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Synthesis of barium titanate nanopowder using polymeric precursor method

V. Vinothini [a], Paramanand Singh [b], M. Balasubramanian [a,*]

[a] Composites Technology Centre, Indian Institute of Technology, Chennai 600036, India
[b] Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Chennai 600036, India

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Abstract

Barium titanate powder was prepared by a polymerized complex method based on the Pechini type reaction route, where barium and titanium ions were polymerized in mixed solution of citric acid, ethylene glycol, to form a transparent resin, which was used as a precursor. Barium titanate powder was formed by heat treating the polymeric precursor in air at 500–900 °C. The thermal decomposition of (Ba, Ti) polymeric precursor was studied by thermal analysis. The crystal structure was investigated by X-ray powder diffractometry and Raman spectroscopy. The particle size and morphology of $BaTiO_3$ were examined by X-ray diffraction and transmission electron microscopy. Cubic $BaTiO_3$ with some traces of hexagonal phase was present at 500 °C and tetragonal $BaTiO_3$ at 600 °C and above. However, Raman spectrum showed a mixture of cubic, tetragonal and hexagonal $BaTiO_3$ at 500 °C and tetragonal $BaTiO_3$ at 600 °C and above. X-ray line broadening studies of 900 °C heat-treated powders showed average crystallite size of 20 nm. Agglomerated spherical grains are observed at 600 °C. The sintering behavior and dielectric properties of the nanopowders were also studied.

Keywords: A. Precursors: organic; C. Dielectric properties; D. Perovskites; D. $BaTiO_3$ and titanates

1. Introduction

The demand for high quality electronic ceramics increases rapidly which have led to greatest sophistication in the processing of these materials in powder synthesis stage and subsequent densification [1]. The bulk property of any material, whether it is a metal, semi conductor or an insulator, changes when the crystallite size reduces from macro to molecular level. Some of the physical properties that change due to this size reduction are (i) lowering of melting point, (ii) decrease of onset sintering temperature, (iii) shift in the luminescence peak towards lower λ, (iv) disappearance of ferroelectric and ferromagnetic properties, (v) enhancement of electronic and ionic conductivity [2]. In traditional ceramic processing, the resulting microstructure has a wide grain size distribution, multiple phases and inevitably some degree of porosity. These are due to inhomogenity and impurity incorporation in the powder processing stage. The successful synthesis of barium titanate nanopowder with their unique dielectric properties largely depends on the purity and crystal structure that greatly influences on the properties. Low temperature, wet chemical route 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 [1].

In co-precipitation and hydrothermal methods, stoichiometry deviations and formation of biphasic solid solutions have been reported [3]. Also the high temperature required for achieving complete solid solution in some of the low temperature methods such as sol–gel and metallo-organic decomposition makes them less favourable. Many of these problems can be overcome by using low temperature polymeric precursor method. The advantage of this technique is the quasi-atomic dispersion of constituent components, which facilitates synthesis of the crystallised powder with ultrafine particle size and high purity at low

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* Corresponding author. Fax: +91 44 2257 0039.
E-mail address: mbala@iitm.ac.in (M. Balasubramanian).

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temperature. Barium titanate, a ceramic material with high dielectric constant used for the manufacture of multilayer ceramic capacitors, thermistors and electro-optic components has several crystallographic modifications [4]. $BaTiO_3$ exists as tetragonal ferroelectric phase with high dielectric constant at room temperature and undergoes phase transformation at 125 °C where it becomes cubic paraelectric phase [5]. The phase transformation occurs even at room temperature, as the size of the crystallite size decreases. The transformation temperature may vary as with synthesis route [6].

Three major contributions are devoted to study the reaction mechanism for the $BaTiO_3$ formation [7–9]. The first of them [7] assumed that a solid state reaction between the nanocrystalline $BaCO_3$ and TiO_2 lead to the formation $BaTiO_3$ as the final reaction product. The other two contributions [8,9] concluded that $BaTiO_3$ formed directly by thermal decomposition of an intermediate phase ($Ba_2Ti_2O_5 \cdot CO_3$) above 635 °C. Such a conclusion has recently been questioned by Cho [10], who proposed a different mechanism for $BaTiO_3$ formation reaction. In the present work, the main aim is to synthesis homogeneous nanosized Barium titanate and the characterization of precursor and calcined powders. Sintered compacts will be made to study the sintering behaviour and dielectric properties. Such information would be useful to device manufacturers especially those involved with thin layer dielectrics.

2. Experimental procedure

The experimental procedure is similar to the one used by Cho and Hamada [11]. The titanium solution was prepared by dissolving titanium tetraisopropoxide (Aldrich 97%) to a solution of citric acid (SRL, 99.5%) and ethylene glycol (SRL, 98%), mixed in a molar ratio of 1:4. The required quantity (Ba:Ti = 1:1) of $BaCO_3$ (Qualigens, 99%) was dissolved in this solution. This solution was heated at 90 °C with a constant stirring until it became clear transparent yellow solution. This solution was heated at 200 °C for 5 h in an oven to promote polymerization and remove solvents. With continued heating at this temperature the solution became more viscous with a change in color from pale yellow to brown, but without any visible formation of precipitation or turbidity and finally solidified into dark brown, glassy resin. Charring the resin at 400 °C for 2 h in an electric furnace resulted in a black solid mass, which was lightly ground into a powder, using Agate Mortar and pestle. The powder obtained in this way is referred to as "precursor". The precursor was heat treated at 500–900 °C in air for 5 h, in Al_2O_3 boat.

The dark brown glassy resin was used to carry out the thermal analysis study with a simultaneous thermal analyser (Netzch STA 409 PC) at a heating rate of 10 °C in air. This equipment records differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The precursor powder was heat-treated at various temperatures (500–900 °C) and the phases were analysed by powder X-ray diffractometry (XRD) using Cu Kα radiation (SHIMODZU, Model XD-1). To obtain grain size from X-ray line broadening, the Scherers formula was used. Raman spectroscopy (BRUKER FRA 106) was also used to investigate the phases present in the powders. The particle size was determined using Transmission electron microscopy (PHILIPS CM 12 STEM UNIT). The powders were compacted into pellets (with few drops of 10% polyvinyl alcohol) at 100 MPa and then sintered at 1300 °C for 3 h. The density of the sintered disks was obtained by the Archimedes method. Dielectric properties were measured on sintered disks coated with silver paste using LCR meter (ZENTECH LCZ 1061).

3. Results and discussions

Fig. 1 shows the TGA and DTA curves for the (Ba, Ti) polymeric resin heated from room temperature to 900 °C. Up to 140 °C, the DTA curve shows a small endothermic peak. Above that temperature, the thermal decomposition of (Ba, Ti) polymeric precursor starts and is a multi-step exothermic

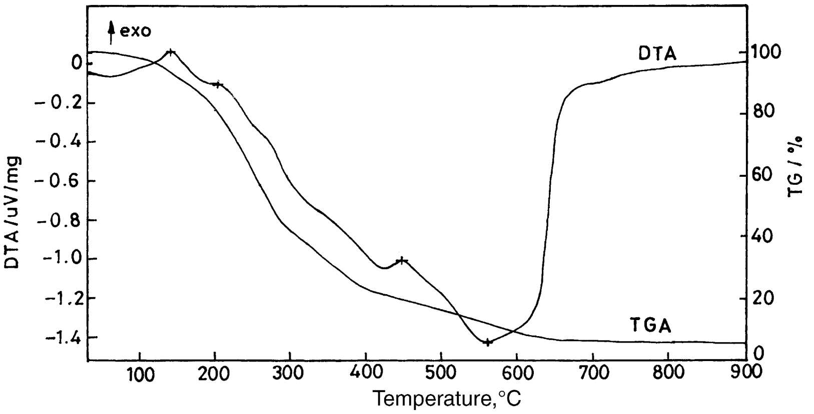

Fig. 1. DTA and TGA results of precursor powders.

reaction process, which is completed at about 640 °C. According to the TGA results, the thermal decomposition process is characterized by apparent loss in sample weight over the temperature ranges from 200 to 320 °C, 320 to 510 °C and 510 to 660 °C. Each step in the TGA curve corresponds (except the first one) to an exothermic peak in the DTA curve. The maxima of these exothermal reactions can be located at about 555 °C. There is no weight loss after 640 °C. As previously reported elsewhere [12] no weight gain was registered through the thermal decomposition of the precursor. The main reactions occurring with increasing temperature in the formation of $BaTiO_3$ from (Ba, Ti)-citrate polyester resin precursors, are the following: (a) dehydration of the polymeric resin precursors, (b) decomposition/oxidation of the dehydrated polymeric resin precursor with the formation of the intermediate phases, and (c) formation of barium titanate as a consequence of the reaction between the previously formed intermediate by products [13].

The XRD results (Fig. 2) indicate the formation of cubic phase of $BaTiO_3$ with some traces of hexagonal phase when heated at 500 °C. The tetragonal phase of $BaTiO_3$ is predominantly present when heated above 600 °C. The first appearance of $BaTiO_3$ with a single tetragonal phase was detected for the sample heated at 600 °C. The complete transformation of precursor into tetragonal $BaTiO_3$ was achieved after 5 hrs at 900 °C as indicated by the separate 0 0 2 and 2 0 0 peaks in the Fig. 2. Presence of cubic phase is not possible to ascertain, due to the line broadening of XRD peaks, as a result of the combined effects of crystallite size, non-uniform strain, and instrumental broadening.

To further verify the above statement on phase development with increasing calcination temperature, the powders were characterized using Raman Spectroscopy. Fig. 3 shows Raman Spectra of precursor powders calcined for 5 hrs in static air at 500–900 °C. The sharper band at 1064 cm^{-1} is found in the samples heated up to 700 °C,

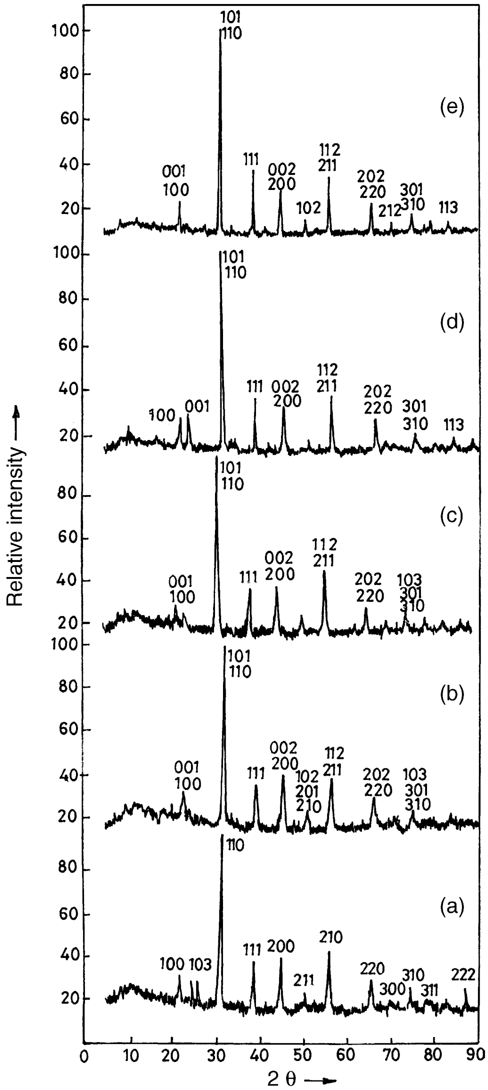

Fig. 2. X-ray diffraction patterns of precursor powder calcined at different temperatures for 5 h: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C.

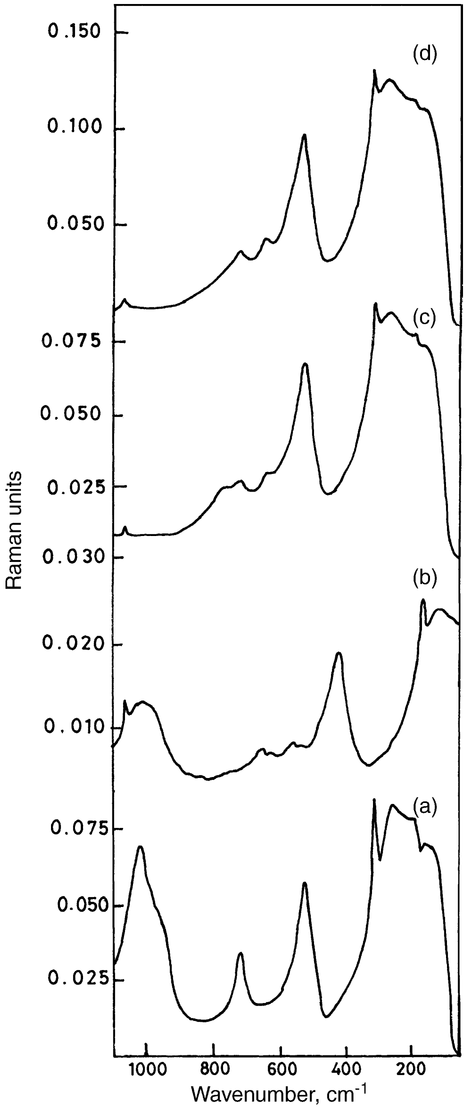

Fig. 3. Raman spectra of precursor powder calcined at different temperatures for 5 h: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 900 °C.

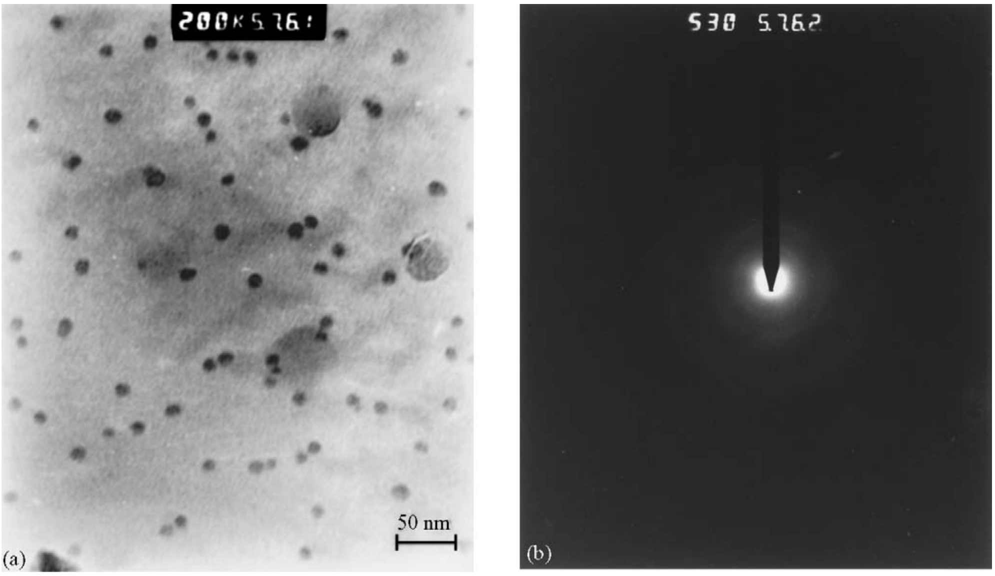

Fig. 4. Transmission electron microscopy of precursor powder calcined at 900 °C: (a) microstructure and (b) SAD pattern.

which represents the CO_3^{2-} symmetric stretching mode in the intermediate phase ($Ba_2Ti_2O_5\cdot CO_3$). The absence of peak at 1054 cm^{-1} infers the absence of $BaCO_3$. The small peak at 638 cm^{-1} for samples heated at 500 °C represents high temperature $BaTiO_3$ hexagonal phase. The absence of peak at 147 cm^{-1} precludes the anatase phase. All of them exhibit distinct bands at about 721, 520, 306 and 260 cm^{-1} wave number which are characteristics of the $BaTiO_3$ with tetragonal structure [13]. The appearance of a peak at 306 cm^{-1} in the sample heat treated at 500 °C indicates, at least on a local scale, asymmetry of TiO_6 octahedra within the $BaTiO_3$ structure exist which is contrary to the XRD results. So these powders are having tetragonal structure rather than cubic structure. As Duran et al [13] suggested, the symmetry of crystals observed by Raman spectroscopy indicates a local and dynamic symmetry, and the symmetry determined by XRD measurement is average and static symmetry.

The grain size of the 900 °C heat-treated samples were calculated from X-ray studies using the Schererr formula. The average particle size was calculated to be around 20 nm for samples heated at 900 °C. TEM shows (Fig. 4) agglomerated spherical grains at 600 °C. Well defined $BaTiO_3$ particles of about 15 nm size are formed when heated for 5 hrs at 600 °C. The selected area electron diffraction pattern shows hazy circles as the powders are

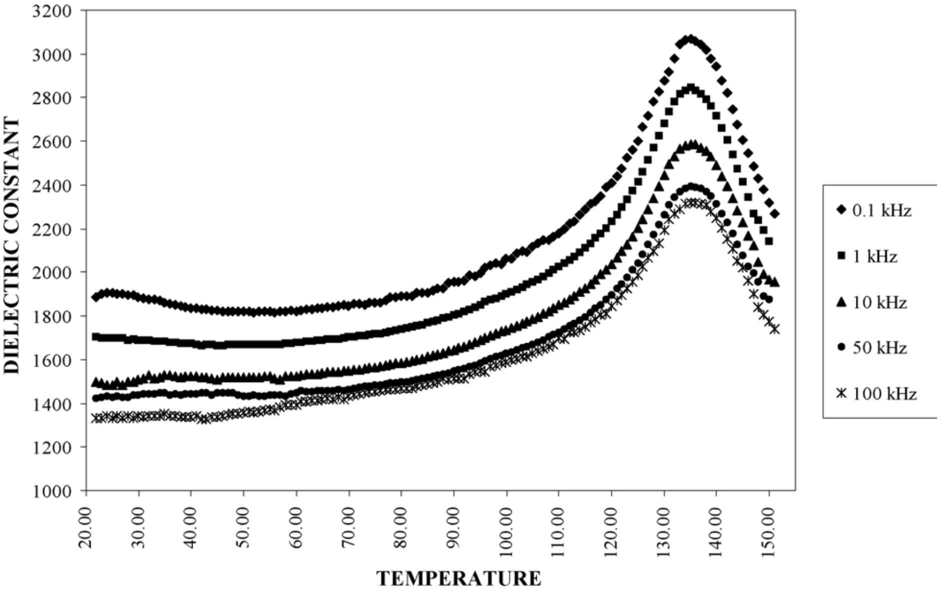

Fig. 5. Variation of dielectric constant as a function of temperature measured at various frequencies.

nano-crystalline. On increasing the heat treatment temperature grain growth takes place resulting in slight increase in particle size.

The sintered compacts at 100 MPa pressure have density of ~92% theoretical density. The dielectric constant of the sintered disk of barium titanate as a function of frequency and temperature were studied. Fig. 5 shows the variation of the dielectric constant as a function of temperature measured at various frequencies. The dielectric constant at 1 kHz is 1700 at room temperature and 2840 at transition temperature, which decreases as frequency increases. Earlier report on $BaTiO_3$ prepared by sol–gel method show that a dielectric constant of 500–600 and 700–900 (at 1 MHz) for samples sintered at 1200 and 1300 °C (30 min), respectively [14]. $BaTiO_3$ prepared by the oxalate precursor route gave dielectric constant of 1620. Thus, the method of synthesis and sintering temperature affect the dielectric constant to a greater extent. The $BaTiO_3$ prepared by this route gives very high dielectric constant without lowering transition temperature.

4. Conclusions

Barium titanate ($BaTiO_3$) was synthesised by heat treating polymeric precursor in air at 500–900 °C for 5 h. The first appearance of $BaTiO_3$ with single phase was detected for the sample heated at 600 °C. The XRD analysis indicated the presence of cubic $BaTiO_3$ with some traces of hexagonal phase at 500 °C and tetragonal phase after 600 °C without any traces of $BaCO_3$ and TiO_2. Raman spectrum suggested that the tetragonal structure might be slightly sustained in the nano $BaTiO_3$ particles. The sintered compacts have density of ~92% theoretical density and the dielectric constant was found to be 1700 at room temperature and 2840 at transition temperature for 1 kHz, which decreases as frequency increases.

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