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The Supplementary Document for the paper “Superspin Glass Mediated Giant Spontaneous Exchange Bias in a Nanocomposite of BiFeO_3 - $\text{Bi}_2\text{Fe}_4\text{O}_9$ ”

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This supplementary document contains detailed results from high resolution powder x-ray diffraction (XRD), transmission electron microscopy (TEM), and magnetic measurements. They are organized as follows: first, we are showing the room temperature x-ray diffraction data refined by FullProf. The refinement yields the microstructural details such as (a) crystallite size, strain and (b) volume fraction of each phase as well as crystallographic details such as (a) lattice parameters, (ii) atom positions, (iii) bond length and angle etc. In Fig. 1 of this supplementary document, the Rietveld refined x-ray diffraction data are given. In Table-I we give the detailed results of the refinement. The average grain size for BiFeO_3 phase is ~ 112 nm whereas that for $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase is ~ 19 nm in sample-A. In sample-B, the grain size for BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ phases turn out to be ~ 30 nm and ~ 8 nm, respectively. In sample-C, the average grain size for BiFeO_3 phase is ~ 12 nm. The volume fraction of $\text{Bi}_2\text{Fe}_4\text{O}_9$ phase in sample-A is $\sim 6\%$ whereas for sample-B and C they are $\geq 10\%$, and $\leq 3\%$.

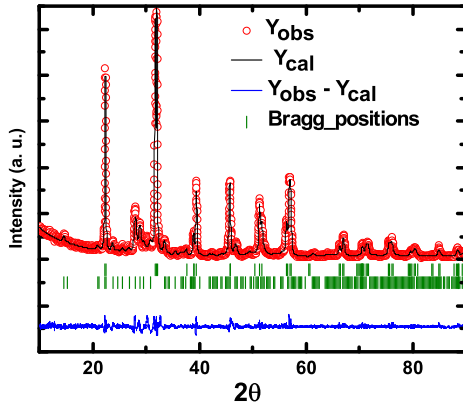


FIG. 1: (color online) The room temperature x-ray diffraction pattern of the nanocomposite. The pattern has been refined by FullProf.

In Fig. 2, we show the bright and dark field (BF/DF) TEM images of the sample-A. A comparison of the BF/DF images shows an intimate mixing of the two phases which has given rise to a high interface density in

sample-A. The selected area electron diffraction (SAED) patterns as well as high resolution TEM (HRTEM) images have also been recorded. The particles are single crystalline. The spots in the SAED images have been indexed by taking into consideration the distance between the lattice planes d , angle between the planes ϕ , as well as the Weiss zone law. Detailed study of the SAED patterns helped in identifying the zone axes for both the BiFeO_3 and $\text{Bi}_2\text{Fe}_4\text{O}_9$ particles. The tilt between the crystals turn out to be $\sim 19^\circ$ for a test case. The convergent beam electron diffraction (CBED) patterns have also been recorded (data not shown) at a few places of the composite. The diffraction spots have been indexed accurately using the method described above. However, a detailed mapping of the variation in tilt across the entire matrix of the nanocomposite could not be completed due to lack of satisfactory images from different regions of the nanocomposite. The scale of mixing of the phases and the resolution at which the images could be captured differed by a large extent at many places.

In Fig. 3, we show the (a) full hysteresis loops corresponding to the data shown in Fig. 1a of the main paper and (b) the full hysteresis loops corresponding to the data shown in Fig. 1b of the paper. Likewise in Fig. 4, we show the full hysteresis loops corresponding to the Figs. 1c and 1d of the paper. The full hysteresis loops measured under zero-field cooled condition for determining the SEB in sample-B are shown in Fig. 5a. The asymmetry in the SEB at 5 K for sample-B, depending on the sign of the starting field and the path followed in tracing the loop, is shown in Fig. 5b. The Fig. 5c shows the variation in SEB and coercivity H_C with field at 5 K for the sample-B. In Fig. 6 of this document, we show the hysteresis loops measured following field cooling under $+5\text{T}$. In Fig. 7a, we show the hysteresis loops measured following zero-field cooling for sample-C. Fig. 7b shows the blown-up portion of the loops around the origin.

Apart from checking the memory effect and its time dependence at lower temperatures (discussed in the main text), we have examined its presence in sample-A at $T_w \sim 100$ K as well. In Fig. 8, we show the characteristic dip at ~ 100 K which signifies the presence of superspin glass moments even at ~ 100 K. We have also verified the presence of superspin glass moments in sample-B below

TABLE I: Structural details of the phases in the nanocomposite from FullProf refinement of x-ray diffraction data.

Phase	Lattice Parameters (Å)	Ions	Wyckoff Positions	x	y	z	Bonds	Length (Å)	Bonds	Angle (°)	Crystallite Size	Volume Fraction
BiFeO ₃ (R3c)	a = 5.579(5) c = 13.863(7)	Bi	6a	0.0	0.0	0.0	Bi-O	2.282(3)	Fe-O-Fe	152.19(7)	111.9	93.89
		Fe	6a	0.0	0.0	0.2251(5)	Bi-O	2.499(5)	O-Bi-O	72.36(4)		
		O	18b	0.4392(3)	0.01530(6)	-0.0482(4)	Fe-O	1.918(5)				
							Fe-O	2.165(3)				
Bi ₂ Fe ₄ O ₉ (Pbam)	a = 7.976(6) b = 8.479(9) c = 6.008(3)	Bi	4g	0.1624(3)	0.1597(5)	0.0	Bi-O	2.461(3)	Fe-O-Fe	129.79(5)	19.3	6.11
		Fe1	4f	0.5	0.0	0.2669(3)	Bi-O	2.295(2)	O-Bi-O	65.72(3)		
		Fe2	4h	0.3682(5)	0.3356(7)	0.5	Bi-O	2.438(3)				
							Fe-O	2.092(4)				
		O1	2b	0.0	0.0	0.5	Fe-O	2.092(4)				
		O2	8i	0.3722(7)	0.2147(6)	0.2425(6)	Fe-O	1.545(7)				
		O3	4h	0.1337(4)	0.4039(2)	0.5	Fe-O	2.016(4)				
		O4	4g	0.1534(6)	0.4303(6)	0.0						

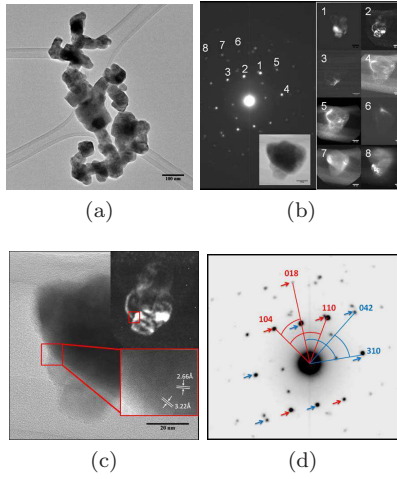


FIG. 2: (color online) (a) A representative bright-field TEM image of the nanocomposite; (b) the SAED patterns showing diffraction spots from both the phases; the dark-field images (marked by numbers) in the side panel shows the regions of the particles corresponding to the diffraction spots; inset shows the bright-field image of the region; the bright-field/dark-field images together with electron diffraction patterns from the regions show the dispersion of the phases and the interfaces in the nanocomposite; (c) a representative bright-field TEM image of an interface; top inset shows the dark-field image of the region while the bottom inset shows the HRTEM image of different orientation of the lattice fringes at the interface; (d) electron diffraction spots with their indexing corresponding to the pattern shown in (b); red and blue colors indicate the BiFeO₃ and Bi₂Fe₄O₉ phases, respectively.

the blocking temperature $T_B \sim 60$ K. In Fig. 9, we show the characteristic dip at $T_w \sim 21$ K in differential magnetization versus temperature plot signifying the memory

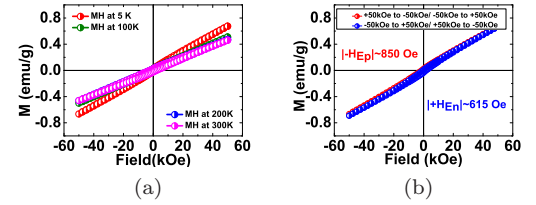


FIG. 3: (color online) (a) The complete form of the hysteresis loops measured under zero-field cooled condition to determine the spontaneous exchange bias (SEB) in sample-A; the portion near the origin is blown up in Fig. 1a of the main text to highlight the extent of SEB; (b) the complete form of the hysteresis loop measured at 5 K under zero-field cooled condition following two different paths - starting with +5T and -5T to show the difference in the extent of SEB (ΔH_E) depending on the sign of the starting field; a portion near the origin is blown up in Fig. 1c of the main text to highlight the asymmetry in SEB at 5 K.

effect. As expected, for sample-B no signature of this memory effect could be seen at ~ 100 K which is above T_B .

Finally, we discuss the importance of demagnetization prior to the measurement of the magnetic properties. The sample has been demagnetized by the following protocol: application of an oscillating field with varying amplitude; the amplitude reduces from maximum to zero. For example, for a demagnetizing field 1000 Oe, the amplitude is brought down to zero in the following sequence: (+1000)-(-900)-(+800)-(-700)...(+50)-(-40)...(+5)-(-4)-(+3)-(-2)-(+1)-(0). In Fig. 10, we show the difference in the ZFC, FC, and remanent magnetization for sample-A measured before and after demagnetization.

In order to check whether there is any trapped flux or

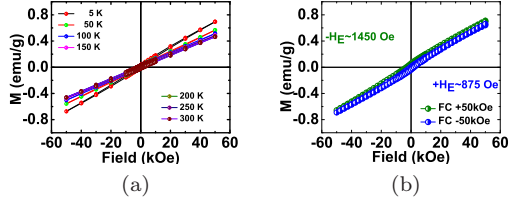


FIG. 4: (color online) (a) The complete form of the hysteresis loops measured following field cooling under a field of +5T to determine the conventional exchange bias (CEB) in sample-A; the portion near the origin is blown up in Fig. 1c of the main text; (b) the complete form of the hysteresis loops, measured at 5 K following field cooling under +5T, using two different tracing paths - one with +5T as the starting field and another with -5T as the starting field. It shows the difference in the extent of CEB (ΔH_E) depending on the sign of the starting field; a portion near the origin is blown up in Fig. 1d of the main text to highlight the asymmetry in CEB at 5 K.

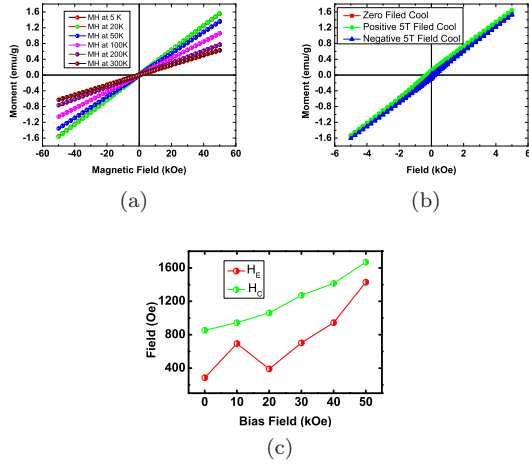


FIG. 5: (color online) (a) The hysteresis loops measured at different temperatures under zero-field cooled condition to determine the SEB in sample-B; (b) the hysteresis loops measured at 5 K via two different paths - with +5T or -5T as the starting field; (c) the field dependence of spontaneous exchange bias H_E and coercivity H_C at 5 K for sample-B.

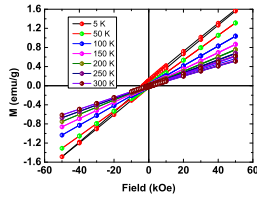


FIG. 6: (color online) The hysteresis loops measured at different temperatures following field cooling under +5T to determine the CEB in sample-B.

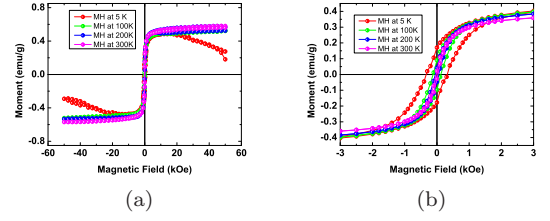


FIG. 7: (color online) (a) The hysteresis loops measured at different temperatures under zero-field cooled condition in sample-C; (b) portion of the loops near the origin is blown up.

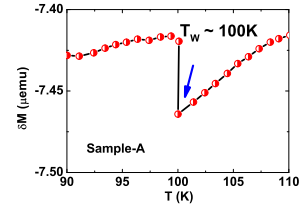


FIG. 8: (color online) The memory effect observed in sample-A at ~ 100 K.

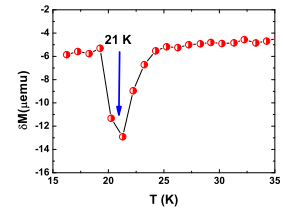


FIG. 9: (color online) The memory effect observed in sample-B at ~ 21 K; no such effect has been observed at ~ 100 K, i.e., above T_B (~ 60 K). This confirms the presence of superspin glass moments in sample-B as well below T_B .

not, we have measured the magnetization of a diamag-

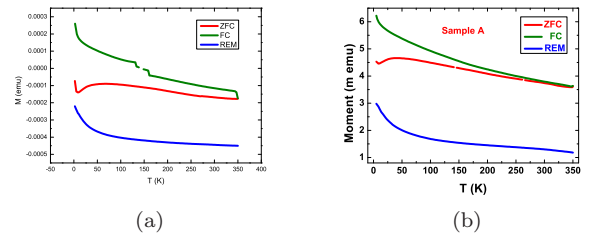


FIG. 10: (color online) The ZFC, FC, remanent magnetization measured in sample-A at (a) before and (b) after demagnetization.

netic sample - sapphire. The result is shown in Fig. 11. This result shows that no trapped flux is present.

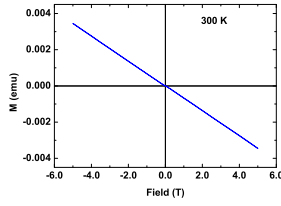


FIG. 11: (color online) The magnetization - field loop for diamagnetic sapphire at 300 K which confirms the absence of trapped flux.

The SEB has also been measured at 300 K, for a test case, after zero-field cooling from ~ 700 K which is well above the magnetic transition point T_N (~ 590 K) for sample-A. The result is shown in Fig. 12. The measurement of the loop, of course, could be done at 18 kOe. The SEB is found to be ~ 81 Oe which is quite consistent with what has been measured at 300 K after running the demagnetization protocol. The magnetization versus temperature plots for both sample-A and B are given in Fig. 13 which shows the T_N for them.

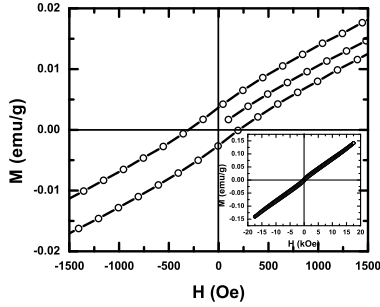


FIG. 12: (color online) The portion of hysteresis loop at 300 K blown up to show the SEB. This has been measured after ZFC from 700 K. inset shows full loop.

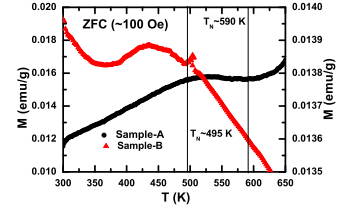


FIG. 13: (color online) The ZFC magnetization versus temperature plots for sample-A and B are shown

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