List of Figure

Figure 1.1 Schematic illustration of the orientation of magnetic moments in materials [source
http://electrons.wikidot.com/magnetism-iron-oxide-magnetite]
Figure 1.2 Schematic illustrations of multiferroics defined from the combination of ferroelectric
and magnetic properties[1]
Figure 1.3 Classification of "ferroic" orders according to symmetry [9]
Figure 1.4 Origin and microscopic mechanism of ferroelectricity in type-I multiferroics (a) In
mixed perovskite, a d^0 ion (green circles) cause for ferroelectricity and magnetic d^n ions (red
circles) responsible for magnetism. (b) Ferroelectricity due to lone pairs (c) Charged-ordered
ferroelectricity in multiferroics and (d) Geometrically frustrated ferroelectricity [1]40
Figure 1.5 Different types of spin structures relevant for type-II multiferroics. (a) Sinusoidal spin
wave, in which spins have to point along one direction but vary in magnitude. This structure is
centrosymmetric, and consequently, the value of ferroelectricity is zero. (b) The cycloidal spiral
with the wave vector $Q = Q_x$ and spins rotating in the (x,z)-plane. It is in this case where one
finds non-zero polarization, $P_Z \neq 0$. (c) In a so-called proper screw; the spins rotate in a plane
perpendicular to Q. Here, the inversion symmetry is broken, but most often it does not produce
polarization although in some instances it might [1]
Figure 1.6 Co/Mn Ising chain with two states of spin ordering in Ca ₃ CoMnO ₆ . Ions are displaced
from ideal positions (broken circles) leading to an electric polarization [21]
Figure 1.7 (a) Magnetoelectric coupling. (b) Direct magnetoelectric effect[24]45
Figure1.8ABX3perovskitestructure.(Source:
https://nptel.ac.in/courses/113104005/lecture4/4_2.htm)

Figure 1.9 Schematic diagram of crystal structure of BFO unit cell. The unit cell can be pictured
as a pseudo-cubic structure which is outlined in blue. Two pseudo-cubic structures are needed to
describe the rhombohedral unit cell.(b) Schematic diagram of the magnetic lattice of BiFeO3
showing G-type antiferromagnetic cell where the nearest neighbor spins are antiparallel. The Fe
spin resides in pseudo-cubic. (c) Schematic diagram of the arrangement of the macroscopic order
parameter (P, L, and M) of the thin film [24]
Figure 1.10 Evolution of the tolerance factor and density of the RMnO3 phase as a function of
ionic radius [41]
Figure 1.11 Phenomenological picture of exchange bias for and AF-FM bilayer [50] 55
Figure 2.1 Flow chart of solid state method
Figure 2.2 The phase formation of prepared samples has been studied by using Rigaku-MiniFlex-
II DESKTOP powder X-ray diffractometer with Cu K α radiation (λ = 1.54 Å) at 30 kV and 15
mA. Crystal structures of each composition were recorded at 2 Θ angle between 20 and 80° with
a step size of 0.02. X-ray diffraction analysis revealed all the important parameters such as
crystalline structure, lattice parameters, unit cell volume, atomic packing fraction etc70
Figure 2.3 (a)Energy level diagram showing states involved in Raman signal. The line thickness
is roughly proportional to the signal strength from the different transitions. (b) Renishaw micro
Raman spectroscope
Figure 2.4 UV-Vis.set up
Figure 2.5 MPMS3 set up
Figure 2.6 A Sawyer-Tower circuit for the measurement of ferroelectric hysteresis loop
Figure 2.7 Transitions that contribute to XAS edges
Figure 2.8 Typical components of modern XAS beamline

Figure 3.1 Rietveld refinement profiles of X-ray diffraction patterns of $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ and
$Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.45}Ti_{0.05}O_3$ samples. The dots represent the observed data while solid line
through dots s the calculated profile, vertical tics below curves represent allowed Bragg-
reflections for the wurtzite phase. The difference is given below the vertical tics
Figure 3.2 Room-temperature micro-Raman spectra of (a) $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ and (b)
$Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.45}Ti_{0.05}O_3$ samples
Figure 3.3. Magnetization vs. applied magnetic field variation of (a) $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ and
(b) $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.45}Ti_{0.05}O_3$
Figure 3.4 Temperature dependence of the in-phase component of ac susceptibility measured
under a field of 500 Oe under the field-cooled condition for $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ and
$Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.45}Ti_{0.05}O_3$
Figure 3.5. (a) Survey scan (b) Bi4f, (c) Fe2p, (c) Fe3s and Mn3s, (d) Mn2p, (f) Fe2p and (g)
La3d core level X-ray photoemission spectra for Bi0.5La0.5Fe0.5Mn0.5O3 at 300 K
Figure 3.6 (a) Survey scan, (b) Bi4f, (c) Fe2p, (d) Fe3s and Mn3s, (e) La3d, (f) Mn2p, and (g)
Ti2p and Bi4d core level X-ray photoemission spectra for Bi0.5La0.5Fe0.5Mn0.45Ti0.05O3 at
300 K
Figure 3.7. Variation of ϵ' and $tan(\delta)$ with respect to temperature at 1kHz , 10khz , 50kHz ,
$100 kHz, 1 MHz \ and \ 2 MHz \ for \ (a) Bi_{0.5} La_{0.5} Fe_{0.5} Mn_{0.5} O_3 \ and \ (b) \ Bi_{0.5} La_{0.5} Fe_{0.5} Mn_{0.45} Ti_{0.05} O_3 \ . \ 103 Mn_{0.45} Ti_{0.45} O_3 \ . \ 103 Mn_{0.45} O_3 \ . \ $
Figure 4.1 Rietveld refinement profiles of X-ray diffraction patterns of $Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.5}O_3$ and
$Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.40}Al_{0.1}O_3$ samples
Figure 4.2. Room-temperature micro-Raman spectra of Bi _{0.5} La _{0.5} Fe _{0.5} Mn _{0.5} O ₃ and Bi
$_{0.5}La_{0.5}Fe_{0.5}Mn_{0.40}Al_{0.1}O_3$ samples

Figure 4.3. Variation of ε' and $tan(\delta)$ values with respect to temperature at
1KHz, 10 KHz, 50 KHz, 100 KHz, 1 MHz and 2 MHz for (a)Bi _{0.5} La _{0.5} Fe _{0.5} Mn _{0.5} O ₃ and (b)
$Bi_{0.5}La_{0.5}Fe_{0.5}Mn_{0.40}Al_{0.1}O_3.$ 112
Figure 5.1. Rietveld refinement of the XRD data of the composite 0.7BFO-0.3TMO. Inset shows
the Williamson-Hall plot to calculate the microstrain
Figure 5.2. AFM (left) and MFM (right) image of the 0.7BFO-0.3TMO Composite 125
Figure 5.3. ZFC and FC magnetization vs. temperature plots for (a) 0.7BFO-0.3TMO and (b)
0.8BFO-0.2TMO composites under an applied magnetic field of 1000 Oe. Inset: the dM/dT vs T
plots for the respective sample. The arrows in the insets point towards the spin reorientation
transition temperature T*
Figure 5.4. The M-H loop of (a) 0.7BFO-0.3TMO and composite measured at different
temperature across 5-300 K after field cooling (1 T) from a higher temperature. Insets (a) and (b)
show close view of the M-H loops around zero field measured at 275 K and 80 K respectively.
Figure 5.5 The temperature dependence of exchange bias field (H_{SEB}) and coercivity of 0.7BFO-
0.3TMO
Figure 5.6 Isothermal remnant magnetization (IRM) and the virgin loop of magnetization vs.
magnetic field of the composite 0.7BFO-0.3TMO
Figure 5.7 Fe $L_{2,3}$ XAS and XMCD spectra of (a) 0.7BFO-0.3TMO at 300 K (b) 0.8BFO-
0.2TMO at 300 K (c) 0.7BFO-0.3TMO at 180 K (d) 0.8BFO-0.2TMO at 180 K. XMCD signal
was multiplied by 5 in all the cases for better visualization. Inset in (a) and (b) shows the
comparison of t_{2g} peak of L_3 edge and L_2 edge of the composites with standard $\alpha\mbox{-}Fe_2O_3$
respectively

Figure 5.8 Mn L_{2.3} XAS and XMCD spectra of (a) 0.7BFO-0.3TMO at 300 K (b) 0.8BFO-0.2TMO at 300 K (c) 0.7BFO-0.3TMO at 180 K (d) 0.8BFO-0.2TMO at 180 K. XMCD signal was multiplied by 5 in case of (a) and (b) for better visualization. Inset in (a) shows the comparison between XAS spectra from 0.7BFO-0.3TMO, 0.8BFO-0.2TMO and standard α -Figure 6.1 (a) temperature dependent Raman spectra of the BFO-TMO composite. (b) Variation of Raman shift of the stretching vibration with temperature. The red line shows the fitting according to eq. 6.1. Inset in figure 6.1(a) shows the x-ray diffraction pattern of the sample 0.7BFO-0.3TMO. Inset in figure 6.1(b) shows the variation of $\delta\omega$ and $[-M^2/{M_0}^2]$ with Figure 6.2 Temperature dependent real part of dielectric constant of BFO-TMO. Inset shows Figure 6.3. Variation of (a) ε' (b) ε'' and (c) tan δ with frequency of the composite BFO-TMO. (d) Variation of real part of dielectric constant with and without magnetic field. Inset in(b) shows ε " variation of frequency fitted with an equation consisting both Debye and Maxwell-Wagner contribution. Inset in (d) shows Variation of % MD with magnetic field at 250 K and measuring Figure 6.4. Typical impedance plot (Cole-Cole plot) of BFO-TMO composite at (a) 300 K (b) 275 K (c) 225 K and (d) 200 K. The red lines in the plots show the fitting of the data as per eq. 5. Figure 7.1 (a)-(c): FESEM images from fractured surfaces of the single phase BFO, TMO and composite 0.7BFO-0.3TMO respectively and insets shows the corresponding calculation of

grains size by eimage j software. (d) EDXA graph of the composite 0.7BFO-0.3TMO with its
chemical composition in the insets
Figure 7.2 FTIR spectrum of the composite 0.7BFO-0.3TMO recorded at 300 K 172
Figure 7.3 (a) XPS survey scan of 0.7BFO-0.3TMO at 300 K. Deconvoluted detail spectra of (b)
Fe 2p (c) O 1s(d) Mn 2pof composite 0.7BFO-0.3TMO.Detail spectra of (e) Tb 3d and (f) Bi 4f.
Figure 7.4. Tauc plot for the determination of the optical band gap of the composite 0.7BFO-
0.3TMO at room temperature. The black dashed arrow is guide to the eye, showing the extracted
bad gap. The inset shows the absorption spectrum of the composite from which the Tauc plot has
been estimated 177
Figure 7.5 (a) Schematic diagram of the band structure. Inset shows the XPAS valence spectra of
the composite 0.7 BFO-0.3 TMO. The red line is guide to the eye showing the position of the edge
of the valence band. (b) Valence band XPS spectrum of the composite at 300 K. (c) UPS
spectrum of the composite at room temperature
Figure 7.6 Temperature dependent resistivity of the composite0.7BFO-0.3TMO. Inset (a) lnp vs.
$1/T$ plot showing Arrhenius plot. Inset (b) lnp Vs. $(1/T)^{1/4}$ showing the plot for variable range
hopping 182
Figure 7.7 Room temperature M-H loop of the composite 0.7BFO-0.3TMO. Inset shows the
room temperature M-H loop of pure BiFeO ₃
Figure 8.1 Room temperature X-ray diffraction (XRD) with Rietveld refinement pattern of
BLFMCO sample. The hollow dots correspond to the observed data (Yobs.), solid red lines pass
through these dots represents the calculated data (Ycal.), and solid blue lines represent the
difference between these two, i.e. (Yobs. – Ycal)

Figure 8.2 Characteristics Raman spectra measured at room temperature for polycrystalline (a)
BLFMO (b) BLFMCO samples
Figure 8.3 (a)Temperature dependence of magnetic moment (M-T curves) of BLFMCO sample
measured under an applied field of 500Oe under field cooling (FC) and Zero-field cooling (ZFC)
conditions
Figure 8.4 Magnetization(M) vs. magnetic field(H) hysteresis loops measurement of sample
BLFMCO obtained at different temperatures (i) 300K (ii) 200K (iii) 80K () 2K. (Insets shows the
enlarged view of M-H curves)
Figure 8.5. Spontaneous Wasp-waisted Magnetic hysteresis loop of sample BLFMCO at 80K.
Figure 8.6 Dielectric constant vs. temperature plots of BLFMCO samples. (The corresponding
loss tangent is presented in the inset of Figure 8.6)
Figure 8.7 Dielectric constant vs. temperature variation of BLFMCO sample under the magnetic
field of 1T. (The corresponding loss tangent is presented in the inset of Figure 8.5