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Dielectric and piezoelectric properties of (La, Mg, F) and (Mg, Mn, F) doped PZT ceramics under low and high sollicitations

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Abstract

The hysteretic behavior of the charge coefficient d_{33} under high mechanical stress and of frequency constant N_{33} during the temperature cycle −40°C–+80°C can be cancelled by fluorine oxygen substitution in the lattice of Mg-doped PZT. These fluorine doped materials also exhibit a high mechanical quality factor and low dielectric losses. The drawback is that they have a lower d_{33} coefficient and are difficult to pole. Mn doping in B site or La doping in A site, in the ABO_3 type perovskite structure are known to increase the d_{33} coefficient and the poling ability. This result is observed on (Mg, F) co-doped PZT with Mn and with La content of 1.5 mol%. In the same manner, Mn doping enhances the hysteretic behavior and the losses while La doping does not significally changes the (Mg, F) co-doped PZT characteristics except the fluorine content for which the losses and the hysteresis are the lowest.

Keywords: Dielectric properties; Hysteresis; Piezoelectric properties; PZT

1. Introduction

Non-linearities and hysteresis in PZT ceramics are related to the capacity of domain wall to move under external sollicitations.[1] This mobility can be reduced by pinning centers which consist of defect dipole in the lattice i.e. B site acceptor ion–oxygen vacancies, B site acceptor ion–fluorine ion in anionic site.[2,3] The latter is less mobile and so more efficient to prevent hysteretic behavior, especially under high mechanical stress. Previous works[4] have shown that some (Mg, F) co-doped PZT with a specific fluorine ion content ($y_{0\mathrm{exp}}$) have a low d_{33} dependence under uniaxial stress up to 120 MPa and a non hysteretic behavior during the temperature cycle −40°C–+80°C. They also present the lowest mechanical and piezoelectric losses. These performances are very interesting for power applications or sensors devices. If we assume that these materials are stoichiometric without cationic nor anionic vacancies, the electroneutrality leads to the theoretical expression $y_{0\ \mathrm{theo}} = 2x + z$ where x and z are respectively the molar content of Mg^{2+} and Ti^{3}.[3] $y_{0\ \mathrm{exp}}$ is well estimated by the latter relation if we consider that z is around 1 mol%. The drawback of this solution is that the d_{33} coefficient is decreased and that these materials cannot be easily poled above 150°C. Mn substitution in B site or La substitution in A site are well known to enhance the d_{33} coefficient and the ability to be poled. The objective of this work is to compare the performances of (Mg, F), (La, Mg, F), (Mn, Mg, F) co-doped PZT in term of their ability to be poled, their dielectric and piezoelectric properties and their stability under high uniaxial stress sollicitation and during a temperature cycle.

2. Experimental

The general chemical formulas for the investigated compositions are:

$Pb_{0.8975}(Ba, Sr)_{0.11}(Zr_{0.52}Ti_{0.48}Mg_{0.0075})$
$O_{3(1.0075)-\delta-y}\square_{\delta}F_{y}$

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$Pb_{0.8975-w}(Ba, Sr)_{0.11}La_w(Zr_{0.52}Ti_{0.48}Mg_{0.0075})$
$O_{3(1.0075)-\delta-y}\square_\delta F_y$
$Pb_{0.8975+t}(Ba, Sr)_{0.11}(Zr_{0.52}Ti_{0.48}Mg_{0.0075}Mn_t)$
$O_{3(1.0075)-\delta-y}\square_\delta F_y$.

They have been prepared for three values of La content: $w=0.5$, 0.75 and 1.5 mol% or for two values of Mn content: $t=0.75$ and 1.5 mol% and for different values y of F content. The method of synthesis used a wet route based on coprecipitation of oxalates and hydroxides discussed elsewhere.[5] The raw materials for doping were magnesium acetate, manganese (II) acetate, lanthanum (III) acetate and lead fluoride. This process leads to a good homogeneity of the composition due to the high reactivity of precursors and the low temperature of the PZT formation (around 600°C). Rods with 6.35 mm in diameter and 15 mm high and discs with 16 mm in diameter and 2 mm thick have been obtained from the PZT powders mixed with PVA binder, pressed under 1000 kg/cm^2 and sintered in sealed alumina crucible with $PbZrO_3$ powders at an optimal temperature around 1230°C. The samples were electroded by brushing with silver paste and firing at 700°C. The poling process has been realized in a silicon oil bath under a DC electrical field of 2 kV/mm applied during 1 min. All the measurements were made 24 h after poling. The sample ability to be poled is controlled by measuring the d_{33} coefficient with the help of the d_{33} meter, for two temperatures of the oil bath: 130°C or 150°C.

The mechanical quality factor Q_m (in inverse ratio of mechanical losses) at low sollicitations level is calculated with the help of a network analyzer HP4194A, by the standard method of electrical equivalent circuit, for the longitudinal frequency.

The dielectric losses $tg\delta$ are measured on a disc with a conventional Schering Bridge at 1 kHz, under 400 V/mm.

The evolution of d_{33} versus uniaxial stress which gives evidence of the domain wall motion ability is studied using a measurement unit developed in our laboratory and described elsewhere.[6] The temperature dependence of the N_{33} coefficient (in direct ratio to the longitudinal mode frequency) is studied by means of a HP4194A analyzer and of an oven in the range −40°C, +80°C, at low input electrical field.

3. Results

3.1. (La, Mg, F) co-doped PZT

The evolution of $tg\delta$ and Q_m versus the fluorine ion content y is given in Fig. 1, for three values w of La content and for the (Mg, F) co-doped PZT%. The $tg\delta$ curves present a minimum when Q_m reaches a maximum value, for a certain fluorine ion content y_0, which decreases as the La content x increases. The $tg\delta$ curve for $w=0.75$ mol% is not given in Fig. 1 due to its similarity with the one obtained for $w=0.5$ mol%. Only for $w=1.5\%$, with the fluorine ion content y_0 (1%), the evolution of d_{33} coefficient versus uniaxial stress presents a slight piezoelectric hysteresis (Fig. 2). With La doping, the N_{33} coefficient curves shown in Fig. 3 are non hysteretic, except for the first heating and cooling period. Finally, it is obvious from Table 1 that these materials cannot be correctly poled with the oil bath temperature of 130°C if $w<1.5$ mol%.

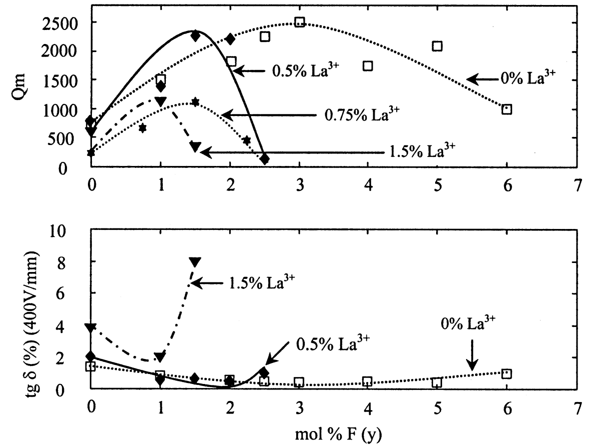

Fig. 1. Evolution of $tg\delta$ and Q_m for La doping of (La, Mg, F) co-doped PZT.

3.2. (Mg, Mn, F) co-doped PZT

The evolution of $tg\delta$ and Q_m versus the fluorine ion content y is given in Fig. 4, for $t=0.75$ mol% and 1.5 mol%, for the (Mg, Mn, F) co-doped PZT with Mg = 0.75 mol%. It completely differs from the results with (Mg, F) or (La, Mg, F) co-doped PZT. Q_m is higher when the material is not doped with fluorine ions. $tg\delta$ reaches a minimum value for $t=0.75$ mol% and $y=0.75$

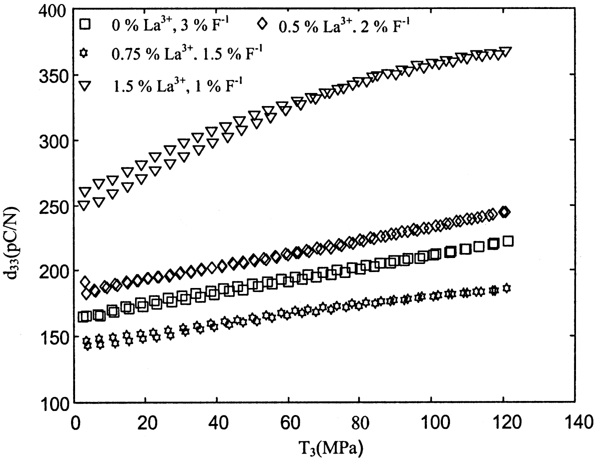

Fig. 2. Evolution of d_{33} versus uniaxial stress T_3, for La doping of (La, Mg, F) co-doped PZT.

mol% and for $t=1.5$ mol% and $y=1.5$ mol%. The corresponding Q_m values keep reasonable, respectively 870 and 700. Except for the composition with $t=0.75$ mol% and $y=0.75$ mol%, the evolution of d_{33} coefficient versus uniaxial stress is fully hysteretic (Fig. 5).

The temperature dependence of the N_{33} coefficient (Fig. 6) sometimes presents a slight hysteresis during the first heating and cooling period and the curve slope is related to the fluorine ion content. Finally, except for one composition, it is obviously that Mn doping facilitates the poling process at medium temperature (cf. Table 2).

Table 1
Polarisability of (La, Mg, F) co-doped PZT versus poling process temperature for the optimal formulations

w (mol%)	y (mol%)	$d_{33}^{130°C}$ (pC/N)	$d_{33}^{150°C}$ (pC/N)
0	3	110	180
0.5	2	100	180
0.75	1.5	110	150
1.5	1	280	270

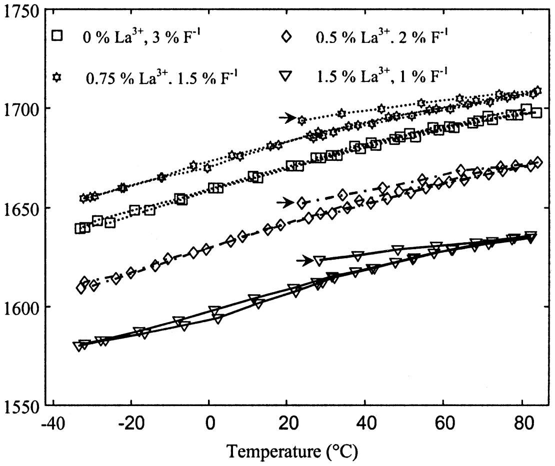

Fig. 3. Evolution of N_{33} during the temperature cycle, for La doping of (La, Mg, F) co-doped PZT.

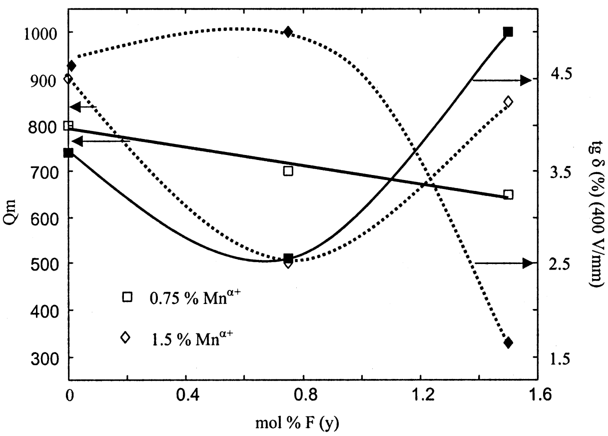

Fig. 4. Evolution of $tg\delta$ and Q_m as a function of F content, F(y), for Mn doping of (Mg, Mn, F) co-doped PZT.

4. Discussion

When the fluorine ion content y is increased in these (La, Mg, F) co-doped PZT, the Mg-fluorine ion defect dipoles progressively takes the place of Mg-$V_{\ddot{0}}$ defect dipoles. The former are certainly less mobile than the latter under high sollicitation, which could explain the

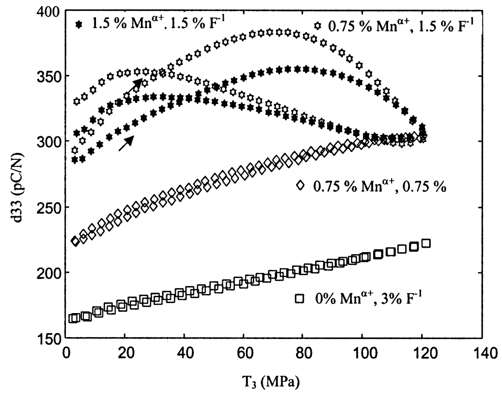

Fig. 5. Evolution of d_{33} versus uniaxial stress T_3, for Mn doping of (Mg, Mn, F) co-doped PZT.

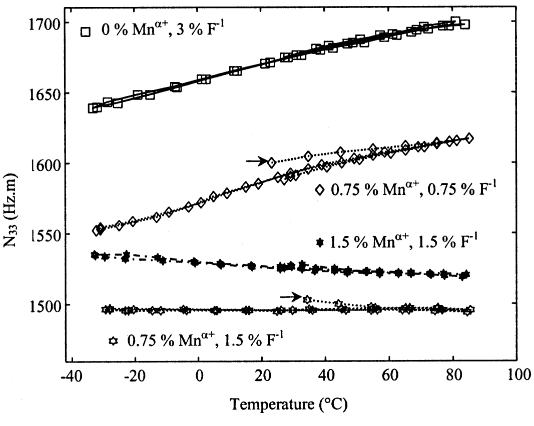

Fig. 6. Evolution of N_{33} during the temperature cycle, for Mn doping of (Mg, Mn, F) co-doped PZT.

Table 2
Polarisability of (Mg, Mn, F) co-doped PZT versus poling process temperature for the optimal formulations

t (mol%)	y (mol%)	$d_{33}^{130°C}$ (pC/N)	$d_{33}^{150°C}$ (pC/N)
0	3	110	180
0.75	0.75	80	220
0.75	1.5	325	320
1.5	0.75	260	280

enhanced stability observed on d_{33} coefficient curves versus uniaxial stress. For the same reason, the dielectric and mechanical losses are drastically reduced. The hardest PZT would correspond to a stoichiometric material without oxygen vacancies for the optimal fluorine ion content y_0. The experimental value of y_0 can be well estimated by the electroneutrality relation written as follow $y_0 = 2x + z - w$ if we assumed that the Ti^{3+} content[3] (z) is around 1 mol% . All these observations could clearly indicate that the La doping effect consists of the compensation of the Mg valency state 2+ in B site and so of the decrease of the y_0 value, due to its valency state 3+ in A site. This behavior leads to a decrease of pinning centers. The thermal stability of the N_{33} coefficient seems to be more sensitive to the number of pinning centers than the mechanical stability of d_{33}. This result is related with previous one discussed elsewhere[3] and for which the thermal stability of N_{33} for (Mg, F) co-doped PZT was enhanced with increasing both fluoride and magnesium contents.

For Mn doping, the previous explanations would only be in good agreement with the behavior of the doped PZT with Mn = 0.75 mol% and F = 0.75 mol%. Several hypothesis could be proposed to explain the characteristics of the other formulations:

- Influence of the tetragonal/rhombohedral phase ratio. In the case of (Mg, Mn, F) co-doped PZT, the change of the N_{33} curve slope with varying amounts of fluorine is an evidence of the evolution of this phases ratio.[7] Previous works[6] had pointed out that the d_{33} coefficient stability versus uniaxial stress is very sensitive to this ratio.
- Influence of the multi valency states of Mn,[8] which modify the number of pinning centers in accordance with a rule not yet known.
- Position of the Mn ion in the material which would be related to its content[8] and which would consequently modify the number of pinning centers.

5. Conclusions

The experimental results clearly show that the ability to be poled and the PZT coefficient stability under high solicitation cannot be easily and simultaneously obtained. The former is enhanced when the domain walls move easily whereas the latter needs pinning centers to decrease their mobility.

This study points out that La doping, even if it decreases the number of pinning centers, always leads for $w < 1.5$ mol% to hard materials, with low losses and a great stability of d_{33}, especially for the stoichiometric formulations without oxygen vacancy. Mn doping mechanism is not yet well understood but it is obvious that for some applications where the performance in term of d_{33} coefficient stability stays in a medium range, it leads to interesting characteristics and generally enhances the polarisability.

Acknowledgements

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