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Evidence of macro–micro domain transition in poled PMN–PZT ceramics

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Abstract

The dielectric properties of unpoled and poled $Pb_{0.88}Ba_{0.06}Sr_{0.06}(Mg_{1/3}Nb_{2/3})_{0.37}Zr_{0.375}Ti_{0.255}O_3$ (modified PMN–PZT) ceramics were investigated. It was found that the dielectric constant increased while the loss tangent decreased after poling. A frequency independent abrupt transition in the dielectric constant and loss tangent responses was observed for the poled ceramics. This abnormal behavior was believed to be correlated with the macro–micro domain transition and the corresponding pyroelectric measurement exhibited a narrow peak at the normal-relaxor transition temperature T_{nr}. Furthermore, the presence of double-loop-like hysteresis and two types of current peaks at a temperature slightly higher than T_{nr} showed another strong evidence of this transition.

Keywords: Microdomain; Macrodomain; Piezoelectric ceramics; Relaxor

1. Introduction

Relaxor ferroelectric ceramic $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) with complex perovskite structure has been widely employed in the fields of multilayer capacitors, actuators and transducers because of its high dielectric permittivity, broad ferroelectric–paraelectric transition, and strong frequency dependency of dielectric properties [1,2]. The solid solution of PMN with normal ferroelectric $Pb(Zr,Ti)O_3$ (PZT) system has attracted special attention due to the lower sintering temperature and superior dielectric and piezoelectric properties [3–5]. In general, short-range, nonstoichiometric 1:1 ordering on the B-site sublattice of the $Pb(B'_{1/3}B''_{2/3})O_3$-type perovskites produces a B-site compositional fluctuation occurring on a nanometer scale and is believed to be responsible for the diffuse phase transition (DPT) and an absence of macroscopic polarization characteristics of relaxors [1,6–9].

On the other hand, it is well known that the dielectric and piezoelectric properties of PMN–PZT ceramics show strong composition and field dependences due to their complex domain structures and unstable phase behaviors [3–5]. Moreover, the depolarization temperature of relaxors (T_d) is much lower than the dielectric permittivity maximum temperature (T_m) which may be attributed to a transformation between polar nanodomains and normal micron-sized domains(i.e., the relaxor-normal or microdomain–macrodomain transition) [10,11]. Earlier studies conducted by Keve and Bye [12] confirmed this behavior in PLZT ceramics. And subsequently, similar spontaneous normal to relaxor ferroelectric transformations have been observed in $Pb(Ni_{1/3}Nb_{2/3})O_3$–$PbTiO_3$–$PbZrO_3$ [13], $Pb(Sc_{1/2}Nb_{1/2})O_3$ [14], La-modified $Pb(Zn_{1/3}Nb_{2/3})_{0.3}$–$(Zr_{0.55}Ti_{0.45})_{0.7}O_3$ [15] and $(K,Na)(Nb,Sb)O_3$–$LiTaO_3$–$BaZrO_3$ [16] lead-free ceramics. Even though these interesting phenomena have been observed, their physical nature has not been clarified yet. Dai et al. [17,18] attributed the spontaneous normal-relaxor transition to the tetragonal stress, which induces the macro–micro domain switching under the thermal drive. However, Kim and Jang [19] demonstrated that the

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spontaneous normal-relaxor transition in La-modified $PbTiO_3$ stemmed from the B-site vacancy. Recently, Deng et al. [20] provided some evidences that the interior stresses due to oxygen deficiency induce the spontaneous normal-relaxor transition in the specimen sintered in reductive ambient. Nevertheless, there is limited information on the macro–micro domain transition behaviors of PMN–PZT ceramics and the relationship between the normal-relaxor transition and electric properties is rarely discussed for this system.

The objective of this work is thus to characterize the normal-relaxor ferroelectric transition and its effect on the electric properties in poled and unpoled PMN–PZT system by choosing $Pb_{0.88}Ba_{0.06}Sr_{0.06}(Mg_{1/3}Nb_{2/3})_{0.37}Zr_{0.375}Ti_{0.255}O_3$ ceramics. The pyroelectric and ferroelectric responses were also conducted. It is expected to present some experimental evidences to clarify the field-induced and spontaneous macro–micro domain transition for the poled PMN–PZT ferroelectrics.

2. Experimental procedure

$Pb_{0.88}Ba_{0.06}Sr_{0.06}(Mg_{1/3}Nb_{2/3})_{0.37}Zr_{0.375}Ti_{0.255}O_3$(abbreviated as modified PMN–PZT hereafter) ceramics were prepared by the conventional solid state reaction method as described in details in the previous report [3]. Phase composition of the samples was characterized using X-ray diffraction (XRD) (Rigaku RAX-10, Tokyo, Japan). Microstructures of fresh fracture of as-sintered samples were observed by scanning electron microscopy (SEM) (TM3000, Hitachi, Tokyo, Japan). The samples were poled at 80 °C in a silicon oil bath under a dc field of 5 kV/mm for 15 min. Dielectric properties of poled and unpoled ceramics were measured using a HP4284A LCR meter (Hewlett-Packard, Palo Alto, CA). And the pyroelectric coefficient was characterized with a Keithley 6517 A electrometer using Byer and Roundy [21] method by heating the poled specimens at fixed heating rate ($dT/dt = 2$ °C/min in present study). Measurements of the ferroelectric polarization and strain were performed using a ferroelectric tester (aixACCT TF Analyzer 1000) in silicon oil at a frequency of 1 Hz. The measurements were conducted from room temperature to 155 °C.

3. Results and discussion

The X-ray diffraction pattern and the SEM micrograph of the fracture surface of the sintered ceramics are shown in Fig. 1. Pure perovskite structure without any secondary impurity phases could be confirmed. Moreover, regular shaped grains with clear grain boundaries and partly transgranular fracture can be found. The microstructure of the ceramics was dense with the average grain size of about 4 μm.

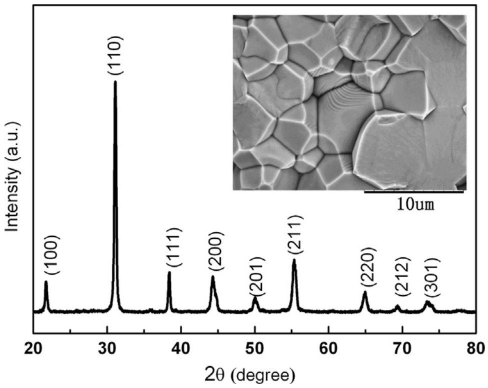

Fig. 1. XRD pattern and the SEM photo of the modified PMN–PZT ceramics.

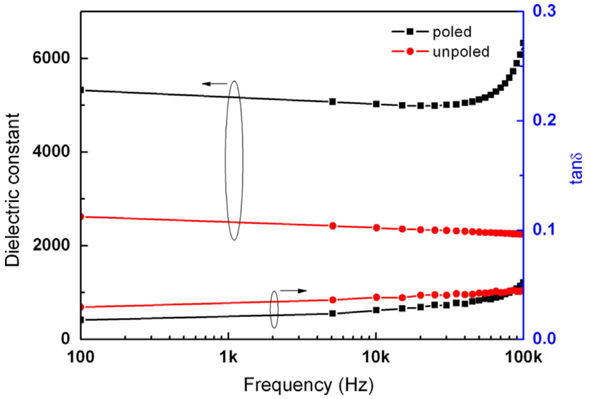

Fig. 2. Frequency dependences of dielectric constant and loss tangent of poled and unpoled modified PMN–PZT ceramics.

Fig. 2 shows the frequency dependence of dielectric constant and loss tangent of the poled and unpoled modified PMN–PZT ceramics observed from 100 Hz to 100 kHz. Obviously, the sample after poling possesses higher dielectric constant and lower loss tangent than that before poling. This enhanced dielectric constant may be ascribed to the improved domain wall mobility after poling [22]. The unpoled samples have a large number of domain walls and are highly self-clamped [23]. During the poling process, the domain wall density decreased drastically due to the electric field induced macrodomain polarization. The lower domain wall density reduces the clamping effect among the domain walls and increases the domain wall mobility. This improved domain wall mobility may play a dominant role on the dielectric constant and thus the dielectric constant increases after poling. However, the exact reason for the reduced dielectric loss in the poled ceramic is unclear at present and needs further investigation. Possibly, the reduced dielectric loss could be attributed to the freezing process of polar microdomains and alters of the domain walls density after poling. The abrupt increase in the dielectric constant and loss tangent near 100 kHz was related to the resonance behavior in the relative permittivity after poling. This result demonstrated that poling is an effective way to remarkably enhance the dielectric constant and simultaneously reduce the loss tangent for PMN–PZT ceramics without complicated composition adjusting, which is promising for some specific applications. More details about the effect of the poling process on domain evolution behaviors can be found in the following part.

Fig. 3(a) and (b) illustrate the dielectric responses for unpoled and poled samples, respectively. The dielectric responses for both ceramics are characterized by diffuse phase transition and frequency dispersion around the dielectric constant peak temperature (T_m), which are typical features of

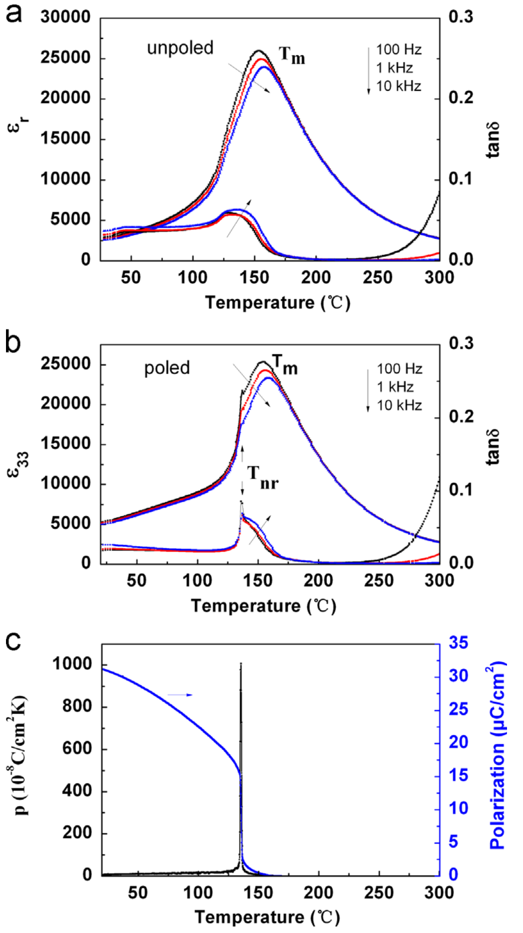

Fig. 3. Temperature dependence of the dielectric constant and loss tangent of (a) unpoled (b) poled modified PMN–PZT ceramics and (c) temperature dependence of the pyroelectric coefficient and calculated polarization of the poled samples.

relaxor ferroelectrics [1]. The maximum value of the dielectric constant decreases with increasing frequency, while that of the dielectric loss tangent increases. This feature may be attributed to the presence of local compositional fluctuation on a microscopic scale, giving rise to the disruption of long-range ferroelectric order into polar microregions with different local Curie temperatures [7,8,17]. Interestingly, a sudden transition at ~136 °C indicated as T_{nr} in Fig. 3 (b) was observed in the poled sample. This T_{nr} implies the spontaneous switching from a normal to a relaxor ferroelectric state, which corresponds to the decay of a macrodomain state to a microdomain state in the heating run. The maximum loss tangent of the poled ceramics was observed in the vicinity of T_{nr}, correlating well with the dielectric anomaly prior to T_m. Furthermore, it is found that the T_{nr} does not change with frequency, and the frequency dependence of dielectric constant becomes weaker in the $T < T_{nr}$ region. This peculiar behavior may be explained as follows: during the poling process, the microdomains coupled and transformed into macrodomain states exhibiting normal ferroelectric characteristic with the frequency independent dielectric responses, however, this field-induced state is unstable and will disrupt into microdomains again with the thermal fluctuation above T_{nr} [10]. The remarkable frequency dispersion of the dielectric responses for the temperature range between T_{nr} and T_m indicates a microdomain relaxor state. The field induced micro–macro domain transition may account for the reduced domain wall density and enhanced domain wall mobility, which give rise to the highly increased dielectric constant after poling (Fig. 2). To further confirm the macro–micro domain transition characteristic, the pyroelectric coefficient and the corresponding polarization P_r calculated from the integration of the pyroelectric coefficient are plotted in Fig. 3 (c). It is well known that the pyroelectric current peak for normal ferroelectrics represents the transition from ferroelectric phase to paraelectric phase. Nevertheless, in the case of the modified PMN–PZT ceramic, the temperature of pyroelectric coefficient maximum coincides with the T_{nr}, implying that this poled PMN–PZT ceramics depolarized at a temperature significantly lower than T_m. A very sharp drop of the polarization (from ~15.8 μC/cm^2 to ~1.4 μC/cm^2) was detected near T_{nr} corresponding to the first order phase transition [24]. This sharp pyroelectric peak is due to the depolarization of macrodomains, which split into microdomains with random polarization orientations at T_{nr}, hence the apparent polarization drops down to nearly zero. It should be noted that the peak of the pyroelectric coefficient was extremely narrow, in accordance with the dielectric behaviors as shown in Fig. 3(b). It is verified that the macro–micro domain transition is a sudden structure transformation which is totally different from the diffuse phase transition around T_m. Therefore, the depolarization mechanism of this PMN–PZT ceramic was related to the macrodomain to microdomain transition rather than the ferroelectric to paraelectric phase transition or the diffuse ferroelectric phase transformation.

In order to gain further evidence of macro–micro domain transition, we measured the temperature-dependent hysteresis (*P*–*E*) loops, and the resultant selected curves are shown in Fig. 4. A saturated square hysteresis loop was observed for the poled sample at 25 °C, showing a relatively large coercive field (E_c) and remnant polarization (P_r). This is a typical characteristic of normal ferroelectric that contains long-range interaction between dipoles and exhibits macrodomain state. The P_r observed from the room temperature *P*–*E* loop is approximately 33 μC/cm^2, which is analogous to the magnitude calculated from the pyroelectric measurement (~31.17 μC/cm^2). The similarity of these two values further verified that the ceramic depolarized totally at the macro–micro domain transition temperature. As the temperature increased, both the P_r and E_c decreased due to the thermal assisted domain switching. At 140 °C, which is slightly higher than T_{nr}, double-loop-like hysteresis was observed, indicating a field-induced micro–macro domain transition. The long-range order of macrodomains can be induced by electric field. However, upon removing the field, the macrodomains spontaneously decay into microdomains again due to the unstable macrodomain state at high temperature. The corresponding bipolar electric field induced strain loops as shown in Fig. 4(b) changed from a butterfly shape to a parabolic electrostrictive behavior when the temperature varied from 125 °C to 140 °C,

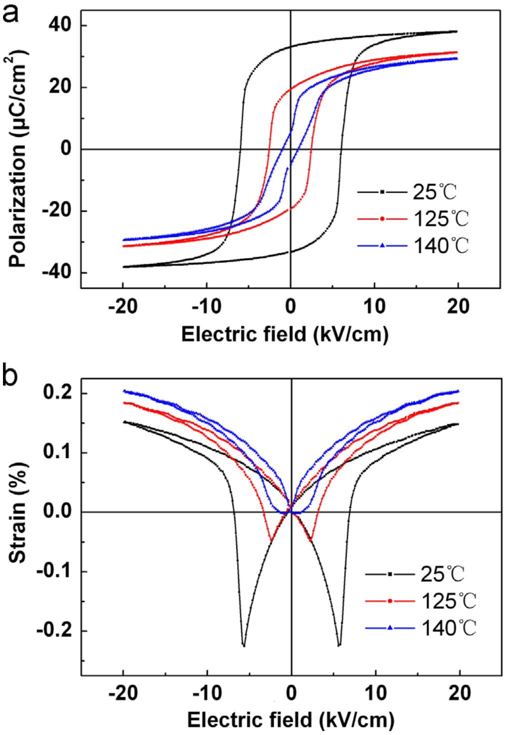

Fig. 4. (a) *P–E* loops and (b) *S–E* loops as a function of temperature of poled modified PMN–PZT ceramics.

which involves the T_{nr}. The negative strain in the *S–E* curve vanished at 140 °C indicative of disappearance of long-range ferroelectric domains. This further confirmed the microdomain nature at 140 °C.

A more intuitive and convenient method to investigate the transition behaviors of PMN–PZT ceramics before and after T_{nr} is to measure the current–electric field (*I–E*) loops at different temperatures. Fig. 5 shows the *I–E* loops at 125 °C and 140 °C, respectively. It is well known that the current peaks mainly originate from the domain switching process [25]. Around E_c, the rate of change of the polarization reaches its maximum and this lead to a sharp increase of the current density. At 125 °C, only two peaks were observed, corresponding to the domain switching around ± Ec. Whereas, two types of peaks were obtained at 140 °C (a temperature slightly higher than T_{nr}) as indicated by P_1 and P_2 in Fig. 5. As the temperature rose up to T_{nr}, the macrodomains became unstable and collapsed into microdomains. Thus, the P_2 peak is believed to be related with the electric field-induced micro–macro domain transition and the switching of the induced ferroelectric domains. While the P_1 peak is due to the spontaneous macro–micro domain transition which is consistent with the depolarization of the electric field induced metastable macrodomain state. These four peaks give rise to a double-loop-like hysteresis as shown in Fig. 4(a). All these results indicated that T_{nr} is actually the temperature of macrodomain–microdomain transition.

4. Conclusion

The dielectric response of poled and unpoled modified PMN–PZT ceramics was investigated. It was found that the dielectric constant increased while the loss tangent decreased after poling. A macro–micro domain transition in poled ceramics was confirmed by means of dielectric, pyroelectric and ferroelectric measurements. This transition temperature T_{nr} is frequency independent and the frequency dependence of dielectric constant becomes weaker at $T < T_{nr}$, implying a sudden structure transformation around T_{nr}. The corresponding pyroelectric and dielectric loss tangent both show maximum at the macro–micro domain transition region, indicating that the depolarization mechanism of this PMN–PZT ceramic can be ascribed to the macro–micro domain transition rather than the ferroelectric–paraelectric or the broad ferroelectric-relaxor phase transformation. A double hysteresis loop as well as four typical current peaks was observed near T_{nr}. The combination of these results indicates that a macro–micro domain transition exists in the poled PMN–PZT ceramics.

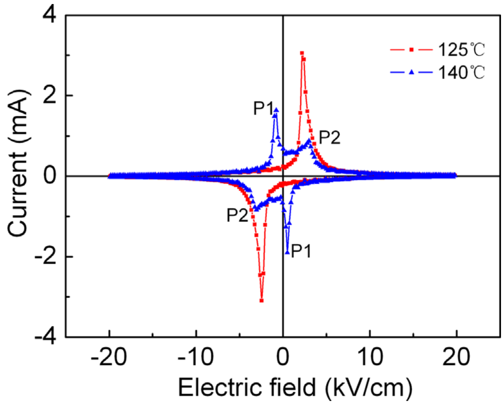

Fig. 5. *I–E* loops measured at 125 °C and 140 °C for poled samples.

Acknowledgments

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References

[1] L.E. Cross, Relaxor ferroelectrics, Ferroelectrics 76 (1987) 241–267.

[2] S.E. Park, T.R. Shrout, Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals, Journal of Applied Physics 82 (1997) 1804–1811.

[3] L. Wang, R.H. Liang, C.L. Mao, M. Gao, G. Du, F. Cao, G.S. Wang X.L. Dong, Investigation of phase structure and electrical properties of doped PMN–PZT ceramics prepared by different methods, Journal of the American Ceramic Society 95 (2012) 445–448.

[4] V. Koval, C. Alemany, J. Briancin, H. Brunckova, K. Saksl, Effect of PMN modification on structure and electrical response of *x*PMN-(1–*x*) PZT ceramic systems, Journal of the European Ceramic Society 23 (2003) 1157–1166.

[5] R. Yimnirun, S. Ananta, P. Laoratanakul, Dielectric and ferroelectric properties of lead magnesium niobate-lead zirconate titanate ceramics prepared by mixed-oxide method, Journal of the European Ceramic Society 25 (2005) 3235–3242.

[6] A. Glazounov, A. Tagantsev, A. Bell, Evidence for domain-type dynamics in the ergodic phase of the $PbMg_{1/3}Nb_{2/3}O_3$ relaxor ferroelectric, Physical Review B 53 (1996) 11281–11284.

[7] N. Setter, L.E. Cross, The role of B-site cation disorder in diffuse phase transition behavior of perovskite ferroelectrics, Journal of Applied Physics 51 (1980) 4356–4360.

[8] P. Groves, Structural phase transitions and long-range order in ferroelectric perovskite lead indium niobate, Journal of Physics C: Solid State Physics 19 (2000) 111–128.

[9] C.S. Hong, S.Y. Chu, C.C. Tsai, C.C. Hsu, The indirect synthesized method induced relaxor state to ferroelectric characteristics for $Pb_{0.95}La_{0.05}(Fe_{2/3}W_{1/3})_{0.65}Ti_{0.35}O_3$ ceramics, Ceramics International 38 (2012) 4123–4130.

[10] H. Fan, Z. Xu, L. Zhang, X. Yao, Dielectric behavior of poled complex perovskite relaxor ferroelectrics, Chinese Science Bulletin 42 (1997) 169–172.

[11] Y. Xi, C. Zhili, L.E. Cross, Polarization and depolarization behavior of hot pressed lead lanthanum zirconate titanate ceramics, Journal of Applied Physics 54 (1983) 3399–3403.

[12] E.T. Keve, K.L. Bye, Phase identification and domain structure in PLZT ceramics, Journal of Applied Physics 46 (1975) 810–818.

[13] M.S. Yoon, H.M. Jang, Relaxor-normal ferroelectric transition in tetragonal-rich field of Pb $(Ni_{1/3}Nb_{2/3})O_3$-$PbTiO_3$-$PbZrO_3$ system, Journal of Applied Physics 77 (1995) 3991–4001.

[14] F. Chu, I. Reaney, N. Setter, Spontaneous (zero-field) relaxor-to-ferroelectric-phase transition in disordered Pb $(Sc_{1/2}\ Nb_{1/2})\ O_3$, Journal of Applied Physics 77 (1995) 1671–1676.

[15] X. Zeng, A. Ding, G. Deng, T. Liu, X. Zheng, W. Cheng, Normal-to-relaxor ferroelectric transformations in lanthanum-modified lead zinc niobate–lead zirconate titanate (PZN–PZT) ceramics, Journal of Physics D: Applied Physics 38 (2005) 3572–3575.

[16] R. Zuo, J. Fu, S. Lu, Z. Xu, Normal to relaxor ferroelectric transition and domain morphology evolution in (K, Na)(Nb, Sb)O_3-LiTaO3-BaZrO_3 lead-free ceramics, Journal of the American Ceramic Society 94 (2011) 4352–4357.

[17] X. Dai, A. DiGiovanni, D. Viehland, Dielectric properties of tetragonal lanthanum modified lead zirconate titanate ceramics, Journal of Applied Physics 74 (1993) 3399–3405.

[18] X. Dai, Z. Xu, D. Viehland, Normal to relaxor ferroelectric transformations in lanthanum-modified tetragonal-structured lead zirconate titanate ceramics, Journal of Applied Physics 79 (1996) 1021–1026.

[19] T.Y. Kim, H.M. Jang, B-site vacancy as the origin of spontaneous normal-to-relaxor ferroelectric transitions in La-modified $PbTiO_3$, Applied Physics Letters 77 (2000) 3824–3826.

[20] G. Deng, G. Li, A. Ding, Q. Yin, Evidence for oxygen vacancy inducing spontaneous normal-relaxor transition in complex perovskite ferroelectrics, Applied Physics Letters 87 (2005) 192905-1–192905-3.

[21] R.L. Byer, C.B. Roundy, Pyroelectric coefficient direct measurement technique and application to a nsec response time detector, Ferroelectrics 3 (1972) 333–338.

[22] C.-H. Wang, L. Wu, Effect of sintering and poling conditions on the properties of 0.125Pb $(Mg_{1/3}Nb_{2/3})O_3-0.875Pb(Zr_{0.5}Ti_{0.5})O_3$ ceramics doped with $4PbO{\cdot}B_2O_3$, Ceramics International 19 (1993) 391–398.

[23] B. Peng, Z. Yue, L. Li, Evaluation of domain wall motion during polymorphic phase transition in (K,Na)NbO_3-based piezoelectric ceramics by nonlinear response measurements, Journal of Applied Physics 109 (2011) 054107-1–054107-6.

[24] G. Robert, M. Demartin, D. Damjanovic, Phase diagram for the 0.4Pb $(Ni_{1/3}Nb_{1/3})O_3$–0.6Pb(Zr,Ti)O_3 solid solution in the vicinity of a morphotropic phase boundary, Journal of the American Ceramic Society 81 (1998) 749–753.

[25] D. Damjanovic, Ferroelectric,dielectric and piezoelectric properties of ferroelectric thin films and ceramics, Reports on Progress in Physics 61 (1998) 1267–1324.