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Multiferroic Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$-BaTiO$_3$ nanostructures: Magnetoelastic coupling, dielectric, and fluorescence


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Multiferroic nanostructures of Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$-BaTiO$_3$ (NZF/BT) have been prepared by two synthesis routes, i.e., chemical combustion (CNZF/BT) and hydrothermal (HNZF/BT). The synthesis of CNZF/BT results in nanoparticles of average size 4 nm at 500 °C annealing. However, the synthesis of HNZF/BT with hydrolysis temperature 180 °C/48 h shows nanowires of diameter 3 nm and length >150 nm. A growth mechanism in the fabrication of nanoparticles and wires is given. X-ray diffraction is used to identify the crystalline phase. The transmission electron microscopy shows the dimensions of NZF/BT nanostructures. The ferromagnetism, ferroelectricity, and magnetoelectric coupling show more enhancements in HNZF/BT nanowires than CNZF/BT nanoparticles. The observed polarization depends upon shape of nanostructures, tetragonal phase, and epitaxial strain. The tension induced by the surface curvature of nanowire counters the near-surface depolarizing effect and meanwhile leads to unusual enhancement of polarization. The ferromagnetism depends upon superficial spin canting, spin pinning of nanocomposite, and oxygen vacancy clusters. The magnetoelectric coefficient as the function of applied dc magnetizing field under ac magnetic field 5 Oe and frequency 1093 Hz is measured. The nanodimensions of NZF/BT are observed dielectric constant up to 120 MHz. The optical activity of NZF/BT nanostructures is shown by Fluorescence spectra. © 2014 AIP Publishing LLC.

I. INTRODUCTION

Multifunctionality of magnetoelectric (ME) multiferroic (MF) provides significant potentials for applications such as spintronics, memory, and sensors, to the next-generation multifunctional devices. The reported work of MF shows spintronics, memory, and sensors, to the next-generation multifunctional devices.1–3 The synthesized spintronic systems via stress mediation.8 A large magnetoelectric output voltage has been observed in Pb based MF composites. But recently, owing to concerns regarding the environmental pollution and its toxicity to human beings,9 Pb based MFs are prohibited. Therefore, extensive research is going on worldwide to find Pb free MF composites with high value of ME coefficient. The MF composite of ferroelectric, BaTiO$_3$ (BT), and ferrites has been recently found to exhibit large ME response at room temperature and low magnetic field.1,8,10–12 The ME behavior is strongly dependent on their microstructure and coupling interaction across ferromagnetic-ferroelectric interface. Among various perovskite based MFs, the tetragonal phase of BT nanostructure rarely exists and resides stress near grain boundaries for enhancement of polarization.13 The twinning behavior of polycrystals, which reduce the bulk strain energy, contributes to the resulting twin structure.14 In the recent work,15 we have reported large ferromagnetism in Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ ferrite nanostructure and therefore become a suitable candidate for MF composite.

The MF BT nanostructures (nanoparticles, nanowire, nanorods, etc.) prepared by different synthesizing routes are divided into two categories: First is by adjusting appropriate
stoichiometric ratio as well as concentration of polymer acting as surfactant, etc.\textsuperscript{3,11,13} The second process is hydrothermal, which is surfactant free, and the size and shape of nanostructure depends on the adjustment of pH value, hydrolysis time, and temperature.\textsuperscript{7,16}

In the present paper, we have prepared MF composite of Ni\textsubscript{0.6}Zn\textsubscript{0.4}Fe\textsubscript{2}O\textsubscript{4}-BaTiO\textsubscript{3} (NZF/BT) nanostructure by two different routes, i.e., chemical combustion and hydrothermal. The resulting structural, microstructural, ferroelectric, ferromagnetic, ME coefficient, dielectric, and optical properties have been investigated.

II. EXPERIMENTAL DETAILS

A. Chemical combustion synthesis of Ni\textsubscript{0.6}Zn\textsubscript{0.4}Fe\textsubscript{2}O\textsubscript{4}-BaTiO\textsubscript{3} (CNZF/BT) composite

The CNZF/BT precursor was prepared by mixing the magnetic NZF and ferroelectric BT phases together from nickel nitrate (Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), zinc nitrate (Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O), ferric nitrate (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O), barium nitrate (Ba(NO\textsubscript{3})\textsubscript{2}), tetra-\textit{n}-butyl orthotitanate (C\textsubscript{16}H\textsubscript{36}O\textsubscript{4}Ti), polyethylene glycol (PEG), and urea taken in desired stoichiometric ratios. The process involves two steps: First, the nitrates of nickel, zinc, and iron were added to PEG and kept stirring at room temperature for homogenous mixing called solution A. Second, tetra-\textit{n}-butyl orthotitanate was dissolved in ethanol, and then, barium acetate was added and stirred at room temperature for homogenous mixing called solution B. Both the solution A and B were mixed dropwise with continuous stirring and raised the room temperature to 50°C. Urea was added to it, and the temperature was then raised to 70°C till combustion takes place. Overall, possible chemical reaction is summarised in Fig. 1(a). All nitrates were acting as oxidising agents and PEG and urea were reducing agents. Brown powder so obtained was washed with a mixture of ethanol and water (double distilled) and finally, subjected to annealing at 500°C for 5 h.

B. Hydrothermal synthesis of Ni\textsubscript{0.6}Zn\textsubscript{0.4}Fe\textsubscript{2}O\textsubscript{4}-BaTiO\textsubscript{3} (HNZF/BT) composite

The precursor of HNZF/BT composite mixed together from magnetic (NZF) and ferroelectric (BT) using nickel chloride (NiCl\textsubscript{2}·6H\textsubscript{2}O), zinc chloride (ZnCl\textsubscript{2}·6H\textsubscript{2}O), iron chloride (FeCl\textsubscript{3}), barium acetate (Ba(C\textsubscript{2}H\textsubscript{5}OO)\textsubscript{2}), and KOH as the starting materials. These chlorides of nickel, zinc, and iron were dissolved in mixture of ethanol and distilled water and taken as solution one. Tetra-\textit{n}-butyl orthotitanate was dissolved in ethanol, and then, barium acetate was added to it and taken as solution two. Both of solutions were mixed and subjected to stirring at room temperature for homogenous mixing for 2 h at room temperature. The pH was adjusted to 13 by the addition of mineralizer KOH with stirring. The final solution was poured into Teflon lined steel autoclave, which was kept for heating in programmed furnace at 180°C for 48 h. The resultant material was washed several times with ethanol–water mixture for purification and then dried at 80°C for 8 h in an oven. A detailed of hydrothermal synthesis of NZF/BT is also given in Fig. 1(b).

C. Characterization

The crystalline structure was analyzed by X-ray diffraction (XRD) by using X’Pert PRO PANalytical system and microstructure by transmission electron microscopy (TEM) by using HITACHI H-7500. For electrical measurements, the NZF/BT crystalline powder prepared from both of the synthesis routes was pressed into pellets of thickness ~0.5 mm by the cold isostatic pressing method with a pressure of 5 bar for 10 min and then sintered at 1000°C for 5 h. There may be possibility in the morphology that the resulting specimens have slight growth in their dimensions of grains, which was already described and shown by SEM images in our previous work of PbTiO\textsubscript{3} and BaTiO\textsubscript{3} based MF systems.\textsuperscript{3,17} Polarization under the influence of applied electric field was measured using a Radiant Technologies ferroelectric test system. Magnetization of the NZF/BT was measured at room temperature using Lakeshore 7304 vibrating sample magnetometer. The ME coupling coefficient was measured by the dynamic field method by a system built in-house. A buffer and high-pass filter circuit to reduce the background voltage noise are employed in the measurement set-up to detect the induced ME voltage across the sample thickness. The room temperature dielectric measurement was performed on CNZF/BT and HNZF/BT specimens with frequency varying from 20Hz to 120 MHz using Precision Impedance analyzer (Wayne Kerr 6500B). The photoactivity is shown by fluorescence spectrum of the composite at room temperature using Edinburgh FLSP920 spectrofluorophotometer.

III. RESULTS AND DISCUSSION

The XRD patterns of both CNZF/BT and HNZF/BT composites revealed the presence of spinel and perovskite...
phases together corresponding to NZF and BT, respectively, as shown in Fig. 2. The spinel phase of NZF shown by diffraction angle 2θ = 30.18°, 35.87°, 37.33°, 43.39°, 49.45°, 53.93°, and 57.33° corresponds to (220), (311), (222), (400), (331), (422), and (511), respectively. While 2θ = 21.93°, 22.18°, 31.51°, 39.14°, 44.97°, 45.21°, 50.91°, 55.75°, and 56.24° corresponds to (001), (100), (101), (111), (002), (200), (201/210), (112), and (211), respectively, indicating tetragonal polycrystalline phase of BT. The reflections 001/100 and 200/002 are the splitting of cubic into tetragonal phase. Using the CHEKCELL lattice constant refinement program, the lattice parameters of both phases are summarized in Table I. The distortion ratio c/a of tetragonal phase is 1.007 and 1.0083, respectively, for CNZF/BT and HNZF/BT composite. As shown in Fig. 1(a), the CNZF/BT consists of nanoparticles of very small size having cubic like faces of average diameter 4 nm.

However, Fig. 3(b) shows the nanowires like structure consisting of large number of nanowires. The observed average diameter of HNZF/BT wire is 3 nm, and the length is greater than 150 nm. The inset of Figs. 3(a) and 3(b) shows the random distribution of ferroelectric (BT) and magnetostrictive (NZF) phases into a single nanocrystal. This can be achieved by mixing ceramic precursors for each phase together, forming a blended MF solution. When combustion/hydrothermal/calcination, such a solution will produce biphasic MF nanostructure with a random distribution of grains in each phase. Such type of distribution of MF phases is given in the recent reported work.18

Figures 1(a) and 1(b) show the possible growth mechanism for small nanoparticles of CNZF/BT and nanowires of HNZF/BT composite. In case of CNZF/BT [Fig. 1(a)], the chemical combustion was used where the nanofabrication temperature (annealing) is low (500°C), resulting in small growth of grains. Generally, nitrates serve as excellent providers of oxidising environment, while the urea and PEG serve as reducing and chelating agents. PEG too gets chelated with metal ions. Formation of ammonium nitrate by the reaction of urea with metal nitrate ions helps in lowering of ignition temperature and provides combustion at low temperature with ease. PEG too gets chelated with metal ions and help in combustion process. As combustion takes place, flame release of gases like oxides of nitrogen and carbon dioxide, and water leads to shattering of material into nanosize product. Figure 1(b) is the HNZF/BT composite showing the fabrication of nanowires by hydrothermal synthesis using ethanol as solvent. This solvent plays a key role to create various shapes because ethanol has such ability due to its high coordinating nature towards the metal cation. The main reason for the particles coarsening or Ostwald ripening process is the surface energy reduction.19 This process involves formation of small crystalline nuclei in a suspension which is supersaturated, and then, it is followed by crystal growth, in which the bigger particles will grow at the cost of the smaller ones due to the energy difference between large and smaller particles. The hydrothermal synthesis leads to particle coalescence if treated for longer period of hydrolysis temperature (180°C for 48 h), due to an increased number of coalescence occasions. Addition of KOH helps in precipitation of material and provides basic environment for the reaction. The role of oriented attachment in hydrothermal conditions is that under dispersed conditions, the anisotropic particles are formed by successive collisions without grain rotation and can lead to various particle shapes. The final

Fig. 2. XRD pattern of CNZF/BT and HNZF/BT nanostructure.

Figure 3 reveals the TEM images at different magnification of CNZF/BT and HNZF/BT composite. As shown in Fig. 3(a), the CNZF/BT consists of nanoparticles of very small size having cubic like faces of average diameter 4 nm.

![Figure 3](image_url)

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![Figure 2](image_url)

Figure 2 shows the XRD pattern of CNZF/BT and HNZF/BT nanostructure.

Figure 1(b) is the HNZF/BT composite showing the fabrication of nanowires by hydrothermal synthesis using ethanol as solvent. This solvent plays a key role to create various shapes because ethanol has such ability due to its high coordinating nature towards the metal cation. The main reason for the particles coarsening or Ostwald ripening process is the surface energy reduction.19 This process involves formation of small crystalline nuclei in a suspension which is supersaturated, and then, it is followed by crystal growth, in which the bigger particles will grow at the cost of the smaller ones due to the energy difference between large and smaller particles. The hydrothermal synthesis leads to particle coalescence if treated for longer period of hydrolysis temperature (180°C for 48 h), due to an increased number of coalescence occasions. Addition of KOH helps in precipitation of material and provides basic environment for the reaction. The role of oriented attachment in hydrothermal conditions is that under dispersed conditions, the anisotropic particles are formed by successive collisions without grain rotation and can lead to various particle shapes.

### Table I. Values of lattice parameters a of NZF and BT (a and c), diameter (d), length (l), spontaneous polarization (P_s), saturation magnetization (M_s), maximum magnetoelectric coefficient (\(c_E\)), and dielectric constant (\(\varepsilon_r\)) of NZF/BT nanostructures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constant</th>
<th>Multiferroic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NZF a (Å)</td>
<td>BT a (Å)</td>
</tr>
<tr>
<td>CNZF/BT</td>
<td>8.395</td>
<td>3.995</td>
</tr>
<tr>
<td>HNZF/BT</td>
<td>8.441</td>
<td>3.998</td>
</tr>
</tbody>
</table>
particle can result from several attachment events along the same surface, giving an uncontrollable shape in agglomerates. It is believed that the present case involves under dispersed conditions; the steric hindrance may have led to effective collisions in only one crystallographic direction due to different ionic radii of all metal ions resulting into formation of nanowires like structure.

Figures 4, 5(a), and 5(b) show the coexistence of ferroelectricity and ferromagnetism of CNZF/BT and HNZF/BT nanostructure, respectively, by measuring polarization versus electric field (P-E) and magnetization versus magnetizing field (M-H) hysteresis curves at room temperature. The P-E hysteresis loops measured at room temperature on poled specimen of CNZF/BT composite with 50 Hz frequency of polarization [Fig. 4(a)] results in the value of spontaneous polarization, \( P_s = 16.51 \mu \text{C/cm}^2 \), remanent polarization, \( P_r = 7.54 \mu \text{C/cm}^2 \), and coercive field, \( E_c = 13.97 \text{kV/cm} \). However, the values of \( P_s = 24.37 \mu \text{C/cm}^2 \), \( P_r = 11.78 \mu \text{C/cm}^2 \), and \( E_c = 15.54 \text{kV/cm} \) are observed in HNZF/BT composite [Fig. 5(a)]. These values of \( P_r \) for both the samples of NZF/BT composite are given in Table I and shows improvement than reported work of BT based composites, which are explained as: first; the surface defects by large value of surface to volume ratio of nanostructures. Second, the polycrystalline phase of BT is tetragonal. This tetragonal phase with nanograins has twin structure by which the stress residing near grain boundaries can easily control depolarization field, and therefore, the long-range interactions support the development of homogeneous polarization; and the elastic constraints form strain energetic and its stress relieving twinning mechanism. Hence, the enhancement in ferroelectric polarization is possible. Third is the epitaxial strain growth between ferrite and ferroelectric interface introduced by the lattice mismatch between cubic phase of spinel (NZF) and tetragonal (BT) result in large ferroelectric polarization. It has also been observed that the NZF/BT composite prepared by hydrothermal synthesis have higher value of polarization than those by chemical combustion, which is explained based on the shape of nanostructure. The HNZF/BT composite has 1D nanowire like structure and the ferroelectric polarization in such type of 1D system is explained on the basis of First-principles density functional theory using local density approximation Hellmann-Feynman theorem by Cai et al. for their ferroelectric system of perovskite PbTiO$_3$ nanowires. By this assumption, the surface compressive stress caused by 1D shape produces an effective tensile in the length direction in nanowires and then leads to a big off-center displacements that enhances the spontaneous polarization. This enhancement in polarization is attributed to the competition between itself surface tension and near-surface depolarizing effect.

Figures 4 and 5(b) show the ferromagnetic behaviors of NZF/BT composites by measuring M-H hysteresis at room temperature. The values of saturation magnetization (\( M_s \)) are
12.26 and 18.35 emu/g, and coercive field ($H_c$) are 81.93 and 69.56 Oe, respectively, for CNZF/BT and HNZF/BT nanocomposites, and are also given in Table I. In both of these composites of NZF/BT, the nanostructural grains show ordered magnetic structure (soft ferromagnetic) causing a non-linear hysteric character because the large surface to volume ratio of nanograins leads to superficial spin canting, spin pinning, or broken exchange bonds. It is possible from microstructure that the area of NZF nanograins are percolated by a large number of small BT particles, causing an increasing number of disordered regions at the interface, and therefore, the magnetic properties of NZF/BT nanocomposite are determined not only by the NZF concentration but also by the degree of connectivity of the two-phase component grains. The HNZF/BT shows nanowire like structure resulting in higher magnetization than CNZF/BT nanoparticles. This is explained by the effective exchange interactions between the unpaired electrons spins, originating from the surface defects such as oxygen vacancy clusters instead of single neutral oxygen vacancies associated with the nanoparticles.

Multiferroicity is the coexistence of ferroelectricity and ferromagnetism gives ME coupling whose strength is measured in terms of magnetoelastic coefficient ($\kappa_\ell$) under a static magnetic field $H_{dc}$, superimposed with a small ac magnetic field $H_{ac}$. The $\kappa_\ell$ is given by $\kappa_\ell = V_{out}/H_{ac} \times t$, where $t$ is the sample thickness and $V_{out}$ is the induced ME voltage. The variations of $\kappa_\ell$ with $H_{dc}$ at ac magnetic field frequency of 1093 Hz and $H_{ac}$ magnetizing field of 5 Oe for both the composites of NZF/BT nanostructure measured at room temperature are shown in Figs. 4 and 5. The maximum value of $\kappa_\ell$ is 78.57 and 102.54 mV/cm Oe, respectively, for CNZF/BT and HNZF/BT. These values of $\kappa_\ell$ are given in Table I and show improvement than the reported work of BT based composites. Generally, the value of $\kappa_\ell$ linearly increases to a maximum value and then decreases linearly to zero with varying $H_{dc}$ of applied magnetic field. But, in the present case of NZF/BT, the $\kappa_\ell$ is non-linearly varying and also observe stability at certain value of applied $H_{dc}$ magnetic field depends on two factors: first, the two-phase nanostructural composite coupled by interfacial strain where ME behavior is strongly dependent on their nanograins and the coupling interaction across the piezoelectric/magnetostrictive interface. It is expected that a residual stress generated can be responsible for the eventual nucleation, evolution, and coalescence of voids, which strongly hinder the domain reorientation, and therefore control the resulting polarization of ME. Second, the dependence of magnetoelastic yield on the bias field, $H_{dc}$, may be ascribed to the nonlinear magnetoelastic stress coupling because it is believed that a bias field favors a parallel spin alignment for all magnetic domains so that the magnetoelastic response is more significant.

Figure 6 shows the variation of dielectric constant ($\varepsilon_r$) and dielectric loss (tan $\delta$) of CNZF/BT and HNZF/BT nanocomposites measured at room temperature in the frequency range of 20 Hz–120 MHz. Both of the composites showing variation in the dielectric constant in the low frequency region is explained on the basis of space charge polarization due to inhomogeneous dielectric structure. These inhomogeneities exist due to impurities, porosity, and grain structure.
indicates dielectric dispersion following the Maxwell-Wagner type interfacial polarization.35,36

Figure 7 shows fluorescence spectrum of NZF/BT nanocomposites at room temperature. It is well known that the point defects, oxygen vacancies, and interstitials are key factors responsible for emission spectrum. In case of BT, the charge transfer spectra from the central Ti$^{3+}$ ion to a neighbouring O$^{2-}$ ion inside octahedron of TiO$_6^{2-}$ from intrinsic defects result into luminescence in the BT system.37 While in case of NZF ferrite, first blue band observed is due to interstitial and defect emission, while system corresponding second band is due to their phase formation.38 Composite HNZF/BT via hydrothermal synthesis shows remarkable high intensity of blue, green, yellow, and red band emissions than CNZF/BT.

IV. CONCLUSION

The MF NZF/BT composite has been successfully synthesized by chemical combustion and hydrothermal routes. The growth mechanism in the formation of small nanoparticles of CNZF/BT is given by the use of nitrates as oxidising agent, and PEG and urea as reducing agent during combustion and annealing. The nanowires of HNZF/BT are formed due to different ionic radii of metal ions, and Ostwald ripening and annealing. The nanowires of HNZF/BT are formed due to different ionic radii of metal ions, and Ostwald ripening and annealing.

The TEM images show that the average particle size is 4 nm for CNZF/BT, and for HNZF/BT nanowires, the average diameter is 3 nm and length is >150 nm. The value of $P_s = 16.51$ and 24.37 $\mu$C/cm$^2$, and $P_e = 7.54$ and 11.78 $\mu$C/cm$^2$, and $E_e = 13.97$ and 15.54 kV/cm, respectively, observed for CNZF/BT and HNZF/BT. The values of $M_s$ are 12.26 and 18.35 emu/g, respectively, measured for CNZF/BT and HNZF/BT. The maximum value of $\varepsilon_r$ is 78.57 and 102.54 mV/cm Oe, respectively, observed for CNZF/BT and HNZF/BT MFs. The value of $\varepsilon_r$ at 10 MHz is 31 and 55, respectively, measured for CNZF/BT and HNZF/BT. The point defects, oxygen vacancies, and interstitials give the emission spectrum of NZF/BT nanocomposite.