## **Table of Contents**

Acknowled	gements	•••••	i
Table of Co	ontents	•••••	. iii
List of Figu	ıres	•••••	.vii
List of Tab	les	X	xiii
List of Abb	previations	•••••	XXV
List of Sym	ıbols	X	xvii
Preface		X	xxi
Chapter 1	Introduction and Literature Review	•••••	1
1.1	Introduction		1
1.2	Ferroics		1
1.3	Ferromagnetism		2
1.4	Antiferromagnetism and Ferrimagnetism		3
1.5	Ferroelectricity		5
1.6	Antiferroelectricity and Ferrielectricity		6
1.7	Quantum Paraelectrics		7
1.8	Spin-Glasses, Dipole glasses and Relaxors		9
1.9	Multiferroics		.14
1.10	The Hexaferrites		.15
1.10.1	Crystal Structure		.15
1.10.2	Multiferroicity in Hexaferrites		19
1.10.3	Technological Applications of Hexaferrites	•••••	23
1.11	Recent Advances in M-type Hexaferrites	•••••	24
1.12	Objectives of the Present Work		33
Chapter 2 BaFe <sub>12</sub> O <sub>19</sub>	Synthesis of Polycrystalline and Single-Crystal G	rowth	of .35
2.1	Introduction		35
2.2	Experimental		36
2.3	Synthesis of BaFe <sub>12</sub> O <sub>19</sub> Polycrystalline Samples		36
2.3.1	Optimization of Calcination Temperature		37

2.3.2	Optimization of Sintering Temperature	38
2.4	Details of Crystal Growth of BaFe <sub>12</sub> O <sub>19</sub>	39
2.4.1	Crystallinity and Phase Purity of Single Crystals	39
2.4.2	Chemical Composition of Single Crystals	41
2.4.3	Iodometry Titration	42
2.5	Room Temperature Crystal Structure of BaFe <sub>12</sub> O <sub>19</sub>	43
2.6	Conclusions	47
Chapter 3	Magnetic Ground State of BaFe <sub>12</sub> O <sub>19</sub> : Evidence for Noncollinea	ır
Magnetic S	tructure and Incommensurate Conical Modulation	49
3.1	Introduction	49
3.2	Current Understanding of the XAS Spectra at the Fe L <sub>2,3</sub> -edges	51
3.3	Current Understanding of X-ray Magnetic Circular Dichroism (XMCD) at	
the Fe L <sub>2</sub>	,3-edges	54
3.4	Experimental	59
3.5	Results and Discussion	60
3.5.1	XAS and XMCD Study at the Fe $L_{2,3}$ -edges at 1.2 K	60
3.5.2	Neutron Diffraction Study at 1.5 K	68
3.6	Conclusions	71
Chapter 4	Evidence for Spin Canting in BaFe <sub>12</sub> FO <sub>19</sub> at T > 1.5 K	73
4.1	Introduction	73
4.2	Experimental	74
4.3	Results and Discussion	75
4.3.1	DC Magnetization Studies	75
4.3.2	XAS and XMCD Studies at the Fe L <sub>2,3</sub> -edges from 1.2 to 30 K	79
4.3.3	Variation of the Magnetic Moment obtained from XMCD and dc	
Magne	tization Measurements with Temperature	84
4.3.4	XAS Studies at the Oxygen (O) K-edge	88
4.3.4	4.1 XAS Study at Oxygen K-edge at 1.2 K	88
4.3.4	4.2 XAS Spectra at the Oxygen K-edge as a Function of Temperature	91
4.4	Conclusions	94
4.4 Chapter 5	Conclusions Evidence for Four Spin-Glass Transitions in BaFe12O19 due 1	94 to
4.4 Chapter 5 Successive	Conclusions Evidence for Four Spin-Glass Transitions in BaFe12O19 due t Freezing of Transverse and Longitudinal Spin Components	94 to 101
4.4 Chapter 5 Successive 5.1	Conclusions Evidence for Four Spin-Glass Transitions in BaFe12O19 due t Freezing of Transverse and Longitudinal Spin Components Introduction	94 to 101 101

5.3	Magnetic Susceptibility Studies
5.3.1	Evidence for the Freezing of the Transverse Component of the Spins104
5.3.2	Evidence for the Freezing of the Longitudinal Component of the Spins114
5.3.3	Signatures of the Spin-Glass Transitions in the Single-Crystal Neutron
Diffrao	ction Studies
5.3.4	The Outlook
5.4	Conclusions
Chapter 6 Transverse	Characteristics of the Spin-Glass Transitions Associated with e and Longitudinal Freezing Using Polycrystalline Samples133
6.1	Introduction
6.2	Experimental
6.3	AC susceptibility $\chi(\omega, T, H, t)$ Studies on BaFe <sub>12</sub> O <sub>19</sub> 136
6.3.1	Comparison of $\chi(\omega, T)$ of Polycrystalline and Single-Crystalline Samples136
6.3.2 Powde	Confirmation of Ergodicity Breaking for the two Transitions in BaFe <sub>12</sub> O <sub>19</sub> or
6.3.3	Evidence for the Gabay-Toulouse (G-T) and Almeida-Thouless (A-T) lines143
6.3.4 Magne	Evidence for the None-Exponential Relaxation: Isothermal Remanent etization (IRM)
6.3.5	Study of Aging, Rejuvenation and Memory Effect in BaFe <sub>12</sub> O <sub>19</sub> 148
6.4	Conclusions
Chapter 7 Evidence f	Role of Incommensurate Longitudinal Conical Modulation and or Another Spin-Glass Transition in BaFe12O19153
7.1	Introduction
7.2	Experimental
7.3	Results and Discussion
7.3.1 Magne	Evidence for a High-Temperature Diffuse Magnetic Transition: tization and Specific Heat Studies156
7.3.2 Diffrae	Signature of the Diffuse Magnetic Transition in Single-Crystal Neutron ction Patterns
7.3.3	Confirmation of the Spin Glass Character of the Diffuse Magnetic Transition 165
7.4	Conclusions
Chapter 8	Emergent Kagome Spin Configurations in the Basal Plane of
BaFe <sub>12</sub> O <sub>19</sub>	as a Function of Temperature175
8.1	Introduction
8.2	Experimental

8.3	Previous Predictions for Spin Canting in BaFe <sub>12</sub> O <sub>19</sub> 17	77
8.4	Neutron Powder Diffraction Studies	78
8.4.1	The Irreducible representation for $Fe^{3+}$ in $BaFe_{12}O_{19}$	30
8.4.2 Repres	Isotropy Subgroups for the Combination of Different Irreducible sentations	33
8.4.3	Details of the Rietveld Refinement	34
8.4.3	3.1 Results of Rietveld refinements	35
8.4.4	Evidence for Geometrical Frustration in the Magnetic Structure of $BaFe_{12}O_{19}18$	37
8.5	Genesis of Randomness in BaFe <sub>12</sub> O <sub>19</sub> 19	<del>)</del> 2
8.5.1	Evidence for magnetoelastic strain in BaFe <sub>12</sub> O <sub>19</sub> 19	<del>)</del> 3
8.5.2	Role of the Exchange Anisotropy	<del>)</del> 9
8.5.3	The Origin of the Incommensurate Conical Spin-Glass Phase	)0
8.6	Conclusions	)2
Chapter 9	Quantum Phase Transition in Ba(1-x)CaxFe12O1920	)5
9.1	Introduction	)5
9.2	Experimental	)7
9.3	Results and Discussion	)9
9.3.1	Evidence for chemical pressure generated by $Ca^{2+}$ substitution	)9
9.3.2	Effect of Ca <sup>2+</sup> Substitution on Quantum Critical Behaviour of BFO21	14
9.3.3	Evidence for Quantum Electric Dipole Glass State in Ca <sup>2+</sup> Substituted BFO21	18
9.3.4	Evidence for Quantum Electric Dipole Liquid (QEDL) Phase	21
9.4	Conclusions	27
Chapter 10	Summary and Suggestions for Future Work	29
10.1	Summary	29
10.2	Suggestions for Future work	32
References		35
List of Pub	lications	93

## **List of Figures**

Figure 1.1: Variation of magnetization and susceptibility below and above Curie
temperature (T <sub>c</sub> ) [38]
Figure 1.2: A few examples of Ising antiferromagnets [41]4
Figure 1.3: Variation of susceptibility and inverse susceptibility of an antiferromagnetic
materials [38]. AF: antiferromagnetic and P: paramagnetic5
Figure 1.4: Typical hysteresis loop for an antiferromagnetic material [46]7
Figure 1.5: Variation of dielectric constant with temperature for a quantum
paraelectric [49]
Figure 1.6: Schematic representation of magnetic spin in triangular lattice by considering
(a) ferromagnetic and (b) antiferromagnetic nearest neighbour interactions [62]9
Figure 1.7: Static (dc) susceptibility (M/H) vs temperature (T) plots of CuMn system
with different magnetic impurity concentration (Mn) [61]10
Figure 1.8: The temperature dependence of real part of ac-susceptibility of CuMn alloy
system. Inset shows frequency dispersion across the freezing temperature. Peak position
shifts to higher temperature side with increasing frequency [61]11
Figure 1.9: Schematic representation of the temperature variations of the odd harmonics
$(\chi_1, \chi_3 \text{ and } \chi_5)$ in ac susceptibility [63]12
Figure 1.10: Thermoremanent magnetization (TRM) plot of Ca(Fe <sub>1/2</sub> Nb <sub>1/2</sub> )O <sub>3</sub> recorded at
15 K for 1000 Oe applied magnetic field using wait time of 1000 s [75]
Figure 1.11: Ternary phase diagram for the hexaferrites16
Figure 1.12: The arrangement of the different layers of $O^{2-}$ and $Ba^{2+}$ ion within the unit
cell of BaFe <sub>12</sub> O <sub>19</sub> M-type hexaferrite [98]17
Figure 1.13: Unit cell of BaFe <sub>12</sub> O <sub>19</sub> [98]18
Figure 1.14: S, R and T blocks [12]19

Figure 1.15: Schematic proposed magnetic structures of magnetoelectric Y-type
hexaferrites. (a) collinearly ferrimagnetic [91], (b) the proper-screw [91] and (c)
longitudinal-conical [101] magnetic structure. The short and long arrows indicate the
effective moment in S and L blocks, respectively [91,101]
Figure 1.16: Schematic (a) proposed transverse-conical [101] magnetic structures of Y-
type hexaferrites and (b) cycloid type magnetic structure [91]
Figure 1.17: Practical applications of hexagonal ferrites [12]24
Figure 1.18: Trigonal bipyramid polyhedra25
Figure 1.19: Temperature dependence of reciprocal susceptibility of BaFe <sub>12</sub> O <sub>19</sub> single-
crystal measured with dc field of 1000 Oe applied parallel (H // c) and perpendicular (H //
ab) to the c-axis [137]28
Figure 1.20: (a) Variation of the magnetic viscosity $S$ with temperature. Inset shows the
behaviour of S on the zoomed scale [28]. (b) The c-axis dielectric permittivity $\varepsilon_c$ as a
function of temperature for $BaFe_{12}O_{19}$ . Inset of (b) shows the same plot with a
logarithmic scale in temperature [14]
Figure 1.21: The $kT^{-1}$ versus $T^2$ plot in the lowest temperature region in the presence of 0
T and 14 T applied along c-axis. The inset shows the Arrhenius plot of $k^* = k - \beta T^3$ below
~125 mK [7]
Figure 2.1: XRD profiles of BaFe <sub>12</sub> O <sub>19</sub> calcined at 1273 K and 1373 K. The position of
impurity peak due to $Fe_2O_3$ is marked with (*)
Figure 2.2: XRD profile for BaFe <sub>12</sub> O <sub>19</sub> , sintered at different temperatures. The position of
the impurity peak of $Fe_2O_3$ is marked with arrow
Figure 2.3: (a) Image of the as-grown crystal and (b) Laue diffraction recorded on the
single-crystal of BaFe <sub>12</sub> O <sub>19</sub>

Figure 2.4: Comparison of XRD pattern on powder obtained after crushing the singlecrystals and sintered samples of BaFe<sub>12</sub>O<sub>19</sub>. The arow shows the position of the most Figure 2.5: Comparison of neutron powder diffraction (NPD) pattern collected on sintered samples with XRD pattern collected on powder obtained after crushing the single-crystals and sintered samples of BaFe<sub>12</sub>O<sub>19</sub>, at room temperature. The Q = 2.32 Å<sup>-1</sup> marked with arrow is the position of most intense nuclear peak of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> at 300 K. .....41 Figure 2.7: Observed (filled red circles), calculated (continuous black line), and difference (bottom green line) profiles obtained from Rietveld refinement using P6<sub>3</sub>/mmc space group for (a) powder and (b) single-crystal samples of  $BaFe_{12}O_{19}$ . The vertical bars Figure 3.1: Schematic representation of (a) collinear magnetic structure of  $BaFe_{12}O_{19}$ , (b) coordination polyhedra for Fe<sup>3+</sup> ions in BaFe<sub>12</sub>O<sub>19</sub> and (c) longitudinal conical magnetic structure due to precession of the net moment in the R and R' blocks about the c-axis for Figure 3.2: XAS spectra of (a)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, GaFeO<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> [200,201], (b) LaFeO<sub>3</sub> [201], (c) Ba<sub>0.5</sub>Sr<sub>1.5</sub>Zn<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> [6] and (d) SrFe<sub>12</sub>O<sub>19</sub> [202] at the Fe L<sub>2.3</sub>-edges. 53 Figure 3.3: Atomic multiplet calculation based simulation of XAS spectra at the L<sub>2,3</sub>edges of Fe at different Wyckoff position in SrFe<sub>12</sub>O<sub>19</sub> [202] with octahedral (OH), Figure 3.4 The Stoner model for the splitting of 3d valence band of transition metal in ferro/ferrimagnetic materials [205].....55

Figure 3.5: XMCD signal at the Fe L-<sub>3,2</sub>-edges measured in the (a)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> [206], (b) GaFeO<sub>3</sub> [200], (c) CoFe<sub>2</sub>O<sub>4</sub> [207] and (d) SrFe<sub>12</sub>O<sub>19</sub> [202]. OH, TPB and TH stand for Figure 3.6: XMCD spectra at the Fe L<sub>2,3</sub>-edges calculated for each iron cation of SrFe<sub>12</sub>O<sub>19</sub> [202]. OH, TPB and TH stand for octahedral, trigonal bipyramid and Figure 3.7: (a) XAS spectra recorded at the Fe  $L_{2,3}$ -edges measured at 1.2 K on a singlecrystal of BaFe<sub>12</sub>O<sub>19</sub> in NI geometry using right ( $\sigma_+$ ) and left ( $\sigma_-$ ) circularly polarised Xray beams. The dotted lines represent the linear background. (b) Normalised XAS spectra and (c) XMCD signal. OH and TH in (c) is stand for octahedral and tetrahedral Figure 3.8: (a) XAS spectra recorded at the Fe L<sub>2,3</sub>-edges measured at 1.2 K on a singlecrystal of BaFe<sub>12</sub>O<sub>19</sub> in grazing incidence geometry without field using right ( $\sigma_+$ ) and left  $(\sigma_{-})$  circularly polarised X-ray beams. The dotted lines represent the linear background. (b) Normalised XAS spectra and (c) XMCD signal......64 Figure 3.9: (a) XAS spectra recorded at the Fe L<sub>2,3</sub>-edges measured at 1.2 K on a singlecrystal of BaFe<sub>12</sub>O<sub>19</sub> in grazing incidence geometry with field of 0.5 T using right ( $\sigma_+$ ) and left  $(\sigma_{-})$  circularly polarised X-ray beams. The dotted lines represent the linear Figure 3.10: (a) The XMCD signal and (b) sum XAS along with their integration measured in grazing incidence geometry without field at 1.2 K. The dotted line in (b) is Figure 3.11: (a) The XMCD signal and (b) sum XAS along with their integration measured in grazing incidence geometry with field of 0.5 T at 1.2 K. The dotted line in (b) is the two-step-like function used for edge jump removal before XAS integration. ...67

Figure 3.12: M-H curve measured at 2 K on single-crystal under various field applied (a) Figure 3.13: Single-crystal neutron diffraction pattern recorded along 001 reciprocal lattice row at 1.5 K depicting a magnetic peak around 003 position. The inset shows the triplet character of the magnetic peak with reflections at l = 3 and  $l = 003 - \tau_1$  and  $003 + \tau_2$ Figure 4.1: (a) Variation of the dc magnetization  $M_{\perp c}$  and  $M_{//c}$  measured with a field of 500 Oe applied parallel ( $_{//}$ ) and perpendicular ( $_{\perp}$ ) to the c-axis of the crystal. (b) The first derivative plot of  $M_{\perp c}$  and  $M_{//c}$  with respect to the temperature. (c) Curie-Weiss fit for Figure 4.2: Magnified view of the temperature dependence of  $M_{\perp c}$  and  $M_{//c}$  in the 2 K to 300 K range, measured with a dc field of 500 Oe, during the warming cycle on a ZFC crystal. The inset shows the occurrence of a magnetic transition at low temperatures on a Figure 4.3: Variation of the magnetic anisotropy parameter A =  $\left(\frac{M_{\perp c}}{M_{\prime lc}}\right)$  with temperature. Figure 4.4: XAS spectra and XMCD signals at the Fe L<sub>2.3</sub>-edges measured in the NI geometry without dc magnetic field bias measured at (a) 30 K, (b) 13.5 K, (c) 5.5 K and (d) 1.2 K. TH and OH in (a)-(d) stand for the tetrahedral and octahedral environments of Figure 4.5: XAS spectra and XMCD signals of Fe at the L<sub>2,3</sub>-edges measured in the GI geometry without dc magnetic field bias (H = 0 T) at (a) 30 K, (b) 13.5 K, (c) 5.5 K and 

Figure 4.6: XAS spectra and XMCD signals of Fe at the L <sub>2,3</sub> -edges measured in the GI
geometry with a biasing magnetic field of $H = 0.5 \text{ T}$ at (a) 30 K, (b) 13.5 K, (c) 5.5 K and
(d) 1.2 K. OH in (a)-(d) stand for octahedral environments of Fe
Figure 4.7: Comparison of the variation of the component of moments (a) longitudinal
(M//c) and (b) transverse components (M $_{\perp c}$ ) calculated using XAS, XMCD signal and dc
magnetization measurements on the single-crystal
Figure 4.8: XAS spectra of oxygen at the K-edge recorded in normal incidence geometry
at 1.2 K
Figure 4.9: Schematic representation of splitting of 3dFe <sup>3+</sup> orbitals in BaFe <sub>12</sub> O <sub>19</sub> due to
crystal field and exchange-correlation effects at 1.2 K90
Figure 4.10: (a) XAS spectra at the O K-edge recorded in the NI geometry at various
temperatures. (b) XAS spectra on a zoomed scale. Peaks A1, A2, A3 and A4 in (b) are
labelled as $t_{2g-bottom}$ , $t_{2g-top}$ , $e_{g-bottom}$ and $e_{g-top}$ , respectively. All the curves in (a) are shifted
along the y-axis by 0.025
Figure 5.1: (a) Variation of the ZFC and FC magnetization $(M_{\perp c})$ measured with dc field
of 500 Oe applied perpendicular to the c-axis of the crystal. (b) Evolution of
thermoremanent magnetization $M_{\perp c}(t)$ of a 1000 Oe FC crystal with time at 40 K. (c)
Temperature dependence of real $\chi'_{\perp c}$ and imaginary $\chi''_{\perp c}$ parts of the ac susceptibility
measured at 545 Hz with an ac field drive of 3 Oe applied perpendicular to the c-axis of
the crystal105
Figure 5.2: Temperature dependence of (a) real $\chi'_{\perp c}(\omega, T)$ and (b) imaginary $\chi''_{\perp c}(\omega, T)$
parts of ac susceptibility measured at various frequencies using an ac drive field of 3 Oe
applied perpendicular to c-axis of the crystal; (c) depicts the lower temperature anomaly
in $\chi''_{\perp c}(\omega, T)$ on a zoomed scale. The solid continuous lines through the data points in (c)
are the fitted curves

Figure 5.3: Variation of the  $ln(\tau)$  with  $1/T'_f$ . The continuous solid line through the data points is the result of the least-squares fit for Vogel-Fulcher law using  $\chi'(\omega, T)$  data....110 Figure 5.4: (a) Optimization of  $T'_{SG}$ . The minimum in (a) corresponds to the lowest variance with  $T'_{SG} \sim 46.035$  K. (b) The least-squares fit for the power-law for ln( $\tau$ ) versus  $ln((T_f'-T_{SG}')/T_{SG}')$  plot using  $\chi'(\omega,T)$  data.....111 Figure 5.5: The  $ln(\tau)$  vs  $1/T_f''$  plots for the (a) higher and (b) lower temperature transitions obtained from the  $\chi''_{\perp c}(\omega, T)$  data. The solid line is the least-squares fit for the Vogel-Fulcher law for the two transition with the best fit parameters given along with the Figure 5.6: Optimization of  $T_{SG}^{\prime\prime}$  for (a) the higher temperature and (b) the lower temperature transitions. The minimum in the two curves gives the optimised critical spin-Figure 5.7: The  $ln(\tau)$  vs  $ln((T''_f - T''_{SG})/T''_{SG})$  plots for the power law type spin dynamics for the (a) higher and (b) lower temperature spin-glass transitions seen in  $\chi''_{\perp c}(\omega, T)$  data. The Figure 5.8: Temperature dependence of real  $\chi'_{//c}$  and imaginary  $\chi''_{//c}$  part of ac susceptibility measured at frequency 200 Hz using ac field of 3 Oe applied along the caxis of the crystal. Inset shows the variation of  $\chi'_{//c}$  on the zoomed scale......115 Figure 5.9: (a) Temperature dependence of the real  $\chi'_{//c}$  part of ac susceptibility measured at various frequencies using an ac drive field of 3 Oe applied parallel to the c-axis of the crystal. All the curves in (a) are shifted by 0.012 emu/gOe x 10<sup>-2</sup> along the y-axis and solid continuous line through the data points is a guide to the eyes. The  $\ln(\tau)$  versus  $1/T'_f$ plot for the two anomalies are shown in (b) for ~ 25 K and (c) for ~ 15 K transitions observed in  $\chi'_{//c}$ . The continuous solid line in (b) and (c) is least-squares fit for Vogel-Fulcher law......116

Figure 5.12: Peak profile of 006 Bragg reflection at (a) 1.5 K, (b) 10 K, (c) 50 K, (d) 100 K, (e) 200 K and (f) 300 K: The continuous solid lines through the data points (filled circles) are the fits for the back-to-back two exponential functions......121 Figure 5.13: Peak profile of 101 Bragg reflection at (a) 1.5 K, (b) 10 K, (c) 50 K, (d) 100 K, (e) 200 K and (f) 300 K: The continuous solid lines through the data points (filled circles) are the fits for the back-to-back two exponential functions......121 Figure 5.14: Temperature dependence of the integrated intensity of 006 Bragg reflection (a) on the full scale and (b) on the magnified scale, obtained from the neutron diffraction data collected on the single-crystal of BaFe<sub>12</sub>O<sub>19</sub>. Broken lines in (a) and (b) are guide to the eyes, while the continuous solid line (black coloured) in (a) is the fit for the square of Figure 5.15: Temperature dependence of the integrated intensity of 101 Bragg reflection (a) on the full scale and (b) on the magnified scale, obtained from the neutron diffraction data collected on the single-crystal of BaFe<sub>12</sub>O<sub>19</sub>. Broken lines in (a) and (b) are guide to the eyes, while the continuous solid line (black coloured) in (a) is the fit for the square of Figure 5.17: Variation of C<sub>P</sub>/T with square of the temperature (T)......126 

Figure 6.1: Temperature dependence of  $\chi'_{//c}$  and  $\chi''_{//c}$  measured at 700 Hz with an ac field drive of 3 Oe applied (a) parallel (//) to the c-axis and (b) perpendicular ( $\perp$ ) to the c-axis of the BFO crystals. This figure has been reproduced from chapter 5. (c) This figure depicts the real  $\chi'$  and imaginary  $\chi''$  parts of ac susceptibility measured at 700 Hz on powder samples at an ac drive field of 3 Oe. The continuous solid line through the data points (filled circles) is guide to the eyes. The dotted vertical lines indicate the first two Figure 6.2: (a) The evolution of ac susceptibility measured on powder sample at (a) 200 Hz with different ac drive fields and (b) comparison of ac susceptibility measured at 50 Hz using ac drive field of 3 Oe and 13 Oe. Successive curves in (a) are shifted vertically by 0.0001 emu/gOe for clarity. The continuous solid line through the data points is guide Figure 6.3: Temperature dependence of the real part of ac susceptibility ( $\chi'(\omega, T)$ ) of the powder sample at various frequencies. Successive curves are shifted vertically by 0.00015 Figure 6.4: The  $ln(\tau)$  versus  $1/T'_f$  plots for the (a) transverse and (b) longitudinal component of the spins. The continuous solid line through the data points is the Vogel-Figure 6.5: Optimization of the spin-glass transition temperature  $(T'_{SG})$  for (a) transverse and (b) longitudinal freezing......141 Figure 6.6: The  $\ln(\tau)$  vs  $\ln(T'_f - T'_{SG})/T'_{SG}$  plots for the freezing of the (a) transverse and (b) longitudinal components of the spins. The continuous line through the data points is the power-law fit......142 Figure 6.7: The  $\chi'(\omega=200$ Hz, T) plot for powder sample under different dc biasing 

Figure 6.8: The T-H diagram showing the Gabay-Toulouse (G-T) with  $m = (2.0 \pm 0.04)$ and de Almeida-Thouless (A-T) with  $m = (0.65 \pm 0.001)$  lines. The continuous line through the data points in the T-H plane is the least-squares fit to the Equation (6.1) and Figure 6.9: Evolution of iso-thermoremanent ac susceptibility  $\chi'(\omega = 200 \text{Hz})$  with time at (a) 40 K and (b) 10 K under 50 Oe dc biasing field. The solid lines (black coloured) through the data points in (a) and (b) are Kohlrausch-Williams-Watt (KWW) stretched exponential equation fits......147 Figure 6.10: Evolution of isothermal remanent ac susceptibility  $\chi'(\omega=200 \text{Hz})$  with time at (a) 40K and (b) 10K under 50 Oe dc biasing field measured with intermediate quenching to 35K and 5K, respectively. The solid lines (black coloured) though the data points in (a) Figure 7.1: Variation of magnetization with temperature measured for a BFO singlecrystal for dc fields of (a) 500 Oe and (b) 1000 Oe applied parallel to the c-axis, and (c) 500 Oe applied perpendicular to the c-axis. The continuous line through the data points are guide to the eyes, whereas the dash-dot line in (c) shows the deviation from the linear behaviour of  $M_{\perp c}$  for 200 < T < 300 K. Panels (a) and (b) depict the results of both ZFC Figure 7.2: (a) Variation of  $\chi^\prime and \, \chi^{\prime\prime}$  with temperature measured at 700 Hz and 745 Hz for an ac drive field of 3 Oe applied (a) parallel and (b) perpendicular to the c-axis, respectively. The continuous lines through the data points are guide to the eyes while the dash-dotted lines for  $\chi''(T)$  curves depict departure from the linear trend below 200 K. The dashed-dotted line in  $\chi'_{//c}$  in (a) has been drawn to highlight the diffuse peak superimposed over the nearly linearly decreasing trend of the background value......158

Figure 7.3: $C_P/T$ versus $T^2$ semi-log plot of BaFe <sub>12</sub> O <sub>19</sub> without any dc field bias. Inset
shows the variation of C <sub>P</sub> with temperature159
Figure 7.4: Variation of the integrated intensity of (a) 101 and (b) 006 Bragg reflections
with temperature. The continuous solid line shows the Brillouin fits for the integrated
intensities unlike the plotted lines through the data points are guide to the eyes
Figure 7.5: The evolution of the magnetic satellite peaks of BFO as a function of
temperatures. The peak position of each satellite is marked with dotted lines. The
continuous solid line through the data points is the deconvoluted profile162
Figure 7.6: (a) The variation of the magnetic satellite peak positions, $(003 - \tau_1)$ and $(003 + \tau_2)$
$\tau_2$ ), with temperature. (b) The variation of the integrated intensity of the magnetic satellite
peak at $(003 + \tau_2)$ position with temperature. The continuous solid lines are guide to the
eyes
Figure 7.7: (a) Variation of magnetization measured on zero-field cooled BFO powder at
100 Oe dc field. (b) Variation of $\chi'$ and $\chi''$ with temperature measured on BFO powder at
700 Hz with an ac drive field of 3 Oe166
Figure 7.8: (a) The variation of $\chi$ " with temperature at 700 Hz. The continuous line below
the peak in $\chi''(T)$ is the fitted curve for modelling the rising background value of $\chi''(T)$
above 100 K. The panel (b) depicts the rising background-subtracted peaks in $\chi''(T)$ at
various frequencies
Figure 7.9: (a) Variation of $ln(\tau)$ versus $1/T_{SG}^{\prime\prime}$ while the solid line is the least-squares fit
for Vogel-Fulcher law. (b) Optimization of $T_{SG}$ and (c) depicts the $ln(\tau) vs ln((T_f'' - T_{SG}'')/t)$
$T_{SG}^{\prime\prime}$ ) plot along with the fit to the power-law type spin dynamics for $T_{SG}$ = 173.3 K168
Figure 7.10: Variation of the dc magnetization of the zero-field cooled powder samples of
$BaFe_{12}O_{19}$ measured during the warming cycle using a dc field of (a) 100 Oe, (b) 300 Oe,
(c) 500 Oe, (d) 700 Oe, (e) 1000 Oe and (f) 1500 Oe. Arrows in (a)-(c) indicate the peak

Figure 7.12: Evolution of iso-thermoremanent ac susceptibility  $\chi'(\omega = 200 \text{Hz})$  with time measured at 100 K under 50 Oe dc biasing field. The solid lines through the data points is Kohlrausch-Williams-Watt (KWW) stretched exponential equation fit. .....171 Figure 7.13: Evolution of isothermal remanent ac susceptibility  $\chi'(\omega = 200 \text{ Hz})$  with time measured at 100 K under 50 Oe dc biasing field measured with intermediate quenching to 95 K. The solid lines (black coloured) though the data points are guide to the eyes. .....172 Figure 8.1: Neutron powder diffraction patterns recorded at various temperatures. Inset shows a zoomed around the forbidden of 003 peak position. All the curves are shifted Figure 8.2: Isotropy subgroup tree for the magnetic space group P6<sub>3</sub>/mm'c'......184 Figure 8.3: The temperature variation of the (a)  $\chi^2$  and (b) R<sub>M</sub>-factor obtained from the Rietveld analysis of neutron diffraction pattern collected at different temperatures......186 Figure 8.4: Observed (filled red circles), calculated (continuous black line), and difference (bottom green line) profiles obtained from the Rietveld refinement using neutron diffraction data at (a) 300K with  $\Gamma_{2a}$ , (b) 100K with  $\Gamma_{2(a \oplus b)}$ , (c) 50K with  $\Gamma_{2 \oplus b}$  $\Gamma_3$ , (d) 10K with  $\Gamma_2 \oplus \Gamma_3$  and (e) 10K with  $\Gamma_2 \oplus \Gamma_4$  for BaFe<sub>12</sub>O<sub>19</sub>. The vertical tick marks Figure 8.5: Magnetic spin configurations obtained from Rietveld refinement of the magnetic structure using irrep  $\Gamma_{2(a \oplus b)}$  (a) longitudinal and (b) transverse components of the canted spins at 300 K and 250 K.....189

Figure 9.3: Variation of (a) lattice parameters a, c, (b) unit cell volume V and (c) bond
lengths Fe2-O1 and Fe2-O3 of $Ba_{(1-x)}Ca_xFe_{12}O_{19}$ in the composition range $0 \le x \ge 0.10$ .
Figure 9.4: Variation of the real ( $\epsilon$ ') and imaginary ( $\epsilon$ ") parts of the dielectric permittivity
of $Ba_{(1-x)}Ca_xFe_{12}O_{19}$ at 300 kHz for different $Ca^{2+}$ concentrations with $x = (a) 0$ , (b) 0.03,
(c) 0.05, (d) 0.07 and (e) 0.10. Insets in (a)-(e) show the variation of $\varepsilon$ ' on the zoomed
scale
Figure 9.5: Variation of ac susceptibility of BCFO-x216
Figure 9.6: Variation of dielectric peak temperature ( $T_c$ ) at 300 kHz of $Ba_{(1-x)}Ca_xFe_{12}O_{19}$
as a function of $Ca^{2+}$ concentration (x). Inset shows variation of glass transition
temperature ( $T_g$ ) as a function of $Ca^{2+}$ concentration (x)
Figure 9.7: Variation of the real ( $\epsilon$ ') part of the dielectric permittivity of Ba <sub>(1-x)</sub> Ca <sub>x</sub> Fe <sub>12</sub> O <sub>19</sub>
for (a) $x = 0$ , (b) $x = 0.03$ , (c) $x = 0.05$ , (d) $x = 0.07$ and (e) $x=0.10$ measured at various
frequencies
Figure 9.8: Non-Arrhenius behaviour of temperature dependence of relaxation time $(\tau)$
shown in $ln(\tau)$ versus 1/T plot of $Ba_{(1-x)}Ca_xFe_{12}O_{19}$ for (a) x=0.05, (b) 0.07 and (c) 0.10.
The continuous line in insets (a)-(c) shows fit for $\ln(\tau)$ vs $\ln(T_{max} - T_g/T_g)$ plot using
power law dynamics $\tau = \tau_0 (T_{max} - T_g/T_g) - z\nu$ characteristic of a dipolar glass transition.
Figure 9.9: Curie-Weiss fit (black solid line) to temperature dependent permittivity (red
circles) of $Ba_{(1-x)}Ca_xFe_{12}O_{19}$ for x = (a) 0.00, (b) 0.03, (c) 0.05 (d) 0.70 and (e) 0.10223
Figure 9.10: Variation of the magnitude of Curie-Weiss temperature $ \Theta_{cw} $ of Ba <sub>(1-</sub>
<sub>x)</sub> Ca <sub>x</sub> Fe <sub>12</sub> O <sub>19</sub> with concentration (x)224
Figure 9.11: Specific heat of BaFe <sub>12</sub> O <sub>19</sub> as a function of temperature. Inset depicts the
specific heat measured at different fields on a magnified scale

Figure 9.12: $C_p/T^{3/2}$ vs $T^{3/2}$ plot where solid line represents the linear fit. Inse	et shows the
non-Debye part of the specific heat at different magnetic fields	225
Figure 9.13: Boson peak at ~ 2.7 K in $BaFe_{12}O_{19}$	

xxii

## List of Tables

Table 1.1: Chemical formula, sequences of S, R, and T blocks, and space groups for
different type of hexaferrites [12]15
Table 1.2: magnetic models for M-type hexagonal ferrites 27
Table 2.1: Average chemical composition of BaFe <sub>12</sub> O <sub>19</sub> in atomic wt% obtained from the
EDX analysis42
Table 2.2: Asymmetric unit of the hexagonal phase of BaFe <sub>12</sub> O <sub>19</sub> in space groups
P6 <sub>3</sub> /mmc
Table 2.3: Positional coordinates, lattice parameters, and agreement factors obtained by
Rietveld refinement using powder XRD data of BaFe <sub>12</sub> O <sub>19</sub> 45
Table 2.4: Positional coordinates, lattice parameters, and agreement factors obtained by
Rietveld refinement using single-crystal XRD data of BaFe <sub>12</sub> O <sub>19</sub> 46
Table 2.5: Comparison of our structural parameters with those reported in literature using
single-crystal data46
Table 2.6: Interatomic distances (Å) obtained from Rietveld refinement powder XRD data
of BaFe <sub>12</sub> O <sub>19</sub>
Table 3.1: Energy of valleys and peaks in experimentally observed XMCD at the Fe L <sub>3</sub> -
edge for SrFe <sub>12</sub> O <sub>19</sub> [202]
Table 3.2: Energy of valleys and peaks at the Fe L <sub>3</sub> -edge of calculated XMCD profiles of
SrFe <sub>12</sub> O <sub>19</sub> [202]
Table 4.1: Energy of the valleys and peaks in the XMCD profile of Fe at the L3-edge
measured in NI geometry with $H = 0$ T
Table 4.2: Energy of valleys and peaks in the XMCD profile of Fe at the L3-edge
measured in GI geometry with $H = 0$ T

Table 4.3: Energy of valleys and peaks in the XMCD profile of Fe at the L <sub>3</sub> -edge
measured in GI geometry with $H = 0.5 T$
Table 4.4: Energy of the peaks $t_{2g}$ and $e_g$ bands observed at the O K-edge spectra recorded
in NI geometry at various temperatures
Table 4.5: Energy of the $t_{2g}$ and $e_g$ bands observed at the O K-edge spectrum recorded in
NI geometry at various temperatures
Table 4.6: Change in crystal field and exchange splitting energies with increase in
temperature
Table 5.1: List of parameters obtained after least-square fit to the Vogel-Fulcher and
power-law dynamics to spin relaxation time
Table 8.1: Basis vectors of the irreducible representation $\Gamma_n$ for magnetic ion (Fe <sup>3+</sup> )
named as Fe1 at 2a Wyckoff site with fractional coordinate (x=0, y=0, z=0) and Fe2 at
2(b) Wyckoff site with fractional coordinate (x=0, y=0, z=0.25)181
Table 8.2: Basis vectors of the irreducible representation $\Gamma_n$ for magnetic ion Fe3 and Fe4
at $4f_{iv}$ (4f1) site with fractional coordinate (x=1/3, y=2/3, z=0.0272) and at $4f_{vi}$ (4f2) site
with fractional coordinate (x=1/3, y=2/3, z=0.1904), respectively
Table 8.3(a): Basis vectors of the irreducible representation $\Gamma_n$ for 6 out of 12 equivalent
position of Fe5 at 12k site with fractional coordinate (x=0.168, y=2x, z=-0.1082)182
Table 8.3(b): Basis vectors of the irreducible representation $\Gamma_n$ for the remaining six
equivalent positions of Fe5 at the 12k site with fractional coordinate (x=0.168, y=2x, z=-
0.1082)
Table 9.1: Atomic positions obtained from the Rietveld refinement for different
compositions