Synthesis and Crystal Structure of Barium Titanyl Oxalate, BaTi(O)(C₂O₄)₂·5H₂O: A Molecular Precursor for BaTiO₃

Wendell E. Rhine* and Robert B. Hallock

Ceramics Processing Research Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

William M. Davis

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Winnie Wong-Ng

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Single crystals of barium titanyl oxalate (BTO), $BaTi(O)(C_2O_4)_2\cdot5H_2O$, were grown by slowly evaporating water from a dilute solution of barium nitrate and ammonium titanyl oxalate, $(NH_4)_2Ti(O)(C_2O_4)_2\cdot H_2O$, at pH 1. The molecular structure of BTO was determined by single-crystal X-ray crystallography. The chemical formula is more accurately described as $Ba_2Ti_2O_2(C_2O_4)_4\cdot10H_2O$ in order to account for the number of unique atoms in the structure. Seven of the ten water molecules are associated with barium atoms, and the remaining three waters occupy interstitial sites in the structure and are not coordinated to either titanium or barium atoms. The compound readily loses water beginning at room temperature, depending on drying conditions and/or relative humidity; hence in the past the compound has been referred to most often as the tetrahydrate, $BaTi(O)(C_2O_4)_2\cdot4H_2O$. Crystal data: $C_8H_{20}Ba_2O_{28}Ti_2$, $M = 934.65$, monoclinic, space group $P2_1/n$ (No. 14), $a = 13.367$ (1) Å, $b = 13.852$ (1) Å, $c = 14.023$ (1) Å, $\beta = 91.61$ (2)°, $V = 2595.6$ Å³, $Z = 4$, $D_{calc} = 2.392$ g/cm³, $R = 0.064$, and $R_w = 0.069$.

Introduction

Barium titanate, $BaTiO_3$, is a major component of high dielectric constant ceramics for capacitor manufacture. The microstructure and, consequently, dielectric properties of barium titanate are very dependent on stoichiometry with regard to the Ba/Ti ratio.[1] One of the most studied methods for controlling the stoichiometry of barium titanate is to use a molecular precursor such as barium titanyl oxalate (BTO).

Barium titanyl oxalate was first reported by Pechard[2] in 1893 as a crystalline compound of the formulation 2-$(C_2O_4H_2)\cdot BaO\cdot TiO_2$ (i.e., the tetrahydrate), and it was isolated as the product of the reaction between potassium titanyl oxalate and barium chloride. Rosenheim and Schutte[3] reported the dihydrate as the product of the same reaction. Barium titanyl oxalate was not further investigated until after the emergence of $BaTiO_3$ as an important dielectric material during World War II.

In 1956, Clabaugh et al.[4] realized the potential for conversion of BTO to stoichiometric $BaTiO_3$; however, they reported that Pechard's[2] method for the synthesis of BTO resulted in incomplete substitution of Ba for K and resulted in a barium-deficient product. The Ba:Ti stoichiometry in BTO and in the resulting $BaTiO_3$ were found to be very dependent on reaction conditions, and an optimized synthesis was developed which involved the addition of barium chloride (0.675 mol/3 L = 0.225 M) and titanium tetrachloride (0.668 mol/3 L = 0.223 M), with

barium in 1% excess, to a hot aqueous solution of oxalic acid containing 10% excess of the amount required for the formation of BTO (final volume = 3 L). Under these conditions, barium titanyl oxalate tetrahydrate with a Ba:Ti ratio of unity was reproducibly prepared and converted to high-purity stoichiometric $BaTiO_3$ at 900 °C.[4]

Since the report by Clabaugh et al.[4] in 1956, the use of BTO to prepare stoichiometric barium titanate has been widely investigated and is the subject of more than 40 publications or patents. Most of the reported syntheses are similar to that of Clabaugh et al.[4] but differ in the concentrations of reagents or temperatures used.[5-8] Clabaugh et al.[4] carried out the precipitation at 80 °C, while others have used lower temperatures and obtained similar results.[13,14,16,17] Several investigators have tried using

(1) See for example: (a) Uchino, K.; Sadanaga, E.; Hirose, T. *J. Am. Ceram. Soc.* 1989, 72, 1555–1559. (b) Kulcsar, F. *J. Am. Ceram. Soc.* 1956, 39, 13–17. (c) Hu, Y. H.; Harmer, M. P.; Smyth, D. M. *J. Am. Ceram. Soc.* 1985, 372–376. (d) Beauger, A.; Mutin, J. C.; Niepce, J. C. *J. Mater. Sci.* 1984, 19, 195–201 and references therein.

(2) Pechard, M. E. *Compt. Rend.* 1893, 116, 1513–1516.

(3) Rosenheim, A.; Schutte, O. *Z. Anorg. Chem.* 1901, 26, 239–257.

(4) Clabaugh, W. S.; Swiggard, E. M.; Gilchrist, R. *J. Res. Natl. Bur. Stand.* 1956, 56, 289–291.

(5) Fang, T.-T.; Lin, H.-B. *J. Am. Ceram. Soc.* 1989, 72, 1899–1906.

(6) Strishkov, B. V.; Lapitskii, A. V.; Vlasov, L. G. *J. Appl. Chem. USSR (Engl. Trans.)* 1960, 33, 1986–1990; 1961, 34, 646–648; *Zh. Prikl. Khim.* 1960, 33, 2009–2014; 1961, 34, 673–674.

(7) Orlyanskii, Yu. N. *J. Appl. Chem. USSR* 1968, 44, 1752–1755; *Zh. Prik. Khim.* 1968, 44, 1730–1734.

(8) Kudaka, K.; Iizumi, K.; Sasaki, K. *Am. Ceram. Soc. Bull.* 1982, 72, 1236.

(9) Yamamura, H.; Watanabe, A.; Shirasaki, S.; Moriyoshi, Y.; Tanada, M. *Ceram. Int.* 1985, 11, 17–22.

(10) Rhine, W. E., Saegusa, K., Hallock, R. B., Cima, M. J. Control of Ceramic Powder Composition by Precipitation Techniques. In *Ceramic Powder Science III Ceramic Transactions*; Messing, G. L., Hirano, S., Hausner, H. American Ceramic Society: Columbus, 1990; Vol. 12, p 107.

(11) Pfaff, G.; Schmidt, F.; Ludwig, W.; Feltz, A. *J. Thermal Anal.* 1988, 771–779.

(12) Bhattacharjee, S., Paria, M. K.; Maiti, H. S. *Ceram. Int.* 1990, 16, 211–214.

(13) Strishkov, B. V.; Lapitskii, A. V.; Vlasov, L. G.; Tsvetkov, A. I. *Dokl. Akad. Nauk SSR (Engl. Trans.)* 1960, 133, 973–975; Russ. orig 133, 1347–1349.

(14) Strizhkov, B. V.; Lapitskii, A. V.; Simanov, Yu. P.; Vlaskov, L. V. *Russ. J. Inorg. Chem.* 1962, 7, 1128–1130.

(15) Gallager, P. K.; Schrey, F. *J. Am. Ceram. Soc.* 1963, 46, 567–573.

(16) Gopalakrishnamurthy, H. S.; Subba Rao, M.; Narayanan Kutty, T. R. *J. Inorg. Nucl. Chem.* 1975, 37, 891–898; 1875–1878.

titanyl nitrate instead of titanium tetrachloride as the titanium source,[5,9,10] and some workers have reported varying degrees of success in preparing BTO from ethanolic solutions.[5,9,11,12]

A majority of researchers have reported BTO as the tetrahydrate, in agreement with the original work of Pechard;[2] however, a close examination of the literature shows that the BTO obtained often contained more than 4 mol of water. Strishkov's[6,13] analytical and TGA data were consistent with 4.4 mol of water, and in a later paper he referred to BTO as $BaTi(O)(C_2O_4)_2 \cdot 4.5H_2O$.[14] Gallager and Schrey[15] reported an "extra few percent of moisture present" in one of their preparations. Gopalakrishnamurthy and co-workers[16] reported that the degree of hydration of BTO varied depending on the relative humidity of the surrounding atmosphere from 4.5 waters at 50% relative humidity to 4.8 waters at 90% relative humidity. Yen et al.[17] recently studied the low-temperature decomposition of BTO assuming it was the tetrahydrate. They observed that BTO was still crystalline after losing 2.9 waters of hydration.

A number of different X-ray powder diffraction patterns have been reported for BTO,[5,6,8,9,12,14,17,18] in addition to several reports of amorphous forms of BTO.[5,9,12] One attempt to prepare BTO in ethanol led to the isolation of a product which gave an X-ray diffraction pattern similar to barium nitrate.[9] The exact composition of this product is not known, but the X-ray powder diffraction pattern was reported to be that of BTO, since this precipitate could be thermally decomposed to barium titanate. In a recent paper, Fang and co-workers[5] reported that the products of the reaction between $Ba(NO_3)_2$ and $TiO(NO_3)_2$ in an ethanolic solution of oxalic acid were a mixture of barium nitrate and $Ti(OH)_2(C_2O_4)$.

The most widely accepted X-ray diffraction pattern for BTO is based on the work of Kudaka et al.[8] and is tabulated for the range 10–30° 2θ on JCPDS card 36-682;[19] however, Yen and co-workers[17] recently calculated unit cell parameters for BTO as $a = 14.954$ Å, $b = 19.332$, $c = 13.9332$, $\beta = 106.43°$, and $Z = 12$, based on the monoclinic system $P2/m$. Louër et al.[18] recently published another analysis of the high-resolution powder pattern of BTO based on a monoclinic cell, and the calculated unit cell parameters were $a = 14.044$ (2) Å, $b = 13.812$ (2) Å, $c = 13.382$ (2) Å, and $\beta = 91.48$ (1)°.

Although BTO has been recognized as a crystalline compound for nearly 100 years, it has never been structurally characterized, and its very existence as a discrete compound remains the subject of debate in the current literature.[5,20,21] To ascertain the nature of this widely studied compound, we grew single crystals of BTO and determined its crystal structure by X-ray crystallography.

Experimental Section

Preparation of $(NH_4)_2Ti(O)(C_2O_4)_2 \cdot H_2O$. An ethanol solution of titanium ethoxide (109.96 g, 0.482 mol, Dynamit Nobel Chemicals, Rockleigh, NJ) was added slowly with stirring to a solution containing 60.74 g (0.482 mol) of oxalic acid dihydrate (Alfa Products, Danvers, MA) and 68.64 g (0.483 mol) of am-

monium oxalate monohydrate (Mallinckrodt Inc., Paris, KY) in 600 mL of water at 80 °C. The overall reaction leading to the synthesis of $(NH_4)_2Ti(O)(C_2O_4)_2 \cdot H_2O$ is

$$Ti(OEt)_4 + H_2C_2O_4 + (NH_4)_2C_2O_4 + 3H_2O \rightarrow$$
$$(NH_4)_2Ti(O)(C_2H_4)_2 \cdot H_2O + 4EtOH$$
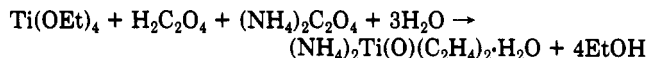
The mixture was initially turbid, but a clear solution was usually obtained after stirring at 80 °C for 1 h. If the solution was still turbid, a small amount of oxalic acid was added, and the solution turned clear in a few minutes. The resulting solution was filtered to remove trace solids and allowed to cool to room temperature. A volume of *n*-propanol approximately equal to twice the volume of aqueous solution was then added while stirring. When stirring was stopped, the mixture separated into two layers, and the product crystallized from the aqueous layer upon setting. The product was isolated by filtration, and the crystalline precipitate was washed with *n*-propanol. The yield of purified $(NH_4)_2Ti(O)(C_2O_4)_2 \cdot H_2O$ was greater than 80%. Elemental analysis for $C_4H_{10}N_2O_{10}Ti$: calcd C, 16.34 (found, 16.37); H, 3.34 (3.36); N, 9.53 (9.49).

Preparation of $BaTi(O)(C_2O_4)_2 \cdot 5H_2O$ (BTO). Ammonium titanyl oxalate (0.45 g, 1.5 mmol) was dissolved in 250 mL of water, and the pH was adjusted to 1 with nitric acid. In a separate flask, barium nitrate (0.38 g, 1.5 mmol) was dissolved in 250 mL of water, and the pH was adjusted to 1 with nitric acid. The ammonium titanyl oxalate solution was added to the barium nitrate solution, and the mixture remained free of precipitate. Water was allowed to evaporate slowly from an open Erlenmeyer flask, and crystals of $BaTi(O)(C_2O_4)_2 \cdot 5H_2O$ nucleated, grew, and became visible after several months. The crystals, which begin to lose water even at room temperature, were isolated by filtration and air-dried at room temperature. Elemental analysis for $BaTi(O)(C_2O_4)_2 \cdot 4.5H_2O$, $C_8H_{18}Ba_2Ti_2O_{27}Ti_2$: calcd C, 10.48 (found, 10.48); H, 1.98 (1.95); Ba, 29.96 (29.59); Ti, 10.45 (10.28); Ba/Ti mol ratio = 1.003. Samples that were analyzed for water content after shorter drying times contained more water with 5 waters being the upper limit.

X-ray Diffraction Study. A colorless prism of BTO having approximate dimensions of $0.15 \times 0.15 \times 0.15$ mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 54.9°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26° with a takeoff angle of 2.8°. Scans of $(0.80 + 0.35 \tan \theta)°$ were made at speeds ranging from 0.9 to 8.0°/min (in ω). Moving-crystal, moving-counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 3.0 to 3.5 mm and a vertical slit set to 4.0 mm. The diameter of the incident beam collimator was 0.8 mm, and the crystal-to-detector distance was 17.3 cm. For intense reflections, an attenuator was automatically inserted in front of the detector.

Of the 6462 reflections collected, 6203 were unique ($R_{int} = 0.081$); equivalent reflections were merged. The intensities of three representative reflections, which were measured after every 60 min of X-ray exposure time, remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient of BTO for Mo Kα radiation is 36.9 cm^{-1}. The data were corrected for Lorentz and polarization effects, but azimuthal scans of several reflections indicated no need for an absorption correction. A correction for secondary extinction was applied (coefficient = 0.10047×10^{-7}).

The structure was solved by a combination of the Patterson method and difference Fourier methods.[22] The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement[23] was based on 3883 observed reflections

(17) Yen, F.-U.; Chang, C. T.; Chang, Y.-H. *J. Am. Ceram. Soc.* **1990,** *73* [11], 3422–27.

(18) Louër, D.; Boultif, A.; Gotor, F. J.; Criado, J. M. *Powder Diffr.* **1990,** *5,* 162.

(19) Joint Committee on Powder Diffraction Standards, Set 36-682, Philadelphia, PA.

(20) Fang, T.-T.; Lin, H.-B.; Hwang, J.-B. *J. Am. Ceram. Soc.* **1990,** *73,* 3363–3367.

(21) Osseo-Asare, K.; Arriagada, F. J.; Adair, J. H. *Ceram. Trans.* **1988,** *1,* 47.

(22) Structure solution methods: (a) Calabrese, J. C.; PHASE—Patterson Heavy Atom Solution Extractor. University of Wisconsin—Madison, Ph.D. Thesis, 1972. (b) Beurskens, P. T. DIRDIF: Direct Methods for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1 Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands.

1210 *Chem. Mater., Vol. 4, No. 6, 1992*

Rhine et al.

$[I > 3.00\sigma(I)]$ and 362 variable parameters, and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.064$$

$$R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2} \right]^{1/2} = 0.069$$

The standard deviation of an observation of unit weight[24] was 1.66. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ vs $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$, and various classes of indexes showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.19 and -3.12 $e^-/\text{Å}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_{calc};[26] the values for $\Delta f'$ and $\Delta f''$, were those of Cromer.[27] All calculations were performed using the TEXSAN[28] crystallographic software package from Molecular Structure Corp.

Calculated Powder Diffraction Pattern of BTO. A simulated powder diffraction pattern was computed based on the single-crystal data, using a local Siemen's version of POWD10.[29] All calculations used Cu $K\alpha_1$ radiation with a wavelength of 1.540 598 1 Å and Smith's tabulation of the Cromer and Waber atomic scattering factors.[30,31] Intensities (values reported for $I_{cal} > 1$) were referred to peak height values and were derived from a Cauchy profile with a tabulated width at half-height determined at NIST.[29] Anomalous dispersion corrections were applied to the heavy atoms Ba and Ti.

Results and Discussion

The preparation of BTO has been the subject of a number of papers. Clabaugh et al.[4] state in their original paper that when a solution of $BaCl_2$ is added to a solution of $TiCl_4$ and oxalic acid at 80 °C, a precipitate forms immediately which dissolves and reprecipitates as BTO. In this effort, we prepared BTO via reactions of $(NH_4)_2Ti$-$(O)(C_2O_4)_2 \cdot H_2O$ with barium salts under a variety of conditions, but we encountered difficulty obtaining a precipitate with 1.00:1.00 stoichiometry (i.e., BTO free of other byproducts).[32] However, by working at room temperature in dilute solution at pH 0–1.5, we were able to achieve slow crystallization of stoichiometric BTO.

In the method used to grow crystals for this work, a clear solution was obtained when a stoichiometric amount of

(23) Least-squares function minimized: $\sum w(|F_o| - |F_c|)^2$ where $\sum w = 4F_o^2/\sigma^2(F_o^2); \sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$; S = scan rate; C = total integrated peak count; R = ratio of scan time to background counting time; B = total background count; Lp = Lorentz/polarization factor; $p = p$ factor.

(24) Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$; where N_o = number of observations; N_v = numbers of variables.

(25) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(26) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(27) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(28) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

(29) Smith, D. K.; Nichols, M. C.; Zolensky, M. E. A Fortran IV Program for Calculating X-ray Powder Diffraction Pattern. Version 10. College of Earth and Mineral Sciences: Pennsylvania State University, 1983.

(30) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.

(31) Cromer, D. T.; Mann, J. B. Los Alamos Scientific Laboratory, LA4403, 1970.

(32) Rhine, W. E.; Hallock, R. B.; Cima, M. *J. Ceram. Trans.* **1992**, *26*, 8.

Table I. Crystallographic Data for $Ba_2Ti_2(C_2O_4)_4 \cdot 10H_2O$

empirical formula	$C_8H_{20}Ba_2O_{28}Ti_2$
formula weight	934.65
crystal color, habit	colorless, prism
crystal dimensions (mm)	0.150 × 0.150 × 0.150
crystal system	monoclinic
space group	$P2_1/n$ (No. 14)
lattice parameters	$a = 13.367$ (1) Å
	$b = 13.852$ (1) Å
	$c = 14.023$ (1) Å
	$\beta = 91.61$ (2)°
unit cell volume	2595.6 Å^3
Z	4
D_{calc}	2.392 g/cm^3
no. of reflections	
measured	6462
unique ($R_{int} = 0.081$)	6203
observed ($I > 3.00\sigma(I)$)	3883
$2\theta_{max}$	54.9°
R	0.064
R_w	0.069
absorption coefficient	36.9 cm^{-1}

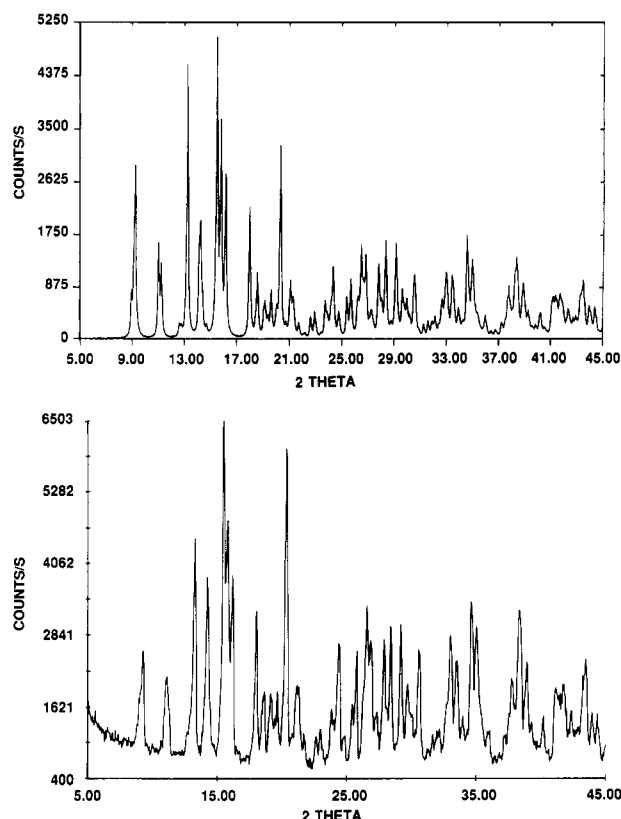**Figure 1.** Calculated (a, top) and observed (b, bottom) powder X-ray diffraction patterns for BTO.

$Ba(NO_3)_3$ was added to a dilute solution ($<10^{-3}$ M) of ammonium titanyl oxalate as long as the pH was less than 1.5. If the pH was not adjusted by adding acid, a precipitate formed immediately and did not redissolve. X-ray diffraction patterns of precipitates obtained at pHs of 4–5 indicated the precipitates were amorphous.[10] When the initial pH was below 0, crystals of $Ba(NO_3)_2$ were isolated instead of BTO.

Recently, aqueous stability diagrams have been calculated for the $Ba-Ti-C_2O_4-H_2O$ system based on thermodynamic modeling. According to this work, BTO is thermodynamically unstable relative to titanium oxide or hydrous oxide, especially at low ($<10^{-2}$ M) metal ion concentrations; its existence is suggested to be due to complexation with chloride ion or to its precipitation as a metastable phase.[21] The fact that the crystals of BTO grew

Figure 2. Asymmetric unit of BTO; O(10), O(101), and O(102) occupy interstitial positions in the unit cell and are not shown.

Figure 3. $[Ti(O)(C_2O_4)_2]_4^{8-}$ eight-membered ring component of BTO.

slowly out of solution over several months suggests that BTO is a thermodynamically stable compound. The results suggest that the precipitate which initially forms, as observed in this work and reported by Clabaugh et al.,[4] is the kinetically controlled product and dissolves under acidic conditions (pHs less than 1.5). From our results,[32] the products isolated immediately after combining reagents are titanium-rich. Similar results have been reported by Orlyanski,[7] and most successful preparations use a 1-5% excess of barium in the solutions.[4,8]

Calculated X-ray Powder Diffraction of BTO. X-ray diffraction from single crystals showed that BTO crystallizes in the monoclinic space group $P2_1/n$. The crystal data are listed in Table I. The calculated powder diffraction pattern of $BaTi(O)(C_2O_4)_2 \cdot 5H_2O$ for $5° < 2\theta < 40°$, based on the single crystal data (Table I), is shown in Figure 1, along with the observed pattern for crushed crystals of $BaTi(O)(C_2O_4)_2 \cdot 4.5H_2O$ dispersed on silicon grease. The calculated diffraction pattern is in excellent agreement with the observed pattern, and it is quite similar to patterns published by Kudaka et al.[8] and Louër et al.,[18] although some differences in relative intensities are noted, perhaps due to slight deviations from stoichiometry or to varying degrees of hydration between samples prepared under different conditions. The calculated and observed data for $BaTi(O)(C_2O_4)_2 \cdot 4.5H_2O$ and the calculated data for $BaTi(O)(C_2O_4)_2 \cdot 5H_2O$, including d spacings, 2θ, intensity, and hkl values, are tabulated for $2\theta < 40°$ in Table II. The cell constants determined from the single-crystal X-ray diffraction results and the calculated powder pattern are in good agreement with those reported by Louër et al. except for the assignments for the a and c axis, which have been reversed. Since Louër et al. prepared their sample by Clabaugh et al.'s method and our crystals were grown at room temperature, the temperature of the reaction does not appear to affect the cell constants and, therefore, the structure or stoichiometry of the oxalate. Also, no significant effect due to the degree of hydration was observed in the calculated intensities.

Crystal Structure of BTO. Positional and isotropic thermal parameters are given in Table III, and intramolecular bond distances and bond angles are given in Tables IV and V, respectively. To account for the number of unique atoms in the structure, BTO is formulated as $Ba_2Ti_2O_4(C_2O_4)_4 \cdot 10H_2O$; an ORTEP diagram of the asymmetric unit is shown in Figure 2. The overall structure of BTO is rather complex and not easily viewed in its
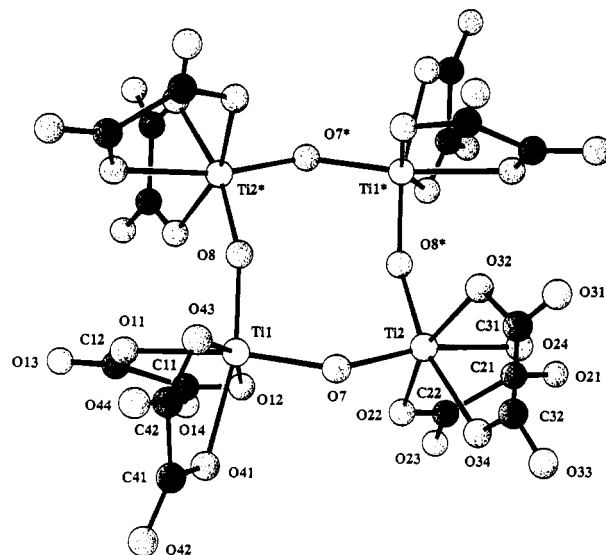
entirety. The $[Ti(O)(C_2O_4)_2]_4^{8-}$ anions contain eight-membered Ti-O rings composed of two pairs of nonequivalent $Ti(O)(C_2O_4)_2^{2-}$ moieties which are related by an inversion center (Figure 3).

The Ti-O eight-membered ring observed in BTO is typical of the structures of many titanyl compounds; in fact, very similar $[Ti(O)(C_2O_4)_2]_4^{8-}$ anions are found in the closely related compounds $(NH_4)_2Ti(O)(C_2O_4)_2 \cdot H_2O$[33] and $K_2Ti(O)(C_2O_4)_2 \cdot 2.25H_2O$.[34] Some other examples of titanyl compounds with Ti-O ring structures include [TiO-$(acac)_2]_2$,[35] $Cs_4[Ti_4O_4(C_6H_6NO_6)_4] \cdot 6H_2O$ ($C_6H_6NO_6$ = nitrilotriacetic acid),[36] and $[CpTiOCl]_4$.[37] The compounds $[CpTiOCl]_4$ and $Cs_4[Ti_4O_4(C_6H_6NO_6)_4] \cdot 6H_2O$ are tetrameric titanyl compounds with eight-membered Ti-O rings similar to those found in BTO. All of the tetramers except $[CpTiOCl]_4$ have C_i symmetry and exist in the chair form. The $[CpTiOCl]_4$ complex, on the other hand, has D_2 symmetry and exists in a form that the authors describe as two butterfly wings, which could be referred to as the boat form of the eight-membered ring (all four Ti atoms lie on the same side of the plane defined by the four oxygen atoms). $[TiO(acac)_2]_2$ is a dimer with octahedral coordination about the Ti atoms and four-membered Ti-O rings composed of edge-shared octahedra.[37]

The rings in these compounds consist of alternating long and short Ti-O bonds and are presumably the result of oligomerization of Ti=O bonds to form compounds with Ti=O→Ti bonds. In BTO the differences between the long and short distances are less than observed for the ammonium, potassium, and cesium compounds (Table VI), and they are almost equivalent [i.e., 1.81 (1), 1.802 (8), 1.809 (8), 1.799 (9) Å], which suggests complete delocalization to form Ti-O-Ti bonds rather than unequal Ti= O→Ti bonds. Isolated Ti=O bonds have only been observed in a few sterically hindered compounds;[38,39] the

(33) Van de Velde, G. M. H.; Harkema, S.; Gellings, P. J. *Inorg. Chim. Acta* **1974**, *11*, 243–252.

(34) Haddad, M.; Brisse, F. *Can. Mineral.* **1978**, *16*, 379–385.

(35) Smith, D.; Caughlan, C. N.; Campbell, J. A. *Inorg. Chem.* **1972**, *11*, 2989.

(36) Wieghardt, K.; Quiltltzsch, U.; Weiss, J.; Nuber, B. *Inorg. Chem.* **1980**, *19*, 2514–2519.

(37) Petersen, J. L. *Inorg. Chem.* **1980**, *19*, 181.

(38) (a) Guilard, R.; Lecomte, C. *Coord. Chem. Rev.* **1985**, *65*, 87–113. (b) Hill, J.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chem.* **1989**, *19*, 2514–19.

(39) Meyer, J. M. *Inorg. Chem.* **1988**, *27*, 3901.

Table II. Calculated and Observed d Spacings for BTO

2θ(cal)	2θ(obs)	d(cal)	d(obs)	I(cal)[a]	I(cal)[b]	I(obs)	hkl
8.97	8.80	9.853	10.040	16	17	6	0 1 1
9.26	9.30	9.539	9.502	58	63	30	1 0 1
11.04	11.10	8.006	7.964	32	29	23	-1 1 1
11.25	11.35	7.856	7.790	25	25	12	1 1 1
12.62	12.65	7.009	6.992	5	6	6	0 0 2
12.77			6.926	5	5		0 2 0
13.24	13.30	6.681	6.652	91	90	67	2 0 0
14.25	14.30	6.209	6.189	39	41	50	0 2 1
14.71	14.80	6.018	5.981	5	5	4	2 1 0
15.48	15.50	5.719	5.712	100	100	100	-1 1 2
15.78	15.85	5.610	5.587	73	65	73	1 1 2, 1 2 1
16.16	16.20	5.480	5.467	55	54	56	2 1 1
17.99	18.05	4.926	4.911	44	42	44	0 2 2
18.59	18.65	4.769	4.754	22	21	20	2 0 2
19.18	19.15	4.624	4.631	13	12	17	-2 1 2
19.38			4.577	8	6		-2 2 1
19.62	19.65	4.520	5.514	16	14	19	2 2 1
19.94			4.427	11	10		-1 0 3
20.04	20.35	4.364	4.361	64	58	94	0 1 3, 1 0 3
20.74	20.80	4.280	4.267	6	5	6	-3 0 1
21.08	21.10	4.211	4.207	20	15	20	3 0 1
21.29	21.30	4.170	4.168	14	12	20	1 1 3, -1 3 1
21.72	21.75	4.089	4.083	5	4	3	-3 1 1
22.19			4.003	2	1		-2 2 2
22.62	22.65	3.928	3.923	7	6	7	2 2 2
22.94	23.00	3.873	3.864	9	8	10	0 2 3
23.40	23.40	3.798	3.798	1	1	2	2 3 0
23.73	23.80	3.746	3.736	13	11	15	3 2 0, -1 2 3
23.90			3.720	9	8		-1 3 2
24.36	24.40	3.652	3.645	24	22	35	2 3 1, 2 1 3
24.81	24.80	3.586	3.587	9	7	7	3 1 2
25.40	25.40	3.504	3.504	14	13	17	0 0 4
25.70	25.75	3.463	3.457	20	18	33	0 4 0
26.30	26.20	3.385	3.399	14	13	16	2 2 3
26.49	26.50	3.362	3.361	31	29	45	0 4 1, -1 3 2
26.85	26.85	3.318	3.318	28	25	35	2 2 3, 2 3 2
27.29	27.30	3.266	3.264	9	8	13	-1 4 1, -3 0 2
27.82	27.85	3.202	3.201	25	21	35	-1 3 3, 3 3 0
28.04			3.180	14	12		3 0 3, 1 3 3
28.35	28.40	3.145	3.140	33	30	38	4 1 1, -2 0 4
28.79	28.75	3.099	3.103	6	5	2	3 1 3
29.14	29.15	3.062	3.061	32	29	39	-1 2 4, -2 1 4
29.64	29.65	3.011	3.011	17	14	19	-2 4 1
29.99	30.05	2.978	2.971	13	12	11	-4 1 2
30.20			2.957	8	7		-3 2 3
30.63	30.60	2.916	2.919	21	19	28	4 1 2
31.25			2.860	4	4		-2 2 4
31.60	31.65	2.829	2.825	6	5	3	-2 4 2
31.91			2.802	5	5		2 4 2, 2 2 4
32.15	32.15	2.782	2.782	7	6	3	0 4 3
32.69	32.65	2.737	2.740	13	12	9	-3 1 4, 4 2 2
32.99	33.00	2.713	2.712	22	21	31	1 5 0, 1 4 3
33.45	33.45	2.677	2.677	21	19	23	1 1 5
33.95	33.95	2.639	2.639	10	9	6	-5 0 1
34.31			2.612	6	6		5 0 1
34.61	34.65	2.590	2.587	35	32	42	-3 2 4, -5 1 1
35.00	35.05	2.562	2.558	26	25	35	-3 4 2, -4 2 3
35.38	35.45	2.535	2.530	9	8	9	-1 5 2
35.99	36.00	2.493	2.493	7	7	5	5 2 0
36.41			2.466	2	2		-5 2 1
36.75			2.444	3	2		5 2 1
37.22	37.20	2.414	2.415	5	5	6	1 4 4
37.81	37.70	2.378	2.384	18	15	25	-4 4 1
38.44	38.40	2.340	2.313	27	25	45	1 5 3, 3 4 3
38.88	38.90	2.314	2.313	19	17	30	3 5 1, -5 1 3
39.27	39.30	2.292	2.290	9	8	11	5 0 3, -5 3 1
39.62	39.55	2.273	2.277	4	3	4	5 3 1

[a] Calculated intensities for BaTi(O)(C₂O₄)₂·5H₂O. [b] Calculated intensities for BaTi(O)(C₂O₄)₂·4.5H₂O.

majority of titanyl compounds undergo oligomerization to form species with rings composed of Ti═O→Ti bonds.

The Ti–O bond distances in different titanyl compounds serve as a measure of the degree of delocalization of the Ti═O bonding electrons in the ring compounds. Although Ti═O bond distances of 1.62–1.66 Å are observed for

sterically hindered monomeric titanyl compounds,[38,39] X-ray diffraction structures of a number of titanyl complexes containing Ti–O rings indicate that a Ti–O bond distance of approximately 1.8 Å can be considered "normal" for these compounds (Table VI). The Ti–O bond distance in the ring is 0.18 Å longer than that observed for

Barium Titanyl Oxalate

Chem. Mater., Vol. 4, No. 6, 1992 1213

Table III. Positional and Isotropic Thermal Parameters for BTO

atom	x	y	z	B(eq)
Ba(1)	0.03349 (6)	0.06976 (6)	0.23622 (6)	1.97 (3)
Ba(2)	−0.03464 (6)	0.33780 (6)	0.04450 (5)	1.42 (3)
Ti(1)	−0.1273 (2)	0.3772 (2)	0.4723 (1)	1.22 (9)
Ti(2)	0.0820 (2)	0.3889 (2)	0.6171 (1)	1.24 (9)
O(1)	0.078 (1)	−0.090 (1)	0.351 (1)	8.0 (1)
O(2)	0.116 (1)	−0.063 (1)	0.109	8.0 (1)
O(3)	−0.1474 (7)	0.1064 (9)	0.3291 (7)	3.3 (5)
O(4)	0.2452 (9)	0.082 (1)	0.2744 (8)	4.3 (6)
O(5)	−0.0922 (9)	−0.072 (1)	0.178 (1)	6.3 (8)
O(6)	0.064 (1)	0.134 (1)	0.4196 (9)	4.9 (7)
O(7)	−0.0434 (6)	0.3609 (6)	0.5738 (5)	1.3 (3)
O(8)	0.1061 (6)	0.4956 (7)	0.5482 (6)	1.8 (4)
O(9)	−0.1965 (8)	0.4585 (8)	−0.0263 (9)	4.0 (6)
O(10)	0.673 (1)	0.073 (1)	0.829 (1)	8.0 (1)
O(11)	−0.2058 (6)	0.3730 (6)	0.3399 (6)	1.7 (4)
O(12)	−0.0255 (6)	0.3255 (7)	0.3842 (5)	1.5 (3)
O(13)	−0.1847 (6)	0.3507 (8)	0.1837 (6)	2.3 (4)
O(14)	0.0099 (7)	0.2887 (7)	0.2355 (6)	2.3 (4)
O(21)	0.3854 (6)	0.3479 (7)	0.6141 (6)	2.3 (4)
O(22)	0.1432 (6)	0.2957 (7)	0.5299 (6)	1.8 (4)
O(23)	0.2878 (7)	0.2424 (7)	0.4713 (6)	2.1 (4)
O(24)	0.2330 (6)	0.3907 (7)	0.6628 (6)	1.9 (4)
O(31)	0.0127 (7)	0.4664 (7)	0.8867 (6)	2.4 (4)
O(32)	0.0511 (6)	0.4698 (6)	0.7333 (6)	1.5 (4)
O(33)	0.0157 (8)	0.2626 (7)	0.8699 (6)	2.7 (5)
O(34)	0.0685 (7)	0.2858 (6)	0.7231 (6)	1.6 (4)
O(41)	−0.1854 (6)	0.2343 (7)	0.4799 (6)	1.7 (4)
O(42)	−0.3242 (7)	0.1540 (8)	0.5165 (8)	3.1 (5)
O(43)	−0.2585 (6)	0.3975 (6)	0.5343 (6)	1.7 (4)
O(44)	−0.4009 (6)	0.3274 (8)	0.5779 (7)	2.5 (4)
O(101)	0.637 (1)	0.425 (1)	0.091 (1)	7.0 (1)
O(102)	0.787 (2)	0.222 (1)	0.735 (1)	10.0 (1)
C(11)	−0.0482 (9)	0.320 (1)	0.2946 (9)	1.6 (5)
C(12)	−0.1552 (8)	0.350 (1)	0.2677 (9)	1.5 (5)
C(21)	0.2934 (9)	0.348 (1)	0.608 (1)	1.7 (5)
C(22)	0.240 (1)	0.291 (1)	0.5285 (9)	1.6 (5)
C(31)	0.0328 (9)	0.4245 (9)	0.8112 (8)	1.3 (5)
C(32)	0.040 (1)	0.317 (1)	0.8027 (8)	1.7 (5)
C(41)	−0.273 (1)	0.227 (1)	0.5094 (9)	1.7 (5)
C(42)	−0.3168 (8)	0.324 (1)	0.5458 (8)	1.5 (5)

Table IV. Bond Distances (Å) between Non-Hydrogen Atoms in BTO

atom	atom	dist	atom	atom	dist
Ba(1)	O(1)	2.79 (2)	Ti(2)	O(8)	1.799 (9)
Ba(1)	O(2)	2.80 (1)	Ti(2)	O(22)	1.971 (9)
Ba(1)	O(3)	2.824 (9)	Ti(2)	O(24)	2.101 (9)
Ba(1)	O(4)	2.87 (1)	Ti(2)	O(32)	2.030 (8)
Ba(1)	O(5)	2.69 (1)	Ti(2)	O(34)	2.073 (8)
Ba(1)	O(6)	2.74 (1)	O(11)	C(12)	1.27 (1)
Ba(1)	O(14)	3.05 (1)	O(12)	C(11)	1.29 (1)
Ba(1)	O(21)	2.822 (9)	O(13)	C(12)	1.23 (1)
Ba(1)	O(44)	2.80 (1)	O(14)	C(11)	1.23 (1)
Ba(2)	O(9)	2.89 (1)	O(21)	C(21)	1.23 (1)
Ba(2)	O(13)	2.844 (8)	O(22)	C(22)	1.30 (1)
Ba(2)	O(14)	2.811 (9)	O(23)	C(22)	1.24 (1)
Ba(2)	O(21)	2.96 (1)	O(24)	C(21)	1.28 (1)
Ba(2)	O(23)	2.790 (9)	O(31)	C(31)	1.24 (1)
Ba(2)	O(31)	2.923 (9)	O(32)	C(31)	1.29 (1)
Ba(2)	O(31)	2.891 (9)	O(33)	C(32)	1.25 (1)
Ba(2)	O(33)	2.761 (9)	O(34)	C(32)	1.27 (1)
Ba(2)	O(42)	2.85 (1)	O(41)	C(41)	1.27 (1)
Ba(2)	O(44)	2.93 (1)	O(42)	C(41)	1.23 (2)
Ti(1)	O(7)	1.802 (8)	O(43)	C(42)	1.30 (1)
Ti(1)	O(8)	1.81 (1)	O(44)	C(42)	1.22 (1)
Ti(1)	O(11)	2.107 (9)	C(11)	C(12)	1.53 (2)
Ti(1)	O(12)	1.997 (8)	C(21)	C(22)	1.53 (2)
Ti(1)	O(41)	2.131 (9)	C(31)	C(32)	1.50 (2)
Ti(1)	O(43)	1.999 (8)	C(41)	C(42)	1.56 (2)
Ti(2)	O(7)	1.809 (8)			

Table V. Bond Angles around Ti(1), Ti(2), O(7), and O(8)[a]

atom	atom	atom	angle
O(7)	Ti(1)	O(8)	98.7 (4)
O(7)	Ti(1)	O(11)	167.4 (4)
O(7)	Ti(1)	O(12)	91.3 (3)
O(7)	Ti(1)	O(41)	93.7 (4)
O(7)	Ti(1)	O(43)	102.0 (4)
O(8)	Ti(1)	O(11)	87.9 (4)
O(8)	Ti(1)	O(12)	98.0 (4)
O(8)	Ti(1)	O(41)	166.4 (4)
O(8)	Ti(1)	O(43)	94.3 (4)
O(11)	Ti(1)	O(12)	77.0 (3)
O(11)	Ti(1)	O(41)	81.1 (3)
O(11)	Ti(1)	O(43)	88.1 (3)
O(12)	Ti(1)	O(41)	87.3 (4)
O(12)	Ti(1)	O(43)	160.3 (4)
O(41)	Ti(1)	O(43)	77.5 (3)
O(7)	Ti(2)	O(8)	100.0 (4)
O(7)	Ti(2)	O(22)	92.7 (4)
O(7)	Ti(2)	O(24)	168.1 (4)
O(7)	Ti(2)	O(32)	100.4 (4)
O(7)	Ti(2)	O(34)	89.7 (4)
O(8)	Ti(2)	O(22)	97.0 (4)
O(8)	Ti(2)	O(24)	88.2 (4)
O(8)	Ti(2)	O(32)	91.2 (4)
O(8)	Ti(2)	O(34)	166.2 (4)
O(22)	Ti(2)	O(24)	77.6 (3)
O(22)	Ti(2)	O(32)	163.1 (4)
O(22)	Ti(2)	O(34)	92.3 (4)
O(24)	Ti(2)	O(32)	88.0 (3)
O(24)	Ti(2)	O(34)	83.8 (4)
O(32)	Ti(2)	O(34)	77.3 (3)
Ti(1)	O(7)	Ti(2)	142.1 (5)
Ti(1)	O(8)	Ti(2)	156.4 (5)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

is still shorter than expected for a single Ti–O bond and, as proposed by van de Velde et al.,[33] a significant amount of dπ–pπ bonding may be involved in these bonds. All of the tetrameric titanyl compounds are isoelectronic and have 12 bonding electrons.

As van de Velde et al. discussed in their paper on the structure of ammonium titanyl oxalate,[33] the bond angles around O7 and O8 help to define the structure of the eight-membered ring in BTO. It can be described as existing in a chair conformation due to the Ti–O–Ti angles of 142.1 (5)° around O7 and 156.4 (5)° around O8. The four oxygen atoms form a diamond with sides of 2.74 and 2.77 Å and angles of 68.8° and 111.1°. The titanium atoms Ti(2) and Ti(2*) lie within this plane of oxygen atoms. As in the ammonium titanyl oxalate,[33] the Ti atoms nearly form a square with sides of 3.415 (3) and 3.532 (3) Å and angles of 88.7 (5)° and 91.2 (5)°.

The non-bonding distances listed in Table VII give a good description of the eight-membered rings in various titanyl compounds, and the distances between opposite oxygen or titanium atoms help to illustrate the geometry of the rings. The distances between oxygen atoms in the Cs compound are 3.90 and 4.04 and are the closest to being identical among the known tetrameric titanyl compounds. It is interesting that the Ti–O distances in this Cs complex are the most unequal (1.74 and 1.91).[36] The O1–O1* and O2–O2* distances in BTO are the most dissimilar, being 4.54 and 3.11, and the Ti–O distances are the closest to being the same in this titanyl oxalate. The differences in bond distances between complexes indicate that the eight-membered ring is easily distorted and is flexible enough to accommodate various cations.

an isolated Ti=O bond. This difference of 0.18 Å is the expected value, assuming that a Ti=O bond has a bond order of twice a Ti–O bond.[40,41] The Ti–O bond, however,

(40) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 228, 240, 256.

(41) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* 1941, *63*, 37.

1214 *Chem. Mater., Vol. 4, No. 6, 1992*

Rhine et al.

Table VI. Ti–O Bond Distances and Ti–O–Ti Bond Angles in Titanyl Complexes

	Ti–O bond distances				bond angles			
					TiOTi	OTiO	TiOTi	OTiO
$(NH_4)_2TiO(Ox)_2$[33]	1.840 (7)	1.788 (8)	1.855 (6)	1.785 (7)	152.1 (5)	96.4 (3)	139.2 (4)	96.8 (3)
$K_2TiO(Ox)_2$[34]	1.820	1.788	1.839	1.790	165.5	98	148.4	98.5
$CsTiO(NTA)$[36]	1.88 (1)	1.78 (1)	1.91 (1)	1.76 (1)	169.8 (6)	100.1 (6)	148.8 (6)	100.1 (6)
$CsTiO(NTA)$[36]	1.91 (1)	1.74 (1)	1.90 (1)	1.74 (1)	168.5 (6)	101.3 (6)	161.9 (6)	100.7 (6)
$BaTiO(Ox)_2$	1.81 (1)	1.802 (8)	1.809 (8)	1.799 (9)	156.4 (5)	98.7 (5)	142.1 (5)	100.0 (5)
$CpTiO(Cl)$[37]	1.797 (1)	1.801 (3)	1.792 (3)	1.800 (1)	169.1 (4)	104.1 (4)	158.2 (2)	102.9 (1)

Table VII

bond	$BaTi(Ox)_2$	$(NH_4)_2Ti(Ox)_2$[33]	$K_2Ti(Ox)_2$[34]	$CsTiO(NTA)$[36]	$CsTiO(NTA)$[36]	$CpClTiO$[37]
	Distances between Nonbonding Atoms in Titanyl Complexes					
O1–O2	2.73	2.712 (9)	2.753	2.79	2.79	2.837 (4)
O1–O2*	2.76	2.717 (9)	2.762	2.82	2.82	2.854 (4)
Ti1–Ti2	3.415 (3)	3.411 (2)	3.473	3.63	3.59	3.529 (1)
Ti1–Ti2*	3.532 (3)	3.521 (2)	3.545	3.53	3.63	3.577 (1)
O1–O1*	4.54	4.353 (9)	4.31	4.30	4.04	4.226 (5)
O2–O2*	3.11	3.243 (9)	3.44	3.61	3.90	3.811 (5)
Ti1–Ti1*	4.860 (5)	4.717 (2)	4.83	5.03	5.09	4.959 (1)
Ti2–Ti2*	4.966 (4)	5.080 (2)	5.09	5.11	5.13	4.959 (1)
	Bond Angles					
O1–O2–O1*	111.1	106.6 (4)	102.8	100.1	92.0	95.9
O2–O1–O2	68.8	73.4 (3)	77.3	80.0	88.0	83.8
Ti1–O2–Ti2*	156.4 (5)	152.1 (5)	165.5	168.5	169.9	169.1 (1)
Ti1–O1–Ti2	142.1 (5)	139.2 (4)	148.4	148.8	161.9	157.2 (2)

The octahedral coordination around the Ti atoms in BTO is distorted, and it is similar to the geometry observed for the ammonium and potassium titanyl oxalates.[33,34] The O–Ti–O angles range from 77° to 100°, and Ti(1) is most coplanar with oxygen atoms O12, O11, O7, and O43 (the sum of equatorial angles is 358.4°). Ti(2) is most coplanar with oxygen atoms O22, O32, O24, and O7 (the sum of equatorial angles is 358.7°). As in the other structures which have a Ti–O eight-membered ring, the Ti–O bond lengths exhibit the trans effect. The Ti–O bonds trans to the titanyl–O bond are always longer [2.107 (9), 2.101 (9), 2.073 (8), and 2.131 (9) Å] than the other Ti–O bonds [1.971 (9), 1.997 (8), 2.030 (8), and 1.997 (8) Å]. The average Ti–O oxalate distance is 2.050 (9) Å. The average Ti–O bond trans to the titanyl oxygen is 2.103 (9) Å, and the average Ti–O bond length cis to the titanyl oxygens is 1.998 (8) Å. However, the average Ti–O bond distance for Ti(1) is 1.974 (9) Å and for Ti(2) is 1.964 (9) Å, which are similar to the average Ti–O distance of 1.96 Å found in TiO_2.[42]

The bonding and structure of the eight-membered ring in ammonium titanyl oxalate have been discussed by van de Velde et al.,[33] who have suggested that in addition to a σ bond there is $d\pi$–$p\pi$ bonding via a two-electron, three-center bond. Petersen[43] and Prout et al.[44] have considered molecular orbital arguments and show that, for compounds such as $[Cp_2L]_2MO$ (M = Ti or Zr), one unfilled hybridized orbital is available to accept electron density from oxygen lone pairs. Consequently, to form the tetramer, each titanium atom must have two empty orbitals available for bonding with two oxo oxygens. Of the nine hybrid orbitals on each Ti atom, six are involved in σ bonding with the four oxalate ions and the two bridging oxo groups. Thus, three metal orbitals remain per Ti atom to accept π electron density.

Degree of Hydration of BTO. The crystal structure of BTO reveals that it crystallizes initially as the pentahydrate at room temperature; therefore, our results support

the conclusions of Gopalakrishnamurthy and co-workers,[16] who reported that the degree of hydration of BTO prepared by Clabaugh's et al.[4] method (precipitated at 80 °C) varies, depending on the relative humidity of the surrounding atmosphere from 4.5 waters at 50% relative humidity to 4.8 waters at 90% relative humidity. The crystals of BTO used in our study were air dried on a frit at room temperature, and the crystals used for the X-ray structure and the sample submitted for elemental analysis contained nine waters of hydration, reflecting the loss of water at room temperature. Therefore, in the crystal used for the X-ray structure determination, the results indicated the interstitial water sites were only partially occupied. On the basis of research by Yen et al.,[43] removing the waters of crystallization as well as those coordinated to the Ba atoms has very little affect on the diffraction intensities, and since our cell constants are similar to those reported by Louër et al., there is currently no published evidence that the cell constants are affected by water content. In this effort, the effect of water content on the observed cell constants or calculated intensities was not investigated. In addition, the effect of water content on the calculated intensities (Table II) was considered as insignificant.

In the BTO molecule, seven of the ten waters are coordinated to the two barium atoms. As shown in Figure 4, the two nonequivalent Ba atoms, Ba(1) and Ba(2), are bridged by three oxalate oxygens, and the two equivalent Ba(2) atoms are bridged by two oxalate oxygens. Ba(1) is coordinated to six oxygen atoms from water molecules, in addition to three oxalate oxygens, making it nine-coordinate. Ba(2) is ten-coordinate and is associated with one water and nine oxalate oxygens. The average Ba–O bond distances of 2.82 (1) Å for Ba(1) and 2.87 (1) Å for Ba(2) agree well with the sum of the ionic radii for oxygen and nine- and ten-coordinate barium ions, respectively.[45] The remaining three water molecules per unit cell are defined by oxygen atoms O(10), O(101), and O(102), which are located at interstitial sites in the structure and are not closely associated with the barium or titanium atoms. These interstitial waters are not shown in the ORTEP

(42) Cromer, D. T.; Harrington, K. *J. Am. Chem. Soc.* **1955**, *77*, 4708.
(43) Petersen, J. L. *J. Organomet. Chem.* **1979**, *166*, 179.
(44) Prout, K.; Cameron, T. S.; Critchley, R. A.; Denton, B.; Rees, G. V. *Acta Crystallogr. Sect. B* **1974**, *30*, 2290.

(45) Huheey, J. E. *Inorg. Chem.* pp 74, Harper and Row: New York, 1972. Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1970**, *B26*, 1076.
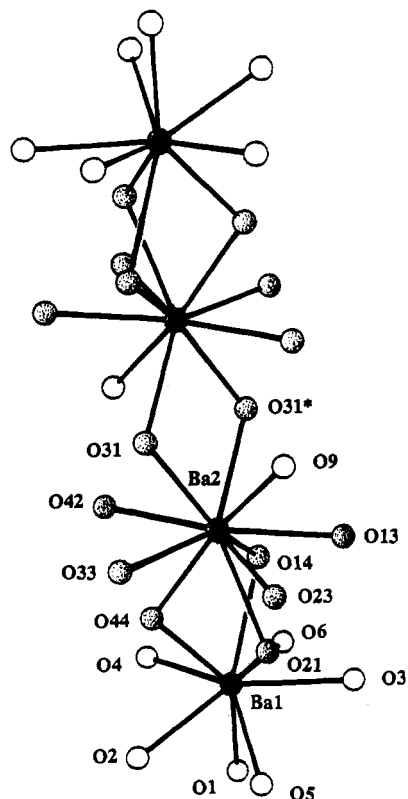
Figure 4. Coordination around the barium atoms in BTO.

diagrams. The shortest Ba–Ti distance is 5.841 (2) Å, between Ba(1) and Ti(1).

TGA data on different samples of BTO prepared by the same method in our laboratory usually show between ten and nine waters of hydration at room temperature. On the basis of the crystal structure data, we would expect the interstitial waters to be the most readily lost. The TGA data in Figure 5 show that 0.7 waters were lost during drying at room temperature, and water loss continued as the temperature was raised above room temperature. At slow heating rates, an additional 1.3 waters were lost below 40 °C and the third water of crystallization was lost by 45 °C. Another five waters were lost by 60 °C, while the two remaining molecules of water were not completely lost until about 150 °C. According to the structure, two of the waters (O5 and O6) bonded to Ba(1) have shorter Ba–O bond distances [2.69 (1) and 2.74 (1) Å] than the other coordinated waters [av = 2.82 (1) Å]. We assume that these two waters are more strongly bonded and are therefore difficult to remove. Also, Yen et al.[43] have shown that BTO is still crystalline when all the waters but these last two have been removed.

IR Spectra. The IR spectra of BTO agree with the crystal structure and show that it does not contain isolated Ti=O bonds. Titanyl compounds possess a Ti=O stretching frequency in the range 1050–950 cm^{-1}. This absorption band has been observed for the monomeric compound, (octaethylporphorin)Ti=O,[38] but is not observed in BTO. The IR spectra of ammonium oxalate, ammonium titanyl oxalate (ATO) and BTO are shown in Figure 6. The vibrational frequencies of BTO were observed at 1705, ν_{as} (C=O); 1424, ν_{s} (C–O, C–C); 1279, ν_{s} (C–O) + δ (O–C=O); 910, ν_{s} (CPO) + δ (O–C=O); and 824 cm^{-1}, δ (O–C=O) + ν (M–O). The IR spectra of the ammonium titanyl oxalate is also shown in Figure 6, and the vibrational frequencies of ammonium titanyl oxalate were observed at 1690, ν_{as} (C=O); 1401, ν_{s} (C–O, C–C); 1244, ν_{s} (C–O) + δ (O–C=O); 896, ν_{s} (C–O) + δ (C–C=O); 880,
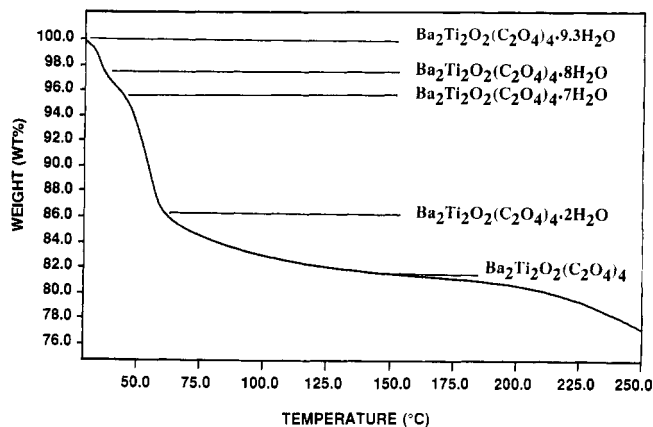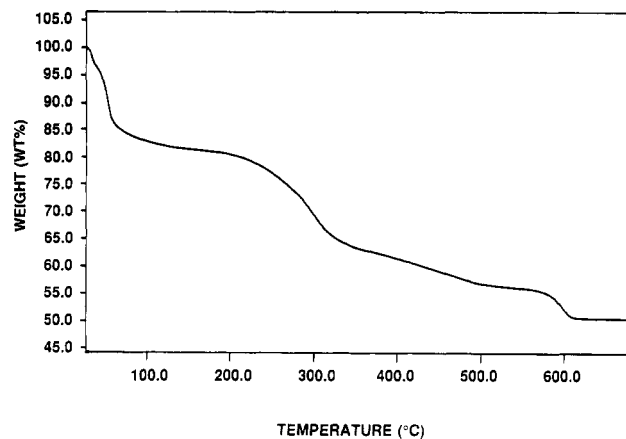

TEMPERATURE (°C)

Figure 5. TGA of BTO in air at 0.5 °C/min (a, top) to 650 °C and (b, bottom) to 250 °C.
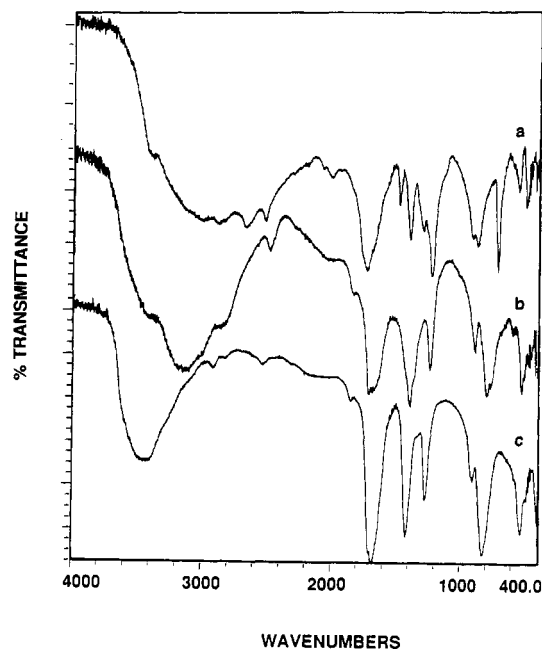

WAVENUMBERS

Figure 6. Diffuse reflectance FTIR spectra of (a) ammonium oxalate, (b) ammonium titanyl oxalate, and (c) barium titanyl oxalate.

778 cm^{-1}, δ (O–C=O) + ν (M–O). The assignments for the IR vibrations are those of Brisse and Haddad.[46] The absorption bands for BTO occur at lower frequencies than the same bands for the ammonium titanyl oxalate. Structurally there is no significant difference in the bond

(46) Brisse, F.; Haddad, M. *Inorg. Chim. Acta* **1977**, *24*, 173.

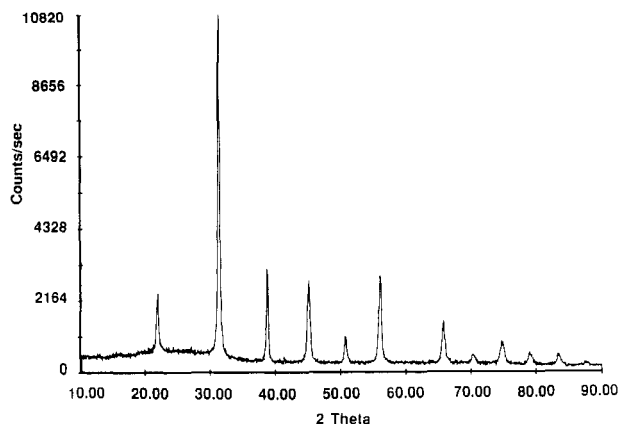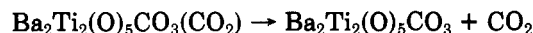1216 *Chem. Mater., Vol. 4, No. 6, 1992*
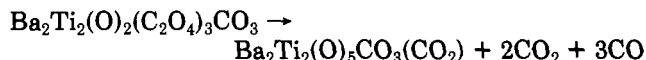
Rhine et al.

Figure 7. X-ray diffraction pattern of barium titanate obtained from BTO at 850 °C.

lengths observed for the oxalate groups in BTO and ATO, and the reason for the shift in vibrational frequencies is not clear.

Thermal Decomposition of BTO. The decomposition of BTO has been extensively studied by many different research groups, and the various proposed decomposition schemes have been reviewed.[47] According to the work of Swilam and Gadalla,[48] conversion of BTO to $BaTiO_3$ requires heating 6 h at 600 °C, 1 h at 700 °C, and less than 0.5 h at 800–900 °C. Essentially, our results agree with theirs. Although the TGA indicates that decomposition is complete by 700 °C at a heating rate of 10 °C/min, we have observed that the decomposition products obtained after heating BTO to 850 °C at 10 °C/min (no hold) contain both phase pure $BaTiO_3$ and a small amount of amorphous material as shown by the broad peak between 15 and 35° in the X-ray diffraction pattern shown in Figure 7. Heating to 900 °C at 10 °C/min (no hold) resulted in complete conversion to barium titanate. TEM micrographs of the products also showed that some amorphous particles were present in the product heated to 850 °C, but

only crystalline particles were observed in the product heated to 900 °C.

Gopalakrishnamurthy et al.[16] have proposed that the decomposition of BTO proceeds through the following intermediates:

$$Ba_2Ti_2(O)_2(C_2O_4)_4 \rightarrow Ba_2Ti_2(O)_2(C_2O_4)_3CO_3 + CO$$

$$Ba_2Ti_2(O)_2(C_2O_4)_3CO_3 \rightarrow$$
$$Ba_2Ti_2(O)_5CO_3(CO_2) + 2CO_2 + 3CO$$

$$Ba_2Ti_2(O)_5CO_3(CO_2) \rightarrow Ba_2Ti_2(O)_5CO_3 + CO_2$$

$$Ba_2Ti_2(O)_5CO_3 \rightarrow 2BaTiO_3 + CO_2$$

This proposed mechanism suggests that nonequivalent barium atoms are present in the intermediates. Since the X-ray structure showed that BTO contains two nonequivalent barium atoms, it supports the above mechanism. In the structure of BTO, Ba(1) is 5.84 Å from Ti(1) and 6.95 Å from Ti(2), while Ba(2) is almost equidistant from Ti(1) and Ti(2*), 6.18 and 6.12 Å, respectively. Since the barium atoms are different, it is reasonable that any intermediates would retain the basic structure and that the two Ba atoms may interact with CO_2 differently to form the intermediate carbonates. Therefore, $Ba_2Ti_2O_5$-CO_3 is a reasonable composition for the decomposition product responsible for the plateau in the TGA between 500 °C at 570 °C. Yen et al.[17] have observed broad X-ray diffraction peaks for products heated to 500 °C, indicating some weakly crystalline intermediates, but there is currently no conclusive evidence that complete segregation occurs to form crystalline $BaCO_3$, $BaTi_2O_5$, or TiO_2 during decomposition of BTO, and $BaTiO_3$ is the only crystalline phase observed upon decomposition as indicated by Figure 7.

Supplementary Material Available: Experimental details for data collection and structure refinement, all calculated atomic coordinates, anisotropic thermal parameters, all nonessential bond lengths and angles, and conformational angles (19 pages); listing of *h*, *k*, *l*, F_o, and F_c (27 pages). Ordering information is given on any current masthead page.

(47) Sharma, A. K.; Kaushik, N. K. *Thermochem. Acta* **1985**, *83*, 347.
(48) Swilam, M. N.; Gadalla, A. M. *Trans. J. Brit. Ceram. Soc.* **1975**, *75*, 159.