Sol−Gel Synthesis of Free-Standing Ferroelectric Lead Zirconate Titanate Nanoparticles

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Lead zirconate titanate (PZT), $PbZr_xTi_{1-x}O_3$, crystals have attracted broad interest due to their piezoelectric and electrooptic properties. PZT has a distorted perovskite structure below about 350 °C with a ferroelectric tetragonal or rhombohedral phase and consequently displays a spontaneous polarization. The polarization direction of the PZT crystal switches between two stable polarization states corresponding to the positive and negative electric bias. This particular feature makes PZT a candidate for nonvolatile ferroelectric random-access memories (NVFRAMs).[1] PZT in free-standing nanoparticulate form is certainly desirable for use as memory bits in two- and three-dimensional information storage devices. We herein report the synthesis of free-standing 10−30 nm PZT nanoparticles with a modified sol−gel method. As far as we know, this is the first time that free-standing PZT nanoparticles have been synthesized.

PZT nanoparticles in a free-standing form are crucial for addressing some important fundamental issues such as the finite size effect on their ferroelectric properties. The finite size effect has been considered to have some major impact on the properties such as lowing the phase transition temperature.[22] Although the size effect has been studied, substantial disagreements exist.[3−5] One of the main problems has been that the materials used in size effect studies were sintered ceramic powders or films containing PZT particles. Those PZT particles had a strong physical connection with each other. Such strong interparticle connections certainly have made the ferroelectric domain structures of the materials rather complex. Systematic studies on free-standing ferroelectric nanoparticles will facilitate our understanding of the size effect on ferroelectric properties.

The sol−gel method has been widely used in preparing materials as nanoparticles, films, and bulk forms.[6,7] It is arguably the most common synthesis technique for the preparation of ferroelectric materials.[8−15] In our synthesis process, lead acetate, titanium(IV) ethoxide, and zirconium(IV) butoxide have been used as the starting reagents. A typical synthesis experiment started with dissolving 10 g of lead acetate, $Pb(C_2H_3O_2)_2{\cdot}3H_2O$ (Fisher, ACS certified grade), in 100 mL of pure acetic acid and the solution was refluxed overnight. Then more than 90% of the acetic acid was distilled to minimize the amount of water in this Pb starting reagent. The remaining ∼7−8 mL concentrated solution was transferred into a glovebox and subsequently mixed with 600 mL of 2-propanol. Zirconium(IV) butoxide (6.13 g), $Zr[O(CH_2)_3CH_3]_4$ in 1-butanol (80 wt %, Aldrich), was added followed by adding 2.83 g of titanium(IV) ethoxide, $Ti(OCH_2CH_3)_4$ in ethanol (Ti ∼20%, Aldrich), with a Ti:Zr molar ratio maintained at 1:1. The Zr and Ti concentration was 0.020 M each and the lead concentration was 0.044 M in the final solution. Slightly higher lead concentration was intended to compensate the loss of Pb in the subsequent thermal treatment. The solution was stirred at 50 °C overnight to reach a transparent form before it was taken out of the glovebox. By slowly adding ammonia with an Ar gas to bubble through a 29.6% (w/w) ammonium hydroxide solution, the pH of this solution was increased to allow the nanoparticulate precursor to slowly grow. Meanwhile, the solution was kept at 80−90 °C under vigorously stirring. A white precipitate slowly appeared after a few hours. The growth process of the PZT nanoparticulate precursor usually lasted for 3−5 days. At the end, 300 mL of 29.6% (w/w) ammonium hydroxide was added to raise the pH level in the solution above 10 and the nanoparticle growth was completed. Then, the nanoparticulate precipitate was separated out by centrifugation and washed with absolute ethanol several times. After drying the product in a vacuum oven at 100 °C overnight, a white fine powder was obtained, which was in an amorphous phase as shown by X-ray diffraction studies. A tube furnace was used to heat this amorphous precursor of nanoparticulate PZT. The temperature of the furnace was raised to 700 °C at a ramp of 0.1−0.3 °C/min in Ar atmosphere. After heat treatment for 12 h at 700 °C, the nanoparticles were heated at 500−600 °C in air for 1−1.5 h to burn out the black carbon residue on the nanoparticle surface. For forming a stable suspension, the surface of nanoparticles was modified with tartrate ligands.

X-ray diffraction studies have shown that the heat treatment of the solid precursor has to be conducted at 650 °C or higher to obtain PZT nanoparticles with a distorted perovskite structure. The chemical composition of the nanoparticles has been determined by chemical analysis by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The composition of the nanoparticles varies slightly from batch to batch. The ratio of Pb to (Zr + Ti) is 1:1. However, the ratio of Zr to Ti can vary from 0.54/0.46 to 0.50/0.50.

Figure 1 shows a transmission electron microscopy (TEM) micrograph of the PZT nanoparticles recorded using a Joel 100C transmission electron microscope. The inset in Figure 1 displays the high-resolution TEM micrograph of a single PZT nanoparticle under a Hitachi HF-2000 field-emission transmission electron microscope, which combining with electron diffraction confirms that each nanoparticle is a single crystal with no evidence indicating the existence of defects such as grain boundary,

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Table 1. Characteristic Structural Parameters Determined from the Rietveld Refinement of X-ray Diffraction for PZT Nanoparticles[a]

phase	space group	phase fraction	*a* (Å)	*b* (Å)	*c* (Å)	α (deg)	% Zr	% Ti	U_{iso}(all)	χ^2	$R(f^2)$
rhombohedral	R_{3cR}	0.25	5.7612	*a*	*a*	59.82	0.54	0.46	0.0223	3.02	0.140
tetragonal	P_{4mm}	0.75	4.0110	*a*	4.1259	90	0.54	0.46	0.0223		

[a] To reduce dependencies, chemical composition and thermal displacement parameters were constrained for both phases.

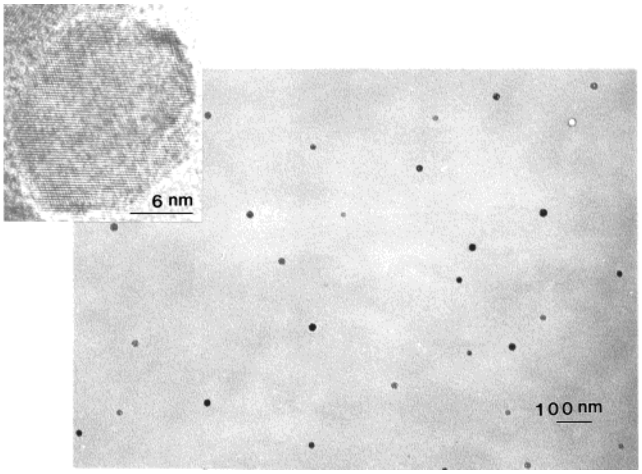

Figure 1. Transmission electron micrograph of PZT nanoparticles with a size of 17 ± 3 nm. The inset shows a single nanoparticle under high-resolution TEM.

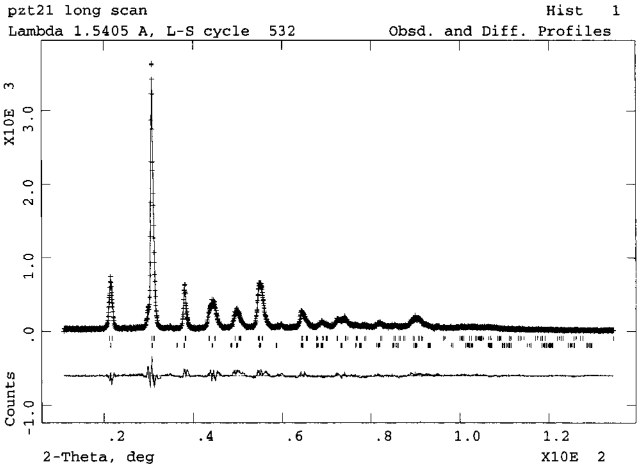

Figure 2. X-ray diffraction pattern of 30 nm PZT nanoparticles. Below the pattern, the first and second row of sticks mark the peaks from the rhombohedral and tetragonal phase, respectively.

dislocation, and stacking fault. The PZT nanoparticles currently can be prepared from about 10 to 30 nm. A size distribution of 20% or less is usually achieved without any particular size separation procedures. The nanoparticles displayed in Figure 1 have a composition of $Pb(Zr_{0.50}Ti_{0.50})O_3$. TEM studies clearly show that these PZT nanoparticles are free-standing individual particles. These nanoparticles can be suspended in a solution for extended periods, which also is an indication of the free-standing nature of nanoparticles. Although pure perovskite PZT nanoparticles are usually obtained when the solid precursor is heated at or above 650 °C, the interparticle sintering will occur if the heat treatment is conducted in oxygen or air. Free-standing crystalline PZT nanoparticles are produced when the precursor is heated in a nitrogen or argon atmosphere. The slow increase of temperature from room temperature to 650−700 °C is essential for achieving a relatively uniform temperature surrounding the nanoparticles during the heating process to avoid the interparticle sintering.

Figure 2 is an X-ray diffraction pattern obtained by using a Bruker D8 X-ray powder diffractometer. It shows that the nanoparticles have a pure perovskite PZT structure. It is well-known that ferroelectric PZT materials can have two phases related to the perovskite structure.[16] One has a tetragonal unit cell and the other has a rhombohedral cell. The morphotropic phase boundary (MPB) for these two phases locates around a Zr:Ti ratio of 0.50:0.50. The Rietveld refinement on the X-ray diffraction pattern has been conducted to determine the phase(s) of PZT nanoparticles by using the General Structure Analysis System (GSAS) program. The whole pattern fitting is also displayed in Figure 2. The results from the Rietveld refinement are summarized in Table 1. The diffraction peaks in the X-ray pattern are broadened compared to the bulk materials. This peak broadening can originate from the reduced size of nanoparticulate samples and/or the lattice strain in the sample. The refinement results indicate that the peak broadening is from the reduced crystal size in our PZT nanoparticles. The perovskite PZT nanoparticles have a mixture of tetragonal and rhombohedral phases. The tetragonal crystal phase is the predominant one. The coexistence of these two phases in PZT materials has been attributed to the equal free energies for tetragonal and rhombohedral phases at MPB.[17,18] It has also been suggested that the mixing of two phases originates from compositional inhomogeneity.[19,20] Further studies on the origin of such a coexistence of two phases are currently pursued on the PZT nanoparticles in our laboratory.

In summary, free-standing PZT nanoparticles have been synthesized by using a modified sol−gel method. The Rietveld refinement of the X-ray diffraction pattern reveals that the tetragonal phase is the predominant phase in these nanoparticles. Characterization of the ferroelectric properties of these PZT nanoparticles is currently being carried out. Also, the possible size effect to the ferroelectric domain structure and the ferroelectric properties is being explored. The studies on PZT nanoparticles in a free-standing form will certainly elucidate the mechanism of ferroelectric properties in reduced dimensions. They will also facilitate the applications of ferroelectric nanoparticles in advanced technologies.

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