Impact of surfactants on Pb (Zr0.53Ti0.47) O₃ nanocrystal formation

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Abstract
In this article, we studied how surfactants can impact Pb (Zr0.53Ti0.47)O₃ (PZT) nanocrystal formation to result in interesting nanohexagon and nanorod shapes of PZT crystal. The PZT nanohexagons/nanorods with typical diameters and bounding lengths within the nanometer range were synthesized by sintering the mixture of PZT crystals. After annealing at 800 °C for 3 h, PZT nanohexagons were formed with Tween 20. Using the same sol–gel method and growth condition but with Tween 20 replaced by Triton X-100, PZT nanocrystals were formed having nanorod shapes. Their single-crystalline nanostructures and compositions were confirmed by high resolution transmission electronic microscopy (HR-TEM), X-ray diffraction (XRD) and Raman Spectra. The results of this study demonstrated new insight on how surfactants impact the morphology of PZT formation.

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1. Introduction

The lead zirconium titanate (PZT) is a prototypical ferroelectric material, which is able to convert mechanical vibrations to electric signals or vice versa. PZTs are broadly used in actuators, sensors and transducers [1–4] due to its high Curie temperature, electric signals or vice versa. PZTs are broadly used in actuators, sensors and transducers [1–4] due to its high Curie temperature, high dielectric constant and high breakdown strength. PZT is also a perfect material for applications in micro-electromechanical systems (MEMS) and nano-electromechanical systems (NEMS). Due to its outstanding piezoelectric property, different shape and size of PZT are required for a wide range of applications; therefore, great efforts have been invested to obtain the PZT microstructures and nanostructures with different morphologies. Synthesis methods for PZT nanocrystals include the traditional soft chemistry methods, hydrothermal reactions and sol–gel process etc. [5,6].

The sol–gel process [7] for synthesis of inorganic nanostructural crystals has proved to be a successful method due to its higher degree of homogeneity compared to the other methods. The sol–gel process requires lower reaction temperatures than the traditional soft chemistry methods and allows the production of solid material from liquid by using a sol or a gel as an intermediate product. In the sol–gel process, thin films or fibers could be directly synthesized from solution by powderless process of transformation of molecular precursors into an oxide network by condensation reactions is often involved in the synthesis of solid materials via ‘soft chemistry’ processes [5–7]. Moreover, sol–gel routes have made it possible to obtain very thin ferroelectric films with splendid operational and structural characteristics for various applications [8].

Conventionally, template-based synthesis is used to organize PZT nanocrystals. Their sizes and shapes are controlled by the use of a porous membrane. Steven et al. [9] have grown uniform sized and almost unidirectionally aligned PZT nanorods in polycarbonate (PC) membranes with the pore sizes between 100 and 200 nm. PZT nanotubes have been successfully made in nanochannel alumina (NCA) and silicon templates respectively by using pore wetting misted chemical solution deposition [10,11]. Zhang et al. have fabricated Pb (Zr0.53Ti0.47)O₃ nanowires in NCA template via the sol–gel process [12]. Wang et al. made PZT fibers with diameter ranging from 500 nm to a few microns by executing metallo-organic decomposition and electrospinning techniques [13]. However, it is difficult to assemble PZT nanorods, nanotubes, nanofibers or nanowires as functional devices due to the difficulty in producing high-quality ferroelectric nanostructures with controllable size and crystallinity. Therefore, a general method for producing well-crystallized nanostructures of perovskite oxides would be of great interest. Peng showed that increasing or removing metal ions from crystallites were enabled by temperature change due to the rapid absorption or desorption of surfactant molecules from nanocrystal surface [14]. The sizes and morphologies of the nanocrystals could be controlled by careful selection of the kind of surfactant and its concentration. Xu et al. developed a polymer-assisted method,
which produced 150–175 nm wide and 1–1.6 μm long single crystal line tetragonal perovskite PZT nanorods only using poly (vinyl alcohol) (PVA) [15]. They also made 40 nm wide and 1.7–3.5 μm long single crystalline tetragonal perovskite PZT nanowires by combining poly(acrylic acid)(PAA) and poly(vinyl alcohol) (PVA) [15].

In this paper, we propose a surfactant-assisted synthesis method to control the morphology of single-crystalline PZT, either in nanohexagon or in nanorod shapes. Experiments were designed to understand the growth mechanism of the nanostructure formation. To our best knowledge, no method for preparation of single crystalline PZT nanohexagons/nanorods has been reported in the literature.

2. Materials and methods

**Synthesis of PZT nanocrystals:** All chemical reagents used in synthesis were purchased from Sigma-Aldrich, USA. They were of analytical grade and were used without further purification. PZT crystals with a composition of Pb(Zr0.53Ti0.47)O3 were synthesized by a modified sol–gel method [4]. The starting materials were zirconium nitrate ZrO(NO3)2·6H2O, lead acetate hydrate Pb(CH3COO)2·3H2O and titanium isopropoxide Ti(OC4H9)4. The ratio of Pb:Zr:Ti was 1:0.53:0.47.

Firstly, 4.0 g Pb(AC)2·3H2O and 2.37 g ZrO(NO3)2·6H2O were dissolved in 100 ml 2-methoxyethanol and stirred at 100 °C for 30 min to obtain a transparent solution in the 200 ml round glass flask. Secondly, 1.89 g Ti(OC4H9)4 was added to the precursor, and the mixture was stirred at 150 °C for 2 h to form PZT-sol. The PZT-sol was then stirred and distilled at 125 °C under slight vacuum to remove solvent and achieve homogeneity. A light yellow gel was obtained after 3 h. The PZT-gel was further dried by removing 2-methoxyethanol under vacuum for 18 h until totally dry PZT-gel was obtained. After cooling the sample down to room temperature, the dried gel was crushed into fine powders and the PZT nanocrystals were formed by sinterting them at 700 °C for 24 h. PZT nanocrystals were randomly selected and analyzed by X-Ray Diffraction.

**Synthesis of PZT nanohexagons:** The formation of nanohexagons was induced by a surfactant-salt-assisted process. Specifically, the

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**Fig. 1.** (a) XRD pattern of PZT nanocrystals (inset: TEM image and the SAED pattern of PZT nanocrystals and (b) TEM images of PZT sintered with NaCl only. Neither nanorods nor nanohexagons were found.
obtained PZT nanocrystals and NaCl were crushed and mixed for 30 min. Liquid surfactant Tween 20, PZT, and NaCl with the mass ratio of PZT:NaCl:Twe 20 = 1:5:10 were added. The mixture was then sonicated (intensity of 239 W, model FS30H, Fisher Scientific Inc.) in a water bath for 15 min before being preheated at 110°C for 1 h. The obtained starting materials were sintered at 300°C for 2 h, then increased to 800°C at a constant rate of approximately 8°C/min for annealing 3 h in the open air. Finally, the products were washed by distilled water 5 times in order to remove any remaining NaCl. The sample was dried at 60°C for 4 h.

**Synthesis of PZT nanorods:** The synthesis procedure of PZT nanorods followed the same steps as that for PZT nanohexagons. The difference is the surfactant Tween 20 was replaced by Triton X-100. The other difference is PZT:NaCl:Triton X-100 = 1:5:10 M ratio is required for synthesizing nanorods, while PZT:NaCl:Tween 20 = 1:5:10 mass ratio is needed for making nanohexagons.

### 3. Results and discussion

**Synthesis of PZT nanocrystals:** Transmission Electron Microscopy (TEM) images and its corresponding Selected Area Electron Diffraction (SAED) pattern of the prepared PZT nanocrystals are shown in the inset of Fig. 1a. It can be clearly seen that the sample entirely consists of PZT nanoparticles, and no large-size nanoparticles or strong agglomerates were observed. In addition, these nanoparticles are relatively uniform in size (with an average grain size of 6.8 nm) and mostly spherical in shape. The diffraction rings in the SAED pattern (inset of Fig. 1a), provided additional evidence that these nanoparticles were highly crystallized. X-ray diffraction (XRD) patterns of the synthesized PZT powders are displayed in Fig. 1a. The results from XRD shows that the PZT powders have the composition of Pb(Zr0.52Ti0.48)O3 because their peaks are in line with the morphotropic phase boundary (MPB) as we expected. The sharp and strong reflection peaks in Fig. 1a illustrate that the prepared PZT nanoparticles have been highly crystallized during the sintering process. It is also clear that all the diffraction lines are in monoclinic phases, which agrees with the standard value based on XRD software calculation. It can be concluded that the fabricated PZT nanocrystals have monoclinic perovskite structure, which illustrates that the PZT nanocrystals are of highly compositional homogeneity.

**Surfactant effect on PZT nanocrystal formation—Nanohexagon formation:** The prepared PZT nanocrystals were then mixed with Tween 20 and NaCl to fabricate PZT nanohexagons. The XRD spectrums of the PZT-Tween 20 sintered at different temperatures are (3 h at 750°C, 800°C and 850°C, respectively) shown in Fig. 2a. Even though the intensities of each XRD pattern does not show clear differences, only the PZT-Tween 20 sintered at 800°C for 3 h gave us PZT nanohexagons (refer to Fig. 2b).

Instead of varying temperature, we have also sintered the sample at 800°C but varied sintering times. Compared to the patterns of PZT-Tween 20 sintered at 2 h 30 min, 3 h, 3 h 30 min, 4 h 30 min and 6 h, the perovskite peaks of PZT-Tween 20 became slightly sharper as we prolonged the sintering time (data not shown), indicating higher extent of crystallinity and larger grain
size [16–18]. However, nanohexagon shape appears only when sintering PZT-Tween 20 for 3 h at 800 °C, but not at other conditions (refer to Fig. 2b).

**Nanorod formation:** To make PZT nanorods, the prepared PZT nanocrystals were mixed with Triton X-100 and NaCl. Fig. 3a shows the XRD patterns of the PZT-Triton X-100 at different sintering times. We have also investigated the effect by varying temperatures (data not shown). The perovskite peaks of PZT-Triton X-100 shifted slightly when the sintering time was prolonged, which means the molar ratio of Pb:Zr:Ti was no longer at the morphotropic phase boundary. In addition, we discovered that nanorod shape appears only when the sintering condition was set for 3 h and 800 °C (refer to Fig. 3b).

**Characterizing PZT nanohexagons/nanorods:**

- **Raman spectra of PZT nanohexagons:** Fig. 2c shows the Raman spectra of PZT nanohexagons. The test setting included: (i) excitation laser wavelength—780 nm; (ii) exposure time—10 sec; (iii) Charge Coupled Device (CCD) detector and (iv) backscattering geometry. The locations of the Raman shift peaks of PZT nanohexagons closely match the typical Raman peaks of perovskite PZT [19,20]. By comparing the Raman spectra of PZT crystals and nanohexagons, the spectra of PZT nanohexagons are lower in intensity. Furthermore, the Raman modes of A1(2TO), E(2TO) and A1(3LO) noticeably shift to lower frequencies (194, 313 and 723 cm⁻¹) while the mode A1(3TO) and the silent mode B1 + ET only downshift slightly. The weakening of intensity and downshifting in frequency of the Raman spectra can be attributed to the mode-soften behaviors [19], indicating a phase transition between PZT nanocrystals and PZT nanohexagons.

- **Raman spectra of PZT nanorods:** Fig. 3c shows the Raman spectra of PZT nanorods. The parameters used for the tests were the same for the PZT nanohexagons. Similar to the PZT nanocrystals, the locations of the Raman shift peaks of PZT nanorods match the typical Raman peaks of perovskite PZT [19,20]. The weakening in intensity and downshifting in frequency of the Raman spectra indicate that there is a phase transition between PZT nanocrystals and PZT nanorods [19].

**Crystal structure of PZT nanohexagons nanorods—TEM images of PZT nanohexagons:** Fig. 2b shows the shape of the PZT nanohexagons synthesized using surfactant Tween 20 and NaCl, from which we can clearly see the hexagon structure of the nanoscale PZT. The PZT nanohexagons, with typical diameters around 480–540 nm and boundary lengths ranging from 230 to 260 nm have been successfully fabricated. In order to explore the crystal structure of the PZT nanohexagon, a cubic region of the nanohexagon was selected. A HRTEM image with high magnification was acquired within this cubic area, and the selected area electron diffraction (SAED) pattern of the corresponding region is shown in this figure. As can be seen, a well-organized pattern instead of diffraction rings is present, indicating that the nanohexagon has single crystal structure. Moreover, the SAED patterns obtained from different areas of the individual hexagon are almost identical. The clear lattice fringes in the enlarged cubic area demonstrate the single crystalline structure of the PZT nanohexagon, which is in line with the SAED results.

**TEM images of PZT nanorods:** Fig. 3b shows the HRTEM image of a single PZT nanorod. To investigate the crystal structure of the PZT nanorods, a cubic region of the nanorod was selected. A HRTEM image with high magnification was taken in this cubic area, and Nano-Beam Diffraction (NBD) Pattern of the corresponding area is shown in Fig. 3b. A pattern of well-organized spots was observed instead of diffraction rings as represented in the NBD pattern of the PZT nanorods, indicating that the nanorod is a single crystal. The clear lattice fringes in the enlarged cubic area illustrate their single crystalline structure.

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**Fig. 3.** (a) XRD patterns of PZT-Triton X-100 at different reaction temperatures. (b) High-resolution TEM image of an individual PZT nanorod and its corresponding Nano-Beam diffraction (NBD) pattern. (c) Raman Spectra of PZT nanorods versus PZT nanocrystals and (d) Proposed mechanism of nanorod growth.
Influence of the surfactants and NaCl on the formation of PZT nanohexagons: In order to identify the influence of the surfactants and NaCl on the formation of PZT nanohexagons or nanorods, one more experiment was performed with the same starting PZT nanocrystals and annealing condition (3 h and 800 °C). This time, only NaCl was mixed with PZT nanoparticles, with no surfactant added. When the product was examined by TEM, only irregular-shaped nanoparticles were observed, and neither nanorods nor nanohexagons were found (see Fig. 1b). Since no specific morphologies of PZT nanocrystals could be formed in the absence of surfactants, it is believed that the surfactant Triton X-100 and Tween 20 play critical roles in the formation of nanohexagons and nanorods.

Mechanism of forming PZT shape—Nanohexagon formation: The formation of PZT-nanohexagon in the mixture of Tween 20 and sodium chloride is related to Tween 20 chemical structure. Tween 20 (Polyisorbate 20) is an amphiphilic molecule with hydrophobic tail of hydrocarbon alkyl and hydrophilic tail of polyethylene glycol (PEG). The hydrophilic tail contains four branch chains of PEG. These PEGs will be completely stretched if surrounding temperature is high enough. The stretching angle between two PEG chains could equal the angle of nanohexagon. In the mixture of PZT nanocrystal, Tween 20 and sodium chloride, strong interactions exist between PEG and PZT nanocrystals. Therefore, PZT nanocrystals adsorbed specifically around the PEG component of Tween 20, and then nanohexagon structure was formed when temperature reaches 800 °C. Fig. 2d describes the hypothesis of the formation mechanism of PZT-nanohexagon.

Mechanism of PZT nanorod formation: According to the Oswald ripening mechanism in [21], under the combined effects of NaCl flux and surfactants, the fine powders dispersed and re-deposited on larger particles, which formed the PZT nanorods along an axial direction shown in Fig. 3d. The components in the flux could move around more easily due to the viscosity of the melt compound which was effectively reduced by adding NaCl [22]. Therefore, the NaCl flux provided a favorable liquid environment for the growth of PZT nanorods. The surfactant Triton X-100 prevented small nanoparticles from aggregating into large particles by forming a “shell” surrounding the small nanoparticles and the nanorod. The Triton X-100 gradually burns in the sintering process, which emitted light smoke. After the Triton X-100 burnt out, the PZT nanorods will be crystallized into single crystal.

4. Conclusion

The sol–gel process is one of the most extensively studied methods to fabricate PZT nanocrystals for microactuators and piezoelectric transducers. We have investigated the growth of single-crystalline PZT nanohexagons and PZT nanorods assisted by surfactants using a modified sol–gel process. The growth of PZT nanohexagons/nanorods is very sensitive to the sintering time, temperature and surfactant ratio. For instance, PZT nanohexagons and nanorods were formed only at 800 °C for 3 h. Single-crystalline PZT nanohexagons with diameters of about 480–540 nm and bounding lengths of approximately 230–260 nm were synthesized when Tween 20 was used. Introduction of surfactant has proved critical in the formation of single-crystalline PZT nanohexagons and nanorods. Our proposed process is a promising technique to produce single-crystalline PZT nanostructures of different morphologies.

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