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Structural and dielectric characterization of Sr substituted Ba(Zr,Ti)O_3 based functional materials

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ABSTRACT Single phase Sr substituted $BaZr_{0.1}Ti_{0.9}O_3$ (also known as BZT) ceramics with a formula $Ba_{1-x}Sr_xZr_{0.1}Ti_{0.9}O_3$ ($x = 0.10$, 0.20, 0.30, 0.40 and 0.50) are prepared using a solid state reaction of mixed oxides at 1250 °C for 15 h. Analysis of XRD patterns of the ceramic powders show that Sr substitutes into Ba sites and reduces the lattice parameter. The powders are sintered at 1600 °C for 6 h to investigate the microstructure and functional properties. It is found that strontium substitution significantly modifies the microstructure and greatly influences the dielectric properties. The increase in Sr content reduces the ceramic grain size and results in spherical grains. With an increase in Sr content, the Curie temperature is lowered, and the relative permittivity maximum is increased and broadened. In $Ba_{1-x}Sr_xZr_{0.1}Ti_{0.9}O_3$ with $x = 0.30$, the relative permittivity reached a maximum of 26 600 and with further increase of Sr content, the relative permittivity is lowered and the phase transition is found to be broad and diffused. The ferroelectric hysteresis characteristics are discussed in detail.

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1 Introduction

Modified barium titanate ($BaTiO_3$) compounds have been of great interest since $BaTiO_3$ was discovered to be a ferroelectric with a wide variety of electrical properties. In recent years, materials of high dielectric constant have been in great demand for use in memory devices, capacitors, and high *k*-dielectrics among other applications [1, 2]. Barium strontium titanate (BST) is a perovskite based ferroelectric and has been widely studied because of its high dielectric constant and the Ba/Sr ratio, which is a dependant variable of the phase transition temperature (T_C) [3–6]. The T_C and dielectric properties of these compounds can be modified by substituting isovalent and aliovalent ions for both Ba (A-site) and/or Ti (B-site) ions in $BaTiO_3$ [2]. The substitution of Zr^{4+} in place of Ti^{4+} has shown the decrease in leakage current in the $BaTiO_3$ based compounds [7]. It is reported that Ba (Zr,Ti)O_3 compounds also have good dielectric and ferroelectric properties [8–10]. It is of great interest to investigate the influence of Sr substitution in these to formulate compounds with tailor made dielectric and ferroelectric properties. A letter was reported on the processing of (Ba,Sr)(Zr,Ti)O_3 ceramics [11] and two other reports on the influence of dopants on the semiconductor properties of (Ba,Sr)(Zr,Ti)O_3 ceramics are available [12, 13]. However, no reported literature is available, hitherto, on the dielectric and microstructural characteristics of Sr substituted Ba(Zr,Ti)O_3 compounds.

In the present work, $BaZr_{0.1}Ti_{0.9}O_3$ compound was taken as the host compound for the substitutional studies of Sr, because of its high dielectric constant and superior ferroelectric properties among Ba(Zr,Ti)O_3 based compounds [14, 15]. The Sr content is varied from 10 mol % to 50 mol % by maintaining the Ba(Sr)/Ti ratio equal to 1.0.

2 Experimental

Samples were prepared using the solid state mixed oxide route using powders of $BaCO_3$ (99.9%), $SrCO_3$ (99.9%), TiO_2 (99.9%) and ZrO_2 (99.9%). The powders were weighed as per stoichiometry (with the Sr content varying from 10 mol % to 50 mol % in steps of 10 mol % in $BaZr_{0.1}Ti_{0.9}O_3$) and mixed thoroughly in agate mortar for 2 h. Distilled water is added while mixing the ingredients to ensure homogeneous mixing. The mixed powder slurry is dried in an oven at 150 °C to remove water. The dried mixture is ground and heat treated in closed alumina crucibles at 1250 °C for 15 h. The heat treated powder is characterized to observe the $Ba_{1-x}Sr_xZr_{0.1}Ti_{0.9}O_3$ (BSZT) single phase formation using X-ray diffraction (SHIMADZU) with a scan rate of 0.02 degree/step and with a step time of 2 s. Furthermore, the BSZT powders are compacted into disc shaped pellets of 10 mm diameter and 2 mm thickness at a compaction pressure of 300 MPa. The pellets are then sintered at 1600 °C for 6 h in a high temperature furnace (Nabertherm). The densities of the sintered pellets are measured using Archimedes principle. The sintered pellets are polished to a mirror finish on both sides and etched thermally for microstructural investigation using a scanning electron microscope (JEOL). For the electrical properties study, the polished pellets are metallized with silver paste on both sides and dried in an oven. These metallized pellets are used to measure the dielectric properties as a function of temperature and frequency using an impedance analyzer (HP 4192A). The room temperature ferroelectric

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hysteresis behaviour of the selected compounds in the unpoled condition is measured using a modified Sawyer–Tower circuit.

3 Results and discussion

3.1 *Phase formation*

The phase formation is confirmed by X-ray diffraction study and the XRD patterns of BSZT with varying Sr content (10 mol % to 50 mol %) are shown in Fig. 1. From the figure, the single phase formation without any impurity phase for all the Sr contents can be clearly observed. This confirms the complete solid solubility of Sr (up to $x = 50$ mol %) in BZT and this is in agreement with the reported literature [16]. The close observation of the X-ray diffraction data indicate shifts in diffraction peaks toward higher 2θ values (Fig. 2). This indicates the reduction of the lattice parameter with an increase in the Sr content. The reduction in the lattice parameter can be explained because of the low ionic radius Sr^{2+} ion (1.44 Å) substituting the higher ionic radius Ba^{2+} ion (1.61 Å). This also clearly confirms the substitution of Sr^{2+} in Ba^{2+} sites without the possibility of substituting at Ti^{4+}/Zr^{4+} sites as the ionic radii of Ti^{4+} and Zr^{4+} are 0.61 Å and 0.72 Å respectively that are much smaller than that of Sr^{2+} or Ba^{2+}.

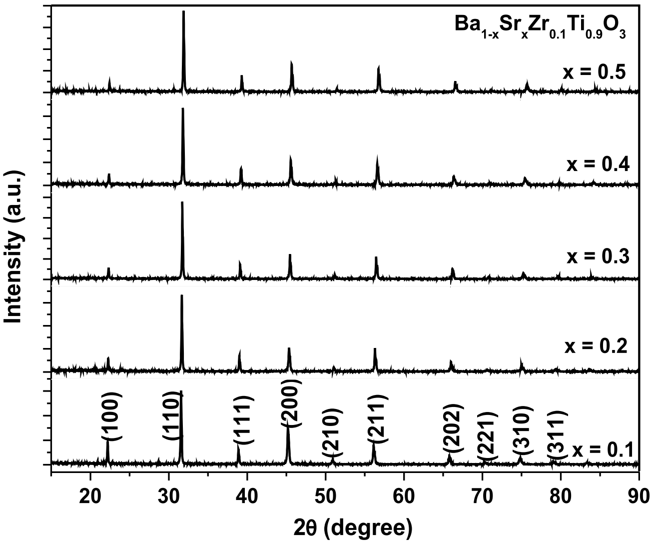

FIGURE 1 X-ray diffraction patterns of Sr (10–50 mol %) substituted $BaZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at 1250 °C for 15 h

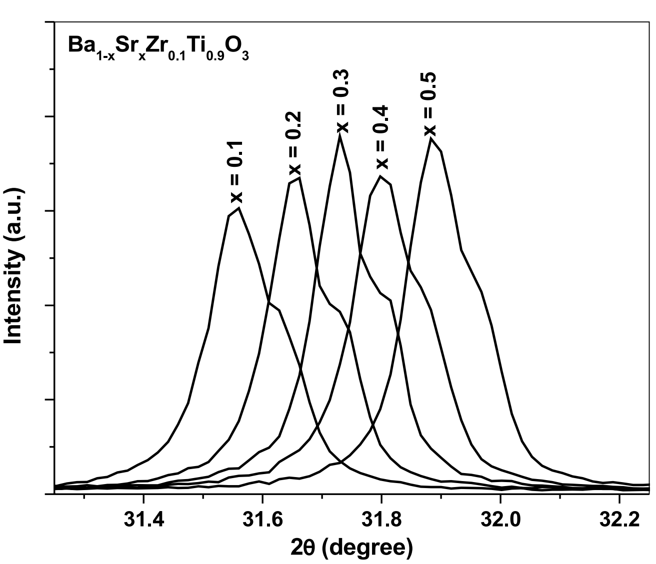

FIGURE 2 X-ray diffraction patterns of Sr (10–50 mol %) substituted $BaZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at 1600 °C for 6 h

3.2 *Microstructure*

The microstructural details of the Sr (0 mol % $\leq$ Sr $\leq$ 50 mol %) substituted BZT ceramics are shown in Figs. 3a–d. Figure 3a shows the microstructure of the parent compound and Fig. 3b shows the microstructure of the 10 mol % Sr substituted BZT ceramic. It can be observed that the grain size is very widely distributed from submicron size to more than 100 μm with irregular shaped grains with a change in Sr content in BZT. As the Sr content is increased, the grain size distribution is narrowed down and the grains became more spherical as can be observed from Figs. 3c–d. The smaller grains merge with each other with the increase in Sr content and grow into larger ones thereby increasing the fraction of the larger grains in the overall microstructure. The maximum density achieved in these compounds with different Sr contents (10 mol % to 50 mol %) varied from 93% to 96% of the theoretical density. All the ceramics have triple point porosity which is commonly observed in solid state oxide mixing processed ceramic materials.

3.3 *Dielectric properties*

The effect of Sr substitution on the dielectric constant of BZT compound as a function of temperature is shown in Fig. 4. With increasing Sr content, the Curie temperature (T_C) of the BZT compound decreases linearly (Fig. 5). The decrease in T_C is very steep with the increase in Sr content. The dielectric constant at T_C initially increased with the increase in Sr content and reached a maximum of $\sim 26\,600$ at 30 mol % of Sr. With further increase in Sr content, the dielectric constant at T_C decreased. The 10 mol % Sr substituted BZT exhibited a broad phase transition and with further increase in the Sr content the phase transition was sharp at 30 mol % Sr. With further increase in Sr beyond 30 mol % the phase transition broadened further (the full width at half maximum (FWHM) of the transition peaks for 10, 30 and 50 mol % Sr are 60.3°, 23.6° and 36.8° respectively). This can be explained by considering the amount of paraelectric (cubic) and ferroelectric (tetragonal, rhombohedral and orthorhombic) phases that exist in the compound along with the amount of structural distortion (due to the ionic size differences between Ba^{2+} and Sr^{2+}) that can result from the introduction of Sr in to the BZT compound. The effect of Sr and Zr isovalent substitution on the three phase transition temperatures (rhombohedral to orthorhombic – T_{RO}, orthorhombic to tetragonal – T_{OT} and tetragonal to cubic – T_{TC}) in $BaTiO_3$ was explained previously [2]. With an increase in the Sr content, T_{TC} is reduced drastically and T_{OT} decreases moderately, whereas T_{RO} is slightly increased. However, an increase in the Zr content strongly decreases the T_{TC} and increased the T_{OT} and T_{RO}. Since the base compound in the present case is 10 mol % Zr substituted $BaTiO_3$, the three transition temperatures approach each other. Further substitution

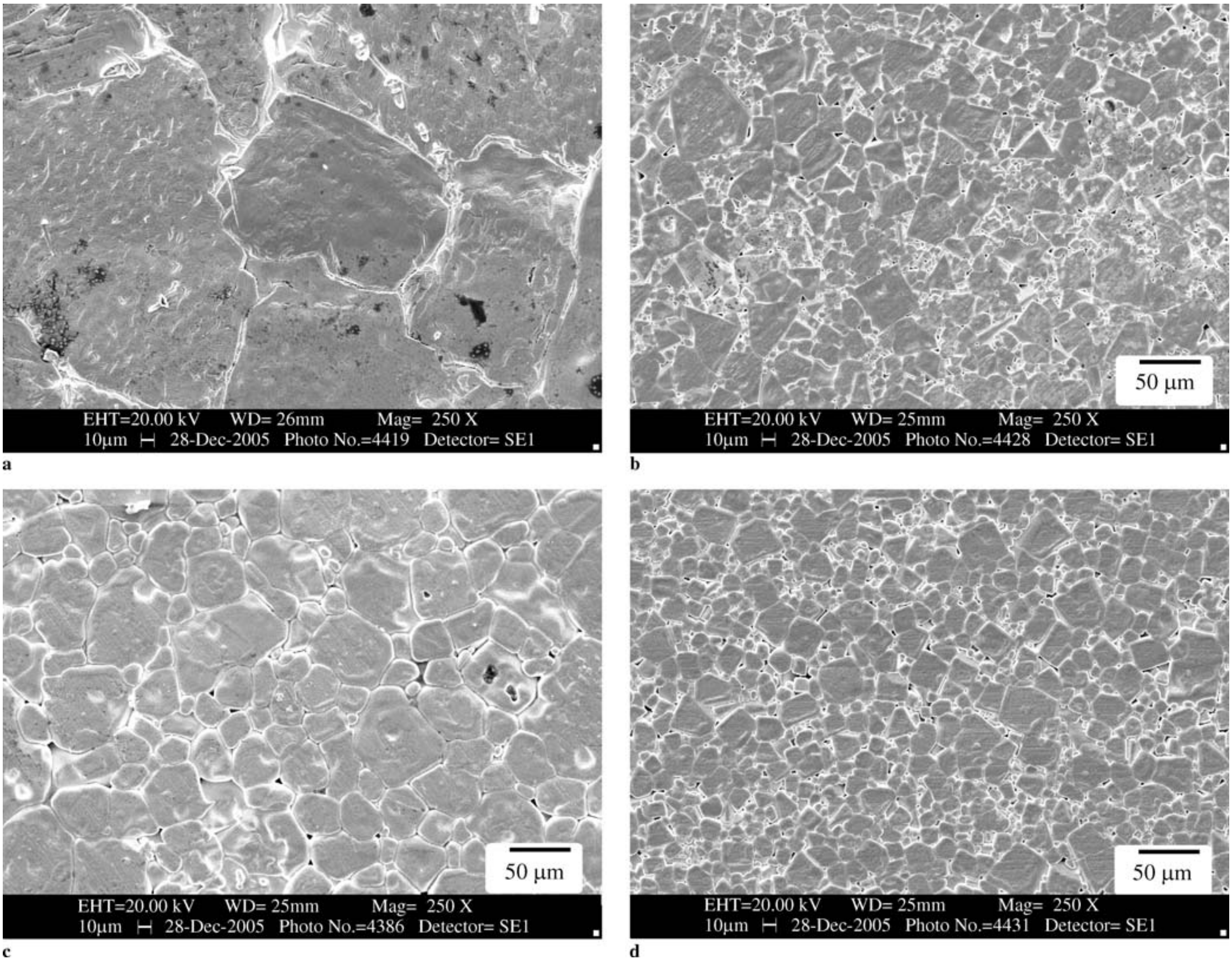

FIGURE 3 SEM pictures of the $Ba_{1-x}Sr_xZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at 1600 °C for 6 h. (**a**) $x = 0.0$, (**b**) $x = 0.10$, (**c**) $x = 0.30$ and (**d**) $x = 0.50$

of Sr brings them much closer. This explains the decrease in the dielectric maximum and broadening of the phase transition in compounds with Sr content of more than 30 mol %. It is also observed that the room temperature dielectric constant is extremely high for the 30 mol % Sr substituted BZT compound (∼ 14 000). Figure 6 shows the dielectric loss behaviour of the BZT compound substituted with different Sr contents ($10 - 50$ mol %). It can be observed that the compound with 10 mol % Sr substitution has two loss peaks and this could be due to the merger of the low temperature phase transitions with the high temperature phase transition, that are usually observed in the case of $BaTiO_3$ [2]. With further increase in Sr content, the two peaks are found to be merged and a single large peak appears for 30 mol % Sr substituted BZT. The high loss of this composition is associated with a high dielectric constant. Beyond 30 mol % of Sr substitution, the dielectric loss is considerably decreased to 0.05. The low loss coupled with high dielectric constant make these materials suitable for many ferroelectric device applications.

Figure 7 shows the frequency dependence of the dielectric behavior as a function of temperature for 30 mol % Sr substituted BZT compound. It can be observed that with increase in frequency the dielectric maximum at the transition is reduced, which is commonly observed in this type of material. The dielectric constant as a function of Sr content at T_C and room temperature are given in Fig. 8. It can be observed that the dielectric constant both at T_C and room temperature is a maximum for the 30 mol % Sr substituted BZT compound ($Ba_{0.7}Sr_{0.3}Zr_{0.1}Ti_{0.9}O_3$). All the Sr substituted compounds (except 50 mol % of Sr substituted compound) have a room temperature dielectric constant of more than 4000 which make these compounds potential candidates for device applications.

3.4 *Ferroelectric properties*

Figure 9 shows the room temperature ferroelectric hysteresis curves and Table 1 summarizes the parameters viz., Curie temperature, remanent polarization (P_r) and coercive field (E_c) for all the Sr substituted BZT compounds. All these measurements were carried out in the unpoled sample condition. The P_r and E_c values initially are found to increase with the increase in Sr content. The increase in Sr content increases the structural distortion initially and there by increases the ferroelectric phase which in turn increases the polarization in the ceramics. The maximum P_r value (8.52 $\mu C/cm^2$) is observed

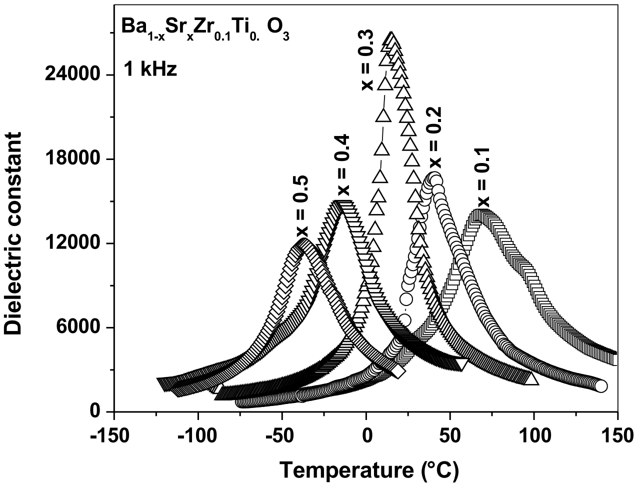

FIGURE 4 Dielectric constant as a function of temperature for different Sr substituted (10–50 mol %) $BaZr_{0.1}Ti_{0.9}O_3$ ceramics prepared by the solid state mixed oxide route and sintered at 1600 °C for 6 h

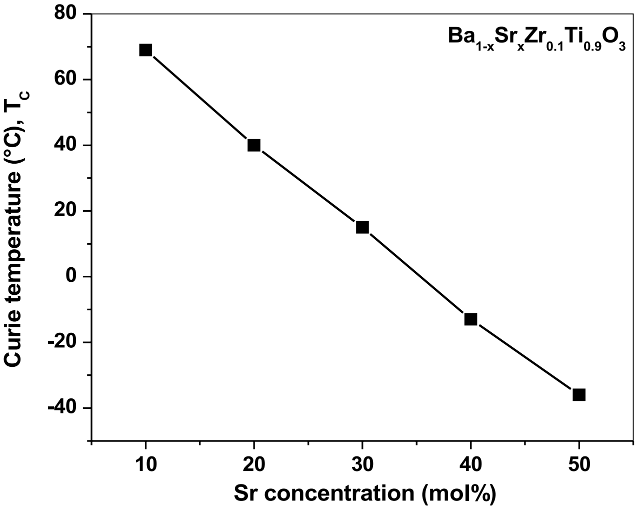

FIGURE 5 Effect of Sr concentration on the Curie temperature of the Sr substituted (10–50 mol %) $BaZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at 1600 °C for 6 h

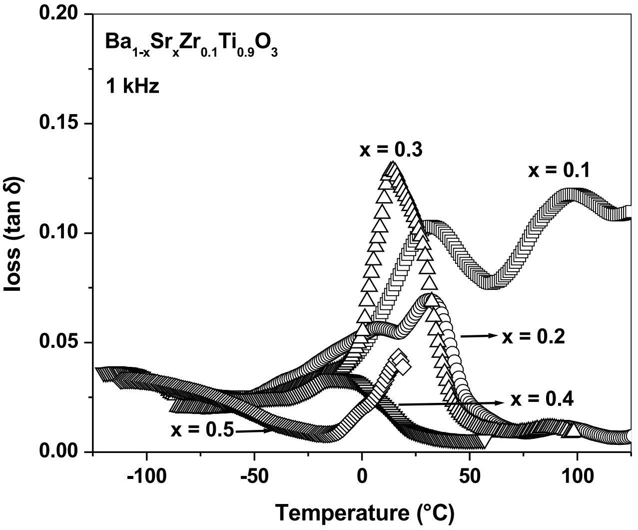

FIGURE 6 Dielectric loss as a function of temperature for $BaZr_{0.1}Ti_{0.9}O_3$ compound substituted with different Sr contents (10–50 mol %) and sintered at 1600 °C for 6 h

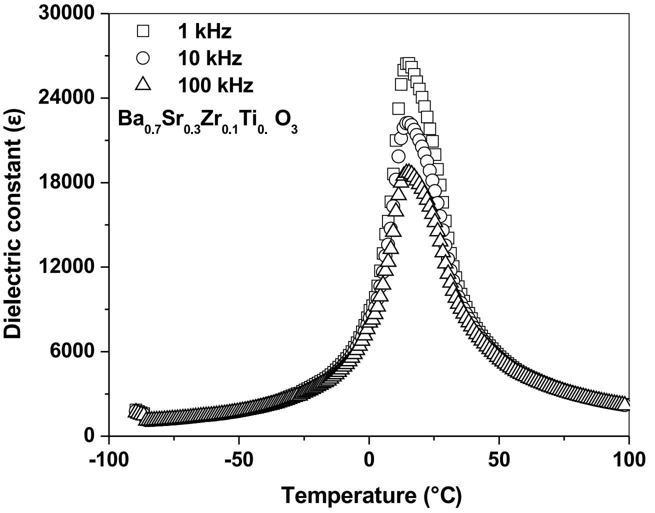

FIGURE 7 Dielectric constant as a function of temperature for 30 mol % Sr substituted $BaZr_{0.1}Ti_{0.9}O_3$ ceramics prepared by the solid state mixed oxide route and sintered at 1600 °C for 6 h

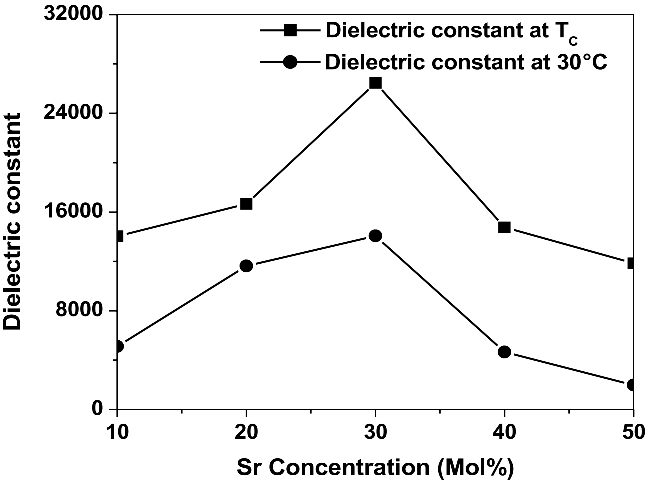

FIGURE 8 Effect of Sr concentration on the dielectric constant at the Curie temperature (T_C) and at room temperature of Sr (10–50 mol %) substituted ceramic sintered at 1600 °C for 6 h

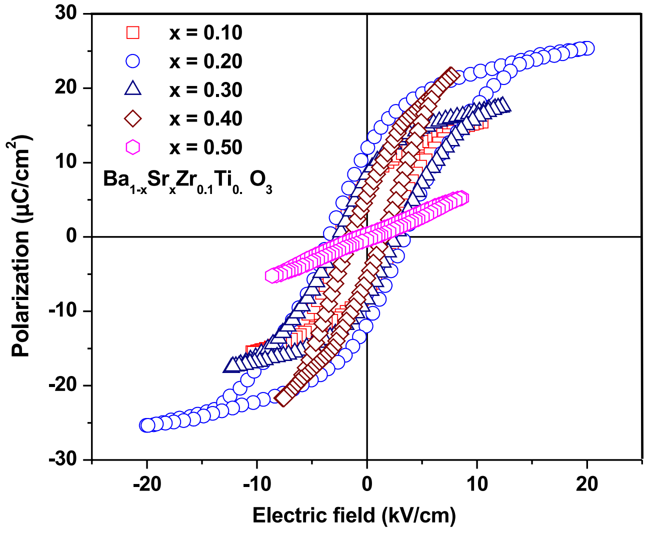

FIGURE 9 Room temperature ferroelectric hysteresis behaviour of Sr (10 mol % to 50 mol %) substituted $BaZr_{0.1}Ti_{0.9}O_3$ ceramics sintered at 1600 °C for 6 h and in the un-poled condition

mol% of Sr	T_C(°C)	Remanent polarization ($\mu C/cm^2$)	Coercive field (kV/cm)
10	69	8.23	2.62
20	40	11.82	3.21
30	15	8.52	2.60
40	−13	5.23	1.68
50	−36	0.26	0.62

TABLE 1 Details of Curie temperature (T_C), remanent polarization, and coercive field of Sr (10 mol % to 50 mol %) substituted $BaZr_{0.1}Ti_{0.9}O_3$ compositions sintered at 1600 °C for 6 h

for 20 mol % Sr substitution whereas the dielectric maximum (26 600) was observed for 30 mol % Sr substitution. It can be seen from the Table 1 that the T_C of 20 mol % Sr substituted BZT is 40 °C, which is close to room temperature at which measurements are carried out. This effectively results in the measurement of hysteresis behaviour at the T_C of the compound, at which maximum polarization is observed. However, the T_C for 30 mol % Sr substituted BZT is 15 °C which is quite below the hysteresis measurement temperature. Beyond the T_C the amount of paraelectric phase is very high and hence the polarization values are low. Moreover, the measurements were carried out in the unpoled condition and hence, the ferroelectric components that exist in the material may not add up for complete polarization. With further increase beyond the 20 mol % of Sr, the paraelectric phase increases in amount at room temperature and this results in the decreasing polarization values for Sr contents greater than 20 mol %. At 50 mol % of Sr content, the curve is almost linear and no hysteresis is observed.

4 Conclusions

Single phase Sr (10−50 mol %) substituted $BaZr_{0.1}Ti_{0.9}O_3$ ceramics were prepared successfully without any impurity phase. X-ray diffraction studies confirmed the substitution of Sr^{2+} ion in the Ba^{2+} ionic site to form a complete solid solution. Substitution of Sr^{2+} resulted in a wide grain size distribution resulting in irregularly shaped grains. With an increase in the Sr^{2+} content, the grain size distribution was narrowed down and the grains became round in shape. It was also observed that the T_C of the $BaZr_{0.1}Ti_{0.9}O_3$ decreased steeply with increase in the Sr^{2+} content on substitution. High dielectric maximum is observed in the case of 30 mol % Sr^{2+} substituted $BaZr_{0.1}Ti_{0.9}O_3$ ceramic, and the dielectric maximum decreased with a further increase in Sr content. It is observed that all the Sr^{2+} substituted $BaZr_{0.1}Ti_{0.9}O_3$ compounds (except 50 mol % of Sr substituted compound) exhibit a dielectric constant of more then 4000 at room temperature. The highest remanent polarization in this series of compounds is observed in 30 mol % Sr^{2+} substituted $BaZr_{0.1}Ti_{0.9}O_3$ ceramic (8.52 $\mu C/cm^2$).

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