Inorg. Chem. **2007**, *46*, 7423–7427

Inorganic Chemistry

Article

Morphology-Controlled Synthesis of Lead Titanate Powders

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Received March 25, 2007

A simple and high-yield synthetic route was developed to synthesize the different-shaped $PbTiO_3$ powders. Spherical, rod, and cubic shapes of $PbTiO_3$ were achieved from the precursors of spherical and rod TiO_2/$K_2Ti_4O_9$ compounds with PbO in the NaCl–KCl melts at the temperatures from 700 to 900 °C, respectively. Raman spectroscopy, X-ray diffraction, thermal field emission scanning electron microscopy, and transmission electron microscopy were used to investigate the structure and morphology. Moreover, the formation mechanism of $PbTiO_3$ with controlled morphologies was analyzed. PbO diffused to the TiO_2 surface in the molten salts, followed with the nucleation and growth of $PbTiO_3$; thus, morphology control of $PbTiO_3$ was realized through controlling the shapes of the titanium source. Raman spectra of the as-synthesized $PbTiO_3$ showed mode-softening behaviors of E(1TO) related to the weakening in ferroelectricity.

Introduction

In recent years, there has been increasing interest in the synthesis of monodispersed metal oxide particles with controlled morphology. Such particles are desired for a variety of applications including the fabrication of ceramic−polymer composites for electronic applications and as a reinforcement phase in polymer and brittle-matrix composites.[1,2]

Lead titanate ferroelectric material ($PbTiO_3$) or simply PT, which exhibits a perovskite structure and a Curie temperature of 490 °C, is one of the most important members in the ferroelectric and piezoelectric families. Because of its high Curie point, low relative permittivity, and high spontaneous polarization, tetragonal $PbTiO_3$ is used as a stable piezoelectric material at high temperature and frequency.[3−5] Unfortunately, pure $PbTiO_3$ was found difficult to synthesize as a mechanically robust, high-density, monolithic ceramic. The problems typically encountered include Pb loss, porosity, and microcracking, in extreme cases leading to spontaneous fracture. Much attention has been devoted to the synthesis of PT powder or thin film using different methods. Many methods have been used to obtain lead titanate powders, such as the sol−gel method,[6,7] the Pechini method,[8] coprecipitation[4,9] and hydrothermal synthesis,[1,10] besides the traditional solid-state reaction of mixed oxides.[11] In all these methods, calcination at more or less high temperature was needed to get pure crystallized ferroelectric $PbTiO_3$, involving the formation of hard aggregates, which was unfavorable for sintering.

Molten-salt synthesis (MSS) is one of the simplest techniques to prepare pure, stoichiometric ceramic powders of multicomponent oxides.[2,12−16] Because of the small

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10.1021/ic700966n CCC: $37.00

diffusion distances of oxide mixtures in molten salts, the high reactivity of salts, and the high mobility of species, completed reactions can be achieved in a relatively short time.[16,17] In addition to possessing a relatively low formation temperature, molten salts could stabilize different polymorphs when compared to other synthesis methods.[18] Another important advantage of the MSS method is that it is amenable to the ability to control powder morphology.[19−21] The objectives of the present work are to synthesize well-defined crystalline $PbTiO_3$ powders with different morphologies employing the MSS method and to investigate the effect of additives of chloride melts on the particle morphology and size of the derived $PbTiO_3$. The effects of the various titanium sources on $PbTiO_3$ morphology were studied, and the mechanism of $PbTiO_3$ formation was involved. Furthermore, the present work proposed a general and useful way to synthesize functional complex oxides in shape control such as (Pb, La)-TiO_3 and (Pb, La)(Zr, Ti)O_3.

Experimental Section

Four series samples of $PbTiO_3$ powders (PT-I, PT-II, PT-III, and PT-IV) were prepared in different precursors. PT-I, PT-II, and PT-III were prepared using spherical TiO_2, rod-shaped TiO_2, and rod-shaped $K_2Ti_4O_9$ as the precursors reacted with PbO in a NaCl−KCl flux, respectively. And PT-IV was prepared by treating PT-I with NP-9 nonionic surfactant, adding in a NaCl flux. Analytically grade reagents TiO_2, PbO, NaCl, KCl and K_2CO_3 were used. The reagent of TiO_2 with spherical shape was used as the spherical titanium source directly. The rod-shaped TiO_2 compound was prepared from rod-shaped $K_2Ti_4O_9$.[22,23] Mixtures of K_2CO_3 and TiO_2 in a molar ratio of 1:3 were heated at 1000 °C for 18 h and then washed with hot deionized water several times to remove residual K_2CO_3. The main product $K_2Ti_4O_9$ was washed in a hot HCl solution for 2 h to extract K_2O, and the resultant phase was $TiO_2\cdot nH_2O$, which was heated for 1 h at 550 °C to prepare the rod-shaped TiO_2 compound.

To prepare PT-I, PT-II, and PT-III powders, the typical synthesis procedure is as follows. The stoichiometric amounts of oxides were mixed by ball-milling for 1 h in an ethanol medium prior to the addition of the salt and then dried at 120 °C for 2 h. NaCl−KCl (50% mol KCl) was used as the medium melt in the MSS route. The mixed ceramic starting powders were mixed with salt at a 1:1 weight ratio by hand-grinding in a mortar and pestle for 30 min and were then heated in the alumina crucibles to the designated temperature at a rate of 5 °C/min. Finally, the samples were cooled in the furnace to room temperature. As-synthesized powders were washed for several times with hot deionized water until no free chloride ions were detected by silver nitrate solution to ensure complete removal of the salt. The obtained PT-I, PT-II, and PT-III powders were dried at 120 °C for 4 h and then characterized by X-ray diffraction (XRD), thermal field emission scanning electron microscopy (FE-SEM), etc.

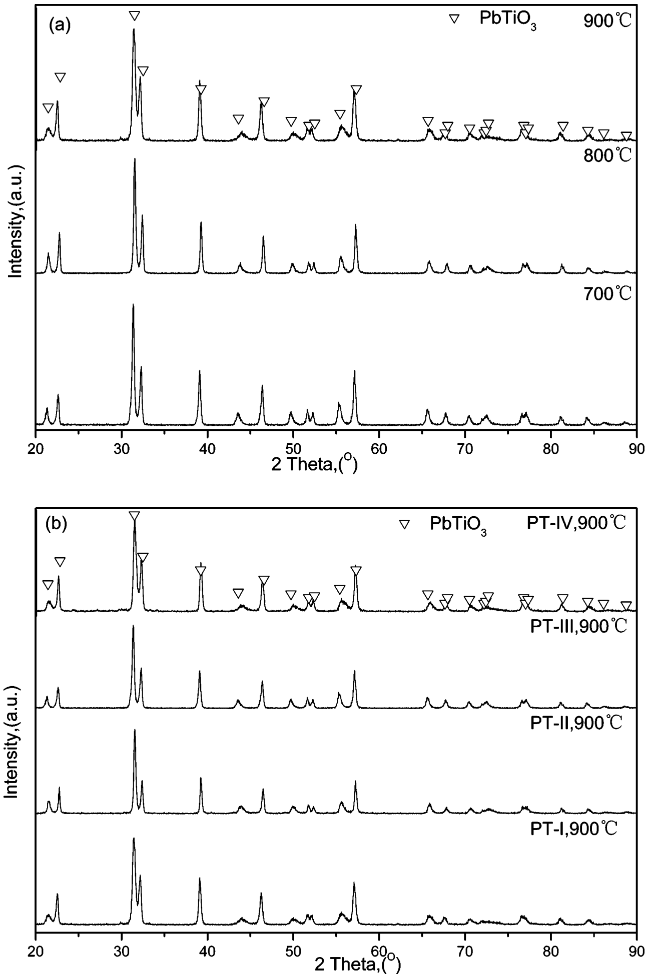

Figure 1. XRD patterns of $PbTiO_3$ powders prepared by MSS. (a) PT-I heated at different temperatures; (b) PT prepared with different precursors at 900 °C.

Table 1. Lattice Parameters of the $PbTiO_3$ Powder Prepared by MSS

series	*a* (*b*), nm	*c*, nm	*c*/*a*	cell volume, nm^3
PT-I	0.3903(6)	0.4136(5)	1.059	0.06348
PT-II	0.3908(4)	0.4105(4)	1.050	0.06271
PT-III	0.3901(5)	0.4115(8)	1.051	0.06274
PT-IV	0.3906(7)	0.4115(9)	1.053	0.06282

To prepare PT-IV, the obtained PT-I powder and NaCl were added to the liquid nonionic surfactant polyoxyethylene (9) nonylphenol ether (NP-9); their molar ratio was 1:5:10.[24] The mixture was then milled (mortar/pestle) for 30 min, sonicated for 10 min, and now preheated at 300 °C. The starting powders were afterward annealed at 900 °C for 2 h in open air. In this work, we extended this method to the synthesis of rod-shaped lead titanate powder. Last, the products were washed by distilled water for several times to get rid of NaCl and dried at 120 °C.

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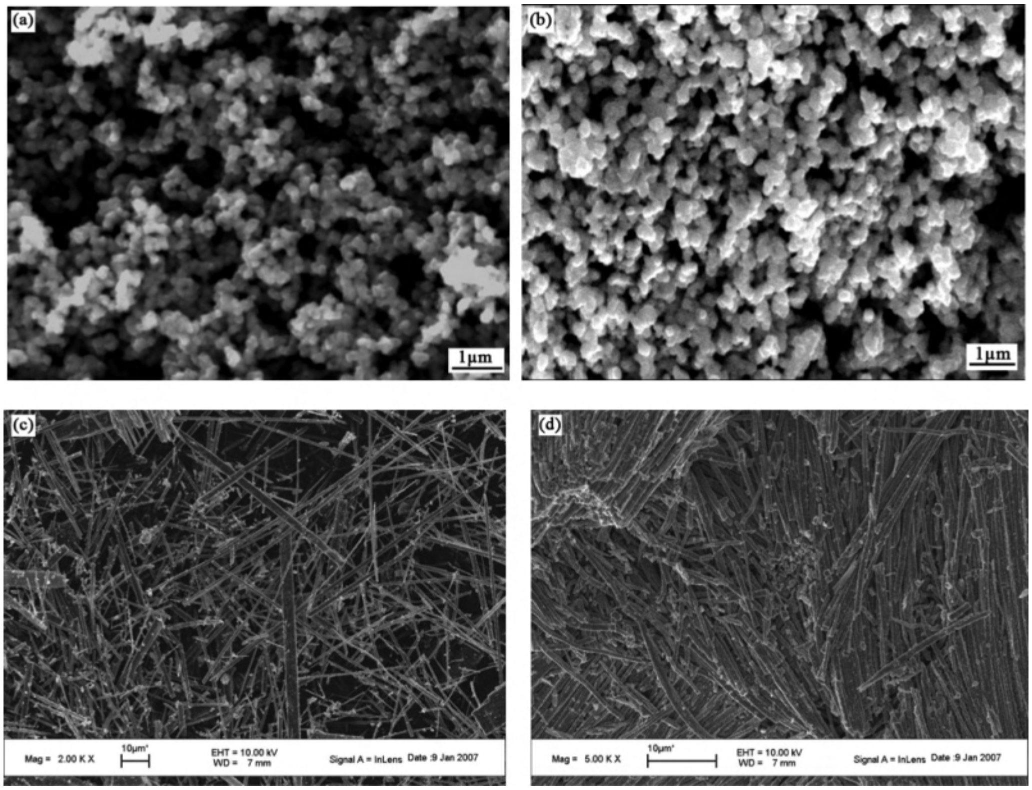

Figure 2. FE-SEM photographs of TiO_2 and $PbTiO_3$ (PT-I, PT-II) from different titanium sources heated at 900 °C for 2 h: (a) spherical TiO_2, (b) PT-I from spherical TiO_2, (c) rod-shaped TiO_2, and (d) PT-II from rod-shaped TiO_2.

Phase analyses were carried out on a 21 kW extra-power powder XRD device (model: M21XVHF22, Mac Science, Yokohama, Japan) at room temperature using Cu Kα radiation. The morphology and compositions of particles were investigated using a transmission electron microscopy device (TEM) (model: JEM-100CXII, JEOL, Japan) and a thermal field emission scanning electron microscope (FE-SEM) (model: LEO-1530, LEO, Germany) equipped with an energy-dispersive X-ray spectrometer (EDS). Raman scattering measurements were performed on a JY-T64000 Raman spectrometer (JY Company, France) under backscattering geometry.

Results and Discussion

Precursors $TiO_2/K_2Ti_4O_9$ with different shapes were mixed with PbO in NaCl−KCl salts ($TiO_2/K_2Ti_4O_9$ + PbO/NaCl−KCl weight ratio = 1). The mixed powders were calcined in a muffle furnace at various predefined temperatures from 700 to 900 °C for 2 h. Figure 1 shows the XRD patterns of the $PbTiO_3$ powders prepared under different conditions. The PT-I, PT-II, PT-III, and PT−IV samples were pure tetragonal $PbTiO_3$ after heating from 700 °C. From the XRD data, lattice constants a and c of the four PTs were calculated and tabulated in Table 1. The ratio value of c/a is slightly lower than that of PT prepared by the conventional solid-state reaction (1.063). It is mainly due to a decrease of the parameter c, which decreases the anisotropy and facilitates an improvement of the material's mechanical properties.

The morphologies of PT prepared from different titanium sources at 900 °C are shown in Figure 2. When the uniform spherical TiO_2 was used as the titanium source, the homogeneous and non-agglomerated PT-I spherical particles were obtained (see parts a and b of Figure 2). If the rod-shaped TiO_2 was used as the starting material, the rod-shaped PT-II particle was achieved (see parts c and d of Figure 2). The present results indicate that the size and morphology of TiO_2 particles determine the morphology of the $PbTiO_3$ particles. The formation of two shapes of $PbTiO_3$ implies that lead ions diffused through the $PbTiO_3$ layers on the surface of TiO_2 to form PT, which was explained by a template formation mechanism.

Rod-shaped $K_2Ti_4O_9$ was used as the titanium source and heated with PbO in the NaCl−KCl melt at 900 °C for 2 h. However, the cubic shape of PT-III was obtained (see Figure 3). The equiaxial PT-III grains in Figure 3b might be ascribed to a "breaking up" of the rod-shaped titanium source particles before the reaction, and the broken trace is observed in Figure 3c. On heating, the rod-shaped $K_2Ti_4O_9$ was broken up into cubic TiO_2 and reacted with PbO according the following reaction

$$\begin{aligned} &K_2Ti_4O_9 + 4PbO \rightarrow \\ &\qquad 4TiO_2 + K_2O + 4PbO \rightarrow 4PbTiO_3 + K_2O \quad (1) \end{aligned}$$

Thus, the cubic $PbTiO_3$ particles would be formed in the template formation mechanism, too.

As reported previously,[20,25−27] reactant solubility in the molten salt plays an important role in MSS, which affects the reaction rate and the morphologies of the as synthesized grains critically. If both reactants are soluble in the molten

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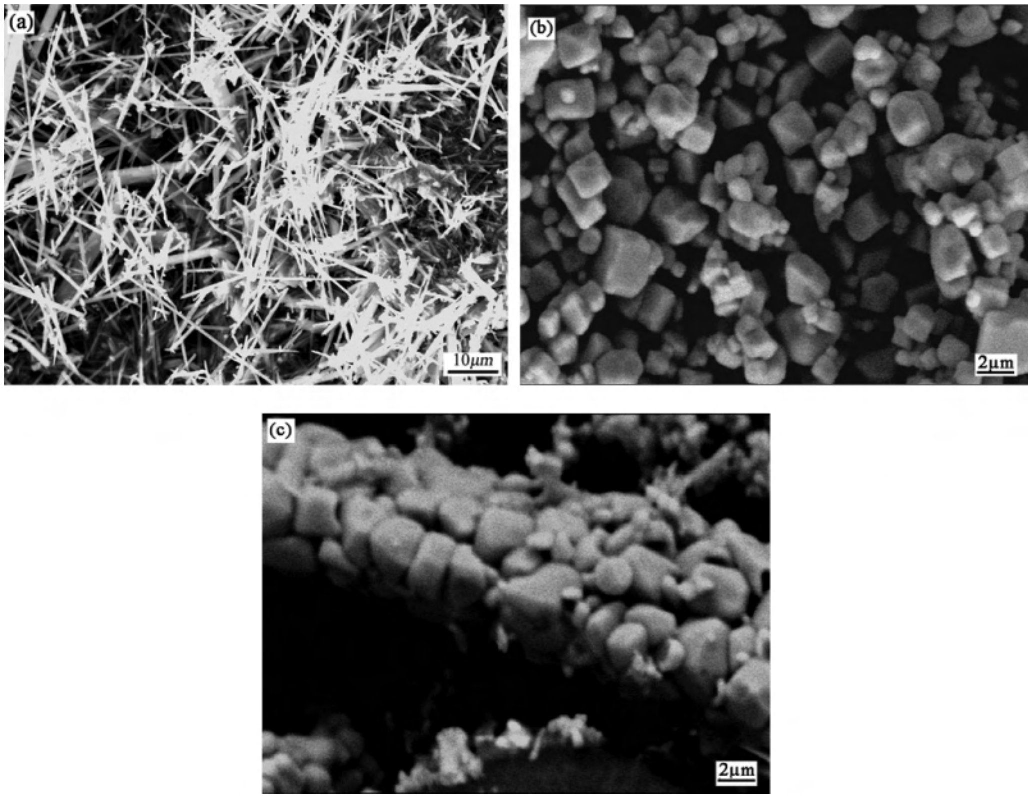

Figure 3. FE-SEM photographs of (a) $K_2Ti_4O_9$, (b) $PbTiO_3$ (PT-III) from $K_2Ti_4O_9$, and (c) typical morphology of PT-III.

salt, then the product will be readily synthesized via precipitation from the salt containing the dissolved reactants (“dissolution−precipitation” mechanism). In this case, the morphologies of product grains will generally be different from those of the reactants. On the other hand, if one reactant is much more soluble than another, it will primarily dissolve into the salt and then diffuse onto the surfaces of the less soluble reactant and react in situ to form the product phase. In this case, the morphology of the synthesized grain will, to a large extent, retain that morphology of the less-soluble reactant (“template formation” mechanism). The melting point of NaCl−KCl with a molar ratio of 1:1 is 657 °C, which was shown in the phase diagram of NaCl−KCl.[28] The solubility of PbO in NaCl−KCl salts was 1.4×10^{-5} and 3.0×10^{-5} mol·g^{-1} chlorides at the temperatures of 800 and 900 °C[14], respectively, while TiO_2 does not dissolve in alkali chlorides.[29] In our case, the fact that the morphologies of $PbTiO_3$ were similar to those of the starting TiO_2 material implied that titanates were formed at the TiO_2 particles surfaces (see Figure 4).

One-dimensional (1D) single-crystal $PbTiO_3$ (PT-IV) powders were obtained by the MSS method with the surfactant NP-9, as seen in Figure 5. The FE-SEM and TEM images indicate that the $PbTiO_3$ crystals are straight, with diameters of 0.1−1 μm and lengths of up to a few micrometers. The formation of the rods can be affected by the character of the starting materials, such as the particle size and/or chemical activity, because the dissolution rate of the material depends on such characters. Its selected-area electron diffraction (SAED) pattern showed that the $PbTiO_3$ rods were single-crystalline with tetragonal crystal structure, which corresponds to the starting material of PT-I. The surfactant NP-9 acted as a dispersing agent, surrounding the single-crystal rods to prevent them from aggregating, and that promoted the fabrication of the 1D rod-shaped structure.[24,30−33] The NP-9 molecules were gradually burnt-off in the process of annealing, accompanied by the emission of light smoke, and the rod-shaped particles of PT-IV further crystallized at 900 °C.

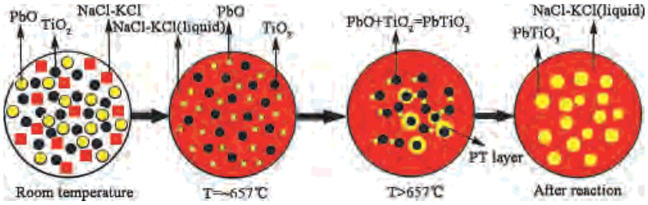

Figure 4. Schematic diagram of the synthesis of $PbTiO_3$ in molten salts.

To confirm the phase of $PbTiO_3$ with different morphologies, $PbTiO_3$ powders were characterized using a Raman spectrometer. Figure 6 illustrates the Raman spectra of $PbTiO_3$ prepared by the MSS method in comparison with that of the bulk crystals prepared by the solid-state reaction.

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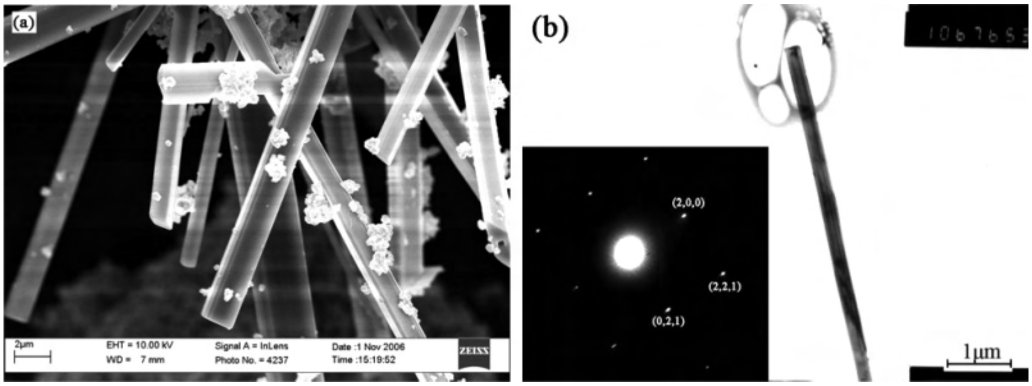

Figure 5. FE-SEM (a) and TEM (b) images of $PbTiO_3$ (PT-IV) with SAED pattern.

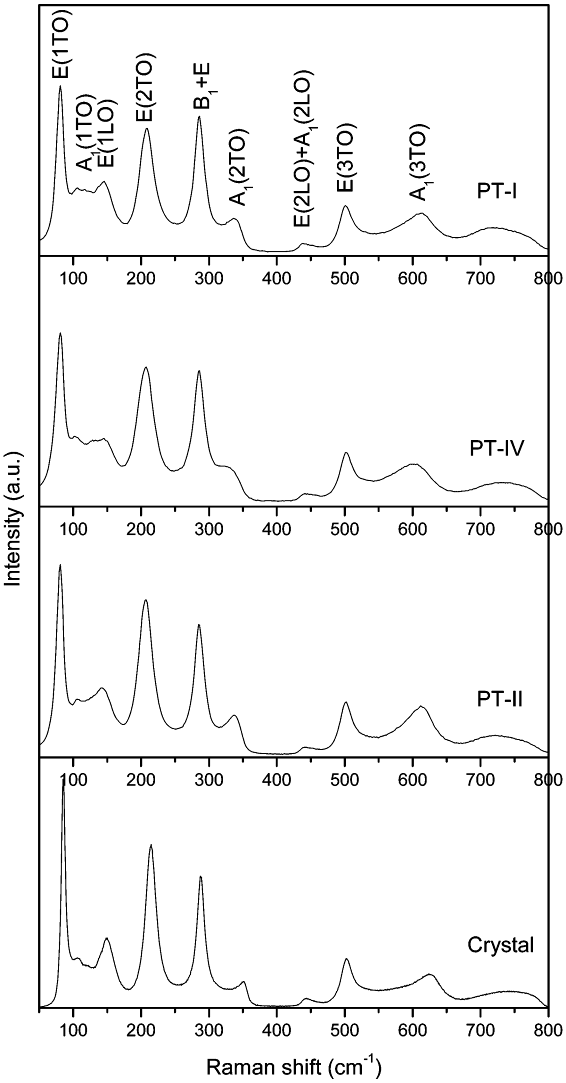

Figure 6. Raman spectra of the $PbTiO_3$ samples prepared by MSS and bulk crystal $PbTiO_3$ methods.

The Raman intensity for $PbTiO_3$ prepared by MSS was apparently lower than that for $PbTiO_3$ prepared by solid-state reaction, and the modes also shifted to lower frequencies, especially for the modes E(1TO), A_1(2TO), E(2TO), and high-frequency mode A_1(3TO), whereas the mode A_1(1TO) and the silent mode $B_1 + E$ was downshifted slightly in PT-IV and the mode A_1(2TO) was enhanced slightly in PT-I and PT-II. The Raman spectra intensities and frequencies of PT-I and PT-IV are similar. The intensity weakening and frequency downshifting of Raman peaks caused by morphology or grain-size-induced effect might be described as mode-softening behaviors, which imply a weakening in ferroelectricity.[24] The weakening in ferroelectricity was related to the decrease of the tetragonality, which was in accordance with the change of lattice parameters.

Conclusions

A novel and simple synthetic approach was developed to synthesize different-shaped $PbTiO_3$ powders and single-crystal rods. Spherical, rod-shaped, and cubic $PbTiO_3$ samples were prepared from the spherical and rod $TiO_2/K_2Ti_4O_9$ compounds with PbO in the NaCl−KCl salts sintered at the temperatures from 700 to 900 °C, respectively. It was shown that PbO was the faster-dissolving component of the starting oxides and TiO_2 was insoluble in alkali chlorides, and the formation of lead titanate proceeded by the dissolution of PbO, transportation through the molten salts, and finally, reaction at the TiO_2 surface. The initial shape of the TiO_2 particles, therefore, determined the final shape and dimensions of the product. A two-step molten-salt sythesis (MSS) method gave rod-shaped single-crystal $PbTiO_3$. The single-crystal rods were straight with diameters of 0.1−1 μm and lengths of up to a few micrometers. Raman spectra of three $PbTiO_3$ samples prepared by the MSS method were studied, and the mode-softening behaviors of E(1TO) indicated the probable weakening in ferroelectricity.

Acknowledgment. This work was supported by the National Nature Science Foundation of China (Nos. 20571009 and 20331030) and Funds of Ministry of Education of China for PCSIRT.

IC700966N