Magnetoelectric spin-glass transition(s) in pure and disordered $BiFeO_3$

Cite as: AIP Advances **8**, 101409 (2018); https://doi.org/10.1063/1.5042131
Submitted: 30 May 2018 . Accepted: 13 August 2018 . Published Online: 30 August 2018

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(Received 30 May 2018; accepted 13 August 2018; published online 30 August 2018)

We present here the results of a comparative study of the spin glass (SG) transition in pure and disordered ($0.80BiFeO_3$-$0.20BaTiO_3$ or 0.80BF-0.20BT) $BiFeO_3$. It is shown that the anomalous frequency dependence of ac susceptibility in the SG phase of BF is not linked with the spin cycloid as it is present even after its destruction in 0.80BF-0.20BT solid solution. Our neutron scattering studies on disordered BF reveal the presence of long-range ordered (LRO) antiferromagnetic (AFM) peak and decrease in the ordered magnetic moment from the overall Brillouin function behaviour around the SG transition suggesting that some spin components are getting detached from the AFM phase. Further, the SG transition is accompanied with anomalies in the unit cell volume and ferroelectric polarization around the SG transition temperature, highlighting the presence of magnetoelastic and magnetoelectric couplings, respectively. All these results suggest that the SG phase of BF is intrinsic to the system and is not due to nano-sized impurities. https://doi.org/10.1063/1.5042131

I. INTRODUCTION

$BiFeO_3$ (BF) continues to attract immense interest as a room temperature multiferroic with the highest ferroelectric and magnetic transition temperatures (T_C ~1100 K and T_N ~643 K) in the family of multiferroics[1] with tremendous potential for multifunctional devices.[2] However, the crystal structure of the paraelectric phase[3–5] on the high temperature side and the magnetic ground state at low temperature[1] side are both controversial. A proper understanding of both the phases is a must for developing a suitable Hamiltonian[6] which can predict the properties of BF at intermediate temperatures accurately. In the present work, our focus is on the low temperature magnetic transitions. Several workers have reported a spin-glass (SG) transition in both poly and single crystals of BF with a freezing temperature T_f ~25K.[7–9] However, doubts have been raised about the intrinsic nature of the SG phase of BF and instead it's origin has been attributed to the presence of nanosized superparamagnetic (SPM) clusters of some impurity phase.[10,11] Even if the SG transition is intrinsic on account of its obsevation in single crystals also, which are believed to be free from such impurities,[8] the frequency dependence of the real (χ'(ω, T)) and imaginary parts (χ"(ω, T)) of the ac susceptibilty χ(ω, T) of this SG phase is quite anomalous when compared to the conventional SG systems in both single and polycrystalline samples.[12] For example, the χ'(ω, T) of the well-known SG systems decreases with increasing frequency around the freezing temperature T_f,[12] whereas it increases in case of pure BF.[8,9] Further, the χ''(ω, T) shows a negative cusp near T_f ~ 30K with a peak temperature that lies above the peak temperature of χ'(ω, T). In all conventional SG systems, the temperature corresponding to the peak in to the peak in χ''(ω, T) is always lower than the peak temperature of χ'(ω, T).[12] These unusual features of the SG phase in BF have been attributed to the presence of incommensurate modulated magnetic spin cycloid cycloid structure.[8]

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Recently, we have shown that the SG transition in the disordered (1-x) $BiFeO_3$-x$BaTiO_3$ ((1-x)BF-xBT) solid solution system is intrinsic to the system as it is accompanied with magnetoelectric and magnetoelastic couplings, both of which were determined using microscopic probes like neutron and x-ray diffraction and are therefore not affected by impurity clusters. More interestingly, it was shown that there are two SG transitions in the disordered solid solutions corresponding to the freezing of the longitudinal ($\mathbf{q}_{\parallel}$) and trnaseverse ($\mathbf{q}_{\perp}$) components of the $3dFe^{3+}$ spins which lead to Almeida-Thouless[13] and Gabay-Toulouse[14] type criticalities in the T-H plane as per the theoretical predictions for SG transition in disordered Heisenberg systems with small single-ion anisotropy.[15] In this paper, we summarise the controversial aspects of SG transition in pure BF[9] and compare them with the results presented on the disorderd BF-xBT system described in Ref. 16.

II. RESULTS AND DISCUSSION

The details of the sample preparation as well as neutron diffraction, x-ray diffraction and magnetic measurements are given elsewhere.[9,16] Single-phase powder and sintered ceramic samples of $BiFeO_3$ are rather difficult to prepare because of the narrow temperature range of stability of the perovskite phase and the volatile nature of Bi^{3+} that promotes the formation of impurity phases like $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$.[17] Figs. 1(a) and (b) compare the room-temperature x-ray powder diffraction (XRD) patterns of BF and 0.80BF-0.20BT powders. It is evident from the figure that the 0.80BF-0.20BT sample is single phase at XRD level but the diffraction pattern of pure BF contains tiny peaks corresponding to an impurity phase $Bi_2Fe_4O_9$ with a peak intensity that is 1.4 % of the strongest 220_{pc} peak of BF with respect to the doubled pseudocubic (pc) unit cell. The singlet and doublet nature of 400_{pc} on one hand and 222_{pc} and 440_{pc} on the other confirm the rhombohedral structure in the R3c space group for both BF and 0.80BF-0.20BT.

Pure BF shows linear M-H response typical of an antiferromagnetic (AFM) phase whereas a hysteresis loop opens up in 0.80BF-0.20BT with a remnant magnetization M_r ~0.13emu/g and coercivity H_c ~3055 Oe, as can be seen from Fig. 1(c). These numbers are in agreement with the previous reports.[18] The magnetic structure of BF, as determined by neutron diffraction is known to be G-type antiferromagnetic with canted spins.[19] However, inspite of the weak ferromagnetic component arising out of the canted spins, BF shows linear M-H plot (see Fig. 1(c)) because of the superposition of an incommensurate modulated cycloidal spin structure with an approximate period λ~62nm.[19] On substituting Fe^{3+} with Ti^{4+} in (1-x)BF-xBT solid solutions, the spin cycloid gets destroyed and leads to release of the canted ferromagnetic component giving rise to a M-H loop with non-zero M_r and

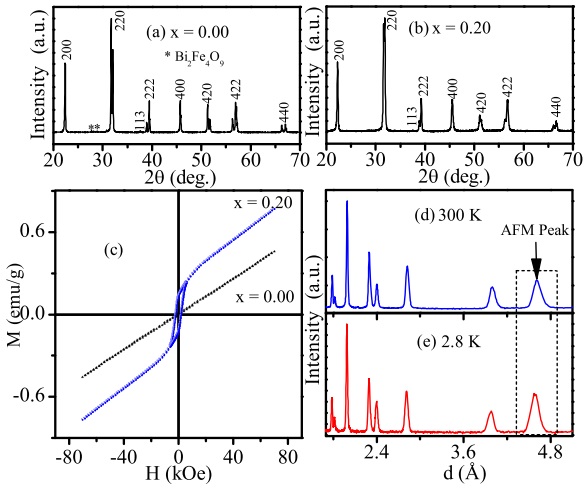

FIG. 1. X-ray diffraction patterns collected at room temperature for **(a)** $BiFeO_3$ (BF) and **(b)** 0.80$BiFeO_3$-0.20$BaTiO_3$ (0.80BF-0.20BT). All the indices are written with respect to the doubled pseudocubic cell **(c)** M-H hysteresis loops of BF and 0.80BF-0.20BT (after Ref. 16) at 300K. **(d-e)** Neutron powder diffraction patterns for 0.80BF-0.20BT at 300K and 2.8K (after Ref. 16). The long-range ordered (LRO) antiferromagnetic (AFM) peak is marked with an arrow.

H_c shown in Fig. 1(c). The absence of spin-cycloid is verified by neutron powder diffraction (NPD) pattern shown in Fig. 1(d) which does not show the magnetic satellite peaks.[20]

Even though the spin cycloid of BF has been destroyed by BT substitution, the frequency dependence of the SG transition remains anomalous in 0.80BF-0.20BT also. This is shown in Fig. 2 which compares the variation of χ' (ω, T) and χ'' (ω, T) of BF and 0.80BF-0.20BT. It is evident from the figure that the peak value of χ'(ω, T)) around the SG transition increases with increasing frequency for both the samples. Further, the χ''(ω, T) shows negative cusp around 30K with a peak temperature above the peak temperature corresponding to χ'(ω, T). Thus, the anomalous nature of the SG phase is not linked with the spin cycloid as conjectured in the literature.[8] We believe, in agreement with Ref. 8, that this anomalous behavior may be due to resonant absorption in the ac susceptibility measurement circuit.

We now proceed to discuss the spin dynamics of BF and 0.80BF-0.20BT which is used to distinguish between SG freezing and SPM blocking[12] to confirm the ergodicity breaking at critical SG transition temperature T_{SG} at which the slowest spin dynamics diverges. For this, we analyze the shift in the peak temperature of χ (ω, T) as a function of frequency using the χ'(ω, T) data in Fig. 2(a) and (c). The spin relaxation time (τ) was taken as inverse of the measuring angular frequency ω (=2πf) corresponding to the peak temperature T_f in the χ' (ω, T). For SPM blocking,[21] τ follows simple Arrhenius law, $\tau = \tau_0 \exp(E_a/k_B T)$ where τ_0 is the inverse of attempt frequency, E_a the activation energy and k_B the Boltzmann constant. The ln(τ) vs (1/T) plot for SPM blocking should therefore be linear. The non-linear nature of the experimentally observed plots shown in the inset of Fig. 2(a) and (c) rules out SPM blocking in both BF and 0.80BF-0.20BT. Spin-glass systems[21] show a characteristic critical temperature T_{SG} at which the slowest spin dynamics diverges signalling the ergodic symmetry breaking. The spin dynamics in SG systems is often modelled using Vogel-Fulcher (V-F) law $\tau = \tau_0 \exp(E_a/k_B\ (T-T_{SG})$. The continuous solid line in the insets of Fig. 2(a) and (c) depict the V-F law fit for the two samples. The excellent fit confirms SG freezing with SG transition temperature $T_{SG}\sim$ 20 and 18.6K for BF and 0.80BF-0.20BT, respectively. The activation energy E_a = 0.8 and 0.65 meV for BF and 0.80BF-0.20BT, respectively, are comparable to the activation energies reported for the SG systems like $Eu_{1-x}Sr_xS$.[21] Our ac susceptibility results thus confirm the existence of a SG transition temperature T_{SG} in BF and 0.80BF-0.20BT at which the ergodicity is broken. Our results also show that the earlier report[8] of $T_{SG} > T_f$ in BF is incorrect. In fact, the T_{SG} has to be lower than T_f (ω) as it corresponds to the divergence of the time scale associated with the slowest spin dynamics.

One can verify the intrinsic nature of the SG transition using neutron and x-ray powder diffraction data in several ways. For example, one can capture the change in ordered magnetic moment at the SG

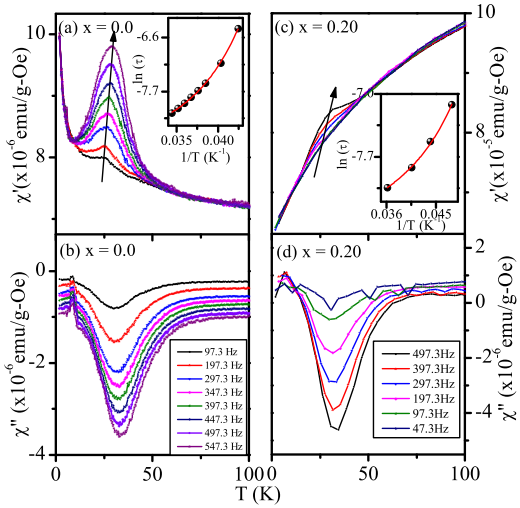

FIG. 2. **(a-d)** Temperature dependence of the real and imaginary parts of the ac susceptibility χ (ω, T) at various frequencies for BF and 0.80BF-0.20BT (after Ref. 16). Insets in (a) and (c) depict ln (τ) vs 1/T plot for BF and 0.80BF-0.20BT, respectively. Solid line is the least squares fit for Vogel-Fulcher law.

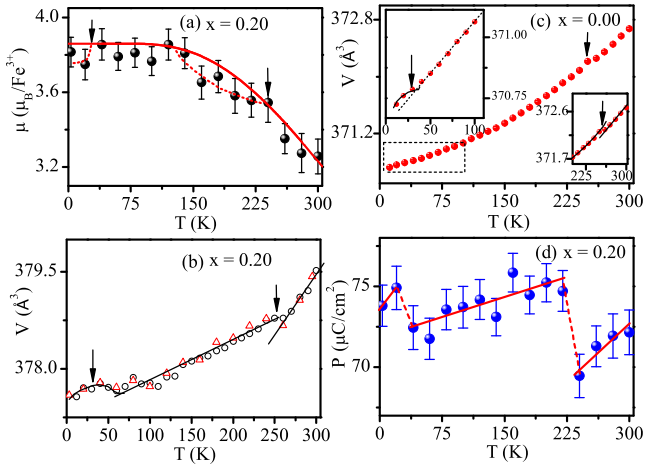

FIG. 3. Variation of **(a)** ordered magnetic moment of $3dFe^{3+}$ of 0.80BF-0.20BT, **(b)** unit cell volume (V(Å^3)) of 0.80BF-0.20BT (after Ref. 16) **(c)** unit cell volume (V(Å^3)) of BF and **(d)** ferroelectric polarization (P) of 0.80BF-0.20BT (after Ref. 16) with temperature. The solid line in (a) represents Brillouin function fit. The arrows in (b) and (c) mark the transition temperatures with anomalies in the unit cell volume.

transition by Rietveld refinement of the magnetic structure using neutron diffraction data at various temperatures. We show in Fig. 3(a) the variation of ordered magnetic moment for 0.80BF-0.20BT obtained from the data given in Ref. 16. The solid line in this curve is the Brillouin function fit. One can clearly see a decrease in the ordered magnetic moment around T_f ~30K in this figure. There is another SG transition in 0.80BF-0.20BT with T_f ~240K around which also one sees a slight diminution in the value of the ordered moment with respect to the Brillouin function behaviour. Such a decrease of moment implies detachment of some component of the ordered moment which takes part in SG freezing. In such a situation, the LRO phase should coexist with the SG phase[14–16] as predicted theoretically for both the Ising and Heisenberg systems. This was verified in Ref. 16. Fig. 1(e) shows the presence of AFM peak even at 2.8K in 0.80BF-0.20BT. In pure BF, neutron diffraction studies by other workers have confirmed the existence of the LRO AFM phase down to 4K.[22,23] However, no study has so far been made to study the detachment of some component of the ordered moment around the SG transition similar to 0.80BF-0.20BT.[16]

One can also confirm the intrinsic nature of SG transition by looking for change in the unit cell volume across the SG transition using neutron and/or x-ray powder diffraction techniques for systems with strong spin-orbit coupling driven magnetoelastic effect as discussed in Ref. 16 for 0.80BF-0.20BT. We show in Fig. 3(b) and (c) the variation of unit cell volume as a function of temperature obtained from x-ray powder diffraction data for 0.80BF-0.20BT (after Ref. 16) and BF. For the former, one can clearly see that the slope changes around the two SG transitions due to magnetoelastic coupling at the SG transition. We also observe a similar change, though much weaker, for BF shown in Fig. 3(c) (see insets for the magnified view) around 30K and 250K. In multiferroic systems like BF and 0.80BF-0.20BT, the intrinsic nature of the SG transition can be verified by looking for change in ferroelectric polarization (P) also around the SG transition due to magnetoelectric coupling. Ferroelectric (FE) polarization can be calculated accurately using Born effective charges and atomic positions obtained by Rietveld analysis of neutron diffraction data. Neutrons are preferred since they can locate oxygen positions more precisely than x-rays. Such a study was carried out in Ref. 16 for 0.80BF-0.20BT and we depict in Fig. 3(d) the temperature dependence of FE polarization from reference 16. Two clear discontinuities in P vs T plot are seen around the two SG transitions confirming magnetoelectric coupling at these transitions. The above results suggest the need for a careful study of the magnetic and nuclear structure of BF as a function of temperature using neutron diffraction measurements at low temperatures to unambiguously confirm the intrinsic nature of the SG transition similar to 0.80BF-0.20BT summarized above after Ref. 16.

Unlike the (1-x)BF-xBT system where the magnetic sublattice has disorder, the occurrence of a SG phase in a homogeneously ordered system like BF without any quenched-in disorder and

randomness is intriguing as all the existing models of SG transitions are based on the concept of disorder, randomness and frustration.[12] While SG transition has been observed in homogeneous Heisenberg systems without any disorder in the presence of geometrical frustration,[24] there is no experimental evidence for geometrical frustration in BF. Thus, even if the SG phase of BF may be intrinsic, the existence of SG transition would remain enigmatic from the point of view of its origin.

III. CONCLUSIONS

We have shown that the anomalous frequency and temperature dependence of the ac susceptibility at the SG transition of $BiFeO_3$ (BF) is not linked with the spin cycloid as it is present even after the destruction of the spin cycloid in disordered BF with 20% $BaTiO_3$ substitution (0.80BF-0.20BT). Neutron scattering studies reveal coexistence of LRO AFM and SG phase on the same magnetic sublattice in 0.80BF-0.20BT and removal of some component of the spins which take part in SG freezing. We have also presented evidence for change in unit cell volume around the SG transition in BF and 0.80BF-0.20BT highlighting the presence of magnetoelastic coupling at the SG transition. In addition, we also presented temperature variation of FE polarization, obtained from the analysis of neutron diffraction data, for 0.80BF-0.20BT which reveal sharp changes across the SG transition. All these observations confirm that the SG phase is intrinsic to 0.80BF-0.20BT and is not due to nano-sized impurities. For BF, there is a need to carry out neutron diffraction study as a function of temperature to provide unambiguous confirmation of the intrinsic nature of the SG transition similar to 0.80BF-0.20BT.[16]

ACKNOWLEDGMENTS

The authors acknowledge the collaboration with Dr. S. D. Kaushik and Dr. V. Siruguri, UGC-DAE Consortium for Scientific Research, Bhabha Atomic Research Centre (BARC), Mumbai-400085, India for neutron powder diffraction.

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