CHAPTER 4: Magnetodielectric Relaxation in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$

4.1 Introduction

As discussed in previous chapter, HTO and DTO show multiple dielectric relaxations in temperature dependent dielectric permittivity measurement. It has been found that at higher temperatures viz. 90 K and 36 K dielectric relaxations are originated from the crystal field induced structural distortions at the oxygen positions of the lattice. As explained in the chapter 1 section 1.7 that symmetry constraints of $Fd\bar{3}m$ space group suggests that low temperature dielectric relaxation may be induced from magnetism [87], [88]. Magnetic studies of these compounds show the lack of magnetic ordering even at low temperatures. However, below 4 K, underlying magnetic dipolar and exchange interactions stabilizes disordered spin ice state, in which each corner shared tetrahedra formed by Ho/Dy ions follows the local 2in-2out spin structure [17], [41], [127]. In 2012, Khomskii proposed that in these compounds only 3in-1out spin structure can induce ferroelectricity via magnetostriction phenomena [128]. In section 3.2.3 it has been described that temperature dependent lattice volume shows an anomalous increment below 30 K in both HTO and DTO. This suggests the involvement of complex mechanism could be responsible for low temperature ferroelectricity. These observations motivate to investigate the underlying phenomena responsible for the emergence of low temperature ferroelectricity in these compounds. In this chapter, the low temperature dielectric relaxation and possible underlying phenomena responsible for the emergence of ferroelectricity in HTO and DTO is being presented.

4.2 Results and Discussion

4.2.1 Low-temperature dielectric analysis

Figure 4.1 shows the temperature dependence of the real (ε') and imaginary (ε") part of the dielectric permittivity of HTO measured in 3-300 kHz frequency range. The observed spectra show a systematic shift in the peak position with increasing frequency in both ε' and ε". It has been found the magnitude of dielectric relaxation increases with frequency followed by a peak shift towards higher temperature. This behavior is more prominent in ε" where this peak shift and an increment in the peak height which rapidly decreases with frequency below 5 K. Shifting in dielectric relaxation temperature with frequency shows lattice distortion induced electric polarization [115] whereas variation in the peak height of ε" suggests the change in net polarization due to change in either magnitude/density of the distorted lattice sites [129]. The nature of frequency dispersion behavior by using the Arrhenius equation is shown in the inset of the figure 4.1 (a). It shows the ln (τ) vs. $1/T_m$ plot, where, T_m is the temperature at which ε" has its maximum value. It has been found that frequency dispersion behavior follows the Arrhenius behavior with a deduced value of characteristic relaxation time, $\tau_0 = 3.7\times10^{-9}$ sec and activation energy, $Ea/k_B = 45.8 \pm 0.7$ K (3.9 ± 0.06 meV). The obtained value of the activation energy is closed to the activation energy for spin ice freezing (~30 K (2.5 meV)) [42]. The order of relaxation time and linear nature of frequency dispersion suggests that observed relaxation is originated from the non-interacting electric dipoles of the ionic polarization due to a subtle change in the ionic positions in the crystal structure [113], [130].

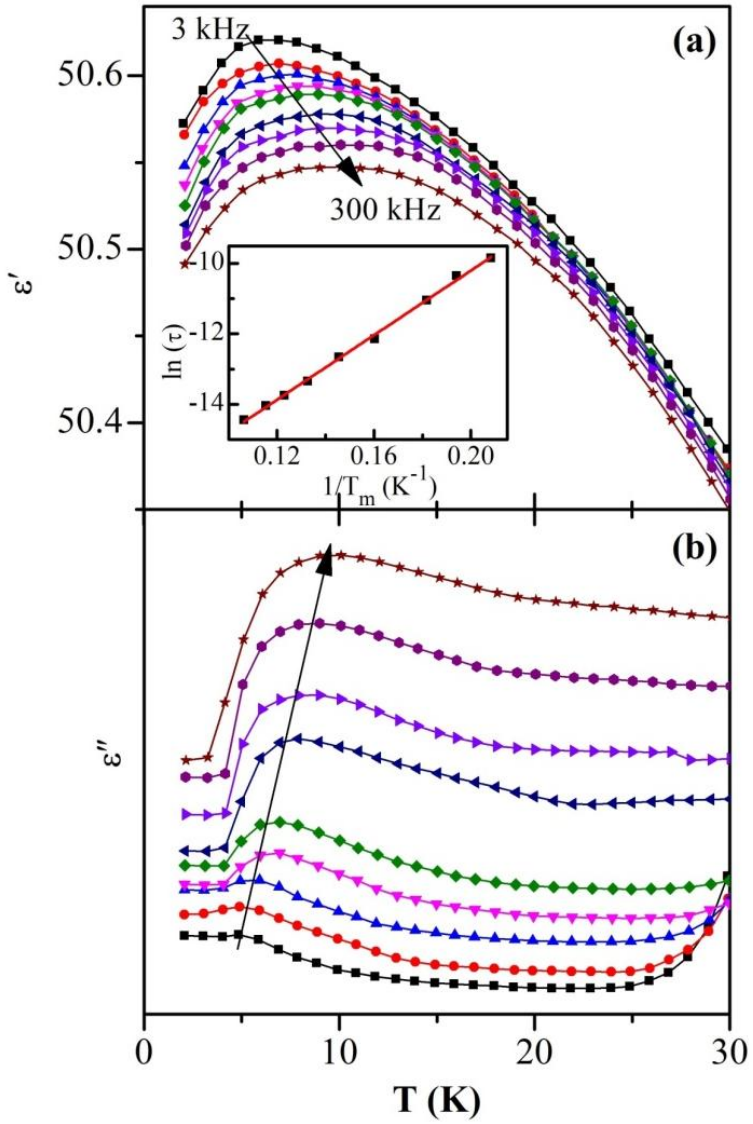

Figure 4.1: Temperature dependence of the real (ε') and imaginary part (ε'') of the dielectric permittivity of $Ho_2Ti_2O_7$ compound measured in 3-300 kHz frequency range. Inset of the figure 3(a) shows the Arrhenius nature of ln (τ) Vs $1/T_m$ plot for the observed relaxation.

Similar to HTO, temperature-dependent dielectric permittivity of DTO has been analysed for low temperature range (2-32 K). Figure 4.2 shows the temperature-dependent ε' and ε'' of DTO, measured at different frequencies (1-300 kHz range). For the measured temperature and frequency range, two successive relaxations termed as T_{m1} and T_{m2} are observed in ~4-9 K and ~17-26 K temperature range in contrast to the single relaxation as observed in HTO. It

has been found that for DTO, T_{m1} relaxation shows frequency dispersion, the increment in the width and magnitude with increasing applied frequency. The observed similarity in the nature of T_{m1} relaxation suggests having the similar origin of dielectric relaxation as that of the HTO at 4K. Furthermore, other than the 4 K dielectric relaxation, DTO shows another transition around 17-26 K. This T_{m2} relaxation is distinguishable only in ε", shows strong frequency-dependent behavior without any variation in the peak width and magnitude.

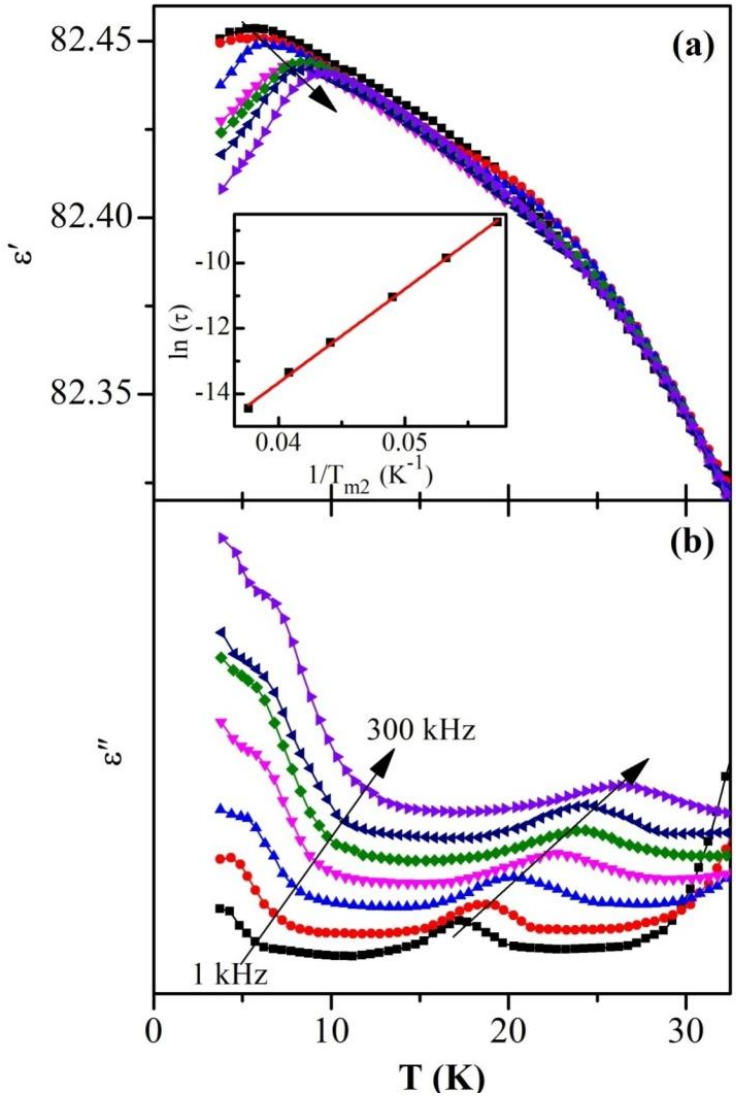

Figure 4.2: Temperature dependent real (ε') and imaginary part (ε'') of the dielectric permittivity of $Dy_2Ti_2O_7$ measured in 1-300 kHz frequency range. Inset of the fig. 7(a) shows the Arrhenius nature of ln (τ) Vs $1/T_{m2}$ plot for the higher temperature dielectric relaxation.

To analyze the shifting in T_{m2} (temperature at which peak take place in ε") with frequency, a linear fit of ln (τ) vs $1/T_{m2}$ plot using Arrhenius law has been done and shown in the inset of figure 4.2 (a). The deduced values of characteristic relaxation time τ_0 and activation energy E_a/k_B are 1.2×10^{-11} sec and 286 ± 5.5 K (24.6 ±0.4 meV), respectively. The order of τ_0 suggests that observed relaxation is associated with polar lattice [113], [130]. It has been noticed that in magnetic ac susceptibility of DTO, a thermally quenched spin freezing observed at 16 K having an activation energy of ~240 K (20.6 meV) [41], [61]. Similarities in the relaxation temperature and activation energy, for both dielectric and magnetic properties of DTO suggest that T_{m2} relaxation is associated with the thermal quenching of the Ising spin occurring at 16 K.

4.2.2 Magnetodielectric and magneto-volume study

Observations described in section 4.2.1 indicate that below 30 K, dielectric relaxations of HTO and DTO are most likely associated with its complex magnetism. To confirm the magnetic origin of dielectric relaxation, temperature-dependent dielectric permittivity of HTO has been performed in presence of 0.5 T of applied magnetic field. Figure 4.3 shows the temperature dependence of the ε' and ε" of HTO measured at 200 kHz, in presence of 0 T and 0.5 T magnetic field. It has been found that, on the application of magnetic field, ε' decreases with a simultaneous increase in ε" with decreasing temperature. This magnetic field dependency of the dielectric permittivity indicates the possible magnetoelectric coupling as observed by Lin et al. [88] and Saito et al [90] as well along the similar line.

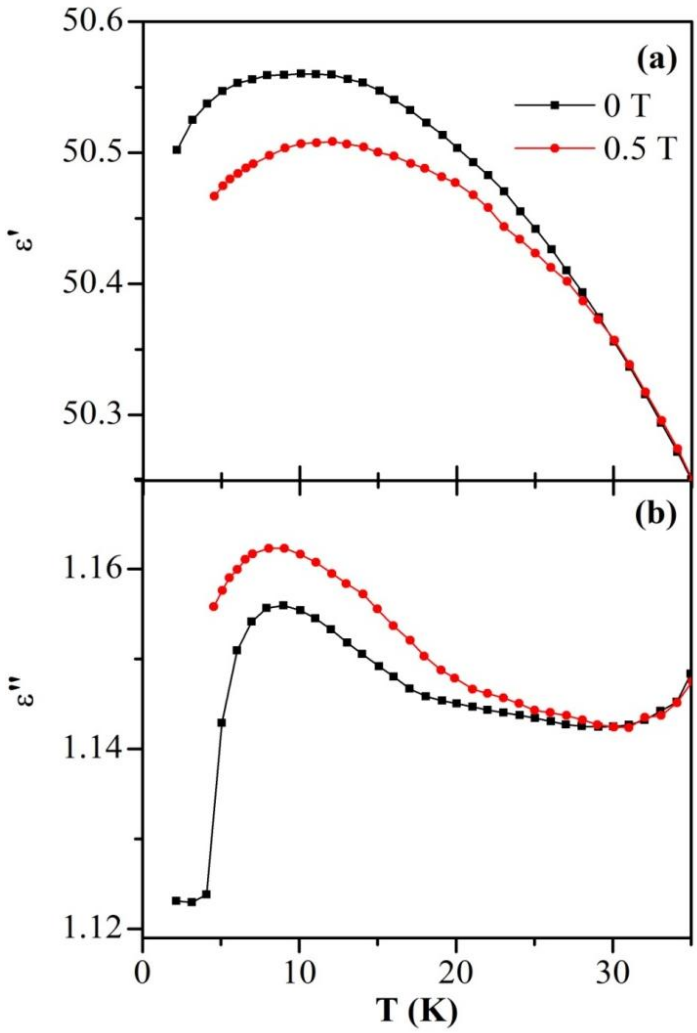

Figure 4.3: Temperature dependence of the real (ε') and imaginary (ε'') part of the dielectric permittivity of $Ho_2Ti_2O_7$ compound measured at 200 kHz for 0 T and 0.5 T magnetic field.

As the obtained value of τ_0 suggests that these dielectric relaxations are governed by lattice distortion [113], [130] and gets affected on the application of external magnetic field, it is likely that magnetovolume effects (MVE) plays a major role in case of HTO and DTO. This MVE can be further quantified by the physical variable of spontaneous volume magnetostriction (SVMS), $\Delta V/V$ % (ω_s), which presents the effect of magnetism on unit cell volume. The SVMS has a $M(T)^2$ dependence and can be represented as [124], [131],

$$\omega_s(T) = 3\int \alpha_m(T)dT = kC_{mV}\{M(T)^2 + \xi(T)^2\} \quad (4.1)$$

Where, $\alpha_m(T)$ is the magnetic contribution to linear coefficients of thermal expansion at temperature T, k and C_{mV} are the compressibility and the magnetovolume coupling parameter, and M(T) and ξ(T) are the amplitudes of local magnetic moment and spin fluctuations, respectively.

The value of ΔV has been obtained from the difference of the observed and calculated value of lattice volume as shown in the figure 3.9 of chapter 3. In order to obtain the value of spontaneous magnetization, the temperature-dependent magnetization at an applied field of 7 T of HTO and DTO as shown in figure 4.4 has been used. Figure 4.5 shows the percentage change in lattice volume ω_s with square of magnetization (M^2) of HTO and DTO.

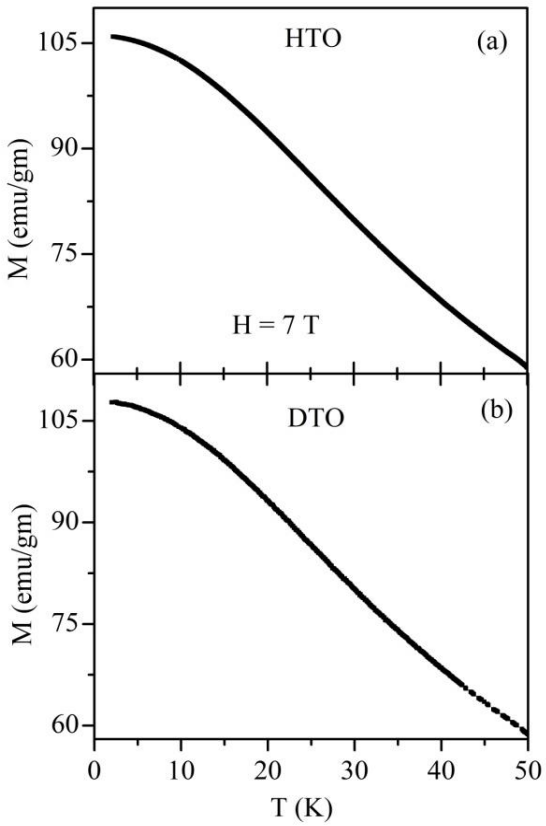

Figure 4.4: Temperature dependence of the magnetization measured at an applied magnetic field of 7 T for (a) $Ho_2Ti_2O_7$ and (b) $Dy_2Ti_2O_7$.

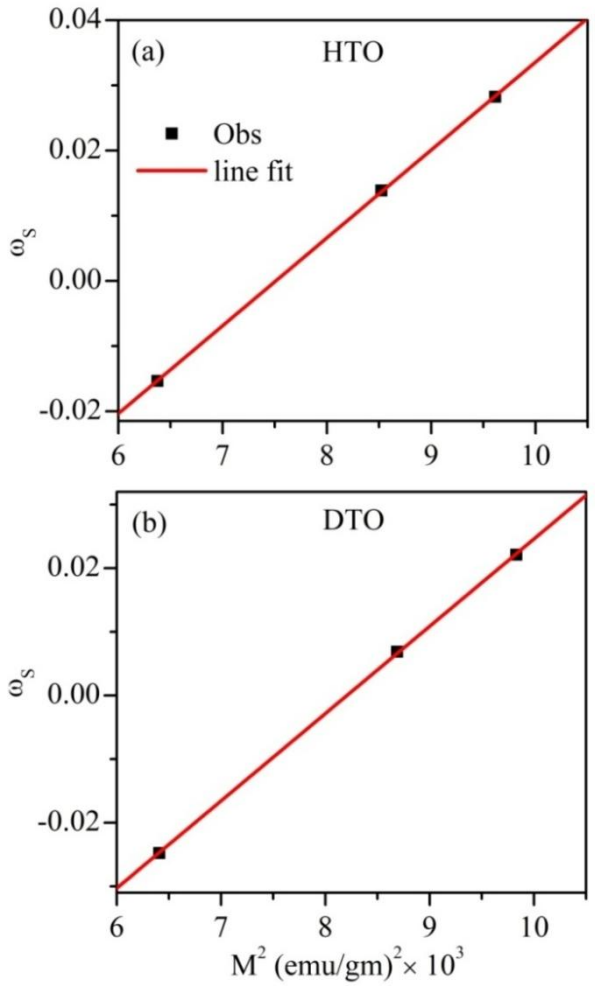

Figure 4.5: Percentage change in the lattice volume with square of magnetization with linear fit (solid blue line) for (a) $Ho_2Ti_2O_7$ and (b) $Dy_2Ti_2O_7$.

The linear correlation of ω_s vs. M^2 is generally taken as a good evidence of magnetostriction. In the present case also, we find a linear correlation in ω_s vs. M^2. This observation indicate that the HTO and DTO is going through a magnetostriction phenomenon at a temperature around 30 K which in turn become responsible for the anomalous increment in the lattice volume and dielectric relaxations.

Since, unlike to other magnetically ordered compound geometrically frustrated HTO and DTO fail to show any fixed magnetic ordering in the temperature range of this study i.e. 30-2 K. This suggests that observed anomalous behavior in lattice volume and dielectric relaxation

likely to originate from its complex spin dynamics. In these compounds, the Ising nature of spin below ~30 K [132] constrains the total microstates to 16 having three possible spin structure termed as 2-fold degenerate 4in-4out, 6-fold degenerate 2in-2out, and 8-fold degenerate 3in-1out/1in-3out. According to equal a priori probability, these spin structures can be assigned a weight factor or density 2/16, 6/16 and 8/16, respectively. At a temperature below 4 K, magnetic dipolar and exchange interaction stabilized the spin ice state in which each corner shared tetrahedra follow 2in-2out spin structure. This means that below 4 K, density of other spin structure (3in-1out and 4in-4out) rapidly decreases. Theoretical study performed by Jubert et al. [133] confirms this observation through their modeled Metropolis dynamics. It has been found that density of 4in-4 out and 3in-1out spin structure goes to zero above 6 K and 1 K, respectively. As pointed out by Khomskii [128], out of the three possible spin structures, only 3in-1out spin structure can induce electric dipoles via magnetostriction phenomena. This means that nature of dielectric relaxation should qualitatively correlate with the density of 3in-1out spin structure. The variation in peak height of ε" and its rapid fall below 5 K as shown in figure 4.1 (b) and 4.2 (b), follows the similar trend as density of 3in-1out spin structure shown by the Jubert et al. This similarity giving a further indication about the origin of low-temperature dielectric relaxation induced through lattice distortions origination from the 3in-1out spin structure.

4.3 Conclusion

In summary, observed anomalous relaxation in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ is associated with the formation of electric dipoles by magnetostriction mechanism. It has been found that induced electric dipoles are non-interacting in nature whose density decreases rapidly below 5 K. The variation in the density of electric dipoles is associated with the rapid decrease in the density

of 3in-1out spin structure with temperature. Due to the dynamic nature of the 3in-1out spin structure, its associated electric dipoles are also dynamic in nature leading to a relaxor type ferroelectric behavior. These observations and dependency of the dielectric relaxation on magnetic field suggesting the magnetic field as a control variable for the so-called magnetoelectricity of these compounds.