Chem. Mater. **1992**, *4*, 847–851

Raman Spectroscopic and Thermoanalytical Studies of the Reaction of $Ba(OH)_2$ with Anatase and Titanium Oxide Gels

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Received February 25, 1992. Revised Manuscript Received May 27, 1992

The reactivity of hydrated barium hydroxide with anatase and an amorphous TiO_2 gel is compared using vibrational spectroscopy and thermoanalytical methods. At a 1:1 stoichiometric ratio, $Ba(OH)_2$ reacts with anatase to form Ba_2TiO_4 at ~450 °C followed by formation of $BaTiO_3$ above 700 °C. In contrast, the amorphous TiO_2 gel reacts with $Ba(OH)_2$ to form an amorphous $BaTiO_3$-like structure under ambient conditions. Upon heating, Ba_2TiO_4, $BaTiO_3$, and $BaTi_2O_5$ are formed from the $BA(OH)_2$–TiO_2 gel at Ba/Ti stoichiometries of 2, 1, and 0.5, respectively.

Introduction

Barium–titanate compounds continue to be the subject of intense research activity due to their wide range of applications in the electronics industry.[1] Recent emphasis has been on new synthetic routes in order to generate high-quality powders under mild conditions.[2] It has become increasingly clear that the structure and reactivities of the titanium and barium precursors play an important role in determining the composition, morphology, and properties of the final product.[3] Thus, more studies have been focusing on the mechanism of formation of compounds in the BaO–TiO_2 system.[4] In this paper, we report on the use of Raman spectroscopy in conjunction with thermogravimetric methods to examine the intermediates produced in the solid-state reaction between $Ba(OH)_2$ and crystalline TiO_2 (anatase) and an amorphous titanium oxide gel. There have been several recent studies on Raman spectroscopy of titanates. These include examination of phase transitions of barium polytitantes and the identification of titanate oligomers in aqueous solution, on SiO_2 surfaces, or in the formation of sodium and potassium titanates.[5] This is the first Raman study of the comparison of the intermediates formed in the reaction between $Ba(OH)_2$ and titanium dioxide, though such methods have been examined for synthesis purposes.[6]

Experimental Section

All chemicals, $Ba(OH)_8\cdot 8H_2O$, TiO_2(anatase), CH_2Cl_2, $TiCl_4$, and NaOH, were analytical grade chemicals obtained from Aldrich Chemical. TiO_2 gel was made by mixing a 2.5 M aqueous solution of NaOH with $TiCl_4/CH_2Cl_2$ and then washing extensively with deionized water. Starting materials for barium–titanates were made by mixing fresh TiO_2 gel and $Ba(OH)_2\cdot 8H_2O$ in appropriate stoichiometries in the presence of CH_2Cl_2. Drying was conducted using CO_2-free dryed air generated by a Balstron air filter. Simultaneous thermogravimetric (TG)/differential thermal analysis (DTA) is a technique which performs TG and DTA measurements on a single sample at the same time as this sample is subjected to a programmed temperature cycle. The Seiko TG/DTA320 used is a module of the SSC5200 thermal analysis system. It covers the temperature range from room temperature through 1500 °C. The Raman spectra were obtained using radiation of 514.5 nm from an argon ion laser (Spectra Physics 171). Power at the sample was ~20 mW. A Spex double monochromator (Spex 1403) was used to discriminate against scattered radiation. The Raman light was detected using a Ga–As photomultiplier tube with photon counting. Typical slit widths were 6 cm^{-1} and scanning times ranged from 1 to 3 s/cm^{-1}. Diffuse reflectance IR spectroscopy was performed using a Bio-Rad 40 FTIR spectrometer.

Results and Discussion

The three sections below focus on (a) the reaction of $Ba(OH)_2$ with anatase, (b) with an amorphous titanium oxide gel, and (c) a discussion that contrasts and compares the two processes.

(a) $Ba(OH)_2$ and Anatase. Equimolar mixtures of $Ba(OH)_2\cdot 8H_2O$ and anatase were intimately mixed and heated. Raman spectra were obtained at room temperature after the various heat treatments. Figure 1 shows the spectra for samples heated in air to 450, 700, and 900 °C and maintained at these temperatures for 12 h. Initial changes are observed in the spectrum at 450 °C with the appearance of bands at 295 and 760 cm^{-1}. These bands are assigned to Ba_2TiO_4, based on both the literature[5b] and examination of pure Ba_2TiO_4. The other bands at 195, 395, 513, and 637 cm^{-1} are characteristic of anatase.[5h] At 700 °c, the bands due to Ba_2TiO_4 grow, and bands characteristic of $BaTiO_3$ at ~516 (note increased intensity compared to TiO_2 bands) and 714 cm^{-1} [5b] are observed for the first time. These bands become dominant at the expense of Ba_2TiO_4 at 900 °C. The results suggest that the formation of $BaTiO_3$ proceeds through the intermediate Ba_2TiO_4 which is consistent with the observations for $BaCO_3$–anatase system.[4a,f,7] The major difference when compared

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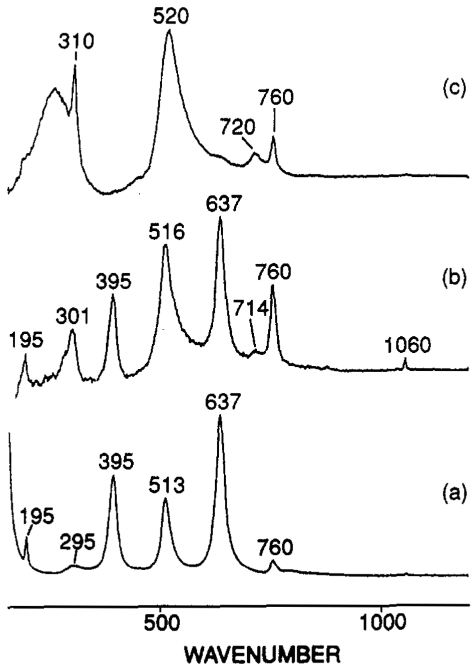

Figure 1. Raman spectra of $Ba(OH)_2$–anatase after heating for 12 h at (a) 450, (b) 700, and (c) 900 °C.

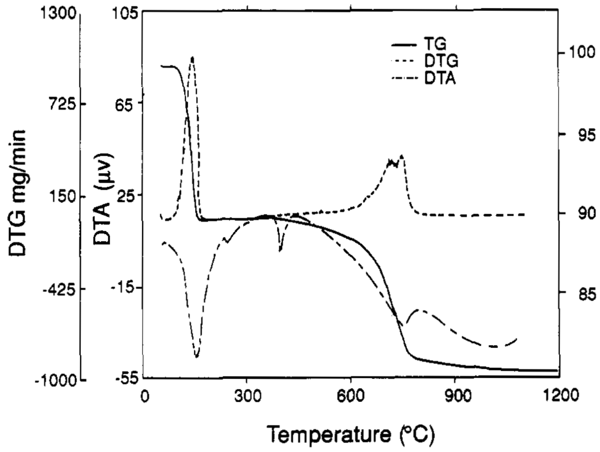

Figure 2. Simultaneous TG/DTA data for $Ba(OH)_2$ in argon; heating rate 20 °C/min.

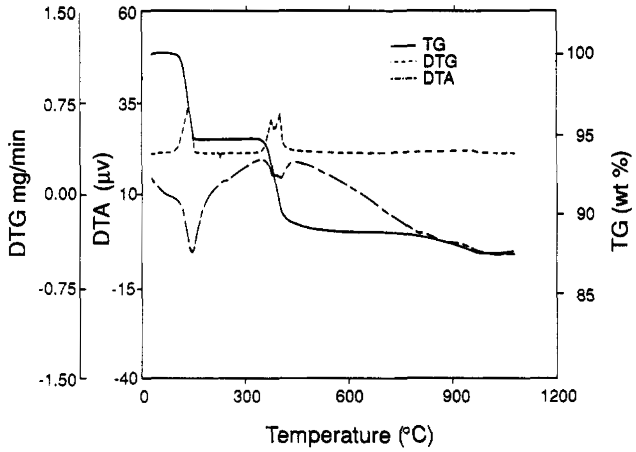

Figure 3. Simultaneous TG/DTA data for $Ba(OH)_2$–anatase; heating rate 20 °C/min.

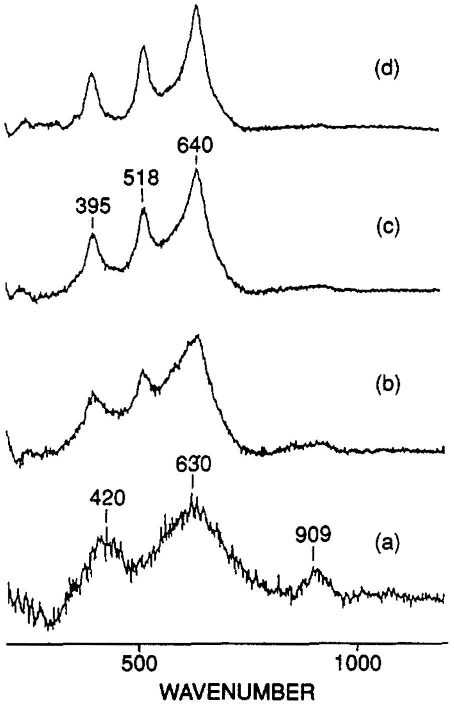

Figure 4. Raman spectra of (a) TiO_2 gel and after heating the TiO_2 gel at (b) 100 °C for 2 h (c) 200 °C for 6 h and (d) 300 °C for 6 h.

with the $BaCO_3$–anatase system appears to be the lower temperature at which Ba_2TiO_4 is formed.[4a] A weak Raman peak at 1060 cm^{-1} due to the formation of carbonate species is observed.

The TG/DTA data for $Ba(OH)_2$ and its mixture with anatase are shown in Figures 2 and 3, respectively. Three different transitions are observed for $Ba(OH)_2$ in Figure 2. The TG curve clearly indicates that the stable material examined was the monohydrate of the $Ba(OH)_2$ formed in flowing Ar. The three transitions correspond to an endothermic dehydration at 150 °C, a phase transition in the anhydrous material at 400 °C, and dehydroxylation at 720 °C.[8] Upon mixing with anatase, however, the dehydroxylation temperature is dramatically lowered and sharpened (see Figure 3). The phase transition now occurs in the same temperature range as dehydroxylation. This greatly enhanced reactivity is indicative of the simultaneous dehydroxylation and reaction with anatase to form an intermediate phase, Ba_2TiO_4, as observed in the Raman spectrum. The enhanced reactivity occuring simultaneously with a phase transformation suggests the presence of a "Hedvall effect" in this system. Hedvall's[9a] assertion that a solid substance is more reactive when undergoing a phase transformation has been a controversial topic (see ref 9b and references therein). At a heating rate of 20 °C/min, the final reaction continues to about 1000 °C.

(b) $Ba(OH)_2$–TiO_2 Gel System. The amorphous TiO_2 gel was prepared by hydrolysis of $TiCl_4$ and its Raman spectrum (Figure 4a) shows broad bands at 420, 630, and 909 cm^{-1}. Upon heating this gel (Figure 4b), characteristic peaks at 395, 518, and 640 cm^{-1} due to anatase begin to emerge at 100 °C and the conversion is almost complete at 300 °C. The bands of the gel at 420 and 630 cm^{-1} are assigned to Ti–O stretching modes and resemble the pattern of anatase. The band at 909 cm^{-1} is assigned to the Ti–O stretching mode of Ti nonbonded oxygens, since

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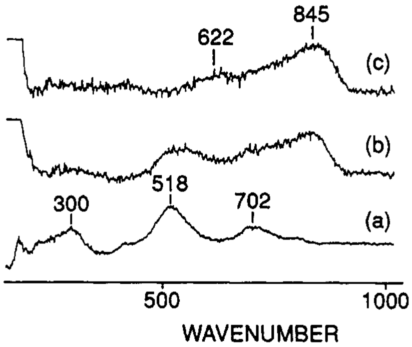

Figure 5. Raman spectra of room-temperature-dried sample of $Ba(OH)_2$-TiO_2 gel at Ba/Ti ratios of (a) 2, (b) 1, and (c) 0.5.

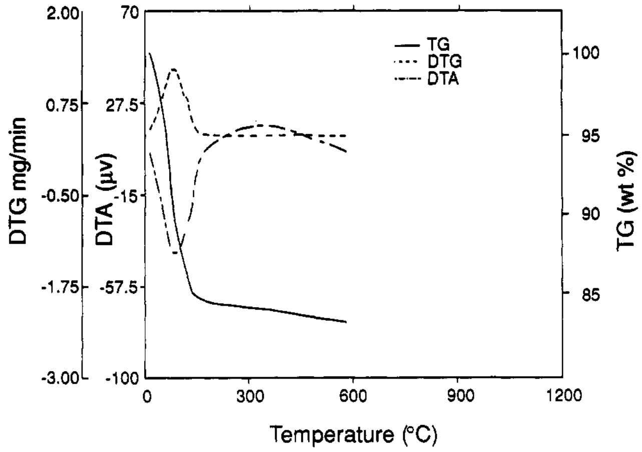

Figure 6. Simultaneous TG/DTA data for $Ba(OH)_2$-TiO_2 gel (1:1 stoichiometry) in argon; heating rate 20 °C/min.

it disappears on heating as condensation begins to occur.[10]

The amorphous TiO_2 gel reacts with $Ba(OH)_2$ upon mixing without any heat treatment. The product of this reaction depends on the Ba/Ti ratio. At a Ba/Ti ratio of 2, the product is characterized by Raman bands at 300, 518, and 702 cm^{-1}, whereas for a Ba/Ti ratio 1/2, broad bands at 622 and 845 cm^{-1} are observed. At a Ba/Ti ratio of 1, bands due to both species are observed. These spectra are shown in Figure 5a–c. The reaction between $Ba(OH)_2$ and gel is also evidenced by the changes in the TG/DTA as well as the infrared spectra shown in Figures 6 and 7, respectively. As compared to dehydroxylation temperatures of about 760 and 360 °C in case of $Ba(OH)_2$ by itself and upon mixing with anatase, in the case of the reaction with the TiO_2 gel, the weight loss is complete by about 150 °C. It is clear that the TiO_2 gel is very reactive toward $Ba(OH)_2$ under ambient conditions. This is also apparent from the diffuse reflectance infrared spectra in the 2500–4000-cm^{-1} region (Figure 7). The broad O–H stretching band in TiO_2 gel is replaced by a sharp band at 3653 cm^{-1} upon interaction with barium hydroxide. This is indicative of the formation of a product with a well-defined non-H-bonded –OH functionality on the surface.

The $Ba(OH)_2$-TiO_2 gel samples evolve to different compounds in the BaO–TiO_2 system upon heating. Raman spectra provide information about this progression and are shown in Figures 8–10. For all three gels having a Ba/Ti ratios of 2/1, 1/1, and 1/2, the initial product upon heating is $BaTiO_3$ as evidenced by the appearance of Raman bands at 300, 520, and 720 cm^{-1}. At higher temperatures, the 2/1 Ba/Ti ratio is completely converted to Ba_2TiO_4, the 1/1 Ba/Ti ratio remains as $BaTiO_3$, and the 1/2 ratio shows

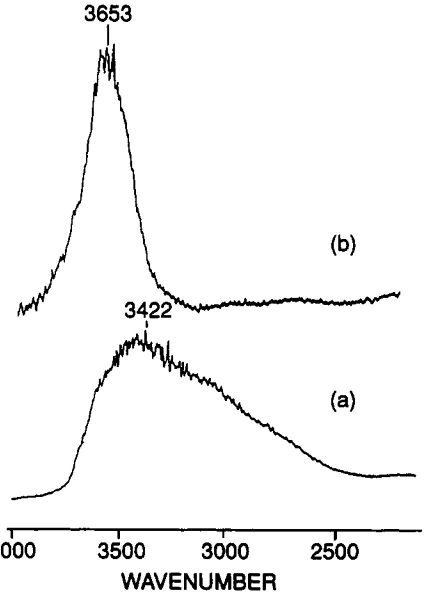

Figure 7. Infrared spectra of dried (a) TiO_2 gel and (b) $Ba(OH)_2$-TiO_2 gel (1:1 stoichiometry).

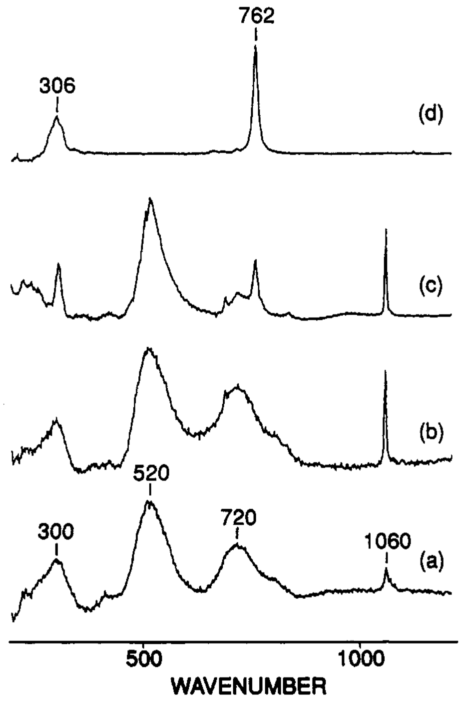

Figure 8. Raman spectra of products obtained by heating $Ba(OH)_2$-TiO_2 gel (Ba/Ti = 2) at (a) 200 °C for 30 min, (b) 450 °C for 18 h, (c) 700 °C for 10 h, and (d) 900 °C for 20 h.

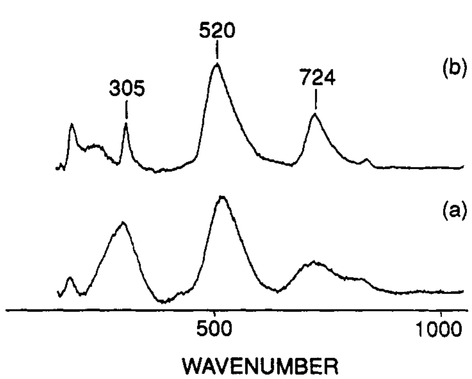

Figure 9. Raman spectra of products obtained by heating $Ba(OH)_2$-TiO_2 gel (Ba/Ti = 1) at (a) 200 °C for 30 min and (b) 450 °C for 18 h.

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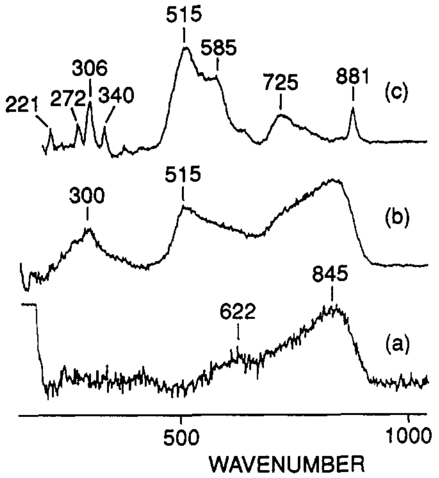

Figure 10. Raman spectra of products obtained by heating $Ba(OH)_2$–TiO_2 gel (Ba/Ti = 0.5) at (a) 200 °C for 30 min (b) 450 °C for 18 h, and (c) 700 °C for 10 h.

Raman bands at 221, 272, 340, 585, and 881 cm^{-1}, characteristic of $BaTi_2O_5$, along with the bands of $BaTiO_3$. The sharp peak at 1060 cm^{-1} is due to the formation of carbonate.

Comparison of Reactivity of $Ba(OH)_2$ with Anatase and TiO_2 Gel. There is clearly a significant difference in the reactivity of $Ba(OH)_2$ with anatase and the TiO_2 gel. This relates to the structure of the two materials. The structure of anatase is well defined—it belongs to the D_{4h}^{19} space group and contains 2 TiO_2 units/unit cell.[11] The oxygen atoms are arranged around Ti in an octahedral configuration. Anatase is characterized by Raman bands at 195, 395, 513, and 637 cm^{-1}.[12] The rigidity of the crystalline framework necessarily requires that chemical reaction begin on the surface and proceed toward the core of the particle. The structure of the amorphous TiO_2 gel is poorly defined. There have been several papers on amorphous TiO_2 gels prepared by hydrolysis of various inorganic and organic Ti precursors. The literature has many molecular descriptions for these materials.[13] There is considerable water retained in the gel, as evidenced by the broad infrared band at 3400 cm^{-1} (Figure 7) and also from previous TG studies.[13] The Raman spectrum shows broad bands at 420, 630, and 909 cm^{-1}. The band at 909 cm^{-1} can be assigned to Ti–O nonbridging bond stretches, since it disappears on heating, presumably due to condensation. The ease with which the TiO_2 gel transforms to an anatase-like structure (below 100 °C) and the broad Raman bands at 625 and 400 cm^{-1} that resemble anatase also suggest that the framework of the gel must be similar to that of anatase (Figure 4). Thus the gel can be thought of as anatase-like with surface Ti–OH groups and with considerable H_2O in the framework. This relatively open network of water may form enhanced diffusion paths for Ba^{2+} to penetrate to the reaction sites, in contrast to the well-formed anatase particles.

The fact that a rapid reaction occurs between $Ba(OH)_2$ and the TiO_2 gel as compared to anatase is evidenced from the vibrational and TG data. Since the experiments were done in air, small amounts of $BaCO_3$ were formed, as estimated by the Raman band at 1060 cm^{-1}. The TG data were, however, taken in argon. Because the amount of $BaCO_3$ formed in the synthesis experiment is small, the general conclusions reached here should not be influenced. Changes are observed immediately after mixing $Ba(OH)_2$ at room temperature with TiO_2 gel. These changes also depend on the Ba/Ti ratio (Figure 5). For a Ba/Ti ratio of 2, the Raman spectrum appears to be that of disordered $BaTiO_3$, indicating an atomic level mixing. This is similar to the case of $SrTiO_3$ which is immediately formed by reaction of $Sr(OH)_2$ and TiO_2 gel.[6b] In the case of Ba/Ti = 1, bands resembling $BaTiO_3$ are observed at 520 and 700 cm^{-1} along with the band at 845 cm^{-1} due to polymeric Ti–O–Ti. At the Ba/Ti ratio of 0.5, no $BaTiO_3$ is formed. Instead the bands are those of polymeric titanates.[5a] However, these bands do not match those of the amorphous anatase-like gels, clearly showing that the presence of $Ba(OH)_2$ has altered the gel structure. This interaction is also evident in the infrared spectrum of the TiO_2 gel before and after reaction with $Ba(OH)_2$ (1:1 ratio). The H_2O band is readily lost and instead a well-defined non-H-bonded O–H stretching band is observed (Figure 7). Clearly, the incorporation of Ba^{2+} into the TiO_2 structure leads to weaker complexation with H_2O, and its ready loss upon room-temperature drying. The thermal analysis also shows that dehydroxylation temperature is lowered to ~ 150 °C in this material (Figure 6). The hydroxyl groups at 3653 cm^{-1} are linked to the Ti center since $Ba(OH)_2$ exhibits sharp bands at 3278 and 3496 cm^{-1}.[14] In contrast to the TiO_2 gel, there is no reaction observed between $Ba(OH)_2$ and anatase at room temperature.

The heat treatment of the (Ba + Ti) materials also differs dramatically in the two cases. For anatase, the intermediate formed is Ba_2TiO_4, whereas in all cases in the gel (Ba/Ti = 2–0.5), $BaTiO_3$ is the primary intermediate product. In the anatase system, Ba_2TiO_4 reacts with TiO_2 to form $BaTiO_3$. For the gel, the 2:1 Ba:Ti material ultimately forms Ba_2TiO_4 by reaction of $BaTiO_3$ with $Ba(OH)_2$. The 1:1 ratio remains as $BaTiO_3$, whereas the 1:2 ratio results in $BaTi_2O_5$ by reaction of $BaTiO_3$ with TiO_2.

Clearly, the rapid incorporation of Ba^{2+} into the TiO_2 gel structure leads to $BaTiO_3$ as an intermediate in all cases. On the other hand, the slow incorporation of Ba^{2+} into anatase leads to $BaTi_2O_4$ as an intermediate. Thus atomic scale mixing of $Ba(OH)_2$ and TiO_2 gel is possible due to the porous nature, as well as the high reactivity of the Ti-nonbonded oxygen atoms. Direct reaction between $Ti(OH)_6{}^{2-}$ and Ba^{2+} has been proposed as the primary reaction in the hydrothermal synthesis.[4b] The presence of $Ti(OH)_6{}^{2-}$ in the TiO_2 gel cannot be confirmed from the IR due to the broad H_2O bands. After reaction with $Ba(OH)_2$, there is evidence for non-H-bonded –OH groups on the Ti surface. The Raman data indicate that the gel is anatase-like, so it is unlikely that we have $Ti(OH)_6{}^{2-}$ as the primary species in the gel. It is interesting to note the reaction of $Ba(OH)_2$ with TiO_2 soot leads directly to $BaTiO_3$.[4c] Thus, the formation of Ba_2TiO_4 is related to the inability of the Ba^{2+} to diffuse rapidly through the TiO_2 matrix. An analogous situation was reported in the formation of $BaSnO_3$, where Ba_2SnO_4 is formed as an intermediate in conventional processing but not via a coprecipitated precursor.[15] Either the use of highly porous TiO_2 gel as in this study or reactive TiO_2 soot leads to the direct formation of $BaTiO_3$.

Therefore, in conclusion this study has shown the following: (a) Hydrolysis of $TiCl_4$ results in a TiO_2 gel that contains H_2O and is anatase-like in structure. (b) The TiO_2

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gel thus formed is reactive toward $Ba(OH)_2$ under ambient conditions and results in formation of an amorphous $BaTiO_3$-like structure. (c) $Ba(OH)_2$ is unreactive toward anatase until 450 °C, when it forms Ba_2TiO_4 and finally $BaTiO_3$ between 700 and 900 °C. (d) The complex formed by reaction of $Ba(OH)_2$ and TiO_2 gel evolves to Ba_2TiO_4, $BaTiO_3$, and a mixture of $BaTiO_3$ and $BaTi_2O_5$ upon heating the 2:1, 1:1, and 1:2 Ba/Ti ratio materials.

Second-Order Nonlinear Optical Properties of *N*-(4-Nitrophenyl)-(*s*)-prolinol-Doped Sol–Gel-Processed Materials

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Received January 22, 1992. Revised Manuscript Received April 20, 1992

The sol–gel-processing technique has been used to prepare a new material for nonlinear optics. The second-order nonlinear optically active molecule *N*-(4-nitrophenyl)-(*s*)-prolinol has been doped to an inorganic oxide matrix in relatively high concentration. Electric field poling was successfully employed to introduce noncentrosymmetry required for second-order nonlinearity. Studies using in situ poling allowed the formulation of conditions under which stable poled orientation was achieved. Second harmonic generation and electrooptic modulation studies have been conducted on this material.

Introduction

The application of nonlinear optical processes to photonics has drawn great interest to the search for new nonlinear optical (NLO) materials.[1-3] These applications require high optical quality materials with low dielectric constant, high optical damage threshold, and high and stable optical nonlinearities. Organics are promising nonlinear optical materials because their molecular structure can be tailored to achieve large optical nonlinearity. They also offer advantages over inorganic materials in material processing and fabrication in the form of thin films, optical fibers, and optical wave guides, etc.

For applications involving second-order nonlinear optical processes, a stringent symmetry requirement is imposed upon the materials, i.e., the active molecular units must be arranged in a noncentrosymmetric fashion to show nonzero second-order nonlinear coefficients. Single crystals with proper symmetry, grown from both inorganic and organic materials, have been shown to perform effectively in second-order nonlinear optical processes. For organic polymers and polymeric materials fabricated in the form of thin films, the noncentrosymmetry is achieved by electric field poling.[4] In this process, a strong electric field is applied across the material to orient the molecules, with nonzero dipole moments, in the direction of the electric field. Conventionally, nonlinear optically active groups are either attached to polymer backbones or simply doped into polymers.[4,5] In both cases, the fast relaxation of the nonlinear optical units back to random orientation prevents these materials from practical applications. Pure polymers doped with nonlinear optically active molecules often do not form good-quality films. Different methods have been proposed to improve the optical quality of these materials and to achieve stable second-order nonlinear optical coefficients. For example, Ye et al. showed that hydrogen bonding can lead to a considerable increase in stability by establishing a weak cross-linked network.[6] Robello et al.[7] and Eich et al.[8] showed that cross-links in multifunctional acrylic systems and diepoxide-diamine condensation reactions, respectively, can also lead to considerable increase in the stability of poled structures. A major concern using this approach is the loss of optical quality.

Sol–gel processing is a technique which enables the preparation of amorphous or crystalline inorganic oxides starting from solutions of suitable precursor compounds, usually alkoxides, through their reaction with water.[9] This technique offers many advantages for material processing,[10,11] among them the inorganic–organic composite

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