

# Dielectric and piezoelectric properties in fluoride-doped PMNT ceramics

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**Abstract** The effect of fluoride (LiF, MgF<sub>2</sub> and their mixture) on microstructure and electrical properties of 0.68 Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–0.32 PbTiO<sub>3</sub> (PMNT) ceramic was investigated. The X-ray study has shown each sample to be a pseudo-cubic perovskite single phase. Microstructure analysis has shown the fluoride-doped PMNT ceramics exhibit a typical liquid phase sintering character, and the fracture of LiF containing PMNT ceramics is transgranular fracture. The dielectric constants of fluoride-doped PMNT ceramics are higher than that of pure PMNT ceramic. The LiF containing PMNT ceramics have more apparent diffusion phase transition (DPT) and frequency dispersion than pure and MgF<sub>2</sub>-doped PMNT ceramics. These results may be ascribed to structural disorder and compositional fluctuations in solid solution. The LiF containing PMNT ceramics have better piezoelectric properties than the other two samples. The values of  $d_{33}$  and  $K_p$  for LiF-doped PMNT ceramic arrive to 624 pC/N and 68%, respectively.

**Keywords** PMNT · Fluoride · Microstructure · Dielectric and piezoelectric properties

## 1 Introduction

Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–PbTiO<sub>3</sub> (PMN–PT) ceramics are very promising materials for the application of electromechanical transducers for their excellent dielectric and piezoelec-

tric properties [1], especially for the composition close to the morphotropic phase boundary (MPB), which contains about 30–35 mol.% of PT [2]. However, PMN–PT ceramics are the same as PZT ceramics can be doped by donor (soft dopant) or acceptor (hard dopant) ions for modifying dielectric and piezoelectric properties. A lot of studies have been made on the influence of different cationic substitutions on the crystalline network and the piezoelectric properties. Recently, some works have been realized on the anionic or dual cationic–anionic substitutions in PZT ceramics for changing greatly the electromechanical properties of the PZT ceramics and improving their stability under high electric field and uniaxial stress [3]. Lithium fluoride (LiF), moreover, had already been used with success to decrease sintering temperature and realize the dual cationic–anionic substitutions in perovskite materials such as KTa<sub>1–x</sub>Nb<sub>x</sub>O<sub>3</sub> (KTN) [4], BaTiO<sub>3</sub> [5], CaZrO<sub>3</sub> [6] and PMNT [7] ceramics.

In this paper, fluoride-doped 0.68 Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–0.32 PbTiO<sub>3</sub> (PMNT) ceramics were firstly prepared and characterized in term of microstructure and electrical properties. The use of fluoride (LiF, MgF<sub>2</sub> and their mixture) is justified taking into accounts its capability to sinter PMNT ceramics at low temperature and the dual cationic–anionic substitutions in PMNT ceramics.

## 2 Experimental procedure

The starting materials PbO, 4MgCO<sub>3</sub>·Mg(OH)<sub>2</sub>·4H<sub>2</sub>O, Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, MgF<sub>2</sub> and LiF were Shanghai products of analysis purity grade. The 0.68 Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–0.32 PbTiO<sub>3</sub> (PMNT) powder was synthesized by a modified two-stage columbite approach [8]. Various mixtures were then prepared from PMNT, LiF and MgF<sub>2</sub>

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powders. The initial composition of these samples is listed in Table 1. The mixed powders added with 5 wt% of polyvinyl alcohol (PVA) were dry ground using an agate mortar, passed through 60-mesh sieves, and pressed into (12 mm in diameter and 5 mm in thick) disks at 150 MPa. The binder was burnt-out by heating up to 600 °C for 2 h, and then the disks were sintered at different temperature (Table 1) for 3 h in a multiple-enclosure crucible setup sealed with the PMNT perovskite powder to minimize PbO volatilization. The ceramics were cut to slice for 0.5 mm thick. X-ray diffraction (Rigaku D/Max-2400, CuK $\alpha$  radiation, Japan) analysis has been carried out for ceramics. The fracture surface of ceramics was examined by scanning electron micrographs (JEOL JSM-5800, Japan). Both sides of the specimens were polished and electroded, then fired in air at 550 °C for 30 min to form silver electrode for electrical measurements. A HP4284A impedance analyzer was used to measure the dielectric constants and losses as a function of temperature on heating from 25 °C to 250 °C at frequencies of 0.1, 1, 10, 100 kHz. The ceramics were poled using a DC field of 2 kV/mm at 25 °C for 10 min. The values of the piezoelectric constant  $d_{33}$  were determined using a  $d_{33}$ -meter.

### 3 Results and discussion

The XRD study has shown each sample to be a pseudocubic perovskite single phase. The structure of pure PMNT ceramic is only slightly affected by fluorides. The lattice parameter ( $a$ ) of fluoride-doped PMNT ceramics at 25 °C is around 4.021 Å, which is very close to that of pure PMNT ceramic (~4.024 Å).

The SEM photographs of ceramics are shown in Fig. 1. The pure PMNT ceramic (sample A) has fine (~2  $\mu$ m) grains and mainly shows intergranular fracture character. However, the fracture of LiF containing PMNT ceramics (sample B and D) is transgranular fracture. It is shown that the conjunct strength of grains is firm. This may be mainly ascribed to the formation of liquid phase melted by LiF additive at lower temperature (~848 °C). The PMNT grains were incorporated with each other to form the dense

structure and large grain in the role of the liquid phase. The fracture character of MgF<sub>2</sub>-doped PMNT ceramic (sample C) is between sample A and sample B, owing to the melting point (~1248 °C) of MgF<sub>2</sub> is higher than that of LiF. The grain size of fluoride-doped PMNT ceramics (~10  $\mu$ m) is much larger than that of pure PMNT ceramic. From above analysis, all the fluoride-doped PMNT ceramics show a typical liquid phase sintering character.

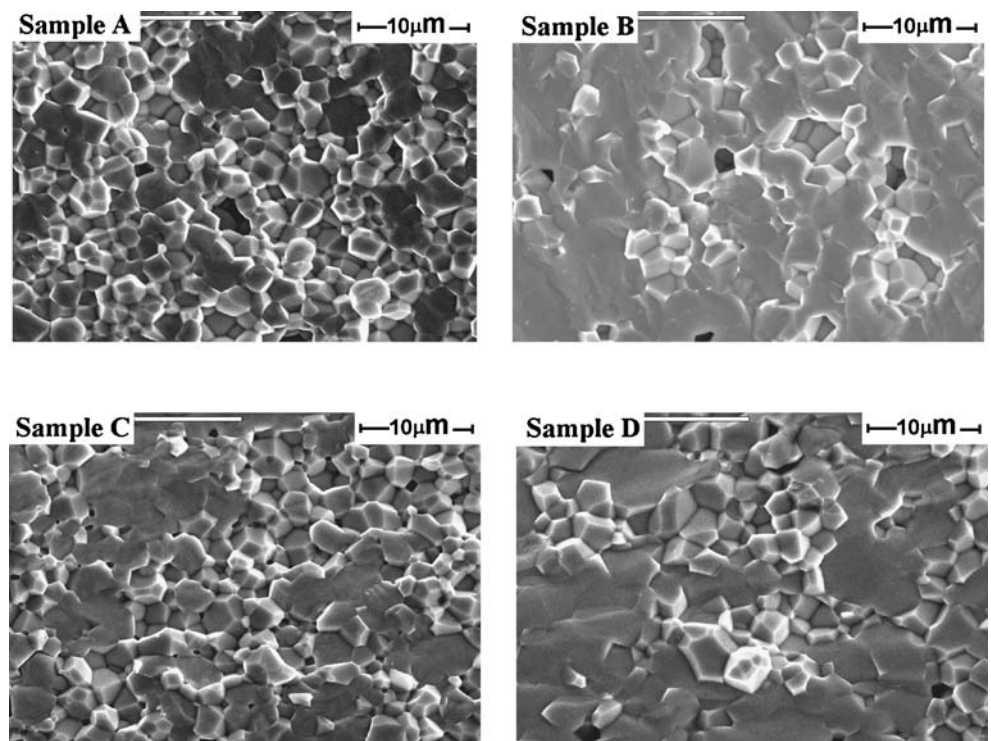
Figure 2 shows temperature dependence of  $\epsilon_r$  and  $\tan\delta$  at different frequencies (0.1–100 kHz) for ceramics. Strong frequency dispersion for sample A–C has been observed only near  $T_m$  (the temperature of maximum dielectric constant), but that for sample D has been observed from room temperature to  $T_m$ . The dielectric characteristics for a measurement frequency of 1 kHz are listed in Table 1.

The values of dielectric constant and dielectric loss for fluoride-doped PMNT ceramics are higher than that of pure PMNT ceramic. This result is ascribed to  $T_m$  shifts to lower temperature. The value of  $T_m$  for sample D (~102 °C) is much lower than that of sample A (~144 °C), and an apparent broadening and lowering of the maximum dielectric constant  $\epsilon_{rm}$  occurs for sample D.  $\Delta T = T_{m/100\text{kHz}} - T_{m/0.1\text{kHz}}$ , where  $\Delta T$  can be used to figure frequency dispersion. The values of  $\Delta T$  for fluoride-doped PMNT ceramics are higher than that of pure PMNT ceramic (~2 °C), especially for sample D, the value of  $\Delta T$  arrives to 9 °C. Therefore, the fluoride-doped PMNT ceramics have more apparent frequency dispersion than pure PMNT ceramic. All the results may be ascribed to the fluoride addition. The role of fluoride in PMNT ceramics is similar to the LiF in KTa<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> ceramics [4], where, LiF firstly melted at 848 °C, and then rapidly moved in the grain boundaries of the ceramics, finally, LiF is localized probably partially at the grain boundary and other parts of LiF react with the grain by anionic (F<sup>-</sup>O<sup>2-</sup>) substitution coupled with a cationic substitution in order to keep the electric neutrality. So the frequency dispersion and diffusion phase transition (DPT) of fluoride-doped PMNT ceramics may be attributed to structural disorder and compositional fluctuations in solid solution, which are originated from the liquid phase at grain boundary and the dual cationic–anionic substitution.

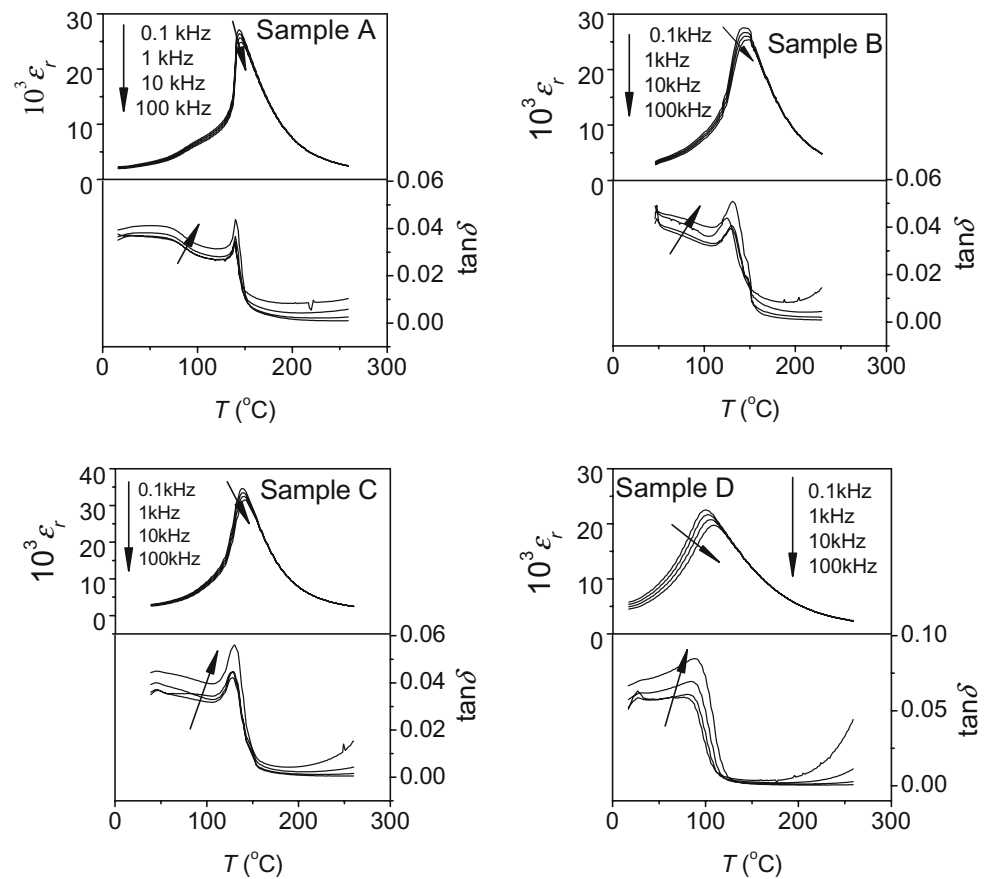
**Table 1** Initial composition, dielectric and piezoelectric characteristics for ceramics (1 kHz).

Sample	Initial compositions of the samples in moles	$T_{\text{sint}}$ (°C)	$\epsilon_r$ (25 °C)	$\tan\delta$ (25 °C)	$T_m$ (°C)	$\epsilon_{rm}$ ( $T_m$ )	$\Delta T$ (°C)	$K_p$ (%)	$d_{33}$ (pC/N)
A	PMNT	1240	2,298	0.037	144	26,406	2	51	326
B	0.97PMNT–0.03LiF	1100	3,090	0.046	139	26,691	4	68	624
C	0.97PMNT–0.03MgF <sub>2</sub>	1200	2,642	0.036	140	33,445	3	43	312
D	0.94PMNT–0.03MgF <sub>2</sub> –0.03LiF	1100	5,826	0.058	102	21,645	9	55	583

**Fig. 1** SEM photographs of fracture surface for ceramics



**Fig. 2** Temperature dependences of dielectric constant ( $\epsilon_r$ ) and loss ( $\tan\delta$ ) at different frequencies for ceramics



The value of piezoelectric planar coupling coefficient  $K_p$  can be calculated using formula 1 [9]:

$$K_p \approx 1.125 \sqrt{\frac{f_a^2 - f_r^2}{f_r^2}} \quad (1)$$

The values of resonant frequency  $f_r$  and anti-resonant frequency  $f_a$  were measured by a resonant–anti-resonant method using a HP4192A complex impedance analyzer. The piezoelectric characteristics for ceramics are shown in Table 1. It showed that the LiF containing PMNT ceramics (sample B and D) have better piezoelectric properties than the other two samples. Therefore, LiF can greatly improve the piezoelectric properties of PMNT ceramics. The values of  $d_{33}$  and  $K_p$  for sample B arrive to 624 pC/N and 68%, respectively, which are far larger than those of the pure PMNT ceramic (326 pC/N and 51%). The values of  $d_{33}$  and  $K_p$  for MgF<sub>2</sub>-doped PMNT ceramic (sample C) are very closed to that of pure PMNT ceramic.

#### 4 Conclusions

The fluoride-doped PMNT [0.68 Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–0.32 PbTiO<sub>3</sub>] ceramics have been prepared by solid state reaction between PMNT and fluoride (LiF, MgF<sub>2</sub> and their mixture). The X-ray study has shown each sample to be a pseudo-cubic perovskite single phase, and the structure of pure PMNT ceramic is only slightly affected by fluoride. Microstructure analysis has shown that LiF plays an important role in the ceramic densification. Moreover, the

fracture of LiF containing PMNT ceramic is transgranular fracture. The LiF containing PMNT ceramics have more apparent diffusion phase transition (DPT) and frequency dispersion than pure and MgF<sub>2</sub>-doped PMNT ceramics. The LiF containing PMNT ceramics have better piezoelectric properties than the other two samples. The values of  $d_{33}$  and  $K_p$  for sample B arrive to 624 pC/N and 68%, respectively. All these results can be ascribed to the liquid phase at grain boundary and the dual cationic–anionic substitution.

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