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The influence of anions on the products of $BaTiO_3$ under hydrothermal conditions

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Tetragonal $BaTiO_3$ has been prepared from a reactive titanium source, tetrabutyl titanate, with barium acetate in alkaline aqueous solution at temperatures as low as 200–240 °C. Various methods, such as X-ray diffraction, differential scanning calorimetry and scanning electron microscopy have been used to investigate the effects of alkalinity, anions, reactivity of the titanium source and degrees of fill, on the particle sizes and morphologies of $BaTiO_3$ generated hydrothermally. The most appropriate KOH concentration is about 1.0 $mol\,l^{-1}$ in which $BaTiO_3$ is the stablest phase in the BaO–TiO_2 system. Compared with chloride and nitrate ions, the acetate ion accelerates the formation of large-grained particles of $BaTiO_3$ more prominently. A more reactive titanium source and a higher fill can promote the formation of tetragonal $BaTiO_3$.

1. Introduction

Hydrothermal synthesis offers many advantages over conventional sintering methods as described by Lencka and Riman [1]. Fine and uniform particles of $BaTiO_3$ with higher purity and without agglomeration have been obtained by using hydrothermal synthesis [2]. The hydrothermal synthesis of $BaTiO_3$ has been reported by a number of researchers [1–7]. In these reports, tetragonal $BaTiO_3$ has not been reported to be produced at temperatures lower than 250 °C. However, it was reported by Kajiyoshi *et al.* [6] and Christensen [7] that the tetragonal form could be directly obtained by the hydrothermal method at temperatures higher than 400 °C. It was claimed by Dutta and Gregg [8] that tetragonal $BaTiO_3$ could be prepared at a temperature as low as 250 °C after 1 week in the presence of chloride anions. Unfortunately, we failed to obtain tetragonal $BaTiO_3$ whilst repeating Dutta's experimental procedure.

In addition, there have been no reports of the influence of nitrate or acetate anions, the reactivity of the titanium source, and the degrees of fill, on the particle sizes and morphologies of $BaTiO_3$ so far. In the present work, the above various effects on the as-synthesized particles of $BaTiO_3$ are examined, and the tetragonal crystals of $BaTiO_3$ were prepared under milder hydrothermal conditions.

2. Experimental procedure

2.1. Synthesis method

The hydrothermal reaction was carried out in a Teflon-lined stainless steel autoclave with the total concentration of titanium and barium at 0.5 $mol\,l^{-1}$. The degree of fill was 80% unless specifically mentioned. After barium and titanium sources with certain Ti/Ba ratio were placed in the autoclave, it was sealed without any agitation of the solution. After heating for various periods in an oven, the autoclave was quenched quickly by immersion in water, and then opened. The product was filtered off, washed with distilled water and kept in a desiccator until dry.

2.2. Characterization

The product phase was identified by powder X-ray diffraction (XRD) using a Kigaku D/MAX-IIIA powder diffractometer with CuK_α radiation ($\lambda = 0.1548$ nm). The relative height and full-width at half-maximum (FWHM) of the (1 1 1) diffraction peak were adopted to compare the crystal and particle sizes.

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Particle sizes and micrographs were determined by scanning electron microscopy (SEM). Calorimetry measurements were taken with a Perkin–Elmer 7 Series thermal analysis system.

3. Results and discussion

3.1. Alkalinity and Ti/Ba ratio

The mixture, tetrabutyl titanate and $BaCl_2$, $Ba(NO_3)_2$ or $BaAc_2$, in the ratio Ti/Ba of 1:1, produced TiO_2 after hydrothermal reaction at 240 °C. From a thermodynamics point of view, $BaTiO_3$ can only be formed from a strong alkaline condition, i.e. at $pH > 13$ [1]. The alkalinity plays an important role in the crystallization of $BaTiO_3$ under hydrothermal conditions. Fig. 1 shows the relationship between the heights of (1 1 1) reflection peak and the concentrations of KOH. Acceptable concentrations of KOH for $BaTiO_3$ formation are $0.5–2.5\ mol\,l^{-1}$. However, a solution with a much higher KOH concentration would easily absorb CO_2 from the ambient atmosphere [1]. According to Fig. 1, the KOH concentration was fixed at a constant value, $1.0\ mol\,l^{-1}$, in the following experiments.

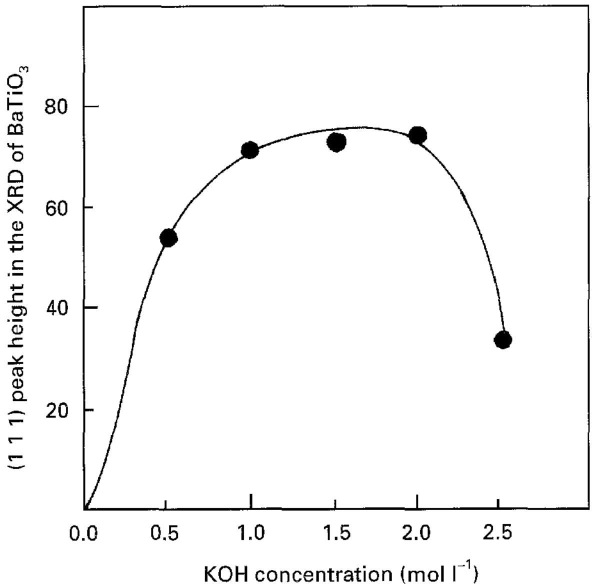

Figure 1 The influence of KOH concentration on the crystallization of $BaTiO_3$ under hydrothermal conditions.

Barium polytitanate was prepared by annealing the as-obtained product of the hydrothermal reaction between barium and titanium sources, with a Ti/Ba ratio of greater than 1 [9]. No pure barium polytitanate was isolated from KOH aqueous solution using the hydrothermal method at 240 °C for 2 days, but a mixture of $BaTiO_3$ and TiO_2 was obtained when the Ti/Ba ratio was greater than 1; when the Ti/Ba ratio was lower than 1, only $BaTiO_3$ crystal phase could be found in the XRD pattern, and extra unreacted $Ba(OH)_2$ remained in the solution, was washed by filtration and/or existed in an amorphous state. All of the above experimental results imply that $BaTiO_3$ is the stablest crystal phase of the $BaO–TiO_2$ family under alkaline hydrothermal conditions.

3.2. The effects of anions

The FWHM (2θ) of the (1 1 1) diffraction peak of $BaTiO_3$ which was converted from TiO_2 with $Ba(OH)_2$, $BaCl_2$, $Ba(NO_3)_2$ or $BaAc_2$ at 240 °C for 4 h in the $1.0\ mol\,l^{-1}$ KOH hydrothermal system is 0.289°, 0.226°, 0.225° or 0.204°, respectively; and the

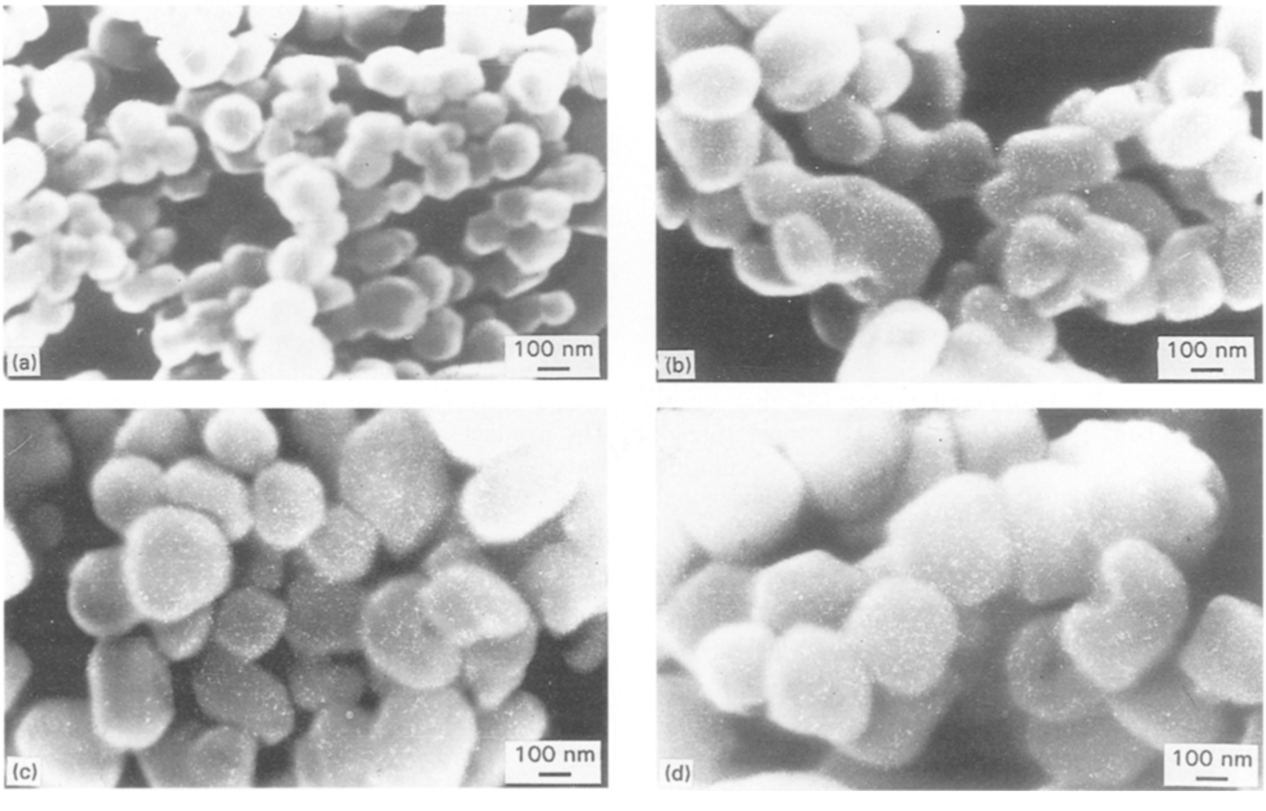

Figure 2 Scanning electron micrographs of $BaTiO_3$ prepared hydrothermally from TiO_2 with (a) $Ba(OH)_2$, (b) $BaCl_2$, (c) $Ba(NO_3)_2$, or (d) $BaAc_2$ at 240 °C, for 1 week.

FWHM is 0.244°, 0.212°, 0.206° or 0.194°, respectively, while at 240 °C for 1 week. The particle sizes of $BaTiO_3$ crystals from $BaAc_2$ starting material, have the largest values (Fig. 2). These results demonstrate that Cl^-, NO_3^- or Ac^- anions can facilitate the formation of larger crystals of $BaTiO_3$ under hydrothermal conditions; of these, Ac^- anions have the greatest effect.

The (2 0 0) reflection remains unsplit in the XRD of the $BaTiO_3$ (Fig. 3) and no thermal transitions can be observed between 50 and 200 °C in the DSC curves of $BaTiO_3$, which was prepared from TiO_2 with $BaCl_2$, $Ba(NO_3)_2$ or $BaAc_2$ at 240 °C for 1 week. These experimental results indicate that the $BaTiO_3$ did not exhibit the tetragonal form as reported by Dutta and Gregg [8].

3.3. Synthesis of tetragonal $BaTiO_3$

The powder diffraction pattern in the range 44°–46° (2θ) for $BaTiO_3$ produced from $BaAc_2$ and tetrabutyl at 240 °C for 2 days is shown in Fig. 4a. The (2 0 0) reflection is split with a lower-angle peak which is indexed at (0 0 2). There is an evident endothermic transition on heating and an exothermic transition on cooling at 128 and 121 °C, respectively, in the DSC curves for the as-prepared $BaTiO_3$ powder (Fig. 5). The average change in enthalpy corresponding to the transition (Curie point) between tetragonal and cubic structure was about 420 mJ g^{-1}. These experimental results confirm that the $BaTiO_3$ was tetragonal at room temperature. The unit cell parameters *a* and *c* were about 0.4002 and 0.4030 nm; the ratio *c*/*a* was 1.008. A scanning electron micrograph is shown in

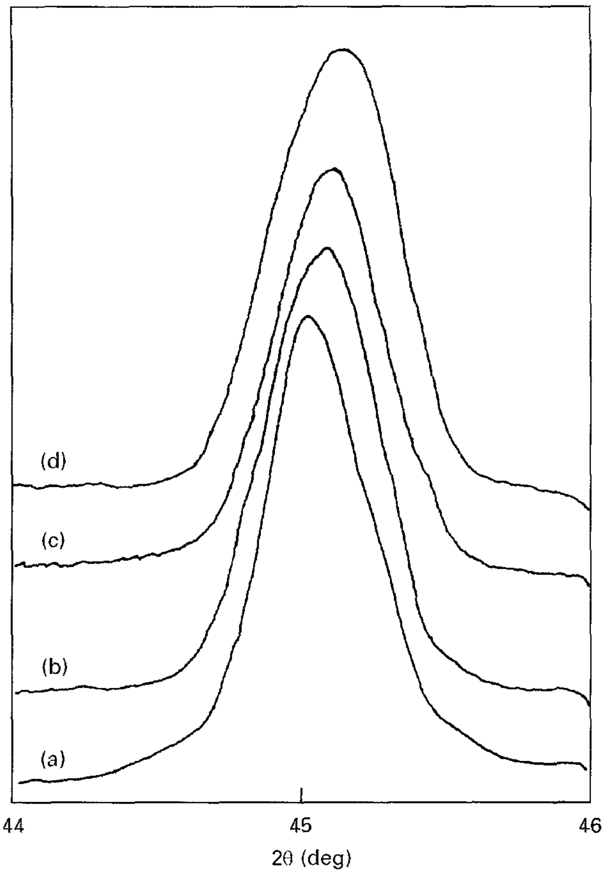

Figure 3 XRD of $BaTiO_3$ synthesized hydrothermally from TiO_2 with (a) $Ba(OH)_2$, (b) $BaCl_2$, (c) $Ba(NO_3)_2$, or (d) $BaAc_2$ at 240 °C for 1 week.

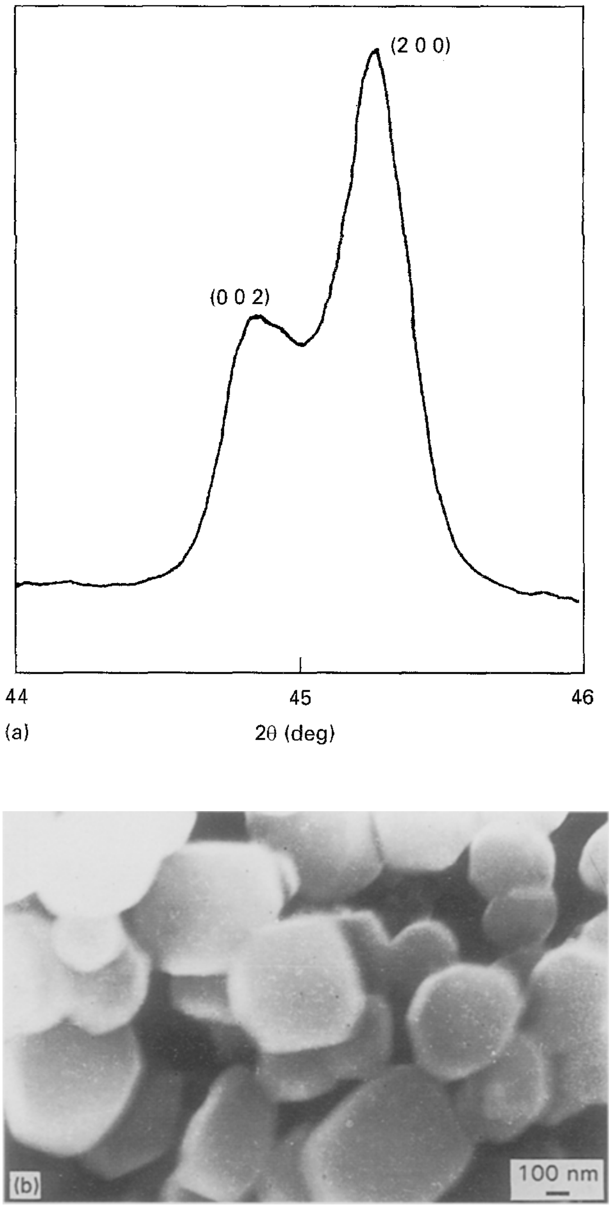

Figure 4 (a) XRD and (b) scanning electron micrograph of $BaTiO_3$ formed from tetrabutyl titanate with $BaAc_2$ at 240 °C for 2 days.

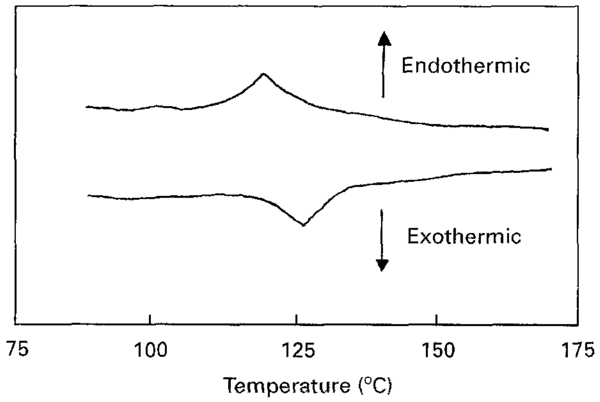

Figure 5 DSC traces of $BaTiO_3$ generated from tetrabutyl titanate with $BaAc_2$ at 240 °C for 2 days: (a) during the heating cycle, (b) during the cooling cycle.

Fig. 4b. The above results imply that the reactive starting material, such as tetrabutyl titanate which substitutes more unreactive TiO_2, will lower the nucleation temperature, as described elsewhere [3], speed crystal growth and enhance the formation of larger $BaTiO_3$ particles; in turn, tetragonal $BaTiO_3$ can be obtained under much milder hydrothermal conditions. That the (2 0 0) reflection of $BaTiO_3$ produced from $BaAc_2$ and tetrabutyl titanate after only one week at 200 °C, also exhibits a shoulder at lower angle (Fig. 6a), indicates that the $BaTiO_3$ product contained tetragonal phase. The scanning electron micrograph is shown in Fig. 6b.

When comparing the micrograph in Fig. 7 of $BaTiO_3$ prepared at 240 °C for 1 week with that in Fig. 4b, it is easy to see that the particle-size distribution is not so uniform as that in Fig. 4b. The adherence of some smaller crystals to a larger crystal (Fig. 7) indicates that the $BaTiO_3$ crystals are not monodispersed. This phenomenon is consistent with the basic crystallization mechanism, involving crystal growth, dissolution and reprecipitation. In the primary hydrothermal reaction state, the system is in a state of supersaturation, nucleation and growth is the dominant process, and the $BaTiO_3$ particles become increasingly larger until dissolution and growth (reprecipitation) reaches a state of dynamic equilibrium. From that moment on, the larger crystals continue to increase in size, while the smaller crystals become increasingly smaller, because the solubility of the larger crystals is less than that of the smaller crystals. Now it is not difficult to comprehend that too long a hydrothermal crystallization will result in the formation of polydispersed crystals. Therefore, the hydrothermal crystallization should be controlled to an appropriate duration in order to produce mono-dispersed powdery material.

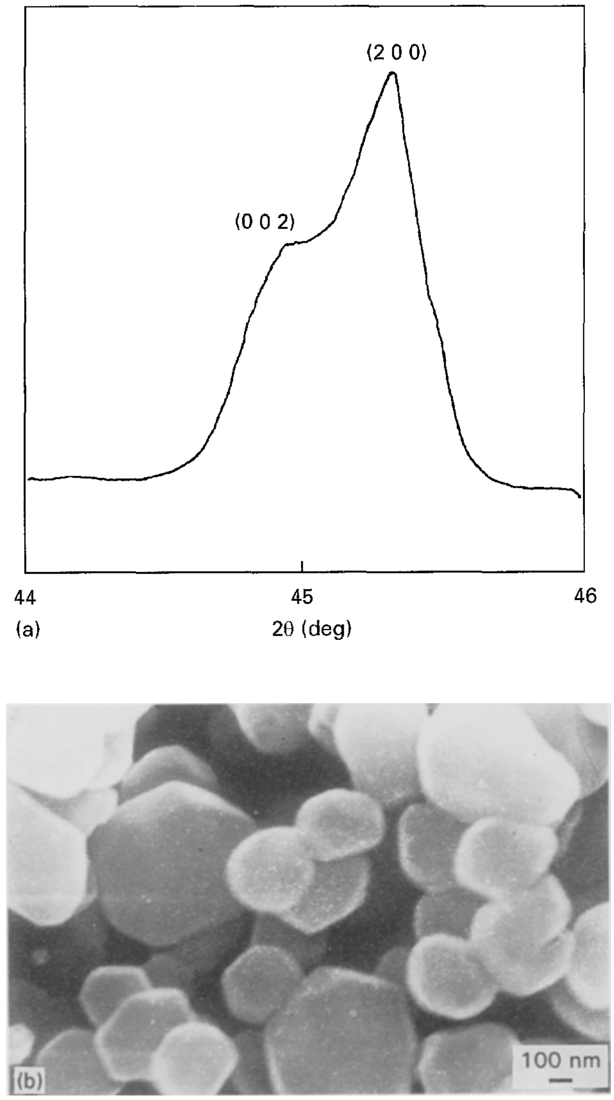

Figure 6 (a) XRD and (b) scanning electron micrograph of $BaTiO_3$ synthesized from tetrabutyl titanate and $BaAc_2$ at 200 °C for 1 week.

3.4. Degrees of fill

One of the most noticeable advantages of hydrothermal crystallization is the use of the autogenous pressure in the sealed reaction vessel to promote the

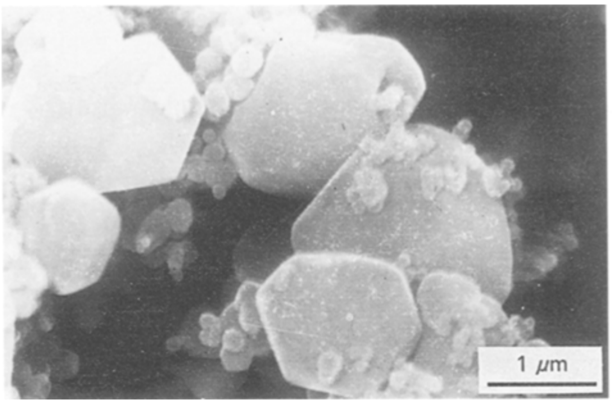

Figure 7 Scanning electron micrograph of the hydrothermally synthesized $BaTiO_3$ from tetrabutyl titanate and $BaAc_2$ at 240 °C for 1 week.

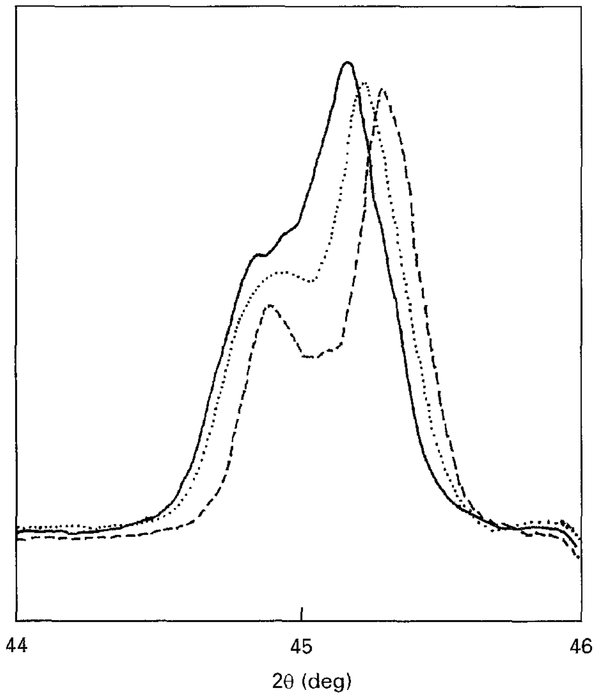

Figure 8 The influence of degrees of fill on the production of tetragonal $BaTiO_3$: (——) 20%, (···) 45%, (– – –) 80%.

nucleation and growth of the required product. A higher degree of fill increases the pressure of the reaction system dramatically, and facilitates the generation of tetragonal $BaTiO_3$. Fig. 8 elucidates the effects of degrees of fill on the formation of tetragonal $BaTiO_3$.

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