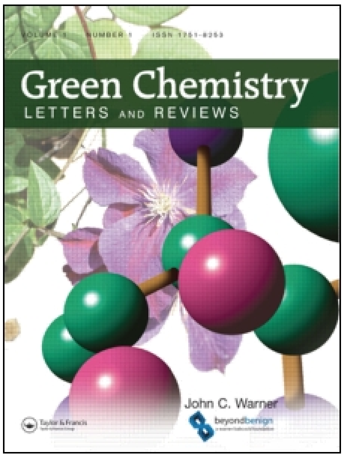

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Generality of the environmentally benign catecholate method to the synthesis of barium-based perovskites

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RESEARCH LETTER

Generality of the environmentally benign catecholate method to the synthesis of barium-based perovskites

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Barium titanate, barium zirconate, and barium hafnate are essential components of the electroceramic industry. Barium titanate is essentially used as multi-layered ceramic capacitors in computers, aerospace, and communication technologies. Barium zirconate is one of the most inert, stable, and corrosion-resistant perovskite employed in superconducting applications. Barium hafnate is used as a component of hybrid ceramic structures for high-temperature applications. The goal of this research was to apply a more environmentally benign synthesis design to the production of barium-based perovskites. The catecholate method, originally applied to the synthesis of barium titanate, was utilized as the approach for the synthesis of barium zirconate and barium hafnate. This developmental process consumed naturally occurring isomorphic forms of metal oxides and no post-sintering treatment was necessary. It resulted in the absence of by-products in most steps while achieving superior stoichiometric control over the barium-to-X (X = Ti, Zr, Hf) molar ratio compared to previous methods.

Keywords: stoichiometric control; catechol; materials science; electroceramics; hafnate and zirconate ceramics

Introduction

Perovskites, in particular those barium-based, are an important class of compounds in the electroceramic industry due to their intriguing properties such as ferroelectricity, superconductivity, charge ordering, and the interplay of structural, magnetic and transport features. These compounds have applications ranging from capacitors, components in electric circuits that temporarily store energy to sensors for thermal cameras. Barium titanate ($BaTiO_3$) is the most investigated member of the perovskite family due to its high-dielectric constant (*1*). It is essentially used for multi-layered ceramic capacitors in computers, aerospace, and communication technologies (*2–5*). Barium titanate ceramics, when properly doped, are also semi-conductive and they exhibit an anomalous sharp jump of resistivity at the Curie temperature (*6*). The positive temperature coefficient of resistivity leads to the production of thermistors, level sensors, and self-regulating heaters (*4,6*). Barium titanate also has excellent ferroelectric properties which allow it to be used in the production of chip capacitors (*7,8*). Another member of the barium-based perovskite family, barium zirconate, is one of the most inert, stable, and corrosion-resistant perovskites employed in superconducting applications for multi-layer ceramic capacitors (*9*). Barium zirconate exhibits special properties such as resisting harsh conditions, when synthesizing superconductors at high temperature or growing crystals (*10,11*). The production of barium zirconate powders is of interest to advanced materials applications such as protonic conductors for fuel cells, dielectric for electronic systems, and buffer layers for coated conductors (*11*). Among the family of transition metals in group 4B in the periodic table, hafnium behaves chemically like zirconium. The only notable physical difference between these two elements is their density. Hafnium is about twice as dense as zirconium. Along with cadmium and boron, hafnium is used in the control rods for nuclear reactors due to having neutron-absorbing properties. Although hafnium is not as popular as zirconium or titanium it seems that the element is rising in fame, as more developments are made.

Previous production methods for these barium-based oxides included hydrothermal method (*1,3,6,7,12,13*), solid-state (*14–18*), high-gravity reactive precipitation (*4,5*), spray coprecipitation (*8*), polymerized complex reaction (*19*), low-temperature aqueous preparation (*20*), aqueous coprecipitation reaction (*21*), sol–gel (*22*), oxalate processing (*10*),

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hydrolysis (*23*), thermal decomposition (*24*), and the catecholate method (*2*). All of the synthetic pathways previously mentioned presented inferior stoichiometric control over the barium-to-X (X = Ti, Zr, Hf) ratio compared to the catecholate method. For example, barium titanate samples prepared via conventional hydrothermal synthesis led to barium-to-titanium ratios of 0.68 and 1.6 compared to a ratio of 0.88 obtained via the catecholate method. In addition, many steps in their procedures were environmentally unfriendly. The nature of the titanium precursors employed is of concern due to chemical, safety, and environmental problems. The use of titanium tetrachloride is undesirable because of pH-dependent hydrolytic instability (*25*). For example, the same concern exists for the alkoxide family of precursors used in hydrothermal processes. Titanium tetrachloride is a corrosive and highly toxic material that requires special handling, storage, and disposal. Titanium tetrachloride is highly irritating to the skin, eyes, and mucous membranes in humans and has high to extreme acute toxicity via inhalation. Due to its strong Lewis acidity it reacts exothermically with even weak bases and explosively with water with release of HCl. An additional concern is the nature of the solvents employed, including organic solvents such as alcohols and aromatics such as toluene with poor environmental compatibility.

It has been demonstrated that naturally occurring isomorphic forms of titanium oxide, TiO_2 can be directly converted into $[NH_4]_2[Ti(C_6H_4O_2)_3]$ (aq), which is a key intermediate in the generation of molecular precursors to $BaTiO_3$ (*2,26*). Extension of this procedure to other oxide systems will allow development of a versatile and greener methodology for the synthesis of electroceramics.

The goal of this study was to extend the catecholate method, which was originally applied to the synthesis of barium titanate (*2*), to the synthesis of barium zirconate and barium hafnate. Titanium, zirconium, and hafnium all have similar chemical properties: they have four valence electrons; are Curie temperature shifters; are found abundantly in nature; and are able to form alloys, composite materials, and oxides which suggest that these elements would form complexes in a similar manner. The extension of this method would allow the use of environmentally benign precursors such as naturally occurring zirconium and hafnium oxides and a minimum amount of toxic or corrosive chemicals compared to previous procedures. Temperature and length of calcination were optimized so no post-sintering treatment would be necessary as often the case in traditional methods. It is also predicted that the molar stoichiometric ratio of barium-to-X (X = Ti, Zr, or Hf) to be 1-to-1 would be respected. In this article the generality of the greener catecholate method to the synthesis of barium zirconate and barium hafnate is successfully demonstrated.

Results and discussion

^{1}H NMR spectroscopy data

The ^{1}H NMR spectra of the three ammonium catecholate salts of titanium, zirconium and hafnium in DMSO exhibited resonances due to:

- the aromatic protons of the catecholate ligands represented by two quartets at 5.9 ppm and at 6.2 ppm;
- the ammonium ion protons represented by one singlet at 7.1 ppm; and
- the protons of the water of crystallization as confirmed by the presence of a singlet at 3.4 ppm.

The ^{1}H NMR spectrum of the ammonium catecholate salt of titanium is shown in Figure 1 as an example.

The ^{1}H NMR spectra of the three barium catecholate intermediates in D_2O exhibited resonances due to:

- the aromatic protons of the catecholate ligands represented by two quartets at 6.5 and 6.7 ppm. Occasionally, two additional small peaks between 6.8 and 7 ppm were present accounting for some “free” catechol; and
- the protons of water of crystallization at 4.9 ppm.

The ^{1}H NMR spectrum of the barium catecholate intermediate is shown in Figure 2 as an example.

Infrared spectroscopy data

Figure 3 shows the IR spectra of the titanium family of compounds. Several distinct features were observed on IR spectrum of the ammonium catecholate salt of titanium:

- a sharp peak at 3569 cm^{-1} and a sharp band at 1480 cm^{-1} corresponding to the carbon–carbon double bond in catechol coordinated to a metal ion demonstrating the formation of a complex. Effectively, the wavenumber for the C=C bond in “free” catechol appears at 1585 cm^{-1};
- a broad band between approximately 2798 cm^{-1} and 3258 cm^{-1} accounting for the presence of the ammonium ion as well as water of crystallization; and
- a band at 1254 cm^{-1} which is a possible indicator of titanium–oxygen stretch.

On the IR spectrum of the hydrate of barium titanyl catecholate:

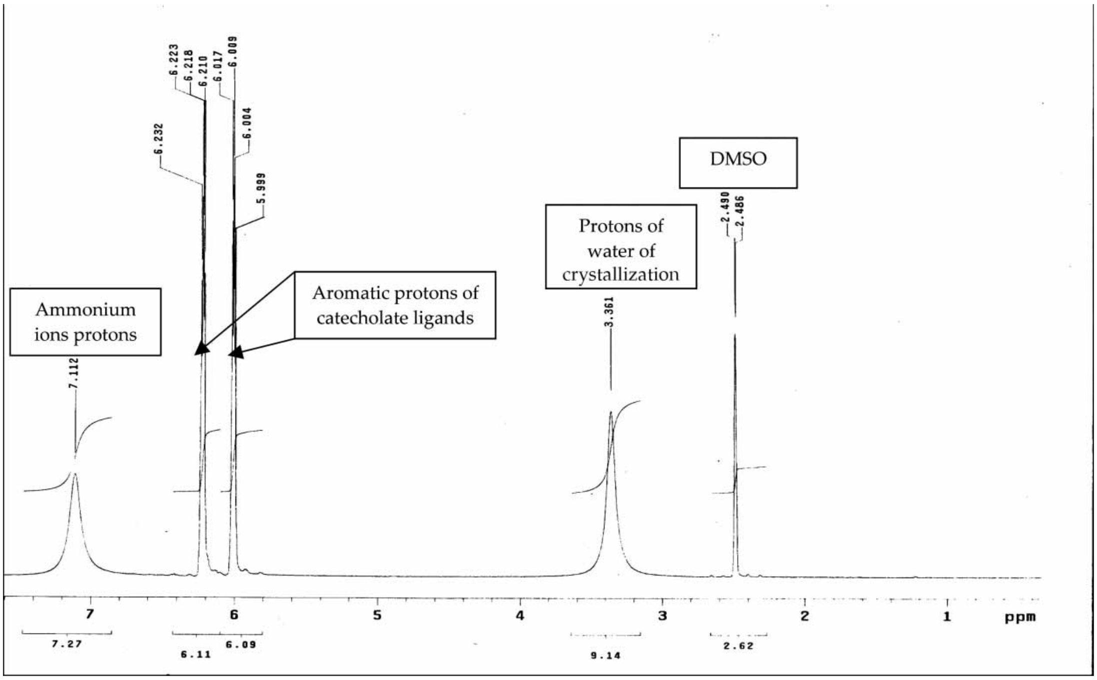


Figure 1. ^{1}H NMR spectrum of the ammonium catecholate salt of titanium in DMSO.

- the broad ammonium ion and water of crystallization band began to narrow to range from approximately 3014 cm^{-1} to 3434 cm^{-1} due to the ammonium ions no longer present;
- the sharp peak at approximately 3577 cm^{-1} and a sharp peak representing the carbon–carbon double bond in coordinated catechol at approximately 1475 cm^{-1} demonstrated the formation of a complex; and
- a peak possibly indicated a titanium–oxygen stretch at 1246 cm^{-1}.

The IR spectrum of the final product ($BaTiO_3$) showed:

- the broad band had narrowed to 2929 cm^{-1} $-$3303 cm^{-1} indicating the absence of ammoniumion; and
- no indication of the carbon–carbon double bond characteristic of coordinated catechol.

The IR spectra related to zirconium-based and hafnium-based compounds shown in Figures 4 and 5, showed three distinct and similar bands, respectively:

- First, a broad band appeared at approximately 3290 cm^{-1}–2469 cm^{-1} indicating the presence of the ammonium ion as well as the water of crystallization in the spectra for the ammonium intermediates. In the spectra of the barium intermediates and the final products, $BaZrO_3$ and $BaHfO_3$, this band began to narrow significantly with a range of 3165 cm^{-1}–2786 cm^{-1} as the ammonium ion disappeared and water of crystallization became less present in these compounds.
- The second sharp band appeared at approximately 1550 cm^{-1} accounting for the presence of coordinated catechol to zirconium or hafnium.
- The third distinctive band appearing in all three, zirconium and hafnium spectra at approximately 1500 cm^{-1}–1020 cm^{-1} indicated the presence of the possible zirconium–oxygen or hafnium–oxygen stretch.

X-ray powder crystallography and inductively coupled plasma–optical emission spectroscopy (ICP–OES) data

The X-ray powder patterns of the three final products were compared to existing patterns in the JCPDS database. X-Ray powder crystallography pattern of barium titanate indicated the purity of the compound solely made of $BaTiO_3$ (Figure 6). The molar ratio of barium-to-titanium expected to be 1:1 in $BaTiO_3$ was confirmed by ICP–OES. In fact, after the synthesis was reproduced three times, the average of molar ratios Ba:Ti was 0.88 with a standard deviation of 0.03. Knowing that intensive preparation is necessary to dissolve these powders for ICP–OES analysis a result of 0.88 is highly encouraging.

X-Ray powder crystallography analysis performed on $BaZrO_3$ confirmed the presence of $BaZrO_3$ (Figure 7). The molar ratio of barium-to-zirconium expected to be 1:1 in $BaZrO_3$ was confirmed by ICP–OES. In

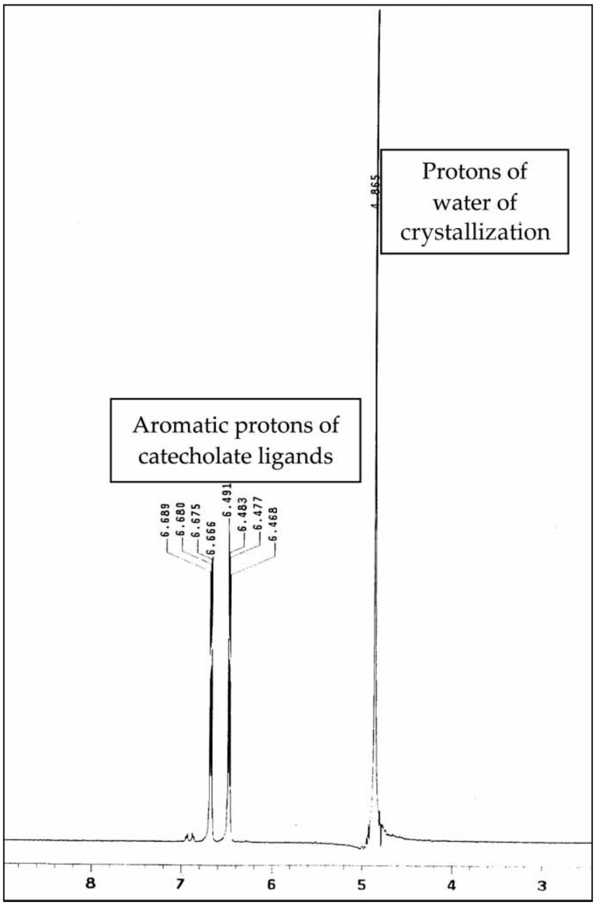


Figure 2. ^1H NMR spectrum of the barium titanyl catecholate compound in D_2O.

fact, after the synthesis was reproduced three times, the average of molar ratios Ba:Zr was 1.15 with a standard deviation of 0.01. X-Ray powder crystallography data regarding $BaHfO_3$ suggested the presence of $BaHfO_3$ as well as unreacted HfO_2 (Figure 8). This was consistent with the fact that the average of molar ratios Ba:Hf was 0.60. The higher than expected hafnium content is due to unreacted HfO_2. Again,

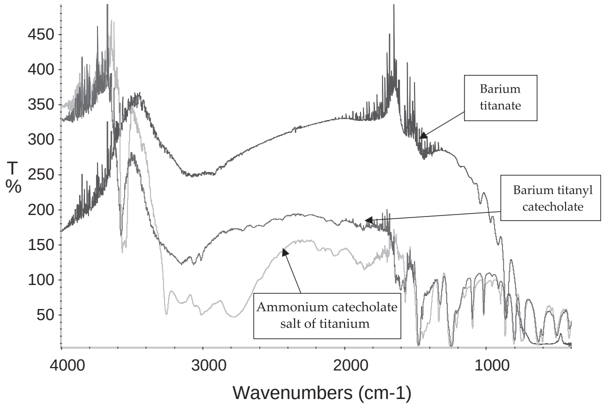


Figure 3. IR spectra of the barium family of compounds.

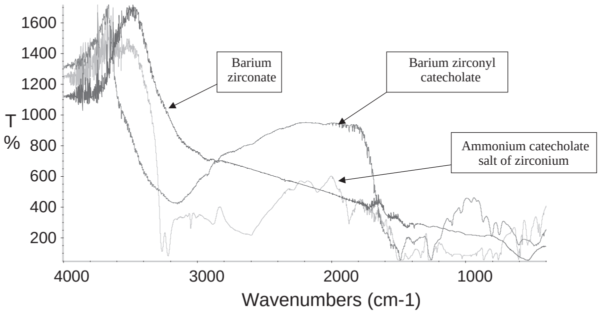


Figure 4. IR spectra of the zirconium family of compounds.

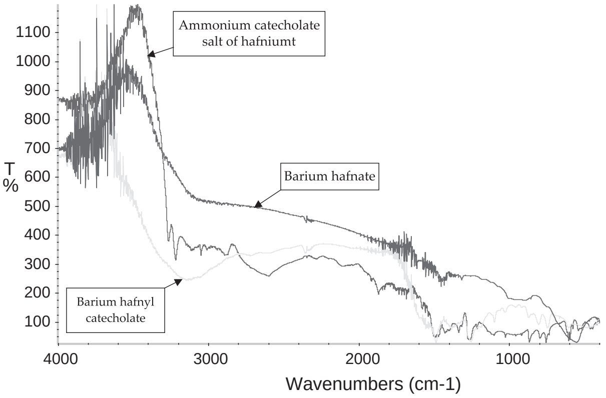


Figure 5. IR spectra of the hafnium family of compounds.

the intensive preparation for dissolution may have also accounted for some loss of barium in the final analysis. Furthermore, it is expected that the reproduction of this synthesis at 400°C for two hours instead of 480°C for 30 minutes will dramatically increase the dissolution time and the stoichiometric control as it was the case for the zirconium compounds.

The catecholate method proved successful in the synthesis of barium zirconate. The application of the catecholate method to the synthesis of barium hafnate is promising. Since the ionic strength of the sulfuric acid/ammonium sulfate solution is high, the ammonium catecholate complexes of titanium, zirconium, and hafnium precipitate quantitatively from solution (>97% based on Ti) and are isolated by simple filtration. The complexes may then be re-dissolved in water in which they are freely soluble. A simple acid–base reaction between the ammonium salt and the barium hydroxide leads to formation of the barium titanyl/zirconyl/hafnyl catecholates with generation of water and ammonia as the only by-products as shown in Scheme 1.

$$[NH_4]_2[Ti(C_6H_4O_2)_3]+Ba(OH)_2\bullet 8H_2O \rightarrow Ba[Ti(C_6H_4O_2)_3]+2\ NH_3+10\ H_2O$$

Scheme 1. Acid–base reaction between ammonium salt and barium hydroxide.

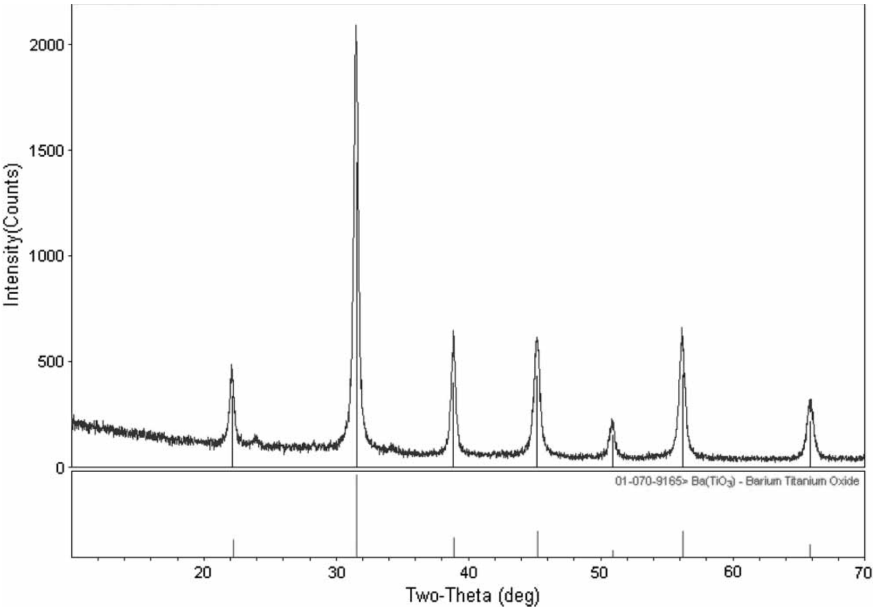


Figure 6. X-Ray diffraction pattern for barium titanate and matching pattern.

The environmental impacts of this new procedure are persuasive. Table 1 show the advantages and disadvantages of the most common processes compared to those of the catecholate pathway.

The 12 Principles of Green Chemistry (*27*) were integrated in this developmental catecholate process:

- The nature of the precursors used eliminated chemical, safety, and environmental concerns. Titanium tetrachloride as well as alkoxide precursors

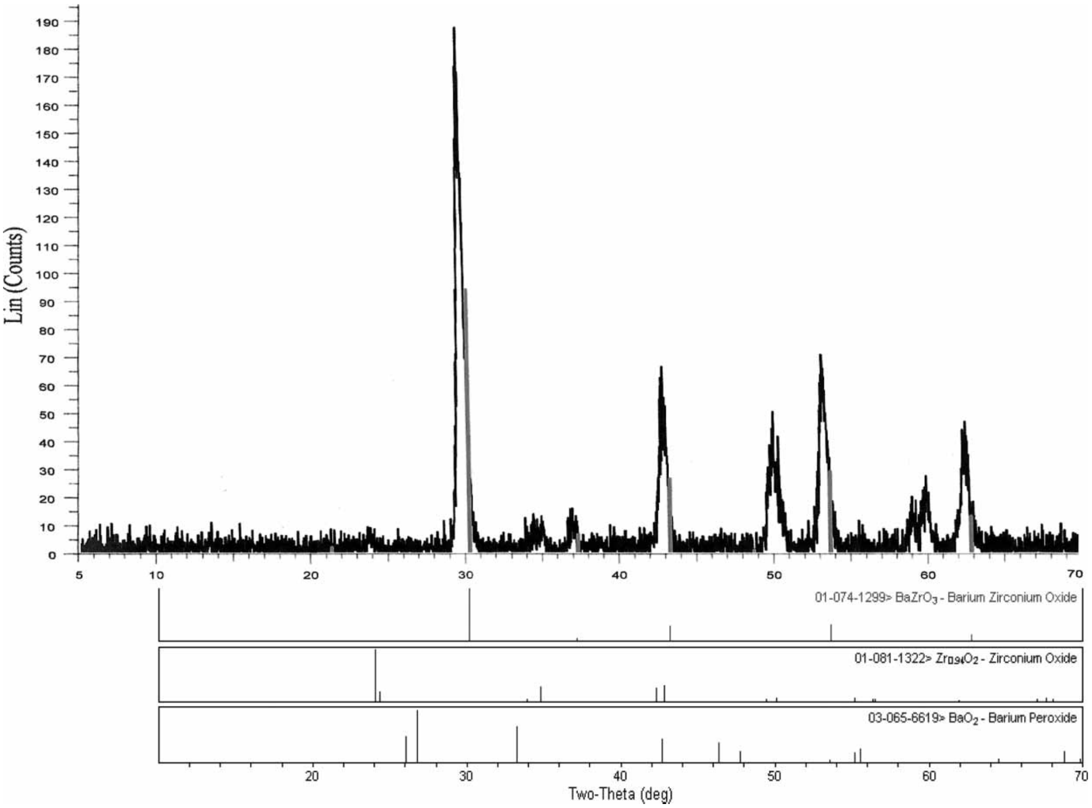


Figure 7. X-Ray diffraction pattern for barium zirconate and matching patterns.

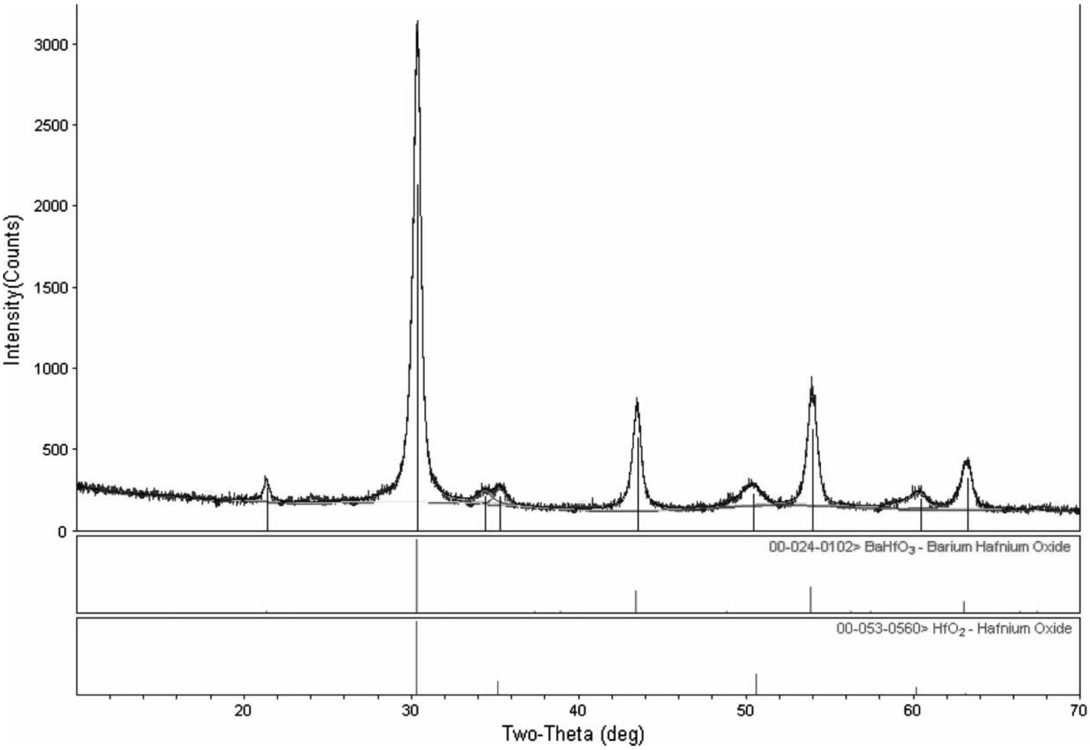


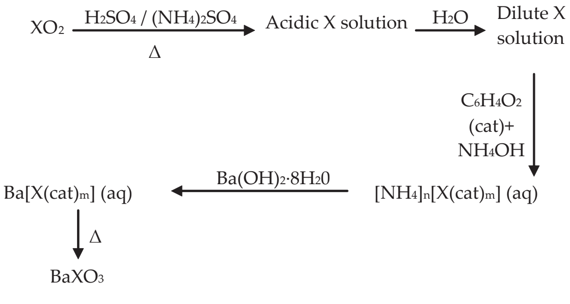
Figure 8. X-Ray diffraction pattern for barium hafnate and matching patterns.

employed in previous research generated concerns over their pH-dependent hydrolytic instability as well as their corrosivity, toxicity, special handling, storage, and disposal. Less toxic and corrosive chemicals, such as TiO_2, ZrO_2, or HfO_2, which are found abundantly in nature and which were used with no further purification, and catechol ($C_6H_4O_2$) which is produced from D-glucose, were used in this method as opposed to precursors such as $TiCl_4$ previously employed.

- The nature of solvents employed in this procedure removed the use of organic solvents such as alcohols and aromatics with poor environmental compatibility. Furthermore, the ligand (catechol) employed in complexation reactions also originated from environmentally benign synthesis.
- This method also eliminated by-products such as CO_2 or $BaCO_3$ which were common side products to barium titanate in previous synthetic methods. The energy required for calcination was minimized in this developmental process. In the catecholate method the calcination temperature and lengths of calcination were optimized so that no post-sintering treatment was necessary while maintaining a superior control of the stoichiometry.

Experimental

The synthesis of the ammonium catecholate salt of titanium, of the barium titanyl catecholate compound and of barium titanate followed what was previously published (*2*). The titanium dioxide used in this experiment was a mixture of anatase and rutile with 97% Ti with no further purification. Modifications of this procedure are reported below for the synthesis of barium zirconate and barium hafnate. The general scheme for this procedure is shown in Scheme 2 below (*n* and *m* are coefficients dependent on the nature of X):



Scheme 2. Generalization of the catecholate method.

Synthesis of ammonium catecholate salts of zirconium and hafnium

Zirconium oxide and hafnium oxide were used with no further purification. Zirconium oxide, baddeleyite, (0.520 g) or hafnium oxide (0.520 g), ammonium sulfate (8.38 g), and sulfuric acid (21.5 mL) were mixed in a 300-mL crucible and heated at approximately

Table 1. Advantages and disadvantages of traditional processes vs. those of the catecholate method in terms of nature of precursors, calcination temperature, production of by-products, and control over molar stoichiometric ratio.

Method	Advantages	Disadvantages
Hydrothermal (1, 3, 6, 7, 12, 13)	– Direct synthesis	– Strong alkali hydroxide solutions (pH = 13) – High-temperature sintering (850°C–1250°C) – Inferior stoichiometric control (molar ratios Ba:Ti of 0.68 and 1.6 in some cases)
Solid-state (*14–18*)	– Environmentally benign precursors (alkaline earth titanates and zirconates)	– High-calcination temperatures (800°C) and sintering temperatures (up to 1700°C) – CO_2 as side product
High-gravity reactive precipitation (*4, 5*)	– $BaTiO_3$ precipitate formed instantaneously through a 15-minute process carried out in air at 85°C	– Precursors such as $TiCl_4$ not environmentally friendly – High-sintering temperatures (up to 1300°C)
Spray coprecipitation (*8*)	– Time efficient	– Environmentally unfriendly precursors such as $TiCl_4$ and NH_3 – Wide range of temperatures (400–1200°C) in sintering step – Inferior stoichiometric control (molar ratio Ba:Ti of 0.84)
Polymerized complex reaction (*19*)	– Low-calcination temperatures	– $BaCO_3$ side product – Citric acid and ethylene glycol as precursors
Low-temperature aqueous preparation (*20*)	– Simple procedure – Time efficient	– $TiCl_4$ as precursor
Aqueous coprecipitation reaction (*21*)	– Lower temperatures – Nitrogen utilized to hinder the formation of an unwanted side product	– Titanium n-propoxide as precursor – Lengthy procedures
Sol–gel (*22*)	– Molecular level mixing of elements – Lower temperatures – Short procedures	– Additional phases present such as $BaCO_4$ and $BaTi_2O_4$ – High-calcination temperatures (> 1000°C)
Oxalate processing (*10*)	– Simple procedure	– Issue in control of the speciation of solution complexes – Stability of solution speciation to pH
Hydrolysis (*23*)	– Water as solvent	– Tetrabutylzirconate and aluminium sec-butoxide as precursors – Excess quantity of water
Thermal decomposition (*24*)	– Time efficient	– Urea as a precursor – High calcination (1200°C) and sintering temperatures (1500°C)
Developmental catecholate pathway (*2*)	– Environmentally friendly precursors – No post-sintering treatment necessary – Absence of by-products in most steps of the synthesis – Superior control of stoichiometry	– High-calcination temperatures compared to some traditional methods

400°C for two hours for the zirconium oxide and at 480°C for 30 minutes for the hafnium oxide. The crucible was removed from heat once a clear solution was obtained. This procedure was performed twice.

The two resulting clear solutions were combined and mixed with distilled water (130 mL) and transferred to a 250-mL bypass-dropping funnel. Ammonium hydroxide (400 mL) was poured into a three-necked round-bottomed flask which was equipped with a nitrogen inlet, a glass stopper, and the bypass-dropping funnel. The ammonium hydroxide solution was stirred under nitrogen for one hour. Catechol (4.31 g) was then added. After it had completely dissolved, the dilute acidic X (IV) solution (with X = Hf or Zr) was added steadily to the ammonium hydroxide solution. The brown solution was then stirred under nitrogen for four hours. When stirring was ceased, the precipitate was allowed to settle for at least 20 minutes. Thorough vacuum filtration was performed and the resulting brown precipitate was allowed to air dry overnight. The yield of ammonium tetra (catecholate) zirconium (IV) was approximately 2.50 g and the yield of ammonium tetra (catecholate) hafnium (IV) was approximately 2.50 g.

Synthesis of barium zirconyl and hafnyl catecholate compounds

Ammonium tetra (catecholate) zirconate (IV) (0.824 g) or ammonium tetra (catecholate) hafnate (IV) (0.820 g) and 100 mL distilled water were mixed in a 250-mL round-bottomed flask until the ammonium compound was dissolved. Then barium hydroxide octahydrate (0.580 g) was added. The round-bottomed flask was equipped with a water condenser and placed in a sand bath at 60°C–70°C. The contents of the flask were stirred for two hours. The flask was removed from the sand bath and allowed to cool to room temperature. The brown solution was filtered using vacuum filtration and a dark brown solution was obtained. The brown solution was then transferred to a 250-mL round-bottomed flask, and placed in an oven (1305U Model by VWR International®) at 112°C overnight. The yield of barium zirconyl catecholate was approximately 0.040 g and the yield of barium hafnyl catecholate was approximately 0.130 g.

Synthesis of barium XO_3 with $X = Zr$ or Hf

The dark brown solid was then transferred to a ceramic boat and placed in a tube furnace (Type F21100 by Thermolyne®) at 700°C for six hours. The calcination process produced white powders of barium zirconate (0.020 g) and barium hafnate (0.065 g).

Characterization and instrumentation

The ammonium and barium catecholate intermediates of the titanium, zirconium, and hafnium compounds were analyzed by ^1H NMR spectroscopy using dimethyl sulfoxide (DMSO) as the solvent for the ammonium intermediates and D_2O as the solvent for the barium hydrate intermediates. Data were collected on a Bruker 400 MHz NMR spectrometer. Barium XO_3 with $X = Ti$, Zr, or Hf, as well as the ammonium and barium hydrate intermediates based on $[NH_4]_4[X(cat)_4]$ and $Ba[X(cat)_4]$ (where cat stands for catecholate), were all characterized by infrared spectroscopy using Avatar™ 360 FT IR e.s.p. Spectrometer by Thermo Nicolet® using a KBr pellet and by X-Ray powder diffraction using a Scintag XDS-2000 instrument and PANalytical X'Pert Pro in Bragg–Brentano parafocusing geometry. The inductively coupled plasma–optical emission spectroscopy (ICP–OES) analyses were performed by Robertson Microlit Laboratories, Madison, NJ.

Conclusions

The environmentally benign catecholate method which was originally applied to the synthesis of barium titanate was extended successfully to the synthesis of barium zirconate and barium hafnate. The use of "greener" starting materials, optimized temperature and lengths of calcination, and control over the stoichiometric molar ratio contributed to the environmental advantage of this procedure. This study demonstrated that solution-phase chemistry and precipitation methods can be exploited in the synthesis of electroceramic materials and they offer a more benign-by-design alternative to the more traditional solid-state procedure. It is anticipated that the generation of lead salts as precursors to lead zirconate and therefore the generation of PZTs (lead zirconate titanates $Pb(Zr_x\ Ti_{1-x})O_3\ 0 < x < 1$) from TiO_2 to ZrO_2 will be successful using this greener procedure.

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