STM JOURNALS

**Research & Reviews: Journal of Physics**
ISSN: 2278-2265(online), ISSN: 2347-9973(print)
Volume 4, Issue 1
www.stmjournals.com

# Fabrication and Parametric Analysis of Thermal Sensing Dielectric PZT Thick Film Nano Ceramic Device Developed by SOL GEL Technique

***Kushal Roy****
Department of Electronics and Communication Engineering, Haldia Institute of Technology, ICARE Complex, PO HIT Haldia, West Bengal, India

## *Abstract*

*Extensive investigation carried out during earlier half of twentieth century, prominently established that the ionic radius of an atom gets reduced to significant levels with decrease in coordination number. The findings of Goldsmith and Pauling showed that ionic radii contracts by 4, 6 and 12% when coordination number is reduced from 12 to 8, 6 and 4 respectively. It is obvious that coordination number reduction takes place at the surface partly owing to surface tension phenomena. Recent past has seen extensive study in this field as it is realized that it plays a vital role in oxygen chemisorption, hence affecting various material properties when nano scaled particle size is considered. $Pb[Zr_x,Ti_{(1-x)}]O_3$, popularly known as PZT has remained a point of attraction for the scientists and researchers in the field of synthetically developed engineering material since its discovery by Jaffe et al. Last few decades have seen various devices like miniature relays, smart structures, memories etc., all utilizing, to a major extent the well-known piezoelectric and pyroelectric properties found in PZT. After being reported about various parametric changes in piezoelectric coefficient, polarization and dielectric constant K by addition of some foreign ions lead to the further classification of PZTs as hard and soft PZTs. As reported by various authors, soft PZTs have highly enhanced piezoelectric properties which makes them highly suitable for fabrication of various electrical and electronic devices owing to high gain and better response, but on the other hand hard PZTs are reported to have highly decreased dielectric constants and piezoelectric coefficients leading their incapability to serve as an effective material for fabrication of actuators. However a considerable linearity in the variation of K is reported in these hard doped materials, which can indirectly be utilized for other low gain and low response systems. It is also been reported that when miniaturizing a device, the grain size plays an important role in governing various parameters like dielectric constant, Curie temperature, polarization etc. of the composite material. Due to the complexity and various independent constraints involved, the origin of grain size effect is yet to be understood well . In the presented work, the author investigates the nature of variation in Curie temperature, dielectric constant, and polarization of the composite material $Pb[Zr_x,Ti_{(1-x)}]O_3$, for x=0.6, 0.7 and 0.8 and the effect of hard dopant $Mg^{+2}$, with an objective to develop a composite solid solution of hard doped PZT which can be used as a temperature sensing element, when incorporated in a capacitive arrangement using simple electronic circuitry. Some interesting results are hereby obtained when the variation of polarization, dielectric constant and Curie temperature is studied in detail with the variation in grain size.*

***Keywords****: PZT thermal sensors, XRD, hard doping, SOL-GEL fabrication technique*

**Author for Correspondence* E-mail: profkushalroy@hotmail.com

## INTRODUCTION

### Synthesis of $Pb[Zr_xTi_{1-x}]O_3$ Nanoceramics using Sol-Gel Technology Followed by Addition of Dopants

The synthesis of $Pb[Zr_xTi_{(1-x)}]O_3$ nanocramics is carried out by Sol-Gel process with the raw materials lead acetate trihydrate $Pb(CH_3COO)_2.3H_2O$, zirconium propoxide $Zr(C_3H_7O)_4$ and titanium iso-propoxide $Ti[(CH_3)_2CHO]_4$.

To start with, lead acetate is dissolved in acetic acid in proper stochiometric ratios for different values of x, (x=0.6, 07 and 0.8) and is heated

  

at 110°C for an hour to remove water and then cooled down to 70°C. With constant stirring using magnetic stirrer, zirconium propoxide followed by titanium isopropoxide is added in a calculated ration corresponding to x=0.6, 0.7 and 0.8 respectively, to the above mixture. Ethylene glycol is added to the above mixture in the ratio of 1 ml of glycol to 10 gm of lead acetate. The initial reaction had to be completed before glycol is added since residual zirconium propoxide and titanium isopropoxide alcolyze with glycol to form a condense solid [1]. A small amount of distilled water is added to get the final sol. The sol is kept at 70°C for 24 h to get the clear transparent gel. The gel is then dried in a controlled oven at 100°C for 48 h to get a light brown powder. The oven dried gel is calcined at 550°C for 5 h. After proper grinding the sample powders corresponding to different values of x that is $Pb[Zr_{0.6}Ti_{0.4}]O_3$, $Pb[Zr_{0.7}Ti_{0.3}]O_3$ and $Pb[Zr_{0.8}Ti_{0.2}]O_3$ are each divided into four parts by weight. To three parts 3, 5, 7 weight % MgO was added followed by proper mixing. The samples were cold pressed at a pressure of $6x10^7$ kg/m$^2$ using a hydraulic press to form disks shaped pallets 1–2 mm thick. These pallets were calcined at 700°C for 5 h, followed by sintering at 1300°C for 2 h. $PbZrO_3$ powder was used as a setter during sintering in order to prevent PbO loss or vaporization at higher temperatures. Density of each sample was calculated by dimensional measurement of thickness and diameter using precision Instruments.

## EXPERIMENTAL RESULTS AND DISCUSSIONS

### Determination of Lattice, Parameters and Nature of Curie Temperature Variation

Lattice parameter of each developed sample of $Pb[Zr_xTi_{(1-x)}]O_3$ corresponding to x=0.6, 0.7 and 0.8 are determined by well-known Scherrer's formula with the help of X ray Diffractograms shown in Figures 1(a), (b) and (c) respectively, thereby studying the nature of Curie temperature variation with the variation in grain size (N). Interestingly, it is noted by the author after studying the nature of variation, that the Curie temperature falls significantly, however the nature of fall is slow for N>15, but is drastic for N<15, where N is the number of layers. The lattice parameter, shown in Table 1 is approximately found to be 0.4 nm which is in accordance with the value reported by Glazer *et al.* [2]. Therefore the grain size for N=15 is about 12 nm. As shown in Figure 2 the nature confirms slight irregularity in the variation for the 80/20 composition near N=10 to 12 and nonlinear variation for N=30 and above. Therefore the composition PZT(80/20) is considered as unsuitable by the author for the fabrication.

***Table 1:*** *Lattice Parameters and Structures of the Samples Developed by the Dielectric Material as Uniform Variation of Curie Temperature is an Essential Requirement in Achieving the Desired Results.*

| Sample | Structure | Lattice Parameters |
|---|---|---|
| PZT (60/40) | Rhombohedral, a=b=c, $\alpha=\beta=\gamma\neq90^o$ | a=0.409(1) nm, $\alpha=\beta=\gamma=89.96(1)^o$ |
| PZT (70/30) | Rhombohedral, a=b=c, $\alpha=\beta=\gamma\neq90^o$ | a=0.400(2) nm, c=0.415(9)nm$\alpha=\beta=\gamma=89.86(5)^o$ |
| PZT (80/20) | Rhombohedral, a=b=c, $\alpha=\beta=\gamma\neq90^o$ | a=0.411(6) nm, c=0.405(1)nm$\alpha=\beta=\gamma=89.90(6)^o$ |

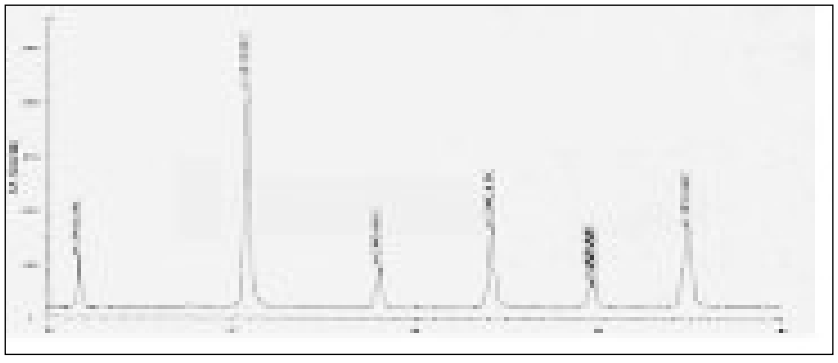

***Fig. 1(a):*** *XRD graph of PZT 70/30 Composition.*

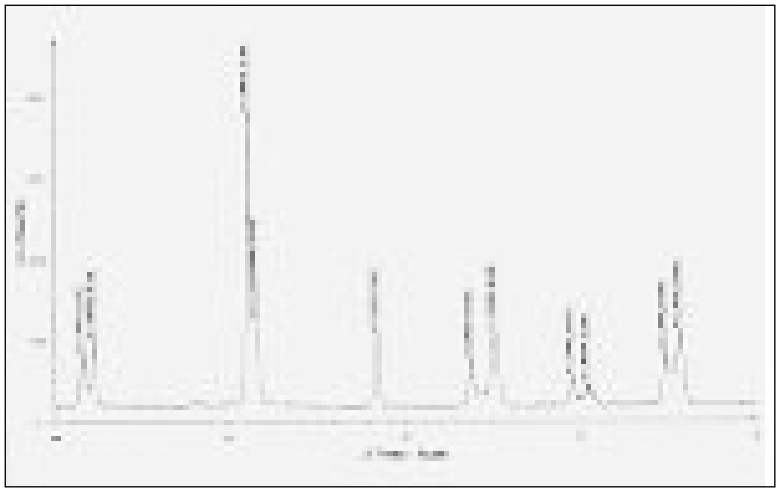

***Fig. 1(b)*** *XRD graph of PZT 60/40 composition*

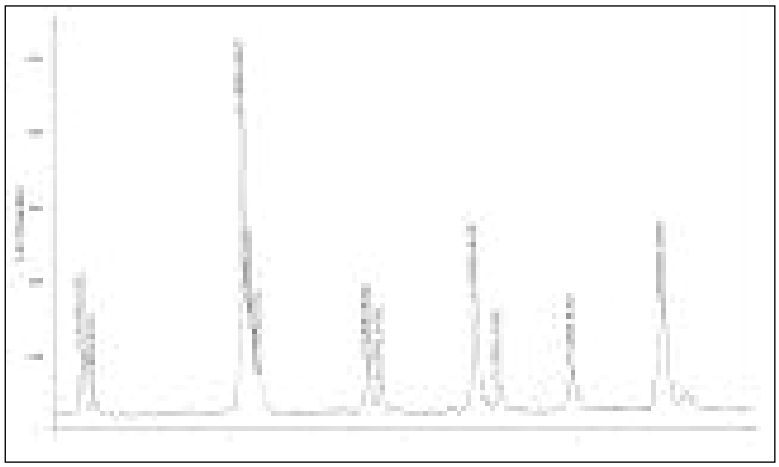

***Fig. 1(c)*** *XRD graph of PZT 80/20 composition*

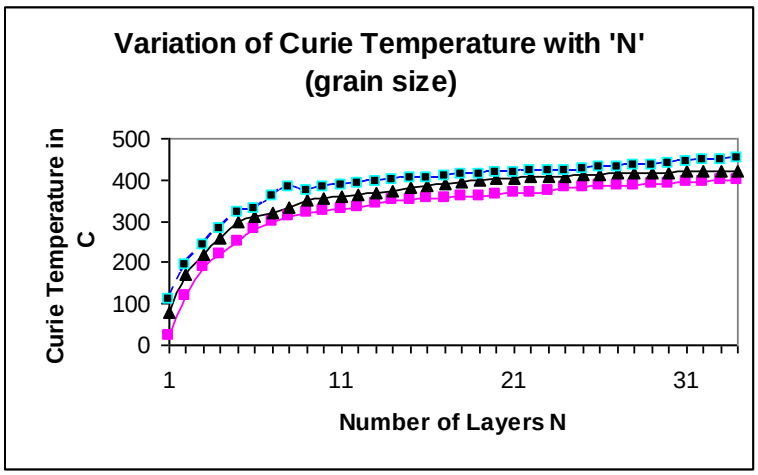


***Fig. 2:*** *Variation of Curie Temperature with N (Pink, Black and Green Denotes the Composition 60/40, 70/30 and 80/20 Respectively).*

**Study and Analysis of the Variation in Spontaneous Polarization with Grain Size**

For ferroelectric phase $F_T$ it has been well established by various authors that [3, 4]

$$P_1^2=P_2^2=0;\ P_3^2\neq 0 \quad (1)$$

Using the well-known LGD Theory we have;

$$P_3^2=-\alpha_{11}^2+[\alpha_{11}^2-3\alpha_{111}(\alpha_1-Q_h\sigma_p]^{1/2} \quad (2)$$

$$3\,\alpha_{111}$$

Where the values of $\alpha_{11}$, $\alpha_{111}$, $\alpha_1$, $Q_h$, $\sigma_p$ are obtained from the Gibb's Free Energy Function for $Pb[Zr_x,Ti_{(1-x)}]O_3$ given in Table 2.

***Table 2:*** *Values of the Coefficients of Gibbs Free Energy at 25°C for* $Pb[Zr_x,Ti_{(1-x)}]O_3$.

| Gibb's Coefficient | X=0.6 | X=0.7 | X=0.8 |
|---|---|---|---|
| $T_C(^OC)$ | 418.4 | 440.2 | 459.1 |
| $\alpha_1(10^7 mF^{-1})$ | –8.34 | –12.47 | –14.84 |
| $\alpha_{11}(10^7 m^5C^{-2}F^{-1})$ | 3.61 | 0.65 | –3.05 |
| $\alpha_{111}(10^8 m^9C^{-4}F^{-1})$ | 1.859 | 2.348 | 2.457 |

The room temperature spontaneous Polarization curve, with variation in N (grain Size) for different values of x is shown in the Figure 3.

After thorough study of the nature of spontaneous polarization variation with grain size for different prepared compositions it is observed that the composition 80/20 gives an anomalous behavior for N=22 to 28, within this region it is henceforth not suitable for achieving the desired objective. Whereas though the composition 60/40 gives nearly constant value on P for all N>10, but the initial value for N<10 falls very steeply in comparison to the composition 70/30, hence after thorough study and investigations of these variations, the best suitable composition considered by the author is corresponding to x=0.7; $Pb[Zr_{0.7},Ti_{0.3}]O_3$. Author would like to mention here that the variation of P with N follows the same trend as established by Chattopadhyay *et al.* for $PbTiO_3$ [5].

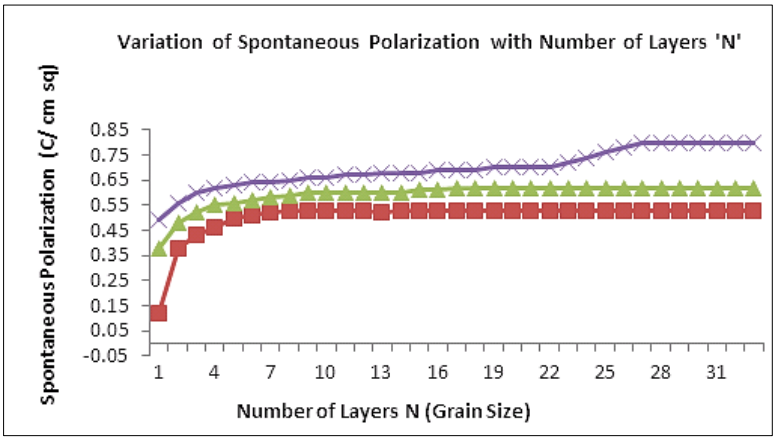


***Fig. 3:*** *Variation of Spontaneous Polarization with N (Pink, Yellow and Green Denotes the Composition 60/40, 70/30 and 80/20 Respectively).*

**Study and Analysis of the Variation of Dielectric Constant with N (Grain Size)**

Variation of Dielectric Constant K with grain size for different compositions is studied and plotted in Figure 4. this curve confirms that the choice of the material composition as mentioned above by the author is appropriate out of the three compositions corresponding to x=0.6, 07 and 0.8 chosen.

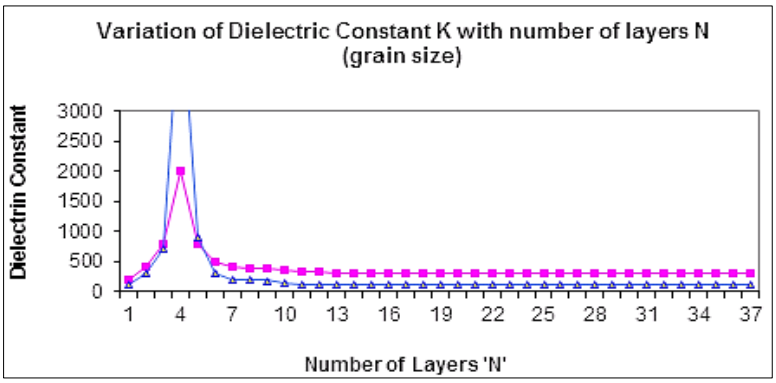


***Fig. 4:*** *Variation of Dielectric Constant K with N (Pink and Blue Corresponding to the Composition 60/40 and 70/30 Respectively).*

As observed from the curve, the value of the dielectric constant from N=3 to 6 gives anomalously high value for the composition corresponding to x=0.6, whereas in comparison though the value of dielectric constant value is very high for x=0.7, (approximately 2000), still remains within the measurable range. It has been established by various authors that $Pb[Zr_xTi_{(1-x)}]O_3$ has a non-linear variation of dielectric constant with temperature [6], which further increases by addition of soft dopants. This enhanced non linearity in dielectric constant is not desirous for designing of temperature sensors, hence author in this paper investigates the effect of hard doping of $Mg^{+2}$ on the chosen sample corresponding to x=0.7, that is $Pb[Zr_{0.7},Ti_{0.3}]O_3$.

**Study and Analysis of the Variation of Dielectric Constant with Temperature**

The sample $Pb[Zr_{0.7},Ti_{0.3}]O_3$ is variably doped with 3, 5 and 7 weight % $Mg^{+2}$ and the results obtained is shown in Figure 5. It is observed that with increase in percentage doping of $Mg^{+2}$, the value of dielectric constant K falls significantly when compared with the undoped sample, with a significant increase in linearity. At 7% $Mg^{+2}$ doping; the material gives linear variation over a wide range of temperature, and interestingly the room temperature dielectric constant variation follows the same nature as the variation of density of the sample as shown in Figure 6. This is further confirmed from the SEM microphotographs of the sample $Pb[Zr_xTi_{(1-x)}]O_3$.

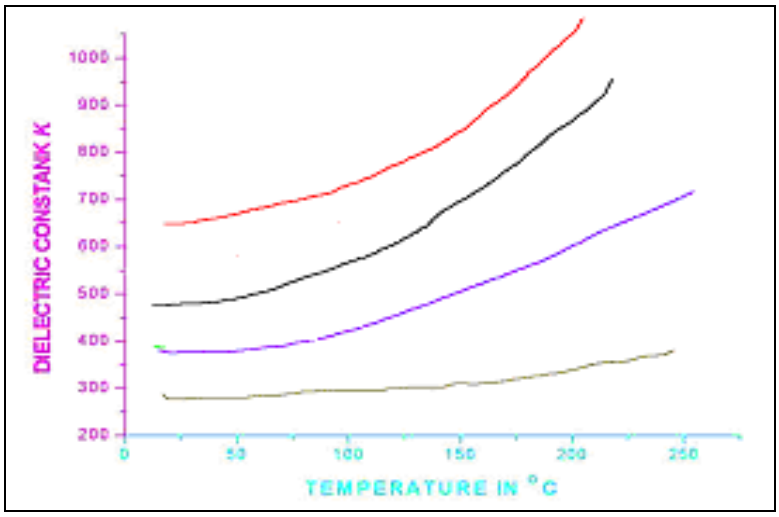


***Fig. 5:*** *Variation of Dielectric Constant K with Temperature (Red, Black, Violet and Brown Curves Corresponds to the Undoped, 3%, 5%, 7% Doped Samples Respectively).*

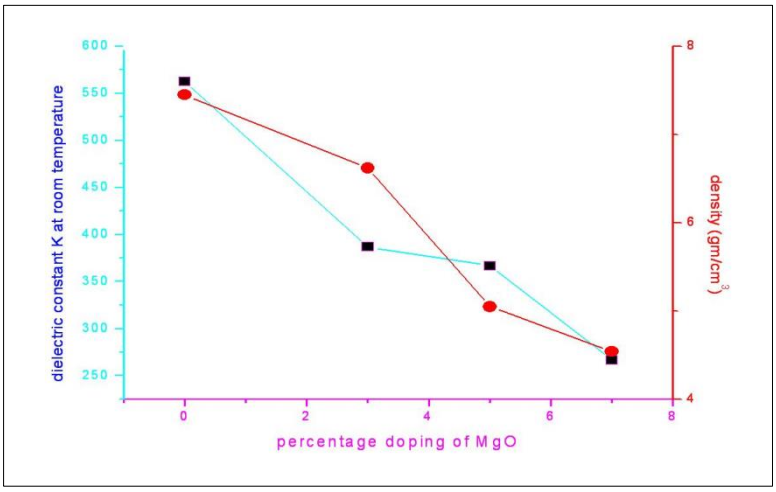


***Fig. 6:*** *The Green and Red Curves Corresponds to Variation of K and Density in gm/cc Respectively with Percentage Doping.*

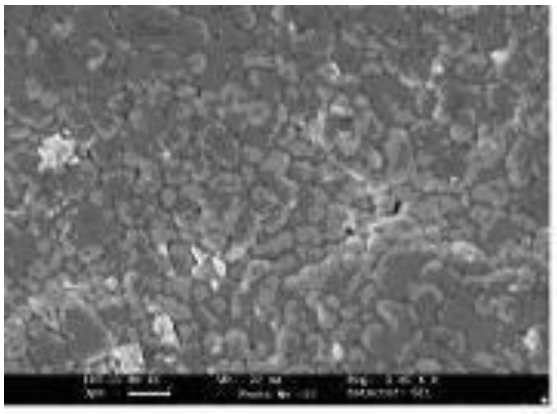

***Fig. 7:*** *SEM Microphotograph of* $Pb[Zr0.7,Ti0.3]O_3$.

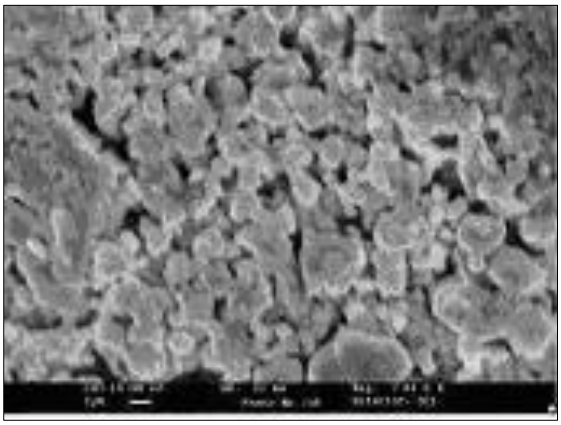

***Fig. 8:*** *SEM Microphotograph of* $Pb[Zr_{0.7},Ti_{0.3}]O_3$ *Doped with 7%* $Mg^{+2}$.

After close investigation the SEM photographs shown in Figures 7 and 8 confirm the reason for the fall in dielectric constant values and density of the samples, as it is clearly visible that the $Pb[Zr_{0.7}Ti_{0.3}]O_3$ has well defined grain boundaries and the domains are well packed whereas for the sample $Pb[Zr_{0.7}Ti_{0.3}]O_3$ doped with 7% $Mg^{+2}$ the packing of domains is loose with considerable porosity.

## CONCLUSION

It is finally concluded that all the samples of $Pb[Zr_x,Ti_{(1-x)}]O_3$ for x=0.6, 0.7 and 0.8 synthesized by Sol-Gel process are homogeneous and formed in single rhombohedral phase. The sample corresponding to x=0.7 is highly compact, dense and have well defined grain boundaries as seen from the SEM microphotographs (Figure 7) and after thoroughly studying the results obtained from various experiments the author confirms that the composition corresponding to x=0.7, $Pb[Zr_{0.7}Ti_{0.3}]O_3$ is best suited as base material for the high dielectric constant makes it suitable for dielectric capacitor applications. Variable $Mg^{+2}$ doping decreases the dielectric constant values considerably. Also it is evident from Figure 5, that though the dielectric constant decreases significantly on increasing the doping percentage of $Mg^{+2}$ there is significant improvement of linearity in the variation of dielectric constant with temperature, this is of great significance in designing thermal sensors as the complexity involved in the electronic circuitry to compensate for the non linearity can be reduced to significant level. Out of all samples 7% $Mg^{+2}$ doped PZT is found to be best suitable and optimum among all the samples developed, for the development of a dielectric material which, if incorporated in capacitor type configuration can effectively serve as efficient thermal sensors, with a view to its linear variation of K over a wide range of temperature of 25–250$^{o}$C. However the author would like to mention here that the percentage doping of $Mg^{+2}$ cannot be increased beyond a certain level as it may affect adversely the sensitivity and resolution of the temperature measurement system due to extremely less value of dielectric constant 'K'.

## ACKNOWLEDGEMENTS

The author would like to thank Dr. K.L. Yadav Asst. Professor, Dept. of Applied Physics for providing the Research Scheme and to Institute Instrumentation Center, Indian Institute of Technology Roorkee for SEM and XRD Instrumentations. Also author would like to express his sincere gratitude to all departments of Haldia Institute of Technology, Haldia W.B. for extending his cooperation in the above presented work.

## REFERENCES

1. Goldsmith VM. *Ber. Deut. Chem. Ges*. 1927; 60:1270p.
2. Glazer AM, Mabud SA. *Acta Crystallogr. B.* 1978; 38: 1060p.
3. Pauling L. *J. Am. Ceram. Soc.* 1947; 69: 542p.
4. Cross LE. *Ferroelectric Ceramics-Tutorial Reviews, Theory, Processing and Applications*. Setter N, Colla EL. (Ed.), Birkhauser Verlag, Basel. 1993.

5. Shannigrahi SR, Choudhary RNP, Acharya HN, *et al. J. Appl. Phys*. 1999; 85(3): 1713–1720p.
6. Haung C-L, *et al. Solid State Communication, Elsevier*. 2003.

## AUTHOR BIBLIOGRAPHY

Born December the 13th 1979, Graduated in the year 2002, gold medalist, **B.E.Tel.E (*Hons*.)** from Government Engineering College Ujjain, Madhya Pradesh. All India first Rank holder in, 'Post Graduate Studies and Research **(PGS&R)** Entrance Examination, henceforth post graduated in the year 2004 from Indian Institute of Technology, Roorkee 247667, Uttarakhand, India with **M. Instrumentation. Phil** Degree. Currently **pursuing extensive research for his PhD** in the field of Nano Material Technology. The author has **four** Research Papers in the related area, out of which **3** are in renowned International Conferences like **IEEE-ISIC-07**, Hotel Orchard **Singapore** (September 2007), **IEEE METAMATERIALS Congress, Rome**, Italy (October 2007) etc. Other than Nano Material Fabrication Technology, author also possesses immense interest in **Cosmology.**

**Cite this Article**
Kushal Roy. Fabrication and Parametric Analysis of Thermal Sensing Dielectric PZT Thick Film Nano Ceramic Device Developed by SOL GEL Technique. *Research & Reviews: Journal of Physics*. 2015; 4(1): 31–37p.

  