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Dielectric and piezoelectric properties of low temperature synthesized iso-valent modified BT ceramics

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Abstract

$Ba_{(1-x)}Y_xTiO_3$ (where Y = Ca, Mg and Sr, x = 0.02, 0.04, 0.06 and 0.08) ferroelectric ceramic samples were synthesized in single perovskite phase by modified solid state reaction (MSSR) route. For single perovskite phase formation and dense grain morphology, 900 °C and 1300 °C were optimized as calcination and sintering temperatures. With the increase of substitutions% of Ca in BCT ceramic samples, the position of T_c increases slightly, whereas with the increase of Mg and Sr substitution% in BMT and BST systems, the position of T_c decreased but remains above RT. Decreased processing temperature with low temperature coefficient of capacitance made BCT ceramic samples useful for dielectric applications. Symmetric nature of the S–E loops indicated the increase of piezoelectric nature with the increase of Ca substitution% in BCT system.

Keywords: C. Dielectric Properties; MSSR; Perovskite; Strain vs. electric field

1. Introduction

In the early 1940s, barium titanate (BT) was first discovered as a ferroelectric system and since then a great deal of efforts had been devoted to study the dielectric and piezoelectric properties of BT based systems [1–6]. BT system is lead free and environmental friendly [7,8] and it is chemically and mechanically very stable. BT system exhibits ferroelectric properties at and above room temperature (RT) and it can be easily synthesized and used in the form of ceramic polycrystalline ceramics [9]. BT ceramics are widely used in the fabrication of multilayer ceramic capacitors (MLCC) and in the piezoelectric transducers applications. Efforts are going on to further modify the dielectric and piezoelectric properties of BT based ceramics. For this purpose, substitution of iso-valent ions for the host lattice cations in BT perovskite lattice plays a significant role in these modifications [10]. These substitutions results in new solid solutions with BT and alter its structural features, resulting in a shift in phase transition temperature along with modified dielectric and piezoelectric properties.

In order to increase volume efficiency, the dielectric layers of BT system and inner electrodes are stacked layer by layer to form a multilayered structure. This is known as a multilayer ceramic capacitor (MLCC). In order to use low-cost metal electrodes, such as Ni and Cu for replacing the more expensive Ag–Pd system inner electrode in multilayer ceramic capacitors (MLCC) the $BaTiO_3$ based compounds must be sintered at a temperature low enough to suppress electrode oxidation [11,12]. It is known that the processing temperature and microstructure of a ferroelectric ceramics depends on the synthesis route used. The purity of the starting precursors affects the processing temperatures and hence the material properties. In case of BT ceramics, solid state route requires high calcination temperature to get perovskite phase and often results in the formation of multiphase and inhomogeneous powders [13–16]. High energy ball milling [17] is also reported to produce 10 nm particle size but the approach suffers from small batch size, high processing time and energy consumption. The complex double metal salts methods involve the use of solid precursors for the manufacture of pure $BaTiO_3$ ceramics. This process involves the use of costly materials, multisteps, uncontrolled particle size and interparticle agglomeration. Pechini's autocombustion method is reported to produce 10 nm particle sizes but the approach suffers from small batch volume.

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Hydrothermal process [18] also involves the incorporation of costly materials. In modified solid state reaction (MSSR) route we have tried to combine the advantages of solid state reaction and chemical routes.

Therefore, in the present work study of structural, dielectric and piezoelectric properties of iso-valent ion substituted BCT, BMT and BST ferroelectric ceramic samples synthesized by MSSR route is carried out.

2. Experimental procedure

Iso-valent ion substituted $Ba_{(1-x)}Y_xTiO_3$ (where Y = Ca, Mg and Sr, $x = 0.02$, 0.04, 0.06 and 0.08) ceramics were synthesized by modified solid state reaction (MSSR) route. In the present work for $x = 0.02$, 0.04. 0.06 and 0.08, we have used BCT1, BCT2, BCT3, BCT4, BMT1, BMT2, BMT3, BMT4, BST1, BST2, BST3 and BST4 notations. Barium acetate trihydate, calcium acetate, strontium acetate, magnesium acetate (all from Aldrich, USA) and fumed titanium oxide were used as starting precursors. Stoichiometric proportion of barium acetate and calcium/strontium/magnesium acetates 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 fumed titanium oxide was mixed in the transparent solutions and stirred for 4 h. The flowchart of the synthesis process is shown in Fig. 1. Iso-valent ion substituted BCT, BMT and BST ceramic samples were calcined at 900 °C for 4 h and single perovskite phase formation was confirmed by X-ray diffraction (XRD) technique. These calcined powders were pressed at 60 MPa for pelletization and sintering for each composition was done at 1300 °C for 4 h. In order to examine the phases present XRD analyses of the powder and pellets were performed on a PW 3020 Philips with Cu Kα radiation ($\lambda = 1.5405$ Å). These pellets were polished and silver paste was applied on the surfaces for doing electrical characterization. ε_r and tanδ at a fixed frequency were measured as the function of temperature using Hioki 3532-50 LCR HiTESTER. The strain vs. electric field is measured by an MTI-2000 photonic sensor (Mech. Tech. Inc.). The MTI-2000 photonic probe modules contain two sets of optical fibers. Light-transmitting fibers and light receiving fibers are bundled together. The displacement is based on the interaction between the field of illumination of the transmitting fibers and the field of view of the receiving fibers.

3. Results and discussion

Fig. 2(a–c) shows the XRD patterns of calcined powders of iso-valent substituted BCT, BMT and BST ceramic samples. Single perovskite phase without any trace of secondary phase

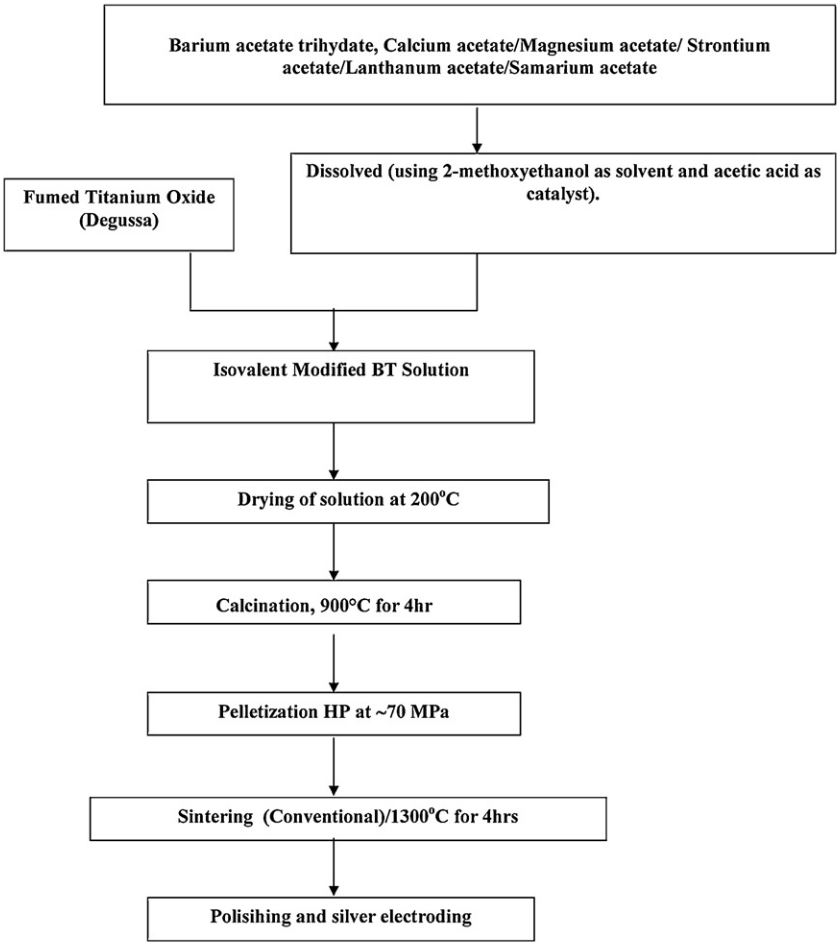

Fig. 1. Flow chart of synthesis of iso-valent modified BT ceramics by MSSR route.

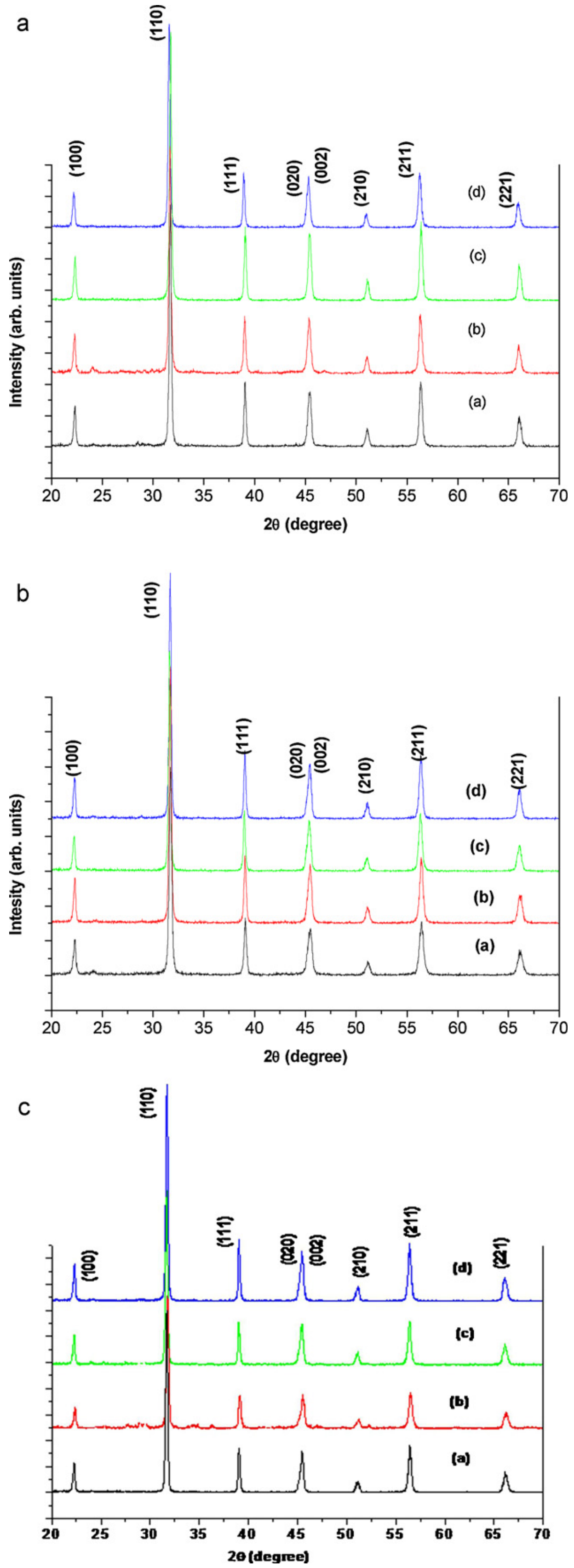

Fig. 2. (a) XRD patterns of (a) BCT1, (b) BCT2, (c) BCT3 and (d) BCT4 samples. (b) XRD patterns of (a) BMT1, (b) BMT2, (c) BMT3 and (d) BMT4 samples. (c) XRD patterns of (a) BST1, (b) BST2, (c) BST3 and (d) BST4 samples.

developed in BCT, BMT and BST ceramic samples at 900 °C calcinations temperature. Calcination temperature of the iso-valent ions substituted BCT, BMT and BST ceramic samples, synthesized by MSSR route, is significantly lower than the BT based systems processed through SSR route [10,19]. Lowering of calcination temperature in these ceramic samples is attributed to the fine particle size of the starting precursors. It can be clearly seen from Fig. 2(a–c) that the intensities of XRD peaks is increasing with the increase in Ca, Mg and Sr substitution% in BCT, BMT & BST ceramic samples. This suggests that Ca, Mg and Sr ions in BCT, BMT and BST ceramic samples are mixing well. The ionic size of Ca^{2+} (0.99 Å), Mg^{2+} (0.66 Å) and Sr^{2+} (1.12 Å) ions is smaller than the replacing Ba^{2+} (1.34 Å) ions in BCT, BMT and BST ceramic samples. Reactivity of a particle increases with the decrease of particle size [20,21]. Therefore, with the increase of incorporation of smaller ionic size Ca^{2+}, Mg^{2+} and Sr^{2+} ions in place of larger size Ba^{2+} ions in BCT, BMT and BST ceramic samples, the reactivity between precursors increases, which give rise the increase in crystallinity and the increase of XRD peaks intensities. The diffraction lines of BCT, BMT and BST sintered ceramics were indexed in different crystal systems and unit cell configurations using a computer program package 'Powdmult' [22]. The appropriate structure was chosen for which the standard deviations, $\Sigma\,\Delta d\ (=d_{obs} - d_{cal})$, where '$d$' is interplaner spacing is found to be minimum. The structures of these ceramics are given in Table 1. In BCT, BMT and BST systems a tetragonal structure is found. The tetragonality (c/a ratio) increases with the increase of Ca substitution% and it decreases with the increase in Mg and Sr substitution% in BCT, BMT and BST ceramic samples, respectively. Tetragonality is a measure to specially characterize the lattice structure of materials with a tetragonal structure. The tetragonality is dependent directly on grain size and indirectly on material processing. Generally, tetragonality decreases with decreasing grain size. Here, with the increase of Ca substitution% in BCT ceramic samples the grain size increases, which leads to increase in tetragonality in BCT ceramic samples. Whereas, with the increase of Mg and Sr substitution% in BMT and BST ceramic samples, the grain size decreases which leads to decrease in tetragonality in these systems [23].

Fig. 3 (a–c) shows the scanning electron micrographs (SEM) of iso-valent substituted BCT, BMT and BST ceramic samples. The average grain size is calculated by using the linear intercept method and is given in Table 1. The grain size and uniformity of the grains increases with the increase of Ca substitution% in BCT system, indicating the good solubility of Ca in BCT system. With the increase in Sr and Mg substitution% in BST and BMT ceramic samples, the grain size decreases. Earlier, same type of grain size dependence has been reported in case of Mg substitution in BST ceramics [24].

Fig. 4(a–c) represents the effect of simultaneous variation of temperature and Ca, Mg and Sr substitution% on dielectric properties of BCT, BMT and BST ceramic samples. RT values of ε_r at 1 kHz frequency of these ceramics are given in Table 1. Value of ε_r at 1 kHz frequency of sintered BCT samples first decreases and then increases with the increase in temperature.

Table 1
Structural, dielectric and piezoelectric parameters of iso-valent modified BT ceramics.

System	BCT1	BCT2	BCT3	BCT4
Structure	Tetragonal $c/a = 1.0150$	Tetragonal $c/a = 1.0158$	Tetragonal $c/a = 1.0162$	Tetragonal $c/a = 1.0167$
Grain size (μm)	10	18	22	27
ε_r at 1 kHz	1231	1422	1270	1104
d_{33} (pm/V)	27	137	228	230
System	BMT1	BMT2	BMT3	BMT4
Structure	Tetragonal $c/a = 1.0134$	Tetragonal $c/a = 1.0131$	Tetragonal $c/a = 1.0128$	Tetragonal $c/a = 1.0136$
Grain size (μm)	1.33	1.23	1.14	0.7
ε_r at 1 kHz	1465	1470	1482	1576
d_{33} (pm/V)	91	86	258	172
System	BST1	BST2	BST3	BST4
Structure	Tetragonal $c/a = 1.0142$	Tetragonal $c/a = 1.0138$	Tetragonal $c/a = 1.0131$	Tetragonal $c/a = 1.0120$
Grain size (μm)	2.05	1.29	1.17	0.94
ε_r at 1 kHz	1473	2131	2170	2374
d_{33} (pm/V)	280	210	228	315

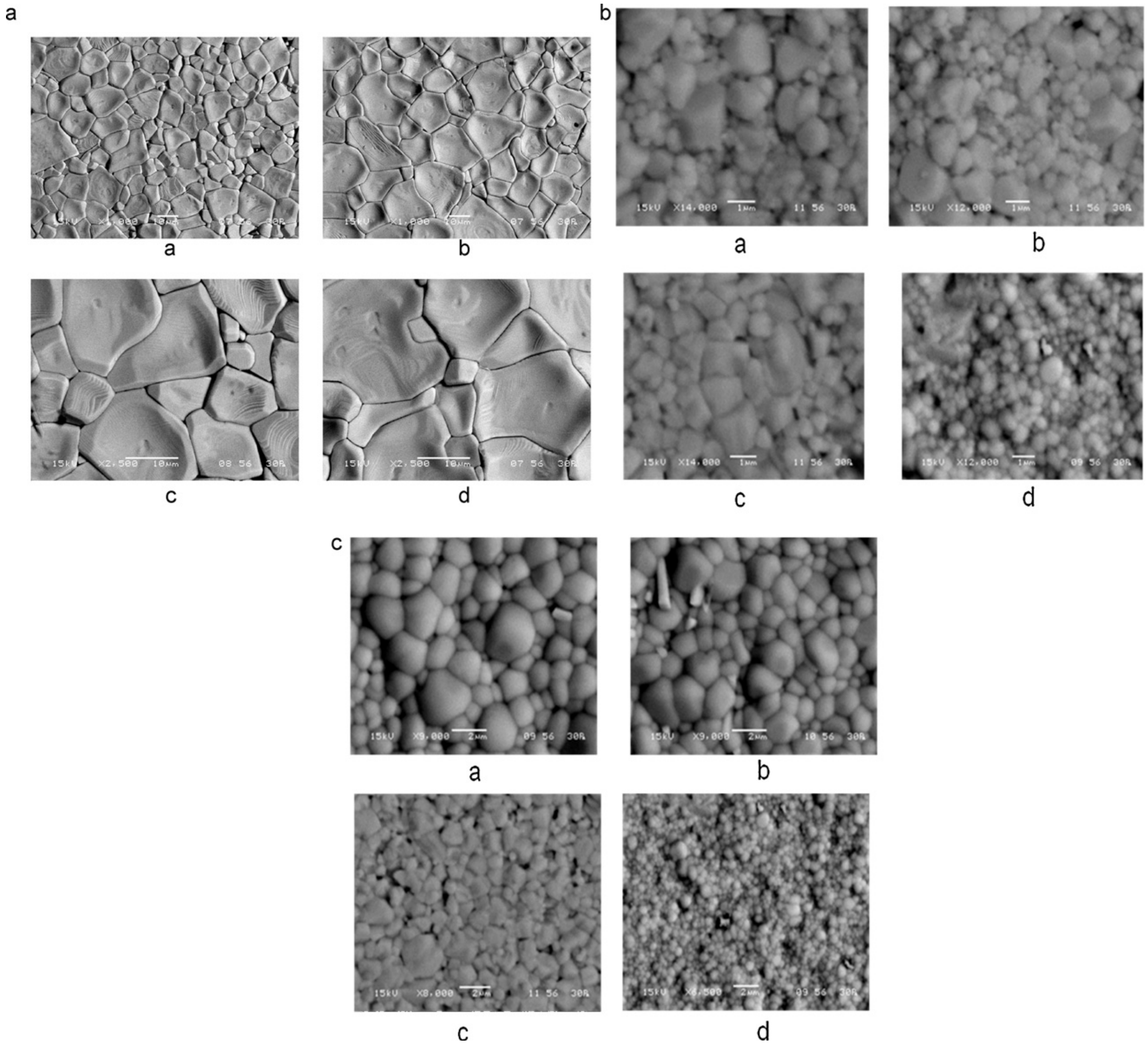

Fig. 3. (a) SEM micrographs of sintered SEM micrographs of sintered (a) BCT1, (b) BCT2, (c) BCT3 and (d) BCT4 samples. (b) SEM micrographs of sintered SEM micrographs of sintered (a) BMT1, (b) BMT2, (c) BMT3 and (d) BMT4 samples. (c) SEM micrographs of sintered (a) BST1, (b) BST2, (c) BST3 and (d) BST4 samples.

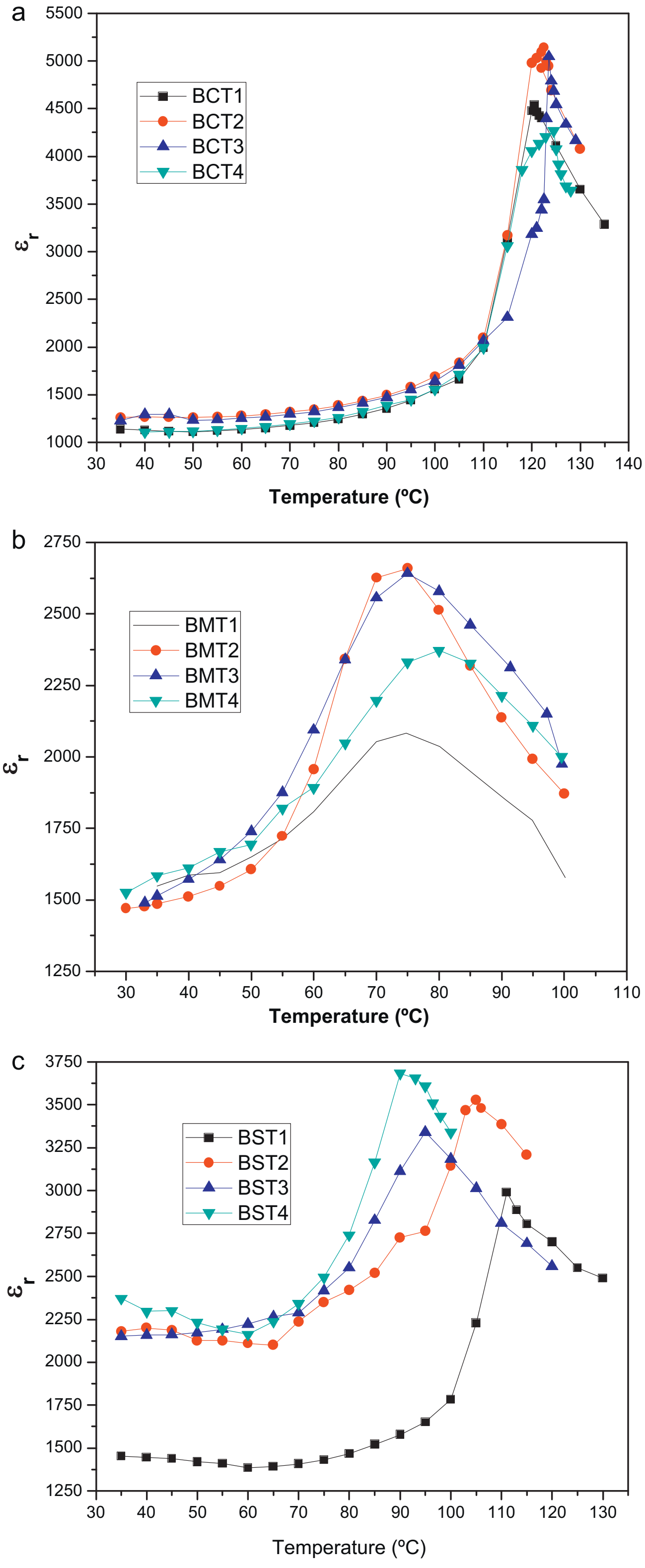

Fig. 4. (a) Temperature variation of ε_r at different frequencies of sintered BCT samples. (b) Temperature variation of ε_r at different frequencies of sintered BMT samples. (c) Temperature variation of ε_r at different frequencies of sintered BST samples.

The initial decrease in ε_r with the increase in temperature of BCT ceramic samples suggest that the orthorhombic to tetragonal structure transformation temperature, $T_{(o\text{–}t)}$, is just below room temperature [25]. Since, near $T_{(o\text{-}t)}$ temperature, value of ε_r is maximum than nearby temperatures [7]. Here, the value of ε_r of BCT, BMT and BST ceramic samples is more than the same systems synthesized by other routes [10,19]. The temperatures corresponding to maximum ε_r and where the structure of the material transform from non-cubic to cubic structure is known as Curie temperature (T_c) [7,26]. It can be seen from the Fig. 4(a) that with the increase of Ca substitution% in BCT samples, the transition temperature increases. This is also confirmed by XRD study. With the increase of Ca substitution% in BCT ceramic samples, the tetragonality (determined by X-ray diffraction study and given in Table 1) increases. It is also well established that the increase in tetragonality leads to increase in T_c [7]. This explains the increase of T_c with the increase of Ca substitution% in BCT samples. With the increase of Ca substitution% in BCT samples, the value of ε_r at RT first increases and then beyond 4% substitution of Ca, it decreases. As reported earlier, with the increase of Ca substitution% 4 in BCT samples, Ca can go to Ti sites, which would lead to creation of oxygen vacancies [27]. These oxygen vacancies would pins the movement of the ferroelectric domains walls and hence result in the decrease in dielectric constant [28]. It can be seen from Fig. 4(b) that with the 2% substitution of Mg in BMT samples, the transition temperature (T_c) decreases to 75 °C and it does not decrease with the further increase in Mg substitution%. Whereas, as shown in Fig. 4(c), with the increase of Sr substitution% in BST system, the position of T_c decreases gradually from 111 to 90 °C. The same type of dielectric phenomena is observed in earlier reports on Mg and Sr substitution in BMT and BST samples [29–31]. With the increase of Mg and Sr substitution% in BMT and BST samples, the value of ε_r at 1 kHz and at RT increases (given in Table 1). This is due to the decrease in T_c. Lowering of T_c shifts the position of temperature corresponding to $\varepsilon_{r\max}$. towards the RT side and hence there is increase in ε_r value at RT with the increase in Mg and Sr substitution% in BMT and BST systems [7,26]. The highest value of ε_r at 1 kHz and at RT is found in BST4 ceramic samples.

Fig. 5(a–c) shows the strain vs. electric field loops of the iso-valent substituted BCT, BMT and BST ceramic samples synthesized by MSSR route. Development of butterfly shape loops hints towards the piezoelectric nature of these samples [32]. Symmetric nature of the S–E loops increases with the increase in Ca substitution% in BCT samples hinting towards the increase in piezoelectric nature [33]. Again symmetric nature increases but hysteresis of the S–E loops decreases with the increase in Mg and Sr substitution% in BMT and BST samples. This decrease of S–E hysteresis hints that with the increase of Mg and Sr substitution% in BMT, BST systems, these ceramics are transforming from piezoelectric to electrostrictive nature [33]. This is as per XRD and dielectric study, where we have reported that with the increase of Mg and Sr substitution% in BMT and BST systems, the tetragonality decreases. Piezoelectric coefficient, d_{33}, has been calculated from converse piezoelectric effect,

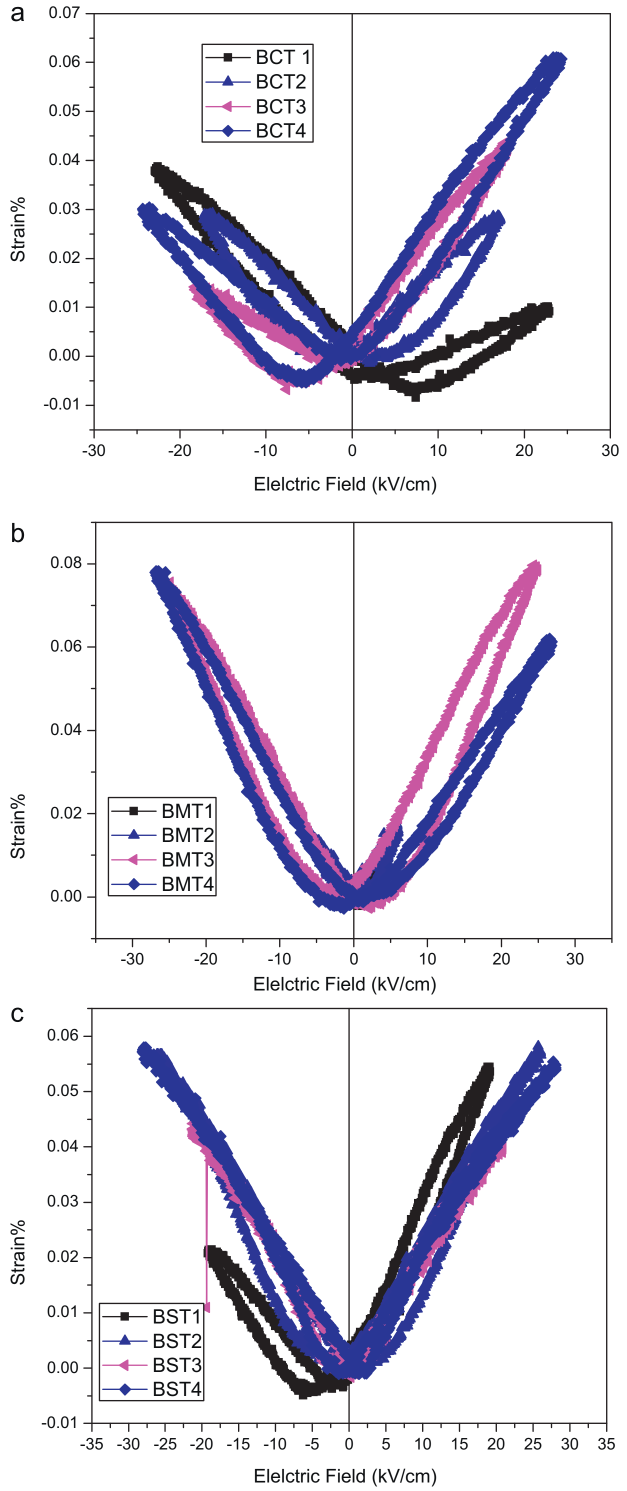

Fig. 5. (a) Strain versus bipolar electric field loop of (a) BCT1, (b) BCT2, (c) BCT3 and (d) BCT4 samples. (b) Strain versus bipolar electric field loop of (a) BMT1, (b) BMT2, (c) BMT3 and (d) BMT4 samples. (c) Strain versus bipolar electric field loop of (a) BST1, (b) BST2, (c) BST3 and (d) BST4 samples.

i.e. by using the slope of the strain vs. electric field plot in the higher field region, using the relation [34]

$$d_{33} = \left(\frac{\Delta \text{strain}\%}{\Delta \text{electric field at higher side}} \right) \qquad (1)$$

The d_{33} piezoelectric coefficient, calculated from the slope of strain vs. electric field plots are given in Table 1. Among iso-valent modified samples, a piezoelectric coefficient as high as 315 pm/V is found in BST4 system suggesting its importance for piezoelectric applications.

4. Conclusions

Dense iso-valent ion substituted BCT, BMT and BST ceramic samples were synthesized in single perovskite phase at lower processing temperatures by MSSR route. Increase in XRD peak intensity with the increase of Ca, Mg and Sr substitution% in BCT, BMT and BST ceramic samples suggested the increase of crystallinity. Negligible temperature coefficient of capacitance from RT to 70 °C in BCT1, BCT2 and BCT3 samples made these ceramic samples important candidates for capacitors applications. A piezoelectric coefficient ~315 pm/V is found in BST4 ceramic samples suggesting its importance for piezoelectric applications.

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