International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jpms.htm
2014 Vol. 4 (4) October-December, pp. 71-78/Bongane and Gawali
Research Article

EFFECT OF PARTICLE SIZE AND TEMPERATURE ON DIELECTRIC PARAMETERS OF PLZT CERAMICS AT 9.85 GH_Z

***Bongane B.K. and Gawali P.G.**
Department of Physics, B. S. College, Basmathnagar, Dist: Hingoli- 431512, India
**Author for Correspondence*

ABSTRACT

The dielectric properties of $(Pb_{0.93}\,La_{0.07})\,(Zr_{0.60}\,Ti_{0.40})\,O_3$ have been carried out at the X-band microwave frequency. The composite material was prepared by using solid state reaction method. The dielectric constant (ε'), dielectric loss (ε''), quality factor ($Q = \frac{1}{tan\delta}$), relaxation time (τ) and conductivity (σ) of PLZT having particle sizes 500, 250, 176.5 and 125 microns have been studied at different temperatures i.e. -10^0,$+10^0$,$+30^0$ and $+50^0$c. The experimental dielectric values have been verified by using correlation formulae's of Landau-Lifshitz-Looyenga and Bottcher. It founds the good agreement with experimental values.

Keywords: *Relative Permittivity, Ferroelectric, Relaxation Time, Dielectric Constant, Quality Factor*

INTRODUCTION

Recent development in the perovkite type ferroelectric ceramics have attracted much attention due to the greatly enhanced dielectric, piezoelectric and pyroelectric performances and strain induced by electric field level compared to normal ceramic solid solutions.

Lead Lanthanum Zirconate Titanate (PLZT) materials consist of a wide range of homogeneous ABO_3 composition existing with the basic lead zirconate-lead titanate solid solution system. Because of the complete miscibility between lead zirconate and lead titanate and the substantial solubility and lanthanum oxide in the system, it is possible to custom make various combination of chemical compositions to get specific desirable properties. The electro-optic applications of PLZT ceramics depends on the composition. It show hysteresis loops with a very high coercive field (EC). For $E < E_c$ materials exhibit linear electro-optic behavior. PLZT ceramics are also useful for optical memory applications (Radheshyam, 2004).

The PLZT unit cell consists of a corner-linked network of oxygen octahedral with Zr^{+4} and Ti^{+4} ions occupying B sites within the octahedral cage and the Pb^{+2} and La^{+3} ions occupies A sites created by the linked octahedral. As a result of the different valances between Pb^{+2} and La^{+3} some of the A sites and B sites are vacant to maintain electrical neutrality in the structure.

The 7% La-doped Pb $(Zr_{.60}\,Ti_{0.40})\,O_3$ ceramic PLZT (7/60/40) composition is one of the most important of piezoelectric applications due to its extremely high piezoelectric and electromechanical coupling co-efficient. PLZT is an important piezoelectric material which has high values of piezoelectric co-efficient, dielectric constant, dielectric loss and good piezoelectric effect in the morphotropic phase boundary (MPB) has been observed in polycrystalline PLZT which is higher than that of polycrystalline PZT.

It was shown that the satisfactory electro-optical properties of PLZT could be achieved only by a suitable procedure of PLZT synthesis initial work on the synthesis of PLZT was done using mixed oxides. Several methods like chemical co-precipitation, solid state reaction, hydrothermal reaction, polymer precursor and a high energy mechanochemical milling process, have been reported in the literature to prepare PLZT compositions. The traditional solid state reaction (SSR) method, allows the mixing of the components at a molecular level and results in materials with high compositional homogeneity. The sintering temperature of PLZT by SSR method is about 1250^OC and PLZT can be used for variety of applications such as thin-film capacitors, multilayer bulk stack devices or integrated memory, to avoid inter-diffusion between layers (Himanshu, 2006).

It is also will documented in the literature that the various properties such as dielectric constant and dielectric loss tangent of PLZT ceramics are dependent on density, grain size, microstructure and temperature.

The aim of this paper is concerned with the microstructure of (7/60/40) PLZT ceramic prepared by the SSR method and studied /discussed dielectric, electrical properties of PLZT ferroelectric materials.

Ferroelectric crystal shows a spontaneous electric polarization. This polarization can be reversed by an electric field. Ferro electricity also depends upon the dielectric behavior of the crystal. The rapid advance in the manufacturing of electromagnetic devices has led to a particular need for ceramics with tenable dielectric constants and low losses at microwave frequencies. Ferro electric materials possess significant tunability i.e. change of dielectric constant under applied electric field. The use of high – permittivity ferroelectric ceramic and films in most microwave devices require that they posses frequency dependent permittivity's and show low dielectric loss. The origin of the relaxation phenomenon has been attributed to the existence of domain structure, inherent to ferroelectric (Burfoot, 1967).

Among the ferroelectrics ($P_bLaZ_rT_iO_3$) has been much studied for its numerous scientific and industrial applications, such as in dielectric capacitors, transducers.

Ferroelectric materials have large range of applications, dielectric, piezoelectric, pyroelectric and electro-optical material. The high dielectric permittivity of Peroviskite material has stimulated their applications in ferroelectric non-volatile memories (FeRAM), dynamic random access memories (DRAM) and even more important in the microwave domain (Lines, 1977)

The electro optic applications of PLZT ceramics depends on the composition. PLZT ceramic compositions in the tetragonal ferroelectric (Ft) region show hysteresis loops with a very high coercive field (Ec). This composition exhibit linear electro optic behavior for E<Ec. PLZT ceramic composition in the rhombohedral ferroelectric (Fr) region of the PLZT phase diagram have loops with a low coercive field. PLZT ceramic are useful for optical memory applications the transparent nature of PLZT has led to its use in electro optic applications.

MATERIALS AND METHODS

Synthesis of Material

PLZT composite material was prepared for microwave studies by using solid state reaction method. In SSR method, the solid reactants react chemically without presence of any solvent at high temperatures yielding a product which is stable. The advantage of SSR method is that final product in solid form is structurally pure with the desired properties depending on the final sintering temperatures. This method is environment friendly and no toxic an unwanted waste is produced after the SSR is complete. The steps involved in SSR are

i) Take weighed appropriate high purity starting materials, fine grain powders in stoichiometric properties.
ii) Mix them together, thoroughly using agate mortar and pestle or ball milling.
iii) Heat the solid powder mixture (calcinations) at elevated temperatures in air using muffle furnace.
iv) Report the calcinations process twice with intermittent grinding.
v) Final powder is ready.

The high purity AR grades Pb3O4 La2O3ZrO2TiO2 were used as starting materials for the solid state reaction (Raju *et al.*, 2010). These constituents were weighed and mixed thoroughly. The composite material was prepared for 50gm. Pb_3O_4 $La_2O_3ZrO_2$ & T_iO_2 are estimated as per $(Pb_{0.93}\ La_{0.07})$ $(Zr_{0.60}\ Ti_{0.40})$ O_3 so that total molecular wt is 329.824gm. Then after estimating the samples of weights Pb_3O_4 $La_2O_3ZrO_2$ & T_iO_2 had taken as 212.536, 11.40, 73.932 and 31.956 gms respectively out of 50 gms. Then this was mixed in stoichiometric proportion has been grinded about 3½ hours continuously using agate mortar for first calcinations.

This mixture was initially sintered at temp 800^0c for a time about 4 hours in a muffle furnace. Then after first calcinations the sample was again grinded or 1½ hrs and kept about 4 hrs. at 1250^0c for final

sintering. The chemical reaction at high temperature take place, through solid state reaction giving a stable sample product free of residual reactants as shown below (Gawali, 2014)

$Pb_3O_4 + La_2O_3 + ZrO_2 + T_iO_2 \rightarrow$ Pb La Zr T_iO_3

Material Preparation for Dielectric Studies

For the determination of dielectric parameters of PLZT were prepared by using sieves of different sizes. Like 500, 250, 176.5, 125 microns particle sizes. All the samples transferred into the glass bottles and labeled according to their particle size. To determine the relative packing factor (δr) densities for each powder sample is measured, measurement of dielectric parameters (ε′) and (ε″) for these powder samples were carried out using reflectometer technique at 9.85 GHz microwave frequency and at temperatures (-10^0c, $+10^0$c, $+30^0$c & $+50^0$c).

For the accurate measurement of wavelength in dielectric (λ_d), sample is introduced in the dielectric cell in steps. Applying constant force of 98N on the sample, and for each time the corresponding output power is measured by using crystal pick in the directional coupler. The relationship between reflected power and sample height is approximately given by a sinusoidal curve. The distance between two adjacent minima of the curve gives half the dielectric wavelength (λ_d).

Determination of Molecular Parameters

The dielectric constant (ε′) and loss factor (ε″) for PLZT powder at microwave frequency are determined by using relations (Yadav, 1992)

$$\epsilon_p^{'} = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \quad \text{..... (1)}$$

$$\epsilon_p^{"} = \frac{2}{\pi}\left(\frac{\lambda_0}{\lambda_c}\right)^2 \frac{\lambda_g}{\lambda_d}\left(\frac{d_{\rho mean}}{d_n}\right)^2 \quad \text{..... (2)}$$

Where λ_0 is the free space wavelength

λ_d is the wavelength in dielectric

λ_c is the cutoff wavelength of waveguide

λ_g is the guide wavelength

The conductivity (σ_p) and relaxation time (τ_p) are obtained by using following relations (Cross, 1993; Lines and Glass, 1977; Gawali and Bongane, 2014; Gawali and Bongane, 2013).

$$\sigma_p = \omega\epsilon_0\epsilon^{"} \quad \text{..... (3)}$$

$$\tau_p = \epsilon^{"}/\omega\epsilon^{'} \quad \text{..... (4)}$$

Where w = 9.85 GHz angular frequency of measurement ε_0 is the permittivity of free space.

The values of $\epsilon_s^{'}$ and $\epsilon_s^{"}$ for bulk materials can be co-related by using the relations given by Bottcher and Landau – Lifshitz – Looyenga (L-L-L, 1960).

RESULTS AND DISCUSSION

Table 1 shows values of permittivity ($\epsilon_p^{'}$) and loss factor ($\epsilon_p^{"}$) along with values of relative packing fraction (δr) for different particle sizes and temperatures. There is systematic increase in $\epsilon_p^{'}$ and $\epsilon_p^{"}$ with increasing δr and systematic decrease in $\epsilon_p^{'}$ and $\epsilon_p^{"}$ with increasing temperature. This is expected because at higher values of δr the interparticle hindrance offered to the dipolar motion for a compact medium is much higher than less bounded particles (Gawali, 2013)

The calculations of quality factor (Q x F) where f is resonant microwave frequency are also mentioned in table 1. It is found decrease in Q x F values for decreasing particle size and by increasing temperature the Q x F values increases.

The values of relaxation time (τ_p) and conductivity (σ_p) are increases systematically by increasing δr and decreases by increasing of temp. It is due to, when polar molecules are very large, then under the influence of high frequency the rotary motion of polar molecules of a system is not sufficiently rapid to attain equilibrium with field.

The increase in τ_p by increasing δ_r is due to increasing hindrance to the process of polarization. The increase in σ_p suggests that at higher compaction, no micro cracks develop in sample due to high mechanical pressure.

Table 1: Values of ε'_p, ε''_p, Q x F, τ_p and σ_p of PLZT at different temperatures and particle sizes

Temperature (^{o}c)	Relative packing factor (δr)	ε'_p	ε''_p	$Q=1/tan$	Q x F GHz	τ_p (P.S.)	σ_p
-10	0.84	28.29	5.99	4.73	46.59	3.42	3.28
	0.88	37.95	9.28	4.09	40.29	3.95	5.08
	0.94	41.27	11.05	3.76	37.04	4.30	6.05
	1.00	44.59	12.83	3.48	34.28	4.65	7.02
10	0.84	24.03	5.04	4.77	46.98	3.39	2.76
	0.88	30.32	7.25	4.18	41.17	3.86	3.97
	0.94	33.33	7.85	3.98	39.20	4.06	4.29
	1.00	34.35	8.85	3.79	37.33	4.26	4.63
30	0.84	19.83	3.64	5.45	53.68	2.96	1.99
	0.88	22.26	4.91	4.53	44.62	3.57	2.69
	0.94	22.69	5.27	4.31	42.45	3.75	2.88
	1.00	23.13	5.63	4.11	40.48	3.94	3.08
50	0.84	16.55	1.88	8.82	86.88	1.83	1.03
	0.84	18.69	3.16	5.91	58.21	2.73	1.73
	0.94	19.69	3.74	5.30	52.20	3.05	2.05
	1.00	20.68	4.32	4.80	47.28	3.37	2.36

Table 2: Measured and calculated Values of ε'_s and ε''_s, for solid bulk from PLZT at different temperatures and packing fractions.

Temperature (^{o}c)	Relative packing factor (δr)	Measured value ε'_P	Calculated from Bottcher's ε'_s	Calculated from L-L-L ε'_s	Measured value ε''_p	Calculated from Bottcher's ε''_s	Calculated from L-L-L ε''_s
- 10	0.84	28.29	36.71	34.72	5.99	8.48	7.88
	0.88	37.95	45.93	42.86	9.28	11.98	11.32
	0.94	41.27	45.20	41.95	11.05	12.49	12.14
	1.00	44.59	44.59	41.25	12.83	12.83	12.83
+ 10	0.84	24.03	31.10	29.46	5.04	7.12	6.62
	0.88	30.32	36.62	34.23	7.25	9.34	8.84
	0.94	33.33	36.47	34.47	7.85	8.86	8.62
	1.00	34.35	34.35	33.48	8.85	8.85	8.85
+ 30	0.84	19.83	25.58	24.55	3.64	5.13	4.78
	0.88	22.26	26.80	25.35	4.91	6.31	5.98
	0.94	22.69	24.78	23.45	5.27	5.95	5.79
	1.00	23.13	23.13	21.88	5.63	5.63	5.63
+ 50	0.84	16.55	21.27	20.94	1.88	2.64	2.47
	0.88	18.69	22.45	21.73	3.16	4.05	3.85
	0.94	19.69	21.48	20.71	3.74	4.21	4.10
	1.00	20.67	20.68	19.32	4.32	4.32	4.32

As temp increases, τ_p decreases may be due to increase in the effective length of dipole. Again increase in temp, causes an increase in energy loss due to the large number of collisions and thereby decreasing τ_p.

Table 2 indicates the measured and computed values of ε'_s and ε''_s for bulk from powder measurements. The results reported at $\delta r = 1$ are those measured on the finest crushed powder sample packed at very closely in a sample holding dielectric cell at 98N force, so minimum voids between the particles.

The smallest particle size 125 micron or less assumed this system as solid bulk for getting correlation between powder and solid bulk. The correlation formulae of Landau – Lifshitz – Looyenga and Bottcher were used.

The bulk values ε'_s and ε''_s are very much closer to measured values.

Conclusion

X-ray diffraction patterns of PLZT were recorded using X-ray diffractometer with Cu.ka (λ= 1.5418 A^0) radiation.

The XRD patterns for the PLZT are shown in Figure 1. The Sharp and single diffraction peaks indicate homogeneity and better crystallization of the samples. The x-ray analysis indicates that the PLZT has single phase with tetragonal structure. All the reflection peaks were indexed using observed interplaner spacing d and lattice parameters of PLZT were determined using a least squares refinement method. A good agreement between calculated and observed of values of all diffraction lines of PLZT suggests that (there is no change in the basic crystal structure) prepared sample is pervoskite ferroelectric material and it useful for electro optic waveguide.

There is fair agreement between the values obtained experimentally and theoretically. It is found the values calculated from the co-relation formulae of Landau – Litshitz – Looyenga and Bottcher between power and solid bulk works well.

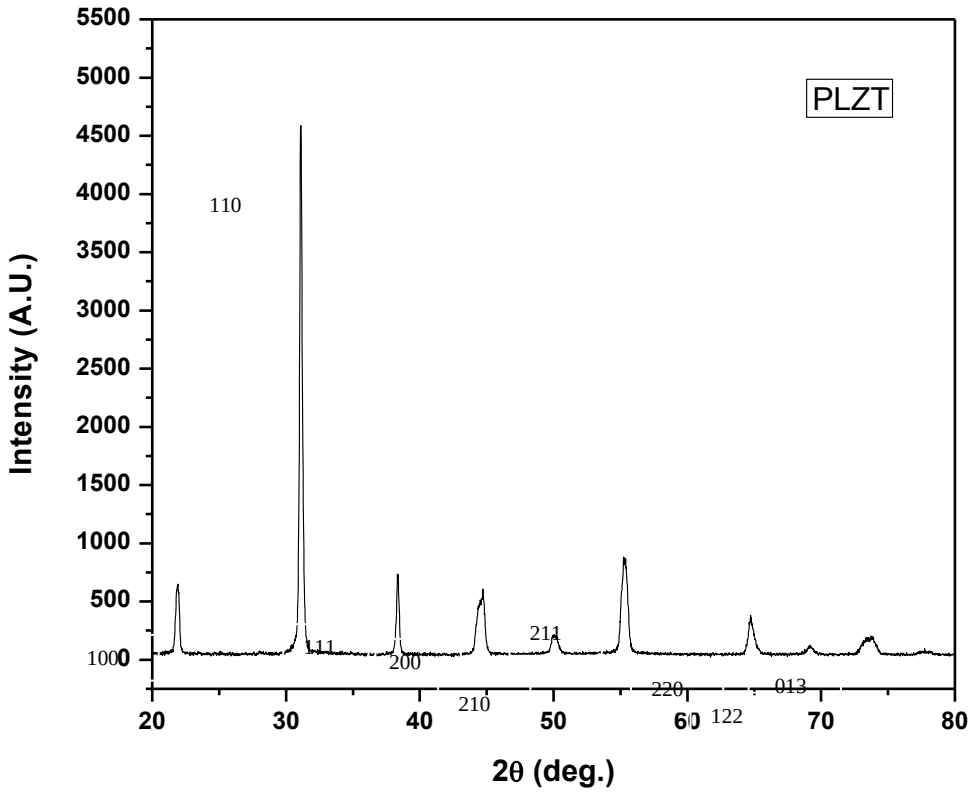

Figure 1: X-ray diffraction pattern of PLZT calcinated at 1250^{O}C/4 h.

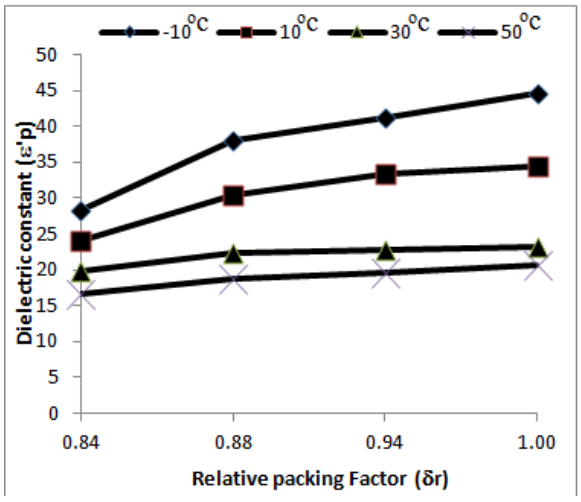

Figure 2: δr Vs ε'

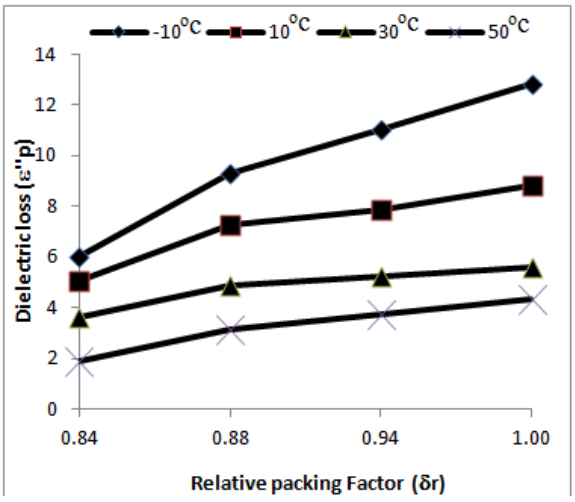

Figure 3: δr Vs ε''

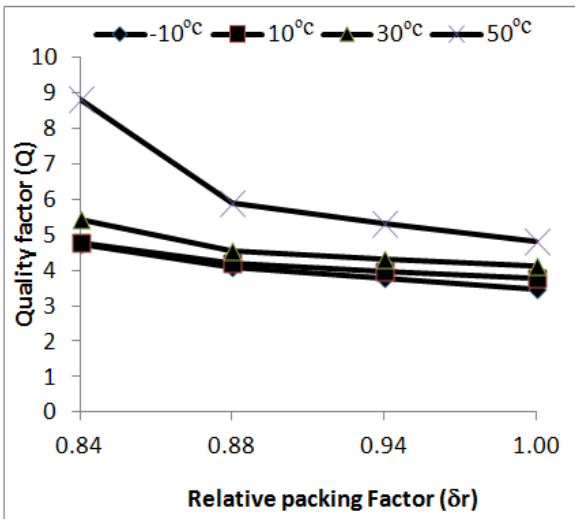

Figure 4: δr Vs Q

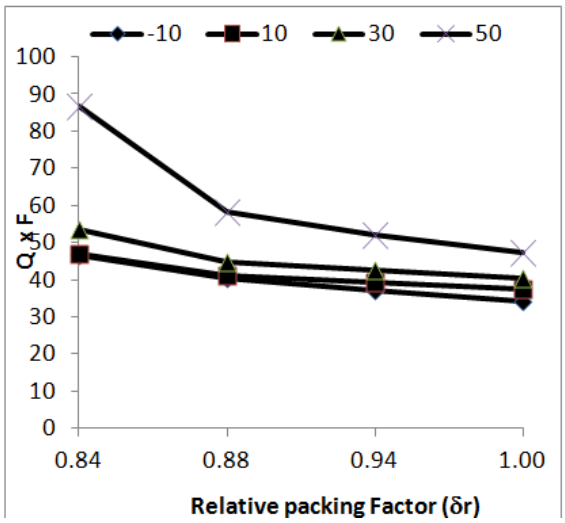

Figure 5: δr Vs Q x F

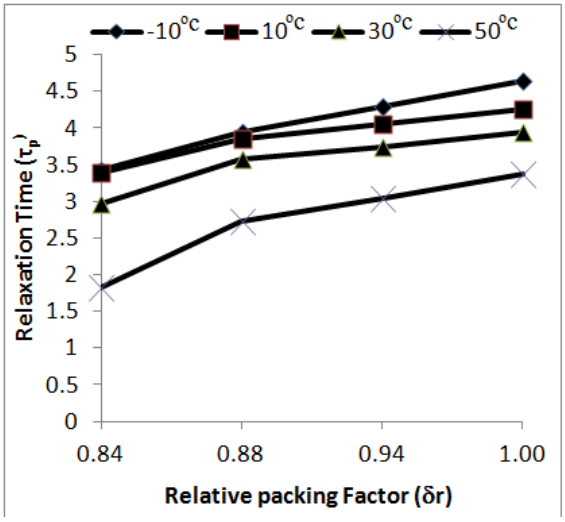

Figure 6: δr Vs τ_p

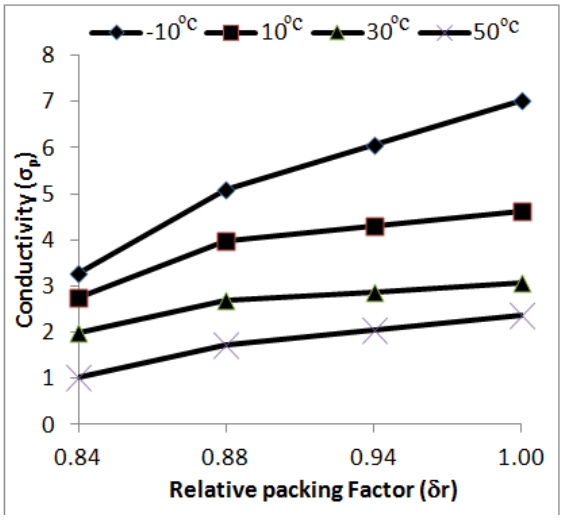

Figure 7: δr Vs σ_p

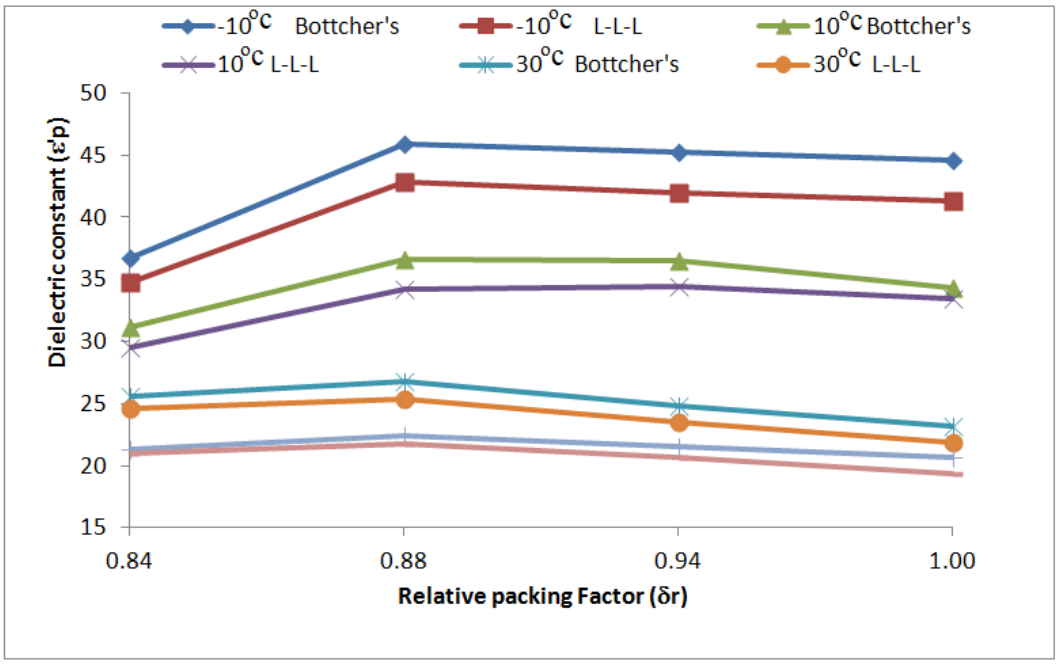

Figure 8: δr Vs ε' (Bott., L.L.L.)

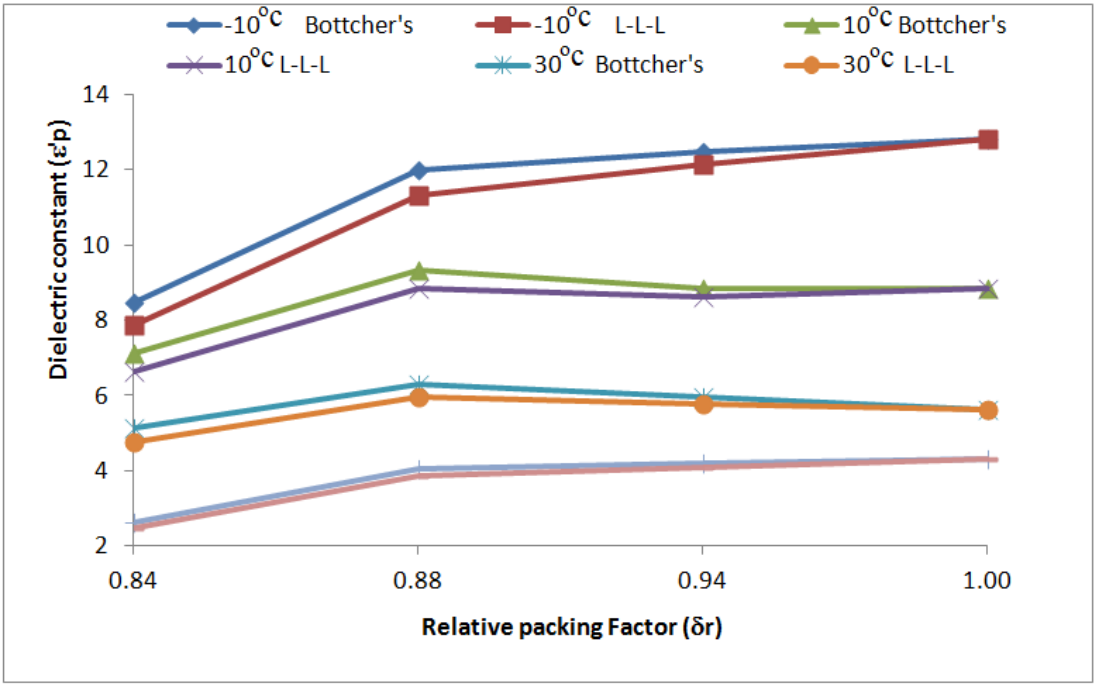

Figure 9: δr Vs ε'' (Bott., L.L.L.)

REFERENCES

Bongane BK and Gawali PG (2012). Dielectric behaviour of n-decanol ethanolamine mixture at microwave frequencies. *Journal of the Indian Chemical Society* **89**(9) 1209-1213.

Burfoot JC (1967). *Ferroelectrics* (van Nostrand, Newyork).

Ceraqueira M and Nasar RS (2000). Sintering and characterization of PLZT (9/65/35). *Ceramic International* **26** 231-236.

Chandra Prakash and Thakur OP (2003). Effect of samarium modification on structural and dielectric properties of PLZT ceramics. *Science Direct, Materials Letters* **57** 2310-2314.
Cross LE (1993). *Ferroelectric Ceramics: Tutorial Reviews, Theory, Processing and Applications* (Birkhauser verlag, Basel).
Gawali PG and Bongane BK (2013). Dielectric behaviour of some pulses using reflect metric technique at 9.85 GHz. *Indian Journal of Applied Research* **3**.
Gawali PG and Bongane BK (2014). Microwave dielectric properties of $(Ba_{0.5}\,Pb_{0.5})\,Tio_3$ With various temperature and particle sizes. *Bionano Frontier (communicated*).
Himanshu AK (2006). Dielectric Study of the barium zinc niobate, synthesized by solid reaction technique. *Indian Journal of Pure and Applied Physics* **391**.
James AR *et al.*, (2010). Chemical synthesis, structural, Thermo-Physical and electrical Property characterization of PLZT ceramics. *Journal of Alloys and Compounds* **496** 624-627.
Jihua Zhang and Chuanren Yang (2011). Microstructure and electrical properties of PLZT ceramics from Pb_3O_4 as the lead source. *Journal of Alloys and Compounds* **509** 2838-2841.
Lines ME and Glass AM (1977). *Principles and Applications of Ferroelectric and Related Materials* (Claredon press, Oxford).
Megaw HD (1957). *Ferroelectricity in Crystals* (Methuen, London).
Radheshyam Rai and Seema Sharma (2004). Structural and dielectric properties of Sb-doped PLZT ceramics. Ceramics International **30** 1295-1299.
Raju K and Venugopal Reddy P (2010). Synthesis and characterization of microwave processed PZT materials. *Current Applied Physics* **10** 31-35.
Ravindra Singh (2007). Preparation and characterization of ferroelectric / Piezoelectric thin films of PLZT/ ZnO and their integration with MEMS processing. M. Phil thesis, IIT Delhi.
Silva PS Jr And Gareiva D (2009). *Material Science and Engineering A.*
Stojanovic BD *et al.*, (2001). Microstructure of Organo metallic derived PLZT ceramics. *Journal of the European Ceramic Society* **21** 1491-1494.
Ukrit Chaimongkon and Theerachai Bongkarn (2011). The effects of firing temperatures and barium content on phase formation, microstructure and dielectric properties of lead barium titanate ceramics prepared via the combustion technique. *Current Applied Physics* **11** 570-576.
Wein–Duo Yang (2001). PZT / PLZT ceramics prepared by hydrolysis and condensation of acetate precursors. *Ceramics International* **27** 373-384.
Yadav JS and Gandhi JM (1992). Simple microwave technique for measuring the dielectric parameters and their powders. *Indian Journal of Pure and Applied Physics* **30** 427.