

Lead Hafnate (PbHfO₃) Perovskite Powders Synthesized by the Oxidant Peroxo Method

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Perovskite lead hafnate (PbHfO₃, PH) nanoparticles that were free from halides and organics were synthesized via the oxidant peroxo method. Stoichiometric amounts of hafnium nitrate (HfO(NO₃)₂) and lead nitrate (PbHfO₃) were dissolved in a diluted hydrogen peroxide (H₂O₂) aqueous solution, which was slowly added to a solution of H₂O₂ and ammonia (NH₃) (pH 11). The lead–hafnium precipitate obtained was filtered and washed, to eliminate all nitrate ions. The precipitate was dried, ground, and calcined at temperatures of 400°–900°C. A tetragonal intermediate phase was identified using X-ray diffractometry and Raman spectroscopy during the calcination process, followed by the crystallization of the orthorhombic PH phase at ~700°C.

I. Introduction

THE synthesis of lead-based oxides has been extensively studied, because of the wide range of technological and industrial applications of these compounds.^{1–3} However, only a few studies exist about the synthesis of lead hafnate (PbHfO₃, hereafter referenced as PH), despite the fact that it is structurally similar to lead zirconate (PbZrO₃, PZ) at room temperature and, therefore, has potential ferroelectric applications.^{4–6} The use of conventional solid-state reaction techniques for the preparation of lead-based oxides requires high temperatures, which often results in powders with undesirable characteristics, such as large particle size, a broad particle-size distribution, partially sintered agglomerates, and low chemical homogeneity that is due to the volatilization of lead. For these reasons, wet-chemical methods can be excellent techniques for the synthesis of these multicomponent powders.

Several wet-chemical methods have been reported for the synthesis of lead-based oxides. Recently, Camargo *et al.* developed a new method for the synthesis of lead-based perovskites nanoparticles (such as lead titanate (PbTiO₃),⁷ lead zirconate titanate (Pb(Zr,Ti)O₃, PZT),⁸ and PbZrO₃ (PZ)⁹) that were free of halides and carbon. This process is called the “oxidant peroxo method” (OPM), because it is based on the oxidation–reduction reaction between the Pb(II) ion and water-soluble metal-peroxide complexes at high pH. The major advantages of this method over the previously reported peroxide-based methods include (i) a simple experimental procedure that permits us to work under ambient atmosphere, (ii) the use of aqueous solvents and starting reagents that can be handled easily and safely, (iii) the total absence of organics and halides, and (iv) no generation of toxic

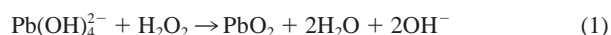
and corrosive hydrochloric acid (HCl) gas during the process. In this communication, we report on the synthesis of PH nanoparticles via the new method, OPM. The products have been characterized using a combined analysis of Raman spectroscopy and X-ray diffractometry (XRD).

II. Experimental Procedure

An aqueous solution that contained lead(II) nitrate (Pb(NO₃)₂) and hafnium nitrate (HfO(NO₃)₂) was prepared with a molar ratio of [Pb]:[Hf] = 1:1 (100 mL; 0.6 mol/L for total cations), followed by the addition of hydrogen peroxide (H₂O₂) (20 mL, 34%). A solution of H₂O₂ (80 mL, 34%) and ammonia (NH₃) (20 mL, 28%) was prepared and stirred in an ice bath. When the lead–hafnium (Pb–Hf) solution was slowly added dropwise into the H₂O₂–NH₃ solution, an exothermic reaction occurred immediately; gas was evolved and an orange precipitate was formed. After the addition of all the Pb–Hf solution, the precipitate was filtered and washed with an aqueous solution of NH₃ (10%), to eliminate the nitrate ions. All Pb and Hf cations were precipitated, with a yield of ~100%. The washed precipitate was dried at a temperature of 50°C for 5 h and ground; then, the dry precipitate (0.50 g) was calcined at 400°–900°C in a closed alumina boat, using a heating rate of 10°C/min. A 23-mg sample of the dry precipitate was characterized using thermogravimetric (TG) analysis (Model TG-DTA 2000/Control Model TAPS-1000, MAC Science, Tokyo, Japan) in static air in the temperature range of 30°–800°C, using a heating rate of 5°C/min; the specimen was placed in a platinum crucible. XRD measurements were conducted using an XRD diffractometer (Model MXP^{3V}, MAC Science). A CuK α radiation source was used to record XRD patterns from the samples at room temperature. XRD intensities were recorded at 2 θ angles of 15°–75° and an angular velocity of 0.25°/min. Visible laser light (wavelength of 514.532 nm) was used for Raman measurements, using a spectrometer (Model T64000, Jobin Yvon/Atago Bussan, Longjumeau, France) with a liquid-nitrogen-cooled charge-coupled device (CCD) detector. The room-temperature spectra in the range of 13–700 cm⁻¹ were measured using a triple monochromator with a grating of 1800 grooves/mm with a backscattering geometry. The power of the laser beam on the samples was adjusted to 10 mW.

III. Results and Discussion

It is well-known that the Pb(II) ion can be oxidized to the Pb(IV) ion using H₂O₂ at high pH, as described by Eq. (1):



Camargo and co-workers^{7–9} developed a technique, called the “oxidant peroxo method” (OPM), to synthesize lead perovskites by applying Eq. (1) to obtain an amorphous precipitate with a controlled molar ratio between Pb and other cations, such as Ti and Zr; these perovskites are completely free of halides and carbon. Titanium and zirconium are able to form water-soluble peroxo

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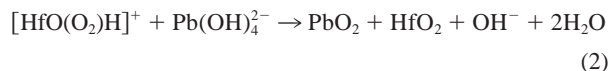
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complexes, and these peroxy complexes can act as the oxidant agent on the lead. Hafnium also can form a similar peroxy complex; Eq. (2) shows the proposed reaction for the formation of the Pb-Hf amorphous precipitate that is used as a precursor for the synthesis of PH powder.



Several similarities were observed between the synthesis of PH and the synthesis of PZ via OPM, e.g., the presence of an intermediate tetragonal phase in powders that were calcined up to 700°C and the detection of the desired perovskite phase at low temperature (at ~500°C, after the weight loss was completed in the TG analysis).⁹ Chemical methods that use chelating organics or nonaqueous solvents often result in crystallization of the PZ phase in the same temperature range, from 500°C to 800°C.^{10,11}

Figure 1 shows the TG curve of the Pb-Hf dry precipitate with a molar ratio of [Pb]:[Hf] = 1:1. The TG curve resulted in a continuous weight loss of 19.5% from 30°C to 492°C. Elemental analysis of the dry precipitate detected only oxygen and hydrogen. Similar curves were obtained for different heating rates; these curves showed that the thermal decomposition of the precipitate was a continuous process, without steps. No detectable mass change was observed at >500°C. This result is consistent with that reported for the synthesis of different lead perovskites via OPM.⁷⁻⁹

XRD patterns of the powders that were calcined for 1 h at 400°–900°C are shown in Fig. 2. Lead hafnate (PH) with an orthorhombic phase was obtained, as indicated by solid circles in the XRD patterns. Unit-cell dimensions ($a = 1.17122$ nm, $b = 0.41005$ nm, and $c = 0.58481$ nm) were calculated from the XRD pattern of the powder that was calcined at 900°C; these lattice parameters were indexed with the TREOR90 program that is built from PowderX software.¹² The broad diffraction peaks, which are probably due to the small crystallite size (indicated by open squares in Fig. 2), correspond to an intermediate tetragonal phase that formed at low temperature, with characteristic peaks at 29°, 35°, 50°, and 60°. This intermediate phase also has been identified in the wet-chemical synthesis of PZ;^{9,14} however, this phase is often erroneously reported as being cubic, based only on XRD evidence. Although XRD is not sensitive enough to distinguish between the tetragonal and cubic phases with small particle size, the tetragonal phase can be distinguished from the cubic phase using Raman spectroscopy.¹⁵ The small peak at 24.6° (indicated by solid squares) corresponds to the lead(II) oxide (PbO) phase, which results from the decomposition of the lead(IV) oxide (PbO₂) at high temperature.

Figure 3 shows the Raman spectrum of the Pb-Hf dry precipitate and the spectra of the powders that were calcined at 400°–700°C. A typical Raman spectrum of the PH phase was obtained

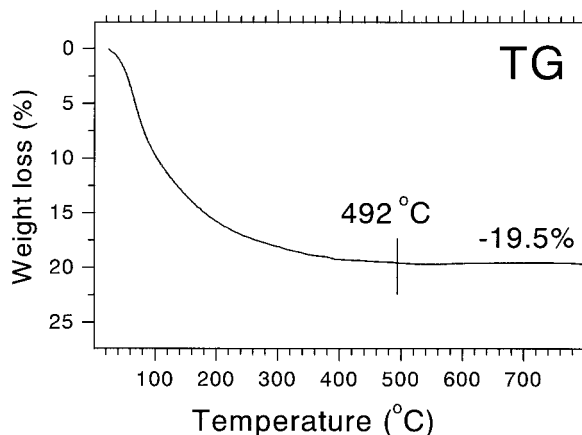


Fig. 1. TG curve of the dry precipitate (23 mg), from 30°C to 800°C, using a heating rate of 5°C/min.

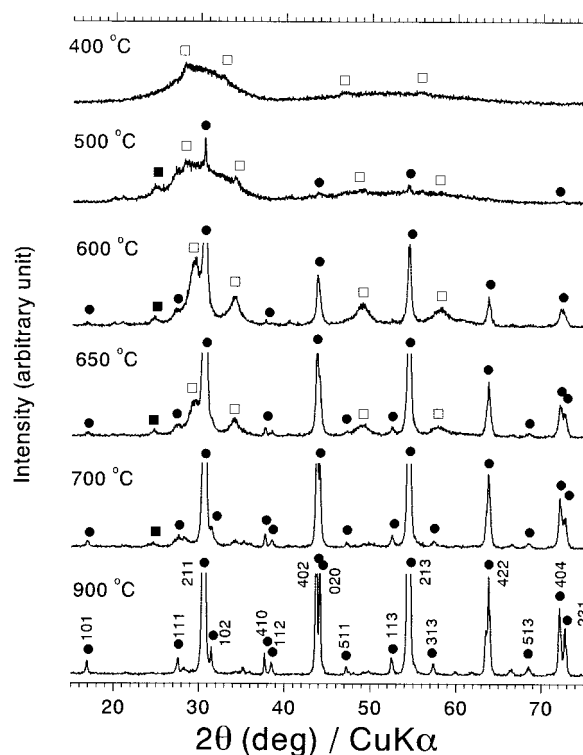


Fig. 2. XRD patterns of the powders calcined for 1 h at 400°–900°C (●) PH phase, (■) PbO phase, and (□) tetragonal intermediate phase).

only when the powders were calcined at $\geq 700^\circ\text{C}$. This spectrum is in good agreement with the previously reported Raman spectrum for the orthorhombic PH phase.¹⁶ On the other hand, the Raman spectra of the powders that were calcined at temperatures up to 600°C show broad bands, probably because of the small size of

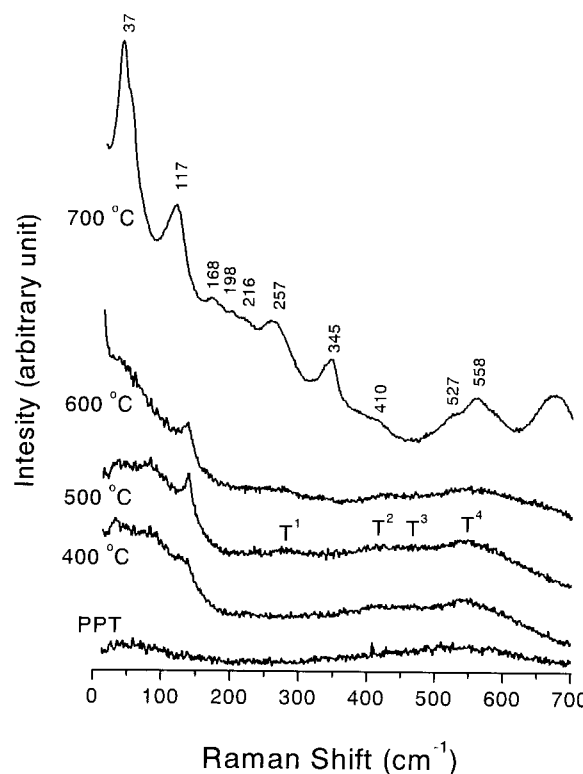


Fig. 3. Raman spectrum of the dry precipitate (indicated by PPT), and the spectra of the powders calcined for 1 h at 400°–900°C. Peaks labeled “T¹” through “T⁴” indicate extra peaks from the tetragonal intermediate phase.

particles. Extra peaks (noted as T¹ through T⁴ in the spectrum of the powder that was calcined at 500°C in Fig. 3) could be observed; these peaks were assigned to a tetragonal intermediate phase.

IV. Conclusions

Ultrafine lead hafnate (PbHfO₃, PH) powders with an orthorhombic structure were successfully prepared using a new technique called the “oxidant-peroxo method”; this method previously has been used to obtain lead titanate, using a precursor that was free of carbon and halides. The PH phase was first formed at ~600°C via an intermediate tetragonal phase, as determined by X-ray diffractometry and Raman spectroscopy. Thermogravimetric analysis revealed a smooth and continuous weight loss from 30°C to 492°C. An orthorhombic PH phase was obtained at annealing temperatures of ≥700°C; the presence of this phase was confirmed unequivocally via Raman spectroscopy.

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