Chapter 7

Conclusions and Future Scope

Rare earth titanate pyrochlores are an exciting field of continuing research and host a diverse range of magnetic properties. The studies have suggested that perturbation through substitution in these systems provides a better understanding of experimental findings in the context of magnetism and the underlying spin dynamics. This final chapter aims to summarize the main experimental results and conclusions that can be drawn from the work presented here, along with a brief glimpse of future research prospects.

This thesis explores 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 and present its effect on the magnetic and electronic properties. The pure phase of polycrystalline powder samples, $Dy_2Ti_2O_7$ and $Er_2Ti_2O_7$ and its Mn-doped derivatives of the form $Dy_2Ti_{2-x}Mn_xO_7$ (x = 0, 0.05, 0.10, 0.15, 0.20) and $Er_2Ti_{2-x}Mn_xO_7$ (x = 0, 0.10, 0.20) were synthesized. All the compounds crystallize in the cubic pyrochlore structure (space group $Fd\bar{3}m$, No. 227).

Since Mn is a transition metal with multiple possible oxidation states and is a Jahn-Teller active element, which makes it highly tunable to modify magnetic properties in materials. Mn doping in the system introduces new interactions as compared to the pure system, and it can influence the magnetic and electronic properties which makes this system more interesting to be further studied. Here the Jahn-Teller distortions is studied using the high-resolution x-ray diffraction pattern. The distortion typically involves displacements of neighboring atoms, leading to changes in bond lengths and bond angles. This affects the material's magnetic and

electronic properties. Further it can modify the magnetic exchange interactions between Mn ions and neighboring spins, altering magnetic ordering temperatures, magnetic ground states, and spin dynamics.

The major findings of the presented thesis work are listed below: -

1. We have studied low-temperature magnetic ordering and spin dynamics for the polycrystalline compound $Dy_2Ti_{2-x}Mn_xO_7$ (x= 0, 0.05, 0.10, 0.15, 0.20). The dc susceptibility result shows bifurcation in FC and ZFC in dc susceptibility measurement as we increase the concentration of Mn at the Ti site in $Dy_2Ti_2O_7$. The temperature variation of inverse susceptibility $\chi^{-1}(T)$ and weak hysteresis observed in the data collected on cooling (FCC) and warming (FCW) confirms the GP-like state. The GP-like state is inferred from magnetic frustration with Mn inclusion at the Ti site. There is an emergence of a new relaxation feature around 5 K (T*) along with the enhancement of spin ice freezing (T_i) in ac susceptibility measurement with Mn substitution even in the absence of any dc magnetic field, which was not observed in the case of $Dy_2Ti_2O_7$. The peak T* can be related to Dy-Mn interactions and the modulation of the crystal electric field at low temperatures. The low-temperature synchrotron x-ray diffraction study confirms the absence of structural phase transition in this system. Debye Gruineisen fit shows that crystal field energy dominance set in at higher temperature with Mn inclusion in $Dy_2Ti_2O_7$. Such a small perturbation in the composition leads to magnetic ordering above the transition temperature. Nevertheless, the evolution of Griffiths phase behaviour associated with the compositional inclusion of Mn at the Ti site in $Dy_2Ti_2O_7$ and the differences are displayed in spin dynamic of the doped $Dy_2Ti_2O_7$. Our current understanding of these

strongly correlated systems still has considerable challenges. Further neutron experiments and theoretical calculations may help to fully understand the system.

2. Optical study of $Dy_2Ti_{2-x}Mn_xO_7$ system shows that an increase in the percentage inclusion of Mn results in a sequential reduction in the band-gap from 3.82 eV to 2.45 eV as obtained by experimental result (UV-Visible spectroscopy). We obtained a more promising and agreed validation between the experimental and theoretical using LDA-1/2 approximation. x-ray photoelectron spectroscopy (XPS) result indicates the presence of a mixed state of Mn (Mn^{3+} and Mn^{4+}), which is explained using Jahn-Teller distortion. The presence of mixed state results in an intermediate (mid-band) Mn state between VB and CB with immediate inclusion of Mn at the Ti site in the $Dy_2Ti_{2-x}Mn_xO_7$ system. These results establish the optical band gap tunability through Mn inclusion at Ti site in $Dy_2Ti_{2-x}Mn_xO_7$. These results provide perturbation as an excellent tool to tailor the band gap in such system. Such system can be used for spin ice base magnetooptical applications.
3. We have investigated the structural and low-temperature magnetic properties of the $Er_2Ti_{2-x}Mn_xO_7$ pyrochlore system. The ac susceptibility measurements reveal evidence of spin-freezing in $Er_2Ti_2O_7$. This high field spin freezing peak in $\chi'(T)$ is a consequence of single moment saturation. This spin freezing becomes more pronounced with the increase in the applied dc-magnetic field and, most interesting aspect is the observation of such spin-freezing that has not been reported earlier. Further, we have studied the effect of Mn doping on Ti site in $Er_2Ti_2O_7$. With the increase in Mn concentration from x = 0.1 to x = 0.2, this peak suppresses and shifts towards the higher temperature side.

4. Following a similar methodology as we used to study the optical and electronic properties of Mn-doped Ising system, i.e., $Dy_2Ti_2O_7$, we performed the analogous study for Mn-doped XY pyrochlore, i.e., $Er_2Ti_2O_7$. We started with ab initio calculation using DFT to study the electronic structure of the valence Band (V.B.) and conduction Band (C.B.), band gap energy (E_g), orbitals involved in hybridization and DOS for the system. Raman spectrum shows the alterations in the local crystal field and symmetry of the system caused by the Mn substitution. In the high-resolution The Mn 2p spectrum shows the coexistence of two oxidation states of Mn, namely Mn^{3+} and Mn^{4+}. An increase in the percentage inclusion of Mn in $Er_2Ti_{2-x}Mn_xO_7$ results in a sequential reduction in bandgap from 3.84 eV (x = 0) to 2.76 eV (x = 0.1) and subsequently 2.57 eV (for x = 0.2) as obtained by experimental results. The band gap calculated using theoretical approach (density functional theory calculations) using LDA-1/2 approximation matches well with the experimental band gap value obtained using a Tauc plot in U.V. Visible absorption spectroscopy. It establishes the optical band gap tunability through Mn inclusion at Ti site. Such a system can be used for magneto-optical applications.

7.1 Suggestions for Future Work

Extended X-ray absorption fine structure (EXAFS) can provide information about the local atomic environment around the Mn ions. Beyond pyrochlore, there are certain other systems where we can study similar substitutions, such as perovskites and spinels.

There are few open questions that remain to be investigated in these systems which are summarized below.

1. A detailed investigation of the magnetic structure through neutron diffraction experiments is essential to establish a unified magnetic phase diagram for the precise orientation of short-range spin orientation.
2. It would be interesting to see the crystallographic changes and magnetic properties of such systems at relatively much lower temperatures, where spin ices are known to freeze and fall out of equilibrium.
3. New systems need to be synthesized to fine-tune the dipolar and exchange interactions to induce long-range ordering.

In conclusion, the results present in the thesis show that the pyrochlores are quite sensitive to perturbation. Mn doping at Ti site strongly influences the low-temperature spin dynamics and electronic structure of the pyrochlore system. Optical and electronic studies using theoretical and experimental approaches establish the band gap tunability in these pyrochlore system. At the end, we hope that our investigation will certainly lead to new and exciting possibilities in studying the effects of perturbation in pyrochlores systems.