Structural and Dielectrical Properties of Nb-doped PZTN Ceramics

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Polycrystalline samples of PZTN with the compositions $Pb_{1.1-x/2}$ $(Zr_{0.53}$ $Ti_{0.47})_{1-x}$ Nb_xO_3 (where x=0.00, 0.01, 0.02, 0.03, 0.04, and 0.05) has been prepared by solid state reaction method. X-ray diffraction studies suggest that the compounds are in rhombohedral phase. Pyrochlore value and surface morphology was studied by scanning electron microscope (SEM). Detailed studies of dielectric constants as a function of temperature (40°C-500°C) and frequency (100Hz-1MHz) suggest that the compound do not have relaxor behavior and undergoes diffuse type of phase transition.

Keywords: Dielectric, ceramics, XRD, SEM.

1. INTRODUCTION

Since the discovery of ferroelectric ceramics in 1950s, lead-based perovskites have emerged as one of the most widely studied and technologically important classes of ferroelectric oxides. Among these, the lead zirconate (PZT) perovskite ferroelectric ceramic of general formula ABO_3 (A=mono or divalent, B= tri, tetra or penta-valent cations) is an excellent material for device applications [1-4]. In the Past, a considerable amount of work has been done to study the effect of various dopants in varying concentrations (x) at the A and B sites of PZT [5-8] and to modify the properties of the material for different piezoelectric devices. The majority of the dopants were iso-valent, super-valent and sub-valent as no work on the effect of double doping with different ions at Pb^{+2} sites (a) and structural and dielectric properties has been done [9]. We, present here our study on the $Pb_{1.1-x/2}$ $(Zr_{0.53}$ $Ti_{0.47})_{1-x}$ Nb_xO_3 (where x=0.00, 0.01, 0.02,0.03, 0.04, and 0.05). Also, some of the critical properties of PZT were optimized by the addition of Nb^{5+}, can be considered as donor dopant PZT materials [10].

2. EXPERIMENT

The compositions $Pb_{1.1-x/2}$ $(Zr_{0.53}$ $Ti_{0.47})_{1-x}$ Nb_xO_3 (where x=0.00, 0.01, 0.02,0.03, 0.04, and 0.05) were prepared by solid state reaction method, using analytical grade reagents PbO, ZrO_2, TiO_2, and Nb_2O_3 as starting materials. The stoichiometric amounts of individual reagents were homogeneously mixed in an agate mortar with acetone media to achieve a fine powder. The well mixed powder was then calcined at 1000^0C for 3 hours in an alumina crucible. Calcined powder was pressed into circular pellets of 1-2 mm thick and 7mm

diameter at pressure of 19×10^6 N/m^2 using uniaxial hydraulic press. These pellets were then sintered at 1100^0C for 3 hours. Crystal structure and phase identification of sintered pellets was carried out by X-ray diffractometer (Bruker D8 Advance) using Cu-Kα radiation (λ=1.5418 A^0) and microstructure was analyzed by using scanning electron microscope (LEO 435 VP). Lattice parameter were also calculated and refined using least square method. Sintered pellets were polished, silver pasted on both the sides and then dried at 200^0C for 30 minutes before measurements. Dielectric measurements were conducted on an automated HIOKI 3522.50 LCR meter. Dielectric permittivity was measured in the frequency range 100Hz-1MHz as a function of temperature in a temperature range 40^{o}C-500^{o}C, where the sample undergoes the ferroelectric to para-electric phase transition.

3. RESULTS AND DISCUSSIONS

The phase formation of the sintered $Pb_{1.1-x/2}$ $(Zr_{0.53}$ $Ti_{0.47})_{1-x}$ Nb_xO_3 (Where x=0.00, 0.01, 0.02, 0.03, 0.04, and 0.05) ceramics is revealed by X-ray diffraction (XRD) shown in Figure 1. All the XRD peaks of six different doped PZT compounds are similar to the results obtained earlier [11,12]. All these observations are found to be consistent. The linear particle size (P) has been calculated from the strong reflection peak using the Scherrie's equation and data is reported in Table 1, $P=K\lambda/\beta_{1/2}\cos\theta$ where K=0.89, and $\beta_{1/2}$ = half width. The decrease in particle size broadens the dielectric peak [13], and increase in pyrochlore phase value. Surface morphology was studied by scanning electron microscope (SEM), the sample were broken/coated with gold and placed in vacuum (10-5 torr) chamber of the electron microscope.

A typical scanning electron microscope of flat surface of the investigated ceramic (where x=0.00, 0.01, 0.02, 0.03, 0.04, and 0.05) is shown in Figure 2.The average grain size determined by linear interception method is given in Table 1.

It was observed from the results that grain size decreases and increases from x =0.00, 0.01, 0.02, 0.03, 0.04, and 0.05. Figure 3 shows the variations of dielectric constant (ε) with temperature for all the six compositions doped PZTN. The dielectric constant of all compositions was found to increase with increasing temperature up to a value, called transition temperature (T_c) and thereafter it decreases. The T_c was found to be different for all six compositions. Also, the T_c was found to be independent of measured frequency (100Hz-1MHz). However, the magnitude of dielectric constant was found to be highly depending on both doping and measured frequency range [14-16]. Detailed studies of this phenomenon were carried out by Isupov [17]. Figure 4 shows the variation of dielectric loss tan(δ) with temperature (40^{o}C-500^{o}C) at (100 Hz—1MHz) for the different doped PZTN compositions. The dielectric loss was found to be very small and decreasing with frequency. Also, above 400^{o}C, a sharp increase in tan(δ) was observed. This growth in tan(δ) is due to an increase in both conduction of residual as well as absorption currents [18-20]. In polar substances, apart from dipole losses due to electrical conduction which increase with temperature, dielectric losses are present.

Table 1: Structural Parameters of doped $Pb_{1.1-x/2}$ $(Zr_{0.53}$ $Ti_{0.47})_{1-x}$ Nb_xO_3.

x Composition	A (A^0)	α (^{0})	Density gm/cm^3	Particle Size SEM (μm)	Particle Size XRD (nm)	Pyrochlore value Δ %
A, x=0.00	5.06551	91.79	5.286	1.51	15.368	4.03
B, x=0.01	5.04454	91.98	5.512	1.31	15.31	6.71
C, x=0.02	4.91944	91.13	5.420	1.48	13.146	8.33
D, x=0.03	5.06720	91.75	5.934	1.45	11.728	15.39
E, x=0.04	5.06720	91.91	5.804	1.25	14.416	14.38
F, x=0.05	5.06939	91.12	5.337	1.38	14.418	16.18

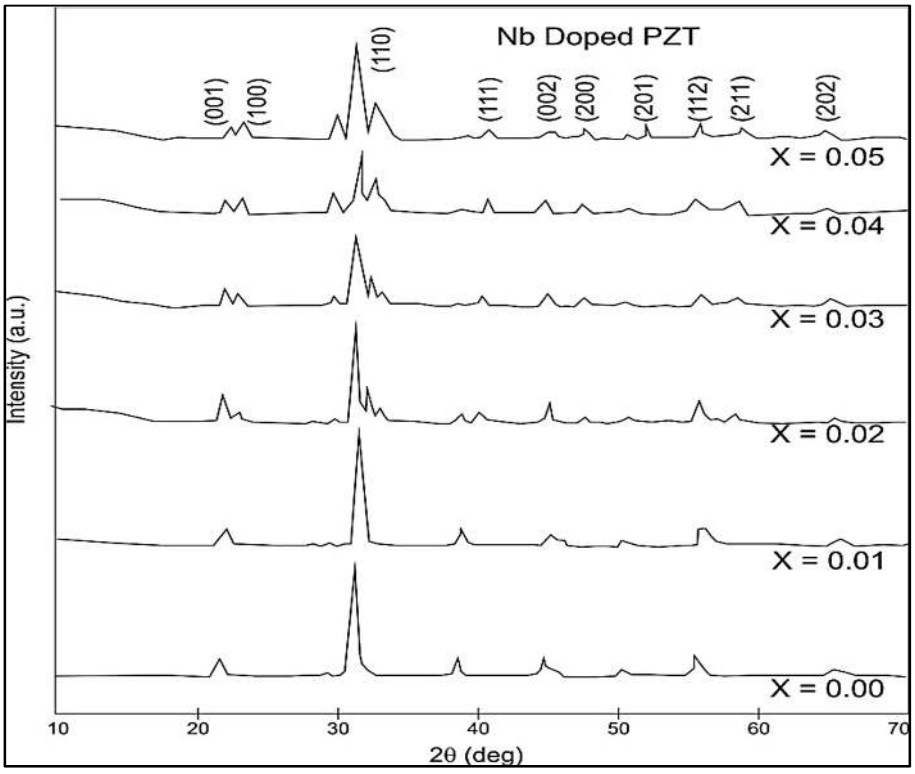


Fig. 1: XRD of $Pb_{1.1-x/2}$ $(Zr_{0.53}$ $Ti_{0.47})_{1-x}$ Nb_xO_3 Calcined at 1000 ^{0}C for 3 hrs.

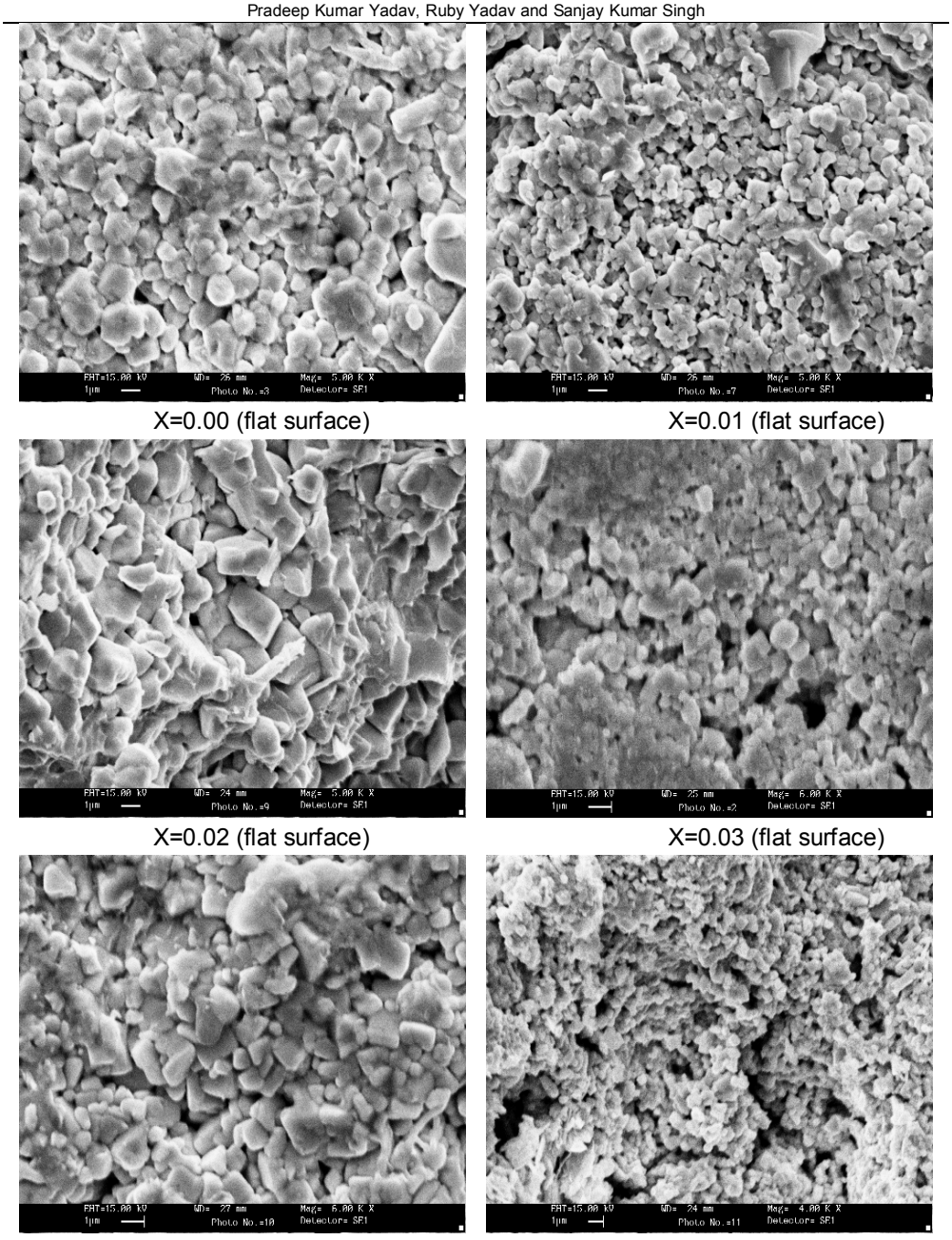
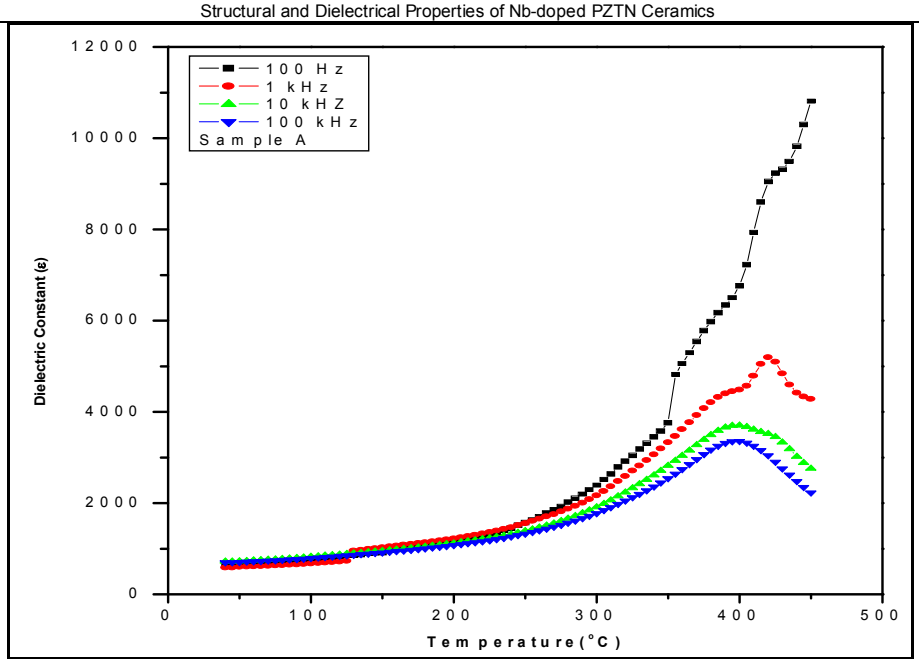
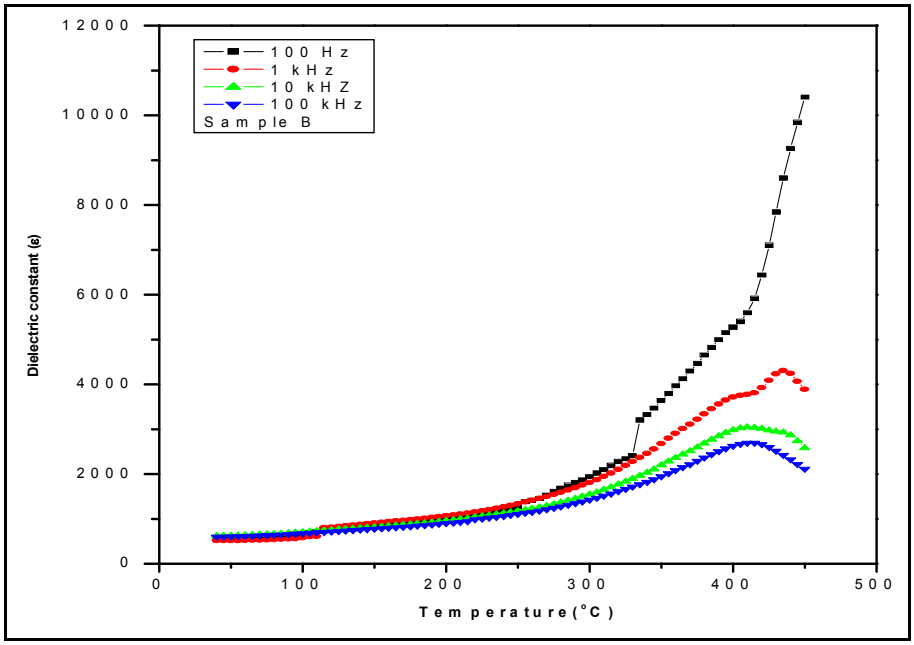
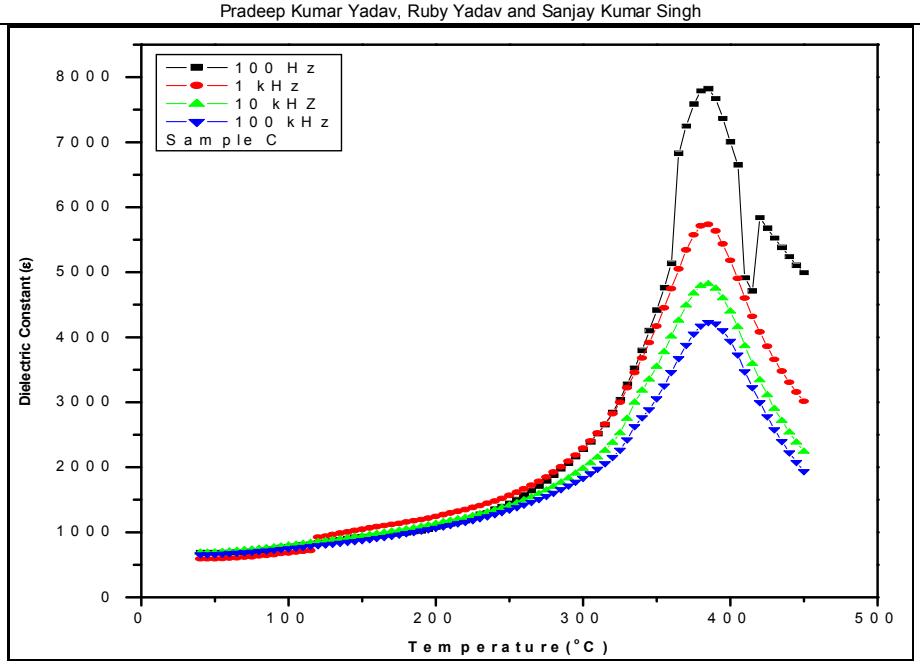
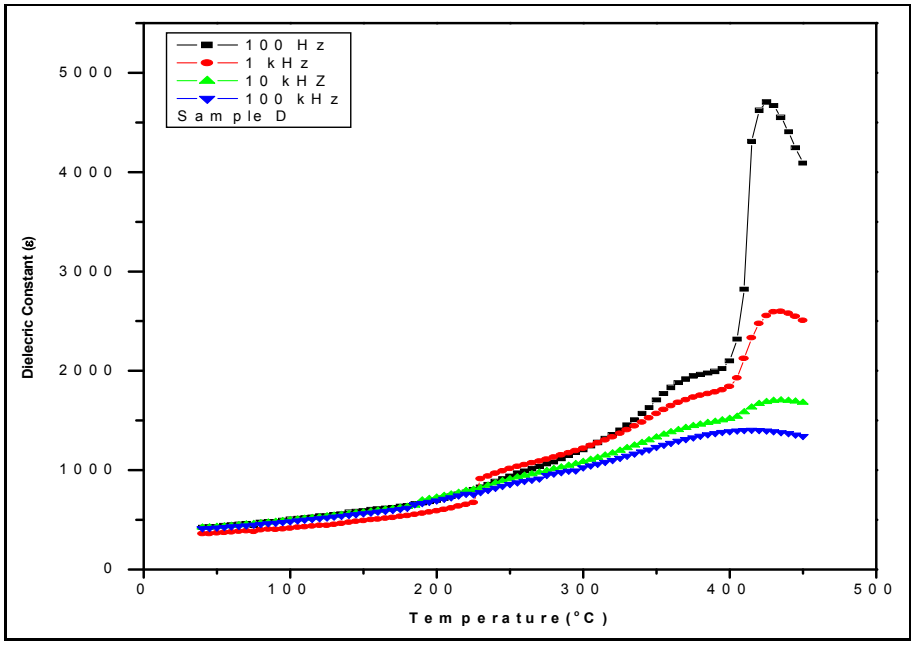


Fig. 2: SEM of $Pb_{1.1-x/2}(Zr_{0.53}\ Ti_{0.47})_{1-x}\ Nb_xO_3$ sintered at 1200^0C for 3 hrs.


12000
10000
8000
6000
4000
2000
0
100 Hz
1 kHz
10 kHZ
100 kHz
Sample A
Dielectric Constant (ε)
0
100
200
300
400
500
Temperature(°C)


12000
10000
8000
6000
4000
2000
0
100 Hz
1 kHz
10 kHZ
100 kHz
Sample B
Dielectric constant (ε)
0
100
200
300
400
500
Temperature(°C)


100 Hz
1 kHz
10 kHZ
100 kHz
Sample C
Dielectric Constant (ε)
Temperature(°C)
0
1000
2000
3000
4000
5000
6000
7000
8000
0
100
200
300
400
500


100 Hz
1 kHz
10 kHZ
100 kHz
Sample D
Dielecric Constant (ε)
Temperature(°C)
0
1000
2000
3000
4000
5000
0
100
200
300
400
500

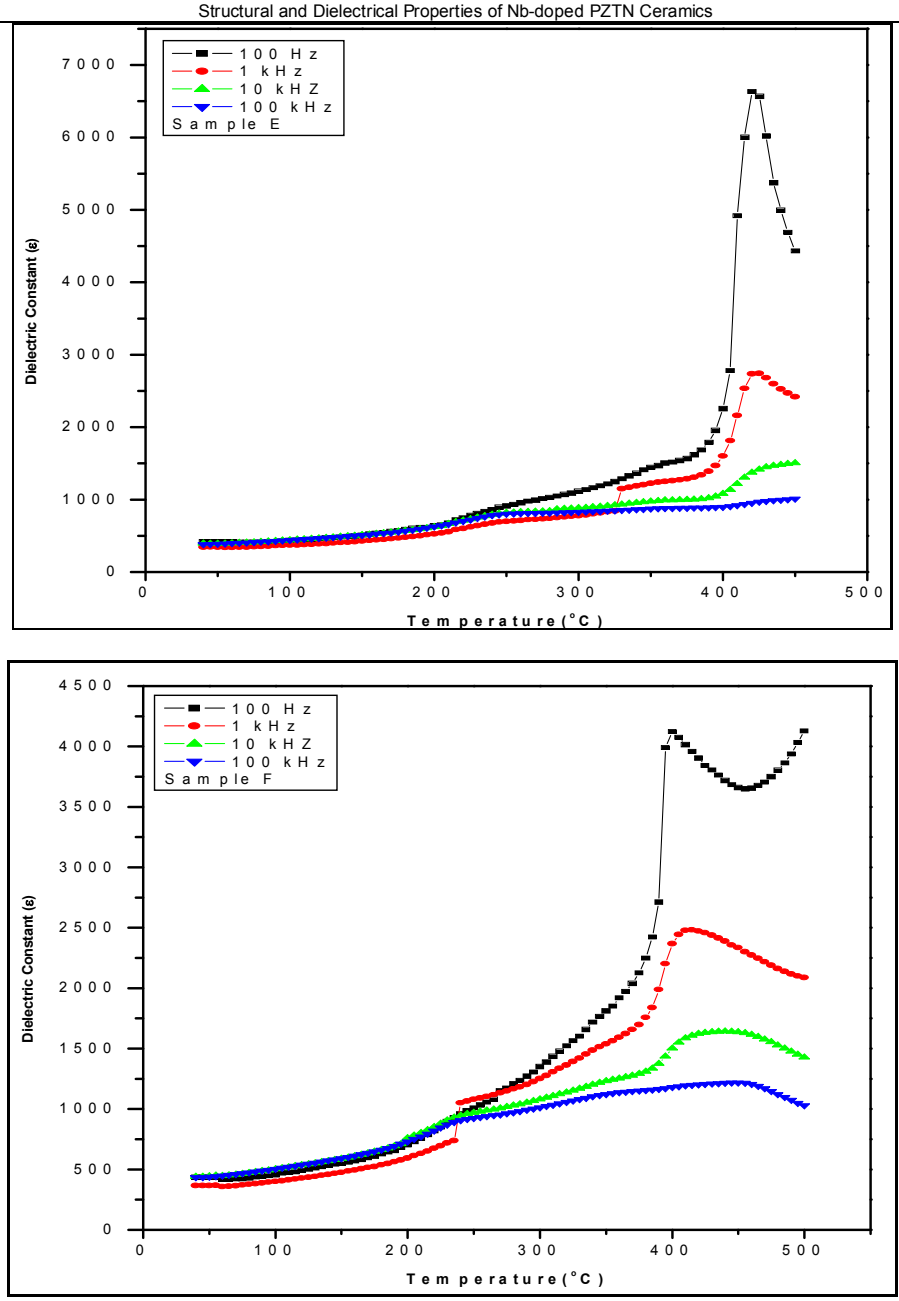
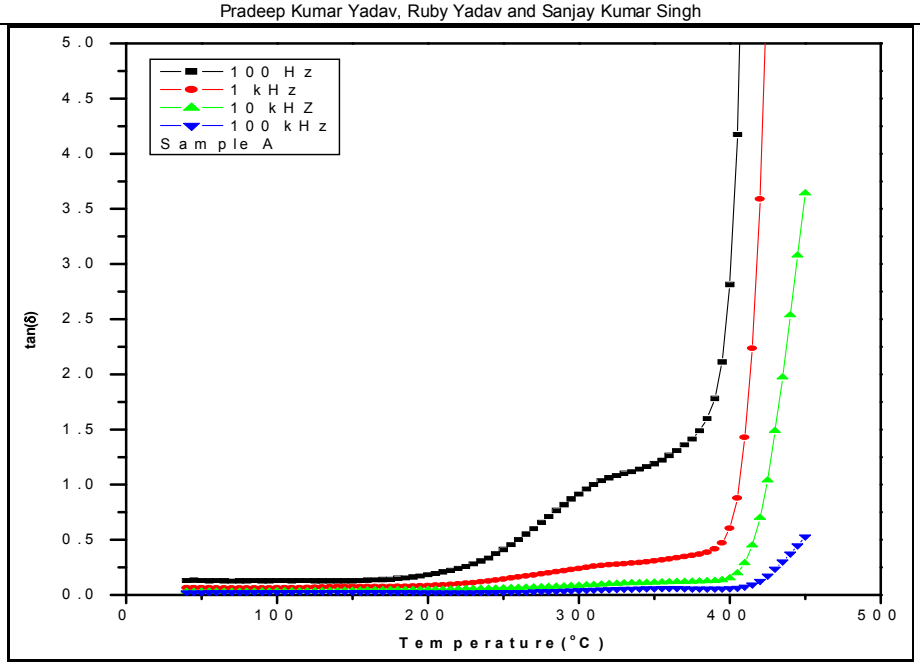
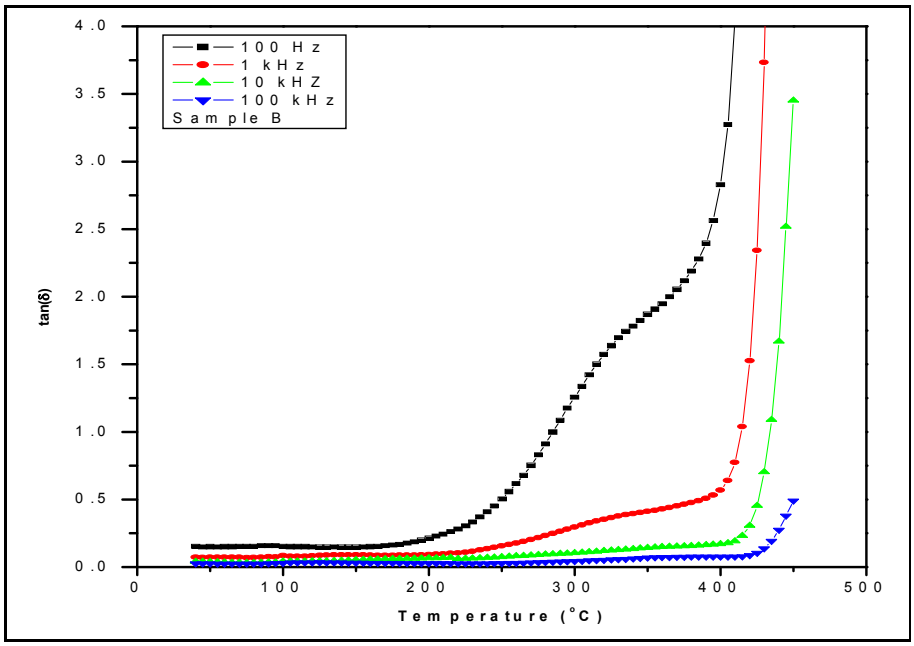
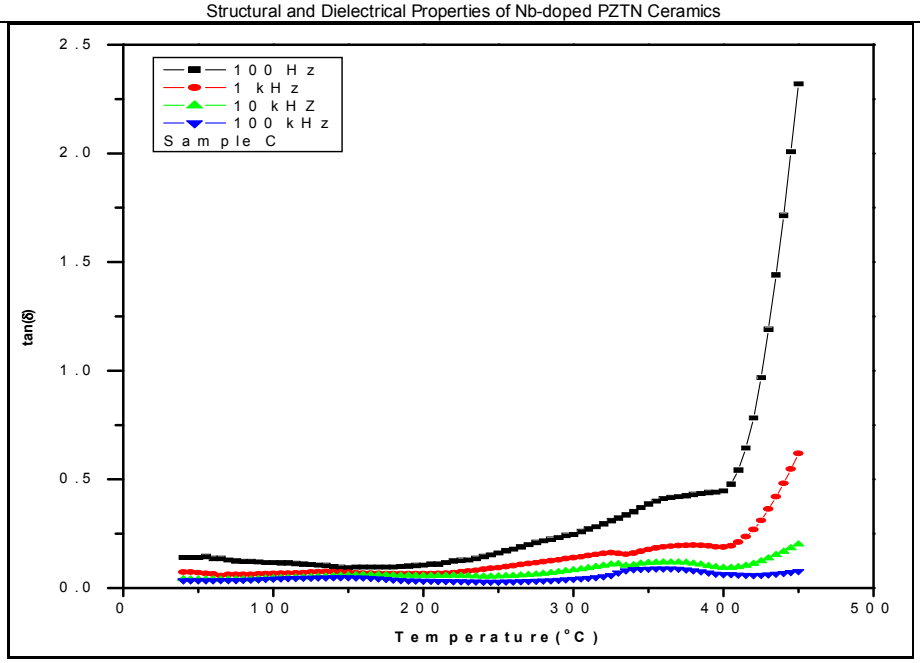
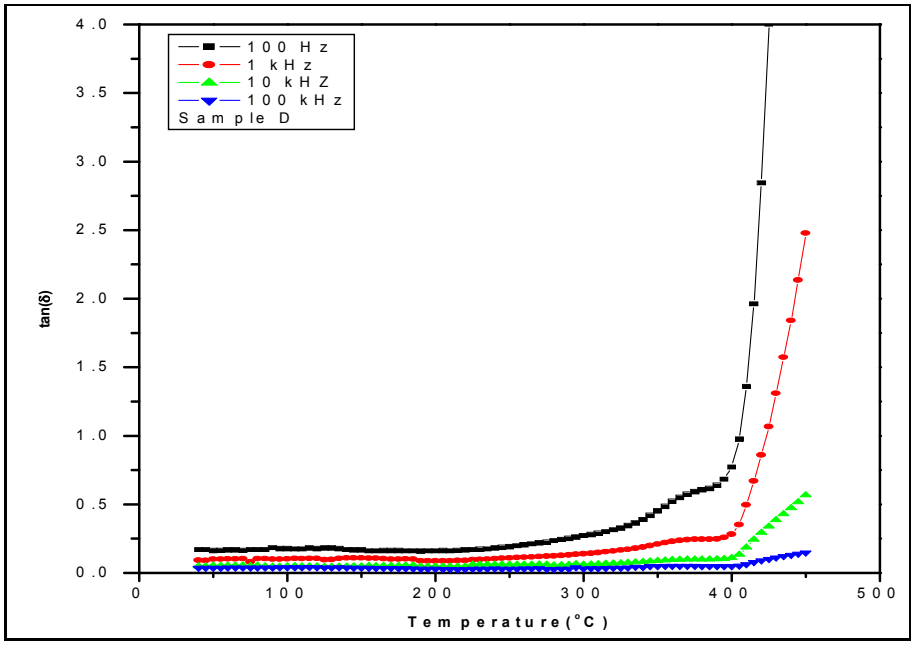


Fig. 3: Dielectric constant of $Pb_{1.1-x/2}(Zr_{0.53}Ti_{0.47})_{1-x}Nb_xO_3$ as a function of temperature at different frequencies (where x=0.00, 0.01, 0.02, 0.03, 0.04, and 0.05 respectively).


100 Hz
1 kHz
10 kHZ
100 kHz
Sample A
tan(δ)
Temperature(°C)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500


100 Hz
1 kHz
10 kHZ
100 kHz
Sample B
tan(δ)
Temperature (°C)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500


100 Hz
1 kHz
10 kHZ
100 kHz
Sample C
tan(δ)
Temperature(°C)
0.0
0.5
1.0
1.5
2.0
2.5
0
100
200
300
400
500


100 Hz
1 kHz
10 kHZ
100 kHz
Sample D
tan(δ)
Temperature(°C)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
0
100
200
300
400
500

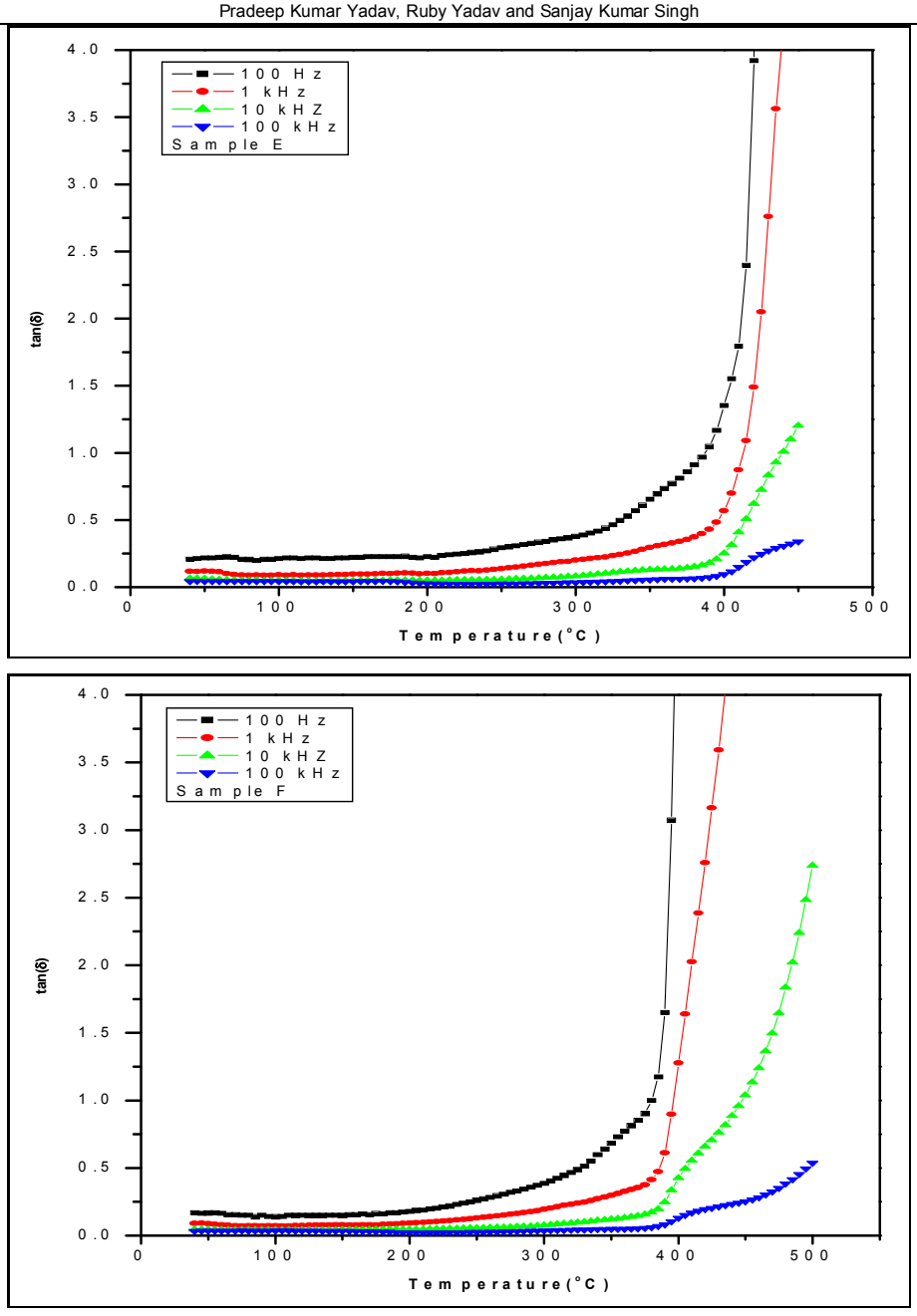


Fig. 4: Dielectric loss in $Pb_{1.1-x/2}(Zr_{0.53}Ti_{0.47})_{1-x}Nb_xO_3$ vs temperature at different frequencies (where x=0.00, 0.01, 0.02, 0.03, 0.04, and 0.05 respectively).

4. CONCLUSION

The effect of Nb doping on structural and dielectric properties of PZT, has observed single phase rhombohedral structure, some pyrochlore phases, size of x-ray, size of SEM and detailed studies of dielectric constant and losses as a function of temperature (40^{o}C-500^{o}C) and frequency (100Hz-1MHz). The present study suggests that the compounds do not have relaxor behavior and undergoes diffuse type of phase transition.

REFERENCES

[1] J.M. Herbert; “Ferroelectric Transducers and Sensors”, Gordon and Breach Science Publishers, London, pp. 299-300, 1982.

[2] C. Kittel; “Domain boundary motion in ferroelectric crystals and the dielectric constant at high frequency”, Phys. Rev, Vol. 83(2), pp. 458, 1951. DOI: 10.1103/Phys.Rev.83.458.

[3] J.F Scott; “Ferroelectric Memories”, Springers, Berlin, 2000.

[4] B. Jaffe, W.R. Cook Jr. and H. Jaffe; “Piezoelectric Ceramics”, Academic press, London & New York, 1971.

[5] N. Setter and E.L. Colla (*Eds.*); “Ferroelectric ceramics: Tutorial review theory, processing and applications”, 1st Ed. Birkhauser Verlag, Basel, 1993.

[6] S. Yokoyama, Y. Ito, K. Ishihara, K. Hamada, S. Ohnishi, J. Kudo and K. Sakiyama; “High Temperature etching of PZT/PE/TiN structure by high density ECR plasma”, Japan J. Appl. Phys, Vol. 34(2B), pp. 767, 1995.

[7] D.L. Polla and L.F. Francis; “Ferroelectric Thin Films in Micro-electromechanical Systems Applications”, MRS Bulletin, Vol. 21, pp. 59-65, 1996.

[8] N. Neumann, R. Kohler and G. Hofmann; “Pyroelectric thin Film sensors and arrays based on P(VDF/TrFE)”, Integrated Ferroelectrics, Vol. 6(1-4), pp. 213-230, 1995. DOI: 10.1080/10584589508019366

[9] G.H. Haertling; “Ferroelectric ceramics: History and Technology”, J. Am. Ceram. Soc., Vol. 82(4), pp. 797-818, 1999.

[10] S.B. Majumdar, B. Roy, R.S. Katiyar and S.B. Krupanidhi; “Effect of neodymium (Nd) doping on the dielectric and ferroelectric characteristics of Sol-gel derived lead zirconate titanate (53/47) thin films”, J. Appl Phys, Vol. 90(6), pp. 2975, 2001.

[11] A.K. Saha, D. Kumar, O. Prakash, A. Sen and H.S. Maiti; “Effect of Phosphorus edition on the sintering and dielectric properties of Pb ($Zr_{0.52}$ $Ti_{0.48}$)O_3”, Materials Res. Bull., Vol. 38(7), pp. 1165-1174, 2003.

[12] C. Pramila, T.C. Goel and P.K.C. Pillai; "Piezoelectric, Pyroelectric and Dielectric properties of La- and Sn- doped PZT ceramics", Mater. Sci. Lett., Vol. 12(21), pp. 1657-1658, 1993.

[13] D.L. Corker, R.W. Whatmore, E. Ringaard and W.W. Wolny; "Liquid Phase sintering of PZT ceramics", J. Eur. Ceram. Soc., Vol. 20(12), pp. 2039-2045, 2000.

[14] J.G. Wan, X.W. Wang, Y.J. Wu, M. Zeng, Y. Wang, H. Jiang, W.Q. Zhou, G.H. Wang and J.M. Liu; "Magnetoelectric $CoFe_2O_4$-$Ph(Zr,Ti)O_3$ composite thin films derived by a sol-gel process", Appl. Phys. Lett., Vol. 86, pp. 122501, 2005.

[15] X.X. Wang, K. Murakami, O. Sugiyama and S. Kaneko; "Piezoelectric properties, densification behaviour and microstructural evolution of low temperature sintered PZT ceramic with sintering aids", J. Eur. Ceram. Soc., Vol. 21(10-11), pp. 1367-1370, 2001.

[16] V.A. Isupov, "Some problems of diffuse ferroelectric phase transitions", Ferroelectrics, Vol. 90(1), pp. 113-118, 1989.

[17] H.J. Hwang, M. Yasuoka, M. Sando and M. Toriyama; "Fabrication, sinterability and mechanical properties of Lead Zirconate Titanate/Silver composites", J. Am. Ceram. Soc., Vol. 82 (9), pp. 2417-2422, 1999.

[18] T. Hayashi, T. Inoue and Y Akiyama; "Low temperature sintering and properties of (Pb, Ba Sr) (Zr, Ti, Sb) O_3, piezoelectric ceramics using sintering aids", Jpn. J. Appl. Phys., Vol. 38(9S), pp. 5549, 1999.

[19] D. Viehland, M. Wuttig and L.E. Cross; "The glassy behaviour of relaxor ferroelectrics", Ferroelectrics, Vol. 120(1), pp. 71-77, 1991.

[20] S. Ke, H. Huang and H. Fan, "Relaxor behaviour in $CaCu_3Ti_4O_{12}$ ceramics", Appl. Phys. Lett., Vol. 89(18), pp. 182904, 2006. DOI:10.1063/1.2374682