Preface

In recent year's geometrically frustrated magnetic system drawn tremendous attention because of its exotic magnetic behaviours such as-spin liquids, spin glass, spins ice. It occurs due to failure of simultaneous minimization of competing magnetic interactions between the localized magnetic moments or spin. This failure gives a large degeneracy to the system ground state instead of single non-degenerate ground state. In this degenerate ground state spin fluctuating by thermal/quantum fluctuations and retain a dynamic state without any long-range ordered phase transition. Due to lack of magnetic ordering, magnetically frustrated systems are exceptionally sensitive to small perturbations and quantum effects, hence their tendency to shows various unusual phenomena, for instance, fractional particle excitations (magnetic monopole) and emergent gauge fields.

In the context of magnetic frustration, geometrically frustrated $Ho_2Ti_2O_7$ (HTO) and $Dy_2Ti_2O_7$ (DTO) are one of the most studied compounds for its exotic spin ice behaviour. In these compounds, lattice architecture constrained the Ho/Dy rare-earth spin in their Ising doublet ground state due to which each spin constrained to fluctuate in a correlated manner along their local <111> crystallographic axis of the $Fd\bar{3}m$ space group. Such specific properties ease the quantum/thermal fluctuation to drive the Ising spin via local transformation. At low temperatures, due to underlying dipolar interaction, these locally constrained dynamic Ising spins form local 2in-2out spin structure which are geometrically frustrated and termed as spin ice state because they mimic the hydrogen ion arrangement in water ice.

Low temperature ac susceptibility of HTO and DTO shows two distinct spin freezing at ~16 K (T_f) and ~4 K (T_{ice}), respectively. Though in case of HTO, these freezing are only observed in the presence of an external magnetic field. The broad range non-magnetic and magnetic (Tb, Yb) dilution study suggest that both observed spin freezing is robust in nature which is weakly affected by altered crystalline field and magnetic interactions. Furthermore, it has been observed that both T_f and T_{ice} freezing strongly depends on the strength of the applied magnetic field, however, spin ice freezing (T_{ice}) vanishes above an applied field of 1 T for both the compounds.

Along with these exotic magnetic properties, these cubic compounds also possess the multiple ferroelectric transitions of different origin. In polycrystalline HTO two ferroelectric transitions are observed at ~60 K and ~23 K, however in case of single crystal of HTO, only one transition, originating at ~28 K has been observed. On the other hand, in polycrystalline DTO, two ferroelectric transitions at ~25 K and ~13 K have been observed. It was concluded that ferroelectric transitions, at ~60 K in case of polycrystalline and ~28 K in case of single crystal of HTO and at ~25 K in polycrystalline DTO, has structural origin. Whereas, low-temperature ferroelectric transition around 23 K (for HTO) and 13 K (for DTO) has been dedicated to originate from the magnetism of the system. It is therefore imperative to investigate the nature and origin of ferroelectric transitions observed in these compounds.

The specific objectives of the present thesis work are as following

- Study of nature and origin of ferroelectric transitions in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$.
- Investigation of parameters affecting the spin dynamics in these frustrated compounds.
- Study the nature of fluctuation (quantum/classical), drives the spin dynamics at low temperature and effect of magnetic perturbations in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$.

- Study the quantum correlation and its associated scrambled quantum information in quantum critical region in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$.

To investigate the physical properties of $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$ and their doped samples, detailed structural, dielectric and magnetic studies have been performed.

The major aim of the present thesis is to investigate the exotic ferroelectric and magnetic behaviour of $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. This thesis includes in **Chapter 1,** an introduction to the fundamental concepts of geometrically frustrated $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ spin ice materials and a brief review made on their structural, magnetic and ferroelectric properties. This chapter also reviews the dynamic magnetic properties in classical and quantum region and factors affecting the spin dynamics of $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$.

The details of the sample preparation for synthesizing the pure phase $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$ & their doped samples and experimental techniques used for the characterization of phase, structural, dielectric, optical and magnetic properties have been discussed in **Chapter 2.**

Chapter 3 describes the nature of dielectric relaxations observed far away from the magnetic spin ice phases in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. A detailed structural and dielectric study has been performed to uncover the underlying phenomena responsible for the emergence of these relaxations in these compounds.

In **Chapter 4** nature of low temperature anomalous dielectric relaxation observed in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ has been extensively examined. Through magneto-capacitance and magnetostriction study origin of these relaxations has been revealed.

Chapter 5 contains a detailed structural, dielectric, optical and magnetic analysis on $Dy_{2-x}Fe_xTi_2O_7$ to investigate the control parameters which affect the spin dynamics of $Dy_2Ti_2O_7$.

Experimental findings explicitly show that instead of crystal field, spin dynamics are non-monotonically depends on the magnetic perturbations.

In **Chapter 6** an investigation made on to classify the quantum critical region in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ through magnetic field vs. spin freezing temperature phase diagram. The obtained results have been explained in terms of quantum criticality of quantum materials. The good agreement of experimental findings with previous findings shows the new pathway to determine the quantum-classical crossover region in quantum materials via ac susceptibly studies.

Chapter 7 describes the measurement protocol to uncover the quantum correlation and its associated scrambled quantum information in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. Experimental findings show the effect of external stimuli, underlying spin correlation and magnetic interaction on the scrambled quantum information in these compounds. It has been explicitly shown that how macroscopic properties of these materials behave entirely different in the thermalized and non-thermalized state with temporal evolution.

Chapter 8 summarizes the main findings of the present work and lists a few suggestions for future investigations.

The main findings of the presented thesis work are listed below:

1. Dielectric relaxations observed in $Ho_2Ti_2O_7$, $Dy_2Ti_2O_7$ are diffuse and Debye-like in nature which is distinctly related with the crystal field induced lattice distortions at O1 and O2 oxygen sites.
2. The low temperature dielectric relaxation in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ is associated with local spin structure of complex magnetism via magnetostriction mechanism.

3. In $Dy_2Ti_2O_7$, spin dynamics is non-monotonically depends on the nature of neighboring magnetic ion's spin due to underlying spin-spin correlation.
4. Quantum critical behaviour has been established in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$. It has been found that competing magnetic interaction is one of the preliminary factors affecting the quantum critical point in these compounds.
5. The measurement protocol quantifying the quantum-classical correspondence has been established. In quantum state, scrambled quantum information is strongly depending on the external stimuli, magnetic interactions and spin correlations.