Hydrothermal synthesis of fine perovskite PbTiO₃ powders with a simple mode of size distribution

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Perovskite phase PbTiO₃ powders were hydrothermally synthesized so as to be fine and homogeneous in physico-chemical properties. Such powders are currently used in the fabrication of electronic ceramic components. The powders were successfully synthesized using a strong alkali as catalyst. Borderline synthesizing conditions, such as temperature and time, were established and their effects on geometrical properties, like mean particle size were determined. Polyacrylamide as an additive was found to be effective for the synthesis of the powders with a simple mode of particle-size distribution.

1. Introduction

Ceramic powders of metal oxides have been used as materials to fabricate various electronic components, e.g. capacitors and sensors. The powders have been prepared with conventional processing techniques, so-called breaking-down methods. The recent pursuit of size reduction and high performance of the electronic components has called for powders which are fine, pure and homogeneous in physico-chemical properties [1]. Chemical preparation of the ceramic powders is advantageous over conventional techniques in enabling desired properties to be obtained [2]. Hydrothermal synthesis of the ceramic powders is a chemical preparation regarded as being superior to the other methods for several reasons [3].

Perovskite-type lead titanate, PbTiO₃, has excellent electronic properties, like ferroelectricity and so on. Thus, its powders have been utilized as materials of several electronic components. In general, the finer the ceramic powders the better the electronic properties of the fabricated components. Too fine a powder, however, are unfavourable for powder processing. As a compromise, submicrometre powders are currently considered to be suitable particle sizes. Besides such fineness, unimodal size distribution also is advantageous for fabrication of the electronic components. As far as the authors know, PbTiO₃ powders, although chemically prepared [1, 4, 5], have not been synthesized so as to carry the favourable properties.

In the present paper, hydrothermal synthesis conditions to prepare such favourable powders are discussed.

2. Experimental procedure

2.1. Materials

Lead nitrate and titanium tetrachloride (extra pure grade) were used as raw materials. Lead nitrate was dissolved in deionized water to give a solution of 1.0 M, which was kept in a bottle. Into titanium tetrachloride in a flask immersed in chilled water, deionized water was added slowly and 1.5 M titanyl solution was prepared. The solution was kept in a brown bottle. Several alkalis were used to catalyse the hydrothermal synthesis. They were of a guaranteed grade of sodium hydroxide and potassium hydroxide, 25% ammonia solution and lithium hydroxide monohydrate. They were used as aqueous solutions of 8 M concentration, except for the lithium hydroxide. The lithium hydroxide was partly soluble in water at room temperature, so it was used as a saturated solution–solid mixture containing an amount equivalent to 8 M.

To control the particle size of the PbTiO₃ powders the effectiveness of various additives was investigated. Several water soluble polymers were used as additives, their solubilities being tested against strongly basic aqueous solutions at room temperature. Those appearing to be soluble were employed. They were polyacrylamide (PAAm) and polyvinyl alcohol (PVA). The former was purchased with 10 wt % aqueous solution and the latter with resin; both were used as received. The mean molecular weights were 5.0×10^3 for the latter and unknown for the former.

2.2. Procedure of hydrothermal synthesis

Hydrothermal synthesis is a type of chemical reaction, so that its rate is accelerated at elevated temperatures. Elevated temperatures will hereafter be called reaction temperatures. Synthesis times during the period when the temperature in a reaction vessel was kept at an elevated temperature will be called a reaction time.

Amounts, equivalent to the atomic ratio of lead and titanium in $PbTiO_3$, of the titanyl and the lead nitrate solution were taken out of the bottles. They were poured into 60 ml of the alkali solutions to give a concentration of 1.0 M. The additives for controlling particle sizes of the powders, if necessary, were added to the alkali solution at amounts which were equivalent to weight per cents from 0.1 to 1.0 in the made-up solution. The made-up solution was fed into a 300 ml reaction vessel which was equipped with a magnetically driven stirrer. Nitrogen gas was flowed through the vessel to displace the air in it, and the vessel was pressurized to 5.07 MPa. It was heated up to a given reaction temperature, which was held for a given reaction time. After that it was cooled down to room temperature and then the contents in it were collected. For removal of lead hydroxide and lead oxide, possibly by-products of the unconverted reactants, the collected mixtures were washed with dilute acetic acid followed by deionized water, and finally filtered. The residue was dried overnight at 70 °C before being characterized.

2.3. Characterization of prepared powders

Morphological properties of the prepared powders were observed by scanning electron microscopy (SEM). Their crystalline structures were analysed by X-ray diffraction (XRD). The size distribution was measured by SEM and a laser scattering and diffraction method (LSDM). The size distribution obtained with LSDM, however, was used only as qualitative information, because the refractive index necessary for LSDM to determine the distribution as absolute values was not available for $PbTiO_3$ particles. Thus, LSDM was applied assuming a refractive index of 1.0. The size distribution with SEM was obtained as follows: Ca. 100 particles were sampled on SEM micrographs and their sizes were determined as two-directional arithmetic mean diameters.

For comparison, purchased perovskite $PbTiO_3$ powders of which the purity was more than 99 wt % were utilized.

3. Results and discussion

3.1. Borderline conditions for synthesizing perovskite phase $PbTiO_3$

Alkalis have been found to catalyse thermal synthesis of some perovskite-type metal oxides [7]. Thus, their effectiveness was studied for the present synthesis.

Fig. 1 shows XRD patterns of prepared and purchased powders. The patterns indicate that both sodium and potassium hydroxides gave $PbTiO_3$ as the only perovskite phase. The sharpness of the patterns suggests that both alkalis produced more crystalline
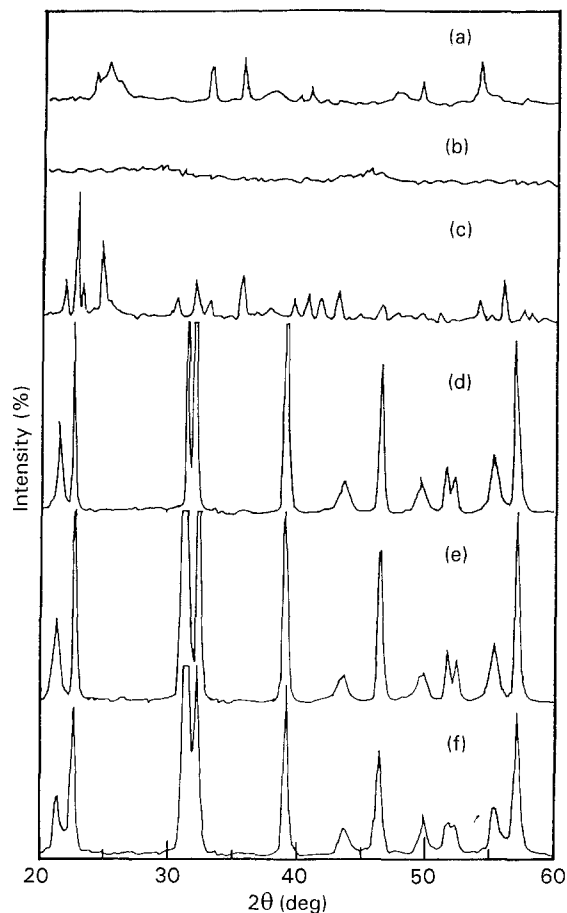
Figure 1 XRD patterns of $PbTiO_3$ powders purchased (f) and synthesized without (a) and with [(b)–(e)] addition of 8 M solution of various alkalis: (b) $LiOH \cdot H_2O$; (c) NH_4OH; (d) NaOH; (e) KOH. Any synthesis was carried out at 200 °C for 2 h.

powders than the purchased powders. The ammonia solution did not provide such crystalline powders as the alkalis, and gave mixtures containing a crystalline structure like the pyrochlore phase rather than the perovskite one. The patterns further revealed that there was no catalytic activity of lithium hydroxide monohydrate. This may be partly responsible for its rather low solubility. Thus, perovskite phase $PbTiO_3$ was synthesized catalytically by the strong alkalis as well.

In light of the above findings, subsequent experiments were carried out using potassium hydroxide as the strong alkali. The milder the synthesizing conditions are the more advantageous the commercial production of the powders, so long as produced powders can carry the desired properties. Thus, borderline conditions for synthesis of the $PbTiO_3$ powders which were well-crystallized and consisted of only the perovskite phase, were studied by XRD analysis.

Firstly, the effects of reaction temperatures were investigated. Fig. 2 shows XRD patterns of the powders which were prepared at various reaction temperatures while the other conditions were held constant. The figure reveals that although the $PbTiO_3$ powders appeared to have been synthesized as low as 150 °C, those with the perovskite phase only began to form at 170 °C, and reaction temperatures higher than 200 °C
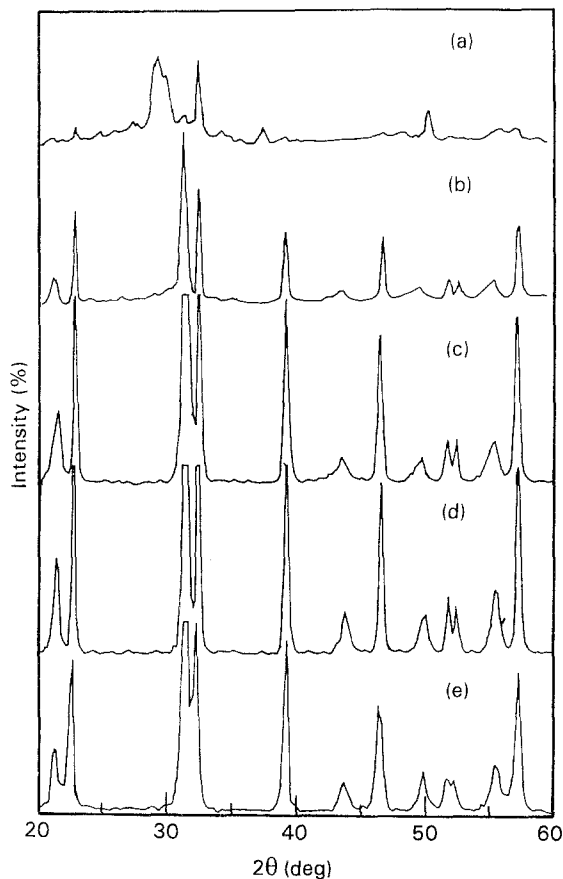
Figure 2 XRD patterns of PbTiO₃ powders purchased (e) and synthesized at different reaction temperatures (°C): (a) 150; (b) 170; (c) 200; (d) 300. Any synthesis was carried out for 8 h.

Figure 3 XRD patterns of PbTiO₃ powders purchased (e) and synthesized under the influence of 8 M potassium hydroxide solution for different reaction times (h): (a) 2; (b) 4; (c) 6; (d) 8. Any synthesis was carried out at 200 °C.

were necessary for the synthesis of the powders crystallized to a similar degree to the purchased powders.

For studies on the effects of reaction time, the powders were prepared at different reaction times at 200 °C of the borderline reaction temperature. Fig. 3 shows XRD patterns of the prepared powders. From the figure, it can be seen that reaction times longer than 2 h were found to be necessary for the synthesis of the desired powders.

Finally, the effects of alkali concentration were investigated. Fig. 4 shows XRD patterns of powders prepared as the concentration was varied. The figure suggests that 4 M was the borderline alkali concentration.

From the above results it is apparent that the synthesis of the desired PbTiO₃ powders required the influence of strong alkalis, and the borderline synthesis conditions were as follows: a strong alkali concentration, higher than 4 M; a reaction temperature over 200 °C; a reaction time longer than 2 h.

3.2. Effects of reaction conditions on geometrical properties of perovskite PbTiO₃ particles

For the promotion of higher performance and the facility of commercial production of the electronic components, particles of the feed powder needed to be uniform in geometrical properties, such as shape and size. Thus, it is important to discuss how synthesizing
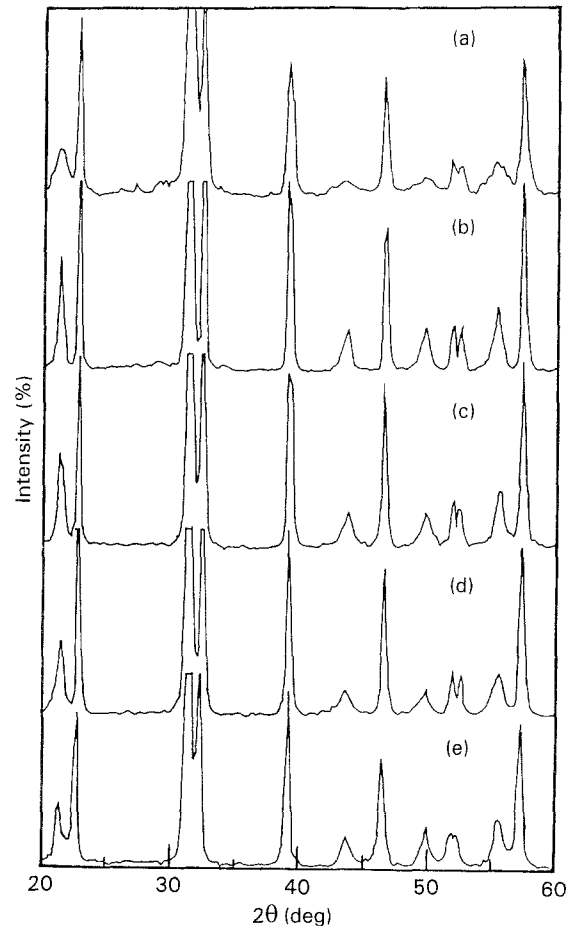
conditions affect geometrical properties of the PbTiO₃ powders. The powders were prepared under different synthesizing conditions beyond the borderline conditions found above.

Fig. 5 shows SEM micrographs of particles of the powders prepared under various reaction temperatures with the other conditions held constant. The figure reveals that at any given reaction temperature particles agglomerated rather distributed their size, and were dimetric. It also shows that their mean sizes decreased with an increase in the reaction temperature: a few micrometres at the lowest temperature of 200 °C and a few tenths of micrometres at the highest temperature of 400 °C. Such a change in the mean particle size may be explained as follows: (1) the particle size in crystallization is controlled mainly through two rate processes of nucleation and grain growth, which compete for chemical species; (2) their rates must be affected in individual dependences on the reaction temperature; (3) at higher reaction temperatures the former process was probably faster than the latter, and thus the particle growth was delayed.

Fig. 6 shows SEM micrographs of particles prepared at different reacting times. The agglomeration, size distribution and shape of the particles are observed to be similar to those in Fig. 5. The mean particle size was found to tend to increase with longer reacting times: a few tenths of micrometres at the
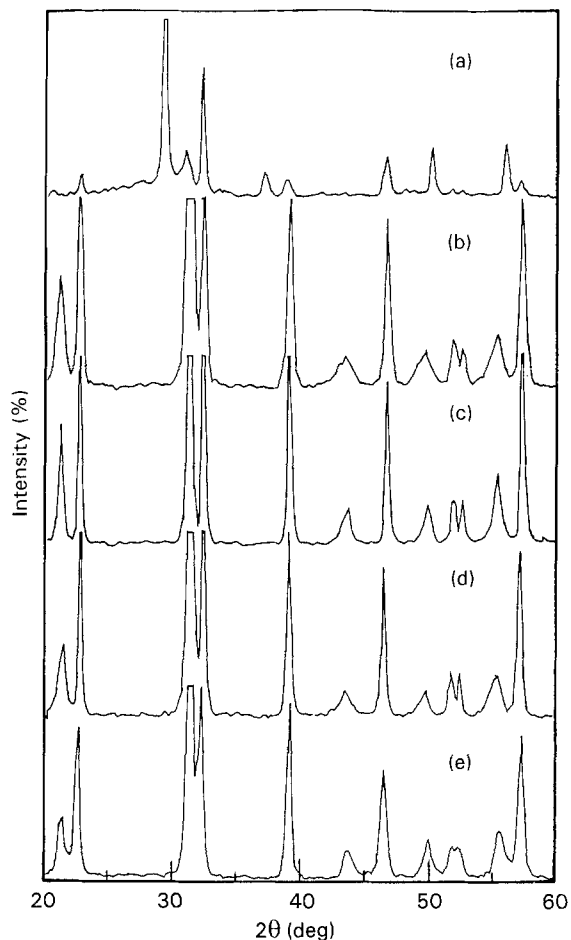
Figure 4 XRD patterns of PbTiO₃ powders purchased (e) and synthesized under the influence of potassium hydroxide solution of different concentrations (M): (a) 2; (b) 4; (c) 6; (d) 8. Any synthesis was carried out at 200 °C for 8 h.

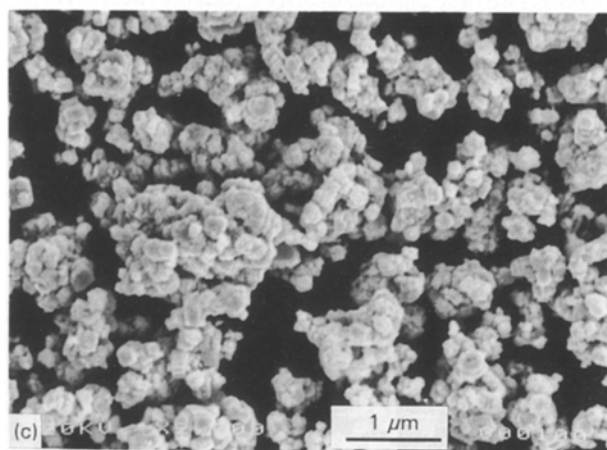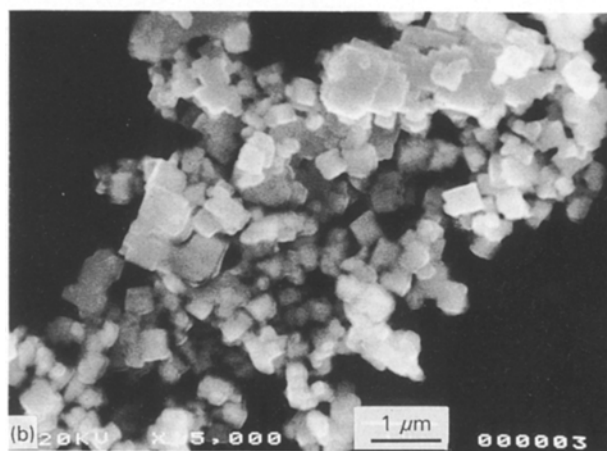*Figure 5* SEM micrographs of PbTiO₃ powders synthesized under the influence of 8 M potassium hydroxide at various reaction temperatures (°C): (a) 200; (b) 300; (c) 400. Any synthesis was carried out for 8 h.

shortest time of 2 h and several micrometres at the longest time of 10 h. From a discussion similar to that applied above, such properties are regarded as being responsible for the grain growth being faster than the nucleation under these reaction conditions. Fig. 7 shows SEM micrographs of particles synthesized at various alkali concentrations. Characteristics similar to those in Fig. 6 were observed for the particle agglomeration and so on. The mean particle size increased with an increase in the alkali concentration, although rather large particles were found even at lower alkali concentrations of 4 and 6 M. To confirm such particle growth with an increase in alkali concentration, the particle size distribution for some of the powders was measured by LSDM. Fig. 8 shows the results. The figure reveals that, at any alkali concentration, particle sizes ranged from 2 to 15 μm, those at the maximum frequencies increased with an increase in the alkali concentration. Thus, that particle growth increased with an increase in alkali concentration was confirmed.

Therefore, it can be concluded that higher alkali concentrations and longer reaction times give larger powder particles, whilst higher reaction temperatures give smaller ones. These findings correspond to those for the hydrothermal synthesis of PZT powder [8].
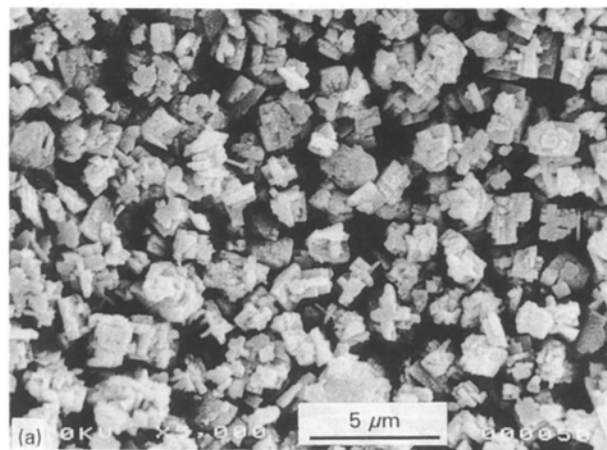
However, particle agglomeration and particle size distribution appear to be significant and cannot be ignored when choosing reaction conditions, for example, reaction temperature.

3.3. Particle size control

As described earlier, powders containing particles distributing their sizes in a simple mode at the sub-micrometre level are favourable for the fabrication of electronic components. However, the experimental
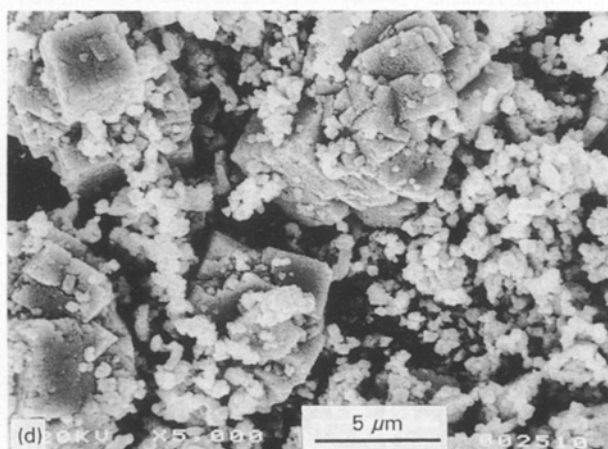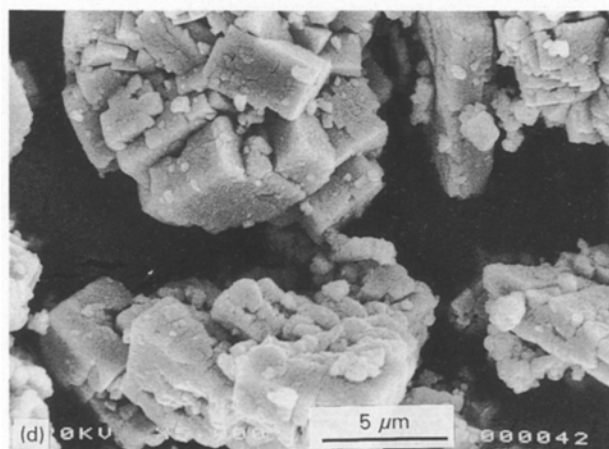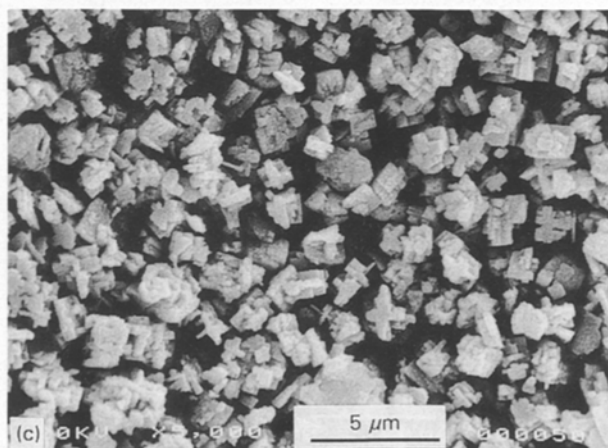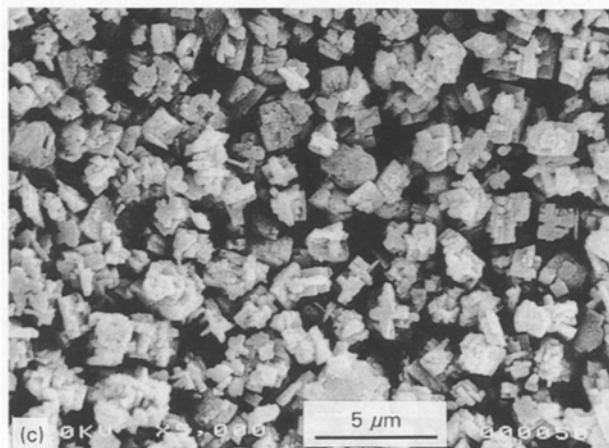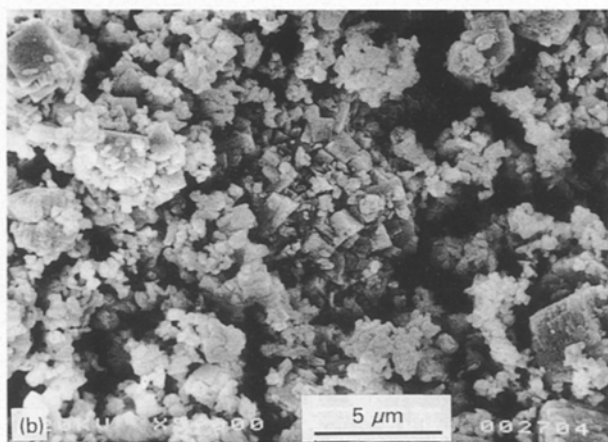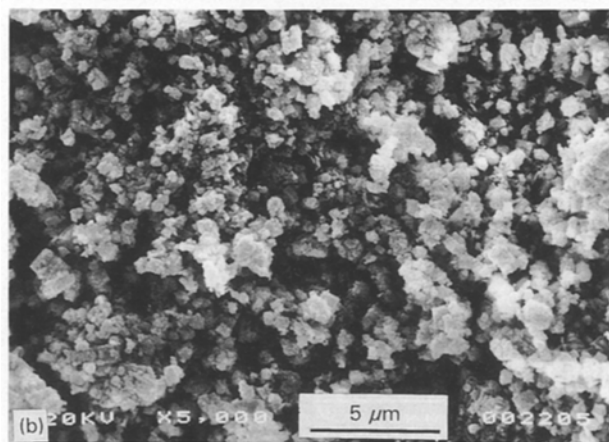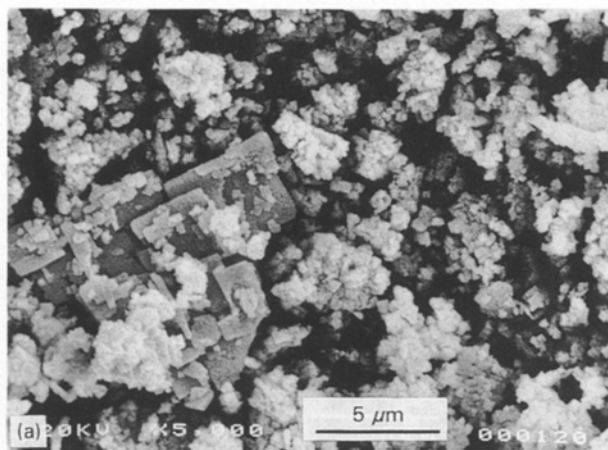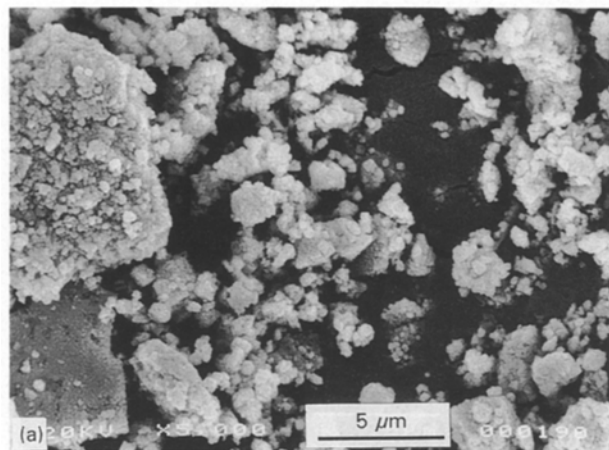
Figure 6 SEM micrographs of $PbTiO_3$ powders synthesized under the influence of 8 M potassium hydroxide solution for various reaction times (h): (a) 2; (b) 3; (c) 8; (d) 10. Any synthesis was carried out at 200 °C.

Figure 7 SEM micrographs of $PbTiO_3$ powders synthesized under the influence of potassium hydroxide solution of various concentrations (M): (a) 4; (b) 6; (c) 8; (d) 12. Any synthesis was carried out at 200 °C for 8 h.
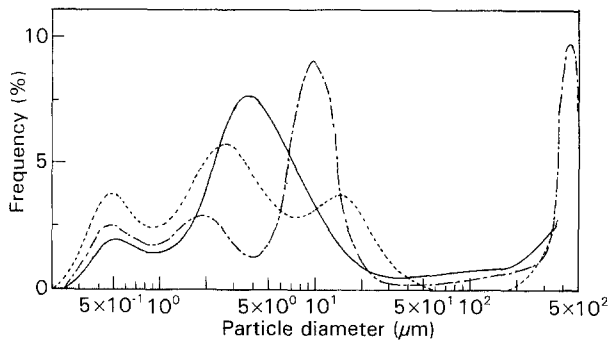
Figure 8 Particle size distribution, determined by a LSDM, of PbTiO₃ powders corresponding to those shown in Fig. 7:- - -, 6 M; —, 8 M; — · —, 12 M.
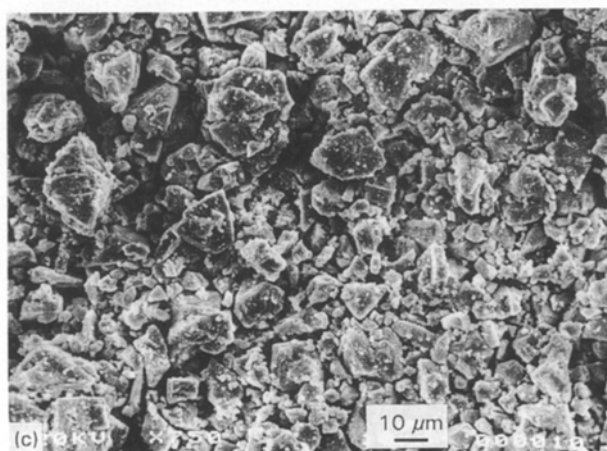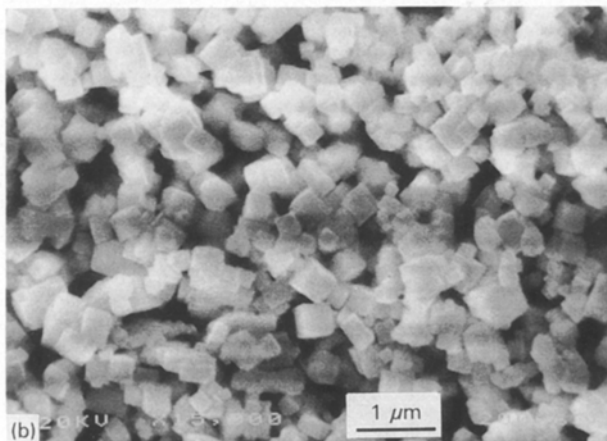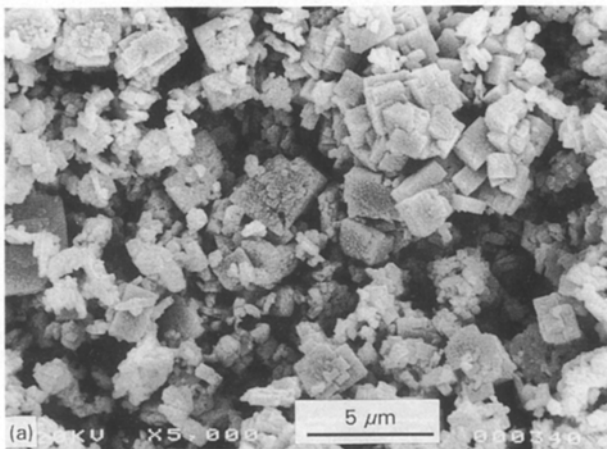

Figure 9 SEM micrographs of PbTiO₃ powders purchased (c) and synthesized at 200 °C corresponding to those in Fig. 9: (a) without PAAm additive; (b) with PAAm additive.

results described above suggest that it may be impossible to realize their unimodal size distribution by choosing only the reaction conditions. To control the particle size the first thing to do is to prevent particles from agglomerating. Thus, dispersing effects of the additives are discussed.

When PVA was added, any prepared powder was found (by XRD analysis) to contain undefined crystal phases other than the perovskite. Thus, no further investigation was made into PVA addition.

PAAm produced powders consisting only of the perovskite phase, which affected the particle size distribution. The effects were obtained adequately with addition of 0.1 wt % of PAAm. Fig. 9 shows SEM micrographs of the powders prepared with and without PAAm addition, with the other reaction conditions held constant. Fig. 9 also shows an SEM micrograph of the purchase powder. The micrographs clearly indicate the addition effect on mean particle size and particle size distribution. The mean particle size decreased from a few micrometres to the submicrometre level on addition of PAAm; the size distribution shifted from a complex mode to a simple one. For clarification of the effect LSDM measurements were made. Fig. 10 shows the results. It clearly indicates a decrease in mean particle size and a shift to simple modes of size distribution as additive effects. However, the mean particle sizes observed on the SEM micrographs appeared to be different to those recorded by LSDM measurements. This was caused by uncertainty in the LSDM measurements, which were induced from the use of an arbitrarily chosen refractive index of PbTiO₃ powders. Thus, the real particle size distribution was measured directly from the SEM micrographs. Fig. 11 shows the measured size histogram of particles synthesized at 200 °C. The figure indicates that PAAm addition lowered the mean particle size from 1.7 to 0.5 μm and made the mode of particle size distribution simple. Such additive effects may be explained in terms of stabilization of the finer
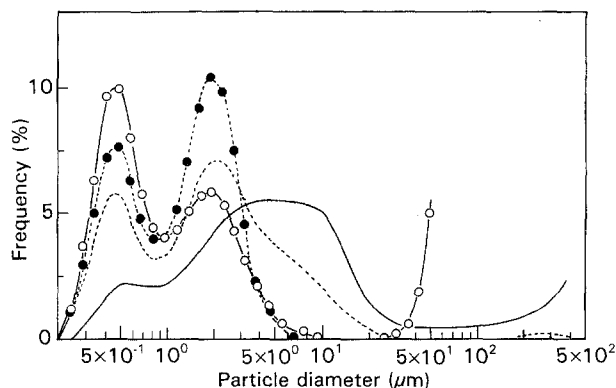

Figure 10 Effect of polyacrylamide addition on particle size distribution, determined by a LSDM, of PbTiO₃ powders synthesized under the influence of 6 M potassium hydroxide solution, where o — o and ● — ● are with PAAm addition and —— and - - - are without PAAm addition. Any synthesis was carried out for 6 h, but at different reaction temperatures: ● — ● and - - - at 300 °C; o — o and —— at 200 °C.
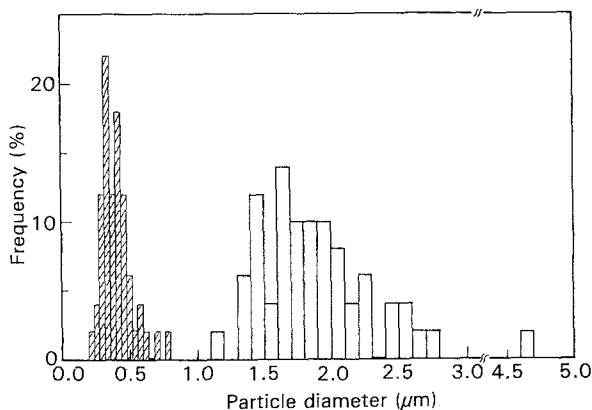
Figure 11 Particle size histograms from the SEM micrographs shown in Fig. 10, of PbTiO₃ powders synthesized at 200 °C: ◫ without PAAm additive; □ with PAAm additive.

particles of PbTiO₃ through steric effects of PAAm molecules adsorbed on them.

4. Conclusion

Hydrothermal synthesis was studied for use in preparing the perovskite PbTiO₃ powders which are suitable for the fabrication of compact electronic components with high performances.

To synthesize powders which were well crystallized and consisted of a single perovskite phase addition of a strong alkali, such as potassium hydroxide, was required. The synthesis conditions beyond 4 M alkali concentration, 2 h reaction time and 200 °C reaction temperature were found to be necessary. The observed effects of reaction conditions on the geometrical properties of PbTiO₃ particles were as follows: (1) higher reaction temperatures decreased powder particle sizes; (2) longer reaction times and higher alkali concentrations increased particle sizes. The prepared powders distributed their particle size in a multi-mode way when no counter-measure was present. When polyacrylamide was added to the hydrothermal synthesis, as a counter-measure, the mean particle size fell to submicrometre levels and were distributed in a simple mode.

Acknowledgements

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