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Electromechanical Properties of PMN-PT and PZT Ceramics at Cryogenic Temperatures

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Abstract—Space borne observation requires extremely high resolution systems with large dimensions. The design of such systems implies associating sensing and actuation systems to insure a highly stable positioning of optical components. However, the currently used PZT materials for piezoelectric actuation show strongly diminished strain at cryogenic temperatures. This work explores the performances of PMN-xPT piezoelectric materials at cryogenic temperatures. Temperature dependence of PMN-xPT ceramics is compared with hard PZT (PZT-4) and soft PZT (PZT5H) ceramics from RT to 10 K. PMN-PT tetragonal compositions exhibit stable piezoelectric constant in the 250-100 K range. The highest values of piezoelectric constant are observed for PMN-38PT in the 200-50 K range. All ceramics exhibit decreasing performances versus cooling temperature. This behaviour is attributed to a “freezing out” of extrinsic contributions to piezoelectricity [12] but is also due to a contribution of quantum effects [13, 14]. The mechanical quality factor (Q_m) increases very quickly from 50 K to 10 K for all samples. This fact could be due to low relaxation processes at very low temperatures.

Keywords- piezoelectric, cryogenic temperatures, ceramic, PMN-PT, PZT

I. INTRODUCTION

Piezoelectric ceramics currently provide the key functional element in devices employed in an exceptionally wide range of applications, including transducers, sensors, signal-processing and voltage transformers. For several decades, the material of choice for the majority of these applications has been polycrystalline ceramics based on $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) due to their unequalled piezoelectric constants and coupling coefficients at room temperature. In space applications, cryogenic actuation is required but the currently used PZT materials do not meet the requirements.

At room temperature, properties of PZT ceramics are optimized using compositions that correspond to the morphotropic phase boundary (MPB). Commercially available “hard” and “soft” PZT compositions exhibit poor piezoelectric performances at temperatures below 100 K. For example, soft PZT has a k_{31} of about 25% and a $-d_{31}$ below 50 pC/N at 30 K

compared with values of about 35% and about 250 pC/N, respectively, at room temperature [1]. At 30 K, PZT piezoelectric ceramics do not meet present demands and have only 25% of their room temperature efficiency [2].

Despite the need for stable actuators at cryogenic temperature, electromechanical properties at very low temperature (below 30 K) are rarely reported. In 1983 the dielectric and piezoelectric properties of modified PZT ceramics from 4.2 K to 300 K were measured [1]. Properties of perovskite materials from 300 K to 30 K were investigated for several compositions of PLZT (La-modified PZT) [3]. Recently, dielectric loss anomalies at low temperatures in PMN-xPT systems were reported [4,5]. Dielectric relaxation and phase transition at cryogenic temperature were also studied [6]. Piezoelectric activity of relaxor-PT ceramics and single crystals at cryogenic temperatures were reported, and the intrinsic and extrinsic contributions were explained [7].

Cryogenic actuators were developed by Xinetix for Nasa application [8]. Multilayer actuators based on electrostrictive materials such as PMN ceramics and PMN-PT single crystals were fabricated and tested [9]. Landolt and Börnstein was used to select materials that exhibited large dielectric constant below 100 K.

The purpose of this work is to complete the previous studies on PMN-xPT ceramics, which were focused on dielectric properties, by investigating the evolution of electromechanical properties from 300 K to 10 K in the composition range from 25% to 42%. Properties of commercial PZT ceramics were also studied in the same conditions.

II. EXPERIMENTAL PROCEDURE

Samples of composition $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ with $x = 0.25, 0.345, 0.38, 0.42$, (hereafter designated xPT, with x in %) were synthesized using the columbite precursor technique [10]. The precursor oxide columbite powder was mixed with PbO and TiO_2 in the appropriate proportions. Each composition was ball-milled for 2h in water, and calcined under oxygen at 800°C for 4 h to form the perovskite phase.

The calcined powders were re-milled and pressed into about 1 mm thick green-disks. The green-disks were sintered under oxygen at 1140°C for 4 h in an alumina crucible to form densified ceramics ($d = 99.9\%$ of the theoretical density). In order to compensate the loss during the sintering process, the atmosphere was saturated in PbO. X-ray diffraction patterns recorded with an Inel CPS 120 Detector with Cu K α radiation show pure perovskite phases.

The hard PZT4 (TLZ1) and the soft PZT5 (TLZ6) ceramics studied in this work are provided by Thales Underwater Systems Pty Limited (Sydney, Australia). The Curie points of TLZ1 and TLZ6 are 320°C and 200°C, respectively.

Electromechanical properties on transversal (31) mode were recorded on plates. Plates of 8x1 mm² surface and 1 mm thickness were machined. Electrodes were deposited by silver pasting onto the surface. The PMN-PT samples were poled by the field cooling method from 180°C to 40°C with an electric field of 200 V/mm. The TLZ1 samples were poled at 120°C applying an electric field of 2.2 kV/mm. TLZ6 samples were poled by field cooling from 120°C to 70°C under 2 kV/mm. The electromechanical properties were calculated from the resonance spectra in accordance with the CENELEC standards [11] with the resonance technique using a HP4294A impedance/gain phase analyzer (40 Hz - 110 MHz). Samples studied in this work were placed in a LHe cryostat from Air Liquid. The temperature can go down from 300 K to 10 K.

III. RESULTS

A. PMN-xPT

Fig. 1 and Fig. 2 show the variation of the dielectric constant ϵ_{33}^T and of the dielectric loss ($\tan \delta$) versus the decreasing temperature. All values diminish and drop at very low temperature for the four PMN-xPT compositions. At 10 K, all samples exhibit a ϵ_{33}^T lower than 500 with the highest values for PMN-PT tetragonal composition. ϵ_{33}^T is equal to 240, 320, 390, 420 for PMN-25PT, PMN-34.5PT, PMN-38PT, PMN-42PT, respectively.

In the RT to ~50 K temperature range, the variations of the dielectric constant ϵ_{33}^T and the dielectric loss ($\tan \delta$) of PMN-xPT ceramics show different behaviors. For the PMN-25PT

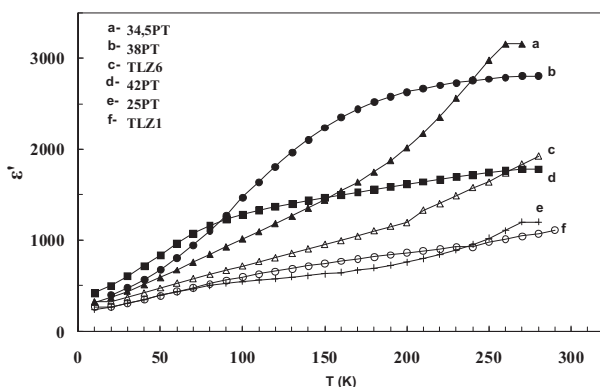


Figure 1. Evolution of the dielectric constant at 1 kHz for PMN-PT and PZT ceramics, as a function of the temperature from 300 K to 10 K.

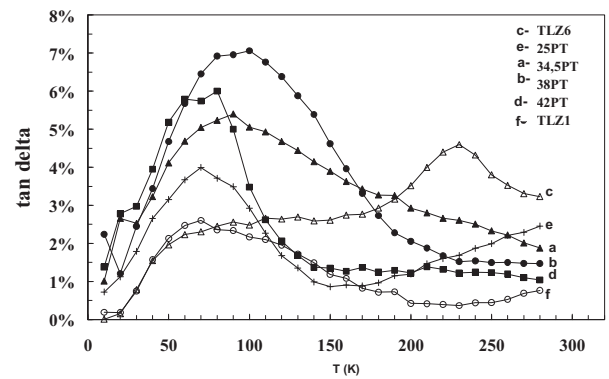


Figure 2. Temperature dependence of the dielectric losses for PMN-PT and PZT ceramics, as a function of the temperature from 300 K to 10 K.

ceramic exhibiting pure rhomboedral structure, as shown on the Fig. 1e, the decrease of the dielectric constant is moderate. The dielectric curve shows a slope change near 70 K. The same behaviour was observed for the pure PMN-42PT tetragonal composition PMN-42PT. The dielectric constant shows a slight decrease between RT to 80 K and then a stronger decrease with decreasing temperature (Fig. 1d).

For the other two compositions in the tetragonal structure near morphotropic phase boundary ($x = 0.38$) and in the MPB ($x = 0.345$), the behaviour of the materials is different. Indeed, the PMN-38PT composition exhibits high value and relative stability of the dielectric constant from 300 K to 200 K and then decreases strongly when the temperature is lowered down to 10 K (Fig. 1b). For the composition in the MPB (PMN-34.5PT), the dielectric constant decreases quickly with cooling temperature (Fig. 1a).

As reported by Singh [15] and Ragini [16], the low temperature transitions involving two ferroelectric phases could not give rise to prominent anomalies in dielectric constant curve while the temperature dependence of elastic modulus (s_{31}) or piezoelectric resonance frequency clearly exhibit transitions.

Fig. 3 presents the variation of the resonance frequency, f_m , with temperature from 500 K to 10 K for PMN-xPT ceramics. These data complete those reported up to 150 K by Singh [15]. Ferroelectric–paraelectric transition leads to sudden drop of

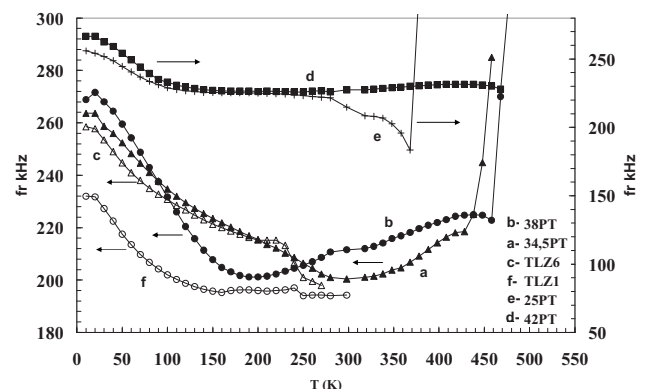


Figure 3. The resonance frequency for PMN-xPT and PZT ceramics, as a function of the temperature from 300 K to 10 K. The curves d and e ($x=0.25$ & 0.42) are in the right axis. The curves a, b, c and f are in the left axis.

resonance frequency at 378 K, 458 K, 468 K and 478 K, respectively. The values, close to the T_{max} , are consistent with the Vegard law, which increases with the increasing PT content. PMN-xPT ceramics compositions show a T_{max} at 385 K, 435 K, 455 K, and 500 K for $x=0.25, 0.345, 0.38,$ and $0.42,$ respectively.

At temperatures below 300 K, compositions of $x = 0.25$ and 0.42 show a behaviour like normal solids for which the elastic modulus (s_{ij}), and hence resonance frequency $f_r (f_r \propto (s_{ij}^{-1/2}))$, is expected to increase on cooling from higher temperature side. For both, variation of f_r show a clear changing slope near 70 K and another one near 300 K for $x = 0.25$. For the two other compositions ($x = 0.38$ and 0.345), f_r decreases with decreasing temperature, showing a minimum around 160 K and 300 K. The fact reveals lattice instability due to a soft mode near structural phase transition [16]. This clearly indicates a phase transition from the room temperature tetragonal phase to monoclinic phase for $x = 0.38$ and from monoclinic M_A to monoclinic M_C for $x = 0.34$. For two other compositions ($x = 0.25$ and 0.42), show behaviour like normal solids for which, the elastic modulus, and hence f_m , is expected to increase on cooling from higher temperature side. For both, variation of f_m show a clear slope change near 70 K and another one near 300 K for the former. The slope change at 300 K, observed for $x=0.25$ would be related to phase transition from rhombohedra to monoclinic structure [15].

Concerning the dielectric loss variation (Fig. 2), the 0.25 composition shows a decrease from RT down to 160 K then start to an increase to reach a maximum near 70 K. The 0.42 composition shows the same strong peak near 70 K, while the other compositions ($x = 0.38$ and 0.345) exhibit much larger and stronger peaks centered near 100 K.

The temperature dependence of the coupling efficiency and the piezoelectric constant, presented on Fig. 4, show the same variation as the dielectric constant. The piezoelectric constant (d_{31}) decreases moderately for $x = 0.25$ and rapidly for $x = 0.345$ when the temperature decrease from RT to 10 K. For $x = 0.38$ and 0.42 , the piezoelectric constants are stable between RT and about 120 K and 80 K, respectively, before dropping at 10 K, down to a value of d_{31} equal to 30 pC/N for both.

B. PZT

The temperature dependence of the piezoelectric coefficient and the dielectric constant of PZT ceramics are shown on fig 1-4. The piezoelectric constants are listed on the table I.

The same behaviour as PMN-xPT was observed. The dielectric constant decreases from RT to 10 K but the slopes are different for the soft and the hard PZT. Hard PZT ceramic presents moderate variations (Fig. 1f) while soft PZT ceramic shows strong decrease (Fig. 1c). The dielectric loss values are lower than those of PMN-PT ceramics (Fig. 2). Indeed, for the

TLZ6 soft ceramic, the losses are above to 3% at room temperature, and below at 2% at 50 K and then very low (0.01%) at 10 K. For the TLZ1 hard ceramic, the losses, very low at room temperature (0.76%), increase up to a maximum at 60 K (2.5%) and then decrease down to a very low value (0.19%). The maximum of dielectric loss peaks (Fig. 3c, 3f) are also lower than that of PMN-PT ceramics.

The temperature dependence of the piezoelectric coefficient d_{31} is very similar to that of the dielectric constant except for the decrease from room temperature to 10 K. TLZ1 and TLZ6 have a good coupling coefficient of about 37% at room temperature, 22% at 10 K, 33% at RT and 22% at 10 K respectively. The k_{31} is relatively stable and, at a temperature of about 50 K, the value diminishes.

IV. DISCUSSION AND CONCLUSION

Dielectric and electromechanical properties of piezoelectric ceramics diminish when the temperature decreases. On lowering the temperature down to near 150 K, the decrease may be due to the sequence tetragonal-monoclinic M_C - monoclinic M_B transitions and a long range monoclinic order [15].

At very low temperature, the behavior could be due to a "freezing out" of extrinsic contributions (i.e., ferroelectric domains wall motion) to piezoelectricity [12] and probably also due to a quenched chemical disorder and polar nanoregions. Polar nanoregions (PNRs) with a size of 60 Å and chemically ordered regions of Mg^{2+} and Nb^{5+} with a size of 20 Å, were reported [17] for pure PMN and PMN-6PT relaxor compositions, while any super lattice structures were observed for higher PT contents. The substitution of Ti^{4+} in PMN-xPT suppresses the chemically ordered regions and enhances the size of PNRs.

On the other hand, the thermal conductivity [17] of ferroelectric $PbTiO_3$ shows a peak at 65 K while that of relaxor PMN exhibits a broader incident near 10 K and plateau near 100 K. The behaviors are typical of crystalline dielectric solids for $PbTiO_3$ and glasslike amorphous materials, which is attributed to the presence of polar nanoregions for PMN. PMN-PTs, behave like PMNs, are partially crystallized glasses and this suggests enhanced elastic mismatch arising from the coexistence of PNRs and mesoscopic ferroelectric domains.

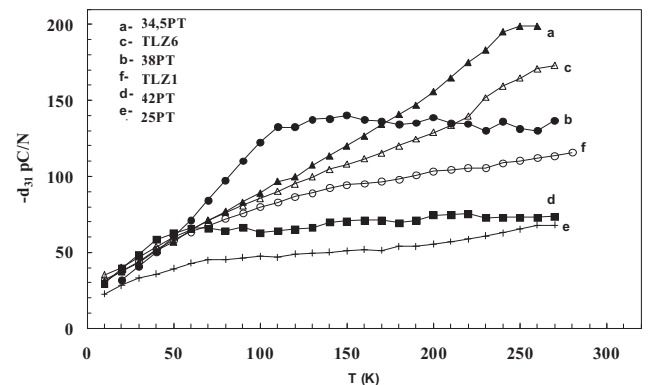


Figure 4. Temperature dependence of the piezoelectric coefficient $-d_{31}$, of PMN-xPT and PZT ceramics.

TABLE I. PIEZOELECTRIC PROPERTIES FOR PMN-PT AND PZT

	ϵ_{33}^T			$-d_{31}$ (pC/N)			k_{31} (%)		
	RT	100 K	20 K	RT	100 K	20 K	RT	100 K	20 K
PMN-42PT	1781	1280	501	74	63	39	19.5	21.2	10
PMN-38PT	2800	1470	397	140	122	32	24	27.5	11
PMN-34.5PT	3200	1010	373	200	89	37	34	28	17
PMN-25PT	1200	545	263	68	47	28	22	22.7	15.5
TLZ1 (PZT4)	1110	595	270	116	80	35	32.7	31	22
TLZ6 (PZT5)	2000	715	327	173	89	40	36.5	32	23

This thermal conductivity peak of PT at 65 K [17] could be related to the strong incident observed in dielectric loss variations of PMN-xPT (70 K and 100 K) observed on this work. The dielectric loss peaks are also consistent with the slope change near 70 K for that the quality factors increase very quickly [18] i.e. the mechanical losses exhibit strong decrease near 70 K. Further studies are necessary to clarify the behavior.

The dielectric constant coefficient ϵ_{33}^T , the piezoelectric coefficient d_{31} and the coupling factor coefficient k_{31} of PMN-PT at 100 K and 20 K are listed in table I.

PZT and PMN-xPT present nearly the same piezoelectric performances at very low temperatures (20 K). At low temperatures, the tetragonal phase PMN-38PT shows better performances with relatively stability from 300 K to 100 K.

Further studies are in progress by doping tetragonal PMN-PT compositions both in ceramic and single crystal.

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