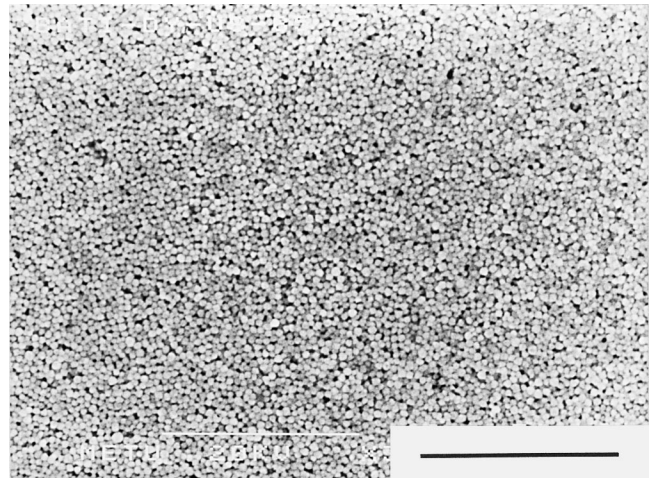

Fig. 3—An SEM micrograph of Dy:$BaTiO_3$ powders synthesized at 90 °C (bar = 10 μm).

The Dy-doped (0.8 at. pct) $BaTiO_3$ powders were synthesized according to the flow chart given in Figure 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 pct 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 Figure 2 (trace D: without NH_4OH (TiO_2 present), trace C: with a NH_4OH addition). The particle morphology of the as-recovered Dy-doped $BaTiO_3$ powders (dispersed in isopropanol by a Misonix XL2015 ultrasonic disrupter and then evaporated to dryness on a small piece of Al foil) is shown in the SEM micrograph of Figure 3. Dy-doped $BaTiO_3$ powders had monodisperse, spherical particles of about 200 nm average particle diameter.

The SEM micrographs given in Figures 4(a) through (f) permit visual comparison of the strong role of Dy, added at the nominal level of 0.8 at. pct, in hydrothermally synthesized $BaTiO_3$ powders. Pure $BaTiO_3$ powders produced according to the processing flow chart of Figure 1(a), which were heated at the temperatures of 1200 °C, 1300 °C, and 1400 °C in an air atmosphere for

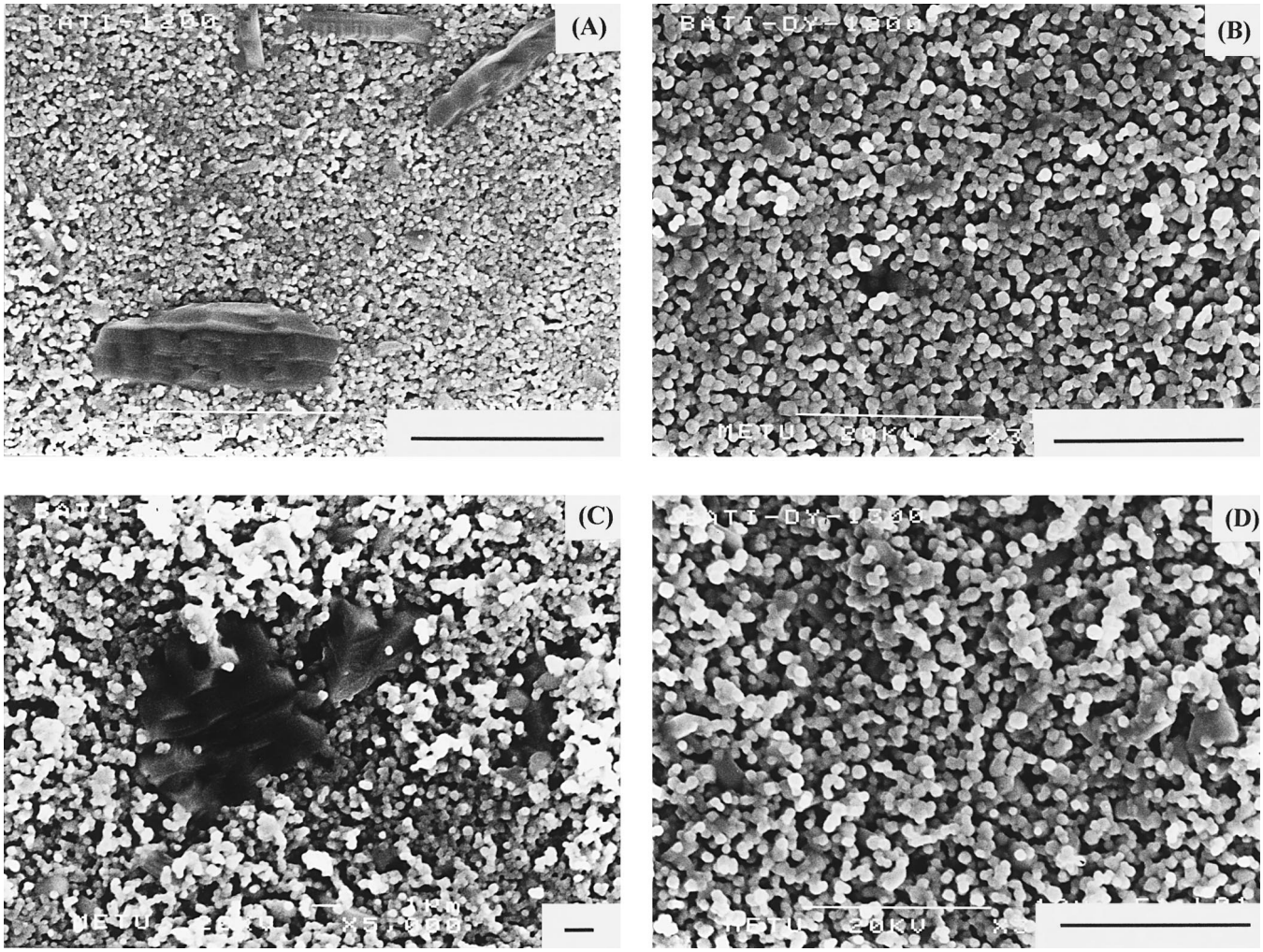

Fig. 4—A series of SEM micrographs of $BaTiO_3$ powders: (*a*) pure, 1200 °C, bar = 10 μm; (*b*) Dy-doped, 1200 °C, bar = 10 μm; (*c*) pure, 1300 °C, bar = 1 μm; (*d*) Dy-doped, 1300 °C, bar = 10 μm; (*e*) Pure, 1400 °C, bar = 10 μm; (*f*) Dy-doped, 1400 °C, bar = 10 μm; and (*g*) Dy-doped, 1500 °C, bar = 10 μm.

6 hours displayed anomalous grain growth, as shown in Figures 4 (a), (c), and (e), respectively. 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 shown in the micrographs of Figures 4(b), (d), and (f), respectively. On the other hand, Dy:$BaTiO_3$ pellets heated at 1500 °C for 6 hours had the typical microstructure of Figure 4(g).

It is known[15] that even the slightest excess of TiO_2 in the initial, powder-processing suspensions of barium hydroxide and titania causes exaggerated grain growth (with occasional grains of sizes in the range from 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 with 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.

IV. CONCLUSIONS

The experimental conditions and parameters of the hydrothermal synthesis of pure and 0.8 at. pct 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. Submicron-sized, monodisperse, spherical particles (with an average particle size of 200 nm) of $BaTiO_3$ were obtained.

The recovered precipitates were already crystalline and cubic with the space group of *Pm*-3*m*. A tentative XRD pattern (to replace the current PDF 31-174 of the ICDD database) for the cubic form of pure $BaTiO_3$ was suggested in this study. Doping with 0.8 at. pct Dy 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 °C to 1400 °C.

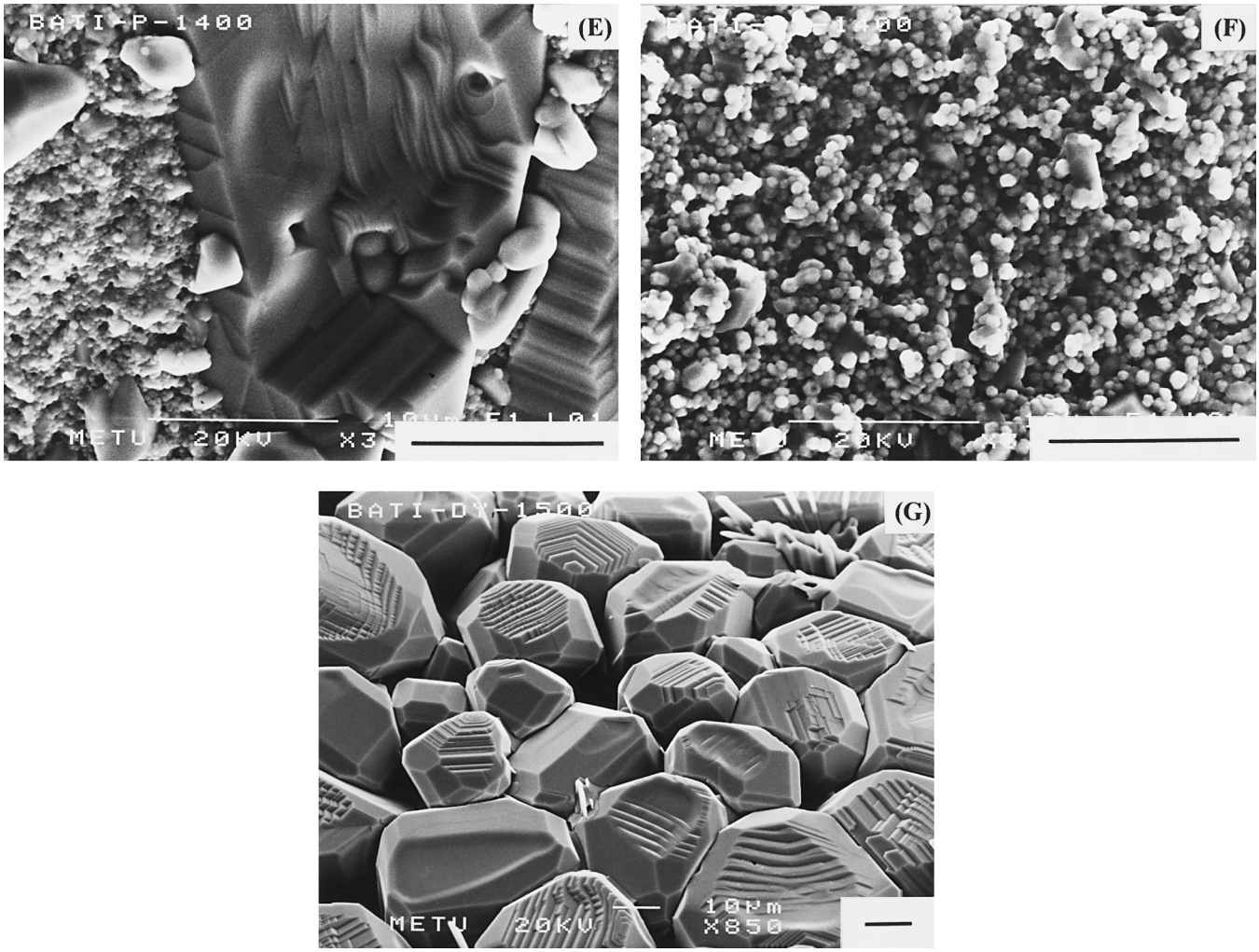

Fig. 4—Continued. A series of SEM micrographs of $BaTiO_3$ powders: (*a*) pure, 1200 °C, bar = 10 μm; (*b*) Dy-doped, 1200 °C, bar = 10 μm; (*c*) pure, 1300 °C, bar = 1 μm; (*d*) Dy-doped, 1300 °C, bar = 10 μm; (*e*) Pure, 1400 °C, bar = 10 μm; (*f*) Dy-doped, 1400 °C, bar = 10 μm; and (*g*) Dy-doped, 1500 °C, bar = 10 μm.

REFERENCES

1. A. Yamaji, Y. Enomoto, K. Kinoshita, and T. Murakami: *J. Am. Ceram. Soc.*, 1977, vol. 60, pp. 97-101.
2. T. Murakami and A. Yamaji: *Am. Ceram. Soc. Bull.*, 1976, vol. 55, pp. 572-75.
3. Y. Enomoto and A. Yamaji: *Am. Ceram. Soc. Bull.*, 1981, vol. 60, pp. 566-70.
4. N.W. Thomas: *Acta Cryst.*, 1989, vol. B45, pp. 337-44.
5. R.C. Buchanan: *Ceramic Materials for Electronics*, Marcel Dekker, Inc., New York, NY, 1986, pp. 101-18.
6. K. Kinoshita and Y. Yamaji: *J. Appl. Phys.*, 1976, vol. 47, pp. 371-73.
7. S. Malbe, J.C. Mutin, and J.C. Niepce: *J. Chem. Phys.*, 1992, vol. 89, pp. 825-43.
8. J.H. Peterson: U.S. Patent No. 2,216,655, Oct. 22, 1940.
9. E.B. Slamovich and I.A. Aksay: *J. Am. Ceram. Soc.*, 1996, vol. 79, pp. 239-47.
10. M.M. Lencka and R.E. Riman: *Chem. Mater.*, 1993, vol. 5, pp. 61-70.
11. A.C. Tas: Patent Pending, Turkish Patent Institute, Ankara, Turkey, Application No 96-00539.
12. A. Sakthivel and R.A. Young: "Rietveld Analysis of X-Ray Powder Diffraction Patterns: Program DBWS-9411 PC," Version: Mar. 1995, Georgia Institute of Technology, Atlanta, GA.
13. D.E. Appleman and H.T. Evans: "Least-squares and Indexing Software for XRD Data," U.S. Geological Survey, Computer Contribution No. 20, U.S. National Technical Information Service, Washington, DC, Document PB-216188, 1973.
14. H. Hsiang and F. Yen: *J. Am. Ceram. Soc.*, 1996, vol. 79, pp. 1053-60.
15. A.C. Caballero, C. Moure, P. Duran, and J.F. Fernandez: *Ceram. Trans.*, vol. 32, pp. 201-10; *in Dielectric Ceramics: Processing, Properties, and Applications*, K.M. Nair, J.P. Guha, and A. Okamoto, eds., The American Ceramic Society, Westerville, OH, 1993.