Dielectric And Piezoelectric Studies Of PLZT Prepared By A Novel Method

Hari Mohan Singh*, A.K. Sharma* and Anil Govindan#
*DAV (P.G.) College Bulandshahar, Uttar Pradesh,
#MMH College Ghaziabad, Uttar Pradesh

The dielectric and piezoelectric studies were carried on La doped Lead Zirconate Titanate PZT (PLZT) ceramic prepared by the method of homogenous precipitation. The material showed better dielectric constants and piezocoefficients compared to the solid state sintering method. The important point is the fine particle size and hence sintering at lower temperature. The dielectric behavior is typical of polar dielectrics with a perovskite structure. The PLZT samples with 8 % La exhibits the maximum figure of merit needed for under water sonar applications.

1. INTRODUCTION

Electronic ceramics (Electroceramics) are used as active components to control voltage and electrical currents, and in passive components, such as capacitors and resistors to control electrical currents or voltages. It is also used in electromechanical applications, such as ferrite magnets and piezoelectric devices. According to a report [1] mentioned in the literature the significance of electroceramic materials can be gauged with respect to the present demand of the same in the global market and projected demand in the future.

High dielectric ceramics used in industrial applications are Barium Titanate, PZT, PMN, etc. Most of them are relaxor ferroelectrics and are either perovskites or those with tungsten bronze structure. Ceramics manufactured from formulations of lead Zirconate / Lead Titanate (Lead Zirconate Titanate – PZT) exhibit greater sensitivity and higher operating temperatures, relative to ceramics of other compositions, and therefore "PZT" materials currently are the most widely used piezoelectrics [2].

The study mentioned in this paper is (i) to obtain PLZT ceramic powders prepared by homogeneous precipitation with the chemical composition corresponding to the x/52/48 ratio, where x = 0 to 20 mole percent of La, and (ii) to study their basic dielectric and piezoelectric properties. The ferroelectric ceramics have a number of properties, which make them very useful in a variety of applications.

Doping of La to the basic PZT system results in many effects, such as enhanced dielectric and piezoelectric properties, increased squareness of the P–E hysteresis loops, decreased coercive field (Ec) and transparency [3] etc.

Donor dopants of higher charge, like a La^{3+} ions, enhance domain wall mobility and result in improved remnant polarization, coupling factors, dielectric constants, dielectric loss tangent and increased optical transparency of electrically "soft" PZT material [4,5].

The chemical composition of PLZT is given by the formula [6]:

$$Pb_{1-x}La_x(Zr_{1-y}Ti_y)_{1-x/4}V_{0,25x}O_3,$$
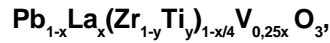
The composition of PLZT is routinely represented by the notation x/(1-y)/y, which denotes the amount of La/Zr/Ti, given in mole fractions or mole per cent. The study reveals the influence of La^{3+} dopant on PZT ceramics and their basic dielectric and piezoelectric properties.

2. EXPERIMENTAL

The preparation of the samples is represented in the form of a flow chart in Fig. 1.

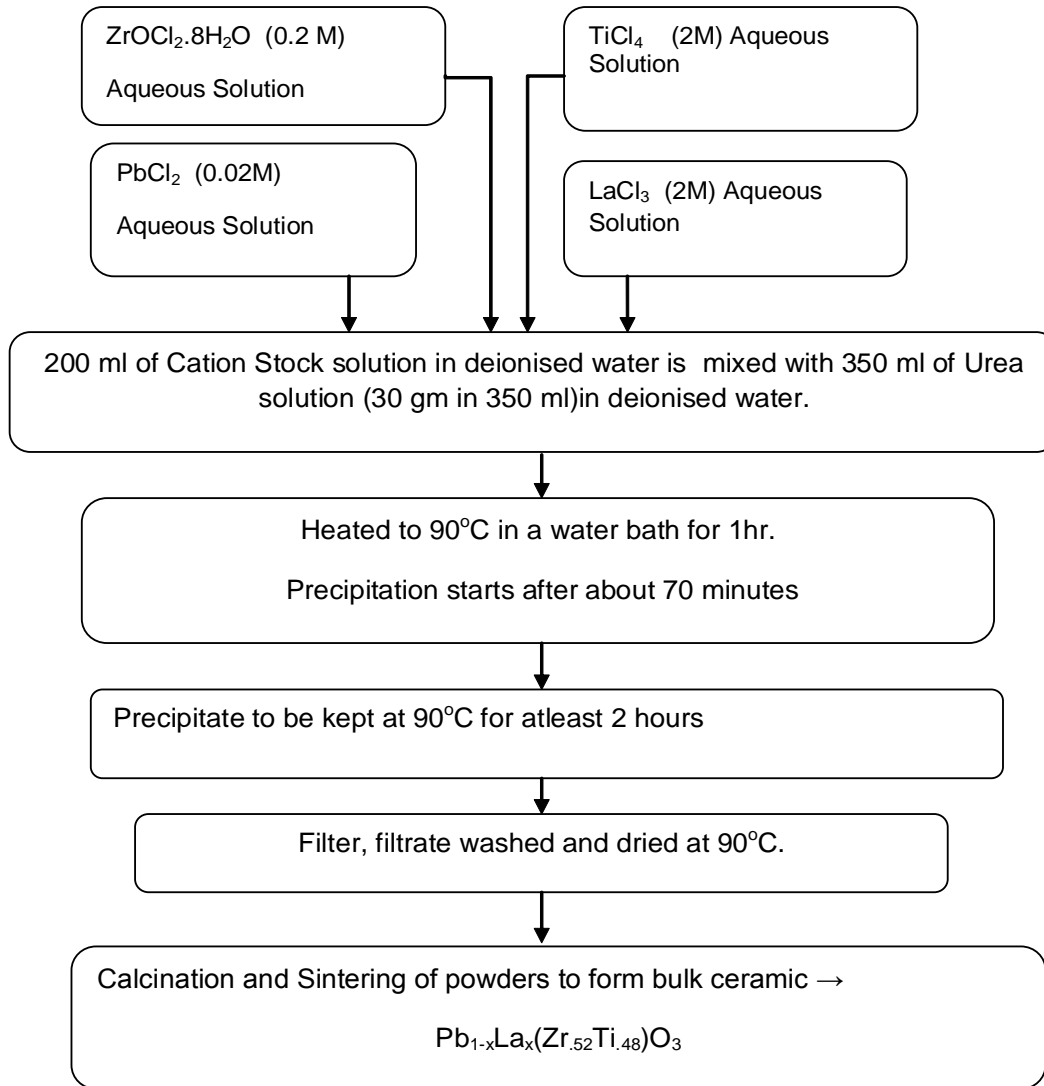**Flow Chart for the Preparation of PLZT samples for characterization**

$ZrOCl_2.8H_2O$ (0.2 M) Aqueous Solution

$TiCl_4$ (2M) Aqueous Solution

$PbCl_2$ (0.02M) Aqueous Solution

$LaCl_3$ (2M) Aqueous Solution

200 ml of Cation Stock solution in deionised water is mixed with 350 ml of Urea solution (30 gm in 350 ml)in deionised water.

Heated to 90°C in a water bath for 1hr.

Precipitation starts after about 70 minutes

Precipitate to be kept at 90°C for atleast 2 hours

Filter, filtrate washed and dried at 90°C.

Calcination and Sintering of powders to form bulk ceramic →

$Pb_{1-x}La_x(Zr_{.52}Ti_{.48})O_3$

Fig. 1

As the initial materials, the following high-purity salts of precursors were chosen:

(a)   Lead(II) Chloride, $PbCl_2$ (203572-10G)
(b)   Lanthanum(III) Chloride $LaCl_3$.$7H_2O$ (203521-25G)
(c)   Zirconium(IV)oxycloride $ZrOCl_2$.$8H_2O$ (205028-10G) [Zirconyl Chloride]
(d)   Titanium(IV) Chloride, $TiCl_4$ (254312)
(e)   Urea, CH_4N_2O (reagent grade) (299367)
(f)   Deionized water (Locally available, very high purity)

The numbers given in the bracket are the catalogue numbers assigned to the particular salt of a particular purity and fineness.

The stoichiometric mixture of the components was prepared by measuring the aqueous solutions prepared, since all the aqueous solutions are of different molarity, it was precalculated as to how much solution of each component should be added to get the correct stoichimetry.

Cation stock solutions for different La percentage were thus prepared. Around 200 ml of the cation stock was then mixed in a beaker into which 350 ml of Urea solution prepared by dissolving 30 gm of urea in 350 ml of deionized water, was added and mixed thoroughly. The resulting solution was then heated to about 90^0C in a water bath to avoid excessive heating and to ensure uniform heat from all sides. When the temperature reaches to about 70^0C a slight turbidity appears, this is the onset of precipitation. As it reaches 90^0C precipitates gets denser. The precipitates are oxides of the cations intimately mixed and of very small particle size. It is kept at that temperature for about 2 hrs. so that the precipitation is complete. After that the precipitates are filtered off washed in deionised water and dried at 90^0C in a vacuum oven. The dried precipitates are then ground in an agate mortar to remove any agglomerates formed. The powder obtained is now a fine mixture of oxides or carbonates, whose level of mixing are not possible by mechanical methods like ball milling etc., even if possible it may take days on end to reach this level. This mixture of oxide precursors were calcined at 800^0C for 6 hours yeiding the desired ceramic powder. The ceramic powders were then mixed with, 0.5% by weight of the mixture, poly vinyl alchohol and compacted into discs of thickness 1mm and diameter 20 mm. Poly Vinyl Alchohol (PVA) acts as a binder in forming the discs, eventually getting evaporated out of the matrix at elevated temperatures during the sintering process. The heating rate during the sintering process was maintained a constant till it reaches 1200^0C. Altogether there were eleven different sets of ceramic pellets from zero to 20 mole percent of lanthanum content with increment of 2 mole percent with subsequent set. The characterization was subsequently carried out.

3. RESULTS AND DISCUSSION

The density of the sol gel prepared and sintered ceramic was measured by the Archimedes principle. This is almost in concordance with expected values, because La is much less dense than Pb, and it is clear that La is replacing Pb in the lattice. Also an almost linear dependence is exhibited which is graphically represented in Fig. 2.

The real part of the dielectric permittivity and loss tangent tan δ are plotted against temperature in Celsius at different frequencies for the various samples, the plots are as shown below Fig. 3-12. The real part of dielectric permittivity implies the usefulness of the material in electrical energy storage (electrical capacity). While the imaginary part of the dielectric permittivity indicates the extent of electrical energy leakage, that may occur in the material with respect to time. The imaginary part of the permittivity also, to an extent, is linked to the ac conductivity of the material. The lesser the value of the imaginary part the better for capacitor applications.

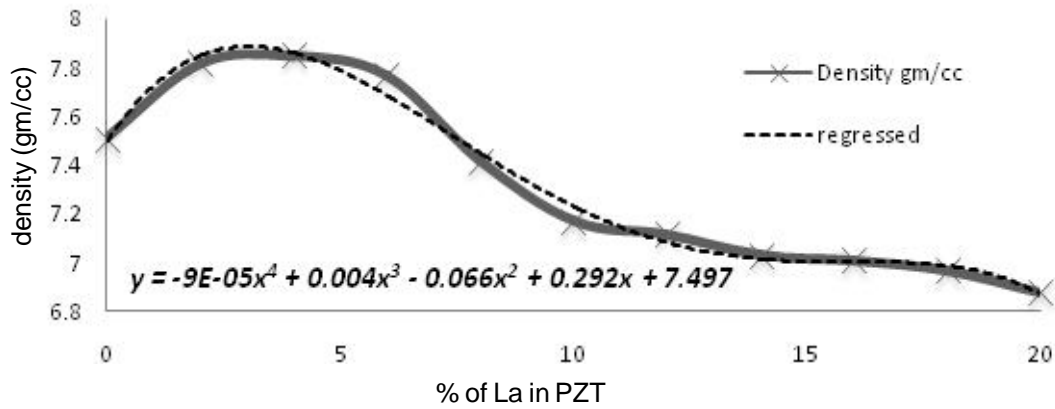**Plot of La mole percent in PLZT versus its density in gm/cc**

$$y = -9E\text{-}05x^4 + 0.004x^3 - 0.066x^2 + 0.292x + 7.497$$

% of La in PZT

Fig. 2

Plot of dielectric constant (ε') as a function of temperature at different frequencies for PLZT 0/52/48 ceramic systems
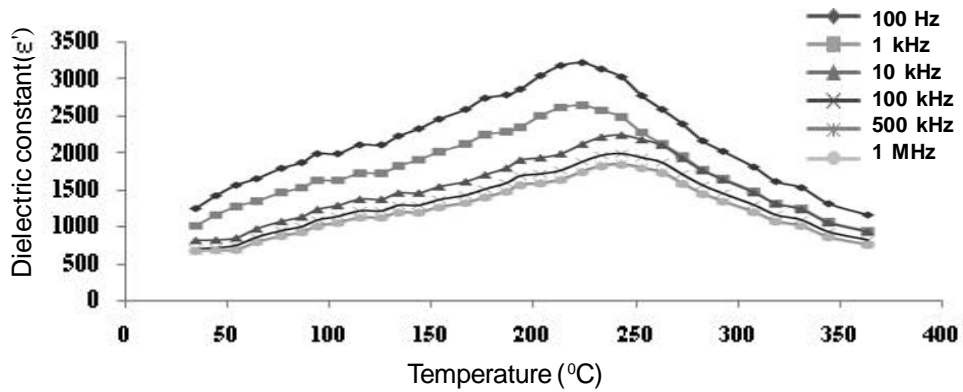

Fig. 3

Plot of dielectric constant (ε') as a function of temperature at different frequencies for PLZT 2/52/48 ceramic systems
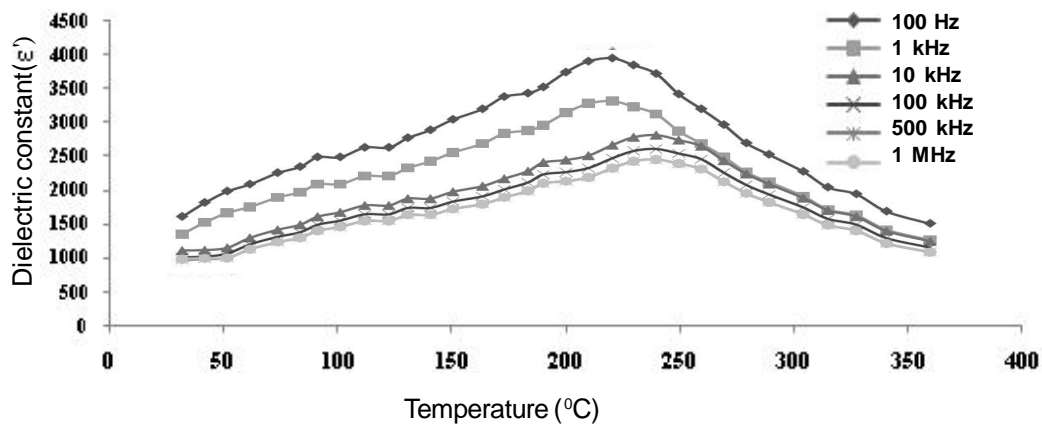

Fig. 4

The dielectric relaxation mechanism can be estimated from the representative plots given in Fig 3-12. As expected the dielectric constant (ε) or the real part of the dielectric permittivity decreases A maxima beyond 200^0C and 250^0C is exhibited by the ceramics. This is due to the activation of soft modes at that temperature, which is a characteristics of polar dielectrics specially in perovskite ferroelectric of ABO_3 type.

Plot of dielectric constant (ε') as a function of temperature at different frequencies for PLZT 8/52/48 ceramic systems
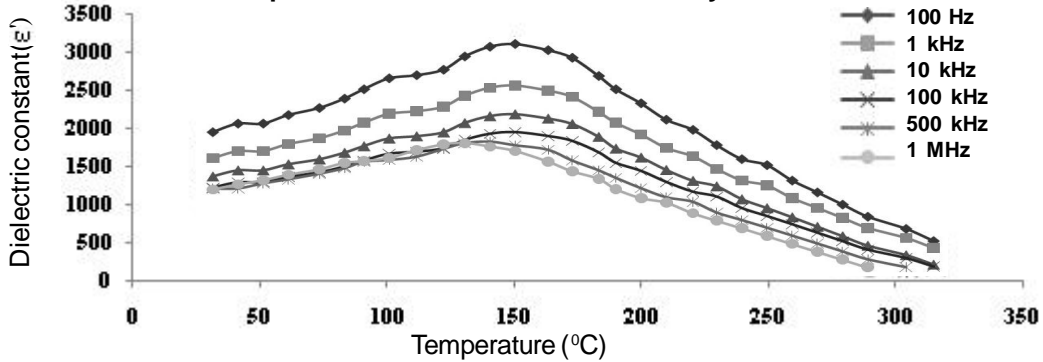
Fig. 5

Plot of dielectric constant (ε) as a function of temperature at different frequencies for PLZT 18/52/48 ceramic systems
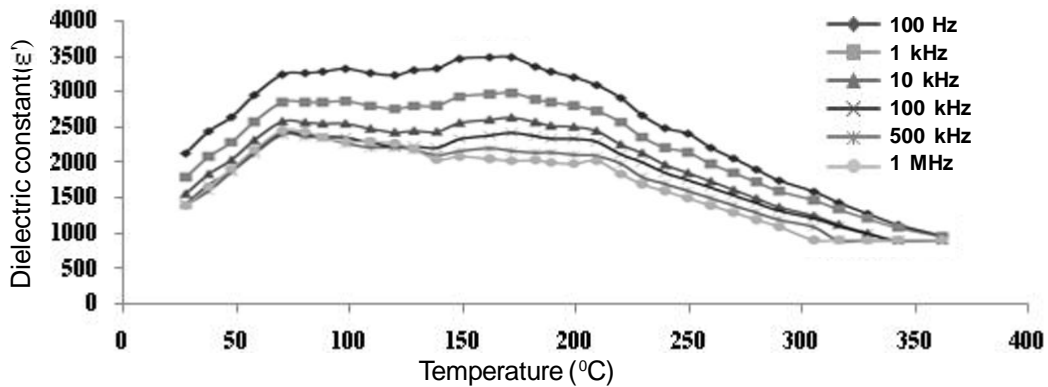

Fig. 6

Plot of dielectric constant (ε') as a function of temperature at different frequencies for PLZT 20/52/48 ceramic systems
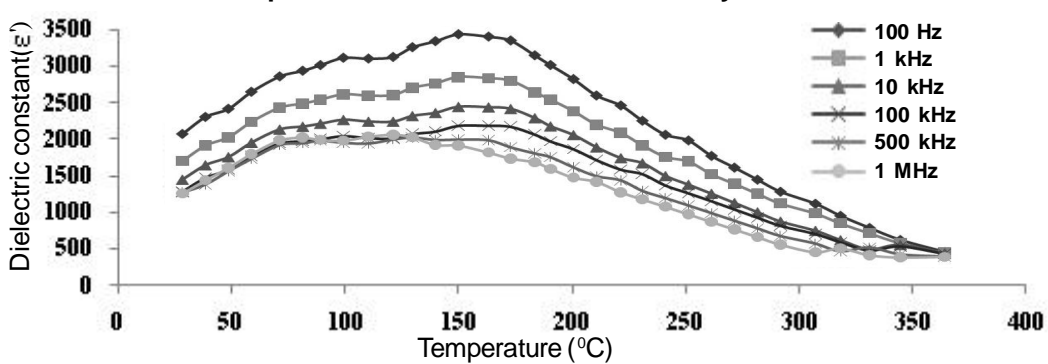

Fig. 7

Loss tangent (tan $\delta = \varepsilon''/\varepsilon'$) as a function of temperature and frequency of PLZT 0/52/48 ceramic
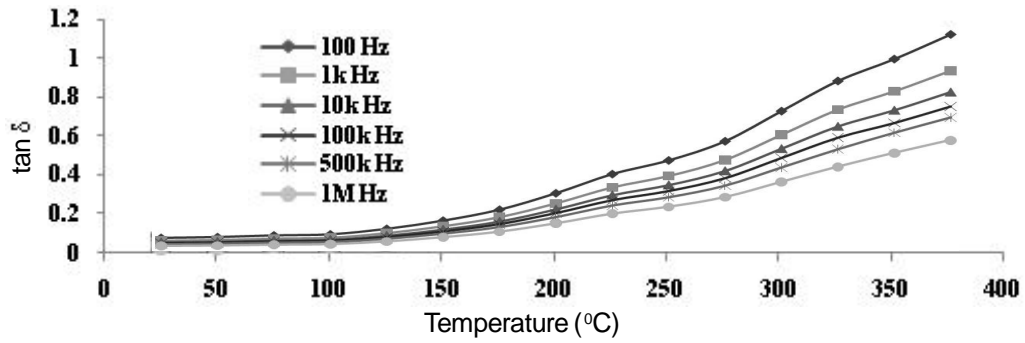

Fig. 8

Loss tangent (tan $\delta = \varepsilon''/\varepsilon'$) as a function of temperature and frequency of PLZT 2/52/48 ceramic
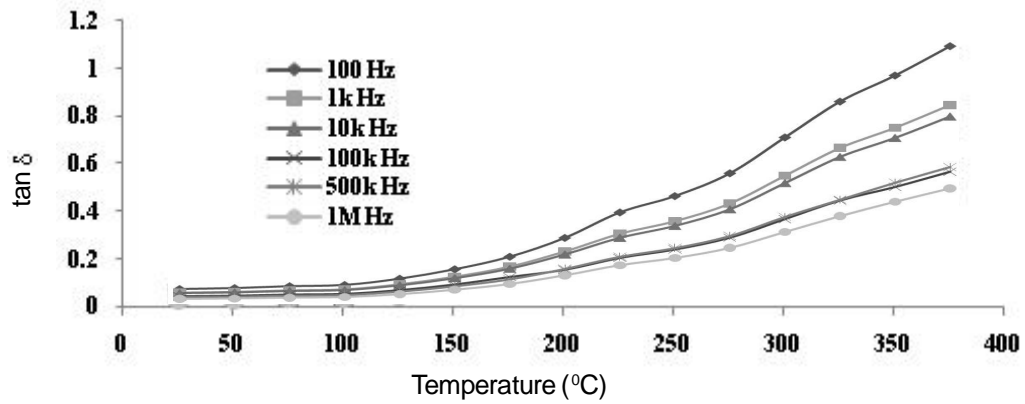

Fig. 9

Loss tangent (tan $\delta = \varepsilon''/\varepsilon'$) as a function of temperature and frequency of PLZT 6/52/48 ceramic
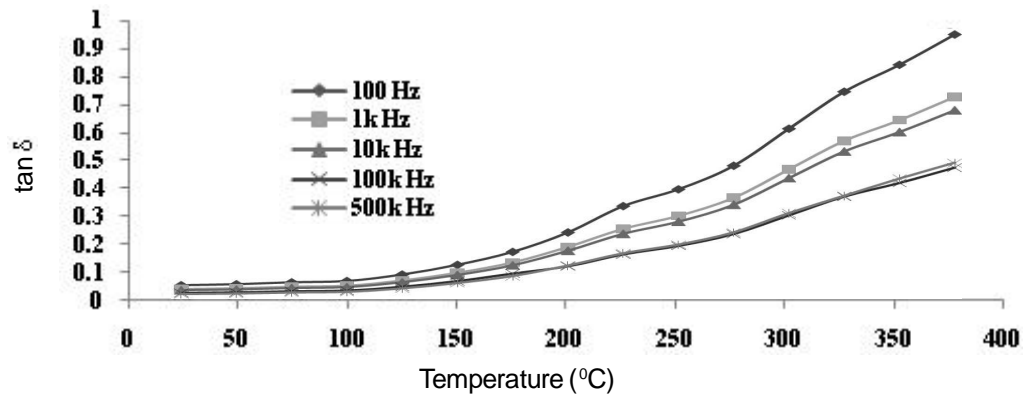

Fig. 10

Loss tangent (tan $\delta = \varepsilon''/\varepsilon'$) as a function of temperature and frequency of PLZT 18/52/48 ceramic
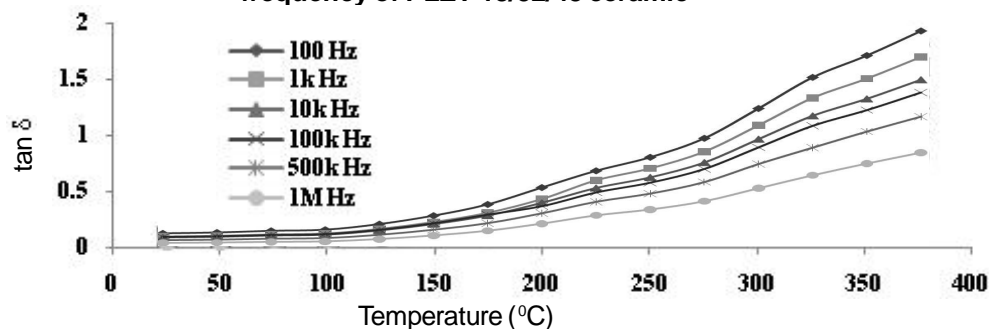

Fig. 11

Loss tangent (tan $\delta = \varepsilon''/\varepsilon'$) as a function of temperature and frequency of PLZT 20/52/48 ceramic
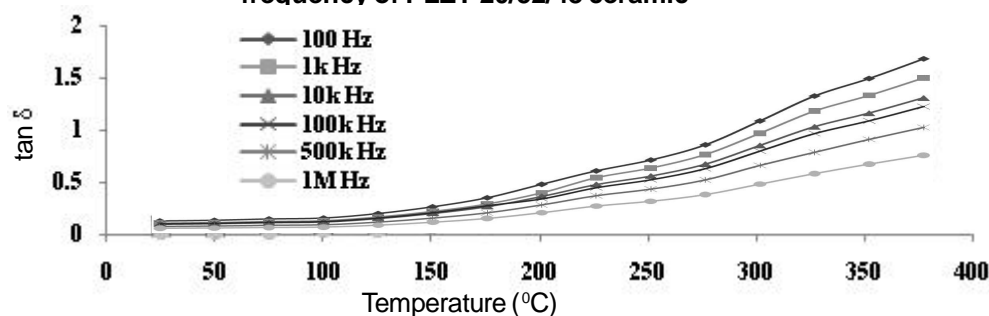

Fig. 12

It can be observed from the Table 1 that 8/54/48 composition has the maximum figure of merit as well as highest piezo d_{33} coefficient. Although the d_{33} values decreases steadily with the increase of La in the ceramic, the piezo figure of merit which is the parameter looked for when designing a sonar system[7], shows a peak at 8% La, implying that composition best suited for transducer application, this is due to the fall in ε accompanied by a fall in the numerical value of d_{31}. Value of d_h and g_h therefore increased and hence the effect.

Table 1 Piezocoefficients of PLZT x/52/48

Samples	d_{33} (pC/N)	d_{31} (pC/N)	d_h (pC/N)	g_h (10^{-3} Vm/N)	$d_h g_h$ (10^{-12} m²N⁻¹)	k_p	k_t	$Z = \rho v$ (106 kgm⁻²s⁻¹)
PLZT 0/52/48	380	-176	28	16.4	459.2	0.55	0.68	37
PLZT 2/52/48	400	-160	80	19.5	1560	0.58	0.68	37
PLZT 4/52/48	452	-152	148	22.6	3344.8	0.64	0.72	37
PLZT 6/52/48	475	-142	191	27.3	5214.3	0.65	0.75	34
PLZT 8/52/48	530	-131	268	35.2	9433.6	0.71	0.77	32
PLZT 10/52/48	424	-120	184	42.1	7746.4	0.69	0.81	32
PLZT 12/52/48	410	-90	230	37.4	8602	0.66	0.76	33
PLZT 14/52/48	405	-65	275	31.6	8690	0.64	0.72	32
PLZT 16/52/48	405	-54	297	23.2	6890.4	0.60	0.71	32
PLZT 18/52/48	403	-49	305	17.1	5215.5	0.60	0.65	32
PLZT 20/52/48	397	-43	311	14.3	4447.3	0.57	0.66	31

4. REFERENCES

[1] Report on 2009-2014, "*Outlook for Advanced Ceramics in India*", Icon Group International, ISBN:000061514G, December 2008.

[2] Jaffe B., Cook W. R. and Jaffe H., "*Piezoelectric Ceramics*", Academic Press New York, ch 7, pp. 135, 1971.

[3] Jiang Q.Y., Subbarao E.C., Cross L.E., "*Effect of composition and temperature on electric fatigue of La doped zirconate titanate ceramics*", J. Appl. Phys., Vol. 75, No. 11, pp. 7433, 1994.

[4] Xu Y., "*Ferroelectric Materials and Their Applications*", Elsevier, Amsterdam, 1991.

[5] Pereira M., Mantas P.Q., "*Preparation of PLZT materials using powders from aqueous coprecipitation*", Key Eng. Materials, Vol.132–136, pp.1123-1126, 1997.

[6] Haertling G.H., "*PLZT electrooptic materials and applications—a review*", Ferroelectrics, Vol. 75 , pp. 25, 1987.

[7] Su´arez-G´omeza A. and Durruthy M.D., "*Suitability of the PLZTN 54/46 ceramic system for designing pulse-echo sensors*", Revista Mexicana de F´isica S, Vol. 52, No. 2, pp. 36–38, 2006.