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Hydrothermal synthesis of fibrous lead titanate powders

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A fibrous lead titanate ($PbTiO_3$) powder with light-yellow colour has been prepared by hydrothermal synthesis. The influences of Pb/Ti ratio (0.3 to 1.0) in the mixture and reaction time on the formation of fibrous $PbTiO_3$ under hydrothermal conditions have been investigated. The preferable conditions for preparing fibrous perovskite-type $PbTiO_3$ from fibrous potassium titanate are that the Pb/Ti ratio is 1.0, reaction temperature 150 °C and time 72 h. The particles of fibrous powder of perovskite type are usually less than 2 μm in diameter and more than 50 μm in length. The fibrous morphology is essentially unchanged up to about 650 °C, but it disappeared after heating to 1000 °C.

1. Introduction

Lead titanate ($PbTiO_3$) is an eminent ferroelectric ceramic with high Curie temperature ($T_c = 490\,^\circ C$), high pyroelectric coefficient, low dielectric constant and high spontaneous polarization. The usual methods for preparing $PbTiO_3$ fine powders include a chemical coprecipitation method [1, 2], a sol–gel method [3] and a hydrothermal method [4, 5]. For the formation of $PbTiO_3$ with the perovskite structure, calcination at high temperature ($> 500\,^\circ C$) is necessary in the first two methods. These $PbTiO_3$ particles are usually spherical and exhibit extensive agglomeration.

Lead titanate synthesized by the hydrothermal method exhibits different crystal structures, for example perovskite-type (hereafter referred to as the PT phase), pyrochlore-type and tetragonal body-centred-type $PbTiO_3$ [6]; also $PbTiO_3O_7$ [4] and various morphologies depending on the reaction conditions. The preparation of pure tabular $PbTiO_3$ with fine grain size via the hydrothermal technique has been reported [6, 7]. Tabular $PbTiO_3$ with a perovskite structure is formed directly in solution. The main plane of the tabular $PbTiO_3$ particle is the (001) plane, and its aspect ratio is usually greater than 10.

Cheng *et al.* [5] and Suzuki *et al.* [7] have reported the hydrothermal synthesis of acicular $PbTiO_3$. However, they did not obtain long, acicular particles or "fibrous" $PbTiO_3$. The particles were normally 1 μm long.

The preparation of fibrous $BaTiO_3$ by the hydrothermal technique has been reported [8]. The fibrous particles of thermal $BaTiO_3$ were formed by ion-exchange reaction. The fibres were normally 50 to 100 μm long, and under the most favourable conditions, fibres 200 to 300 μm long were produced. The aspect ratio of the fibrous $BaTiO_3$ was usually greater than 50 to 100.

The purpose of this study is to investigate the possibility of preparing pure, fine powders of fibrous $PbTiO_3$ by the hydrothermal method and to clarify the effects of preparation conditions on the formation of $PbTiO_3$.

2. Experimental procedure

Fibrous potassium titanate, $2K_2O \cdot 11TiO_2 \cdot 3H_2O$, hereafter referred to as the XI phase (Kyusyu Taika-renga Co., Bizen, Japan) and lead hydroxide ($Pb_2O(OH)_2$) were used as starting materials. A mixture of $2K_2O \cdot 11TiO_2 \cdot 3H_2O$ and $Pb_2O(OH)_2$ in a given Pb/Ti ratio was placed in a silver crucible with 120 cm^3 water and placed in an autoclave. The hydrothermal synthesis of the $PbTiO_3$ was conducted at 150 °C for 24–72 h. After the autoclave apparatus was cooled at a rate of 5 °C min^{-1}, the product was

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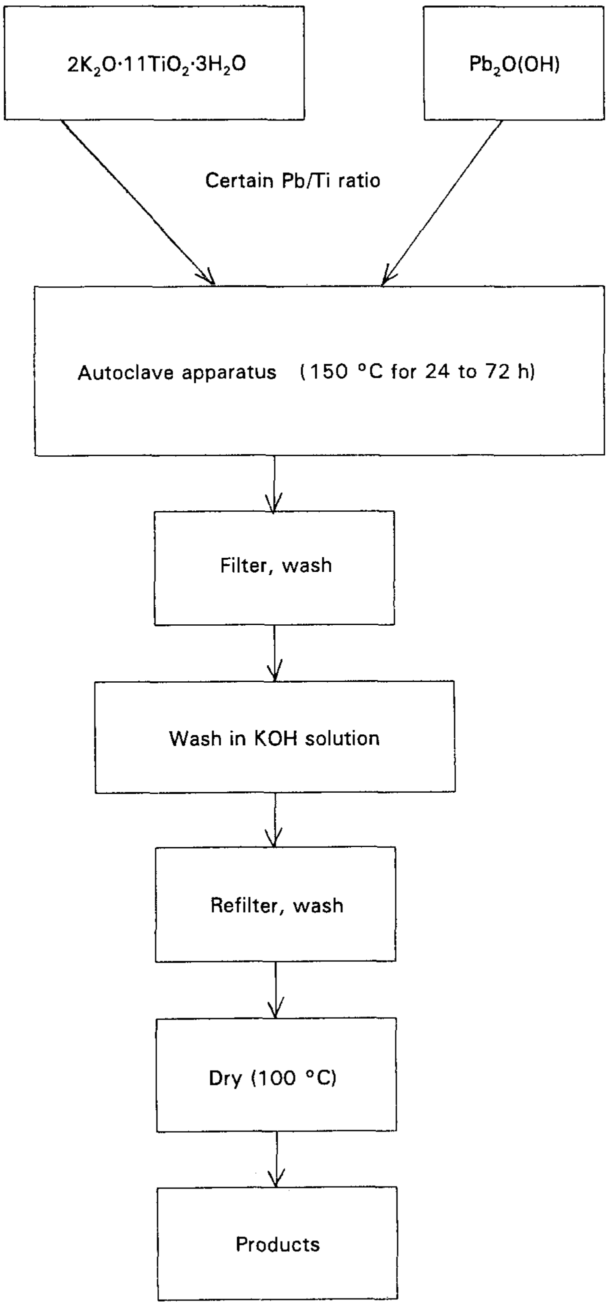

Figure 1 Diagram of process for preparing fibrous $PbTiO_3$.

filtered and washed with deionized water and 10% KOH solution to remove residual PbO. The product was then refiltered, washed until the pH becomes ~ 7, and dried at 80 °C for 24 h. The process is summarized in Fig. 1.

The synthesized powders were analysed by means of X-ray diffraction (XRD) using CuK_α radiation with a nickel filter and a graphite monochromator, fixing the scanning speed at $1° \, 2\theta \, \mathrm{min}^{-1}$ with a diffractometer (Model RAD-2C, Rigaku Co., Tokyo) to determine the phases present in the crystalline products. The morphology of the $PbTiO_3$ particles was observed using scanning electron microscopy (SEM) (JSM-T300, Jeol Co., Tokyo). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were also conducted (TG/DTA 300, Seiko Electronics Co., Tokyo).

3. Results and discussion

We examined the influences of Pb/Ti ratio in feedstock and reaction time on the formation and crystal growth of fibrous $PbTiO_3$ in hydrothermal conditions.

To study the effects of Pb/Ti ratio on the formation of fibrous $PbTiO_3$, a set of experiments was conducted at a constant reaction time of 24 h while varying the Pb/Ti ratio in the range of 0.3 to 1.

The results show that, when the Pb/Ti was 1, pure fibrous PT-phase $PbTiO_3$ powders were produced. If Pb/Ti was 0.3, a fibrous mixture (XI phase and PT phase) was formed. The relevant results are listed in Table I.

Table I shows that when the Pb/Ti ratio is 1, pure fibrous PT-phase $PbTiO_3$ is formed. The hydrothermal synthesis reaction of $PbTiO_3$ was conducted in a strongly basic solution. $Pb_2O(OH)_2$ and PbO are amphoteric substances, showing a minimum solubility at a pH of 9.34. The solubility of $Pb_2O(OH)_2$ and PbO increased with increased pH and temperature of solution by forming the soluble species $Pb(OH)_3^-$. Therefore, many Pb^{2+} ions were in solution under conditions of high pH and temperature. According to the mechanism of forming fibrous $PbTiO_3$ from fibrous $2K_2O \cdot 11TiO_2 \cdot 3H_2O$ by ionic exchange under hydrothermal conditions, it is reasonable to assume that the formation of $PbTiO_3$ was due to the exchange reaction between Pb_2^+ ions and K^+ ions under the hydrothermal conditions of high pH (KOH), temperature, and pressure (4–5 $\mathrm{kg\,cm^{-2}}$). The formation of the PT phase may require a higher Pb_2^+ concentration than that of K^+. Therefore, for the formation of pure PT phase the required Pb/Ti ratio must be higher than that of the mixture phase.

The reaction time had a great effect on the rate of forming PT-phase $PbTiO_3$ and on crystallite growth. The XRD patterns of the products at different times are given in Fig. 2, which shows that PT-phase $PbTiO_3$ began to form at 24 h. However, the ionic exchange of potassium ion and lead ion was not complete after 24 h. Igarishi *et al.* [9] reported these phenomena. The longer the time, the higher was the ratio of forming PT-phase $PbTiO_3$. The reaction was usually completed after 72 h. During the initial stage of reaction, $Pb_2O(OH)_2$ did not dissociate to lead ions in 150 °C water. However, K^+ ion dissolves in reaction water from fibrous $2K_2O \cdot 11TiO_2 \cdot 3H_2O$ and $Pb_2O(OH)_2$ dissociates to lead ion in K^+ containing water.

The fibrous $PbTiO_3$ with PT phase was formed under hydrothermal conditions with a long reaction

TABLE I Influence of Pb/Ti ratio and reaction time on the formation of $PbTiO_3$

Sample No.	Pb/Ti (mole ratio)	Reaction time (h)	Product phase
1	0.3	24	XI + PT
2	1.0	24	XI + PT
3	1.0	72	PT

Reaction temperature $T = 150$ °C.

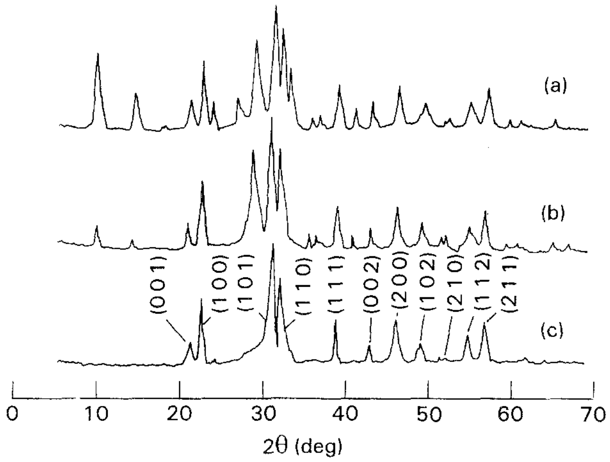

Figure 2 XRD patterns of products at different Pb/Ti ratios and reaction times. (a) Pb/Ti = 0.3, 24 h; (b) Pb/Ti = 1, 24 h; (c) Pb/Ti = 1, 72 h.

time. It forms light yellow, fibrous crystallites with a diameter usually less than 2 μm and a length larger than 50 μm. Fig. 3 shows scanning electron micrographs of the crystallites. Fig. 3c shows that the fibrous particles are constructed of smaller cubic crystallites in a parallel arrangement along their long axes. In the TG curve of PT phase there is a weight loss of ~ 2.7 wt % at 325 °C (Fig. 4). This phenomenon is attributed to the desorption of crystallite H_2O in the fibrous sample. No weight loss was observed at the phase-transformation temperature (~ 500 °C) [5] in the TG–DTA curves of the PT phase. These results showed that calcination at high temperature is not necessary in the formation of PT-phase $PbTiO_3$ by hydrothermal reaction.

The (1 1 0) line widths (β) at half peak intensity in the XRD pattern of the PT phase were used to characterize the average grain size of samples from the Scherrer formula. The D value is the average crystal size in the (1 1 0) direction. The relative intensity ($I_{1\,1\,0}$) of the (1 1 0) peak was used to represent the relative crystallinity of the samples. The average grain size, D, of sample No. 3 (Table I) was calculated from the formula

$$D = \frac{K\lambda}{\beta\cos\theta} = \frac{0.9 \times 0.15405}{0.0104 \times \cos(22.4/2)} = 13.5\ \text{nm}$$

where $\beta = 0.6(\text{deg}) = 2\pi \times 0.6/360$ (radian). The crystal structure of PT-phase $PbTiO_3$ may be more complicated, since Fig. 3c shows grain sizes of 1.3–2.8 μm.

Fig. 4 illustrates the thermal analysis diagram of PT-phase $PbTiO_3$ from which the remanent H_2O and PbO have been removed. The TG curve consists of two weight losses at about 325 and 920 °C. The weight loss at 325 °C is attributed to the desorption of crystal water from the fibrous $PbTiO_3$. The weight loss at 920 °C is smaller and is attributed to the evaporation of PbO.

SEM analysis of the samples after heating to 650 and 1000 °C confirms a phase transformation from fibrous to sintered $PbTiO_3$. The relevant SEM photographs are shown in Fig. 5. After heating to 650 °C, the fibrous shape of the samples is essentially unchanged. Fibrous PT-phase $PbTiO_3$ is light yellow in colour.

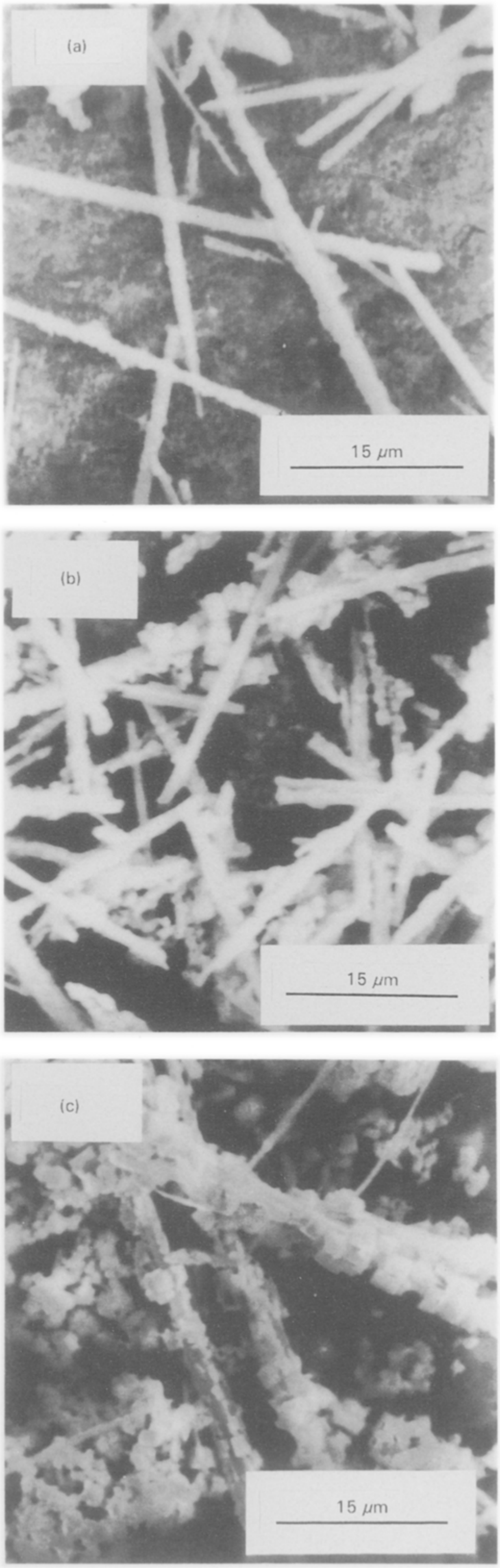

Figure 3 SEM micrographs of fibrous $PbTiO_3$: (a) Pb/Ti = 0.3, 24 h; (b) Pb/Ti = 1, 24 h; (c) Pb/Ti = 1, 72 h.

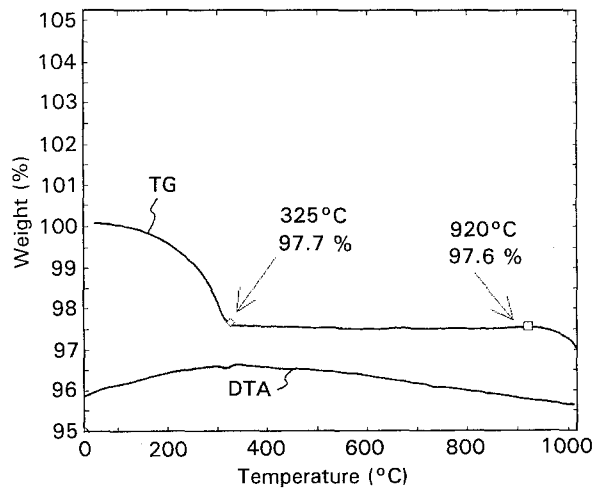

Figure 4 Thermal analysis diagram of fibrous $PbTiO_3$ (sample No. 3).

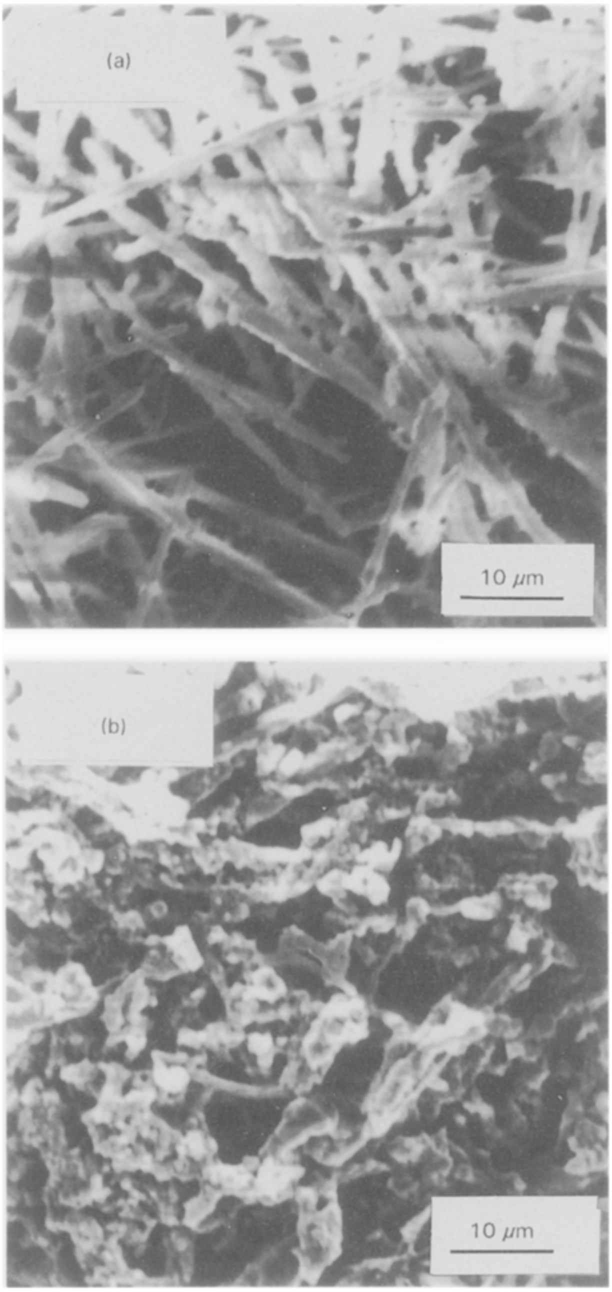

Figure 5 SEM micrograph of fibrous $PbTiO_3$ after heating at (a) 650 °C and (b) 1000 °C.

After heating at 1000 °C, the fibrous shape of the samples is changed and the colour is light green. Increasing the temperature should accelerate the evaporation of PbO, but the grain surface may be sintered and agglomeration occurs. The remanent PbO in the sample acts as a flux, promoting sintering of the fibrous $PbTiO_3$.

Cheng *et al.* [5] reported that the crystal system in acicular $PbTiO_3$ prepared by hydrothermal synthesis is tetragonal body-centred. This difference may have been due to lead deficiency in the sample.

In the transformation from tetragonal body-centred phase to perovskite phase, calcination at 605 °C was unavoidable. This procedure resulted in a lead-deficient sample which caused an increase in the transformation temperature. The transformation temperature from tetragonal body-centred phase to perovskite phase is higher than from the amorphous phase (by sol–gel method [5]) to perovskite phase, when it is about 500 °C. The ion exchange from XI phase to PT phase can be accompanied by a larger removal of the framework, but the difference between the energies of the two crystal lattices is not large because the reaction temperature at 150 °C is low.

4. Conclusion

Pure PT-phase lead titanate ($PbTiO_3$) has been prepared by a hydrothermal method. PT-phase $PbTiO_3$ is in the form of light yellow, fibrous crystallites with an axis diameter usually less than 1 μm and length larger than 50 μm. The XI phase can be converted to perovskite-type (PT) phase at 150 °C, and its fibrous shape remains essentially unchanged. A heat of phase transformation is not observed and weight loss occurs in the relevant temperature range. The preferable conditions for preparing pure fibrous PT-phase $PbTiO_3$ are Pb/Ti = 1, reaction temperature 150 °C, and time 24 to 72 h, with potassium titanate as a starting material. The hydrothermal technique provides the possibility for preparing $PbTiO_3$ fine powders with aspherical symmetry in their morphology.

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