CHAPTER 8: Summary and Suggestions for Future Work

8.1 Conclusions

In the present work a detailed structural, dielectric and magnetic analysis of $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$ and their doped derivatives has been presented. The findings of the thesis can be summarized as follows.

Dielectric measurements of $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ reveal that both the compounds exhibit multiple dielectric relaxations having a magnetic and non-magnetic origin. The dielectric relaxations observed at 90 K and 36 K in both $Ho_2Ti_2O_7$, and $Dy_2Ti_2O_7$ are diffuse and Debye-like in nature. It has been found that both relaxations observed in both compounds are distinctly related to lattice distortions at both oxygen sites. Symmetry analysis of $Fd\bar{3}m$ space group suggest that structural distortions at oxygen positions have an electronic origin, showing the coupling of electronic and structural parameters in these compounds. Due to this coupling, a pronounced change in crystal field distorts the oxygen position along with splitting of multipolar order parameter as reflected in the form of 90 K and 36 K dielectric relaxation and deviation in lattice volume from Debye-Grüneisen behavior in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$.

An investigation made on low-temperature anomalous dielectric relaxation shows that observed relaxation is associated with 3in-1out/1in-3out spin structure via magnetostriction mechanism. Due to the dynamic nature of spin, magnetism induced electric dipoles are non-interacting in nature. The temperature and magnetic field dependence of the density of 3in-1out/1in-3out spin structure facilitate these parameters to control multiferroic properties of $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. The observed magnetoelectricity of these materials makes them as a

novel candidate for multifunctional materials having fast switching capability which can be controlled by temperature and magnetic field.

Magnetic and dielectric relaxation studies of $Dy_{2-x}Fe_xTi_2O_7$ highlight the importance of the local environment, which affects the exotic freezing observed in $Dy_2Ti_2O_7$ for a narrow range of dilution ($0 \leq x \leq 0.15$). It has been found that both ~16 K and ~4 K spin freezing are highly susceptible for the substituted Fe ion instead of robust in nature as reported previously. The effects of substituted Fe ion are investigated in terms of altered crystal field and magnetic perturbations. Optical analysis reveals that effect of altered crystal filed on electric states of Dy ions is negligible which confirms that in $Dy_2Ti_2O_7$ spin dynamics of very sensitive to the substituted Fe spin. ac susceptibility of x= 0.05 and 0.15 composition measured at different dc field shows the recovery of spin freezing in presence of the external magnetic field, as observed in $Dy_2Ti_2O_7$ but their nature is quite modified. These observations lead us to conclude that in these compounds' spins are strongly correlated with each other due to which spin dynamics are very sensitive to the nature of neighbouring magnetic ion's spin. This dependency facilitates to tune and control the spin dynamics and its associated magnetoelectric properties through in these compounds by a magnetic field.

Magnetic spin freezing observed in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$are investigated in terms of "quantum criticality" through the H-T phase diagram. It has been found that in $Ho_2Ti_2O_7$ both single ion spin freezing temperature (T_f) and spin ice freezing temperature (T_{ice}) lies in the quantum critical region whereas, in $Dy_2Ti_2O_7$, only T_{ice} lies in the quantum critical region. The obtained values of the critical field suggest higher effective energy barrier for spin relaxation in $Dy_2Ti_2O_7$ in comparison to $Ho_2Ti_2O_7$. This finding is further confirmed from the ac susceptibility study of B-site Mn substituted $Ho_2Ti_{1.9}Mn_{0.1}O_7$ and

$Dy_2Ti_{1.9}Mn_{0.1}O_7$ where T_{ice} freezing is more prominently affected in comparison to the single ion freezing T_f. These observations lead us to conclude that competing magnetic interaction acting in different temperature regime are one of the preliminary factors responsible for the alteration in a quantum critical point in these compounds. This observed dependencies of the low-temperature phases on a non-thermal external variable, open a new route to investigate the underlying physics of geometrically frustrated magnetic materials in terms of quantum criticality at non-zero temperatures.

The crucial external variables responsible for classical behaviour of spin in the quantum critical region in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ has been revealed through ac susceptibility study. An external magnetic field set bound on dephasing of quantum correlations by increasing the thermalization time and bring it to measurement time scale. Due to increment in thermalization time, scrambled quantum information associated with quantum correlations are partially maintained as observed in the form of thermal hysteresis in ac susceptibility measurement. Exponential decay of $\Delta\chi'$ with applied frequency evident that applied frequency also dephases the quantum correlations similar to thermalization phenomena and works as a control variable for quantum and classical nature of spin in these compounds. The analysis of temperature-dependent variation in $\Delta\chi'$, I(T) and R(T) lead us to conclude that strengthen in spin correlation enhances the quantum correlation whereas magnetic interaction induced spin constrained suppress the quantum correlations. It has been found that unlike to classical behaviour where macroscopic properties are stationary and universal with respect to widely differing initial conditions, in the quantum correlated state, macroscopic properties are depending on the initial conditions and varies with temporal evolution. The anomalous sensitivity of quantum correlation on external stimuli (magnetic field and frequency),

provides an effective tool to control the classical and quantum behaviour of these compounds. The so observed control over macroscopic properties of these quantum materials suggests them to study in more depth for future applications. Further, our finding opens a new approach to study the exotic quantum behaviour of other quantum magnetic materials in terms of quantum correlations.

8.2 Scope for future work

The present work has reported the nature of dielectric relaxations having crystal field and magnetic origin. Further, through H-T phase diagram classification of the quantum critical region in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ spin ice compounds has been done. Explain the cause of classical nature of spin in quantum critical region where spin dynamics are governed by the quantum fluctuations in a correlated manner, which is very sensitive for external stimuli. Based on these findings, present work can be extended in the following ways.

- Low-temperature neutron scattering studies of synthesized samples can be performed to understand the structural, dielectric and magnetic behaviour.
- Detailed studies are required to understand the PL and UV-vis spectra of HTO and DTO.
- Low-temperature (>2 K) dielectric and magnetic study needed to understand the magnetodielectric mechanism in both HTO and HTO.
- Study the ferroelectricity of other geometrically frustrated cubic materials.
- Study of Fe substituted $Dy_{2-x}Fe_xTi_2O_7$ compounds and other geometrically frustrated quantum magnets in terms of quantum criticality and quantum correlation.
- Investigation of governing crucial variables, affect the quantum correlations and its associated quantum information in other geometrically frustrated quantum materials.