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Synthesis and Characterization of $BaTi(OC_6H_5)_6\cdot 2DMF$, a Single-Source Sol–Gel Precursor to $BaTiO_3$ Gels, Powders, and Thin Films

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Barium titanate, $BaTiO_3$, is a scientifically and technologically important dielectric material,[2] and several solution chemical routes to $BaTiO_3$ have been developed that offer advantages over traditional powder processing techniques.[3] Among these various approaches, sol–gel processing of alkoxides has proven to be a particularly flexible technique for preparing $BaTiO_3$ gels,[4] powders,[5] and films.[6] The chemistry involved in these sol–gel procedures is poorly understood and hence difficult to control, however, since the precursor solutions employed in each case contain barium titanium complexes of unknown composition and structure. By contrast, the sol–gel processing of simple oxides such as SiO_2 and TiO_2 is relatively well understood and can be approached in a systematic fashion, since the corresponding alkoxide precursors $Si(OR)_4$ and $Ti(OR)_4$ are known and their chemistry has been studied in detail.[7] Operating on the hypothesis that the sol–gel processing of $BaTiO_3$ might be similarly simplified if the analogous alkoxide precursors $BaTi(OR)_6$ were available, we have attempted to prepare such complexes and study their chemistry. In the course of these investigations, we have found that the problems associated with the preparation of alkyl $BaTi(OR)_6$ complexes[8] can be circumvented using aryl derivatives, and we report here the synthesis and characterization of the solvated phenoxide $BaTi(OC_6H_5)_6\cdot 2DMF$, DMF = *N,N*-dimethylformamide, a viable sol–gel precursor to $BaTiO_3$ gels, powders, and thin films.

Reaction of barium metal with 6.6 equiv of phenol in diethyl ether solution followed by addition of 1 equiv of $Ti(OPr^i)_4$ yielded a dark brown solution that was stirred for 24 h in an inert atmosphere. All volatiles were then removed under reduced pressure, and the resulting brown solid was crystallized from DMF/diethyl ether. In this fashion, analytically pure $BaTi(OC_6H_5)_6\cdot 2DMF$ (**1**) was prepared in 73% yield based on titanium.[9] A structure determination[10] using X-ray diffraction techniques revealed that crystals of **1** grown from 1,2-$C_2H_4Cl_2$ solution are composed of discrete tetranuclear $[BaTi(OC_6H_5)_6(DMF)_2]_2$ molecules and dichloroethane solvent molecules of crystallization. The crystal structure contains two rigorously centrosymmetric and crystallographically independent $[BaTi(OC_6H_5)_6(DMF)_2]_2$ molecules, one of which is shown in Figure 1. Here, the 12 phenoxy ligands are distributed equally among three distinct structural types: four are μ_3-bonded through their oxygens to one Ti^{IV} and two Ba^{II} centers, four are μ_2-bonded to one Ti^{IV} and one Ba^{II} center, and four are terminally bonded to a single Ti^{IV} center. Each d^0 Ti^{IV} ion is octahedrally coordinated to a pair of *cis*-μ_3-phenoxides, a pair of *trans*-μ_2-phenoxides, and a pair of cis terminally bonded phenoxide ligands. Each Ba^{II} center achieves a coordination number of eight by bonding to the oxygens of all four μ_3-phenoxides and a pair of μ_2-phenoxides as well as the oxygens from a pair of DMF ligands. Here, bicapped trigonal prismatic coordination geometry is adopted: the four μ_3-phenoxide and two DMF oxygens bonded to each Ba^{II} lie at the vertexes of a distorted trigonal prism and the μ_2-phenoxide oxygens cap a pair of its "square" faces. The third "square" face is defined by the four μ_3-phenoxide oxygens and is common to both Ba^{II} ions in the cluster. The structure(s) adopted by compound **1** in the solution state is unclear. Carbon-13 NMR spectra of compound **1** in DMF solution show resonances for only one type of phenoxy group and one type of DMF molecule at ambient temperature.[9] The three sets of resonances anticipated for a fully resolved spectrum of the dimer shown in Figure 1a are not observed, even at −60 °C.

Hydrolysis of the barium titanium phenoxide solvate **1** in polar organic solvents yields stable sols which, upon addition of sufficient water, form brown-yellow transparent gels. A systematic variation of solvent polarity, degree of hydrolysis, and pH allows gel time and gel

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(8) Several $BaTi(OR)_6$ double alkoxides have been claimed in the literature, but recent research reported by Turevskaya et al. has demonstrated that these claims, unsupported by single-crystal X-ray diffraction studies, are unjustified: Turevskaya, E. P.; Yanovskaya, M. I.; Lymar', V. K.; Turova, N. Ya. *Russ. J. Inorg. Chem.* **1993**, *38*, 563.

(9) Anal. Calcd for $C_{42}H_{44}N_2BaTiO_8$: C, 56.68; H, 4.98; N, 3.15; Ba, 15.43; Ti, 5.38. Found: C, 57.00; H, 4.68; N, 3.32; Ba, 15.60; Ti, 5.51. ^{13}C NMR (125.8 MHz, DMF, 20 °C) 30.9 (NCH_3); 36.0 (NCH_3); 116.3 (*p*-C_6H_5); 120.9, 128.1 (*o*-, *m*-C_6H_5); 162.8 (NCHO); 167.9 (*ipso*-C_6H_5).

(10) For detailed results of the X-ray crystallographic study, see the paragraph at the end of this paper regarding supporting information.

(11) 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.

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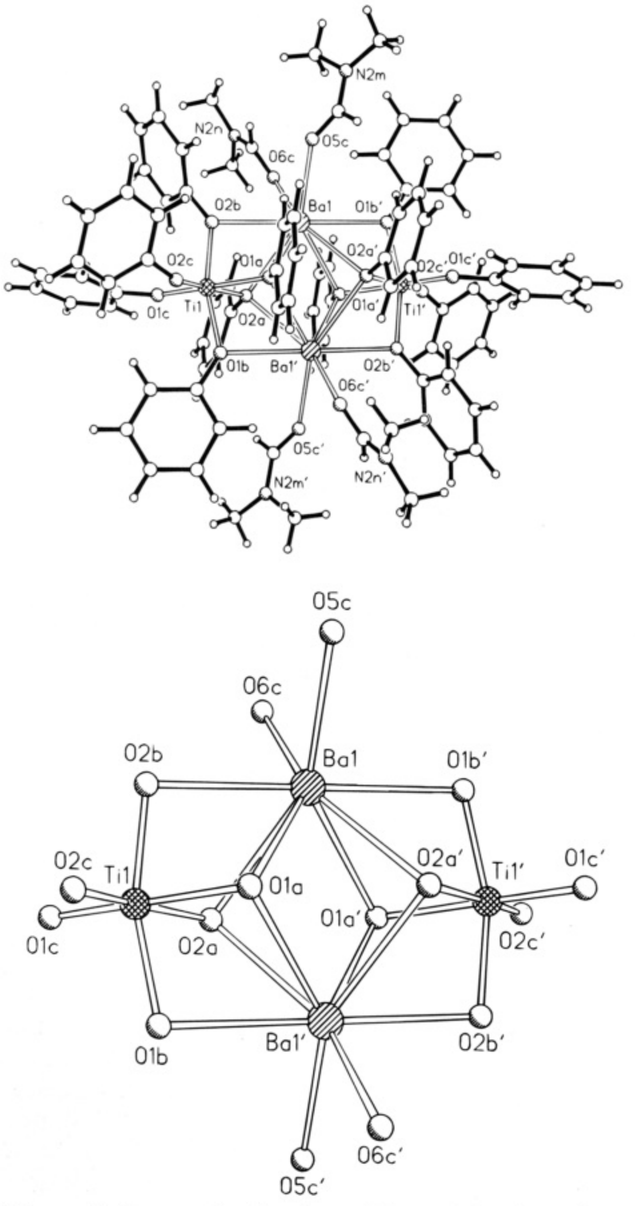

Figure 1. Perspective drawings of (a, top) the first of two crystallographically independent $[BaTi(OPh)_6(DMF)_2]_2$ molecules present in crystalline $[BaTi(OPh)_6(DMF)_2]_2 \cdot 1.5C_2H_4Cl_2$ and (b, bottom) the $Ba_2Ti_2O_{16}$ core of this molecule. Barium and titanium atoms are represented by large-sized diagonally lined and cross-hatched spheres, respectively. Oxygen and nitrogen atoms are represented by medium-sized shaded spheres; carbon and hydrogen atoms are represented by medium-sized and small open spheres, respectively. Selected atoms are labeled and those atoms labeled with a prime are related to those labeled without primes by the crystallographic inversion center located at $(0, {}^1/_2, 0)$ in the unit cell. Average[11] bond lengths for the two crystallographically independent $Ba_2Ti_6O_{16}$ cores are 2.864 (5, 20, 40, 4), 2.815 (5, 25, 40, 8), and 2.662 (8, 25, 31, 4) Å for the μ_2-phenoxy, μ_3-phenoxy, and DMF oxygen Ba−O bonds, respectively, and 2.044 (5, 12, 25, 4), 1.984 (6, 14, 27, 4), and 1.829 (6, 11, 13, 4) Å for the μ_3-phenoxy, μ_2-phenoxy, and terminal phenoxy Ti−O bonds, respectively.

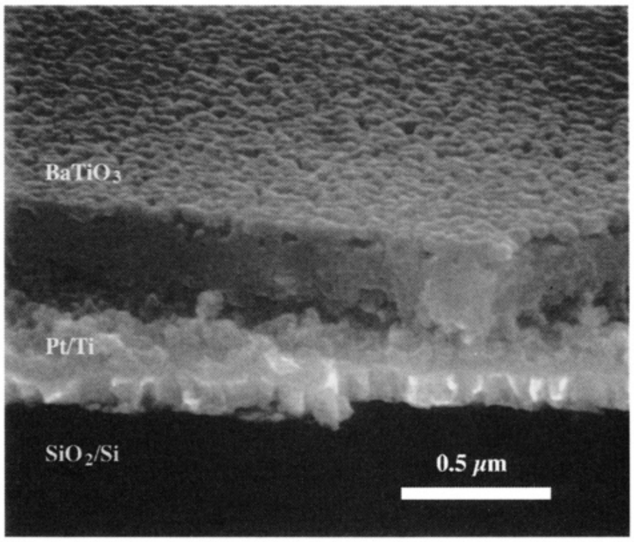

Figure 2. Scanning electron micrograph of a 0.4 μm thick $BaTiO_3$ film obtained from 10 depositions of compound **1** (0.25 M) plus 3 equiv of water and 0.11 equiv of HNO_3 in 1/1 (V/V) DMF/toluene solution on a platinized silicon substrate after heat treatment in air at 750 °C (for details of the procedure, see ref 12).

texture to be independently manipulated. For example, a gel time of 6 h is observed upon hydrolysis of a 0.22 M solution of **1** in 1/1 (V/V) DMF/THF with 12 equiv of water at ambient temperature. The gel time is reduced to 30 min by addition of 0.064 equiv of HCl; use of 1/1 (V/V) DMF/toluene as the solvent but no acid addition reduces the gel time to 2 min. Cloudy, i.e., particulate gels are obtained under more acidic conditions. For example, hydrolysis of a 0.22 M solution of **1** in 1/1 (V/V) DMF/toluene with 9 equiv of water containing 0.33 equiv of HCl yields a translucent, cloudy gel after 6 h at ambient temperature. The gels prepared from **1** are transformed into $BaTiO_3$ at 600 °C, and spin-casting of sols prepared from hydrolyzed **1** yields dense $BaTiO_3$ films after heat treatment at 750 °C (see Figure 2). In both cases, nanocrystalline[13] cubic material is formed according to X-ray diffraction measurements.[14]

Barium titanium phenoxide, $BaTi(OPh)_6 \cdot 2DMF$, shows great promise as a single-source sol−gel precursor for $BaTiO_3$ dielectric thin films. Preliminary electrical measurements[15] have revealed that thin films (200−250 nm) prepared on platinized silicon under optimized conditions display dielectric properties (dielectric constant $K = 210$, loss tan $\delta = 0.03$ at 1 kHz and 0.5×10^6 V/m ac, 25 °C), electrical resistivities ($>10^{11}$ Ω m), and dielectric strenghts ($>10^8$ V/m dc) at ambient temperature comparable to high-quality sol−gel-derived $BaTiO_3$ thin films described in the literature.[6i] We are currently investigating the relationship between processing conditions and electrical properties.

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Supporting Information Available: Crystal structure report, listings of positional and thermal parameters, listings of bond lengths and angles, and perspective structure drawings for $[BaTi(OC_6H_5)_6(DMF)_2]_2 \cdot 1.5C_2H_4Cl_2$ (42 pages); structure factor tables (29 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.

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