Journal of Asian Ceramic Societies

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tace20

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To cite this article: Vijay Bijalwan, Ilya Sokolov & Pavel Tofel (2021) Poling procedures and piezoelectric response of $(Ba_{0.85}Ca_{0.15}Zr_{0.1}T_{0.9})O_3$ ceramics, Journal of Asian Ceramic Societies, 9:1, 206-213, DOI: 10.1080/21870764.2020.1860438

To link to this article: https://doi.org/10.1080/21870764.2020.1860438

JOURNAL OF ASIAN CERAMIC SOCIETIES
2021, VOL. 9, NO. 1, 206–213
https://doi.org/10.1080/21870764.2020.1860438

Poling procedures and piezoelectric response of $(Ba_{0.85}Ca_{0.15}Zr_{0.1}T_{0.9})O_3$ ceramics

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ABSTRACT

The goal of the current report was to find the optimal poling conditions: poling field, poling time and poling temperature for lead-free $(Ba_{0.85}Ca_{0.15}Zr_{0.1}T_{0.9})O_3$ ceramic. It has been noticed that the low poling field (< 2 kV/mm) was insufficient for obtaining ideal poling state ($\theta = 90°$) due to the incomplete switching of domains and thus low piezoelectric properties ($d_{33} \leq 438$ pC/N and $k_p \leq 49\%$). However, relevance of higher poling voltage (> 2 kV/mm) may induce electric breakdown and physical defects such as cracks in the sample, which also leads degradation of piezoelectric properties. The optimal poling field, poling time and poling temperature was found to be 2 kV/mm, 10 min and 24°C, i.e., near room temperature, respectively to achieve nearly ideal poling state ($\theta = 86°$) obtained by impedance spectra, and thus enhanced piezoelectric constant $d_{33} = 505$ pC/N and $k_p = 56\%$ at room temperature. The O-T phase transition point was identified at 32.6°C, for which a peak value of $d_{33(E=0V)} = 622$ pm/V was realized.

ARTICLE HISTORY
Received 14 September 2020
Accepted 28 November 2020

KEYWORDS
Poling conditions; piezoelectric constant; impedance spectra; lead-free piezoelectric ceramics

1. Introduction

In recent years, lead-free piezoelectric materials are receiving a considerable attention for the alteration of lead zirconate titanate (PZT)-based materials. In 2009, Liu and Ren [1] discovered $(Ba_{0.85}Ca_{0.15}Zr_{0.1}T_{0.9})O_3$ (BCZT) system, which show similar piezoelectric properties than that of PZT. BCZT ceramic exhibits a temperature-dependent morhotropic phase boundary (MPB) and show very high piezoelectric constant ($d_{33} > 600$ pC/N). However, such high piezoelectric constant is not easy to achieve and can be influenced by different processing techniques [2], sintering conditions [3,4] and poling conditions [5–8]. For polycrystalline ceramics, the domain orientations are randomly distributed, which gives a zero net polarization. Therefore, electrical poling is required by applying a DC field for certain amount of time and temperature that can align polar axis toward the direction of an applied field resulting net piezoelectric response. However, the poling conditions for BCZT ceramic are scattered in the literature [5,6,9,10] and is worth to compile a detailed report particularly focused on it. Therefore, the prime focus of the current research is to optimize the poling conditions such as poling field, poling time, and poling temperature to achieve enhanced piezo-response. Poling studies carried out by Su et al. [5]and Wu et al. [9] have reported high piezoelectric properties for BCZT ceramics when poled at very high poling field of 4 kV/mm and poling temperature of 40°C. Li et al. [10] discovered optimal piezoelectric properties when BCZT ceramic was poled at 120°C, which is higher than the Curie temperature (T_C). On the other hand, Praveen et al. [6] showed that a poling field of 3 times coercive field (E_C), which is approximately as low as 0.4 kV/mm to obtain $d_{33} > 600$ pC/N.

Therefore, in this article, we compiled a detailed report on the influence of wide range of poling field, poling time, and poling temperatures on the piezoelectric properties of BCZT ceramic using a standard DC poling in silicon oil. The effect of lower and excessive poling field on piezoelectric and ferroelectric properties is discussed and the optimized poling conditions for BCZT ceramic has been identified.

2. Experimental procedure

$(Ba_{0.85}Ca_{0.15}Zr_{0.1}T_{0.9})O_3$ ceramics were synthesized by conventional solid-state reaction technique. Raw powders of $BaCO_3$ (99.5%, Dakram, UK), $CaCO_3$ (99.9%, Lachner, Czech Republic), TiO_2 (99.5%, Dakram, UK) and ZrO_2 (99.5%, Dakram, UK) were used as starting powders. Thereafter, these powders were mixed in horizontal ball-mill with zirconia balls and ethanol followed by drying at 90°C/24 h. The dried powder was calcined at 1250°C/4 h. Then the calcined powder was re-milled and ~ 2 wt% each of the two binders,

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Duramax B1000 (Product No. 74,821, Chesham Chemicals Ltd., UK) and B1007 (Product No. 74,823, Chesham Chemicals Ltd., UK), were added during last hour of milling followed by drying. The green samples of ~ 1 mm thickness were prepared by uniaxial pressing (150 MPa) and sintered at 1520°C/4 h at a heating and cooling rate of 3°C/min. Relative density (~ 95%) were calculated by Archimedes method (EN623-2) and then expressed as a percentage of the theoretical density (TD) of 5.72 g/cm^3 obtained from XRD results. The phase structure of sintered specimens was analyzed by X-Ray equipment (SmartLab Rigaku, Japan) that was set up in Bragg-Brentano geometry using Cu-Kα radiation (λ = 1.54 Å) equipped with a 1D detector (D/teX-Ultra). Quasi-static piezoelectric constant, d_{33}, was measured by Berlincourt d_{33} meter (YE2730A, Sinocera, China) after poling in silicon oil at different poling fields 0.4, 0.6, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6 kV/mm, different poling times 10, 20, 30 min and various poling temperatures 24, 28, 33, 38, 43, 48°C. The ferroelectric properties (measured at 1 Hz), planar coupling coefficient (k_p) and temperature-dependent piezoelectric constant $d_{33(E=0)}$ were examined by using a piezoelectric evaluation system (AixPES, aixACCT, Germany).

3. Results and discussion

3.1. Phase characterization

The room temperature XRD patterns (2θ = 20°-70°) were obtained for BCZT ceramics between 0.4 and 3.6 kV/mm poling fields for 10 min as illustrated in Figure 1(a). BCZT ceramics formed a pure perovskite phase and no trace of impurity or secondary phase was detected, which directs that the equilibrium of the ferroelectric phase was reached in BCZT ceramics. The peak splitting of (022)/(200) between 2θ = 44.4–45.6° (Figure 1(b)) and the formation of triplet (004)/(040)/(222) between 65.2–66.4 (Figure 1(c)) suggests the presence of the orthorhombic (O) phase. Therefore, the BCZT ceramic shows O-phase at room temperature, regardless of applied poling field, which clearly indicates that the poling field do not affect phase structure of BCZT ceramic. Similar pure O-phase are previously reported by Fu et al. [11] for $(Ba_{0.89}Ca_{0.11}Zr_{0.1}T_{0.9})O_3$, Bijalwan et al. [12] and Keeble et al. [13] for $(Ba_{0.85}Ca_{0.15}Zr_{0.1}T_{0.9})O_3$ ceramics at room temperature.

3.2. Optimization of poling conditions: piezoelectric and ferroelectric properties

Poling is necessary step for any polycrystalline piezoelectric ceramics to get their piezo-response. For this, electrical poling is required by which an external electric filed is supplied and randomly oriented ferroelectric domain aligned or becomes polarized with a non-zero polarization developed along applied field direction. Poling conditions such as poling voltage, poling temperature and sufficient poling time is required to get optimal piezoelectric response of BCZT ceramics [6]. Figure 2(a) depicts impedance spectra of BCZT ceramics at different poling voltage (ranges from 0.4 to 3.6 kV/mm) at room temperature for 10 minutes. Upon poling, the phase angle (θ) first increases from 79.2° (poling field, 0.4 kV/mm) to 86° (poling field, 2 kV/mm) and then decreases to 83.4° with further increase in the poling field. Beyond 2.4 kV/mm, θ values stabilized between 82.1° and 82.7°. The highest θ = 86° is realized for BCZT sample poled at 2 kV/mm for 10 min, which indicates that the sample is approaching toward ideal poling state (θ = 90°). The low d_{33}

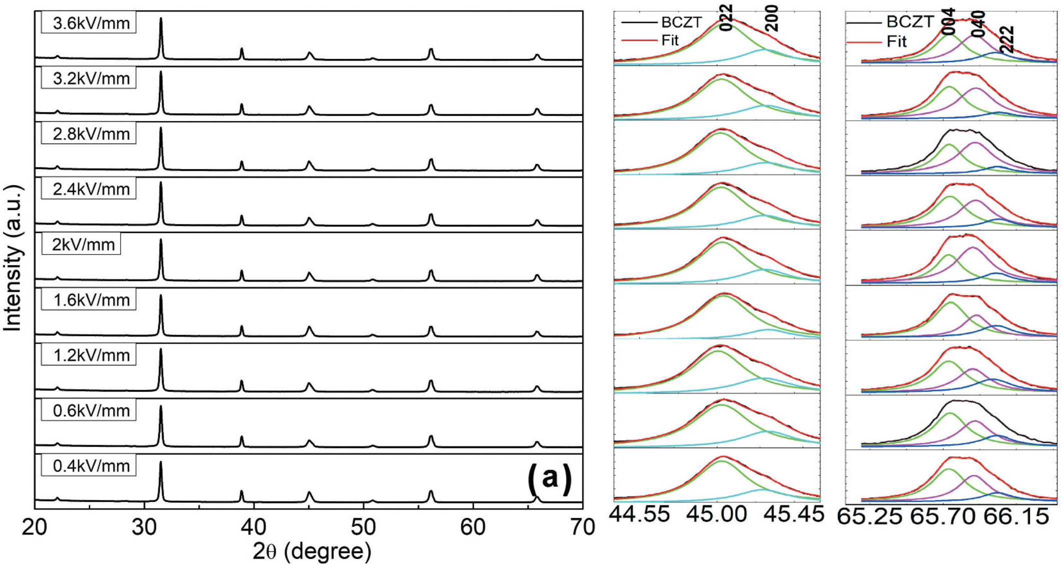

Figure 1. (a) X-ray diffraction patterns in the 2θ range of 20°-70°, (b) Enlarged view in the 2θ range of 44.6°-45.6°, (c) Enlarged view in the 2θ range of 65.2°-66.4° for BCZT ceramics at various poling fields.

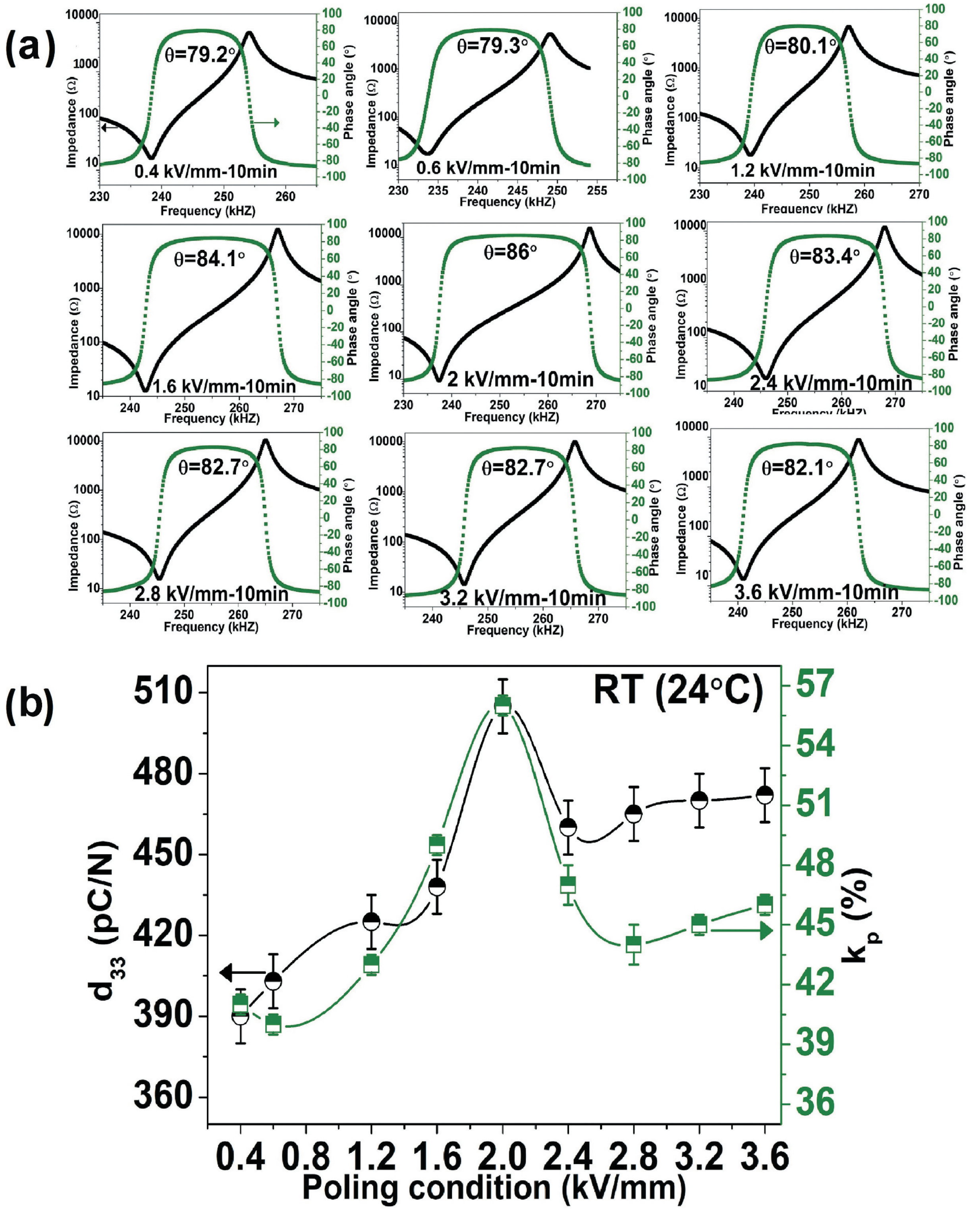

Figure 2. (a) Impedance spectra, (b) Piezoelectric constant and planar coupling coefficient of BCZT ceramic at various poling fields.

values at poling field (< 2 kV/mm) can be ascribed to the incomplete switching of domains. Relevance of higher poling voltage (> 2 kV/mm) seemed also inefficient to reach the ideal poling state; however, it may induce electric breakdown and physical defects such as cracks in the sample leading to the reduction in the electrical properties [14]. The comparison of various poling conditions and corresponding piezoelectric response is shown in Table 1.

In response of approaching ideal poling state (θ = 86°), the piezoelectric constant d_{33} and planar coupling coefficient k_p reached the peak value of 505 pC/N and 56%, respectively, for the sample poled at 2 kV/mm for 10 min as shown in Figure 2(b). There was a clear correlation found between degree of poling (phase angle values) and piezoelectric properties. The poling voltage for BCZT ceramic in this study was found to be lower compared to the PZT-5 H (poling

Table 1. Summary of piezoelectric properties of BCZT ceramic at different poling fields.

Material and conditions	Poling field (kV/mm)	Phase angle (°)	d_{33} (pC/N)	k_p (%)
BCZT (Poled at 24°C for 10 min)	0.4	79.2	390	41
	0.6	79.3	403	40
	1.2	80.1	425	43
	1.6	84.1	438	49
	2.0	86.0	505	56
	2.4	83.4	460	47
	2.8	82.7	465	44
	3.4	82.7	470	45
	3.6	82.1	472	46

voltage ~ 4.1, kV/mm, d_{33} = 464 pC/N), BNT-BT (poling voltage ~ 4 kV/mm, d_{33} = 119 pC/N) and KNNS-BHNH (poling voltage ~ 2.3 kV/mm, d_{33} = 429 pC/N) [7]. Tao et al. [7] found optimal poling voltage for BCZT ceramic as 1.6 kV/mm, while d_{33} was found as low as 381 pC/N.

Electric field dependent polarization curves (P-E loops) were measured at 1 Hz as shown in Figure 3(a), which represents ferroelectric behavior of BCZT ceramics. The remnant polarization (P_r) values first increases from 10.74 μC/cm^2 to a maximum of 12.5 μC/cm^2 for the sample poled at 2.4 kV/mm for 10 min (24°C). However, similar P_r value, 12.43 μC/cm^2 was also attained for the sample poled at 2 kV/mm as depicted in Figure 3(b). Further increase in poling voltage led to the saturation in the P_r values (12.18–12.38 μC/cm^2). The coercive field (E_C) was found below 0.2 kV/mm for BCZT ceramics at different poling fields, which indicate the soft behavior of BCZT ceramics.

The optimized poling voltage for BCZT samples is further optimized with holding time during poling. For this, BCZT sample (poling voltage, 2kV/mm) poling time was prolonged i.e. 20 min and 30 min as represented in Figure 4(a). When the poling time is increased from 10 to 30 min, the phase angle value reduced from 86° (poling time, 10 min) to 83.4° (poling time, 30 min). As a result, the d_{33} value decreased from 505 pC/N to 480 pC/N and similarly, k_p values reduced from 56% to 50%. The decrease in k_p values can also be confirmed by decrease in the anti-resonance frequency (f_r) as depicted in Figure 4(b). Therefore, large poling time was not found to be efficient so as to enhance piezoelectric properties of BCZT ceramics. Figure 5(a) shows the variation in d_{33} and k_p values of BCZT samples poled at different poling temperatures. The

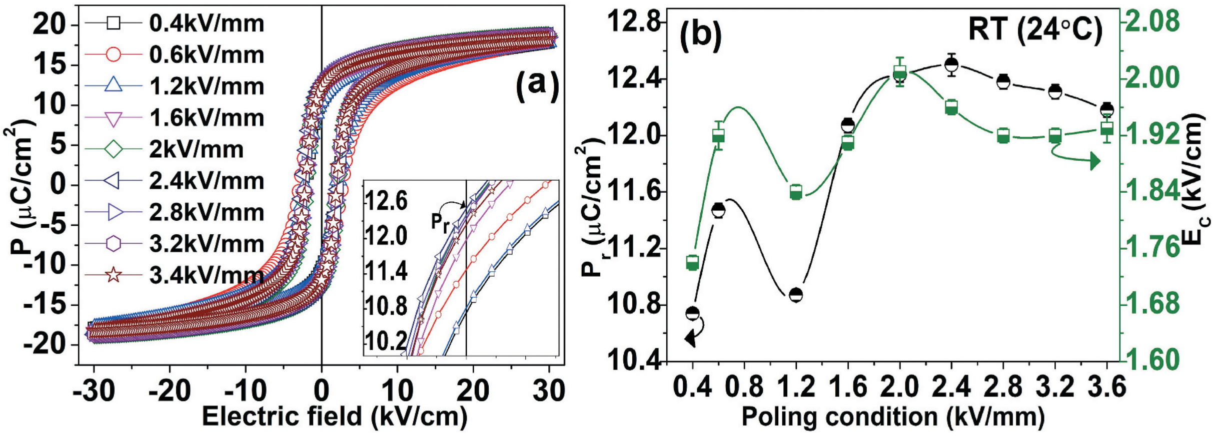

Figure 3. (a) P-E hysteresis loops, and (b) Remnant polarization and coercive field of BCZT ceramic at different poling fields.

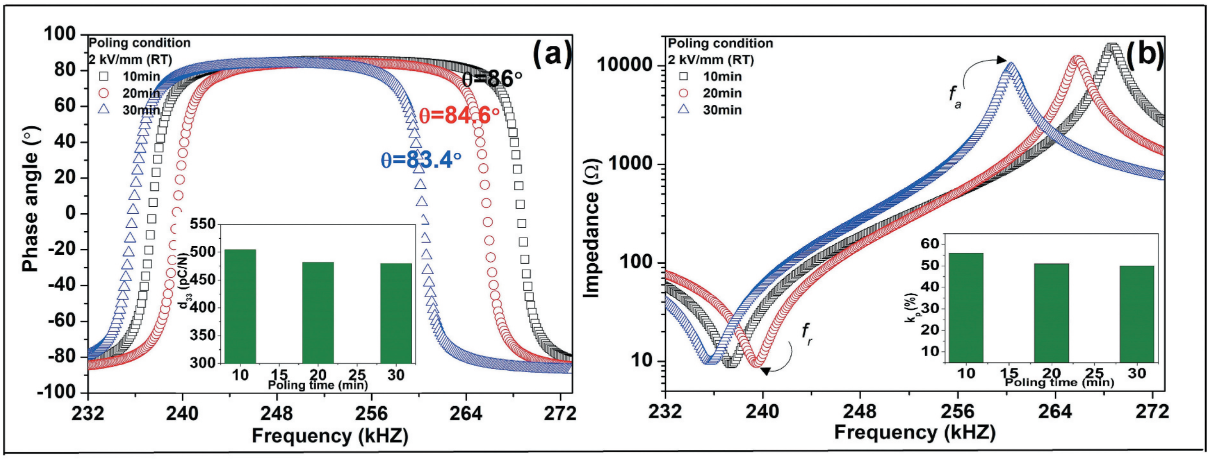

Figure 4. (a,b) Impedance spectra and corresponding piezoelectric constant and planar coupling coefficient (both in insets) at different poling times.

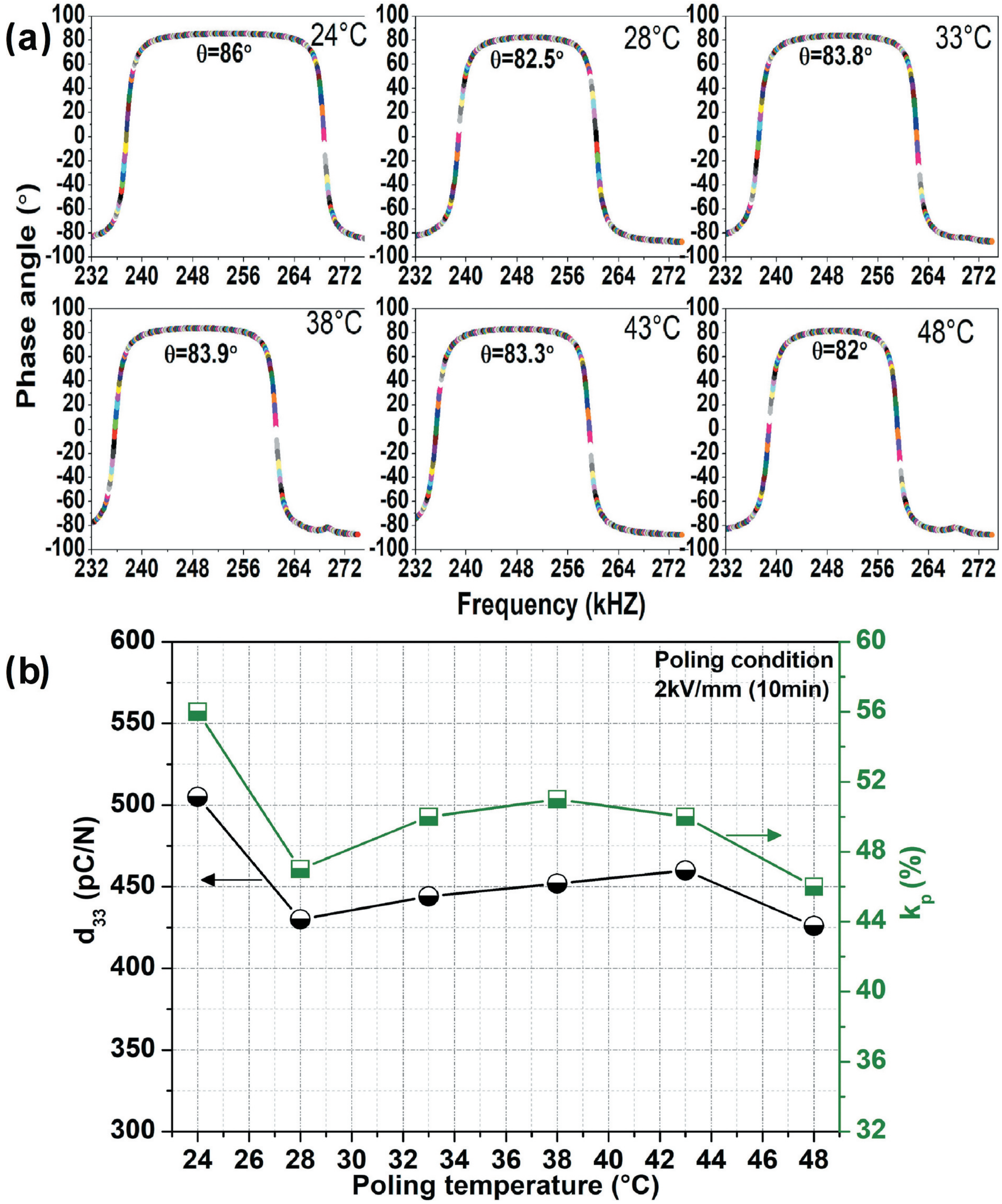

Figure 5. (a) Impedance spectra, and (b) Piezoelectric constant and planar coupling coefficient at different poling temperatures for BCZT ceramic.

maximum d_{33} and k_p values were kept for the samples poled at room temperature i.e. 24°C as represented in Figure 5(b). When poling temperature further increased, the d_{33} values first decreases and then stabilized in the range of 426–460 pC/N. It is evident from the above results that the highest d_{33} and k_p values were obtained for the BCZT sample poled at 24°C (poling field, 2 kV/mm and poling time, 10 min). The comparison of different poling conditions with piezoelectric properties are summarized in Table 2.

3.3. *Temperature-dependent dielectric, piezoelectric and ferroelectric curves*

The temperature dependence of relative permittivity and $d_{33(E=0)}$ of unpoled BCZT ceramic is depicted in Figure 6(a,b). Two dielectric peaks near room temperature and around 100°C were observed corresponding to the O -T and T – C phase transitions, respectively (Figure 6(a)). Similar two distinct peaks were also observed for $d_{33(E=0)}$ vs. T plot, which agree well with

Table 2. Comparison of poling conditions with piezoelectric properties of BCZT ceramic.

Material	Poling field (kV/mm)	Poling Temperature (°C)	Poling time (min)	Phase angle (°)	d_{33} (pC/N)	k_p (%)
BCZT	2	24	10	86.0	505	56
			20	84.6	482	51
			30	83.4	480	50
BCZT	2	28	10	82.5	430	47
		33		83.8	444	50
		38		83.9	452	51
		43		83.3	460	50
		48		82.0	426	46

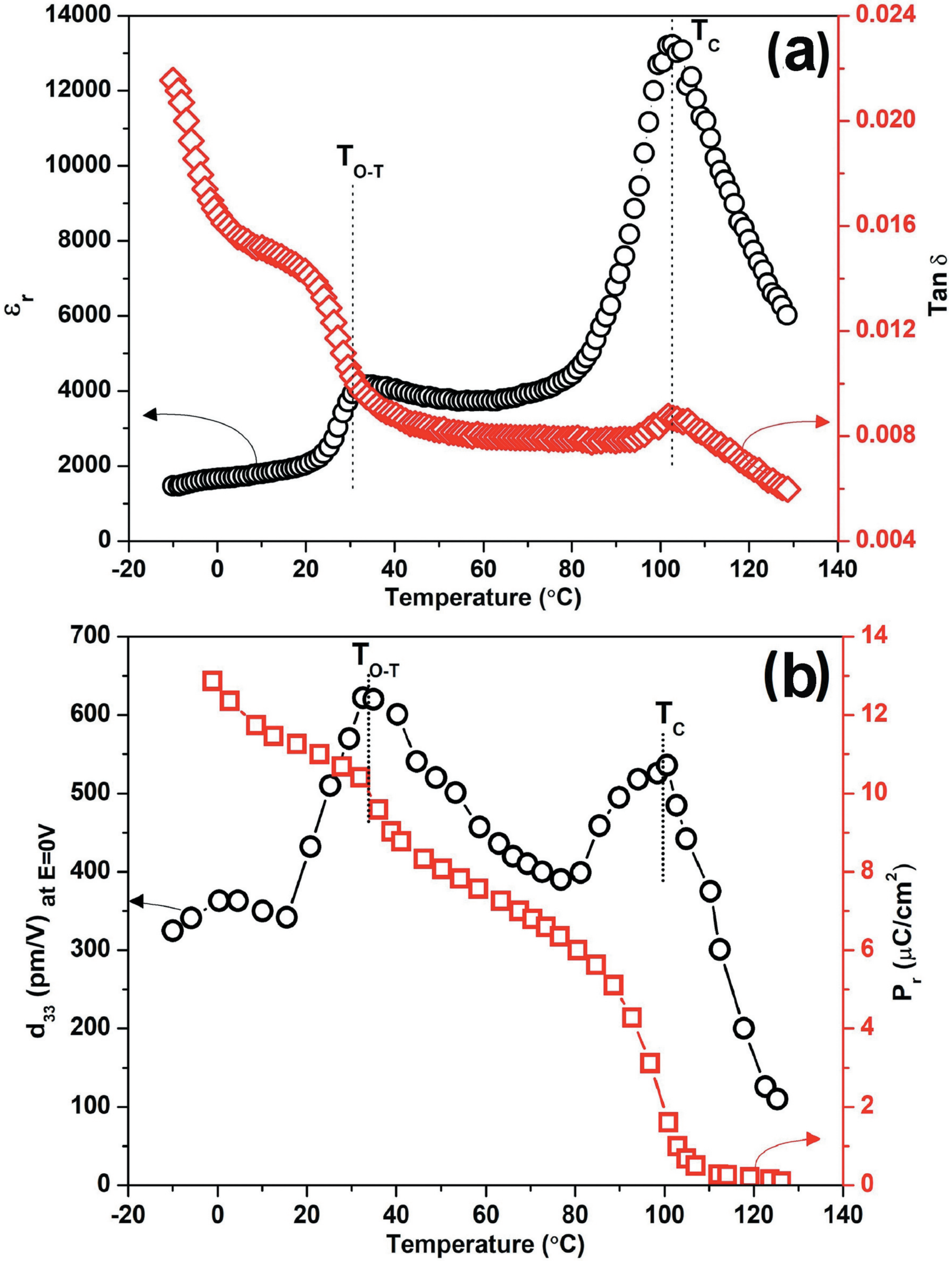

Figure 6. (a) Temperature-dependent dielectric permittivity, and (b) Piezoelectric constant and remnant polarization for BCZT ceramic.

the dielectric measurements. The piezoelectric coefficient was evaluated at zero bias voltage $d_{33(E=0)}$ on unpoled samples and therefore this could be the reason in obtaining low $d_{33(E=0)}$ = 444 pm/V at 24°C as compared to the d_{33} value attained by quasi-static method. If the samples are poled, then similar value of d_{33} can be obtained by indirect method [15,16]. The $d_{33(E=0)}$ values rapidly increased when it approached toward O – T phase transition temperature ($T_{O\text{-}T}$ = 32.6° C), and attained maximum value of 622 pm/V. This higher values of $d_{33(E=0)}$ is due to the domain volume fractions of the two phases. Such a phenomenon suggests that the higher piezoelectric response of BCZT ceramic can be obtained at $T_{O\text{-}T}$ than in single ferroelectric phase. This behavior of d_{33} against temperature is reflected to be a macroscopic illustration of the evolution of temperature-dependent spontaneous polarization [17]. Peaks at phase transition temperatures are strongly ascribed to the lattice softening and structural relaxation, that guide to an enlarged mobility of domains and rare sensitivity to the external stress or electric filed. This is also termed as "constrained negative stiffness effect" in the literature [17], which may contribute to the peaks near phase transitions and thus improved piezoelectricity.

Theoretical analysis has shown that the high piezoelectric response can be induced by the constrained negative stiffness because of the coupling between electric and strain field [18]. Negative stiffness can be induced in $BaTiO_3$-based ceramics the following way; it is relevant at the macroscopic scale and is anticipated in the context of Landau theory of ferroelastic transformations: when temperature is reduced down from a value above the transition temperature, then spontaneous strain and temperature having single minimum slowly flattens and acquire two or more minima i.e. potential wells. The curvature of the spontaneous strain (energy function of strain) denote an elastic modulus. Therefore, the curve flattening signifies a softening of the modulus close to the critical temperature, while the reversed curvature depicts a negative stiffness at small strain.

4. Discussion

Optimized poling conditions, (poling field, poling time, and poling temperature) of a piezoelectric material is attributed to the alignment of the ferroelectric as well as ferroelectric domains upon an applied electric field, which is essential to enhance the piezoelectric properties of the BCZT ceramic. It is believed that a suitable poling temperature may also assist accumulation of charge carriers at the grain boundaries that can heighten the piezo-response of the samples [5,10] and it was found to be near RT, i.e. 24°C in the current study. The low poling field makes the switching inadequate as in the case between 0.4 and 1.6 kV/mm poling field. However, excessive poling field and poling time tends to over-pole the sample, which may initiate physical defects and ultimately to the dielectric breakdown of the BCZT sample [14]. This could explain the decrease in the d_{33} values when sample poled over poling field > 2 kV/mm (Figure 2(b)) and excessive poling time > 10 min (Figure 4(a,b)) in the current study. Poling dependence study by Su et al. [5] and Praveen et al. [6] revealed that the optimal poling voltage for BCZT ceramics is approximately two or three times of the E_C and poling temperature in the range of 30–40°C reaching d_{33} values > 600 pC/N and they ascribed it to the multiphase coexistence. Wu et al. [9] reported optimal d_{33} = 423 pC/N at poling voltage and poling temperature 4 kV/mm and 40°C, respectively. Our previous work also shows the d_{33} value ~ 420 PC/N, when BCZT ceramic poled at 3 kV/mm for 10 min [19]. However, in the current study the BCZT ceramics show d_{33} = 505 pC/N at 24°C (RT), when sample poled at 2 kV/mm for 10 min and d_{33} = 622 pC/N (assumed from the value $d_{33(E=0)}$ = 622 pm/V) at $T_{O\text{-}T}$ = 32.6°C. Keeping in mind that $T_{O\text{-}T}$ is not the poling temperature but phase transition point, which is the main reason for obtaining similar high d_{33} values previously reported [1,6]. Change in poling field did not affect the phase structure of BCZT ceramic in the current study as confirmed by XRD spectra.

5. Conclusion

In summary, high piezoelectric properties (d_{33} = 505 pC/N and k_p = 56%) were attained at the optimized conditions i.e., 2 kV/mm for 10 min at 24°C i.e., room temperature. Also, piezoelectric constant $d_{33(E=0)}$ = 622 pm/V was measured at 32.6°C, the point at which orthorhombic-tetragonal phase transition occurs. The crystal structure remains unaffected with the poling field and time. This work notably finds the appropriate poling conditions for BCZT ceramics to reach ideal poling state and thus heighten the piezoelectric response.

Acknowledgments

The authors gratefully acknowledge the support of the Czech Science Foundation (project No. 18-20498S) The research has also been financially supported by the Ministry of Education, Youth and Sports of the Czech Republic under the projects CEITEC 2020 (LQ1601) and CzechNanoLab Research Infrastructure (LM2018110).

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Grantová Agentura České Republiky [18-20498S]; Ministerstvo Školství, Mládeže a Tělovýchovy [LQ1601]; CzechNanoLab Research Infrastructure [LM2018110].

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