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Synthesis and characterization of calcium modified barium titanate ceramics by partial precipitation route

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ABSTRACT

Calcium modified BaTiO₃ (BT) ferroelectric system was synthesized by partial precipitation route. For single perovskite phase and dense grain morphology formation 900°C and 1300°C temperatures were optimized as calcination and sintering temperatures, respectively. Dense packing of grains with average grain size ~13.3µm was observed in Ba_{0.96}Ca_{0.04}TiO₃ system. Room temperature (RT) dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of Ba_{0.96}Ca_{0.04}TiO₃ ferroelectric system at 1 kHz were found to be ~1425 and 0.04, respectively. Development of polarization vs. electric field (PE) loop with $P_r \sim 5.8 \mu\text{C}/\text{cm}^2$ and $E_c \sim 3.5 \text{ kV}/\text{cm}$ confirmed the ferroelectric nature of the Ba_{0.96}Ca_{0.04}TiO₃ samples. Transition temperature (T_c) was found to be ~120°C at 1 kHz with relaxor behavior. © 2009 Trade Science Inc. - INDIA

KEYWORDS

Ceramics;
X-ray diffraction;
Ferroelectricity.

1. INTRODUCTION

Recently, lead-free materials have attracted much attention with the rising demand of the global environment protection. A great deal of efforts had been devoted to study the dielectric properties of barium titanium based materials^[1-6]. Modified BaTiO₃ ceramics are widely used in the fabrication of multilayer ceramic capacitors and nonvolatile memory devices because of their high dielectric constant and low dissipation factor. Many efforts have been made to modify the dielectric properties of these ceramics. Substitution of isovalent ions for the host lattice cations in perovskite lattice plays a significant role in these modifications. These materials form solid solutions with BaTiO₃ and alter its structural

features, resulting in a shift in phase transition temperature along with modified dielectric properties^[7]. Being a lead free ferroelectric system, modified barium titanate is an environmentally friendly material, thus making it a good candidate for various applications such as capacitors, positive temperature coefficient resistors, high-density optical data storage, ultrasonic transducer, piezoelectric devices and semiconductors^[8].

Processing temperature and microstructure of the ferroelectric ceramics depends on the synthesis route used. The purity of the starting precursors affects the processing temperatures and hence the material properties. Generally, in ceramics prepared from complex solid solution systems, the compositional fluctuation as well as the purity among ceramic particles is very im-

portant^[9]. The modified BT solid solutions are conventionally synthesized through solid-oxide route^[10-13]. Chemical solution methods are also used to produce more homogeneous, finer particle size and low impurity level powders than that produced by the solid-oxide method^[14-16]. But, the chemical synthesis route is very complex. On the other hand, the solid-oxide synthesis has advantages with respect to the use of relatively low-cost raw materials and simple processing steps. Both chemical and solid state reaction routes have relative advantages and disadvantages over each other. It becomes imperative to devise some other synthesis process to combine the advantages of both these routes. Therefore, in the present study, modified chemical route is used to get the benefit of both solid state reaction and chemical routes. In this process, barium acetate trihydrate, calcium acetate and TiO₂ powders were used for the synthesis of Ba_{0.96}Ca_{0.04}TiO₃ samples to get some of the benefits of both the solid-oxide and chemical routes.

In the present paper, Ba_{0.96}Ca_{0.04}TiO₃ system was synthesized in single perovskite phase by modified chemical route. The structural, surface morphological, dielectric and ferroelectric properties have also been discussed.

2. EXPERIMENTAL

In modified chemical route, barium acetate trihydrate, calcium acetate and titanium oxide (all from Aldrich, USA) were used as precursors along with 2-methoxy ethanol as solvent and acetic acid as catalyst. Barium acetate and calcium acetate were dissolved and transparent solution was prepared using 2-methoxy ethanol as the solvent and acetic acid as the catalyst. Finally, the stoichiometric proportion of titanium oxide was mixed in the transparent solutions and stirred for 4 hrs. After drying the slurry in oven, BT samples were calcined at 900°C for 4 hrs and single perovskite phase formation was confirmed by X-ray diffraction (XRD) technique. In order to examine the phases present in the modified Ba_{0.96}Ca_{0.04}TiO₃ system, XRD analyses of the powder and pellets were performed on a PW 3020 Philips with Cu K α radiation ($\lambda=1.5405\text{\AA}$). The modified Ba_{0.96}Ca_{0.04}TiO₃ powder was pressed at 60MPa for pelletization and sintering was done at

1300°C for four hours. These pellets were polished and silver paste was applied on the surfaces for doing electrical characterization. Surface morphology of the samples was studied using Jeol T-330 Scanning Electron Microscope. Relative dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) were measured as the function of frequency using Hioki 3532-50 LCR HiTESTER. Using a Sawyer Tower circuit, hysteresis (P-E) loops were taken with a computer interfaced loop tracer.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the TGA/DSC graph of Ba_{0.96}Ca_{0.04}TiO₃ powder. A weight loss of ~10.23% was observed up to 200°C, which is attributed to the evaporation of absorbed water and solvent. A large wt. loss ~16% around 300°C is due to the decomposition of acetyl and bonded alkyl groups and their combustion^[17]. The weight loss at around 800°C (5.65%) is due to the decomposition of residual BaCO₃. When the temperature was higher than 900°C, the weight of the Ba_{0.96}Ca_{0.04}TiO₃ dry gels no longer decreased, which

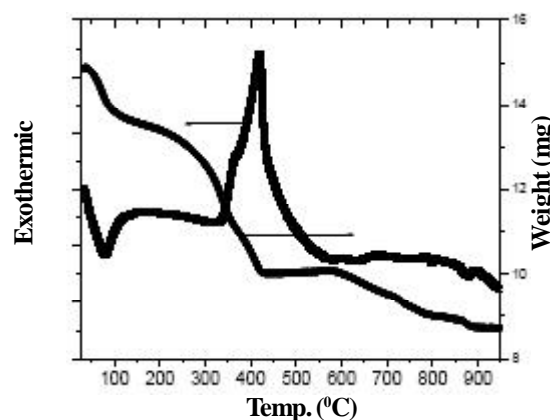


Figure 1: DTA-TGA curves of BCT (96/04) powder

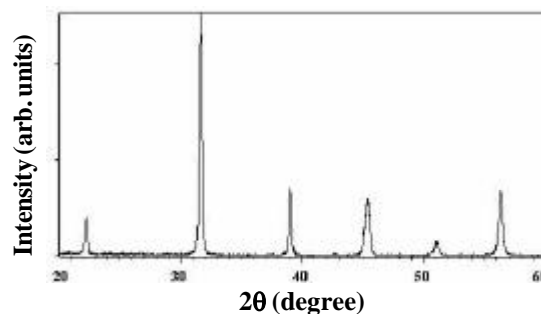


Figure 2: XRD pattern of Ba_{0.96}Ca_{0.04}TiO₃ system calcined at 900°C for 4 hrs

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hints about the calcination temperature to be $\sim 900^\circ\text{C}$.

Figure 2 shows the room-temperature XRD pattern of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ sample synthesized by modified chemical route. The diffraction pattern shows the intense lines of perovskite phase. The peaks in XRD patterns are found to be sharp, distinct indicating good homogeneity and crystallization of the system^[18]. In $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ samples, synthesized by modified chemical route, single perovskite phase peaks are obtained at 900°C calcination temperature, which is significantly lower than the earlier reports on modified BT system synthesized by solid state reaction route^[19,20]. At this calcination temperature, there is no trace of secondary phase. Low calcinations temperature in $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ samples synthesized by modified chemical route can be attributed to the fine particle size of the precursors. In this route, mixing between the precursors is taking place at atomic level. Lower the particle size higher is the ratio of surface area to volume. Since surfaces are higher energy regions, they will always act to minimize their area, and thus lower their energy when possible^[21], which leads to lower calcinations temperature. In addition, the difference in particle size between the precursors used may also accelerate the calcination reaction and lower the processing temperature. Since in this modified chemical route, the particle size for barium acetate and calcium acetate is of nano meter size order and titanium oxide is of micro meter size order^[22].

Figure 3 illustrates the SEM micrographs of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ samples synthesized by modified chemical route. Presence of pore free uniform grains in $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ ceramic samples suggest the advantage of using modified chemical route over conventional solid state reaction route. Average grain size, estimated by linear intercept method, was found to be $\sim 13.3\mu\text{m}$ in $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ ceramic samples.

Figure 4 shows the frequency dependence of ϵ_r and $\tan\delta$ at room temperature (RT) of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ ceramic samples. At RT, values of ϵ_r and $\tan\delta$ at 1kHz are found to be 1425 and 0.04, which is comparable to earlier reports on modified BT system^[23]. Initially, both ϵ_r and $\tan\delta$ decreases with the increase in frequency. The fall in ϵ_r arises from the fact that polarization does not occur instantaneously with the application of the electric field, which is further due to the inertia of the

dipoles and the delay in response towards the impressed alternating electric field leads to dielectric loss and decline in ϵ_r . At low frequencies, all types of polarization contributes and as the frequency is increased, polarizations with large relaxation times cease to respond and hence the decrease in ϵ_r ^[24]. At lower frequencies ϵ_r is maximum because the contributions from the space charge polarization is large. The space charge polarization arises by the accumulation of charges mainly due to vacancies of oxygen at the grain boundaries and at the electrode interface. At higher frequencies, contributions from the polarizations having high relaxation time ceases resulting in the decrease in ϵ_r ^[25]. The same type of frequency-dependent dielectric behaviour is found in many other ferroelectric ceramic systems^[26,27].

Figure 5 shows the temperature variation of ϵ_r at different frequencies (0.1 kHz-1 MHz) of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ samples. Values of ϵ_r at different frequencies increases with the increase in temperature and transition temperature (T_c) at 1kHz was found to be around $\sim 120^\circ\text{C}$, which increases with the increase in frequency.

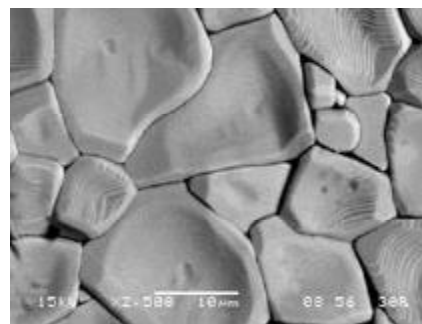


Figure 3 : SEM micrographs of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ sample

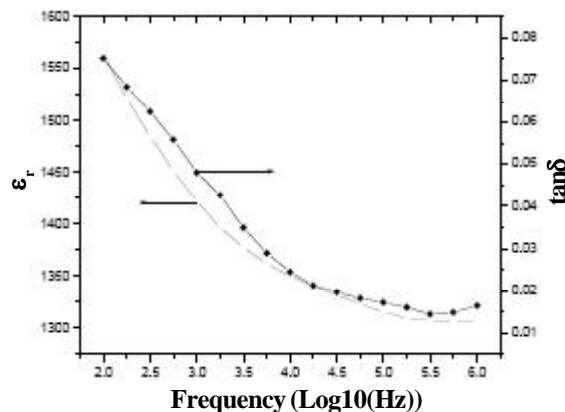


Figure 4: Variation of (a) ϵ_r and (b) $\tan\delta$ with frequency of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ system sintered at 1300°C

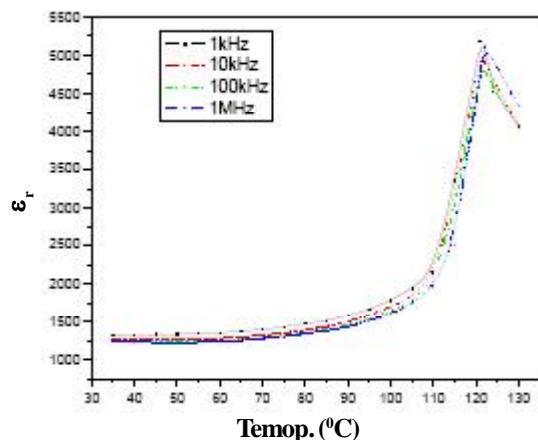


Figure 5: Temperature variation of ϵ_r of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ system at different frequencies

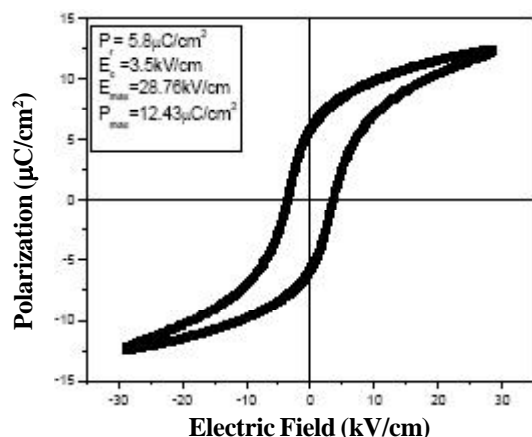


Figure 6: P-E hysteresis loop of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ system sintered at 1300°C

This is a typical characteristic behavior of relaxor ferroelectric systems^[28]. This suggests the introduction of microscopic inhomogeneous behavior with the substitution of Ca^{2+} ions^[29]. Earlier reports have shown transition of normal to relaxor behavior with Ca^{2+} substitution more than 10% in BT system^[30]. A series of impurity doped BaTiO_3 systems such as Sn, Hf, Ce and Y have also shown a ferroelectric to relaxor behaviour at higher doping concentrations^[31]. Here, modified chemical route involves starting powders of different sizes (barium acetate and calcium acetate are of nano meter size order and titanium oxide is of micro meter size order). This hints that starting powder size mismatch is contributing in the introduction of microscopic inhomogeneous nature in the modified BT system. It can be seen from figure 5 that ϵ_r at different frequencies increases with the increase in temperature. ϵ_r of any ma-

terial, in general, is influenced by dipolar, electronic, ionic and interfacial polarizations^[32]. Interfacial polarization increases due to the creation of crystal defects and dipolar polarization decreases due to the increase in randomness of the dipoles with temperature. However, the temperature effect on ionic and electronic polarizations is very small^[25]. The increase in ϵ_r with temperature suggests the increase in interfacial polarization. At T_c , values of ϵ_r at 1 kHz was found to be ~ 5200 .

Figure 6 shows the (P-E) loop of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ sample. Here, development of ferroelectric hysteresis loop hints towards the ferroelectric nature of the material. The coercive field E_c and remnant polarization P_r are found to be $\sim 3.5\text{kV/cm}$ and $5.8\mu\text{C/cm}^2$, respectively. The value of P_r is in agreement with the earlier reports whereas the value of E_c is smaller than the earlier reported value^[33]. Since, smaller the grain size more is the field required to switch the direction of domains. Therefore, this small value of E_c can be attributed to larger grain size^[34].

4. CONCLUSIONS

Single perovskite phase formation study of $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ system was carried out by modified chemical technique. 900°C processing temperature was optimized as the calcination temperature for single perovskite phase formation. Presence of pore free dense homogeneous grain distribution in $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ ceramic samples hints towards the advantage of modified chemical route. Room temperature values of ϵ_r and $\tan\delta$ at 1kHz were found to be ~ 1425 and 0.04 , respectively. T_c with relaxor type of behavior was found to be $\sim 120^\circ\text{C}$. Development of P-E hysteresis loop suggests the ferroelectric nature of the $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{TiO}_3$ system.

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