**PAPER • OPEN ACCESS**

# Multiferroic properties of lead-free $0.2(Ni_{0.8}Zn_{0.2}Fe_2O_4)$-$0.8(Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3)$ magnetoelectric composite

View the article online for updates and enhancements.

# Multiferroic properties of lead-free 0.2(Ni$_{0.8}$ Zn$_{0.2}$Fe$_2$O$_4$)-0.8(Ba$_{0.85}$Ca$_{0.15}$Zr$_{0.1}$Ti$_{0.9}$O$_3$) magnetoelectric composite

**Anu V Nair, S. Vishnunarayanan, K S Vaishnavi, Pittala Suresh and P S Anil Kumar**[1]
*Department of Physics,*
Indian Institute of Science, Bangalore – 560012, Karnataka, India

E-mail: anil@iisc.ac.in

**Abstract.** In this work the structural, electric and magnetic characteristics of 0.2(Ni$_{0.8}$ Zn$_{0.2}$Fe$_2$O$_4$ (NZF))-0.8 (Ba$_{0.85}$Ca$_{0.15}$Zr$_{0.1}$Ti$_{0.9}$O$_3$ (BCZT)) multiferroic composite is investigated. The constituent phases were synthesized by sol-gel process, and mixed in an appropriate ratio to form the composite. The XRD data and Rietveld refinement confirm that the composite exists in cubic+tetragonal+orthorhombic mixed phases. The *P-E* loop of the composite shows a finite loop opening with a decrease in the polarization compared to the pure BCZT. The *M-H* loops show a saturated loop at an applied field ~ 1 kOe and the values of magnetization decreased nearly by four orders, compared to the pure NZF.

## 1. Introduction

Multiferroics having ferroelectricity, ferromagnetism are of great interest in recent days due to its unique property called magnetoelectric (ME) coupling, in which a cross-coupling exists between electric and magnetic orders. Such materials are very much promising for the spintronic and memory device applications [1]. However, such materials are very rarely available in nature. Particularly, the single-phase multiferroic materials (for example BiFeO$_3$) at room temperature show weak coupling constant due to which the realization of practical applications becomes very difficult. However, the ME coupling can be improved by forming the composite using suitable piezoelectric phase and magnetostrictive phase. In the magnetoelectric composite, strain mediated coupling is possible which is very strong compared to the single-phase materials due to the product property of composites [2, 3]. The magnetostrictive Zinc doped Nickel Ferrite (Zn$_{0.2}$Ni$_{0.8}$Fe$_2$O$_4$) (NZF) is one of the most attractive ferrites in terms of its high magnetic permeability, electrical resistivity, and Curie temperature [4, 5]. The ferroelectric phase selected for the study is Barium-Calcium-Zirconate-Titanate (Ba$_{0.85}$Ca$_{0.15}$Zr$_{0.1}$Ti$_{0.9}$O$_3$) (BCZT) which is a lead-free piezoelectric material. This ceramic exhibits a very high piezoelectric coefficient d$_{33}$ ≈ 620 pC/N [6]. The high piezoelectric property of BCZT is due to the morphotropic phase boundary (MPB) caused by the co-existence of the cubic (C), rhombohedral (R) and tetragonal (T) phases [6, 7]. In the conventional solid-state method, for the formation of BCZT, very high sintering temperatures > 1350 °C are needed and achieving good density is a challenging task. The wet chemical methods like sol-gel, hydrothermal are very effective to reduce the phase formation temperature and to achieve high density at relatively low sintering temperatures. Therefore, the sol-gel method is considered to prepare both BCZT and NZF phases. In this study, a ME composite constituting of 20% magnetostrictive NZF phase and 80% piezoelectric BCZT phase is

---

[1]    To whom any correspondence should be addressed.

prepared using the sol-gel method. The structural, electric and magnetic properties of the composite are investigated.

## 2. Experimental Procedure

The Nickel Zinc Ferrite ($Zn_{0.2}Ni_{0.8}Fe_2O_4$) (NZF) and Barium–Calcium–Zirconate-Titanate ($Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3$) (BCZT) ceramics are synthesized by the sol-gel method. The precursors used for the preparation of the ferrite phase are Nickel Nitrate, Zinc Nitrate, and Ferric Nitrate. Stoichiometric amounts of the precursors are dissolved in deionized water and magnetically stirred. Citric acid is used as the chelating agent. The stirred solution is heated at 250 °C in air to make the powder. The powder is pre-calcined at 600 °C for 10 hours to remove all the nitrates and further, heated at 900 °C for 10 hours to form the required phase. In order to prepare the piezoelectric phase, the precursors of Barium nitrate, Calcium Nitrate, Zirconium Oxynitrate and Titanium Isopropoxide are considered in the stoichiometric amounts. The precursors are dissolved in deionized water separately, stirred thoroughly. Titanium Isopropoxide alone is dissolved in ethylene glycol under a nitrogen atmosphere to avoid the formation of $TiO_2$ and stirred thoroughly to obtain a clear solution. All the solutions are mixed and citric acid is used as the chelating agent. The mixture is heated at 250 °C in the air till all the solvents evaporate. The obtained powder is calcined at 1350 °C.

The $0.2(Zn_{0.2}Ni_{0.8}Fe_2O_4)$-$0.8(Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3)$ composite (0.2NZ-0.8BCZT) is prepared by mixing the 20 % NZF with 80 % BCZT powders obtained through above process. The composite thus obtained is sintered at 1000 °C for 24 hours.

The crystalline structure and phase formation of the ceramics are investigated using X-Ray Powder Diffraction (XRD) (Cu $K_\alpha$ = 1.5406 Å). The room temperature ferroelectric measurements are done using Radiant precision premier II Ferroelectric Tester. The magnetic properties of the ceramics are investigated using Quantum Design PPMS-VSM. The hysteresis loop is recorded at room temperature by sweeping the external field between -4 T and +4 T.

## 3. Results and Discussion

### 3.1. Structural analysis

The room temperature X-ray diffraction of the 0.2NZ-0.8BCZT is shown in Figure 1. The XRD of the composite is compared with that of pure NZF and BCZT compounds. The planes corresponding to both the magnetostrictive, NZF and the piezoelectric, BCZT phases are observed in the XRD spectra, implying the composite phase formation. Moreover, no unidentified peaks are observed in the XRD, which indicates the absence of any new phase evolved during sintering of the composite [2]. The low intensity for the NZF phase diffraction peaks relative to the BCZT can be attributed to the lower composition of the NZF phase in the composite. The XRD data is refined by the Rietveld Method using the FullProf Software to obtain more information on the crystal structure. The structure model is considered by incorporating NZF and BCZT phases. Generally, NZF exists in the cubic structure with the *Fd-3m* space group while BCZT possesses the mixed structures, tetragonal with *P4mm* and orthorhombic with *Amm2* space group. A very good agreement is obtained between the experimental data and the structural model, confirmed by the *R-* values and goodness of fit (mentioned in figure 2). From the refinement, the obtained lattice parameters, cell volume for the NZF and BCZT phases of the composite are listed in Table 1.

Further, the lattice strain of the composite is investigated using Williamson Hall Analysis. The Williamson Hall equation is defined by $\beta \cos\theta = K\lambda/D + 4\varepsilon \sin\theta$, where $K$ is the shape factor; $\beta$ is the full width at half maximum for a particular $\theta$; $D$ is the average crystallite size and $\varepsilon$ is the lattice strain. The plot of $\beta \cos\theta$ vs $4 \sin\theta$ is given in Figure 2. The slope of the graph gives the microstrain and the crystallite size can be calculated from the intercept. The strain obtained from the graph is ~ 0.0009 and the crystallite size calculated from the intercept is ~ 40 nm. This microstrain is coupled with the polarization in these samples, which will be discussed in the later part of the manuscript.
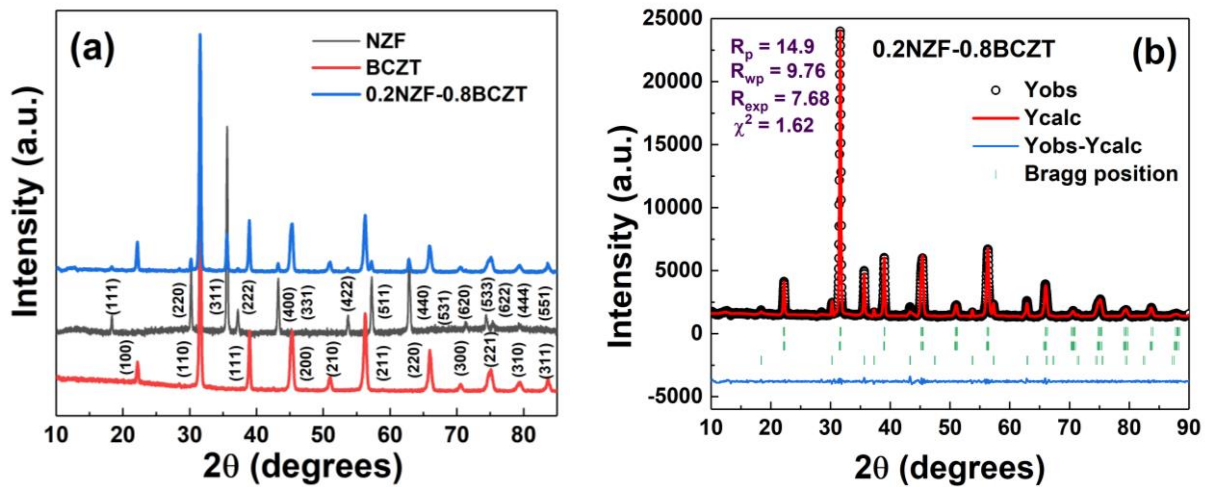
**Figure 1.** (a). The XRD data of 0.2NZ-0.8BCZT, (b). The Rietveld Refinement of 0.2NZ-0.8BCZT. The observed and calculated patterns are shown by circles and lines, respectively. The difference between the observed and calculated patterns is shown by the blue line at the bottom of each panel. The vertical bars represent the Bragg peak positions.

**Table 1.** Refined structural parameters for 0.2NZ-0.8BCZT

| Structures | $a$ (Å) | $b$ (Å) | $c$ (Å) | Cell volume (Å³) |
|---|---|---|---|---|
| Cubic | 8.3549 | 8.3549 | 8.3549 | 583.21 |
| Tetragonal | 3.9928 | 3.9928 | 4.0135 | 63.98 |
| Orthorhombic | 3.9895 | 5.6707 | 5.6816 | 128.53 |
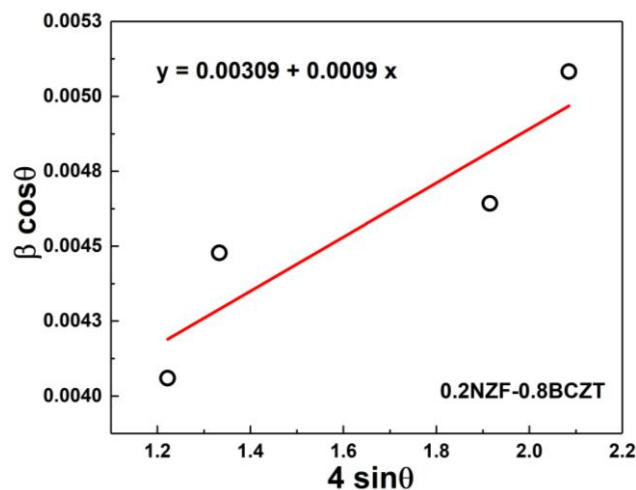


**Figure 2.** Williamson Hall plot of 0.2NZ-0.8BCZT.

### 3.2. Electric properties

Figure 3 shows the ferroelectric hysteresis loops of the pure BCZT and 0.2NZ-0.8BCZT measured at room temperature. The remnant polarization ($P_r$) of the composite and the BCZT are 0.3 μC/cm$^2$ and 1.57 μC/cm$^2$ respectively. The coercive field ($E_C$) of the 0.2NZ-0.8BCZT and the BCZT are 10.66 kV/cm and 4.92 kV/cm respectively. The polarization at high field ($P_{max}$) is reduced to 1.28 μC/cm$^2$ for the composite from 6.73 μC/cm$^2$ in comparison to the BCZT. The reduction of the $P_r$

and $E_C$ of the composite is attributed to the conducting nature of the NZF. The NZF is centrosymmetric and does not have any polarization whereas BCZT being a non-centrosymmetric compound, contributes to the observed polarization. Figure 4 shows the room temperature dielectric constant ($\varepsilon$) and the dielectric loss (tanδ) of the composite measured in the frequency range 20Hz-2MHz. It is observed that there is an increase in the ε and tan δ of the composite with a decrease in frequency. The value of $\varepsilon$ for the composite at 1 MHz is 107.
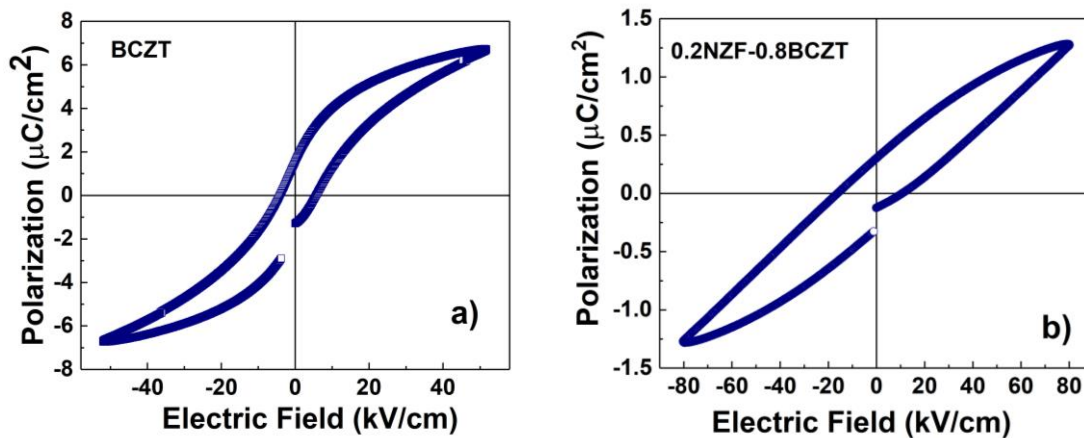


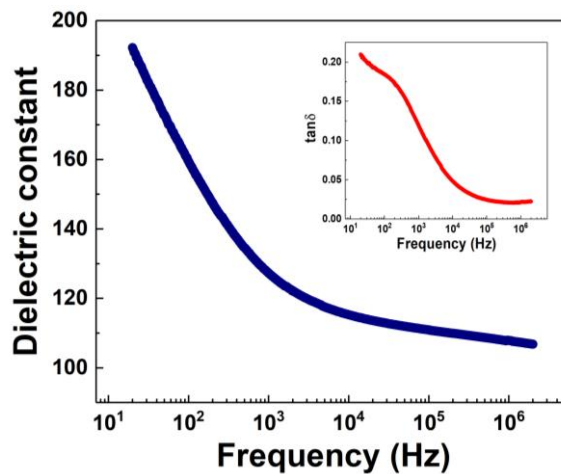**Figure 3.** The P-E loop of a) BCZT and b) 0.2NZ-0.8BCZT measured at room temperature.



**Figure 4.** Dielectric constant of 0.2NZ-0.8BCZT. The inset shows the dielectric loss of the composite at room temperature.

*3.3. Magnetic properties*
Figure 5 shows the *M-H* loops of the composite and pure NZF recorded at room temperature. The saturation magnetization ($M_s$) for the pure NZF and the 0.2NZ-0.8BCZT are 68 emu/g and 13 emu/g respectively. The remnant magnetization ($M_r$) of the NZF is 5.82 emu/g and for the composite is 1.16 emu/g and the coercive field ($H_C$) for the NZF and the 0.2NZ-0.8BCZT are below 100 Oe. The value of the magnetization of the composite is reduced nearly five times to that of pure NZF, indicating that the value of magnetization is scaled to the NZF phase fraction and BCZT has no contribution in the magnetic properties.
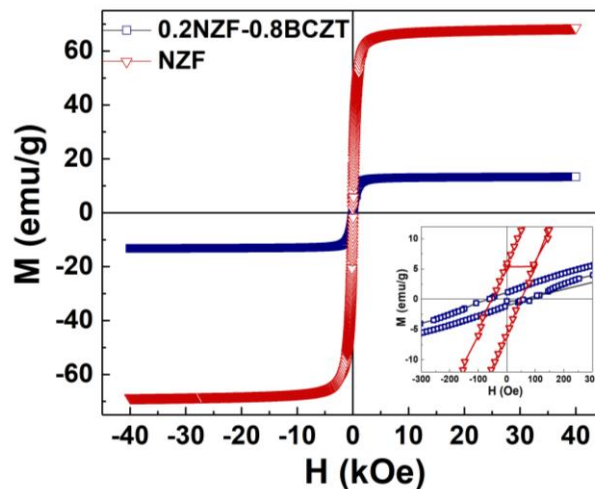
**Figure 5.** The magnetic hysteresis loops of NZF
and 0.2NZ-0.8BCZT at room temperature.

## 4. Summary

The polycrystalline samples of $0.2(Zn_{0.2}Ni_{0.8}Fe_2O_4)-0.8(Ba_{0.85}Ca_{0.15}Zr_{0.1}Ti_{0.9}O_3)$ composites are synthesized through sol-gel method. The crystal structure is confirmed by refining the XRD data to the mixed phases of cubic, tetragonal and orthorhombic phases. The calculated lattice strain and crystallite size of the composite using Williamson-Hall analysis are ~ 0.0009 and ~ 40 nm respectively. The *P-E* loop measurements show a ferroelectric type of behavior for BCZT and the composite. The values of ferroelectric polarization are decreased for the composite, due to the non-polar nature of NZF. The dielectric constant of 0.2NZF-0.8BCZT is found to be 107 at 1MHz. The $M_s$ and $M_r$ of the pure NZF are 68 emu/g and 5.82 emu/g, which are reduced to 13emu/g and 1.16 emu/g for the 0.2NZ-0.8BCZT, respectively. Thus the composite show good ferroelectric and magnetic characteristics which are absent in the individual compounds. Therefore, 0.2NZF-0.8BCZT befits a room temperature multiferroic and is expected to have a good ME coupling through the strain mediation. This coupling effect is much desirable for magnetic field sensors, magnetic recording heads, multiferroic solar cells, multiferroic gyrators, thermal energy harvesters etc. [8].

**Acknowledgments**

**References**
[1]   Spaldin N A and Fiebig M 2015 *Science* **309** 391.
[2]   Praveen P J, Vinitha Reddy M, Dinesh Kumar S, Subramanian V and Das D 2018 *Cer. Inter.* **44** 4298.
[3]   Streubel R, Köhler D, Schäfer R and Eng Lukas M 2013 *Phys. Rev. B*. **87** 054410.
[4]   Ali M A, Uddin M M Khan M N I, Chowdhury F U Z, Hoque S M and Liba S I 2017 *Chin. Phys. B*. **26** 077501.
[5]   Shinde T J, Gadkari A B and Vasambekar P N 2013 *J. Mag. Mag. Mater.* **333** 152.
[6]   Rafiq M A, Rafiq M N and Saravanan K V 2015 *Cer. Inter*. **41** 11436.
[7]   Liu W, Ren X 2009 *Phys, Rev. Let*. **253** 257602.
[8]   Vopson M M 2015 *Crit. Rev. Sol. Mater. Sci.* **40** 223.