

## Barium Titanium Glycolate: A New Barium Titanate Powder Precursor

Victor W. Day,\*<sup>1a</sup> Todd A. Eberspacher,<sup>1a</sup>  
Matthew H. Frey,<sup>1b</sup> W. G. Klemperer,<sup>\*,1c</sup>  
Shurong Liang,<sup>1c</sup> and David A. Payne<sup>\*,1b</sup>

Department of Chemistry, University of Nebraska  
Lincoln, Nebraska 68588  
The Beckman Institute for  
Advanced Science and Technology  
Departments of Chemistry and  
Materials Science and Engineering  
University of Illinois, Urbana, Illinois 61801

Received November 16, 1995

The preparation of  $\text{BaTiO}_3$  preceramic powders by calcination of barium titanium coordination complexes as opposed to  $\text{BaCO}_3/\text{TiO}_2$  mixtures offers advantages in terms of processibility and phase purity that are well-documented.<sup>2</sup> The chemistry of the complexes employed is far from simple, however. Preparation of barium titanyl oxalate,<sup>3</sup>  $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 5\text{H}_2\text{O}$ , requires strict control of reaction temperature, reaction time, and solution composition if material with the proper stoichiometry is to be obtained.<sup>4</sup> Barium titanium citrate,<sup>5</sup>  $\text{BaTi}(\text{C}_6\text{H}_6\text{O}_7)_3 \cdot 6\text{H}_2\text{O}$ , can easily be prepared in pure form but utilizes a complex organic ligand. Finally, barium titanium catecholate,<sup>6</sup>  $\text{BaTi}(\text{C}_6\text{H}_4\text{O}_2)_3 \cdot 3\text{H}_2\text{O}$ , requires a multistep preparation involving either concentrated sulfuric acid or equally corrosive  $\text{TiCl}_4$ , while barium titanium alkoxides<sup>7</sup> and phenoxides<sup>8</sup> require inert-atmosphere techniques for their preparation.<sup>9</sup> We recently reported a new barium titanium glycolate complex,  $\text{BaTi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}$ ,<sup>8</sup> which is easily prepared from simple starting materials using benchtop procedures developed by others for the synthesis of analogous complexes  $\text{BaSi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 3.25\text{C}_2\text{H}_6\text{O}_2$ ,<sup>10</sup>  $\text{Na}_2\text{Ti}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2$ ,<sup>11</sup> and  $\text{K}_2\text{Ti}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 2.5\text{C}_2\text{H}_6\text{O}_2$ .<sup>11</sup>

(1) (a) University of Nebraska. (b) Department of Materials Science and Engineering, University of Illinois. (c) Department of Chemistry, University of Illinois.

(2) (a) Hilton, A. D.; Frost, R. *New Eng. Mater.* **1992**, *66*, 67, 145. (b) Phule, P. P.; Risbudi, S. H. *J. Mater. Sci.* **1990**, *25*, 1169. (c) Hennings, D. *Brit. Ceram. Proc.* **1989**, *41*, 1.

(3) (a) Clabaugh, W. S.; Swiggard, E. M.; Gilchrist, R. *J. Res. Natl. Bur. Std.* **1956**, *56*, 289. (b) Bind, J. M.; Dupin, T.; Schafer, J.; Titeux, M. *J. Met.* **1987**, *39*, 60. (c) Rhine, W. E.; Hallock, R. B.; Davis, W. M.; Wong-Ng, W. *Chem. Mater.* **1992**, *4*, 1208.

(4) For a discussion of these problems, see ref 2a, pp 152-3, and ref 2c, p 4.

(5) (a) Pechini, M. P. U.S. Patent 3,231,218; 1966. (b) Hennings, D.; Mayr, W. *J. Solid State Chem.* **1978**, *26*, 329. (c) Hutchins, G. A.; Maher, G. H.; Ross, S. D. *Am. Ceram. Soc. Bull.* **1987**, *66*, 681.

(6) (a) Ali, N. J.; Milne, S. J. *Br. Ceram. Trans. J.* **1987**, *86*, 113. (b) Davies, J. A.; Dutremez, S. *J. Am. Ceram. Soc.* **1990**, *73*, 1429.

(7) (a) Kirby, K. W. *Mater. Res. Bull.* **1988**, *23*, 881. (b) Yanovsky, A. I.; Yanovskaya, M. I.; Limar, V. K.; Kessler, V. G.; Turova, N. Ya. *J. Chem. Soc., Chem. Commun.* **1991**, 1605. (c) Tarevskaya, E. P.; Yanovskaya, M. I.; Lymar', V. K.; Turova, N. Ya. *Russ. J. Inorg. Chem.* **1993**, *38*, 563. (d) Suyama, Y.; Nagasawa, M. *J. Am. Ceram. Soc.* **1994**, *77*, 603. (e) Gaskins, B.; Lannutti, J. J.; Finnen, D. C.; Pinkerton, A. A. *Acta Crystallogr.* **1994**, *C50*, 1387.

(8) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Liang, S. *Mater. Res. Soc. Symp. Proc.* **1994**, *351*, 177.

(9) Note that some recently-reported 1:1 barium titanium diketonate alkoxide complexes fail to yield  $\text{BaTiO}_3$  upon heating, liberating volatile titanium complexes instead: Kessler, V. G.; Hubert-Pfalzgraf, L. G.; Daniele, S.; Gleizes, A. *Chem. Mater.* **1994**, *6*, 2336.

(10) Hoppe, M. L.; Laine, R. M.; Kampf, J.; Gordon, M. S.; Burggraf, L. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 287.

(11) Gainsford, G. J.; Kemmitt, T.; Lensink, C.; Milestone, N. B. *Inorg. Chem.* **1995**, *34*, 746.

Here, we provide details concerning the synthesis and structure of this new complex and report successful calcination into  $\text{BaTiO}_3$  preceramic powders that sinter into polycrystalline, tetragonal  $\text{BaTiO}_3$  having good dielectric properties.

Barium titanium glycolate (BTG) could be prepared by reaction of ethylene glycol with any of several barium reagents (BaO or Ba metal) and titanium(IV) reagents ( $\text{TiO}_2$  or titanium isopropoxide). In a typical preparation, 6.0 g of barium oxide fine powder was added to 30 mL of ethylene glycol with vigorous stirring. The reaction was exothermic, and the reaction mixture was allowed to cool to ambient temperature with stirring over 30 min. The reaction mixture was then diluted with 40 mL of 2-propanol, and a small amount of suspended solid material was removed by centrifugation. Titanium isopropoxide (9.0 mL) was then added with vigorous stirring, and the reaction mixture was stirred for 30 min. The product (18.6 g, 96% yield based on Ti) precipitated from solution and was collected by filtration, washed with 2-propanol (30 mL) and dried in *vacuo*.<sup>12</sup> It was formulated  $\text{BaTi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}$  using elemental analysis<sup>12</sup> and thermogravimetric analysis (see below).<sup>13</sup> Although BTG can be prepared in an aerobic atmosphere, it is hygroscopic and should be stored in a desiccator.

A single-crystal X-ray diffraction study of BTG was performed using crystals grown by cooling a hot saturated ethylene glycol solution to ambient temperature.<sup>14</sup> This study showed that crystalline BTG is composed of

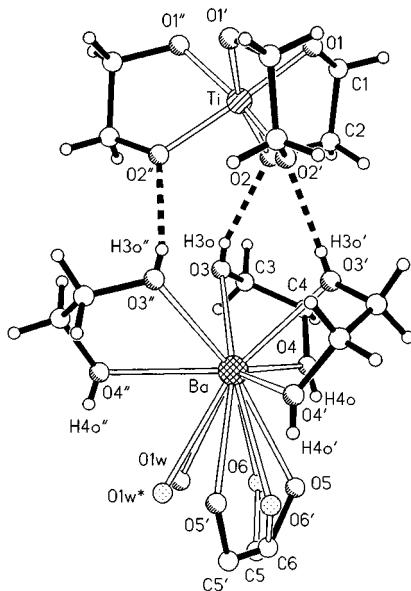
(12) Anal. Calcd for  $\text{BaTiC}_{14}\text{H}_{38}\text{O}_{15}$ : Ba, 21.74; Ti, 7.58; C, 26.62; H, 6.06. Found: Ba, 21.61; Ti, 7.58; C, 26.92; H, 6.09. IR ( $\text{cm}^{-1}$ , KBr) 3600-3000 s, br; 2935 m; 2866 m; 2824 m; 2653 m; 2534 m; 1967 w; 1928 w; 1638 m, br; 1454 m, br; 1379 m; 1355 m; 1335 m; 1236 m; 1222 m; 1119 sh; 1085 s; 1050 s; 911 m; 880 s; 818 m; 601 s; 530 sh; 512 s; 453 s.

(13) A different, anhydrous product,  $\text{BaTi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2$ , is obtained when Ba metal and titanium isopropoxide are used as reactants and the preparation is carried out in a dry nitrogen atmosphere.

(14) Single crystals of  $[\text{Ba}^{II}(\text{HOCH}_2\text{CH}_2\text{OH})_4(\text{OH}_2)][\text{Ti}^{IV}(\text{OCH}_2\text{CH}_2\text{O}_3)]$  are, at  $20 \pm 1$  °C, rhombohedral, space group  $R\bar{3}c-C_{3v}^6$  (No. 161) with  $a = 18.530(6)$  Å,  $\alpha = 27.36(2)$ °,  $V = 1186(1)$  Å<sup>3</sup>,  $Z = 2$  formula units ( $d_{\text{calcd}} = 1.769$  g cm<sup>-3</sup>;  $\mu_{\text{a}}(\text{Mo K}\alpha) = 2.05$  mm<sup>-1</sup>). The computer programs and procedures used for data collection, data reduction, structure solution, and refinement of BTG have been reported elsewhere.<sup>15</sup> A total of 923 independent reflections having  $2\theta(\text{Mo K}\alpha) 50.7^\circ$  (equivalent of 0.8 limiting Cu K $\alpha$  spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (1.0° wide)  $\omega$  scans and graphite-monochromated Mo K $\alpha$  radiation. The structure was solved using the "heavy atom" technique with the Siemens SHELXTL-PC software package. The resulting structural parameters have been refined to convergence ( $R_1$  (unweighted, based on  $F$ ) = 0.030 for 639 independent absorption-corrected reflections having  $2\theta(\text{Mo K}\alpha) < 50.7^\circ$  and  $I > 3\sigma(I)$  using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all ordered and one disordered (O<sub>6</sub>) non-hydrogen atoms and isotropic thermal parameters for the remaining disordered non-hydrogen atoms and all included hydrogen atoms. The hydroxy hydrogens on the ordered ethylene glycol ligands (H<sub>30</sub> and H<sub>40</sub>) were located from a difference Fourier and refined as independent isotropic atoms. Methylene hydrogen atoms on the ordered glycol and glycolate ligands were included in the structural model at fixed idealized tetrahedral positions with a C-H bond length of 0.96 Å and an isotropic thermal parameter 20% greater than the equivalent isotropic thermal parameter of the carbon atom to which it is bonded.

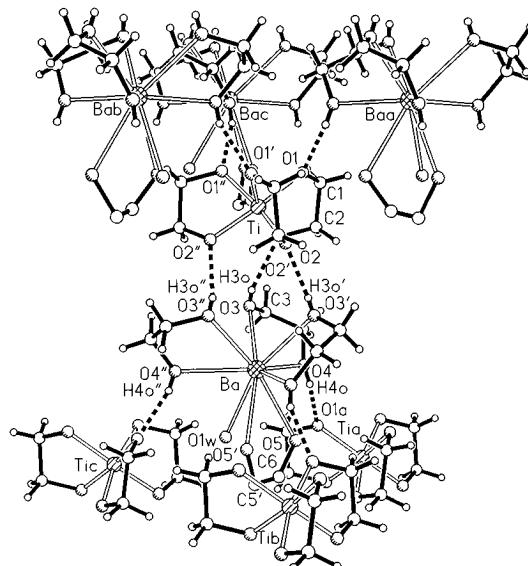
(15) (a) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; R. Planalp, P.; Schiller, P. W.; Yagasaki, A.; Zhong, B. *Inorg. Chem.* **1993**, *32*, 1629. (b) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125.

(16) The first number in parentheses following an average value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average value.



**Figure 1.** Perspective drawing of the hydrogen-bonded  $[\text{Ti}(\text{OCH}_2\text{CH}_2\text{O})_3]^{2-}/[\text{Ba}(\text{HOCH}_2\text{CH}_2\text{OH})_4(\text{H}_2\text{O})]^{2+}$  anion/cation pairs present in crystals of  $\text{BaTi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}$ . For purposes of clarity, the  $\text{Ba}^{II}$  ion is represented by a large cross-hatched sphere, the  $\text{Ti}^{IV}$  ion by a large striped sphere, oxygen atoms by medium-sized shaded or dotted spheres, and carbon and hydrogen atoms by medium-sized and small open spheres, respectively. The view is nearly perpendicular to the crystallographic  $C_3$  axis which passes through both metals and relates atoms labeled with and without primes (' or '). Since the  $\text{Ti}^{IV}$  and  $\text{Ba}^{II}$  ions both lie on a crystallographic  $C_3$  axis in the unit cell, the water molecule and fourth ethylene glycol which are coordinated to Ba are necessarily disordered in the lattice as described in the text. The  $[\text{Ti}^{IV}(\text{OCH}_2\text{CH}_2\text{O})_3]^{2-}$  anion adopts a *lel* conformation with average<sup>16</sup>  $\text{Ti}-\text{O}$  bond lengths of 1.93-(2,1,1,2) Å. The average<sup>16</sup>  $\text{Ba}-\text{O}_3$  and  $\text{Ba}-\text{O}_4$  bond length is 2.76(1,1,1,2) Å and the bond length from Ba to the disordered oxygens ( $\text{O}_5$ ,  $\text{O}'_5$  and  $\text{O}_{1w}$ ,  $\text{O}'_{6w}$  and  $\text{O}_{1w*}$ ) is 2.82(10,2,2,2) Å.

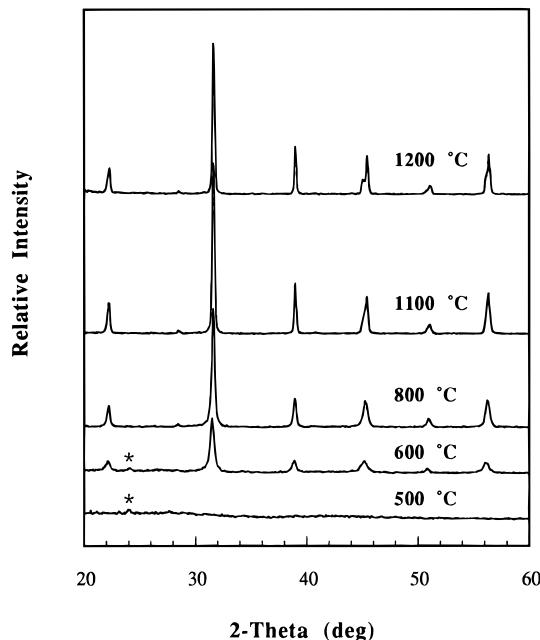
hydrogen-bonded pairs of octahedral  $[\text{Ti}^{IV}(\text{OCH}_2\text{CH}_2\text{O})_3]^{2-}$  anions and 9-coordinate  $[\text{Ba}^{II}(\text{HOCH}_2\text{CH}_2\text{OH})_4(\text{OH}_2)]^{2+}$  cations like those shown in Figure 1. The  $[\text{Ti}^{IV}(\text{OCH}_2\text{CH}_2\text{O})_3]^{2-}$  ions lie on a crystallographic  $C_3$  axis with the chelating glycolate ligands adopting *lel* ring conformations. Since the  $\text{Ba}^{II}$  centers also lie on this crystallographic  $C_3$  axis, the water molecule and the fourth ethylene glycol molecule which are coordinated to Ba are necessarily disordered in the lattice. Electron density maxima in difference Fourier maps can be interpreted by invoking two different disordered configurations for these two ligands. Two different arrangements for the oxygen atoms of these two ligands about the  $C_3$  axis give reasonable  $\text{Ba}-\text{O}$  and interligand  $\text{O}\cdots\text{O}$  separations on the  $\text{Ba}^{II}$  coordination sphere:  $\text{O}_5$ ,  $\text{O}'_5$ , and  $\text{O}_{1w}$  form one equivalent set while  $\text{O}_6$ ,  $\text{O}'_6$ , and  $\text{O}_{1w*}$  form the other. When the (disordered) carbons for the fourth glycol are included, one produces the two ligand configurations at  $\text{Ba}^{II}$  shown in Figure 1. The first configuration has  $\text{O}_{1w}$  and the  $\text{O}_5\text{C}_6\text{C}_5\text{O}'_5$  glycol coordinated to Ba, and the second configuration has  $\text{O}_{1w*}$  and the  $\text{O}_6\text{C}_5\text{C}_6\text{O}'_6$  glycol coordinated to Ba. Although the hydrogen centers on the disordered glycol and water molecules could not be located or refined, the hydroxyl hydrogens on oxygens  $\text{O}_3$  and  $\text{O}_4$  were located from a difference Fourier synthesis and refined as independent isotropic atoms. The three hydrogens bonded to the  $C_3$ -related  $\text{O}_3$  glycol oxygens are used to form the hydrogen-



**Figure 2.** Perspective drawing of the pseudotetrahedral array of hydrogen-bonded counteranions surrounding each cation and anion in crystals of  $\text{BaTi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}$ . The viewing direction and atom representation are the same as those of Figure 1. Only one set of disordered water and ethylene glycol ligands are shown coordinated to  $\text{Ba}^{II}$ . The  $\text{O}_{1a}\cdots\text{O}_4$  and  $\text{O}_2\cdots\text{O}_3$  separations are 2.58 and 2.64 Å, respectively; the  $\text{O}_{1a}\cdots\text{H}_{4o}-\text{O}_4$  and  $\text{O}_2\cdots\text{H}_{3o}-\text{O}_3$  angles are 157° and 160°, respectively.

bonded ion pair shown in Figure 1, and those bonded to glycol oxygen  $\text{O}_4$  are used to form hydrogen bonds to three adjacent  $[\text{Ti}^{IV}(\text{OCH}_2\text{CH}_2\text{O})_3]^{2-}$  anions as shown in Figure 2. These hydrogen bonds thus generate a distorted tetrahedral array of four  $[\text{Ti}^{IV}(\text{OCH}_2\text{CH}_2\text{O})_3]^{2-}$  anions surrounding a single  $[\text{Ba}^{II}(\text{HOCH}_2\text{CH}_2\text{OH})_4(\text{OH}_2)]^{2+}$  cation in the crystal. Since they also generate a distorted tetrahedral array of  $[\text{Ba}^{II}(\text{HOCH}_2\text{CH}_2\text{OH})_4(\text{OH}_2)]^{2+}$  cations around each  $[\text{Ti}^{IV}(\text{OCH}_2\text{CH}_2\text{O})_3]^{2-}$  anion, the lattice can be viewed as a trigonally distorted zinc blend arrangement of  $[\text{Ba}^{II}(\text{HOCH}_2\text{CH}_2\text{OH})_4(\text{OH}_2)]^{2+}$  cations and  $[\text{Ti}^{IV}(\text{OCH}_2\text{CH}_2\text{O})_3]^{2-}$  anions with one short 5.39 Å  $\text{Ba}\cdots\text{Ti}$  separation (the one within the hydrogen-bonded ion pair of Figure 1) and three longer 6.17 Å  $\text{Ba}\cdots\text{Ti}$  separations around each metal ion in the lattice. Alternatively, the structure can be viewed as comprised of ion pairs of the type shown in Figure 1 occupying a trigonally distorted fcc lattice.

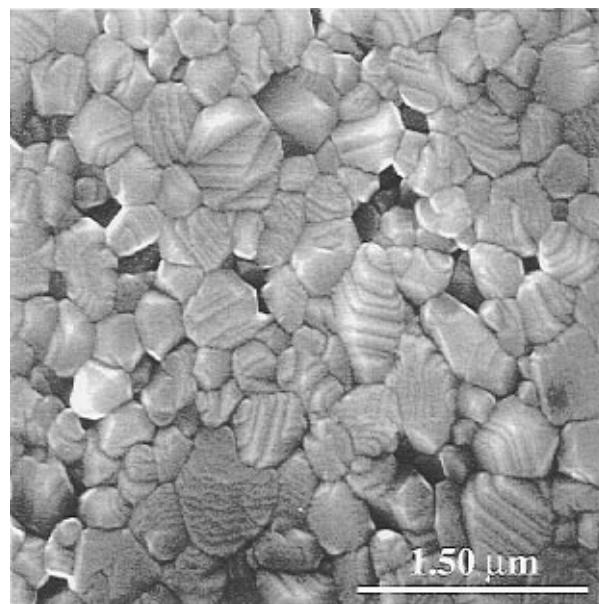
Thermogravimetric analysis of  $\text{BaTi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}$  in  $\text{N}_2$  at 10 °C/min showed clear weight loss rate maxima at 67, 120, and 360 °C. The 4% weight loss observed between 25 and 82 °C corresponds to loss of a single water molecule per formula unit (3% calculated), the 39% loss between 82 and 310 °C to four ethylene glycol molecules (39% calculated), and the 19% weight loss between 310 and 1000 °C to conversion of three glycolate ligands into three oxide ligands (21% calculated). Thermal conversion of BTG in air into crystalline  $\text{BaTiO}_3$  was monitored by X-ray powder diffraction and observed at about 600 °C, a temperature typically observed for barium titanate complexes.<sup>2</sup> The diffraction patterns shown in Figure 3 were measured from samples heated to the temperature indicated at 10 °C/min, held at that temperature for 60 min, and then cooled to ambient temperature. The diffraction patterns show only a barely detectable line at  $2\theta = 24.1^\circ$



**Figure 3.** Cu K $\alpha_1$  X-ray powder diffraction patterns of BTG after calcining at the temperatures indicated. Asterisks in the 500 and 600 °C patterns label a very weak line assigned to BaCO<sub>3</sub>.<sup>18</sup> The remaining diffraction lines correspond to barium titanate with the perovskite structure.<sup>19,20</sup>

for BaCO<sub>3</sub><sup>17</sup> at 500 and 600 °C. Transformation of apparently cubic nanocrystalline BaTiO<sub>3</sub> into tetragonal BaTiO<sub>3</sub> was evident at 1200 °C from the splitting of the  $2\theta = 22.2^\circ$  (100), 45.2° (200), 50.9° (210), and 56.0° (211) peaks.<sup>18,19</sup>

Barium titanate powders obtained by calcining BTG at 900 °C for 2 h were dry pressed at 270 MPa and then heat treated, without the use of additives, for 2 h at 1300 °C. The material thus obtained was then sliced, polished, and thermally etched (1200 °C for 1 h) for examination by SEM. The micrographs obtained showed a bimodal grain size distribution characteristic of exaggerated grain growth during BaTiO<sub>3</sub> sintering,<sup>20</sup> with exaggerated grain diameters of ca. 20  $\mu\text{m}$  in a fine-grain (ca. 0.5  $\mu\text{m}$ ) matrix. Figure 4 illustrates the fine-grain



**Figure 4.** SEM micrograph of the sintered ceramic obtained from BTG-derived BaTiO<sub>3</sub> powder as described in the text.

matrix, where some grain pull-out occurred during sample preparation. Electrical measurements obtained from thin-sliced (0.72 mm) samples yielded dielectric properties ( $K = 2260$ , loss tan  $\delta = 0.01$  at 1 V/cm, 1 kHz, 25 °C) characteristic of polycrystalline barium titanate having this microstructure.<sup>21</sup> We are currently optimizing these properties through variation of the calcining and sintering conditions.

**Acknowledgment.** This research was supported through the Frederick Seitz Materials Research Laboratory by the U.S. Department of Energy, Division of Materials Science, under Contract DEFG02-91ER-45439. X-ray powder diffraction and electron microscopy were carried out in the Center for Microanalysis of Materials, University of Illinois, which is supported by the U.S. Department of Energy under grant DEFG02-91-ER45439.

**Supporting Information Available:** Crystal structure report, listings of positional and thermal parameters, listings of bond lengths and angles, and perspective structure drawing for BaTi(C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>)<sub>3</sub>·4C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>·H<sub>2</sub>O (15 pages); structure factor tables (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

CM950547Q

(17) Bell, A. M. T. *Superconduct. Sci. Technol.* **1990**, *3*, 55.  
 (18) (a) Naka, S.; Nakakita, F.; Suwa, Y.; Inagaki, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1168. (b) Powder Diffraction File Card No. 31-0174. Joint Committee on Powder Diffraction Standards, 1994.  
 (19) Powder Diffraction File Card No. 5-626. Joint Committee on Powder Diffraction Standards, 1993.  
 (20) Kingery, W. D.; Bowen, H. K.; Ulmann, D. R. *Introduction to Ceramics*, 2nd ed.; John Wiley & Sons: New York, 1976; p 461.  
 (21) Kinoshita, K.; Yamaji, A. *J. Appl. Phys.* **1976**, *47*, 371.