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Peroxide-Based Route Free from Halides for the Synthesis of Lead Titanate Powder

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$PbTiO_3$ has been successfully synthesized at reduced temperatures (500−700 °C) using neither organics (including alkoxides) nor undesirable halides. Water-soluble peroxytitanic complexes $[Ti(OH)_3O_2]^-$ were prepared by the reaction between titanium metal and hydrogen peroxide at $pH = 11$. A solution of lead nitrate was added to the peroxytitanic acid solution and an amorphous precipitate of lead and titanium was formed, which was filtered and washed to eliminate the nitrate ion. The precipitate was calcined between 200 and 700 °C in a closed alumina boat. The precipitate was characterized by ICP, TG, Raman spectroscopy, XRD, and SEM, and the calcined lead titanate was characterized by BET, Raman spectroscopy, XRD, and SEM. The amorphous precipitate showed a small weight loss (11.45%). Powders calcined at temperatures higher than 500 °C showed pure tetragonal $PbTiO_3$ perovskite phase on the XRD patterns and Raman spectra and a large surface area in the range of 6−22 $m^2\ g^{-1}$. The average diameter of the particles was calculated from the SEM image as 100 nm.

Introduction

The perovskite $PbTiO_3$ (referred to as PT) is an important ferroelectric material widely used in the electronic industry, mainly as solid solutions with other lead-based perovskites.[1−4] Although pure PT cannot exist as a well-sintered ceramic body because of its high degree of tetragonality,[5] highly dense samples of solid solutions beteween PT and typical relaxors, like $Pb(Mg_{1/3}Nb_{2/3})O_3$, can be obtained.[1−4]

Much attention has been paid during the past decade to the synthesis of PT by wet-chemical methods,[6−8] for instance, the hydrolysis of double alkoxide of lead and titanium,[9] the mixture of titanium alkoxide and lead acetate[10] or titanium alkoxide and lead glycolate,[11] and the polymerizable complex (PC) method,[12,13] rather than the conventional solid-state reaction technique. However, all of these chemical routes require a large quantity of organics, sometimes reaching almost 80% of the total weight.[14] During the burning of the organics, the local temperature can be higher than the nominal temperature because of the exothermic reaction, resulting in the formation of strongly agglomerated particles.[15]

Another wet-chemical technique, originally called the peroxide-based route (PBR), was developed.[16−18] Safari et al.[19] synthesized PT powder by the peroxide based route where an aqueous solution of hydrogen peroxide, lead nitrate, and titanium tetrachloride was treated with ammonia solution to form a precipitate, which was subsequently heat-treated at 900 °C to obtain crystalline PT powder. Although several alkaline earth titanates, stannates, and zirconates were synthesized using the PBR technique, all of the previously reported studies had several disadvantages relating to the presence of chloride ion, which include (i) possible degradation of electronic properties of the final material due to a small concentration of residual chloride,[20] (ii) poor densification of ceramics due to chloride, (iii) generation of corrosive HCl gas during the processing, and (iv) working under an inert atmosphere to avoid the hydrolysis of metal chlorides.[17,18]

In this article, the synthesis of an amorphous titanium−lead compound from a chloride-free aqueous

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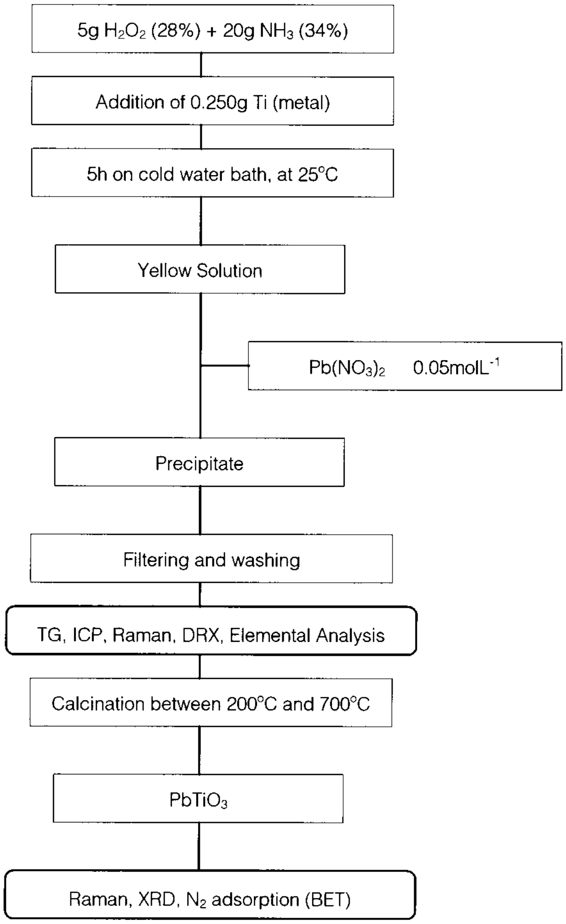

Figure 1. Flowchart for preparing $PbTiO_3$ by a peroxide-based route (PBR). The mole ratio of lead and titanium is (1:1 Pb:Ti).

solution is reported. This amorphous Ti−Pb compound was used as a precursor for the low-temperature synthesis of pure crystalline $PbTiO_3$ without the use of a dry and inert atmosphere.

Experimental Section

The flowchart in Figure 1 summarizes the synthesis of PT. A mixture of 5 g of hydrogen peroxide (28%, Tomiyama High Purity Chemicals, Japan) and 20 g of ammonia aqueous solution (34%, E.L.M., Japan) was prepared. This solution was put into a cold water bath and 0.250 g of titanium metal powder (98%, Wako Pure Chemical Ind. Ltd, Japan) was added. After 5 h, all titanium metal powder was dissolved with gas evolution, changing the color of the solution from colorless to yellow transparent solution containing the peroxytitanato $[Ti(OH)_3O_2]^-$ ion.[21] If the water bath is not used, the solution temperature increses because of the exothermic nature of the titanium dissolution and the hydrogen peroxide will be decomposed. An aqueous solution consisting of 0.729 g of lead nitrate (99.9%, Wako Pure Chemical Ind. Ltd, Japan) and 50 mL of distilled water was quickly added to the peroxytitanato solution, resulting in a vigorous evolution of gas. After a few seconds, an orange precipitate was formed and the solution lost its yellow color. This precipitate was filtered and washed with diluted ammonia solution (10%) to eliminate the nitrate ions. The washed precipitate was dried at 50 °C for 5 h. The dried precipitate was ground and characterized by elemental analysis (carbon, hydrogen, nitrogen, and oxygen), micro-Raman spectroscopy, thermal analysis, and X-ray diffraction. Then, the precipitate was dissolved in diluted hydrochloric acid (HCl, 0.5 mol L^{-1}) and subjected to inductively coupled plasma (ICP) atomic emission spectroscopy. The precipitate was calcined in the temperature range between 200 and 700 °C for 1 h with a heating rate of 10 °C min^{-1} in a closed alumina boat. The calcined powder was characterized by Raman spectroscopy and X-ray diffraction. The surface area was determined by the BET method (Horiba SA-9601, using a mixture of 30% N_2 and 70% He). A model T-64000, Jobin Yvon/Atago Bussan, France/Japan Raman spectrometer with a liquid-nitrogen-cooled CCD detector was used with a 514.5-nm line of Ar laser (visible region) for excitation (10 mW and 10 s of acquisition time). Dynamic thermogravimetry (TG) (TG-DTA-2000/Control model TAPS-1000, MAC-Science, Japan) was carried out in air between 30 and 650 °C, with a heating rate of 1 °C min^{-1}, using 6.25 mg of sample in a platinum crucible. The powders were characterized by XRD, in a 2θ range from 5° to 75°, using Cu Kα radiation (MXP^{3va}, MAC-Science, Japan). The powder morphology as well as the microstructure of the samples were studied with scanning electron microscopy (SEM) (Hitachi S-4500 scanning microscope, Japan).

Results and Discussion

It is known that aqueous solutions of Ti(IV) and hydrogen peroxide give an intense orange color in concentrated solutions, characteristic of peroxo complexes, such as peroxytitanato $[Ti(OH)_3O_2]^-$ ion, often called peroxytitanic acid.[22] The mechanism of the peroxytitanic acid formation from the titanium metal is very complex and not completely understood.[23] However, at pH = 11, the reaction can be described by eq 1:

$$Ti^0 + 3H_2O_2 \rightarrow [Ti(OH)_3O_2]^- + H_2O + H^+ \qquad (1)$$

Hydrogen peroxide in excess is necessary to stabilize the solution of peroxytitanic acid. The excess of H_2O_2 decomposes slowly with evolution of oxygen gas. When most of the H_2O_2 is consumed, a yellow gel usually forms spontaneously,[21] even in neutral solution. On the other hand, if a solution of lead is added to the peroxytitanic acid solution at high pH, an amorphous precipitate containing lead and titanium is formed. The soluble lead tetrahydroxide $[Pb(OH)_4]^{2-}$ forms in the presence of excess OH^- and reacts immediately with hydrogen peroxide, raising the oxidation state of the lead from Pb(II) to Pb(IV) (eq 2):

$$Pb(OH)_4^{2-} + 2H_2O_2 \rightarrow PbO_2 + 2H_2O + 2OH^- \qquad (2)$$

The oxidation of lead tetrahydroxide to lead dioxide can also occur in the presence of peroxytitanic acid since the peroxy group (O_2^{2-}) present in the $[Ti(OH)_3O_2]^-$ molecule can act as an oxidant. The precipitate can be described as a mixture of amorphous PbO_2 and TiO_2, as proposed by eq 3:

$$Pb(OH)_4^{2-} + [Ti(OH)_3O_2]^- \rightarrow PbO_2 + TiO_2 + 2H_2O + 3OH^- \qquad (3)$$

Elemental analysis (carbon, hydrogen, nitrogen, and oxygen) for the precipitate shows the presence of a small quantity of nitrogen and carbon (see Table 1), probably

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Table 1. Results from Elemental Analysis (Hydrogen, Carbon, Oxygen, and Nitrogen) [The Values Are the Percentage in Mass of the Volatile Material; The Final Power Was Pure PT]

element	percentage in mass (%)
hydrogen	0.73
carbon	0.69
oxygen	9.96
nitrogen	0.07
total volatile	11.45

due to the absorption of N_2 and CO_2 gases from the atmosphere. The chemical composition of the precipitate was calculated from the ICP and elemental analyses as [$Pb_4Ti_4O_{14}$·$3H_2O$], which is very close to the theoretical composition [$Pb_4Ti_4O_{16}$] resulting from the amorphous stoichiometric mixture of PbO_2 and TiO_2. The small difference in the amount of oxygen between the theoretical and the experimental result can be explained by the possible mixture of Pb(II) and Pb(IV) in the precipitate.[22,23]

In Figure 2, a small weight loss (11.8%) was detected between 30 and 475 °C on the TG curve of the precipitate, very close to the weight loss calculated from the elemental analysis (11.45%). Because of the absence of organics and their combustion, the local temperature is not increased. From the viewpoint of avoiding agglomeration, it is thus a particular advantage of this method compared to the previously reported sol–gel methods.[12,13]

As shown in Figure 3A, no crystalline phase was identified on the X-ray diffraction pattern of the amorphous precipitate. On the X-ray pattern of the powder calcined at 450 °C/1 h (Figure 3B), one can observe small peaks from the $PbTiO_3$ formed at low temperature, in agreement with results of the synthesis of PT by the PC method.[12,13] On the X-ray pattern of the powder calcined at 500 °C (Figure 3C) and the powder calcined at 700 °C for 1 h (Figure 3D) only PT may be identified. Despite the low crystallinity of the powder calcined at 500 °C when compared to the powder calcined at 700 °C, it should be stressed that only the tetragonal $PbTiO_3$ (PT) is observed (JCPDS 6–452).

Usually, when a sol–gel method is used, two crystalline phases can be formed, a metastable cubic pyrochlore and the perovskite (PT).[6] It is of particular importance that, on X-ray patterns in the Figure 3, there are no diffraction peaks from phases others than the PT. On the other hand, the use of Raman spectroscopy as a complementary technique can provide additional information about the presence of small amounts of secondary phases.[24] The Raman spectrum of the powder calcined at 700 °C for 1 h (Figure 4C) reproduces the well-known perovskite phase.[10] Bersani et al.[10] have reported, using X-ray and Raman spectroscopy, that the amorphous powder crystallizes at 600 °C, giving lead–titanium pyrochlore phase, and only at 700 °C PT is formed. However, pyrochlore phase is observed neither in Figure 3 nor in Figure 4. The characteristic Raman spectrum of the PT is easily observed on the Figure 4B, for the powder calcined at 500 °C for 1 h, without the presence of secondary phases. The absence of a very sharp peak at 145 cm^{-1}, characteristic for the pyrochlore phase,[10] on Figures 4B and 4C is conclusive for the direct formation of the PT phase from the amorphous powder.

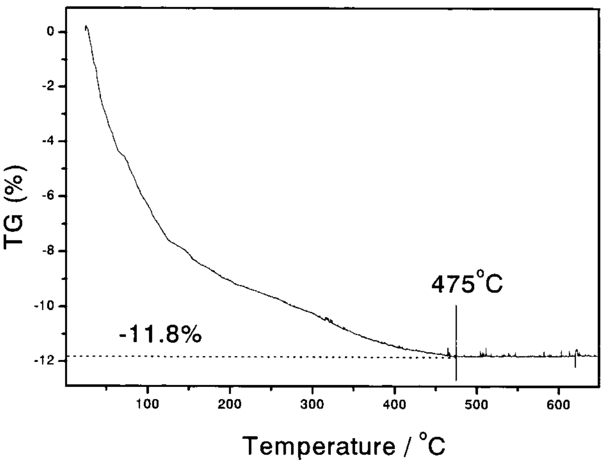

Figure 2. Thermogravimetriy (TG) curve of the precipitate powder, using 1 °C min^{-1} as the heating rate and 6.25 mg of sample in a platinum crucible.

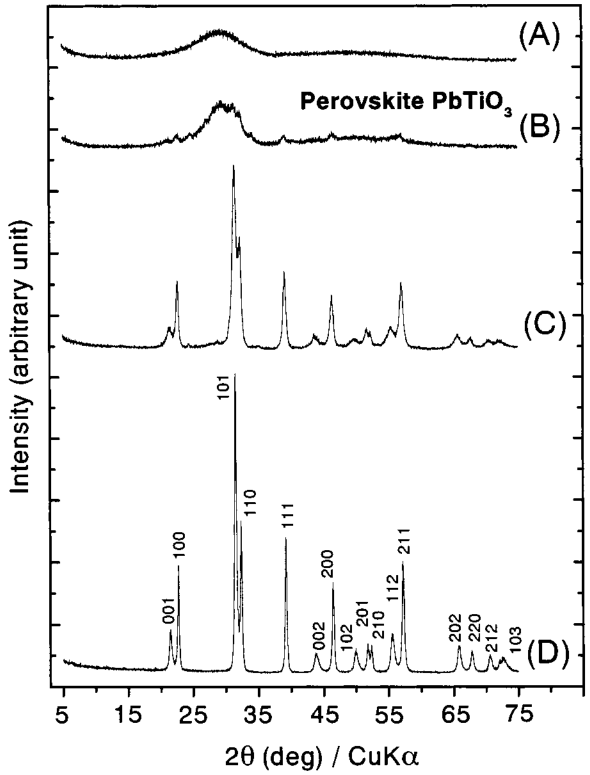

Figure 3. X-ray diffraction pattern of the (A) precipitate powder, (B) $PbTiO_3$ calcined at 450 °C for 1 h, (C) $PbTiO_3$ calcined at 500 °C for 1 h, and (D) $PbTiO_3$ calcined at 700 °C for 1 h. The heating rate used was 10 °C min^{-1}.

Figure 5 compares the SEM pictures of the amorphous precipitate (Figure 5A) and the crystalline PT powder (Figure 5B). The amorphous powder shows a uniform particle size with average diameter (D_{SEM}) of 100 nm. On the other hand, the PT powder calcined at 700 °C for 1 h (Figure 5B) shows the presence of particle growth, resulting in two classes of particles, one with average diameter (D_{SEM}) of 100 nm and the other with 200 nm. The size of the particles can also be estimated by the equivalent mean diameter (D_{BET}) calculated by the eq 4, where ρ_t is the theoretical density of the PT

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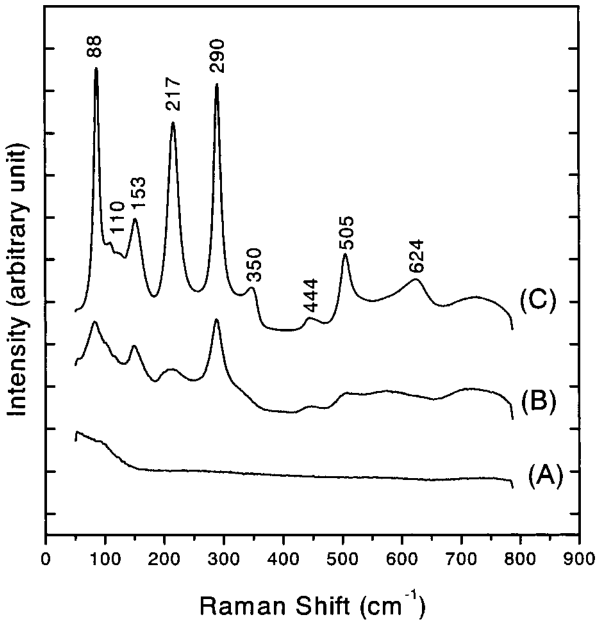

Figure 4. Raman spectra of (A) precipitate powder, (B) $PbTiO_3$ calcined at 500 °C for 1 h, and (C) $PbTiO_3$ calcined at 700 °C for 1 h, using the 514.5-nm line of Ar laser.

($\rho_t = 7.97$ g cm^{-3}).[25,26]

$$D_{BET} = \frac{6}{\rho_t S_{BET}} \qquad (4)$$

Table 2 shows the results of specific surface areas determined by the BET method (S_{BET}) and the equivalent particle diameter (D_{BET}), together with those reported by Shrout et al. (reactive calcination method)[27] and Peterson and Slamovch (hydrothermal processing).[28] The values of D_{SEM} and D_{BET} are comparable, which can be interpreted as the absence of agglomerates.[29] Although nanoparticles can be synthesized by other wet-chemical techniques,[9−20,27,28] Table 2 shows that the use of the PBR route results in higher S_{BET} for the same temperature of calcination, smaller particles, and therefore more reactive powder. Therefore, it is feasible to prepare pure $PbTiO_3$ phase with a high surface area using neither organics nor undesirable halides from an aqueous solution, which is a major advantage over the other methods reported before.

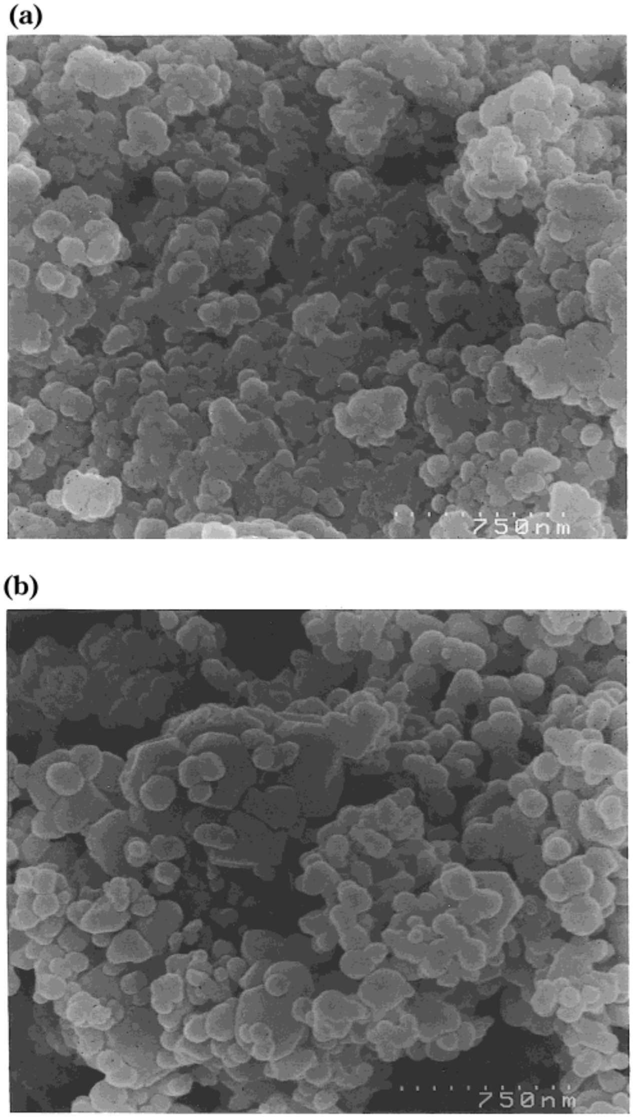

Figure 5. Scanning electron microscopy (SEM) of (A) precipitate powder and (B) $PbTiO_3$ calcined at 700 °C for 1 h.

Table 2. Specific Surface Area (S_{BET}) and Mean Equivalent Diameter (D_{BET}) of the PT Powder Calcined at Different Temperatures

temperature (°C)	S_{BET} (m^2 g^{-1})	D_{BET} (nm)
500	21.78	34.55
600	11.75	64.05
700	5.83	129.1
625[a]	1.8	400
200[b]	4.4	170

[a] Reference 24 (reactive calcination method). [b] Reference 25 (hydrothermal processing).

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