HYDROTHERMAL PROCESSING OF $BaTiO_3$/POLYMER FILMS

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ABSTRACT

Hydrothermally derived films of $BaTiO_3$ were fabricated by reacting thin layers of titanium organometallic liquid precursors in aqueous solutions containing $Ba(OH)_2$ and having a high pH. Cubic submicron polycrystalline films of $BaTiO_3$ (thickness ≈ 1 µm) were formed at 70°C. Low concentrations of block copolymers of polybutadiene and polystyrene were incorporated into the liquid precursor to prevent precursor film cracking. Higher polymer concentrations allowed fabrication of polymer/ceramic composite films by virtue of the low temperature used in hydrothermal processing.

BACKGROUND

Over the last decade efforts have increased to develop practical analogs to organic-polymer/ceramic composites found in nature.[1] Composites of polymers and ceramics are used in a wide variety of applications. Ceramic particles are introduced into elastomers to enhance the polymer's mechanical properties,[2] while composites of polymers with SiO_2 or TiO_2 are being evaluated as waveguides,[3] and for other optical applications.[4] Below we discuss how one may use hydrothermal processing not only to fabricate ceramics, but also to form thin film composites containing polymers and ceramics. Small additions of Kraton D1102*, a block copolymer of polystyrene and polybutadiene (70% polybutadiene by weight, MW ≈ 30,000) were used to maintain the mechanical integrity of low molecular weight precursor films during drying, while larger additions led to the formation of a colloidal dispersion of $BaTiO_3$ particles in a polymeric matrix after hydrothermal processing.

Hydrothermal processing is a route to fabricate ceramics below 100°C. It involves the formation of crystalline materials from reactants in an aqueous medium under strongly alkaline conditions. Hydrothermal processing is used to fabricate large single crystals of quartz via seeding, and in the formation of zeolites from aluminosilicate gels.[5] In 1988, Lilley and Wusirika fabricated monosized powders of $BaTiO_3$ by dispersing TiO_2 powders in a concentrated solution of $Ba(OH)_2$.[6] Dogan et al. used transmission electron microscopy (TEM) to observe the formation of hydrothermally derived $BaTiO_3$ powders in a solution of $Ba(OH)_2$ with TiO_2 particles.[7] Their observations showed that the TiO_2 initially dissolved in the aqueous $Ba(OH)_2$, and led to the nucleation of nanometer-sized $BaTiO_3$ particles in cubic phase.

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Calculations defining the thermodynamics of hydrothermal processing were performed by Lencka and Riman.[8] They derived stability diagrams outlining the requirements to synthesize $BaTiO_3$ among other materials. Their results showed that successful fabrication of $BaTiO_3$ required a $pH > 12$, and a barium concentration on the order of 10^{-4} molal or higher. The modelling showed that it is possible to fabricate $BaTiO_3$ at room temperature, although this has yet to be done experimentally. Finally, they demonstrated the importance of eliminating CO_2 from the reaction vessel to avoid the formation of $BaCO_3$.

Yoshimura and coworkers were the first to demonstrate the utility of hydrothermal processing to form thin films by fabricating a variety of perovskite materials.[9] They produced films of $BaTiO_3$ by depositing sputtered titanium metal films onto polymer or glass substrates, followed by a combined hydrothermal/electrochemical treatment at temperatures in excess of 100°C using an autoclave. Bendale et al. used a hydrothermal/electrochemical approach to grow films of $BaTiO_3$ on titanium metal substrates at temperatures as low as 55°C.[10] Their study indicated that a layer of titanium oxide acted as a precursor for the formation of $BaTiO_3$. Consistent with hydrothermal processing of powders, $BaTiO_3$ film fabrication was favored in highly alkaline CO_2 free environments.

Our approach uses hydrothermal processing to form films of $BaTiO_3$ from organometallic liquid precursors. $BaTiO_3$ film thickness is determined by the thickness of the precursor layer, which is in turn controlled by the rheology of the liquid precursor. As shown below, liquid precursors allow one to coprocess polymers with the $BaTiO_3$ films given a suitable solvent for both polymer and precursor. All processing described below is performed at 70°C, and without an applied electric field. The absence of an electric field simplifies both the processing procedure, and the interpretation of $BaTiO_3$ film formation.

EXPERIMENTAL PROCEDURE

Hydrothermally derived films of $BaTiO_3$ were fabricated by reacting films of titanium metal organic liquid precursors in aqueous solutions containing barium and having a $pH > 12$. Films of titanium diisopropoxide bis(ethylacetoacetate)[#] (TIBE) were fabricated by spin coating a thin layer (< 1 μm) of the precursor (diluted 1:1 by volume with toluene) onto a glass substrate (300 μm thickness, 10 x 10 mm). In order to facilitate handling, the substrates were attached with double sided tape to 10 mm x 15 mm x 2 mm slides of PMMA. The PMMA slide was in turn attached to a spin coater (a modified router), and enough precursor was applied with a pipette to cover the substrate. The spin coater was run at 10 kRPM for 5 s, and a second coating of precursor was applied. The film was dried in a dessicator into which was placed a small beaker of toluene to slow evaporation. Despite this, the films invariably cracked during drying. In order to reduce the extent of film cracking, Kraton D1102 was dissolved into the TIBE/toluene solution. Additions of the polymer ranged from 2% to 80% by weight relative to TIBE, solutions with larger polymer concentrations were further diluted with toluene to facilitate spin coating. To examine the infiltration of the aqueous $Ba(OH)_2$ solution into the hydrophobic block copolymer, a relatively thick precursor/polymer film (50/50

[#] Gelest Chemical Co., Tullytown, PA 19007

TIBE/toluene, film ≈ 100 μm thickness) was fabricated by casting the precursor solution on water.

$Ba(OH)_2$ solutions were made from H_2O that had been boiled for 15 min to remove dissolved CO_2. After dissolution of $Ba(OH)_2$ in warm H_2O (> 50°C) the solution was filtered, to remove any $BaCO_3$ formed on the solution surface, into a polyethylene bottle. The bottle was flushed with nitrogen, sealed, and kept in an oven at 40°C or higher (depending on the concentration of $Ba(OH)_2$) to avoid precipitation of $Ba(OH)_2$.

$BaTiO_3$ and $BaTiO_3$/polymer films were fabricated by placing the coated substrates into $Ba(OH)_2$ solutions, flushing the bottle with nitrogen, and placing the bottle in an oven. The substrates were held on the bottom of the bottle using a piece of teflon for ballast. All films described below were treated at 70°C in 1 M $Ba(OH)_2$ for 4 h, except for the thick film which was treated for 24 h. The films were characterized by XRD using Cu Kα radiation, and a scan rate of 0.75°/min from 15° to 65° 2θ. Microstructural observation was conducted in a scanning electron microscope (SEM) by mounting the films on aluminum stubs with carbon paint and gold coating the film surface. The thick film was fractured in liquid nitrogen before viewing in the SEM.

RESULTS AND OBSERVATIONS

Morphological changes during drying of the TIBE/toluene films were observed using an optical microscope. As the films dried, an interconnected network of cracks developed within the film (Fig 1a). Additions of 8 wt% Kraton D1102 (relative to TIBE) reduced the number density of cracks (Fig. 1b), and further additions of polymer eliminated the film cracking altogether. Observations at higher magnification (Fig. 1c) indicated that cracking initiated at dust particles, scratches, or other heterogeneities, followed by propagation and subsequent linking up of the cracks. Additions of polymer prevented the formation of a crack network by limiting the extent that the cracks could propagate from their nucleation sites (Fig. 1d).

The hydrothermal conditions used above to fabricate $BaTiO_3$ films were well within the region of $BaTiO_3$ stability described by Lencka and Riman.[8] The $BaTiO_3$ films were transparent, but showed colorful interference patterns in reflected light much like soap bubbles and oil films. Fracture surfaces indicated that the films had a thickness between 0.5 and 1.0 μm. XRD of the films corresponded to the pattern for cubic $BaTiO_3$. Microstructural observation using the SEM (Fig. 2a) showed a continuous film that appeared dense, and having a narrow grain size distribution within the limits of 0.1 and 0.2 μm.

Adding small amounts of polymer (< 10 wt. %) did not change the film's microstructure. Further additions of polymer led to a weaker XRD pattern as the proportion of $BaTiO_3$ in the film decreased. Fig. 2b shows a typical microstructure for the polymer loaded $BaTiO_3$ films, in this case the precursor containing 40% polymer relative to TIBE. $BaTiO_3$ particles were present as a colloidal dispersion in a matrix of polymer, the particles appearing to sit close to or on the surface of the film. The particle size decreased monotonically with increased polymer loading; comparing Figs. 2a and 2b one observes a decrease in particle size of approximately 50%. Freeze fracture observations of the thin spin coated films were inconclusive as to whether $BaTiO_3$ particles could be found below the surface of the film.

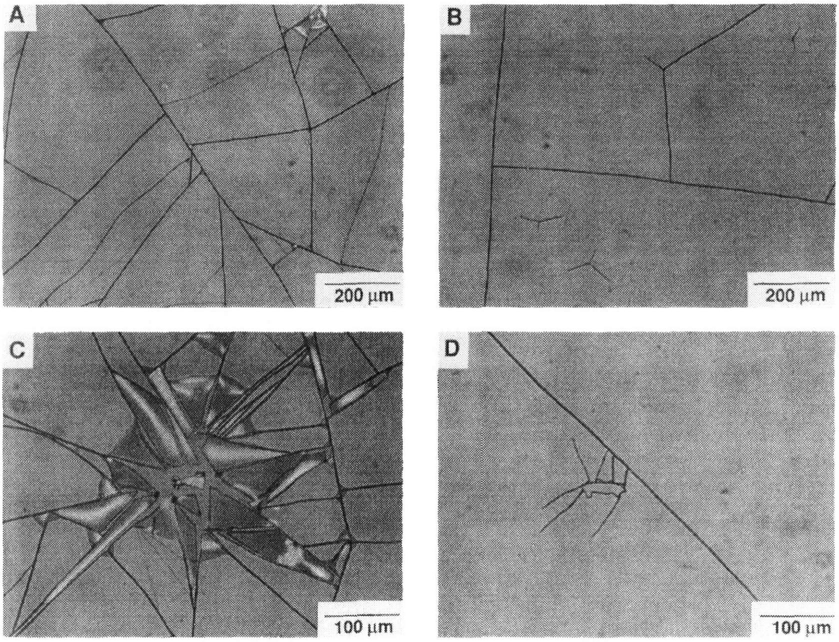

Figure 1: Spin coated films of TIBE/toluene (1:1 by volume), a) no polymer, b) 8 wt. % D1102, c) crack nucleation site, no polymer, d) 8 wt. % D1102.

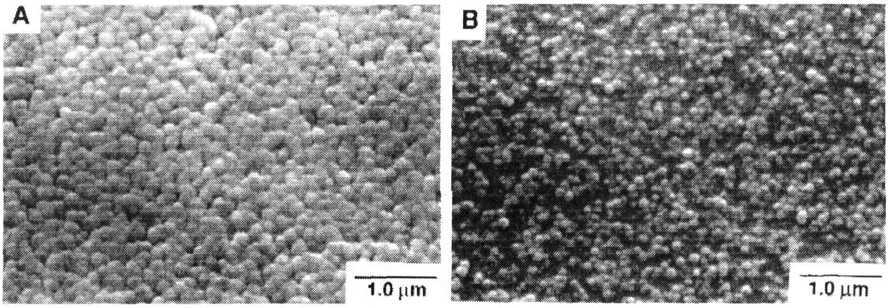

Figure 2: Precursor films treated in 1 M $Ba(OH)_2$ at 70°C for 4h to form $BaTiO_3$: a) TIBE/no polymer, b) 40 wt. % D1102 relative to TIBE.

Thicker films fabricated to facilitate freeze fracture again had particles on the film surface (Fig. 3a). XRD of the thick films showed a weak pattern for cubic

$BaTiO_3$, and energy dispersive spectroscopy (EDS) of the surface indicated that the particles contained barium and titanium, although the exact proportion of the two could not be determined due to peak overlap. The $BaTiO_3$ particles were inhomogeneously distributed across the film's surface, areas containing a large number of $BaTiO_3$ particles next to regions with relatively few particles. This was due to segregation of the TIBE from the polymer during film fabrication as the toluene slowly evaporated. Segregation was unlikely in the thin spin coated TIBE/polymer films because the solvent evaporated rapidly. The fracture surface of the film exhibited spherical particles 0.75 - 1.0 µm in diameter (≈ 3 times as large as the particles on the surface) randomly distributed throughout the polymeric matrix (Fig. 3b). In most cases the fracture path went through the particles implying a strong bond between the particles and the matrix. EDS of the fracture surface indicated the presence of titanium, but no barium was detected.

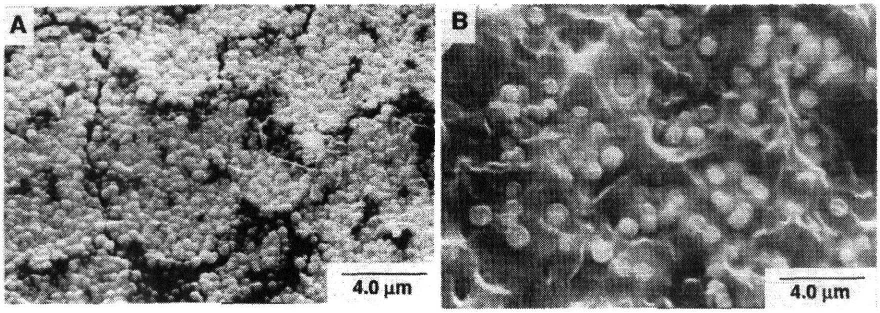

Figure 3: Thick polymer/TIBE film treated in 1M $Ba(OH)_2$ at 70°C for 24h: a) film surface, b) fracture surface.

DISCUSSION

Studies of the drying of gels have shown that the shrinkage associated with the drying of a film on a rigid substrate leads to the development of stresses that are relieved by the formation of cracks within the film.[11] The addition of a high molecular weight linear polymer causes the formation of an interconnected network of polymer chains in the film. The polymer network prevents cracking by increasing the fracture toughness of the film. Further, stresses developed during drying may be relieved by the movement of polymer chains rather than by cracking. In the experiments described above, a relatively large fraction (≈ 10 wt. %) was required to eliminate film cracking. Increasing the molecular weight of the polymer should cause a network of chains to form at a lower volume fraction, thereby decreasing the amount of polymer required to prevent cracking.

The $BaTiO_3$ films formed by hydrothermal processing were transparent because they had a small grain size, and any porosity in the film was too fine to scatter light. The relationship between processing conditions (i.e., pH, temperature, $[Ba]^{2+}$) and microstructure are discussed in detail elsewhere.[12] The $BaTiO_3$ phase is in cubic form even though the thermodynamically stable form of

$BaTiO_3$ at room temperature is tetragonal. This phenomenon, attributed to a particle size effect, has been observed in a number of fine grain titanates,[13,14] but its origin has yet to be understood. The critical particle size for the transition from cubic to tetragonal $BaTiO_3$ was reported as ≈ 0.15 µm in two studies.[13,14] However, the presence of grain boundaries and residual stresses make the assessment of films more complicated than free particles.

In both the spin coated (thin) and cast (thick) polymer/TIBE films $BaTiO_3$ was observed on the film surface after hydrothermal treatment. The observation of barium free particles on the fracture surface of the thick film indicates that hydrolyzing agents (H_2O, OH^-) could diffuse through the polymer to promote the formation of TiO_2 particles, but barium was insoluble in the polymer matrix. This scenario is supported by the work of Calvert and Broad who noted that if the reagent is not soluble in the polymer only surface reactions can occur.[15] Further, by placing both barium and titanium directly into the polymer by forming PMMA films with mixed Ba/Ti alkoxides, they precipitated $BaTiO_3$ particles in the bulk by placing the films in boiling $Ba(OH)_2$.[15] For the TIBE/polymer films described above, $BaTiO_3$ will form only when titanium diffuses to the surface and reacts with the aqueous $Ba(OH)_2$ solution.

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