

To one and all!!!

CERTIFICATE

It is certified that the work contained in the thesis titled "**Role of chemical pressure on the magnetic and electronic properties of magnetically frustrated holmium titanates and germanates**" by **Ms. Manjari Shukla** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy, and SOTA for the award of Ph.D. Degree.

Dr. Chandan Upadhyay

(Supervisor)

School of Materials Science & Technology

Indian Institute of Technology

(Banaras Hindu University)

DECLARATION BY THE CANDIDATE

I, "**Manjari Shukla**", certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of "**Dr. Chandan Upadhyay**" from July 2015 to Feb 2021, at the School of Materials Science & Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any others work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

Date:

Place: Varanasi

(Ms. Manjari Shukla)

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

Dr. Chandan Upadhyay
(Supervisor)
School of Materials Science & Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

Dr. Chandana Rath
(Coordinator)
School of Materials Science & Technology
Indian Institute of Technology
(Banaras Hindu University)
Varanasi

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: **ROLE OF CHEMICAL PRESSURE ON THE MAGNETIC AND ELECTRONIC PROPERTIES OF MAGNETICALLY FRUSTRATED HOLMIUM TITANATES AND GERMANATES**

Name of the Student: **Ms. Manjari Shukla**

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the "Doctor of Philosophy" degree.

Date:

Place: Varanasi

(Ms. Manjari Shukla)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated.



ACKNOWLEDGEMENTS

The conglomeration of inspiration, guidance, and support from many individuals had led towards the successful completion of this work. Therefore, I would like to take this opportunity here and acknowledge all, who had been instrumental during my research.

*It's an inordinate pleasure to express my deep sense of gratitude to my supervisor **Dr. Chandan Upadhyay**, School of Materials Science and Technology, Indian Institute of Technology (BHU), for his excellent support, skilled guidance, an abundance of patience, and his persistent encouragement for endeavour of achieving high standards in work. I consider it my proud privilege to have the opportunity to work with him.*

I express my regards to Dr. Sunil Mishra, Department of Physics (IIT BHU) who had always provided the support, guidance, and suggestions for necessary improvements in my thesis work.

I would like to thank all the teachers at the School, Prof. Dhananjai Pandey, Prof. Pralay Maity, Prof. Rajiv Prakash, Dr. Chandana Rath, Dr. Akhilesh Singh, Dr. Bhola Nath Pal, Dr. Ashish Kumar Mishra, Dr. Shrawan Kumar Mishra, Dr. Sanjay Singh and Dr. S. R. Singh for their support at all moment during the progress of my research.

I am thankful to Dr. Soma Banik from RRCAT, Indore and Dr. Rajan Pandey from VIT, Vellore for their help in measurements. I acknowledge CIF, IIT (BHU), the technical and non-technical staff members of CIFC for their help in my research work. Financial assistance from the IIT (BHU) to participate in conference is also acknowledged. I am also grateful to all office staff of the school and authorities of IIT (BHU), for their kind help during the period of my stay to complete the thesis work.

I express thanks to my seniors Dr. Pappu Kumar, Dr. Pinki Singh, Dr. Pramod Kumar Yadav and Dr. Priyanka Tiwari for their discussion related to my research issues.

I am thankful to Dr. Devesh Shukla, for his excellent co-operation and support during entire Ph. D days.

I express my sincere thanks to my school friends Mr. Chandan Mishra, Ms. Neha Rai, Mr. Akash Pandey and Mr. Siddharth Kaushik for their pleasant company, care, and encouragement.

I acknowledge my superb and delightful juniors Mr. Abhishek Tripathi and Mr. Rajnikant Upadhyay. Their fondness, prudence and thoughtfulness has always kept me going all way through. Special mention to my dear friend Ms. Astha Upadhyay and for being a wonderful companion in this journey called "life".

*My deep and sincere gratitude to my father **Shri Ram Yagya Shukla** and mother **Smt. Kanchan Shukla**, for their selfless love and providing me the opportunities and freedom to go with my own experiences. I acknowledge my brother Madhav Shukla for his continuous optimism and Alok Shukla for always being there for me as a friend. I express my all respect and gratitude to my late grandmother.*

I offer my humble gratitude to Almighty for giving me the courage and strength to complete my research work in his holy abode Kashi. Lastly, I thank the founder, Mahamana Pt. Madan Mohan Malviyaji for providing this glorious place to work.

Date:

Place: Varanasi

(Manjari Shukla)

INDEX

CONTENT	PAGES
Certificate.....	i
Declaration by the candidate & Certificate by the supervisor	iii
Copyright transfer certificate	v
Acknowledgements.....	vii
Index	ix
List of figures.....	xiii
List of tables.....	xxiii
List of abbreviations	xxv
Preface	xxvii
Chapter 1 INTRODUCTION AND LITERATURE REVIEW	1
1.1 Introduction	1
1.2 Magnetic interactions	5
1.2.1 Dipolar Interaction.....	6
1.2.2 Exchange Interaction	7
1.3 Magnetic frustrations	12
1.3.1 Frustration in two-dimension.....	13
1.3.2 Frustration in three-dimension.....	17
1.4 Pyrochlore lattice	18
1.4.1 Magnetic interactions in specific to Pyrochlore Lattice	21
1.5 Spin ice.....	22
1.6 Spin relaxation apart from spin-ice in different spin frustrated systems	23
1.6.1 Unconventional long-range ordering	23
1.6.2 XY antiferromagnetic (Long-range ordering via an order by disorder mechanism).....	25
1.6.3 Spin Glass	26
1.6.4 Spin liquid/Cooperative paramagnetism ($Tb_2Ti_2O_7$)	28
1.7 Spin ice: in the context of $Ho_2Ti_2O_7$	29

1.8	Experimental signatures of spin ice: [(Dy/Ho) ₂ Ti ₂ O ₇]	34
1.9	Application of chemical pressure in magnetically frustrated systems (dipolar spin ice model)	43
1.10	Previous results in relevance to the application of chemical pressure.....	46
1.11	Holmium pyrogermanate	48
1.12	Applications and motivations	53
1.13	Thesis aim.....	54
Chapter 2	SYNTHESIS AND CHARACTERIZATIONS	57
2.1	Introduction.....	57
2.2	Stability-field/Structure-stability Map for the synthesis of A ₂ B ₂ O ₇ materials	58
2.3	Solid –state synthesis route.....	60
2.4	Characterization techniques	63
2.4.1	x-ray diffraction (XRD).....	63
2.4.2	Synchrotron x-ray diffraction (SXR).....	69
2.4.3	Magnetic Measurements.....	69
2.4.4	Density Functional Theory (DFT).....	72
2.4.5	x-ray electron spectroscopy (XPS).....	78
2.4.6	Ultraviolet Photoelectron Spectroscopy (UPS).....	80
2.4.7	UV Visible absorption Spectroscopy	80
2.4.8	Photoluminescence emission Spectroscopy	81
Chapter 3	ROBUST SPIN ICE FREEZING IN MAGNETICALLY FRUSTRATED Ho ₂ Ti ₂ O ₇ AND CRYSTAL FIELD-PHONON COUPLING	85
3.1	Introduction.....	85
3.2	Structural analysis.....	87
3.2.1	Rietveld refinement of HRXRD pattern of Ho ₂ Ge _x Ti _{2-x} O ₇	89
3.2.2	Role of positive chemical pressure on the structure	90
3.3	Magnetic properties	92
3.3.1	Temperature dependent magnetization.....	92
3.3.2	Field dependent magnetization.....	95
3.3.3	Temperature dependent ac-susceptibility	96
3.4	Low temperature SRXRD measurement for Ho ₂ Ge _{0.1} Ti _{1.9} O ₇	104
3.5	Crystal field-phonon coupling	105
3.6	Conclusions.....	107

Chapter 4	STRUCTURAL ANALYSIS OF $\text{Ho}_2\text{Ge}_2\text{O}_7$ AND EFFECT OF NEGATIVE CHEMICAL PRESSURE UPON ITS MAGNETIC PROPERTIES.	109
4.1	Introduction	109
4.2	Structural analysis	111
4.2.1	Rietveld refinement of obtained HRXRD pattern of $\text{Ho}_2\text{Ge}_2\text{O}_7$	111
4.2.2	Role of negative chemical pressure on the crystal structure of $\text{Ho}_2\text{Ge}_2\text{O}_7$	116
4.3	Magnetic properties of $\text{Ho}_2\text{Ge}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$	118
4.3.1	Temperature dependent magnetization.	119
4.3.2	Field dependent magnetization	121
4.3.3	Temperature dependent ac-susceptibility	124
4.4	Conclusions	129
Chapter 5	ROLE OF CHEMICAL PRESSURE UPON THE ELECTRONIC STRUCTURE OF $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$	131
5.1	Introduction	131
5.2	Structural analysis of $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$	132
5.3	Electronic structure calculation through DFT calculations.....	135
5.3.1	Density of state (DOS) calculations of $\text{Ho}_2\text{Ge}_2\text{O}_7$	136
5.3.2	Density of state calculations of $\text{Ho}_2\text{Ti}_2\text{O}_7$	137
5.3.3	Evolution of total DOS for $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$	138
5.3.4	Band structure of $\text{Ho}_2\text{Ge}_2\text{O}_7$	140
5.3.5	Band structure of $\text{Ho}_2\text{Ti}_2\text{O}_7$	143
5.4	Electronic structure analysis of $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$: experimental characterizations .	145
5.4.1	Ultraviolet photoelectron Spectroscopy.....	146
5.4.2	x-ray photoelectron spectroscopy	148
5.5	Conclusions	151
Chapter 6	OPTICAL PROPERTIES OF $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ SYSTEM	153
6.1	Introduction	153
6.2	Optical studies on $\text{Ho}_2\text{Ti}_2\text{O}_7$ system	154
6.2.1	Ultraviolet-visible spectroscopy	155
6.2.2	Photoluminescence spectroscopy	160
6.3	Conclusions	166
Chapter 7	CONCLUSIONS AND FUTURE SCOPE.....	169
7.1	Conclusions	169

7.2 Suggestions for future work.....	171
REFERENCES	173
List of Publications.....	187

LIST OF FIGURES

- Figure 1.1 Dipolar Spin Ice Model (DSIM) which presents the possibility for inducing long-range ordering by varying the complex dipolar and exchange interaction in spin disordered systems.[26] 4
- Figure 1.2 Dipole-dipole interactions of parallel magnetic moments. Top: vector representation of dipoles interacting at a fixed separation, r , and various orientations relative to the z -axis. Bottom: plot of the value of $y = 3\cos^2\theta - 1$ as a function of θ . [30] 6
- Figure 1.3 (a) Ferromagnetic and (b) antiferromagnetic Ising type spins on the vertices of a square lattice. Both types of spin coupling on this lattice site result in an unfrustrated system. 14
- Figure 1.4 (a) Ferromagnetic and (b) antiferromagnetic interaction between the spins on the vertices of a triangular lattice.[37] 15
- Figure 1.5 (a) $J_{nn} \gg J_{nnn}$ and (b) $J_{nn} \ll J_{nnn}$ condition on a square lattice site result in an unfrustrated system, whereas (c) $J_{nn} \sim J_{nnn}$ ends up with frustrated "plaquettes" of a square planar lattice.[31] 16
- Figure 1.6 (a) Edge-sharing and (b) Corner-sharing (Kagome) triangular lattices having disordered spin arrangement. [31] 16
- Figure 1.7 (a) The simplest example of 3D frustration is antiferromagnetically coupled spin on the vertices of a tetrahedral lattice. (b) The array of such spin arrangements within the lattice constitutes the frustrated pyrochlore lattice. (c) The pyrochlore lattice consists of an alternating kagome and triangular planar layers stacked along a $\langle 111 \rangle$ direction.[18], [31]17
- Figure 1.8 (Top) Cubic pyrochlores ($A_2B_2O_7$; A = rare earth metal ion & B = d block transition metal ion) with A and B ions residing on two distinct interpenetrating corner-sharing tetrahedral sublattices. (Bottom) Three-dimensional pyrochlore lattice along with the Wyckoff sites assigned to these atomic positions according to the International tables of crystallography.[18] 19

Figure 1.9 (a) Crystal structure of the magnetic ions in the rare-earth pyrochlores. (b) Local environment of a rare-earth ion showing the surrounding oxygen ions. The local XY plane of the ion, as well as the C_2 and C_3 rotation axes of the D_{3d} site symmetry group. [11] 20

Figure 1.10 (a) dc-susceptibility data for $Gd_2Ti_2O_7$ showing Curie–Weiss behavior at $T \sim 10$ K and no sign of long-range order till $T \sim 1$ K. (b) Presence of two-phase transitions at 0.9 and 0.7 K (zero applied field) from heat capacity data on $Gd_2Ti_2O_7$ (top). Induction of new transitions in applied fields (bottom).[42] 24

Figure 1.11 (a) The 1 k magnetic structure for $Gd_2Ti_2O_7$, which is consistent with the neutron diffraction data above 0.7K. (b) The 4k magnetic structure of $Gd_2Ti_2O_7$ consistent with both the Bragg and diffuse neutron diffraction data below 0.7 K. The dark spheres represent Gd ions with a full ($7.0\mu_B$) ordered moment while the grey spheres carry only a $1.9 \mu_B$ ordered moment. [42] 24

Figure 1.12 (a) Specific heat versus temperature for $Er_2Ti_2O_7$. (b) Inverse of the magnetic susceptibility of an $Er_2Ti_2O_7$ crystal versus temperature in a large temperature range. The solid line results from a fit with the Curie Weiss law. A field of 1 mT is applied along a diagonal of the cubic crystal structure. The inset shows the low-temperature range of the data. [44] 26

Figure 1.13 Spin dynamics in $Y_2Mo_2O_7$. (a) Neutron spin echo results for $Y_2Mo_2O_7$ at temperatures spanning $T_f = 22.5$ K determined from static magnetization data. Note that within this time window, spin freezing is not fully established until 10 K. (b) Frequency-dependent ac susceptibility χ' for $Y_2Mo_2O_7$ showing classical spin-glass behavior. (c) dc-susceptibility showing $T_f \sim 22.5$ K. [18], [31] 27

Figure 1.14 (a) The temperature dependence of the inverse susceptibility for $Tb_2Ti_2O_7$, along with a fit of the high-temperature regime of this data to a Curie-Weiss form. The inset shows the assumed local arrangement of moments on a single tetrahedron. (b) The variation with temperature of the muon spin relaxation rate for $Tb_2Ti_2O_7$ in a longitudinal applied field of 0.005 T. The inset shows the single exponential relaxation of the muon polarization at various temperatures. [47] 28

Figure 1.15 (Top panel) The normalized intermediate scattering function $S(q, t)/S(q, 0)$ as measured through neutron scattering experiment, integrated in the range $0.5^\circ A^{-1} \leq q \leq 1.0^\circ A^{-1}$

at various temperatures. (Bottom panel) as a function of q , showing negligible q dependence. [36] 30

Figure 1.16 ac-susceptibility data taken on a single crystal of $\text{Ho}_2\text{Ti}_2\text{O}_7$. (Top) The high-temperature peak position as a function of $\log f$ at different fields. Inset: Arrhenius behavior of the low-temperature feature in the same field. (Bottom) Frequency dependence of the ac susceptibility (imaginary part) measured in an applied dc field $B = 1$ T parallel to the $\langle 111 \rangle$ axis. [36] 31

Figure 1.17 (a) The curves of M-T (magnetization vs. temperature) for both ZFC and FC sequences under the magnetic field $H = 0.1$ kOe and 5 kOe, respectively. The inset indicates the MT curves under $H=0.1$ kOe with the T-range of (2–100) K. (b) Magnetic hysteresis loop at 2 K in the H-range of (-20–20) kOe. [27] 33

Figure 1.18 Limiting low-temperature state is characterized by a residual entropy, $S = 1.68$ J/mol. K known as zero point or residual entropy being observed in $\text{Dy}_2\text{Ti}_2\text{O}_7$. [53] 35

Figure 1.19 (a) "2 in-2 out" orientation, the letter 6 in bracket indicates six possible states. Adjacent to it is the "1 in-3 out" spin orientation, and this orientation has eight degenerate states. Last is the "all-in-all-out" configuration having two degenerate states. (b) Assigning an energy $+J_{\text{eff}}$ to an 'in-in' or 'out-out' pair and $-J_{\text{eff}}$ to an 'in-out' pair yields energies $E (2:2) = -2J_{\text{eff}}$, $E (3:1) = 0$ and $E (4:4) = +6J_{\text{eff}}$. [54] 35

Figure 1.20 Neutron scattering data for $\text{Ho}_2\text{Ti}_2\text{O}_7$. (Left) Unusual temperature dependence of the magnetic Bragg peaks measured in an applied field of 2 T. (Right) The two sets of peaks (full and open circles) respectively suggest the $q = 0$ and $q = X$ magnetic shown as (a) and (b). [54] 36

Figure 1.21 χ^{-1} vs. T plot for $\text{Ho}_2\text{Ti}_2\text{O}_7$ providing the value of $\theta_{\text{CW}} = +1.9 \pm 0.1$ K in accordance with Curie-Weiss law. [57] 37

Figure 1.22 (a) Two oxygen atoms (O') are responsible for driving the local Ising anisotropy and sets a strong crystal-field effect along the $\langle 111 \rangle$ axis of the tetrahedron. (b) Strong axial symmetry of the magnetic site has along a local $\langle 111 \rangle$ direction. [58] 39

Figure 1.23 (a) The local coordinate frame x_0, y_0, z_0 (red arrows) used to describe the transverse magnetic field B (green arrow) and its direction angle Φ in Eq. (1.35). (b) Splitting of the ground-state doublet under the influence of a purely transverse magnetic field. The red curves correspond to the non-Kramers behavior of $\text{Ho}_2\text{Ti}_2\text{O}_7$. (c) Splitting of the ground-state doublet $\Delta E_{01} = E_1 - E_0$ versus the magnitude of the transverse field. [58] 42

Figure 1.24 Crystal field spectrum of $\text{Ho}_2\text{Ti}_2\text{O}_7$ features six doublets (solid lines) and five singlets (dashed-dotted lines). In meV, bottom to top, the series of doublets is 0, 21.96, 25.99, 59.59, 71.51, and 76.80, while the series of singlets is 20.42, 27.71, 69.36, 69.94, and 80.52. [58] 43

Figure 1.25 The two competing phases for spin-ices: (a) the $Q = 0$ "all in-all out" phase and (b) the spin-ice "two in-two out" phase [59]. 44

Figure 1.26 (a) Real and imaginary parts of the ac susceptibility of $\text{Dy}_2\text{Ge}_2\text{O}_7$ (black lines) and $\text{Dy}_2\text{Ge}_{1.875}\text{Si}_{0.125}\text{O}_7$ (red lines) at frequencies of 16 Hz (solid lines), 270 Hz (dashed lines), and 770 Hz (dash-dotted lines). (b) Spin-relaxation time τ as a function of the inverse peak temperature T_P used for Arrhenius fit.[21] 47

Figure 1.27 (a) Temperature dependence of the magnetic specific heat c_{mag} per mol of Dy of the $\text{Dy}_2\text{Ge}_2\text{O}_7$ and $\text{Dy}_2\text{Ge}_{1.875}\text{Si}_{0.125}\text{O}_7$ samples. (b) Temperature dependence of the molar entropy of $\text{Dy}_2\text{Ge}_2\text{O}_7$ and $\text{Dy}_2\text{Ge}_{1.875}\text{Si}_{0.125}\text{O}_7$ at zero fields and 1, 2, and 4 T. [21] 47

Figure 1.28 The real (χ') and imaginary part (χ'') of ac-susceptibility of $\text{Dy}_{2-x}\text{Yb}_x\text{Ti}_2\text{O}_7$ measured at $H = 10\text{kOe}$. [61] 48

Figure 1.29 Crystal structure of $\text{Ho}_2\text{Ge}_2\text{O}_7$ (a) the rare earth Ho sublattice showing the right-handed helices centred on fourfold screw axes parallel to the c -axis; the edge-sharing triangles connecting the Ho atoms are shaded. The different colored atoms illustrate the four Ho atoms around the fourfold screw axis. (b) the Ho-O and (c) Ho-Ge coordination polyhedra, with Ho—red (dark gray) and O/Ge—white/light blue (light gray): there are five O in a highly distorted pentagon in the ab plane, and two more O, one above and one below. (d) Magnetic spin configuration showing eight Ho ions in four equivalent ab planes. [28] 50

Figure 1.30 ac-susceptibility data for single crystal of $\text{Ho}_2\text{Ge}_2\text{O}_7$ when magnetic field is applied parallel to ab axis; (b)-(e) $\nu = 10, 102, 103,$ and 104 Hz data for $H = 0.1, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0,$ and 1.2 T.[28]	51
Figure 1.31 Inverse magnetic susceptibility of $\text{Ho}_2\text{Ge}_2\text{O}_7$ (single crystal) for $H = 0.1$ T and $H ab$ (circles) and $H c$ (triangles) together with the calculated average inverse susceptibility (line). Inset: low temperature anisotropic susceptibilities. (b) Specific heat for $\text{Ho}_2\text{Ge}_2\text{O}_7$ measured at zero and applied field (0.5 T). (c) $T = 2$ K $M(H)$ isotherms for $H ab$ (circles) and $H c$ (triangles). [28]	52
Figure 2.1 In the sample series $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$, positive and negative chemical pressure has been applied through the substitution of Ge^{4+} in $\text{Ho}_2\text{Ti}_2\text{O}_7$ and Ti^{4+} in $\text{Ho}_2\text{Ge}_2\text{O}_7$ respectively.	58
Figure 2.2 Possibility of the all the elements that could produce $\text{A}_2\text{B}_2\text{O}_7$ cubic pyrochlore phase. [18]	59
Figure 2.3 Stability field map for the synthesis of $\text{A}_2\text{B}_2\text{O}_7$ magnetically frustrated systems. [18]	59
Figure 2.4 Flowchart for standard solid-state route adopted for the sample synthesis.	60
Figure 2.5 Room temperature high resolution x-ray diffraction pattern HRXRD pattern for $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 2, 1.9, 1.75, 1.5$ & 1).	62
Figure 2.6 Room temperature high resolution x-ray diffraction pattern (HRXRD) pattern for $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0, 0.05, 0.1, 0.15, 0.25$ & 0.5).	62
Figure 2.7 Schematic representation of incident and diffracted X-rays from the crystal lattice.	64
Figure 2.8 Schematic representation of photoluminescence emission.	82
Figure 3.1 (a) Dependence of the specific heat peak position on T . (b) Dependence of $T_{\text{peak}}/D_{\text{nn}}$ on $J_{\text{nn}}/D_{\text{nn}}$ ratio. The open symbols are experimental results, and the solid lines are the theoretical calculations from the dipolar spin-ice model.[60]	86

Figure 3.2 A part of pyrochlore lattice containing two O' atoms connected through the shared Ho³⁺ atom of the adjacent tetrahedra. 88

Figure 3.3 The projection of pyrochlore lattice along [111] direction highlighting the strong axial symmetry containing the O' oxygen ions (red spheres) and magnetic Ho³⁺ (blue spheres) ions only. 88

Figure 3.4 Room temperature high resolution X-ray diffraction (HRXRD) pattern of Ho₂Ge_xTi_{2-x}O₇ for (a) x = 0 (b) x= 0.1 (c) 0.15 (d) 0.25. 89

Figure 3.5 Room temperature high resolution x-ray diffraction data (HRXRD) indicating the shift of (222), (440), (622) and (662) peaks towards higher Q value and with increase in chemical pressure for (a) x = 0 (b) x = 0.1 (c) x = 0.1 (d) x = 0.25) in Ho₂Ge_xTi_{2-x}O₇. 90

Figure 3.6 Temperature dependence of dc susceptibility curve of Ho₂Ge_xTi_{2-x}O₇ (x = 0, 0.1, 0.15 and 0.25) samples in the range of (2-200) K for (a) H = 100 Oe (b) and 1000 Oe. The inset shows the corresponding inverse susceptibility curve obtained from dc χ for ZFC data. 92

Figure 3.7 Magnetic field dependence of magnetization of Ho₂Ge_xTi_{2-x}O₇ (x = 0, 0.1, 0.15 and 0.25) at T = 2 K for H (magnetic field) ranging from -70 to 70 kOe. 95

Figure 3.8 Real part of ac-susceptibility of Ho₂Ge_xTi_{2-x}O₇ for (a) x = 0 (b) x= 0.1 (c) x= 0.15 (d) x= 0.25 measured at H = 0.1, 0.5, 1, 5, 7.5, 10, 20 and 50 kOe at an applied ac-frequency of 500 Hz. 96

Figure 3.9 Variation of ac susceptibility with temperature for Ho₂Ge_xTi_{2-x}O₇ (x = 0, 0.1, 0.15 and 0.25) for an applied field of (a) H = 7.5 kOe (b) H = 10 kOe (c) H = 20 kOe (d) H = 50 kOe at 500 Hz. Single ion freezing temperature (T_s) is shifted towards the low lower temperature with increasing chemical pressure effect. 98

Figure 3.10 Frequency independence of ac susceptibility of Ho₂Ge_xTi_{2-x}O₇ for (a) x = 0 (b) x= 0.1 (c) x= 0.15 (d) x= 0.25 for applied dc magnetic field H = 7.5 kOe. 99

Figure 3.11 Shift in the single ion freezing temperature (T_s) against external applied magnetic field for Ho₂Ge_xTi_{2-x}O₇ (x = 0, 0.1, 0.15 and 0.25) system. 100

Figure 3.12 Variation of single ion freezing temperature (T_s) with composition in $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ (x value = 0, 0.1, 0.15 and 0.25) at an applied magnetic field of (a) $H = 7.5$ kOe (b) $H = 10$ kOe (c) $H = 20$ kOe (d) $H = 50$ kOe for an applied frequency of 500 Hz. 100

Figure 3.13 Spin ice freezing (T_{ice}) remains unaffected with the increase in chemical pressure for $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0, 0.1, 0.15$ and 0.25) system. 101

Figure 3.14 Low temperature synchrotron x-ray diffraction pattern of $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0.1$) at (a) $T=150$ K, (b) $T= 70$ K, (c) $T=30$ K (d) $T=15$ K. 104

Figure 3.15 Debye Grüneisen fit of $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0.1$) indicating the deviation from its linear behavior below 30 K. 105

Figure 3.16 Temperature dependence of the unit-cell volume of SrRuO_3 . The solid line represents the contribution of the phonon fitted using the Debye function. [86] 107

Figure 4.1 Room-temperature high-resolution x-ray diffraction pattern of powdered $\text{Ho}_2\text{Ge}_2\text{O}_7$ along with the fitted $[\text{P}4_12_12(\text{tetragonal})$ space group] and the difference between the observed and calculated fit. 112

Figure 4.2 3D-structure of $\text{Ho}_2\text{Ge}_2\text{O}_7$ depicting $[\text{Ge}_2\text{O}_7]^{6-}$ unit in which Ge^{+4} ion is coordinated with four dis-equivalent oxygen with Ge-O4-Ge unit in common having a bridging angle of $133.3(4)^\circ$. 113

Figure 4.3 Crystal structure of $\text{Ho}_2\text{Ge}_2\text{O}_7$ showing (a) infinite helical chain of magnetic rare-earth atom in a single unit cell having 8 Ho^{3+} atoms with 2 Ho^{3+} atom in each of the four layers parallel to the crystallographic ab plane. (b) The pentagonal bipyramidal structure around the rare-earth ion is constituting the HoO_7 unit along with GeO_4 tetrahedra. 114

Figure 4.4 Position of magnetic ion within a helix of a unit cell of $\text{Ho}_2\text{Ge}_2\text{O}_7$. It shows four Ho^{3+} ions arranged in a pattern of common edge-sharing two triangles further corner joined with the next Ho_4 plaquette. Shared edges have been marked with a red line. 115

Figure 4.5 Room temperature refined high-resolution x-ray diffraction pattern of powdered $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ using the $\text{P}4_12_12$ space group. 116

Figure 4.6 Room temperature high-resolution x-ray diffraction pattern for (a) $\text{Ho}_2\text{Ge}_2\text{O}_7$ and (b) $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ indicating the shift of (201), (004), (212), (105), and (321) peaks towards lower angle side. 118

Figure 4.7 Temperature dependence of dc-susceptibility curve of $\text{Ho}_2\text{Ge}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ in the range of (2-200) K for (a) $H = 100$ Oe & (b) $H = 1000$ Oe. Inset contains the corresponding inverse susceptibility curve to obtain θ_{CW} fitted through Curie-Weiss law in the linear temperature range of (25-50) K with further extrapolating the χ^{-1} vs. T plot. 119

Figure 4.8 Magnetic field dependence isothermal magnetization of $\text{Ho}_2\text{Ge}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ at $T = 2$ K for H ranging from -70 to 70 kOe. 122

Figure 4.9 Temperature dependence of real part of the ac-susceptibility of $\text{Ho}_2\text{Ge}_2\text{O}_7$ without any application of magnetic field at the characteristic frequency of 50, 100, 300, 500, 700, and 900 Hz. 124

Figure 4.10 Real part of ac-susceptibility of for (a) $\text{Ho}_2\text{Ge}_2\text{O}_7$ and (b) $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ as a function of temperature (2-40) K at an applied magnetic field of 0.5, 1.0, 5.0, 7.5, 10, 20 and 50 kOe (applied frequency = 500 Hz). 125

Figure 4.11 The variation in the single ion freezing temperature with a magnetic field for (a) $\text{Ho}_2\text{Ge}_2\text{O}_7$ and (b) $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$. 127

Figure 4.12 The ac-susceptibility plot of $\text{Ho}_2\text{Ge}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ at an applied magnetic field of (a) $H = 5$ kOe (b) $H = 7.5$ kOe (c) $H = 10$ kOe (d) $H = 20$ kOe (e) $H = 50$ kOe. 128

Figure 5.1 Calculated optical band gap values (open down triangles) and distortion parameter x (solid up triangles). [93] 133

Figure 5.2 Density of States (DOS) of $\text{Ho}_2\text{Ge}_2\text{O}_7$ (a) Partial DOSs of Ho (6s, 5p and 5d); Ge (4s, 4p and 4d) and O (2s, 2p and 3d) states along with total DOS obtained from standard LDA and (b) total DOS from LDA half. 136

Figure 5.3 Density of States (DOS) of $\text{Ho}_2\text{Ti}_2\text{O}_7$ (a) Partial DOSs of Ho (6s, 5p and 5d); Ti (4s, 4p and 3d) and O (2s, 2p and 3d) states along with total DOS obtained from standard

LDA (local density approximation) and (b) total DOS from LDA half involving self-energy correction method. 137

Figure 5.4 Total DOS of (a) $\text{Ho}_2\text{Ge}_2\text{O}_7$ along with B site Ti^{4+} substitution for $x=1.75$ ($\text{Ho}_2\text{Ge}_{1.75}\text{Ti}_{0.25}\text{O}_7$) (b) $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 2, 1.75, 1.25, 1.5$ and 1) and (c) $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0, 0.25, 0.5$ and 0.75). 139

Figure 5.5 Band structure of $\text{Ho}_2\text{Ge}_2\text{O}_7$ obtained from (a) Standard LDA (local density approximation) having band gap of 3.98 eV with direct transition involving Γ symmetric point; (CBM – Conduction band minima; VBM – Valence band maxima) and (b) LDA half, (Ge and O atoms) involving self-energy correction method having band gap of 6.11 eV with indirect transition along Γ to X symmetry point of Brillouin zone. 141

Figure 5.6 Symmetry points along with the phonons involved in indirect-transitions in the Brillouin zone for $\text{Ho}_2\text{Ge}_2\text{O}_7$ (space group; 92). 142

Figure 5.7 Band structure of $\text{Ho}_2\text{Ti}_2\text{O}_7$ obtained from (a) Standard LDA (local density approximation) having band gap of 2.74 eV with direct transition involving Γ symmetric point; (CBM – Conduction band minima; VBM – Valence band maxima) and (b) LDA half, (O atoms) involving self-energy correction method having band gap of 4.33 eV with indirect transition along Γ to X symmetry point of Brillouin zone. 143

Figure 5.8 Symmetry points along with the phonons involved in indirect-transitions in the Brillouin zone for $\text{Ho}_2\text{Ti}_2\text{O}_7$ (space group; 227). 144

Figure 5.9 Valence band spectra of $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ obtained from UPS spectra recorded at photon energy of 21.2 eV. (a) ($x = 2, 1.9$ and 1.75). Feature A marks the dominance of O-2p -11.8 eV, B; (Ge-4p at -8 eV), C; (Ho-4f at -4 eV) and D; (Ti-3d at 2 eV) state (b) ($x = 0, 0.1$ and 0.25). Feature A, B and C marks the hybridized s state of O, Ti and Ho at -9, -11 and -13 eV, D; (O-2p at -6 eV) and E and F; (Ho-4f at -4 eV). Positions have been designated according to the order of cross section assigned to these orbitals at $h\nu = 1.2$ eV. 146

Figure 5.10 Core level spectra along with valence state of (a) $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 2, 1.9$ and 1.75) (b) $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0, 0.1$ and 0.25) showing Ho 4f, $5p_{1/2}$, and $5p_{3/2}$; O 2s; Ge 3d and Ti 3p core and valence levels obtained from XPS. 148

Figure 6.1 Luminescence spectra of $\text{Ho}_2\text{Ti}_2\text{O}_7$ single crystal after excitation at 488 nm (top and middle) and 1064 nm (bottom). [51] 155

Figure 6.2 Dependence of composition on room temperature UV-Visible absorption spectra of $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x=2, 1.9, 1.75, 1.5, 1, 0.5, 0.25, 0.1, 0$) sample series. Inset shows the clear intensity variation in the Ho^{3+} absorption states with B site Ge^{4+} and Ti^{4+} substitution. 156

Figure 6.3 Variation in Band gap (eV) with subsequent increase in Ti^{4+} concentration in $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$. 159

Figure 6.4 Dependence of Photoluminescence emission (PLE) spectra of (a) $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x=2, 1.9, 1.75$ and 1.5) (b) $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x=1, 0.5, 0.25, 0.1$ and 0) powdered sample series with increasing Ti^{4+} concentration in $\text{Ho}_2\text{Ge}_2\text{O}_7$ and Ge^{4+} in $\text{Ho}_2\text{Ti}_2\text{O}_7$ respectively upon excitation with 290 nm on Ho^{3+} emission states. 161

Figure 6.5 Variation in Photoluminescence Emission spectra of Ho^{3+} ; $^5\text{F}_5$ to $^5\text{I}_8$ emission in $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 2, 1.9, 1.75, 1.5, 1, 0.5, 0.25, 0.1$ and 0) pyrochlore oxide using excitation wavelength of 450 nm. 163

Figure 6.6 Schematic energy level scheme of Ho^{3+} , Ti^{4+} and Ge^{4+} excited states and involved emission mechanism in $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 2, 1.9, 1.75, 1.5, 1, 0.5, 0.25, 0.1$ and 0) for both excitation wavelengths of 290 nm and 450 nm. 166

LIST OF TABLES

Table 3.1 Lattice parameters and magnetic-interaction parameters for six pyrochlore spin-ices. [60]	86
Table 3.2 Bond length and bond angles of $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0, 0.1, 0.15$ & 0.25) series obtained from Rietveld refinement of HRXRD data.	91
Table 3.3 Value of dipolar interaction and Curie Weiss temperature for $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0, 0.1, 0.15$ & 0.25) sample series obtained from Curie Weiss fitting at 100 and 1000 Oe. The values in bracket represent the error.	93
Table 4.1 Curie-Weiss temperature, magnetic ground state, lattice parameter and anisotropy exhibited in few $\text{A}_2\text{B}_2\text{O}_7$. [59]	110
Table 4.2 Wyckoff positions of space group = P4_12_12 . [89]	111
Table 4.3 Wyckoff positions of $\text{Ho}_2\text{Ge}_2\text{O}_7$ obtained from refinement using space group = P4_12_12 ; Lattice parameters ($a = b$) = $6.80662(5)$ Å, $c = 12.3803(1)$ Å; Obtained values of $\chi^2=3.62$, $R_{\text{wp}}=15.7$, $R_{\text{p}}= 12.7$ and $R_{\text{e}}=8.26$.	112
Table 4.4 Bond length and bond angles as obtained from the 3D structure of $\text{Ho}_2\text{Ge}_2\text{O}_7$ generated from VESTA.	115
Table 4.5 Wyckoff positions of $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ obtained after refinement using space group = P4_12_12 ; Lattice parameters ($a = b$) = $6.8080(1)$ Å, $c = 12.3840(2)$ Å; Obtained values of $\chi^2=15.64$, $R_{\text{wp}}=35.2$, $R_{\text{p}}= 23.9$ and $R_{\text{e}}=8.91$.	117
Table 4.6 Bond length and bond angles of $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ as obtained from using the tools VESTA.	117
Table 4.7 Curie Weiss temperature for $\text{Ho}_2\text{Ge}_2\text{O}_7$ & $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$ obtained from Curie Weiss fitting at 100 and 1000 Oe. The values in bracket represent the error.	121

Table 5.1 The “x” parameters for $A_2Ti_2O_7$ ($A = Sm-Lu$), the variation created a change in the band gap values. [93]	132
Table 5.2 Cubic phase composition along with structural distortion parameters i.e., bond length and bond angle of $Ho_2Ge_xTi_{2-x}O_7$ ($x = 0, 0.1$ and 0.25)	135
Table 5.3 Band gap energies of $Ho_2Ge_xTi_{2-x}O_7$ ($x = 2, 1.9, 1.75, 1.5, 1, 0.5, 0.25, 0.1$ and 0) obtained from theoretical data (DFT calculations).	140
Table 5.4 Transitions involved along the symmetry points of the Brillouin zone in $Ho_2Ge_2O_7$ obtained from the band structure calculation through standard LDA and LDA – 1/2 (Ge and O atoms) method that involves self-energy correction.	142
Table 5.5 Transitions involved along the symmetry points of the Brillouin zone in $Ho_2Ti_2O_7$ obtained from the band structure calculation through standard LDA and LDA – 1/2(O atoms) method that involves self-energy correction.	145
Table 6.1. Band gap energies of $Ho_2Ge_xTi_{2-x}O_7$ ($x = 2, 1.9, 1.75, 1.5, 1, 0.5, 0.25, 0.1$ and 0) obtained from both experimental (through Tauc plot using UV-Visible absorption spectra data) and theoretical data (DFT calculations).	158
Table 6.2 Transitions associated from vibrational states of 5F_5 (D_7, D_6, D_1, D_1) to 5I_8 ($Z_{10}, Z_{11}, Z_8, Z_{11}$) of Ho^{3+} obtained at 652, 659, 663 and 669 nm in PLE (Photoluminescence emission) spectra with excitation wavelength of 450 nm.	165

LIST OF ABBREVIATIONS

AFM	Antiferromagnetic
BE	Binding energy
CB	Conduction band
CTT	Charge transfer transition
CF	Crystal field
DFT	Density functional theory
D_{nn}	Nearest neighbor dipolar interaction
DOS	Density of states
DSIM	Dipolar spin ice model
emu/g	Electron mass unit per gram
eV	Electron volt
FC	Field cooled
FM	Ferromagnetic
GGA	Generalized gradient approximation
GSA	Ground state absorption
H	Magnetic field
HRXRD	High resolution x-ray Diffraction
J_{nn}	Nearest neighbor exchange interaction
K	Kelvin

keV	Kilo electron volt
kOe	Kilo Oersted
LDA	Local density approximation
LMCT	Ligand to metal charge transfer
M	Magnetization
M-H	Magnetization versus magnetic field
M-T	Magnetization versus temperature
MPMS	Magnetic Property Measurement System
M_s	Saturation magnetization
RE	Rare earth
RRKJ	Rappe-Rabe-Kaxiras-Joannopoulos
SQUID	Superconducting Quantum Interference Device
SXRD	Synchrotron x-ray diffraction
UPS	Ultraviolet photoelectron spectroscopy
UV-Vis	Ultraviolet-Visible
VB	Valence band
VESTA	Visualization for electronic structural analysis
XPS	x-ray photoelectron spectroscopy
ZFC	Zero field cooled

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 ($T \sim 2$ K and $T \sim 15$ 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 $\text{Ho}_2\text{Ge}_2\text{O}_7$ is 5.2 eV, and that for $\text{Ho}_2\text{Ti}_2\text{O}_7$ 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 ($\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$). 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 $\text{Ho}_2\text{Ge}_2\text{O}_7$ 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 $\text{Ho}_2\text{Ge}_2\text{O}_7$ to be classified as a classically frustrated spin disordered system. On the other hand, for the conventional cubic pyrochlore $\text{Ho}_2\text{Ti}_2\text{O}_7$, 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 $T \sim 15$ 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 $\text{Ho}_2\text{Ge}_2\text{O}_7$, as well as that of its negative chemical pressure induced derivative $\text{Ho}_2\text{Ti}_{0.1}\text{Ge}_{1.9}\text{O}_7$, indicates the archetypical signature of ice-like spin correlation at $T \sim 2$ K. Effect of negative chemical pressure in $\text{Ho}_2\text{Ge}_2\text{O}_7$ matrix decreases the low temperature short-range ferromagnetic spin correlation at $T \sim 2$ 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 $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ ($x = 0, 0.1, 0.15$ & 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 $T \sim 15$ K is attributed to crystal field-phonon coupling.
3. Distinct shrinkage effect in the matrix of $\text{Ho}_2\text{Ti}_2\text{O}_7$ 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 $\text{Ho}_2\text{Ge}_2\text{O}_7$. 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 $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$ 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 $\text{Ho}_2\text{Ge}_x\text{Ti}_{2-x}\text{O}_7$.

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 $\text{Ho}_2\text{Ge}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ 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 $\text{Ho}_2\text{Ge}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ 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 ($T \sim 2$ 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 $\text{Ho}_2\text{Ti}_2\text{O}_7$. This crystal field-phonon coupling is prominent at $T \sim 15$ K, which is reflected through the shift of single ion spin freezing temperature ($T \sim 15$ K) towards lower temperature with an increase in chemical pressure.

Chapter 4 deals with the structural analysis of $\text{Ho}_2\text{Ge}_2\text{O}_7$ 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 $\text{Ho}_2\text{Ti}_x\text{Ge}_{2-x}\text{O}_7$ indicates the lattice volume expansion, and this effect decreases the dipolar interaction in the $\text{Ho}_2\text{Ge}_2\text{O}_7$ matrix. ac-susceptibility presents two spin relaxation, one at $T \sim 3$ K corresponding to ice-like spin freezing at second at $T \sim 15$ 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 $\text{Ho}_2\text{Ti}_x\text{Ge}_{2-x}\text{O}_7$. Computational approach had been used for the density of state (DOS) and band structure calculation of $\text{Ho}_2\text{Ti}_x\text{Ge}_{2-x}\text{O}_7$. 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 ($\text{Ho}_2\text{Ti}_x\text{Ge}_{2-x}\text{O}_7$) on the electronic states of the subsystems had been discussed in detail.

The thorough understanding of the optical properties of $\text{Ho}_2\text{Ti}_x\text{Ge}_{2-x}\text{O}_7$ 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.