Investigation the dielectrical and electromechanical properties of PZT thin films

M. R. Benam
Department of Physics, Payame Noor University of Mashhad, Mashhad, Iran.

Abstract
We have studied thedielectric and electromechanical properties of pure and doped $Pb(Zr_{0.53}Ti_{0.47})O_3$thin films.Samples were prepared bya sol-gel method and werecalcined at temperatures of 700ºC for two hours in a Pb-rich atmosphere.It was observed a negligible effect occurs during the tetragonal–rhombohedral transition in the preparedpure and doped PZT thin films.The optimal amount of electrical parameters were obtained to be 945, 323 pC/N, 40 mV/N, and 300 for dielectric constant, charge constant, Voltage constant, and Quality factor, respectively. Also the electromechanical coupling factor (kp) was found to be0.49for the doped- PZT thin film.

Keywords: Piezoelectric properties, PZT, Dielectric properties, electromechanical.

I. Introduction

Lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ or (PZT) ceramics with a general formula of ABO_3possess outstanding piezoelectric, pyroelectric and ferroelectric properties [1, 2]. Special attention is given tomodified PZT systems at compositions near their morphotropic phase boundaries (MPB) between Ti-rich tetragonal and Zr-rich rhombohedral phaseswith monoclinic phases[3].The effect of doping on various physical and chemical properties of this material has been identified and this effect has been extensively exploited to improve their performance. 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 such as La^{3+} and W^{6+} (forsite A) and Nb^{5+}, Sb^{5+} (for site B)leading to the creation of site A vacancies in the lattice [7-10]. The soft PZTs normally have a higher permittivity, larger losses, and betterpiezoelectric coefficients and are easy to pole. Thus,they can be usedfor applications with high piezoelectric properties. Doping PZT ceramic with small amount of Nb (approximately2 %wt.) significantly increases the dielectric constant and piezoelectric coefficients [11, 12]. The fatigue behaviour of PZT has been also 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,P_r,a small leakage current, and good fatigue endurance. However, very little information is available on the effect of Y^{+3} andNb^{+5}co-doping on microstructure and piezoelectric coefficient of PZT ceramics [15].
In this study, we studied the effect of Nb andY co-doping on dielectric and piezoelectric properties of PZT thin films.

II. Experimental

The raw materials lead acetate, zirconium oxynitrate, titanium isopropoxide, niobium oxalate, and yttrium nitrate (which all have been purchased from Sigma – Aldrich) were used to prepare the pure and doped PZT thin films. The samples were fabricated according to the formula: $Pb_{0.97}Y_{0.03}(Zr_{0.52},Ti_{0.48})_{0.97}Nb_{0.03}O_3$.
For this propose a solution of citric acid and nitric acid was prepared. To get this solution, the citric acid was dissolved in minimum water then the nitric acid was added to the citric acid solution in the room temperature. After that, the titanium iso-propoxide was added to the solution and stirred to get a clear solution fallowing by adding the niobium oxalate and yttrium nitrate. The amounts of the acids were measured as below:

$$\frac{M_{Citricacid}}{M_{Metal\ Cation}} = 2.5 \quad and \quad \frac{M_{Nitric\ acid}}{M_{Citricacid}} = \frac{1}{3}$$

In the other hand, the lead nitrate and zirconium oxynitrate were dissolved in minimum water at 50 °C separately. After that, the lead nitrate and zirconium oxynitrate were added to the titanium isopropoxide solution gradually. The pH of the obtained clear solution was adjusted to 7 by adding ammonia solution and following that the prepared solution was refluxed at 100 °C for 2h. The obtained solution was spin coated on silicon substrate and the calcined at 700 ºC for 2 h.
The prepared pure and doped PZT thin films were characterized by X-ray diffraction (XRD, Philips, X'pert, Cu Kα).The piezoelectric constant, d_{33}, was measured bya d_{33} meter (Penne baker, Model 8000,USA) and the voltage constant,g_{33}, was

calculated from following equation:

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

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

$$k_p^2 = \frac{2.54(f_a - f_r)}{f_r} - \left(\frac{(f_a - f_r)}{f_r}\right)^2 \quad (2)$$

$$Q_m^2 = \frac{f_a^2}{[2\pi f_r Z_r C(f_a^2 - f_r^2)]} \quad (3)$$

where f_a is anti-resonance and f_r is resonance frequency of samples.

III. Results and discussions

IV. Results of XRD patterns:

The phase formation and orientation of pure and doped PZT samples were investigated using X–ray diffraction analysis in the range of 5-45 degreesas shown in Fig.1.The XRD results reveal the coexistence of a perovskite–type tetragonal and rhombohedral crystalline phaseswhich is free from a pyrochlore phase. X-ray patterns show that tetragonality hasbeen increased with doping level x=0.03, since at 2θ=32° an extra peak has appeared next to the main peak [17]. In this case the tetragonal phase prevails over as the balance between the tetragonal andrhombohedral crystalline phases is disturbed. Generally, high-piezoelectric activity at the MPB is attributed to the large number of thermodynamically equivalent states allows a high degree of alignment of ferroelectric dipoles.

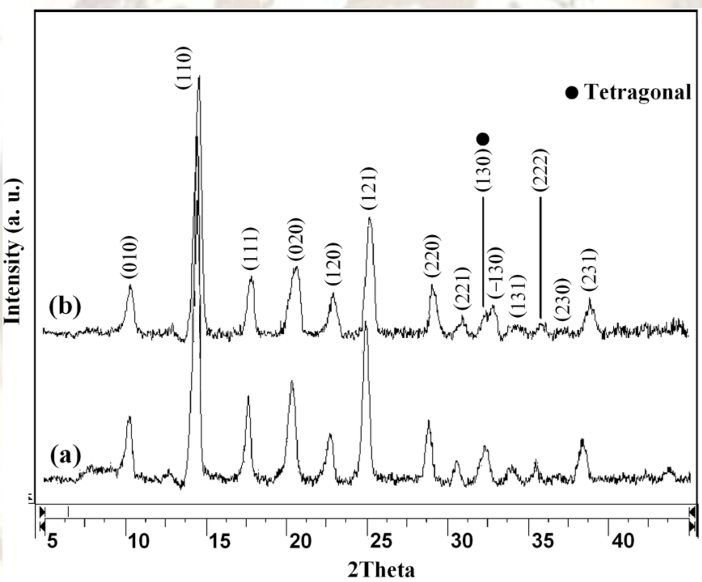

Fig .1XRD patterns of (a) pure and (b) $Pb_{0.97}Y_{0.03}(Zr_{0.53}Ti_{0.47})_{0.97}Nb_{0.03}O_3$ samples.

This high degree of alignment and enhanced polarizability at the MPB results in a dramatic enhancement of dielectric and piezoelectric properties approaching the MPB. Recently, it has been shown that the monoclinic structure could be pictured as provided a bridge between the rhombohedral and tetragonal structures, which makes the movement of polarization easier [6].

Piezoelectric coefficients

The electrical properties, such as the electromechanical and piezoelectric ones, are systematically evaluated for samples. In the case of co-doping, the d_{33}coefficients reach to value of323 pC/N and k_p to 490; whereas they are 180 pC/N and 380 for pure one, respectively. The $Q_m$is decreased whereas the g_{33}increase with doping content comparing to the pure sample. At room temperature thevalue of Q_m and g_{33}were obtained to be 450 and 30 mV/N for pure PZT sample and 300 and 40 mV/N for doped PZT sample, respectively.The results were summarized in Table 1.

Dielectric constants

It was obtained that the dielectric constants of pure PZT sample increase by doping of Nb and Y then has reached maximum of 945 comparing to the value of 600 for pure sample. The number of Pb vacancies in PZT is closely related to the types and valence of dopants. This is due to the Pb vacancies that are compensated by electrons produced by the donor dopants [15]. Doping Y^{+3} will createmore Pb^{+2}

vacancies in order to maintain electro neutrality. The results have been compared with the results of other researchers (Table. 1).

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

Compound	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
$Pb_{0.89}(BaSr)_{0.11}(Zr_{0.52}$-$Ti_{0.48})_{0.99}Mn_{0.01})O_3$+%1F [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	-
$Pb_{1.03-x}Y_x[(Zr_{0.52}Ti_{0.48})_{1-x}Nb_x]O_3$ (x=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	-	-	-	-
$0.15[Pb(Ni_{1/3}Nb_{2/3})O_3]$–$0.85[Pb(Zr_{1/2}Ti_{1/2})O_3]$ +%1Y_2O_3 [20]	1616	-	-	0.47	128
Present Work					
Pb $(Zr_{0.53}Ti_{0.47})O_3$	600	180	30	380	450
$Pb_{0.97}Y_{0.03}[(Zr_{0.53}Ti_{0.47})_{0.97}Nb_{0.03}]O_3$	945	323	40	490	300

Conclusion

Dielectric and electromechanical properties of pure and Y and Nb-doped $Pb(Zr_{0.53}Ti_{0.47})O_3$ thin filmswere measured**.** We showed that the Piezoelectric properties of PZT thinfilms increased with doping. The optimal amount of electrical parameters were obtained to be 945, 323 pC/N, 40 mV/N, and 300 for dielectric constant, charge constant, Voltage constant, and Quality factor, respectively. Also the electromechanical coupling factor (kp) was found to be 0.49 for the doped- PZT thin film.

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References

[1] Jaffe B., Cook W.R. And Jaffe H., *Piezoelectric Ceramics*, Academic Press Inc., New York, 1971.
[2] Okazaki K., *Ferroelectrics*, 41 (1982), 77.
[3] Berlincourt D., *J. Accost. Soc. Am.*, 91 (1992), 3034.
[4] Singh V., Kumar H.H., Kharat D.K., Hait S. And Kulkarni M.P., *Mater. Lett.*, 60 (2006), 2964.
[5] Hizebry A., Attaoui H.El., Saˆadaoui M., Chevalier J. And Fantozzi G., *J. Euro. Ceram. Soc.*, 27 (2007), 557.
[6] Boucher E., Guiffard B., Lebrun L. And Guyomar D., *Ceram. Inter*. 32 (2006), 479.
[7] Helbig U., *J. Euro. Ceram. Soc*., 27 (2007), 2567.
[8] Santos D.M., Sim˜oes A.Z., Zaghete M.A., Santos C.O., Varela J.A. And Longo E., J. *Mater. Chem.Phys*., 103 (2007), 371.
[9] Kulcsar F., *J. Am. Ceram. Soc*., 42 (1959), 49.
[10] Kulcsar F., *J. Am. Ceram. Soc*., 42 (1959), 343.
[11] Miura K. And Tanaka M., *J. Appl. Phys*., 36 (1997), 226.
[12] Dimos D., Schwartz R.W. And Lockwood S.J., *J. Am. Ceram. Soc*., 77 (1994), 3000.
[13] Griswold E.M., Sayer M. And Amm T., *Can. J. Phys*.,69 (1991), 260.
[14] Li C., Liu M., Zeng Y. And Yu D., Sens. *Actuators A*, 58 (1997), 245.
[15] Zhang R.F., Zhang H.P., Ma J., Chen Y.Z. And Zhang T.S., *Sol. St. Ion*., 166 (2004), 219.
[16]"*Http://Www.Americanpiezo.Com/Piezo_Theory/Resonance_Frequency.Html* ". Apc International, Ltd. Determining Resonance Frequency. 1998-2009.
[17] Piticescu R.M., Mitoseriu L., Vivianiand M. And Poladian V.M., *J. Euro. Ceram. Soc.*, 25 (2005), 2491.
[18] Durruthy-Rodríguez M.D., Pérez-Fernández L.D., Peláiz-Barranco A. And Calderón-Piñar F., *Appl. Phys. A*, 95 (2009), 423.
[19] Prasatkhetragarn A., Unruan M., Ngamjarurojana A., Laosiritaworn Y., Ananta S. And Yimnirun R., *Current Appl. Phys*., 9 (2009), 1165.
[20] Kang S.H., Lee D.S., Lee S.Y., Kim I.W., Kim J.S. And Park E.C., *Ceram. Inter*., 30 (2004), 1453.