INDEX

CONTENTPAGES	5
Certificate	i
Declaration by the candidate & Certificate by the supervisori	ii
Copyright transfer certificate	v
Acknowledgementsv	ii
Indexi	X
List of figuresxi	ii
List of tablesxxi	ii
List of abbreviationsxx	v
Prefacexxv	ii
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 frustrations1	2
1.3.1 Frustration in two-dimension	3
1.3.2 Frustration in three-dimension	7
1.4 Pyrochlore lattice	8
1.4.1 Magnetic interactions in specific to Pyrochlore Lattice	1
1.5 Spin ice2	2
1.6 Spin relaxation apart from spin-ice in different spin frustrated systems	3
1.6.1 Unconventional long-range ordering	3
1.6.2 XY antiferromagnetic (Long-range ordering via an order by disorder mechanism)	5
1.6.3 Spin Glass	6
1.6.4 Spin liquid/Cooperative paramagnetism (Tb ₂ Ti ₂ O ₇)2	8
1.7 Spin ice: in the context of $Ho_2Ti_2O_7$	9

1.8	Experimental signatures of spin ice: [(Dy/Ho)2Ti2O7]	
1.9 model	Application of chemical pressure in magnetically frustrated systems (dipo	lar spin ice 43
1.10	Previous results in relevance to the application of chemical pressure	
1.11	Holmium pyrogermanate	
1.12	Applications and motivations	53
1.13	Thesis aim	54
Chapter	2 SYNTHESIS AND CHARACTERIZATIONS	
2.1	Introduction	
2.2	Stability-field/Structure-stability Map for the synthesis of A2B2O7 mater	ials 58
2.3	Solid –state synthesis route	60
2.4	Characterization techniques	63
2.4.	1 x-ray diffraction (XRD)	
2.4.2	2 Synchrotron x-ray diffraction (SXRD)	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 Ho ₂ Ti ₂ O	3 ROBUST SPIN ICE FREEZING IN MAGNETICALLY FRUSTRA 7 AND CRYSTAL FIELD-PHONON COUPLING	ATED 85
3.1	Introduction	85
3.2	Structural analysis	
3.2.	1 Rietveld refinement of HRXRD pattern of Ho ₂ Ge _x Ti _{2-x} O ₇	89
3.2.2	2 Role of positive chemical pressure on the structure	
3.3	Magnetic properties	
3.3.	1 Temperature dependent magnetization	
3.3.	2 Field dependent magnetization	
3.3.	3 Temperature dependent ac-susceptibility	
3.4	Low temperature SRXRD measurement for Ho ₂ Ge _{0.1} Ti _{1.9} O ₇	
3.5	Crystal field-phonon coupling	105
3.6	Conclusions	107
School o	f Materials Science and Technology, IIT (BHU), Varanasi	Page x

Chapter	· 4	STRUCTURAL ANALYSIS OF Ho ₂ Ge ₂ O ₇ AND EFFECT OF NEGAT	IVE
CHEMI		2 PRESSURE UPON ITS MAGNETIC PROPERTIES	109
4.1	Intr	roduction	109
4.2	Stru	uctural analysis	111
4.2	.1	Rietveld refinement of obtained HRXRD pattern of Ho ₂ Ge ₂ O ₇	111
4.2	.2	Role of negative chemical pressure on the crystal structure of Ho ₂ Ge ₂ O ₇	116
4.3	Ma	gnetic properties of Ho ₂ Ge ₂ O ₇ and Ho ₂ Ti _{0.1} Ge _{1.9} 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	Cor	nclusions	129
Chapter	5 5	ROLE OF CHEMICAL PRESSURE UPON THE ELECTRONIC	121
SIRUC	IUK	1 - i	131
5.1	Intr	roduction	131
5.2	Stru	uctural analysis of Ho ₂ Ge _x $I_{12-x}O_7$	132
5.3	Ele	ctronic structure calculation through DFT calculations	135
5.3	.1	Density of state (DOS) calculations of Ho ₂ Ge ₂ O ₇	136
5.3	.2	Density of state calculations of Ho ₂ Ti ₂ O ₇	137
5.3.3		Evolution of total DOS for Ho ₂ Ge _x Ti _{2-x} O ₇	138
5.3.4		Band structure of Ho ₂ Ge ₂ O ₇	140
5.3	.5	Band structure of Ho ₂ Ti ₂ O ₇	143
5.4	Ele	ctronic structure analysis of Ho2GexTi2-xO7: experimental characterization	ıs .145
5.4	.1	Ultraviolet photoelectron Spectroscopy	146
5.4	.2	x-ray photoelectron spectroscopy	148
5.5	Cor	nclusions	151
Chapter	· 6	OPTICAL PROPERTIES OF Ho2GexTi2-xO7 SYSTEM	153
6.1	Intr	roduction	153
6.2	Opt	tical studies on Ho ₂ Ti ₂ O ₇ system	154
6.2	.1	Ultraviolet-visible spectroscopy	155
6.2	.2	Photoluminescence spectroscopy	160
6.3	Cor	nclusions	166
Chapter	7	CONCLUSIONS AND FUTURE SCOPE	169
7.1	Coi	nclusions	169
School	of Ma	aterials Science and Technology, IIT (BHU), Varanasi Pa	age xi

E

7.2	Suggestions for future work	
REFER	ENCES	
List of	Publications	

LIST OF FIGURES

Figure 1.1 Dipolar Spin Ice Model (DSIM) which presents the possibility for inducing longrange 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 <111> 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 ~10 K and no sign of long-range order till T ~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 (7.0µ_B) ordered moment while the grey spheres carry only a 1.9 µ_B ordered moment. [42]

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 Tf =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~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]

Figure 1.15 (Top panel) The normalized intermediate scattering function S(q, t)/S(q, 0) as measured through neutron scatteringexperiment, integrated in the range $0.5^{\circ}A^{-1} \le q \le 1.0^{\circ}A^{-1}$ *School of Materials Science and Technology, IIT (BHU), Varanasi* Page | xiv 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 Ho₂Ti₂O₇. (Top) The hightemperature 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 <111> 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 Dy₂Ti₂O₇. [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 $+J_{eff}$ to an 'in–in' or 'out–out' pair and $-J_{eff}$ to an 'in-out' pair yields energies E (2:2) = $-2J_{eff}$, E (3:1) = 0 and E (4:4) = $+6J_{eff}$. [54] 35

Figure 1.20 Neutron scattering data for $Ho_2Ti_2O_7$. (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]

Figure 1.21 χ -1 vs. T plot for Ho₂Ti₂O₇ providing the value of $\theta_{CW} = +1.9 \pm 0.1$ 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 <111> axis of the tetrahedron. (b) Strong axial symmetry of the magnetic site has along a local <111> 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 Ho₂Ti₂O₇. (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 $Ho_2Ti_2O_7$ 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]

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 $Dy_2Ge_2O_7$ (black lines) and $Dy_2Ge_{1.875}Si_{0.125}O_7$ (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 Dy₂Ge₂O₇ and Dy₂Ge_{1.875}Si_{0.125}O₇ samples. (b) Temperature dependence of the molar entropy of Dy₂Ge₂O₇ and Dy₂Ge_{1.875}Si_{0.125}O₇ 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 Dy_{2-x}Yb_xTi₂O₇ measured at H = 10kOe. [61] 48

Figure 1.29 Crystal structure of Ho₂Ge₂O₇ (a) the rare earth Ho sublattice showing the righthanded 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 $Ho_2Ge_2O_7$ when magnetic field is applied parallel to ab axis; (b)-(e) v = 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 Ho₂Ge₂O₇ (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 Ho₂Ge₂O₇ 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 $Ho_2Ge_xTi_{2-x}O_7$, positive and negative chemical pressure has been applied through the substitution of Ge^{4+} in $Ho_2Ti_2O_7$ and Ti^{4+} in $Ho_2Ge_2O_7$ respectively. 58

Figure 2.2 Possibility of the all the elements that could produce $A_2^{3+}B_2^{4+}O_7^{2-}$ cubic pyrochlore phase. [18] 59

Figure 2.3 Stability field map for the synthesis of A₂B₂O₇ 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 $Ho_2Ge_xTi_{2-x}O_7$ (x = 2, 1.9, 1.75, 1.5 &1). 62

Figure 2.6 Room temperature high resolution x-ray diffraction pattern (HRXRD) pattern for $Ho_2Ge_xTi_{2-x}O_7$ (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.

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_{peak}/D_{nn} on J_{nn}/D_{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.

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.

Figure 3.4 Room temperature high resolution X-ray diffraction (HRXRD) pattern of $Ho_2Ge_xTi_{2-x}O_7$ 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.

Figure 3.7 Magnetic field dependence of magnetization of $Ho_2Ge_xTi_{2-x}O_7$ (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 $Ho_2Ge_xTi_{2-x}O_7$ 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.

Figure 3.9 Variation of ac susceptibility with temperature for $Ho_2Ge_xTi_{2-x}O_7$ (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 $Ho_2Ge_xTi_{2-x}O_7$ 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 (Ts) with composition in Ho₂Ge_xTi_{2-x}O₇ (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 Ho₂Ge_xTi_{2-x}O₇ (x = 0, 0.1, 0.15 and 0.25) system. 101

Figure 3.14 Low temperature synchrotron x-ray diffraction pattern of $Ho_2Ge_xTi_{2-x}O_7$ (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 $Ho_2Ge_xTi_{2-x}O_7$ (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 SrRuO₃. 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 $Ho_2Ge_2O_7$ along with the fitted [P4₁2₁2(tetragonal) space group] and the difference between the observed and calculated fit. 112

Figure 4.2 3D-structure of Ho₂Ge₂O₇ depicting $[Ge_2O_7]^{6-}$ 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) °. 113

Figure 4.3 Crystal structure of $Ho_2Ge_2O_7$ showing (a) infinite helical chain of magnetic rareearth 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 GeO₄ tetrahedra. 114

Figure 4.4 Position of magnetic ion within a helix of a unit cell of $Ho_2Ge_2O_7$. It shows four Ho^{3+} ions arranged in a pattern of common edge-sharing two triangles further corner joined with the next Ho₄ 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 $Ho_2Ti_{0.1}Ge_{1.9}O_7$ using the P4₁2₁2 space group. 116

Figure 4.6 Room temperature high-resolution x-ray diffraction pattern for (a) $Ho_2Ge_2O_7$ and (b) $Ho_2Ti_{0.1}Ge_{1.9}O_7$ 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 Ho₂Ge₂O₇ and Ho₂Ti_{0.1}Ge_{1.9}O₇ 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 $Ho_2Ge_2O_7$ and $Ho_2Ti_{0.1}Ge_{1.9}O_7$ 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 $Ho_2Ge_2O_7$ 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) $Ho_2Ge_2O_7$ and (b) $Ho_2Ti_{0.1}Ge_{1.9}O_7$ 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) Ho₂Ge₂O₇ and (b) Ho₂Ti_{0.1}Ge_{1.9}O₇. 127

Figure 4.12 The ac-susceptibility plot of Ho₂Ge₂O₇ and Ho₂Ti_{0.1}Ge_{1.9}O₇at 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 $Ho_2Ge_2O_7$ (a) Partial DOSs of Ho (6s, 5pand 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 $Ho_2Ti_2O_7$ (a) Partial DOSs of Ho (6s, 5pand 5d); Ti (4s, 4p and 3d) and O (2s, 2p and 3d) states along with total DOS obtained from standard

School of Materials Science and Technology, IIT (BHU), Varanasi

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

Figure 5.4 Total DOS of (a) $Ho_2Ge_2O_7$ along with B site Ti^{4+} substitution for x=1.75 ($Ho_2Ge_{1.75}Ti_{0.25}O_7$) (b) $Ho_2Ge_xTi_{2-x}O_7$ (x = 2, 1.75, 1.25, 1.5 and 1) and (c) $Ho_2Ge_xTi_{2-x}O_7$ (x = 0, 0.25, 0.5 and 0.75).

Figure 5.5 Band structure of Ho₂Ge₂O₇ 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 Ho₂Ge₂O₇ (space group; 92). 142

Figure 5.7 Band structure of $Ho_2Ti_2O_7$ 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 Ho₂Ti₂O₇ (space group; 227). 144

Figure 5.9 Valence band spectra of $Ho_2Ge_xTi_{2-x}O_7$ 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 hv = 1.2 eV. 146

Figure 5.10 Core level spectra along with valence state of (a) $Ho_2Ge_xTi_{2-x}O_7$ (x = 2, 1.9 and 1.75) (b) $Ho_2Ge_xTi_{2-x}O_7$ (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 $Ho_2Ti_2O_7$ 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 $Ho_2Ge_xTi_{2-x}O_7$ (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 $Ho_2Ge_xTi_{2-x}O_7$. 159

Figure 6.4 Dependence of Photoluminescence emission (PLE) spectra of (a) $Ho_2Ge_xTi_{2-x}O_7$ (x=2, 1.9, 1.75 and 1.5) (b) $Ho_2Ge_xTi_{2-x}O_7$ (x=1, 0.5, 0.25, 0.1 and 0) powdered sample series with increasing Ti⁴⁺ concentration in $Ho_2Ge_2O_7$ and Ge^{4+} in $Ho_2Ti_2O_7$ respectively upon excitation with 290 nm on Ho^{3+} emission states. 161

Figure 6.5 Variation in Photoluminescence Emission spectra of Ho³⁺; ${}^{5}F_{5}$ to ${}^{5}I_{8}$ emission in Ho₂Ge_xTi_{2-x}O₇ (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 $Ho_2Ge_xTi_{2-x}O_7$ (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 $Ho_2Ge_xTi_{2-x}O_7$ (x = 0, 0.1, 0.15 & 0.25) seriesobtained from Rietveld refinement of HRXRD data.91

Table 3.3 Value of dipolar interaction and Curie Weiss temperature for $Ho_2Ge_xTi_{2-x}O_7$ (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 anisotropyexhibited in few A2B2O7. [59]110

Table 4.2 Wyckoff positions of space group = $P4_12_12$. [89] 111

Table 4.3 Wyckoff positions of Ho₂Ge₂O₇ obtained from refinement using space group = P4₁2₁2; Lattice parameters (a = b) = 6.80662(5) Å, c = 12.3803(1) Å; Obtained values of χ^2 =3.62, R_{wp}=15.7, R_p= 12.7 and R_e=8.26. 112

Table 4.4 Bond length and bond angles as obtained from the 3D structure of Ho2Ge2O7generated from VESTA.115

Table 4.5 Wyckoff positions of Ho₂Ti_{0.1}Ge_{1.9}O₇ obtained after refinement using space group = P4₁2₁2; Lattice parameters (a = b) = 6.8080(1) Å, c = 12.3840(2) Å; Obtained values of χ^2 =15.64, R_{wp}=35.2, R_p= 23.9 and R_e=8.91. 117

Table 4.6 Bond length and bond angles of $Ho_2Ti_{0.1}Ge_{1.9}O_7$ as obtained from using the tools VESTA. 117

Table 4.7 Curie Weiss temperature for Ho2Ge2O7 & Ho2Ti0.1Ge1.9O7 obtained from CurieWeiss fitting at 100 and 1000 Oe. The values in bracket represent the error.121

School of Materials Science and Technology, IIT (BHU), Varanasi

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., bondlength 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 ${}^{5}F_{5}$ (D₇, D₆, D₁, D₁) to ${}^{5}I_{8}$ (Z₁₀, Z₁₁, Z₈, Z₁₁) of Ho³⁺ obtained at 652, 659, 663 and 669 nm in PLE (Photoluminescence emission) spectra with excitation wavelength of 450 nm. 165