Role of Mn Doping on the Electromechanical Properties of [001] Domain Engineered Single crystals

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ABSTRACT: We studied the influence of Mn doping on electromechanical properties of PZN–*x*PT with *x* = 7% and 9%. Single crystals oriented along the [111], [011] and [001] directions were poled by a "field cooling" process with an applied electric field of 1 kV/cm. It is shown that Mn doping has a significant influence on the single domain crystals in both cases. It modifies the phase symmetry of single domain PZN–7PT from orthorhombic to rhombohedral. It reduces permittivity perpendicular to polarization direction of single domain PZN–9PT by about 40%. This change in the properties of the bulk material is the main cause for the decrease of permittivity observed in [001] poled PZN–9PT crystals. Further effects of doping on the properties of [001] domain engineered crystals are a decrease of the piezoelectric coefficient, a hardening of the material and an increase of the mechanical quality factor.

Keywords: piezoelectric, single crystal, PZN-PT, manganese, domain engineering

1. INTRODUCTION

The high electro-mechanical properties of relaxor-based single crystals such as PZN–PT and PMN–PT suggest that these materials could contribute noticeably to increase the performances of piezoelectric transducers in acoustic imaging and sonars. [001] domain engineered single crystals in particular exhibit very high piezoelectric coefficients due to the very high contribution of domain coexistence. However, their low mechanical quality factor Q_m makes them unsuitable for high power applications. Doping these compounds with acceptor cations has been found to enhance Q_m and many researches are currently being carried out in this direction [1-4]. It was shown in particular that Mn doping changes the overall behavior of PZN–4.5PT from a soft to a harder material [4]. In PZN–8PT crystals, doping improves substancially the fatigue behavior [2]. In this paper, we investigate the influence of Mn doping on structure, domain structure and electromechanical properties of PZN-7PT and PZN-9PT single crystals.

2. EXPERIMENTAL PROCEDURE

Crystals of PZN–7PT and PZN–9PT with and without MnO_2 additions (1% mol) have been grown by the flux technique. All crystals were oriented along pseudocubic [001], [101] and [111] directions using a Laue back scattering configuration. Samples were cut and polished. Cr/Au electrodes were sputtered on the appropriate faces of the sample for dielectric and electromechanical measurements. Before poling, all samples were heated up to 400°C for 2 hours to release stress induced by polishing.

Composition and homogeneity of the samples were controlled by T_C measurement. All samples were poled using the field cooling method (FC) [5] with a DC field of 1 kV/cm, from the cubic phase down to room temperature.

Electrical impedance of the samples was measured on an Agilent 4294A impedance analyzer and electromechanical coefficient were calculated according to the standard IRE method.

3. INFLUENCE OF Mn DOPING ON STRUCTURE AND PROPERTIES OF SINGLE DOMAINS

3.1 Single domain symmetry

Single domains are the building blocks of multidomain structures and it is therefore of interest to study the influence of doping on single domains.

In PZN–PT, rhomboedral, orthorhombic, monoclinic and tetragonal phases across the morphotropic phase boundary (8-10%) [6] are very close in energy. The ferroelectric phase of a given sample is therefore very sensitive to its nature (powder, single crystal), its composition and the poling process [7-9]. A first task is to determine the most stable single domain state at room temperature for each sample. This is based on the assessment that the weakest permittivity is usually obtained when its measured along the polarization direction of the single domain.

This is best illustrated by the PZN-9PT crystals poled along the [101] direction (fig. 1). PZN-9PT undergoes two phase transitions during cooling under an electric field of 1 kV/cm. A first transition is obtained from the paraelectric cubic phase to a ferroelectric tetragonal phase. In this configuration, 2 polarisation directions are energetically equivalent and the resulting domain structure consists of 2 families of tetragonal domains. We call this domain structure 2T. A second transition, associated with a sharp drop in

permittivity occurs at 300K. This low temperature ferroelectric phase is monoclinic as demonstrated from X–ray diffraction studies for undoped PZN-9PT [8,10]. The monoclinic unit cell however is obtained from a very slight distortion of an orthorhombic cell. We therefore assumed an orthorhombic symmetry for the determination of electromechanical poperties in the following.

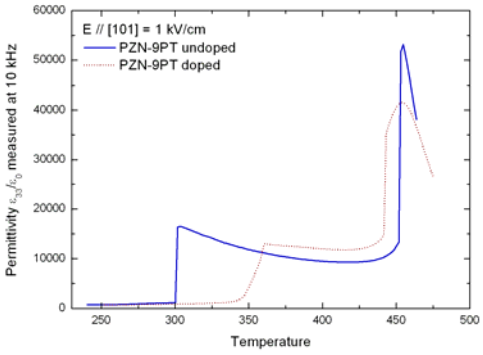

Fig.1: Permittivity versus temperature during the polarization (FC) for doped and undoped PZN-9PT.

Introduction of Mn dopant induces a shift of the transition temperature for both phase transitions. The low phase transition temperature is shifted by 60K from 300K to 360K. X-ray diffraction confirms that the structure at room temperature is monoclinic as in the undoped case, with very similar lattice parameters. Mn doping has therefore only a very small effect on the lattice parameters of PZN-9PT.

The permittivity tensors for doped and undoped crystals are given in table I. Longitudinal permittivity (ε_{33} - along the polarization direction) is reduced by about 15%. More dramatic is the effect of doping upon transverse permittivity (ε_{11} and ε_{22} - perpendicular to the polarization direction), which are reduced by about 40%.

Table I: Permittivity of doped and undoped PZN-9PT single domains at room temperature

Direction	PZN-9PT	PZN-9PT:Mn
[101]	ε_{11} = 9400	ε_{11} = 5720
[010]	ε_{22} = 21000	ε_{22} = 11900
[101]	ε_{33} = 900	ε_{33} = 760

PZN-7PT behaves differently, as it might be expected since it lies closer from the morphotropic phase boundary. Poling of undoped PZN-7PT along the [101] direction is pretty similar to PZN-9PT and a [101] single domain is expected (Fig.2). However, Mn doping modifies the evolution of permittivity during poling along [101]. Like in the previous case, transition temperatures are shifted. In addition, the curve is considerably smoothed around the low temperature phase transition (Fig.2). Last, the room temperature permittivity after poling is much higher than in the undoped case (1900 versus 1000). This suggests that the crystal reaches a multidomain structure instead of the expected single-domain state.

On the other hand, if we compare evolutions of permittivity during poling for undoped and doped PZN-7PT along the [111] direction, the opposite trends are observed: doping results in a sharper transition and a lower permittivity. Those observations suggest that the single domain is rhombohedral in doped PZN-7PT rather than orthorhombic as in the undoped case. Moreover transverse permittivity is found to be isotropic with $\varepsilon_{11} = \varepsilon_{22} = 7550$ as expected in a rhombohedral symmetry. Full permittivity tensors for doped and undoped crystals are given in table II. Permittivity is on the average lower in doped crystals than in undoped crystals.

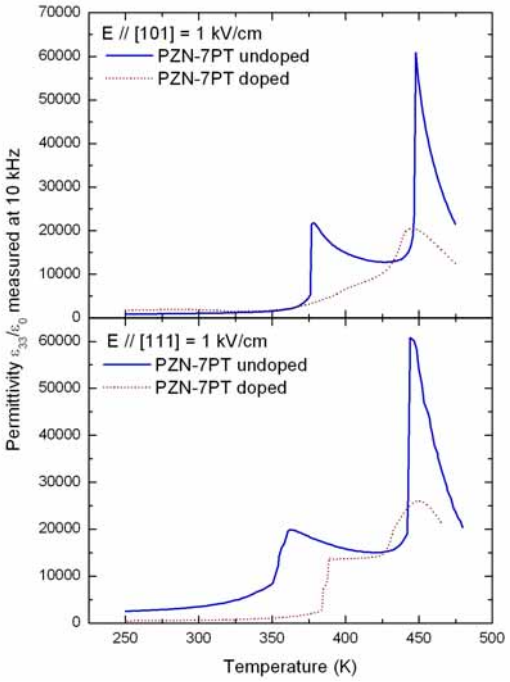

Fig.2: Permittivity versus temperature during the polarization for doped and undoped PZN-7PT. Electric field is applied along [101] (top) and [111] (bottom).

Table II: Permittivity of doped and undoped PZN-7PT single domains at room temperature

PZN-7PT	PZN-7PT:Mn
[110] // ε_{11} = 7400	[110] // ε_{11} = 7550
[110] // ε_{22} = 26000	[112] // ε_{22} = 7550
[110] // ε_{33} = 950	[111] // ε_{33} = 655

Mn doping on both PZN–7PT and PZN–9PT single crystals results in an overall permittivity reduction especially for transverse permittivity. In PZN-7PT, the effect is even more significant since it changes the symmetry of the single domain state at room temperature.

3.2 Electromechanical properties

Piezoelectric coefficient d_{33}, electromechanical coupling coefficient k_{33}, elastic compliance s_{33}^E for all single domain crystals are given in table III. Although the symmetry of the single domain state changes upon doping for PZN-7PT and not for PZN-9PT, the electromechanical properties of single domain states are affected in the same way in both cases. The mechanical quality factor increases, and the elastic compliance decreases (hardening of the material), with a decrease of the piezoelectric coefficient.

All results obtained on single domain crystals show that Mn doping have an influence not only on permittivity but also on other electromechanical properties.

Table III: Electromechanical properties of single domains at room temperature

	PZN-9PT [101]	PZN-9PT:Mn [101]
k_{33} (%)	60	70
d_{33} (pC/N)	250	230
s_{33}^E (pm²/N)	18	16
Q_m	300	500
	PZN-7PT [101]	PZN-7PT:Mn [111]
k_{33} (%)	58	37
d_{33} (pC/N)	240	75
s_{33}^E (pm²/N)	17	7
Q_m	135	630

4. [001] DOMAIN ENGINEERED SINGLE CRYSTALS

4.1 [001] multidomain structure

Permittivity versus temperature during the field cooling of PZN-9PT crystals is shown on figure 3. The two phase transitions are visible. The lowest permittivity is obtained in the tetragonal phase as the polarization lies along the [001] direction with domain structure 1T. The second phase transition occurs approximately at room temperature. The structure of the low temperature phase is multidomain 4M with 4 equivalent families of monoclinic domains as shown in [10]. X-ray diffraction study confirmed that this is also the case for doped PZN-9PT, with lattice parameters very close to the undoped crystal.

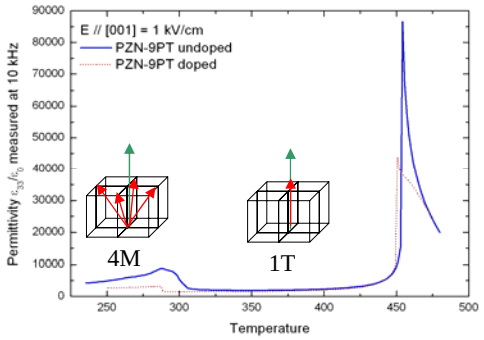

Fig.3: Permittivity versus temperature during poling (FC) for doped and undoped PZN-9PT.

As far as PZN-7PT is concerned, multidomain structures expected from single domain symmetries are 4O and 4R for undoped and doped crystals respectively. The evolution of permittivity during the poling process is given on figure 4. The undoped case is qualitatively very similar to the PZN-9PT, supporting the assumption of a 4O domain structure. In contrast, the anomaly due to the low temperature transition does not appear clearly for the doped crystal. In addition, permittivity increases by a factor of 2 when the poling field is switched off. This reveals the instability of the induced domain structure, which will be discussed in the following.

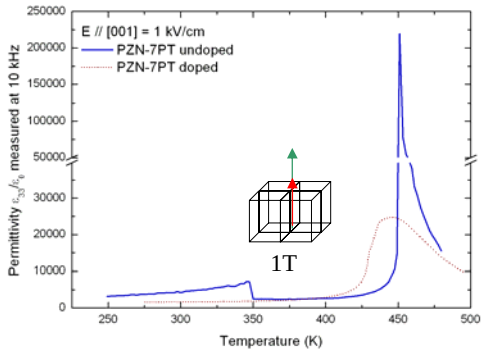

Fig.4: Permittivity versus temperature during the polarization for doped and undoped PZN-7%PT.

4.2 Permittivity and electromechanical properties along [001]

Permittivity of PZN-9PT at room temperature along the [001] direction amounts to $4950\varepsilon_0$ and $3600\varepsilon_0$ for undoped and doped crystals respectively. These values may be compared to those calculated by a simple rotation of the single-domain axes: $5150\varepsilon_0$ and $3240\varepsilon_0$ [11]. The gap between calculated and measured values is small and might be attributed to a weak domain wall contribution. Moreover, the reduction of longitudinal permittivity upon Mn doping is essentially accounted for by this calculation. This shows that it can be attributed to the intrinsic influence of Mn-doping through the decrease of ε_{11}.

In undoped PZN-7PT, the permittivity of the [001] poled crystal is in agreement with its predicted value ($4240\varepsilon_0$ measured versus $4175\varepsilon_0$ calculated). In the doped case, the measured permittivity is significantly lower: $3440\varepsilon_0$ measured versus $5170\varepsilon_0$ calculated. A contribution of domain coexistence can be invoked to explain this difference, but it would be very strong contrary to the other cases where it seems to be weak. Another hypothesis would be that the phase symmetry in the [001] domain engineered crystal is different from the expected 4R multidomain structure. The rhombohedral phase could be distorted into à monoclinic phase and the polar moment tilted to approach [001] as observed in PZN–8PT [7]. A detailed X-ray diffraction study would be needed to identify precisely the phase symmetry.

Further comparisons between electromechanical properties of undoped and doped [001] domain engineered single crystals of both compositions are given in table IV. Even though a direct comparison of doped and undoped PZN-7PT is in principle not really possible because of the uncertainty on the structure, the same trends are seen in both cases. The properties of the longitudinal mode reveal a reduction of permittivity and piezoelectric constant, a reduction of the compliance and an increase of the mechanical quality factor. Those trends were also observed on rhombohedral PZN–4.5PT by Kobor *et al.* [3].

Table IV: Electromechanical properties of domain engineered crystals at room temperature

	PZN-9PT	PZN-9PT:Mn
$\varepsilon_{33}/\ \varepsilon_0$	4950	3600
k_{33} (%)	91	94
d_{33} (pC/m²)	2900	1900
s_{33}^E (pm²/N)	223	126
Q_m	66	200
	PZN-7PT	PZN-7PT:Mn
$\varepsilon_{33}/\ \varepsilon_0$	4240	3440
k_{33} (%)	90	87
d_{33} (pC/m²)	1900	1490
s_{33}^E (pm²/N)	120	95
Q_m	100	470

5. DISCUSSION AND CONCLUSION

In order to determine the intrinsic effect of Mn doping on properties of PZN-PT single crystal close to the morphotropic phase boundary, symmetry and electromechanical properties of single domain crystals, i.e. without any domain wall, were studied. We have shown that Mn doping on PZN-PT close to the morphotropic phase boundary has a tremendous effect on single domain crystals. In PZN-7PT, it favors a rhombohedral single domain state and probably affects the domain structure of [001] domain engineered states. In PZN-9PT, it has almost no effect on the phase symmetry but reduces drastically the transverse permittivity, which causes a reduction of the longitudinal permittivity in [001] multidomain crystals.

This shows that the influence of Mn doping on high performance multidomain piezoelectric single crystals cannot be only interpreted as an influence on domain wall motions but should also take into account the intrinsic contributions, i.e. its influence on the properties of the bulk material. A comprehensive determination of the electromechanical tensor of the single domain state is needed to discriminate between these two different effects.

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[11] In this case, longitudinal permittivity for a multidomain crystal is given by $\varepsilon_{11} \sin^2\theta + \varepsilon_{33} \cos^2\theta$ where $\theta = 45°$ and 54.73° for the 4O and 4R domain structure respectively.