PREFACE

After the discovery of implications of Anderson's resonating-valence-bond (RVB) theory to high-temperature superconductors, frustrated magnetism developed wide-spread recognition. Experimentally, the absence of phase transition at Curie-Weiss temperature signals the possibility of unconventional low-temperature physics. The study of the nature of low-temperature spin-dynamics in such magnetically frustrated systems helps to discover new properties and new exotic states namely spin-ice, gapped or gapless spin-liquids, spin nematics, etc.

Low-temperature spin-dynamics are effectively controlled through dipolar and exchange interaction along with the crystal electric field. Cubic pyrochlores (space group = $Fd\bar{3}m$) and tetragonal pyrogermanates (space group = $P4_12_12$) belonging to a class of spin disordered systems had been synthesized. Structural analysis establishes an entirely different ligand arrangement around the central rare earth metal ion for both these systems. The parameters affecting the nature of spin fluctuations had been studied. Further perturbation had been created in the interaction Hamiltonian through the application of chemical pressure in the parent matrix of holmium pyrotitanates and pyrogermanate for studying the nature of spin fluctuations (classical/quantum) driving the spin dynamics at a lower temperature (T ~ 2 K and T ~ 15 K). Thereafter modification in chemical potential manifests remarkable effects in magnetic properties, and had been elaborately discussed.

Further, the electronic structure had been calculated, and the band gap (E_g) had been

determined. E_g for $Ho_2Ge_2O_7$ is 5.2 eV, and that for $Ho_2Ti_2O_7$ is 3.7 eV which puts them in an insulator class of materials and could be efficiently exploited for various applications where optical and magnetic properties are combined. The absorption and emission (optical) spectral studies reflect a high probability of forbidden transition between the 4f states of Ho^{3+} ion that suitably such systems in the category of materials for quantum information storage and biological imaging applications.

The comprehensive objective of this thesis was to synthesize pure phase holmium titanate, and holmium germanate and its chemical pressure applied derivatives ($Ho_2Ge_xTi_{2-x}O_7$). Thereafter a thorough understanding of its structural, magnetic, electronic, and optical properties had been presented. Both the dipolar and exchange interaction had been tuned to induce long-range ordering. The dipolar interaction decreases in $Ho_2Ge_2O_7$ with the application of negative chemical pressure effect, and the low-temperature spin dynamics (~ 2 K) is of ferromagnetic origin. The ac-susceptibility measurement suggested $Ho_2Ge_2O_7$ to be classified as a classically frustrated spin disordered system. On the other hand, for the conventional cubic pyrochlore $Ho_2Ti_2O_7$, the magnetic ground state is spin-ice, and this freezing relaxation is robust to the application of positive chemical pressure effect, classifying it as a quantum spin-ice system.

The specific objectives of the Ph.D. thesis are as follows:

1. Structural and magnetic analysis of the holmium pyrogermanates and holmium titanates using various characterization tools.
2. Investigation of the parameters (magnetic interactions, i.e., J_{nn} and D_{nn}) which affects the spin dynamics at low temperatures.
3. Studying the nature of the spin fluctuations (quantum/classical) that drives the spin

dynamics at low temperature (~2 K) and at T ~ 15 K through perturbations in the interaction Hamiltonian by the application of chemical pressure.

4. Calculation of the electronic structure i.e., the density of states and band structure, along with the determination of band gap using both theoretical (density functional theory) approach as well as via an experimental method.

Important findings of the present thesis are as follows: -

1. The magnetic response of $Ho_2Ge_2O_7$, as well as that of its negative chemical pressure induced derivative $Ho_2Ti_{0.1}Ge_{1.9}O_7$, indicates the archetypical signature of ice-like spin correlation at T ~ 2 K. Effect of negative chemical pressure in $Ho_2Ge_2O_7$ matrix decreases the low temperature short-range ferromagnetic spin correlation at T ~ 2 K. Dominance of the debilitation of exchange interaction over dipolar interaction is established through the enhancement in Curie-Weiss temperature.

2. The magnetic analysis of $Ho_2Ge_xTi_{2-x}O_7$ (x = 0, 0.1, 0.15 & 0.25) shows a reduction in the value of Curie-Weiss temperature from 0.33 K to -0.04 K (for an applied magnetic field of 100 Oe) with an increase in positive chemical pressure, indicating the dominance of the evolution of antiferromagnetic exchange interaction over ferromagnetic dipolar interaction. The single-ion spin freezing mechanism at T ~ 15 K is attributed to crystal field-phonon coupling.

3. Distinct shrinkage effect in the matrix of $Ho_2Ti_2O_7$ upon Ge^{4+} substitution results in the modifications of band gap value. The band gap of 5.20 eV drastically drops to 3.92 eV with immediate Ti^{4+} substitution in $Ho_2Ge_2O_7$. Density of state (DOS) calculation indicates that the upper valence band is formed due to the hybridization

of the O-2p state with that of Ho-5p & Ti-3p state, whereas conduction band primarily consists of Ho-5d state hybridized with Ti-3d & Ge-4d states. The evolution of the total DOS for $Ho_2Ge_xTi_{2-x}O_7$ shows that valence band edge is more sensitive than the conduction band to the change in chemical pressure. It proves that chemical pressure is an excellent tool to tailor the band gap and fine-tune the intermediate electronic states in $Ho_2Ge_xTi_{2-x}O_7$.

4. Photoluminescence spectra present four favored sub-level vibrational transition corresponding to $^5F_5$ (D_7, D_6, D_1, D_1) to $^5I_8$ (Z_{10}, Z_{11}, Z_8, Z_{11}) electronic levels at 652, 659, 663, and 669 nm for Ho^{3+} using an excitation wavelength of 450 nm along with other emission peaks for transition within 4f states of Ho^{3+} ion. Such fine control over emission spectra can find applications in devices where precise wavelengths are required.

The major aim of the work was to synthesize and crystallographically analyse the above-mentioned spin frustrated magnetic systems and to further study the low-temperature spin dynamics. **Chapter 1** of this thesis presents the basic introduction to magnetic frustration as well as the magnetic interactions that play a role at low temperatures for the establishment of magnetic ground state. This chapter also includes the signatory features of $Ho_2Ge_2O_7$ and $Ho_2Ti_2O_7$ in relevance to their magnetic and structural properties as obtained through various characteristics tools. Further, the role of chemical pressure (modification in interaction Hamiltonian) in context to dipolar spin ice model (DSIM) for inducing long-range ordering has also been discussed.

The optimization of various synthesis parameters in order to obtain the pure phase $Ho_2Ge_2O_7$ and $Ho_2Ti_2O_7$ is described in **Chapter 2**. The duration for mechanical mixing

(high energy ball mill), temperature for thermochemical reaction, pressure condition for pellet formation, binder removal temperature, as well as the sintering and annealing temperatures, all have been properly optimized to ensure the maximum reproducibility of the samples.

The robust nature of the spin ice freezing (T ~ 2 K) for conventional cubic pyrochlore has been established in **Chapter 3**. Low-temperature synchrotron x-ray diffraction pattern indicates an anomaly in lattice volume below 30 K, the curve of lattice volume vs. temperature when fitted using Debye-Grüneisen equation established crystal field-phonon coupling in $Ho_2Ti_2O_7$. This crystal field-phonon coupling is prominent at T ~ 15 K, which is reflected through the shift of single ion spin freezing temperature (T ~ 15 K) towards lower temperature with an increase in chemical pressure.

Chapter 4 deals with the structural analysis of $Ho_2Ge_2O_7$ along with the study of the effect of modulation in magnetic interaction upon the spin relaxation at a lower temperature. The high-resolution x-ray diffraction pattern of $Ho_2Ti_xGe_{2-x}O_7$ indicates the lattice volume expansion, and this effect decreases the dipolar interaction in the $Ho_2Ge_2O_7$ matrix. ac-susceptibility presents two spin relaxation, one at T ~ 3 K corresponding to ice-like spin freezing at second at T ~ 15 K due to single-ion anisotropy attributed to the thermal origin. The M-H (magnetization vs. field) behavior at 2 K indicates a ferromagnetic spin correlation.

In **Chapter 5**, we have tried to appraise the relationship between the structural and electronic properties of $Ho_2Ti_xGe_{2-x}O_7$. Computational approach had been used for the density of state (DOS) and band structure calculation of $Ho_2Ti_xGe_{2-x}O_7$. The electronic

structure of valence band (V.B.), conduction band (C.B.), band gap energy (E_g), orbitals involved in hybridization, influence of the B site substitution ($Ho_2Ti_xGe_{2-x}O_7$) on the electronic states of the subsystems had been discussed in detail.

The thorough understanding of the optical properties of $Ho_2Ti_xGe_{2-x}O_7$ with its linkage to crystal structure is described in **Chapter 6.** UV-Visible spectroscopy presents the maximum cross-section for absorption at a wavelength of 454 nm. Using the excitation wavelength of 450 nm, luminescence peaks of precise wavelength had been obtained at a wavelength of ~ 675 nm. The sensitivity of the band gap to the composition makes these materials extremely interesting from the point of view of the fundamental problem regarding energy band structure in solid-state physics.

The whole of the thesis work is summarized in **Chapter 7** along with the future work suggestions.