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Unraveling dielectric abnormality based on the effect of defect dipoles in Cr ion doped multipurpose properties of BCT ceramics

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Abstract

With the motive of unraveling the effect of Cr incorporation on the structural, microstructural, dielectric, ferroelectric, energy storage, and magnetic properties of BCT (Barium Calcium Titanate) ceramics have been investigated. $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($0.000 \leq x \leq 0.020$) powder samples have been prepared using classical solid-state reaction method. Cr doped BCT ceramics showed a single phase perovskite structure having a tetragonal phase without phase transformation from $P4mm$ to $Pm-3m$ after the addition of Cr. With increased Cr content, the tolerance factor, lattice parameters, unit cell volume, c/a ratio, and grain size have been found to decrease. Both Debye-Scherrer and Williamson-Hall plot methods confirmed the reduction of crystallite size on increased Cr doping in BCT lattice. A dielectric anomaly “hump” (~ 447 K) has been observed at low frequencies in the paraelectric region due to the presence of acceptor induced defect dipoles. The temperature-dependent dielectric properties of prepared BCT ceramic with Cr compositions possess diffused phase transition (DPT) and the width of DPT is increased. Room temperature energy storage density achieved the maximum value of 190.35 mJ/cm^3 for the composition $x = 0.005$ at an electric field of 55 kV/cm . For the Cr composition of $x = 0.015$ and an electric field of 10 kV/cm , the highest energy storage efficiency (η) of about 60.5% has been obtained at room temperature. % Temperature coefficient of capacitance has been obtained to vary between $\pm 15 \%$ in the temperature range of 303 K to 523 K . Cr doped ceramic samples exhibit room temperature ferromagnetism at low magnetic fields and diamagnetism at a higher value of

magnetic fields. These results suggest prepared ceramics as a suitable lead-free material for X8R multilayer ceramic capacitor devices and energy applications.

Keywords: Cr doped BCT, ferroelectric properties, energy storage density, dielectric properties, defect dipoles, magnetic measurements

1 Introduction

With the functionality of ferroelectric materials, they can be adapted to wide-ranging applications, including multilayer ceramic capacitors (MLCCs), sensors, transducers, actuators, and energy storage devices [1–5]. The rapidly growing demands of energy storage technologies have promoted the development of materials with high energy storage density and high energy storage efficiency [6–9]. The usage of ferroelectric ceramic materials in electrical and electronic devices is fast blooming as a potential material for energy storage applications [6,9–11]. The majority of ferroelectric ceramic capacitors employ Lead (Pb) containing materials such as PbTiO_3 (lead titanate oxide), PZT (lead zirconate titanate), and their derivative compositions [12]. Lead-based compositions of ferroelectric ceramic capacitors offered outstanding energy storage properties. But the presence of highly precarious Lead (Pb) raised concerns regarding detrimental effects on human health and the environment, and forbid their usefulness [3,13,14]. New ceramic compositions need to be designed to replace Pb and derive the improved performance of Lead-free materials in a variety of achievable properties [13,15,16]. For the last few decades, the enthralling research into Lead-free ceramics has been conducted [17]. Currently, the search for Lead-free dielectric ceramics with ergonomic properties is focused on the compositions of BaTiO_3 , which is a well-studied perovskite ferroelectric material due to its enormous practical applications [13,18–21]. Modification in the structure and properties of BaTiO_3 can be made by doping with a variety of dopant ions (dopant engineering) for fetching multiple applications from doped ceramic materials [5,15,20,22–27]. The properties of ceramic materials are highly dependent on final crystal symmetry, choice of dopant, the disparity in ionic radii between host/parent and dopant cations, doping concentration, and preparation conditions [28]

The A-site substitution of smaller ionic radii Ca^{2+} (1.34 Å) in BaTiO_3 is caused by replacing Ba^{2+} ions with larger ionic radii (1.61 Å) within its solid solution limit. BCT (Ca doping in BaTiO_3) ceramics support the diffused temperature dependence of dielectric constant, provide higher breakdown strength, and better piezoelectric properties [2,14,29–32]. Moreover, doping effect of

Ca on temperature-dependent transitions of BaTiO₃, tetragonal- cubic transition temperature (at ~ 120 °C) shows negligible variation, but lowers the transition temperature of tetragonal-orthorhombic (at ~ 5 °C) and orthorhombic- rhombohedral (at ~ -80 °C) phase [1,15,30,33]. Further, Ca doping also prevents the formation of an undesired hexagonal phase and greatly improves the performance of BaTiO₃ ceramics [1,30,34].

Cr ions are non- polluting transition metals having high chemical reactivity and meliorates the performance of perovskite ceramics. Cr doping brings significant improvement in stabilizing the crystal structure through the formation of solid-solution, enhances the aging effect, decrease dielectric losses, and tune transducer properties of ceramic systems [14,26,30,35]. Cr ions can exist in Cr²⁺, Cr³⁺, Cr⁴⁺, Cr⁵⁺ and Cr⁶⁺ oxidation states with ionic radii 0.80 Å, 0.615 Å, 0.55 Å, 0.49 Å and 0.44 Å respectively in six coordinated octahedral [24,36]. The difference between ionic radii of substituted cations and dopant ions must be within $\pm 15\%$ to form a stable solid-solution [30]. The ionic radii of Cr³⁺ (0.615 Å) is very close to Ti⁴⁺ (0.62 Å) which makes this configuration highly favorable in the BCT system [24]. Therefore, it is expected that Ti ions can be doped by Cr ions in the BCT lattice. Cr₂O₃ is an acceptor dopant that generates positively charged holes or oxygen vacancies when doped into the BCT matrix. The literature, however, still lacks information about the effect of Cr doping on the properties of BCT ceramics. In the present work, lead-free ceramic compositions of Ba_{0.80}Ca_{0.20}Ti_{1-3x/4}Cr_xO₃ ($0.000 \leq x \leq 0.020$) have been prepared through classical solid-state reaction method. The doping effect of Cr content on BCT solid solution has been unraveled by exploring structural, microstructural, dielectric, ferroelectric, energy storage, and magnetic properties.

2 Sample preparation and Experimental methods

Lead free ceramic powder samples Ba_{0.80}Ca_{0.20}Ti_{1-3x/4}Cr_xO₃ with different doping levels ($x = 0.000, 0.005, 0.010, 0.015$ and 0.020) have been prepared using classical solid-state reaction method. The analytical grade constituent powders BaCO₃, TiO₂, Cr₂O₃ (procured from HiMedia, 99% pure), and CaCO₃ (Merck, 99% pure) have been weighed in desired molar proportions as per the stoichiometric composition. Their mixture has been obtained by grinding the powder samples into agate mortar and pestle. Then mixed powder was milled in distilled water using high energy ball mill for 4 hrs at 500 rotations/min. The obtained liquid mixture (slurry) has been dried overnight at 120 °C in the oven. The mixed dried sample powder has been subjected to calcination

at 1100 °C for 4 hrs in a high-temperature muffle furnace. The calcined powders were ball milled, dried, and Calcined again following the above-mentioned procedure. After calcination, powders were uniaxially pressed into disk pellets of 1-2 mm thickness and a diameter of 10 mm under a pressure of 0.5 ton/sq. in. for 2 minutes. The pelletized calcined products have been sintered at 1350 °C for 4 hrs. All the characterizations have been carried out on the sintered samples. The crystallographic structure of prepared compositions has been examined using Rigaku Miniflex-II X-ray diffractometer over the angular range (2θ) 20 - 80°. The $\text{CuK}\alpha$ radiations ($\lambda \sim 1.540560 \text{ \AA}$) from the copper tube has been used for investigation. The phase identification and lattice parameters were calculated by Rietveld refinement of XRD data performed employing Full Prof software 2015. The morphology and microstructure images from the fractured surface of sintered samples have been observed using Scanning Electron Microscope (FE-SEM, Carl Zeiss Supra 55). For dielectric and ferroelectric measurements, the polished surfaces of disk pellets were coated with a silver paste to make electrodes. The dielectric measurements have been performed using impedance analyzer (Keysight - E4990A) in the frequency range of 500 Hz to 100 kHz. The ferroelectric (P-E) measurements have been carried out using a P-E loop tracer (Marine, India). The room temperature magnetization vs. magnetic field (M-H) loops have been measured using a Microscience E-29 Vibrating Sample Magnetometer (VSM).

3. Results and discussion

3.1 Analysis of crystal structure

The XRD diffraction pattern of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($x = 0.000, 0.005, 0.010, 0.015$ and 0.020) ceramics have been recorded on crushed powder samples at room temperature, are displayed in Fig. 1 (a). In Fig. 1 (a), XRD patterns evidence the well-defined single-phase perovskite tetragonal structure. Obtained XRD patterns are also free from any impurity phase of oxides and show no structural transformation from the tetragonal (P4mm) phase after Cr doping in the BCT lattice at room temperature. It indicates that samples are well crystallized and diffusion of Cr and Ca ions at Ti and Ba lattice positions into the BCT host matrix, respectively, suggesting the formation of a solid-solution. All the peaks in XRD diffraction patterns of BCT samples doped with Cr ions have been identified to tetragonal phase using JCPDS card number 81-2205 (BaTiO_3). The characteristic peaks located at diffraction angle $2\theta \sim 45.5^\circ$ corresponds to the (002) and (200) crystalline planes of tetragonal (P4mm) symmetry of unit cell. The enlarged part of characteristic

tetragonal diffraction peaks is shown in Fig 1 (b). It is also visible from Fig. 1 (b) that no significant change in diffraction peak intensities was observed with increasing the incorporation of Cr contents (x) which verified the prevailing of tetragonal structure for all prepared samples. All the diffraction peaks show a shift towards higher 2θ with respect to bare ($x = 0.000$) BCT sample for increasing incorporation of Cr. This shifting of diffraction peaks indicates that lattice parameters (a, c) and unit cell volume (a^2c) decreases with doping of Cr ions at the lattice site of Ti in BCT ceramics. As the shifting of diffraction peaks towards the higher angle side is a clear indication of a decrease in unit cell volume and lattice parameters. This is due to the incorporation of lower size Cr^{3+} ions (0.615 Å) in the Ti^{4+} (0.62 Å) site of the BCT lattice.

Goldsmith's tolerance (t) factor has been determined for the estimation of degree of distortion of host perovskite structure on the basis of ionic radii in BCT perovskite doped with Cr ions. The t for x mol Cr-doped BCT (doping level dependence of t) was calculated using chemical formula $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$, considering Cr^{3+} in the lattice is given by [1]

$$t = \frac{(0.80R_{\text{Ba}} + 0.20R_{\text{Ca}} + R_{\text{O}})}{\sqrt{2}((1-3x/4)R_{\text{Ti}} + xR_{\text{Cr}} + R_{\text{O}})} \quad (1)$$

where, R_{Ba} , R_{Ca} , R_{Ti} , R_{Cr} , and R_{O} represents the ionic radii of Ba (1.61 Å), Ca (1.34 Å), Ti (0.62 Å), Cr (0.615 Å), and O (1.40 Å) ions which have been taken from the table of ionic radii proposed by Shannon. The calculated t values of prepared ceramic samples are tabulated in Table 1. From Table 1, values of tolerance factor (t) have been found to decrease from 1.0347 to 1.0332 with increased Cr dopant concentration in BCT lattice. This implies that tetragonality (c/a ratio) decreases with increasing Cr content. The obtained t values also indicate that the stability of perovskite structure has been increased with an increase in amount of Cr content.

3.1.1 Debye Scherrer and W-H plot method for determination of crystallite size

Broadening of Bragg's diffraction peaks is related to the finite size of a crystal (crystallite size), instrumental factors, structural defects, and strain in the lattice. Using the Debye Scherrer equation and Williamson Hall (W-H) plot method, extensive analysis of XRD patterns was conducted. The incorporation effect of Cr ions on the crystallite size was also studied in BCT lattice. The average crystallite size of prepared samples has been calculated using Debye Scherrer

and W-H plot method for comparative analysis, which are stated in equation (2) and (3, 4) respectively [1,37]. Lattice strain values were obtained only from the W-H plot ($\beta \cos \theta$ vs. $4 \sin \theta$).

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\eta \sin \theta \quad (3)$$

$$D = \frac{0.89\lambda}{\text{Intercept}} \quad (4)$$

where, D is average crystallite size, $\lambda \sim 1.54056 \text{ \AA}$ (wavelength of Cu (K_α) radiation), $k \sim (0.89)$ is shape factor, β is FWHM (full width at half maxima), θ is the diffraction angle and η is lattice strain. Fig. 2 shows the graph of the W-H plot, which is plotted between $\beta \cos \theta$ (along y-axis) and $4 \sin \theta$ (along x-axis). Debye Scherrer gives crystallite size while the W-H plot gives both the strain and crystallite size of all Cr doped BCT ceramics. The intercept and slope values were further used to calculate crystallite size and strain values for prepared samples. The calculated values of D and η are tabulated in Table 1. From the Scrutiny of data presented in Table 1, it has been observed that the crystallite size obtained using both methods shows a decreasing trend with an increase in Cr content. This variation in crystallite size (given in Table 1) is due to the increase in FWHM of diffraction peaks, change in strain, and bond length values with an increase in substitution of Cr contents. Moreover, when Ti^{4+} ions with larger ionic radii are doped with smaller size Cr^{3+} ions, there would be shrinkage of the lattice which results in the variation of lattice strain [38]. The decrease in crystallite size is an indication of increase in structural defects which would restrict grain growth.

3.1.2 Rietveld Refinement

Rietveld refinement method has been used to determine the precise lattice parameters and for the quantitative phase analysis of Cr doped BCT ceramics. The obtained XRD data of bare and Cr doped BCT ceramics were fitted considering tetragonal symmetry belonging to $P4mm$ space group using Full Prof software (2015). For the tetragonal perovskite structure of Cr – BCT samples, Ba/ Ca atoms are at 1a (0, 0, 0), Ti/Cr atoms at 1b (0.5, 0.5, $0.5 \pm \Delta z$), O1 atoms at 1b (0.5, 0.5, $0.5 \pm \Delta z$) and O2 atoms at 2b (0.5, 0, $0.5 \pm \Delta z$) represents the Wyckoff sites and atomic positions respectively. Since atoms are moved along z-direction within the tetragonal unit cell, the

cell becomes elongated along c – axis. Refinement of z atomic position of Ti/Cr, O1, and O2 atoms are thus taken into account whereas the position of Ba/Ca atoms is assumed to be fixed. The procedure details of theoretical fitting (Rietveld refinement) of XRD patterns have been discussed in our previous work [1,2]. The single tetragonal phase has been verified for all BCT samples doped with Cr ions. The fitting excellence of peaks can be analyzed by the quality of fit (χ^2) along with low values of reliability parameters (R_p and R_{wp}). All the obtained results are in accordance with the XRD studies. Fig. 3 displays the Rietveld refinement fitted patterns of all prepared compositions. In Fig. 3, the experimental data (Y_{obs}) and theoretically fitted (Y_{cal}) XRD patterns are denoted by open black and solid red symbols, respectively. The solid blue line at the bottom shows the difference between experimental and calculated XRD patterns. Vertical lines (pink color) denote the Bragg's peak position corresponding to P4mm space group. The lattice parameters, volume, position coordinates, reliability parameters, and quality of fit (χ^2) for each composition, as obtained from Rietveld fitting of experimental XRD data are presented in Table 2. The bond length values of Ba/Ca – O, Ti/Cr – O, O-O atoms and the number of bonds for all ceramic compositions are reported in Table 3. From the perusal of data presented in Table 2, refined lattice parameters as well as unit cell volume have been found to decrease with increasing doping content of Cr^{3+} at Ti^{4+} sites due to the lower ionic radii of Cr. The refined structural parameters are in accordance with the shifting of diffraction peaks. It has also been found that c/a ratio decreases on replacement of larger size Ti ions by Cr ions of smaller size with increasing doping content in the BCT matrix. The reduction in c/a ratio implies a decrease in tetragonality and the emergence of crystal structure towards stable perovskite structure [2]. The refined 3D tetragonal structure model for $Ba_{0.80}Ca_{0.20}Ti_{1-3x/4}Cr_xO_3$ ceramics was constructed using a CIF file with the help of VESTA software. Fig. 4 illustrates the typical tetragonal structure model for $x = 0.000$ and $x = 0.020$ compositions of prepared ceramics, where, green, dark blue, light blue, pink, and red-colored spheres represent Ba, Ca, Ti, Cr, and O atoms respectively. As seen from Fig. 4, Ba, and Ca atoms are occupying the corner positions, Ti atoms occupy the body center position and Cr dopants are shown replacing for Ti in Fig. 4 (b). From Fig. 4, refined model ($x = 0.020$) confirmed that dopant Cr^{3+} ions have entered the Ti^{4+} sites (octahedral position) in BCT ceramics. Data presented in Table 3, shows the variation in bond length values on the incorporation of Cr ions implies lattice deformation due to the induced strain in the BCT lattice.

3.1.3 Density measurement

Archimedes Principle has been utilized for the calculation of experimental density ($d_{\text{exp.}}$) of samples. X-ray density (d_{xrd}) has been calculated using lattice parameters (obtained from Rietveld refinement). Porosity has been determined for prepared samples using the following relation [39]

$$\text{Porosity (\%)} = \left(1 - \frac{d_{\text{exp}}}{d_{\text{xrd}}} \right) \times 100 \quad (5)$$

For all prepared compositions, the density and porosity values as a function of Cr content are summarized in Table 2. From the perusal of data presented in Table 2, it has been observed that density increases for $x = 0.005$ and then gradually decreases with increasing incorporation of Cr at Ti sites. It has also been observed that experimental density ($d_{\text{exp.}}$) values are smaller than those of x-ray density (d_{xrd}) for all prepared samples. This could be ascribed to the existence of pores which can develop during the sintering process. Opposite variation trend has been found for porosity, sample with composition $x = 0.005$ shows low porosity whereas other samples show increased porosity with increased Cr doping. This might be due to the incorporation of Cr ions having smaller ionic radii in comparison to Ti ions (larger size), results in the displacement of neighboring atoms from their position and causes the shrinkage of lattice [39]. Thus, increased compositional fluctuations would lead to increased porosity.

3.2 Analysis of structural morphology

The SEM micrographs of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ for all compositions varying from $x = 0.000$ to 0.020 are presented in Fig. 5 to probe their morphology and average grain size. The SEM images of BCT samples doped with Cr ions reveal that grains appear in polyhedral form/shape with varying sizes and have been heterogeneously distributed with certain voids. Heterogeneous distribution of grain size indicates the nucleation rate is much rapid than grain growth rate [40]. Grain boundaries of all Cr doped BCT samples are clearly visible in the SEM images. The average grain size was calculated from Image J software using SEM micrographs. It has been observed that average grain size firstly increases from $5.80 \mu\text{m}$ to $10.78 \mu\text{m}$ when $x = 0.005$ and then decreases from $10.78 \mu\text{m}$ to $5 \mu\text{m}$ on increasing the incorporation of Cr content from $x = 0.005$ to $x = 0.020$, as displayed in Histograms of Fig. 5. The average grain size value for all prepared samples have been tabulated in Table 1. This decrease in grain size is due to the adhesion of Cr^{3+}

ions onto the surface and grain boundaries with increased Cr content [41]. These Cr^{3+} ions attached to the surface hinders the grain growth and results in the reduction of grain size.

3.3 Dielectric study

3.3.1 Temperature dependence of dielectric constant

In order to check the dielectric response of prepared ceramic samples, temperature-dependent dielectric studies have been carried out. The temperature-dependent dielectric constant behavior of all Cr compositions as a parameter of frequency ranging from 500 Hz – 100 kHz has been carefully examined (presented in Fig. 6). The temperature-dependent ϵ' of Cr doped BCT ceramics at 10 kHz are shown in Fig. 7. It can be seen from the ϵ' vs. T plots that there is a gradual increase in ϵ' up to tetragonal (P4mm) to cubic (Pm-3m) phase transition temperature (T_c), and then drop in ϵ' is clearly visible in the paraelectric region. An additional dielectric anomaly “hump” (located around 447 K) at low frequencies in the paraelectric region has been observed for Cr content ($x = 0.005 - 0.020$). However, no such anomaly is observed in the dielectric curve of BCT sample with composition $x = 0.000$. This appeared anomaly in acceptor (Cr^{3+}) doped samples could be associated with the dielectric relaxation mechanism induced by orientation polarization of defect dipoles [42,43]. As lower valence (Cr^{3+}) transition metal ions are incorporated at the Ti^{4+} sites (octahedral position) of BCT lattice due to the resemblance of their ionic radii. Thus, in case of doping with Cr^{3+} ions for Ti^{4+} ions, oxygen vacancies ($V_o^{\bullet\bullet}$) have been formed in order to compensate for the charge misfit in the BCT ceramics. Also, Cr^{3+} ions at Ti^{4+} sites can associate with neighboring oxygen vacancies, and dipoles (Cr_{Ti}' or $\text{Cr}_{\text{Ti}}' - V_o^{\bullet\bullet}$) will be produced, named as defects dipoles and given by the following reaction [43]:

Furthermore, the external electric field would orientationally polarize ($\text{Cr}_{\text{Ti}}' - V_o^{\bullet\bullet}$) defect dipoles (can change their orientation), results in net polarization and creates a hump in the dielectric curve [44]. In addition, the orientation polarization of these oxygen vacancies are associated with defect dipoles typically occurs at high temperatures and low frequencies due to higher volume and lower mobility of oxygen vacancies [43]. This dielectric anomaly almost disappeared at higher

frequencies. Therefore, a relaxed hump is formed in ϵ' vs. T curve due to thermal fluctuation to the polarization response of prepared samples. The hump size is found to be related to the concentration of oxygen vacancy that accumulates on grain surface, grain boundaries, and domain walls of the ceramics [42]. The transition temperature (T_c) of the prepared ceramic compositions have been determined from the dielectric peak at higher frequencies to discern circumvent the polarization effect of defect dipoles. From the perusal of data presented in Fig. 7, T_c has been observed to shift to a lower temperature (from 404 K to 413 K) and also a lower values of $\epsilon'_{\max}$ at T_c with increased Cr content (x) in BCT ceramics. While the observed change in T_c seems to be quite small, this is reasonable from the perspective of low Cr doping content (up to 2 mol %). The variation in T_c is also directly related to the number of oxygen vacancies ($V_O^{\bullet\bullet}$) in the acceptor doped ceramics. Additionally, dopant Cr^{3+} ions for Ti^{4+} ions are highly compatible with the lattice structure of BCT because of their resemblance to ionic radii and electronegativity, which establishes a stable transition temperature for prepared ceramics. With increased Cr doping, the reduction in maximum of dielectric constant ($\epsilon'_{\max}$) at T_c may be attributed to decrease in grain size as observed by SEM micrographs analysis. Furthermore, the effect of decreasing $\epsilon'_{\max}$ is probable due to formation of oxygen vacancies that usually pin the ferroelectric domain walls motion at higher Cr doping level. The values of ϵ'_{RT} , $\epsilon'_{\max}$ at 10 kHz and T_c are summarized in Table 4.

3.3.2 Frequency dependence of dielectric constant

From Fig. 6 (a- e), the dielectric constant analysis shows that phase transition temperature (T_c) does not shift as a function of frequency. Thus, T_c value is independent from the frequency effect which is an indication of the classical ferroelectric nature of studied ceramic samples. But, $\epsilon' - T$ plot shows a decrease of $\epsilon'_{\max}$ along with the disappearance of anomaly peak with increasing frequency from 500 Hz to 100 kHz. Thus, it can be inferred that the intensity of both dielectric peaks in $\epsilon' - T$ plot decreases but does not show position shift and retains a broad shape around phase transition temperature with increased frequency.

3.3.3 Diffused phase transition behavior

Dielectric constant (ϵ') has been found to be independent of temperature and frequency at low temperatures (below T_c). On careful observation of ϵ' vs. T curve above T_c , the phase transition is broadened over a certain temperature interval and seemed to have frequency dependence. To

examine the characteristic of ferroelectric phase transition in prepared ceramics, ϵ' - T curves were fitted with Power Law at various frequencies. Bare and Cr doped BCT ceramics may obey Power law in the paraelectric region. The Power law is described by the following relation [1]

$$\frac{\epsilon'_c}{\epsilon'} = \left(1 + \frac{(T - T_c)^\gamma}{2\delta_c^2} \right) \quad (7)$$

where, δ_c is the broadening parameter, γ is the degree of relaxation which is expected to be 1 for ideal ferroelectrics, $1 < \gamma < 2$ for diffused phase transition (DPT) and 2 for relaxor ferroelectrics, T_c is transition temperature and ϵ'_c is a maximum dielectric constant value. To elucidate the dielectric phenomenon in bare and Cr doped BCT solid solution by Power law, ϵ' vs. T plot at different frequencies is presented in Fig. 6 (a - e). Fig. 8 (a - e) shows the experimental dielectric constant data along with curves above T_c generated by fitting the data to Power law for all prepared ceramic compositions. The Power law curve excellently fits the presented ϵ' vs. T data with best fit parameter R^2 in the range 0.9982 - 0.9994. Two parameters γ and δ_c obtained by fitting the experimental ϵ' data to equation (7) and the graph [Fig. 9 (a) - (b)] has been plotted for γ and δ_c as function of Cr composition and frequency (for composition $x = 0.015$). The obtained values of γ from Power Law fit appear to be within the range of 1 and 2 for different doping content of Cr in BCT which clearly indicates the diffused nature of phase transition. This is ascribed to the presence of polar microscopic regions over a temperature range. The γ and δ_c values show an increasing trend with an increase in Cr doping content due to the compositional fluctuations. Even though, γ and δ_c have been found to increase with an increase in frequency and similar behavior has been obtained for all Cr doped BCT ceramics.

3.3.4 Determination of temperature interval of DPT

Diffused phase transitions (DPT) occur due to the merging of ferroelectric and paraelectric phases in a wide temperature range and may arise because of small compositional fluctuations of microscopic regions [45]. Width of phase transition (D') represents the degree of relaxation/diffusiveness. DPT includes the temperature range from $T \leq T_c$ to $T \geq T_c$. Temperature range of diffused phase transition can be determined directly from the $\partial\epsilon'/\partial T$ (derivative of ϵ' vs. T) curve. The degree of diffusiveness in ϵ' vs. T plot is calculated by temperature range between extrema of $\partial\epsilon'/\partial T$ by following relation [45]

$$D' = T_{(\partial\epsilon'/\partial T)_{\min}} - T_{(\partial\epsilon'/\partial T)_{\max}} \quad (8)$$

where, $T_{(\partial\epsilon'/\partial T)_{\max}}$ and $T_{(\partial\epsilon'/\partial T)_{\min}}$ denotes the temperature at which $\partial\epsilon'/\partial T$ attains highest and lowest, respectively. These temperature values indicate a rapid variation of the prepared sample's dielectric constant owing to polar microscopic regions. Fig. 10 (a) - (e) shows the ϵ' vs. T and $\partial\epsilon'/\partial T$ vs. T curves for bare and Cr doped BCT ceramics. The D' value of all prepared compositions is presented in Table 4. It is apparent from Fig. 10 and the values presented in Table that samples possess diffused phase transitions and the diffusiveness degree increases with increasing Cr content in BCT lattice. The increased width of diffused phase transition could be related to the decreased average grain size with an increase in Cr doping.

3.3.5 Dielectric loss

Fig. 11 presents the variation of dielectric loss as a function of temperature at different frequencies for all samples with Cr doping contents. The curves of dielectric loss ($\tan\delta$ vs. T) in Fig. 11 show the occurrence of two loss peaks similar to the dielectric anomaly observed in $\epsilon' - T$ curve. The behavior of the first dielectric loss peak is corresponding to the tetragonal-cubic phase transition but at a slightly lower temperature than T_c . Additional loss peak (located in paraelectric regime) behavior is also associated with dielectric losses caused due to the existence of defect dipoles. By examining the shape of the $\tan\delta - T$ curve, it has been observed that dielectric loss anomaly (related to defect dipoles) is present at the higher temperature side of tetragonal to cubic phase transition. However, the occurrence of hump around 447 K in $\tan\delta$ vs. T curve is more pronounced as compared to $\epsilon' - T$ curve. The intensity of dielectric loss peaks corresponding to tetragonal - cubic phase and anomaly due to the formation of defect dipoles varies as a function of increasing frequency. It can also be noticed that at higher frequencies the effect of defect dipoles weakens and thus a reduction in the intensity of anomaly loss peak. This could be ascribed to the fact that the contribution of orientation polarization of defect dipoles decreases with an increase in the frequency of applied field, resulting in low dielectric loss [46]. An overall reduction in dielectric losses near T_c has been observed with an increase in Cr content. This may be linked with the diminution of average grain size in prepared samples. The dielectric loss ($\tan\delta_{DD}$) occurred at high temperatures is due to the presence of defect dipoles, which might be because oxygen vacancies begin to move and lead to electric conduction in samples [46]. Also, increasing the

doping level of Cr content often induces an increased concentration of oxygen vacancy, resulting in a gradual increase in dielectric loss with Cr content at a higher temperature. Thus giving rise to defect dipole induced dielectric losses. Further, in higher temperature region and at low frequencies, the larger values of dielectric losses may be due to conduction losses that decline as the frequency of applied field rises [2]. A summary of dielectric loss values such as $\text{Tan}\delta_{\text{RT}}$, $\text{Tan}\delta_{\text{Tc}}$, and $\text{Tan}\delta_{\text{DD}}$ at a frequency of 10 kHz for all prepared Cr doped BCT samples is presented in Table 4.

3.3.6 Temperature coefficient of capacitance

Temperature coefficient of capacitance (T_{CC}) of bare and Cr doped BCT ceramics have been evaluated in the temperature range 303 K to 523 K, using the following formula [1]

$$\%T_{\text{CC}} = \left(\frac{C_T - C_{T-1}}{C_{T-1}} \right) \times 100 \quad (9)$$

where, C_T is capacitance value at operating temperature T and the C_{T-1} corresponds to capacitance value at $T-1$ temperature. Fig. 12 displays the fashion of variation of T_{CC} with temperature at a frequency of 10 kHz. Looking at a plot of T_{CC} vs. T for all Cr doped samples, it was found that variance of T_{CC} is initially positive up to 363 K then becomes highly positive around T_c and appears negative above 423 K. The overall variance of T_{CC} in the prescribed temperature range is within $\pm 10 \%$. In the temperature range near T_c , a higher Cr ($x = 0.020$) doped sample possesses the lowest T_{CC} about $\pm 7.65 \%$. This implies that the incorporation of Cr content can enhance the temperature stability of dielectric properties of BCT ceramics. The prepared material yields room temperature $\epsilon' \sim 629 - 793$ and ϵ' at $T_c \sim 2915 - 4368$, with low dielectric loss (< 0.07) and temperature coefficient of capacitance (T_{CC}) of $\pm 15 \%$ from 303 K to 523 K. Thus the system of Cr doped BCT MLCCs could be a possible contender for the future generation of X8R devices [47].

3.4 Effect of Cr doping on ferroelectric properties of BCT ceramics

3.4.1 Electric field induced ferroelectric evolution

The measurement of hysteresis loops (P-E) directly depends on the electric field. To access its influence on ferroelectric properties at room temperature, the electric field has been increased. Fig. 13 (a) – (e) shows the electric-field induced hysteresis loops of all prepared samples measured

with the applied electric field up to 50 - 60 kV/cm at 50 Hz and room temperature. With increasing electric field values, standard ferroelectric loops have been observed. The P-E loops are unsaturated and small under low electric fields. Larger P-E loops have been attained upon application of higher electric fields, which becomes more and more saturated. It has been observed that for all Cr doped compositions, remnant polarization (P_r), saturation polarization (P_s), and coercive field (E_c) gradually increase with an increase in electric field values. Moreover, Cr doping in BCT ceramics shows enhancement in dielectric breakdown strength up to 60 kV/cm with increased doping content.

3.4.2 Composition induced ferroelectric evolution

The room temperature polarization hysteresis loops of Cr doped BCT ceramic samples are shown in Fig. 14. It can be seen from Fig. 14 that well behaved ferroelectric (P-E) loops have been observed for all prepared compositions. This suggests that the crystal structure of prepared bare and Cr doped BCT samples is in the ferroelectric phase at room temperature. The remnant polarization (P_r) and maximum polarization (P_{max}) were obtained varying from 8.984 $\mu\text{C}/\text{cm}^2$ to 10.838 $\mu\text{C}/\text{cm}^2$ and 14.507 $\mu\text{C}/\text{cm}^2$ to 20.037 $\mu\text{C}/\text{cm}^2$ for the studied Cr “x” content, respectively. Firstly, the P_r and P_{max} values decrease up to $x = 0.010$ and then increases with an increase in Cr content. The variation in polarization is generally influenced by many contributing factors such as c/a ratio, grain size, grain boundary, oxygen vacancy, phase transition, and defect dipoles [1]. The dependence of P_r and P_{max} on Cr content (up to $x = 0.010$) was found to be associated with decreased tetragonality (c/a ratio) and average grain size. The c/a ratio (obtained from Rietveld refinement) decreases as well as grain size reduction is observed from SEM micrographs with increased Cr content. A lower value of c/a ratio will result in lower polarization. Also, a decrease in grain size leads to an increase in the number of grain boundaries which causes interference in polarization between grains [1]. Thus, a reduction in polarization is observed in prepared samples up to $x = 0.010$. However, for higher Cr doping content ($x \geq 0.015$), P_r and P_{max} variation is not consistent with that of tetragonality and reduced grain size. This may be attributed to the dominance of defect polarization effect. As the number of defect dipoles increases by coupling of Cr^{3+} with oxygen vacancies on increasing incorporation of Cr content. These defect dipoles get aligned along the direction of spontaneous polarization which contributes to the overall increase in polarizability [48]. The ferroelectric parameters namely remnant polarization (P_r), maximum

polarization ($P_{\max}$), and coercive field (E_c) with Cr content at 50 kV/cm are presented in Table 5. From the data presented in Table 5, it is observed that E_c of ceramic samples continuously increases with increase Cr (up to $x = 0.015$) content. This increase in E_c can be attributed to the formation of oxygen vacancies on Cr^{3+} doping for Ti^{4+} ions of BCT. These oxygen vacancies diffused into the domain boundaries and induce a pinning effect on boundaries and reduce the domain wall movement. Thus coercive field increases and prepared material behave as hard ferroelectrics. However, a drop in E_c for higher Cr doping content ($x = 0.020$) is due to the dominance of the effect of defect dipoles on the ferroelectric domains. The defect dipoles and oxygen vacancies migrate into domain boundaries because of their moderate mobility, even at lower temperature than phase transition temperature. Such defect dipoles can pin the movement of the domain and may result in the formation of small wavy domains, rather than large domain structures [49]. As a Consequence, the coupling effect between domain walls and grain boundaries gets reduced and would weaken the pinning of domain wall motion which contributes to the reduction of E_c [43].

3.4.3 Temperature induced ferroelectric evolution

The temperature-dependent hysteresis loops of prepared ceramic compositions were measured at an applied field of 50 - 60 kV/cm with a frequency of 50 Hz. The typical hysteresis loops for Cr doped BCT compositions with $x = 0.000$, $x = 0.010$ and $x = 0.020$ at different temperatures (room temperature to 383 K) are presented in Fig. 15 (a - c). From the perusal of data presented in Fig. 15, it can be observed that P-E loops are well saturated indicating normal ferroelectrics, and are highly temperature-dependent showing evidence of soft ceramics. As the temperature rises, P-E hysteresis loops of Cr doped BCT ceramics tend to be thinner and thinner, accompanied by a gradual decrease of both P_r and E_c , suggesting deterioration of ferroelectric properties. This variation trend of P_r and E_c usually occurs in most of the ferroelectric materials. The decrease in P_r and E_c is ascribed to energy barrier reduction for the reorientation of domains and to maintain poled state at higher temperatures.

3.5 Effect of Cr doping on energy storage properties of BCT ceramics

For the overview of energy storage performance of Cr doped BCT ceramics, P-E loops have been used to determine the energy storage density (W_{rec}), loss density (W_{loss}), and also energy storage efficiency (η) with variation of electric field and temperature. P-E loop diagram shown in Fig. 16 (a), demonstrates the W_{rec} , W_{loss} enclosed by purple and sky blue colored area respectively.

The W_{rec} , W_{loss} , and η have been calculated from the hysteresis area in 1st quadrant using relations [50]

$$W_{rec} = \int_{P_r}^{P_{max}} E dP \quad (10)$$

$$W_{loss} = \int_0^{P_r} E dP \quad (11)$$

$$\eta = \frac{W_{rec}}{W_{rec} + W_{loss}} \times 100 \quad (12)$$

where, W_{rec} , W_{loss} , η , E , P_{max} , and P_r represents the energy storage density, energy loss density, energy storage efficiency, electric field, maximum polarization and remnant polarization respectively.

3.5.1 Effect of electric field on energy storage properties

The room temperature evolution of energy storage properties (W_{rec} , W_{loss} and η) with an applied electric field (50 - 60 kV/cm) for different compositions of Cr doped BCT has been shown in Fig. 16 (b - d). From the perusal of data presented in Fig. 16 (b - d), it has been found that W_{rec} , W_{loss} , and η are increasing overall with an increase in the applied electric field. Table 5 summarizes the values of W_{rec} , W_{loss} , and η obtained at a 50 kV/cm as a function of Cr content. The W_{rec} , W_{loss} , and η found to be varying from 107.20 to 177.88 mJ/cm³, 138.51 to 228.77 mJ/cm³, and 35.87 to 56.22 % respectively with Cr (x) content. The variation of W_{rec} has been observed to be similar to the difference between P_{max} and P_r with increased Cr content. The W_{rec} decreases up to $x = 0.010$ and then increases. Since there is a large difference between P_{max} and P_r , energy storage density would be high. An overall decrease in energy storage efficiency (η) has been observed with Cr content due to the increase in energy loss density (W_{loss}). The maximum energy storage density at room temperature has been achieved to be 190.35 mJ/cm³ for $x = 0.005$ at an applied electric field of 55 kV/cm. The highest efficiency of about 60.5 % has been obtained for Cr content “ $x = 0.015$ ” at 10 kV/cm.

3.5.2 Effect of temperature on energy storage properties

Temperature-dependent stability is a significant feature that needs to be considered for the practical applications of prepared ceramics for energy storage. For this, temperature-induced ferroelectric hysteresis loops have been used to study the variation of energy storage properties with temperature. Fig. 17 (a - c) is a plot of energy storage density (W_{rec}), energy loss density (W_{loss}), and efficiency (η) versus temperature change for BCT samples of different Cr contents (x). It can be seen from Fig. 17 (a - c) that W_{rec} and η increases with an increase in temperature because of a decrease in W_{loss} (as P-E loops become thinner with temperature). Table 5 summarizes the values of W_{rec} , W_{loss} , and η at 353 K at an electric field of 50 kV/cm. The maximum energy storage density has been obtained to be 238.25 mJ/cm³ with an efficiency of about 56.01 % at 353 K for the Cr composition $x = 0.015$. Moreover, Cr doped BCT ceramic compositions offer stable energy storage density in the temperature range of 303 K to 353 K. Thus, Cr ($x = 0.015$) doped composition of BCT can be a potential candidate for energy storage applications at an elevated temperature.

3.6 Magnetic Measurements

M-H loops have been analyzed to observe the doping effect of Cr (d^n - electrons) on the ferromagnetic property of parent BCT ceramics. The room temperature magnetic field dependence of magnetization for bare and Cr doped BCT ceramic samples is displayed in Fig. 18 (a - e), with an inset of partial amplification at low magnetic fields. Results of the M-H loop reveal that bare BCT sample exhibits diamagnetic behavior with an applied magnetic field, suggesting Ti ions are in 4+ oxidation state with d^0 electrons (empty d- orbitals). In Cr doped BCT samples, M-H loops show both diamagnetism and ferromagnetism at room temperature [51]. At low applied magnetic fields, the feeble ferromagnetic character of ceramic samples is dominant. At a higher magnetic field, the diamagnetic contribution is dominating the magnetic signal in Cr doped BCT samples. When acceptor Cr^{3+} ions are incorporated at the Ti^{4+} site of BCT lattice, charge compensation occurs and results in the creation of oxygen vacancies and defect dipoles. The oxygen vacancies or defects in doped BCT ceramics serve as a medium for magnetic interactions and are assumed to induce ferromagnetism [1]. The observed ferromagnetic behavior of prepared ceramic samples at low applied fields revealed that oxygen vacancies provide short-range ferromagnetic exchange interactions and increases with an increase in Cr content [40]. However, at higher fields, high magnetic energy overcomes the short-range exchange interaction energy which is dominated by

diamagnetism [40]. Moreover, for the subtraction of sample holder's diamagnetic contribution, the diamagnetic correction has been done to the obtained M-H loops as shown in Fig. 19 (a - d) from $x = 0.005$ to $x = 0.020$. For this, linear fit gives the diamagnetic slope at high fields and then a straight line with slope is subtracted from the raw M-H curve. This yields the magnetization curve for prepared ceramic samples. The obtained values of remnant magnetization (M_r) from M-H loops are 0.0393, 0.0467, 0.0569 and 0.0270 memu/g and coercive field (H_c) values are 173.09, 150.21, 171.01 and 168.29 Oe for $x = 0.005$, 0.010, 0.015 and 0.020 respectively.

4 Conclusions

The present research focuses on unraveling the effect of Cr doping on structural, morphological, dielectric, ferroelectric, energy storage, and magnetic properties of BCT ceramics. The XRD patterns confirm that a single-phase tetragonal structure has been formed in all prepared samples. Rietveld analysis of XRD indicates that lattice parameters and unit cell volume decrease with increasing content of Cr. XRD analysis also shows that tolerance factor and crystallite size calculated using Debye-Scherrer and W-H plot methods decreases by increasing the Cr doping content. SEM micrographs display the presence of well-developed polyhedral shaped grains. The grain size of samples decreased with an increase in the concentration of Cr content. For doped samples, temperature-dependent dielectric constant and dielectric loss curves show the presence of defect dipole induced anomaly at lower frequencies in the paraelectric region. All the prepared ceramic samples have been found to exhibit DPT and also the width of DPT has been observed to increase with increased Cr content in BCT lattice. The T_{CC} values lie within $\pm 15\%$ along with low dielectric losses ($\tan\delta < 0.07$), which presents the Cr doped BCT ceramics as a potential material for X8R MLCCs. The ferroelectric hysteresis loops show an increasing trend of P_r and E_c with an electric field and a decreasing trend with an increase in temperature. P-E loops reveal the presence of defect dipole effect on the variation of P_r and E_c with Cr content. An overall increase in energy storage parameters such as W_{rec} , W_{loss} , and η has been observed with an increasing function of applied electric field and temperature. For ceramic sample with $x = 0.005$ composition, the highest $W_{rec} \sim 190.35 \text{ mJ/cm}^3$ at 55 kV/cm has been attained, and maximum storage efficiency of about 60.5 % has been achieved at 10 kV/cm for the sample $x = 0.015$ at room temperature. However, ceramic composition with $x = 0.015$ also presents better temperature-dependent energy storage properties ($W_{rec} \sim 238.25 \text{ mJ/cm}^3$, $\eta \sim 56.01\%$ at 353 K). Room temperature M-H loop of

Cr doped samples shows the ferromagnetism at low magnetic fields and diamagnetism at high magnetic fields. The diamagnetic correction has been applied to the M-H loops to obtain the magnetic parameters such as remnant magnetization (M_r), saturation magnetization (M_s), and coercivity (H_c). The prepared ceramic compositions in this study could be used for possible future multipurpose systems in X8R MLCCs, energy storage applications, and as a multiferroic material.

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Fig. 1 (a) X-ray diffraction patterns of bare and Cr doped $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($0.000 \leq x \leq 0.020$) samples; (b) magnified view of (002) and (200) peaks near $2\theta \sim 45.5^\circ$.

Fig. 2 (a) – (e) Williamson-Hall (W-H) plots of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($0.000 \leq x \leq 0.020$) ceramics.

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Fig. 4 Typical crystal structure of (a) bare BCT and (b) Cr doped BCT with $x = 0.020$ drawn by VESTA software using CIF generated during Rietveld refinement.

Fig. 5 SEM micrographs of all $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics with grain size distribution.

Fig. 6 Temperature dependence of dielectric constant ($\epsilon' - T$) of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics measured at different frequencies (500 Hz to 100 kHz).

Fig. 7 Temperature dependence of dielectric constant ($\epsilon' - T$) of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics measured at 10 kHz.

Fig. 8 Temperature dependence of dielectric constant ($\epsilon' - T$) curves at different frequencies fitted according to Power Law for all $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics.

Fig. 9 (a) Plot of γ and δ_c as a function of Cr content at 10 kHz and (b) plot of γ and δ_c as a function of frequency for typical composition with $x = 0.015$.

Fig. 10 Variation of ϵ' vs. T along with $\partial\epsilon'/\partial T$ vs. T of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics at 10 kHz.

Fig. 11 Temperature dependence of dielectric loss ($\tan\delta$ vs. T) of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics measured at different frequencies.

Fig. 12 Temperature dependence of temperature coefficient of capacitance ($\% T_{cc}$ vs. T) of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics at 10 kHz

Fig. 13 (a) - (e) Room temperature ferroelectric (P-E) hysteresis loops at different electric fields of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($0.000 \leq x \leq 0.020$) ceramics.

Fig. 14 Room temperature ferroelectric (P-E) hysteresis loops of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($0.000 \leq x \leq 0.020$) ceramics at an electric field of 45 kV/cm.

Fig. 15 Typical P-E hysteresis loops recorded at various temperatures for Cr doped BCT ceramic composition with $x = 0.000$, $x = 0.010$ and $x = 0.020$.

Fig. 16 (a) Schematic diagram for the calculation of energy storage properties from ferroelectric P-E hysteresis loops; (b) – (d) electric field strength dependence on W_{rec} , W_{loss} and η of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics.

Fig. 17 Variation of calculated (a) W_{rec} , (b) W_{loss} and (c) η with temperature for $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics.

Fig. 18 M-H loops recorded at room temperature and inset showing magnified view at low magnetic fields of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($0.000 \leq x \leq 0.020$) ceramics.

Fig. 19 M-H loops of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($0.005 \leq x \leq 0.020$) ceramics obtained after excluding diamagnetic contribution.

Figures

Figure 1

(a) X-ray diffraction patterns of bare and Cr doped $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ($0.000 \leq x \leq 0.020$) samples; (b) magnified view of (002) and (200) peaks near $2\theta \approx 45.5^\circ$.

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(b) $x = 0.020$

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Typical crystal structure of (a) bare BCT and (b) Cr doped BCT with $x = 0.020$ drawn by VESTA software using CIF generated during Rietveld refinement.

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Temperature dependence of dielectric loss ($\text{Tan}\delta$ vs. T) of $\text{Ba}_{0.80}\text{Ca}_{0.20}\text{Ti}_{1-3x/4}\text{Cr}_x\text{O}_3$ ceramics measured at different frequencies.

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Typical P-E hysteresis loops recorded at various temperatures for Cr doped BCT ceramic composition with $x = 0.000$, $x = 0.010$ and $x = 0.020$.

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