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EFFECT OF Zno-TeO_2 GLASS DOPING ON STRUCTURAL AND DIELECTRIC PROPERTIES OF $BiFeO_3$ PREPARED BY SOLID STATE METHOD

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ABSTRACT

Impurity phase formation and large leakage current values have been major problems for technological applications of multiferroic $BiFeO_3$ compounds. In this study, excess amount of Bi was added to compensate the loss of Bi in the samples during sintering. Zinc tellurite (ZT) glass added $BiFeO_3$ samples was prepared by conventional solid state method with the composition of (1-x)$BiFeO_3$ - (x)ZnO-TeO_2 (x = 0, 0.03, 0.05, 0.10) samples. XRD analysis showed that the addition of 2 mol% excess amount of Bi to $BiFeO_3$ has suppressed the formation of secondary phases such as $Bi_2Fe_4O_9$ during sintering. No secondary phase peaks were observed in ZT glass added samples. SEM images showed that the grain morphology changed from angular faceted in $BiFeO_3$(with 2 mol% excess) to rounded grains in ZT glass was added samples. Dielectric properties of samples were measured in the frequency range of 100 Hz to 1 MHz at room temperature. The dielectric constant of ZT glass added $BiFeO_3$ has improved due to increased grain boundary resistance and oxygen vacancies as a result of ZT glass addition. The insulating ZT glass reduced grain to grain contact at the grain boundary resulting in reduced dielectric loss at higher ZT glass addition.

Keywords: $BiFeO_3$, dielectric properties, ZnO-TeO_2 glass

INTRODUCTION

Multiferroic materials which exhibit at least two ferroic orders simultaneously have received great attention for advanced technologies applications. Coupling between these two orders provide distinctive technique of switching electric polarization using magnetic field and magnetic polarization by electric field. These properties are very interesting as it could be implemented in various devices and applications. Bismuth ferrite, $BiFeO_3$ is a single phase multiferroic compound which has a ferroelectric behaviour with Curie transition temperature (Tc) of 850^{o}C and antiferromagnetic Neel temperature (T_N) of 380^{o}C. $BiFeO_3$ shows antiferromagnetic G-type spin configuration and has superimposed incommensurate periodical cycloid spin structure of 642 nm [1-3].

However, one of the main obstacles for $BiFeO_3$ applications is the presence of secondary phases such as $Bi_2Fe_4O_9$, $Bi_{25}FeO_{40}$ and $Bi_{36}Fe_{24}O_{57}$ [4]. Formation of secondary phases such as sillenite $Bi_2Fe_4O_9$, due to evaporation of Bi during processing, at the grain boundaries of $BiFeO_3$ could result in large leakage currents and high dielectric losses compared to single phase $BiFeO_3$ [5]. One of the methods employed to overcome this problem is to add excess Bi to compensate the loss of Bi from sintering.

Previous reports suggested that addition of glass resulted in lowering dielectric loss for $CaCu_3Ti_4O_{12}$ [6] and decreased in electrical conductivity for MgCuZn ferrites [7]. It is reported that the presence of insulating glass phase at the grain boundary would reduce inter granular leakage and result in lower dielectric losses. Therefore, it can be expected that small amount of highly insulating glass addition to the $BiFeO_3$ could electrically isolate $BiFeO_3$ grains from each other and increase the grain boundary resistivity of the sintered product. Furthermore, glass addition can aid in liquid-phase-sintering at low temperature due to low melting point of glass which gives additional advantage by suppressing Bi evaporation and impurity formation at $BiFeO_3$ grain boundaries [8].

Tellurite based glasses exhibit high dielectric constant, low melting point and low glass transition temperature, T_g compared to other glass systems [9-10]. In addition, ZnO-TeO_2 (ZT) glass has the higher resistivity compared to another tellurite glass such as TeO_2-V_2O_5, TeO_2-WO_3 and TeO_2-CuO [11]. ZT glass is one suitable candidate which can be considered for the addition due to its high resistivity and low melting point. To the best of our knowledge, there are no reports on synthesis of ZT glass added $BiFeO_3$ and its effect on dielectric properties.

EXPERIMENTAL

$BiFeO_3$ ceramic samples with and without glass addition were prepared separately using solid state method. High purity Bi_2O_3 and Fe_2O_3 (99.9% Sigma Aldrich) powders were weighed with 2 mol % excess Bi_2O_3 than stoichiometric $BiFeO_3$. Here onwards $BiFeO_3$ with 2 mol% excess bismuth will be referred to as $BiFeO_3$(2Bi) for easy reference. The powder was mixed using agate mortar for 2 hours for homogenization. Then the powder was calcined at 800^{o}C for 4 hours. 0.3ZnO-0.7Te_2O (ZT) glass was prepared from ZnO and TeO_2 (99.9% Sigma Aldrich) powders via melt quenching method. These powders were melted at 900^{o}C for 150 min and quenched to 300^{o}C in a stainless steel mould. Subsequently, powdered ZT glass was added to calcined $BiFeO_3$-2Bi powders with the composition of (1-x)$BiFeO_3$(2Bi)-xZn-TeO_2 where x=0, 0.03, 0.05, 0.1 mol% and mixed in an agate mortar. The mixture was then pressed into pellets and sintered for 4 hours at 850^{o}C. The phase analysis of the samples was carried out using X-Ray diffraction (XRD) with Cu Kα (λ=1.5406Å) radiation. The microstructure and morphology of the samples were examined by employing a Scanning Electron Microscope (SEM). The dielectric constant and dielectric loss of the samples was measured using LCR meter (Hioki Model 3532-50) at room temperature.

RESULTS AND DISCUSSION

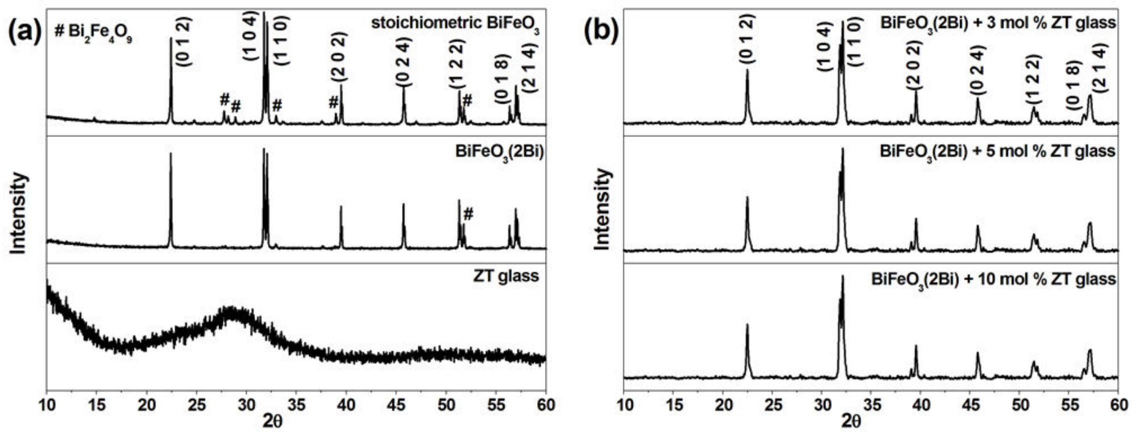

Figure 1 X-Ray Diffraction pattern of (a) stoichiometric $BiFeO_3$, $BiFeO_3$(2Bi), and ZnO-TeO_2 glass (b) ZnO-TeO_2 glass with different mol % + $BiFeO_3$(2Bi) sample

The XRD patterns of stoichiometric $BiFeO_3$, $BiFeO_3$(2Bi), and ZnO-TeO_2 (ZT) glass samples were shown in Figure 1(a). XRD patterns were indexed based on standard rhombohedral perovskite $BiFeO_3$ JCPDF data card (86-1518). ZT glass XRD pattern showed amorphous structure without any sharp peaks corresponding to crystalline phases (Figure 1(a)). XRD peaks corresponding to secondary impurity phase ($Bi_2Fe_4O_9$) were observed along with pure $BiFeO_3$ peaks in the stoichiometric $BiFeO_3$ sample. On the contrary, no secondary phases were observed in the XRD patterns of samples prepared with 2 mol% excess Bi, as the addition of excess Bi has compensated for the Bi evaporation and arrested the formation of Fe rich secondary phase during sintering process. XRD patterns of ZT glass added $BiFeO_3$(2Bi) were shown in Figure 1(b). ZT glass added sample showed XRD peaks corresponding to $BiFeO_3$ and no secondary phase peaks were observed. Lattice parameters (*a* and *c*) and lattice volume of all samples were calculated from XRD data and tabulated in Table 1. The value of lattice parameter and lattice volume of the samples increased with ZT glass addition. This could be due to diffusion of elements from ZT glass into $BiFeO_3$(2Bi) during sintering.

Table 1: Lattice parameter of (1-x)$BiFeO_3$(2Bi)-xZn-TeO_2 for x=0, 0.03, 0.05, 0.1 mol%

Composition	*a* [Å]	*c* [Å]	Lattice volume [$Å^3$]
x=0	5.308	12.312	346.889
x=0.03	5.310	12.367	348.701
x=0.05	5.312	12.378	349.274
x=0.10	5.320	12.381	350.412

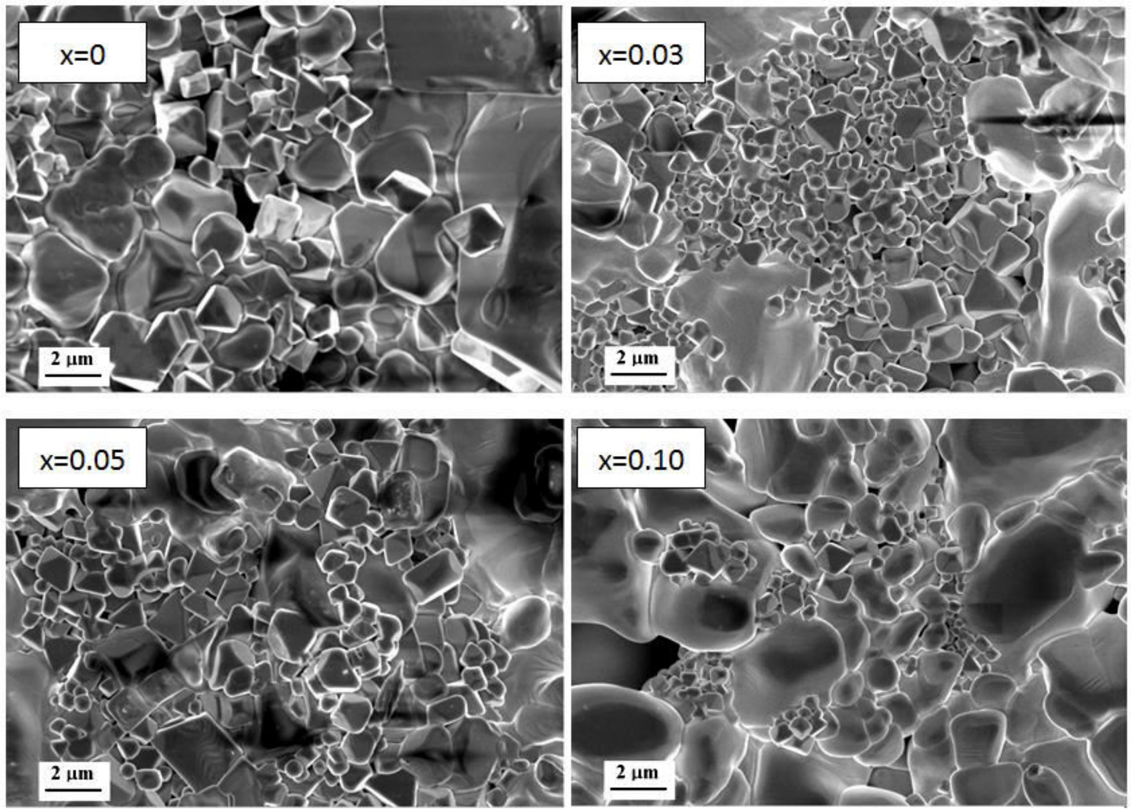

Figure 2: SEM micrograph of (1-x)$BiFeO_3$(2Bi)-xZn-TeO_2 (a) x=0 (b) x=0.03 (c) x=0.05 (d) x=0.10 mol%

Scanning electron micrographs (SEM) of (1-x)$BiFeO_3$(2Bi)-xZn-TeO_2 samples were shown in Figure 2 (a-d). Grains with angular crystallographic facets were observed in the micrographs indicating recrystallization during sintering. $BiFeO_3$(2Bi) samples displayed an average grain size of 4-5 µm and ZT glass addition has resulted in decreased grain size. Sample with 0.03mol% ZT glass addition has showed an average grain size of 1-2 µm and the grain size increased to 6-7µm at 0.1 mol% ZT glass addition, which is highest among all the sample prepared in this study. Furthermore, the grain morphology is seen to change from angular faceted to rounded grains with the addition of ZT glass to $BiFeO_3$(2Bi). Initial decrease in grain size with 0.03mol% ZT glass addition could be attributed to the grain boundary pinning by the glass during sintering. However, increase in grain size with the higher amounts glass addition to $BiFeO_3$(2Bi) could be attributed to the improved inter grain contact due to the presence of liquid phase and grain wetting by the glass during sintering. Furthermore, $BiFeO_3$ grain wetting by glass phase and possible chemical interaction between two phases would result in reduced surface energy and resulted in rounded grains compared to $BiFeO_3$(2Bi) samples, which has displayed angular crystallographic faceted grains.

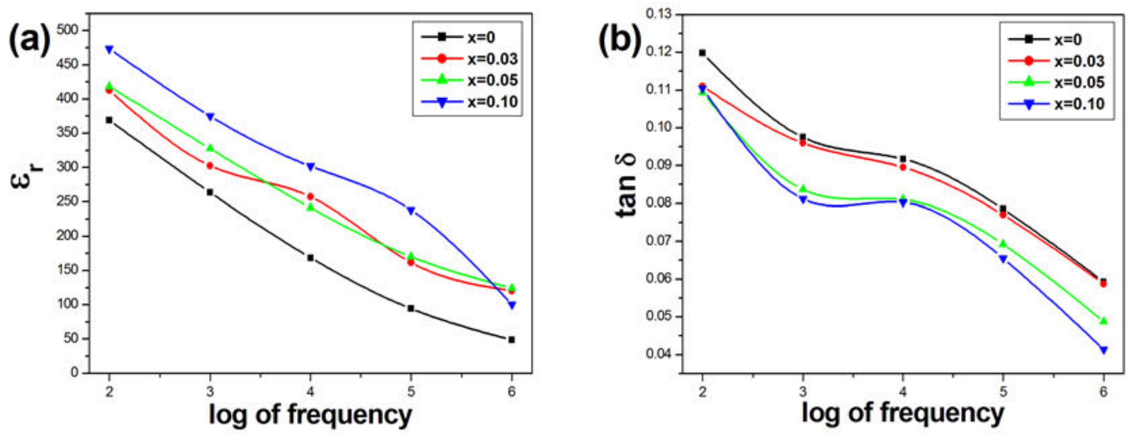

Figure 3 (a) Dielectric constant (ε_r) and (b) dielectric loss (tan δ) of (1-x)$BiFeO_3$(2Bi)-xZn-TeO_2 at room temperature

Dielectric constant (ε_r) and dielectric loss (tan δ) values obtained from impedance analysis of the sintered $BiFeO_3$(2Bi) and ZT glass added $BiFeO_3$(2Bi) samples over the frequency range of 100Hz to 1MHz at room temperature were illustrated in Figure 3. The value of dielectric constant for all the samples is seen to decrease with increasing frequency until 1MHz. This could be attributed to dielectric relaxation phenomena where the heavy dipoles tend to lag behind the alternating frequency as the frequency is increased to higher values. Grain conductivity, grain boundary resistivity, dielectric constant and dielectric loss values calculated from impedance spectroscopic data were shown in Table 2. The internal barrier layer capacitance (IBLC) model suggests that the dielectric constant is greatly dependent on the grain size, grain boundary dielectric constant and grain boundary thickness as shown in Eq. 1 [8].

$$\varepsilon_r' = \varepsilon_{gb}\left(\frac{d_g + d_{gb}}{d_{gb}}\right) \qquad (1)$$

Where ε_{gb} is the dielectric constant of the grain boundary layer, d_g and d_{gb} are the thickness of the grain and grain boundary layer respectively. According to the equation, large grain size, thicker grain boundaries and higher grain boundary resistance would result in enhanced dielectric constant of the ceramics.

According to the Table 1, grain boundary resistivity is higher than the grain resistivity by more than two orders for $BiFeO_3$(2Bi). In ceramic materials the concentration of oxygen vacancies increases with the increase in temperature during sintering process according to the Eq. 2.

$$O_0^x \leftrightarrow \frac{1}{2} O_2 + V_o^{\cdot\cdot} + 2e^{'} \quad (2)$$

Where O_0^x represents oxygen ions in the lattice, O_2 is oxygen gas, $V_o^{\cdot\cdot}$ represents oxygen vacancy with double positive charges and $e^{'}$ is electron [12].

During cooling, reoxidation takes place via grain boundaries due to high atomic diffusion rate at grain boundaries compared to grain interiors and often this reoxidation process is partial as the diffusion rates drop at low temperatures. This results in reoxidized regions adjacent to grain boundaries and grain interiors with oxygen vacancies. As a result, grain interiors display higher conductivity and higher polarizability due to dipole formation compared to reoxidized grain boundary regions. Conducting grains surrounded by high resistance grain boundaries confirms towards IBLC model of dielectric constant. Grain boundary resistance is seen to increase with the increased ZT glass addition to $BiFeO_3$(2Bi) samples. The high resistance ZT glass wets the grain boundary regions of $BiFeO_3$ grains during sintering and contributes towards improved grain boundary resistance of ZT doped $BiFeO_3$(2Bi) samples. A minor increase in grain resistance was also observed with ZT glass addition, which could be attributed to possible diffusion of elements from glass into $BiFeO_3$ grains during sintering as shown in the changes of lattice parameters and lattice volume in Table 1.

$BiFeO_3$(2Bi) samples with 0.03 mol% ZT glass addition have shown higher dielectric constant values compared to $BiFeO_3$(2Bi) samples. The value of dielectric constant is seen to increase further as the composition of ZT glass increased as shown in Table 2. The further increase in dielectric constant values with the addition of ZT glass to $BiFeO_3$(2Bi) samples could be attributed to the higher grain boundary resistance and increase in grain size according to the IBLC model. The addition of ZT glass into $BiFeO_3$(2Bi) also resulted in decreased dielectric loss values as shown in Table 2. The decrease in grain-to-grain contact due to the presence of insulating ZT glass at the grain boundaries would reduce leakage and result in decreased dielectric loss values. Samples with 0.1 mol% ZT glass have showed smallest dielectric loss value of 0.081 compared to all other samples.

Table 2: Grain boundary resistivity (ρ_{gb}), grain resistivity (ρ_g), dielectric constant (ε_r) and dielectric loss (tan δ) at frequency 1000Hz of ZT glass added $BiFeO_3$(2Bi)

Composition	Grain boundary resistivity, ρ_{gb} [Ωm] $\pm$ 0.001	Grain resistivity, ρ_g [x 10^{-2} Ωm] $\pm$ 0.01	Dielectric constant [ε_r] $\pm$ 0.001	Dielectric loss [tan δ] $\pm$ 0.001
x=0	502.875	95.08	263.869	0.097
x=0.03	597.675	95.29	302.915	0.095
x=0.05	692.852	95.47	327.821	0.083
x=0.1	790.561	97.21	375.202	0.081

CONCLUSIONS

Microstructure and dielectric characteristics $BiFeO_3$(2Bi) and ZT glass added $BiFeO_3$(2Bi) were studied and results were shows addition of excess Bi has compensated for the Bi evaporation and detained the formation of secondary phase during sintering process. The average grain size of ZT glass added samples increased as glass composition increased. The grains structure also changed from angular faceted to rounded grains. Addition of ZT glass into $BiFeO_3$(2Bi) promoted high resistivity grain boundary and high grain conductivity which conforms to the IBLC model which resulted in higher value of dielectric constant as the composition of glass increased. On the other hand, the dielectric loss also showed reducing trend with ZT glass addition as insulating ZT glass act as a barrier layer which reduced the grain to grain contact in the samples.

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