Dielectric characterization of BTO-derived barium titanate (BaTiO₃) ceramics

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Ultrafine barium titanate (BT) powders, produced by controlled pyrolytic decomposition of ‘BTO’ (precipitated by a novel chemical route) in air at 700°C/5 hr, are sintered in the form of pellets at 1250°C/4 hr to get ceramic compacts with density ~ 91%. These compacts show nearly uniform microstructure with average grain size ~ 4.00 μm, dielectric constant (ε') ~ 1250, tan δ, (T = 121°C) ~ 7600 and tan δ = 1.5 × 10⁻².

The preparation of stoichiometric submicron size ceramic powders at low temperatures using chemical methods is an area of considerable interest and technological significance. The synthesis of electronic materials having high dielectric constant ε' and low dielectric loss (e.g. BaTiO₃) is of particular importance for the manufacture of capacitors and sensors.

Three low-temperature methods have been reported for the preparation of barium titanate in the literature. These are: (1) sol-gel process, (2) modified alkoxide synthesis, and (3) chemical coprecipitation. In sol-gel and modified alkoxide routes, controlled hydrolysis reactions of metal alkoxides have been used to prepare monodisperse oxide powders of controlled size and shape. During the hydrolysis of mixed (Ba & Ti) precursors, two main problems are encountered: (i) irregular chemical bonding with two metals and (ii) heterogeneous polycondensation. In addition, the starting chemicals are costly.

To overcome these difficulties, we have reported a simple chemical method to precipitate a molecular precursor, namely BaTiO(C₂O₄)₂.4H₂O (BTO), using water soluble salts — barium acetate and potassium titanyl oxalate. The well-characterized ‘BTO’ precipitate was further converted to submicron (0.2 μm) size spherical stoichiometric BT powders by pyrolytic decomposition in air in the temperature range 550°C-700°C. Resulting BT powders were characterized using various techniques.

The primary objective of the present investigation is to further characterize BT in the form of sintered ceramic compacts for dielectric/ferroelectric properties. The temperature dependence of dielectric constant (ε') and loss factor (tan δ) support strongly the formation of high quality BT powders and compacts.

**Experimental**

The detailed experimental procedure adopted during the present studies is summarized in a processing flow-chart (Fig. 1).

The well-characterized potassium-free (conc. < 10 ppm) dry precipitate of ‘BTO’ was calcined in air at 700°C/5 hr to obtain stoichiometric BT powders. These powders were then cold-pressed into discs (diameter = 20 mm, thickness = 2 mm) at a pressure of 5 tons/sq. inch with 2% PVA binder. The discs were sintered as a stack of four pieces in air at 1250°C/4 hr. The furnace was then allowed to cool at its natural cooling rate.

XRD and SEM techniques were used to identify crystalline phases and microstructure in the final ceramic BT compacts.

The sintered compacts were then lapped up to 0.5 mm thickness with fine emery powder paste. These...
lapped compacts were coated with conducting silver paint on both sides and fired in air at 600°C/2 hr to cure the paint.

Dielectric measurements were done employing a commercial LCR bridge at 1 kHz frequency. The temperature dependence of dielectric constant (ε) and loss factor (tan δ) were studied to estimate the Curie temperature (Tc, °C). Finally the values of the spontaneous polarization (Ps), coercive field (Ec) and break down voltage (Ed) were determined from hysteresis-loop measurements using a (home-built) Sawyer-Tower circuit9.

**Results and discussion**

The pressed pellets of these powders showed green density ≈ 60%, which increased after sintering at 1250°C/4 hr, to density (5.5 g/cm³) ≈ 91% of theoretical density of BT.

Fig. 2 shows the XRD plot of a sintered ceramic disc. The distinct separation between reflections of the (002, 200) planes is also clearly seen in Fig. 2. The lattice parameters of the unit cell are, a = 3.99Å, c = 4.026Å with c/a ratio = 1.009. These values match well with reported data10 for the tetragonal phase of BT. Furthermore, no extra lines are observed corresponding to any additional phases of the Ba-Ti-O system.

Fig. 3 shows the microstructure developed during sintering-cycle of the green pellet. It shows (i) nearly
uniform microstructure with well-defined grains, (ii) average grain size \( \approx 4 \mu m \) and (iii) presence of pores resulting in low densification. The average grain diameter \( D \) was determined by the linear intercept method\(^{12}\) using the correction by Mendelson\(^{12}\).

After confirming the format on of ohmic contacts on the BT ceramic disc, the DC-resistivity was found to be \( 2.16 \times 10^{-11} \) \( \Omega \) cm. At room temperature \( (T = 30^\circ C) \), dielectric constant \( (\varepsilon_{RT}) = 1250 \) with tan \( \delta = 1.5\% \) were obtained at \( 1 \) kHz frequency. These values of the dielectric parameters are comparable with the reported values on polycrystalline BT ceramics synthesized by various other chemical synthesis route\(^{13-18}\).

The temperature dependence of the dielectric constant \( (\varepsilon) \) and tan \( \delta \) was measured using heating and cooling cycles. Fig.4a shows that the dielectric constant \( (\varepsilon) \) is nearly constant up to \( 95 \pm 1^\circ C \) and then increases rapidly to a maximum value of \( \approx 7200 \) at \( 121 \pm 1^\circ C \). It drops down to 4000 around \( 140^\circ C \). The temperature corresponding to \( \varepsilon_{max} (T_c) \) is \( 121^\circ C \). During cooling cycle, the nature of the \( \varepsilon \) vs T behaviour was found to be similar to that observed during heating cycle with \( \varepsilon_{max} = 7600 \) at \( T_c = 121 \pm 1^\circ C \). The temperature dependence of tan \( \delta \) values was the same during heating and cooling cycles with tan \( \delta \) values \( \approx 1.2-1.5 \times 10^{-2} \) (Fig.4b).

The values of \( \varepsilon_{max} \) during heating and cooling cycles are lower than the reported values of \( \varepsilon_{max} (> 10,000) \) for best ceramic samples reported in the literature\(^{17}\) for their help in recording XRD and SEM micrograph of dense BT compacts. Attempts to control processing parameters during various stages of chemical synthesis to improve further dielectric performance parameters are underway.

Conclusions

Ceramic processing of ultrafine BT powders (made from BTO precursor) via a novel chemical route resulted in good ceramic compacts exhibiting better performance parameters.

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References

10 ASTM Card No.5-0626 for BaTiO₃.
11 Fullman R L, Trans AIME (USA), 197 (1953) 447.