Reactions between PbO and TiO_2 under Hydrothermal Conditions

Shoji KANEKO and Fumio IMOTO

Department of Industrial Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu 432

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The phase relation of products obtained by the reaction between PbO and TiO_2 under hydrothermal conditions up to 500 °C and 500 kg/cm² for 5h has been investigated. The yield and crystallographic properties of purified $PbTiO_3$ depend upon the PbO/TiO_2 mole ratio (Pb/Ti ratio) in raw mixtures as well as the reaction temperature. Both $PbTiO_3$ and $PbTi_3O_7$ are synthesized at a remarkably low temperature under hydrothermal conditions, as compared with the ignition process in air. Pure and well-crystallized $PbTiO_3$ is obtained by heat-treating above 400 °C at Pb/Ti ratios greater than 1.0 and by dissolving excess PbO with acetic acid. $PbTi_3O_7$ coexists occasionally with $PbTiO_3$ to some extent at Pb/Ti ratios less than 1.0, but appears as a single phase in the temperature range 100—450 °C at the Pb/Ti ratio 0.33. The unit cell volume of $PbTiO_3$ prepared at lower temperature is considerably large, suggesting a loosely-packed structure. The compound is always of tetragonal form containing no metastable cubic form.

Three compounds, Pb_2TiO_4,[1] $PbTiO_3$,[2] and $PbTi_3O_7$[3] have been reported in the system PbO–TiO_2, although the phase diagram has not been completed so far. The existence of Pb_2TiO_4 was denied by Matsuo and Sasaki.[4] Aykan[3] found a novel compound $PbTi_3O_7$ by the reaction between PbO and TiO_2 in the TiO_2-rich region. Kato *et al.*[5] analyzed the structure in detail using a single crystal prepared by a flux method. Lobachev[6] also found a new phase in the system PbO–TiO_2–KF–H_2O under hydrothermal conditions and determined the composition as $PbTi_3O_7$ by chemical analysis. His X-ray data, however, were insufficient, differing from those of other investigators.[3,5]

$PbTiO_3$ has a tetragonal form at room temperature, the axial ratio (c/a=1.065) being the largest of perovskite-type compounds. It is transformed reversibly from tetragonal to cubic around 490 °C (Curie point),[7] and is important as a component of complex perovskite-type compounds, especially piezoelectrics such as PZT ceramics.[8]

In previous papers[9,10] dealing with the reaction of oxides under hydrothermal conditions, it was shown that the crystallization and anatase-rutile transformation of TiO_2 was markedly accelerated, and fine-grained (below 200 Å) $BaTiO_3$ of tetragonal form easily synthesized. A hydrothermal reaction seems to be suitable for the preparation of inorganic powders containing a volatile component such as PbO.

We have investigated the phase relation of the products by the reaction between PbO and TiO_2 in order to find the optimum conditions for the preparation of pure $PbTiO_3$ under hydrothermal conditions.

Experimental

Starting Materials and Procedures. Hydrous titanium dioxide (TiO_2: 83.6 wt%, H_2O: 10.8 wt%, SO_3: 5.6 wt%) was prepared by the neutralization of titanium sulfate with aqueous ammonia (sulfate-process). This compound (TiO_2: 91.9 wt%, H_2O: 8.1 wt%) was also prepared by the hydrolysis of titanium tetrachloride with heating at about 100 °C (chloride-process). Both of them were considered to be the most reactive source of TiO_2.

Hydrous titanium dioxide and guaranteed reagent lead monoxide (purity 99.0 wt%, Koso Chemical Co., Ltd.) were weighed to prepare a mixture of a certain PbO/TiO_2 mole ratio (Pb/Ti ratio). A gold vessel containing raw materials and water was placed in a cylindrical autoclave of 100 cm³ volume, and subjected to various conditions up to 500 °C and 500 kg/cm² for 5 h. Products were washed several times with 5% acetic acid and distilled water by decantation in order to remove excess PbO, then dried at 80 °C in an oven.

Chemical Analysis. Dried products were analyzed by the following method. About 0.6 g of a sample is accurately weighed and dissolved in 20 ml of hot sulfuric acid with 6 g of ammonium sulfate. After cooling, lead sulfate is precipitated by addition water and filtered off for weighing. Hydrous titanium dioxide is precipitated from the filtrate by addition of aqueous ammonia. After filtration and ignition, the precipitate is weighed as total TiO_2, *i.e.*, unreacted TiO_2 and TiO_2 in $PbTiO_3$. The yield of $PbTiO_3$ is calculated by

$$\text{Yield (\%)} = \frac{\text{Weight of } TiO_2 \text{ in } PbTiO_3 \text{ equimolar to } PbSO_4}{\text{Weight of total } TiO_2} \times 100. \quad (1)$$

X-Ray Diffraction. The products were identified by means of X-ray diffraction using Geigerflex, Type D-2* with nickel-filtered Cu $K\alpha$ radiation. The crystallite size was calculated from Scherrer's equation[11] with Warren's correction, employing half value widths of $PbTiO_3$ (110) and Si (111) reflections. Lattice constants of tetragonal $PbTiO_3$ were determined by (110) and (200) reflections using Si as an internal standard.

Results and Discussion

Reaction Products under Various Conditions. Poorly-crystallized $PbTiO_3$ was formed at Pb/Ti ratio 1.0 and 200 °C, with an unknown phase X and a small amount of lead sulfate attributed to the sulfate ion contained in hydrous titanium dioxide[9] (Fig. 1). Above 300 °C, the unknown phase disappeared with increase of $PbTiO_3$. $PbTiO_3$ appeared as a single phase in a considerably wide temperature range. Under hydrothermal conditions, the synthesis of $PbTiO_3$ was initiated at a temperature as low as 170 °C, which was much lower than 550 °C in the ignition process reported by Okazaki *et al.*[12] and somewhat higher than 60 °C in the wet synthesis of $BaTiO_3$.[13] Figure 2 shows a similar

* Rigaku Denki Co., Ltd. Tokyo, Japan.

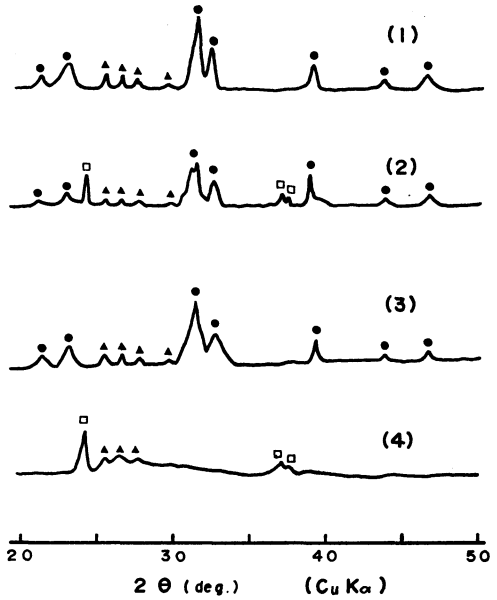

Fig. 1. X-Ray diffraction patterns of the products. (1) Pb/Ti ratio=1.0, 300 °C, (2) Pb/Ti ratio=1.0, 200 °C, (3) Pb/Ti ratio=0.8, 300 °C, (4) Pb/Ti ratio=0.8, 200 °C. ●: $PbTiO_3$, ○: $PbTi_3O_7$, ▲: $PbSO_4$, □: unknown phase.

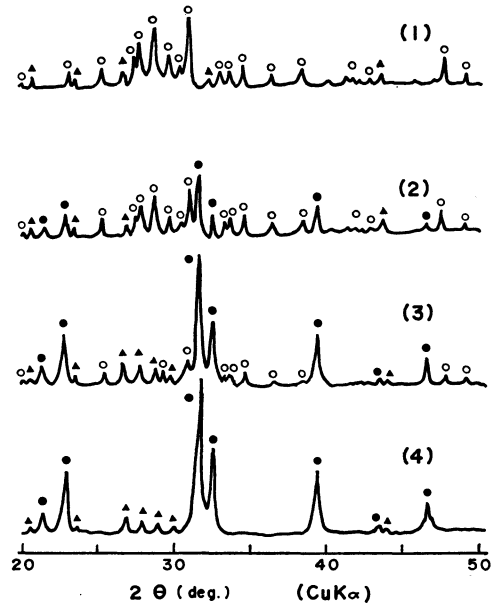

Fig. 2. X-Ray diffraction patterns of the products at various Pb/Ti ratios and 400 °C. (1) Pb/Ti ratio=0.33, (2) Pb/Ti ratio=0.5, (3) Pb/Ti ratio=0.7, (4) Pb/Ti ratio=1.0. ●: $PbTiO_3$, ○: $PbTi_3O_7$, ▲: $PbSO_4$.

phase relation at 400 °C. $PbTi_3O_7$ was observed as a single phase at Pb/Ti ratio 0.33. $PbTi_3O_7$ and $PbTiO_3$ coexisting at Pb/Ti ratios 0.45—0.7, the latter predominated high Pb/Ti ratio.

The relationship between Pb/Ti ratio, temperature and phase is shown in Fig. 3. The diagram is divided into four zones: (1) coexistence of amorphous and unknown phases, (2) $PbTiO_3$, (3) $PbTi_3O_7$, and (4) coexistence of $PbTiO_3$ and $PbTi_3O_7$. It is remarkable that $PbTi_3O_7$ was solely obtained in a wide and low temperature range 100—450 °C under hydrothermal conditions, as compared with the narrow temperature range 800—850 °C in the ignition process in the air.[3]

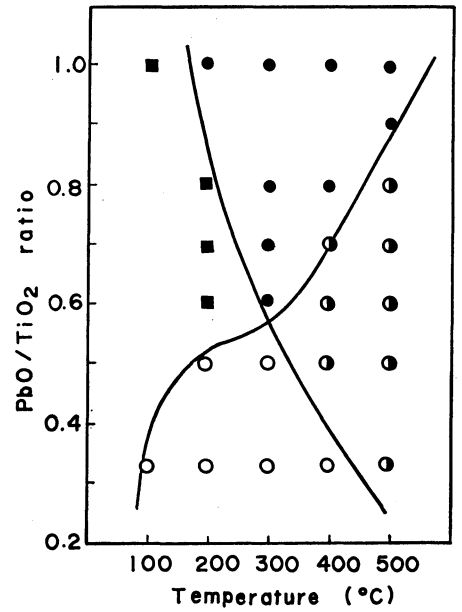

Fig. 3. Phase relation in the reaction between PbO and TiO_2 under hydrothermal conditions. ■: Amorphous and unknown phase, ●: $PbTiO_3$, ○: $PbTi_3O_7$, ◑: $PbTiO_3+PbTi_3O_7$.

Crystallographic Properties of $PbTiO_3$. In the lattice constants of $PbTiO_3$, a for the specimens treated at lower temperatures is slightly smaller than the value

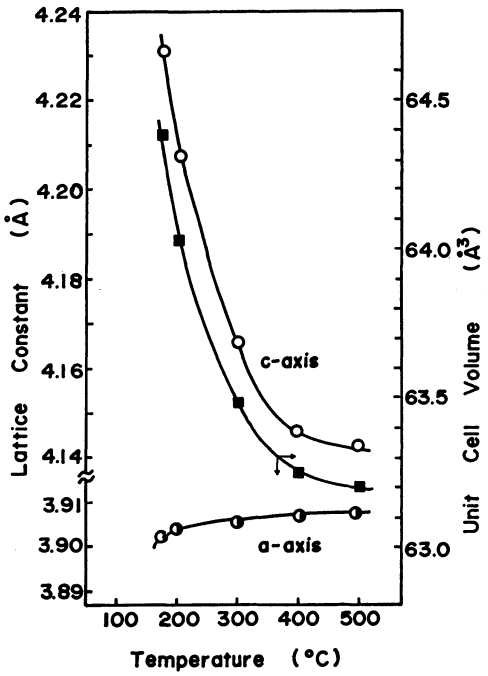

Fig. 4. Variations of lattice constants and unit cell volume of hydrothermal $PbTiO_3$ with reaction temperature.

reported** whereas c is relatively larger (Fig. 4), indicating that the unit cell expands to the direction of c-axis by loose packing of each ion. With increase in temperature, c decreases markedly and the axial ratio (c/a) gradually approaches the value 1.065,** the unit cell volume (a^2c) changing in a similar way to c. In contrast, hydrothermal $BaTiO_3$, as well as wet-synthesized $BaTiO_3$,[13,14] are of cubic form presumed to be a metastable state, being transformed into tetragonal form with increase in temperature.[11] The difference between $PbTiO_3$ and $BaTiO_3$ seems to arise primarily from the difference in ionic properties of lead and barium. The tolerance factor, or the fraction of ion packing, in $PbTiO_3$ is smaller than that in $BaTiO_3$; each ion in the former moves more easily around than that in the latter in the crystal lattice. In addition, lead ion is more readily polarized than barium ion. The anisotropy of the crystal structure is more enhanced in $PbTiO_3$.

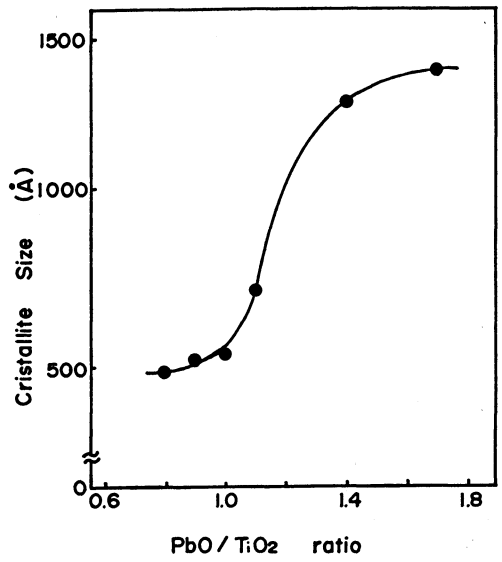

Fig. 5. Crystallite size of hydrothermal $PbTiO_3$ at 500 °C as a function of Pb/Ti ratio.

The crystallite size of $PbTiO_3$ increases from 500 to 1400 Å with increase in the Pb/Ti ratio (Fig. 5). The size of starting hydrous titanium dioxide is about 80 Å, the reaction temperature being too low to expect crystal growth by the solid state reaction. Thus the crystal growth suggests that the hydrothermal reaction proceeds through the solution-precipitation mechanism based on the large dissolving power of hydrothermal media.

TiO_2 obtained by the chloride-process was also examined as a starting material to avoid the formation of the by-products resulting from impurities. As shown in Fig. 6, the specimens prepared from TiO_2 by the chloride-process generally give sharper X-ray profiles than those for the specimens prepared from TiO_2 by the sulfate-process. No preheating TiO_2 by the sulfate-process contains both H_2O and SO_3. It loses almost H_2O at about 570 °C, then releasing SO_3 and crystallizes completely. On the other hand, no preheating TiO_2 by the chloride-process contains H_2O alone and loses it at 300 °C.[9] When used no preheating TiO_2 or TiO_2 preheated at 600 °C, the X-ray profiles of $PbTiO_3$ were sharp [Fig. 6(1)], but when used TiO_2 preheated at 400 °C, the profile was broad. When used no preheating TiO_2, the profile was very sharp, but when used TiO_2 preheated over 400 °C, the profiles were rather broad [Fig. 6(2)]. If we assume that the sharper X-ray profile

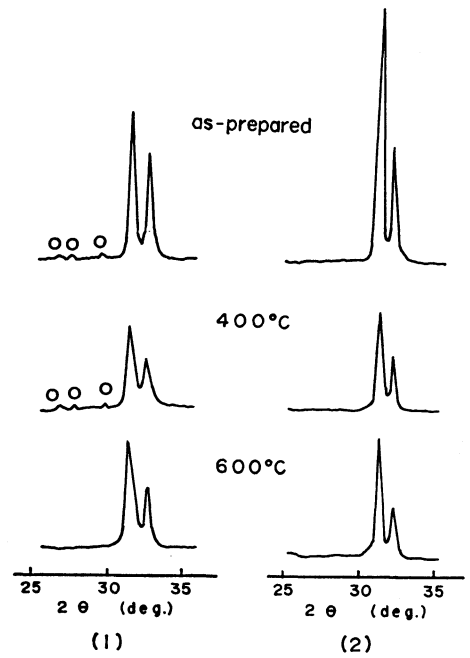

Fig. 6. X-Ray profiles of hydrothermal $PbTiO_3$ prepared from two kinds of TiO_2 pre-heated at various temperatures. (1) TiO_2 prepared by the sulfate-process, (2) TiO_2 prepared by the chloride-process. ○: $PbSO_4$.

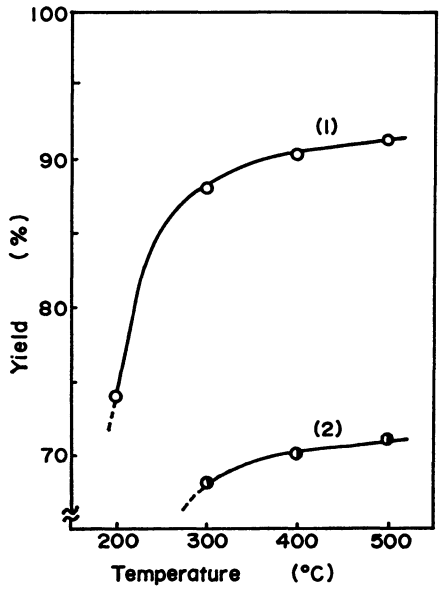

Fig. 7. Relationship between yield of hydrothermal $PbTiO_3$ and reaction temperature. (1) Pb/Ti ratio=1.0, (2) Pb/Ti ratio=0.8.

** From "Powder Diffraction File, Card No. 4-0477," lattice constants a and c of $PbTiO_3$ are 3.899 Å and 4.153 Å, respectively. Unit cell volume, $a^2c=63.138$ Å^3 and axial ratio, $c/a=1.065$ are calculated from these values.

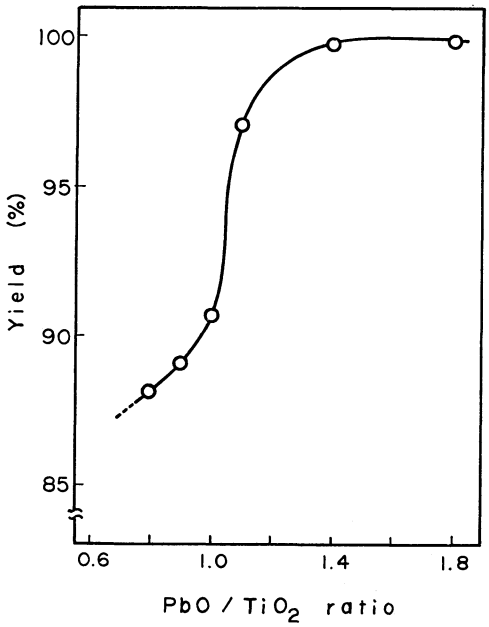

Fig. 8. Relationship between yield of hydrothermal $PbTiO_3$ and Pb/Ti ratio at 500 °C.

is related to better crystallinity, OH or H_2O on the surface of TiO_2 promotes crystallization, while the sulfate ion retards it. For the preparation of pure and well-crystallized $PbTiO_3$ it is advantageous to use no preheating TiO_2 by the chloride-process containing much H_2O and no sulfate ion.

Yield of $PbTiO_3$. At the Pb/Ti ratios 0.8—1.0, the yield increases with in temperature, the reaction proceeding almost completely up to 400 °C (Fig. 7). The yield was 90.7% at the Pb/Ti ratio 1.0 and 400 °C. However it is estimated to be over 95% after the correction for the consumption of PbO by the preferential reaction with sulfate ion contained in hydrous titanium dioxide converting to lead sulfate. Figure 8 shows the relation between yield and the Pb/Ti ratio at 500 °C. When the Pb/Ti ratio exceeds 1.0, the yield reaches 100% after the correction described above. The yield changes considerably with the Pb/Ti ratio and reaction temperature.

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