

Effect of Y^{3+} and Nb^{5+} co-doping on dielectric and piezoelectric properties of PZT ceramics

A. K. ZAK^{*}, A. JALALIAN, S. M. HOSSEINI,
A. KOMPANY, T. SHEKOFTEH NARM

Department of Physics, Materials and Electroceramics Laboratory,
Ferdowsi University of Mashhad, Mashhad, Iran

The effect of co-doping of $Pb_{1-x}Y_x[(Zr_{0.53}Ti_{0.47})_{1-x}Nb_x]O_3$ bulk materials ($0 \leq x \leq 0.03$) with Y^{3+} ions and Nb^{5+} on their dielectric and piezoelectric properties was investigated. Samples fabricated by conventional oxide mixing (OM) were sintered at 1250 °C for 2 h in a Pb-rich atmosphere. During the tetragonal–rhombohedral transition in the doped PZT ceramics a negligible effect was observed after additions of Y^{3+} and Nb^{5+} ions. The co-doping with both ions was noted to inhibit grain growth and promote densification and electrical properties. The optimal doping level was found to be at $x = 0.015$, for which the electric permittivity of 907, the piezoelectric constant of 323 pC/N, g_{33} of 40 mV/N, Q_m of 272 and the electromechanical coupling factor (k_p) of 0.49 were obtained.

Keywords: *piezoelectric properties; PZT ceramics; dielectric properties*

1. Introduction

Lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) ceramics of a general formula ABO_3 possess outstanding piezoelectric, pyroelectric and ferroelectric properties [1, 2]. Special attention is given to modified PZT systems having compositions near their morphotropic phase boundaries (MPB), between Ti-rich tetragonal and Zr-rich rhombohedral phases with monoclinic phases [3].

The effect of doping on various physical and chemical properties of this material was identified and extensively exploited to improve the performance of the material. Many aliovalent compositional alterations to PZT have been studied, either with higher valence substitutions (donors) or with lower valence ions (acceptors) [4]. PZT ceramics can be doped with ions to form “hard” and “soft” PZTs. Hard PZTs are doped with acceptor ions such as K^+ , Na^+ (for site A) and Fe^{3+} , Al^{3+} , Mn^{3+} (for site B), creating oxygen vacancies in the lattice [5, 6]. Soft PZTs are doped with donor ions

^{*}Corresponding author, e-mail: alikhorsandzak@gmail.com

such as La^{3+} and W^{6+} (for site A) and Nb^{5+} , Sb^{5+} (for site B) leading to the creation of site A vacancies in the lattice [7–10]. Soft PZTs normally have higher permittivity, larger losses, better piezoelectric coefficients and are easy to pole. Thus, they can be used for applications requiring very high piezoelectric properties. Doping PZT ceramic with a small amount of Nb (ca. 2 wt. %) significantly increases the electric permittivity and piezoelectric coefficients [11, 12]. The fatigue behaviour of PZT has also been improved by the addition of Nb [13]. Yttrium doping is another way to improve the properties of PZT ceramics. Li et al. [14] have shown that Y-doped PZT has a large remnant polarization, a small leakage current, and good fatigue endurance. However, very little information is available on the effect of Y^{3+} and Nb^{5+} co-doping on the microstructure and piezoelectric coefficient of PZT ceramics [15].

In this study, we studied the effect of Nb and Y co-doping on the grain size, structure as well as on dielectric and piezoelectric properties of PZT ceramics.

2. Experimental

PbO , ZrO_2 , TiO_2 , Nb_2O_5 , and Y_2O_3 (Merck, >99% purity) were used to fabricate the samples were fabricated according to the formula: $\text{Pb}_{1-x}\text{Y}_x(\text{Zr}_{0.53}\text{Ti}_{0.47})_{1-x}\text{Nb}_x\text{O}_3$ ($0.01 \leq x \leq 0.03$). 5 % wt. excess of PbO was added to compensate for the loss of lead (Pb) during the final heat treatment. The mixed powder was ball-milled for 3 h in ethanol using zirconia balls and a Teflon jar, and then the mixture was dried at 100 °C. Calcinations were carried out at 900 °C for 2 h with the heating rate of 4 °C/min. For granulation, 3 wt. % of poly(vinyl alcohol) (PVA) was added to the PZT powder as a binder which was then pressed into disc-shaped pellets, each having the diameter r of 11 mm and the thickness of ca. 2 mm under the pressure of 250 MPa. The sintering temperature was 1250 °C and the isothermal sintering time was 2 h, under the heating rate of 4 °C/min. The samples were characterized by X-ray diffraction (XRD), and a scanning electron microscope (SEM) was used to study the microstructures of the sintered pellets. The electric permittivity K_{33} was deduced from the capacitance, measured at the frequency of 100 Hz. The specimens were poled for 30 min in silicone oil at 120 °C under the field of 2.5 kV/mm, and they were cooled to room temperature before the electric field was removed. All electromechanical measurements were performed one week after poling. The piezoelectric constant d_{33} was measured with a d_{33} meter (Penne Baker, model 8000, USA) and the voltage constant g_{33} was calculated from the following equation:

$$g_{33} = \frac{d_{33}}{\epsilon_0 K_{33}} \quad (1)$$

Other piezoelectric parameters such as mechanical quality factor Q_m and coupling factor k_p were calculated from the impedance–frequency curves [16].

$$k_p^2 = \frac{2.54(f_a - f_r)}{f_r} - \left(\frac{(f_a - f_r)}{f_r} \right)^2, \quad Q_m^2 = \frac{f_a^2}{\left[2\pi f_r Z_r C (f_a^2 - f_r^2) \right]} \quad (2)$$

where f_a is the antiresonance frequency and f_r is the resonance frequency of disk shape PZT samples.

3. Results and discussion

3.1. XRD patterns

The phase formation and orientation of pure and doped PZT samples were investigated by X-ray diffraction analysis in the range of 20 – 100° , using CuK_α radiation as shown in Fig. 1.

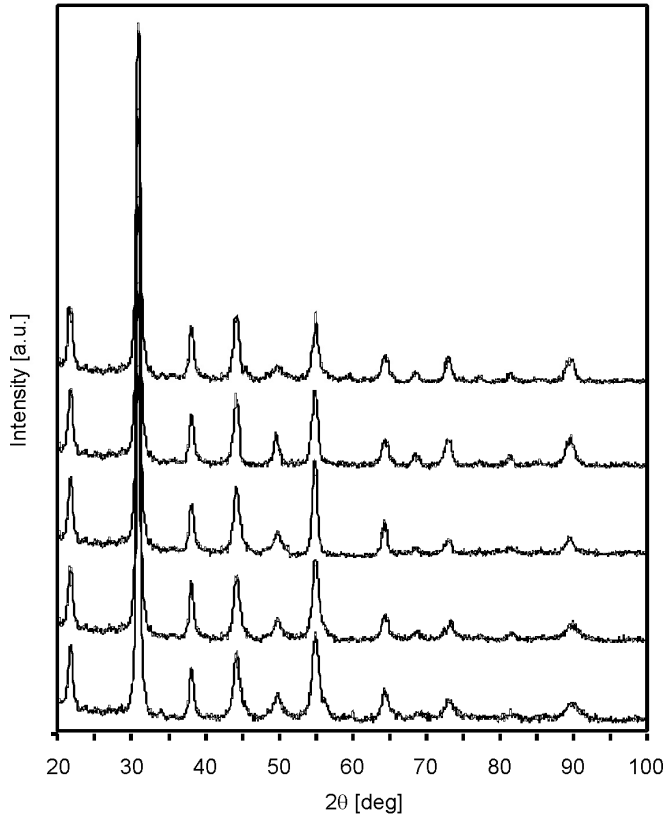


Fig. 1. XRD patterns of $Pb_{1-x}Y_x(Zr_{0.53}Ti_{0.47})_{1-x}Nb_5O_3$ samples: a) $x = 0.0$, b) $x = 0.01$, c) $x = 0.015$, d) $x = 0.02$, and (e) $x = 0.03$

The XRD results reveal the coexistence of a perovskite type tetragonal phase with a rhombohedral one, free from a pyrochlore phase. X-ray patterns show that tetragonality is increased with doping levels $x = 0.01$ and $x = 0.03$, since at $2\theta = 73^\circ$ an extra peak appears next to the main peak [17]. In these cases, the balance between the tetragonal and rhombohedral crystalline phases is disturbed, but tetragonal phase prevails. Maximal tetragonality in doped PZT occurs at $x = 0.01$, and corresponds to maximum intensity of the XRD peaks. Generally, high-piezoelectric activity at the MPB is attributed to the a number of thermodynamically equivalent states, which allows a high degree of alignment of ferroelectric dipoles. Such a high degree of alignment and enhanced polarizability at the MPB results in a dramatic enhancement of dielectric and piezoelectric properties near the MPB. Recently it has been shown that the monoclinic structure could be pictured as providing a bridge between rhombohedral and tetragonal structures, which makes the polarization easier [6].

3.2. Surface morphology

Typical SEM images of pure and doped PZT with Y and Nb ($x = 0.015$) are shown in Figs. 2 and 3. The SEM results indicate that the average grain size of doped PZT is smaller in comparison with pure PZT, and it was found to be about $3\mu\text{m}$.

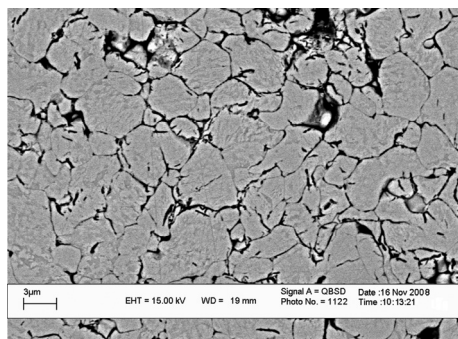


Fig. 2. Typical SEM images of polished and subsequently etched pure PZT ceramics (Zr/Ti ratio 53/47) sintering at 1250°C for 2 hours

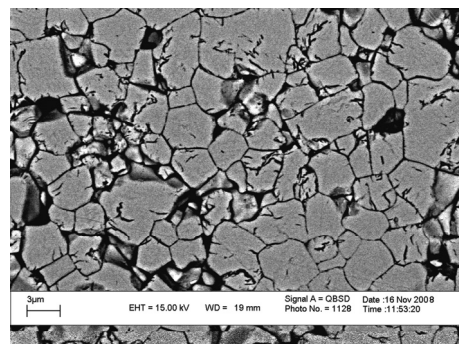


Fig. 3. Typical SEM image of polished and subsequently etched doped PZT ($x = 0.015$) ceramics (Zr/Ti ratio 53/47) sintering at 1250°C for 2 hours

3.3. Piezoelectric coefficients

Electrical properties such as the electromechanical and piezoelectric properties, were systematically evaluated with respect to the Nb and Y ratio. Table 1 shows the values of the d_{33} piezoelectric coefficient g_{33} , the mechanical quality factor Q_m and the coupling coefficient k_p for various x values of Nb and Y co-doped PZT. In the case of co-doping, the d_{33} and g_{33} coefficients reach a maximum value at $x = 0.015$ and their evolution versus ratio are very similar. The k_p increases as x increases, and reaches

a maximum at $x = 0.02$, then it decreases for higher values of x . The Q_m increases upon x increasing. At room temperature, the optimum value of d_{33} is 323 pC/N and that of k_p is 0.49, corresponding to $x = 0.015$.

Table 1. Dielectric and piezoelectric properties of PZT doped with various elements

Compound	ρ [g/cm ³]	K_{33}	d_{33} [pC/N]	g_{33} [mV/N]	k_p	Q_m
Pb (Zr _{0.55} Ti _{0.45}) _{0.975} Nb _{0.025} O ₃ [4]	—	679	233	—	0.45	122
Pb _{0.092} La _{0.08} (Zr _{0.55} Ti _{0.45}) _{0.975} Nb _{0.025} O ₃ [4]	—	1978	338	—	0.58	73
Pb _{0.89} (BaSr) _{0.11} (Zr _{0.52} –Ti _{0.48}) _{0.99} Mn _{0.01} O ₃ +1%F [6]	—	1650	340	—	0.8	—
Pb _{0.89} (BaSr) _{0.11} (Zr _{0.52} –Ti _{0.48}) _{0.99} Mn _{0.01} O ₃ [6]	—	1190	260	—	0.7	—
Pb _{1.03-x} Y _x [(Zr _{0.52} Ti _{0.48}) _{1-x} Nb _x]O ₃ (0.02) [15]	—	1380	—	—	0.6	—
Pb _{1.03} [(Zr _{0.52} Ti _{0.48}) _{1-y} Nb _y]O ₃ ($y = 0.02$) [15]	—	925	—	—	0.48	—
Pb(Zr _{0.52} Ti _{0.48}) _{0.975} Nb _{0.025} O ₃ [17]	—	—	—	—	0.27	—
0.8Pb(Zr _{1/2} Ti _{1/2})O ₃ –0.2Pb(Co _{1/3} Nb _{2/3})O ₃ [19]	—	716	—	—	—	—
0.15[Pb(Ni _{1/3} Nb _{2/3})O ₃]–0.85[Pb(Zr _{1/2} Ti _{1/2})O ₃] +1%Y ₂ O ₃ [20]	7.53	1616	—	—	0.47	128
Present work						
Pb _{1.03-x} Y _x [(Zr _{0.53} Ti _{0.47}) _{1-x} Nb _x]O ₃ (0.0)	7.54	584	190	37	0.37	453
Pb _{1.03-x} Y _x [(Zr _{0.53} Ti _{0.47}) _{1-x} Nb _x]O ₃ (0.01)	7.64	823	309	42	0.44	267
Pb _{1.03-x} Y _x [(Zr _{0.53} Ti _{0.47}) _{1-x} Nb _x]O ₃ (0.015)	7.56	907	323	40	0.49	272
Pb _{1.03-x} Y _x [(Zr _{0.53} Ti _{0.47}) _{1-x} Nb _x]O ₃ (0.02)	7.56	945	218	26	0.50	303
Pb _{1.03-x} Y _x [(Zr _{0.53} Ti _{0.47}) _{1-x} Nb _x]O ₃ (0.03)	7.42	723	206	32	0.30	305

3.4. Densities and electric permittivities

The electric permittivities of the samples are increased after co-doping with Nb and Y, and attain a maximum value of 945 at $x = 0.02$ (Table 1). Initially, the densities of the doped PZT ceramics increase in proportion with the doping level. Maximum density is attained at $x = 0.010$; for higher values of x , the density is inversely proportional to the doping level. The number of Pb vacancies in PZT is closely related to the types and valence of the dopants. This is due to the Pb vacancies that are compensated by electrons produced by the donor dopants [15]. Doping Y^{3+} will create more Pb^{2+} vacancies in order to maintain electroneutrality. As a result, the densification is enhanced and therefore the densities of the doped PZT ceramics are increased for doping levels ranging from $x = 0.01$ to 0.03. The decrease in the density for $x > 0.01$ may be attributed to the decrease in the diffusivity of Pb vacancies, which results from the cation gradients within the PZT grains and/or the dopant segregation at the grain boundaries. Similar results have been reported when other donor dopants were employed [18]. The results were compared with those of other studies (Table 1).

4. Conclusion

We have considered the effect of Y^{3+} and Nb^{5+} co-doping on the dielectric and piezoelectric properties of the $Pb_{1-x}Y_x[(Zr_{0.53}Ti_{0.47})_{1-x}Nb_x]O_3$ ($0 \leq x \leq 0.03$), namely

(PZT) ceramics. The XRD results reveal the coexistence of a perovskite type tetragonal and a rhombohedral crystalline phases being free from a pyrochlore phase. X-ray patterns show that tetragonality is increased for doping levels $x = 0.01$ and $x = 0.03$, since at $2\theta = 32^\circ$ an extra peak appears next to the main peak. The characterization of ceramic samples showed that significant change in the piezoelectric properties occurs at 0.015 wt. % of dopant in PZT. The optimized piezoelectric parameters were $d_{33} = 323$ pC/N, $K_{33} = 907$, $k_p = 0.49$, $Q_m = 272$, $g_{33} = 40$ mV/N for the modified composition. These parameters were similar to those for the soft PZT materials and are useful for the development of underwater transducers, piezoelectric accelerometers and medical applications.

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