

Hydrothermal Synthesis of BaTiO₃ on a Titanium-Loaded Polymer Support

M. Oledzka,[†] N. E. Brese,[‡] and R. E. Riman^{*,†}

Department of Ceramic and Materials Engineering, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854-8065, and Rohm and Haas Company, 727 Norristown Road, Spring House, Pennsylvania 19477

Received March 22, 1999. Revised Manuscript Received May 13, 1999

A titanium-containing polymer precursor was subjected to aqueous Ba(OH)₂ solutions of concentration varying from 0.02 to 0.5 M and at temperatures from 65 to 200 °C under hydrothermal conditions. Powder X-ray diffraction (XRD) revealed the presence of cubic BaTiO₃ in most of the products, as a result of the mineralization of the polymer. Nucleation of spindlelike BaTiO₃ particles was observed on the polymer surface after reactions lasting 5 h. Sources of possible contamination with carbonates are discussed.

Introduction

Barium titanate (BaTiO₃) is useful for the manufacture of multilayer ceramic capacitors, thermistors and electrooptic components.¹ Therefore, it has been the subject of continuous research, since the discovery of its ferroelectric properties in the 1940s. The hydrothermal method of synthesis offers a simple direct route to obtain anhydrous multicomponent ceramic oxides.^{2,3} In contrast to the conventional solid state route, hydrothermal synthesis takes place at lower temperatures and arguably in a more benign experimental environment. Other advantages of the hydrothermal technology include low cost, high product purity, and the ability to control particle size.³ In addition, thermodynamic modeling of hydrothermal processes has been carried out for several important ferroelectric materials, including BaTiO₃, providing theoretical guidance for designing optimal hydrothermal experiments up to ~300 °C.⁴

As early as 1963, Christensen and Rasmussen reported on the hydrothermal crystal growth of BaTiO₃ (at temperatures of 380–450 °C and pressures of 300–500 atm) from titania gel and an aqueous solution of Ba(OH)₂ with NaOH as a mineralizer.⁵ More recent work by Kutty and Balachandran demonstrated that ultrafine BaTiO₃ powder can be synthesized at temperatures as low as 85 °C.⁶ In a typical hydrothermal process, BaTiO₃ is prepared from an aqueous solution of Ba(OH)₂ (or some other strong base with a soluble barium salt) and such titanium sources as oxide, oxide gels, or metalorganic compounds. Apart from crystal growth and powder

syntheses, the hydrothermal technique has been successfully employed by various groups in the growth of polycrystalline^{7,8} and heteroepitaxial^{9,10} BaTiO₃ thin films at temperatures ranging from 70 to 800 °C.

Calvert and Broad applied the hydrothermal method at ambient pressure and temperature ~100 °C for in situ precipitation of BaTiO₃ in a polymer matrix to produce composites.¹¹ This procedure, inspired by the formation of biominerals such as bone, teeth, or seashells, represents one of the recent trends in materials synthesis, termed biomimetic materials chemistry.¹² The use of polymers as templates for the growth of inorganic materials has been receiving considerable attention. This promising synthetic technique may be used, for example, to produce inorganic thin films under mild conditions¹³ and composites containing nanometer particles,¹⁴ as well as nanosized inorganic compounds with controlled stoichiometry, size, shape, and structure.^{15,16}

Lee et al. recently demonstrated the feasibility of a biomimetic approach in the nanoscale patterning of a barium titanate precursor on a block copolymeric template.¹⁷ Crystalline BaTiO₃, however, did not form as a

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* Corresponding author. E-mail: riman@email.rci.rutgers.edu.

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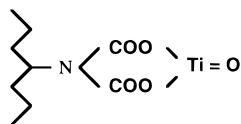


Figure 1. Schematic picture of the polymer precursor used in this work.

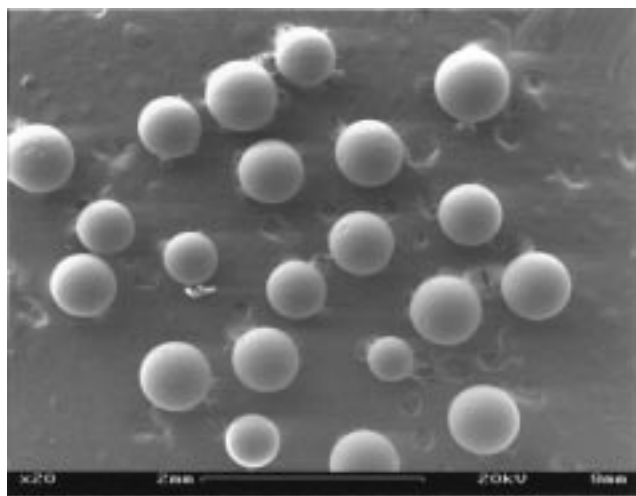


Figure 2. FESEM image of Ti-loaded Amberlite IRC718 polymer beads.

result of this experimental process, even after immersion of the barium titanated films into an alkaline aqueous solution.

The purpose of this study is to investigate the behavior of a titanium-containing polymer as a potential titanium precursor in the hydrothermal synthesis of BaTiO₃. To our knowledge, this is the first use of a titanium-containing resin in the hydrothermal processing of BaTiO₃. Since the final product of the synthetic approach employed here contains both a mineral part (BaTiO₃) and an organic part (the resin), our work in a way can also be considered as a contribution to biomimetic materials and composite chemistry.

Experimental Section

Preparation of Ti-Loaded Polymer. Amberlite IRC718 (Rohm and Haas) is a chelating cation-exchange resin used to remove heavy metal cations from waste and feed streams. The polymer backbone is a copolymer of styrene and divinyl benzene, and it is decorated with aminodiacetic groups adept at chelating transition metals (see Figure 1). A 75 g sample of polymer beads were loaded into a 1 in. diameter glass column that was fitted with a glass frit drain. The beads were slowly rinsed with 250 mL of a 1 N H₂SO₄ solution and then with sufficient purified water to reach an effluent pH = 5. Then 35 g of these wet beads were placed in a 125 mL polyethylene bottle along with 30 mL of an aqueous 20 019 ppm TiOSO₄ (Aldrich) solution and rocked for 18 h on a flatbed shaker. The beads were again placed in a glass column and rinsed with 1 M NH₄OH and purified water to remove any traces of sulfate which would later react with Ba to form BaSO₄. Inductively coupled plasma (ICP) analysis of the effluent on a Bausch and Lomb 3510 spectrometer and X-ray diffraction (XRD) analysis of pyrolyzed material indicated that titanium remained bound to the resin during the rinsing operation. Figure 2 shows the Ti-loaded resin beads.

Hydrothermal Reaction. Polymer beads, Ba(OH)₂ powder (Fisher Scientific, reagent grade), and CO₂-free water were transferred together with a stirring bar into a Teflon container (50 mL, Saville Corporation, Minnetonka, MN) with an inner

Table 1. Experimental Conditions and Results of Powder X-ray Diffraction (XRD) Analysis

reaction no.	Ba(OH) ₂ (mol/L)	<i>t</i> (°C)	time (h)	<i>m</i> _{resin} (g)	results of XRD analysis
1	0.2	65	5	1.41	amorphous
2	0.02	100	5	1.63	amorphous
3	0.1	100	5	2.05	BaTiO ₃
4	0.2	100	5	2.55	BaTiO ₃
5	0.5	100	5	2.55	BaTiO ₃ , BaCO ₃
6	~0.1 ^a	100	25	1.25	BaTiO ₃
7	0.1	150	168	2.60	BaTiO ₃ , BaCO ₃
8	0.2	170	48	0.49	BaTiO ₃
9	0.2	200	5	0.43	BaTiO ₃ , BaCO ₃
10	0.2 ^b	100	5	1.50	SrTiO ₃ , Sr(OH) ₂

^a After 25 h ~2/3 of water evaporated; thus the final Ba(OH)₂ concentration was higher and equal to ~0.3 M. ^b Concentration of Sr(OH)₂.

seal valve. The handling of the reactants was done under an inert gas (Ar) atmosphere, in a CO₂-free glovebox (VAC Vacuum Atmosphere Co., Model DLX-001-S-P, Hawthorne, CA), since carbon dioxide exposure may lead to the formation of a BaCO₃ impurity.⁴ In experiments carried out at temperatures above 100 °C, a pressure vessel (125 mL, Parr Co., Moline, IL) was used. After the synthesis, the beads were washed thoroughly with CO₂-free water and dried overnight in an oven at ~50 °C. During the hydrothermal syntheses, the beads changed color from light to pale brown. The observed change in color was similar for all processing temperatures.

Characterization. A portion of the beads from each hydrothermal run was ground, and the resulting powders were characterized using powder X-ray diffraction. The analyses were performed on a Siemens D-500 diffractometer (Siemens Analytical X-ray Instrument Inc., Madison, WI) using Ni-filtered Cu Kα radiation, in the 20–80° range with a 0.04° step size and 2 s count time. The chemical identity of the products was determined by comparing the experimental X-ray powder patterns to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDS). The surface morphology of the beads coated with carbon was examined with a Leo-Zeiss Gemini 982 field emission scanning microscope (FESEM). Semiquantitative analyses were carried out on a PGT (Princeton Gamma Tech, Princeton, NJ) digital energy dispersive spectroscopy (EDS) spectrometer, using an accelerating voltage ranging from 10 to 15 keV. Peak overlap of the titanium Kα and barium Lα lines was resolved by standardless analysis IMIX software.

Results and Discussion

The resin was reacted with aqueous Ba(OH)₂ solutions of concentration varying from 0.02 to 0.5 M (pH value: 12.30–13.70, respectively) and at temperatures ranging from 65 to 200 °C. High pH and barium concentration on the order of 10⁻⁴ M or higher are necessary for a successful synthesis of BaTiO₃ with a high yield (i.e., above 99.995%), as indicated by thermodynamic calculations of stability diagrams for the hydrothermal Ba–Ti system by Lencka and Riman.⁴ Moreover, a pH at least as high as 9 ensures that Ti ions stay bonded to the resin.¹⁸ Experimental conditions are summarized in Table 1 along with the results of XRD analysis. The obtained XRD patterns compare favorably to JCPDS card No. 5-0626, which indicates the presence of cubic BaTiO₃ in most of the runs (Table 1). Figure 3a shows an XRD pattern of an amorphous polymer precursor, and Figure 3b shows a typical XRD pattern of a hydrothermally processed polymer containing BaTiO₃ (reaction 3). The formation of the cubic BaTiO₃ phase, observed in this work, is quite common in the hydrothermal processing of BaTiO₃ at 250 °C or

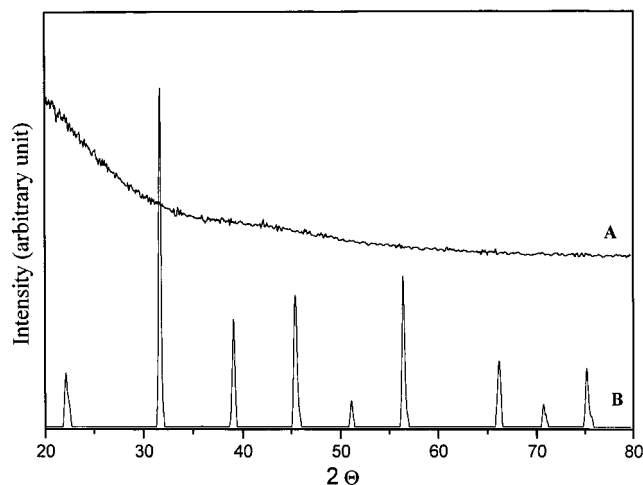


Figure 3. (a) Powder X-ray diffraction pattern of an unreacted polymer. (b) Typical powder X-ray diffraction pattern of a hydrothermally processed polymer, reaction 3 (0.1 M Ba(OH)₂, 100 °C, 5 h).

below.^{19,20} Although the tetragonal polymorph is thermodynamically stable below the Curie point (i.e., 130 °C), particle size, if less than 1 μm, may not be large enough to accommodate the strain caused by a structural transition from cubic to tetragonal phase.¹⁹

Experimental data presented in Table 1 indicate that all experiments carried out at 100 °C or higher temperatures, and at a Ba(OH)₂ concentration of at least 0.1 M, lead to the formation of BaTiO₃, in agreement with theoretical thermodynamic predictions.⁴ FESEM examination of the surface morphology of the polymer beads provides further insight into how the resin reacts with Ba(OH)₂ solution. Figure 4a shows the FESEM image of an unreacted polymer bead. Reactions carried out at 100 °C for 5 h (e.g., reaction 3), which yielded the BaTiO₃ phase, produced many randomly oriented particles attached to the beads' surface. Standardless EDS analysis confirmed their composition to be BaTiO₃. Regardless of the Ba(OH)₂ concentration, the particles exhibit a spindlelike morphology, which is uncommon for the BaTiO₃ particles (Figure 4b). The length of these spindlelike particles seems to be affected by the concentration of the Ba(OH)₂ solution. Higher concentrations (0.5, 0.2 M) produced particles up to 2 μm long, while the solution of a lower concentration (0.1 M) produced particles only up to 1 μm long. However, more experiments should be carried out to unambiguously confirm this relationship between spindle length and Ba(OH)₂ concentration. The formation of spindlelike particles in an early stage of the hydrothermal growth of BaTiO₃, can be explained based on the model of heterogeneous nucleation on a polymeric substrate by chemical accretion, given by Walton.²¹ According to this model, the polymer-bound Ti ions (Figure 1) form anchors for subsequent complexation and cluster formation.²¹ The surface arrangement of the Ti ions may lead

to very specific nucleation features, which indeed was observed in our study as the formation of BaTiO₃ particles with an unusual spindlelike morphology.

An increase in the reaction time (reaction 6) and temperature (reactions 7–9) leads to the coverage of the beads' surface with a thin film, as shown in Figure 4c. For all the reactions the composition of the films was confirmed by the EDS analysis to be that of BaTiO₃ within experimental error. Initially, the EDS analysis was carried out at 15 keV. However, the raw data suggested that approximately five times more barium than titanium was present. Decreasing the accelerating voltage of the EDS analysis to 10 keV, and thus the excitation volume, gave the expected stoichiometry of the BaTiO₃ phase. Therefore, this value of accelerating voltage was used subsequently. Results of EDS analyses performed at these two different values of accelerating voltage indicate that the distribution of titanium and barium ions may not be homogeneous in an area close to the beads' surface. This may be a reason the BaTiO₃ phase covers the surface of a polymer precursor only with a thin layer. That also, in turn, may imply that prior to the hydrothermal processing, titanium ions might reside mostly at the surface of the polymer beads, as would be expected from the rather low loading level. Calcining the Ti-loaded resin (at 650–800 °C for 3 h) results in the pronounced weight loss of 98 wt %, and the formation of mostly TiO₂ rutile (JCPDS card No. 21-1276) and some organic residue. The excess of barium revealed by the EDS analyses at 15 keV is consistent with the excess of Ba(OH)₂ solution that was used in each hydrothermal reaction. It may also suggest the BaTiO₃ layer on a bead surface does not obstruct the diffusion of Ba²⁺ ions inside a bead. Moreover, even if XRD analysis did not detect crystalline BaTiO₃ in the final products, its amount might be below the detection limit of the X-ray diffraction technique (~3 wt %) and/or it may be present in an amorphous form. Subsequent calcination studies of the hydrothermally processed resin confirm this excess of barium; for example, the calcination carried out at 1200 °C for 24 h yielded a final product composed mainly of Ba₂TiO₄ (JCPDS card No. 38-1481) with traces of BaCO₃ (JCPDS card No. 5-0378) and TiO₂ rutile.

The reaction carried out at 65 °C and Ba(OH)₂ concentration of 0.2 M yielded an amorphous product, which might indicate that either the resin may not be sufficiently reactive at 65 °C or that the duration of the hydrothermal synthesis is not long enough. Since FESEM image of this particular product (Figure 4d) shows the presence of many submicron spherical and elongated particles attached to a bead's surface, the synthesis time might be a decisive factor in this reaction. In contrast, FESEM examination of another amorphous product (reaction 2–100 °C and Ba(OH)₂ concentration of 0.02 M) reveals no sign of nucleation on the surface of a bead. According to the thermodynamic predictions for the hydrothermal Ba–Ti system,⁴ such experimental conditions should favor the formation of BaTiO₃. The absence of the BaTiO₃ phase in this case suggests that this particular reaction was, most likely, kinetically inhibited by the low concentration of Ba(OH)₂. All other reactions carried out at 100 °C yielded the BaTiO₃ phase. This indicates that the concentration of the Ba-

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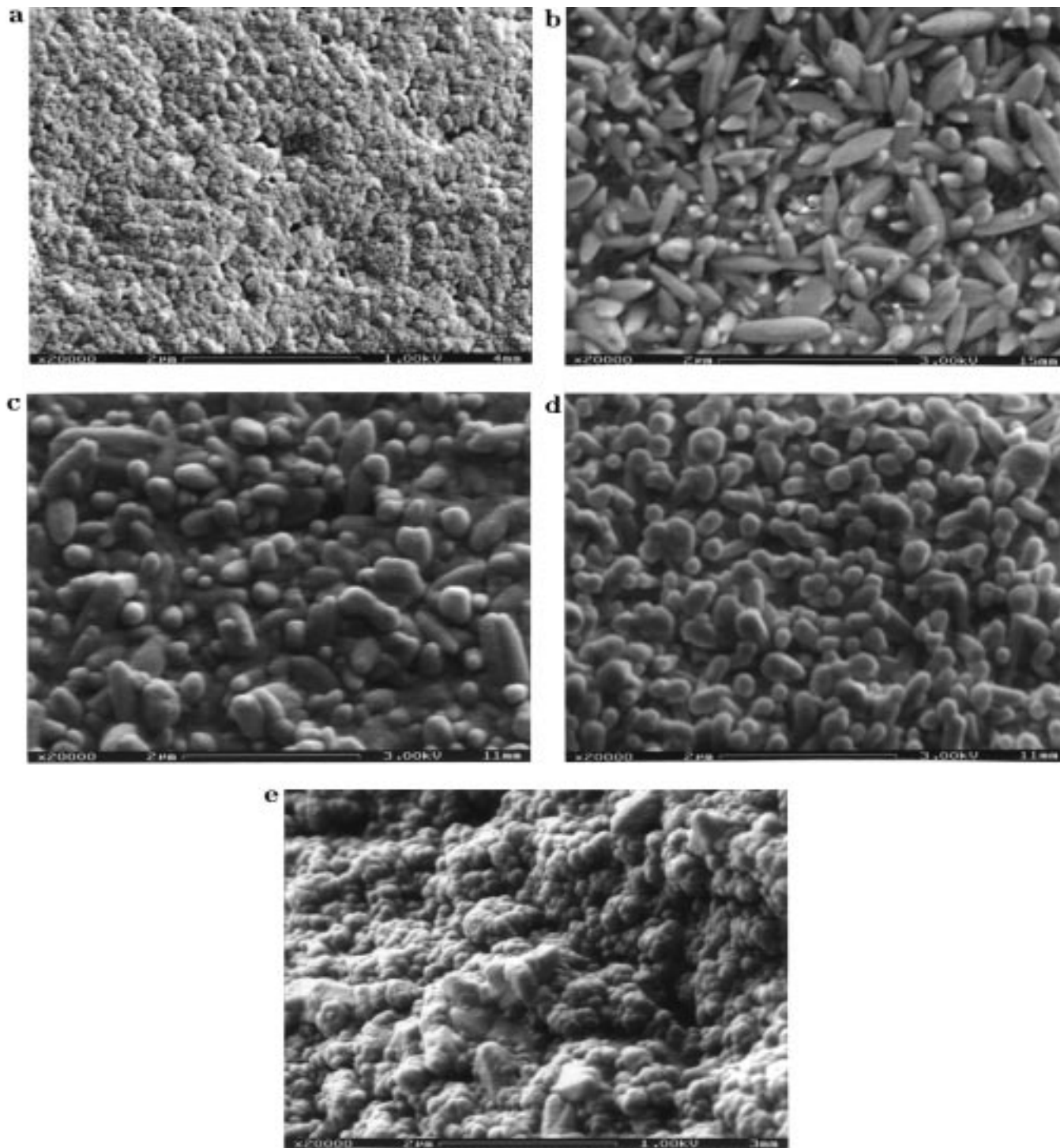


Figure 4. FESEM images: (a) surface of an unreacted polymer; (b) spindlelike BaTiO_3 particles produced in reaction 3 (0.1 M $\text{Ba}(\text{OH})_2$, 100 °C, 5 h); (c) surface covered with BaTiO_3 thin film (reaction 6: ~ 0.3 M $\text{Ba}(\text{OH})_2$, 100 °C, 25 h); (d) submicrometer spherical particles produced in reaction 1 (0.1 M $\text{Ba}(\text{OH})_2$, 65 °C, 5 h); (e) aggregates of SrTiO_3 particles produced in reaction 10 (0.1 M $\text{Sr}(\text{OH})_2$, 100 °C, 5 h).

$(\text{OH})_2$ solution plays an important role in the reactivity of the polymer precursor, and the concentration of the former should be at least 10^{-1} M for the polymer precursor to form the BaTiO_3 phase.

On the basis of the experimental evidence, discussed above, the possible microstructure that forms during the hydrothermal reaction on a polymer surface might be represented by a scheme like that shown in Figure 5.

Despite precautions undertaken to avoid CO_2 absorption during the syntheses (the use of the CO_2 -free water

and the CO_2 -free glovebox), BaCO_3 (JCPDS card No. 5-0378) was observed in some of the products. Various factors may contribute to the contamination of the final product with the carbonate phase.²² First, CO_2 can be introduced with the starting materials (i.e., $\text{Ba}(\text{OH})_2$). Commercially available alkaline-earth metal hydroxides usually contain from 0.4 up to ~ 3 wt % of CO_2 . Thus,

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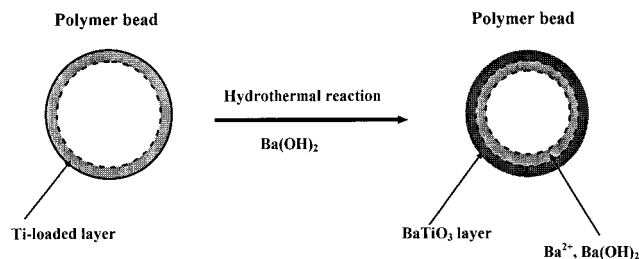


Figure 5. Schematic representation of a possible microstructure that forms on polymer surface as a result of the hydrothermal reaction: cross section of a polymer bead.

solutions with higher Ba(OH)₂ amounts are more likely to produce a carbonate phase. Indeed, reactions 3–5 (Table 1) may serve as an example of this trend. The use of solution with the highest concentration, that is 0.5 M, yielded the final product containing both BaTiO₃ and BaCO₃.

CO₂ can also be introduced after the synthesis during washing and filtration. According to data published by Lencka et al., however, this is unlikely to be the major source of CO₂ contamination.²² In this work, all the final products were washed and filtered in the air. Despite this, the BaCO₃ phase was not always observed in the XRD pattern.

Finally, the polymer itself may be a source of CO₂, either from thermal decomposition under hydrothermal conditions, or the release of incompletely incorporated monomer or oligomer. It is difficult to assess the influence of this factor due to an unavailability of relevant data. However, based on our preliminary experimental data (Table 1), large amounts of BaCO₃ are produced in reaction 9 and 7, which may be an indication that high temperature and long synthesis time, respectively, might affect the polymer's stability in a hydrothermal environment. In addition, we observed that smaller beads were more likely to yield a product containing a BaCO₃ phase.

We also reacted the titanium-containing resin with Sr(OH)₂ solution, employing similar experimental conditions to those used in reaction 4 (Table 1). The final product contained SrTiO₃ (JCPDS card No. 35-0734) as

well as some Sr(OH)₂ (JCPDS card No. 27-847). The presence of Sr(OH)₂ in the hydrothermal product, like in experiments with Ba(OH)₂, can be attributed to the excess of the base used. However, Sr(OH)₂ is less soluble than Ba(OH)₂²³ and as such is more difficult to remove from the final product. Unlike the reaction with the Ba(OH)₂ solution, this process does not produce spindlelike particles but aggregates of submicrometer particles (Figure 4e). In view of identical processing conditions and rather similar chemical behaviors of Sr(OH)₂ and Ba(OH)₂, it is difficult to explain this difference in morphology. Therefore, further research is necessary to elucidate the occurrence of a spindlelike morphology observed for BaTiO₃ phase.

Summary

Titanium-containing Amberlite IRC718 chelating cation-exchange resin was used successfully for the first time as a precursor in the hydrothermal synthesis of BaTiO₃ and SrTiO₃. The 5 h long reactions at 100 °C and Ba(OH)₂ concentrations of at least 0.1 M lead to the mineralization of the polymer surface and nucleation of BaTiO₃ particles with a spindlelike morphology. An increase in a reaction time results in a uniform coverage of the surface with BaTiO₃. The presence of BaCO₃ impurity, observed in some of the final products, may present a technical challenge and limits further practical applications of the resin in, for example, the manufacture of BaTiO₃ thin films.

Acknowledgment. The authors would like to thank Dr. I. Pozsgai for EDS measurement and helpful discussions and Dr. M. M. Lencka for a critical review of the manuscript and helpful discussions. This work was supported by ONR and DARPA. N.E.B. thanks E. Lundquist and E. Langenmayr for materials and helpful discussions.

CM990169F

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