# PREFACE

Frustration is the inability of the system to minimize all of its pairwise interactions simultaneously. In exchange coupled spin systems, frustration often brings about interesting phenomena because it can lead to complex spin configurations and rich phase diagrams. The Pyrochlore oxides are magnetically frustrated systems having the general chemical formula $A_2B_2O_7$ (where A and B are typically trivalent and tetravalent ions, respectively). The topic of investigation in this thesis is the pyrochlore titanates $A_2Ti_2O_7$, where $A^{3+}$ is a magnetic rare earth ion (Dy and Er) and $Ti^{4+}$ is non-magnetic. Geometric frustration arises in the rare earth pyrochlores due to magnetic rare earth ions occupying the vertices of the network of corner-sharing tetrahedra. Over the last few decades, groundbreaking discoveries have unfolded within these materials, spanning superconductivity, spin liquid states, spin ice states, glassy states in the absence of chemical disorder, and metal-insulator transitions. Geometric frustration plays a role in the relevant physics of all these phenomena. Low-temperature spin-dynamics are effectively controlled through dipolar and exchange interaction along with the crystal electric field.

The comprehensive objective of the thesis is to explore the role of perturbation by substituting magnetic ion Mn at a non-magnetic Ti site in an Ising ($Dy_2Ti_2O_7$) and XY ($Er_2Ti_2O_7$) pyrochlore system. The pure phase (space group = $Fd\bar{3}m$) Dysprosium titanate and Erbium titanate and its Mn-doped derivatives ($Dy_2Ti_{2-x}Mn_xO_7$ and $Er_2Ti_{2-x}Mn_xO_7$) have been synthesized. Thereafter a thorough understanding of its structural, magnetic, electronic, and optical properties had been presented.

Important findings of the presented thesis work are listed below: -

**1. Gradual emergence of ordering in the spin-frustrated $Dy_2Ti_{2-x}Mn_xO_7$**

The study of the magnetic properties (static and dynamic) of doped spin ice $Dy_2Ti_{2-x}Mn_xO_7$ (x = 0, 0.05, 0.10, 0.15, 0.20) is presented. Results show that the magnetic properties of the system are significantly affected by the inclusion of Mn at the Ti sites. The dc magnetization shows bifurcation in zero field cooling and field cooled warming data with increased Mn substitution. Such irreversibility in ZFC and FC measurements and its behaviour with the increasing field indicates the spin states to be spin glass, cluster glasses or Griffiths-phase like. A new peak appears in the ac susceptibility data around 5 K (termed as T*), associated with Mn, even at zero applied dc-bias field; this is in addition to the $Dy^{3+}$ spin peak, i.e. single ion peak around 15 K and the spin freezing peak at 3 K as observed in $Dy_2Ti_2O_7$. The peak T* in the ac-susceptibility measurement becomes more pronounced with the increase of Mn doping, indicating the presence of a short-range magnetically ordered state in the paramagnetic state. The result supports the evidence of the Griffiths phase-like state has been observed. The T* peak is thermally driven, as indicated by its frequency dependence susceptibility measurement. Low-temperature structural change in lattice parameters and crystal field phonon coupling has been studied using synchrotron x-ray diffraction. Debye-Grüneisen's temperature-dependent lattice-volume analysis shows the 'crystal field'-phonon coupling emergence at a much higher temperature (70 K) in $Dy_2Ti_{1.8}Mn_{0.2}O_7$ in contrast to 30 K in $Dy_2Ti_2O_7$.

**2. Effect of Mn doping on the electronic and optical properties of $Dy_2Ti_2O_7$: A combined spectroscopic and theoretical study**

Further, the electronic and optical studies on $Dy_2Ti_{2-x}Mn_xO_7$ (x = 0.00, 0.05, 0.10, 0.15, & 0.20) are carried out. This investigation utilizes both theoretical (density functional theory calculations) and experimental (ultraviolet-visible absorption, photoluminescence emission spectroscopy and Raman spectroscopy) approaches. Density functional theory (DFT) calculations were performed considering the local density approximation (LDA) and LDA-1/2 for exchange-correlation interactions. Computed energy band-gap using theoretical formulations is in agreement with experimental results. Experimentally obtained band gap value reduces from 3.82 eV to 2.45 eV with an increase in Mn concentration as x increases from 0 to 0.20. The reduction in band gap value is attributed to the fact that there exists a lack of hybridization between the O-2p orbital and Ti-3d orbital, which is well correlated with the crystallographic data. The presence of a mixed state of Mn (explained using x-ray photoelectron spectroscopy results), resulting in the intermediate Mn state between the valence band (VB) and the conduction band (CB) with immediate inclusion of Mn at the Ti site in $Dy_2Ti_{2-x}Mn_xO_7$ (x = 0.00, 0.05, 0.10, 0.15, 0.20) system.

Furthermore, we extend our study to examine the effect of manganese (Mn) on the magnetic and electronic properties of another class of system, i.e., XY-type pyrochlore ($Er_2Ti_2O_7$).

**3. Low-temperature dynamic spin freezing in $Er_2Ti_2O_7$**

$Er_2Ti_2O_7$ has been proposed as the ⟨111⟩ XY antiferromagnet pyrochlore. The spins of $Er^{3+}$ lie perpendicular to the local ⟨111⟩ axis. We have investigated the structural and low-temperature magnetic properties in doped $Er_2Ti_{2-x}Mn_xO_7$ (x= 0.0, 0.10, 0.20). The low-temperature magnetic behavior is studied using ac and dc magnetic susceptibility

measurements of both the pure material and Mn substituted at the Ti site. The ac susceptibility data reveals the emergence of a peak at T = 15 K in $\chi'(T)$ for fields H > 0.5 T, which becomes more pronounced and shifts to higher temperatures with increasing field. The high field peak in $\chi'(T)$ is a consequence of single-moment saturation.

**4. Optical and electronic structure study of Mn-doped $Er_2Ti_2O_7$**

Finally, we performed the electronic and optical studies on $Er_2Ti_{2-x}Mn_xO_7$ (x = 0.00, 0.10, & 0.20) in similar way as we carried out for Ising system ($Dy_2Ti_2O_7$) through combined, theoretical (density functional theory calculations) and experimental (ultraviolet-visible absorption, photoluminescence emission spectroscopy, and Raman spectroscopy) approaches. The energy band-gap values obtained using theoretical formulations are in close accordance with the experimental results. The band-gap value obtained using the LDA-1/2 approach indicates the insulated ground state of the $Er_2Ti_{2-x}Mn_xO_7$ (x = 0.00, 0.10, & 0.20) system. The band gap value obtained experimentally reduces from 3.84 eV to 2.57 eV as the level of Mn doping increases from 0 to 0.20.

**Chapter 1** of this thesis presents the basic introduction to magnetic frustration and the magnetic interactions that play a role in establishing a magnetic ground state at low temperatures. This chapter also includes the signatory features of $Dy_2Ti_2O_7$ and $Er_2Ti_2O_7$ in relevance to their magnetic and structural properties as obtained through various characteristics tools. Further, the role of perturbation through A and B site substitution has also been discussed.

The synthesis method adopted to obtain the pure phase $Dy_2Ti_2O_7$ and $Er_2Ti_2O_7$ and its doped Mn derivative and experimental techniques adopted to characterize the materials is described in **Chapter 2**.

**In chapter 3**, I have discussed the synthesis of $Dy_2Ti_{2-x}Mn_xO_7$ (x=0, 0.05, 0.10, 0.15, 0.20) and studied the role of Mn on magnetic properties of this Ising type pyrochlore system through magnetization vs. temperature, magnetization vs. the magnetic field, and field and frequency-dependent ac susceptibility measurements.

**Chapter 4** deals with calculating the electronic structure of the pyrochlore $Dy_2Ti_{2-x}Mn_xO_7$ (x = 0, 0.05, 0.10, 0.15, 0.20) system. The study involved the calculation of the density of states and band structure, along with the theoretical determination of the band-gap through DFT. The various states involved in hybridization for band formation were identified. Also, the band-gap of $Dy_2Ti_{2-x}Mn_xO_7$ was experimentally calculated using UV-Visible absorption spectra. The complex pattern of UV-Visible absorption and photoluminescence emission spectra were used to identify the states for the same. The experimental and theoretical band-gap values were in good agreement. It was found that slight perturbation in the magnetic landscape of the system is an excellent tool for tailoring the band-gap values in magnetically frustrated systems.

**In Chapter 5,** we switch to the next class of system, i.e., an XY-type pyrochlore system, and we have discussed the synthesis of $Er_2Ti_{2-x}Mn_xO_7$ (x= 0.0, 0.10, & 0.20) and studied the role of Mn on the structural and magnetic properties of this system, through dc and ac susceptibility measurements.

A thorough understanding of the optical properties of $Er_2Ti_{2-x}Mn_xO_7$ (x= 0.0, 0.10, 0.20) and its linkage to crystal structure is described in **Chapter 6.** It discusses the electronic structure calculation of this another class of system $Er_2Ti_{2-x}Mn_xO_7$ (x= 0.0, 0.10, 0.20). The study involved the calculation of the density of states and band structure, along with the theoretical determination of the band-gap through DFT. The band gap was experimentally calculated

using UV-visible absorption spectra. Good agreement has been found between the theoretical and experimental band-gap values.

The thesis is summarized in **Chapter 7,** along with the suggestions for future work.