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EFFECTS OF SINTERING TEMPERATURE ON STRUCTURAL AND ELECTRICAL PROPERTIES OF FE^{3+} DOPING PZT CERAMICS

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Abstract

The influence of the sintering temperature on the structure and on the hysteresis loops of Fe^{3+} doped $Pb(Zr_xTi_{1-x})O_3$ system has been investigated. Three compositions have been selected in the following mode: one in rhombohedral region, one in MPB region and one in tetragonal region have been obtained by solid state reaction technique. Sintering has been carried out at 1200^0C and 1250^0C respectively. The nature of the phases has been investigated in detail using X-ray diffraction analysis (XRD). All the sintered samples reveal a perovskite type structure. The surfaces have been lapped and metalized in order to obtaine the hysteresis loops at room temperature. The results showed a similar behaviour with "hard" PZT ceramics.

Key words: doped PZT, hard PZT, dielectric properties, piezoelectric properties

1. Introduction

Doped $Pb(Zr_xTi_{1-x})O_3$ (PZT) ceramics due to their piezoelectric properties show a very large interest for applications such as sensors [1], actuators [2], transducers [3] and structural health monitoring [4]. The final piezoelectric properties depend on the: (i) value of Zr^{4+}/Ti^{4+} ratio, (ii) nature of dopants and (iii) doping into A^{2+} or/and B^{4+} site of $A^{II}B^{IV}O_3$ perovskit structure. The piezoelectric properties of doped PZT ceramics can be significantly modified by the addition of a small quantities of dopants. Using the donor dopants leads to obtaining so called "soft" PZT ceramics and using the acceptor dopants leads to obtaining so called "hard" materials [5]. If used dopants (ions) of higher valence for the A site (like Nb^{5+}, La^{3+}) obtained lead vacancies and if used lower

valense for B site (like Fe^{3+}) obtained oxygen vacancies [6]. The lead vacancies influence the mechanism of internal stress because of the reduction of cell parameter ratio, c/a and increase the mobility of the domain walls [7]. The oxygen vacancies lead to realization of complex defects that have an electrical dipole moment. These defects can be re-oriented by spontaneous polarization [8]. The PZT ceramic doped with iron presents lower constants like dielectric constant and loss constant [9]. Therefore, according to Kumar and Mishra [10] addition of Fe_2O_3 in PZNT system brings structural changes in the material and according to Rai et.al.[11] in PLZT doped with Fe increase the transition temperature. Addition of Fe^{3+} in the PZT structure form defect dipoles with partially charge-compensating oxygen vacancies ($Fe'_{Zr,Ti}$–$V^{\bullet\bullet}_O$)$^{\bullet}$ if the doping level is below his solubility limit [12].

In the present research paper, Fe^{3+} modified $Pb(Zr_xTi_{1-x})O_3$ ceramics with a general formula of $\mathbf{Pb(Zr_{1-x}Ti_x)_{0.99}Fe_{0.01}O_3}$ for different ratio Zr^{4+}/Ti^{4+} (where x = 0.42, 0.48, 0.58) have been synthesized. The structural and ferroelectric properties of the materials have been investigated in order to check their applicability as transducer.

2. Materials and Methods

The conventional mixed oxide process have been used to prepare Fe3+ doped Pb(Zr1−xTix)O3 ceramics, with x = 0.42, 0.48 and 0.58. The amount of dopant used was 1 wt.% of Fe2O3. The obtained compositions have been labelled as PZT-Fe1 (x=0.48), PZT-Fe2 (x=0.58) and PZT-Fe3 (x=0.42). The raw materials, consisting in high purity oxides, have been mixed in a ball mill, dried and calcined at 870°C for 4h. After being uniaxial pressed into discs form with a diameter of 11 mm and a thickness of 2 mm the samples were sintered for 2h at 1200 and 1250°C in a close alumina crucible. Then, after lapping, the silver electrodes were applied on both sides of the discs and heat treated at 600°C for 30 min. The densities of the sintered samples have been measured by Archimedes method. To determine the crystalline structure of the sintered samples, X-ray diffractometer (BRUKER AXS D8 Advance) with CuKα radiation and Ni filter has been used. In order to determine the piezoelectric properties all the samples have been polarized at 160°C in a silicon oil under 3-6 kV/mm for 30 min. The densities of the sintered samples have been measured by Archimedes method. The P-E hysteresis loops of the un-poled samples have been measured using the TF analyser 2000 (Aixact System). After 72 h of poling the piezoelectric properties have been determined with an impedance analyser 4294A (Agilent type) [5]. The piezoelectric properties (electromechanical coupling factor kp) have been determined by the resonance-anti-resonance method [13].

3. Results and discussion

Structural anaysis

The XRD patterns of the Fe^{3+} doped PZT sintered at 1200 and 1250°C are shown in Figure 1-3. XRD measurements pointed out that all the compositions sintered at 1250°C have a single perovskite phase, indicating a formation of a solid solution. At 1200°C for PZT-Fe2 and PZT-Fe3 as secondary phase appears and directly observable in the XRD patterns.

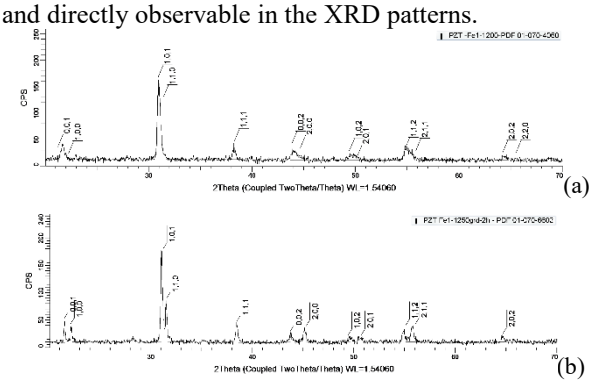


Fig.1: XRD patterns of PZT-Fe1 sintered 2h at (a)1200°C and (b) 1250°C

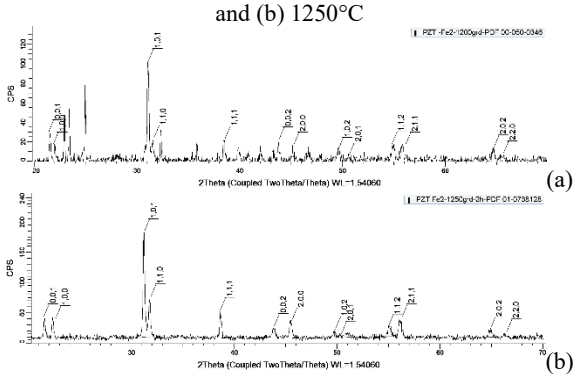


Fig.2: XRD patterns of PZT-Fe2 sintered 2h at (a)1200°C and (b) 1250°C

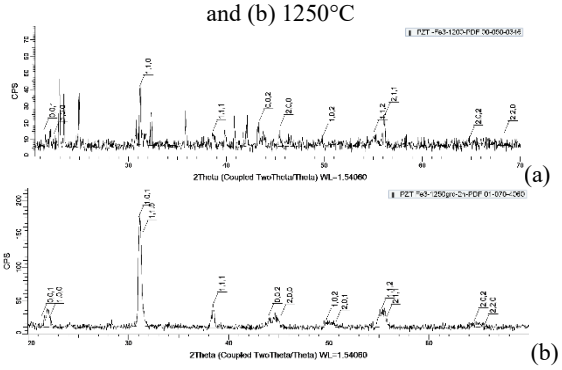


Fig.3: XRD patterns of PZT-Fe3 sintered 2h at (a)1200°C and (b) 1250°C

It is known that for the tetragonal structure the (111) is a single and (200) is a doublet, whereas for the rhombohedral structure (111) is a doublet and (200) is a single [10].

For all the compositions the crystallinity of the structure increases as temperature increases.

Study of the sinterability

Table 1 shows the densities of the PZT-Fe1, PZT-Fe2 and PZT-Fe3 sintered at 1200 and 1250°C. The densities of the samples sintered at 1200°C are in the range of 7.21 and 7.40 g/cm^3. As the sintering temperature increases to 1250°C the density of all samples increases and the results seems to be dependent of the composition. The high density values can be considered as a good indication that all samples can be submitted to electrical characterization.

Table 1: Apparent density and porosity of the all compositions as a function of the sintering temperature

Samples	Sintering temperature [°C]	Apparent density [g/cm^3]	Porosity [%]
PZT-Fe1	1200	7.40	0.87
	1250	7.41	0.86
PZT-Fe2	1200	7.21	0.78
	1250	7.34	0.65
PZT-Fe3	1200	7.24	1.12
	1250	7.40	1.06

Piezoelectric properties

Table 2 reports the obtained values for the piezoelectric factor (the planar coupling factor k_p) at room temperature as a function of the sintering temperature for PZT-Fe1, PZT-Fe2 and PZT-Fe3 compositions. Some compositions (PZT-Fe2 and PZT-Fe3) could not be polarized due to the structural inhomogeneity being the determining factor in this process. It can be observed that the values for the k_p depend on the Zr^{4+}/Ti^{4+} ratio.

PZT-Fe2 and PZT-Fe3 sintered at 1200°C were could not be poled because of the type of structure which depends on the Zr^{4+}/Ti^{4+} ratio. The data are reliable with the values obtained for density and porosity.

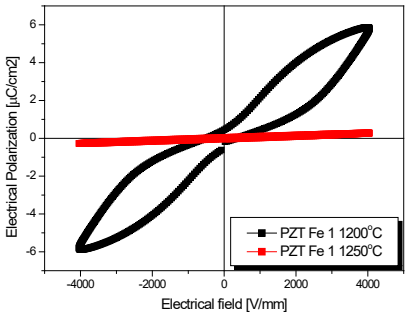
Table 2: The piezoelectric properties for the all compositions as a function of sintering temperature

Samples	Sintering temperature [°C]	f_r [MHz]	f_a [MHz]	k_p
PZT-Fe1	1200	1.9	2.1	0.51
	1250	1.3	1.4	0.44
PZT-Fe2	1200	-	-	-
	1250	1.3	1.5	0.62
PZT-Fe3	1200	-	-	-
	1250	1.4	1.5	0.42

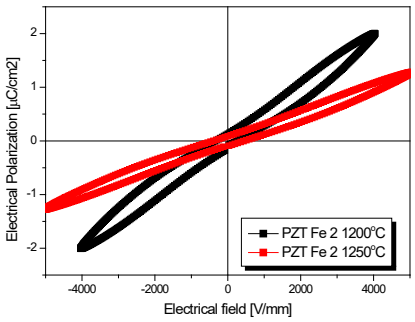
Feroelectric properties

Figure 4 shows the dependence of the hysteresis loops on the sintering temperature for un-poled compositions. In each phase region the hard ceramics characteristics are observed [14, 15]. The shape of the hysteresis loops depends on the nature of the phases obtained in the crystalline structure and it is influenced by the sintering conditions and by the amount of the tetragonal phase. Some P–E loop obtained for the compositions sintered in the air is lossy and not saturated [16]. If the sintering is carried out in air the reorientations of the domains become difficult and development of an unsaturated P–E loop [17] is observed.

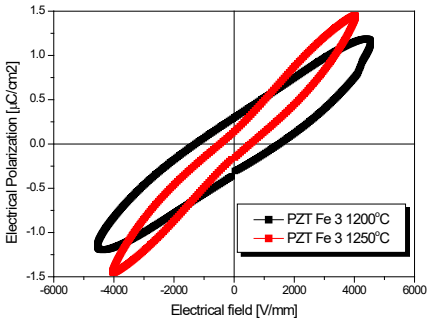
The values obtained for the remanent polarisation (P_r) and for the coercitive field (E_c) for all the sintered compositions are presented in Table 3.



(a)



(b)



(c)

Fig.4: Hysteresis loops obtained for un-poled compositions sintered at 1200ºC and 1250ºC: (a) PZT-Fe1, (b) PZT-Fe2 and (c) PZT-Fe3

Table 3: The values for the remanent polarisation (P_r) and the coercitive field (E_c) obtained for the PZT-Fe1, PZT-Fe2 and PZT-Fe3 compositions function of sintering temperature

Samples	Sintering temperature [°C]	E_c [V]	P_r [μC/cm^2]
PZT-Fe1	1200	346.17	0.45
	1250	808.85	0.05
PZT-Fe2	1200	251.21	0.13
	1250	407.46	0.09
PZT-Fe3	1200	1496.9	0.30
	1250	506.86	0.14

It can be observed that the values obtained for the remanent polarization Pr and the coercitive field Ec increases with increasing of the sintering temperature for the PZT-Fe1 and PZT-Fe2 and decreases with increasing of the sintering temperature for the PZT-Fe3 [16]. The results are in line with the Zr^{4+}/Ti^{4+} ratio.

5. Conclusions

In this research paper, the effect of the manufacturing method, in particular one of the most important parameter like the sintering temperature (1200^0C and 1250^0C), on the hysteresis loops of Fe^{3+} doped Pb(ZrxTi1-x)O_3 structure was studied. Three compositions, with different crystalline structure, were considered during the investigation. X-ray diffraction analysis results make an evidence that all the sintered samples reveal a perovskite crystalline structure. As for the hysteresis loops concern, measured at room temperature, it comes out that the values obtained for the remanent polarization Pr and the coercitive field Ec increases sintering temperature increases for the PZT-Fe1 and PZT-Fe2 samples and decreases as sintering temperature increases for the PZT-Fe3 samples, in line with the Zr^{4+}/Ti^{4+} ratio and according to the studies reported in [16].

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