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Study of Electrical Properties of Lead-free BCZT Ceramic $(Ba_{0.80}Ca_{0.20}Zr_{0.1}Ti_{0.9})O_3$ at Different Sintering Temperatures

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There is a tremendous growth in the demand for high performance lead-free ceramics due to environmental issues. In the present work, the traditional solid-state sintering technique at different sintering temperatures, namely, 1380, 1400 and 1420 ^{o}C has been employed to prepare lead-free $(Ba_{0.80}Ca_{0.20}Zr_{0.1}Ti_{0.9})O_3$ ceramics. Detailed XRD analysis suggests pure perovskite structure for the ceramic synthesized at higher sintering temperature 1420 ^{o}C without any impurities. Density measurement using Archimedes principle shows a trend of increased densification with increasing sintering temperature. Room temperature frequency dependent dielectric constant study indicates high value of dielectric constant (ε_{rt}= 2665-2490) in the frequency range100 Hz-100 kHz for the ceramic sintered at 1420 ^{o}C. Temperature dependent dielectric studies at constant frequency (10 kHz) indicates that ceramic prepared at 1420 ^{o}C has high Curie temperature T_c =77 ^{o}C. Ferroelectric properties of the ceramics are enhanced by raising the sintering temperature from 1380 to 1420 ^{o}C with higher spontaneous polarisation of P_s = 7.68 μC/cm^2 corresponding to 1420 ^{o}C ceramic. The reasonably high values of Curie temperature, room temperature dielectric constant in the large frequency range and improved ferroelectric properties of the ceramic prepared at 1420 ^{o}C indicate that this ceramic can be a good candidate for being developed into commercially viable lead-free ferroelectric material.

Keywords: Lead free; Dielectric properties; Sintering temperature

1 Introduction

For years, the use of lead-based perovskite ferroelectrics, such as (PZT), have been studied mainly as the primary material due to their superior piezoelectric properties[1,2,3], but due to their adverse impact on environment, the quest of alternate lead-free material was started[4,5]. Barium titanate based piezoceramics are one such suitable candidates for replacing lead-based materials due to its high piezoelectric properties[6]. $(Ba_{0.80}Ca_{0.20}Zr_{0.1}Ti_{0.9})O_3$ (BCZT) is one such lead- free material that has shown remarkable piezoelectric properties when prepared under optimised conditions[7]. In the present paper the investigation is carried out to see the impact of different sintering temperatures on the dielectric and ferroelectric properties of BCZT[8].

2 Materials and Methods

$(Ba_{0.80}Ca_{0.20}Zr_{0.1}Ti_{0.9})O_3$ ceramics, abbreviated as BCZT, were synthesized using stoichiometrically weighed raw powders of $BaCO_3$ (99.0% purity), $CaCO_3$ (99.5%), ZrO_2 (99.5%) and TiO2 (99.5%). These powders were firstly mixed using agate mortar and pestle for about 45minutes. The mixture was then dried using an oven at 70 ^{o}C for 24 h. The mixture was grinded before and after calcinations using agate mortar and pestle for about 45 minutes to maintain its homogeneity. In this preparation, double calcination was conducted at 1175 and 1200 ^{o}C for 4h each in air to get purer form of the perovskite structure. (Furnace: Nabertherm P 310, Germany).

The calcined powder was granulated by adding 6wt % Polyvinyl alcohol (PVA) that acts as a binder, then the mixture was pressed under 320 MPa uniaxial hydraulic pressure to form green pellet disks of dimensions 1 mm thickness and 10 mm diameter.

The pellets were kept for 30 minutes at 600 ^{o}C for burning off the PVA before sintering. Sintering was performed at different sintering temperatures, namely 1380, 1400 and 1420 ^{o}C. These sintered pellets were then polished, silver coated and heated at 400 ^{o}C for about 1 h for performing dielectric and ferroelectric measurements.

For examining the crystallographic structure, XRD patterns were obtained using X-ray diffractometer with Cu-kα radiation (1.5406 Å) over 2Θ varying from 20^{o} to 80^{o}. Dielectric properties were studied as a function of frequency and temperature at a testing

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voltage of 1V using Impedance Analyzer (Wayne Kerr 6500B, Germany). Ferroelectric properties were examined with the help of a PE loop tracer system (Marine India) at a working frequency of 50 Hz. No deliquescence was observed when exposed to water for 24 h in any of the ceramic samples prepared. Bulk densities of the samples were estimated using Archimedes' principle.

3 Results and discussion

3.1 X-Ray Diffraction

Figure 1 represents the room temperature X-ray diffraction pattern of $(Ba_{0.80}Ca_{0.20}Zr_{0.1}Ti_{0.9})O_3$ at different sintering temperatures (1380,1400 and 1420 °C). We can clearly see that, the XRD plot for 1420 °C shows pure perovskite form without any secondary peaks. However, at 1380 and 1400 °C sintering temperatures, there are secondary peaks indicating that ceramic is not well prepared.

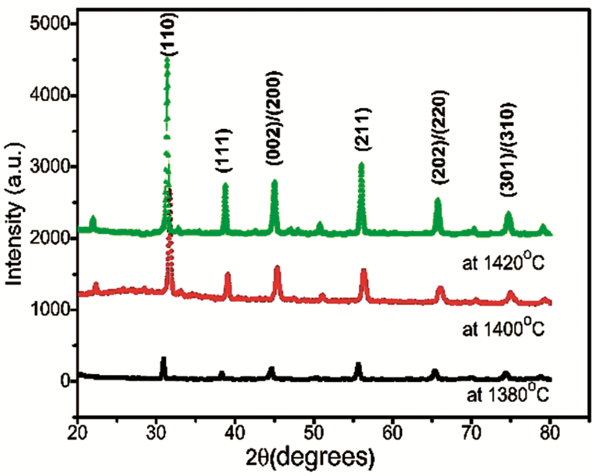

Fig. 1 — XRD pattern of BCZT at different sintering temperatures.

The crystallite size of the ceramics was calculated using Debye-Scherrer formula[9]

$$D = \frac{k\lambda}{\beta cos\theta}$$

where, D=crystallite size, k=shape factor (0.9, taken for spherical particles), λ= wavelength used (Cu-kα=1.5406 Å), β = FWHM (full width at half maximum).

Table 1 summarizes the crystallographic parameters for the ceramics prepared at different sintering temperatures. Interestingly, the crystallite size shows increasing trend with raising sintering temperature and maximizes for 1420 °C (D=28.28nm).

XRD peak for 1420 °C ceramic shows the cell volume as 64.50 Å^3 which is very close to that of the single crystal (64.48 Å^3, JCPDS File No. 891428).

3.2 Dielectric properties

Figure 2(a) shows frequency dependence of dielectric constant at room temperature for ceramics prepared at different sintering temperatures. It is clear from Fig. 2(a) that the dielectric constant is the highest in the frequency range of 100-100 kHz for the

Table 1 — Crystallographic properties of BCZT ceramics

Sintering Temp. (°C)	Lattice parameters (Å) a b c			Cell volume (Å^3) V	Crystallite Size (nm) D
1380	4.06	4.02	3.92	64.03	26.71
1400	3.99	3.97	4.03	64.03	22.38
1420	4.20	4.03	3.98	64.50	28.28

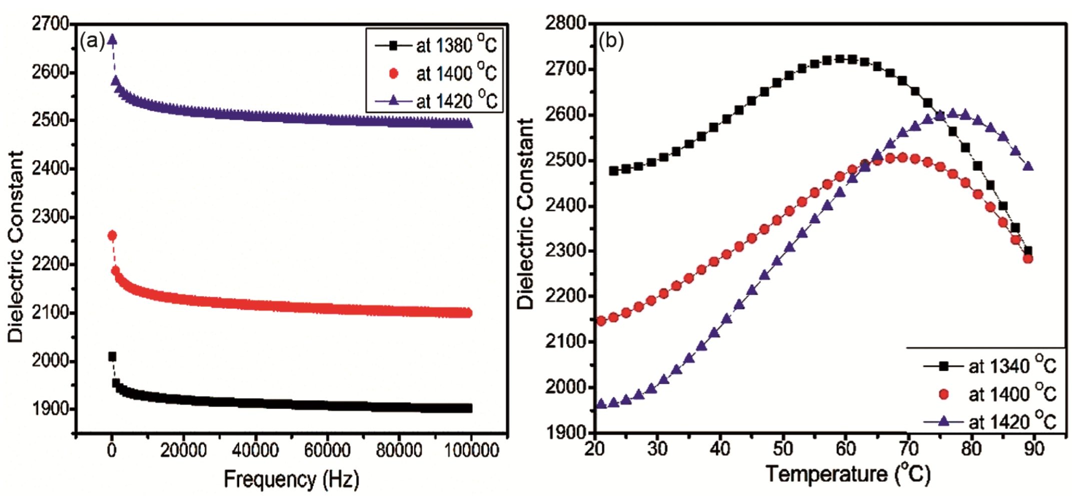

Fig. 2 — (a) Frequency dependence of dielectric constant at different Sintering temperatures.(b) Temperature dependence of dielectric Constant at 10kHz at different Sintering temperatures.

Table 2 — Dielectric & piezoelectric properties of BCZT ceramics

Sintering Temp.(°C)	1380 °C	1400 °C	1420 °C
Density (g/cm^3)	5.111	5.141	5.234
T_C (°C)	59	69	77
ε_r	2004	2260	2665
tan δ	0.012	0.016	0.005
P_r(μC/cm^2)	3.128	2.985	3.394
E_c(kV/cm)	4.557	4.819	4.502
P_S(μC/cm^2)	5.861	6.381	7.680

ceramic sintered at 1420 °C. Each dielectric constant curve shows a sudden drop, this is due to the withdrawal of one of the polarization contributions at higher frequencies.

Table 2 shows that frequency dependence of dielectric loss (*tan δ*) of ceramics prepared at different sintering temperatures. Dielectric loss data indicates that the ceramic prepared at 1420 °C shows lowest dielectric loss in comparison with ceramics prepared at other sintering temperatures, which emphasises that the ceramic sintered at 1420 °C is well densified.

Table 2 also enlists the densities of the ceramics calculated by Archimedes principle, which also supports the results of dielectric loss at 1420 °C.

Fig. 2(b) shows the temperature dependence of dielectric constant at 10 kHz frequency. Here we can see that the dielectric constant increases with increasing temperature and after Curie temperature T_C the dielectric constant starts decreasing. T_C also corresponds to the phase transition from ferroelectric phase to paraelectric phase. Moreover, we can see that the ceramic prepared at 1420 °C shows highest T_C.

Table 2 also shows values of Curie temperature (T_C) and density for different sintering temperatures. The values clearly shows that both Curie temperature (T_C) and density show increasing trends with the increase in sintering temperature and maximises at 1420 °C.

3.3 Ferroelectric properties

Figure 3 represents the room temperature PE-hysteresis curves measured at maximum applied electric field of 26kV/cm at frequency 50Hz.The well-shaped PE-loops confirm the ferroelectric nature of ceramics prepared at different sintering temperatures. The remnant polarisation (P_r) and coercive field (E_C) values listed in Table 2 were determined from Fig 3.

Table 2 shows the variation of remnant polarisation (**P_r**) and coercive field (E_C) at different sintering

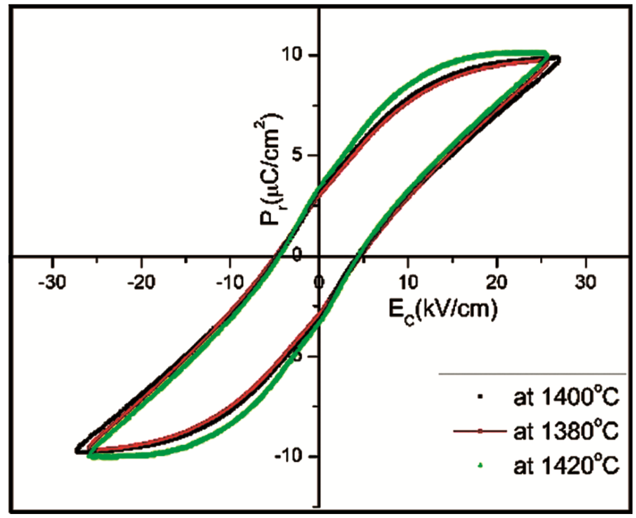

Fig. 3 — PE-hysteresis loops of $(Ba_{0.80}Ca_{0.20}Zr_{0.1}Ti_{0.9})O_3$.

temperatures. These values reveal that both P_r and E_c are greatly influenced by sintering temperature. P_r maximises at 1420 °C while E_c shows the lowest value at this sintering temperature. Furthermore, the ceramic which was prepared at 1420 °C shows the highest value of spontaneous polarisation (P_s).

4 Conclusion

The influence of different sintering temperatures (1380, 1400 and 1420 °C) on the structural, dielectric and ferroelectric properties of $(Ba_{0.80}Ca_{0.20}Zr_{0.1}Ti_{0.9})O_3$ ceramics were investigated. XRD analysis shows that increasing sintering temperature aids in the disappearance of secondary peaks and in the formation of pure perovskite at sintering temperature 1420 °C. The increase of crystallite size and density with increasing sintering temperature suggests the strong influence of sintering temperature on the structural transformation of the ceramics. The large dielectric constant around room temperature (ε_r =2665), high Curie temperature (T_c = 77 °C) and improved ferroelectric properties (P_r = 3.394μC/cm^2, P_s = 7.68μC/cm^2, E_c=4.50 kV/cm) indicate that optimized sintering temperature of the ceramics can be 1420 °C in this investigated temperature range. Further study is underway for exploring the possibility of optimization at higher sintering temperature.

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