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The Supplementary Document for the paper “Superspin Glass Mediated Giant Spontaneous Exchange Bias in a Nanocomposite of BiFeO$_3$-$Bi_2Fe_4O_9$”

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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 $\sim$112 nm whereas that for Bi$_2$Fe$_4$O$_9$ phase is $\sim$19 nm in sample-A. In sample-B, the grain size for BiFeO$_3$ and Bi$_2$Fe$_4$O$_9$ phases turn out to be $\sim$30 nm and $\sim$8 nm, respectively. In sample-C, the average grain size for BiFeO$_3$ phase is $\sim$12 nm. The volume fraction of Bi$_2$Fe$_4$O$_9$ phase in sample-A is $\sim$6% whereas for sample-B and C they are $\geq$10%, and $\leq$3%.

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 $\phi$, 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 Bi$_2$Fe$_4$O$_9$ particles. The tilt between the crystals turn out to be $\sim$19° 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 +5T. 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 $\sim$100 K which signifies the presence of superspin glass moments even at $\sim$100 K. We have also verified the presence of superspin glass moments in sample-B below

\[ \text{FIG. 1: (color online) The room temperature x-ray diffraction pattern of the nanocomposite. The pattern has been refined by FullProf.} \]
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 effect. As expected, for sample-B no signature of this memory effect could be seen at $\sim 100$ 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 ($\Delta H_E$) 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 $\sim$100 K.

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

We have measured the magnetization of a diamag-
magnetic 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 $T_N$ ($\sim 500$ 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 $\sim 81$ 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.

![Magnetization-field loop](image)

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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