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Anne Marteel-Parrish^a; Samantha DeCarlo^a; Danielle Harlan^a; Jonathan Martin^a; Heather Sheridan^a

^a Department of Chemistry, Washington College, Chestertown, MD, USA

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RESEARCH LETTER

Toward a more environmentally benign synthesis of doped barium titanate

Anne Marteel-Parrish*, Samantha DeCarlo, Danielle Harlan, Jonathan Martin and Heather Sheridan

Department of Chemistry, Washington College, 300 Washington Avenue, Chestertown, MD 21620, USA

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Barium titanate is one of the most thoroughly studied members of the perovskite family due to its prominent place in the electroceramic industry. To be used as a capacitor at room temperature, a high-dielectric constant is needed which is achieved through doping. The focus of this research was to develop a more environmentally benign alternative to the doping of barium titanate. The barium source was barium titanyl catecholate, $\text{Ba}[\text{Ti}(\text{cat})_3]$ (aq) and the doping sources were strontium oxalate (SrC_2O_4) and strontium carbonate (SrCO_3). The doping strategies included a solid-state synthetic pathway as well as microwave- and centrifuge-assisted methods which both employed water as the only solvent. The last two benign by design methods were tested with respect to their thermodynamic control over barium-to-strontium stoichiometric ratios. These methods of doping proved to be more environmentally friendly and economical while combining green chemistry and materials science.

Keywords: stoichiometric control; materials science; electroceramics; doped barium titanate

Introduction

Barium titanate is one of the most investigated electroceramics due to its large dielectric constant present in the cubic phase above 120°C and the presence of ferroelectric properties exhibited by its distorted (tetragonal) shape between 5°C and 120°C . Because of its valuable properties barium titanate is the major raw component for the production of multilayer ceramic capacitors used in decoupling, filtering, timing, and many other consumer and scientific applications. It has been established that doping perovskites such as barium titanate allows for a high-dielectric constant to be maintained while lowering the Curie temperature (the temperature of 120°C at which the tetragonal phase of barium titanate changes to the cubic one) (1). Many methods of doping barium titanate have been reported. However, most of these methods have proven to be environmentally unfriendly and did not demonstrate effectiveness in stoichiometric control, which is the biggest dilemma encountered when doping. One method involved strontium carbonate, SrCO_3 , and barium titanyl catecholate, $\text{Ba}[\text{Ti}(\text{C}_6\text{H}_4\text{O}_2)_3]$ (an intermediate in the production of BaTiO_3), as the precursors in the doping process. These reactants were mixed in an aqueous environment with and without reflux and then filtered. The water was removed and the resulting solid was then calcined at 800°C for 12 hours. X-ray powder diffraction analysis showed the barium-to-strontium

molar ratio to be anywhere in the range of 50:50–77:23, therefore yielding an ambiguous and varying stoichiometric ratio (2). Another method employed a sol-gel technique for synthesizing a (Ba,Sr) TiO_3 fluid-like gel, which was then calcined at 900°C via a microwave furnace resulting in a (Ba,Sr) TiO_3 nanopowder. Not only a large amount of energy was needed, but also the stoichiometric control over the final product was a difficult task (3). A wet chemical synthesis technique has been attempted and proved to be much safer while also using less energy. Using titanium alkoxide and alkali earth hydroxides as precursors, this method entailed a water hydrolysis and an acid-base neutralizing reaction. Both of these reactions were effective at low temperatures and ambient pressure, while still maintaining compositional and structural control over the perovskites. Despite the many benefits to this synthesis, including stoichiometric control, the results indicated the presence of an impurity, BaCO_3 , in the analysis of the final powders (4). The polymeric citrate precursor method used citric acid and ethylene glycol as precursors and a pure product was obtained at only 500°C . However, weak tetragonality and no ferroelectric transition were obtained, making this method unsuitable for electroceramic applications (5). Another scheme of synthesis was the microwave-hydrothermal route. The conditions included a strong alkaline environment, with a pH greater than 12, at

*Corresponding author. Email: amarteel2@washcoll.edu

200°C and 200 psi, with a reaction time of approximately 30 minutes. Although the stoichiometry of the resultant powders was maintained, only the cubic structure was observed (6). Yet another hydrothermal route required no calcination, which saved an enormous amount of energy, especially during mass production. However, a precursor gel was produced using TiCl_4 , a toxic and corrosive chemical for the environment (7). One study attempted a one-step synthesis, or a simple direct precipitation method involving temperatures lower than 100°C. The precursor solution included barium acetate, strontium acetate, and titanium tetrabutoxide monomer. Although these precursors are considered stable, they are not environmentally benign. In addition, strict control over pH of the solution was necessary, which illustrated another drawback of this method (8).

In this study, an environmentally benign doping developmental process was investigated, in which the precursor barium titanate catecholate was synthesized using the greener catecholate method (9,10). Davies and Dutremez found that both naturally occurring forms of titanium dioxide (rutile or anatase) undergo reaction with ammonium sulfate followed by complexation with basic solution of catechol to yield an ionic complex, $[\text{NH}_4]_2[\text{Ti}(\text{C}_6\text{H}_4\text{O}_2)_3]$ (aq). The latter precipitates from solution quantitatively and can be isolated by filtration. The subsequent acid–base reaction between the ammonium salt and barium hydroxide leads to formation of $\text{Ba}[\text{Ti}(\text{C}_6\text{H}_4\text{O}_2)_3]$ which is the main precursor used in this method (9). Maintaining stoichiometric control is necessary to attain high-quality doped perovskites, but is still extremely challenging. The electrical properties of barium titanate subject it to a high-sensitivity factor when it comes to manipulating the stoichiometry. The reasons for the problems included solubility differences between the dopant and barium sources, as well as in reaction rates, and errors in weighing small quantities of reagents, etc. (2). Despite the chemical stability of this perovskite, a strategy that displays control over stoichiometry, one that also manages to be more environmentally benign, is needed.

This research focused on exploring a method in which the Ba:Sr ratio was under thermodynamic control in the presence of excess reagent. Introduction of an excess of a solid strontium source, SrX, to a solution of a barium source, BaX, resulted in a cation exchange. The degree to which the cations were exchanged was controlled by the ratio of solubility products of BaX and SrX at the temperature of the solution. While initial BaX concentration was independent of the doping level, it did control the amount of anions, X^{2-} , entering solution. In order to prepare doped barium titanate with particular Ba:Sr ratios, a

strontium source which had the appropriate value for the ratio of the solubility products of BaX:SrX was selected with BaX being the barium titanate catecholate intermediate synthesized from naturally occurring isomorphous forms of titanium dioxide (TiO_2) with no further purification and catechol ($\text{C}_6\text{H}_4\text{O}_2$) (9,10). The two strontium dopants chosen were strontium oxalate (SrC_2O_4) and strontium carbonate (SrCO_3). Both barium and strontium are cations with a +2 charge, and the two elements have similar atomic radii. This parallelism in size helps the formation of similar bond strengths between the two cations (11). The doping strategy used an excess of strontium source in which the barium-to-strontium ratio was 1:10 to study the equilibrium conditions (12). Three different strategies were looked at: first, a simple solid-state technique was attempted, whereby the strontium source and the barium titanate catecholate intermediate were thoroughly mixed and heated in a tube furnace. This technique eliminated a multi-step procedure and the use of additional reagents, energy, and time. Second, a microwave-assisted strategy was investigated. During this process, deionized water was the solvent and only 10% microwave power was needed. Microwave heating has several advantages such as accelerating reaction rates, milder reaction conditions, and lower energy usage. Third, a centrifuge was used to mix the reagents. No heat was needed and once again deionized water was the only solvent. The synthesis and outcomes of the three strategies are detailed as well as the potential of this new doping method from a green chemistry point of view.

Results and discussion

The conditions necessary for each system to come to equilibrium were studied. Reactions were performed for varying lengths of time both with and without microwave heating and with the use of a centrifuge without heating. The methods described above were the results of intensive trials.

The results were focused on finding the appropriate method which would give the ultimate control over the stoichiometric ratio of barium-to-strontium. The stoichiometric ratios are governed by the ratio of the solubility products of the barium-to-strontium sources as shown in Table 1.

The solubility products shown in Table 1 are for dissolution in water. The ionic strength of $\text{Ba}[\text{Ti}(\text{cat})_3]$ (aq) will affect these values but it is estimated that the ratio of solubility products of BaX/SrX will only be slightly affected for reasonable concentrations of barium titanate catecholate.

Table 1. Predicted Ba:Sr molar ratios based on the solubility product values (K_{sp}) at 25°C of corresponding salts.

X^{2-}	K_{sp} (BaX)	K_{sp} (SrX)	K_{sp} (BaX)/ K_{sp} (SrX)	Product $Ba_xSr_yTiO_3$	Predicted Ba:Sr molar ratios
CO_3^{2-}	8.1×10^{-9}	9.4×10^{-10}	8.6	$Ba_{0.88}Sr_{0.12}TiO_3$	7.6
$C_2O_4^{2-}$	1.2×10^{-7}	5.6×10^{-8}	2.1	$Ba_{0.53}Sr_{0.47}TiO_3$	1.1

Note: The IUPAC Solubility Data Series contains solubility data on barium and strontium salts scattered through the volumes dealing with solubilities of solids in liquids.

Table 2 shows the averaged percentages by mass for Ba and Sr as well as the resulting Ba:Sr molar ratios. The averaged percentages are the results of three independent syntheses for each method after the equilibrium conditions have been optimized.

The results of the ICP–OES analysis suggest that the centrifuge-assisted method using strontium oxalate as dopant is the most promising. The solid-state method did not provide any stoichiometric control. The use of a microwave did not allow the stoichiometry of the final doped powders to be effectively controlled. While the centrifuge-assisted method is definitely a step forward especially with the use of strontium oxalate as dopant, several factors can play a role in affecting the stoichiometry: the solubility product constants may have been affected by the presence of a second solute such as $[BaTi(cat)_3]$ which would lower the solubility of the ionic compound, the intense preparation for the ICP–OES analyses may have resulted in the lower barium content in the case of $SrCO_3$ as dopant.

Even if the X-ray powder diffraction patterns provided some insight regarding the different phases present in the final doped powders, it was difficult to confirm the stoichiometry using matching compounds in the existing database. While the X-ray diffraction patterns showed the presence of $Ba_xSr_yTiO_3$, with x ranging from 0.5 to 0.88 depending

on the dopant source, such as the one shown on Figure 1, it was concluded that:

- there were no $SrCO_3$ or SrC_2O_4 byproducts when they were used as dopants in either the centrifuge or the microwave-assisted methods; and
- the use of $SrCO_3$ or SrC_2O_4 as dopants using the microwave-assisted method led to the formation of strontium-doped barium titanate with the expected stoichiometry but additional phases such as barium titanium oxide were also present (Figure 2).

Future experiments are planned to monitor the effect of the temperature and length of time on the presence of additional phases.

The proposed developmental doping processes were compared to previously researched methods in terms of nature of precursors, calcination temperature, production of by-products, and control over molar stoichiometric ratio. Table 3 shows advantages and disadvantages of all methods using strontium as dopant.

The centrifuge- and microwave-assisted new strategies applied many of the green chemistry principles (16). The first principle, referred to as principle three: “wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment,” was put into practice. By using less

Table 2. Molar Ba:Sr ratios obtained via solid-state, microwave, and centrifuge methods based on ICP–OES compositional analysis of Ba and Sr.

	Average percentage (%) of Ba by mass (standard deviation when available)	Average percentage (%) of Sr by mass (standard deviation when available)	Resulting Ba:Sr molar ratios
Solid-state method with $SrCO_3$ as dopant	0.05	0.60	0.09
Solid-state method with SrC_2O_4 as dopant	0.06	0.6	0.1
Microwave method with $SrCO_3$ as dopant	37.6 (2.1)	17.3 (3.6)	1.4
Centrifuge method with $SrCO_3$ as dopant	44.1 (3.5)	11.1 (3.2)	2.5
Microwave method with SrC_2O_4 as dopant	26.7 (1.6)	33.1 (1.1)	0.5
Centrifuge method with SrC_2O_4 as dopant	37.0 (0.50)	23.7 (0.50)	1.0

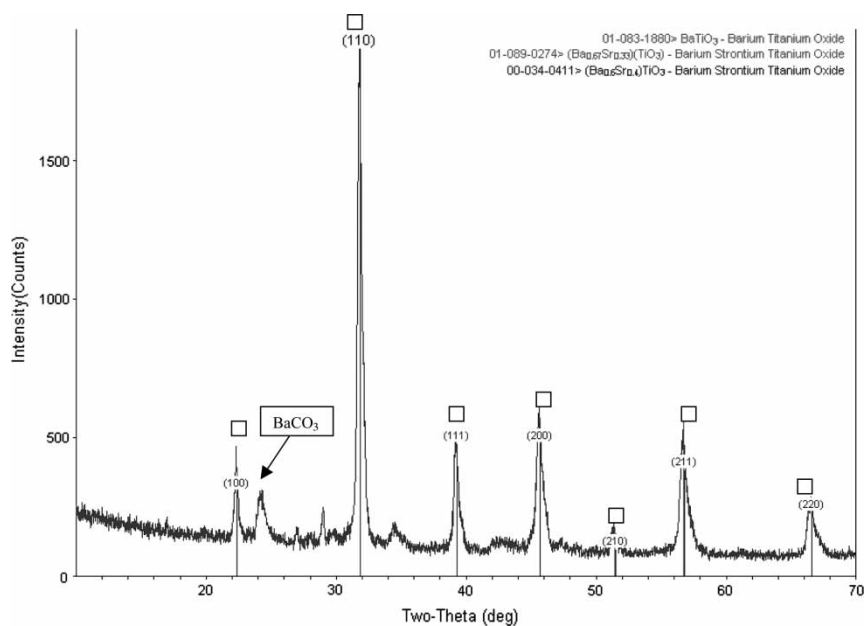


Figure 1. X-Ray powder diffraction pattern of strontium-doped barium titanate using the centrifuge-assisted method. The squares correspond to the strontium-doped barium titanate phase with $x = 50\%$.

toxic chemicals as precursors, these approaches were considered greener than conventional and common methods. An example of a conventional corrosive precursor used frequently in the synthesis of barium-strontium titanates was titanium tetrachloride. Switch-

ing to the naturally occurring isomorphic forms of TiO_2 without further purification and the catecholate method ultimately yielded a less corrosive and more cost-effective product. Another principle of green chemistry adopted in these procedures was principle

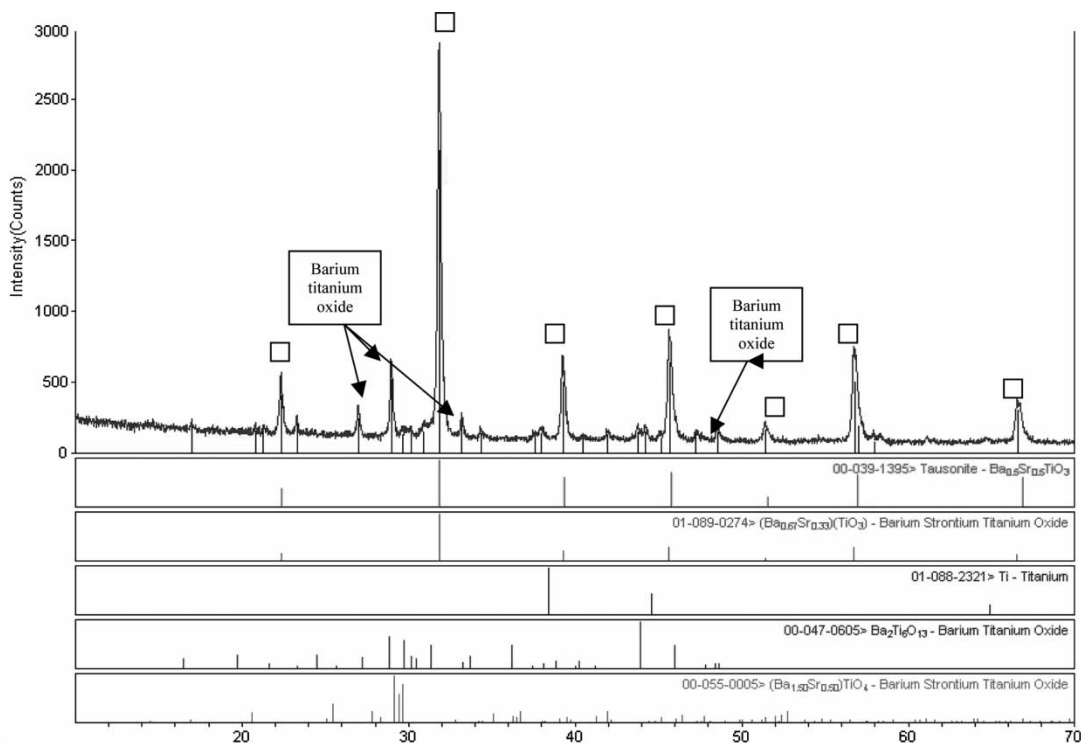


Figure 2. Example of X-Ray diffraction pattern of strontium-doped barium titanate and additional phases using the microwave-assisted method. The squares correspond to the strontium-doped barium titanate phase with $x = 50\%$.

Table 3. Advantages and disadvantages of traditional processes vs. the centrifuge- and microwave-assisted processes in terms of nature of precursors, calcination temperature, production of by-products, and control over molar stoichiometric ratio.

Method	Advantage(s)	Disadvantage(s)
Sol-gel (3)	<ul style="list-style-type: none"> • Smaller amounts of dielectric loss 	<ul style="list-style-type: none"> • Large amount of energy (calcination temperature greater than 900°C) • Inferior stoichiometric control
Wet chemical synthesis technique (4)	<ul style="list-style-type: none"> • Effective at low temperatures and ambient pressure • Compositional and structural control 	<ul style="list-style-type: none"> • Presence of impurity (BaCO₃)
Polymeric citrate precursor method (5)	<ul style="list-style-type: none"> • Citric acid and ethylene glycol precursors • Cubic structure (pure product) found at only 500°C 	<ul style="list-style-type: none"> • Weak tetragonality and no ferroelectric transition obtained making it inapt for the electroceramic industry
(Microwave) Hydrothermal Method (6)	<ul style="list-style-type: none"> • Stoichiometry of powders maintained 	<ul style="list-style-type: none"> • Strong alkaline environment (pH > 12) • Reaction at high pressure 200 psi
Hydrothermal method (7)	<ul style="list-style-type: none"> • Enhanced electrical properties • Able to manipulate the Curie temperature • No calcination (saving energy) 	<ul style="list-style-type: none"> • Precursor gel produced from TiCl₄ (toxic and corrosive chemical)
One-step synthesis/simple direct precipitation method (8)	<ul style="list-style-type: none"> • Temperature < 100°C 	<ul style="list-style-type: none"> • Non environmentally benign precursors • Strict control of pH needed
Mechanosynthesized nanopowders and spark plasma sintering (13)	<ul style="list-style-type: none"> • Grain growth control • Possibility of processing dense nanostructured Ba_xSr_yTiO₃ ceramics • Temperature lower (300°C–400°C) than standard sintering 	<ul style="list-style-type: none"> • BaO₂ strong oxidizer
Solvothermal method (14,15)	<ul style="list-style-type: none"> • Low temperature • Time efficient 	<ul style="list-style-type: none"> • Harmful and non environmentally benign precursors
Centrifuge- and microwave-assisted pathways based on the catecholate method (9)	<ul style="list-style-type: none"> • Environmentally friendly precursors • No post-sintering treatment necessary • Absence of by-products in most steps of the processes • Superior control of stoichiometry • Deionized water as solvent 	<ul style="list-style-type: none"> • Presence of additional phases

five: “the use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.” By using deionized water as the only solvent in the doping process, this principle was thoroughly applied. Principle six: “energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure,” was the next principle implemented. One step of energy conservation that was seen in the proposed methods is instead of using BaTiO₃ after combustion, the intermediate, Ba[Ti(C₆H₄O₂)₃] (aq), was used in the doping process and therefore energy was ultimately saved. In addition, lower temperature, atmospheric pressure, and de-

creased lengths of time were used for calcinations compared with previously researched methods (17). For instance, in the conventional solid-state method for synthesizing barium titanate, temperatures exceeded 1000°C for up to 12 hours (2). In contrast, the proposed strategies required a maximum heat of 800°C for merely four hours. In addition, all of the steps were performed under ambient pressure, and several steps did not require any heat at all. Chemicals, which are readily available in nature, such as titanium oxide, were used in this study allowing principle seven: “a raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable,” to be relevant as well. All of these reasons justify the use of the proposed catecholate method, as well as the centrifuge-assisted doping process, as more

environmentally benign techniques of synthesizing barium–strontium titanates.

Experimental

All the procedures described below are original to the knowledge of the authors and only the optimized procedures with respect to attaining equilibrium conditions are presented.

Solid-state synthesis of strontium-doped barium titanate ($Ba_xSr_yTiO_3$)

Barium titanyl catecholates were synthesized according to the adapted procedure previously published (9,10). Barium titanyl catecholate (0.100 g) and strontium oxalate (0.308 g – Alfa Aesar, 95%) were combined in a mortar and crushed into a fine, brown powder using a pestle. The resulting fine powder was placed in a ceramic boat which was set in a tube furnace (Type F21100 by Thermolyne®) at approximately 800°C for four hours. A white powder (0.2658 g) was obtained.

The same procedure was followed using barium titanyl catecholate (0.100 g) and strontium carbonate (0.259 g – Alfa Aesar, 97.5%). A white powder (0.289 g) was obtained.

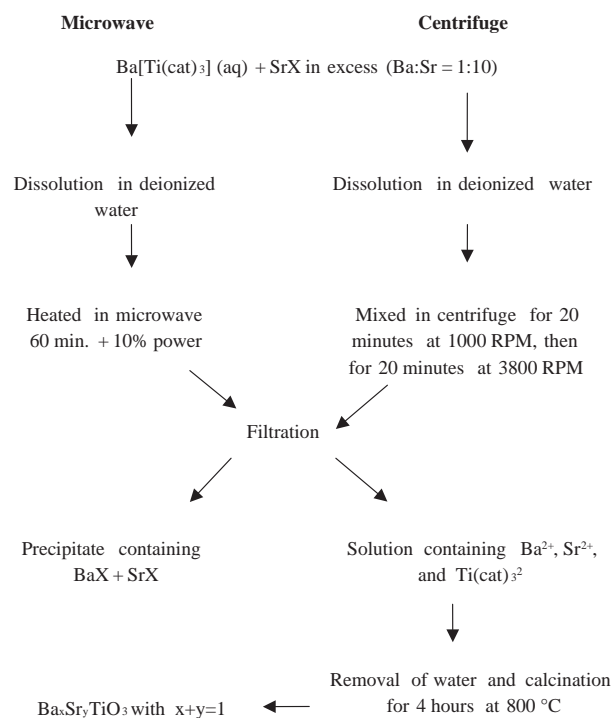
Microwave-assisted synthesis of strontium-doped barium titanate ($Ba_xSr_yTiO_3$)

Barium titanyl catecholate (0.200 g) and strontium oxalate (0.616 g – Alfa Aesar, 95%) were combined in a mortar and using a pestle crushed into a fine brown powder. The powder was then added to 1L of deionized water placed in a 1-L glass beaker and stirred. The beaker was then placed in a microwave (Model R-428JK by Sharp®) and heated for 30 minutes at 10% power. After 30 minutes, the beaker was removed and the solution was stirred for 30 seconds, and then placed back in the microwave for another 30 minutes at 10% power. After 30 minutes, the beaker was removed from the microwave and allowed to cool to room temperature. Once cooled, the brownish solution was filtered twice using vacuum filtration. The resulting solution was put in an oven (1395U Model by VWR International©) overnight at 112°C. The final yield of the solid was 0.1068 g. The resultant solid was put in a ceramic weigh boat and placed in a tube furnace (Type F21100 by Thermolyne®) at approximately 800°C for four hours. A brownish powder (0.0366 g) was obtained. The same procedure was done using barium titanyl catecholate (0.200 g) and strontium carbonate (0.518g – Alfa Aesar, 97.5%). A grayish yellow powder (0.0215 g) was obtained.

Centrifuge-assisted synthesis of strontium-doped barium titanate ($Ba_xSr_yTiO_3$)

Barium titanyl catecholate (0.0333 g) and strontium oxalate (0.103 g – Alfa Aesar, 95%) were combined in a mortar and, using a pestle, crushed into a fine brown powder. The powder was then added to a 50-mL centrifuge tube containing 50 mL of deionized water. This step was repeated three more times. The resulting four tubes were then loaded into a centrifuge (IEC Centra CL2 by Thermo Electron Corporation®) which was run at 1000 RPM for two 10-minute cycles, and then at 3800 RPM for two additional 10-minute cycles. After each 10-minute cycle the precipitate was loosened from the bottom of the tube.

The solutions from the four tubes were then combined in a 250-mL glass beaker and the brownish solution was filtered twice using vacuum filtration. The resulting solution was then placed in an oven (1395U Model by VWR International©) overnight at 112°C. The resulting solid was put in a ceramic weigh boat which was then placed in a tube furnace (Type F21100 by Thermolyne®) at approximately 800°C for four hours. A brownish powder (0.0271g) was obtained. The same procedure was followed using barium titanyl catecholate (0.0333 g) and strontium carbonate (0.0864 g – Alfa Aesar, 97.5%). A grayish yellow powder (0.0282 g) was obtained. Scheme 1



Scheme 1. Microwave- and centrifuge-assisted synthesis of strontium-doped barium titanate.

shows the microwave- and centrifuge-assisted methods.

Characterization and instrumentation

All final products were analyzed by X-Ray powder diffraction using a Scintag XDS-2000 instrument and PANalytical X'Pert Pro in Bragg–Brentano parafocusing geometry. The percentages by mass of barium and strontium were obtained by inductively coupled plasma–optical emission spectroscopy (ICP–OES) and were performed by Robertson Microlit Laboratories, Madison, NJ.

Conclusions

Three new environmentally benign routes of doping involving the use of molecular precursors under conditions where thermodynamic control governs the stoichiometry of the doped ceramics were exploited. Strontium oxalate and strontium carbonate were the two strontium sources used. While the solid-state process was far from providing any stoichiometric control, the centrifuge-assisted method is a promising step further in the synthesis of strontium-doped barium titanate electroceramics. The generation of useful doped semiconductors in a more environmentally benign manner represents a significant advance in ceramics technology.

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