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Raman Spectroscopic Study of the Formation of Barium Titanate from an Oxalate Precursor

Prabir K. Dutta,* P. K. Gallagher, and Jen Twu†

Department of Chemistry, The Ohio State University, 120 West 18th Ave., Columbus, Ohio 43210

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Barium titanyl oxalate ($BaTiO(C_2O_4)_2$) is used commercially as a precursor for the preparation of the ferroelectric ceramic $BaTiO_3$. This study examines the conversion of this mixed oxalate compound to $BaTiO_3$ upon thermal treatment. The molecular structure of the mixed oxalate has been determined by Raman spectroscopy to consist of a Ti_4O_4 ring, in contrast with the earlier reports that this molecule contains a titanyl (Ti=O) unit. The mixed oxalate was heated from room temperature to 800 °C, and the structural changes that occurred were followed by Raman spectroscopy at ambient temperature. As a function of temperature, the bidentate oxalate ligand changes to a bridged oxalate, followed by decomposition to ligated carbonate and then to ionic carbonate. All traces of the ligand disappear beyond 800 °C. The intermediate that exists in the temperature range 250–600 °C is a Ba–Ti amorphous complex. $BaTiO_3$ first appears at 580 °C. The organic ligand serves to provide an atomic level contact between the metal ions, thus providing a route to $BaTiO_3$ formation at lower temperatures.

Introduction

Barium titanate ($BaTiO_3$), a ceramic capacitor with a high dielectric constant, continues to be the subject of intense research activity.[1] In optimizing the applications for electronic materials, the synthesis of high-purity $BaTiO_3$ is essential.[2] Recent emphasis has been on development of methodologies for synthesis under milder conditions, with the goal of producing high-purity, stoichiometric, submicron, monodisperse crystallites that will sinter at lower temperatures.[3] Examples of synthesis methods include hydrothermal synthesis using $Ba(OH)_2$,[4] sol–gel methods using alkoxide precursors[5] and coprecipitation of Ba–Ti salts as citrates[6] or oxalates.[7] These methods have evolved over the past 3 decades and have the advantages of fewer impurities, lower firing temperatures, and better control of electrical properties. The molecular level transformations that lead to the formation of $BaTiO_3$ have been explored only recently, mainly via spectroscopic methods.[8–10] It is expected that as this understanding increases, further optimization as well as development of new methods for synthesis will emerge.

In this study, we focus on the formation of mixed barium–titanium oxalates and their decomposition to form $BaTiO_3$. This is an important process for manufacture of $BaTiO_3$,[11] and previous mechanistic studies have mostly involved thermoanalytical methods.[12–16] Raman spectroscopic studies reported in this paper provide structural information on the starting material and its transformation to $BaTiO_3$. These complement the results from the thermoanalytical methods[12–16] as well as previous infrared spectroscopic studies that have focused on the oxalate ligand.[10,16] A mechanism is proposed to account for the formation of $BaTiO_3$ from the Ba–Ti oxalate compound, and contrasted with the conventional method of preparation using $BaCO_3$ and TiO_2.

Experimental Section

All chemicals, $BaCl_2$, $BaCO_3$, $TiCl_4$, TiO_2 (anatase), oxalic acid, and $BaCl_2$, were analytical grade and obtained from Aldrich Chemical Co. The barium titanyl oxalate was synthesized from the metal chlorides according to the procedure reported by Clabaugh and co-workers.[17] Conventional synthesis of $BaTiO_3$ was done by grinding together $BaCO_3$ and anatase followed by heating to 800 °C. Spectroscopic studies were done on samples at ambient temperatures following heat treatment.

Thermal analysis was performed using a Seiko Model SSC5200 thermal analysis system with the simultaneous TG/DTA 320 module having R type thermocouples. The heating rate was 30 °C min^{-1} in flowing air. The nominal sample size was 15 mg. Platinum sample pans were used.

The Raman spectra were obtained using radiation of 457.9 nm from an argon-ion laser (Spectra Physics 171). The power at the sample was ~20 mW. A Spex double monochromator (Spex 1403) was used to discriminate against elastically scattered radiation. The Raman scattering was detected with a GaAs photomultiplier tube with photon counting. Typical slit widths were 6 cm^{-1}, and scanning times ranged from 1–3 s/cm^{-1}.

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† Present address: Department of Chemistry, Chinese Culture University, Taipei, Taiwan, R.O.C.

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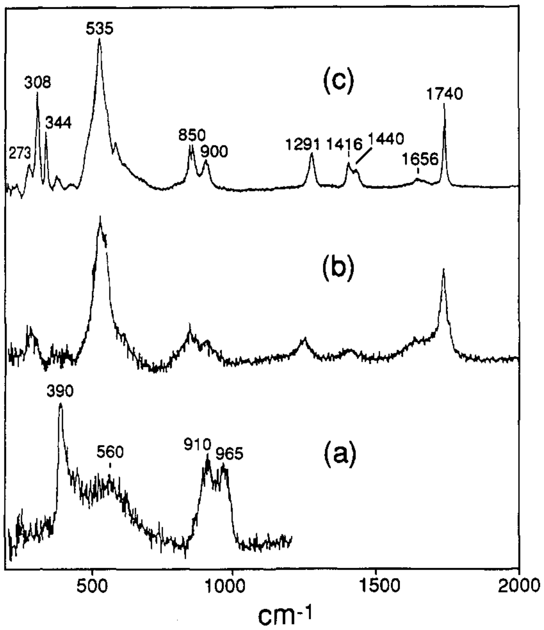

Figure 1. Raman spectra of the reactant solutions used in making BTO: (a) $TiCl_4$ and $BaCl_2$; (b) $TiCl_4$ and oxalic acid. (c) Raman spectrum of solid BTO.

Results

The composition of the mixed oxalate precipitate prepared by the procedure of Clabaugh et al. has been reported to be $BaTiO(C_2O_4)_2{\cdot}4H_2O$ (henceforth abbreviated as BTO).[17] There appears to be some controversy as to the exact molecular structure of this compound, though in most of the literature[10,13–17] it is described by the presence of a titanyl unit (Ti═O). Therefore, to clarify the structure of this oxalate, the Raman spectra of the solution of the precursors necessary to prepare BTO were examined. Figure 1a is the spectrum of an aqueous solution of $BaCl_2$ to which $TiCl_4$ at stoichiometries of 1:1 has been added and is characterized by bands at 390, 560, 910, and 965 cm^{-1}. This spectrum resembles that reported for $TiCl_4$/aqueous solutions.[18] The peak at 965 cm^{-1} is assigned to Ti═O stretching mode of TiO^{2+}, indicating the formation of $TiOCl_2$ by hydrolysis of $TiCl_4$. The bands at 390 and 910 cm^{-1} have been reported in >0.5 M $TiCl_4$ solutions and assigned to Ti–O stretching vibrations of Ti–O–Ti dimer.[18] The broad band at 560 cm^{-1} arises from Ti–O stretches of titanium hydroxy species.[18] These results suggest that the $TiCl_4$ precursor solution contains a mixture of various titanium–oxygen bonded species, including the titanyl ion. Dissolved $BaCl_2$ does not exhibit any features in the Raman spectrum between 200 and 1200 cm^{-1}.

Figure 1b is the spectrum of an aqueous solution of $TiCl_4$/water and oxalic acid, at a stoichiometry of 1:2. Figure 1c is the spectrum of the solid $BaTiO(C_2O_4)_2{\cdot}4H_2O$, obtained as a precipitate by mixing $TiCl_4$, $BaCl_2$, and oxalic acid (1:1:2). The similarity of the spectral pattern shown in Figure 1b,c indicates that the same chemical species is responsible for the spectra in both cases. There is little, if any uncomplexed oxalic acid in these samples, which has prominent Raman bands at 852, 480, and 1750 cm^{-1} in order of decreasing intensity.[19] On the contrary, the band at 1740 cm^{-1} in Figure 1c is considerably more intense than the 480- and 852-cm^{-1} bands. Also, previous infrared studies have confirmed the absence of free oxalic acid in the mixed oxalate crystals.[10]

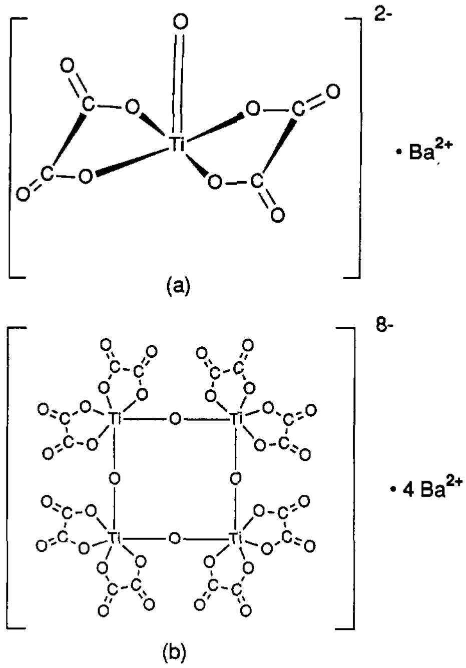

Figure 2. Two possible molecular structures of BTO.

The structure of the mixed Ba–Ti oxalate is usually represented as consisting of a titanyl moiety,[10,12–16] as shown in Figure 2a. However, the Raman spectroscopic data are not consistent with this description. First, both infrared and Raman spectroscopy have shown that titanyl groups (Ti═O) are uncommon.[20,21] Second, in chelated compounds such as TiO(porphyrin), where a true titanyl moiety exists, the Ti═O vibrational frequency appears as a polarized Raman band at 950 cm^{-1}, and no such band is observed in BTO.[21] Thus, the common formulation of $BaTiO(C_2O_4)_2$ as a Ti═O containing moiety is incorrect. Another description of this mixed oxaloto compound based on thermal analysis is a barium hydrogen oxalate into which titanium hydroxy species are inserted.[14] This is also incorrect based on the fact that the $TiCl_4$/oxalate solution has the same Raman spectrum as that of the $BaTiO(C_2O_4)_2$, suggesting that the same species is present in both cases, which necessitates that the Ba^{2+} is merely acting as a cation.

The possible absence of the titanyl unit (Ti═O) in the $BaTiO(C_2O_4)_2$ suggests the presence of an alternate structure. Insight can be derived from the structure of $(NH_4)_2TiO(C_2O_4)_2$ and $K_2TiO(C_2O_4)_2$, which are synthesized under similar conditions as the Ba–Ti salt and have similar stoichiometries, but neither of which contain the Ti═O bond.[21,23] In the case of $(NH_4)_2TiO(C_2O_4)_2$, X-ray diffraction has shown the structure to consist of Ti_4O_4 rings, with each Ti atom coordinated to two oxalate groups.[23] A similar structure for the BTO complex (Figure 2b) is consistent with the spectroscopic data. The bands observed in Figure 1b,c arising from the oxalato ligand

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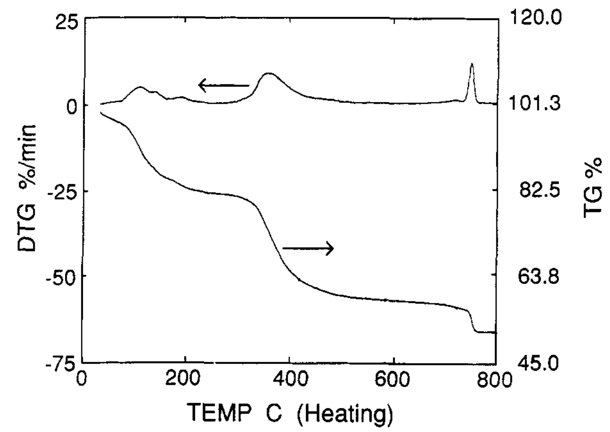

Figure 3. Thermogravimetric analysis of decomposition of BTO.

can be readily discerned by comparison with the Raman spectra of metal oxalato compounds, and $Ti(C_2O_4)_3^{2-}$, in particular.[22] The vibrations at 1740, 1656, 1440, 1416, 1291, and 850 cm^{-1} are assigned to the oxalate ligand.[22] This leaves the bands at 535 and 900 cm^{-1}, which are assigned to Ti–O stretches. In particular, the strong Raman band at 535 cm^{-1} is assigned to the Ti–O vibration of the Ti_4O_4 four-membered ring shown in Figure 2b. Such prominent bands are also observed in zeolites that contain four-membered aluminosilicate rings (T_4O_4, T=Si, Al), e.g., in zeolite A (490 cm^{-1}) and zeolite X (513 cm^{-1}).[24] Bands below 400 cm^{-1} arise from bending modes of CCO, OTiO, and COTi.

Figure 3 shows the thermogravimetric data of the decomposition of BTO to form $BaTiO_3$ and is consistent with previous reports.[10–12] The three weight losses in the temperature ranges of 100, 400, and 750 °C correspond to losses of H_2O, CO + CO_2, and CO_2 respectively. A number of mechanisms have been suggested[10,12–16] based on these data, and we will consider these in the Discussion in light of the Raman data presented below.

Figures 4 and 5 show the Raman spectra obtained under ambient conditions after successively higher temperature treatments of BTO. The BTO begins to lose its structural integrity at 250 °C, as measured by the decrease of the prominent Raman band at 535 cm^{-1} for the Ti_4O_4 unit. Bands at 1452 and 1722 cm^{-1} appear at this temperature. We assign these bands to bridged oxalato species, based on infrared spectra of oxolato bridged metal complexes which show ν(C–O) bands at 1600–1750 and 1350–1450 cm^{-1}.[26] At 340 °C, new bands appearing at 1060, 1355, and 1578 cm^{-1} can be assigned to ligated carbonate, which are expected to have Raman allowed A_1 bands at 303, 772, 1069, and 1376 cm^{-1} for unidentate carbonate and 370, 771, 1038, and 1595 cm^{-1} for bidentate carbonate.[27] The broad band at 770 cm^{-1} observed in the material heated to 340 °C also has contributions from the Ti–O–Ti stretching modes.[9] At 500 °C, the sharp band at 1065 cm^{-1} and the weak band at 1440 cm^{-1} are characteristic of the symmetric and asymmetric stretching modes of ionic carbonate (CO_3^{2-}).[25] In the 600–850-cm^{-1} region, the spectrum resembles the amorphous solid obtained by mixing $Ba(OH)_2$ and TiO_2 gel, and assigned to Ti–O–Ti stretches of amorphous barium titanate.[9]

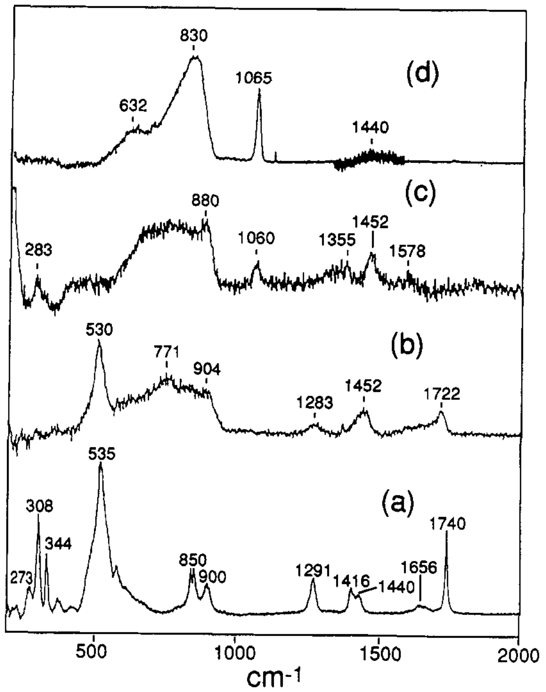

Figure 4. Raman spectra at ambient conditions of (a) BTO and after heating to (b) 250, (c) 340, and (c) 500 °C.

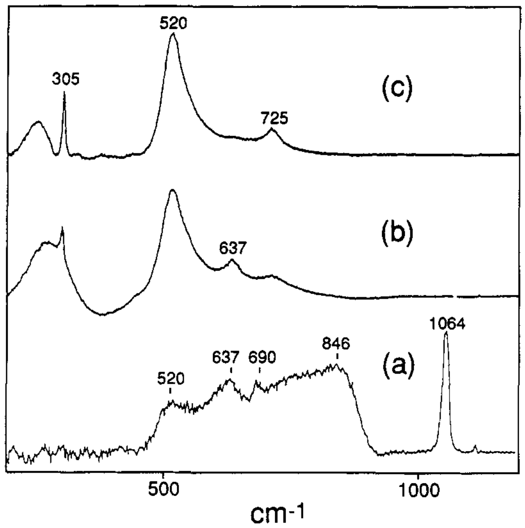

Figure 5. Raman spectra at ambient conditions of BTO heated to (a) 580, (b) 600, and (c) 800 °C.

For samples heated to 580 °C, the $BaTiO_3$ band (520 cm^{-1}) first appears, along with the 1064 cm^{-1}, assigned to ionic carbonate. The assignment of the weak peak at 1111 cm^{-1} is unclear. At 600 °C, the carbonate band disappears, the $BaTiO_3$ bands at 305, 520, and 725 cm^{-1} become prominent, and the band at 637 cm^{-1} is still present, the latter band persisting until the final thermal treatment of 800 °C. A previous infrared study has shown the presence of a band at 1410 cm^{-1} which exhibits behavior similar to the 637-cm^{-1} band, appearing at 375 °C and disappearing at 700 °C.[10] This infrared band was assigned to ionic carbonate, but there is no evidence for ionic carbonate in the Raman spectrum (1060 cm^{-1})[25] at 600 °C (Figure 5b). It appears reasonable to assign both the 637-cm^{-1} band in the Raman region and the 1410-cm^{-1} band in the infrared region as arising from the same CO_2 evolving species, since the thermogravimetric data show that some carbonate

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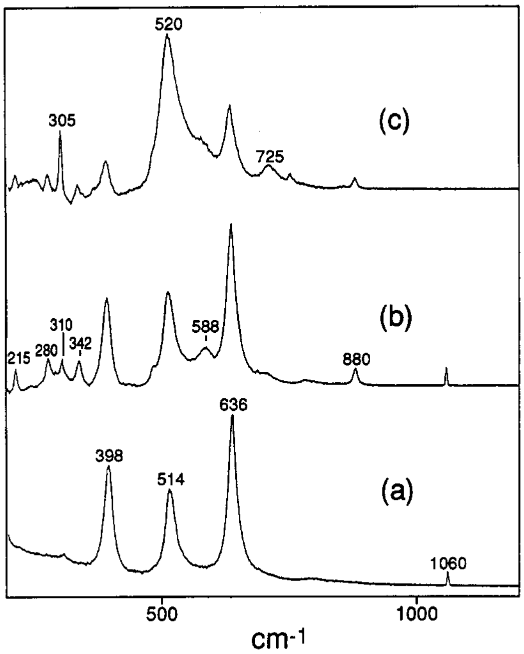


Figure 6. Raman spectra at ambient conditions of a mixture of $BaCO_3 + TiO_2$ heated to (a) 600, (b) 700, and (c) 800 °C.

species must exist up to temperatures of 750 °C. It is difficult from these sparse data to determine the exact nature of this carbonate species. Another possibility is based on the work of Kumar et al.,[8] who reported a Raman band at 636 cm^{-1} during the thermal decomposition of a metalorganic resin to form $BaTiO_3$. They observed this band from ambient temperatures until 729 °C and assigned it to Ti–O stretch of a titanium-based oxide phase. We notice the presence of the distinct 636-cm^{-1} band only after heating to 500 °C. Anatase does have a band in this region,[28] but it also has a strong band at $\sim$400 cm^{-1}, which is not observed. Therefore, it appears reasonable to assign the 637-cm^{-1} band to a carbonate species, rather than an anatase-like phase.

Figure 6 shows the Raman spectra for a $BaCO_3 + TiO_2$ mixture heated for 12 h at 600, 700, and 800 °C in air. The bands for anatase occur at 398, 514, and 636 cm^{-1}, and the band due to carbonate is at 1060 cm^{-1}. No reaction between the reactants occur until 700 °C. At this stage, besides $BaTiO_3$ and unreacted TiO_2 and $BaCO_3$, bands at 215, 342, 588, and 880 cm^{-1} due to $BaTi_2O_5$[29] are also observed. The spectrum at 800 °C is essentially a mixture of TiO_2, $BaTiO_3$, and $BaTi_2O_5$, with all the carbonate having reacted.

Discussion

The above spectroscopic studies show that the evolution of pure $BaTiO_3$ from BTO occurs through a complex mechanism. The presence of discrete titanium species such as TiO_2(anatase), Ba_2TiO_4, and $BaTi_2O_5$ can be excluded since the characteristic vibrational bands due to these species are not observed. There is no doubt that the band due to carbonate ion is observed, but its exact nature of association cannot be ascertained. The observed carbonate band is different from that of $BaCO_3$. Figure 7 compares the Raman spectrum of pure $BaCO_3$ with the carbonate species observed during decomposition of BTO

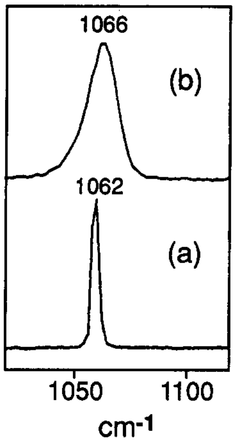
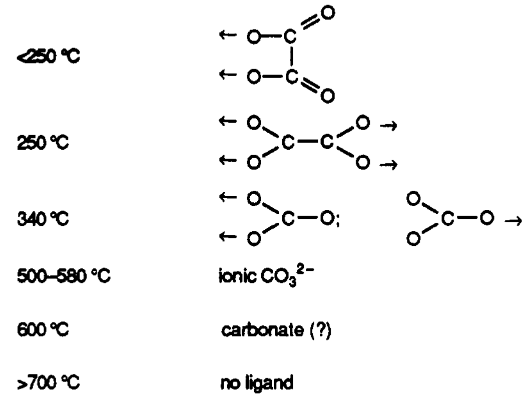


Figure 7. Comparison of the $\nu_1(CO_3^{2-})$ stretching frequency of (a) pure $BaCO_3$ and (b) that formed during the thermal decomposition of $BaTiO_3$ at 500 °C.

Scheme I

Ligands Present during the Thermal Decomposition Process



Barium Titanium Intermediates during the Thermal Decomposition Process

<250 °C	$[TiO(C_2O_4)_2]_4{\cdot}4Ba^{2+}$
250–340 °C	$[Ti–O–Ti–]{\cdot}Ba^{2+}$
340–580 °C	$[–Ti–O–Ti–]{\cdot}Ba^{2+}$ Ba^{2+}
600–700 °C	$BaTiO_3$, $[Ti–O–Ti–]$ Ba^{2+}
>700 °C	$BaTiO_3$

at 500 °C. The band of the latter is broader by a factor of 3 and shifted toward a higher frequency (1066 cm^{-1}), indicating a modified environment. A possibility is that small crystallite sizes of $BaCO_3$ (nanocrystals) are formed. In the case of TiO_2, small crystallites were found to have broader Raman bands.[30] Scheme I emphasizes the multiplicity of species evident from the Raman data, without emphasizing the stoichiometry.

The Ba-Ti species are associated with the ligand throughout the early stages of the heating process, though the exact nature of these complexes cannot be deduced from the Raman data. These studies suggest that an appropriate description of the Ba–Ti intermediate is that the Ba^{2+} is inserted into a Ti–O–Ti polymer network, resembling solids formed by a mixture of reactive titanium

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oxide gel with barium hydroxide.[9] Earlier studies have proposed that the intermediate is a Ba,Ti oxycarbonate phase for preparations from both citrates[8] and oxalates.[16] Similar results were also noted for the formation of $SrTiO_3$ from the corresponding citrate.[31] The role of the ligands primarily is to keep these metal ions in intimate contact.

Comparison of the mixed oxalate decomposition with the conventional $BaCO_3$ and TiO_2 preparation provides an insight into the differences in the reactivities in these two cases. It is important to note that the carbonate formed during the BTO decomposition disappears at temperatures exceeding 600 °C, whereas the carbonate in the conventional preparation only disappears after heating above 700 °C, clearly indicating a difference in reactivities. Pure $BaCO_3$ decomposes at a much higher temperature as compared to the $BaCO_3$ and TiO_2 mixture.[32] Thus, the decomposition temperature of the carbonate progressively decreases as one spans pure $BaCO_3$, $BaCO_3$ plus anatase, and the carbonate formed as an intermediate in decomposition of BTO, clearly illustrating the enhanced reactivity along this progression. Previous studies of the mixed oxide system based on diffraction and thermogravimetric methods has shown the presence of Ba_2TiO_4 as an intermediate,[33] whereas in our study the intermediate is $BaTi_2O_5$. It could arise from the physical nature of our starting materials. Notwithstanding this fact, it is clear that the $BaCO_3$ and anatase lead to intermediate stable phases, primarily arising because of diffusional restrictions between the reactant particles.[33,34] This is evident from the lower activation energy of 46 kcal/mol in the BTO decomposition as compared to 58 kcal/mol in the $BaCO_3$ + TiO_2 system.[35]

In conclusion, the advantage of the BTO preparation stems from the role of oxalate ligand which provides an atomic level contact between the metal ions thus resulting in promoted diffusion of Ba^{2+} within the Ti–O–Ti lattice, and prevents the generation of other distinct crystalline phases prior to formation of $BaTiO_3$.

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