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Review

Low-temperature synthesis and processing of electronic materials in the BaO–TiO_2 system

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The BaO–TiO_2 system contains several technologically important electronic materials. $BaTiO_3$, a ceramic with high dielectric constant, is useful for the manufacture of multilayer ceramic capacitors, thermistors and electro-optic components. Titania rich compounds in this system (such as $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$) are suitable for the manufacture of miniaturized microwave resonators. Conventional processing of these ceramics relies on the solid-state reactions between readily available raw materials (typically TiO_2 and $BaCO_3$) and tends to produce coarse, impure, inhomogeneous and multiphase powders. Low temperature, wet chemical routes offer an exciting possibility for the synthesis of high purity, homogeneous, ultrafine and multicomponent powders from which electronic components with tailored and predictable properties could be prepared. A review of new and emerging techniques for the low temperature, wet chemical synthesis of barium titanates is presented. Salient features of several of these processes based on the use of alkoxides, acetates, citrates, chlorides, hydroxides and oxalates of barium and titanium, and combinations thereof, are described. The reaction pathways for the formation of barium titanates are discussed. A comparative summary of the powder characteristics and electrical properties of the barium titanates obtained by different techniques is presented along with a brief discussion of the economic viability of these processes.

1. Introduction

Barium titanate compounds in the BaO–TiO_2 system are archetypal electronic ceramics with a long history of technological applications in the ceramic capacitors industry. Increasing demands on the quality of electronic ceramics have led to greater sophistication in the processing of these materials both at the powder-synthesis stage and subsequent densification to solid components or thin dielectric layers. In the traditional 'mixing and firing' approach, common to usual ceramic processing, oxides or salts (such as carbonates) are mechanically mixed, calcined, pressed and sintered to yield a solid body. The resulting microstructure has a wide grain-size distribution, multiple phases and inevitably some degree of porosity. Many of these characteristics are symptomatic of inadequate attention to the powder processing stage where inhomogeneity and impurity incorporation normally originate. The growing awareness of the need for scientific elegance in processing electroceramic powders before firing is clear in much of the current emphasis on novel low-temperature synthesis techniques. These emerging methods hold the promise of yielding high-purity, ultrafine powders with predictable dopant levels and a hitherto unattainable degree of compositional homogeneity.

The primary objective of this review is to describe and discuss the salient features of the newly evolving wet chemical techniques for preparation of BaO–TiO_2 powders. The processes are classified on the basis of the starting precursors which form the powders, gels and thin films. The use of inorganic and/or organometallic precursors has previously been reported for the synthesis of $BaTiO_3$ powders. Alkoxides, acetates, chlorides, hydroxides, nitrates, citrates, oxalates of barium and titanium and combinations of these precursors are known to form high-purity submicron powders of $BaTiO_3$, $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$. In the present review we will describe and discuss these processes highlighting the chemistry and the reaction pathways for the evolution of crystalline phases from the precursor powders synthesized by different routes. The extent of constituents mixing at submicron level and the impact on powder characteristics will be reviewed. Finally, a comparative summary of the purity and morphology of powders, as well as the microstructure and electrical properties of the densified ceramic, will be presented with a brief discussion of the economic viability of these processes.

2. BaO–TiO_2 compounds and devices

2.1. Barium titanate ($BaTiO_3$)

$BaTiO_3$ is a ubiquitous electronic ceramic widely utilized in the manufacture of thermistors, multilayer capacitors (MLCs) and electro-optic devices. We shall focus this discussion on the processing of MLCs.

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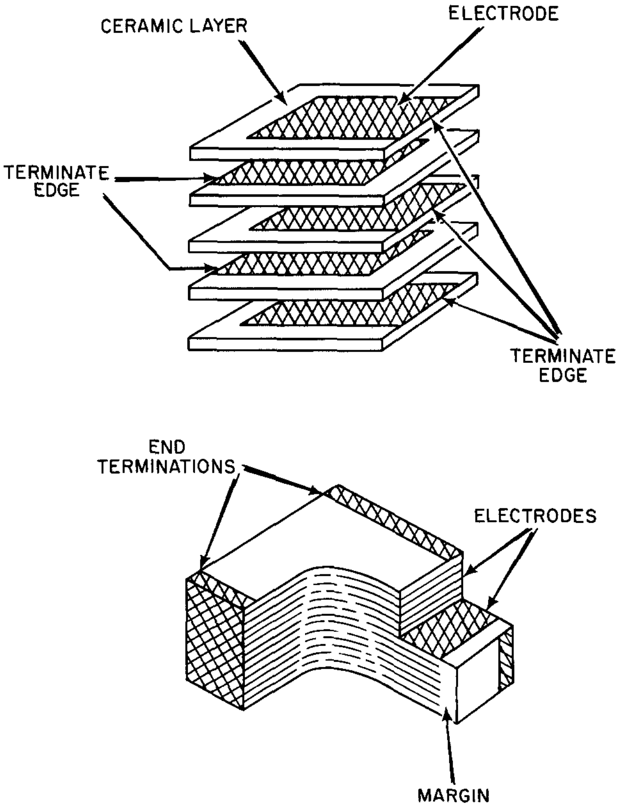

Figure 1 Schematic diagram of a multilayer ceramic capacitor (adapted from ref. 102).

Ceramic capacitors can have a single or multilayer configuration. A multilayer configuration (Fig. 1) consists of several dielectric layers arranged in parallel to obtain a high volumetric efficiency (capacitance per unit volume). Due to the increased miniaturization of future-generation integrated circuits, it is important to develope MLCs with higher levels of volumetric efficiency. One of the major technical barriers to the achievement of reliable MLCs is the lack of a clear understanding of the correlation between the mechanical defects and capacitor failure. The sources of mechanical defects are believed to be (i) poor control and characterization of starting powders; (ii) chemical reactions between dielectric and electrode materials; and (iii) imperfect process control [1]. The major cost-related barrier in the manufacture of MLCs is the high-temperature co-sintering which necessitates the use of expensive noble metal (usually silver/palladium) electrodes (Fig. 1). Metallization accounts for 90% of materials cost and 35% of the total cost of an MLC [1]. Relatively inexpensive non-noble metal electrodes (e.g. nickel, copper) can be used if the MLCs are processed at lower temperatures (below $\approx 1000°$ C).

Reductions in the manufacturing costs associated with the use of non-noble metal electrodes, and the potential for increased reliability and production yield, have provided the impetus for the low-temperature synthesis and processing of $BaTiO_3$ powders. Novel low-firing dielectric compositions, sintering additives (e.g. LiF), sintering in inert/reducing atmosphere and low temperatures synthesis of high purity, homogeneous, ultrafine and sinteractive $BaTiO_3$ powders are some of the areas of active current research.

2.2. Barium polytitantates

Barium tetratitanate ($BaTi_4O_9$) and $Ba_2Ti_9O_{20}$ are the titania-rich compounds in the $BaO–TiO_2$ system that are of considerable interest for microwave dielectric applications, particularly as microwave resonators (Fig. 2). The dielectric constant of these materials is higher (35 to 40) than air which allows miniaturization of microwave resonators. The desired properties of the ceramics for microwave resonators are (i) a dielectric constant greater than 10 and preferably high (35 to 40); (ii) low dielectric loss ($\tan \delta < 10^{-3}$ in the GHz frequency range) and a low-temperature coefficient of the dielectric constant (< 20 p.p.m. $°C^{-1}$). Many of the materials based on combinations of titanates and zirconates (with and without dopants) are being researched to obtain microwave dielectric ceramics with improved dielectric properties.

2.3. Other compounds in the $BaO–TiO_2$ system

A few other compounds in the $BaO–TiO_2$ system appear to be promising, but studies on these materials are somewhat limited due to the difficulties in synthesizing and processing these materials in a single-phase form. Recently, Kirby has reinvestigated and modified the phase diagram of the $BaTiO_3–TiO_2$ system [2] (Fig. 3). Studies similar to those reported by Ritter *et al.* [3] and Millet *et al.* [4] on phase relations of electroceramic materials should also be useful for their synthesis and processing. It must be emphasized that some of these materials, which cannot readily be prepared in a single phase form using the oxide-mix technique, can be synthesized using wet chemical techniques.

3. Conventional processing

Conventional processing of electoceramic materials relies on solid-state reactions between readily available raw materials (typically $BaCO_3$ and TiO_2). The reaction scheme for the formation of $BaTiO_3$,

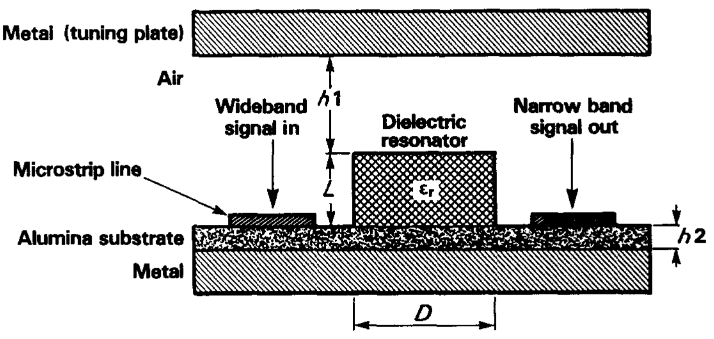

Figure 2 Schematic diagram of a ceramic microwave resonator positioned between two microstrip lines (from ref. 103).

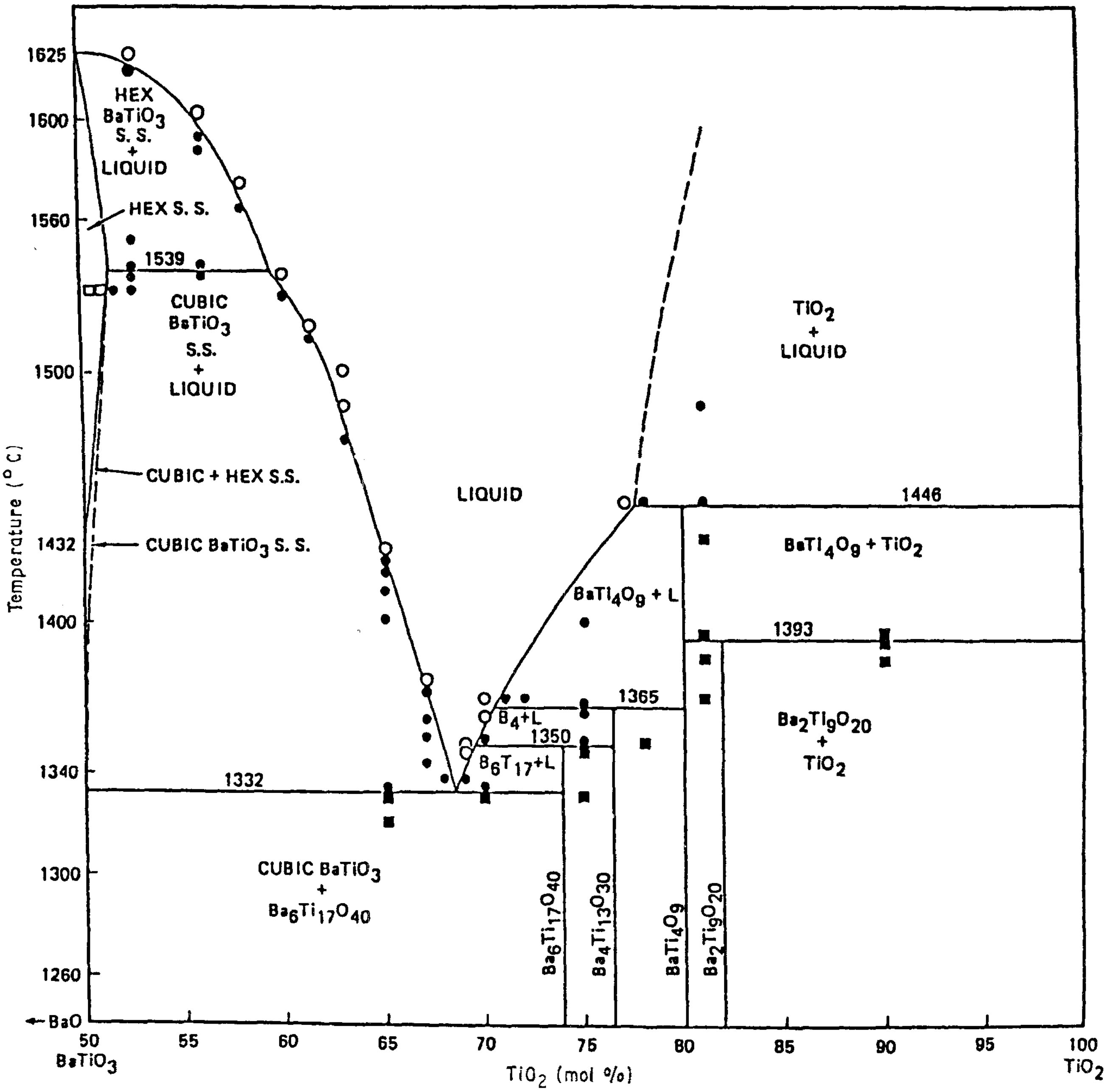

Figure 3 Recently reinvestigated phase diagram of $BaTiO_3$–TiO_2 system (courtesy of Keven Kirby and B. A. Wechsler, Hughes Research, Malibu, California). ○, All liquid; ●, solid and liquid phases; ■, two solid phases; □, one solid phase.

illustrated in Table I, has been discussed in literature [5–9]. The formation of intermediate phases prior to the completion of $BaTiO_3$ formation is noteworthy. Similar mechanisms are known to exist for the synthesis of polytitanates. The high-temperature synthesis of these materials results in the formation of relatively coarse, inhomogeneous and possibly multiphase (such as $BaTiO_3$ calcines containing Ba_2TiO_4) powders.

TABLE I Reactions leading to formation of $BaTiO_3$ from $BaCO_3$ and TiO_2

1. Reaction at the interface by diffusion of Ba into TiO_2
   $BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2$
2. Initial formation of $BaTiO_3$ protective layer on TiO_2 particles limits diffusion of Ba into TiO_2
3. Formation of orthotitanate phase
   $BaCO_3 + BaTiO_3 \rightarrow Ba_2TiO_4 + CO_2$
   $2\ BaCO_3 + TiO_2 \rightarrow Ba_2TiO_4 + 2CO_2$ (less likely)
4. Final formation of $BaTiO_3$
   $Ba_2TiO_4 + TiO_2 \rightarrow 2\ BaTiO_3$
5. Formation of other phases
   e.g. $Ba_6Ti_{17}O_{40}$, $Ba_4Ti_{13}O_{30}$

Also, as a result of the use of relatively impure raw materials and ball-milling operations, impurities such as alumina, silica, sulphur, phosphorus etc. are usually introduced in conventionally prepared ceramics. These impurities are known to have deleterious effects on the electrical characteristics and mechanical properties of barium titanate-based electronic components. The desirability of high-purity $BaTiO_3$ for thermistor and capacitor applications is well documented in the literature and the deleterious effects of impurities on the electrical properties of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ are being studied. For example, the recent study by Mhaisalkar [10] clearly demonstrates the severe degradation of the $BaTi_4O_9$ electrical properties, dielectric loss in particular, as a result of the Al_2O_3 impurity introduced during ball-milling operations. Effects of desirable impurities such as manganese and tungsten on the electrical properties of polytitanates have also been reported [11–12]. Care has to be exercised while using wet chemical techniques as well. Kutty and Murugaraj [13], for example, have reported the stabilization of the $Ba_2Ti_{5.5}O_{13}$ using the hydrothermal route in stainless steel autoclaves. Under apparently identical conditions the same phase could not be obtained in stainless steel autoclaves lined with teflon. They have attributed this phenomenon to the effect of impurities from the stainless steel autoclave. Therefore in order to elucidate, understand and control the useful and undesirable effects of impurities, there is a need to develop protocols for the synthesis of high purity, single phase, homogeneous and sinteractive powders of these polytitanate materials. Several laboratories are currently pursuing research in wet chemical processes for the synthesis of high-purity, submicron, homogeneous and stoichiometric $BaTiO_3$ powders.

4. Emerging low temperature processes for $BaTiO_3$ powders

4.1. Alkoxide-derived powders [22–25]

The pioneering process developed by Mazdiyasni and co-workers [22–25] utilized simultaneous hydrolytic decomposition of titanium ethoxide (derived from titanium isopropoxide) and barium isopropoxide.

The technique resulted in the formation of ultrafine and high-purity crystalline powders of $BaTiO_3$. A calcination treatment (between 500 and 700° C) was necessary to remove the residual carbon and the formation of $BaCO_3$ was avoided as the entire process was conducted under an inert atmosphere. The overall reaction for the formation of $BaTiO_3$ can be written as follows

$$\mathrm{Ti(OC_5H_{11})_4 + Ba(OC_3H_7)_2 + 3H_2O}$$
$$\rightarrow \mathrm{BaTiO_3 + 4C_5H_{11}OH + 2C_3H_7OH}$$

One of the merits of this technique is the relative ease and uniformity with which dopants such as lanthanum, neodymium, scandium, niobium etc. are introduced at the solution stage. Thus the technique can be successfully used to obtain doped and multicomponent $BaTiO_3$-based powders. The oven-dried powders obtained using this technique were crystalline [23]. One of the salient features of this process is the high-purity end product. From the impurity analyses presented in Table II, it is clear that the purity of the alkoxide-derived powders is superior to the thermistor grade $BaTiO_3$ powders prepared by the acetate gel or oxalate process. The problems associated with this process are (i) the high cost of alkoxide reagents; and (ii) the premature hydrolysis of extremely moisture-sensitive barium precursor.

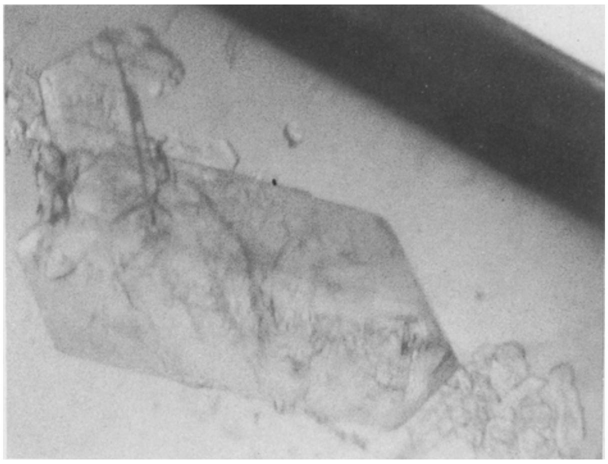

Figure 4 Microphotograph of a Ba–Ti double alkoxide single crystal (from ref. 20, courtesy Kevin Kirby).

4.2. Alkoxide-derived gels [20, 28, 29, 32, 33]

The rate of hydrolysis of the barium and titanium alkoxides can be reduced considerably at very low temperatures [28] and/or alkoxides concentrations to obtain monolithic gels [28, 33]. Amorphous gel powders have also been obtained [31, 32] from alkoxide precursors. These amorphous gels can be converted to crystalline $BaTiO_3$ by heat treatment at higher temperatures (> 400 to 650° C). The mechanism of $BaTiO_3$ formation has not been reported.

4.3. $BaTiO_3$ powders from double alkoxide single crystals

Kirby [20] recently reported synthesis of double alkoxide single crystals of the apparent composition $BaTi(OC_3H_7)_6$ from a barium-rich double isopropoxide solution. Larger (10 × 4.5 × 4 mm) crystals were obtained by seeding the virgin solutions immediately after preparation with smaller crystals from other attempts (Fig. 4). The precise structure and composition of the single crystals are not known, but highly crystalline $BaTiO_3$ powders were obtained by calcination at 800° C. Although novel, the large-scale application of this approach must await further extensive developmental work.

4.4. Use of molecularly modified titanium alkoxide and barium acetate [14, 16–19, 21, 31, 41]

4.4.1. Sol-Precipitation process

We reported a sol–gel as well as a sol-precipitation technique based on the use of these precursors [14, 16, 17]. Figures 5a and b indicate the application of this approach for the preparation of crystalline powders and monolithic gels (section 4.4.2) of $BaTiO_3$. The

TABLE II Impurity analyses of $BaTiO_3$ powders [14]

Impurity*	Alkoxides	Acetate gel	Oxalate	Oxide mix
Silica	< 0.02	< 0.02	0.01	0.12
Alumina	< 0.002	< 0.02	0.01	0.12
SrO	< 0.003	< 0.012	0.02	1.00
Na_2O	< 0.001	< 0.013	n.a.	0.13
CaO	< 0.014	< 0.014	n.a.	n.a.

*Weight percent. n.a. Not analysed.

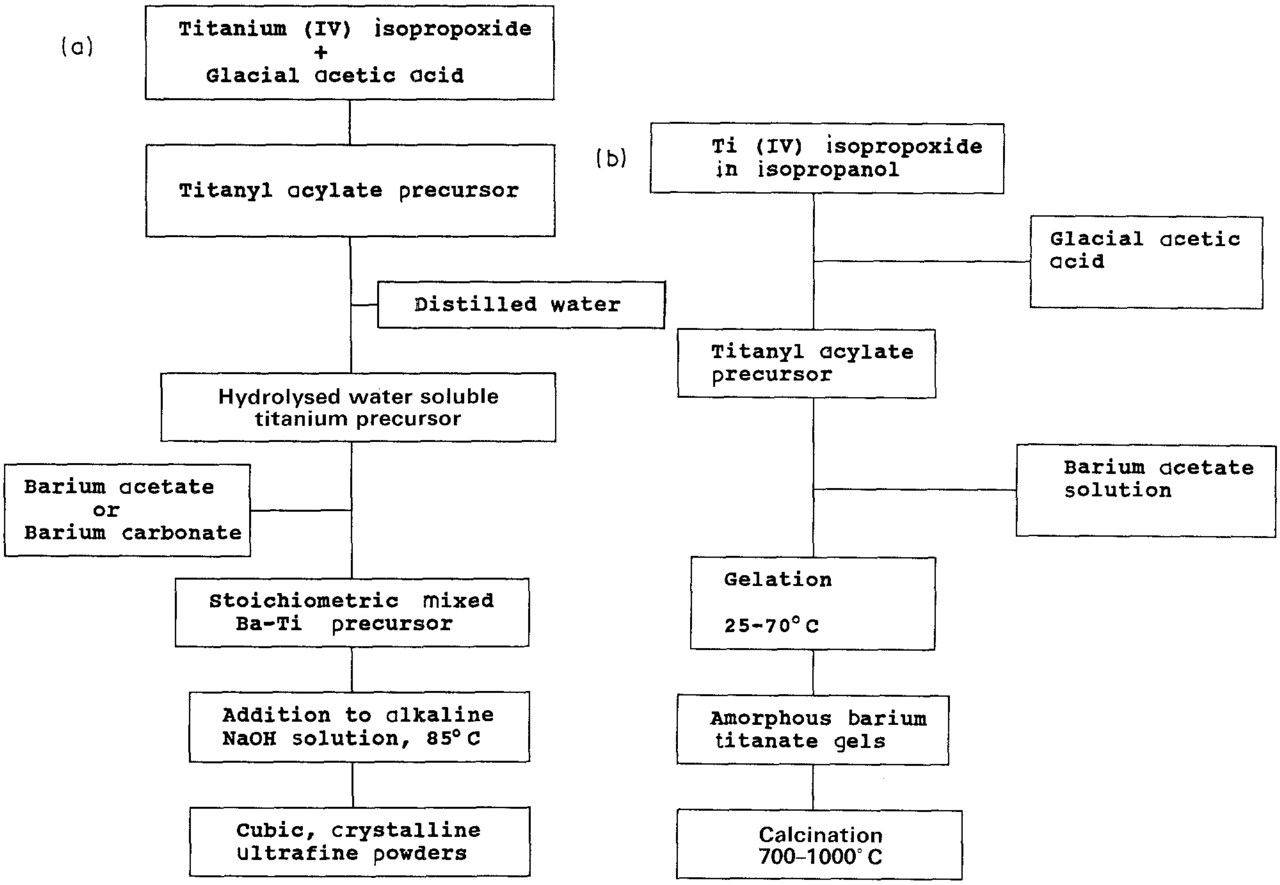

Figure 5 (a) Synthesis of sol-precipitated $BaTiO_3$ powders and (b) preparation of amorphous $BaTiO_3$ gels.

extent of replacement of alkoxy groups by the acetate (CH_3COO) groups depends on the Ac/Ti ratio. Reaction of titanium isopropoxide with excess (Ac/Ti = 10) glacial acetic acid results in a titanyl acylate type precursor. Under acidic conditions this precursor forms a white precipitate believed to be that of polymeric titanyl acylate. This precipitate dissolves in excess water, probably as a result of formation of a hydroxy titanium acylate type compound. Thus the problem of rapid hydrolysis of titanium isopropoxide and formation of hydrous titania can be avoided.

Barium acetate, a moisture-insensitive and inexpensive precursor, can then be dissolved into the hydrolysed titanium acylate-type precursor to obtain a stoichiometric sol. The sol is then added to a highly alkaline solution of sodium hydroxide to obtain high purity, submicron and stoichiometric $BaTiO_3$ powders.

The reaction between titanium alkoxides and acetic acid has been studied in detail by Doeuff *et al.* [40]. The reaction between water and titanyl acylate type precursor as well as the structure of the water-soluble titanium precursor needs further investigation. It is possible that on addition of the titanyl hydroxy acylate-type precursor $Ti(OH)_6^{-2}$ forms under highly alkaline conditions and reacts with Ba^{2+} to form cubic crystalline $BaTiO_3$. This is similar to the reaction mechanism for the synthesis of $BaTiO_3$ from barium hydroxide and titanium isopropoxide discussed in section 4.5. In these processes the possibility of hydrothermal type reactions must also be considered.

Figure 6 shows the morphology of the oven-dried (110° C) and calcined powders derived from this technique. The oven-dried powders consist of agglomerates consisting of very fine (< 100 nm) primary particles. It

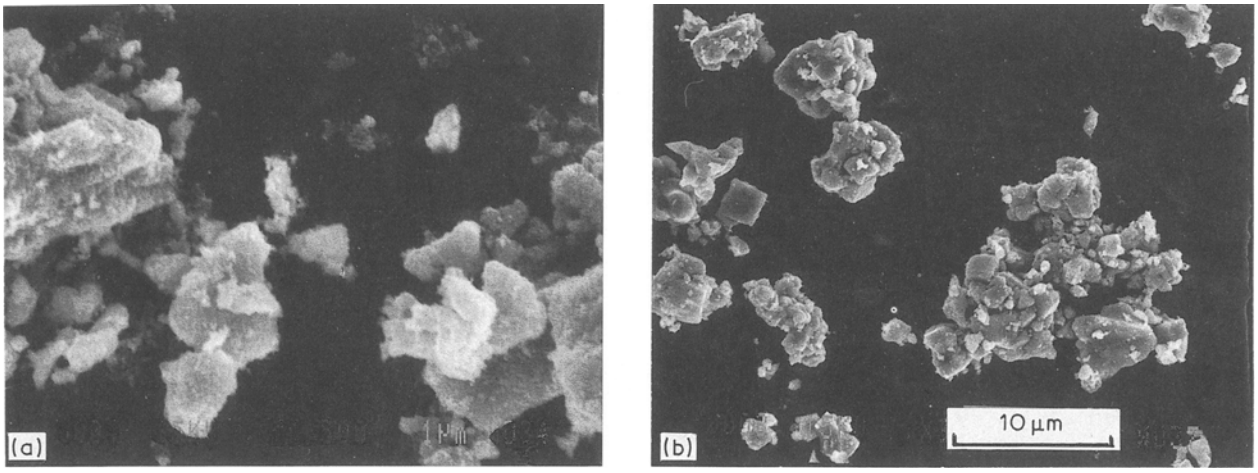

Figure 6 Morphology of sol-precipitated powders. (a) Oven-dried and (b) after calcination, 950° C, 24 h.

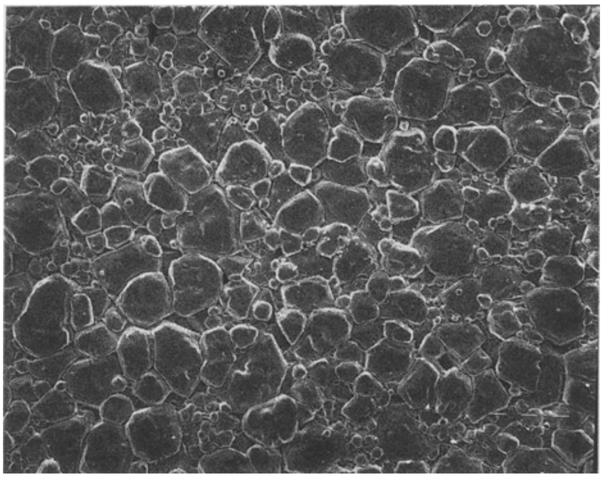

Figure 7 Microstructure of dense $BaTiO_3$ ceramic obtained using sol-precipitated powders (x200).

would be a useful contribution to develop techniques for control and use of the high surface activity of the particles, and avoidance of agglomerate formation in the sol-precipitated powders. The calcination treatment is necessary to decompose the small amount of $BaCO_3$ formed during washing and drying operations as well as to obtain a tetragonal crystal structure [16, 21]. The calcined powders consisting of primary particles ≈ 3 to $5\,\mu m$ in size were sintered at 1350° C to obtain dense ceramics (90 to 96% density) without any sintering additives. A typical microstructure of sintered samples is shown in Fig. 7. The relatively coarse grain size is characteristic of high purity $BaTiO_3$ powders with no sintering additives and grain growth modifiers.

4.4.2. Sol–gel process

In the sol–gel process based on the use of identical precursors, monolithic gels were formed (Fig. 5b). Under acidic conditions, the sol formed from hydrolysed titanyl acylate and barium acetate formed monolithic gels (Fig. 8). Gelation can be enhanced by increasing the temperature [14, 16, 17, 31] and calcination of the gels was studied in detail. Figure 9 shows the evolution of crystalline $BaTiO_3$ from the amorphous gels. Notice the relatively weak reflection corresponding to $BaCO_3$ ($2\theta = 23.9°$) in the temperature range 400 to 500° C. The formation of $BaCO_3$ in this route has also recently been discussed by other researchers [18, 19, 31, 41]. The $BaCO_3$ formed during calcination of the gels also reacts with the amorphous titania (or titania rich metastable phases) to form $BaTiO_3$.

Such phenomena affect the compositional homogeneity of the gel derived ceramics. Prassas *et al.* [42] have observed surface crystallization of Na_2O–SiO_2 gels due to formation of sodium carbonates (reaction of gel surface with CO_2 from air). Furthermore the water itself caused partial dissolution of the gels into a paste like material. The note of caution implicit in these observations is particularly timely, since it is a popular current belief that sol–gel processing results in extremely homogeneous ceramics and glasses. The possibility of segregation of constituents during synthesis, ageing and calcination of gels, and its effects on crystallization behaviour, and compositional homogeneity must be considered carefully.

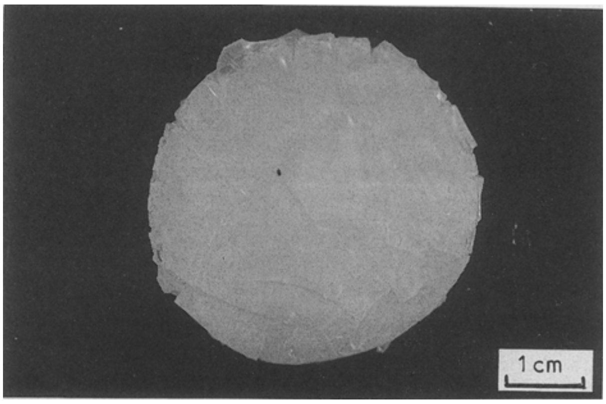

Figure 8 Monolithic $BaTiO_3$ gels derived using barium acetate and modified titanium alkoxide.

Reaction between very fine $BaCO_3$ particles and the titania rich metastable phases, however, may not be the only mechanism for $BaTiO_3$ formation. For example, during the course of pyrolysis a non-crystalline inorganic solid can be formed, which in turn would undergo structural rearrangement to form $BaTiO_3$ crystals. The existence of such an inorganic non-crystalline solid is consistent with Ulrich's observations on formation of pure $BaTiO_3$ glass [43]. Mackenzie [44] has also discussed the synthesis of glassy inorganic oxides and non-Zachariasen behaviour of $BaTiO_3$ and WO_3. We are also using molecular dynamics simulations to gain a theoretical insight into the formation and local structure of amorphous $BaTiO_3$ [45].

In principle, the mechanism of formation of $BaTiO_3$ from very fine, reactive particles of $BaCO_3$ is similar to the synthesis based on conventional processing (Table

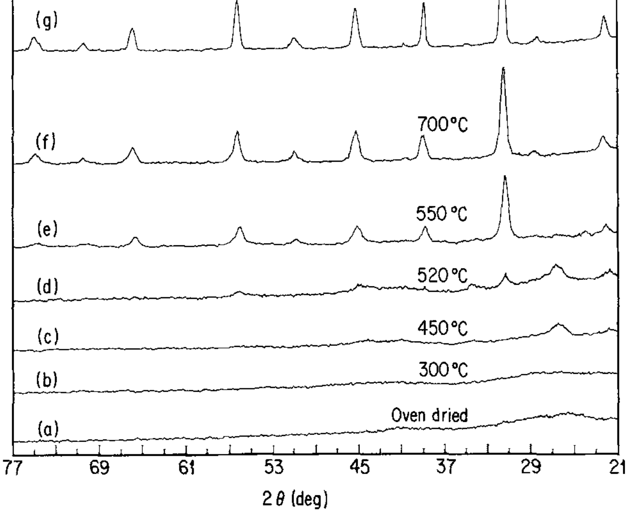

Figure 9 Evolution of crystalline $BaTiO_3$ from amorphous gels.

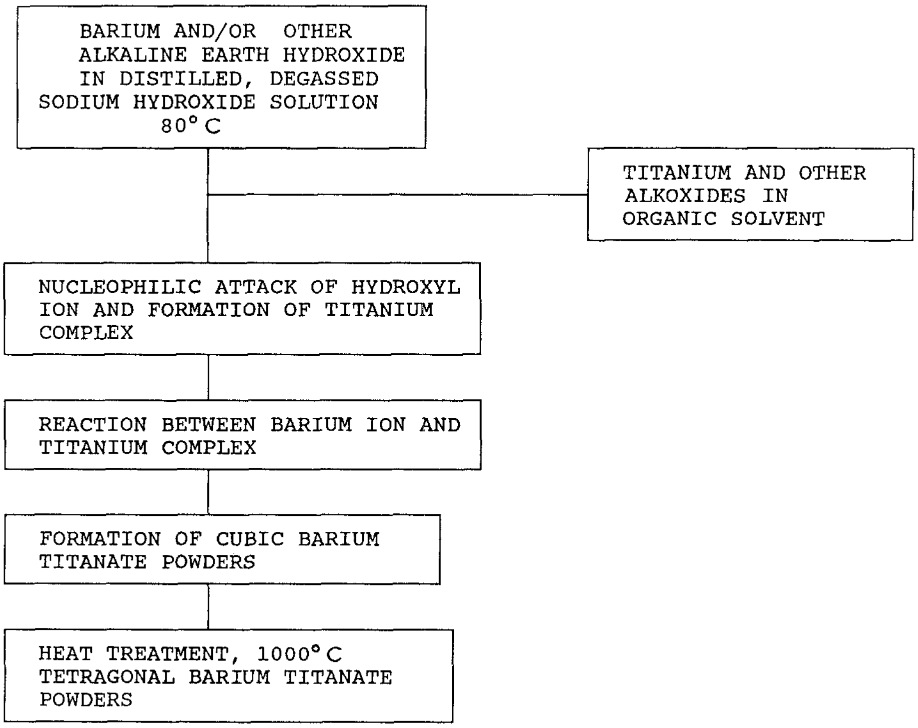

Figure 10 Synthesis of $BaTiO_3$ powders using barium hydroxide and titanium isopropoxide.

I) and the use of oxalates and citrates (to be discussed below). The atomic scale mixing may not be observed in all the regions of samples prepared using these processes. The possibility of crystallization of $BaTiO_3$ from an inorganic amorphous solid obtained during the course of pyrolysis of acetate-derived gels and other precursors to $BaTiO_3$ needs to be examined closely, as it would reflect on the extent of the achievable homogeneity at the atomic scale.

Due to the undecomposed residual $BaCO_3$, sintered $BaTiO_3$ bodies with a relatively porous microstructure (70% density) were obtained. This phenomenon is similar to the densification behaviour of oxalate-derived powders calcined in a CO_2 atmosphere studied by Enomoto and Yamaji [46] where ceramics with low (80%) density were obtained. The calcination of acetate-derived gels at elevated temperatures resulted in denser (85 to 90%) ceramics. Tomandl *et al.* [18] have correctly pointed out the importance of gel calcination treatment to obtain powders with good densification characteristics.

The processes based on the use of barium acetate- and titanyl acylate-type precursors are promising and offer several technological advantages. Barium acetate is a moisture-insensitive, easier to handle and inexpensive precursor that can be synthesized *in situ* by the dissolution of high-grade $BaCO_3$ in acetic acid. As the titanyl acylate type precursor dissolves in water, the subsequent handling of the precursor is easy and the potential problem of formation of hydrous titania is avoided. Wilson *et al.* [21] have patented a sol-precipitation process in which the heat of the reactions is used to eliminate external heating. The technique can also be easily applied to prepare thin $BaTiO_3$ films by dipping or spinning the substrates [19]. This coating technique is simple and inexpensive and better suited for scale-up as compared to other thin film deposition techniques which will be discussed later.

4.5. Use of barium hydroxide [47–54]

Flaschen [47] originally reported a process based on the use of barium hydroxide and titanium isopropoxide for the formation of $BaTiO_3$ powders (Fig. 10). Several publications and patents have appeared in the literature based on this process [47–54]. The process relies on the stabilization of a titanium complex under alkaline conditions and its neutralization by Ba^{2+}

$$Ba^{2+} + Ti(OH)_6^{-2} \rightarrow BaTiO_3 + 3H_2O$$

The mechanism suggested by Kiss *et al.* [48] is the nucleophilic attack by H_2O and OH^- on $Ti(OR)_4$. The presence of OH^- ions is critical for the formation of the titanium complex. The acid-base reaction described above cannot occur in neutral solutions, and hydrous titania is obtained as a result. There is no direct evidence for this reaction and, as mentioned earlier, the possibility of hydrothermal type reactions must be considered.

Under strongly alkaline conditions ($pH > 10$) cubic crystalline powder of $BaTiO_3$ is obtained at low (< 100° C) temperatures which transforms into the thermodynamically stable tetragonal structure after a heat treatment at higher temperatures (> 800° C) and subsequent cooling through the Curie temperature. It is preferable to conduct the process under inert atmosphere to minimize the formation of $BaCO_3$. The technique also requires optimization and control of several parameters such as the pH, temperature, intensity of agitation and rate of addition of the titanium precursor to obtain $BaTiO_3$ with consistent particle size and stoichiometry. The process can also be used to prepare doped $BaTiO_3$ powders.

4.6. Oxalate process [46, 56–64]

One of the best processes for obtaining $BaTiO_3$ powders with precise stoichiometry, in large quantities is the use of the oxalate process. Starting materials $TiCl_4$ and $BaCl_2$ are reacted with water and

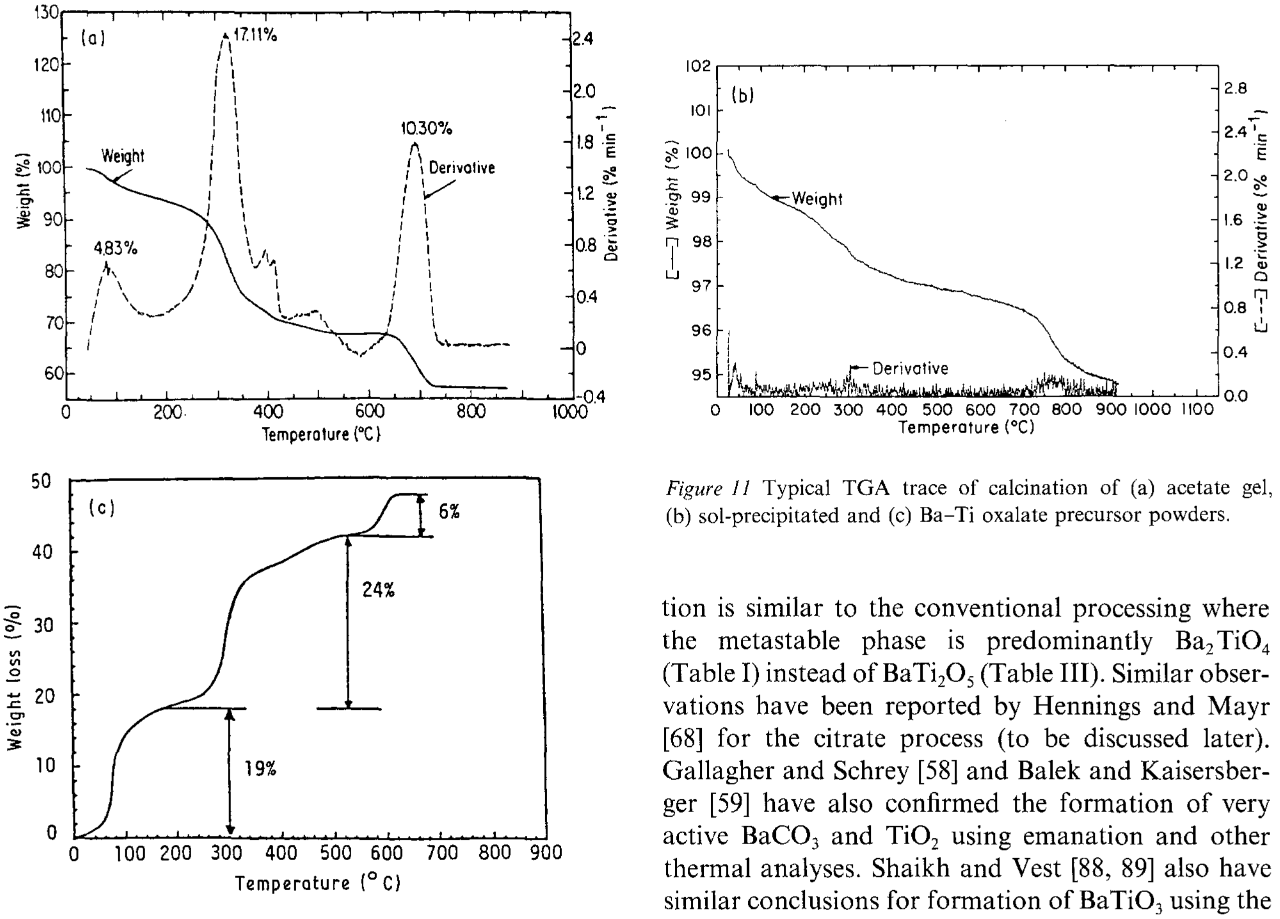

Figure 11 Typical TGA trace of calcination of (a) acetate gel, (b) sol-precipitated and (c) Ba–Ti oxalate precursor powders.

oxalic acid ($H_2C_2O_4$) to precipitate a double oxalate ($BaTiO(C_2O_4)_2 \cdot 4H_2O$). Yamamura *et al.* [56] have reported formation of tetragonal $BaTiO_3$ using $Ba(NO_3)_2$ and $TiO(NO_3)_2$ as starting materials. Thermal decomposition of these oxalates is conducted to obtain fine, stoichiometric powders. The thermogravimetric analysis (TGA) data on the acetate gels and sol-precipitated powders are included for the purpose of comparison (Figs 11a and b) [16]. A typical TGA trace of the decomposition of the double oxalate precursor is shown in Fig. 11c (adapted from [23]). The overall weight loss of the oxalate salt is comparable to the acetate gels and is less than the sol-precipitated powders.

The reactions and intermediates that lead to the formation of crystalline $BaTiO_3$ reported by Bind *et al.* [57] are summarized in Table III. Note that the double oxalate does not convert to $BaTiO_3$ directly. Very fine particles of $BaCO_3$ and $BaTi_2O_5$ formed initially react with each other to form the final product. In this respect, the mechanism of $BaTiO_3$ formation is similar to the conventional processing where the metastable phase is predominantly Ba_2TiO_4 (Table I) instead of $BaTi_2O_5$ (Table III). Similar observations have been reported by Hennings and Mayr [68] for the citrate process (to be discussed later). Gallagher and Schrey [58] and Balek and Kaisersberger [59] have also confirmed the formation of very active $BaCO_3$ and TiO_2 using emanation and other thermal analyses. Shaikh and Vest [88, 89] also have similar conclusions for formation of $BaTiO_3$ using the metallo-organic decomposition (MOD) process. It should also be noted that one of the ways by which $BaTiO_3$ formation occurs in the sol–gel process on the use of barium acetate is also via $BaCO_3$ formation [14, 16, 17, 41]. Thus the complete atomic-level mixing of constituents seems to be doubtful in these processes. Pathways for $BaTiO_3$ from different precursors are schematically shown in Fig. 12. The oxalate process typically results in fine, cubic $BaTiO_3$ powders that on additional heat treatment form soft agglomerates of the tetragonal phase (Fig. 13). This process is commercial and the powders prepared using oxalates are used in thermistor and capacitors industry.

4.7. Citrate process [55, 64–68]

The citrate process also known as the Pechini [55] or the liquid mix (LM) process is similar to the oxalate process. Mulder [65] used tetrabutyl titanate with citric acid and ethylene glycol to obtain an aqueous solution. Barium carbonate dissolved in formic acid and water is then added to the titanium precursor. After adjusting the pH, a 1 : 1 mixed crystalline citrate

TABLE III Synthesis of $BaTiO_3$ using oxalate process [57]

Synthesis of mixed oxalate

$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2\ HCl$

$BaCl_2 + TiOCl_2 + 2\ H_2C_2O_4 + 4\ H_2O \rightarrow BaTiO\ (C_2O_4)_2 \cdot 4H_2O + 4\ HCl$

Thermal decomposition of mixed oxalate

100 to 140°C $BaTiO(C_2O_4)_2 \cdot 4H_2O \rightarrow BaTiO(C_2O_4)_2 + 4H_2O$

300 to 350°C $BaTiO(C_2O_4)_2 \rightarrow 0.5\ BaTi_2O_5^* + 0.5\ BaCO_3 + 2\ CO + 1.5\ CO_2$

600 to 700°C $0.5\ BaTi_2O_5 + 0.5\ BaCO_3 \rightarrow BaTiO_3 + 0.5\ CO_2$

*Misprinted as $BaTiO_5$ [57].

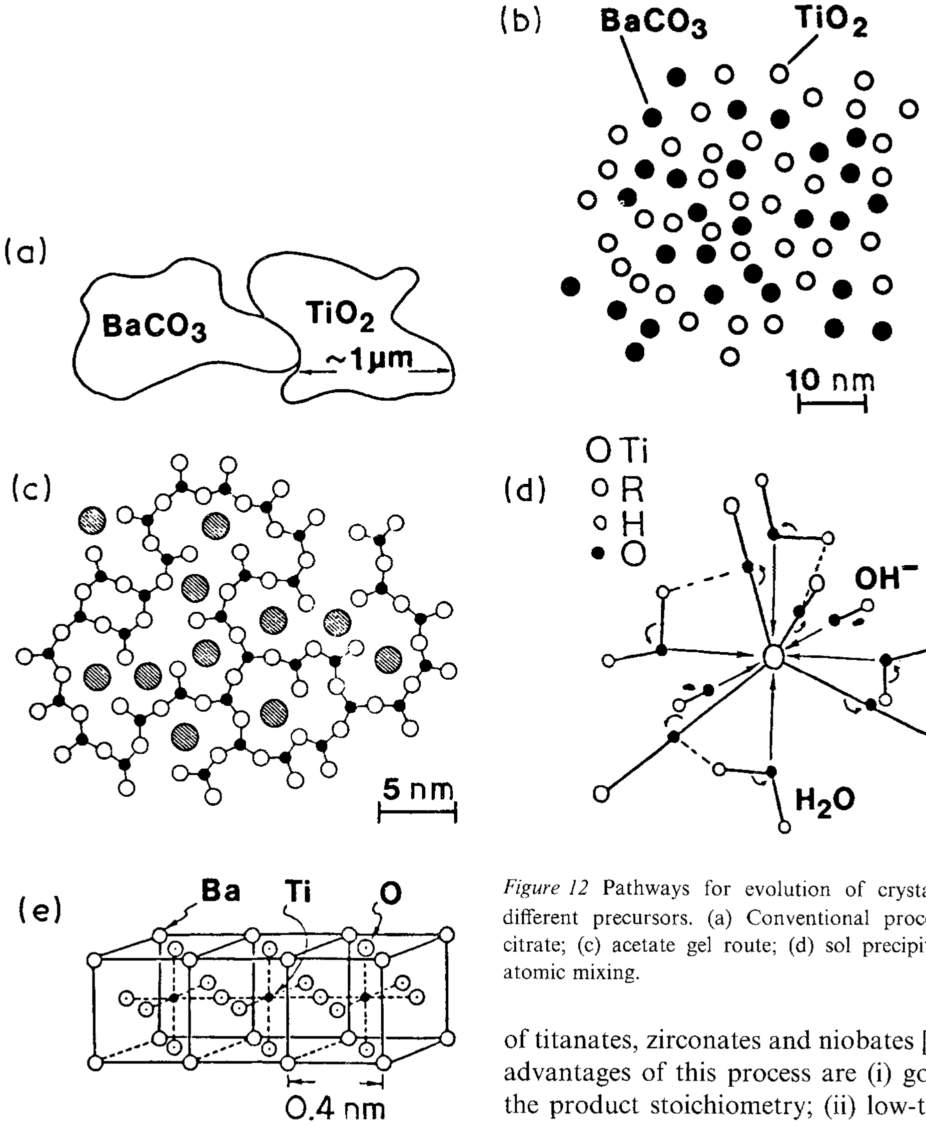

Figure 12 Pathways for evolution of crystalline $BaTiO_3$ from different precursors. (a) Conventional processing; (b) oxalate/citrate; (c) acetate gel route; (d) sol precipitation; (e) complete atomic mixing.

$(BaTi(C_6H_6O_7)_3 \cdot 4H_2O)$ can then be precipitated. Salez *et al.* [66, 67] have optimized the process conditions such as the concentrations of citric acid, ethylene glycol and the molar ratio (Ba + Ti) to (citric acid + ethylene glycol). Heat treatment of this precursor then results in formation of $BaTiO_3$ through solid-state reactions (Table IV) between intermediate species [68]. It is interesting to note that irrespective of the Ba/Ti ratio in the solution, but depending on the pH, a citrate salt with Ba/Ti ratio of 1 : 1 at $pH < 2.6$, or 2 : 1 at $pH > 3.2$ is obtained [68].

The liquid-mix process has been applied to the synthesis of over 100 different oxides including a number of titanates, zirconates and niobates [55]. Some of the advantages of this process are (i) good control over the product stoichiometry; (ii) low-temperature synthesis (typically < 800° C); and (iii) ease of introducing dopants. The high weight losses during calcination, and agglomeration during calcination treatments are some of the demerits associated with this process.

4.8. Hydrothermal synthesis [69–76]

Fine powders of aggregated, submicron $BaTiO_3$ and mixed titanates have been reported by a number of researchers. In their early work Christensen [69] and Kaneko [70] showed that $BaTiO_3$ could be prepared from barium hydroxide solutions and oxide, esters or oxide gels of titanium, when temperatures form 380 to 500° C and pressures from 300 to 500 atm were applied. Recent work of Kutty and co-workers [71–73]

TABLE IV Intermediate formation in citrate process for $BaTiO_3$ powders [68]

Temperature (° C)	Formula
20–100	$BaTi(C_6H_6O_7)_3 \cdot 6H_2O \rightarrow BaTi(C_6H_6O_7)_3 \cdot 2H_2O + 4H_2O$
100–200	$BaTi(C_6H_6O_7)_3 \cdot 2H_2O \rightarrow BaTi(C_6H_6O_7)_3 + 2H_2O$
200–210	$BaTi(C_6H_6O_7)_3 \rightarrow BaTi(C_6H_4O_6)_3 + 3H_2O$ (BaTi) aconitate
210–250	$BaTi(C_6H_4O_6)_3 \rightarrow BaTi(C_5H_4O_4)_3 + 3CO_2$ (BaTi)itaconate
250–360	$BaTi(C_5H_4O_4)_3 \rightarrow TiO_2 \cdot Ba(C_5H_4O_4) + 2C_5H_4O_3$ itaconic anhydride
360	$C_5H_4O_3 + O_2 \rightarrow 2H_2O + 5CO_2$
360–600	$TiO_2 \cdot Ba(C_5H_4O_4) \rightarrow BaCO_3, CO_2, H_2O$ and possibly $(BaCO_3)_x \cdot (TiO_2)_y$, $BaTiO_3$ (above 500° C) $\rightarrow BaTiO_3, CO_2$

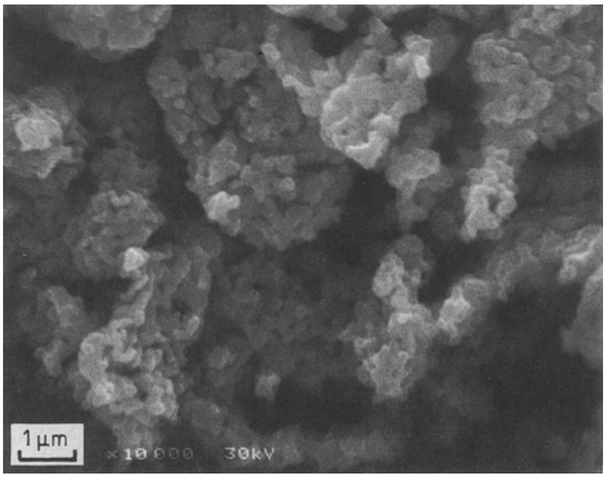

Figure 13 Morphology of oxalate-derived powders, after calcination, 1000° C, 2 h (courtesy of Jim Wilson, Transelco Division, Ferro Corporation, USA).

demonstrates the synthesis of ultrafine $BaTiO_3$ powders at temperatures as low as 85° C. Pressures were close to the water vapour pressure at the temperature of synthesis (15 to 65 atm). Freshly prepared and stearically stabilized (using PVA surfactant) reactive titania gels free of anionic contaminants were used with $Ba(OH)_2$ to obtain $BaTiO_3$ powders with acicular crystals. Although ultrafine powders are obtained using the hydrothermal route, the stoichiometry is affected by the type and amount of solvent and can be difficult to control. According to the study by Maurice and Buchanan [77] the agglomerate characteristics of the hydrothermally prepared powders can result in lower green densities (44%) but higher shrinkage and fired density (98% for Ba/Ti = 0.987).

4.9. Freeze drying [78–80]

Ali and Mline [78] reported a novel $BaTiO_3$ synthesis route based on the calcination of a freeze-dried catechol complex $Ba[Ti(C_6H_4O_2)_3] \cdot 4H_2O$. The catechol complex reagent, an aromatic diol $C_6H_4(OH)_2$, is initially reacted with $TiCl_4$ to obtain a titanium complex, which in turn reacts with $BaCO_3$ to form a water-soluble mixed catechol complex. This catechol complex is separated by freeze drying and is subsequently decomposed at high temperatures to obtain $BaTiO_3$. A flowsheet of this process (Fig. 14) shows the important steps.

The mechanism of evolution of $BaTiO_3$ is not clear. Metastable phases may be responsible for the formation of $BaTiO_3$. This technique utilizes novel chemistry and has potential for the preparation of mixed and doped titanate powders, and clearly deserves further research efforts. The catechol process has also been applied successfully to other alkaline earth titanates [79].

5. Heat treatment of wet chemically derived $BaTiO_3$ powders

Wet chemically prepared powders usually need a relatively high-temperature treatment to (i) obtain stoichiometric, crystalline $BaTiO_3$ (as in acetate, citrate and oxalate processes); (ii) remove any residual solvents, adsorbed water and small amounts of $BaCO_3$; and more importantly (iii) obtain powders with agglomerate size, surface area and crystal structure according to the customer specifications. This heat-treatment step has important effects on the microstructure and electrical properties of $BaTiO_3$.

It may be noted that this and any subsequent heat treatment also has an effect on the relative amounts of

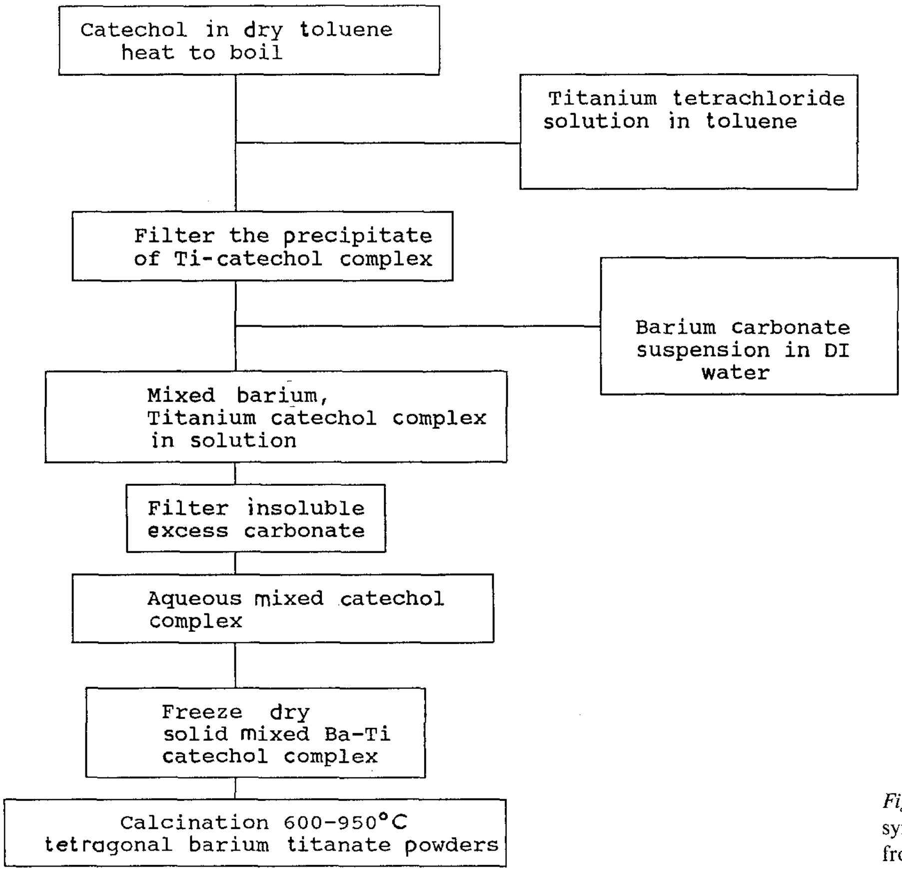

Figure 14 Flowsheet for catechol-based synthesis of $BaTiO_3$ powders (adapted from ref. 78).

the tetragonal and cubic phases present in the ceramic at room temperature. The cubic–tetragonal transformation has important implications related to the 'ageing' of ceramic components. Most low-temperature wet chemical processes result in formation of $BaTiO_3$ powders with a metastable cubic structure (at room temperature). After heat treatment in the range 900 to 1000° C and subsequent cooling through the Curie temperature, powders with thermodynamically stable tetragonal structure can be obtained (at room temperature). Commercially available oxalate-derived powders heat-treated at temperatures above 1100° C, are believed to exhibit tetragonal structure at room temperature. According to Vivekandan *et al.* [73], hydrothermally prepared $BaTiO_3$ powders heated to 1200° C and subsequently cooled through the Curie temperature exhibit a tetragonal structure. They have attributed the relatively higher heat-treatment temperature (to obtain a tetragonal phase at room temperature) to the presence of residual hydoxyl ions in the $BaTiO_3$ powders obtained by a hydrothermal route. At present there is insufficient and conflicting information on the crystal structure (cubic or pseudocubic) of chemically prepared $BaTiO_3$ powders.

6. Thin films [19, 81–91]

Thin solid barium titanate films are of interest for thin-film piezoelectric components, barrier layers for deposition of high T_c superconducting thin films and electro-optic applications. Secondly, thinner dielectric layers offer high volumetric efficiency. Vacuum evaporation, electrodeposition, r.f. sputtering and other techniques have been reported for the preparation of thin dielectric $BaTiO_3$ layers [81–84, 91]. These techniques need sophisticated instrumentation and may also pose geometrical and area constraints. In r.f. sputtering the $BaTiO_3$ target may also be reduced [91]. These techniques are also limited in terms of their ability for large scale production.

Wet chemical techniques have the advantages of using relatively inexpensive and easier to handle reagents and simple equipment. Larger areas with complicated geometries can also be coated successfully. The possibility of dielectric breakdown, decreased mechanical strength and difficulties in preparing multilayered structures may be the limiting factors.

Fukushima *et al.* [84] used barium napthalate and a titanium alkoxide as source materials. A butanol solution of these precursors was spread on a glass or quartz substrate. After evaporation of solvent, a calcination treatment was employed to remove the organics. $BaTiO_3$ films showing interference colours were obtained by calcination above 400° C. Films up to 1 μm thickness were prepared with electrical resistivity of 10^9 ohm cm^{-1}.

Yanovskaya *et al.* [85] and Dosch [86] reported alkoxide-based synthesis of $BaTiO_3$ films deposited on silicon wafers. Nickel and titanium substrates, obtained by r.f. and d.c. sputtering on to silicon wafers, were also used. Barium hydroxide and titanium isopropoxide were used as the starting materials. Hydrolysis of the precursors resulted in formation of crystalline $BaTiO_3$ in the range 450 to 500° C. The current-voltage characteristics of the prepared films have also been described.

Recently Mohallem and Aegerter [19] used barium acetate and titanium isopropoxide for the deposition of thin films by a dipping technique. The chemistry of this process is similar to that reported in our work on the synthesis of $BaTiO_3$ gels [14, 16, 17]. Successive depositions were made to obtain highly adherent and crack-free films up to 400 nm thick. The films were amorphous up to 550° C. Crystallization to an apparently tetragonal structure occurred after heat treatment at 600° C. The refractive index of these films was found to be 2.1 (at 550 nm). This technique utilizes moisture-insensitive precursors that are easier to handle, and also has potential for the preparation of mixed titanate films.

Vest and Singaram [87] have used a metallo-organic decomposition (MOD) process to prepare thin films and powders of $BaTiO_3$. Titanium dimethoxy dineodeconate and barium neodeconate were synthesized from titanium methoxide and barium chloride, respectively. These precursors decomposed to $BaCO_3$ and TiO_2 and reacted to form $BaTiO_3$. The MOD process is different from the sol–gel process in that a gel is never formed. The kinetics and mechanism of $BaTiO_3$ formation using the MOD process have been discussed by Shaikh and Vest [88, 89].

The formation of $BaTiO_3$ in thin films and powder synthesis is quite similar. Due to the increased level of constituents mixing, $BaTiO_3$ formation is typically complete at $\approx$700° C in films derived using the wet chemical approach. For relatively thicker (8000 nm) films synthesized from $BaCO_3$ and TiO_2 powders, the complete crystallization occurs above 1000° C [90]. These observations are consistent with the pathways depicted in Fig. 12. The wet chemical techniques for thin film deposition suffer from two limitations: (i) relatively high crystallization temperatures cause reactions with substrates; and (ii) preparation of thick coatings ($\approx$10 to 15 μm) cannot be achieved in a single step. There is also need to develop protocols for the synthesis of multilayered ceramic structures.

7. Electrical properties

As the electrical properties of $BaTiO_3$ are extremely sensitive to the Ba/Ti ratio, impurities, dopants and the ceramic microstructure, it is difficult to correlate the electrical properties with the process parameters. Maurice and Buchanan [77] made a systematic study of the microstructure and electrical properties of high-purity $BaTiO_3$ obtained by different low-temperature routes (Fig. 15a). The improvement in dielectric properties of $BaTiO_3$ powders obtained from gel calcined at higher temperatures is apparent from the data in Fig. 15b [16]. The combined effects of stoichiometry and agglomerate structure on the microstructure and dielectric properties are difficult to predict for $BaTiO_3$ prepared using different techniques. Therefore, it is difficult to assign a rank of merit to processes on the basis of electrical properties alone. The success of the process from the point of view of a profitable commercial operation would be primarily defined by

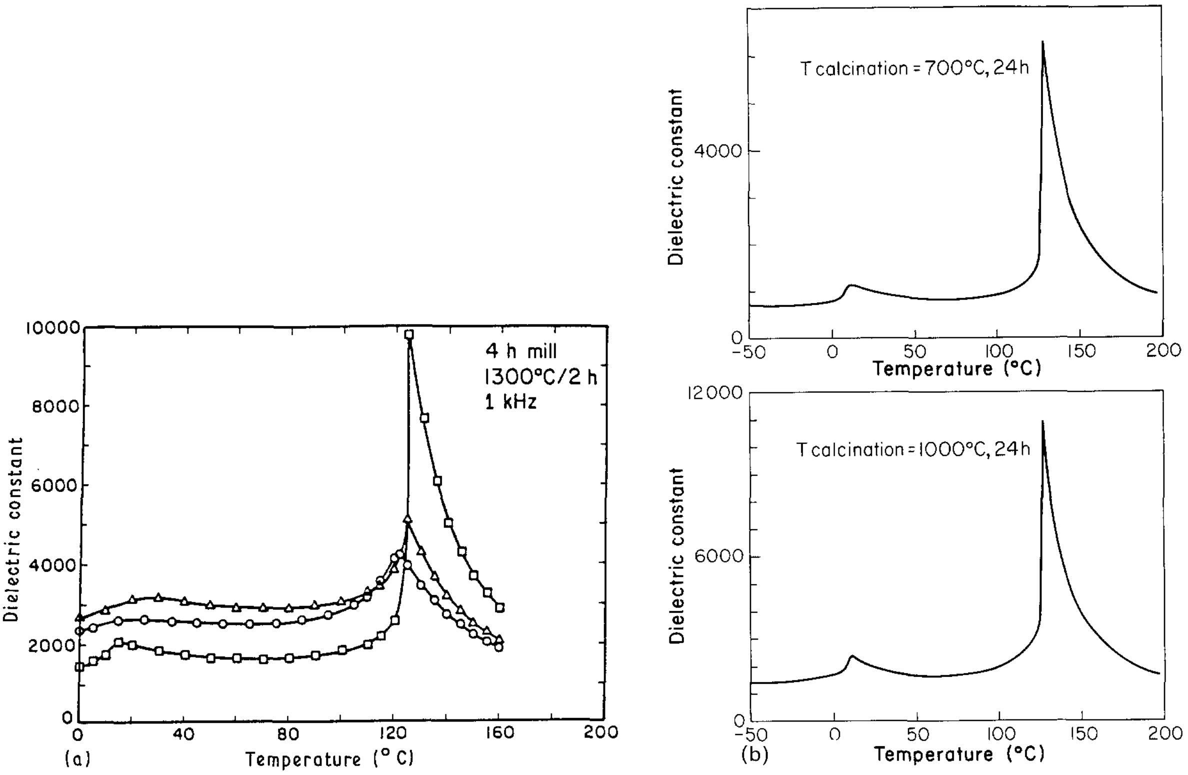

Figure 15 Electrical properties of $BaTiO_3$ synthesized using (a) ○ conventional, △ oxalate and □ hydrothermal (from ref. 77) and (b) acetate gel routes.

the cost and ease of handling of the precursors, as well as the ability of a technique to produce homogeneous fine powders and thin films with good, reproducible electrical properties. Similar considerations would also apply to techniques for polytitanate synthesis.

8. Synthesis of polytitanates [3, 4, 11–13, 17, 37, 92–101]

A relatively limited literature exists on the low-temperature synthesis of polytitanates. Suwa *et al.* [92] investigated the synthesis of various phases (such as $BaTi_4O_9$, $Ba_2Ti_9O_{20}$ etc) in the BaO–TiO_2 system. The synthesis was based on the technique used by Mazdiyasni and co-workers [22–25], namely, the use of barium alkoxide (derived from barium metal) and a titanium alkoxide. Their efforts led to the synthesis of single phase Ba_2TiO_4 and $BaTi_5O_{11}$ materials. Note that these materials cannot be obtained in a single-phase form using conventional 'oxide-mix' process. Ritter *et al.* [3] and Kikuchi and Saito [37] attempted synthesis of various phases in the BaO-TiO_2 system using a BaO-derived alkoxide precursor and titanium isopropoxide. The attempts to synthesize $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ phases always resulted in multiphase materials. Recent work in our laboratories involved simultaneous hydrolytic decomposition of barium isopropoxide (synthesized *in situ*) and titanium isopropoxide (ratio 1 : 4) with a view to synthesizing $BaTi_4O_9$ [17]. Amorphous powders obtained after oven drying were converted to single-phase (as identified by X-ray) 1 : 4 compounds by heat treatment at 1100° C. Heat treatment at lower temperatures resulted in the crystallization of other polytitanate phases (Fig. 16). Further work is being directed to optimize the heat treatment so as to obtain truly single phase ceramics and determination of their dielectric characteristics.

Hirano and Naka [93] have patented an alkoxide-based process with $Ba_2Ti_9O_{20}$- type ceramics for high-frequency applications. The $Ba_2Ti_9O_{20}$ evolves from the precursor powders in a way essentially similar to the evolution of $BaTi_4O_9$ reported in our work [17]. Hydrothermal synthesis of polytitanates has also been attempted [13]. The approach is similar to hydrothermal synthesis of $BaTiO_3$ discussed earlier. Polytitanates with Ba : Ti $>$ 1 : 5 were found to be unstable under hydrothermal conditions. Rutile and $BaTi_4O_9$ were obtained at 1200° C when the starting stoichiometry was 1 : 4.

There are published studies relating to the synthesis of doped and mixed polytitanates using the conventional techniques [11, 12]. O'Bryan *et al.* [94, 95] and other researchers [96–98] have conducted systematic studies on the conventional synthesis, crystal structure and electrical properties of undoped polytitanates. The importance of homogeneous composition in the sintering behaviour of $Ba_2Ti_9O_{20}$ (probably more easily achievable by wet chemical techniques) has been discussed by Jakola *et al.* [99]. The application of sol-gel and other wet chemical processes for the synthesis of these materials is an exciting area that clearly deserves additional research efforts. This approach would be promising, particularly for the synthesis of single-phase $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ without repetitive calcination and grinding treatments that are currently employed in the conventional processing. These low-temperature routes need to be examined closely for the synthesis of undoped and mixed titanates/zirconates to prepare ceramics with tailored electrical properties.

9. Summary

The dielectric properties of $BaTiO_3$ obtained from different powders are sensitive to the combined effects of stoichiometry, trace impurities and

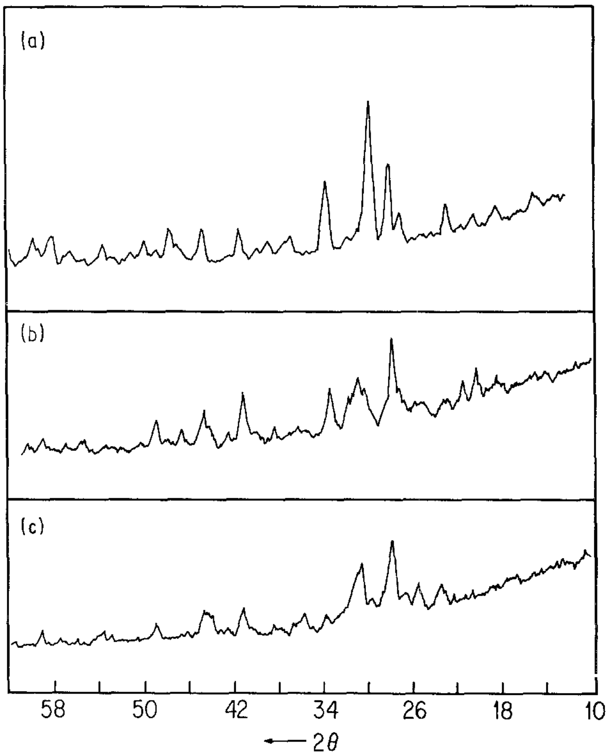

Figure 16 Evolution of polytitanate phases from amorphous barium tetratitanate (1:4) precursor powders. (a) 1100° C, 3 h, $BaTi_4O_9$; (b) 900° C, 31 h, $Ba_4Ti_{13}O_{30}$ and $BaTi_5O_{11}$(tr); (c) 800° C, 24 h, $BaTi_5O_{11}$.

agglomerate structures. Therefore it appears that the various processes can be better evaluated based on the relative ease and cost for the consistent preparation of stoichiometric, homogeneous and interactive $BaTiO_3$ powders. Different inorganic and organometallic precursors can be used to prepare $BaTiO_3$ and polytitanate powders for dielectric and microwave applications.

The oxalate process is commercial and has been used to prepare stoichiometric, high purity $BaTiO_3$ in large quantities. The technique based on the simultaneous hydrolytic decomposition of alkoxides leads to ultrafine, stoichiometric and doped powders. However the cost and use of moisture-sensitive precursors are the limiting factors that would tend to inhibit their commercialization. Hydrothermal synthesis is promising, however, the difficulty in stoichiometry control and the need for special autoclaves are problems. The use of freeze-dried catechol complexes is also an interesting approach for the synthesis of barium and other alkaline earth titanates.

The recent development of a process based on the use of barium acetate and a titanyl acylate-type precursor to obtain crystalline, high-purity $BaTiO_3$ powders seems to be an important development. The process uses relatively inexpensive and moisture-insensitive precursors and has some potential for commercialization. Identical precursors have also been used to prepare $BaTiO_3$ gels and thin films.

Although most wet chemical routes lead to formation of $BaTiO_3$ at low temperatures, a heat treatment is necessary to remove the solvents, residual carbonate (if any) and more importantly to produce powders with the desired agglomerate size, surface area and crystal structure. One problem associated with the wet chemical processes is the formation of agglomerates in the as-prepared and heat-treated powders. It would be a useful contribution to develop techniques to minimize the agglomeration of these particles, so as to use the high surface activity of the powders in a controlled manner.

Wet chemical preparation techniques have been successfully used to deposit thin dielectric layers of $BaTiO_3$. In this area, research efforts are needed to generate thicker and multilayered ceramic structures.

The synthesis of polytitanate-type doped and undoped microwave dielectrics using the wet chemical routes is an exciting area awaiting exploration. Sol–gel synthesis of polytitanates (such as $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$) has been reported. Compounds such as Ba_2TiO_4 and $BaTi_5O_{11}$ that cannot be synthesized as single-phase materials using conventional processing can be prepared using the sol–gel approach. Research efforts on low-temperature synthesis of high-purity, doped and mixed polytitanates for high-frequency applications will also result in ceramics with tailored and controlled electrical properties.

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References

1. "Advanced Ceramic Materials: Technological and Economic Assessment" (Noyes, Park Ridge, New Jersey, 1985).
2. K. KIRBY, personal communication.
3. J. J. RITTER, R. S. ROTH and J. E. BLENDELL, *J. Amer. Ceram. Soc.* **69** (1986) 155.
4. J. M. MILLET, R. S. ROTH and H. S. PARKER, *ibid.* **69** (1986) 811.
5. A. BEAUGER, J. C. MUTIN and J. C. NIEPCE, *J. Mater. Sci.* **18** (1983) 304.
6. B. JAFFE, W. R. COOK and H. JAFFE, "Piezoelectric Ceramics" (Academic Press, New York, 1971).
7. L. K. TEMPLETON and J. A. PASK, *J. Amer. Ceram. Soc.* **42** (1959) 212.
8. H. TAGWA and J. OHASHI, *Denki Kagaku Ky Okai, Showa.* **52** (8) (1984) 485.
9. J. C. MUTIN and J. C. NIEPCE, *J. Mater. Sci. Lett.* **2** (1984) 1591.
10. S. G. MHAISALKAR, M. Sc. thesis, Ohio State University, Ohio, 1987.
11. S. NISHIGAKI *et al. J. Amer. Ceram. Soc.* **71** (1988) C-11.
12. S. NOMURA, K. TOMAYA and K. KANETA, *Jpn J. Appl. Phys.* **22** (1983) 1125.
13. T. R. N. KUTTY and P. MURUGARAJ, *J. Mater. Sci. Lett.* **7** (1988) 601.
14. P. P. PHULE and S. H. RISBUD, *Adv. Ceram. Mater.* **3** (1988) 183.
15. P. P. PHULE, S. RAGHAVAN and S. H. RISBUD, *J. Amer. Ceram. Soc.* **70** (1987) C-108.

16. P. P. PHULE and S. H. RISBUD, *Mater. Sci. Engg.* **B3** (1989) 241.
17. P. P. PHULE and S. H. RISBUD in "Better Ceramics Through Chemistry" Vol. 3, edited by C. J. Brinker, D. R. Clark and D. R. Ulrich (Materials Research Society, Pittsburgh, 1988) p. 275.
18. G. TOMANDL, H. ROSCH and A. STEIGELSCHMITT, *ibid*, p. 281.
19. N. D. S. MOHALLEM and M. A. AEGERTER, *ibid*, p. 515.
20. K. W. KIRBY, *Mater. Res. Bull.* **23** (1988) 881.
21. J. M. WILSON, D. L. COLLER and S. VENKATARAMANI, US patent 4 670 243, June (1987).
22. K. S. MAZDIYASNI and L. M. BROWN, *J. Amer. Ceram. Soc.* **55** (1972) 633.
23. K. S. MAZDIYASNI, R. T. DOLLOFF and J. S. SMITH II, *ibid.* **52** (1969) 523.
24. K. S. MAZDIYASNI, *Amer. Ceram. Soc. Bull.* **63** (1984) 591.
25. K. S. MAZDIYASNI *et al.*, US patent 3 647 364, March (1972).
26. J. C. BERNIER, *Powder Metall. Int.* **18** (1986) 164.
27. J. C. BERNIER *et al.* "High Tech Ceramics, Part B", Materials Science Monograph 38B, edited by P. Vincenzini (Elsevier, Amsterdam, 1987) p. 1443.
28. J. L. REHSPRINGER, P. POIX and J. C. BERNIER, *J. Non. Cryst. Solids* **82** (1986) 286.
29. J. L. REHSPRINGER and J. C. BERNIER, *Mater. Res. Soc. Symp.* **72** (1986) 67.
30. J. L. REHSPRINGER *et al.*, *J. Phys. Colloq.* **C1** (1986) 243.
31. F. CHAPUT and J. P. BOILOT, "High Tech Ceramics, Part B", Materials Science Monograph 38B, edited by P. Vincenzini (Elsevier, Amsterdam, 1987) p. 1459.
32. T. KASAI, Y. OZAKI and S. YAMAMOTO, *Yogyo Kyokaishi* **95** (1987) 1000.
33. T. KASAI and Y. OZAKI, *ibid.* **95** (1987) 912.
34. Y. OZAKI, *Ferroelectrics* **49** (1983) 285.
35. Y. OZAKI and Y. SHINOHARA, Japanese patent JP 62 265118 A2 [87/265118] November (1987).
36. Y. OZAKI, Japanese patent JP 57 82119 A2 [82/82119] May (1982).
37. T. KIKUCHI and T. SAITO, Japanese patent JP 61 21916 A2 [86/21916] January (1986).
38. G. DATTA, H. S. MAITI and A. PAUL in "High Tech Ceramics Part B", Materials Science Monograph 38B, edited by P. Vincenzini (Elsevier, Amsterdam, 1987) p. 1469.
39. *Idem, J. Mater. Sci. Lett.* **6** (1987) 787.
40. S. DOEUFF *et al. J. Non. Cryst. Solids* **89** (1987) 206.
41. A. MOSSET, I. G. LUNEAU and J. GALY, *ibid.* **100** (1988) 339.
42. M. PRASSAS, *et al.* in "Ultrastructure Processing of Advanced Structural and Electronic Materials", edited by L. L. Hench (Noyes Publications, New Jersey, 1984) p. 85.
43. D. R. ULRICH, PhD thesis cited in "Inorganic Glass-Forming Systems" edited by H. Rawson (Academic Press, New York, 1967) p. 202.
44. J. D. MacKENZIE in "Ultrastructure Processing of Advanced Ceramic Materials" edited by J. D. MacKenzie and D. R. Ulrich (Wiley, New York 1988) p. 589.
45. P. P. PHULE, P. A. DEYMIER and S. H. RISBUD, to be published.
46. Y. ENOMOTO and A. YAMAJI, *Amer. Ceram. Soc. Bull.* **60** (1981) 566.
47. S. S. FLASCHEN, *J. Amer. Chem. Soc.* **77** (1955) 6194.
48. K. KISS *et al. J. Amer. Ceram. Soc.* **49** (1966) 291.
49. F. CHAPUT and J. F. BOILOT, *J. Mater. Sci. Lett.* **6** (1987) 1110.
50. H. YAMAMURA *et al. Nippon Kagaku Kaishi.* **7** (1974) 1155.
51. S. UEDAIRA, *et al.*, European patent application EP 104002 Al, March (1984).
52. Japanese patent JP 59 39726 A2 [84/39726] March (1984).
53. K. H. LEE, B. H. LEE and H. S. LEE, *Yoop Hakhoechi* **21** (1984) 323.
54. K. AKIRA *et al.* Japanese patent JP 61 91016 A2 [86/91016] May (1986).
55. M. PECHINI, US patent 3 330 697, July (1967).
56. H. YAMAMURA *et al.*, *Ceram. Int.* **11** (1985) 17.
57. J. M. BIND *et al.*, *J. Metals.* **39** (1987) 60.
58. P. K. GALLAGHER and F. SCHREY, *J. Amer. Ceram. Soc.* **46** (1963) 567.
59. V. BALEK and E. KAISERBERGER, *Thermochim. Acta.* **85** (1985) 207.
60. W. S. CLAUBAUGH, E. M. SWIGGARD and R. GILCHRIST, *J. Res. Nat. Bur. Std.* **56** (1956) 289.
61. Y. H. KIM, J. LEE and H. I. HAN, *Yoop Hakhoechi* **23** (1986) 11.
62. N. G. EROR and H. U. ANDERSON in "Better Ceramics Through Chemistry" Vol 2 (Materials Research Society, Pittsburgh, 1986) p. 571.
63. A. N. VIRKAR, K. BANDYOPADHYAY and A. PAUL, *Trans. Ind. Ceram. Soc.* **44** (1985) 78.
64. M. N. SWILAM and A. M. GADALLA, *Trans. J. Brit. Ceram. Soc.* **74** (1975) 159.
65. B. J. MULDER, *Ceram. Bull.* **49** (1970) 990.
66. H. SALEZ, P. ODIER and B. CALES, *J. Non. Cryst. Solids* **82** (1986) 314.
67. H. SALEZ, B. CALES and P. ODIER, *Mater. Sci. Monogr.* (*High Tech. Ceram.*) **38A** (1987) 491.
68. D. HENNINGS and W. MAYR, *J. Solid State Chem.* **26** (1978) 329.
69. A. N. CHRISTENSEN, *Acta Chem. Scand.* **24** (1970) 2447.
70. S. KANEKO and F. IMOTO, *Nippon Kagaku Kaishi* **6** (1975) 985.
71. T. R. N. KUTTY and R. BALACHANDRAN, *Mater. Res. Bull.* **19** (1984) 1479.
72. P. MURUGARAJ and T. R. N. KUTTY, *ibid.* **20** (1985) 1473.
73. R. VIVEKANADAN, S. PHILIP and T. R. N. KUTTY, *ibid.* **22** (1986) 99.
74. H. OKADA, H. MATSUBAYASHI and F. GOTO, Japanese patent JP 62 72525 A2 [87/72425] March (1987).
75. K. MATSUOKA, S. SAKURAGI and J. YAMAZAKI, *Rep. Res. Lab. Hydrotherm. Chem.* (*Kochi, Jpn*) **2** (1978) 45.
76. L. I. SHVETS, N. A. OVRAMENKO and F. D. OVCHARENKO, *Dokl. Akad. Nauk SSSR* (*Chem.*), **248** (1979) 889.
77. A. K. MAURICE and R. C. BUCHANAN, *Ferroelectrics* **74** (1987) 61.
78. N. J. ALI and S. J. MLINE, *Trans. J. Brit. Ceram. Soc.* **86** (1987) 113.
79. N. J. ALI *et al.*, in "Better Ceramics Through Chemistry" Vol. 3 (Materials Research Society, Pittsburgh, 1988) p. 269.
80. L. A. XUE, F. L. RILEY and R. J. BROOK, *Trans. J. Brit. Ceram. Soc.* **85** (1986) 47.
81. V. DHARMADHIKARI and W. GRANNEMAN, *J. Appl. Phys.* **53** (1982) 8988.
82. C. FELDMAN, *ibid.* **27** (1956) 870.
83. J. PANITZ and C. HU, *Ferroelectrics* **27** (1980) 161.
84. J. FUKUSHIMA, K. KODAIRA and T. MATSUSHITA, *Amer. Ceram. Soc. Bull.* **55** (1976) 1064.
85. M. I. YANOVSKAYA *et al. Izv. Akad. Nauk. SSSR* (*Neorg. Mater.*) **17** (1981) 307.
86. R. G. DOSCH, in "Better Ceramics Through Chemistry", Vol. 1, (Materials Research Society, Pittsburgh, 1984) p. 157.
87. G. M. VEST and S. SINGARAM, "Materials Research Society Symposium Proceedings (Defect Prop. Process. High Technology Nonmetallic Materials") Vol. 60 (Materials Research Society, Pittsburgh, 1986) p. 35.
88. A. S. SHAIKH and G. M. VEST, *J. Amer. Ceram. Soc.* **69** (1986) 682.
89. A. S. SHAIKH and R. W. VEST, *ibid.* **69** (1986) 689.
90. K. H. YEON and H. C. HONG, *Chongi Hakhoe Nonmunchi* **35** (1986) 323.
91. A. MANSINGH and C. V. R. VASANTA KUMAR, *J. Mater. Sci. Lett.* **7** (1988) 1104.
92. Y. SUWA, Y. SUGIMOTO and S. NAKA, *Funtai Oyobi Funmatsuyakin* **25** (1978) 164.

93. S. HIRANO and S. NAKA, Japanese patent - JP 6221758 A2 [87/217158] January (1987); S. HIRANO *et al.* in "Advances in Ceramics", Vol. 19 edited by J. B. Blum and W. R. Cannon. (American Ceramics Society, Westerville, Ohio, 1986) p. 139.
94. H. M. O'BRYAN and J. THOMSON JR., *J. Amer. Ceram. Soc.* **57** (1974) 522.
95. *Idem, ibid.* **58** (1975) 454.
96. J. K. PLOUDRE *et al.*, *ibid.* **58** (1975) 418.
97. W. W. RHODES and J. THOMSON JR., *Amer. Ceram. Soc. Bull.* **55** (1976) 308.
98. D. HENNINGS and P. SCHNABEL, *Philips J. Res.* **38** (1983) 295.
99. T. JAKOLA, A. UUSIMAKI and S. LEPPAVUORI, *Int. J. High Tech. Ceram.* **2** (1986) 195.
100. T. F. LIMAR, A. I. SAVOS'KINA and N. G. KISEL, *Izv. Akad. Nauk. SSSR (Neorg. Mater.)* **12** (1976) 1134.
101. Z. Y. MAKAROVA *et al.*, *Ukr. Khim. Zh.* (in Russian) **51** (1985) 454.
102. Information brochure, "The Capacitor" (AV Ceramics, Myrtle Beach, South Carolina, USA).
103. P. C. OSBOND, R. W. WHATMORE and F. W. AINGER, Proceedings of British Ceramic Society **36** (1985) 167.

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