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Grain size effect on the poling of soft $Pb(Zr,Ti)O_3$ ferroelectric ceramics

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Abstract

The properties of piezoelectric ceramic materials are strongly dependent on the degree of polarization as set by the poling process. As the polarization depends on the domain wall mobility, which in turn depends on the domain size and grain size, the current study focuses on the effect of the grain size on the poling process and dielectric and piezoelectric properties. Polarization and pyroelectric, dielectric and piezoelectric properties of modified donor doped ferroelectric $Pb(Zr,Ti)O_3$ ceramics having different grain sizes have been studied. The dielectric and piezoelectric parameters greatly improved at room temperature with increasing grain size. The Curie temperature (160 °C) is found to shift slightly (by about 7 °C) towards higher temperatures as the grain size increases (2–10 μm). It is concluded that, an optimum choice of a combination of poling field and grain size leads to optimum physical properties. A limited dependence of the dielectric properties on the grain size in non-poled state exists. The dominant contribution to the dielectric properties in the different conditions of the material is discussed.

Keywords: Pb (Zs; Ti) O_3; Poling; Ferroelectrics; Grain size; Domains

1. Introduction

Investigations of the effect of grain size on the phase transition in ferroelectrics date back to the 1950s. Kniekamp and Heywang[2] showed that the ferroelectricity in ($BaTiO_3$) BT single crystals disappears for sufficiently small crystal size. In polycrystalline BT the permittivity increases with decreasing grain size.[3] Coincidently with Kniekamp and Heywang, Känzig and co-workers[4,5] investigated the effect of grain size on T_C for other polycrystalline ferroelectrics. With decreasing grain size in the range of 1–5 μm for sintered samples with high density, it was found that (i) there is a decrease in the dielectric constant, (ii) the dielectric constant peak becomes broader, (iii) the Curie transition temperature T_C rises.

However, with the availability of more advanced chemical preparation techniques (*sol–gel*, *hydrosol*, *aerosol*, *microemulsion*, *etc.*), it is now established that the decrease in the grain size causes (i) a monotonic reduction in the transition temperature T_C contrary to early observation, (ii) the dielectric constant peak becomes wider, (ii) the ferroelectric phase transition becomes increasingly diffuse, (iv) the crystallographic distortion of the unit cell, which characterizes the ferroelectric phase, decreases and tends towards higher symmetry.[6]

Uchino et al.[8] made a detailed study on the variation of the tetragonal distortion (c/a) with particle size in $BaTiO_3$ and have identified the T_C as that temperature at which (c/i) → 1. They estimated the critical size of the crystal below which the ferroelectricity cannot be observed as 120 nm. In a more recent study, Saad et al. showed that the ferroelectricity in BT can be observed in unconstrained materials in samples as small as 70 nm.[9]

Recently, the study of grain size effects (on the *nanometer* scale) in ferroelectric systems has become very important because of their potential applications, especially as non-volatile memory elements. The miniaturization of ferroelectric electroceramic components is accompanied by the necessity of reducing of the grain size. The domain size, domain configuration and domain wall mobility all change with a reducing grain size.[7]

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Table 1
Grain size effects on PZT systems (adopted from Randall et al.[7] and references therein)

Reference	Year	Grain size μm	Dielectric constant ε_r at 25 °C	Piezoelectric property at 25 °C	Transition parameters	Model	Comments
Haertling	1964	2–5	Increases	As E_C increases, P_r decreases			Hot-pressed ceramics
Geseman	1965	3–7		As k_p decreases, P_r decreases			
Webster and Weston	1986	1.7–6	Increases	As k_p and Q_m decrease, P_r decreases		Internal-stress model	Clamping of domain motion
Okazaki and Nagata	1971	1.7–6	Decreases	k_{ij} decreases	As T_C increases, ε_{max} decreases		Porosity effects are also important
Ouchi et al.	1965	1–4		As d_{ij} and k_p decrease, E_C increases	As T_C increases, ε_{max} decreases	Space-charge model	Lanthanum-doped PZT
Martirena and Burfoot	1974	1.8–4.6	Decreases	d_{ij} decreases	As T_C increases, ε_{max} decreases	Gaussian distribution	Hot-pressed niobium-doped PZT
Keizer and co-workers	1973 1975	0.6–10			As T_C increases, ε_{max} decreases	Internal-stress model	Propose hydrostatic effect; lanthanumdoped PZT
Pisarski	1988 1989	3			As T_C increases, ε_{max} decreases		Width of MPB region change
Rossetti	1991				2D T_C increases	2D or 3D stress model	Devonshire theory; thin-film $PbTiO_3$
Yamamoto	1992	0.6–10		As E_C increases, P_r and k_p decrease	As Tc decreases, ε_{max} decreases	PbO grain boundary	Processing dependence

There have been many earlier attempts to investigate the influence of grain size on the piezoelectric properties in PZT ceramics.[7] In general, grain-size studies were limited in a range of 1.0–10 μm in bulk ceramics. The variations in properties with grain size, as summarized in Table 1, showed little consistency. Reasons for the inconsistencies are believed to be related to processing and the control of grain-boundary resistivities that lead to space-charge accumulation, which masks the size–effect response in the ferroelectric grains.[7]

One of the intrinsic microstructural characteristics in ferroelectric PZT ceramics are the internal stresses that develop because of the incompatible strains occurring during the paraelectric-ferroelectric transition.[10] In addition, the thermal expansion anisotropy of tetragonal crystals may also contribute to the stress development. According to the *internal stress model* proposed by Buessem et al.[3] the large internal stress developed during cooling of PZT is released by the formation of a polydomain structure. A polydomain structure is possible if the grain is large enough to contain multiple domains. Consequently the internal stress along the grain boundary would be substantially relieved in large PZT grains by the possible formation of multidomain structure. For small PZT grains, however, the formation of polydomain structure may not occur. Consequently, the internal stress increases during the cooling. Such a stress will not be relieved by the formation of 90° domains and leads to a decrease in T_C.[3]

Very recently we reported on the optimum poling conditions of soft ferroelectric ceramic PZT.[1] The approach was to employ some preconditions of poling followed by evaluation of the degree of polarization by different methods. Using the switching current and pyrocurrent data, insight to the mechanism of polarization in soft ferroelectrics was gained.

The internal stresses can be relieved by increasing the grain size[3,11] as a result of polydomain formation, resulting in easy domain switching (i.e. easier poling). Therefore, the present study focuses on the dependence of the polarization and consequently the dielectric and piezoelectric characteristics on the grain size variation.

2. Experimental

Non-poled soft PZT (PXE52, modified donor doped $PbZr_{0.415}Ti_{0.585}O_3$) ceramic powder coded "*PXE 52″* were

Table 2
Sintering temperature and the corresponding resultant density and mean linear intercept (*Sample standard deviation in brackets*) of PXE 52

Sample name	Sintering temperature (°C)	Grain size (μm)	Density (ρ) g/cm^3
1	1150	2.0 (±0.4)	7.29
2	1175	3.5 (±0.2)	7.72
3	1200	4.5 (±0.4)	7.82
4	1225	5.7 (±0.9)	7.82
5	1250	7.0 (±1.2)	7.93
6	1275	8.6 (±1.1)	7.93
7	1300	9.8 (±2.2)	7.98

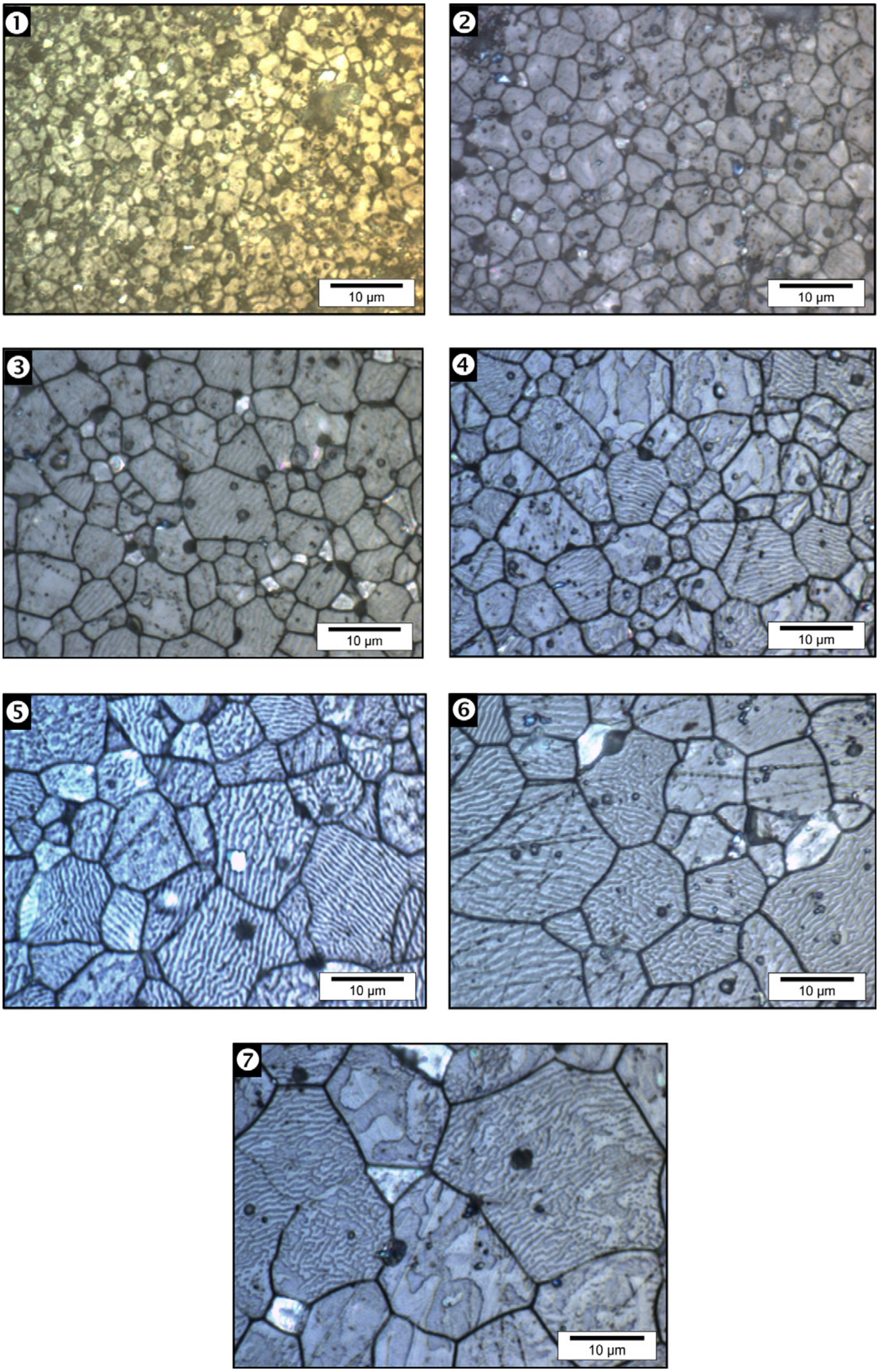

Fig. 1. Optical micrographs of samples (1–7) sintered at different temperatures (1150–1300 °C), see Fig. 2.

provided by Morgan Electro Ceramics B.V. Eindhoven, the Netherlands. The powder was pressed into bars of at least 15 mm in diameter and sintered at different temperatures (1150–1300 °C) in a tube furnace with flowing oxygen. The following sintering profile was applied for all bars. The bar was heated from room temperature to the desired temperature in 8 h and held at this temperature for 4 h and then cooled down to room temperature in 8 h. The sintered bars were diced into discs of 10 mm in diameter. Next, the discs were subjected to clean-firing at 700 °C for 48 h, cleaned in methanol in an ultrasonic bath for 2 min, washed in water and soap and then dried in air. Finally, the discs were electroded with Ni by sputtering for electrical measurements.

The microstructure of the as-prepared samples was investigated using polarized light optical microscopy. First, the sample was molded in a resin before grinding and successive polishing. Thereafter the sample surface was etched as described previously.[1] The grain size d_{GS} was measured using linear intercept method, counting about 100 grains.

Hysteresis loops were observed using a computer-controlled virtual ground method (*Radiant Technologies Inc., RT6000 HVA-z 2000 V amplifier and RT6000 HVS-z high voltage input test system*) using the fast mode (0.4 ms) at room temperature. The maximum applied electric field was 20 kV/cm. The polarization current measurements were carried on non-poled samples at applied electric fields of 3.75, 7.0, and 25 kV/cm at room temperature. The electric field was applied using the Keithley built-in voltage source. The pyroelectric measurement was carried out using the direct method.[12] Experimental details for pyroelectricity measurements are described in detail in reference 1.

The resonance method is commonly used to determine material coefficients of piezoelectric ceramics.[13,19,20] When excited at the resonance frequency f_r, the piezoelectric disc will resonate at a greater amplitude. For the anti-resonant frequency f_a, the impedance of the piezoelectric disc is at a maximum and the oscillation amplitude is at a minimum.[14] By measuring the resonance and anti-resonance frequencies f_r and f_a, along with dielectric parameters, the electromechanical coupling factors k_p, k_{33}, k_{31} and piezoelectric charge constants d_{33} and $-d_{31}$ can be calculated using the equations analyzed in references 14,19,20.

The dielectric and piezoelectric parameters of poled samples were measured using a *HP4294A Precision Impedance Analyzer* at 1 kHz in the temperature range from room temperature up to T_C.

3. Results

The microstructure of polished and etched surface of non-poled samples was analyzed using optical microscopy. Fig. 1 shows the optical micrographs for samples sintered at different temperatures (1150–1300 °C). As shown in Fig. 2 and summarized in Table 2, the grain size and density increased as a function of the sintering temperature. The average grain size ranges from ∼2 μm at 1150 °C to ∼10 μm at 1300 °C.

Fig. 3 depicts the hysteresis loops for the different grain sizes. At first glance, no major change is observed in the gross shape of the loops. The rectangular ratio of the hysteresis loops, defined as P_r/P_{max} where P_r is the remanent polarization and P_{max} is the maximum polarization,[15] did not significantly change. However, the coercive field slightly decreased with increasing grain size, as shown in Fig. 4. For the smallest grain (∼2 μm), $E_C = 8.0$ kV/cm and for the largest grain (∼10 μm) $E_C = 7.5$ kV/cm.

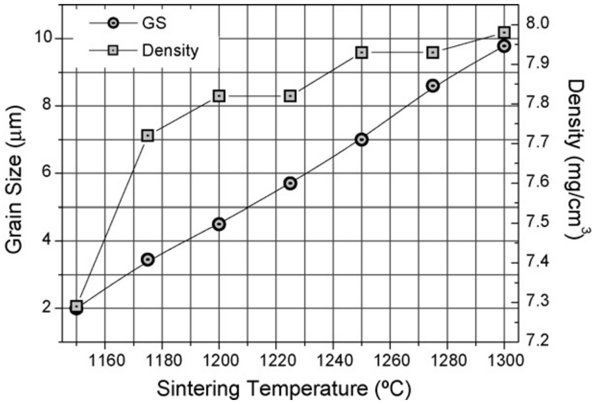

Fig. 2. Grain size and density as a function of sintering temperature for PXE 52. The lines serve as a guide to the eye.

As we discussed previously,[1] the poling field enhances the spontaneous polarization and dielectric properties. Fig. 5 summarizes the main results obtained previously[1] for the poling effect on P_s, ε_r and tan δ. It is clearly shown that when an electric field slightly higher than the coercive field (7.5 kV/cm) is applied at room temperature, a maximum enhancement in properties results. Following the same procedure as applied before,[1] Fig. 6 shows the polarization current as a function of time at a fixed field of 3.75 kV/cm for the different grain sizes. The polarization current profile shows the typical switching peak which is moving towards shorter time as the grain size increases. It is interesting to observe that for grain size ≥4.5 μm although the applied poling field is quite low ($0.5E_C$), the switching peak is observed. This behavior indicates the possibility of complete switching and consequently maximum polarization even at low field if the grain size is large enough. Fig. 7 illustrates the decrease of the switching time t_{sw} with the grain size. As can be expected, t_{sw} becomes probably constant at larger grain sizes than those used in the present work. For the smallest grain size the switching peak was not observed and this can be ascribed to the unrelieved internal stresses developed in fine grains which suppresses the orientation process.[3,10,11] Either the switching may occur at much longer time scale than used in our experiments or the switching process never occurs due to the indomitable counteracting internal stress.

By integrating the polarization current over the poling time, the polarization is obtained and plotted in Fig. 8a. The increasing grain size greatly enhances the polarization from 7.5 μC/m^2 for $d_{gs} = 2$ μm to 40 μC/cm^2 for $d_{gs} = \sim 10$ μm, as illustrated in Fig. 8b. Fig. 9a–c shows the pyroelectric coefficient as a function of temperature for the different grain sizes after different poling fields of 3.75, 7.5, 25 kV/cm, respectively. The pyroelectric activity is remarkably enhanced by increasing the grain size as a result of the increase of the spontaneous polarization. Furthermore, as a typical grain size effect, the inset figures show the shift of the Curie temperature towards higher temperature by increasing the grain size.

As we mentioned previously, the poling field enhances the dielectric properties. Figs. 10–13 show that increasing the grain size enhances the dielectric and piezoelectric

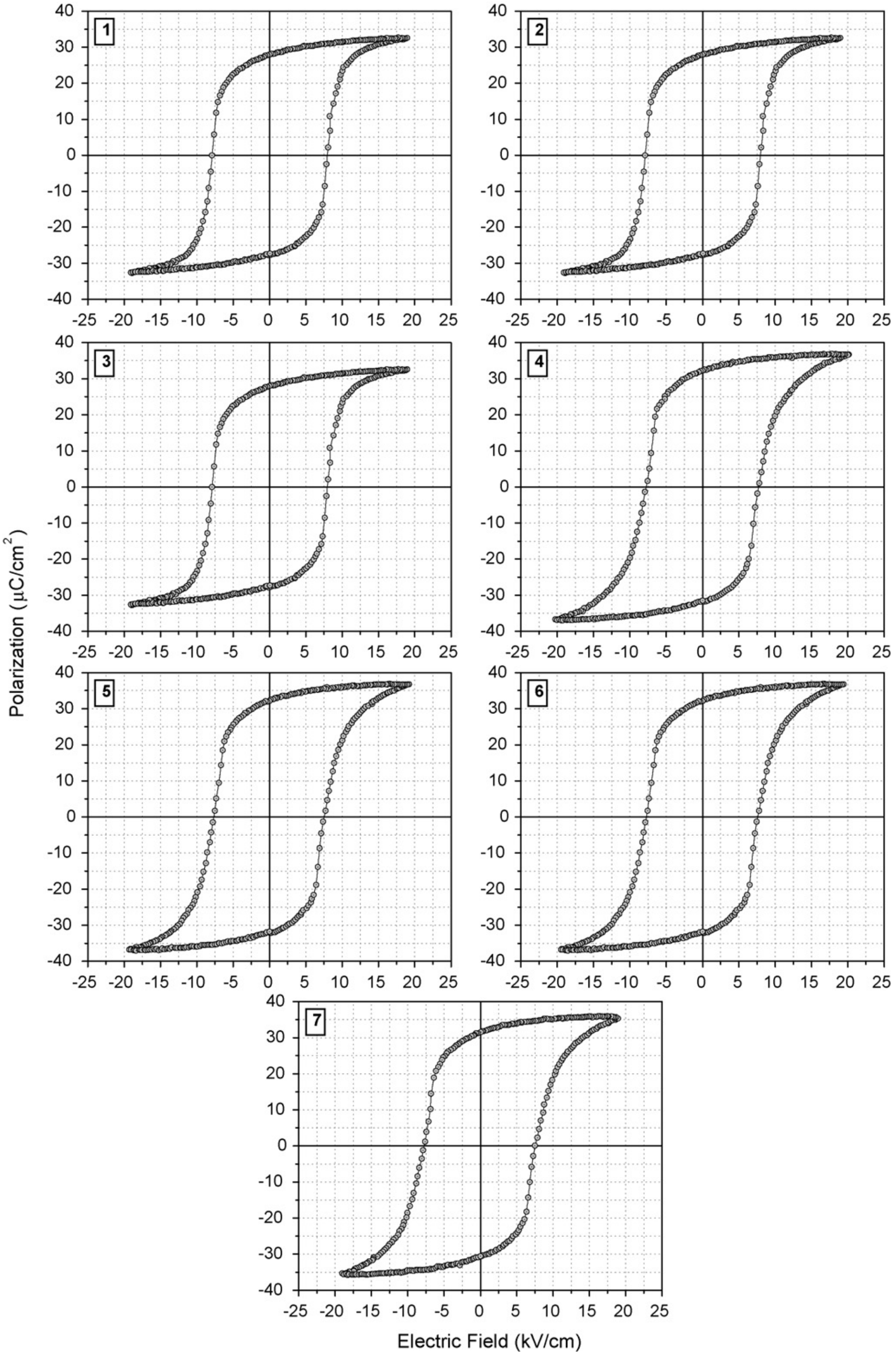

Fig. 3. Hysteresis loops as a function of grain size at room temperature and maximum field of 25 kV/cm.

parameters as a consequence of the improvement made in the polarization. The dielectric constant ε_r and dielectric dissipation factor $\tan\delta$ for poled materials greatly improve with respect to the non-poled case. The piezoelectric properties are also enhanced by increasing the grain size. The ultimate enhancement is a function of the poling field.

It is worth to point out that the dielectric properties (ε_r and $\tan\delta$) for non-poled samples did not considerably change with changing grain size. However, the post-poling properties are noticeably grain size/poling field dependent. This behavior raises the question of what are the effective contributions to the dielectric parameters before and after poling. This question will be discussed in the next section.

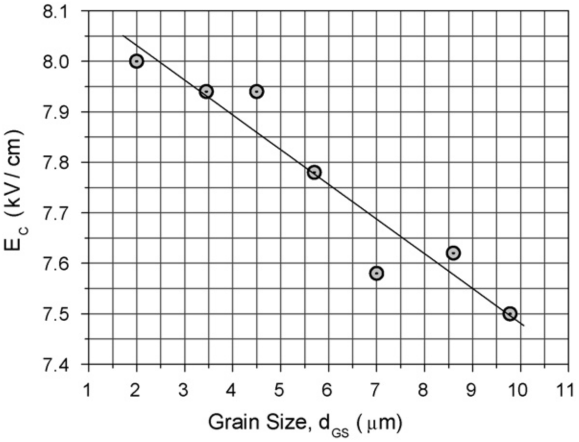

Fig. 4. The variation of coercive field E_C with grain size.

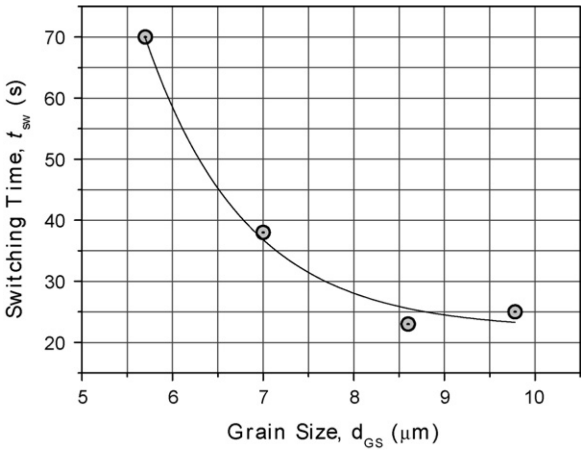

Fig. 7. Decreasing switching time t_{sw} with increasing grain size.

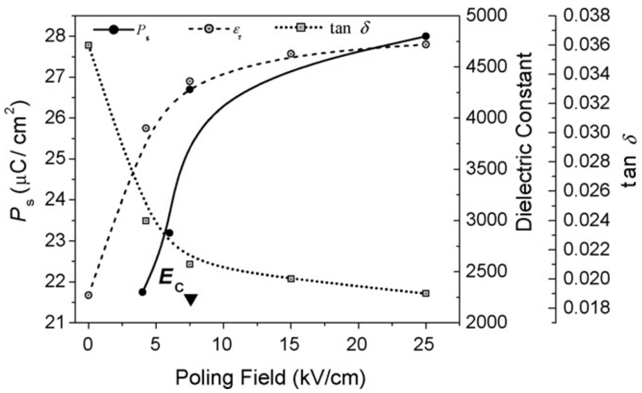

Fig. 5. Summery of poling effect on the polarization and dielectric properties as retrieved from reference 1

4. Discussion

4.1. Limits of the grain size effect

From the results of the dielectric and piezoelectric properties (Figs. 10–13) it can be concluded that by optimum combination of poling conditions and grain size the dielectric properties are significantly enhanced. However, the curves in Figs. 10d–13d show that the effect of increasing the grain size saturates at a certain grain size. This behavior can be explained as follows.[16] During the transformation form the paraelectric phase to the ferroelectric phase, the crystal splits into multiple domains. This splitting is necessary to lower the free energy by reducing the electrostatic and mechanical energy of the spontaneous polarization charges. However, domain splitting cannot be continued without limit because a definite energy is required for the formation of domain

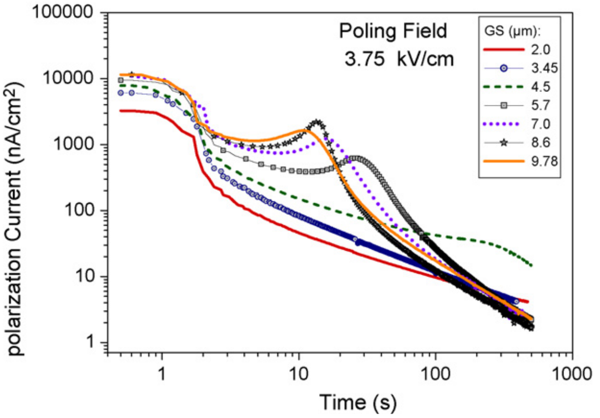

Fig. 6. The poling current as function of time for different grain sizes under applied poling field of 3.75 kV/cm at room temperature.

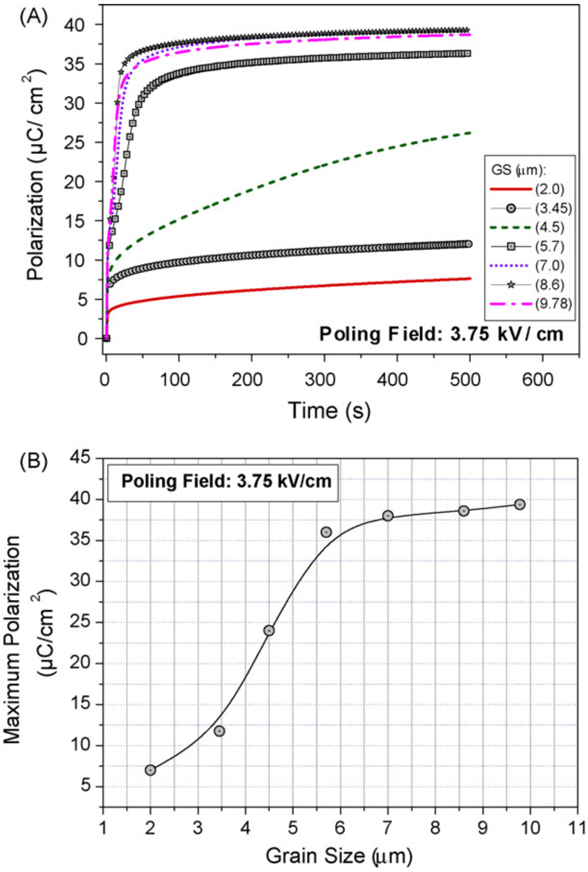

Fig. 8. (A) Polarization as calculated form curves in Fig. 6. (B) Maximum polarization as a function of grain size.

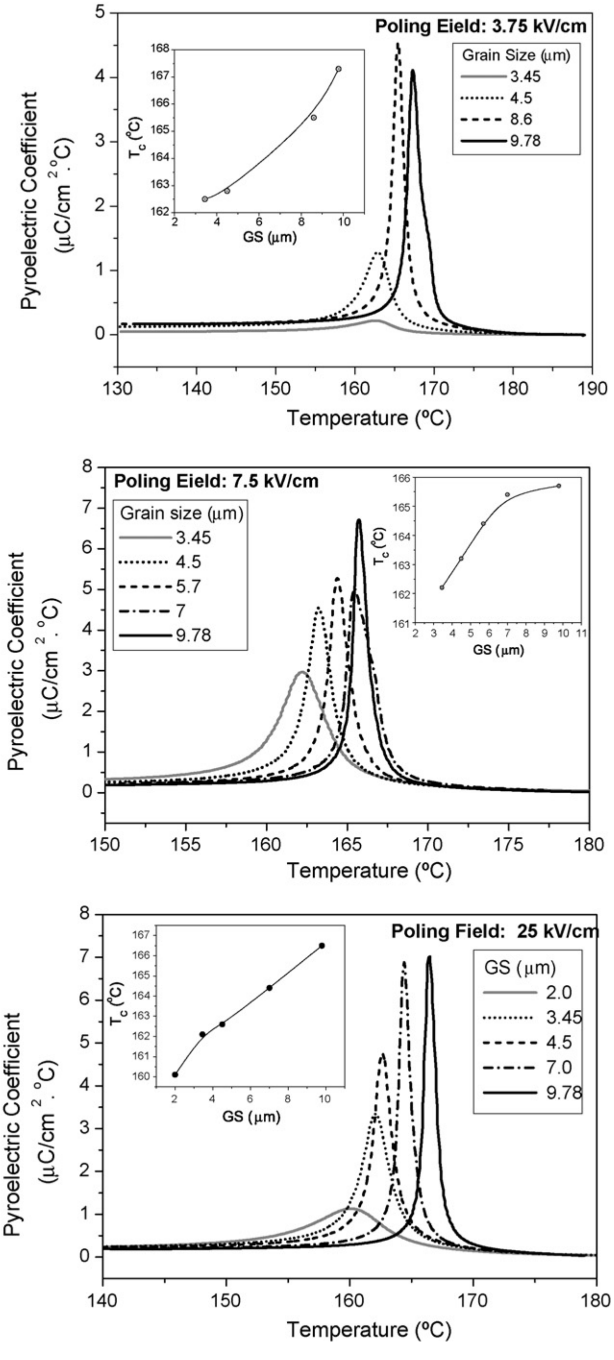

Fig. 9. Pyroelectric coefficient after different poling conditions.

walls. The splitting of a crystal into domains stops when the energy gained by reduction of the electrostatic energy becomes equal to the energy lost in the formation of domain walls.[16]

4.2. *Intrinsic and extrinsic contribution*

There are several polarization mechanisms contributing to the dielectric response;[17,18] (i) *electronic polarization*: the relative displacement of the negatively charged electron shell with respect to the positively charged core; (ii) *ionic polarization*: as observed in ionic crystals and describes the displacement of the positive and negative sublattices under an applied electric field; (iii) *orientation polarization*: the alignment of permanent dipoles via rotational movement; (iv) *space charge polarization (Maxwell–Wagner polarization)*: polarization due to spatial inhomogeneities of charge carrier densities;[20] (v) *domain wall motion*: plays a decisive role in ferroelectric materials and contributes significantly to the overall dielectric response. The total polarization of dielectric material results from all the contributions mentioned above. In bulk ferroelectric ceramics, the room temperature dielectric and piezoelectric properties result from a combination of the *intrinsic* lattice related response and *extrinsic* responses originating from domain wall motion, phase boundary, space charge, *etc*.[18,21–23]

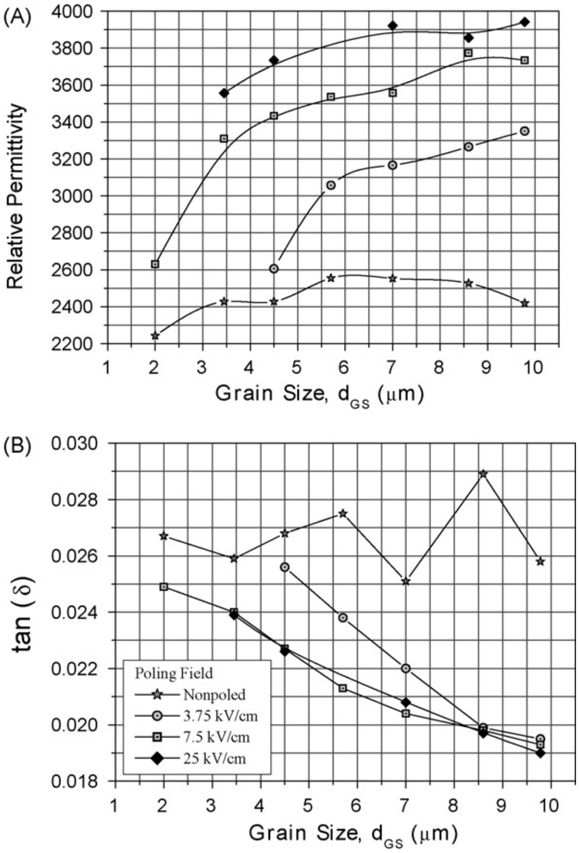

Fig. 10. Room temperature relative permittivity ε_r (A) and dielectric dissipation factor tan δ (B) as a function of grain size at different poling conditions.

$$\varepsilon_r = \varepsilon_{\text{int}} + \varepsilon_{ext} \qquad (1)$$

The extrinsic contributions can be separated in two types: *reversible* and *irreversible*. Both types are presented schematically in Fig. 14. Under a small (*subswitching*) field reversible movement of the wall is regarded as a small displacement either by vibration or bending around a local minimum. When the field becomes high enough to switch the domain, an irreversible contribution is expected.[18]

Small displacements of all types of domain walls will affect the polarization of the material whereas the movement of non-180° walls, in addition to the polarization change, directly contribute to the piezoelectric effect.[24,25,27] Displace-

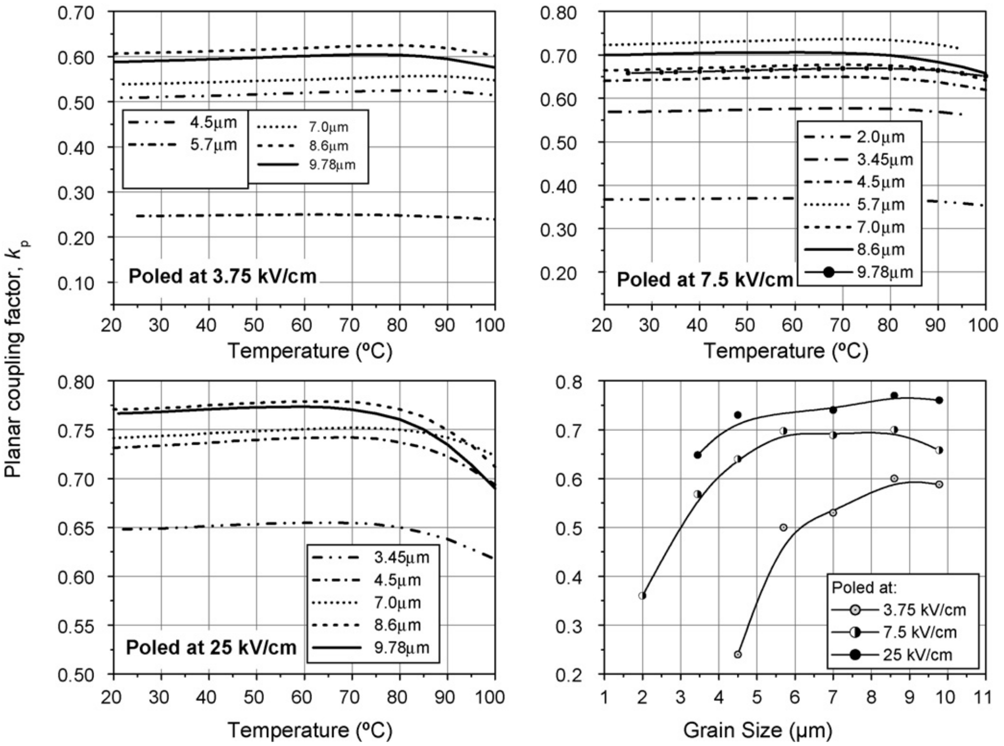

Fig. 11. Planar coupling factor k_p as a function of temperature at different grain sizes after different condition of poling, (A) $E = 3.75$ kV/cm, (B) $E = 7.5$ kV/cm, (C) $E = 25$ kV/cm, (D) k_p as a function of grain size at room temperature.

ment of domain walls also contributes to the dielectric and mechanical losses of ferroelectric materials and, particularly near the phase transition temperature, may dominate other loss mechanisms.[24]

By considering the ε_r–E curve (Fig. 15), the sharp peak at the coercive field is due to high domain wall density and motion (*extrinsic contribution*). At large fields, domain wall contributions are reduced due to a decrease in the number

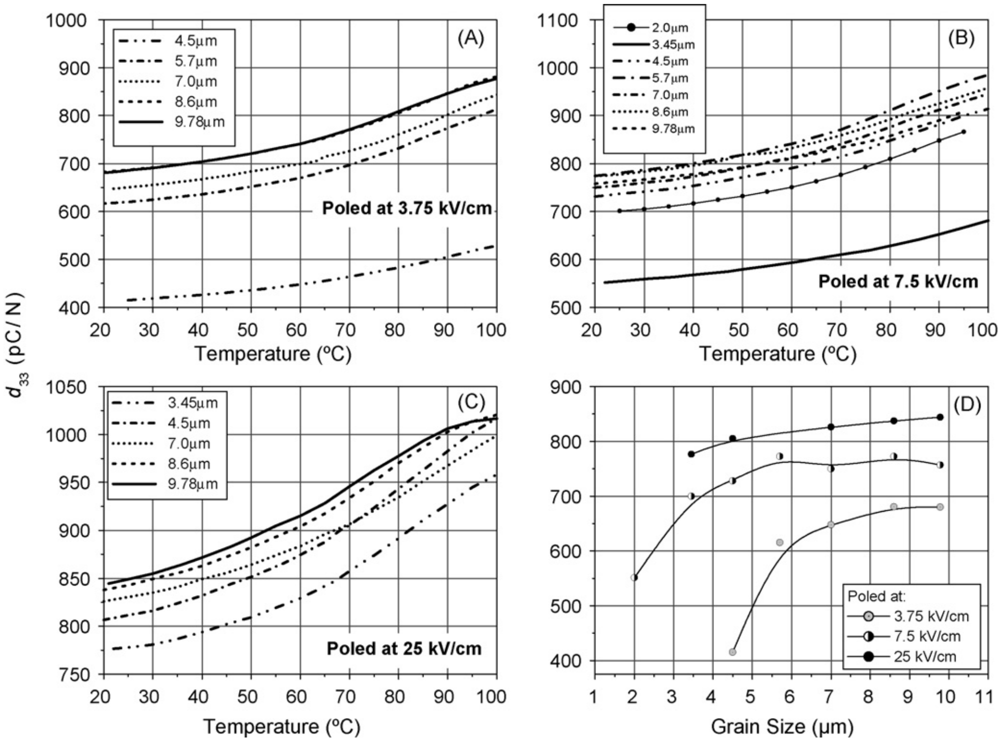

Fig. 12. Piezoelectric charge constant d_{33} as a function of temperature at different grain size after different condition of poling, (A) $E = 3.75$ kV/cm, (B) $E = 7.5$ kV/cm, (C) $E = 25$ kV/cm, (D)) d_{33} as a function of grain size at room temperature.

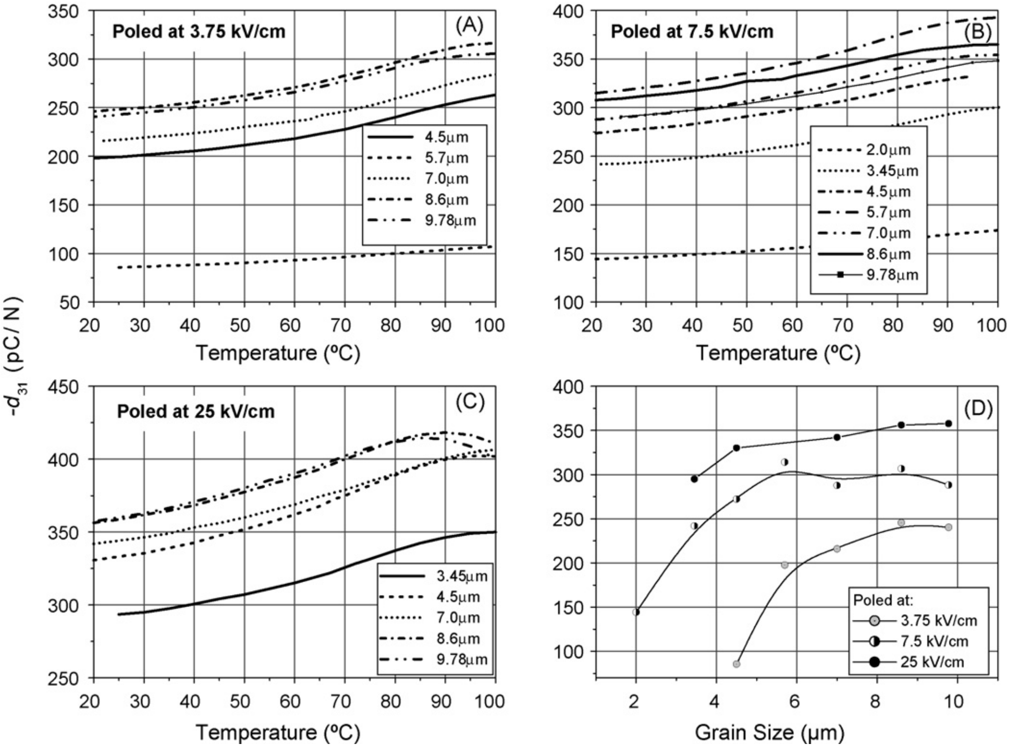

Fig. 13. Piezoelectric charge constant $-d_{31}$ as a function of temperature at different grain sizes after different condition of poling, (A) $E = 3.75$ kV/cm, (B) $E = 7.5$ kV/cm, (C) $E = 25$ kV/cm, (D) $-d_{31}$ as a function of grain size at room temperature.

of domain walls. Therefore, the dielectric constant measured at large applied voltage values will approach the intrinsic dielectric constant.[28,29] Based on the domain wall motion model,[30,31] it was proposed that the losses are due to domain wall motions, and the wall contribution is proportional to the total domain wall area per unit volume. During poling many domain walls are eliminated and do no longer contribute to the loss, so that the loss factor would be expected to reduce.

Cao and Randall[32] indicated that the domain switching process involves transgranular cooperation of domains. Clearly, if this is indeed the general case, the quality of grain boundaries, presence of intergranular phases and porosity will affect domain-wall switching. This may explain, in our case, why the smaller grain materials show lower polarization.

From the Landau–Devonshire phenomenological theory, it has been proposed that for PZT at compositions near the morphotropic phase boundary, the domain-wall contribution accounts for more than half of the room-temperature dielectric and piezoelectric responses.[34]

There is still an extensive debate on how to separate the intrinsic and extrinsic portions from the apparent measured quantities.[24,25,26] Herbiet et al.[22] argued that the extrinsic contribution is the main source of dielectric loss, because the domain wall motion can induce mechanical friction. They derived that the extrinsic contribution to the dielectric property can reach

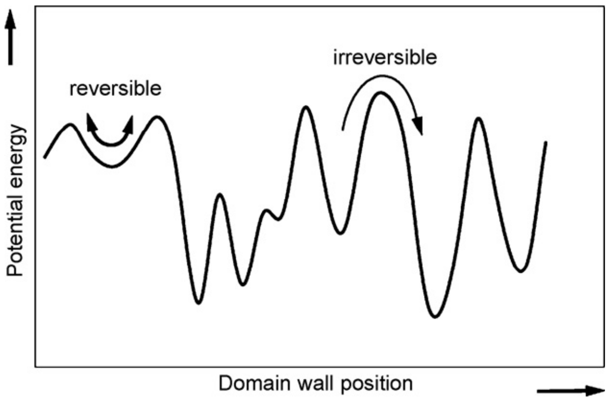

Fig. 14. Schematic of the movement of a domain wall in the lattice potential.

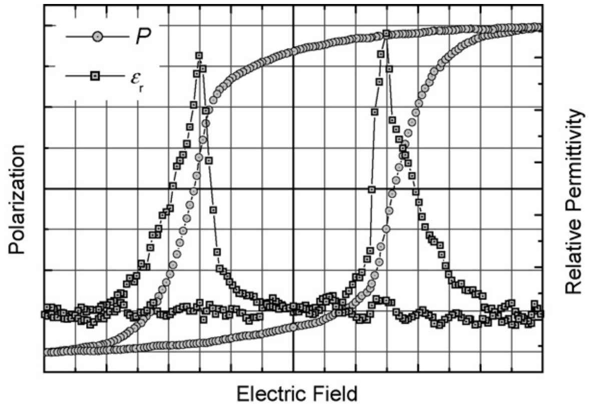

Fig. 15. P–E hysteresis loop and the derivative $(dP/dE) \equiv \varepsilon_r$ as a function of an ac electric field.

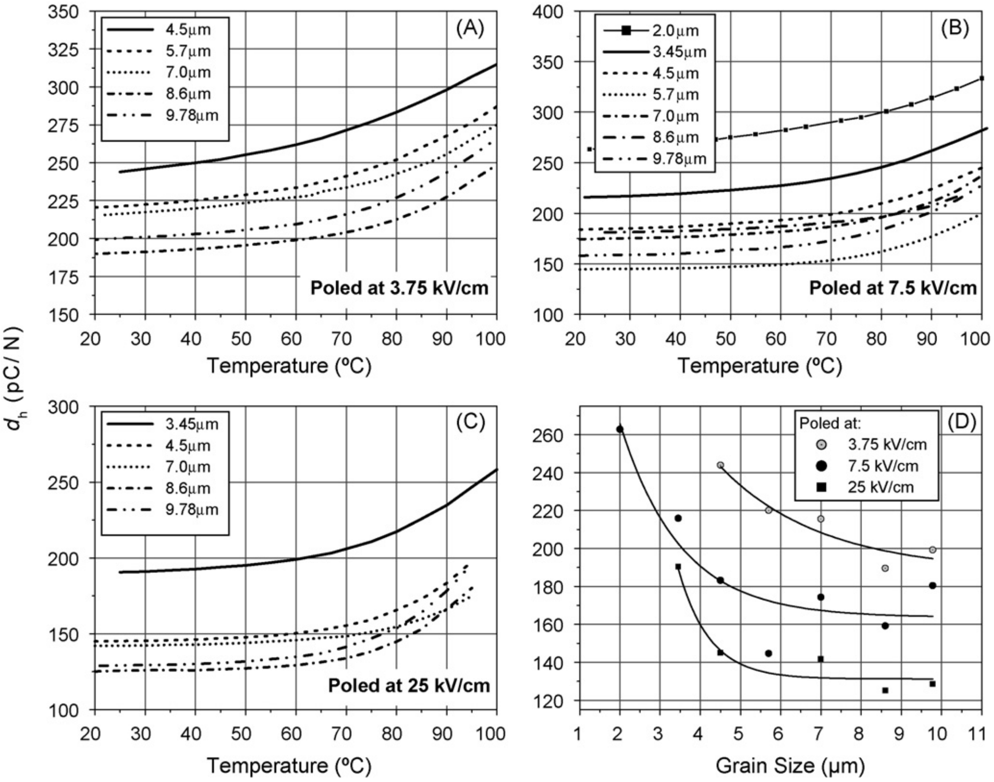

Fig. 16. Hydrostatic piezoelectric charge constant d_h as a function of temperature at different grain size after different condition of poling, (A) $E = 3.75$ kV/cm, (B) $E = 7.5$ kV/cm, (C) $E = 25$ kV/cm, (D)) d_h as a function of grain size at room temperature.

70% of the total at room temperature. A comparable extrinsic contribution percentage was observed in PZT system at room temperature.[33,36]

Experimentally, there are two methods to separate the extrinsic and intrinsic contributions to dielectric and piezoelectric properties in ceramics:[33] One is based on the frequency dispersion characteristics of the dielectric constant and the other is based on freezing out domain wall oscillations at very low temperature so that the dielectric constant converges towards value calculated from the phenomenological theory (which does not account for the domain contribution).[23,36]

Zhang et al.[33] assumed that the intrinsic polarization change will be accompanied by a change in the unit-cell volume while the polarization change induced by domain-wall motion will not cause volumetric changes. As a consequence, the domain-wall motion has no contribution to the hydrostatic response of a material. Accordingly, the change in the hydrostatic piezoelectric coefficient d_h will not be related to the response from domain walls. With this assumption, they calculated the temperature dependence of the dielectric and piezoelectric constants for pure and soft PZT. They attributed most of the increase of these properties to the extrinsic responses. They mentioned that, according to the phenomenological theory,[33,37] the piezoelectric response in a single-domain ferroelectric can be viewed as polarization-biased electrostriction. Hence the intrinsic piezoelectric and dielectric response are related through the electrostrictive coefficient Q_{ij} and remanent polarization P_r.

$$d_h = 2\varepsilon_{33}\varepsilon_o Q_h P_r \tag{2a}$$

where

$$d_h = d_{33} + 2d_{31} \tag{2b}$$

represents the intrinsic hydrostatic piezoelectric coefficient, ε_{33} the intrinsic dielectric permittivity in the direction of the polarization and ε_o the permittivity of free space. Randall et al.[7] argued that Eq. (2a) is not valid for the PZT system, because, if it were true, Q_h should be practically constant, which is not the case. They added that the invalidity of Eq. (2a) in the polycrystalline system is the result of large extrinsic contribution to ε_{33} and accordingly d_h is not purely intrinsic in nature.

However, following the criteria of Zhang et al.,[33] the hydrostatic piezoelectric coefficient d_h was calculated according to Eq. (2b) for all grain sizes and for the different poling conditions, the results of which are shown in Fig. 16. It is clearly seen that d_h is almost constant at and above room temperature up to about 80 °C and increases at still higher temperature. Adding to that, the constant value of d_h with temperature is increasing with increasing poling field. The constancy of d_h according to Zhang et al.[33] is indicating the constant intrinsic contribution over the temperature interval mentioned above. This behavior could mean that Eq. (2a) may be valid over that temperature range and cannot be applied above 80 °C due to the increasing extrinsic contribution.

Since the magnitude of the elastic/dielectric properties is dependent on both intrinsic and extrinsic properties, it is expected that both intrinsic and extrinsic contributions are influenced by grain size variations in the PZT ceramics.[7] Therefore, d_h is plotted as a function of grain size in Fig. 16d. Contrary to what observed by Randall et al.,[7] d_h is found to decrease with increasing grain size, oppositely to the behavior of d_{33} and $-d_{31}$ (the latter which is entirely extrinsic). This behavior can be attributed to suppression of the intrinsic dielectric contribution while the extrinsic grows due to contribution due to the increasing number of domain walls in larger grains. Damjanovic[24] and co-workers[39] have shown that in compressively stressed crystals or crystals biased by an antiparallel field, the intrinsic piezoelectric properties are enhanced. This is equivalent to the case of small grains where depolarizing fields and compressive stresses are be completely compensated by domain walls. Thus, intrinsic effects could be enhanced in small grains by internal stresses and the depolarizing field, while the extrinsic effects become smaller because the domain wall density is smaller. In large grains the internal stresses and depolarizing fields are compensated by domain wall structures, leading to a smaller intrinsic but a larger extrinsic contributions.

Hence we have two oppositely changing effects: a decreasing intrinsic contribution with increasing grain size (represented by d_h) and increasing extrinsic contribution with increasing grain size (represented by d_{33} and $-d_{31}$). This opposite effects of the intrinsic and extrinsic contributions may lead to a constant behavior of the dielectric parameters as a function of grain size in the non-poled state.

5. Conclusions

It was previously[1] found that an electric field slightly higher than the coercive field can efficiently polarize soft PZT-PXE52 to maximum polarization leading to largely enhanced dielectric and piezoelectric properties. In the present work, it was found that, increasing the grain size maximizes the dielectric and piezoelectric properties as compared to properties of grain size often used in practice. However, we noticed a limit for the grain size effect. Thus, an optimum choice of a combination of the poling field and the grain size leads to maximum enhanced properties. It was also found that the extrinsic dielectric contribution increases with increasing grain size due to the increasing number of domain walls.

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