Hydrothermal Synthesis of PbO–TiO$_2$ Solid Solution

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The reactions between PbO and TiO$_2$ in the PbO-rich side of the system PbO–TiO$_2$ were investigated under hydrothermal conditions. The influences of Pb/Ti ratios (1.0–4.0) in the feedstock, reaction temperature (100–160 °C), and pH (11.4–14.2) in the reaction medium on the reaction products have been researched. A new type of PbO–TiO$_2$ solid solution [PT(SS)] can be formed under specific hydrothermal conditions. The Pb/Ti ratio in PT(SS) may be varied within a certain range. The PT(SS)-1 with a tabular morphology and a tetragonal structure is a typical PbO–TiO$_2$ solid solution that is preferentially formed. Its cell parameters are a = 3.911 Å and c = 4.831 Å, and its composition is $PbTi_xO_{1+2x}$ (x = 0.80 ± 0.02). The PT(SS) is converted into the tetragonal perovskite-type PbTiO$_3$ and PbO (litharge or massicot) over 550 °C. A combination of heat treatment and acetic acid wash of PT(SS) could provide a new method for preparing ultrafine PbTiO$_3$ powders.

Introduction

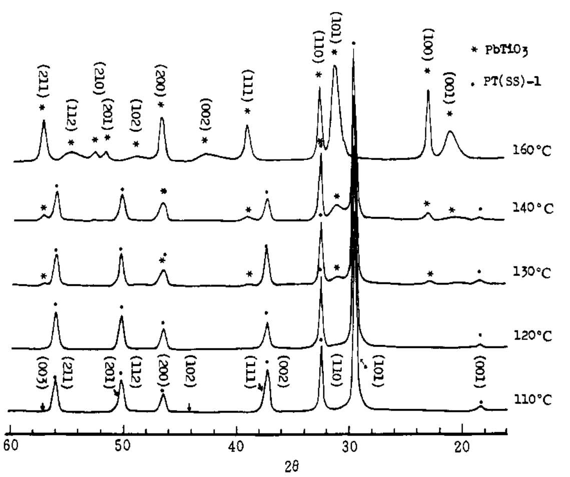

Figure 1. XRD patterns of products formed at 110–160 °C (Pb/Ti ratio = 2.0, pH of 14.0, reaction time = 2 h).

The reactions in the PbO–TiO$_2$ system under hydrothermal conditions are variable. Compounds can be formed with different composition, crystal structure, and morphology. Kaneko and Imoto[1] studied reactions between PbO and TiO$_2$ in the TiO$_2$-rich side of the PbO–TiO$_2$ system under the hydrothermal conditions. PbTi$_3$O$_7$ was observed as a single phase at a Pb/Ti ratio of 0.33. PbTi$_3$O$_7$ and PbTiO$_3$ coexisted at Pb/Ti ratios of 0.45–0.7. They had not provided, however, more detailed data. Suzuki,[2] Takai,[3] and Watson et al.[4] have investigated the hydrothermal synthesis of PbTiO$_3$. We have investigated systematically the reactions between PbO and TiO$_2$ under hydrothermal conditions. The pure tabular PbTiO$_3$ with tetragonal perovskite structure,[5] the pure acicular PbTiO$_3$ with tetragonal body-centered structure,[6] and the starlike (or irregular) Pb$_2$Ti$_2$O$_7$ with cubic pyrochlore structure[5] have been prepared under different hydrothermal conditions. According to the phase diagram of the PbO–TiO$_2$ system,[7] the PbO(ss) (a PbO–TiO$_2$ solid solution) can be formed in the PbO-rich side of the PbO–TiO$_2$ system at higher temperature ($T > 490$ °C). Matsuo et al. determined the dependence of lattice parameters of PbO(ss) on the content of TiO$_2$ in PbO(ss) (TiO$_2$ <12 mol %)[8] and found that the lattice parameters decreased linearly with increasing TiO$_2$ content in PbO(ss). Therefore, this PbO(ss) solid solution is considered statistically to be a result of the partial replacement of Pb^{2+} by Ti^{4+} ions. Kutty et al.[9] reported that they could obtain PbO(ss) free of PbiO$_3$ under hydrothermal conditions (at 160 °C with the initial composition of PbO:TiO$_2$ = 0.85:0.15). The values of cell parameters a and c for PbO(ss) fell on the curve given by Matsuo et al.[8] The content of TiO$_2$ in PbO(ss) was about 9.8 mol %. Takai et al.[3] suggested that the (101) and (110) reflections of PbO(ss) (2θ = 29.3° and 32.3°, respectively, Cu Kα radiation) arise from another form of PbTiO$_3$, and they considered that PbO(ss) can be the first intermediate during hydrothermal precipitation of PbTiO$_3$. Yet detailed structure data have not been published. We have obtained a PbO–TiO$_2$ solid solution phase with a tetragonal structure at 130 °C in the preparation of PZT by the hydrothermal method.[10] Its (101) and (110) reflections (2θ = 29.3° and 32.4°, respectively) were

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1994.

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(7) Jaffe, B.; Cook, W. R.; Jaffe, H. *Piezoelectric Ceramics;* Academic Press: New York, 1971; Chapter 7.

(8) Matsuo, Y.; Sasaki, H. PbO-Rich Side of the System PbO - TiO$_2$. *J. Am. Ceram. Soc.* **1963,** *46*(8), 409–10.

(9) Kutty, T. R. N.; Balachandran, R. Direct Precipitation of Lead Zirconate Titanate by Hydrothermal Method. *Mater. Res. Bull.* **1984,** *19,* 1479.

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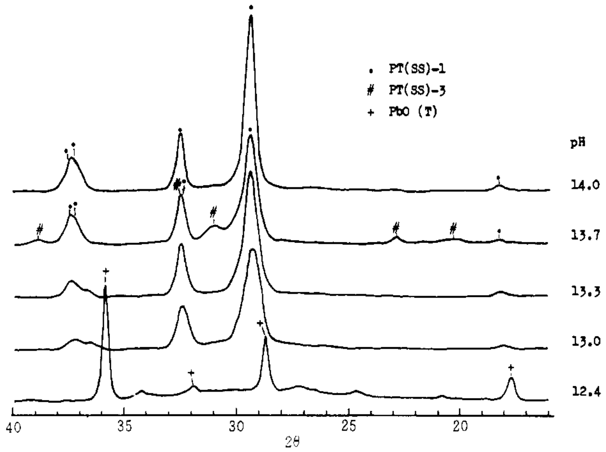

Figure 2. XRD patterns of products formed in the reaction medium of pH 12.4–14.0 (Pb/Ti ratio = 2.0, at 120 °C for 2 h).

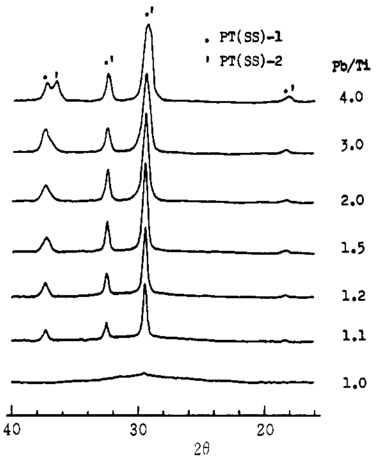

Figure 3. XRD patterns of products formed in the feedstock with various Pb/Ti ratios (pH of 14.0, at 120 °C for 2 h).

Table 1. Influence of Pb/Ti Ratio on 2θ Angle and HHB[a]

	sample A				sample B			
	(101)		(110)		(101)		(110)	
Pb/Ti	2θ	HHB	2θ	HHB	2θ	HHB	2θ	HHB
1.2	29.34	0.26	32.35	0.18				
1.4	29.32	0.27	32.34	0.20	29.33	0.26	32.35	0.18
1.5	29.31	0.30	32.33	0.22				
1.7	29.31	0.36	32.32	0.27	29.33	0.27	32.34	0.21
2.0	29.30	0.38	32.30	0.30	29.34	0.28	32.35	0.22

[a] A and B are the samples before and after treating by 5 v/v % dilute acetic acid of 10 mL/g sample, respectively. The units of 2θ and HHB are degrees. The conditions for preparing samples: pH of 14.0, at 120 °C for 2 h.

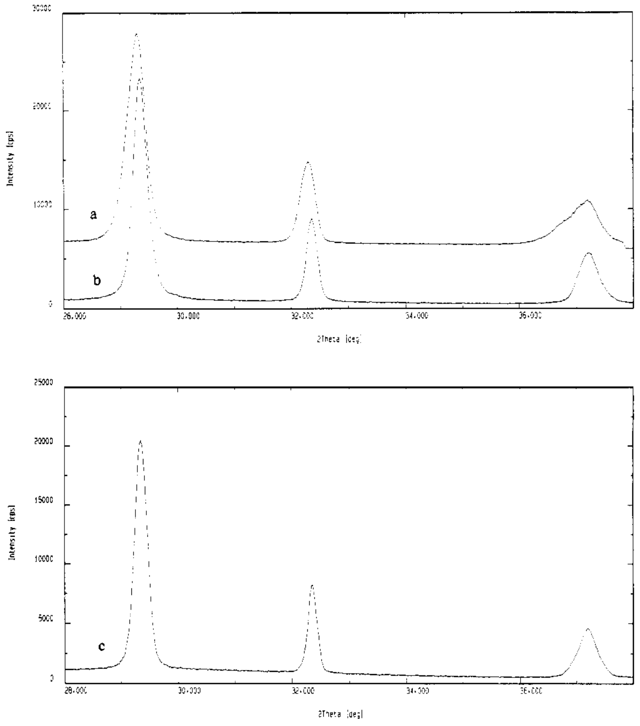

Figure 4. XRD patterns of the sample (Pb/Ti = 2.0) (a) before and (b) after treating by dilute acetic acid and (c) the sample (Pb/Ti = 1.2). * This XRD patterns are obtained using Cu Kα radiation at 40 kV and 100 mA and an automatic monochromator and by scanning at 1° 2θ min^{-1} with a diffractometer (Model Dmax-2000, Rigaku Co., Tokyo, Japan).

Table 2. Powder XRD Data of PT(SS)-1

		2θ (deg)		d (Å)	
(*HKL*)	I/I_0	obsd	calcd	obsd	calcd
001	3	18.35	18.36	4.829	4.831
100	0		22.74		3.911
101	100	29.34	29.38	3.043	3.039
110	39	32.35	32.38	2.763	2.765
002	15	37.20	37.22	2.417	2.415
111	7	37.45	37.47	2.401	2.400
102	0.5	44.10	44.06	2.053	2.055
200	9	46.45	46.44	1.955	1.955
112	15	50.15	50.15	1.819	1.819
201	5	50.35	50.34	1.812	1.812
210	0		52.31		1.749
211	16	55.90	55.91	1.644	1.644
003	0.5	57.20	57.21	1.610	1.610

consistent with those mentioned above by Takai. Yet, the Pb/Ti ratio in this solid solution is more than 1. Thus, it could be a PbO–TiO_2 solid solution instead of another form of $PbTiO_3$. The above results indicated that the PbO–TiO_2 solid solution formed under different conditions could have different compositions. The PbO–TiO_2 solid solution which contains lower content of TiO_2 (<10 mol %) is usually referred to as PbO(ss); for the one comprising higher content of TiO_2 (>10 mol %), we have designated it as PT(SS). The investigation on PT(SS) formed under hydrothermal conditions has been limited. The aim of the present work is to study the reaction between PbO and TiO_2 in the PbO-rich side of system PbO–TiO_2 and the formation of PT(SS) under hydrothermal conditions.

Experimental Procedure

Lead nitrate ($Pb(NO_3)_2$) and titanium butoxide (tetra-*n*-butyl titanate, $Ti[O(CH_2)_3CH_3]_4$) were used as starting materials. *N* (10–40) mL of $Pb(NO_3)_2$ aqueous solution (1.0 mol L^{-1}) and 10 mL of $Ti[O(CH_2)_3CH_3]_4$ ethanol solution (1.0 mol L^{-1}) were added to a reaction medium with a pH of 11.4–14.2 (KOH solution) in certain Pb/Ti ratios. The total volume of the feedstock was kept to 65 mL. The feedstock prepared was charged into a 100-mL Teflon-lined stainless steel autoclave apparatus with electromagnetic stirrer (Peking University Instrument Factory). The hydrothermal reactions were conducted at a temperature range of 100–160 °C for 1–2 h (heating rate 3 °C/min). After the autoclave apparatus was cooled to room temperature in ca. 2 h, the product was filtered, washed with deionized water to neutral pH, and dried. The method is similar to that in ref 6. The chemical agents used in this work were all analytical grade.

The reaction products were analyzed by X-ray diffraction (XRD) using Cu Kα radiation at 40 kV and 20 mA and a graphite

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(10) Cheng, H.; Ma, J.; Zhu, B.; Cui, Y. Reaction Mechanism in the Formation of PZT Solid Solutions under Hydrothermal Conditions. *J. Am. Ceram. Soc.* **1993**, *76* (3), 625–29.

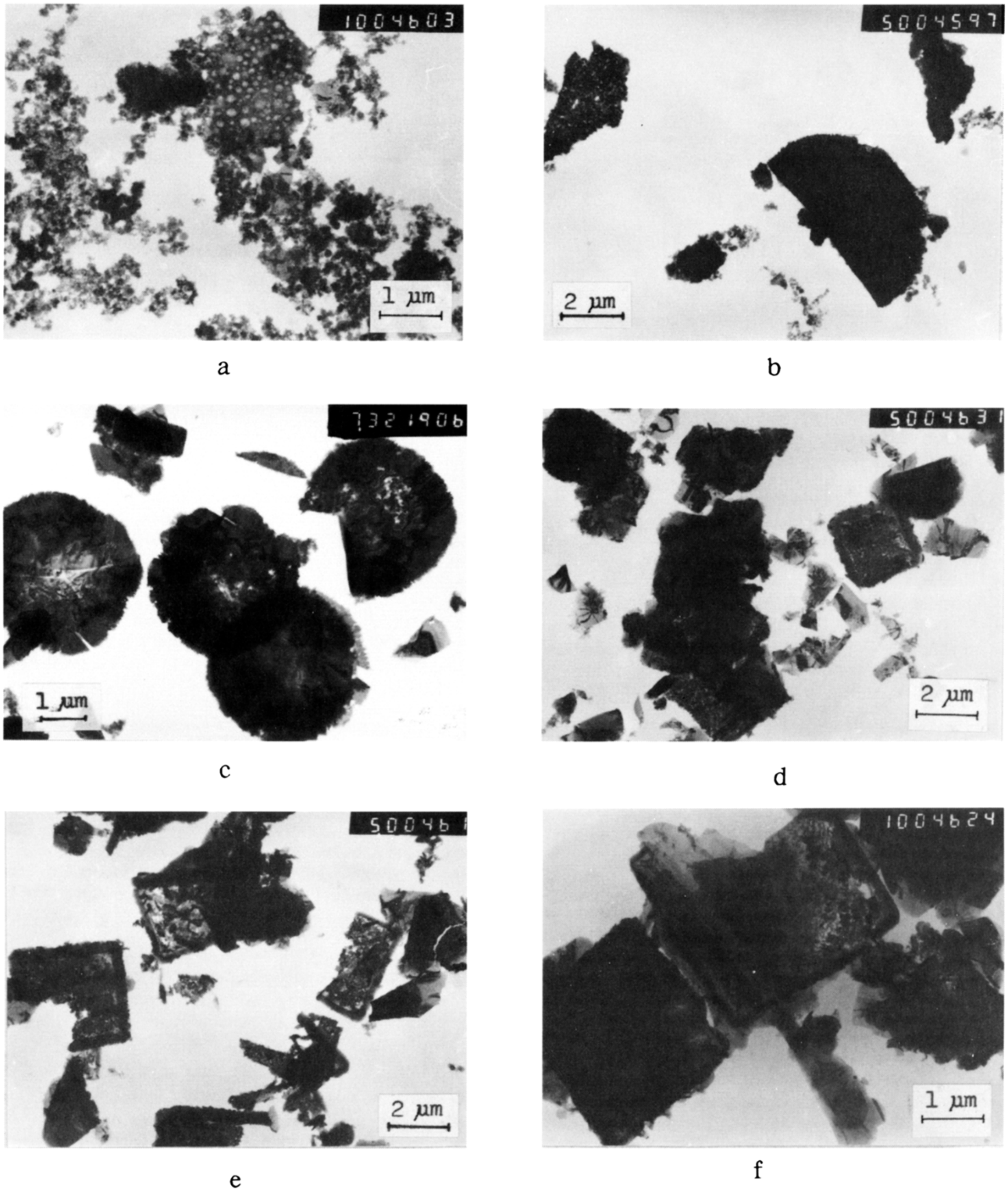


Figure 5. Electron micrographs of products formed in the feedstock with various Pb/Ti ratios: (a) 1.0, (b) 1.1, (c) 1.5, (d) 2.0, (e) 3.0, and (f) 4.0 (pH of 14.0, at 120 °C for 2 h).

monochromator and by scanning at 1° 2θ min^{-1} with a diffractometer (Model D/max-rA and Dmax-2000, Rigaku Co., Tokyo, Japan) to determine the phase of the crystalline products. The morphology of the products was observed using transmission electron microscopy (TEM) (Model JEM-200 CX,JEOL,Ltd., Tokyo, Japan) and scanning electron microscopy (SEM) (Model KYKY-1000B, Beijing, China). Thermal gravimetric analysis (TG) and differential thermal analysis (DTA) were conducted using a thermal analyzer (Rigaku, Japan). The Raman spectra were detected with a Bruker FRA 106 FT-Raman accessory using a Nd:YAG laser (λ = 1064 nm, 200 mW) (Bruker Instrument Inc.). The composition of the crystalline PT(SS)-1 was determined using the chemical analysis method.

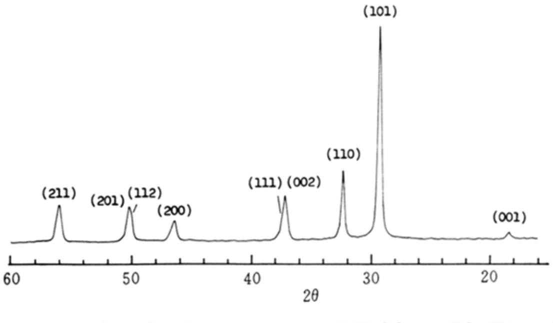
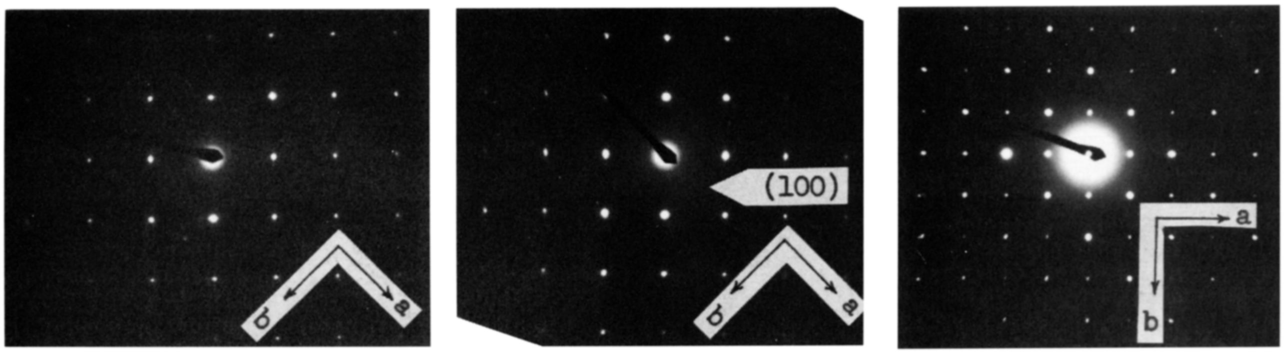


Figure 6. Indexed XRD pattern of PT(SS)-1 (Pb/Ti ratio = 2.0, pH of 14.0, at 120 °C for 2 h).



(a) (b) (c)

Figure 7. Electron diffraction patterns of PT(SS)-1 (a, b) and $PbTiO_3$ (c) in the [001] direction.

Results and Discussion

Influence of Reaction Conditions. We examined the influences of reaction temperature, pH in reaction medium, and Pb/Ti ratio in feedstock on the formation of reaction products.

Reaction Temperature. The effect of reaction temperature on the formation of PT(SS) was examined in the range 100–160 °C, using a Pb/Ti ratio of 2.0, a KOH solution with a pH of 14.0 as reaction medium, and a reaction time of 2 h. The XRD phase analysis showed that the PT(SS) crystallite began to form at ca. 100 °C. When the reaction temperature reached 110 °C, the formation of PT(SS) crystallite is almost complete. If the reaction temperature was higher than 130 °C, the tetragonal perovskite $PbTiO_3$ phase began to appear. The product is mainly the tetragonal perovskite $PbTiO_3$ at 160 °C. The XRD patterns of products formed at 110–160 °C are illustrated in Figure 1. It can be seen that the optimum temperature range for forming PT(SS) is 110–120 °C under the above-mentioned conditions.

pH in Reaction Medium. The pH in reaction medium has a significant effect on the formation of different lead titanate phases. KOH solution was used to adjust the pH in reaction medium. We have examined by XRD and TEM the products formed in the pH range 11.4–14.2 using a Pb/Ti ratio of 2.0, reaction temperature of 120 °C, and reaction time of 2 h.

The experimental results are shown in Figure 2. When pH is <13, no PT(SS) is formed. The product is amorphous at pH = 11.4. Increasing the pH to 12.4 the tetragonal red PbO phase (litharge) appeared, but there was also an amorphous phase. When pH is >13, the PT(SS) began to form, but its XRD peaks are remarkably broad. It could be the result of the coexistence of PbO–TiO_2 solid solution with different compositions and the effect of small crystallite sizes. The major PbO–TiO_2 solid solution phase in the product was PT(SS)-1 (a = 3.91 Å, c = 4.83 Å), and it gradually increased with increasing pH. As pH reached 13.7, besides the major phase, PT(SS)-1, a new PbO–TiO_2 solid solution, PT(SS)-3 (a = 3.90 Å, c = 4.25 Å), appeared. These results were obtained at three different times. With increasing reaction time, the content of PT(SS)-3 in the product would increase. From its broad XRD peaks, the grain size of PT(SS)-3 must be very small (<20 nm). When pH was 13.9–14.2 the PT(SS)-1 phase was obtained, yet there was another PT(SS)-2 phase coexisting with PT(SS)-1 (see next section).

$Pb(OH)_2$ is an amphoteric compound. It begins to be dissolved partly as pH > 11, and its solubility increases markedly as pH > 13 due to formation of the complex ion $Pb(OH)_3^-$ (its overall stability constant log β = 13.3).[11] We observed that if pH is > 13, $Pb(OH)_2$ in the feedstock is easily converted to a metastable orthorhombic PbO (massicot) at room temperature. If pH is <13, the $Pb(OH)_2$ is stable at room temperature, but it can change to the stable tetragonal PbO (litharge) at higher temperature (>100 °C). PT(SS) can be formed under certain hydrothermal conditions only if the metastable PbO (massicot) is present in the feedstock (i.e., the formation of PT(SS) is linked with the presence of PbO (massicot)). It was determined that the solubilities of PbO (massicot) and PbO (litharge) in 1 M KOH solution at room temperature were ca. 0.8 and 0.04 g/100 mL, respectively (i.e., the solubility of PbO (massicot) in KOH solution was much more than that of PbO (litharge)). The PT(SS) is hardly dissolved in KOH solution. Thus, in the case of high pH, Pb species with higher solubility can diffuse into the framework of hydrous titanium dioxide ($TiO_2 \cdot xH_2O$) sol-state precipitate to form PT(SS) by reaction, while the metastable PbO (massicot) can be dissolved to replenish the Pb species in solution. This could be the reason that PT(SS) can form only under high pH conditions.

Pb/Ti Ratio. In addition to reaction temperature and pH in reaction medium, the Pb/Ti ratio in the feedstock also has a great effect on the formation of the product phase. To ensure that the reaction was carried out completely, the reaction conditions employed were a pH of 14 and a reaction temperature of 120 °C for 2 h. The range of Pb/Ti ratios examined was 1.0–4.0. The XRD patterns for the products are shown in Figure 3. It can be seen from Figure 3 that the PT(SS)-1 appears only if a Pb/Ti ratio is >1.0. If the Pb/Ti ratio is <1.0, the product is amorphous even if pH is increased to 14.2. With increasing Pb/Ti ratio (from 1.2 to 2.0) in the feedstock, the half-height breadth (HHB) of the diffraction peak for products gradually increased, while their XRD 2θ angle slightly decreased. The related results are listed in Table 1. When the Pb/Ti ratio is >1.4, it can be observed that a new phase, PT(SS)-2, began to appear from the XRD peak near 2θ = 36.7°, and the cell parameters of PT(SS)-2 slightly increased with increasing Pb/Ti ratio in the feedstock. The XRD pattern of PY(SS)-2 overlapped in part with that of PT(SS)-1, and therefore the diffraction peaks of products broadened. When these samples were treated by 5 v/v % dilute acetic acid solution (10 mL/g

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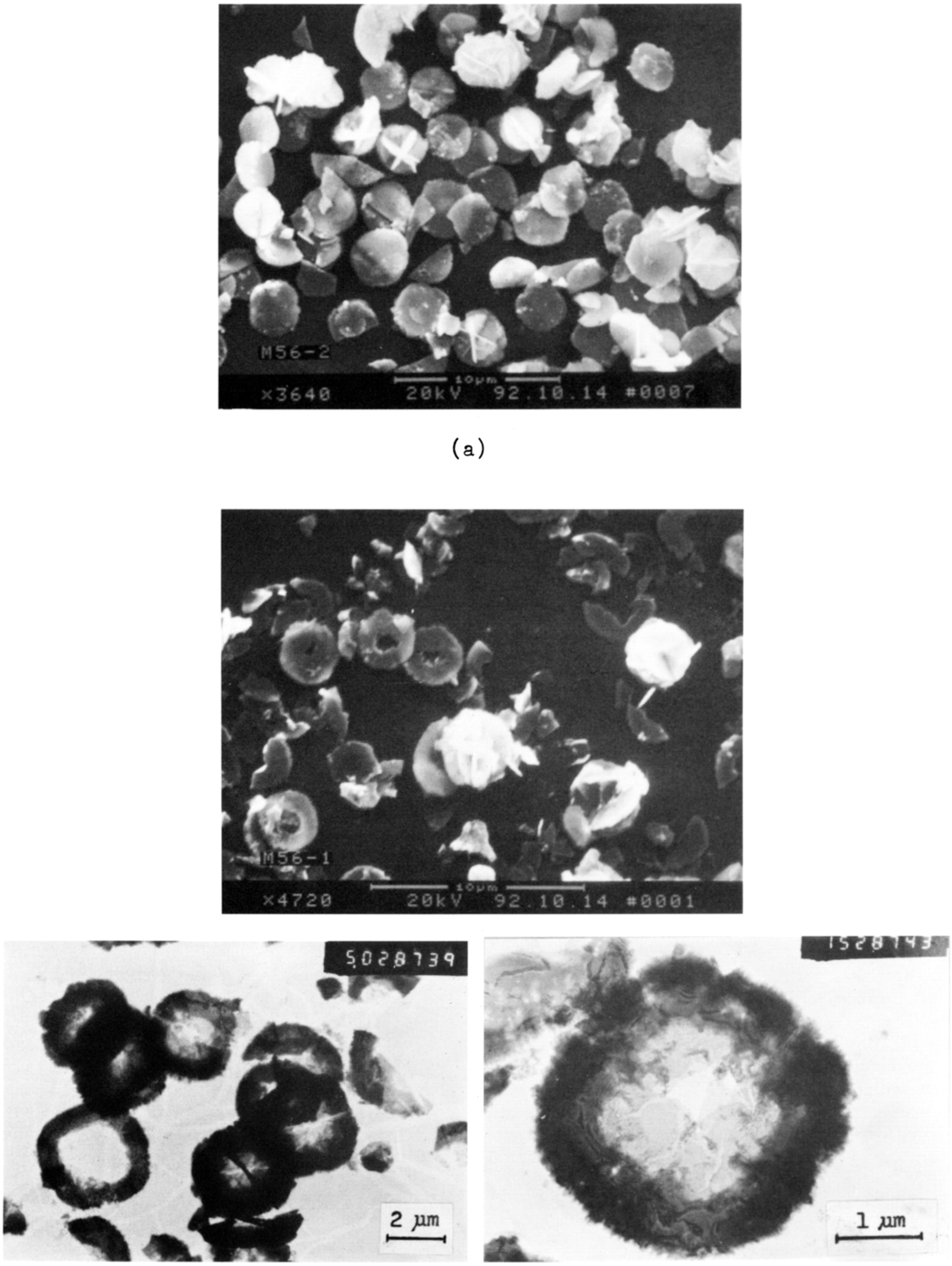
[11] Inczedy, J. *Applications of Complex Equilibria*; Ellis Horwood Limited: Chichester, 1976; p 323.



(a)

(b)

Figure 8. Electron micrographs (SEM and TEM) of PT(SS)-1 particles: (a) before and (b) after treatment by acetic acid.

sample), the HHB of diffraction peaks narrowed obviously and were all close to that of the sample with Pb/Ti ratios of 1.2–1.4. Their XRD 2θ angle also returned to higher angle. These results also are listed in Table 1. The XRD patterns of a typical sample (Pb/Ti = 2.0) before and after treating by dilute acetic acid are shown in Figure 4a,b. For easy comparison, the XRD pattern of the sample (Pb/Ti = 1.2) is shown in Figure 4c. From Figure 4, it can be seen that the XRD peak near $2\theta = 36.7°$ disappeared after treating with dilute acetic acid, and the other XRD peaks

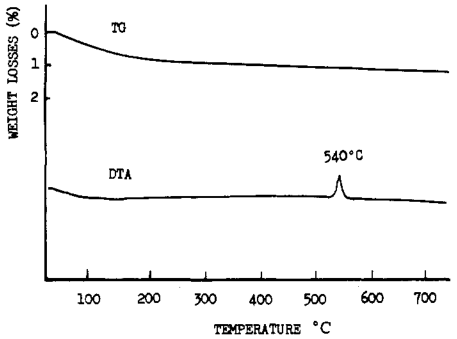


Figure 9. Thermal analysis diagram of PT(SS)-1.

also narrowed. In the above dilute acetic acid, there are a lot of Pb species, but few Ti species are detected. It indicated that a part of PbO in the PT(SS)-2 phase can be dissolved by dilute acetic acid while the PT(SS)-2 changed into the PT(SS)-1. The PT(SS)-2 could be a PbO–TiO_2 solid solution with higher PbO component, and its composition is variable within a certain range. From relatively lower diffraction peak and higher background in Figure 4c, it indicated that the sample (Pb/Ti = 1.2) was not pure and could contain unreacted amorphous titanium species, but no PT(SS)-2 phase was in it. When Pb/Ti ratio was equal to 4.0, the XRD pattern of PT(SS)-2 became more distinct. In this case, both phases PT(SS)-1 and PT(SS)-2 coexisted in the product. The cell parameters *a* and *c* of PT(SS)-2 were ca. 3.95 and 4.93 Å, respectively. The color of products changed gradually from light-yellow to orange with increasing Pb/Ti ratio in the feedstock. When these samples were treated by dilute acetic acid, their color turned light-yellow again. From above results, it can be seen that the composition of product will become more complex with increasing Pb/Ti ratio in the feedstock.

The Pb/Ti ratio in the feedstock also has an effect on the morphology of product particles. The electron micrographs of products formed in the feedstock with various Pb/Ti ratios are shown in Figure 5. When Pb/Ti = 1.0, the products are mainly amorphous small particles. When Pb/Ti ratio is <1.5, the particles have a discoid or fan morphology. As Pb/Ti ratio is >1.5, the morphology of particles changes gradually from discoid to square. From Figure 5 it can be seen that the submicroscopic structure of the particle is becoming more heterogeneous with increasing Pb/Ti ratio in the feedstock. It could be concerned with the cocrystallization of PT(SS) with different compositions. From Figure 5 it also can be seen that the larger particles of PT(SS) are actually polycrystals, and only a few in PT(SS) are single crystals. Some particles were broken by ultrasonic dispersion before examination by TEM.

Composition, Structure, and Transformation of PT(SS). The XRD analysis indicated that the sensitivity for detecting the PbO phase was higher than 1 wt %. Also, no single PbO phase was detected in the XRD patterns of PT(SS) samples. Therefore, it can be affirmed that there was no free crystalline PbO phase in the PT(SS) products.

The PbO–TiO_2 solid solution formed under different hydrothermal conditions has a variable composition within a certain range, and the PT(SS) with different composition could coexist in the product. In these experimental conditions, the preferentially formed solid solution phase was PT(SS)-1. According to above experimental result, the PT(SS)-2, a phase coexisting with PT(SS)-1 in products, can be dissolved by dilute acetic acid to obtain a pure PT(SS)-1 phase. When the sample with Pb/Ti ratio = 2.0 was treted by 5 v/v % acetic acid of 4, 6, 8, and 10 mL/g sample, the relevant contents of dissolved species were 0.18, 0.22, 0.23, and 0.23 g/g sample, respectively. The XRD peaks of the treated samples were getting higher and sharper. Therefore, it could be considered that the sample treated using 5 v/v % acetic acid of 10 mL/g sample was a pure crystalline phase, PT(SS)-1. When the above-treated sample was treated using more concentrated acetic acid (>10 v/v %), it can be further dissolved while its XRD intensity decreased and the background increased. It meant that the framework of PT(SS)-1 was collapsing gradually with removal of the PbO component in PT(SS).

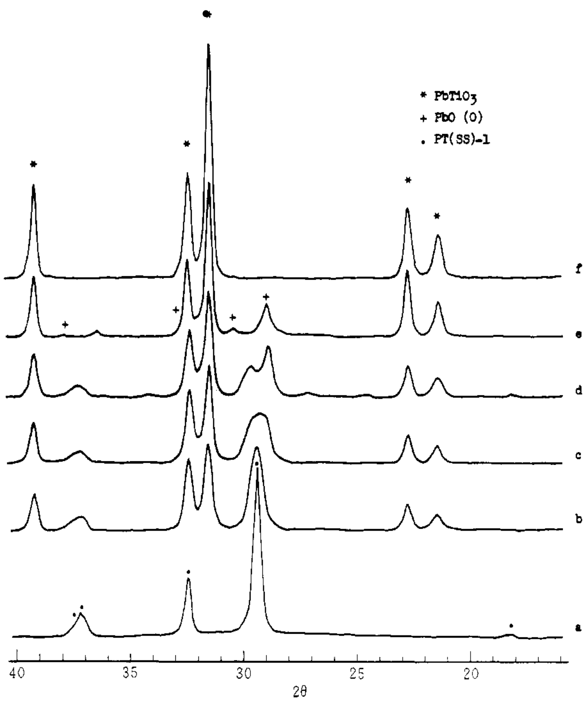


Figure 10. XRD patterns of samples heated at different conditions: (a) PT(SS)-1; (b) 650 °C, 1 h; (c) 650 °C, 2 h; (d) 650 °C, 3 h; (e) 750 °C, 3 h; (f) the sample after removing PbO by acetic acid–$PbTiO_3$.

The PT(SS)-1 is a light-yellow tabular crystallite. Its composition determined using chemical analysis method is $PbTi_xO_{1+2x}$ ($x = 0.80 \pm 0.02$) (no K species was detected). The XRD analysis indicates that the PT(SS)-1 belongs to the tetragonal system. Its indexed XRD pattern is presented in Figure 6. The indexed powder XRD data are listed in Table 2. From Table 2, it can be seen that the observed plane distance (d_o) is in good agreement with the calculated plane distance (d_c). The cell parameters of PT(SS)-1, corrected by the least-squares method, are as follows: a = 3.911 Å, very close to that of $PbTiO_3$, and c = 4.831 Å (1 Å = 0.1 nm), which is longer than c axis of $PbTiO_3$ (a = 3.899 Å, c = 4.1532 Å; see JCPDS-6-452). Figure 7 shows the electron diffraction patterns (EDP) of PT(SS)-1 and $PbTiO_3$ in the [001] direction. It can be observed from Figure 7a,b that the intensity of diffraction points which have $H + K = 2n + 1$ indexes is zero or very weak in the EDP of PT(SS)-1. Comparing parts a and c of Figure 7, the lattice parameter a of PT(SS)-1 and that of $PbTiO_3$ are very close to each other, which is consistent with the results of XRD. The density (D) of PT(SS)-1 was determined to be 6.39 ± 0.02 g cm^{-3} by the specific

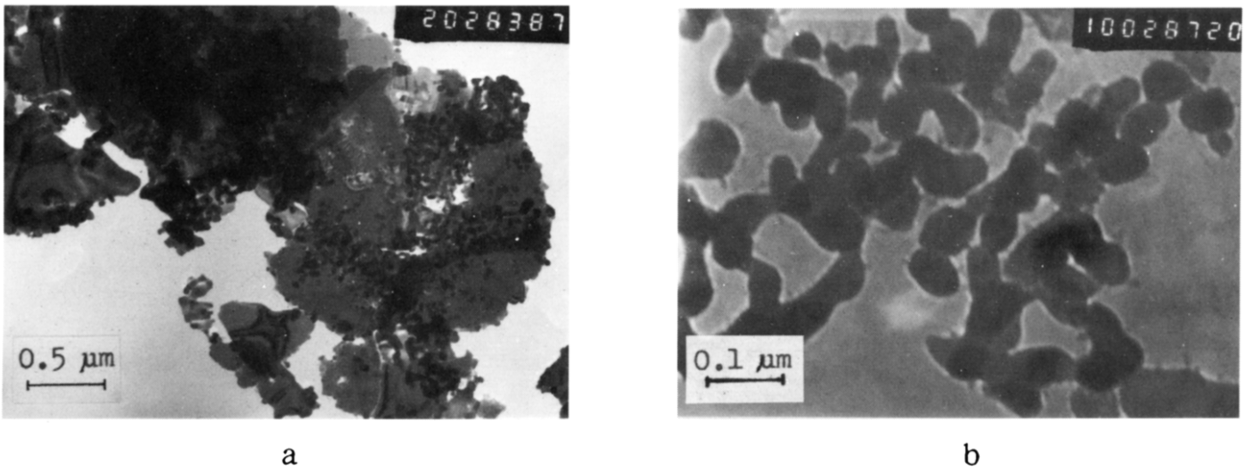


Figure 11. Electron micrograph of the sample (heated over 750 °C): (a) before and (b) after dissolving PbO by acetic acid.

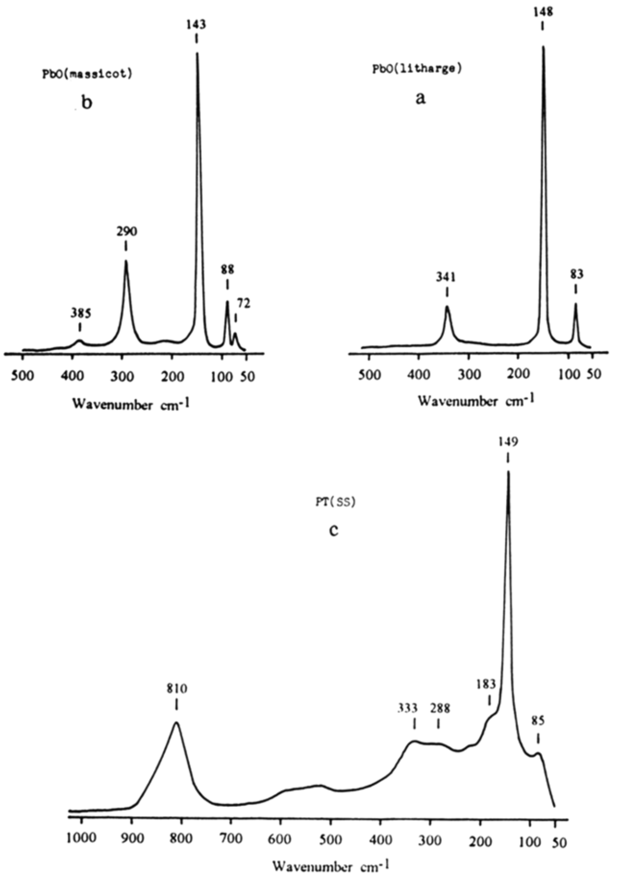


Figure 12. Raman spectra of (a) PbO (litharge), (b) PbO (massicot), and (c) PT(SS).

gravity bottle method. The number of $PbTi_xO_{1+2x}$ ($x = 0.80 \pm 0.02$) units (Z) in a unit cell was calculated from the following formula

$$Z = \frac{DV}{M_{PbO} + 0.80M_{TiO_2}} = \frac{6.39 \times (3.911)^2 \times 4.831 \times 10^{-24}}{287.1/(6.023 \times 10^{23})} = 0.99$$

where V is the cell volume of PT(SS)-1, M is the molecular weight, and N is the Avogadro constant. Therefore, each cell contain 1 unit of $PbTi_xO_{1+2x}$ ($x = 0.80 \pm 0.02$). The TiO_2 unit is statistically distributed in the cell of PT(SS)-1.

The structure of the most PT(SS)-1 particles is imperfect. When the PT(SS)-1 particle was dissolved by acetic acid, the dissolving rate in the center of particle was faster than that on the edge of the particle, resulting in a doughnut-shaped particle being formed (Figure 8). This indicates that there are more structural defects in the central part of the particle.

The TG–DTA curves of the PT(SS)-1 are shown in Figure 9. Besides a very small exothermic peak near 540 °C, no other significant exothermic or endothermic peaks were observed in the range 100–750 °C. The exothermic peak could be due to the transformation from PT(SS)-1 to $PbTiO_3$. The weight loss is ca. 1.2 wt %, and it could be due to either adsorbed water or organics. The XRD patterns of PT(SS) samples treated at different temperature and time are shown in Figure 10. The PT(SS) is converted gradually into perovskite $PbTiO_3$ and PbO (litharge or massicot) over 550 °C. The PT(SS) with a different composition has a similar result, with only the content of $PbTiO_3$ formed being different. As temperature is increased, the conversion will be accelerated. The (101) reflection of PT(SS)-1 ($2\theta = 29.34°$) broadened remarkably as the $PbTiO_3$ phase was formed. This could be due to the collapse of the structural framework of PT(SS)-1 and the change of composition in the solid solution as the $PbTiO_3$ is formed. When the temperature was over 750 °C, the PT(SS) was completely converted into the perovskite $PbTiO_3$ and the PbO (massicot or litharge) phase (Figure 10e). If the sample treated over 750 °C was washed with 10 v/v % acetic acid, the PbO is removed to obtain pure perovskite $PbTiO_3$ fine crystallites with a diameter usually less than 100 nm (Figure 10f). Figure 11 shows the electron micrographs of the sample (treated over 750 °C) before (a) and after (b) dissolving PbO by acetic acid. From Figure 11b, it can be seen that the agglomeration decreased remarkably in the $PbTiO_3$ fine powders due to the separating effect of surrounding PbO. The combination of heat treatment and acetic acid wash could provide a new procedure for preparing ultrafine $PbTiO_3$ particles without agglomeration.

The Raman spectra of PbO (litharge), PbO (massicot), and PT(SS-1) are shown in Figure 12 for comparison. PT(SS) formed under different conditions of Pb/Ti ratio (1.2–2.0) have the same Raman spectra on the whole. A sharp band at 149 cm^{-1} was observed for PT(SS)-1, and it was consistent with the characteristic band of PbO (litharge) at 148 cm^{-1} (a relevant band for PbO (massicot) was at 143

cm^{-1}). It indicated that the structural framework formed by Pb–O bonds in PT(SS)-1 is closer to that in PbO (litharge). There is a broad band near 810 cm^{-1}, which was not observed in PbO and TiO_2.[12] This band could be concerned with a certain Ti–O vibration mode.

From the above discussion, it is likely that the structure of PT(SS) is between the tetragonal perovskite $PbTiO_3$ (a = 3.899 Å, c = 4.153 Å) and the tetragonal PbO (a = 3.9729 Å, c = 5.0192 Å). The tetragonal PbO (litharge) has a layer structure,[13] and the space between its layers is large enough to contain the TiO_2 unit. As the TiO_2 unit is incorporated into an interlayer of PbO (litharge), the distance (c) between layers will shorten due to the enhancement of interlayer binding force, while the cell parameter a of PbO (litharge) will only show a slight change. Thus, the cell parameter a of PT(SS) with different composition is closer, and their cell parameter c decreases with increasing content of TiO_2 in PT(SS). When PT(SS) is heated, Ti^{4+} ions in it shift and concentrate accompanying the displacement of Pb^{2+} and O^{2-} ions to form $PbTiO_3$, while the Ti-deficient PT(SS) returns to the metstable PbO (massicot) or the PbO (litharge).

Conclusion

In the PbO–TiO_2 system, several Pb–Ti complex oxides and solid solutions with various composition, structure, and morphology can be formed under different hydrothermal reaction conditions. A new type of PbO–TiO_2 solid solution phase, PT(SS)-1, preferentially formed under a relatively low reaction temperature (110–120 °C), high pH (>14), and Pb/Ti ratio >1.2. This PT(SS)-1 is a light-yellow crystallite with a tetragonal structure and tabular morphology, and its cell parameters are a = 3.911 Å and c = 4.831 Å. Its composition is $PbTi_xO_{1+2x}$ (x = 0.80 ± 0.02). The Pb/Ti ratio in PT(SS) could be changed within a certain range. The PT(SS) is converted gradually into the tetragonal perovskite $PbTiO_3$ and PbO (litharge or massicot) over 550 °C. A combination of heat treatment and acetic acid wash of PT(SS) could provide a new method for preparing ultrafine $PbTiO_3$ particles.

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