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It is certified that the work contained in the thesis entitled *"DISCOVERY OF NEW LOW TEMPERATURE PHASE TRANSITIONS IN BARIUM HEXAFERRITE"* by *"KESHAV KUMAR"* 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, Candidacy and SOTA for the award of Ph.D. degree.

Date: 19.01.2021

Place: Varanasi

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DECLARATION BY THE CANDIDATE

I, *KESHAV KUMAR*, certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the supervision of **PROF. DHANANJAI PANDEY** for a period from **JULY 2014** to **DECEMBER 2020** at the **SCHOOL OF MATERIALS SCIENCE AND TECHNOLOGY**, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this Ph.D. 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 will fully copied any other's 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.
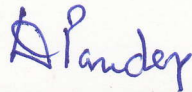
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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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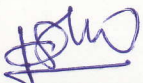
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Date: 19.01.2021   (Keshav Kumar)

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List of Abbreviations

Antiferroelectric	AFE
Antiferromagnetic	AFM
$BaFe_{12}O_{19}$	BFO
$Ba_2Mg_2Fe_{12}O_{22}$	BMFO
Classical Phase Transitions	CPT
Energy Dispersive X-ray spectroscopy	EDX
Ferroelectric	FE
Ferromagnetic	FM
Grazing Incidence	GI
Irreducible Representations	Irreps
Isothermal Remanent Magnetization	IRM
Kohlrausch-Williams-Watt	KWW
Long-Range Ordered	LRO
Left Circularly Polarised	LCP
Magnetic Properties Measurement System	MPMS
Normal Incidence	NI
Neutron Powder Diffraction	NPD
Octahedral	OH
Physical Properties Measurement System	PPMS
Permanent Magnets	PM_s
Right Circularly Polarised	RCP
Superparamagnetic	SPM
Scanning Electron Microscope	SEM

Synchrotron X-ray Diffraction	SXRD
Superconducting Quantum Interference Device	SQUID
Small- Angle Neutron Scattering	SANS
$SrCr_8Ga_4O_{19}$	SCGO
$SrCr_{9p}Ga_{12-9p}O_{19}$	SCGO-p
Spin-Glass	SG
Trigonal Bipyramid	TBP
Thermoremanent Magnetization	TRM
Tetrahedral	TH
Total Electron Yield	TEY
Quantum Phase Transitions	QPT
Quantum Critical Point	QCP
Quantum Electric Dipole Liquid State	QEDL
Quantum Paraelectricity	QPE
X-ray Powder Diffraction	XRD
X-ray Absorption Spectra	XAS
X-ray magnetic Circular Dichroism	XMCD
X-ray Magnetic Linear Dichroism	XMLD

List of Symbols

Absorption Cross-Section	μ
Angstrom	$\mathring{A}$
Anisotropy parameter	A
AC Susceptibility	$\chi(\omega, T)$
Activation Energy	E_a
Almeida-Thouless	A-T
Bohr Magneton	μ_B
Bifurcation/Irreversibility	T_{irr}
Bulk Modulus	B
Dzyaloshinskii-Moriya	D-M
Curie Constant	C
Curie Temperature	T_c
Curie-Wiess Temperature	Θ_{CW}
Characteristic Relaxation Time	τ_0
Critical Exponent.	$z\nu$
Critical Composition	x_c
Coercive Field	H_c
Dielectric Permittivity	ε'
Debye Temperature	θ_D
Electric Dipoles Density	C'
Exchange Interactions	J
Excitation Energy Gap	Δ
Electron Volt	eV

Full-Width at Half-Maxima	FWHM
Frequency	f
Field Cooled	FC
Gabay-Toulouse	G-T
Grüneisen Parameter	γ
Intensity of Incident Electromagnetic Radiation	I_0
Intensity of the Beam After Passing Through the Sample	I_t
Kelvin	K
Longitudinal Component	//c
Transverse Component	$\perp c$
Neel Temperature	T_N
Paramagnetic	P
Propagation Vector	**k**
Phase Shift	ϕ
Magnetic Dipole Operator	m_T^θ
Magnetic Field	H
Magnetization	M
Number of $3dFe^{3+}$ holes	n_h
Remanent Magnetization	M_r
Stretched exponential function exponent	β
Specific Heat	C_P
Spin-Glass Transition Temperature	T_{SG}
Spin-Glass Freezing Temperature	T_f
Saturation Magnetization	M_s

Susceptibility	χ
Spontaneous Electric Polarization	P_s
Thermal Parameters	B
Thickness	t
Unit Cell Volume	V
Vogel-Fulcher Freezing Temperature	T_{VF}
Wavelength	λ
Wait Time	t_w
Wait Temperature	T_w
XAS Spectra Measured using the RCP X-ray Beam	σ_+
XAS Spectra Measured using the LCP X-ray Beam	σ_-
XMCD Signal	$\Delta\sigma = (\sigma_+ - \sigma_-)$
Zero-Field Cooled	ZFC

xxx

Preface

The study of phase transitions in frustrated magnetic systems has been a frontline area of research in solid-state and material sciences. The most commonly investigated source of frustration is frozen-in substitutional disorder leading to a competition between ferromagnetic (FM) and antiferromagnetic (AFM) interactions. Such a competition and randomness in certain situations can prevent the emergence of long-range ordered (LRO) phases and instead give rise to a unique spin-glass state in which the spins are randomly frozen below a frequency (ω) and field (H) dependent peak, usually called as spin-glass freezing temperature (T_f), in the temperature dependence of magnetic susceptibility as a result of ergodic symmetry breaking. Frustration may also arise due to nearest neighbour AFM interactions alone due to the geometry of the lattice for spins arranged on the edge shared triangular (e.g. $YbZnGaO_4$), corner shared triangular or kagome (e.g. $(H_3O)Fe_3(SO_4)_2(OH)_6$ and $SrGa_{12-x}Cr_xO_{19}$), pyrochlore (e.g. $Tb_2Mo_2O_7$), and spinels (e.g. MAl_2O_4 with M = Co, Fe, & Mn) lattices. Such geometrically frustrated systems have evinced enormous attention in recent years as many of them exhibit exotic spin liquid, spin ice and spin-glass transitions even in the absence of any apparent site-disorder. Recent theoretical calculations seem to suggest that in the absence of any site-disorder, and hence randomness, the ground state of the geometrically frustrated systems has macroscopic degeneracy with no phase transition down to the absolute zero temperature. Such systems, however, have the possibility of the degeneracy getting lifted by quantum or thermal fluctuations through an intriguing mechanism known as "order by disorder" even in the absence of site disorder. More recent theoretical studies have shown that even an infinitesimal random disorder in the few body exchange interactions caused by anisotropic exchange interactions due to nearest neighbour bond length variations and/or magnetoelastic strains or dipole-dipole interactions between uncompensated spin or spin

clusters with intra-cluster geometrical frustration, can lift the degeneracy of the ground state and induce exotic phase transitions to spin liquid, spin glass and other complex ordered phases.

Frustration resulting from the geometry of the lattice considered so far in the literature is pre-existing in the paramagnetic high-temperature phase due to its crystal structure. In contrast to the pre-existing geometrical frustration, this thesis presents evidence for emergent geometrical frustration in the LRO phase of an M-type hexaferrite, namely $BaFe_{12}O_{19}$ of immense commercial value worth about 4 billion dollars, at temperatures several hundred Kelvin below the ferrimagnetic transition temperature $T_c \simeq$ 714 K. Further, the genesis of the emergent geometrical frustration as well as its consequences on the low-temperature behaviour of LRO ferrimagnetic phase of $BaFe_{12}O_{19}$ have been investigated in this thesis. A wide-ranging experimental techniques, involving X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) studies, X-ray and neutron powder diffraction studies, single-crystal neutron scattering studies, bulk magnetic susceptibility studies using both dc and ac fields on single crystals and powder samples, dielectric studies as a function of frequency and chemical pressure and specific heat studies on polycrystalline samples, have been employed in these investigations using in-house facilities as well as advanced synchrotron facility at Petra-III, DESY, Hamburg, FRM-II, Garching Germany and ISIS at Rutherford Appleton Laboratory, Harwell Oxford Didcot, UK, all as a function of temperature for T < 300 K.

These studies have unravelled the complexity of the low-temperature phase transition behaviour of $BaFe_{12}O_{19}$ and its ground state. The most significant finding of the present work includes the discovery of as many as five spin-glass transitions involving either the longitudinal or the transverse components of the spins or the precession

dynamics of the longitudinal conical magnetic structure in an ordered compound without any substitutional (site-) disorder and a quantum electric dipole glass state induced by a non-thermal variable. Presently, there no single theory that predicts a succession of five spin-glass transitions in a long-range ordered system with or without any substitutional site disorder. The present findings are expected to stimulate further theoretical and experimental studies in search of emergent geometrical frustration and its consequences in other hexaferrites as well as geometrically frustrated magnetic materials.

The present thesis comprises ten chapters, as outlined below briefly:

Chapter 01 gives a brief introduction and a short review of the relevant literature on hexaferrites.

Chapter 02 gives the details of $BaFe_{12}O_{19}$ powder synthesis, sintering of these powders and crystal growth along with their characterization for phase purity and compositional stoichiometry.

Chapter 03 presents evidence for the non-collinear magnetic structure of $BaFe_{12}O_{19}$ in its ground state using XAS and XMCD studies at 1.2 K and discovery of incommensurate longitudinal conical modulation of the magnetic structure in single-crystal neutron diffraction studies in the ground state of $BaFe_{12}O_{19}$.

Chapter 04 presents evidence for large magnetic anisotropy using dc magnetization studies in the 2 to 950 K temperature range with a peak around 45 K, canting of $3dFe^{3+}$ spins with respect to the c-axis using temperature and incident angle dependent XAS and XMCD studies at the Fe $L_{2,3}$-edges, splitting of the Fe-3d orbitals into e_g and t_{2g} bands due to crystal field effects and their further splitting due to exchange-correlations using XAS studies at the O K-edge and significant change in the exchange splitting around 15 K accompanied with change in the XMCD profile shapes and an upturn in dc magnetization perpendicular to the c-axis.

Chapter 05 presents evidence for four successive spin-glass transitions in $BaFe_{12}O_{19}$ single crystals whose spin dynamics diverges at $T_{SG} \sim 46$ K, ~ 25 K, ~ 15 K and ~ 4 K as per the Vogel-Fulcher and power-law fits for the spin relaxation time, anomalies in the temperature dependence of the specific heat in the C_P/T^3 versus T and C_P/T versus T^2 plots, diminution in the integrated intensities of the *006* and *101* reflections in single-crystal neutron diffraction studies around the spin-glass freezing temperatures and confirmation of the co-existence of the spin-glass phases with the long-range ordered ferrimagnetic phase of $BaFe_{12}O_{19}$.

Chapter 06 investigates in detail various characteristics of the first set of longitudinal and transverse spin-glass phase transitions occurring at higher temperatures, using ac susceptibility studies on polycrystalline samples as a function of temperature, frequency, time, aging and magnetic field. These studies confirm ergodicity breaking at the two critical spin-glass transition temperatures, presence of Gabay-Toulouse (G-T) and Almeida-Thouless (A-T) lines in the T-H plane, non-exponential relaxation of isothermal magnetization and memory and rejuvenation effects below T_{SG}. These results are, surprisingly, in excellent agreement with the theoretically predicted T-H phase diagram for the disordered Heisenberg systems with negative single-ion anisotropy.

Chapter 07 reports the discovery of another spin-glass transition in $BaFe_{12}O_{19}$ as revealed by the divergence of the spin relaxation time at $T_{SG} \sim 173$ K, field (H) dependent shift of the spin-glass freezing temperature $T_f(H)$ along the Gabay-Toulouse line, history-dependent irreversibility of M(T), observation of non-exponential relaxation of the isothermal remanent magnetization as well as memory effects. Using high-resolution single-crystal neutron scattering studies, this chapter also presents evidence for longitudinal incommensurate conical modulation of the magnetic structure of $BaFe_{12}O_{19}$ at all temperatures upto 300 K, except a narrow temperature range ~ 15 K to ~ 35 K,

where the modulation is commensurate. These studies reveal significant change in the integrated intensity of the satellite peaks and modulation wave vector across the spin-glass transition suggesting that this transition may be linked with the precession dynamics of the $3dFe^{3+}$ spins in the longitudinal conical magnetic structure of $BaFe_{12}O_{19}$.

Chapter 08 presents arguments for the deviation from the collinear Gorter model, as confirmed in chapters 3 to 7, due to canting of the spins at the 12k Wyckoff sites of $BaFe_{12}O_{19}$ unit cell, leaving the spins at the other sites aligned parallel or antiparallel to the c-axis as in the Gorter model. These arguments are used for the Rietveld analysis of the temperature-dependent neutron diffraction (NPD) patterns which reveal the emergence of fully frustrated kagome spin configuration as well as another kagome spin configuration with two-fold degeneracy as a function of temperature. Using temperature-dependent powder XRD studies, evidence for the presence of significant anisotropic magnetoelastic strains below 175 K with magneto-volume effect in different temperature ranges is also presented in this chapter. These magnetoelastic strains may provide the desired randomness to the few body exchange interactions in $BaFe_{12}O_{19}$ required in the existing theories of spin-glass transition in geometrically frustrated ordered compounds.

Chapter 09 presents the results of dielectric studies as a function of temperature and frequency from 1.66 K onwards to investigate the quantum critical behaviour of $BaFe_{12}O_{19}$ involving electric dipoles. This chapter provides confirmation of quantum electric dipole liquid (QEDL) like state using dielectric and specific heat studies and reports the discovery of a new quantum electric dipole glass transition induced by a non-thermal variable which is chemical pressure in the present case.

Chapter 10 summarizes the main finding of this thesis and list a few suggestions for future work.