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Effects of sintering temperature and poling conditions on the electrical properties of $Ba_{0.70}Ca_{0.30}TiO_3$ diphasic piezoelectric ceramics

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Abstract

The effects of sintering temperature and poling conditions on the electrical properties of tetragonal and orthorhombic diphasic $Ba_{0.70}Ca_{0.30}TiO_3$ (BCT) lead-free ceramics have been systematically investigated. On the one hand, with increasing sintering temperature from 1270 °C to 1400 °C, the bulk density increases monotonically and the Curie temperature keeps almost constant with the value of ~120 °C, whereas the grain size, the maximum relative dielectric constant, room temperature polarization reach the maximum values for samples sintered at 1340 °C. On the other hand, it is found that the piezoelectric property depends on poling electric field and poling temperature significantly. An enhanced piezoelectric behavior of $d_{33}=126$ pC/N, $k_p=0.29$, and $Q_m=588$ is obtained for the BCT ceramics poled at 100 °C with 30 kV/cm field for 20 min. The aging behavior of the piezoelectric property is also investigated.

Keywords: $Ba_{0.70}Ca_{0.30}TiO_3$; Piezoelectric properties; Poling conditions; Sintering

1. Introduction

Piezoelectric ceramics have been extensively used in various electronic devices such as transducers, sensors, actuators, etc. [1]. Lead-based piezoelectric ceramics exemplified by Pb(Zr,Ti)O_3 close to the morphotropic phase boundary (MPB) play a leading role in the field of electromechanical applications for their superior properties. However, the use of lead-based materials causes serious environmental problems because of the high toxicity of lead oxide [2–4]. Therefore, considerable attention has been devoted to investigating lead-free piezoelectric materials to replace the widely used lead-based counterparts [5–9].

$BaTiO_3$ (BT) based ceramics are one of the promising lead-free candidates showing promising properties [10–14]. Up to now, many BT-based solid solutions have been reported with enhanced dielectric, ferroelectric and piezoelectric properties [11–15]. Among these solutions, $BaTiO_3$–$CaTiO_3$ (BT–CT) is of particular interests because of its unique electric behaviors and the existence of solution limit [16–18]. At room temperature, BT and CT have tetragonal and orthorhombic crystal structure, respectively. It has been established that in BT-rich $Ba_{1-x}Ca_xTiO_3$ solid solutions, the substitution of Ca^{2+} for Ba^{2+} causes a negligible change of Curie temperature (T_C) [18], but strong decrease of the tetragonal–orthorhombic phase transition temperature (T_{O-T}), which leads to improved temperature reliability of dielectric property [19,20]. In addition, there is a solubility limit for the Ca^{2+} substituting for Ba^{2+} around $x=0.23$, above which the solutions have tetragonal and orthorhombic diphasic structures [18,21]. Although $Ba_{1-x}Ca_xTiO_3$ solid solutions have been intensively investigated from the viewpoint of both structure and properties, no detailed studies about the influences of sintering temperature and poling conditions on the electrical properties have been reported, especially for the diphasic compositions, which is of particular importance because based on the diphasic

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$Ba_{0.7}Ca_{0.3}TiO_3$, some lead-free materials with excellent room temperature electric performance have been developed very recently [12–14].

It is noted that piezoelectric ceramics are mostly fabricated by solid state reaction technique. The electrical properties of the ceramics are sensitive to their microstructures, and sintering temperature is one of the key parameters determining the microstructures [22,23]. Moreover, poling, a process involving domain reorientation and domain wall movement driven by an external electric field, is a necessary process to yield macroscopic piezoelectric property. So, it is reasonable that to obtain the best piezoelectric performance, the effects of sintering temperature and poling condition on the electrical properties should be well optimized. On the other hand, piezoelectric aging, which is defined as the spontaneous change of electromechanical properties with time under zero external stress and a constant temperature, is one of the key factors that should be considered for actual application [24,25]. That means the aging behavior of piezoelectric ceramics should be explored in terms of possible device applications.

In this paper, the influences of sintering temperature, poling temperature and poling electric field on the microstructure, dielectric, ferroelectric and piezoelectric properties of diphasic $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics were systematically investigated. The aging behavior of the ceramics was also explored and the possible mechanisms for the aging were discussed.

2. Experimental procedure

$Ba_{0.70}Ca_{0.30}TiO_3$ (BCT) ceramics were prepared by a conventional solid-state reaction method using $BaCO_3$ (99.0%, Alfa Aesar), $CaCO_3$ (99.0%, Alfa Aesar), and TiO_2 (99.0%, Alfa Aesar) as raw materials. The dried raw materials were weighed according to the stoichiometric formula and ball milled in ethanol for 12 h. The dried slurries were calcined at 1050 °C for 3 h and then ball milled in ethanol again for 16 h to obtain homogeneous powder. Disks of 13 mm in diameter and 0.5–1 mm in thickness were pressed under pressure of 100 MPa. 8% polyvinyl alcohol (PVA) was used as binder, which was burnt out by slow heating at 550 °C for 2 h. The disks were sintered at 1270–1400 °C in air for 4 h, followed by a furnace cooling. The density was determined by the Archimedes method.

The crystal structures of the ceramics were identified by X-ray diffraction (XRD) on grounded, unpoled samples with an automated Rigaku D/max 2400 X-ray diffractometer using CuKα radiation. The microstructures were recorded by a scanning electron microscopy (Quanta 200FEG SEM). For electric measurements, the sintered disks were grounded carefully to ensure the parallel surfaces. The circular surfaces of the disks were covered with a thin layer of silver paste and fired at 600 °C for 30 min. The silver layers served as electrodes. The temperature dependence of dielectric property was measured using an Agilent E4980A LCR meter at frequencies ranging from 100 Hz to 1 MHz in a temperature range of 30–250 °C. The ferroelectric polarization–electric field (*P–E*) hysteresis loops were measured with precision premier II (Radiant Tech. USA) in silicone oil. For piezoelectric measurements, Samples were poled in silicone oil at various temperatures (15–110 °C) and under various DC electric fields (10–40 kV/cm) for 20 min, the electric field was maintained during cooling. The piezoelectric constant (d_{33}) was measured using a quasi-static d_{33} meter (Institute of Acoustics, Chinese Academy of Sciences, ZJ-4A, China). The planar electromechanical coupling factors (k_p) and the mechanical quality factor (Q_m) were measured by a resonance–antiresonance method using an impedance analyzer (Agilent 4294 A) and calculated following IEEE standards. The poled samples sintered at 1340 °C for 4 h were placed for days, and then the piezoelectric properties were measured again to study the aging behavior.

3. Results and discussion

Fig. 1 shows the XRD patterns of the BCT ceramics sintered at various temperatures. All ceramics show coexisted tetragonal and orthorhombic phases without any other impurity phases, which is consistent with other report.[18,21,26] Fig. 2(a)–(d) shows the typical SEM microstructures of the BCT ceramics sintered at 1290 °C, 1340 °C, 1380 °C, and 1400 °C, respectively. The small and large grains are attributed to the orthorhombic and tetragonal phases, respectively, [18] as can be seen, the small orthorhombic grains are dispersed among the larger tetragonal grain matrix, this is consistent with the XRD data (Fig. 1) and the previous report on BCT.[18] It is found the averaged tetragonal grain size increases significantly with increasing sintering temperature, reaches the maximum value of 6.2 μm for the samples sintered at 1340 °C, and then decreases. It should be noted this observation is not only self-consistent with the XRD data (Fig. 1) and the corresponding electrical properties shown in the follows, but also in agreement with other reports

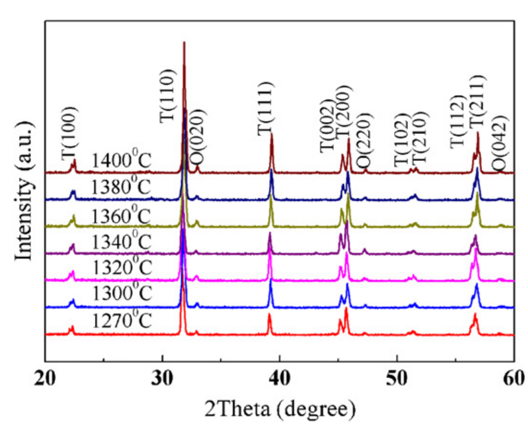

Fig. 1. XRD patterns of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics.

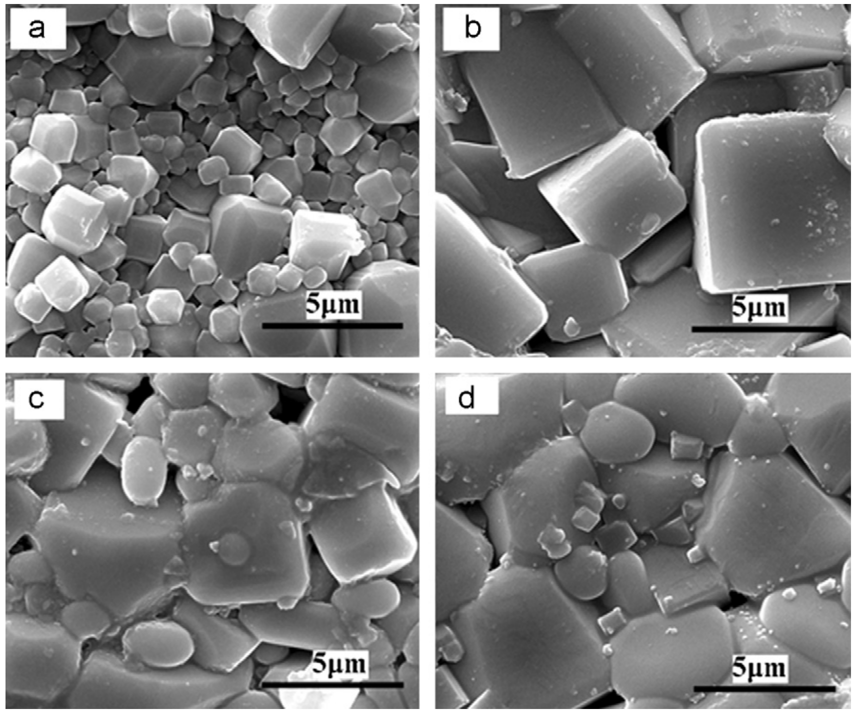

Fig. 2. SEM micrographs of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics sintered at (a) 1290 °C, (b) 1340 °C, (c) 1380 °C and (d) 1400 °C for 4 h.

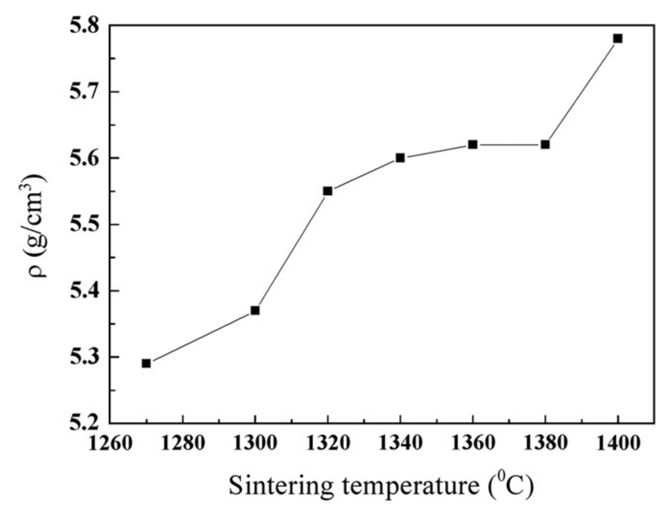

Fig. 3. Density of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics as a function of sintering temperature.

[27,28]. However, the orthorhombic grain size is almost independent on sintering temperature with the constant value of 2.5 μm. Furthermore, increasing the sintering temperature leads to increased density, the bulk density of the BCT ceramics as a function of sintering temperature is shown in Fig. 3.

Fig. 4(a)–(d) shows the typical temperature dependence of the relative dielectric permittivity (ε_r) and dissipation factor tangent (tanδ) of BCT ceramics sintered at 1270 °C, 1340 °C, 1380 °C, and 1400 °C, respectively. The ceramics sintered with other temperatures show the similar $\varepsilon_r - T$ and $\tan\delta - T$ curves. As can be seen, all the samples show sharp ferroelectric-paraelectric transition peaks (T_C) around 120 °C, and the T_C is slightly frequency dependent, indicating the weak relaxor characteristics. The maximum relative dielectric permittivity (ε_m) at T_C of all ceramics measured at 1 kHz is plotted in Fig. 5. It is found the T_C value is almost independent on sintering temperature within the range of 119–124 °C. However, with increasing sintering temperature, ε_m increases, reaches the maximum value of 6890 for the samples sintered at 1340 °C for 4 h, and then decreases. We note this trend is consistent with the change of the tetragonal grain size.

Fig. 6(a) presents the room temperature P–E hysteresis loops of the BCT ceramics sintered at different temperatures measured with the applied field of 70 kV/cm. Well saturated ferroelectric P–E hysteresis loops were observed for all the ceramics. The maximum polarization (P_{max}) and remnant polarization (P_r) of the BCT ceramics as a function of sintering temperature are plotted in Fig. 6(b). Obviously, with increasing sintering temperature, P_{max} and P_r increase, reaches the maximum values of 14.8 μC/cm^2 and 8.0 μC/cm^2, respectively, for the ceramics sintered at 1340 °C, and then decreases to 12.1 μC/cm^2 and 5.2 μC/cm^2 for the ceramics sintered at 1400 °C.

Fig. 7 shows the piezoelectric properties of the BCT ceramics sintered at different sintering temperatures. The ceramics sintered at the temperatures less than 1340 °C have a low d_{33}, k_p, and Q_m values. A maximum d_{33} value, together with a highest k_p value and a highest Q_m value are observed for the ceramics sintered at 1340 °C, which is ascribed to increased grain size of the tetragonal phases sintered at 1340 °C, while little contributed from orthorhombic phase (grain size is nearly independent on sintering temperatue). Actually, if the tetragonal phase is suppressed

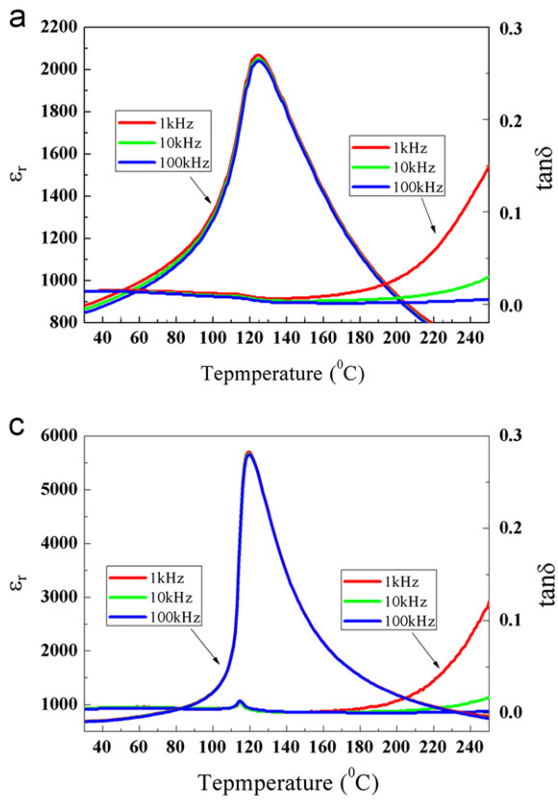

Fig. 4. Typical temperature dependent dielectric properties of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics sintered at (a) 1270 °C, (b) 1340 °C, (c) 1380 °C and (d) 1400 °C.

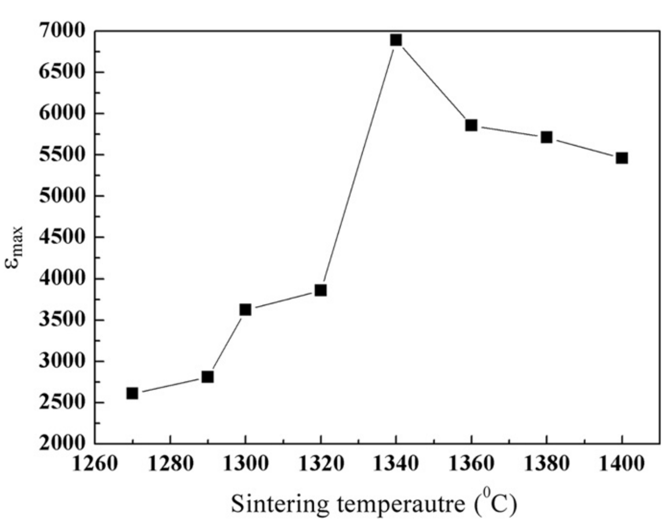

Fig. 5. The maximum relative dielectric permittivity (ε_m) at T_C of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics measured at 1 kHz.

till to form diphasic pseudocubic-orthorhomic phases, the electric properties will be greatly weakened, as will be reported elsewhere. With further increasing sintering temperature, the d_{33}, k_p, and Q_m decreases.

The above mentioned structures, dielectric, ferroelectric and piezoelectric properties are self-consistent. At the beginning, the increase of sintering temperature ($\leq$1340 °C) leads to significantly increased tetragonal grain size (Fig. 2), which promotes ferroelectric property because lager grain size means less amount of grain boundary, while ground boundary will leads to polarization discontinuity between grains and hence decreased polarization [29]. It can be concluded that within our experiments, the optimized sintering temperature for BCT is around 1340 °C.

To optimize the poling conditions, the BCT ceramics sintered at 1340 °C were poled at different poling temperature (T_p) and poling electric field (E_p). Firstly, the ceramics were poled with different T_p but a fixed E_p of 30 kV/cm for 20 min, the results are shown in Fig. 8(a). It can be observed that the piezoelectric properties of BCT ceramics are significantly affected by the T_p. The d_{33}, k_p, *and* Q_m values increase with increasing T_p and reaches maximum simultaneously when poled at 100 °C, and then decrease when T_p approached to 110 °C. At a proper T_p close to but lower than the phase transition temperature, the ferroelectric domains might be metastable, and so it is easy to make domains well oriented by an external field, so more contribution from reoriented domain to piezoelectric property. Accordingly, the piezoelectric property increases with increasing T_P. However, too high T_p means the BCT are close to paraelectric phase, which means the decreased ferroelectric domains and so the reoriented domains decrease, this should be responsible for the decreased piezoelectric property in Fig. 8(a).

On the other hand, with fixed T_p of 100 °C and poling time of 20 min, the E_p dependent piezoelectric properties are shown in Fig. 8(b). The d_{33}, k_p, and Q_m values are low when $E_p \leq 10$ kV/cm because of the inadequate switching of the ferroelectric polarization, and they gradually increase with increase E_p due to the adequate switching of the domain with increasing E_p. Generally, the 180° ferroelectric domain can be easily switched even under low E_p, while the other domains like 90° domain can only be switched under a relatively high electric field. So higher E_p, more switched domains, and higher piezoelectric properties. However, excessive E_p (35 kV/mm in this case) tends to over-pole the samples which lead to physical flaws and eventually to the dielectric breakdown of the samples. Based on the above description, the enhanced piezoelectric properties with d_{33} ~ 126 pC/N, k_p ~0.29, and Q_m ~ 588 could be obtained with the optimum poling conditions of E_p = 30 kV/cm and T_p = 100 °C for 20 min.

For aging investigation, the BCT ceramics sintered at 1340 °C for 4 h were poled and placed at room temperature for days. Fig. 9 shows the relative decrease of d_{33} and k_p with respect to the initial values as a function of aging time. It can be observed that the piezoelectric properties of the samples decrease dramatically within the initial 1000 min after poling, the d_{33} and k_p decrease ~25% and ~20%, respectively. With further increase in aging time, the decrease of both d_{33} and k_p become gradual. One of the possible mechanisms for aging might be as follows. The high internal stress induced by 90° domain wall motion and rotation of ferroelectric domains under electric field tends to force part of oriented domains to switch back after the electric field was removed, [30] after the removal of electric field, the domains switch back dramatically to relax the stress, which corresponds to the significant aging behavior within the initial 1000 s. Then the further relaxation of stress is gradual, leading to gradual aging behavior.

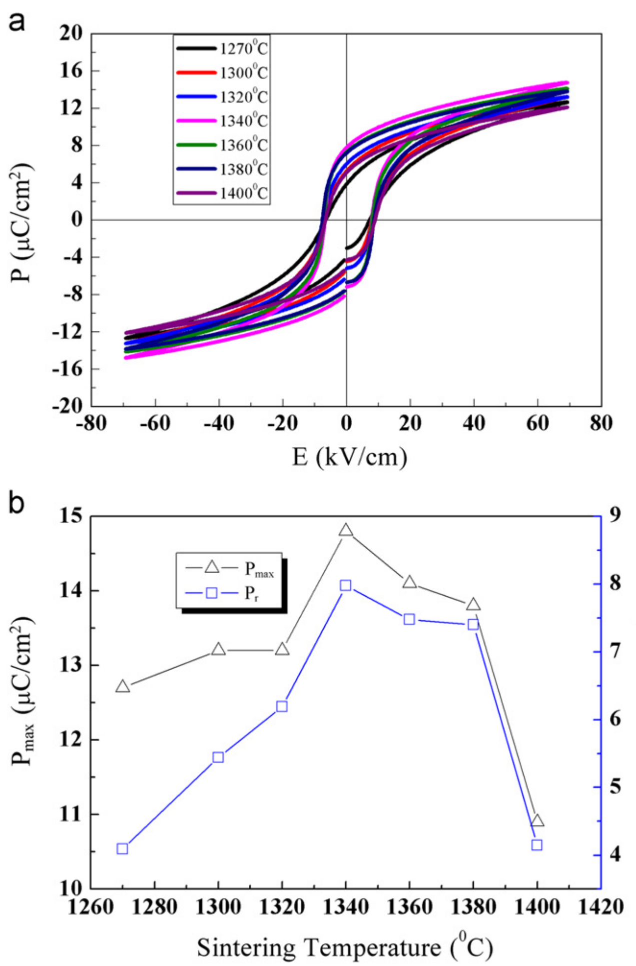

Fig. 6. (a) *P–E* hysteresis loops of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics measured at room temperature, (b) P_{max} and P_r values of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics as a function of sintering temperature.

4. Conclusions

Diphasic $Ba_{0.70}Ca_{0.30}TiO_3$ lead-free piezoelectric ceramics have been prepared with different sintering temperatures and the structures, dielectric, ferroelectric and piezoelectric properties have been systematically investigated, based on the results, the optimized sintering temperature is determined to be close to 1340 °C. With fixed poling time of 20 min, the optimized poling electric field and poling temperature are around 30 kV/mm and 100 °C, respectively. Under the optimized poling conditions, the ceramics sintered at optimized temperature show enhanced piezoelectric behavior of d_{33} ~ 126 pC/N, k_p ~ 0.29 and Q_m

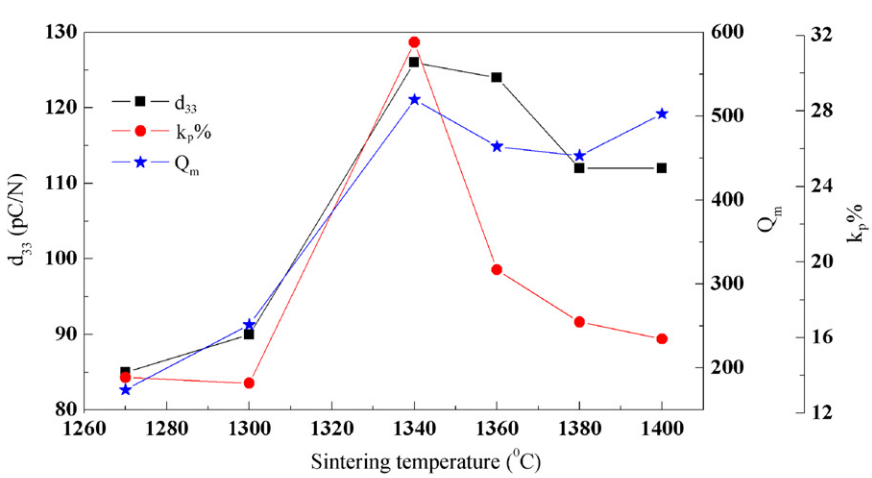

Fig. 7. Piezoelectric properties of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics as a function of sintering temperature.

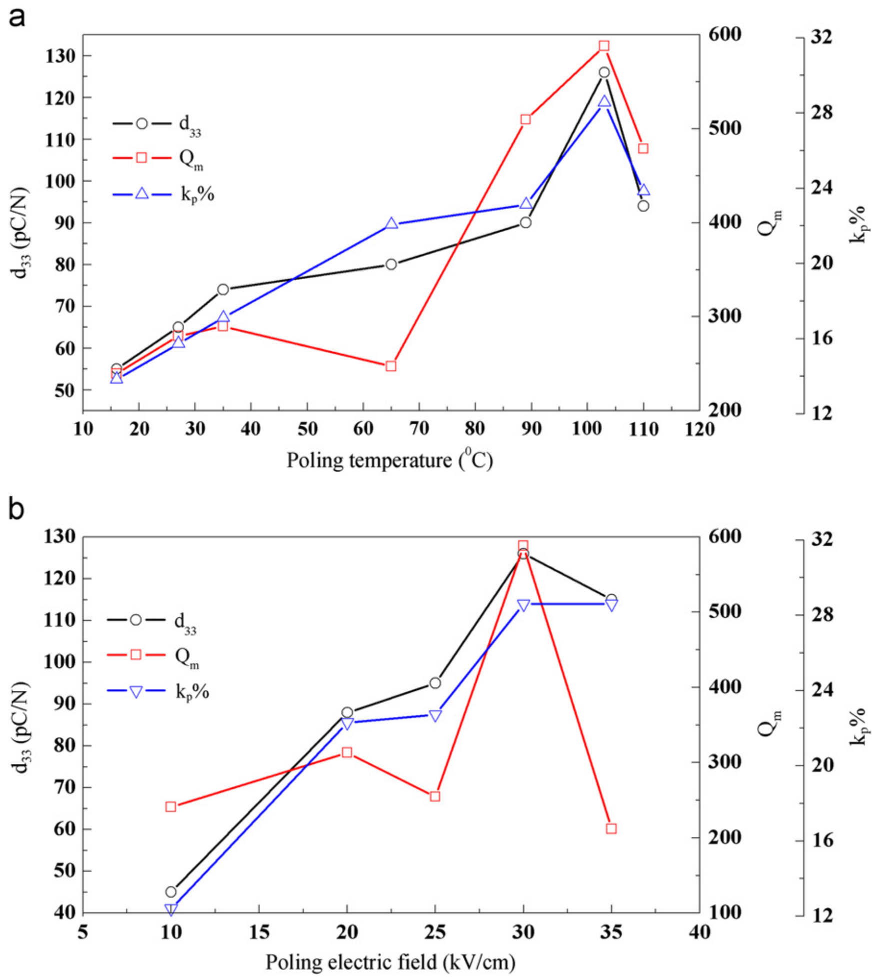

Fig. 8. The piezoelectric properties of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics as a function of (a) the poling temperature with fixed poling electric field of 30 kV/cm, and (b) poling electric field with the poling temperature of 100 °C.

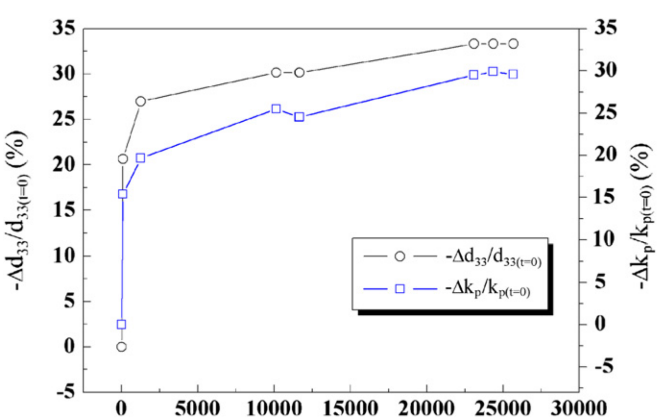

Fig. 9. The aging behavior of the k_p and d_{33} of the $Ba_{0.70}Ca_{0.30}TiO_3$ ceramics.

~588. Aging behavior is investigated and dramatic aging behavior is observed within the initial 1000 s. These results may be helpful for improving the electric properties of BCT-related lead-free materials.

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