Abstract

Multiferroic (magnetolectric or magnetodielectric) materials are greatly focused by the scientific community through worldwide because of their intriguing fundamental physics and novel multifunctional device applications. Magnetolectric or magnetodielectric materials are nothing but the coupling between the two materials having ferroelectric and ferromagnetic phase. Here, in ME or MD materials the electric polarization can be induced by means on application of magnetic field or vice-versa. Coupling between the piezoelectric effect of ferroelectric material and magnetostrictive effect of magnetic material are mainly responsible for the ME effect in the composites. Lead based material like; (PZT) is one of the most studied and widely used ferroelectric materials with its high ferroelectric and piezoelectric properties. But, toxicity of lead containing material hinders its use in many applications. Also, lead based materials are banned in many countries worldwide, therefore search of lead free material having compatible properties to those lead containing material is the big task for a researchers among worldwide. Amongst different lead-free piezoelectric materials such as BaTiO$_3$, (BiNa)TiO$_3$, (KNa)NbO$_3$ and the solid solutions of (Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$-Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ (BCT-BZT) are likely to be the most probable candidates for the replacement of lead based materials.

In the present work, we have synthesized the lead free ferroelectric composite $[x(Ba_{0.7}Ca_{0.3})TiO_3-(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3]$ (BCT-BZT) where $x = 0.15, 0.3, 0.4$ and $0.5$. On the other hand ferromagnetic phase Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO) is selected as a magnetostrictive material to make coupling with ferroelectric BCT-BZT. Here, microwave sintering technique is implemented for the complete formation of ferroelectric, ferromagnetic and magnetodielectric phases. Following ferroelectric, ferromagnetic and magnetodielectric systems are synthesized in bulk phase employing hydroxide co-precipitation method and sintered using microwave sintering technique at 1100 °C and 1200 °C.

1) Ba$_{0.7}$Ca$_{0.3}$TiO$_3$ (BCT)
2) BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (BZT)
3) $[x(Ba_{0.7}Ca_{0.3})TiO_3-(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3]$ (BCT-BZT) for $x = 0.15, 0.3, 0.4$ and $0.5$
4) Co$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ (CNFO)
5) $x[CNFO]-(1-x)[0.5BCT-0.5BZT]$ where $x = 0.1, 0.2, 0.3$ and $0.4$. 
After being sintered the composite and parent phases of these materials are characterized by various techniques. On the other hand thin films of ferroelectric 0.5BCT-0.5BZT and magnetodielectric CNFO-(0.5BCT-0.5BZT) were synthesized by using sol-gel method followed by spin coating.

Here, it is seen that the ferroelectric and magnetodielectric bulk samples processed with microwave sintering technique posses higher density. Ferroelectric composition 0.5BCT-0.5BZT shows higher value of Curie temperature with enhanced dielectric and ferroelectric properties. Existence of rhombohedral and tetragonal crystal structure at room temperature confirms the morphotropic phase boundary (MPB) in BCT-BZT composition. This could be again confirmed from the temperature dependent dielectric properties with existence of two dielectric anomalies. Raman spectra confirm phase transition in the ceramic samples. Co$_{1-x}$Ni$_x$Fe$_2$O$_4$ (where \(x = 0.1\)) were prepared by using the hydroxide co-precipitation method. An obtained precipitate was sintered at 1100 °C by microwave sintering technique. The structural analysis confirms the single-phase cubic spinel structure with Fd-3m space group. The magnetic characterization was carried out at temperature 5k, 150k and 300K. It is seen that the saturation magnetization (Ms) and Bohr magnetron (\(\mu_B\)) has higher values at lower temperature 64.15 emu/gm and 2.69 and decreases at room temperature. Irreversibility is observed between the ZFC and FC curves at 100 Oe.

Magnetodielectric composite of \(x[Co_{0.9}Ni_{0.1}Fe_2O_4]-(1-x)[0.5(Ba_{0.7}Ca_{0.3})TiO_3-0.5Ba(Zr_{0.2}Ti_{0.8})O_3]\) where, \(x = 0.1, 0.2, 0.3, 0.4\) have been prepared by the Co-precipitation method followed by microwave sintering. The properties of the sintered composites are investigated through the different techniques viz. structural, micro structural, dielectric, magnetic, and magneto-dielectric analysis. X-ray diffraction analysis confirms the perovskite phase and spinal phase respectively. The dielectric constant and loss factor of the composites were studied as a function of frequency and temperature. It is observed that the dielectric constant has two anomalies one correspondence to ferroelectric to paraelectric transition below \(~ 130 \, ^\circ C\) of BCT-BZT and second is the magnetic transition of CNFO above \(~ 450 \, ^\circ C\). Both the ferroelectric and ferromagnetic behaviours of the composites are observed at room temperature with strong dependence on the content of magnetic material. Saturation magnetization (Ms) increases with increasing the content of CNFO ferrite. Magneto-capacitance is measured by applying magnetic field up to 1 tesla. Magneto-capacitance increases with increase in the magnetic field. Raman analysis of ferroelectric, magnetic and magnetodielectric compounds confirms the formation of respective phase. With increasing
concentration of the ferrite CNFO values of saturation polarization decreases continuously, this may resulted as increase in ferrite concentration reduces the ferroelectric nature of BCT-BZT and ferroelectric hysteresis loop becomes more circular. Here, it is seen that the MD composites sintered at lower temperature (1100 °C) posses positive magnetocapacitance and the numerical value of magnetocapacitance at maximum applied magnetic field at x=0.2 and 0.4 are high (6-7%). Increasing sintering temperature results in enhancement of linear magnetoelectric coupling coefficient (α). Here the 0.4CNFO-0.6(0.5BCT-0.5BZT) MD composite sintered at 1200 °C shows a ME value (~ 21 mV/Oe.cm). The Saturation magnetisation, magnetic moment and coercive field of the composites increase with increase in CNFO content. Increase in the Hc value with increase in ferrite concentration indicates that the magnetization becomes harder.

0.5BCT-0.5BZT ferroelectric thin film and CNFO-[0.5BCT-0.5BZT] MD thin film deposited on Pt/Ti/Si/SiO$_2$ substrate using spin coating technique. The deposited ferroelectric thin film after annealing at 800 °C, shows perovskite structure with tetragonal crystal structure having lattice parameters $a = b = 4.006$ and $c = 4.068$. On the other hand CNFO-[0.5BCT-0.5BZT] magnetodielectric thin film exhibits both crystal structures, i.e. cubic spinel structure corresponding to ferrite material and perovskite tetragonal crystal structure of ferroelectric phase. Real part ($\varepsilon_r$) and imaginary part ($\varepsilon'$) of dielectric constant were measured at room temperature and plotted against frequency. Dielectric behaviour of thin has similar kind of nature as observed for bulk ferroelectric and magnetodielectric composites. The both thin films are analyzed by Raman spectroscopy for their vibrational modes. Thin films shows similar kind of properties as observed in case of bulk counterparts.

**Keywords:** Lead free ferroelectric; 0.5BCT-0.5BZT; CNFO; microwave sintering; dielectric measurement; ferroelectric properties; magnetic properties; magnetoelectric properties; magnetocapacitance