Tunable magnetic pole inversion in multiferroic BiFeO$_3$-DyFeO$_3$ solid solution

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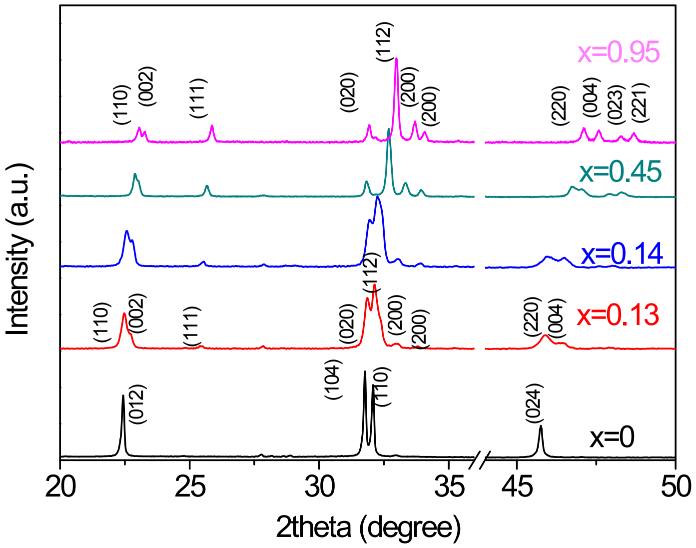


Figure S1 The enlarged XRD pattern of Bi$_{1-x}$Dy$_x$FeO$_3$ solid solutions (x=0, 0.13, 0.14, 0.45 and 0.91). The XRD pattern of BFO (x=0) can be indexed into a rhombohedra structure. The XRD pattern of x = 0.13 shows an orthorhombic phase. The XRD patterns of other BFO-DFO solid solutions (x > 0.13) can all be indexed into the orthorhombic phase. Since the ionic radius of Dy^{3+} ions is smaller than that of Bi^{3+} ions, the substitution of Dy^{3+} for Bi^{3+} decreases the unit cell volume. Consequently, the diffraction peaks shift to higher diffraction angles as the concentration of the Dy^{3+} ions increases.

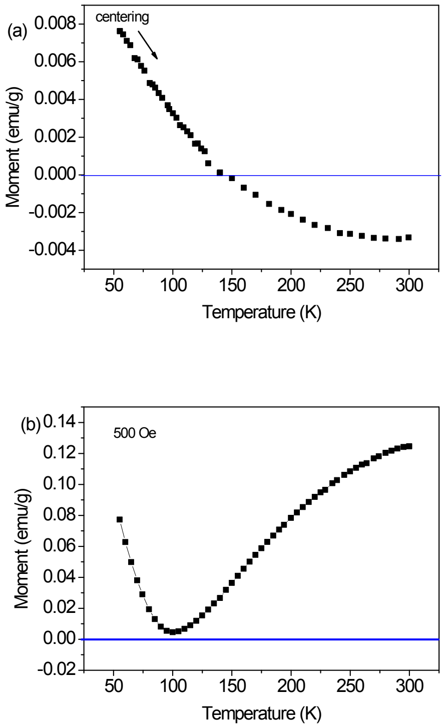
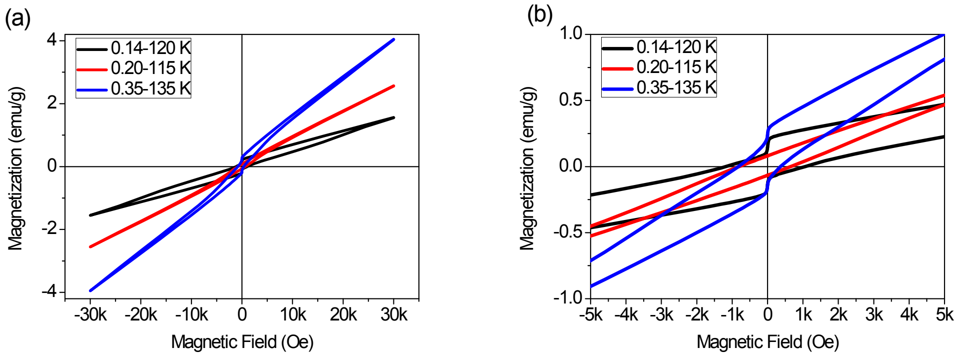


Figure S2 (a) Variation of the magnetization versus temperature for x=0.14 measured following a non-standard FC protocol: the virgin sample is cooled down to 50 K without centering and then magnetized in a weak field (after manually centering the sample holder) and its moment is recorded upon heating, ascertaining the intrinsic nature of the observed magnetic pole inversion. The insets indicate the schematic spin structures in the respective temperature ranges. (b) The field-cooling magnetization versus temperature curve for the x=0.14 sample measured at the field of 500 Oe.

It is worth noting that some extrinsic factors such as sample inhomogeneities and/or magnetization history could cause magnetic pole inversion[1]. In order to ascertain that the magnetization reversal observed above is intrinsic, not only all samples tested are virgin, but also another non-standard FC protocol is employed. For common magnetic measurements using a PPMS, MPMS or VSM system, a typical operation is to *center the sample* before the FC/ZFC protocols. During such operation, a magnetic field is applied to the sample and the magnetic moment is measured to acquire the center position (of the sample holder). After that, the FC/ZFC magnetization curves are recorded upon cooling down. In this measurement procedure, the virgin state of the sample is actually broken and the net magnetization might be initially oriented parallel to the field. If the magnetization reverse is intrinsic, the FC curves measured upon heating from low temperature (50 K) to room temperature (300K) are supposed to pass through zero as well. Therefore, we have developed the following non-standard FC protocol: a virgin sample of BFO-DFO (x=0.14) is cooled down to 50 K without centering and then magnetized in a weak field (after manually centering the sample holder) to record its moment upon heating. The results of such measurements are shown in Figure S2 (a). A positive magnetization is found at low temperature (because of the magnetic field poling) and it passes through zero at about 140 K and becomes negative at higher temperatures at 1 Oe. The magnetization changes its sign at 140 K, which is consistent with the data shown in Figure 1(a). This result confirms that the magnetic pole inversion observed in the BFO-DFO solid solution system is indeed intrinsic. When the external field is increased to 500 Oe, the magnetization exhibits a minimal value but does not pass through zero. This can be explained by magnetic field poling effect: the net moment of the sample is reoriented along the field direction and no negative magnetization is observe[2].

Figure S3 gives the M-H hysteresis loop of these corresponding samples. These M-H hysteresis loop at compensation temperature is typically weak ferromagnetism type, which arise from the DM interaction and paramagnetism of Dy ions.



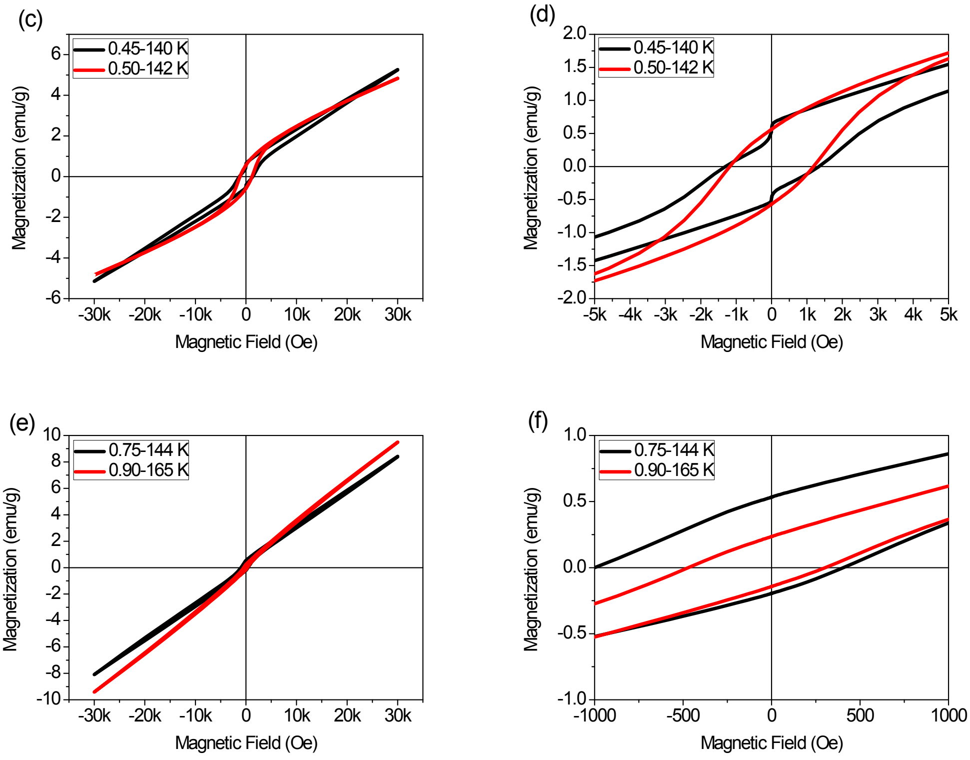


Figure **S3** M-H hysteresis loops of select samples measured at their compensation temperatures, respectively. (a) x=0.14 (black), 0.20 (red) and 0.35 (blue) samples, (c) x=0.45 (black) and 0.50 (red) samples, and (e) x=0.75 (black) and 0.90 (red) samples. (b) (d) and (f) are the enlarged loops.

References:

1. A. A. Belik, *Inorg. Chem.*, 2013, **52**, 2015-2021.
2. P. D. Kulkarni, U. V. Vaidya, V. C. Rakhecha, A. Thamizhavel, S. K. Dhar, A. K. Nigam, S. Ramakrishnan and A. K. Grover, *Phys. Rev. B*, 2008, **78**, 064426.