Bull. Mater. Sci., Vol. 26, No. 4, June 2003, pp. 397–399. © Indian Academy of Sciences.

Dielectric and piezoelectric properties of neodymium oxide doped lead zirconate titanate ceramics

JANARDAN SINGH*, N C SONI and S L SRIVASTAVA[†]

Electroceramics (Ultrasonic Groups), National Physical Laboratory, Dr K S Krishnan Road, New Delhi 110 012, India

[†]Department of Physics and M.N. Saha Centre of Space Studies, University of Allahabad, Allahabad 211 002, India

MS received 18 December 2002; revised 15 March 2003

Abstract. **The dielectric and electromechanical properties of lead zirconate titanate [Pb(Zr, Ti)O_3] ceramic added with neodymium oxide have been systematically studied employing the vector impedance spectroscopic (VIS) technique. The specimens were prepared using the mixed oxide route by adding different mol% of Nd_2O_3 (0·1 to 7 mol%) in [Pb(Zr, Ti)O_3] near morphotropic phase boundary. Piezoelectric equivalent circuit parameters *R, L, C_a* in series and *C_b* in parallel have been determined by simulating /*Z*/ and Θ plots. Electromechanical coupling coefficients and strain constants for the radial modes show a peak at about 3 mol%, the dielectric constant peaks at about 1 mol% and voltage constants peak at about 0·75 mol% of Nd_2O_3.**

Keywords. **Nd doped lead zirconate titanate; piezoelectric properties; ferroelectric materials; electromechanical parameters; vector impedance measurements.**

1. Introduction

The lead zirconate titanate [Pb(Zr, Ti)O_3] ceramics, to which oxides such as La_2O_3, Nb_2O_5, Fe_2O_3, NiO, MnO_2, IrO_2, ThO_2, WO_3, Cr_2O_3 and U_3O_8 have been added and studied by several workers (Jaffe *et al* 1971; Thomann 1972; Troccaz *et al* 1978; Wu *et al* 1982; Heywang and Thomann 1984; Moulson and Herbert 1990; Katiyar *et al* 1994, 1997) due to their wide application in various piezoelectric, ultrasonics and underwater devices along with various actuators and sensors in different fields of science and technology. The effect of addition of rare earth oxides in Pb(Zr, Ti)O_3 ceramics have mostly been related with the incorporation of La^{+3} ions into Pb(Zr, Ti)O_3 ceramics which increases their dielectric constant, electromechanical parameters and dielectric loss and decreases mechanical quality factor. The Pb(Zr, Ti)O_3 ceramics added with La^{+3} ions have been extensively studied for both piezoelectric and electro-optical applications but such studies have not been done with other rare earth oxides. It has been reported that the effect of doping of Sm^{+3} and Nd^{+3} are similar to La^{+3} doped lead zirconate titanate ceramics (Wu *et al* 1982). Some of the dielectric and electromechanical parameters have been reported for few compositions of Nd_2O_3 added to Pb(Zr, Ti)O_3 near to morphotropic phase boundary (Thomann 1972; Tandon *et al* 1992), $Pb_{0·98}$ $Sr_{0·02}$ ($Li_{0·008}$ $W_{0·012}$ $Ti_{0·46}$ $Zr_{0·52}$)O_3 (Wu *et al* 1982) and Pb($Zr_{0·95}$ $Ti_{0·5}$)O_3 ceramics (Xue *et al* 1990). Inspite of these studies relatively meagre information is available regarding the various dielectric and electromechanical parameters at different levels of Nd_2O_3 addition near to morphotropic phase boundary.

It is well known that the electromechanical properties of PZT depend strongly on additives as well as the morphotropic phase boundary. The present investigation was undertaken to study the effect of Nd_2O_3 addition to lead zirconate titanate ceramic at 54/46 Zr/Ti ratio near the morphotropic phase boundary on the various dielectric and electromechanical parameters. The measurements of various electromechanical parameters were carried out by employing vector impedance spectroscopic (VIS) technique.

2. Theory

2.1 *Piezoelectric response*

A single piezoelectric mode is electrically equivalent to *R*, *L*, C_a in series and C_b in parallel (see figure 1) and the equivalent impedance, *Z* of this circuit (Katiyar *et al* 1994, 1997) is given as

$$Z = \frac{w_s Q_m R\,[1 + jQ_m\,(w/w_s) - (w_s/w)]}{j\omega r\,[1 + jQ_m \sqrt{(1 + 1/r)}\,(w/w_p) - (w_p/w)]}\ , \quad (1a)$$

$$= R_e + jX_e, \quad (1b)$$

and the admittance $Y = (1/Z) = G + jB$, where *r* is capacitive ratio,

*Author for correspondence

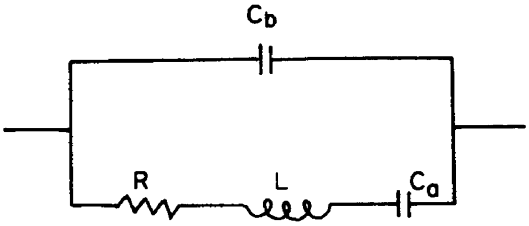

Figure 1. Piezoelectric equivalent circuit.

$$w_s = 2\pi f_s = [1/\sqrt{(L \cdot C_a)}], \tag{2a}$$

the series resonance angular frequency, is equal to (C_b/C_a)

$$w_p = 2p f_p = w_s \sqrt{[1 + (1/r)]}, \tag{2b}$$

the parallel resonance angular frequency.

$Q_m = (\omega_s \cdot L/R)$ is the mechanical quality factor and $M = (Q_m/r) = 1/(w_s C_b R)$ the figure of merit of this circuit. The frequencies at which the reactance, X_e, is zero, are the resonant and anti-resonant frequencies, f_r and f_a, respectively and at the frequency, f_n, Z is maximum and at f_m, Z is minimum.

2.2 *Radial modes and piezoelectric parameters*

Radial modes of the thin discs are particularly important in the piezoelectric ceramics, because they are free from the spurious noise and the interference effects. The planar coupling coefficient, (K_p) of the piezoelectric ceramics may be determined from the measurements of the piezoelectric response on the radial modes. According to IRE standards on piezoelectric crystals (1957 and 1961) the planar coupling coefficient, K_p, can be determined with the help of the following equation

$$\frac{K_p^2}{1-K_p^2} = \frac{[(1-s^E)\, J_1[\Phi(1+\Delta f/f_s)] - \Phi(1+\Delta f/f_s)\, J_0\, [\Phi(1+\Delta f/f_s)]]}{(1-s^E)\, J_1[\Phi(1+\Delta f/f_s)]}, \tag{3}$$

where $\Delta f = (f_p - f_s)$, f_s and f_p are series and parallel resonance frequencies.

J_0 and J_1 are Bessel functions of first kind and of zero order and first order, respectively and s^E the Poisson's ratio, Φ the lowest positive root of the following equation

$$(1 - s^E)\, J_1(\Phi) = \Phi\, J_0(\Phi). \tag{4}$$

It may be noted that (f_m, f_n) and (f_r, f_a) are directly measurable, but not (f_s, f_p). For getting a correct value of K_p using (3), we need f_s and f_p which can be evaluated only when R, L, C_a and C_b, are known.

The coupling coefficient, K_{31}, may be obtained from K_p and s^E:

$$K_{31}^2 = 0{\cdot}5\,(1 - s^E)\, K_p^2. \tag{5}$$

The elastic compliance, s_{11}^E, may be calculated from

$$\frac{1}{s_{11}^E} = \frac{4p^2 a^2 f_s^2 (1 - s E^2)\, r}{\Phi^2}, \tag{6}$$

where 'a' is the radius of the disc and 'r' the density of the material. The piezoelectric strain constant, d_{31}, and the hydrostatic piezoelectric strain constant, d_h, may be calculated from the following equations

$$d_{31} = K_{31}\, (e_{33}^T\, s_{11}^E)^{1/2}, \tag{7}$$

$$d_h = d_{33} + 2d_{31}. \tag{8}$$

We may note that d_{31} is negative.

The piezoelectric voltage constants, g_{31} and g_{33}, may then be calculated from

$$g_{31} = d_{31}/e_{33}^T,\; g_{33} = d_{33}/e_{33}^T, \tag{9}$$

where e_{33}^T is the dielectric permittivity of the material.

3. Experimental

3.1 *Preparation of specimen*

The LR grade ingredients of PbO, ZrO_2, TiO_2, and Nd_2O_3 of the compositions, $Pb(Zr_{0{\cdot}54}, Ti_{0{\cdot}46})O_3$, were prepared by mixing different molar percentages of Nd_2O_3 ($Pb(Zr, Ti)O_3$ + X% Nd_2O_3, X = 0·10 to 7 mol%) with the help of agate mortar, pestle and acetone as medium. An excess of 1·5 wt% lead oxide was added in different molar compositions in order to compensate for the lead losses during calcination and subsequent sintering. The mixed materials were initially fired in air at 850°C for 2 h. The sample in the form of discs of dimension 16 mm diameter and 3 mm thickness was pressed and then sintered at 1250°C for 150 min. The sintered discs were lapped and electroded with fired on silver paint. The electroded discs were polarized using a high d.c. electric field of ~ 3·5 kV/mm while they were immersed in heated silicon oil at about 130°C.

3.2 *Measurements*

The electrical measurements were carried out at room temperature using a Hewlett Packard model HP-4194A vector impedance analyser, which was controlled by their computer model HP-300. Impedance /Z/ and phase angle, Θ, of the samples have been measured at different harmonics of the radial modes in the frequency range 0·15–1·5 MHz. The charge constant, d_{33}, was measured by using a Berlincourt's d_{33} meter model CPDT-3300 (Channel Products Inc. USA).

4. Results and discussion

The piezoelectric equivalent circuit parameters, R, L, C_a and C_b, were obtained from the simulated fitting of /Z/

Table 1. Measured and derived values of dielectric, K_3^T, tan *d*, elastic and electromechanical parameters, s_{11}^E, d_{33}, d_{31}, d_h, g_{33} and g_{31} at different mol% of Nd_2O_3 additions in $Pb(Zr_{0·54}, Ti_{0·46})O_3$.

Sl. no.	Nd_2O_3 (mol%)	K_3^T	tan *d*	K_p	s^E_{11} (× 10^{-12} m^2/N)	d_{33} (× 10^{-12} C/N)	d_{31}	d_h	g_{33} (mV·m/N)	g_{31}
1.	0·10	424	0·006	0·27	15	135	38	59	36	10
2.	0·50	818	0·016	0·51	17	370	104	162	51	14
3.	0·75	748	0·019	0·52	19	380	107	166	57	16
4.	1·00	1296	0·027	0·56	20	405	153	99	35	13
5.	3·00	1218	0·015	0·59	20	422	157	108	39	15
6.	5·00	1026	0·017	0·39	12	257	74	109	28	8
7.	7·00	850	0·017	0·34	12	214	58	98	28	8

and Θ with experimental curves. For the fundamental mode measured values of dielectric constant, K_3^T, loss factor, tan *d*, and piezoelectric parameters, s_{11}^E, d_{33}, d_{31}, d_h, g_{33} and g_{31} (taking the value of $s^E = 0·34$ from Katiyar *et al* 1994, 1997) at different mol% of Nd_2O_3 additions in $Pb(Zr_{0·54}, Ti_{0·46})O_3$ are listed in table 1.

The addition of neodymium causes significant changes on electromechanical properties which may be seen in table 1. The correct values of K_p determined for different labels of Nd^{+3} doping using (3) are also reported (table 1). The piezoelectric parameter, K_p, charge constant, d_{33} and d_{31}, show a peak at 3 mol%, K_3^T peaks at 1 mol% whereas d_h, g_{33} and g_{31} peaks around 0·75 mol% of Nd_2O_3. Thomann (1972) reported K_3^T, and coercive field of one composition of $Pb(Zr_{0·53}, Ti_{0·47})O_3$ + 1 wt% Nd_2O_3 and Tandon *et al* (1992) found that dielectric constant, K_3^T, loss tangent, (tan *d*) increase with addition of Nd_2O_3 and d_{33} and g_{33} peaks at 2 mol% of Nd_2O_3 and peak value of d_{33} reported by them is lower than the values reported here. Maximum values of the elastic, piezoelectric and dielectric parameters i.e. s_{11}^E, d_{31}, g_{31}, K_{31} and dielectric constant, K_3^T, of Nd doped lead zirconate titanate (PZT) reported here are larger than those of Cr doped PZT (Katiyar *et al* 1994) and Mn doped PZT (Katiyar *et al* 1997).

5. Conclusion

With these observed enhanced electromechanical parameters, it may be remarked that the effect of Nd_2O_3 doping is similar to La_2O_3 doped lead zirconate titanate ceramic materials. Since lead zirconate titanate ceramics added with neodymium ions have enhanced dielectric and electromechanical properties, they may therefore find special applications in piezoelectric, ultrasonic and underwater acoustic transducer devices.

Acknowledgements

The author thanks Dr Krishan Lal, Director, National Physical Laboratory, New Delhi for his constant interest and encouragement. One of us (SLS) thanks ISRO, Bangalore, for the grant of a research project entitled “Study of Microwave Ceramics”.

References

Heywang W and Thomann H 1984 *Ann. Rev. Mater. Sci.* **14** 27

IRE Standards on Piezoelectric Crystals 1957 *Proc. IRE* **45** 354

IRE Standards on Piezoelectric Crystals 1961 *Proc. IRE* **49** 1161

Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric ceramics* (London: Academic Press)

Katiyar V K, Srivastava S L and Singh Janardan 1994 *J. Appl. Phys.* **76** 1131

Katiyar V K, Srivastava S L and Singh Janardan 1997 *Ferroelectrics* **193** 21

Moulson A J and Herbert J M 1990 *Electroceramics* (London: Chapman and Hall)

Tandon R P, Singh V and Swami N N 1992 *J. Mater. Sci. Lett.* **11** 327

Thomann H 1972 *Ferroelectrics* **4** 141

Troccaz M, Gonnard P and Eyraud L 1978 *Ferroelectrics* **22** 17

Wu Long, Lee Chung-Chang, Wu Tien Shou and Wei Chung-Chuang 1982 *Ferroelectrics* **41** 157

Xue W R, Schulze W A and Newnham R E 1990 *J. Am. Ceram. Soc.* **73** 1783