

Characteristics of F doped PZT ceramics using different fluorine sources

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Abstract

In this study, some structural and electrical properties of a PZT base composition $\text{Pb}_{0.89}(\text{Ba}, \text{Sr})_{0.11}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ co-doped with 1 mol% manganese and 2 mol% fluorine have been studied. Two different fluorine sources were used: lead fluoride PbF_2 and manganese fluoride MnF_2 . These fluoride salts are added to the co-precipitated precursors powder. Mn dopant was added to the solution as manganese acetate (MnAc) before co-precipitation, when PbF_2 was used. The structural analysis of the sintered ceramics revealed that MnF_2 doping makes the volume of the cubic unit cell (V_c) and the grain size decrease, whereas (MnAc, PbF_2) co-doping makes the apparent density increase and keeps the average grain size and V_c unchanged. Both types of doping reagents largely enhance the piezoelectric activity (high d_{33} and k_{33} coefficients, well saturated Polarization–Electric field loops) but MnF_2 induces both combinatory soft and hard characteristics compared to (MnAc, PbF_2) co-doping. Impedance spectroscopy showed that both types of doping reagents strongly reduce the electrical conductivity with the same conducting species, i.e. the same defect chemistry, confirmed by optical absorption data. Finally, this study shows that in the semi-wet process used, PbF_2 is added homogeneously to the co-precipitated powder. Whatever the fluorine source, only the coexistence of Mn and F dopants is necessary to improve the piezoelectric response.

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1. Introduction

Ferroelectric lead zirconate titanate ceramics $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ abbreviated PZT are widely used in many industrial applications such as medicine or aeronautics due to their excellent electromechanical properties. Generally, the x value lies between 0.50 and 0.54, which corresponds with the morphotropic phase boundary (MPB) where the solid solution $x\text{PbZrO}_3-(1-x)\text{PbTiO}_3$ is a mixture of both tetragonal and rhombohedral phases and gives the best dielectric and piezoelectric properties. However, PZT ceramics are rarely used in their chemically pure form. Classically, the electrical properties are modulated by the incorporation of small amounts of cations (doping). There are two principal categories of dopants [1]:

- Donor dopants which are higher valence substituents like Nb^{5+} or Sb^{5+} in the place of ($\text{Zr}^{4+}/\text{Ti}^{4+}$) or La^{3+} in the place of

Pb^{2+} . They are called softeners and have the following effects of the characteristics of PZT:

- little change in Curie point;
- higher dielectric constant and losses (at room temperature);
- higher charge coefficient d_{33} ;
- much lower mechanical quality factor Q_m ;
- easy to depolarize by mechanical stress.

The excess of positive charge in soft PZT is compensated by lead vacancies.

- Acceptor dopants which are lower valence substituents like Mg^{2+} or Fe^{3+} (B site) or Na^+ (A site). They are called hardeners and cause the following changes of the characteristics of PZT:
 - little change in Curie point;
 - lower dielectric constant and losses (at room temperature);
 - lower d_{33} ;
 - much higher mechanical Q_m ;
 - difficult to depolarize by mechanical stress.

The lack of positive charge in hard PZT is compensated by oxygen vacancies.

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A lot of studies have been made on the cation substituents in PZTs since many years, in particular the transition metal cations but, to the best of our knowledge, few works have been realized on the anionic substituents such as fluorine ion F^- . In the last years, our Laboratory developed PZT ceramics co-doped with Mn or Mg and fluorine [2–4]. In particular, (Mn, F) co-doping improves both dielectric and electromechanical characteristics and the thermal stability of some piezo coefficients [5,6]. Besides, it also makes the mechanical quality factor Q_m increase, which is very interesting for high-power transducer devices [7,8]. The F doped PZT ceramics are usually prepared using lead fluoride PbF_2 as a fluorine source [9] which allows to control F content without adding supplementary foreign cations in the PZT perovskite (Pb ion brought by PbF_2 is a PZT constitutive ion) but the effect of different fluoride salts is unknown, for a given doped composition. So the purpose of the present study is to investigate the influence of other fluoride salts on some structural and electrical properties of the sintered specimens.

2. Sample preparation and experimental procedure

The chosen base composition was $Pb_{0.89}(Ba, Sr)_{0.11}(Zr_{0.52}Ti_{0.48})O_3$ co-doped with 1 mol% Mn and 2 mol% F. The studied PZT compositions were systematically doped with barium and strontium (11 mol%) in A site of the perovskite in order to increase the polarisability and the room temperature dielectric constant. The PZT powder was prepared by co-precipitation in a aqueous solution of oxalic acid. The pH of the solution was adjusted with ammonia. Experimental details are given elsewhere [10]. When necessary, manganese was added to the solution as acetate (MnAc). The fluorine salts used are: lead fluoride PbF_2 and manganese fluoride MnF_2 . They were added to the precursors powder obtained after co-precipitation using a mortar grinder in alcoholic media. The total amount of lead, PbF_2 included (when it is used), corresponds with 0.89 mol in the PZT.

Table 1 gives the different PZT compositions with the final dopants concentrations in the PZT, the corresponding starting reagents and their content.

The precursors powder was dried at 80 °C for 15 h and calcined at 800 °C for 4 h. The resulting powders were pressed into discs and cylindrical rods and the green pellets were sintered at 1230 °C in a lead rich atmosphere to control PbO volatility.

X-ray diffraction (XRD) studies were performed on the crushed sintered ceramics in order to determine the lattice parameter of each composition. XRD measurements were realized using a X-Pert Pro MPD (PANalytical) with an incident monochromator (Cu $K\alpha_1$ radiation) and a real time multiple strip detector X'Celerator in the $\Delta 2\theta$ range = 10–90°. At room

temperature, both rhombohedral and tetragonal phases coexist in every studied PZT due to the Zr/Ti ratio, but the effect of doping on the lattice was determined by the unit cell tetragonal distortion (c/a) of the crushed sintered ceramics. It was chosen to evaluate the lattice parameter “a” in the high temperature cubic phase above the Curie temperature. So, XRD diagrams were recorded at 400 °C using high temperature camera HTK 16 (Anton Paar). The step size in the 2θ range was 0.0167° and the counting time per step was 550 s. Precise lattice parameters were determined using eight of the tetragonal or cubic reflections. The unit cell search and cell parameter refinement have been realized using X'Pert Plus Program (PANalytical).

The density of the PZT ceramics was estimated by the geometrical method. The average grain size was determined using a scanning electron microscopy (SEM Jeol 840). The optical absorption of PZT compositions was measured with UV–vis spectrometer Lambda 35 (Perkin-Elmer).

For the electrical measurements, disc-shaped ceramics (16 mm diameter, 2 mm thickness) and cylindrical ceramics (6.35 mm diameter, 15 mm length) were electroded with silver paste fired at 700 °C and poled in a silicone oil bath at 120 °C with an applied field of 2.5 kV/mm for 5 min. Dielectric and piezoelectric properties of PZT ceramics were measured 24 h using an impedance analyzer (HP 4194 A). The dielectric constant and losses of disc-shaped unpoled ceramics as a function of temperature were measured at a heating rate of 1 °C/min, with an accuracy of ± 1 °C in order to get the Curie temperature T_c . Conductivity measurements were also made on the discs using complex impedance spectroscopy [11] in the temperature range 200–700 °C. Impedance data (real Z' and imaginary Z'' components) were collected at a constant temperature using an impedance analyzer (Solartron) in the frequency range of $f = 10^{-2}$ Hz–1 MHz with an applied voltage of 1 V. Bulk resistance values were extracted from complex plane plots (Z'' versus Z').

3. Results and discussion

3.1. Structural analysis

Table 2 gives the density of the studied ceramics. The co-doped specimen from MnAc and PbF_2 presents the highest density and the density of PZT 2 (co-doping by MnF_2) is slightly lower than that of undoped specimen. The doping reagents dependence of the density may be correlated to the SEM observations in Fig. 1 showing etched surface of the sintered compositions. It is clear that both the undoped PZT and PZT 1 (MnAc, PbF_2) co-doping roughly exhibit the same average grain size, whereas it is markedly decreased by MnF_2 doping (PZT

Table 1
PZT compositions with the starting reagents used

Dopants concentration (mol%)	Mn (1), F (2)	
Sample	PZT 1	PZT 2
Doping reagent	MnAc (1) PbF_2 (1)	MnF_2 (1)

Table 2
Density and structural parameters of the ceramics

PZT	Undoped	PZT 1	PZT 2
Density (g/cm ³)	7.43	7.50	7.40
Tetragonal parameter (c/a)	1.020	1.018	1.018
Volume of cubic unit cell V_c (Å ³)	67.62	67.62	67.55

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