Enhanced Ferroelectric and Dielectric Properties of $BiFe_{0.95}Zn_{0.05}O_3$ Multiferroic Ceramics by Solution Combustion Method (SCM)

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ABSTRACT

Multiferroic $BiFe_{0.95}Zn_{0.05}O_3$ was prepared by a novel solution combustion method (SCM) using metal nitrates (Oxidizers) and glycine (Fuel) as starting materials. The x-ray diffraction (XRD) spectra revels that the sample has rhombhohedral perovskite structure having space group R3c with a small impurity peak corresponding to $Bi_{12}(Bi_{0.5}Fe_{0.5})O_{19.5}$ observed around 30^0 in the 2θ range. The surface morphology of the sample was studied by scanning electron microscope (SEM). The ferroelectric measurement of sample shows maximum saturation polarization $P_s = 0.65 \ \mu C/cm^2$ and remanent polarization of $P_r = 0.27 \ \mu C/cm^2$. The dielectric constant versus temperature measurement shows the dielectric constant ($\varepsilon \sim 35, 33, f= 10kHz, 1MHz$ at RT and $\varepsilon \sim 661, 116, f = 10kHz, 1MHz$ at $T = 400 \ ^0C$) of sample continuously increasing with temperature in range 30 - 400 ^0C and dielectric loss versus temperature plot ($tan\delta \sim 0.046, 0.014, f = 10kHz, 1MHz$ at RT and $tan\delta \sim 4.86, 0.72, \ f = 10 \ kHz, 1MHz$ at $T = 400 \ ^0C$) in the frequency range 10 kHz-1MHz exhibits a good dielectric performance. The dielectric constant and loss as a function of frequency in the range 10 kHz -1 MHz was studied at room temperature.

Keywords: Multiferroic $BiFe_{0.95}Zn_{0.05}O_3$, Solution Combustion Method, Characterizations, Ferroelectric, dielectric Properties.
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INTRODUCTION

Multiferroic materials exhibit electric and magnetic nature together results in ferroelectricity and ferromagnetism in a single phase [1]. Multiferroic materials are gaining much attention because of their potential applications in various fields such as information storage, spintronic, sensors [2], memory, data storage media [3], digital memories, spin filters electrically switchable spin valves [4], microelectronics [5], wireless sensors, high frequency filters [6]. Due to coupling between electric and magnetic parameters results in a novel phenomena known as

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magnetoelectric effect (ME) in which polarization can be switched by applied magnetic field and magnetization can be switched by applied electric field provide an additional opportunities for the fabrication of microelectronic and spintronic devices [7,8]. $BiFeO_3$ have rhombhohedrally distorted perovskite structure with G-type antiferromagnetic behavior below Neel temperature ($T_N \sim 643$ K) and ferroelectric behavior below Curie temperature ($T_C \sim 1103$ K) [9, 10].

Several groups have attempted to enhance the ferroelectricity and magnetism in $BiFeO_3$ with A and B site doping such as Mn [2], La [11], Cr [12], Ti [13] trivalent element dopants but there are only few reports on divalent doped $BiFeO_3$. Xu et.al studied the magnetic and dielectric properties of $BiFeO_3$ and $BiFe_{0.95}Zn_{0.05}O_3$ ceramics they showed that rapid sintering enhances the magnetic properties of $BiFeO_3$ and Zn substitution improves the dielectric properties of $BiFeO_3$ [14]. Khomchenko et.al. reported the frequency dependant dielectric constant and loss measurement at RT depicts semiconducting magnanites and ferrites behavior due to prescence of nonlocalized charge carriers and due to this reason the dielectric permittivity and loss factor decreases with increasing frequency in $Bi_{0.8}A_{0.2}FeO_3$, A = Ca, Sr, Pb ceramics prepared by solid state reaction [15]. Wang et. al. studied the synthesis of $Bi_{1-x}Ba_xFeO_3$ by double sintering technique shows RT ferroelectric hystersis loop with nonsaturated P-E loop until at higher voltage and the dielectric constant verses frequency plot shows higher dielectric constant at lower frequencies and decreases with increasing frequency [16]. Kothari et.al. reported the multiferroic properties of $Bi_{1-x}Ca_xFeO_3$ by solid state reaction in which they have shown the leakage current values increases with increase in Ca doping level results in increase in oxygen vacancies due to charge neutralization of Ca^{2+} at Bi^{3+} site and M-H loop shows remnant magnetization [17]. Fruth et.al.studied the preparation of $BiFeO_3$ ceramic by solution combustion method. The dielectric constant and losses was measured with heating-cooling cycles [18].

In this paper we report the synthesis of $BiFe_{0.95}Zn_{0.05}O_3$ ceramics by solution combustion method using glycine fuel and BFZO ceramic shows remarkably enhanced ferroelectric and dielectric properties than earlier reported results.

MATERIALS AND METHODS

The $BiFe_{0.95}Zn_{0.05}O_3$ multiferroic was prepared by a solution combustion method (SCM). The starting materials $Bi(NO_3)_3.5H_2O$ (CDH, India), $Fe(NO_3)_3. 9H_2O$ (Fischer Scientific), $Zn(NO_3)_2. 6H_2O$ (CDH, India) were used as an oxidizers and glycine (NH_2CH_2COOH) (CDH, India) was used as fuel. The oxidizer (O): fuel (F) ratio was calculated based on the oxidizing valencies of metal nitrates and reducing valency of fuel [19]. The metal nitrates and glycine in stiochimetric ratios were dissolved in distilled water, this solution is then concentrated by heating in a Pyrex dish (150x50mm) on a burner until the excess of free water evaporates and spontaneous ignition occurred with finally a combustion powder is obtained. This powder was grinded and calcined at 650 ^{0}C for 4hrs. In this calcined powders 2% PVA (polyvinyl alcohol) was added as a binder and pellets from synthesized powders were prepared using uniaxial pressing. The pellet was sintered at 670 ^{0}C for 30 min and carried out for further characterization and measurements.

The phase identification of the sintered pellet was performed on X-ray diffractometer (Philips X'Pert PRO) with CuKα radiation in the 2θ range 20-75^0. The surface morphology was studied using scanning electron microscope (SEM, EVO-50). For ferroelectric and dielectric

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measurements the two opposite surfaces of sintered pellet was polished with silver paste. Ferroelectric measurement was performed at room temperature using Precision Premier II, Radiant Technologies, USA. Dielectric constant and loss as a function of temperature measurement was performed on Agilent HP 4192A, Impedance Analyzer and dielectric constant as a function of frequency at room temperature measurement by Agilent 4294A, Precision Impedance Analyzer.

RESULTS AND DISCUSSION

1. Structural Studies

Fig.1 shows the XRD pattern of $BiFe_{0.95}Zn_{0.05}O_3$ (BFZO) ceramic at room temperature. The BFZO sample shows rhombhohedral perovskite structure with space group R3c. All the peaks matches very well with the reported data only the $Bi_{12}(Bi_{0.5}Fe_{0.5})O_{19.5}$ impurity peak appearing at 2θ around 30^0 marked by stars. With increasing doping concentration this secondary phase becomes more intensive because it is very difficult to prepare single phase $BiFeO_3$ [14].
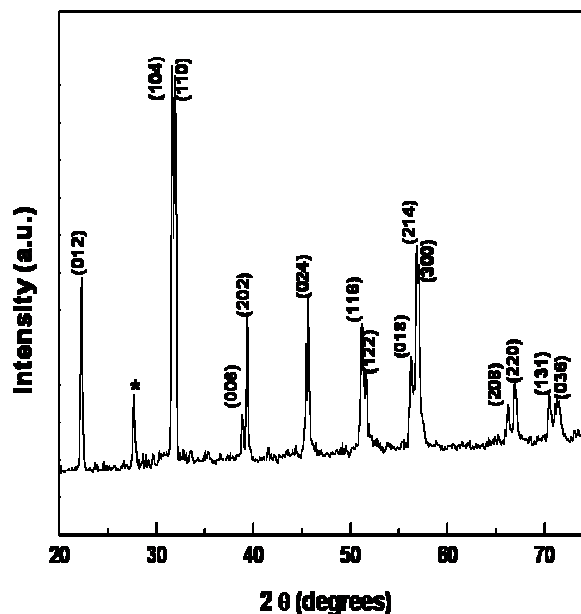

Fig.1. XRD pattern of $BiFe_{0.95}Zn_{0.05}O_3$ sample at RT (* indicates the impurity phase)

2. Surface Morphological Studies

Fig.2 shows the typical surface SEM image of $BiFe_{0.95}Zn_{0.05}O_3$ ceramic sintered at 670^0 C for 30 min, the grains of $BiFe_{0.95}Zn_{0.05}O_3$ are uniform and irregular. The bigger size grains are observed due to agglomeration of small grains with interconnected structure and the average grain size was estimated to be about 200 – 500 nm.

3. Ferroelectric P-E Hystersis Loop

Fig.3. shows the electric field dependant polarization exhibits a clear ferroelectric hystersis loop of $BiFe_{0.95}Zn_{0.05}O_3$ at room temperature (300 K). The loop is very well saturated with

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remarkably enhanced saturation polarization Ps = 0.65 μC/cm^2 and remanent polarization Pr = 0.27 μC/cm^2.
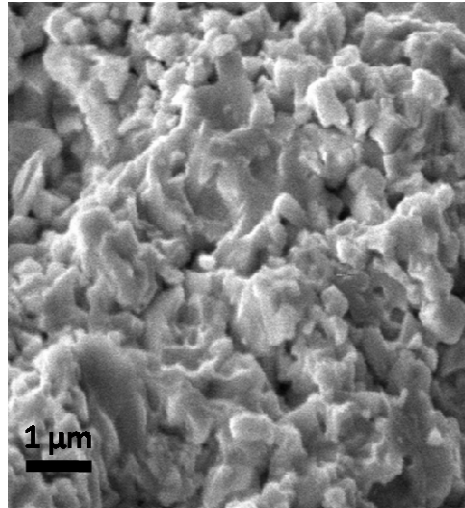
Fig.2. SEM image of BiFe$_{0.95}$Zn$_{0.05}$O$_3$ ceramic

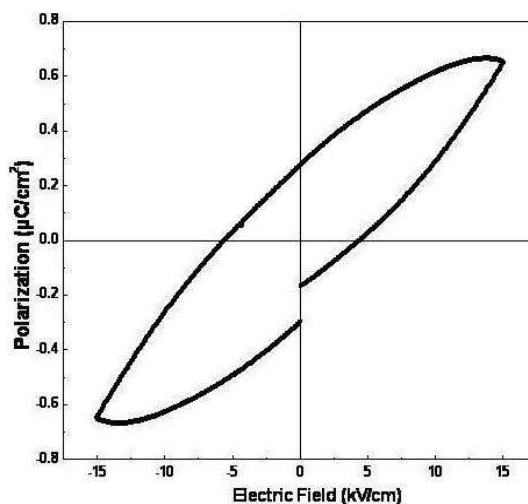**Fig.3. Ferroelectric Hystersis (P-E) Loops of BiFe$_{0.95}$Zn$_{0.05}$O$_3$ at RT.**

4. Dielectric Studies

Fig.4 a) shows the dielectric constant verses temperature plot of BiFe$_{0.95}$Zn$_{0.05}$O$_3$ obtained by combustion method in the temperature range 30 - 400^0 C with corresponding frequencies ranging from 10 kHz - 1MHz at heating cycle shows a continuous increase of dielectric constant with temperature, in this sense only small values of permittivity $\varepsilon \sim$ 35, 33, f= 10kHz, 1MHz at room temperature and $\varepsilon \sim$ 661, 116, f = 10kHz, 1MHz at T = 400 ^{0}C) are observed for BFZO multiferroic ceramic.

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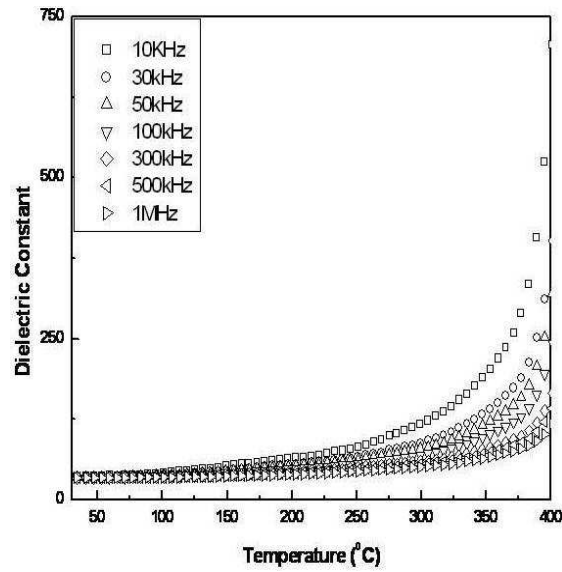**Fig.4 a). Dielectric constant – temperature graph of BiFe$_{0.95}$Zn$_{0.05}$O$_3$, f = 10kHz-1MHz.**

Fig.4 b) shows the dielectric loss verses temperature graph of BiFe$_{0.95}$Zn$_{0.05}$O$_3$ in the temperature range of 30 - 400^0 C with corresponding frequencies ranging from 10 kHz - 1MHz at heating cycle exhibits continuous increment of loss with temperature with corresponding dielectric losses (tanδ ~ 0.015, f = 1 MHz and tanδ ~ 0.050, f = 10kHz at room temperature). This BiFe$_{0.95}$Zn$_{0.05}$O$_3$ multiferroic shows tanδ < 1 at room temperature exhibits good dielectric properties [18].

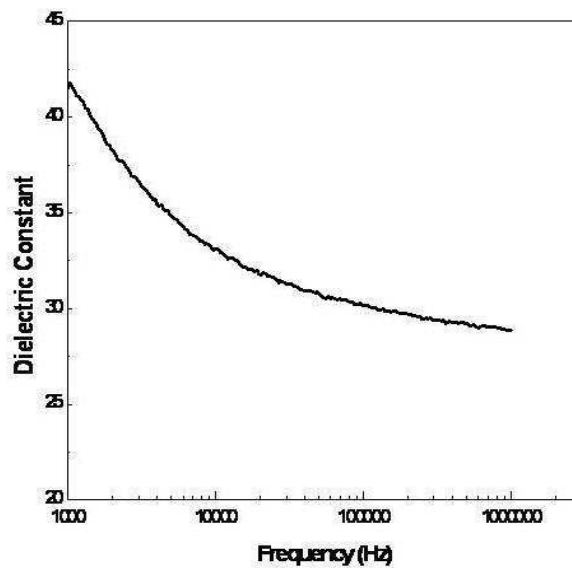**Fig.4 b) Dielectric loss – temperature graph of BiFe$_{0.95}$Zn$_{0.05}$O$_3$, f = 10kHz-1MHz.**

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Fig. 4 c) shows the variation of dielectric constant verses frequency obtained for $BiFe_{0.95}Zn_{0.05}O_3$ sample at room temperature in the frequency range 10 kHz -1 MHz shows the dielectric constant decreases with increasing frequency.
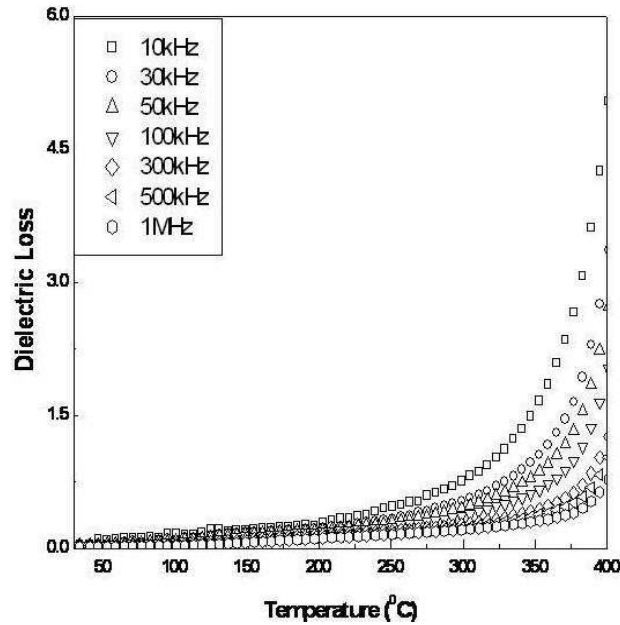

Fig. 4 c) Dielectric constant verses frequency plots of $BiFe_{0.95}Zn_{0.05}O_3$ at RT

Fig.5.2 shows variation of dielectric loss verses frequency obtained for $BiFe_{0.95}Zn_{0.05}O_3$ sample at room temperature in the frequency range 10 kHz -1 MHz shows the dielectric loss decreases with increasing frequency.
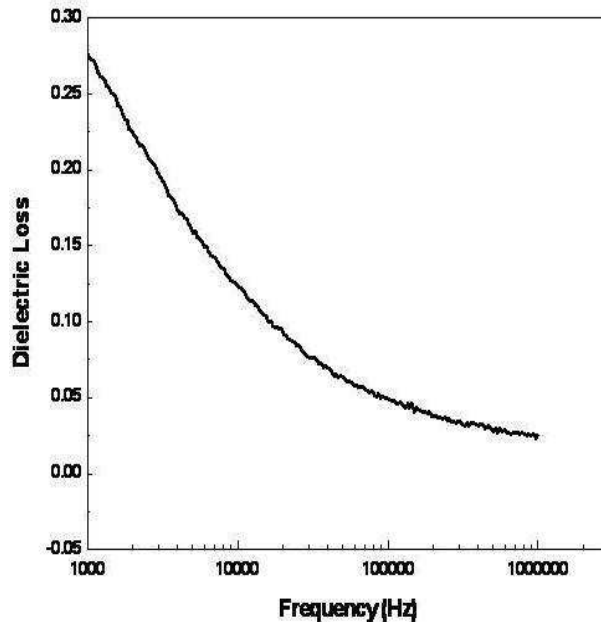

Fig. 4 d) Dielectric loss verses frequency plot of $BiFe_{0.95}Zn_{0.05}O_3$ at RT

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CONCLUSION

In summary, The Zn doped $BiFeO_3$ ($BiFe_{0.95}Zn_{0.05}O_3$) multiferroic ceramic has been successfully synthesized by a solution combustion method (SCM) using glycine fuel. The XRD pattern reveals that the sample has rhombhohedral crystal structure and has good agreement with the reported data. The microstructure of sample shows the grains have uniform, irregular, and agglomerated grains with interconnected structure has been formed. The ferroelectric hystersis loop for Zn substituted $BiFeO_3$ was well saturated with enhanced saturation (P_s) and remanent polarizations (P_r) and finally it was found that the Zn doping at Fe site results an improvement of dielectric constant and dielectric losses.

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