Fabrication and Characterization of Dielectric Properties of BaTiO$_3$/Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ Multiphase Multiferroic

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Abstract—Multiphase multiferroic ceramics based on xBaTiO$_3$ (BTO)/(1-x)Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ (NZFO) system were fabricated employing solid–state synthesis route. The composition of BTO was varied with x= 0.7-0.9 and sintered at 1275ºC or 1275ºC. Employing field emission scanning electron microscopy (FESEM) an improved microstructure has been found for samples sintered at 1275ºC. X-ray diffraction study confirmed the crystalline tetragonal perovskite structure of BTO phase and cubic spinel structure of NZFO phase in fabricated samples at all sintering temperatures. With increasing NZFO content dielectric constant was found to be decreased at the studied frequency range of 100 Hz to 2 MHz at room temperature. Curie temperature has shown to increase significantly with increasing composition of NZFO and broadened.

Index Terms— Multiferroic composites, dielectric constant, Microstructure, BTO/NZFO.

I. INTRODUCTION

Multiferroic (MF) materials simultaneously display more than one primary "ferroic" properties nameply ferroelectricity, ferromagnetism and ferroelasticity [1, 2]. Now-a-days, MF materials have shown a profound interest among the researchers due to its multifunctional characteristics. The most important and interesting MF system is electromagnetic multiferroics where the ferroelectric properties (polarization) are switched by magnetic field and vice versa. These properties are very rare in single phase materials as ferroelectricity or ferromagnetism requires entirely contradictory d-shell requirements [3, 4]. In addition, single phase MF materials have some limitations such as scarcity of materials, difficulty in tailoring its multiferroic responses, high cost involvement of fabricating materials and inherent week coupling between the order parameters at room temperature. In contrast, multiphase multiferroics (MMF) are free from those limitations: relatively cheaper, easier to fabricate, possess superior magneto-electric (ME) coupling response at ambient temperature and tailoring of properties are relatively easy [5]. Moreover, MF composites exhibit product property, which enables its wide range of applications such as, electric generator, magnetic field sensors, waveguides, bi-tunable devices, microwave materials and so on [6, 7].

The constituents of MMF include piezoelectric perovskite ceramics (e.g. BaTiO$_3$, PbZrTiO$_3$) and piezomagnetic spinel ferrites (e.g. NiFe$_2$O$_4$, CoFe$_2$O$_4$) [5-7, 9, 10]. In this research, BTO was used due to its attractive properties like high dielectric constant, low dielectric loss, good thermal stability, low leakage current density, and high piezoelectric coefficient [11-13]. On the other hand, Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ (NZFO) is used here as piezomagnetic constituent which may provide magnetostrictive properties with excellent magnetic and high electrical resistance in high frequency band and better ferromagnetic properties including high Curie temperature and thermo-chemical stability [14]. However, during fabrication of the MMF, some challenges are to be addressed such as the composite should be free from any chemical reactions taken between the constituent phases, the ferromagnetic constituent should possess large resistivity and the microstructural defects such as pores in the composite materials should be kept as low as possible [8]. Some advances have already been made in MMF systems [6-8, 10-13]. But none has taken into consideration the effect of controlling composition and microstructure on the dielectric properties of the fabricated composite. Thus, in the present work, we have fabricated xBTO/(1-x)NZFO composites (x= 0.7, 0.8, 0.9) employing solid state route, optimized sintering parameters to control grain size and to develop defect free microstructure and studied the effect of composition, frequency and temperature on the dielectric properties in these composites.

II. EXPERIMENTAL TECHNIQUE

A. Materials and Synthesis

MMF comprised of xBTO/(1-x)NZFO system (with x= 0.7, 0.8, 0.9) were prepared using solid-state sintering route. At first, NFO (99.9%) and ZFO (99.9%) nano-powder with particle size ~20-50 nm were taken into stoichiometric ratio, mixed thoroughly in a mortar with pestle for several hours and mixed again in a planetary ball-mill with 300 rpm speed for 45 minutes using acetone as mixing medium. The mixed powders were pre-sintered at 850^{0}C at 12 h to form NZFO.

BTO (99.95%) nano-powder of particle size of 100 nm is also pre-sintered at 1000^{0}C for 12 h to increase its particle size. Then, pre-sintered NZFO powder and BTO (99.95%) powder were thoroughly mixed in required proportion in planetary ball-mill and milled again in a pot mill in acetone medium for 18 hours to ensure better mixing of the powders and the milled powders were pressed into pallets with a diameter of 15 mm and thickness of 2 mm at a pressure of 150 MPa. The fabricated pallets were sintered at 1250 ºC or 1275

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ºC in air for 4 h. The % theoretical density was calculated for all the sintered samples. Crystalline structures of both starting materials and fabricated MMF were examined using an X-ray diffractometer (XRD, model Bruker D8 Discover) with Cu Kα1 radiation (λ=1.5406Å, 40kV, 30mA). Grain size and morphology of sintered MMF were examined employing field-emission scanning electron microscope (FESEM) (JEOL JSM-7600). The dielectric properrties were measured as a function of frequency and temperature by an impedance analyzer. The variations of dielectric properties were studied by recording capacitance at different frequencies. To obtain good ohmic contacts, the samples were coated with silver paste.

III. RESULTS AND DISCUSSION

Table 1 shows the % theoretical density of the samples sintered at 1250 ℃ and 1275 ℃. The samples sintered at 1275 ℃ exhibited higher density than that of the samples sintered at 1250 ℃.

**Table 1. Percent theoretical density of the samples sintered at 1250^0C and 1275^0C.**

| Sample	Sintering temperature [^{0}C]	% Theoretical density	Grain size [µm]
0.7BTO/0.3NZFO	1250	83.30	0.50
0.8BTO/0.2NZFO	1250	85.75	0.50
0.9BTO/0.1NZFO	1250	83.35	0.55
0.7BTO/0.3NZFO	1275	95.77	0.65
0.8BTO/0.2NZFO	1275	92.65	0.65
0.9BTO/0.1NZFO	1275	95.95	0.65

Fig. 1 shows XRD patterns of MMF samples sintered at 1275^0C and 1250^0C. The XRD pattern of the samples shows coexistence of both BTO and NZFO phases. The BTO phase has a typical tetragonal perovskite structure and the NZFO phase has a mixed spinel structure. All XRD peaks were identified and any peak related to impurity phases are absent for all sintered samples. The spinel phase of NZFO was confirmed by peaks at diffraction angle 2θ=30.18^0, 35.87^0, 43.39^0 and 57.33^0 corresponding to reflections from (220), (311), (511) and (400) planes respectively. Tetragonal BT phase was detected by peaks at 2θ=21.93^0, 22.18^0, 31.51^0, 39.14^0, 44.97^0, 45.21^0, 50.91^0, 55.75^0, and 56.24^0 corresponding respectively to (001), (100), (101), (111), (002), (200), (201/210), (112), and (211) reflections planes. The twin-peak reflection planes (001)/(100) and (200)/(002) indicator of splitting of cubic into tetragonal phase are not separable anymore. Evidently, NZFO peak observed from (311) and (400) reflections were found to be prominent with increasing NZFO content. Diffraction peaks obtained from samples sintered at 1250^0C exhibited subtle difference.

Fig. 2 shows SEM micrographs of the samples after sintered at 1250℃ and 1275℃. Samples sintered at 1250℃ have shown to have porosity for all compositions. In contrast, samples sintered at 1275℃ have no porosity in their microstructure. Porosity in microstructure has a detrimental effect on the MMF as porosity reduces the mechanical coupling between the ferroelectric and ferromagnetic phases. Grain size varied from 0.50 to 0.55 µm for samples sintered at

1250⁰C. However, samples sintered at 1275⁰C were found to have unaltered grain size of 0.65 µm indicating less pronounce effect of compositional variation.
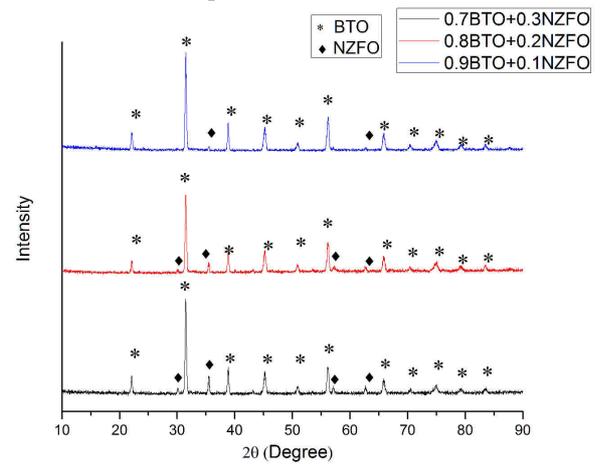
(a)
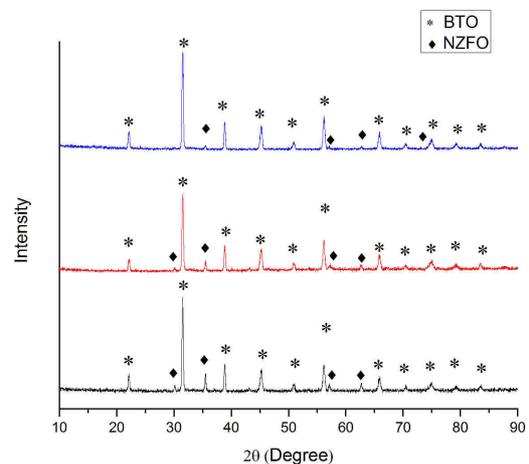
(b)

Fig.1: X-ray diffraction patterns of xBTO/(1-x)NZFO MMF: (a) 1250℃ and (b) 1275℃ .

Next, dielectric response of samples sintered at 1275℃ was measured. Fig. 3 shows the dielectric constant as a function of frequency. From fig.3 we can see, higher values of dielectric constant observed at lower frequencies, which can be explained on the basis of space charge polarization due to inhomogeneous dielectric structure [11].

Dielectric constant has found to be decreased with increasing NZFO content. This result is quite obvious, as the MMF attains its ferroelectric properties only from its constituent BTO phase. Thus, the decrease of BTO content in MMF resulted in diminished dielectric constant. Moreover, NZFO is the low resistant constituent thereby decreasing the dielectric constant value of resulted MMF. However, an improved higher dielectric constant was obtained in this research compared to previously reported experiments [11, 13].
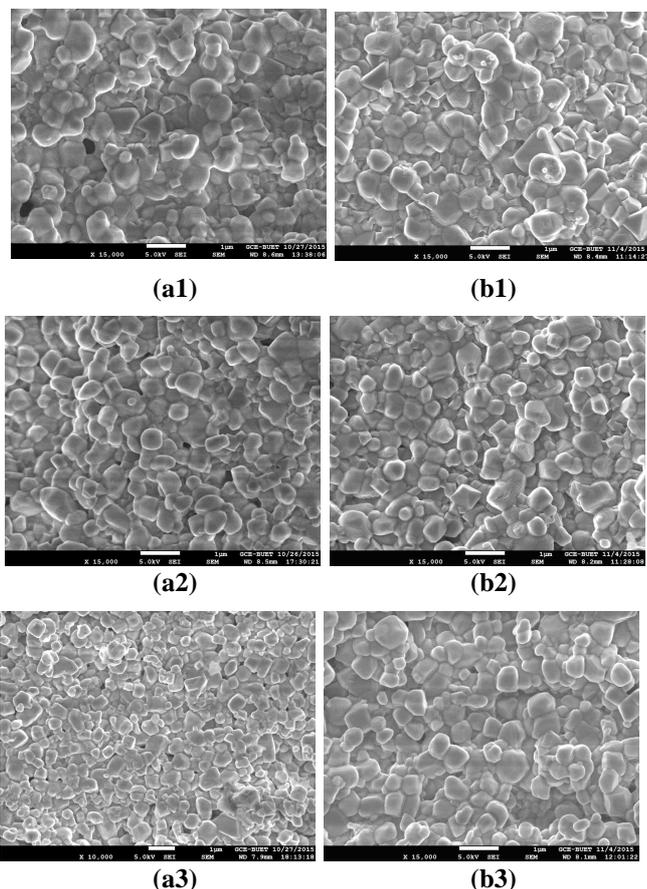
(a1) **(b1)**

(a2) **(b2)**

(a3) **(b3)**

Fig. 2: SEM micrograph of MMF sintered at: 1250ºC (a1-a3) and 1275ºC (b1-b3). x=0.7 (a1, b1), 0.8 (a2, b2) and 0.9 (a3, b3).
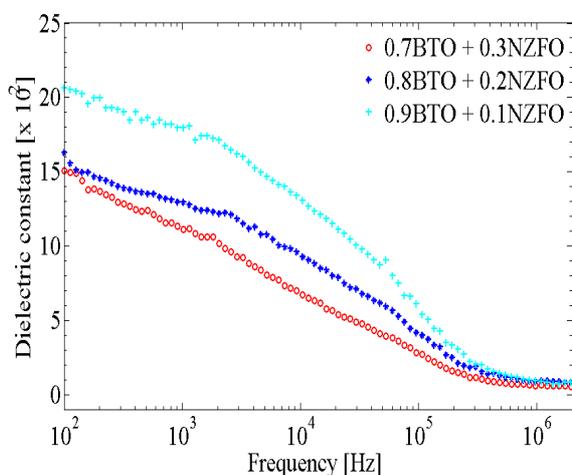
Fig. 3: Variation of dielectric constant as a function of frequency of MMF sintered at 1275ºC.

Shown in Fig. 4 is the temperature dependency of dielectric constant for MMF sintered at 1275 ºC. Evidently, Curie temperature of BTO was 120ºC. Curie temperature for 0.7BTO/0.3NZFO MMF was found to be around 130ºC, for 0.8BTO/0.2NZFO it was around 125ºC and for 0.9BTO/0.1NZFO it was around 122ºC. Curie temperature has shown to be shifted to right with increasing NZFO.
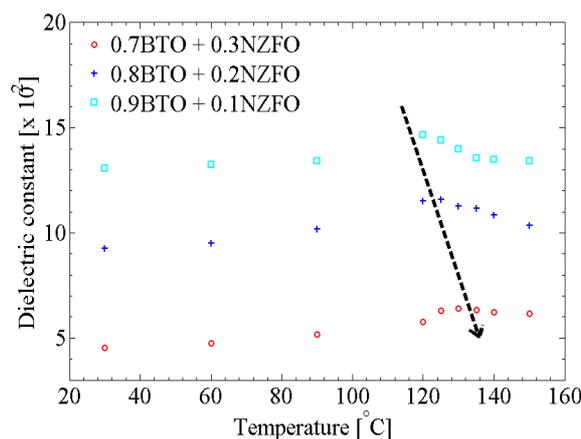
Fig. 4: Variation of dielectric constant as a function of temperature of MMF sintered at 1275ºC.

IV. CONCLUSIONS

Multiphase multiferroics (MMF) were successfully fabricated. XRD analysis confirmed the presence of cubic spinel ferrite phase and the tetragonal perovskite structure of the ferroelectric. An optimal microstructure of MMF was developed using different sintering temperatures and compositional variations. A combination of good theoretical density and grain size was obtained for the samples sintered at 1275ºC. Curie temperature was found to shift at higher temperature with increasing NZFO content. An excellent combination of % theoretical density and dielectric constant value was found for 0.9BTO/0.1NZFO composite sintered at 1275 ºC.

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