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Study of structural, dielectric and electrical properties of sol-gel prepared Zr-modified $BaTiO_3$ ceramic

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ABSTRACT

Polycrystalline samples of Zr doped $BaTiO_3$ with a general formula $Ba(Zr_x Ti_{1-x}) O_3$(x =0.0, 0.05,0.1, 0.2) have been synthesized by sol-gel technique. Structural analysis of the compound shows that there is a slight distortion in the perovskite crystal on Zr doping at Ti -site. Detailed analysis of dielectric constant(E_R) and dissipation factor (tan δ) at different temperatures (room temperature to 200^{0}C) at 10kHz, 100kHz, 1MHz and frequencies(100Hz to 4MHz) shows little relaxor type behavior upto 10 atomic percent Zr doping at Ti-site. A diffuse phase transition is observed in these compositions. D.C. resistivity after Tc shows a slight temperature dependence indicating suitable for temperature sensitive detector. Higher amount of Zr diminishes Ferro-electric property. The competition between randomness and interaction between the polar micro-grains may be the cause of temperature independent of resistivity at higher temperature.

INTRODUCTION

Some ferroelectrics with perovskite structure of general formula ABO_3(A=mono or di, B= tri, tetra or pentavalent ions) have a great technological importance because of their potential applications as dynamical and non-volatile memory components, transducers, sensors and many other active and passive devices. It has been found that the desired device parameters can be obtained by suitable doping of single or multi - elements at A and/or B-site of the perovskite compounds satisfying the following conditions (i) charge neutrality and (ii) tolerance factor t[1] as

$$t = \overline{Y_A} + \overline{Y_O} / \gamma 2\overline{Y_B} + \overline{Y_O} \quad (1)$$

Where Y^-_A is the average ionic radius of A- site atoms, Y^-_B is the average ionic radius of B-site atoms and r_0 is the ionic radius of O^{2-}. To satisfy perovskite structure t should be within the range of 0.8=t=1.1. Barium titanate ($BaTiO_3$), an important member of ABO_3) family, is to date the most extensively investigated ferroelectric material. It is extremely interesting from the viewpoint of the solid state scientist because its structure is far simpler than that of any other ferroelectric known so far thus offering a great promise for better understanding of the ferroelectric phenomenon. $BaTiO_3$ with suitable substitution at Ba-site was found to have semiconducting and PTCR (positive temperature coefficient of resistance) properties. Although a lot of work[2-3] has been done on Ba- site and carrying on this tendency, not much has been reported on Zr modified BaTi03. Since the ionic radius of Zr^{4+}(0.87Å) and Ti^{4+}(1.10Å) are of same order, and valency, this element has been chosen as modifier. Here we report our work on the

synthesis and characterization (structural, dielectric and electrical properties) of $Ba(Zr_x Ti_{1-x}0_3$(x=0.05,0.1,0.2) complex system. The tolerance factor(Goldschmit Scale) t of the compounds were calculated using the equation (1) and were found to be within the range of 0.91-0.924. This clearly shows that the compounds have a distorted perovskite structure (for ideal perovskite, t =1).

EXPERIMENTAL

Sample preparation: Polycrystalline samples of $Ba(Zr_x Ti_{1-x})0_3$[BZT] with different Zr concentrations($0 \le x \le 0.2$) were synthesized as described below. Barium acetate(99.9%, Aldrich, USA), zirconium acetate were taken together in proper stoichiometry and dissolved in minimum quantity of doubly distilled water. To obtain zirconium acetate, an aqueous solution of zirconyl nitrate(99%, Loba Chemic; India) was first converted into its hydroxide form by adding ammonia solution (M/s s.d. fine-chem, India). The hydroxide was then filtered. The precipitate was thoroughly washed with doubly distilled water and kept in a hot water bath after adding acetic acid(99.9%, M/s E-Merck, India) to obtain a clear solution of zirconyl acetate. It was then transferred to a beaker containing the solution of acetates of barium and zirconium. The required volume of titanium isopropoxide(99% pure, M/s E-Merck, Schuchardt, Germany) dissolved in an equal volume of n-butanol (M/s E-Merck India) was taken to which the above mixture of acetates was added slowly with constant stirring by a magnetic stirrer. Finally, 1.5mol of citric acid(99.5%~M/s E-Merck, India» and 1 mol of glycerol (M/s E-Merck, India) were added as a chelating agent for each mol of BZT. The resultant mixture was dried at 60^0C in an air oven for 24h to form a clear transparent gel. The gel was dried at 100^0C for 72 hr. and a light brown powder was obtained. The powdered gels were then calcined at 550^0C for 15hr. The powders were cold pressed into discs (pellets) of 10 mm.diameter and 1-2mm. thickness at a pressure of $5\times10^3 N/m^2$ using a hydraulic press. The pellets were sintered at 1100^0C for 2hrs.

X-ray diffraction

The formation and quality of the desired compounds were checked by X-ray diffraction (XRD) with a powder diffractometer (Philips PW 1877) using Cuk_a radiation (A= 1.5418Å) in a wide range of Bragg angels ($20 \le 2\theta \le 60^0$) at room temperature with the scanning rate 2^0C/min on sintered pellets.

The flat polished surfaces of sintered pellets were electroded with high purity silver paste and dried at 150^0C for 2hrs. before taking any electrical measurements. The capacitance(Cp), dissipation factor(D), absolute value of impedance $|Z|$ and resistance Rp of the compounds were measured in parallel mode using a HIOKI 3235 LCR Hitester (Japan) and a laboratory made three-terminal sample holder as a function of frequency (100Hz - 4MHz) and temperature (30-200^0C). The electrical resistivity of the compounds was studied using a programmable Electrometer(Keithley-617).

RESULTS AND DISCUSSION

The XRD patterns of each member of the family are shown in the figure 1. The experimentally observed (d_{obs}) and calculated d-values(d_{cal}) with their observed intensity ratio (I/I_0) of all four members of the above family are given in TABLE 1. All the reflection peaks were indexed in tetragonal system using observed d-values with the help of a standard computer program,

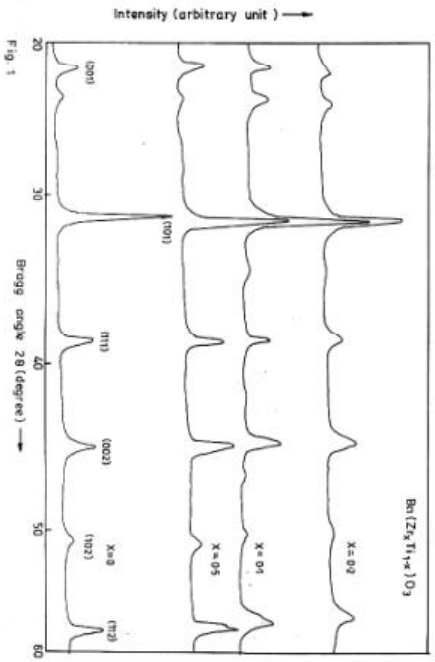

Figure 1: Comparison of XRD patterns of BZT

TABLE 1 : Comparison of observed (o) and calculated (c) values of d (in nm) with I/I_0 in parentheses of $Ba(Zr_xTi_{1-x})O_3$ at room temperature.

hkl		X=0	X=0.05	X=0.1	X=0.2
100	(o)	0.40402(16)	0.40402(16)	0.40402(15)	0.40402(13)
	(c)	0.40406	0.40412	0.40326	0.40287
110	(o)	0.28488(100)	0.28847(100)	0.28444(100)	0.28847(100)
	(c)	0.28346	0.28517	0.28456	0.28753
111	(o)	0.23237(31)	0.23679(31)	0.23266(30)	0.23679(28)
	(c)	0.23130	0.23268	0.23219	0.23404
200	(o)	0.20123(30)	0.20145(31)	0.20145(30)	0.20145(28)
	(c)	0.20081	0.20123	0.20163	0.20143
210	(o)	0.17989	0.18241(11)	0.18016(9)	0.18241(8)
	(c)	0.17947	0.18058	0.18020	0.18288
211	(0)	0.16421	0.16448(38)	0.16448(31)	0.16448(35)
	(c)	0.16376	0.16441	0.16440	0.16498

TABLE 2: Comparison of structural, electrical and dielectric parameters of BZT(x=0.05,0.1 and 0.2)

Parameters	X=0.05	X=0.1	X=0.2
a(nm)	0.4001(3)	0.4024(6)	0.4016(1)
c(nm)	0.4016(1)	0.4041(2)	0.4042(6)
c/a	1.0037	1.0041	1.0065
dc $\rho_{RT}(\Omega m)$	2.3×10^6	6.5×10^6	8.025×10^6
ε_R^{max} (at T_c)	433.5	367.3	330.0
tanδ (at T_c)	0.0365	0.0495	0.0787
T_c (K)	374	362	350
γ	1.46	1.84	-
Average particle size(Å)	303	196	185

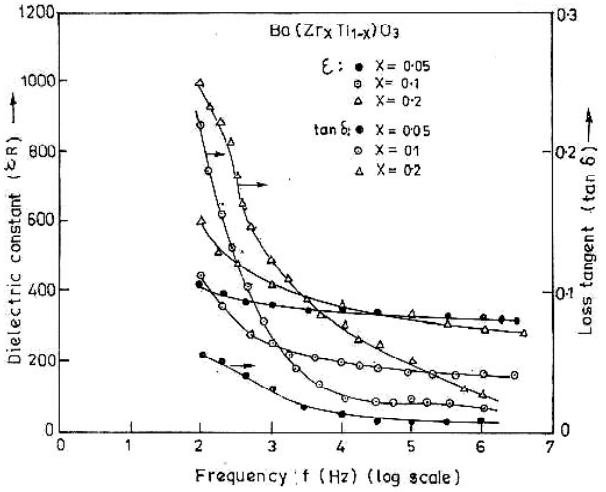

Figure 2: Variation of dielectric constant and loss tangent as function of frequency of BZT at room temperature

''POWD''. The cell parameters refined by least - squares technique, are given in TABLE 2. The average linear particle size of these compounds was calculated by Scherrer's equation[4] [$P=0.89\lambda/\beta_{1/2}\cos\theta$] where $\beta_{1/2}$ is the half-peak width. The cell parameters are changed very little with change in Zr4+ion at Ti - site. As Zr

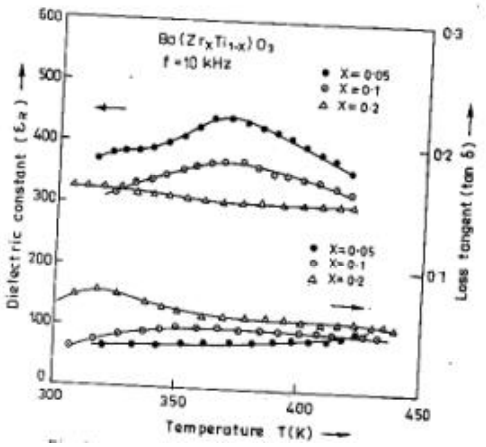

Figure 3: Variation of dielectric constant and loss tangent as function of temperature of BZT at kHz

content increases, the c/a ratio increases and particle size decreases which implies that the cell becomes somewhat distorted which is evident from the splitting and broadening of the peak (211).

Figure 2 shows the frequency variation of real part of dielectric constant(ε_R) and loss tangent (tanδ) of all the doped compounds at room temperature. A decrease in dielectric constant was observed with increases in frequency because at lower frequencies the compounds exhibit different types of polarizations (i.e., interfacial, dipolar, atomic, ionic and electronic). Due to large concentration of defects present in the polycrystalline samples, the space charge polarization increases and there by ε_R of the compounds become high. This extrinsic type of polarization is noticeable in the low frequency (i.e. <70KHz) region but negligible at low temperature[5]. As Zr content increases, the value of dielectric constant ε_R increases due to grain boundary structure of the material. The tanδ first decreases with increase in frequency and becomes lowest ($\approx 10^{-2}$) at 78kHz for compound with x=0.05, whereas it becomes lowest at 82 kHz for compounds with x= 0.1 and 0.2. Again the value of dielectric constants become higher in the frequency range (70-85kHz) which have been shown in figure 5(a) for x=0.05 and 0.1. The peak in frequency vs dielectric response curve in the frequency range 75-85kHz may be due to dipolar resonance of polar grains. Figure 3 shows the temperature dependence of dielectric constant and tan δ for all the doped samples.The dielectric peak gets broadened over small temperature interval for samples containing 5% and 10% Zr con-

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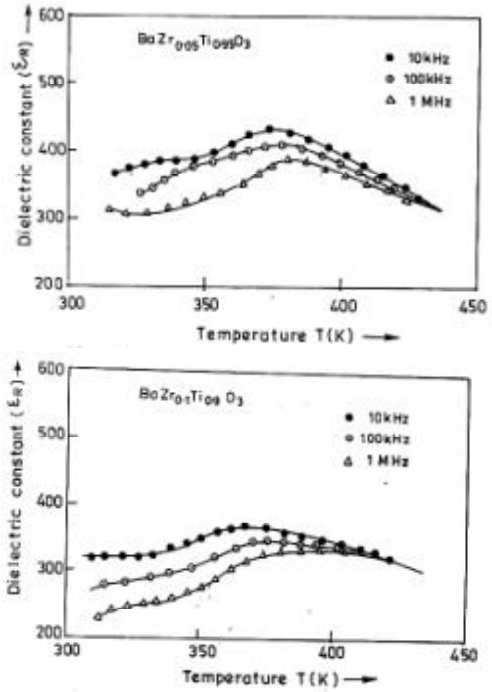

Figure 4(a): Temperature variation of dielectric constant of BZT(5%) at different frequencies (b): Temperature variation of dielectric constant of BZT (10%)at different frequencies

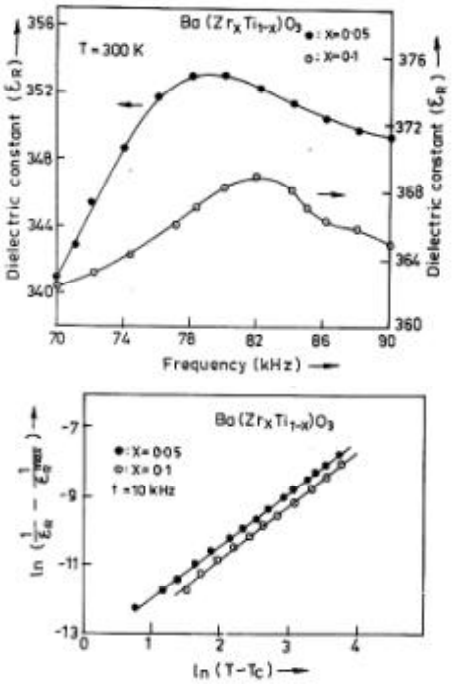

Figure 5(a): Frequency variation of dielectric constant for BZT (x =0.05, 0.1) in the frequency range (70-90kHz)(b): Variation of $\ln(1/\varepsilon_R - 1/\varepsilon_R^{max})$ with ln(T-Tc) of BZT (x= 0.05, 0.1) AT 10Khz

tent-indicating the presence of diffuse phase transition in the compounds. At high temperature, dielectric loss is higher which is due to space charge polarization. From the various experimental techniques, it has been established that diffuse phase transition occurs mainly due to the compositional fluctuation and /or substitutional disordering in the arrangement of cations in one or more crystallographic sites of the structure. This leads to the microscopic inhomogeneity in the compound and causes a distribution of local Curie points. Further, the diffuseness in the dielectric peaks of the compounds is represented by the physical quantity diffusivity, γ, which has been calculated from the following expression[6].

$$(1/\varepsilon_R - 1/\varepsilon_R^{max}) = C\,(T-T_c)^{\gamma} \qquad (2)$$

where ε_R is the dielectric constant at temperature T, ε_R^{max} is its maximum value at Tc and C is a proportionality constant.

The value of γ is around 1 for a normal dielectric (i.e. obeying Curie-Weiss law), and is equal to 2 for completely disordered dielectrics showing DPT[8]. The values of γ calculated from the slope of the curves ($1/\varepsilon_R - 1/\varepsilon_R^{max}$) versus ln ($T-T_c$) shown in figure 5(b) are listed in TABLE 2. The values of γ in our compounds are 1.46 and 1.84 for x=0.05 and 0.1 respectively which shows disorder type phase transition. Higher Zr content probably causes more disorder causing less ferroelectric. Dispersion in dielectric constant with frequency increases with higher concentration of Zr^{+4}.For sample containing 20% Zr the average particle size is 185Å. The smaller grain size also increases the scattering amplitude which may be manifested through increase in dielectric loss, resistivity and thus diminishes ferroelectric property. It has also been observed that ferroelectric-para electric transition temperature(T_c) for compounds(x=0.5, O.1) i.e. the peak in the ε_R versus T curve {Figure 4(a,b)} shifts towards higher temperature side with increasing frequency from 10kHz to 1MHz. This shows slight relaxor behavior of these compounds with low Zr substitution at Ti - site. An inhomogeneous distribution of $Ti^{+4}$and Zr^{+4}may be the origin of its relaxor behavior. The value of ε_R and tan δ for polycrystalline $BaTiO_3$ at room temperature is around 1500 and 1.2 respectively at 10kHz. These values are consistent with the reported values of Marutake et al.[7]. At a particular frequency (10 kHz), the values of ε_R and tanδ of these doped samples are not very high as compared to undoped $BaTiO_3$ which may be due to ran-

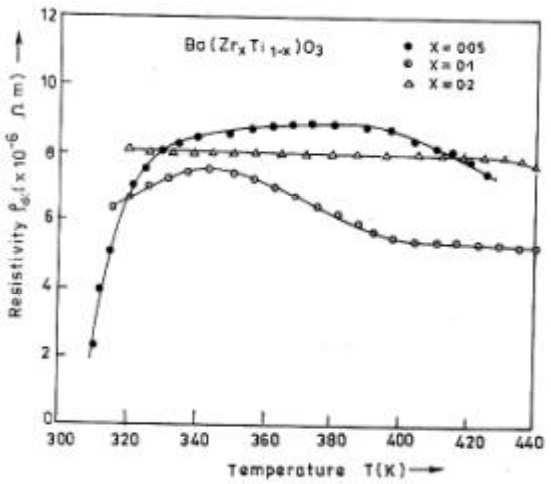

Figure 6: Temperature variation of electrical resistivity of BZT

domness of polar micro-grains.

Figure 6 shows the variation of resistivity ρ as a function of temperature for modified compounds(BZT) at constant biasing electric field (20V/cm). The resistivity increases with increase in temperature and becomes maximum near Tc and then decreases slowly with temperature.

The resistivity above Tc is nearly independent of temperature, which may be due to competition between randomness and interactions between polar micrograins simultaneously[9]. Therefore XRD and resistivity data indicate that ferroelectric property diminishes due to higher degree of distortion at Ti- site due to the higher concentration of Zr^{+4}.On substitution 20% Zr at Ti-site, reasonably constant activation energy over a broad temperature range are most desirable from the standpoint of developing a highly sensitive thermal detector.

CONCLUSIONS

As Zr content increases the c/a ratio increases and particle size decreases indicating distortion of $Ti0_6$ octahedron from the splitting and broadening of the XRD peak(211). The resistivity of the Zr-doped compounds at Ti-sites of $BaTiO_3$ is found to be of the order of $10^8\Omega$cm., which shows temperature independency above Tc. The compounds prepared by sol-gel technique exhibit better homogeneity and formation of a single phase compound. The addition of Zr at Ti-site upto 10 atomic percent produces relaxor ferroelectrics. Larger Zr doping diminishes ferroelectric property, enhances disorder but improves resistivity sensitivity for use as thermal detector. The material with appropriate Zr concentration at Ti-site may be used as a tuned frequency selector in the radio frequency range.

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