



Formation of BaTiO₃ from Barium Oxalate and TiO₂

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Submitted May 28, 2002; Revised January 28, 2003; Accepted October 14, 2003

Abstract. Barium titanate powder has been prepared via a semi-oxalate method that uses barium oxalate and TiO₂ precursors, instead of titanyl oxalate. Barium oxalate was precipitated from nitrate solution onto the surface of TiO₂ powders. Crystallization of BaTiO₃ from the precursors was investigated by TGA, DTA and XRD analysis. It is evident that an intermediate barium oxycarbonate along with BaCO₃, forms between 450–500°C and that decomposes to BaCO₃ again at high temperature. Decomposition of BaCO₃ occurs at much lower temperature, from 600°C onwards, due to the presence of TiO₂. The precursor completely transforms into BaTiO₃ at 900°C. Nanometer size BaTiO₃ crystallites are produced during this synthesis due to the lower calcination temperature. The crystalline morphology of BaTiO₃ is controlled mainly by the morphology of BaCO₃, which formed in the intermediate stage.

Keywords: BaTiO₃ synthesis, oxalate-oxide reaction, reaction kinetics, crystal morphology

Introduction

The compositions of most of the commercial high dielectric constant ceramic materials used for disc or multilayer capacitor are based on BaTiO₃. Fine BaTiO₃ powder can be synthesized by conventional mixed oxide method [1–3], and a number of solution techniques such as oxalate co-precipitation method [4–6], hydrothermal method [7, 8] and the Pechini process [9] etc. The conventional preparation route of dielectric material is solid-state reaction of oxides and carbonates at temperatures as high as 1200°C. At such high calcination temperatures strongly aggregated, coarse grain powders of 1–2 μm grain size are usually formed. Also in the reaction of BaCO₃ and TiO₂, usually a number of intermediate phases like Ba₂TiO₄, BaTi₄O₉ and BaTi₃O₇ are formed [1]. However the formation of intermediate phases can be suppressed by the use of sub-micrometer BaCO₃ [3]. On the contrary, the solution techniques lead to more homogenous, pure phase and stoichiometric BaTiO₃ powders with finer particle size than mixed oxide synthesis, due to the finer scale

of mixing and subsequent lower amorphous to crystalline transformation temperature. Two mechanisms have been suggested for BaTiO₃ formation from solution derived amorphous precursors. Some authors [10] have proposed that metal organic precursors such as oxalate salt BaTiO(C₂O₄)₂·4H₂O decomposes to form a finely divided mixture of BaCO₃ and TiO₂, which subsequently reacts to form BaTiO₃ on heating at 600–700°C in air. Alternatively, it has been proposed that an intermediate barium titanium oxycarbonate forms during the calcination of amorphous oxalate salt [11], with subsequent decomposition of the intermediate to BaTiO₃.

These literature reports clearly show that the mechanism of BaTiO₃ formation is highly dependent on the preparation method. In this paper we present an analysis of BaTiO₃ formation via semi-oxalate method in which the precursor was prepared by precipitating barium oxalate at the surface of TiO₂ particles. TiO₂ powder is used instead of its organometallic salt in this study, because of its easy availability and low cost. There has been no such oxalate-oxide reaction synthesis of BaTiO₃ reported in the literature. The transformation kinetics and morphological development of BaTiO₃ are discussed.

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Experimental Procedure

The starting materials used in the present work included $\text{Ba}(\text{NO}_3)_2$ (>99%, Loba Chemie Pvt. Ltd., India), TiO_2 (>99%, E-Merk, India, $d_{10} = 0.27 \mu\text{m}$, $d_{50} = 0.35 \mu\text{m}$, $d_{90} = 0.48 \mu\text{m}$) and $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ (>99.5%, S.D. Fine-Chem Ltd., India). An aqueous solution of 0.12 molar $\text{Ba}(\text{NO}_3)_2$ was prepared using deionized water. Required amount ($\text{Ba}/\text{Ti} = 1:1$) of TiO_2 powder was added to the $\text{Ba}(\text{NO}_3)_2$ solution with constant stirring. The suspension was ultrasonicated (10 minutes) to break TiO_2 agglomerates. Required amount of oxalic acid (0.4 molar solution) was added drop wise into the mixture under vigorous stirring. The pH of the resultant mixture was adjusted to 6–7 by adding ammonia solution. This process precipitated barium oxalate on the surface of fine TiO_2 (seed) particles by heterogeneous nucleation. It is well known that heterogeneous nucleation is used in coating of ceramic particles with another ceramics [12]. For example, Kyoung R. Han et al. [13] have produced coprecipitate Zr-Ti-hydroxides over SnO_2 particles by simultaneously adding ZrOCl_2 and TiCl_4 mixed solution and NH_4OH -solution to an aqueous slurry of SnO_2 . The necessary condition is that the super-saturation must be controlled so that only heterogeneous nucleation on the seed takes place. If super-saturation is too high, homogeneous nucleation will take place [12]. In the present case super-saturation was controlled by the use of dilute solutions. The resulting precipitates were then washed repeatedly using deionized water, followed by drying at 40°C for 48 hours.

The as dried precursor was characterised using thermo-gravimetric analysis and differential thermal analysis with alumina as a reference at a heating rate of $10^\circ\text{C}/\text{minute}$ in air from room temperature up to 1100°C . The precursor was calcined in air at various temperatures, up to 900°C , followed by phase identification performed at room temperature using a Cu-K_α X-Ray Diffractometer (PW-1830, Philips, Netherlands). To quantify the BaTiO_3 and intermediate BaCO_3 concentrations, calcined powders were uniformly mixed with an internal standard, CaF_2 powder and the resulting mixture was analysed using a step size of 0.02° , 2 with 20 second/step. The relative weight fractions of BaTiO_3 and BaCO_3 were quantified from the ratio of [101] & [110] peak areas of BaTiO_3 and [111] & [021] peak areas of BaCO_3 , respectively, with the [111] peak area of CaF_2 , according to the process described by S. Kumar & G.L. Messing [14]. On the ba-

sis of XRD line broadening at half maxima of the above said peaks, crystallite sizes of BaTiO_3 in the calcined powders were estimated using the Scherrer equation [15]. The morphological development of crystalline BaTiO_3 was studied by optical microscopy (Zeiss Axiotech optical microscope).

Results and Discussion

Figure 1 shows the TGA and DTA traces for the BaTiO_3 precursor. TGA exhibits three apparent decreases in specimen weight in the range $50\text{--}300^\circ\text{C}$, $400\text{--}650^\circ\text{C}$ and $750\text{--}1000^\circ\text{C}$ respectively and a minor increase in weight in the range $650\text{--}710^\circ\text{C}$. The fall in weight over the range $50\text{--}300^\circ\text{C}$ corresponds to a DTA endothermic reaction. The fall over the range $400\text{--}650^\circ\text{C}$ corresponds to a DTA exotherm and the fall over the range $750\text{--}1000^\circ\text{C}$ corresponds to again a DTA endotherm. It is generally accepted that the mechanism of decomposition of barium titanyl oxalate [4, 10, 11] involves the following three steps with increasing calcination temperatures: (1) Dehydration of oxalate precursor (2) Decomposition of dehydrated oxalate to intermediate phases such BaCO_3 , TiO_2 , oxycarbonate, etc. (3) Decomposition of BaCO_3 /oxycarbonate and formation of BaTiO_3 . Three decreases in specimen weight are therefore believe to corresponds to the above three stages, respectively. In this case, the specimen is composed of an equimolar mixture of $\text{Ba}(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ and TiO_2 . There is a close agreement between the overall weight loss of 27.15% observed and that expected on the basis of

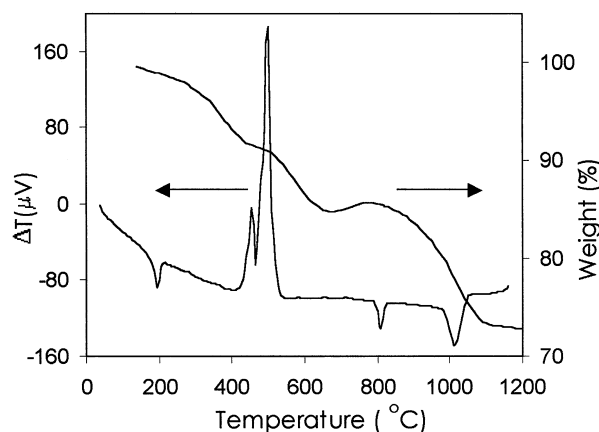
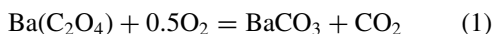
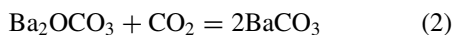


Fig. 1. TGA and DTA of semi-oxalate precursor between 25 and 1100°C in air.

conversion of Ba(C₂O₄)·1H₂O:TiO₂ to BaTiO₃ (27.8% theoretical). The 200°C endothermic peak corresponds to dehydration of Ba(C₂O₄)·1H₂O and 500°C exothermic peak corresponds to oxidation of the organic precursor as per the reaction:



According to the above reaction the weight loss from initial to complete oxidation should be 14.23%. But a weight loss of about 16.29% was observed in this case. The extra weight loss (2.06%) may be due to the formation of little amount of barium-oxycarbonate in the system. A small exothermic peak just before 500°C big exotherm may be due to this oxycarbonate formation. As reported by previous authors [16], the intermediate Ba-Ti-oxycarbonate phase is a metastable and weakly crystalline phase with a stoichiometry close to Ba₂Ti₂O₅CO₃. In the present case, a small amount of barium-oxycarbonate phase with a stoichiometry close to Ba₂OCO₃, may be forming in the system along with BaCO₃ major phase. Jenq-dar Tsay et al. [17] also reported the coexistence of BaCO₃ with the intermediate oxycarbonate phase during the thermal decomposition of barium-titanium citrate. The oxycarbonate phase was not detected in the calcined precursor by the XRD analysis due to its little amount as well as weakly crystalline in nature. The intermediate oxycarbonate was then converted to BaCO₃ at higher temperature by the reaction:



The reaction is associated with a net weight gain. A TGA weight gain of about 2.05% in the range 650–710°C may be due to the above transformation. Also this 2.05% weight gain is very close to the excess weight loss of 2.06% that found in the temperature range 400–650°C. So it can be concluded that the little exothermic peak in the range 400–650°C is due to the oxycarbonate formation and a little amount of oxycarbonate coexists with BaCO₃ during the decomposition of Ba-oxalate-TiO₂ precursor. The 1000°C endothermic peak corresponds to the formation BaTiO₃ by the reaction:



The 800°C endothermic peak is identified as due to the polymorphic transformation of whitrite to

α-BaCO₃ [18], since there was no TGA weight change associated with this endotherm.

To understand the fundamental issues of BaTiO₃ crystallization the precursor was heated in air at temperatures from 500–900°C at 100°C interval for 1 hour. Figure 2 shows the XRD patterns of the precursor and that heated at different temperatures. The precursor powder contains barium oxalate and TiO₂ phases. Above 500°C, BaCO₃ phase appears in the system due to the oxidation of oxalate (reaction 1). The amount of BaCO₃ (peak area) decreases slowly upto 800°C, then rapidly after 800°C. It should be noted that the decomposition of BaCO₃ occurs at much lower temperatures in presence of relatively acidic TiO₂ [4] than does pure BaCO₃ system [19]. That is why the quantity of BaCO₃ decreases from 600°C onwards in this case. The rapid decomposition of BaCO₃ after 800°C may be due to the two following reasons. Firstly, it may be due to small crystallite size of the BaCO₃. Secondly, the polymorphic transformation of whitrite near 800°C, may accelerate its decomposition due to the formation of defects in the crystallites during the transformation (the Hedvall effect) [20]. The precursor was completely transformed into single phase BaTiO₃ at 900°C. To check the intermediate phase formation, the samples were also heat-treated at 50°C interval in the temperature range 500–900°C, without holding at the peak temperature. No traces of intermediate BaO and/or Ba₂TiO₄, BaTi₄O₉ and BaTi₃O₇ phases were detected by XRD at any stages of transformation. So it is concluded that the reaction (3) is responsible for BaTiO₃ formation in this system. X-Ray quantitative estimation of BaTiO₃ (Fig. 3) shows that the quantity slowly increases from 600°C to 800°C and then rapidly from 800°C to 900°C. However the quantity of intermediate BaCO₃ (Fig. 3) increases slightly from 500°C to 600°C and then decreases slowly up to 800°C, and rapidly up to 900°C. The slight increase in its quantity is due to the transformation of oxycarbonate to carbonate (reaction 2) at 600°C for 1 hour. As stated above, the presence of oxycarbonate was not detected by XRD due to its weakly crystalline in nature and small in quantity. The concentration of BaTiO₃ formed was used as a measure of the final stage of the transformation. Taking the transformation to obey first-order reaction kinetics, the velocity constant (*k*) is determined for different temperatures and then activation energy (*E*) is evaluated from the Arrhenius plot (Fig. 4) of 'log *k*' against 1/*T*, according to J. Bera [21]. Figure 4 shows the Arrhenius type dependency of reaction

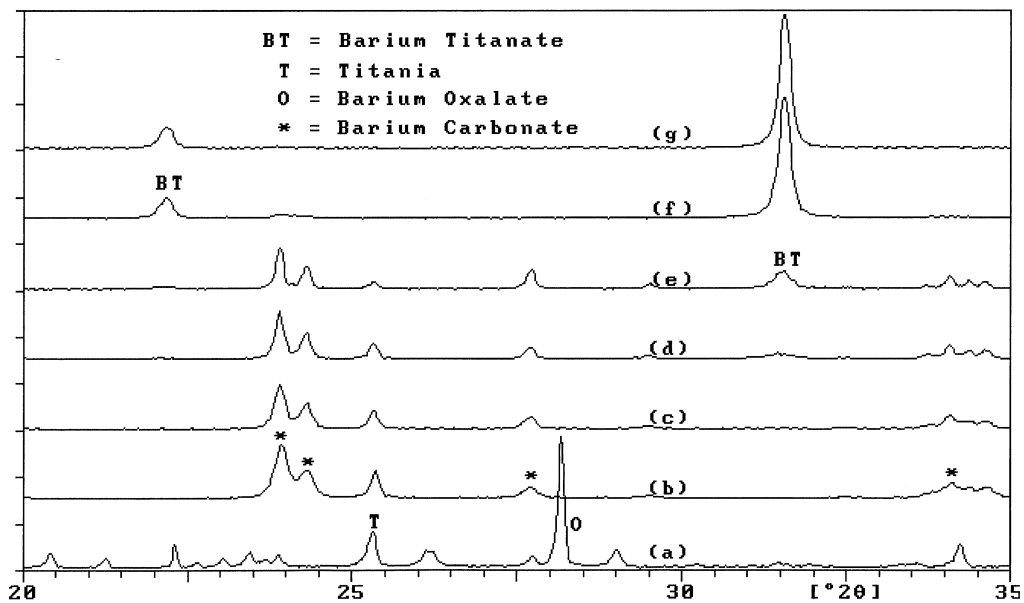


Fig. 2. XRD patterns of (a) semi-oxalate precursor and precursor heated at (b) 500°C/1 h, (c) 600°C/1 h, (d) 700°C/1 h, (e) 800°C/1 h, (f) 900°C/1 h and (g) 900°C/8 hrs.

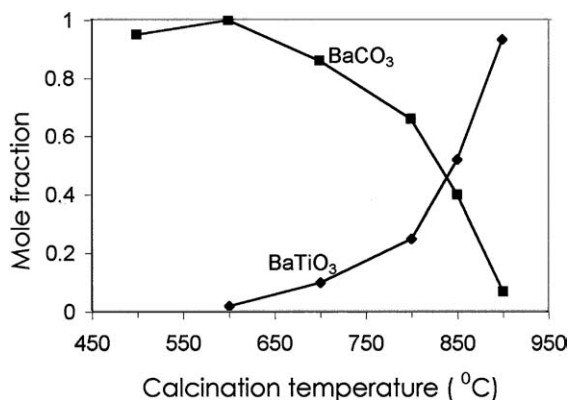


Fig. 3. Non-isothermal transformation kinetics of precursor in static air.

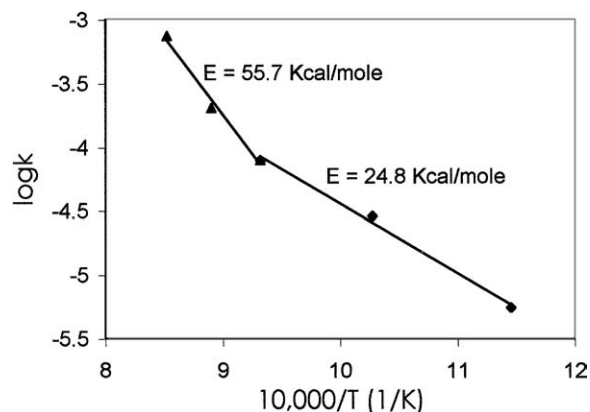


Fig. 4. Arrhenius dependence of reaction rate on calcination temperature for the transformation of precursor to BaTiO₃ in static air.

rate on calcination temperature for BaTiO₃ phase formation.

Which also indicates the two reaction rates (denoted by their different activation energies) for BaTiO₃ formation in the temperature range 600–800°C and 800–900°C, respectively. The transformation of precursor to BaTiO₃ in the lower temperature range may be rate-controlled by the diffusion of CO₂ gas through the BaTiO₃ product layer [14] and have lower activation energy (24.8 Kcal/mole). Transformation re-

action in the higher temperature range may be rate-controlled by Ba²⁺ ion diffusion through the product layer [22] and have higher activation energy (55.7 Kcal/mole).

The BaTiO₃ powders derived in this process was characterized with respect to crystallite size developed as a function of calcination temperature. Figure 5 plots the average crystallite size as a function of calcination temperature. As expected, crystallite size

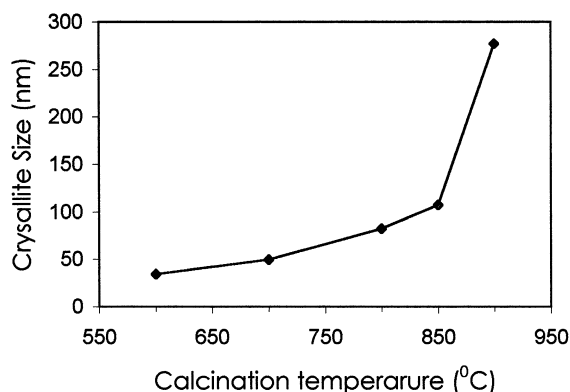


Fig. 5. Average crystallite size of BaTiO₃ estimated on the basis of peak broadening as a function of calcinations temperature for semi-oxalate precursor.

increases with increasing calcination temperature, only the size increases slowly up to 850°C, and then rapidly with temperature. The rapid increase in crystallite size after 900°C may be due to the partial sintering and growth of fine BaTiO₃ crystallites. However, it is possible to prepare BaTiO₃ with crystallite size nearly 300 nm by calcining the precursor at 900°C/1 hr. The lattice parameter determination by XRD showed that BaTiO₃ (900°C/1 hr) has cell pa-

rameters: $c = 4.026$ Å, $a = 3.9949$ Å, with c/a ratio = 1.0078. Which may be considered as composed of tetragonal phase. But that produced at 700°C/1 hr, may be considered as pseudocubic as it has cell parameters: $c = 4.0125$ Å, $a = 4.0026$ Å, with c/a ratio = 1.0025.

The Fig. 6 shows the optical micrograph of raw precursor and precursor calcined at 600°C/1 h and 900°C/8 hrs. The raw precursor has irregularly shaped agglomerated particles (Fig. 6(a)), which is the nature of glassy organic resin [14]. It is well known that BaCO₃ particles have elongated rod like morphology [23]. The intermediate BaCO₃ particle has also an elongated morphology (Fig. 6(b)) in the calcined product. The morphology of completely grown BaTiO₃ crystallite (Fig. 6(c)) is also elongated. This is only possible if the BaTiO₃ shape is inherited from the shape of the intermediate BaCO₃ particles. In our system, it is likely to produce elongated BaTiO₃ by the above mechanism. So, the morphology of BaTiO₃ was more controlled by intermediate BaCO₃ than by TiO₂ morphology. Figure 6(c) shows a rather big crystallite size of the BaTiO₃ due to the strong particle growth during calcination at 900°C for 8 hrs duration and hence, it may be considered as “overcalcined”. Its micrograph is used here to show the crystallization/growth

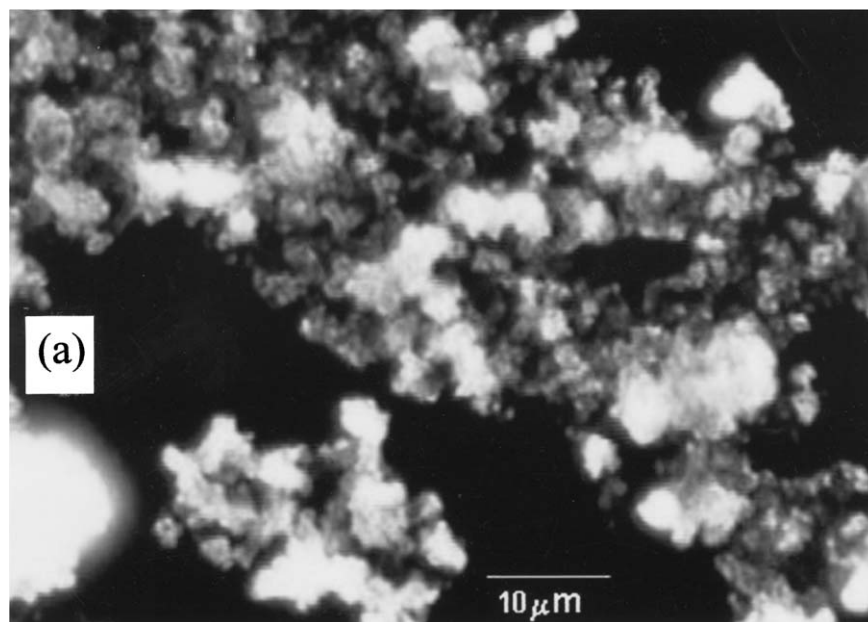


Fig. 6. Optical micrograph of (a) raw precursor powder, (b) precursor calcined at 600°C/1 h and (c) precursor calcined at 900°C/8 hrs.

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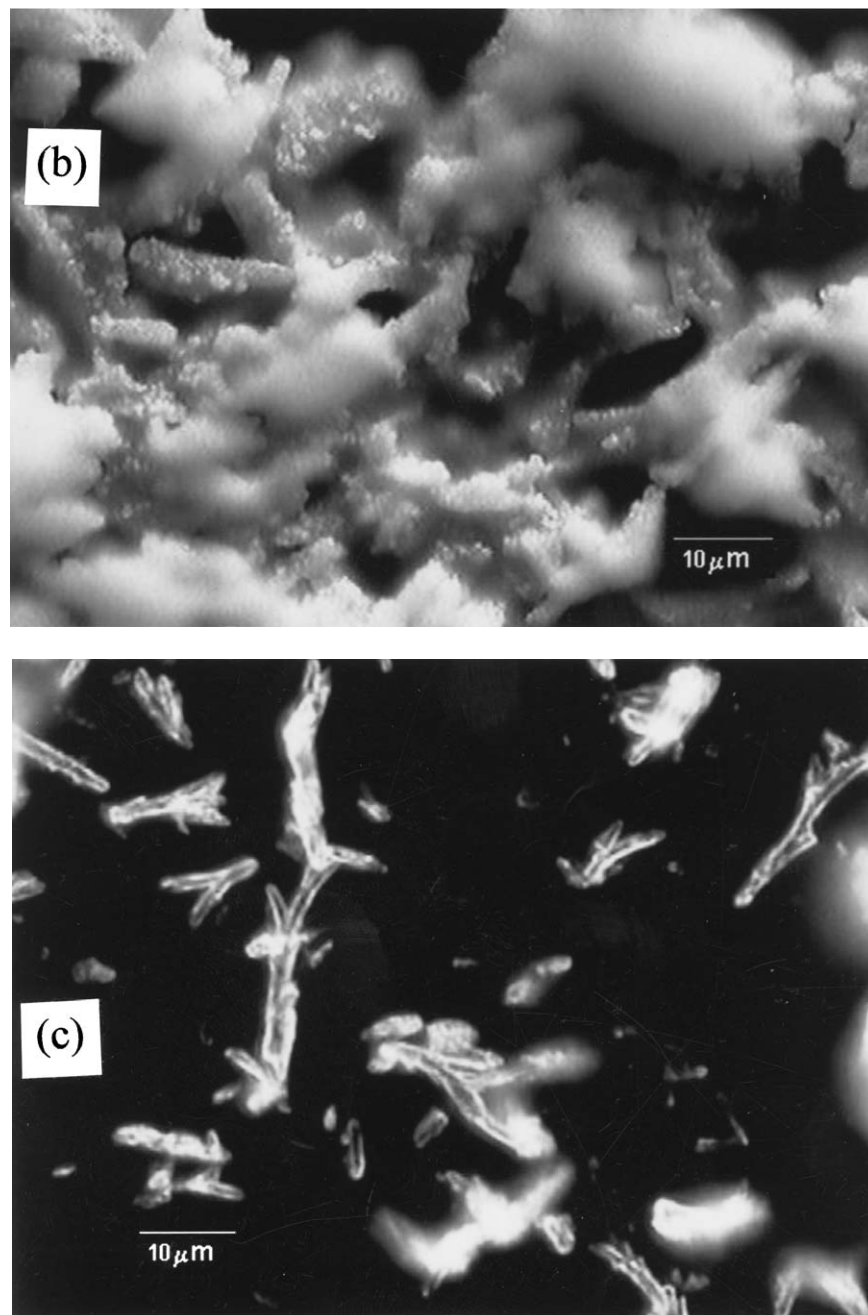


Fig. 6. (Continued).

behaviour of the BaTiO_3 , for better understanding of the process. For capacitor application, the precursor must be calcined at $900^\circ\text{C}/1$ hr or below 900°C /for few hrs, to get fine particle size and soft agglomerates. It is obvious that soft agglomerates are formed dur-

ing low temperature ($\geq 900^\circ\text{C}$) calcination and those agglomerates can be disintegrated by gentle milling [3]. So, a low-temperature synthesis of fine crystallite size BaTiO_3 is possible through this semi-oxalate route.

Conclusion

Semi-oxalate precursors for BaTiO₃ synthesis, containing barium oxalate precipitated on the surface of the TiO₂ particles, have an irregularly shaped agglomerated morphology. Based on DTA, TGA and XRD results, we conclude that upon heating the precursor between 450°C–500°C, an intermediate weakly crystalline barium oxycarbonate forms along with BaCO₃. The intermediate oxycarbonate decomposes to form BaCO₃ in the range 600–700°C. The BaTiO₃ formation is started from 600°C onwards but the kinetics of its formation is higher after 800°C. Up to 800°C the reaction rate may be controlled by CO₂ diffusion and after 800°C that may be controlled by Ba²⁺ ion diffusion. Nanometer size crystallites are produced during low temperature calcination of the precursor. The morphology of BaTiO₃ crystal formation is mainly governed by the morphology of intermediate BaCO₃ particles.

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