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Fluorine-oxygen substitution in MgO-doped lead zirconate titanate ceramics: diffractometric and dielectric studies

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A fluorine-oxygen substitution has been realized in a PZT material with a composition $Pb_{0.89}(Ba, Sr)_{0.11}(Zr_{0.52}Ti_{0.48})O_3$ thanks to the introduction of Mg^{2+} ions in the B-site of the perovskite. Oxygen vacancies may exist in the anionic sublattice if the fluorine rate is lower than the required one for a stoichiometric PZT-type ABO_3. The F–O substitution makes the relative amount of rhombohedral phase in the MgO and F-doped PZT samples decrease and a drastic increase of the Curie temperature is observed. Minimum values of dielectric constant, high level dielectric losses and piezoelectric coefficient are obtained for a fluorine concentration close to the stoichoimetric PZT one.

1. Introduction

Ferroelectric PZT ceramics $Pb(Zr_xTi_{1-x})O_3$ have been studied intensively owing to their electromechanical properties. It is possible to modify these properties and obtain specific characteristics for precise applications by making different cationic substitutions in the ABO_3 type PZT perovskite structure. A lot of studies have been made on the influence of different dopants on the crystalline network and the piezoelectric properties.

On the other hand, few works have been realized on the anionic substitution in the PZT materials, like the fluorine oxygen substitution. Eyraud *et al.* showed that the F–O substitution changed greatly the electromechanical properties of the PZT ceramics and improved their stability under high electric field and uniaxial stress [1, 2].

In this paper, a diffractometric and dielectric study of ceramics with a nominal composition $Pb_{0.89}(Ba, Sr)_{0.11}(Zr_{0.52}Ti_{0.48})O_3$ doped with Mg^{2+} in the B site of perovskite and F^- is proposed.

2. Experimental

PZT powder was prepared by coprecipitation in an aqueous solution of oxalic acid. The starting materials used were high purity lead acetate, barium acetate, strontium acetate (Merck), tetra-*n*-butyl titanate ($Ti(OC_4H_9)_4$) and tetra-*n*-butyl zirconate ($Zr(OC_4H_9)_4$) (Huls). Experimental details are given elsewhere [3]. The precipitate so obtained contains metal hydroxides and lead oxalate. Magnesium acetate (Merck) and sub micrometer sized lead fluoride powder were then added to the dried precipitate. The total amount of lead in the precipitate-PbF_2 included-corresponds to 0.89 mol in the final PZT. The mixture was stirred and crushed in ethyl alcohol for 1 h and dried at 100 °C for 5 h. The precursors powder was then calcined at 600 °C for 10 h and reheated at 800 °C for 4 h to ensure complete reaction.

The PZT powder was mixed with an appropriate amount of PVA binder and then pressed into discs and cylindrical rods under 1000 kg/cm^2. After binder burnout (600 °C, 4 h), the samples were sintered at 1230 °C for 4 h.

Disc-shaped ceramics (16 mm diameter, 2 mm thickness) and cylindrical ceramics (6.35 mm diameter, 15 mm length) were then poled in a silicone oil bath at 150 °C with an applied field of 2.5 kV/mm for 1 min. The room temperature ratio of both rhombohedral and tetragonal phases as well as high temperature unit cell volume in the paraelectric (cubic) phase of the sintered samples were determined by powder X-ray diffraction (Siemens diffractometer) using CoK_α radiation after crushing the ceramics. The amount of rhombohedral phase was calculated measuring the areas of the reflection lines using a monophasic tetragonal PZT $Pb_{0.89}(Ba, Sr)_{0.11}(Zr_{0.48}Ti_{0.52})O_3$ as standard specimen [4].

The $(0\,1\,3)_t$ and $(3\,1\,0)_t$ reflection lines of the tetragonal phase and the $(3\,1\,0)_r$ reflection lines of the rhombohedral phase were used in preference to the $(0\,0\,2)_t$, $(2\,0\,0)_t$ and $(2\,0\,0)_r$ lines in order to get a better precision (Fig. 1).

Dielectric and piezoelectric properties of PZT ceramics were measured 24 h after poling using a LCR meter (HP4284A) for the dielectric constant ε_r of disc-shaped samples, a Schering Bridge for the dielectric losses under high electric field (400 V/mm) and a Piezo-d_{33} Berlincourtmeter for the piezoelectric coefficient d_{33} of cylindrical samples. The Curie temperature corresponds to the maximum value of ε_r measured at 10 kHz, with an accuracy of ±1 °C.

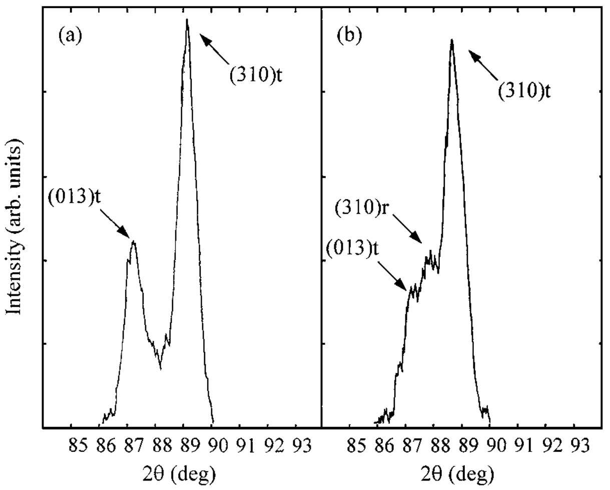

Figure 1 Profile of $(0\,1\,3)_t$, $(3\,1\,0)_r$ and $(3\,1\,0)_t$ reflection lines of: (a) Monophasic tetragonal PZT $Pb_{0.89}(Ba, Sr)_{0.11}(Zr_{0.48}Ti_{0.52})O_3$ and (b) biphasic PZT $Pb_{0.89}(Ba, Sr)_{0.11}[(Zr_{0.52}\,Ti_{0.48})_{0.99}Mg_{0.01}]O_{2.99}\square_{0.01}$.

3. Results and discussion

The theoretical stoichiometric formulation of the PZT doped with an equal amount of MgO and PbF_2 (x mol) is:

$$Pb_{0.89}(Ba, Sr)_{0.11}[(Zr_{0.52}Ti_{0.48})_{1-x}Mg_x]O_{3-2x}F_{2x}$$

If the quantity of PbF_2 (y mol) is lower than the quantity of MgO (x mol), then it is possible to write a new theoretical non-stoichiometric formulation showing extrinsic oxygen vacancies due to the introduction of magnesium in the lattice:

$$Pb_{0.89}(Ba, Sr)_{0.11}[(Zr_{0.52}Ti_{0.48})_{1-x}Mg_x]$$
$$O_{3-x-y}\square_{x-y}F_{2y}$$

3.1. Diffractometric study

The variation of the amount of rhombohedral phase in the MgO-doped PZT samples ($x = 0.01$) with increasing fluorine content is given Fig. 2. The PZT without dopant in B site and in anionic site-initial PZT-was also studied.

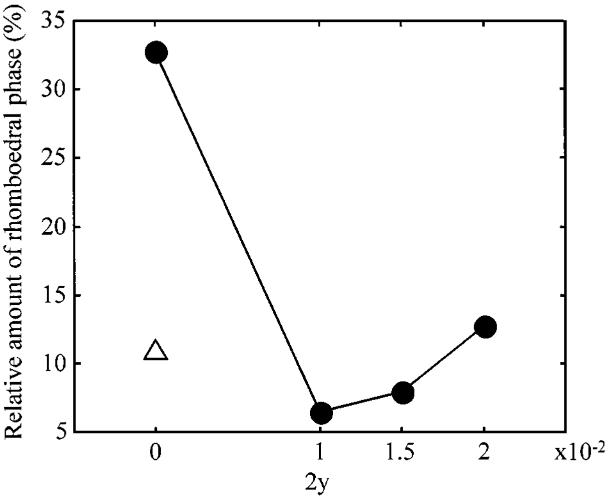

Figure 2 Relative amount of rhombohedral phase with fluorine content for MgO-doped PZT (●) $x = 0.01$. (△) $x = 0$, $y = 0$.

All the PZT samples have a majority of tetragonal phase because of the chosen Zr/Ti ratio and the small amounts of magnesium and fluorine introduced. However, the quantity of rhombohedral phase is approximately three times higher in the MgO-doped PZT without fluorine than in the initial PZT. Concerning the F-doped PZT, the rate of rhombohedral phase varies slightly with the molar percentage of fluorine and is roughly the same one as in the initial PZT.

The F–O substitution modifies the symmetry of the MgO-doped PZT ($x = 0.01$) since the amount of rhombohedral phase is lower in the F-doped PZT materials. This variation may be related to the change of the distortions in the perovskite lattice, e.g. in the BO_6 octohedra and in the AO_3 planes.

In the case of the MgO-doped PZT ($x = 0.01$), the anionic sublattice contains oxygen vacancies which tend to shrink the cell and so make the O–O and A–O distances vary creating rhombohedral distortions [5]. Whereas in the F-doped PZT specimens, the amount of oxygen vacancies is lower or even almost equal to zero.

This hypothesis is confirmed by the high temperature XRD diagrams study which shows that the unit cell volume in cubic phase of the MgO-doped PZT is smaller than in the F- doped PZT and in the initial PZT (Table I).

3.2. Dielectric and piezoelectric studies

Fig. 3 shows the evolution of the Curie temperature (T_c) with the fluorine content for two different MgO rates ($x = 0.0075$ and 0.01). The Curie points of both initial PZT and 3%F-doped PZT are also given. For both series of materials, T_c varies in the same way: large increase for $2y = 0.01$, then slight decrease for $2y = 0.015$ and finally reincrease up to $2y = 0.03$.

TABLE I Variation of the unit cell volume of the PZT samples in the cubic phase ($T = 440\,°C$) with MgO and fluorine content

x	0	0.01	0.01	0.01	0.01
$2y$	0	0	0.01	0.015	0.02
V($Å^3$)	67.750	67.720	67.788	67.754	67.774

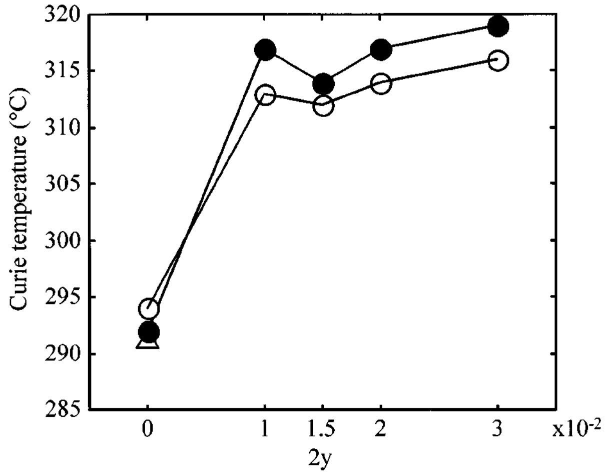

Figure 3 Evolution of T_c with fluorine content for two different MgO concentrations: (○) $x = 0.0075$ and (●) $x = 0.01$. (△) $x = 0$, $y = 0$.

These results are difficult to interpret. A F–O substitution associated with a cationic substitution to ensure electrical neutrality without oxygen vacancies leads to a decrease of the lattice anisotropy and so of T_c because the M–F bond (M = Ti, Zr) is less covalent than the M–O bond [6].

For both series, the slight decrease for $2y = 0.015$ may correspond to the F-doped PZT with a composition close to the stoichiometric one

$$Pb_{0.89}(Ba,\ Sr)_{0.11}[(Zr_{0.52}Ti_{0.48})_{0.9925}Mg_{0.0075}]$$
$$O_{2.985}F_{0.015} \quad \text{and}$$
$$Pb_{0.89}(Ba,\ Sr)_{0.11}[(Zr_{0.52}Ti_{0.48})_{0.99}Mg_{0.01}]O_{2.98}F_{0.02}$$

and consequently to a less important distortion in the perovskite.

The variation of the dielectric constant ε_r versus y for $x = 0.0075$ and $x = 0.010$ is represented Fig. 4.

Both series follow the same evolution: large decrease of ε_r up to $2y = 0.010$–0.015 and then ε_r becomes approximately constant for high fluorine concentration. In the same way, dielectric losses tgδ under high electric field (400 V/mm, 1 kHz) show a similar evolution (Fig. 5): significant decrease of tgδ up to $2y = 0.015$ and above this value, tgδ remains the same. High level measurements (400 V/mm, 1 kHz) were used in preference to low level standard measurements (1 V/mm, 1 kHz) [7] because the increase of dielectric losses with the amplitude of the electric field allows a more marked comparison between the various samples.

So, when $x = 0.0075$ and $x = 0.01$, ε_r and tgδ keep approximately constant minimum values after the significant decrease for $2y \leq 0.015$, corresponding to a Mg and F-doped stoichiometric PZT without oxygen vacancies:

$$Pb_{0.89}(Ba,\ Sr)_{0.11}[(Zr_{0.52}Ti_{0.48})_{1-z}Mg_z]O_{3-2z}F_{2z}$$

These results clearly show the preponderant role of fluorine in the stabilization of ferroelectric domain wall configuration. A MgO-doped PZT contains oxygen vacancies (V_o) which stabilize the spontaneous polarization P_s within each domain by volume effect or domain wall effect [8]. In the case of volume effect, the dopant Mg forms Mg^{2+}–V_o associates with a dipole moment in the direction of the associate axis. These defect dipoles orient themselves in the existing P_s direction and stabilize the domain wall configuration. But under strong external excitations such as uniaxial stress, high electric field and temperature, a new P_s direction develops, anisotropic associated defects may be activated and reorient themselves in the new P_s direction. Consequently, the domain wall configuration is no longer fixed. The increase of the domain wall mobility causes an increase in the dielectric and mechanical losses.

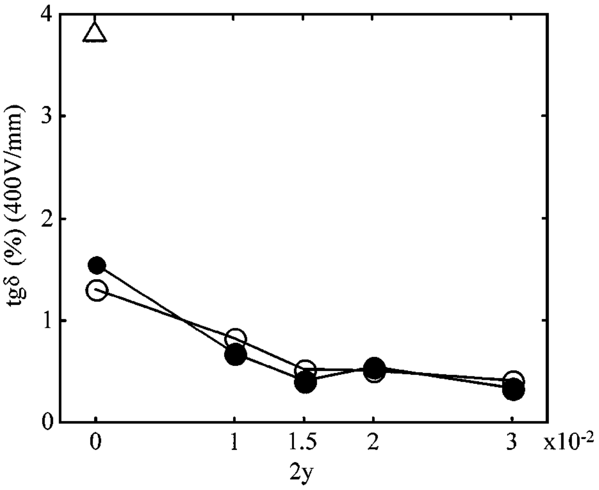

Figure 5 Evolution of tgδ with fluorine content for two different MgO concentrations: (○) $x = 0.0075$ and (●) $x = 0.01$. (△) $x = 0$, $y = 0$.

On the other hand, as oxygen vacancies are the only lattice defects in the perovskite structure that have a significant mobility [9], when fluorine is introduced in the anionic site, defect dipoles Mg^{2+}–F^- are much less mobile than Mg^{2+}–V_o. So, they stabilize the domain wall configuration more, even under high external conditions.

This idea is confirmed by the evolution of the piezoelectric coefficient d_{33} with increasing fluorine concentration (Fig. 6). Under the same conditions—aging of

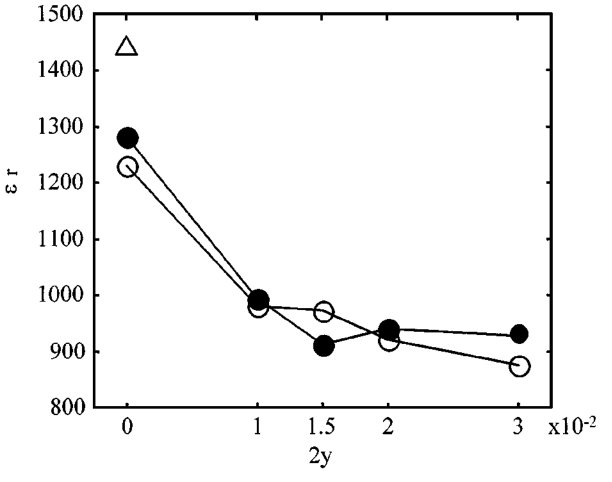

Figure 4 Evolution of ε_r with fluorine content for two different MgO concentrations: (○) $x = 0.0075$ and (●) $x = 0.01$. (△) $x = 0$, $y = 0$.

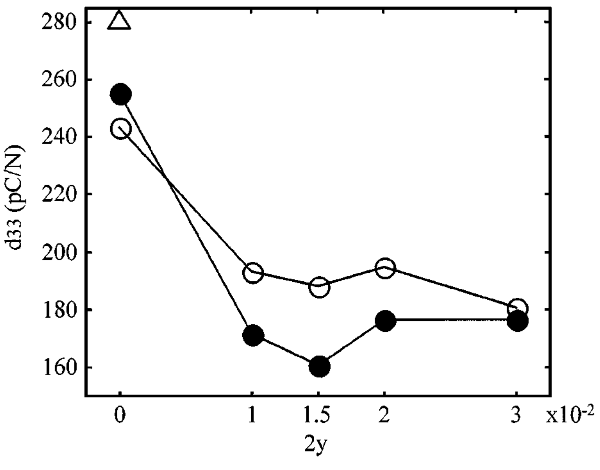

Figure 6 Evolution of d_{33} with fluorine content for two different MgO concentrations: (○) $x = 0.0075$ and (●) $x = 0.01$. (△) $x = 0$, $y = 0$.

the ceramics after poling, temperature, applied poling field—a drastic decrease of d_{33} for F-doped PZT samples can be observed, owing to a stabilized domain configuration by anisotropic defects which cannot easily orient themselves in the direction of the poling field.

4. Conclusion

The introduction of acceptor Mg^{2+} ions in the B site of the PZT materials allowed fluorine—oxygen substitution in the anionic site.

Oxygen vacancies may exist if the fluorine rate is lower than the fluorine rate corresponding to the stoichiometric PZT.

The diffractometric study of MgO and F-doped PZT solutions showed that F–O substitution decreases the amount of rhombohedral phase in the sample; it is also accompanied by a decrease of ε_r, tgδ (400 V/mm) and d_{33} making the material "harder" than the only MgO-doped one. Also, a surprising pronounced increase of T_c is observed.

Further investigations concerning F-doped PZT specimens with higher fluorine concentrations than those corresponding to the stoichiometry should allow a more precise understanding of the mechanism of fluorine—oxygen substitution.

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