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Microstructural and High Tc Dielectric Properties of Microwave Sintered $Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) Ceramic

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Abstract: Nanopowder of $Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) lead free ferroelectric ceramic was synthesized by hydroxide co-precipitation method. As-synthesized powder is sintered using the microwave sintering technique at different temperature 1100°C and 1200°C. Sintered ceramic samples were investigated for its structural, morphological, and temperature dependent dielectric properties. Structural analysis confirms biphasic crystal structure, tetragonal phase corresponding to $BaTiO_3$ lattice and orthorhombic phase resulting from the $CaTiO_3$ lattice. Scanning electron microscope images reveals the formation of grains with higher density. Ferroelectric-Paraelectric transition (Tc) of the material shifts towards higher temperature (Tc ~ 155°C) with maximum dielectric constant and low loss tangent.

Keywords: Ferroelectrics, Microwave Sintering, Dielectric Properties, Microstructure, Phase Transformation

1. Introduction

$BaTiO_3$ (BT) is one of the most important lead-free ferroelectric material and extensively useful material for number of electronic appliances such as multilayer ceramic capacitors, actuators, lead free piezoelectric transducers, infrared detectors, voltage tunable device in microwave electronics and as a charge storage device etc. BT material is known for exhibiting interesting electrical properties like high dielectric constant, low dielectric loss, ferroelectric, piezoelectric and pyroelectric behavior and stands as one of the most useful perovskite oxide compared with other dielectric materials [1]. Addition Sr^{2+}, Ca^{2+} or Zr^{4+} ions at A or B site of $BaTiO_3$ will results in formation of solid solutions like $Ba_{1-x}Sr_xTiO_3$ (BST), $Ba_{1-x}Ca_xTiO_3$ (BCT) and $BaZr_xTi_{1-x}O_3$ (BZT). These solid solutions has improved electrical and mechanical properties and found useful for various applications [2]. Particularly, BZT and BCT materials are used as ceramic capacitors and also founds numerous applications as an electrical material [1-2]. Replacing of Ba^{2+} ions by Ca^{2+} ions at A-site in $BaTiO_3$ lattice results in the prospective lead-free material which can applicable in electro-optic modulators and memory devices [10]. Solid solution of BCT was most used as a multilayer ceramic capacitor also this can be used in various other applications like: dielectric filter, dielectric antenna, dielectric resonator, dielectric duplexer, capacitor and phase shifter [1, 10]. Sintering at particular and desirable temperature is one most important and necessary stage in the development of the ceramic material. Though it is widely used, conventional method of ceramic processing founds drawbacks such as, need of higher sintering temperature (1400 - 1500°C) for longer duration (above 5 hrs), unusual grain growth during heating, etc. On the other hand the microwave sintering technique is superior than conventional sintering (CS) due to its unique characteristics, such as rapid heating, enhanced densification rate and improved microstructure. In the microwave process, the heat is generated internally within the material instead of originating from external sources, and hence there is an inverse heating profile as compared with conventional sintering mechanism. The heating is very rapid as the material is heated by energy conversion rather than by energy transfer, which occurs in conventional techniques. Though the microwave processing of ceramic materials is introduced about 5 decades ago its use is very rare [2-4].

Number of studies on BCT ceramic sample processed with conventional method is available, only few researchers are mentioned the dielectric and microstructural properties of BCT solid solution with microwave processing. Here we have synthesized lead-free $Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) ferroelectric solid solution with microwave processing technique. These ceramic samples are sintered at two temperatures 1100°C and 1200°C respectively. The present paper reports on structural, morphological, and dielectric properties with improved Tc of this microwave sintered material.

2. Materials and Method

2.1. Materials

For synthesis of $Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) nanopowder stoichimetric amounts of barium nitrate $Ba(NO_3)_2$, calcium nitrate $Ca(NO_3)_2{\cdot}4H_2O$, from S-D fine chemicals Ltd. and potassium titanium oxalate $K_2TiO(C_2O_2)_4{\cdot}2H_2O$ from Loba Chemicals having purity ~ 99% are used as starting materials. Here, a mixture of NH_4OH and KOH were used as precipitating agents.

2.2. Synthesis Method

For synthesis of BCT nanopowder hydroxide coprecipitation method was adopted. This synthesis procedure was quite similar as reported earlier [2]. It is seen that It has been observed that the $Ba(OH)_2$ and $Sr(OH)_2$ is fractionally soluble in water but insoluble in alkaline medium. Therefore in each stage of precipitation the pH ~10 was maintained. The obtained precipitate of BCT was dried under infra red light (~ 150°C), this dried precipitate was grinded in an agate mortar for 1 hour to get a fine powder and calcination was carried out at 1000°C for 4 hours. Calcinated powder samples were pressed hydraulically in to disk shaped pellets (about 1cm diameter and 2 mm thickness) after rigours grinding for 2-3 hours using agate mortar, the pressure was maintained at about $50kN/cm^2$. Pressed pellets and remaining pinch of powder were sintered at two different temperatures 1100°C and 1200°C using fast microwave sintering technique for 30 and 20 min respectively. The scheduled sintering time was kept lower by 10 min at higher temperature. Programmable microwave furnace with 1.3 KW, 2.45 GHz and thermally insulated chamber which prevent heat loss was used for this purpose.

2.3. Characterization Techniques

X-ray diffractometer (Rigaku Miniflex-II) is used for structural analysis, whereas morphology is studied by using scanning electron microscope (JEOL JSM-IT-300). Dielectric properties are measured with variation of temperature from 25°C to 200°C at frequency values 100 Hz, 1 KHz, 100 KHz and 1 MHz respectively. Custom made programmable furnace is used for variation of temperature and parallel values of capacitance (Cp) and figure of merit (Q) are measured using precise high frequency LCR meter (Wayne-Kerr 6500B). For measurement of dielectric properties the pellet samples were coated with conducting silver on both sides of surface and dried at 150°C for 2 hours.

3. Results and Discussion

Figure 1 shows room temperature x-ray diffraction pattern of BCT ceramic sample sintered at both temperatures using microwave sintering technique. X-ray diffraction is studied against 2θ angle, scan ranges from 20° to 80° and scan rate was maintained at 3°/min. BCT is a perovskite ceramic, which is a solid solution of $BaTiO_3$ and $CaTiO_3$. At room temperature $BaTiO_3$ exhibits a tetragonal crystal structure while $CaTiO_3$ shows orthorhombic crystal structure [1]. Here, as synthesized BCT ceramic shows more number of diffraction peaks which are corresponding to tetragonal crystal structure of $BaTiO_3$ phase in the BCT ceramic and these observed tetragonal diffraction peaks are in good agreement with JCPDS data card 81-1288. The diffraction patterns observed at 2θ angle 32°, 46° and at 58° having the hkl planes (121), (202) and (042) respectively are results from the orthorhombic crystal structure corresponding to $CaTiO_3$ phase. These diffraction peaks are well matches and are indexed according to the JCPDS data card 75-2100 [4-5]. It could be seen that, the lattice parameter values a and c increase with increase in temperature whereas, tetragonality (c/a ratio) slightly decreases. This may due to increase in the diffusion of Ca^{2+} ions on Ba^{2+} site, as the temperature increases from 1100°C to 1200°C. As rate of diffusion of substituted ions increases with increase in temperature results in formation of complete lattice structure due to this crystallinity of the ceramic material increases. The crystallite size is calculated at most prominent peak of perovskite structure, using Scherer's equation given as,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

Where, D crystallite size, λ is the x-ray wavelength, β is the angle at the full width half maximum (FWHM) and θ the diffraction angle. The crystallite size founds to increase with increase in temperature. Calculated lattice parameters with unit cell volume and crystallite size are listed in table 1.

Table 1. *Parameters obtained from the x-ray diffraction analysis of BCT ceramic sintered at different temperature.*

Sintering Temperature	Lattice parameters			Crystallite Size	Volume
	a(Å)	c(Å)	c/a	(nm)	(a^2c)
1100°C (30 min)	3.9256	4.001	1.0192	35.56	63.87
1200°C (20 min)	3.9487	4.002	1.0134	38.33	63.98

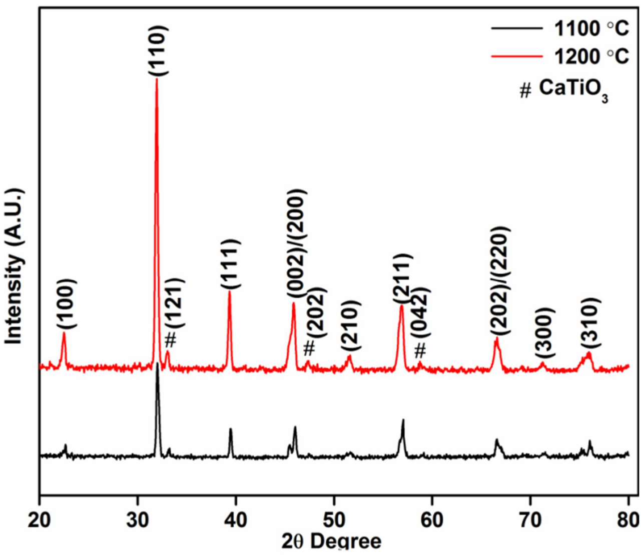

Figure 1. *Room temperature x-ray diffraction pattern of MW sintered BCT at 1100°C and 1200°C.*

Figure 2(a) and 2(b) represent the scanning electron micrographs of BCT ceramic sintered at 1100°C and 1200°C respectively. Microstructural images of ceramic material sintered at both temperatures are show dense morphology; grains are developed with less number of voids. The average grain size is calculated from the SEM images and the observed average grain size is 1.2 μ_m and 1.3 μ_m for ceramic sintered at 1100°C and 1200°C respectively. Observed grain size confirms that numbers of crystallites are gathered together in the formation of grains. The grain size increases with increase in sintering temperature this may attribute due to occurrence of more diffusion of doped ions at higher temperature, this was also observed from the x-ray diffraction analysis. Moreover microwave sintering is a unique technique which provides rapid internal heating to the material under process which results in the enhancement of microstructural properties with high dense nature, and dense microstructure of ceramic material gives the enhanced physical and electrical properties of electroceramics.

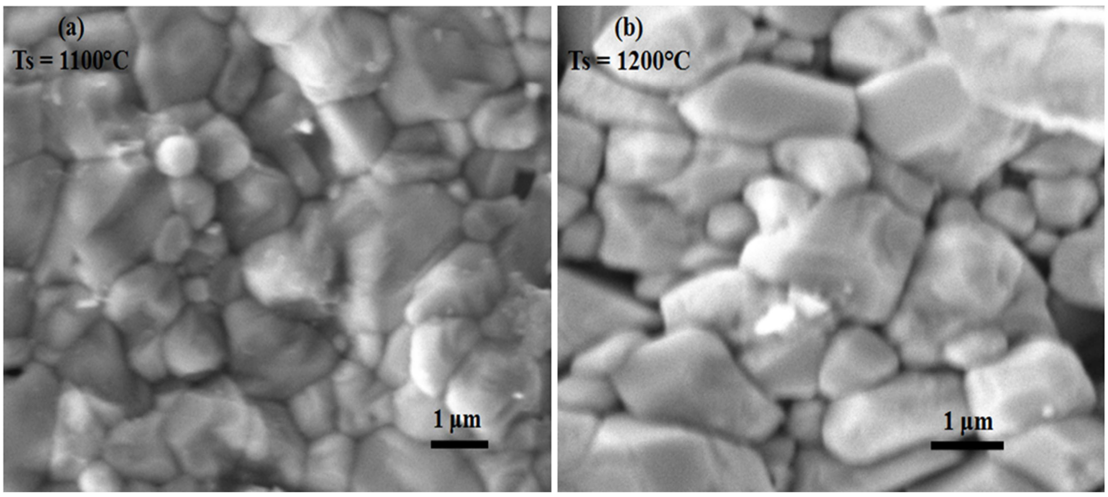

Figure 2. *SEM images of MW sintered BCT (a) 1100°C and (b) 1200°C.*

Figure 3(a) and 3(b) show the variation of dielectric constant (ε_r) with temperature whereas, inset figure show the variation of loss tangent with temperature for BCT ceramic sintered at 1100°C and 1200°C respectively. Here, increment in magnitude (almost double) of dielectric constant was observed for ceramic sintered at 1200°C while the dielectric loss tangent value is low as compared with ceramic sintered at lower temperature (1100°C). This increment in dielectric constant may attributes because of improved microstructure resulted due to more diffusion of Ca^{2+} ions on Ba^{2+} site with increasing temperature this may be resulted due to diffusion of Ca ions fill the voids results high dense microstructure. Density of the material is an very important factor in case of ceramics, higher density of material plays an important role in enhancement of electrical properties [6-7]. Here microwave sintering is also contributes in the improving the physical and electrical properties of ceramic material. With increase in temperature dielectric constant increases for each applied frequency, reaches maximum value (ε_{rm}) at maximum temperature (Tm) also called as Curie temperature and decreases further with increase in temperature leaving a broad dielectric spectra at the maximum temperature. The broadness of dielectric spectra confirms the existence of diffuse phase transition (DPT) in the microwave sintered ceramic material whereas; the behaviour of dielectric constant remains unchanged for both samples.

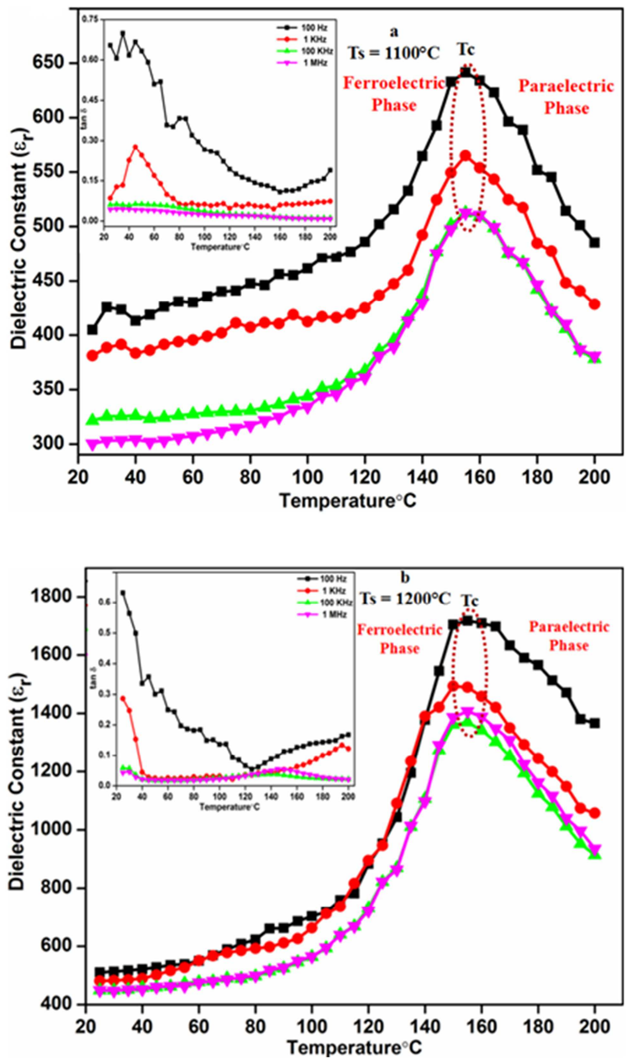

Figure 3. *Variation of dielectric constant (ε_r) for MW sintered BCT ceramic samples (a) 1100°C and (b) 1200°C (inset fig. Show variation of tan δ with temperature).*

The temperature at which the dielectric constant has maximum value and the temperature from which dielectric constant start to decrease are called as transition temperature (Tc), where the transitions of material from ferroelectric to paraelectric phase occurs. It could be seen that, dielectric constant value of BCT ceramic material decreases with increase in applied frequency and Tc shifts slightly towards higher temperature. The dielectric constant of ceramic sample sintered at higher temperature shows less frequency dispersion. This may be due to an arrangement of fine grains results from high temperature heating of ceramic material. Up to the transition temperature material exhibits ferroelectric properties, which is an active region of this material, above the transition temperature the material becomes paraelectric. Therefore materials with high transition point are most important materials for high energy storage application at higher temperature range [8]. The observed Tc value for both the samples (~ 155°C) has higher magnitude than reported earlier [9-10] for similar kind of ceramic materials and even higher than the pure $BaTiO_3$ phase processed with conventional method [11]. Low values 0.05 and 0.2 of loss tangent are observed for microwave sintered ceramic material sintered at 1100°C and 1200°C. The behaviour of dielectric loss tangent was quite similar for both BCT samples sintered at different temperature. Dispersion observed of loss tangent is more at lower frequency value and at higher applied frequency dielectric loss tangent posse's almost constant behaviour. At lower temperature and lower value of frequency dielectric loss tangent is more and decreases with increase in temperature from 25°C to 200°C and frequency from 100 Hz to 1 MHz. These improved electrical properties assign microwave technique as one of most important technique.

4. Conclusions

$Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) lead free ferroelectric material is successfully synthesized by co-precipitation method. Most useful and important microwave sintering technique is used for heating of as synthesized ceramic material at two temperatures 1100°C and 1200°C, keeping very short holding time 30 min and 20 min respectively. Biphasic crystal structure was observed for both samples, tetragonal corresponding to $BaTiO_3$ phase and orthorhombic crystal structure for $CaTiO_3$ phase. Microstructures observed for ceramic processed with microwave technique are very dense and improvement is observed with increasing temperature. High dielectric constant with low dielectric loss observed for ceramic sintered at 1200°C, whereas the phase transition temperature range is enhanced which confirms microwave sintering affects on the active region or working region.

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References

[1] V. Sreenivas Puli, D. K. Pradhan, B. C. Riggs, D. B. Chrisey, R. S. Katiyar. J. Alloy. Compd.; 2014, 584, 369.

[2] Z. Yu, C. Ang, R. Guo, A. S. Bhalla. J. Appl. Phys.; 2002, 92, 1489.

[3] S. M. Mane, P. M. Tirmali, D. J. Salunkhe, P. B. Joshi, C. B. Kolekar, S. B. Kulkarni. J. Mater Sci: Mater Electron.; 2016, 27 (7), 7204.

[4] S. Mane, P. Tirmali, S. Kadam, A. Tarale, C. Kolekar, S. Kulkarni. J. Chin. Adv. Mate. Soci.; 2016, 4 (4), 269.

[5] P. Victor, R. Ranjith, S. B. Krupanidhi. J. Appl. Phys.; 2003, 94 (12), 7702.

[6] R. S. da Silva, J. C. M'Peko, L. da Costa Fontes, A. C. Hernandes. Mate. Res.; 2009, 12 (3), 287.

[7] O. P. Thakur, C. Prakash, D. K. Agrawal. Mate. Sci. Engg. B.; 2002, 96, 221.

[8] O. P. Thakur, C. Prakash, D. K. Agrawal. Mate. Lett.; 2002, 56, 970.

[9] X. Hao. J. Adv. Dielect.; 2013, 3 (1), (1330001) 1.

[10] M. R. Panigrahi, S. Panigrahi. Phys. B.; 2010, 405, 2556.

[11] N. Baskaran, H. Chang. Mate. Chem. Phys.; 2002, 77, 889.

[12] Sonia, R. K. Patel, P. Kumar, C. Prakash, D. K. Agrawal. Ceram. Int.; 2012, 38, 1585.