Grain size dependence of the microstructures and functional properties of (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$) (Zr$_{0.1}$Ti$_{0.9}$) O$_3$ lead-free piezoelectric ceramics

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ABSTRACT

By the solid-state reaction route, (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$) (Zr$_{0.1}$Ti$_{0.9}$) O$_3$ (BCCeZT) lead-free piezoelectric ceramics were prepared. The powder was processed at 1250 ºC for 2 h, and compacted green bodies were then sintered at various sintering temperatures. X-ray diffraction analysis and Raman spectra confirmed the rhombohedral-tetragonal phase coexistence of $x = 0-0.00131$. Addition of CeO$_2$ facilitated development of grain sizes greater than 10 µm at low sintering temperatures. The effects of grain size on the ferroelectric and piezoelectric properties were studied systematically and it was found that a ~ (10–12) µm grain size is critical for the processing of high-performance lead-free BCZT ceramics. CeO$_2$ substitution at the A site may bring down the sintering temperature by about 200 ºC without significant loss of properties. The best properties were obtained for $x = 0.00131$ at a low sintering temperature of 1350 ºC for 4 h exhibiting $d_{33} = 501 ± 10$ pC/N, $e_p = 38.5 ± 1.92$ %, $P_r = 12.19$ μC/cm$^2$, $T_c = 108.1$ ºC, and a large strain of 0.14%. These results show that BCZT ceramics could be promising candidates for the fabrication of lead-free devices.

1. Introduction

For many years, lead-derived piezoelectric materials such as lead zirconate titanate (PZT) have been used for various applications including sensors, fuel injectors, actuators, and transducers due to their excellent piezoelectric properties [1]. Lead-based piezo ceramics contain as much as 60% lead in their composition, which is a major concern due to the toxicity of lead in the environment. The demand for the replacement of these ceramics has emerged as a result, and now research is focused on the development of new lead-free efficient ceramic systems whose properties are comparable to PZT [2–7]. In 2009, Lui and Ren reported a new lead-free ceramic system (Ba$_{0.2}$ Zr$_{0.8}$ TiO$_3$–x(Ba$_{0.7}$ Ca$_{0.3}$)TiO$_3$ (BZT)–x(BCT), are commonly referred to as BCZT that represents excellent piezoelectric properties at $x = 0.5$ [8] that are mainly comparable to those of their lead-based counterparts. This ceramic system has similar morphotropic phase boundaries (MPB) to PZT except for its strong dependence on temperature and stoichiometry. Since its development has been conducted to study its structure and its effect on the functional properties [5,9,10] of lead-free ceramics (including BCZT). The piezoelectric and dielectric properties mainly depend on the grain sizes, and it is commonly believed that their functional properties could be enhanced with proper grain sizes [11–16]. A significant research is being done on lead-free ceramics in which dependence on grain size of their physical and functional properties has been reported. For instance, the grain size effect on the ferroelectric properties and electrostrictive coefficients of Fe$_{3+}$ doped 0.5BCT–0.5BZT ceramics was studied [17]. Long and Yi recently showed that if the grain size is between 8 and 15 µm, higher $d_{33}$ (= 560 pC/N) could be achieved for (Ba$_{0.85}$Ca$_{0.15}$) (Zr$_{0.1}$Ti$_{0.9}$)O$_3$ ceramics [18]. For potassium sodium niobate (K,Na)NbO$_3$-based materials, the particle size effect on their functional properties has been studied recently [19]. So far, a superior $d_{33}$ (~ 570 pC/N) value has been reported recently for a KNN-based material, which they ascribed to the nanoscale domains and high density of ferroelectric domain boundaries [20].

CeO$_2$ is a dopant/additive commonly used in the past for lead-based compositions to enhance the piezoelectric and dielectric properties [21–23]. Currently, CeO$_2$ has been used as an additive in lead-free compositions such as BaTiO$_3$–CeO$_2$ [24], KNN–CeO$_2$ [25], BNB–CeO$_2$ [26], BKT–CeO$_2$ [27], and BKNLT–CeO$_2$ [28] to obtain better piezoelectric properties and densities. Cui et al. [29] used CeO$_2$ as an additive with BCZT lead-free systems mainly to reduce the sintering temperature while maintaining a very high piezoelectric constant of $d_{33} = 600$ pC/N. There are no reports available regarding temperature and grain size dependence on its functional properties when CeO$_2$ is used as an A-site substituent in the ABO$_3$ structure of BCZT perovskite materials.
Therefore, we used CeO$_2$ (in $\times$ mol.) in the A site in the composition (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$) (Zr$_{0.1}$Ti$_{0.9}$) O$_3$ in order to study its crystal structure, its microstructure and the effect on its functional properties, including its ferroelectric properties which were lacking in the previous report [29]. A comprehensive study has been done on temperature and grain size dependence of the piezoelectric and ferroelectric properties. It was discovered that CeO$_2$ addition may reduce the sintering temperature of BCZT ceramics while maintaining significantly high piezoelectric properties.

2. Experimental

(Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$) (Zr$_{0.1}$Ti$_{0.9}$) O$_3$ where x(moles) = 0, 0.0008, 0.00131, 0.02 were fabricated according to the stoichiometric formula by the solid-state reaction method. The initial powder for each batch was prepared as 200 g. BaCO$_3$ (Dakram, UK, 99.9%), CaCO$_3$ (Lachner, CZ, 99.9%), ZrO$_2$ (Dakram, UK, 99.9%), TiO$_2$ (Dakram, UK, 99.9%) and CeO$_2$ (Sigma Aldrich, UK, 99.9%) were used as raw materials. Before milling, the powders were first dried at 220 °C/1h in the laboratory oven (Lenton MMD/0229, UK) and then weighed stoichiometrically. Mixing of the powder was performed in a horizontal ball mill with deionized water for 24 h. The ratio of powder to zirconia milling media to water was 2:1:1. The resulting slurry was dried in an oven at 90°C for 15 h and sieved (300 microns, VWR, UK), after which it was calcined at 1250 °C for 2 h in a zirconia crucible using a muffle furnace (Lenton, 5696, UK). After calcination, the calcined powders were re-milled for 24 h to reduce the particle size and avoid agglomeration. During the last hour of milling, ~ 5 wt.% of each binder, Duramax B1000 (Product No. 74,821, Chesham Chemicals Ltd., UK), and B1007 (Product No. 74,823, Chesham Chemicals Ltd., UK), were added. The resulting powders were then sieved and pressed (Instron, 5507, UK) in a steel die (P. T. No. 3000, Specac, UK) of 13 mm diameter and 1 mm thickness at pressure of 155MPa. Finally, the circular discs were sintered in the muffle furnace at different temperatures. The X-ray diffraction (Equinox 3000, INEL, France) with Cu-Kα radiation ($\lambda = 1.54178$ Å) was conducted to determine and understand the phase structure of the sintered samples. Raman spectra (Renishaw inVia, UK) were used to confirm the phase transformation. The bulk densities were calculated by the Archimedes method using distilled water as a medium.

3. Results and discussions

3.1 Crystal structure

3.1.1 XRD analysis

Figure 1 represents the XRD patterns of pressed samples of (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$) (Zr$_{0.1}$Ti$_{0.9}$) O$_3$ measured at room temperature. All peaks were indexed to tetragonal cells and no secondary phase was observed. Figure 1(b) and 1(c) presents expanded views of the 20 angles between 45°–47° and 65°–68°, respectively. Splitting of the peaks (002)/(200) and (220)/(202) was investigated for the samples $x = 0–0.00131$, with the results suggesting the existence of a tetragonal–rhombohedral (T–R) phase transition [8]. At higher Ce concentrations ($x = 0.02$) the splitting merges to form a single peak, suggesting that the ceramics may have a tendency to transform into another phase, i.e. the pseudo-cubic phase.

Taking tolerance factors into consideration, the small ions [r(R$^{3+}$)] < 0.087 nm will occupy the B site, relatively large ions [r(R$^{4+}$)] > 0.094 nm will occupy the A-sites and moderate ions are believed to occupy both sites [30]. It is well known in the case of another perovskite, BaTiO$_3$, that Ce$^{3+}$ substitutes the A-site while Ce$^{4+}$ substitutes the B-site but that self-compensation occurs when Ba/Ca = 1 [24]. Ce exists in both valence states as Ce$^{3+}$ (0.134 nm) and Ce$^{4+}$ (0.087 nm) [31]; therefore, according to crystal chemistry and the radius matching rule, Ce$^{3+}$ ions may occupy the A-site of either Ca$^{2+}$ (0.134 nm) or Ba$^{2+}$ (0.161 nm) due to the similar ionic radii. Also, Ce$^{4+}$ ions have ionic radii greater than those of the B-site elements, Ti$^{4+}$ (0.060 nm) and Zr$^{4+}$ (0.072 nm). Thus, it is least possible for Ce$^{4+}$ ions to occupy the B-site. Interestingly, when $x > 0$, the intensity peaks are shifted slightly toward higher angles, indicating cell contraction. Since the ionic radii of Ce$^{4+}$ are less than those of Ca$^{2+}$, Ce$^{4+}$ ions might go into the Ca$^{2+}$ positions of the A-site and cause lattice distortion and decreased lattice size.

3 kV/mm for 10 min at room temperature. The dielectric properties were measured by an impedance analyzer (4294, Agilent, USA) at a frequency of 1 kHz, and the piezoelectric constant (d$_{33}$) was measured with a Berlincourt d$_{33}$ m (YE2730A, Sinocera, China) at room temperature. The ferroelectric properties were investigated with the help of AixACCT systems, GmbH (Germany). The sintered samples were polished and thermally etched at 100 °C below their sintering temperatures with ramp up and ramp down temperatures of 20 °C/min. Scanning electron microscopy (JEOL 6060LV, Japan) was used for the investigation of surface morphologies, and the grain size was calculated by the linear intercept method.
3.1.2 Raman spectra

Raman spectroscopy was performed on \((\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Ce}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3\) ceramics to further clarify the effect of Ce content on the phase evolution of the BCZT system and corroborate the XRD results shown earlier. Figure 2 shows room temperature Raman spectra in the range of 50–800 cm\(^{-1}\). Here the R and T phases coexisted for the samples \(x = 0, 0.0008, 0.00131\), in which modes at 93, 151, 201, 248, 294, 524, 726 cm\(^{-1}\) are related to the R phase, especially at 151 and 190 cm\(^{-1}\), while the modes at 248, 294, 524, 726 cm\(^{-1}\) are related to the T phase [32]. No mode at 490 cm\(^{-1}\) was observed which is believed to be a signature of the O phase. This suggests that the 490 cm\(^{-1}\) peak merges with the 524 cm\(^{-1}\) peaks. Therefore, we can assume that the R and T phases coexisted for the samples \(x = 0, 0.0008, 0.00131\), which agrees with the XRD results. Further, for \(x = 0.02\), the intensity of the modes becomes weak at 93 cm\(^{-1}\) and

![Figure 1](image1)

![Figure 2](image2)

**Figure 1.** (a) Room temperature XRD patterns of \((\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Ce}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3\) samples, (b) magnification of Figure 1(a) in the range of 45°–47° and (c) magnification of Figure 1(a) in the range of 65°–68° sintered at 1350 °C for 4 h.

**Figure 2.** Room temperature Raman spectra of \((\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Ce}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3\) ceramics sintered at 1350 °C/4 h.
294 cm\(^{-1}\) and other peaks between them vanish, while the modes at 524, 726 cm\(^{-1}\) peaks remain. In addition, broad modes of 294 cm\(^{-1}\) and 726 cm\(^{-1}\) are features of the pseudo-cubic phase. Similar results were reported in previous studies \[33–35\].

### 3.2 Bulk density, microstructures and grain sizes

It is evident from Figure 3 that as the sintering temperature increases the bulk density increases obviously. Much higher bulk densities (5.40 g/cm\(^3\)) were observed for the samples \(x > 0\) as compared to pure BCZT \((x = 0)\) at the sintering temperature of 1350°C/4h. This shows that a small amount of CeO\(_2\) was useful for improving the densification of the samples. Maximum density was observed for \(x = 0.02\) as 5.75 g/cm\(^3\). It is also noted that the bulk density remains more or less constant for the samples \(x > 0\) at above 1350°C/4h. Thus, a small amount of CeO\(_2\) is useful to improve the densities of BCZT ceramics.

Figures 4 and 5 show microstructures of these ceramics heated at 1350 °C and 1450 °C for 4 h. At 1350 °C, the microstructures of \(x = 0, 0.0008\) and 0.00131 are not dense enough as compared to \(x = 0.02\). It is important to notice that the grain sizes are very small for \(x = 0.02\) and that the microstructure becomes much denser compared to other compositions at different sintering temperatures. At 1450 °C, the grains grow steadily, which brings a moderate increase in the densities of the samples when \(x = 0–0.00131\). Sample \(x = 0.02\) remains sufficiently dense, while no improvement in grain growth was observed. It seems that addition of CeO\(_2\) (less than or equal to 0.00131) enhances grain growth. Grain growth remains steady with CeO\(_2\) addition of \(x = 0.02\). Hence, the amount of CeO\(_2\) in the BCZT composition concerns a change in the grain growth.

In general, grains grow with increase in sintering temperatures and a condition that is valid for \(x = 0–0.00131\). Sample \(x = 0.02\) limits grain growth, irrespective of increase in sintering temperature, which clearly shows that large amounts of CeO\(_2\) are effective in suppressing the melting and grain growth of BCZT ceramics during sintering, which might be due to the accumulation of Ce ions at the grain boundaries. From the above results, it is concluded that CeO\(_2\) has a solubility up to \(x = 0.00131\) in a BCZT system.

Proper grain size is an important for obtaining high piezoelectric properties for BCZT ceramics; the best properties can be obtained with a grain size > 10 μm \[5\] and can deteriorate at a grain size smaller than 10 μm \[36\], which result was found to be valid for the sample \(x = 0.02\), which has a < 1 μm grain size, as shown in Figure 6. At 1350 °C, the average grain size was calculated as about 6 μm for pure BCZT \((x = 0)\), while when Ce contents of 0.0008 and 0.00131 were slowly introduced, the grain sizes were increased in the range of 10–12 μm. A high Ce concentration \((x = 0.02)\) limits grain growth, which might affect the properties of these ceramics. This should be attributable to the donor-type nature of Ce ions.

![Figure 3](image-url) **Figure 3.** Bulk density of \((\text{Ba}_0.85\text{Ca}_{0.15–x}\text{Ce}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3\) ceramics as a function of sintering temperature (4h).
For PZT-based ceramics, donor dopants generally limit grain growth [25,37]. The sintering kinetics can be explained by the lattice diffusion of vacancies from pores to grain boundaries, and donor doping reduces the diffusion coefficient: the vacancies (e.g. A-site vacancies in this case) created by doping are supposed to be bound to the impurity ion (e.g. Ce\(^{3+}\) in the present study). When, Ce content is low (up to \(x = 0.00131\)) the diffusion coefficient may increase, making mass transport strong. As a result, the grains grow, and the structure becomes dense. When Ce content is high (\(x = 0.02\)), meanwhile, the diffusion coefficient weakens due to an excess of A-site vacancies, and mass transportation can be supposed to be lowered and grain growth was limited as a result.

Figure 4. SEM images of \((\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Ce}_x)\) \((\text{Zr}_{0.1}\text{Ti}_{0.9})\) \(\text{O}_3\) ceramics (a) 0, (b) 0.0008, (c) 0.00131, and (d) 0.02 at 1350 °C for 4 h.

Figure 5. SEM images of \((\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Ce}_x)\) \((\text{Zr}_{0.1}\text{Ti}_{0.9})\) \(\text{O}_3\) ceramics (a) 0, (b) 0.0008, (c) 0.00131, and (d) 0.02 at 1450 °C for 4 h.
3.3 Piezoelectric and ferroelectric properties

Figure 7(a) and 7(b) shows the piezoelectric coefficient ($d_{33}$) and planar coupling factor ($k_p$), respectively, of BCZeZT ceramics at different sintering temperatures. As the sintering temperature increases, the $d_{33}$ values sharply increase for $x = 0.0008$ and 0.00131 at 1350 °C and then decrease drastically with further increases in the sintering temperature. At 1350 °C, pure BCZT ($x = 0$) has a $d_{33}$ value of around 290 ± 15 pC/N, while when the Ce concentration is slightly increased ($x = 0.00131$), a peak value of $d_{33} \sim 501 \pm 10$ pC/N is revealed. Further increases in the Ce concentration ($x = 0.02$), ions of Ce caused drastic deterioration of $d_{33}$, which can be attributed to the fine grain size. The planar coupling factor ($k_p$) follows the same trend: the maximum value of $k_p$ was found to be 38.5 ± 1.92% for the sample $x = 0.00131$ but decreased remarkably for the sample $x = 0.02$ sintered at 1350 °C/4h, as shown in Figure 7(b). The piezoelectric properties are summarized in Table 1 at a sintering temperature of 1350 °C/4h.

The $d_{33}$ and $k_p$ of these ceramics decrease remarkably when the CeO$_2$ concentration increases ($x = 0.02$), replacing Ca$^{2+}$ ions and making the lattice distortion ever larger. When Ce$^{3+}$ and Ce$^{4+}$ ions occupy Ca$^{2+}$ positions, vacancies are formed in the lattice and grain growth slows (Also see Figures 4(d) and 5(d)) while the grain size of the BCZT ceramics is

![Figure 6. Average grain size of (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$)(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ ceramics as a function of sintering temperature (4h).](image)

![Figure 7. (a) Piezoelectric constant, $d_{33}$, and (b) planer coupling coefficient, $k_p$, of (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$)(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ ceramics as a function of sintering temperature.](image)
Table 1. Summary of grain sizes, piezoelectric properties and Curie temperatures of (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$) (Zr$_{0.1}$Ti$_{0.9}$) O$_3$ ceramics at 1350 °C/4 h.

| x  | Grain size (μm) | d$_{33}$ (pC/N) | k$_p$ (%) | T$_c$ (°C) |
|----|----------------|-----------------|-----------|------------|
| 0  | 7.6 ± 2        | 290 ± 15        | 26.4 ± 1  | 105.4      |
| 0.0008 | 12.16 ± 2.39 | 490 ± 20        | 37.8 ± 1.69 | 103.2      |
| 0.00131 | 11.26 ± 1.97 | 501 ± 10        | 38.5 ± 1.92 | 108.1      |
| 0.02 | 0.76 ± 0.08    | -               | -         | 72.6       |

lowered as well [38]. In the process of replacing Ca$^{2+}$ by Ce$^{3+}$ and Ce$^{4+}$, moreover, when the CeO$_2$ concentration is low (up to x = 0.00131), Ca$^{2+}$ vacancies are dominantly produced, which results in increased d$_{33}$. When the CeO$_2$ amount of x = 0.02 increase on the other hand, the lattice distortion effect dominates to drastically reduce the piezoelectric properties. Similar results were found previously [38–40].

The relationship between piezoelectric and ferroelectric data can be described logically by [41]:

$$d_{ij} = P_r \varepsilon_r \varepsilon_0 2Q_{ij},$$

(1)

where $d_{ij}$ is the piezoelectric constant, $P_r$ is the remnant polarization, $\varepsilon_r$ is the relative permittivity or dielectric constant), $\varepsilon_0$ is the permittivity in free space and $Q_{ij}$ is the electrostriction coefficient). As is clear from Equation (1), d$_{33}$ is directly proportional to remnant polarization ($P_r$), suggesting that if the $P_r$ increases, d$_{33}$ also increases. In our research, $P_r$ is dependent on grain size (see Figure 8(a)), i.e. when the grain size is large, the $P_r$ parameter has a high value; therefore, based on Equation (1), d$_{33}$ has a higher value. If the grain sizes are fine, then contribution by clusters of grains to polarization will be reduced because of domain wall pinning, which lowers the d$_{33}$ value [42]. As is well documented in the previous literature, a 60–70% contribution to the increase in d$_{33}$ is due to the displacement of domain walls [43]. Thus, it is believed that larger numbers of domain variants as well as displacement of domain walls are much easier to achieve with bigger grain sizes which can actuate a large strain and push enhancement of the piezoelectric constant (here, d$_{33}$ = 501 ± 10 pC/N for x = 0.00131).

P–E hysteresis loops for (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$) (Zr$_{0.1}$Ti$_{0.9}$) O$_3$ are shown in Figure 8(a) sintered at a temperature of 1350 °C for 4h. All samples represent typical ferroelectric loops under a switching frequency of 1Hz. Here we observed that the remnant polarization (P$_r$) is significantly dependent on the grain size. For pure BCZT (x = 0), a $P_r$ value of 7.86 μC/cm$^2$ was observed. When the cerium content was increased to 0.00131, The $P_r$ value also increased to 12.19 μC/cm$^2$. Further increases in the cerium content (x = 0.02) show a significant decrease in the $P_r$ value (3.68 μC/cm$^2$), which was ascribed to the fine grain sizes of the samples.

A study of P–E responses to the grain sizes of ceramics has been proposed by Ohihara [43] in which fractions (f) of grains give rise to polarization reversal or domain switching and which is expressed as follows:

$$f = f_0 \left[ 1 - \exp\left(-G_n d^3/kT\right) \right],$$

(2)

where $f_0$ is the initial polarization or domain of ferroelectric materials, $G_n$ is a constant that represents grain anisotropy energy density, and d is the grain size of the ceramics. Based on these conclusions, f has importance only to the grain size d. Therefore, if the grain size increases, the fraction of grains contributing to the polarization reversal also increases, which brings an improvement in the ferroelectric (P–E) characteristics (see Figure 8(b)).

Figure 8(b) represents the strain-electric field (S–E) loop with a typical butterfly nature. Pure BCZT (x = 0) shows strain on the order of 0.11% with a grain size of 7.6 ± 2 μm. As the Ce concentration increased slightly up to 0.00131, the grain size started to improve (11.26 ± 1.97 μm), which results in better strain characteristics (S = 0.14%). A further increase in the Ce

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**Figure 8.** (a) P–E hysteresis loops and (b) strain hysteresis loops for (Ba$_{0.85}$Ca$_{0.15-x}$Ce$_x$) (Zr$_{0.1}$Ti$_{0.9}$) O$_3$ ceramics sintered at 1350 °C/4 h.
concentration \((x = 0.02)\) gave rise to inferior strain of \(S = 0.07\%\). This may be due to the very small grain size of \(0.76 \pm 0.02 \mu m\).

The variations in grain size influence the domain size, and form the balance of depolarization energy as well as of domain wall energy [44]. The correlation between the domain size \((d)\) and the grain size \((t)\) can be denoted as \(d = \left[\frac{\sigma}{\varepsilon_r P_0^2}\right] \cdot t^{1/2}\), where \(\sigma\), \(\varepsilon_r\), and \(P_0\) are the energy density of the domain wall, the dielectric constant and spontaneous polarization, respectively. It can therefore be concluded that there is a strong dependence of domain size on grain size in perovskite type ferroelectrics, as was confirmed in the previous report [36]. Moreover, another important fact for the grain size effect on the piezoelectric properties of perovskite-type ferroelectrics is influence of the 90° domain walls [45, 46].

Our present results correspond well with to the change in domain size of BCZT ceramics [36] as a function of grain size, showing \(d_{33}\) and \(k_p\) values around 480 pC/N and ~ 40% for ~ 10–12 µm grain sizes and \(d_{33}\) and \(k_p\) values around 50 pC/N and ~ 15% for ~ 0.4–1.5 µm grain sizes [36]. Based on the above findings, increased domain size should be the reason for the enhancement of piezoelectric properties with larger grain size, which is in line with our results. In addition, in sample \(x = 0.02\) (cubic crystal structure from XRD) with grain size < 1 um, no piezoelectric properties were observed. This could result from the strong coupling between the grain boundaries and the domain walls which make domain reorientation extremely difficult and severely constrain the domain wall motion. The ferroelectric properties of these ceramics are summarized in Table 2.

### Table 2. Summary of ferroelectric properties of (Ba\(_{0.85}\)Ca\(_{0.15}\)–\(x\)Ce\(_x\)) (Zr\(_{0.1}\)Ti\(_{0.9}\)) O\(_3\) ceramics at 1350 °C/4 h.

| \(x\) | \(P_r\) (µC/cm\(^2\)) | \(S_{\text{max}}\) (%) | \(E_C\) (kV/cm) |
|------|-----------------|-----------------|-------------|
| 0    | 7.86            | 0.11            | 5.49        |
| 0.0008| 11.29           | 0.13            | 5.16        |
| 0.00131 | 12.19          | 0.14            | 4.57        |
| 0.02 | -               | 0.07            | -           |

### 3.4 Dielectric properties

Figure 9 represents relative permittivity \((\varepsilon_r)\) as a function of sintering temperature for \((\text{Ba}_{0.85}\text{Ca}_{0.15}\text{–\(x\)}\text{Ce}_{x}) \text{(Zr}_{0.1}\text{Ti}_{0.9})\text{O}_{3}\) samples measured at 1 kHz. High relative permittivity \((\varepsilon_r \sim 10,000–12,000)\) was measured for \(x = 0.0008, 0.00131\) samples as compared to pure BCZT \((\varepsilon_r \sim 8000)\). When the Ce content become excessive \((x = 0.02)\), a significant drop in \(\varepsilon_r\) was observed \((\varepsilon_r < 5000)\). The relative permittivity peak became broader for \(x = 0.02\), which leads to a more conspicuous diffuse phase transition (DPT) character. This character may be ascribed to structural change due to the excess Ce content and consequently small grain size \((0.76 \pm 0.08 \mu m)\), which results in low relative permittivity and to a shifting of the ferroelectric-paraelectric phase transition to lower temperatures. This may be due to the pseudo-cubic character, in which tetragonal and cubic phases are believed to be very close to each other with a resulting \(T_C\) shift towards lower temperatures (see Figure 9).

![Figure 9. Temperature-dependent relative permittivity of (Ba\(_{0.85}\)Ca\(_{0.15}\)–\(x\)Ce\(_x\)) (Zr\(_{0.1}\)Ti\(_{0.9}\)) O\(_3\) ceramics sintered at 1350 °C/4 h.](image-url)
4. Conclusions
(Ba_{0.85}Ca_{0.15-x}Ce_x)(Zr_{0.1}Ti_{0.9})O_3 ceramics have been successfully synthesized via a solid-state reaction method. The ferroelectric, piezoelectric, and dielectric properties were systematically studied. It was found that high functional properties can be achieved when the grain sizes are between 10 and 12 µm. XRD and Raman analysis are in close agreement in confirming rhombohedral-tetragonal phase coexistence for x = 0–0.00131. The excellent properties were obtained for x = 0.00131 when sintered at 1350 °C for 4h, resulting in $d_{33} = 501 \pm 10 \text{ pC/N}$, $K_p = 38.5 \pm 1.92$, $P_r = 12.19 \mu C/cm^2$, $S = 0.14\%$, $T_C = 108.1 °C$. The above-mentioned high performances of BCCeZT ceramics suggest that the lead-free piezoelectric ceramics could potentially be useful for the fabrication of various electronic devices.

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