Chapter 6
Electric and Magnetic properties of $Ga_{0.75}Er_{0.25}FeO_3$

6.1 INTRODUCTION

Multiferroic (MF) materials have attracted the interest of researchers due to their fascinating magnetoelectric characteristics and prospective applications to a new form of memory resources device[4]. Multiferroic material includes more than one ferroic orderings in the same phase, such as antiferromagnetic/ferromagnetic/ferrimagnetic, ferroelectric, ferroelastic, and ferrotoroidic. There are only a few materials currently exist that exhibit multiferroicity owing to the mutual exclusion of electrical and magnetic spontaneous polarization[16,242]. The most widely used and studied MF is BFO, which has a ferroelectric transitional temperature of 1103 K and a magnetic transition temperature of 643 K. $BiFeO_3$ exhibits a large magnetization of 0.5–1.0 μB/Fe and significant spontaneous polarisation (Pr ~ 50–60 $\mu C/cm^2$) at room temperature in an epitaxial thin film. The material's tiny ME coupling coefficient and large leakage current, as realized, prevent practical device applications[29]. $GaFeO_3$ (GFO) is one of the most attractive choices among them because of its significant magnetoelectric effect and distinctive magnetoelectric, magneto-optic, and piezoelectric capabilities[243–245]. GFO forms a ferrimagnetically ordered spin structure in the polar orthorhombic Pna21 (also known as Pc21n) space group during crystallization. In the Pna21 configuration, the four Fe^{3+} ions in a unit cell are antiferromagnetically linked along the axis. On the other hand, the intermixed Fe^{3+} ions occupying the Ga sites (or various Fe occupations at the Fe1 and Fe2 sites) can result in a ferromagnetic order with Fe^{3+} ions at the Fe sites, which gives rise to ferrimagnetic ordering at a temperature of 230 K[25,246]. Rado in 1960 found an exceptionally unusual magnetoelectric phenomenon in the bulk GFO [247].

Since the GFO is understood to exhibit significant magneto-crystalline anisotropy, the shape and nature of the magnetic properties strongly depend on the degree of strength of the applied measuring field in comparison to the magnitude and temperature variation of the coercivity, i.e., the magneto-crystalline anisotropy[248]. In recent years, many efforts have been made to develop innovative gallium ferrite compounds and explore their associated characteristics. One can better explain a system's magnetic properties by having a deeper understanding of the electronic structure of the system. We have comprehensively studied the magnetic and dielectric properties as well as the electronic structure at ambient temperature using XPS analysis in the current work with $Ga_{0.75}Er_{0.25}FeO_3$.

6.2 EXPERIMENTAL DETAILS

The standard solid-state reaction approach was used to synthesize the polycrystalline $Ga_{0.75}Er_{0.25}FeO_3$ (GEF25). Highly pure oxides, including Ga_2O_3, Er_2O_3, and Fe_2O_3 were mixed in stoichiometric proportions and grounded in an agate mortar for around 2 hours. Then put this material at 900 °C for 20 hours inside a furnace for heat treatment and then reground for calcination at 1050 °C for 20 hours and intermittent grinding and again put it for calcination at the same temperature for 30 hours and reground and make pellet and then sintered at 1280 °C for 40 hours then cool down to room temperature, all heating process done in air medium. An X-ray diffractometer called the Rigaku Miniflex-II (Cu K) was used to conduct the powder X-ray diffraction (XRD). The structure of the XRD pattern was analyzed using the Rietveld method in Fullprof software. All of the temperature-dependent magnetization measurements utilized the superconducting quantum interference device (SQUID) based magnetic property measuring system (Quantum Design-MPMS). High-resolution X-ray photoemission spectroscopy (XPS) was used to confirm the valence states and composition of the manufactured pellets. The Keysight E4980A (using the usual two-probe approach) precision LCR meter was used to perform dielectric measurements utilizing a He-cooled closed-cycle refrigerator (CCR).

6.3 RESULTS AND DISCUSSION

6.3.1 X-RAY DIFFRACTION STUDY:

Fig. 6.1 is showing the room temperature XRD patterns of GEF25 in the range of 15 to 80º. The XRD profile fitting has been carried out using Fullprof software via the Lebail refinement method. The refinement found that the crystal Lebail fitting matches with two phases i.e., Cubic (Space group: Ia3d) + Rhombohedral (Space group: R-3c) with Chi2: 4.78. Further no other (impurity) phases were observed. The cell parameter for the Cubic phase is a = b = c = 12.3153 Å, and for the Rhombohedral phase, it is a = b = 5.0344 Å, c= 13.6943 Å.

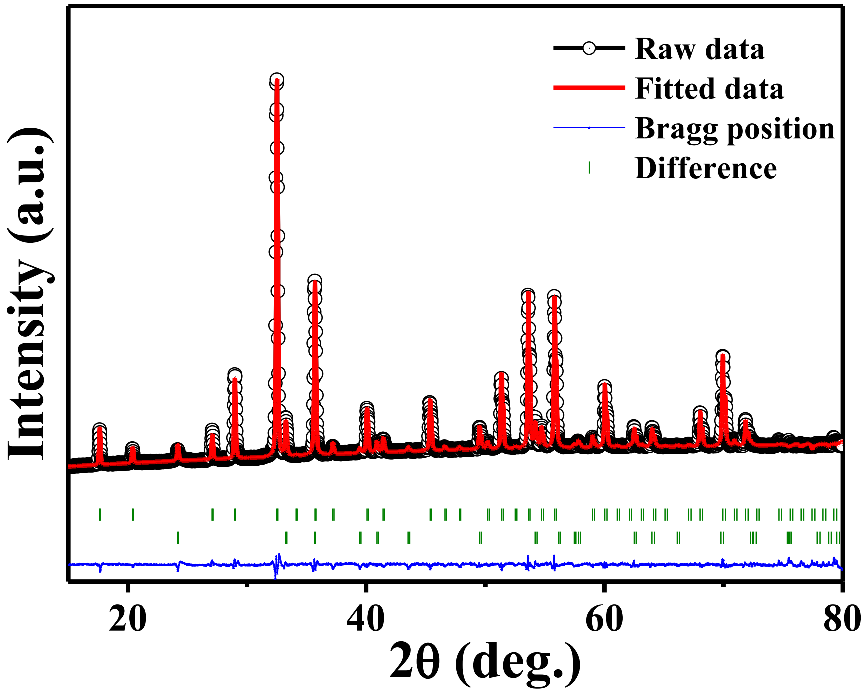

Figure 6.1: *Lebail refinement of the X-ray diffraction data of* $Ga_{0.75}Er_{0.25}FeO_3$ *system at room temperature*

6.3.2 MAGNETIC STUDY:

Figure 6. 2(a) shows the conventional ZFC and FC magnetizations (M) curve with applied dc fields (H) i.e., 100 Oe in the temperature range of 2–300 K. On decreasing temperature,

the magnetization increases and shows a magnetic transition at 293 K [the precise T_C has been determined using the temperature-dependent (dM/dT) curve, which is shown in the inset of Fig. 6. 2(a)]. Interestingly, the transition temperature of the presented system is quite high (T_C =293 K) in comparison to the previously reported T_C (which is in the range of 238 - 249 K) in bulk GFO[248]'. Moreover, the ZFC/FC magnetization exhibits a large bifurcation below T_C, which is showing that the system has strong magnetic frustration. Furthermore, to understand the nature of the magnetic structure properly, we have collected the isothermal field-dependent magnetization (M-H) loop at various temperatures. The M-H loop is depicted in Figure 6. 2(b) for temperatures of 2.2, 10, 100, and 300 K. Magnetic moment saturation has not been attained up to a high applied field of 5T. As we can see from the M-H loop at 2.2 K and 10 K there is a pinched-like shape (also known as wasp-waisted hysteresis).

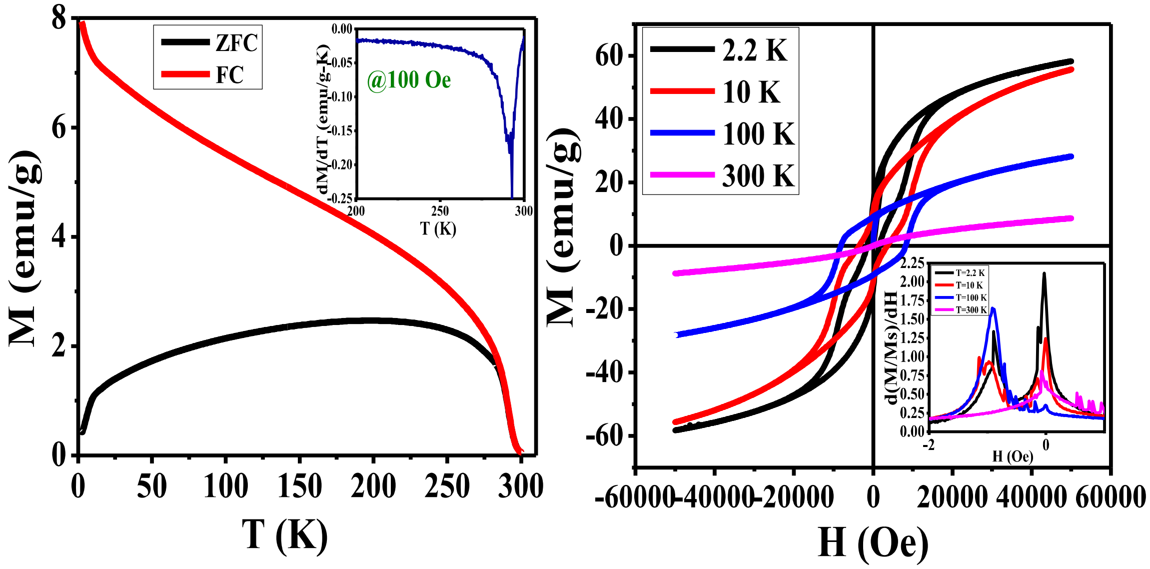

Figure 6.2 :*(a) Moment vs. temperature curves measured for zero field cooling and field cooling conditions at 100 Oe in the temperature range 2K – 300K. The inset demonstrates the dM/dT curve for the* $Ga_{0.75}Er_{0.25}FeO_3$ system. *(b) Isothermal magnetization data (M-H) for the* $Ga_{0.75}Er_{0.25}FeO_3$ *sample, measured at 300 K. The derivative of the magnetization as a function of the applied field is shown in the inset after being normalized with the saturation magnetization.*

Kim et al. obtained nearly identical M-H findings for $GaFeO_3$ and $AlFeO_3$

and subsequently explained the existence of hard and soft magnetic phases[249]. This is possible in GFO since the four cation sites exhibit distinct anisotropy in their magnetic energies, namely the octahedral sites (Fe1, Fe2, and Ga2) have strong anisotropy, whereas the tetrahedral Ga1 site is less anisotropic, and thus these act as hard and soft magnetic phases, respectively. One can observe two switching fields that correspond to hard (peak at comparatively larger fields) and soft (peak at small fields) magnetic phases in the inset of Figure 6. 2 (b), which represents the derivative of the magnetization normalized with M_S as a function of the field[248]. The action of Fe ions on the G1 site is distinct from that of Fe1, Fe2, and G2 sites[249]. In the inset of Figure 6. 2(b) at 100 K we can see that there is only one peak in the d(M/Ms)/dH curve toward the higher field side which shows that there is only a hard magnetic phase, however, at 300 K, there is only one peak at lower field side suggesting that system has only a soft magnetic phase at room temperature.

6.3.3 DIELECTRIC STUDY:

Figures 6. 3(a) illustrate the temperature dependence of the dielectric constant (ε') and the related dielectric loss tangent (tanδ) shown in the inset of Fig. 3(a) at various frequencies (600 Hz,1.2 kHz, 3 kHz, 6 kHz, 12 kHz, 20 kHz, 25 kHz, and 40 kHz) of GEF25. At low temperatures (below 250 K), the ε'-T curve exhibits practically non-dispersive intrinsic polarisation and has a low value of ε' because of the freezing of the electrical dipoles. Beyond 250 K, the material exhibits a step-like rising behavior, and the position of the steps alters towards higher temperatures at a higher frequency, exhibiting a thermally triggered polarisation[229]. At 600 Hz the ε' value is 150 and the maximum tanδ is 0.7 showing the quite low value of the dielectric loss. It is well that the dipolar, electronic, ionic, and interfacial polarisations all contribute to the dielectric constant of any material.

At low frequencies, the dielectric constant is greatly influenced by the interfacial and dipolar polarizations. These two polarizations both depend primarily on temperature. Both electronic and ionic polarizations at high frequencies are frequency independent, they contribute to the dielectric constant in the high-frequency range[250,251]. Figures 6. 3(b) and the inset of Fig. 6. 3(b) depict the frequency (f) dependence of the ε' and tanδ of GEF25 at different temperatures. As we can see from the figure that ε' value decreases as frequency increases this type of behavior is known as Debye-like relaxation[252]. The maximum value of ε' is at 300 K (i.e., 560) and tanδ (i.e. 0.72). The shift of tanδ peaks towards higher frequencies is observed as temperature increases. It's an indication of thermally triggered Debye-like dipolar relaxation[243].

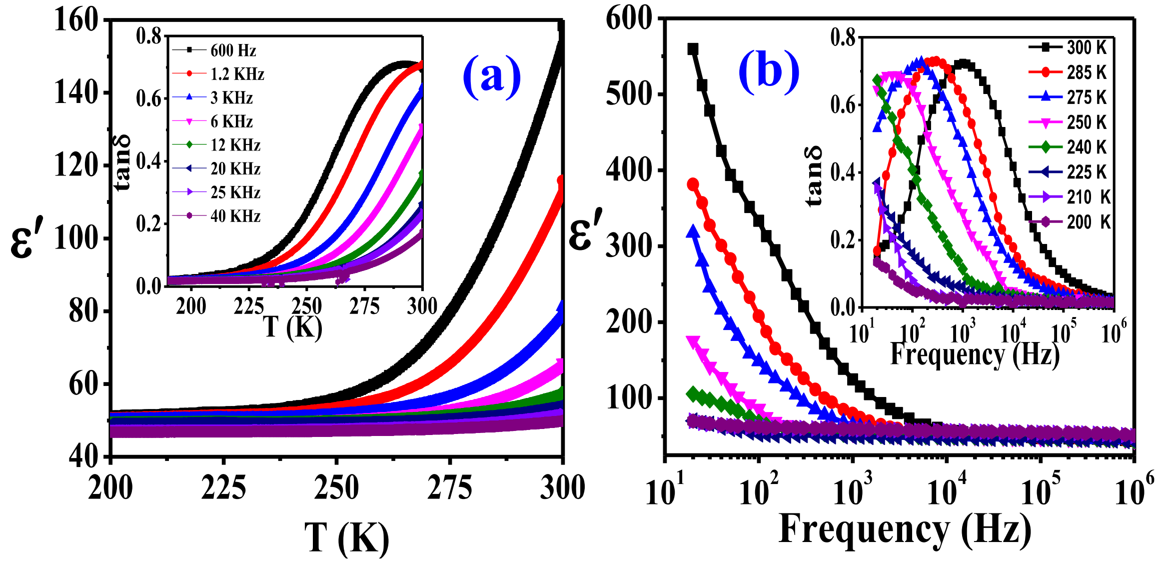

Figure 6.3: *(a) Shown the variation in the dielectric constant, and the inset shows the dielectric loss with frequency at different temperatures. (b) the dielectric constant and the inset show the dielectric loss with the temperature at different frequencies.*

6.3.4 X-RAY PHOTOELECTRON SPECTROSCOPY STUDY:

Figure 6. 4(a) shows the survey spectrum for the GEF25 system, with each peak's elements assigned by the National Institute of Standard Technology database. It verified the existence of Ga, Er, Fe, and O on the GEF25 sample surface. The spectrum demonstrated the sample's purity, which revealed the absence of all other elements except C. The sample's

surface absorbed carbon during contact with air, which is why carbon is always present. To eliminate the charge effect error, the entire analysis was completed after applying a carbon correction with the C1s line positioned at 284.5 eV[196]. Figure 6. 4(b) shows the Fe 2p XPS spectra. The spectra include the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ spin orbiting coupling peaks, which are located at 722.6 eV and 709 eV, respectively, with a doublet separation of 13.6 eV. Fe 2p1/2 and Fe 2p3/2 peak further deconvolute in the double peak i.e. Fe $2p_{1/2}$ (722.56 eV, 729.34 eV), Fe $2p_{3/2}$ (713.34 eV,708.76 eV) respectively. That is compatible with ions of iron having a nominal mixed valance state of Fe^{+2} and Fe^{+3}.

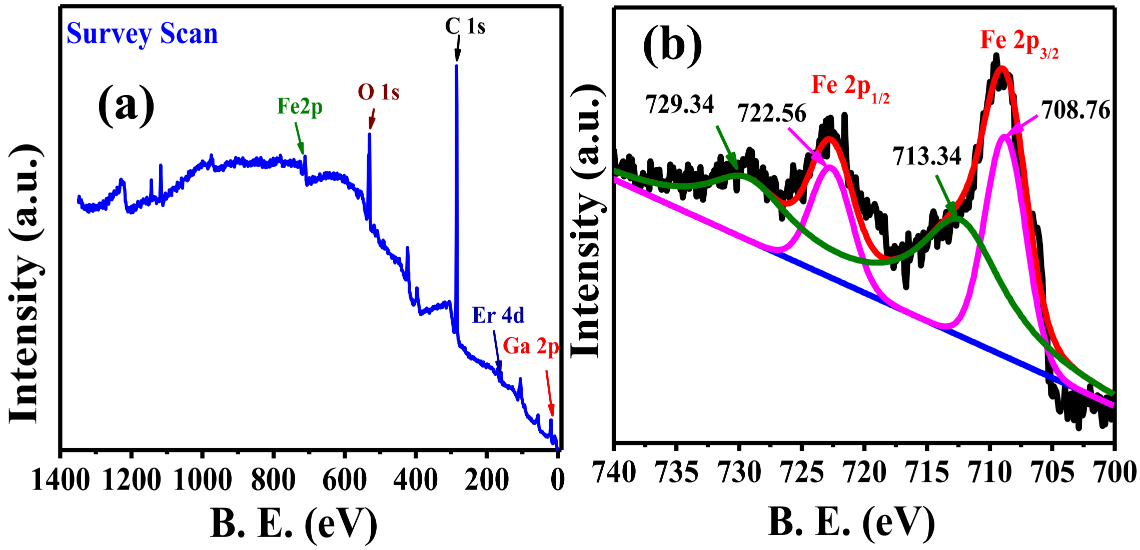

Figure 6.4: *The core level x-ray photoelectron spectroscopy (XPS) of* $Ga_{0.75}Er_{0.25}FeO_3$ *(a) survey scan and (b) Fe 2p respectively.*

6.4 CONCLUSION

The polycrystalline $Ga_{0.75}Er_{0.25}FeO_3$ system prepared by solid-state route crystallizes in mixed-phase i.e., cubic (with space group: Ia3d) + rhombohedral (with space group: R-3c). This system shows a magnetic ordering at a relatively high transition temperature i.e., 293 K. The M-H curve shows a pinched-type behavior at 2.2 and 10 K, because of the presence of two different magnetic phases (i.e., hard and soft magnetic phases). Through the XPS analysis, it was observed that Fe exists in the mixed-valence state (+2, +3), which may be the reason behind the existence of mixed magnetic phases. The dielectric measurement shows that there is Debye-like dipolar relaxation phenomenon is observed.