

Synthesis and Characterization of a Perovskite Barium Zirconate (BaZrO₃): An Experiment for an Advanced Inorganic Chemistry Laboratory

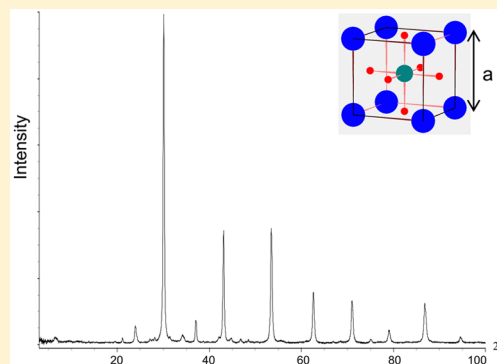
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Supporting Information

ABSTRACT: In this experiment, the students explore the synthesis of a crystalline solid-state material, barium zirconate (BaZrO₃) by two different synthetic methods: (a) the wet chemical method using BaCl₂·2H₂O and ZrOCl₂·8H₂O as the precursors, and (b) the solid-state reaction from BaCO₃ and ZrO₂. BaZrO₃ adopts a perovskite structure with a cubic unit cell. The intermediate and the products are examined by various characterization techniques. The identity and the purity of the products are determined by powder X-ray diffraction technique. The structural information on the products is analyzed by the XRD patterns, where students apply the $\sin^2\theta$ -ratio method to determine the type and dimension of the unit cell. The composition of the Ba²⁺ and Zr⁴⁺ ions in the product is determined by the gravimetric analysis, while the vibrational modes of the product are observed by Infrared Spectroscopy.

KEYWORDS: Upper-Division Undergraduate, Inorganic Chemistry, Solid State Chemistry, Synthesis, X-ray Crystallography, Gravimetric Analysis, IR Spectroscopy, Hands-On Learning/Manipulatives, Laboratory Instruction



BACKGROUND

Several ceramic materials with a perovskite structure often exhibit interesting electronic properties¹ and, therefore, are often called “electroceramics”. These materials have been commonly utilized as insulators,² capacitors,³ and superconductors.⁴ Moreover, recent interests on the applications of these perovskite electroceramic materials have emerged in the area of catalysis⁵ and solar cells.⁶ A perovskite compound has a general chemical formula ABX₃, where A is a large but low charge cation such as Sr²⁺ and Ba²⁺, B is a small but high charge cation such as Ti⁴⁺ and Zr⁴⁺, and X is an anion with low charge such as O²⁻ and I⁻. Many perovskite compounds have been synthesized including CaTiO₃,⁷ SrTiO₃,⁸ SrZrO₃,⁹ and BaZrO₃.¹⁰ Structurally, a perovskite compound displays a crystalline cubic unit cell where the large cations A locate at each of the corners of the unit cell. The small cation B and the anion X reside at the center and on every face of the cubic cell, respectively (Figure 1).

Perovskite electroceramic compounds can be synthesized in various ways, both in solid and solution phase. The solid-state reaction is the most common and the simplest approach where the metal salt precursors are ground and calcined at high temperature. For example, lanthanum cobaltate (LaCoO₃) can be prepared by calcination of a well-mixed sample of lanthanum nitrate hydrate (La(NO₃)₃·nH₂O) and cobalt nitrate hexahydrate (Co(NO₃)₃·6H₂O) at 800 °C in the presence of KOH.¹¹ However, the main disadvantage of this synthetic approach is the low quality of the product.⁸ Various solution phase

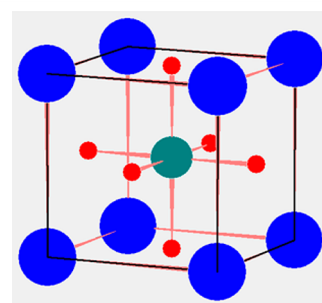


Figure 1. Unit cell of a perovskite compound, ABX₃. A = blue, B = teal, X = red.

reactions including co-precipitation and sol-gel methods have been successfully employed to prepare high-purity perovskite compounds. Calcium titanate (CaTiO₃) has been synthesized by a sol-gel method, in which a solution of calcium oxide (CaO) in acetic acid and a solution of titanium(IV) isopropoxide are mixed. A homogeneous gel is formed after evaporation of the solvent. The desired CaTiO₃ powder is obtained after calcination of the dry gel at 900 °C.¹²

Unfortunately, solid-state chemistry, a crucial component of inorganic chemistry curriculum, is underrepresented in teaching laboratories. Moreover, in recent years no novel teaching

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experiment on the synthesis and the characterization of a perovskite material has been developed. An experiment on the preparation Na_xWO_3 by electrolysis at high temperature from $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, Na_2WO_4 , and WO_3 was published in 1977 by Conroy. The product is characterized by X-ray diffraction (XRD) technique as well as chemical analysis.¹³ An experiment developed in 1987 by Ellis entails a synthesis of superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by a multistep calcination of Y_2O_3 , BaCO_3 , and CuO .¹⁴ A modified experiment on the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_7$ from Y_2O_3 , BaCO_3 , and CuO has been published by Girolami et al.,¹⁵ where a well-mixed mixture is heated at 970 °C for 2–3 h.

This novel experiment offers attractive features due to its simplicity of the synthesis and the breadth of the product characterization. The product is prepared by both solid-state reaction and a reaction in an aqueous phase, which allows the students to draw a comparison between the two synthetic methods. Furthermore, the synthesis component requires standard apparatus and equipment, and only involves one calcination step of 6 h to reliably produce the desired product. This experiment also comprehensively utilizes a wide range of characterization techniques including IR spectroscopy as well as powder XRD and gravimetric analysis, which are not commonly covered in a typical inorganic chemistry laboratory, to analyze the obtained intermediate and products.

■ PEDAGOGICAL GOALS

This experiment, aimed for an advanced inorganic chemistry laboratory taken by upper-division chemistry and biochemistry majors, is designed to replicate a research environment where the students have a freedom to plan and conduct their own experiment under the instructor's supervision. The experiment not only exposes the students to the art of solid-state synthesis, which is not commonly covered in a typical inorganic chemistry laboratory, but also the characterization of crystalline solid-state materials. The pedagogical goals are

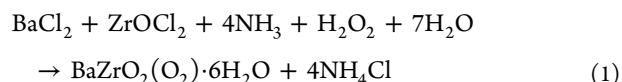
- Students will be familiar with techniques and equipment commonly used for a synthesis of crystalline solid-state materials.
- Students will be able to utilize various characterization techniques to analyze a sample of crystalline solid-state material.
- Students will be able to correctly index a powder XRD pattern of a crystalline material possessing a cubic unit cell.
- Students will be able to appropriately plan an experiment in order to utilize time and resources most efficiently.

■ EXPERIMENT

Due to the nature and the length of this experiment, two 4-h laboratory periods are required. Students could work individually or in a small group. The experiment consists of two main parts: the synthesis of the perovskite barium zirconate (BaZrO_3) and the characterization of the synthesized BaZrO_3 products.

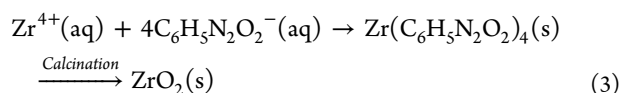
The first week of the experiment involves the synthesis of BaZrO_3 by two different synthetic methods: the wet chemical method and the solid-state reaction. A prelab problem set is assigned to allow the students to determine the quantity of each chemical reagent needed for the experiment as well as the theoretical yield of the product prior to arriving to the laboratory. For the wet chemical method, soluble barium

chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) salts are employed as precursors for the cations in the presence of an oxidizing agent (H_2O_2). Initially, the gel-like amorphous peroxy intermediate, $\text{BaZrO}_2(\text{O}_2) \cdot 6\text{H}_2\text{O}$, is formed, which can be transformed to the crystalline BaZrO_3 product upon calcination under air. The chemical reaction for the formation of the peroxy intermediate is presented in eq 1:¹⁰



For the solid-state reaction, the BaZrO_3 product is prepared by a calcination of a well ground mixture of barium carbonate (BaCO_3) and zirconium(IV) oxide (ZrO_2) solids. The identical calcination conditions of 1000 °C and 6 h are employed in order to obtain an accurate comparison between the two synthetic methods.

The second week of the lab period is devoted to the analyses of the BaZrO_3 products where the students determine (i) the identity, purity, and structural information (XRD); (ii) the composition of Ba^{2+} and Zr^{4+} ions (gravimetric analysis); and (iii) the vibrational mode (IR). For the gravimetric analysis, a small amount of ground BaZrO_3 sample is digested in concentrated H_2SO_4 at medium–high temperature. Once the sample is completely digested and a clear solution is obtained, Ba^{2+} and Zr^{4+} ions are separately and selectively isolated from the solution by means of precipitation as insoluble salts. A precipitation of Ba^{2+} ions as BaSO_4 is achieved by an addition of ethanol. Upon addition of a Cupferron solution, the Zr^{4+} ions remaining in the filtrate are precipitated out of the solution as zirconium cupferrate, $\text{Zr}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_4$.¹⁶ Both BaSO_4 and zirconium cupferrate are then subjected to calcination in a reaction furnace to remove carbonaceous impurities such as remaining filter paper and soot from the sample. In addition, zirconium cupferrate is also transformed to ZrO_2 upon calcination. The chemical equations representing the formation of BaSO_4 and ZrO_2 are presented in eqs 2 and 3.



■ HAZARDS

Safety goggles must be worn at all time during the experiment. Barium chloride dihydrate, Cupferron, and barium zirconate are toxic if swallowed. Cupferron is also a potential carcinogenic material. Zirconyl chloride octahydrate, concentrated ammonia solution, concentrated sulfuric acid, and hydrogen peroxide are corrosive, which can cause severe skin burns and eye damage. Hazards for the peroxy intermediate and zirconium cupferrate are not known, but can be assumed to be toxic if swallowed. Ethanol is flammable. Digestion of barium zirconate sample with concentrated sulfuric acid can produce toxic fumes, and must be conducted in a functional fume hood. Standard precautions such as wearing heat-resisting gloves should be employed when operating a reaction furnace and a drying oven.

RESULTS AND DISCUSSION

Preparation of Barium Zirconate

This experiment was performed individually by nine upper-division chemistry and biochemistry majors from Inorganic Chemistry II (CHEM 483) laboratory in two semesters. During the synthesis by the wet chemical method, a white gel of the peroxo intermediate, $\text{BaZrO}_2(\text{O}_2)\cdot 6\text{H}_2\text{O}$, was instantaneously formed upon mixing of BaCl_2 , ZrOCl_2 , NH_3 , and H_2O_2 solutions. After the peroxo gel was dried and calcined, a white powder product of BaZrO_3 was obtained. The solid-state synthesis of BaZrO_3 from BaCO_3 and ZrO_2 also resulted in a formation of a white powder product. The percent yields for the BaZrO_3 products obtained by the wet chemical method and the solid-state synthesis ranged from 54 to 90% and 82 to 99%, respectively.

Infrared Spectroscopy of Barium Zirconate Products

Due to the absence of organic functional groups, the IR spectra of the synthesized BaZrO_3 products (Supporting Information, S19) did not contain absorption bands typically found in the wavenumber greater than 1000 cm^{-1} . The only absorption band in the IR spectrum of product obtained from the wet chemical method appeared at 500 cm^{-1} , which corresponds to the stretching vibrational mode of Zr–O bonds in BaZrO_3 .¹⁷ However, the IR spectra acquired by some students also exhibited an additional absorption band at 1434 cm^{-1} . This absorption corresponds to a CO stretching band of CO_3^{2-} ion, which is a supporting evidence of a presence of BaCO_3 impurity. Carbonate-containing compound such as BaCO_3 in this experiment is known to be a common impurity due to the presence of the atmospheric CO_2 .¹⁸ The IR spectrum of this product was drastically different from that of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ substrate (3 absorption bands at 3000 , 1500 , and 480 cm^{-1}) and that of the peroxo intermediate (3 absorption bands at 2343 , 1386 , and 432 cm^{-1}), which indicated the complete conversion of the substrate and the peroxo intermediate upon calcination.

The IR spectrum of the product obtained from the solid-state reaction resembled that obtained from the product of the wet chemical method, where the Zr–O stretching band of BaZrO_3 at 500 cm^{-1} and CO stretching band of CO_3^{2-} ions at 1434 cm^{-1} were present. For this synthetic method, the unreacted BaCO_3 substrate was responsible for the CO absorption band. The unreacted ZrO_2 substrate (Zr–O stretching band at 480 cm^{-1}) was unidentifiable by IR spectroscopy due to the similar absorption wavenumber to the BaZrO_3 product.

X-ray Diffraction of Barium Zirconate Products

The XRD pattern of the peroxo intermediate obtained by wet chemical method mainly exhibited no diffraction peaks, which is a characteristic of an amorphous solid. The peroxo intermediate, however, contained BaCO_3 impurity, which was identified by the diffraction peaks in the XRD pattern. The XRD pattern of the final product from the calcination of the peroxo intermediate conclusively confirmed the formation of the crystalline BaZrO_3 ¹⁰ with a presence of small quantity of BaCO_3 (up to 8%) and/or ZrO_2 (up to 20%) impurities. ZrO_2 is also a common impurity for a perovskite zirconate that is formed upon calcination of a peroxo intermediate at high temperature ($\sim 1200\text{ }^\circ\text{C}$).¹⁹ The presence of this ZrO_2 impurity was previously undetected by IR spectroscopy due to the similar wavenumber to the BaZrO_3 product. The XRD pattern of the product from the solid-state reaction contained

diffraction peaks assigned for the unreacted BaCO_3 and ZrO_2 ($\sim 25\%$) in addition to those assigned to the desired BaZrO_3 . The XRD patterns are presented in the Supporting Information, S25–S28.

The $\sin^2\theta$ -ratio method, $\frac{\sin^2\theta_1}{\sin^2\theta_2} = \frac{m_1}{m_2}$, where $m = h^2 + k^2 + l^2$ (see Supporting Information, S10), was applied to index the XRD patterns of the crystalline BaZrO_3 products to obtain the following structural information: (i) the hkl Miller indices for each diffracting peak, (ii) the structural type of the BaZrO_3 unit cell, and (iii) the size of the unit cell. From the obtained XRD patterns, the first diffracting peak at 2θ of 21.18° was assigned with 100 indices. The structural type of the BaZrO_3 unit cell was identified by the hkl indices of the first diffracting peak, which revealed that the BaZrO_3 product adopts a cubic cell structure. The complete hkl assignment of diffracting peaks of BaZrO_3 is presented in the Supporting Information, S13. The size of the BaZrO_3 unit cell is represented by the length of the unit cell, a , which was determined by the d -spacing formula of a cubic cell: $\sin\theta = \frac{\lambda}{2a}\sqrt{(h^2 + k^2 + l^2)}$. On the basis of the obtained XRD patterns, the length of unit cells of the synthesized BaZrO_3 from the wet chemical method and the solid-state synthesis was calculated to be 4.195 \AA , which coincides with the value previously reported of 4.192 \AA ²⁰ (0.07% error).

Gravimetric Analysis of Barium Zirconate Products

The IR spectra of the calcined BaSO_4 and ZrO_2 products are presented in the Supporting Information, S23 and S24. The mole ratio of Ba^{2+} and Zr^{4+} ions was calculated from the masses of the obtained BaSO_4 and ZrO_2 . The class mole ratios for the Ba^{2+} and Zr^{4+} ions ranged from 0.60 to 0.84 for the products obtained from the wet chemical method, and 0.82–1.01 for the products obtained from the solid-state reaction. These results may initially indicate the solid-state reaction as a superior synthetic method for BaZrO_3 since the obtained products exhibited a closer experimental $\text{Ba}^{2+}/\text{Zr}^{4+}$ mole ratio to the ideal mole ratio (1:1). The wide range of Ba^{2+} and Zr^{4+} mole ratios from the products obtained by the wet chemical method was due to the presence of BaCO_3 and ZrO_2 impurities which varied from sample to sample as indicated by IR spectroscopy and XRD. It is to be noted that the Ba^{2+} and Zr^{4+} mole ratio nicely correlated to the results from the XRD; the samples without ZrO_2 impurity produced the Ba^{2+} and Zr^{4+} mole ratios that are closer to the ideal ratio, while the mole ratio of Ba^{2+} and Zr^{4+} ion deviated for the samples that were contaminated with ZrO_2 .

For the BaZrO_3 products prepared by the solid-state reaction, the mole ratios of Ba^{2+} to Zr^{4+} ion did not accurately reflect the purity of the products since the unreacted BaCO_3 and ZrO_2 , which were detected by IR spectroscopy and XRD, were not removed and therefore remained in the products, resulting in the ideal mole ratio of Ba^{2+} and Zr^{4+} ion.

All of the students were able to successfully carry out the experiment, and obtained the desired products within the allocated time. However, the percent yield and the percent purity of the synthesized BaZrO_3 products varied by the synthetic method as well as the students' skills. On the basis of the three characterization techniques employed in this experiment, the wet chemical method was concluded to be a superior method for a synthesis of BaZrO_3 due to the higher purity of the products. From the assessment of the students' lab reports, the achievement of every aforementioned pedagogical

goal was met. Their lab reports showed a comprehensive understanding of the 2 synthetic methods as well as correct interpretations of the characterization data. Every student was able to identify (i) the advantages and disadvantages of each synthetic method; (ii) the identity and percent purity of the product as well as the impurities present by IR spectroscopy, XRD, and gravimetric analysis; and (iii) the type and size of the product's unit cell by XRD. After the conclusion of the experiment, the students were assigned with the XRD pattern of an unknown metal, which they were able to accurately index the diffraction peaks and reveal the identity of the metal.

CONCLUSION

This experiment introduced a concept of the synthesis and the characterization of a crystalline solid-state material. The students successfully conducted the synthesis of BaZrO₃ by two different synthetic methods and became acquainted with a high-temperature reaction furnace for a calcination process. The obtained products were analyzed by three characterization techniques, which revealed the composition and the bonding mode, as well as the structural information on the products.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00924.

Complete list of chemicals and glassware; student handout; IR spectra; XRD patterns of the intermediate and the products; XRD pattern of an unknown metal for the postlab assessment; additional notes for the instructor including details on experimental schedules and calculations for percent yield, Ba²⁺/Zr⁴⁺ mole ratio, background on powder XRD and indexing the XRD pattern of BaZrO₃ (ZIP)

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Notes

The authors declare no competing financial interest.

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