

Effect of microwave processing on structural, dielectric and ferroelectric properties of calcium-doped BaTiO₃ ceramics

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Calcium-doped barium titanate, Ba_(1-x)Ca_xTiO₃ (where x = 0.02, 0.04, 0.06 & 0.08)/BCT1, BCT2, BCT3 & BCT4, ferroelectric ceramics were synthesized by a microwave processing technique. For the formation of a single perovskite phase with a dense grain morphology, microwave sintering temperature was optimized at 1100 °C for 1 h. SEM characterization of the microwave sintered BCT samples showed dense and homogeneous packing of sub-micrometer size grains. The BCT2 system showed the highest room temperature (RT) dielectric constant (ϵ_r). The dielectric property vs. temperature behavior revealed a diffuse phase transition nature. The occurrence of polarization vs. electric field (P-E) loops confirmed the ferroelectric nature of the microwave sintered BCT samples.

Key words: BCT, Ferroelectric materials, Dielectric properties, Perovskite, Diffusivity.

Introduction

Barium titanate (BT) is one of the most important lead-free ferroelectric ceramics due to its outstanding dielectric and ferroelectric properties in applications for multilayer capacitors, thermistors, thermal sensors and electric devices. Much effort has been made to further modify the BT compound by different means in order to achieve stable capacitors with satisfactory operational capacity. Substitution of isovalent ions for the host lattice cations in the BT perovskite lattice plays a significant role in these modifications. BT and its isovalent- substituted ceramics are of great interest because of their interesting properties. With the substitution of dopants like Ca, Sr and Zr [1-3], the transition from a ferroelectric to a paraelectric phase becomes diffuse both in ceramics as well as in single crystal samples. This broadening increases with an increase in the concentration of the dopants. These iso-valent substitutions form new solid solutions with BT and alter its structural features along with modifying the dielectric properties [4-6]. Ca substitution in BT ceramics (BCT) is known as a typical depressor in BT ceramics, which leads to a significant suppression of the dielectric loss ($\tan\delta$) and the temperature coefficient of ϵ_r but only a slight change of Curie point (T_c) [7]. Considering these good dielectric properties, BCT materials are expected as alternative candidates for tunable microwave dielectric materials with low $\tan\delta$ and a small temperature coefficient of ϵ_r . Because of these interesting

properties BCT materials finds their applications as various capacitor materials (including multilayer ceramic capacitors), dielectric filters, dielectric antennae, dielectric resonators, dielectric duplexers, capacitors and phase shifters. Therefore, we can conclude that BCT is an interesting system which finds its use in various applications.

Generally, the performance of functional ceramics significantly depends on the microstructure of the sintered body [8-10]. The processing temperature and microstructure of ferroelectric ceramics depends on the synthesis route used. Modified and unmodified BT solid solutions are conventionally synthesized through a solid state reaction (SSR) route [11-14]. Generally, the processing of ceramics through a SSR route is accompanied by unwanted phases and the processing period is very long and hence with a high energy consumption. Ceramics processed in conventional furnaces generally require rather long times owing to the inertia of furnaces and much energy is lost by radiation. These disadvantages could be avoided by using microwave processing of samples provided that the dielectric losses of the material processed be high enough for the penetration of the waves to be allowed. Therefore, the microwave processing of ceramics can be utilized as an alternative approach to the SSR route because of its potential advantages such as rapid heating, penetrating radiation, more uniform microstructures and higher densities [15, 16]. It is also worth pointing out that the use of microwave allows heating to be started at the core of the sample by contrast to the heating of the samples in conventional furnaces where heating starts at the surface; this could alter the microstructure of the ceramics and dielectric properties.

Therefore, in the present study we report a detailed study on the phase, structure, microstructure, dielectric and ferroel-

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electric characterizations of Ca substituted BT samples sintered by a microwave processing technique.

Experimental

The polycrystalline ceramic samples of Ba_(1-x)Ca_xTiO₃ (where x = 0.02, 0.04, 0.06, 0.08)/BCT1, BCT2, BCT3 & BCT4 compositions were synthesized using high grade reagents BaCO₃, TiO₂, and CaCO₃ powders (all from Aldrich with 99.8% purity). These starting precursors were taken in stoichiometric ratios as the initial raw material. Stoichiometric weights of all the powders were mixed, respectively as per the different compositions and ball milled with acetone for 8 h, using zirconia balls as the grinding media. After drying the slurry in an oven, calcination of the powders was carried out at 1100 °C for 4 h in a conventional furnace and single perovskite phase formation was confirmed by the X-ray diffraction (XRD) technique. The calcined powders were mixed thoroughly with 2 wt% polyvinyl alcohol (PVA) and pressed into disks of diameter ~10 mm and a thickness ~1.5 mm under ~60 MPa pressure. The microwave sintering of the sample was carried out at 1100 °C for 1 h with a heating rate of 25°K·minute⁻¹ by placing the pellets in the centre of a 4.4 kW, 2.45 GHz multi mode microwave cavity. The microwave furnace temperature was recorded using a Raytek non-contact sensor (XRTG5). XRD analysis of the pellets were performed on a PW 3020 Philips diffractometer using Cu K α (λ = 0.15405 nm) radiation in order to examine the phases present in the material. The sintered microstructures were observed using a JEOL T-330 scanning electron microscope (SEM). Silver paste was applied on both sides of the samples for the electrical measurements. Dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) were measured as a function of temperature at different frequencies using a computer interfaced HIOKI 3532-50 LCR-HITESTER. A conventional computer-interfaced Sawyer-Tower circuit was used to measure the polarization vs. electric field (P-E) hysteresis loops at 20 Hz frequency.

Results and Discussion

Fig. 1 shows the DSC/TGA measurements of uncalcined ball milled powder of the BCT2 sample. It can be seen in Fig. 1 that there is an overall weight loss around 14% from room temperature (RT) to 1000 °C. Two processes of weight loss in the temperature ranges RT-700 & 700-1000 °C are attributed to loss of water and loss of CO₂, respectively. Above 1000 °C, no substantial weight loss is observed. Therefore, the DSC/TGA study hints at the formation of a single perovskite phase around 1000 °C. In the present study the calcination temperature was optimized at 1100 °C for four h for single perovskite phase formation in different BCT samples.

Fig. 2 shows the XRD patterns of different Ca substituted BT sintered ceramics. The diffraction patterns show the development of intense lines of the single perovskite phase

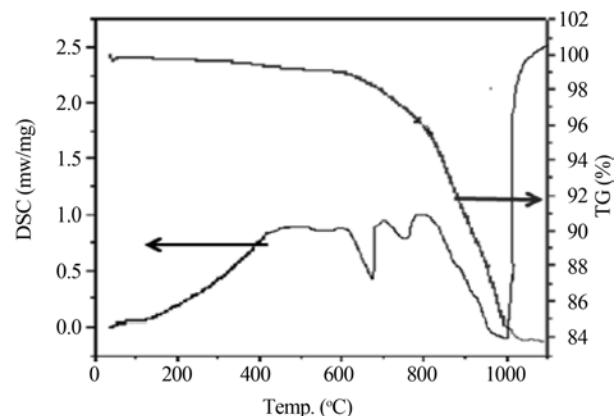


Fig. 1. TGA and DSC curves for the dried BCT2 sample powder.

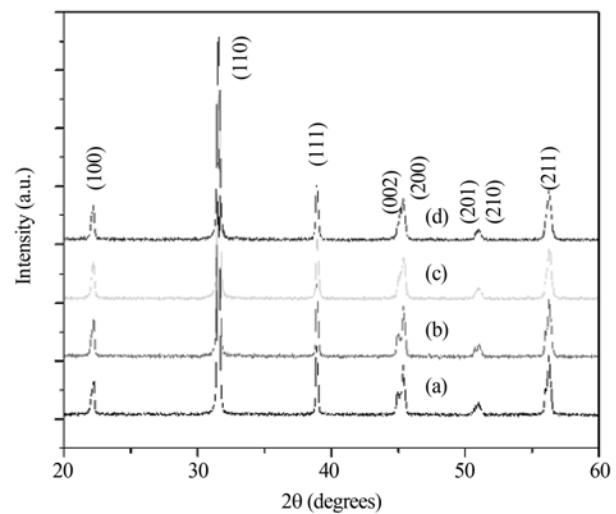


Fig. 2. XRD peaks of MW sintered (a) BCT1 (b) BCT2 (c) BCT3 & (d) BCT4 samples.

peaks for different Ca substitution concentrations in the BT system. XRD diffraction peaks are found to be sharp and distinct, indicating good homogeneity and crystallization of the different BCT ceramics samples [17]. As shown in Fig. 3, the diffraction peak intensity of the most intense peak (20~31.5°) is a maximum for the BCT2 system, whereas first the full width at half maxima (FWHM) gradually increases up to the BCT 2 system and then decreases with an increase in the Ca substitution concentration in the BT system. This indicates the better solubility of the 4%Ca substitution in the BT system. It is well known that the solubility of Ca decreases with an increase in its content in the BT system [18]. It can also be observed in Fig. 3 that the substitution of Ca atoms in the parent material causes shifting towards a higher angle of the most intense peak, which indicates the development of strain in the materials [19]. This shifting of the peak position can be clearly visualized from the normalized diffractogram of the (110) plane, shown in Fig. 3. Fig. 2 also shows the changes of the split 20~45° peak with the variation of Ca substitution concentration in the BT system. As the Ca substitution concentration in the BT system is increased,

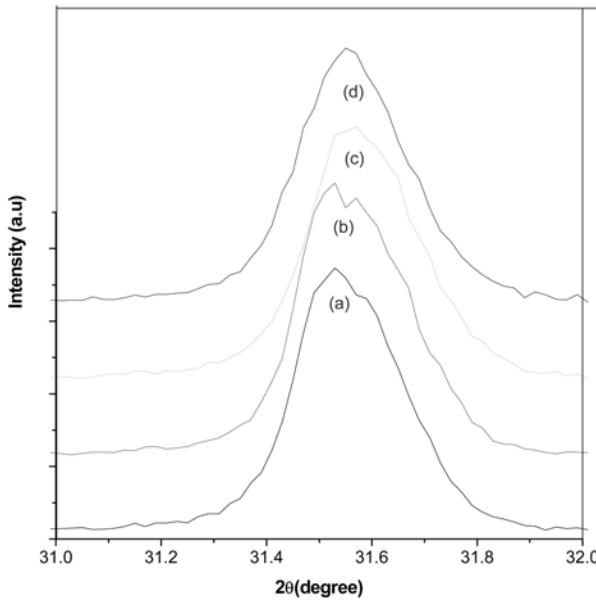


Fig. 3. Enlarged XRD patterns of MW sintered (a) BCT1 (b) BCT2 (c) BCT3 & (d) BCT4 samples.

the well-resolved doublet upto to $x = 0.04$ starts merging, which corresponds to a decrease in the tetragonality of the BCT system [20]. The diffraction lines of Ca substituted BT ceramics were indexed in different crystal systems and unit cell configurations using a computer program package 'Powdmult' [21]. Out of the different structures a suitable structure with lattice parameters, given in Table 1, was selected for different Ca substitution concentrations in the BT system for which standard deviation (SD), $\Sigma \Delta d$ ($= d_{\text{obs}} - d_{\text{cal}}$), where ' d ' is the interplanar spacing, was found to be minimum. The lattice parameters of the unit cell were refined using a least square fit method. This confirms the decrease in tetragonality of the BCT system with an increase in Ca substitution concentration in the BT system.

Fig. 4 gives the SEM micrographs of microwave sintered Ca substituted BT ceramic samples. The presence of pore-free uniform grains suggests the advantage of the using the microwave sintering route. The density, measured by Archimedes method and average grain size, estimated by the linear intercept method, are given in Table 1. The grain size of the microwave sintered Ca modified BT ceramic samples is lower than the same systems processed by a conventional solid state route [22]. Better densification with the formation of finer and uniform grains in the case of microwave sintered samples is due to the rapidity of microwave heating which avoids undesirable grain growth in the BCT ceramic samples. This is the characteristic of microwave processing of ceramics as the heating rate is rapid and the mechanism of heating is different from a conventional sintering process [15, 16]. The grain size decreases with an increase in the Ca substitution concentration in BT ceramic samples. This indicates that an increase in the Ca substitution concentration in the BT

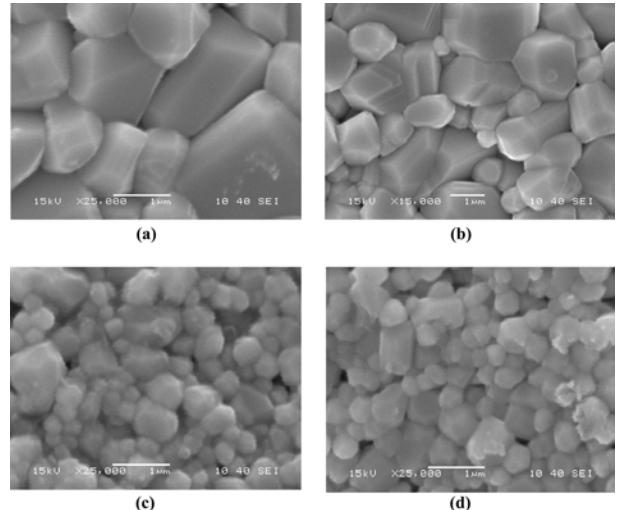


Fig. 4. SEM images of MW sintered (a) BCT1 (b) BCT2 (c) BCT3 & (d) BCT4 samples.

system inhibits grain growth.

Fig. 5 shows the temperature variation of ϵ_r at different frequencies of Ca modified BT samples sintered by the microwave process. The observed T_c decreases with an increase in the Ca substitution concentration in BCT samples. This indicates that the substitution of smaller Ca^{2+} ions (1\AA) at Ba^{2+} ions (1.36\AA) positions causes a decrease of the relative displacement of A site ions with respect to the oxygen octahedral cage in the ABO_3 perovskite type of system. Since T_c is directly related to the square of this relative displacement [23], therefore with an increase in the Ca substitution concentration in BCT samples, the T_c is down shifted. Values of ϵ_r and $\tan\delta$ of different Ca substituted BCT samples at RT are given in Table 1. The RT values of BCT samples at 1 kHz decreases with an increase in the Ca substitution concentration in BCT samples, which confirms the dielectric depressing nature of Ca substitution in the BT system. Values of ϵ_r of different Ca modified BT samples are found to be higher than the same systems synthesized by conventional processing. This can be explained on the basis of a better density and a uniform morphology of the Ca substituted BCT samples. The grain size of the Ca substituted BCT samples is lower than the same systems synthesized by conventional processing. It has been reported earlier that the value of ϵ_r of fine-grained BT samples is higher than coarse-grained BT samples [24]. Since, microwave processed Ca modified BT samples have a sub-micrometer size grain and therefore an increase in ϵ_r . The temperature coefficient of ϵ_r from RT to 80°C is almost zero for BCT2 and BCT3 systems. This confirms the dielectric depressing nature of Ca substitution in BCT systems. With an increase in the Ca substitution concentration in BCT samples, the value of ϵ_r at RT increases up to the BCT3 system and then decreases for the BCT4 system. This can be explained on the basis of a decrease in the grain size and porosity of the BCT samples. An increase in ϵ_r with a decrease in grain size upto $0.65\text{ }\mu\text{m}$ (the BCT3

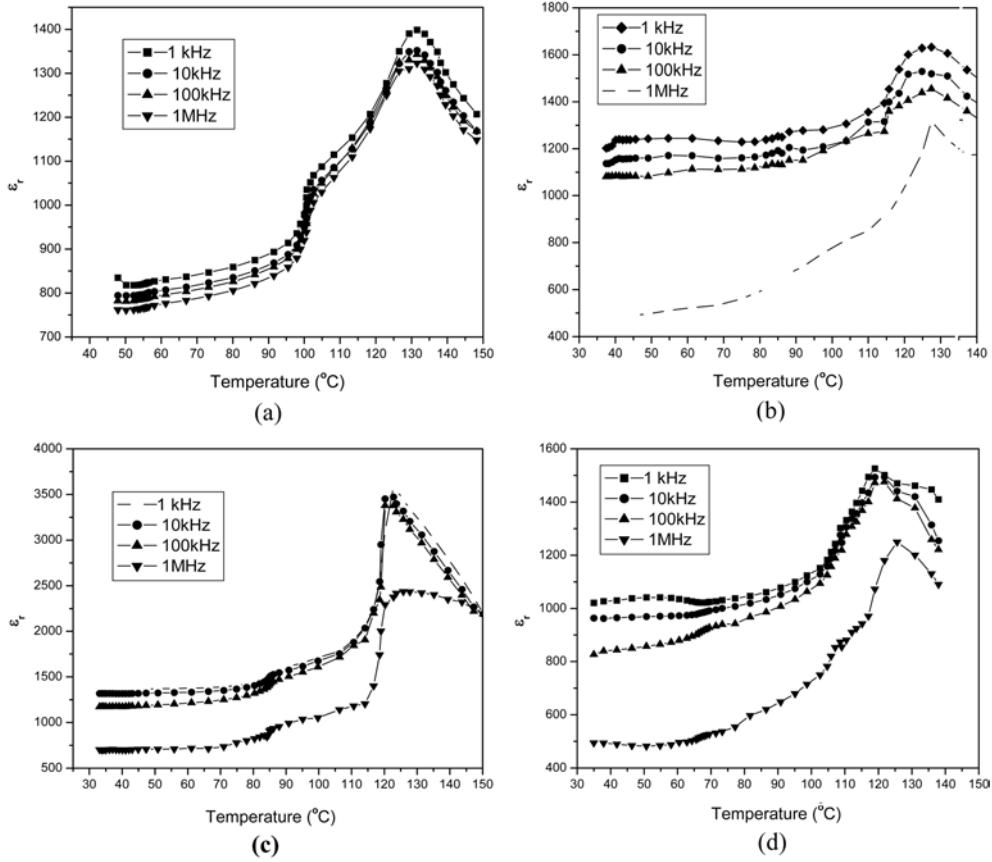


Fig. 5. variation of ϵ_r at different frequencies of MW sintered XRD peaks of MW sintered (a) BCT1 (b) BCT2 (c) BCT3 & (d) BCT4 samples.

system) implies that the internal stress is increasing with a decrease in the grain size, which is also confirmed from the XRD study. The decrease in ϵ_r for a grain size $\sim 0.5 \mu\text{m}$ (the BCT4 system) implies that a contribution from 90° domain walls starts increasing below a 0.65 μm grain size limit. It is known that ϵ_r increases with an increase in the internal stress and it decreases with an increase in the 90° domain wall contribution. Therefore, in the present study, below a 0.65 μm grain size, the 90° domain wall motion contribution to ϵ_r becomes prominent and hence there is a decrease in ϵ_r at RT for the BCT4 system. The same phenomenon has been reported in earlier studies on the BT system [25, 26].

Fig. 6 shows the variation of $\log(1/\epsilon_r/\epsilon_{r \max})$ vs. $\log(T/T_{\max})$ for the Ca substituted BCT samples. From the slope of the graph, a value of 'γ' is calculated. The value of 'γ' for normal ferroelectrics is 1 and it increases with an increase in the diffusivity of the samples. The values of 'γ' are found to be 1.58, 1.87, 1.48 and 1.14, in the BCT1, BCT2, BCT3 & BCT4 systems, respectively. First the diffusivity increases with an increase of Ca incorporation in the BT system and then decreases with a further increase in the Ca substitution concentration in the BCT system. This suggests the introduction of structural disorder and compositional fluctuations by the Ca substitution in BCT systems [27]. The diffuse transition behavior might be due to the larger probability of the Ca²⁺ ions

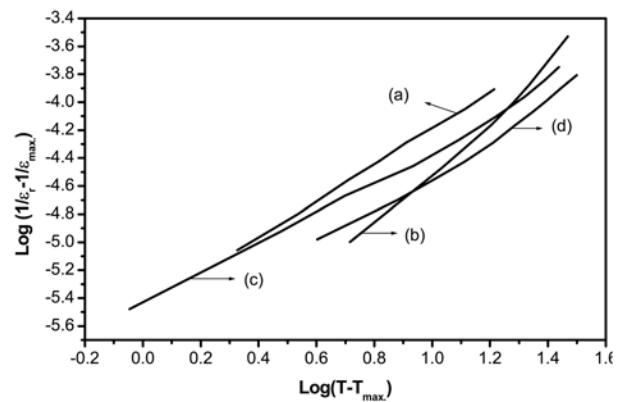


Fig. 6. Variation of $\log(1/\epsilon_r/\epsilon_{r \max})$ vs. $\log(T - T_{\max})$ of (a) BCT1 (b) BCT2 (c) BCT3 & (d) BCT4 samples.

occupying the Ti⁴⁺ sites, eventually introducing larger compositional and structural disorder, which gives rise to a diffuse phase transition.

Fig. 7 shows the P-E hysteresis loops of Ca substituted BCT samples sintered by the microwave processing technique. Development of P-E hysteresis loops confirms the ferroelectric nature of the Ca substituted BCT samples. The remnant polarization (P_r) and coercive fields (E_c) decrease with an increase of the Ca substitution concentration in BCT systems. The values of P_r for BCT systems

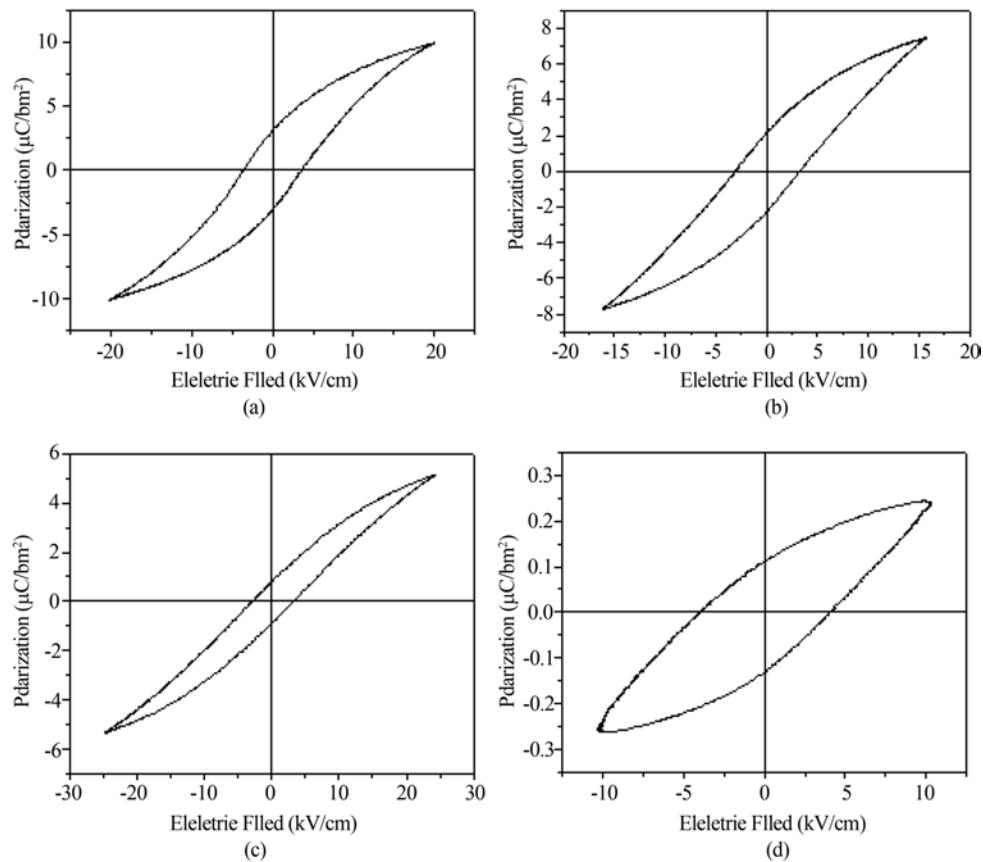


Fig. 7. P-E Hysteresis loops of (a) BCT1 (b) BCT2 (c) BCT3 & (d) BCT4 samples.

Table 1. Effect of variation of Ca substitution concentration in BCT samples on different parameters

System	Structure	Density g/cm ³	T _c (°C)	Grain Size (μm)	ε _r at 1 kHz	tanδ 1 kHz	P _r (μC/cm ²)
Ba _{0.98} Ca _{0.02} TiO ₃	Tetragonal c = 4.0548 a = 3.9901 c/a = 1.0162	5.77	131	1.3	835	0.041	3.1
Ba _{0.96} Ca _{0.04} TiO ₃	Tetragonal c = 4.0538 a = 3.9903 c/a = 1.0159	5.68	127	0.7	1200	0.039	2.2
Ba _{0.94} Ca _{0.06} TiO ₃	Tetragonal c = 4.0537 a = 3.9910 c/a = 1.0157	5.64	123	0.65	1365	0.034	0.84
Ba _{0.92} Ca _{0.08} TiO ₃	Tetragonal c = 4.0378 a = 3.9769 c/a = 1.0153	5.51	119	0.5m	1020	0.025	0.12

are given in Table 1. This decrease in the value of P_r with an increase in the Ca substitution concentration in BCT systems may be due to a decrease in density, grain size and tetragonality of the BCT systems [28, 29].

Conclusions

Calcium-substituted barium titanate ferroelectric ceramics

were synthesized in a single perovskite phase by a microwave processing technique. Tetragonality decreased with an increase in the Ca substitution concentration in BCT systems. The presence of pore-free uniform grains suggested an advantage of using microwave sintering process. The value of T_c and P_r decreased with an increase in the Ca substitution concentration in the BT system. The temperature coefficient of ϵ_r from RT to 80 °C was almost zero for

BCT2 and BCT3 systems indicating an increase in the temperature stability of these compounds. BCT2 showed the highest RT $\epsilon_r \sim 1365$ at 1 kHz. Microwave processing of BCT systems decreased the sintering time significantly while maintaining good dielectric properties.

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