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Solvothermal synthesis and characterization of $PbTiO_3$ powders

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$PbTiO_3$ powders with low agglomeration were solvothermally synthesized in alcohol solution to be free from contamination by foreign ions. Borderline reaction conditions such as temperature and time were established. The use of strong alkali as mineralizer was found to be effective for the synthesis of perovskite phase $PbTiO_3$. The products were characterized in detail by XRD, TEM and other techniques.

$PbTiO_3$ has always appeared as two types of stable phases, the pyrochlore (PY) and perovskite (PE) structures, of which PE-$PbTiO_3$ is a well known ferroelectric material with excellent dielectric, pyroelectric and piezoelectric properties.[1,2] Many papers focused on the hydrothermal process for the synthesis of $PbTiO_3$ powders, which is a chemical preparation regarded as being superior to other methods for several reasons.[3] Hydrothermal synthesis of powders can be defined as the treatment of aqueous solutions or suspensions of precursors at elevated temperature in a pressurized vessel, and the solvothermal process is the hydrothermal reaction carried out in non-aqueous solution. In comparison with the hydrothermal process, solvothermal synthesis might allow the product to be free from foreign anions because the organic solution, having a low relative permittivity, is free from ionic species.[4] Previous work showed that $PbTiO_3$ powders hydrothermally prepared from oxides, salts and alkoxides exhibit different crystal structures and various morphologies[5–8] and the precursor has an important effect on the product,[9] depending on the reaction conditions. However, to our knowledge, all the syntheses of well crystallized $PbTiO_3$ powders have been achieved in aqueous solution and there are no reports on the solvothermal synthesis of $PbTiO_3$ powders. Thus, the objective of this research is to develop a solvothermal process to prepare phase-pure $PbTiO_3$ powders in alcoholic solution such as methanol and 2-methoxyethanol (MOE).

Experimental

Synthesis

All reagents were of analytical grade and were not purified further before utilization.

The general process used to prepare $PbTiO_3$ powders is schematically shown in Fig. 1. Amorphous xerogels consisting of a mixture of equivalent molar amounts of PbO and TiO_2 were prepared using lead acetylacetate [$Pb(acac)_2$] and tetrabutyl titanate [$Ti(OC_4H_9)_4$] as starting materials. To avoid reaction with CO_2, all manipulations were carried out in an N_2 atmosphere. The mixture of $Pb(acac)_2$ and $Ti(OC_4H_9)_4$ in MOE solution, in which the molar ratio of Pb to Ti was 1 : 1 and the sum of the Pb and Ti concentrations was 0.02 mol dm^{-3}, was refluxed for 2 h to obtain a stable solution through an alcohol interchange reaction between the ethoxy and butoxy groups. After concentrating the above solution until a total concentration of metal ions (Pb+Ti) of up to 0.1 mol dm^{-3}, a mixture of MOE and water (volume ratio 4 : 1) was added to the solution, in which the molar ratio of water to whole metal ions was 8 : 1. Upon cooling this solution to room temperature after refluxing for 0.5 h, the transparent solution (sol) gradually transformed to a gel; then aging for 24 h and drying in vacuum at 0 °C resulted in the formation of the precursor xerogel.

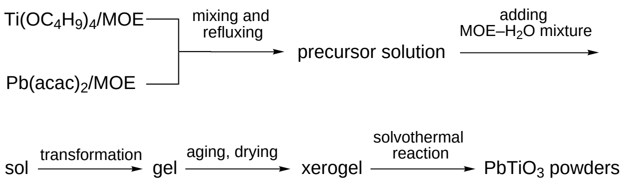


Fig. 1 Flow diagram of the synthesis procedure for the $PbTiO_3$ powders

The precursor xerogel was poured into the solvent to form a suspension solution, and 30.0 cm^3 of the suspension (in which the total Pb+Ti concentration was 0.1 mol dm^{-3}) was fed into a 40.0 cm^3 stainless-steel autoclave with a Teflon liner. N_2 gas was passed through the vessel to displace air. The vessel was heated to a given reaction temperature at which it was held for a planned time. After that, the autoclave was cooled to room temperature, then the precipitate was collected by centrifugation, washed with acetone and dried at room temperature before being characterized.

Characterization

X-Ray diffraction patterns were recorded on a Rigaku D/Max-IIIA diffractometer with nickel-filtered Cu-Kα radiation (λ= 0.15418 nm). A H-8100 IV transmission electron microscope (TEM) equipped with an energy disperse X-ray microanalyzer (EDX) was used to observe the mean size and morphology of the primary particles and laser scattering and diffraction (LSD) was applied to estimate the size distribution of the aggregates of the primary particles. Compositional analyses were carried out on a inductively coupled plasma atomic emission spectrometer (ICP-1000) for metal contents in the product. The BET (Brunauer–Emmett–Teller) surface areas of the final powders were measured on an apparatus made in our laboratory.

Results and Discussion

Crystallization of $PbTiO_3$

In order to investigate the crystallization behavior, xerogels were heated in methanol and MOE at various temperatures for different times to determine the degree of crystallization. The XRD patterns for the xerogels treated in methanol at 200 °C for various times are shown in Fig. 2A and those treated in MOE at 240 °C are shown in Fig. 2B. The starting xerogel was amorphous by XRD. The xerogels heated in methanol for

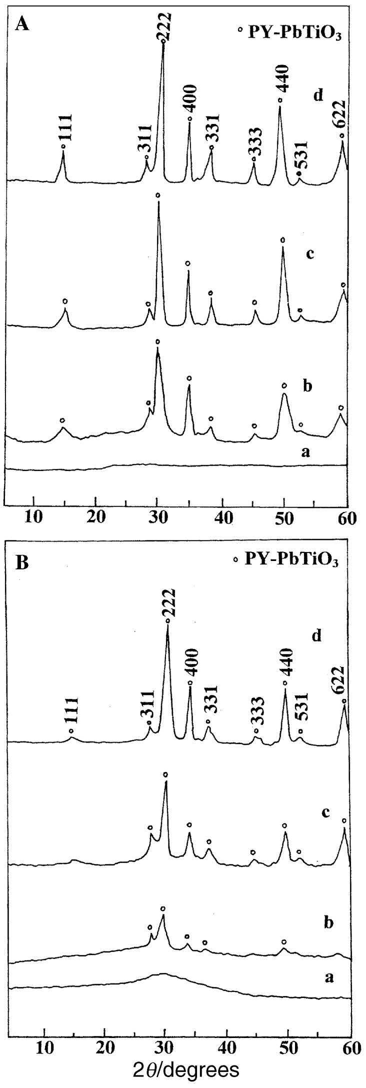


Fig. 2 XRD patterns of the xerogels treated for various times. A: in methanol at 200 °C for (a) 6, (b) 10, (c) 24, (d) 40 h; B: in MOE at 240 °C for (a) 6, (b) 10, (c) 24, (d) 40 h.

10 h showed XRD peaks corresponding to the PY phase and the peak intensity increased with increasing reaction time. When the reaction carried out for 24 h, well crystallized PY-$PbTiO_3$ powders were obtained. However, it was necessary to heat the xerogels at 240 °C for 30 h to prepare pure PY-$PbTiO_3$ powders.

The crystallization behavior of the xerogels in methanol and MOE at various temperatures for 24 h is shown in Fig. 3A and B, respectively. The crystallization proceeded above 160 °C and was greatly accelerated with increasing temperature. Fig. 3 also shows that although the PY-$PbTiO_3$ powders in methanol appeared at 160 °C, those with the PY phase only began to form at 180 °C, and reaction temperatures higher than 200 °C were necessary for the synthesis of phase-pure PY-$PbTiO_3$ powders. In comparison, the crystallization of the xerogel in MOE required higher temperatures; >240 °C was necessary for formation of pure PY-$PbTiO_3$.

Unfortunately, PE-$PbTiO_3$ could not be obtained under the above reaction conditions; however, the same conditions may result in the formation of PE-$PbTiO_3$ in aqueous solution.[10] To synthesize PE-$PbTiO_3$, NaOH and NaOR (R = methyl, 2-methoxyethyl) were applied to catalyze the reaction. NaOH or NaOR was dissolved into the precursor solution, in which the concentration of the alkali was 2.4 mol dm^{-3}. Fig. 4A shows XRD patterns of the products prepared in methanol at 200 °C for various times (other conditions held constant) using NaOH as mineralizer; Fig. 4B reveals those derived from MOE at 240 °C for different times. PE-$PbTiO_3$ appeared in methanol for 10 h reaction, and at least 40 h was required to prepare this pure phase. The borderline reaction conditions for the syntheses of pure PE-$PbTiO_3$ powders are shown in Table 1.

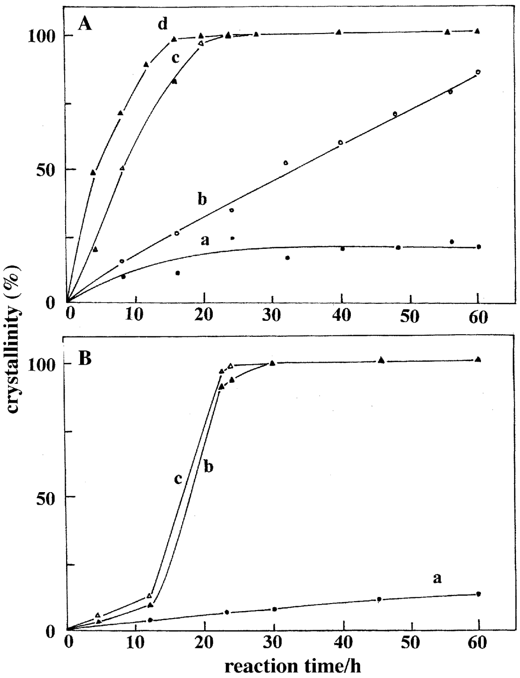
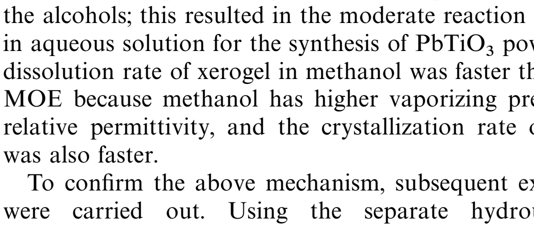


Fig. 3 Crystallization behavior of xerogels at various temperature for 24 h. A: in methanol, (a) 160, (b) 180, (c) 200, (d) 240 °C; B: in MOE, (a) 200, (b) 240, (c) 260 °C.

The reaction conditions for preparing the $PbTiO_3$ powders by the solvothermal method were not more moderate in comparison with those for hydrothermal synthesis.[7] Furthermore, the reaction temperature in MOE solution was higher than that in methanol solution, and the former reaction time was longer than the latter for the synthesis of the phase-pure powders. As a mineralizer, NaOR might be more favorable to catalyze the formation of the PE-$PbTiO_3$ powders. This result might be explained as follows.

The crystallization is proposed to proceed by the dissolution–reprecipitation mechanism as shown in eqn. (1), where the dissolution of xerogels might be the rate controlling stage.[11]



$$\begin{array}{ccc} [Pb(OH)_xO_yTi(OH)_z]_n & & \\ \text{(xerogel)} & & \\ \big\downarrow \text{dissolution} & & \\ Pb^{2+}(aq.)+Ti^{4+}(aq.)+OH^- & \xrightarrow{\text{crystallization}} & PbTiO_3 \\ \text{(solution)} & & \text{(precipitate)} \end{array} \qquad (1)$$

The xerogel dissolved more readily in water because of the higher relative permittivity of water compared with those of the alcohols; this resulted in the moderate reaction conditions in aqueous solution for the synthesis of $PbTiO_3$ powders. The dissolution rate of xerogel in methanol was faster than that in MOE because methanol has higher vaporizing pressure and relative permittivity, and the crystallization rate of $PbTiO_3$ was also faster.

To confirm the above mechanism, subsequent experiments were carried out. Using the separate hydrous oxides $TiO_2 \cdot nH_2O$ and $PbO \cdot nH_2O$ xerogels as precursors for the preparation of $PbTiO_3$ in methanol at 200 °C while other conditions were the same as in the above experiments, pure PY-$PbTiO_3$ powders could be obtained as reaction times of up to 60 h and 80 h were necessary for synthesizing PE-

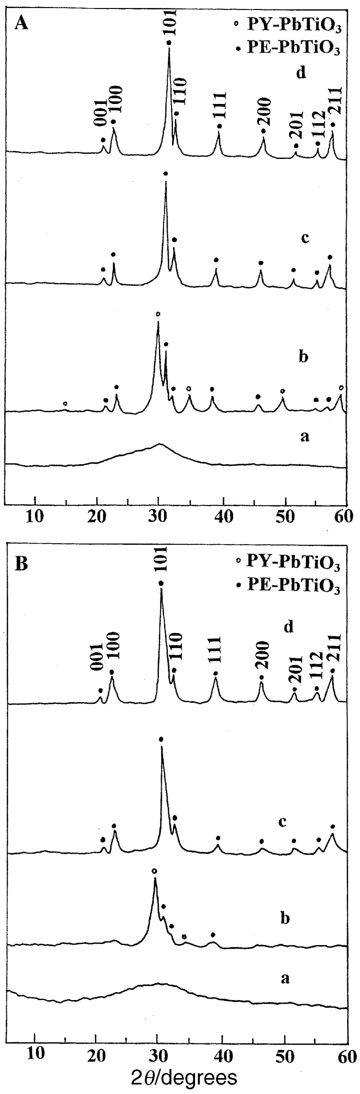


Fig. 4 XRD patterns of the xerogels treated using NaOH as mineralizer. A: in methanol, temperature: 200 °C, time: (a) 2, (b) 10, (c) 40, (d) 50 h; B: in MOE, temperature: 240 °C, time: (a) 2, (b) 10, (c) 50, (d) 60 h.

Table 1 Reaction conditions for preparing the crystalline PbTiO$_3$ powders

sample	solvent	mineralizer	T/°C	t/h	phase
A	methanol	—	200	24	PY
B	MOE	—	240	30	PY
C	methanol	NaOH	200	40	PE
D	methanol	NaOCH$_3$	180	24	PE
E	MOE	NaOH	240	50	PE
F	MOE	NaOMOE	200	40	PE

PbTiO$_3$ powders using NaOH as mineralizer. By increasing the alkali concentration up to 4.8 mol dm^{-3}, pure PE-PbTiO$_3$ powders could be prepared after 60 h reaction time. This result demonstrated that the reaction accelerated with increasing alkali concentration, and the formation of the product must be through one dissolution and transportation process of the precursor species. In fact, the PbO·nH$_2$O xerogel could dissolve in alkali solution even at room temperature and the solubility increase with increasing alkali concentration. Highly concentrated alkali solution resulted in the acceleration of the reaction. In comparison to the separate xerogels, the shorter reaction time for the synthesis of PbTiO$_3$ powders from a single xerogel might be due to the Pb and Ti atoms being homogeneously arranged in the xerogel having a shorter diffusion route to create the PbTiO$_3$ structure.[7] The variation of the crystallinity of PE-PbTiO$_3$ and the precursor species concentration with the reaction time in the process further confirmed the mechanism (Fig. 5). The crystallization of PE-PbTiO$_3$ increased with increasing reaction time, while the Pb^{2+} concentration in solution decreased. This indicates that the formation of the final crystalline powders must be through a recrystallization process.

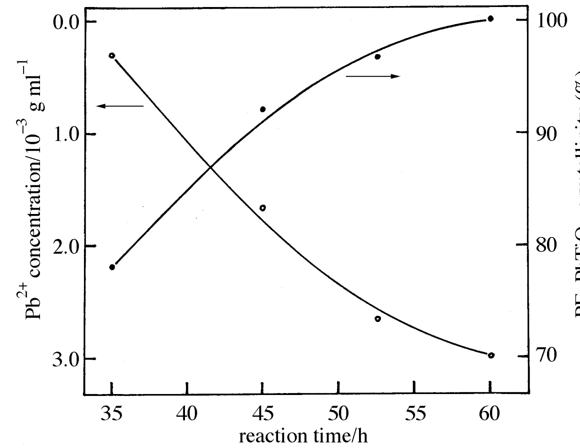


Fig. 5 The crystallinity of PE-PbTiO$_3$ and the Pb^{2+} concentration in the corresponding solution

Particulate properties of PbTiO$_3$ powders

The results of ICP and EDX analyses showed that these PE phase powders after washing with acetone three times did not contain Na$^+$, *i.e.* the products were not contaminated by foreign ions. There were no adsorption bands in IR spectra of the PbTiO$_3$ powders other than their characteristic bands. This also revealed that the organic materials did not affect the products. Using KCl as an internal standard for verifying the positions of the reflections, the samples were scanned from 4 to 60° (2θ) at a scan speed of 0.1° min^{-1}. The unit cell parameters indexed for PY-PbTiO$_3$ derived from different solvents were identical within the analysis error, which were $a = 1.044$ nm, $V = 1.1379$ nm^3, while those for PE-PbTiO$_3$ derived from methanol and MOE were $a = 0.3900$ nm, $c = 0.4154$ nm, $V = 0.06318$ nm^3 and $a = 0.3901$ nm, $c = 0.4154$ nm, $V = 0.06321$ nm^3, respectively. These parameters are a little larger than the standard values.[12] The average particle sizes of these powders were measured according to the TEM observations. High BET surface areas in agreement with the particle size from TEM observations demonstrated that these particles had a low agglomeration. The powders displayed a simple mode of size distribution. The morphology of the PY-PbTiO$_3$ powders with a mean particle size of 8–15 nm appeared spherical, whereas the PE-PbTiO$_3$ particles with a size of 12–24 nm were cubic, which reflected the tetragonal crystallographic habit of the perovskite structure. To further clarify the agglomeration, LSD measurements were carried out. The result shown in Fig. 6 clearly indicates that the particles exhibited a simple mode of size distribution. However, the mean size observed on the TEM photographs appeared to be different from those recorded by LSD measurements. This was caused by uncertainty in the LSD measurements, which was induced by the use of an arbitrarily chosen refractive index of PbTiO$_3$ powders, but they demonstrated the real size distribution of aggregates of primary particles.

Conclusions

The important conclusions of this study may be summarized as follows.

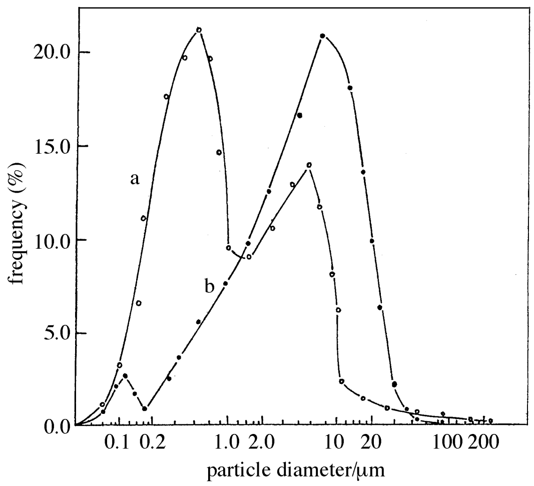


Fig. 6 The particle size distribution, LSD measurements, of the $PbTiO_3$ powders: (a) sample A; (b) sample C

(*a*) Although the crystallization of $PbTiO_3$ in alcohol solution required higher temperatures for longer times, the nanometer-sized, particles in comparison with the micrometer-sized ones derived from aqueous solution, exhibited a lower agglomeration due to the organic materials having a lower relative permittivity, and had a simple mode of size distribution.

(*b*) Like the hydrothermal process, the formation of $PbTiO_3$ proceeds in alcohol solution by a dissolution–reprecipitation mechanism in which the dissolution of precursor was the rate controlling stage; however, the PY-$PbTiO_3$ particles appeared spherical and the PE-$PbTiO_3$ particles had a cubic morphology. It was difficult to synthesize PE-$PbTiO_3$ without using alkaline mineralizer.

(*c*) The reaction conditions were varied for preparing the $PbTiO_3$ powders derived from the different organic solvents. For example, in comparison with those in methanol, the reactions in MOE for the syntheses of the $PbTiO_3$ powders required higher temperatures or longer times due to MOE having lower vaporizing pressure and relative permittivity.

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