



Characterization of Barium Titanate: BaTiO₃ (BT) Ceramics Prepared from Sol-Gel Derived BT Powders

S.B. DESHPANDE, P.D. GODBOLE, Y.B. KHOLLAM & H.S. POTDAR*

Physical and Materials Chemistry Division, National Chemical Laboratory, Pashan, Pune-411 008

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Abstract. Sol-gel synthesis was attempted at room temperature by adding drop wise a clear solution (made by reacting BaCO₃ with glacial acetic acid) to an equi-molar solution of titanium tetrabutoxide in isopropanol (IPA) and acetic acid. The gelation occurred within 30 minutes. The as-dried gel was calcined at 750°C/6 h in air to obtain carbon free BaTiO₃ powders. The resulting BT powders were further pressed into pellets and sintered at 1280°C/4 h in air to get dense ceramics (density ~ 94%). XRD and SEM techniques were used for phase and microstructure analysis respectively. The room temperature relative permittivity (ϵ) of 1280 increased to 7200 (at Curie temperature of 127°C) at 1 kHz frequency. The dissipation factor ($\tan\delta$) ~ 1.6% was observed in these samples. Also, the ferroelectric properties such as spontaneous polarization (P_s ~ 13 $\mu\text{C}/\text{cm}^2$), coercive field (E_c ~ 4.0 kV/cm) and dielectric strength (~34 kV/cm) are estimated for these samples. These performance parameters are compared with the available standard data from the literature.

Keywords: barium titanate, sol-gel processing, relative permittivity, ferroelectricity, microstructure

1. Introduction

Barium titanate (BaTiO₃): BT is a well-known electroceramic material used in the manufacture of thermistors, dielectric ceramic capacitors, multilayer capacitors etc. [1, 2]. There is a renewed interest in evaluating wet chemical methods for the synthesis of very fine BT powders with high purity and high sinterability [3, 4] to improve its electrical properties [5]. Traditionally, BT powders are prepared by classical solid-state reaction, which involves two steps: (1) ball milling of BaCO₃ and TiO₂ and (2) calcination of mixture at higher temperatures around 1100°C to form BT powders via slow diffusion controlled reactions [6]. High-temperature BT powder thus obtained has some drawbacks such as very large particle size, higher impurity content due to repetitive calcination and grinding treatments and also lower chemical reactivity. Therefore, these BT powders are not suitable for enhancing the dielectric properties of ceramics. Many low-temperature wet-chemical meth-

ods such as oxalate process [7–9], hydrolysis of barium titanium alkoxides [10], homogeneous precipitation [11], sol-gel [12], combustion method [13], mixed citrates [14, 15], conventional and microwave assisted hydrothermal (M-H) techniques [16–18] have been tried to prepare high-purity homogeneous and ultrafine BT powders. The oxalate-based process also produces intermediate species during calcination stage which further react at temperature $\geq 800^\circ\text{C}$ via diffusion controlled reactions to yield ultrafine BT powders [19]. These high calcination temperatures give rise to the particle aggregation and thus affect the sinterability of the BT powder. In view of this, the present work describes the sol-gel process wherein the cheaper starting precursors such as titanium tetrabutoxide and barium carbonate are used and all the reactions are carried out at room temperature in acidic semi-aqueous media to form the gels at ambient conditions. The gels are formed by controlled hydrolysis and subsequent polymerization and condensation reactions to form 3-dimensional network forming viscous gel mass that is further dried under ambient conditions to get gel powder. It is definitely a gelation process rather than a sol-precipitation

*To whom all correspondence should be addressed. E-mail: potdar@ems.ncl.res.in

reaction. The advantage of this route is that it helps to produce submicron sized BT particles with high chemical purity and reactivity and narrow size distribution. Also, it helps to maintain homogeneous mixing of two cations at molecular level. There have been reports of wet-chemical methods producing submicron BT powders that will densify with small grain size and yield high dielectric constant without addition of dopants [12, 20]. Therefore, the main emphasis of the present investigation is on the characterization of sol-gel derived BT powders in the form of ceramic compacts for their dielectric and ferroelectric properties and to try to relate them to the observed functional microstructure. All these results are discussed in this paper.

2. Experimental

All the chemicals used for the synthesis were of AR grade. A clear solution obtained by reacting BaCO_3 (0.1 M) with 150 ml of glacial acetic acid (dissolution process was initiated by the addition of few drops of water to initiate the reaction) was added dropwise to the solution of titanium tetrabutoxide (0.1 M) dissolved in 700 ml of IPA and 15 ml glacial acetic acid while constant stirring. The hydrolysis and condensation reactions occurred to form a gel within 30 min. The dried gel powder was calcined at $750^\circ\text{C}/6\text{ h}$ to form BT phase. The calcined powder was cold-pressed into disks ($\sim 2\text{ g}$ each) at 5000 psi in 20 mm die punch set with PVA binder. The pressed disks (green density $\sim 60\%$) were sintered at $1280^\circ\text{C}/4\text{ h}$ in air. The sintered density was found to be $\sim 94\%$ of the theoretical density. XRD characterization of the calcined BT powders as well as sintered compacts (powdered) were carried out using Philips X-ray diffractometer Model 1730 with $\text{CuK}\alpha$ radiation and Ni filter. The slow scans for (200) and (002) reflections were taken from which the 'd' values were measured. The lattice parameters a_o and c_o were calculated by using the equation given below:

$$\sin^2\theta_{(hkl)} = \lambda^2(h^2 + k^2)/4a^2 + \lambda^2(l^2)/4c^2.$$

The crystallite size 'D' was calculated by using the Scherrer equation:

$$D = K\lambda/\beta \cos\theta$$

where, 'K' is constant, ' λ ' is X-ray wavelength, ' β ' is full width at half maximum and ' θ ' is angle of diffraction.

The microstructure developed during calcination and sintering stages was examined using scanning elec-

tron microscope (Leica, Stereoscan 440). For electrical measurements, the sintered disks were lapped up to 0.6 mm thickness, coated on both sides (diameter = 1.4 cm) with conducting silver paint, which was subsequently cured at $600^\circ\text{C}/2\text{ h}$ to develop excellent electrical contacts. Dielectric measurements were carried out employing a commercial LCR bridge at 1 kHz frequency. The Curie temperature (T_c) of the sample was determined from the peak in the relative dielectric constant versus temperature curve. The ferroelectric hysteresis-loop parameters: spontaneous polarization (P_s), remanent polarization (P_r) and coercive field (E_c) were estimated from the loop observed at 50 Hz on a 515 Tektronix oscilloscope with the aid of a home-built Sawyer-Tower circuit [21]. Dielectric strength or breakdown voltage (E_b) of the material was measured from the maximum voltage that the material can withstand without its electrical breakdown. All processing scheme is described in the flowchart (Fig. 1) given below.

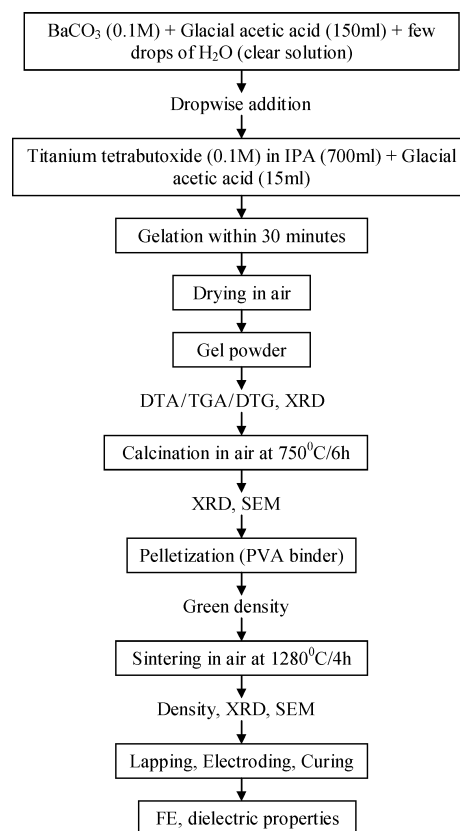


Fig. 1. Flowchart.

3. Results and Discussion

In our earlier paper [22], we have reported the optimization of various preparation conditions to obtain a gel by controlled hydrolysis and condensation reactions in semi-aqueous media between barium and titanium species at ambient conditions. These as-dried gels on decomposition in air produced BaTiO₃ (BT) powders.

The goal of the present work is to further evaluate BT ceramics made from above sol-gel derived BT powders for their dielectric and ferroelectric properties. Fig. 2(a) and (b) shows the XRD patterns of the calcined (750°C/6 h) BT powder and powder made from dense BT ceramics (obtained by sintering at 1280°C/4 h in air) respectively. Fig. 2(a) clearly indicates the formation of cubic BaTiO₃ as major phase [23] with very weak peaks appearing at $2\theta = 23.9^\circ$ and 27.5° which may be assigned to the reflections corresponding to the unreacted BaCO₃ and TiO₂ respectively [23] formed during the pyrolytic decomposition of the hard

gel-mass. The weak peaks observed at $2\theta = 28.6^\circ$ and 29.2° may be assigned to the formation of small amount of BaTi₃O₇/Ba₂TiO₄ [23] during the decomposition of the gel. The formation of metastable cubic phase [JCPDS data File No: 27582] of BT during calcination at 750°C/6 h is not uncommon as the calculated crystallite size (~ 29 nm) is lower than the critical size (60–70 nm) needed for the cubic-tetragonal phase transformation [24, 25]. The XRD density for the calcined powder was found to be ~ 6.005 g/cm³ since the calculated cubic lattice parameter was ~ 4.01 Å. Figure 2(b) shows the XRD pattern of the powder of sintered (1280°C/4 h) pellet, which gave 'd' values matching exclusively with the standard data (ASTM card No. 5-0626) reported for the tetragonal phase of BaTiO₃. The two peaks appearing at $2\theta = 44.8^\circ$ and 45.2° show clear splitting of (002) and (200) reflections corresponding to the tetragonal phase of BaTiO₃. The tetragonal lattice parameters calculated from these two reflections, $a_o = 3.996$ Å and $c_o = 4.030$ Å gave $c/a = 1.0085$. The XRD density for the sintered tetragonal powder was 6.017 g/cm³

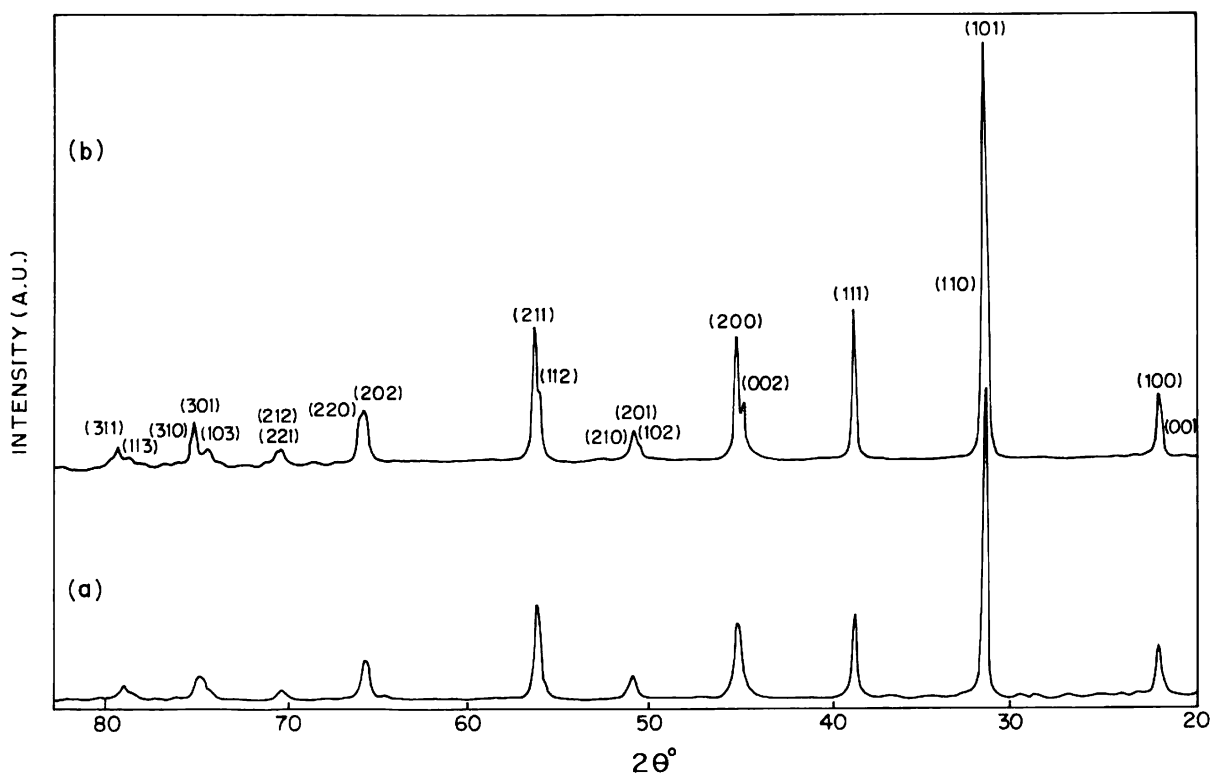


Fig. 2. XRD patterns of (a) gel calcined at 750°C/6 h and (b) powder of pellet sintered at 1280°C/4 h.

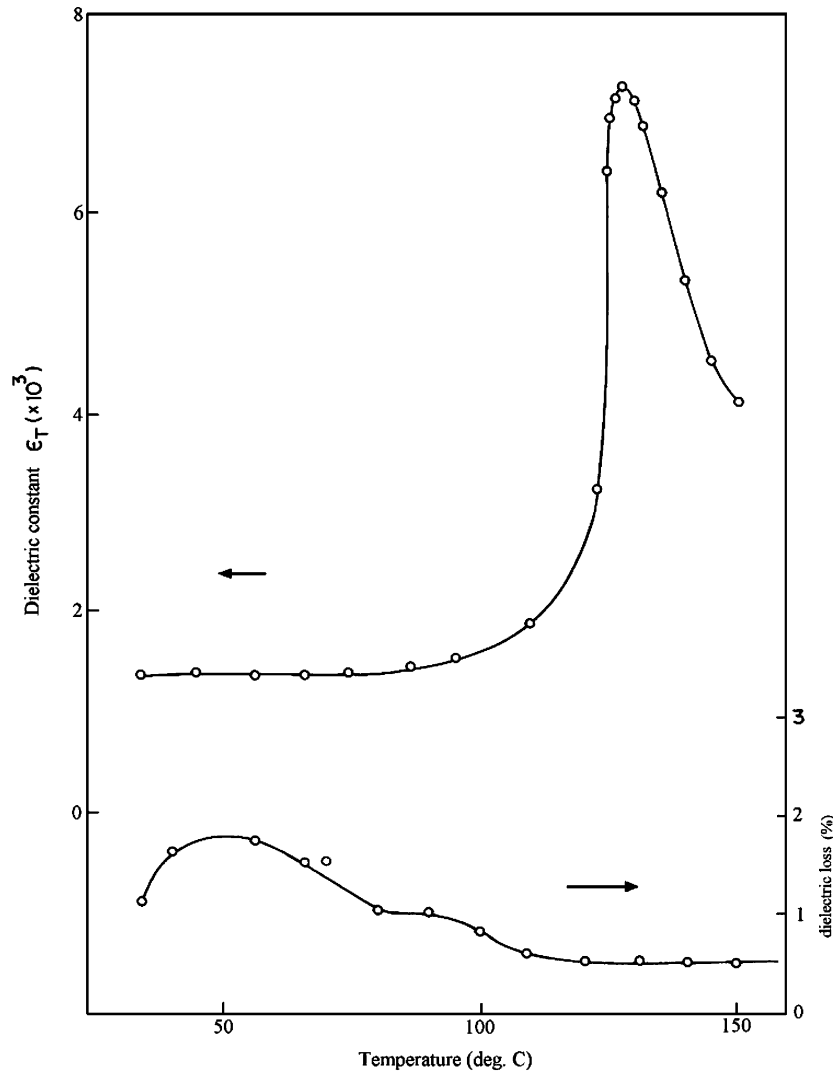


Fig. 3. Variation of dielectric constant (ϵ) and loss ($\tan \delta$) with temperature.

which is in agreement with that reported in the literature [23]. The dielectric and ferroelectric properties were measured on these disks as described in the experimental section. The room-temperature dielectric constant was found to be $\epsilon_{RT} \approx 1280$ with $\tan \delta = 1.6\%$ at 1 kHz frequency. The temperature-dependence of the dielectric constant (ϵ_T) and loss ($\tan \delta$) are shown in Fig. 3. It is evident from this Fig. 3 that the maximum value of dielectric constant obtained is $\epsilon_{\max} = 7200$ at $127 \pm 1^\circ\text{C}$ which is taken as the Curie temperature (T_c) of the material. The dielectric behavior of the material as a function of temperature during heating and cooling cycles was found to be nearly identical. The di-

electric loss ($\tan \delta$) value decreased with temperature and remained nearly constant ($\sim 0.5\%$) at and above 110°C . The dielectric loss increased with decrease in temperature below 100°C . This observation is consistent with the observations reported by T.T. Fang et al. [5] for BaTiO_3 ceramics. This may be either due to slight excess of Ti in BT ceramics wherein injected protons H^+ from adsorbed water tend to reduce Ti^{4+} to Ti^{3+} thereby causing an increase in the dielectric loss factor or may be due to the water vapour adsorbed on the surfaces of the open pore channels as the density of our samples is not very high. The ferroelectric properties estimated from the FE hysteresis loop for our

samples were found to be $P_s = 13.0 \mu\text{C}/\text{cm}^2$, $P_r = 7.0 \mu\text{C}/\text{cm}^2$ and $E_c = 4.0 \text{ kV}/\text{cm}$. The observed value for P_s is quite comparable to the reported value for the ceramic sample [23]. Sharma et al. [26] have reported higher values ($P_s = 19.2$ & $P_r = 11.1 \mu\text{C}/\text{cm}^2$ and $E_c = 8.0 \text{ kV}/\text{cm}$) for the sol-gel derived BT ceramics. These higher values may be due to the higher densification ($>99\%$) in their samples. However, the room temperature dielectric constant (ϵ_{RT}) is lower i.e. <800 than that observed in our samples ($\epsilon_{RT} \approx 1280$). Also, $\epsilon_{\text{max}} = 7200$ value in our sample is found to be much higher than that reported by them for their BT ceramics ($\epsilon_{\text{max}} = 2500$). The dissipation factor ($\tan \delta$) values are quite comparable. Figure 4(a) shows the SEM photograph of the calcined powder ($750^\circ\text{C}/6 \text{ h}$) in air. The BT powders prepared by sol-gel route yielded BT particles having size of about $0.2 \mu\text{m}$. Most of them are in spherical shape and are agglomerated to form soft agglomerates. Figure 4(b) shows the SEM photograph of fractured surface of the pellet sintered at $1280^\circ\text{C}/4 \text{ h}$. It showed varied grain size in the range $5\text{--}15 \mu\text{m}$ with presence of some porosity. This may be due to the uncontrolled nucleation and grain growth processes occurred during sintering at higher temperature in air. From these measurements it appears that the BaTiO_3 powders obtained by the presently described sol-gel route produce grain size in the range of $5\text{--}15 \mu\text{m}$ when sintered at 1280°C in air (with density $\sim 94\%$). These observations are indicative of the fact that highly sinterable BaTiO_3 powders are obtained by the presently described sol-gel process. This argument is supported by the reported fact [27] that dense BaTiO_3 samples with grain size $\sim 10 \mu\text{m}$ are difficult to obtain unless hot pressing or hot isostatic pressing technique is used. The BaTiO_3 powder of the nearly the same particle size usually sinters to 95% of theoretical density under oxygen at 1320°C or at 1350°C under air. Arlt et al. [27] made these important observations in context with the grain size effect on the dielectric properties in BaTiO_3 ceramics produced under different sintering conditions. The highest value of the room temperature dielectric constant $\epsilon_{RT} \sim 4600$ is observed at the grain size in the range of $0.7\text{--}1.0 \mu\text{m}$. At even smaller grain sizes of $\sim 0.28 \mu\text{m}$, the room temperature value decreases to 2500 and the peak (ϵ vs. T plot) gets smeared out. At grain size $\sim 7.0 \mu\text{m}$, the room temperature dielectric constant $\epsilon_{RT} \sim 1800$ with $\epsilon_{\text{max}} \sim 7000$ (at $T_c = 125^\circ\text{C}$) was obtained. Our results for sol-gel derived BT ceramics in present case,

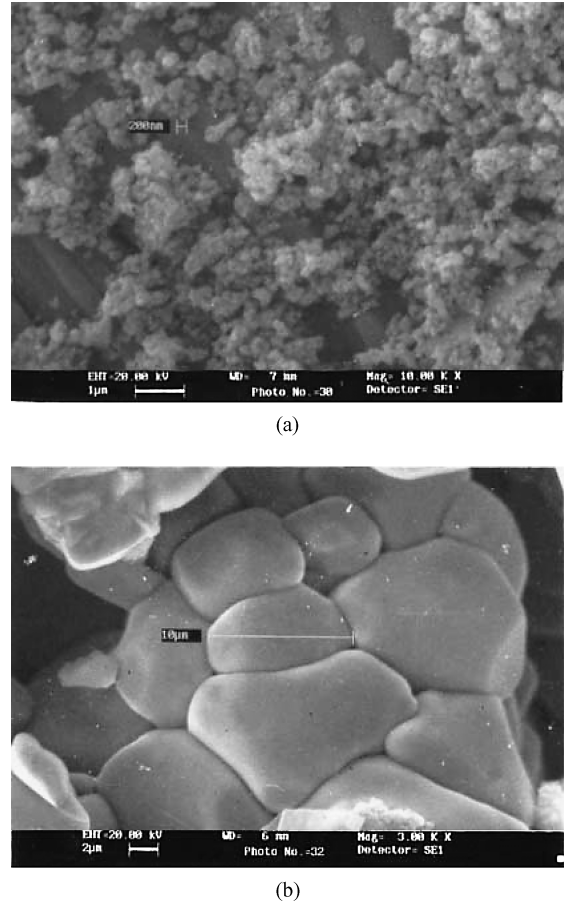


Fig. 4. SEM photographs of (a) gel calcined at $750^\circ\text{C}/6 \text{ h}$ and (b) fractured surface of pellet sintered at $1280^\circ\text{C}/4 \text{ h}$.

$\epsilon_{RT} = 1280$, $\epsilon_{\text{max}} = 7200$ at $T_c = 127^\circ\text{C}$ and grain size in the range of $5\text{--}15 \mu\text{m}$ are quite consistent with the findings of Arlt et al. [27].

Table 1 summarizes the electro-physical properties for our material along with the reported data [23, 28, 29] for single crystals as well as polycrystalline BT ceramics for comparison. It is seen from Table 1 that the ferroelectric and dielectric properties of the sol-gel derived BT ceramics are found to be nearly comparable with those prepared by solid-state reaction route.

4. Conclusion

A simple wet-chemical sol-gel route generated gel-mass at ambient condition, which on subsequent

Table 1. Electrophysical property data on BaTiO₃.

| Parameter | Standard data [23, 26, 27] | | |
|--|----------------------------|-------------|--------------|
| | Single crystal | Ceramic | Present work |
| Relative Density (%) | 100 | 98 | ~94 |
| Symmetry | Tetragonal | Tetragonal | Tetragonal |
| Axial ratio (c/a) | 1.01 | ~1.01 | 1.0085 |
| Spont. Polarization, P_s ($\mu\text{C}/\text{cm}^2$) | 26.0 | 14.6 | 13.0 |
| Coercive Field, E_c (kV/cm) | 1.0 | 2.5 | 4.0 |
| Dielectric Strength, E_b (kV/cm) | >120 | >50 | ~34.0 |
| Dielectric Constant at RT | 2000 | 1400–2100 | ~1280 |
| Dielectric Constant at T_c | 10,000 | 7500–10,000 | ~7200 |
| Dielectric Loss ($\tan \delta$) (%) | 5.0 | 1.0 | 1.6 |
| Curie Temp. T_c ($^\circ\text{C}$) | 121 | ~130 | 127 |

heat-treatment at 750°C/6 h in air, produced submicron sized, stoichiometric, spherical BT powders. The sintering of these powders in the form of pellets gave dense ceramic bodies with 94% density. The ferroelectric/dielectric properties were comparable with the reported standard data for BT ceramics.

Acknowledgments

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