Nonmonotonic Magnetic Field Dependence of Remnant Ferroelectric Polarization in Reduced Graphene Oxide–BiFeO$_3$ Nanocomposite

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1. Introduction

The reconstruction of crystallographic, magnetic, and electronic structures at the interface turns out to be quite an effective way of preserving the multiferroic orders and augmenting the coupling among the order parameters in multiferroics-based heterostructures/composites.[1] Among different heterostructures or composites, graphene/BiFeO$_3$ or reduced graphene oxide–BiFeO$_3$ systems have attracted a lot of attention.[2–6] Large exchange field $B_{ex}$ (of the order from ten to hundred tesla) in graphene/BiFeO$_3$ heterostructure induces proximity effect-driven magnetism.[3,5] Among different heterostructures or composites, graphene/BiFeO$_3$ or reduced graphene oxide–BiFeO$_3$ systems have attracted a lot of attention.[1,5] Large exchange field $B_{ex}$ (of the order from ten to hundred tesla) in graphene/BiFeO$_3$ heterostructure induces proximity effect-driven magnetism.[3,5] While, in graphene/BaMnO$_3$ systems, the magnetic structure of BaMnO$_3$ exhibits change from antiferromagnetic-to-ferromagnetic orientation at the interface.[4] It has also been shown[7] that graphene–methylammonium lead iodide (CH$_3$NH$_3$PbI$_3$) composite exhibits ferroelectricity because of the reconstruction of the crystallographic structure in the interface regions. Given all these results, it is important to examine how reconstruction of magnetic and electronic structures by exchange-coupled surface atoms of graphene...
and nanoscale BiFeO₃ influences the multiferroicity in BiFeO₃. In this article, we report that the reduced-graphene-oxide–BiFeO₃ (RGO/BFO) nanocomposite exhibits significantly different multiferroic properties than what has been observed in bulk and nanoscale BiFeO₃. For example, the ferromagnetic component decreases yet coercivity rises and ferroelectric polarization exhibits remarkable nonmonotonic variation with applied magnetic field (H). In different systems, ferroelectric polarization is found to exhibit both increase and decrease under an applied magnetic field. For example, orthoferrite DyFeO₃ [8] or Z-type hexaferrite Sr₂Co₂Fe₂₄O₄⁴ [9] exhibits a rise in polarization under a magnetic field. Bulk BiFeO₃, on the other hand, exhibits [10] suppression of off-centering of Fe ions (and consequently, suppression of ferroelectric polarization (P)) below the magnetic transition temperature $T_N$ (off centering of Bi ions remains unaffected) as it is driven by negative bulk magnetostriction within the Fe–O–Fe spin structure. Therefore, one observes monotonic suppression of $P$ under $H$. Suppression of $P$ under $H$ is found to continue [11] across a magnetic field range as wide as 0–500 kOe and across a magnetic phase transition from spin cycloid to canted antiferromagnetic structure. In contrast, in the case of the RGO/BFO nanocomposite, the $H$ dependence of $P$ turns out to be nonmonotonic possibly because of field-dependent competition between positive and negative magnetostriiction arising, respectively, in the interface and bulk regions of the nanocomposite. Obviously, this is quite different from the $P$–$H$ patterns observed in bulk or nanoscale BiFeO₃.

2. Results and Discussion

Figure 1 shows the XRD data for Com-H and BFO-H. The data were refined by FullProf. Both Com-H and BFO-H were found to assume $R3c$ space group. BiFeO₃ assumes $R3c$ symmetry due to the presence of polar distortion and antiferrodistortive rotation of FeO₆ octahedra (which was shown [12] to be related to the magnetization) around the axis of polarization [11]. The detailed results of the refinement (lattice parameters, ion positions, and bond lengths) including the fit statistics are given in the supporting information document. The corresponding estimated standard deviation (which signifies the error bar) is also mentioned. Figure 2a,b shows the bright-field TEM and high-resolution TEM (HRTEM) images for Com-H. The image analysis yields the average size of BFO particles to be $\approx$18–20 nm, which is comparable with the particle size of BFO-H (shown in the supporting information). A certain fraction of the BFO particles are anchored onto the RGO layers. The HRTEM image shows the interface between (012) plane of BFO ($d = 0.39$ nm) and the RGO layer with interlayer spacing 0.51 nm. It indicates deposition of graphene layer onto the (100) plane of BiFeO₃. The interlayer spacing of RGO is much larger than that in graphite ($d = 0.37$ nm) due to exfoliation.

The Raman spectrometry of Com-H and BFO-H is shown in Figure 3a–c. The experiments were carried out with both 514 and 785 nm He–Ne laser excitations. It is found that the intensity ratio of the characteristic D and G peaks at 1332 and 1590 cm⁻¹, which, respectively, corresponds to the dangling bonds from defects containing $sp^2$-hybridized orbitals and planar vibration of C ions bonded via $sp^2$-hybridized orbitals, is 1.00 in Com-H. Using the relations [13,14] $I_D = [(1.8 \pm 0.5) \times 10^{-9} \times \lambda^4]/[I_G/I_C]$ and $n_D = 10^{14}/\pi L_D^2$, where $L_D$ is the effective distance between the defects (in nm), $n_D$ is the defect concentration (in cm⁻²), $\lambda$ is the wavelength of excitation, and $I$ is the intensity of the D or G peaks, we find that the defect concentration ($n_D$) and the spacing between the defects ($L_D$) in the RGO layers are $1.98 \times 10^7$ cm⁻² and 12.67 nm, respectively. The corresponding figures for graphite oxide (GO) are $2.77 \times 10^7$ cm⁻² and 10.70 nm, respectively. The decrease in defect concentration and increase in defect spacing in Com-H with respect to GO indicate lesser extent of functionalization of the graphene layer in Com-H.

The characteristic modes of BFO exhibit substantial red- and blueshifts in Com-H. According to group theory, there are 13 Raman-active modes of BFO with the rhombohedral $R3c$ structure, which are defined by the following irreducible representations [15] $\Gamma_{\text{Raman,}R3c} = 4A_1 \oplus 9E$, where four $A_1$ modes are polarized along z-axis and the rest 9 $E$ doubly degenerate modes are polarized along the $x$–$y$ plane. In BFO-H and Com-H (Figure 3b,c), nine active modes could be observed out of the 13 modes. The lineshape of the peaks was fit by Gaussian function. Their assignment together with the modes calculated from first-principles [15] are listed in Table 1.

The lower-order $A_1$ and $E$ modes are related to the Bi–O and Fe–O vibration, while the higher-order peaks arise due to the change in the oxygen motion states. A comparison of the Raman spectra observed in BFO-H and Com-H (Figure 3) reveals that 1) the lower-order modes (till $167$ cm⁻¹), influenced by Bi atoms, do not exhibit any substantial shift, while 2) the modes influenced by Fe ions and oxygen motion states are either red- or blueshifted. For example, the
$A_1(LO)/A_1(TO)$ and $E(TO)$ modes at $\approx 270$, $\approx 306$, and $\approx 443 \text{ cm}^{-1}$ are redshifted by $5$–$13 \text{ cm}^{-1}$, while the $E(LO)/E(TO)$ one at $\approx 337.5 \text{ cm}^{-1}$ is blueshifted by $\approx 13 \text{ cm}^{-1}$ in Com-H. This could be due to the change in the Fe–O bond lengths and the motion states of oxygen. The formation of Fe–C bonds at the BFO/RGO interface (discussed later) could have some influence on the bulk lattice and its distortion. The distortions in the Fe–O bonds have contributions from both polar distortion and antiferrodistortive tilt. The calculation of the Fe–O bond length (supporting information) shows that indeed the difference in the bond lengths decreased in Com-H. A similar observation has earlier been made by others\cite{17} in different perovskite oxide systems. The IR spectra too corroborate these observations together with the confirmation of the formation of RGO and are included in the supporting information document.
The high-resolution XPS data for Bi 4f and Fe 2p are shown in Figure 4a,b, respectively. The Bi 4f7/2 and 4f5/2 spin–orbit doublet peaks are located at 158.4 and 163.7 eV, respectively, which are found to correspond to Bi3+ states from Bi–O bonds. Interestingly, the binding energy of Bi3+ states remains same in both the BFO-H and Com-H samples. It indicates that no substitution has taken place at the Bi3+ sites in the Com-H sample. Of course, an additional weak pair of doublet peaks was observed in Com-H in the lower-binding energy side, which indicates the presence of Bi0 states. To estimate the percentage of Bi0 states in Com-H, we adopted the χ2 iterative fitting of the two pairs of doublet peaks. The Bi0 states 4f orbit doublet peaks are centered at 158.4 and 163.7 eV, respectively, in Com-H in the lower-binding energy side, which indicates the presence of Bi0 states. To estimate the percentage of Bi0 states in Com-H, we adopted the χ2 iterative fitting of the two pairs of doublet peaks. The Bi0 states 4f orbit doublet peaks are centered at 158.4 and 163.7 eV, respectively, in Com-H in the lower-binding energy side, which indicates the presence of Bi0 states.

Table 1. The Raman modes for com-h and BFO-H samples.

| Raman modes | BFO-H [cm⁻¹] | Com-H [cm⁻¹] | Calculated [cm⁻¹] |
|-------------|--------------|--------------|------------------|
| E(LO)       | 173.7        | 171.4        | 171.2            |
| A1(LO)      | 163.7        | 162.8        | 162.7            |
| A1(TO)      | 167.7        | 166.8        | 166.7            |
| A2(TO)      | 153.7        | 152.8        | 152.7            |
| A3(TO)      | 151.7        | 150.8        | 150.7            |
| A4(TO)      | 149.7        | 148.8        | 148.7            |
| A5(TO)      | 147.7        | 146.8        | 146.7            |

The Fe2p3/2 and Fe2p1/2 spin–orbit doublet peaks are located at around 709.6 and 722.9 eV, respectively, with a pair of shake-up satellite peaks located at 8.0 eV above their spin–orbit doublet peaks. We have carefully fitted the spectra using the following fitting parameters for Fe2+: spin–orbit splitting 13.3 eV, branching ratio 2.0, full width at half maximum (FWHM) 2.3 eV; and an integral background was subtracted before fitting. Similarly, the spectra for Fe3+ were fitted by considering spin–orbit splitting 13.8 eV, branching ratio 2.0, and FWHM 3.8 eV. The fitted Fe 2p spectra highlight the characteristic doublet peaks of Fe2+:O species at ≈709.6 and ≈722.9 eV for Fe2p3/2 and Fe2p1/2, respectively, and the doublet peaks of Fe3+:O species at ≈714.4 and ≈725.2 eV for Fe2p3/2 and Fe2p1/2, respectively. It is to be noted that the composite sample shows no change in the peak positions, except for the Fe3+ oxidation state which shows a shift of ≈0.6 eV toward higher binding energy. This chemical shift of Fe3+ arises due to the variation in the electronegativity of Fe and O in the composite sample. The Fe2+:Fe3+ ratio turns out to be 45.4:54.6 and 49.4:50.6 in BFO-H and Com-H, respectively.

Figure 5 shows the C 1s core-level spectra for both BFO-H and Com-H. The spectra corresponding to Com-H were fit using the contribution of the following six components: 1) defects; 2) O==C—O; 3) C==O; 4) C=C; 5) C==C; and 6) Fe—C bonds. The peak at 283.9 eV corresponds to the Fe—C bonds. Existence of this peak proves the presence of Fe—C bonds in the Com-H sample. Figure 6 shows the O 1s peak fit with the contribution from lattice oxygen, oxygen loss, and surface oxygen. Their characteristic peaks appear at lower, intermediate, and higher binding energies. For both the samples, the O 1s peaks were fitted by keeping the peak position, line shape, and the width same. The oxygen loss turns out to be 18.1 and 26.5%, respectively, for BFO-H and Com-H.

We analyzed the C 1s spectra for Com-H quantitatively for determining the concentration of different bonds such as Fe—C, C==C, O==O, O—O, O—C—O and compared the results with those obtained from the analysis of the spectra (Figure 7) for pure GO. The comparison is given in Table 2. The concentration...
of C=C bonds is found to have decreased in Com-H in comparison with that in GO because of the rise in the Fe─C bonds in Com-H. The difference between the concentration of C=C bonds alone in GO and that of C=C and Fe─C bonds (≈3%) in Com-H is accounted for in the rise in C─C bonds in Com-H. Expectedly, the concentration of O─C─O and O─C─O bonds decreased in Com-H because of reduction of GO in the composite. The presence of C─C bonds also indicates that not all the surface carbon ions of graphene are bonded to the Fe ions of BiFeO₃ particles. Therefore, both bonded and nonbonded BiFeO₃ particles coexist in the Com-H sample. As discussed later, relative concentration of the bonded BiFeO₃ particles plays an important role in governing the magnetoelectric properties of the nanocomposite.

To examine the interface region and its variation with the wt% of the RGO in BFO/RGO nanocomposites, we, as well, carried out XPS on the samples containing 0.5 and 2.5 wt% RGO. The XPS data and their fitting together with the results obtained from such analysis have been given in the supporting information. Remarkably, the concentration of the Fe─C bonds is found to vary directly with the wt% of RGO in the nanocomposite. From nearly 24.3% in the sample with 0.5 wt% RGO, the Fe─C bond concentration decreased to nearly 22.7% in Com-H to even ≈6.3% in the sample with 2.5 wt% RGO. Because of higher surface area, the Fe─C bond concentration is higher in the sample containing smaller wt% RGO. As discussed later, this variation influences the magnetic properties significantly.

Figure 8 shows the room-temperature magnetization (M) versus field (H) hysteresis loops for Com-H and BFO-H.
Contrary to the prediction made\(^4\) in the case of graphene/BaMnO\(_3\), the ferromagnetic component is found to have weakened in Com-H. The magnetization (M) does not tend to saturate (M\(_{20\text{kOe}}\) = 0.017 and 0.17 emu g\(^{-1}\), respectively, for BFO-H and Com-H) within the applied field limit (\(\pm 20\) kOe). The coercivity (H\(_C\)), of course, turns out to be much larger in Com-H (H\(_C\) = 38 and 190 Oe, respectively, for BFO-H and Com-H). It is well known now that, for BFO, the nanoparticles exhibit enhancement in the ferromagnetic component because of larger spin canting and incomplete spin spiral (this is effective in particles smaller than \(\approx 62\) nm, the wavelength of the spin spiral in BiFeO\(_3\)). It has been shown\(^1\) from the powder neutron diffraction experiment that the canting angle could enhance to \(\approx 6^\circ\) (from \(\approx 1^\circ\) in bulk sample\(^2\)) in particles of size \(\approx 25\) nm.

In the present case, variation of the ferromagnetic component could result from the change in the charge states of ions and the formation of Fe—C bonds at the RGO/BFO interface in Com-H. The Fe—C exchange coupling interaction (which leads to exchange splitting of the Dirac bands in graphene layer as well as renormalization of the Fe moments in the interface; exchange field was shown\(^3\) to be of the order of 10—100 T at the BiFeO\(_3\)/graphene interface) possibly gives rise to the renormalization of the exchange coupling parameters at the bulk as well which, in turn, could give rise to drop in the spin-canting angle. The ferromagnetic component, therefore, weakens. Interestingly, in spite of weakening of the ferromagnetic component, the coercivity (H\(_C\)) turns out to be larger in Com-H. The pinning of domains by defects appears to be stronger in Com-H. Because of the surface ferromagnetism and core antiferromagnetism, a small amount of exchange bias field (H\(_E\)) could also be observed (H\(_E\) = 31 and \(-25\) Oe, respectively, for BFO-H and Com-H).

We have also examined the magnetic properties of the nanocomposites containing 0.5 and 2.5 wt% RGO. Interestingly, the parameters such as magnetization at 20 kOe field M\(_{20\text{kOe}}\) and saturation magnetization M\(_S\), of course, turns out to be much larger in Com-H (H\(_C\) = 38 and 190 Oe, respectively, for BFO-H and Com-H).

The change in the loop shape results from change in magnetic anisotropy. Using Akulov function M(H) = M\(_S\)[1 - (1/15)](H\(_S\)/H)] and H\(_S\) = 2K/M\(_S\) (M\(_S\) is the saturation magnetization), we could calculate the overall magnetic anisotropy K. The results are given in the supporting information document. Clearly, large variation in K reflects influence of the variation in the interface region in the nanocomposites containing different wt% RGO. Combining the results obtained from the XPS and the magnetic hysteresis loop measurements, it is possible to observe that from pure BiFeO\(_3\) to nanocomposites of BiFeO\(_3\)/RGO containing different wt% RGO, the magnetic properties, such as hysteresis loop shape, anisotropy, H\(_C\), M\(_S\), M\(_{20\text{kOe}}\), exhibit direct correlation with the concentration of the Fe—C bonds.

Multiferroicity in the BFO/RGO nanocomposite was further examined by powder neutron diffraction experiments. The neutron diffraction data were recorded on the Com-H sample at room temperature under different magnetic fields across 0–20 kOe. We considered collinear spin structure. Long spiral length (\(\approx 62\) nm) in BiFeO\(_3\) allows such consideration. The data were refined by FullProf by considering the R3c space group and \(\Gamma_1\) irreducible representation (propagation vector k = 0). Group theory analysis of the spin structure for R3c and propagation vector k = 0 yields three irreducible representations \(\Gamma_1\), \(\Gamma_2\), and \(\Gamma_3\) (reducible representation \(I(\text{Fe, } 6a) = \Gamma_1 + \Gamma_2 + 2\Gamma_3\)). Refinement shows that \(\Gamma_1\) (G-type antiferromagnetic structure) offers the best fitting (supporting information). The refinement is shown in Figure 9. The lattice parameters, magnetic moment, ion positions, and the fit statistics are included in the supporting information document. The variation of the magnetic moment along c-axis (c\(_j\)) with the applied magnetic field together with the collinear spin structure corresponding to \(\Gamma_1\) is shown in Figure 10. The nonmonotonic field dependence of c\(_j\) possibly reflects field-dependent competition between interface and bulk magnetization and consequent renormalization of the average bulk magnetic moment calculated from powder neutron diffraction by considering collinear G-type spin structure \(\Gamma_1\). Interestingly, the lattice volume (V\(_1\)) is found to decrease and then increase (Figure 10), indicating switch from negative to positive magnetostriiction as the applied magnetic field is enhanced across 0–20 kOe. This could be (as discussed later) due to field-dependent competition between bulk and interface magnetic anisotropy. The anticorrelation between c\(_1\) and V\(_1\) is notable. While c\(_1\) (V\(_1\)) increases (decreases) with increase in applied field (H) initially, they exhibit a converse trend thereafter (Figure 10). Such anticorrelation has not been reported in pure BiFeO\(_3\).

We finally discuss the results of the measurement of intrinsic structural off-centering by high-resolution powder neutron diffraction under different magnetic fields. The net off-centering within a unit cell was estimated from the off-centering of Bi and Fe ions (s and t, respectively) along the polarization axis\(^3\) in the hexagonal setting as well as from off-centering of the Bi and Fe ions with respect to their oxygen cages. It is important to point out here that high-resolution neutron diffraction is more effective than XRD in determining the crystallographic structure (including ion positions) which contains lighter ions such as oxygen. The magnetic field (H) dependence of net off-centered displacement (δ) in the unit cell, estimated from the powder neutron diffraction data, is plotted in Figure 11. Interestingly, δ exhibits nonmonotonic pattern of variation with the magnetic field (H) across 0–20 kOe. This is the central result of this paper. We also used the positive-up-negative-down (PUND)

\(^20\) and remanent ferroelectric hysteresis loop protocols\(^21\) for the direct electrical measurement of remanent polarization (P\(_R\)) on an assembly of nanoparticles (supporting information). Interestingly, in spite of the influence of several factors such as the presence of surface defects, poor particle—particle electrical connectivity, poor electrode—nanoparticle connectivity, etc., the net magnetic field dependence of P\(_R\) turns out to conform to the nonmonotonic pattern obtained from the analysis of powder neutron diffraction data. The nonmonotonic nature of P\(_R\) – H in RGO/BFO nanocomposite, therefore, is intrinsic. Pristine BiFeO\(_3\), on the contrary, exhibits monotonic suppression of P\(_R\) with the increase in magnetic field because of negative magnetoelectric coupling\(^19\). Stabilization of the R3c structure in BiFeO\(_3\) yields coupled polarization and magnetization via coupling between polar distortion and antiferrodistortion of FeO\(_6\) octahedra. It has been demonstrated\(^22\) that indeed the deterministic 180° switching of magnetic domains takes place (as a result of that of the ferroelectric domains) under electric field in two steps, first,
Figure 9. Powder neutron diffraction data and their refinement by FullProf; R3c and \( \Gamma_1 \) phases have been considered; the data were recorded at room temperature under different magnetic fields: a) 0 kOe, b) 5 kOe, c) 10 kOe, d) 15 kOe, and e) 20 kOe.

Figure 10. a) The variation of the lattice volume and magnetic moment along c-axis with field obtained from the refinement of neutron diffraction data. b) The spin structure corresponding to \( \Gamma_1 \) irreducible representation.
in-plane rotation by 71° and then out-of-plane rotation by 109°. Piezo- and magnetostriction associated with this complex pathway of domain rotation influences the magnitude of the polarization and magnetization of the domains.

As the magnetic field is swept from zero to a maximum, negative magnetoelastic coupling (arising from influence of negative magnetostriction on piezoelectricity) in pure BiFeO$_3$ yields decrease in polarization with increase in magnetization.\cite{10} Suppression of polarization under magnetic field was observed not just in bulk form of the sample but in nanoscale samples as well.\cite{23} The bulk and surface magnetocrystalline anisotropy ($K_B$ and $K_S$) results in negative bulk and surface magnetostriction ($\lambda_B$ and $\lambda_S$) in nanoscale BiFeO$_3$, assuming R3c structure. Negative magnetostriction leads to negative magnetoelastic coupling, that is, suppression of polarization under magnetic field. In an assembly of single-crystalline nanoparticles, averaging over the domain configurations and the properties, therefore, yields similar decrease (increase) in polarization (magnetization) at any given state. This magnetostrictive suppression of piezoelectricity, observed in pure BiFeO$_3$, can be altered and consequent enhancement of magnetostriction-driven polarization is possible. In BiFeO$_3$/reduced graphene oxide nanocomposite, emergence of Fe–C bonds (from strong hybridization of 3$d_z^2$–$p_z$/3$d_z^2$ orbitals of Fe and $p_z$ orbitals of C) and consequent magnetization at the graphene–BiFeO$_3$ interface regions open up this possibility. It has already been shown$^{[5,24]}$ that the Fe–C bonding leads to the generation of a large exchange field (of the order of 10–100 T) which gives rise to the split of the Dirac bands in the graphene layer as well as proximity-induced magnetization. This exchange field alters the magnetization at the interface reflected in the enhancement of the antiferromagnetic component in RGO/BFO nanocomposite. Change in the magnetic moment at the interface was earlier predicted by theoretical calculations.$^{[25]}$ The anisotropy ($K_I$) associated with this interface magnetization could yield positive surface magnetostriction. This, in turn, could give rise to the rise in $P_R$ with $H$, that is, positive magnetoelastic coupling. It has been shown$^{[26]}$ earlier that indeed the ratio of surface/interface anisotropy and bulk anisotropy ($K_I/K_B$) governs the spin structure significantly.

A different structure emerges as $K_I$ or $K_S$ increases with respect to $K_B$. Therefore, different spin structures at the interface change the magnitude of $K_I$ with respect to that of $K_B$, which, in turn, yields positive interface magnetostriiction. Field-dependent switch from negative to positive magnetostriiction has indeed been observed in the present case (Figure 10). The mapping of lattice volume ($V_L$) with the applied magnetic field (Figure 10) shows decrease and then increase in $V_L$ as the field is swept across 0–20 kOe. This observation underlines the important role of interface magnetization arising from the Fe–C bonds. Of course, how $K_I$, in the present case, yields positive interface magnetostriiction and how the ratio $K_I/K_B$ governs the field-dependent switch in magnetostriiction, from negative to positive, have to be studied in detail separately.

Based on earlier discussion, in Figure 12, we present the schematic of the model which describes the physics behind the observed nonmonotonic $P_R$ – $H$ pattern. The Com-H sample contains both bonded (via Fe–C bonds) and nonbonded (attached via van der Waals bonds) BiFeO$_3$ particles. While magnetostriiction due to symmetric exchange interaction across Fe–O–Fe bonds, in the absence (relevant for BFO-H) and presence of proximity coupling via formation of Fe–C bonds (relevant for Com-H because of the presence of these bonds at the interface regions), yields, respectively, negative and positive magnetoelastic coupling, the field-dependent competition (shown in Figure 12) between the positive and negative magnetoelastic coupling in bonded and nonbonded BiFeO$_3$ particles yields the observed nonmonotonic pattern of variation of $P_R$ with $H$. $P_R$ decreases initially and then rises and finally decreases again as the applied magnetic field is swept from 0 to $\approx$20 kOe. Relative volume fraction of the bonded and nonbonded BiFeO$_3$ nanoparticles, therefore, governs the relative strength of increase and decrease in the $P_R$ as a function of $H$. The coexistence of positive and negative magnetostriictive regions and engineering of their respective volume fractions have earlier been demonstrated$^{[27]}$ within the bulk of the Fe–Ga alloys. This was projected to yield field-dependent switch in ferroelectric polarization in ferroelectric/Fe–Ga alloy multilayer composites. In the present case, reconstruction of the interface

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**Figure 11.** (a) The variation of unit cell off-centered displacement, $s_c - t_c$ (left axis), and net off-centering with respect to the oxygen cages (right axis) obtained from refinement of powder neutron diffraction data; b) section of the R3c crystallographic structure is shown in hexagonal setting to highlight the off-centered displacements of Bi ($s_c$) and Fe ($t_c$) ions along $^{[1]}$.
in reduced-graphene-oxide/BiFeO$_3$ nanocomposite is shown to actually yield the result projected in the study by Gou et al. Engineering of the bulk and interface anisotropies and hence of the bulk and interface magnetostriictions further could yield eventually an interesting custom-designed periodic nonmonotonic pattern of variation of $P_r$ with $H$. This will assume immense significance in the context of the emerging field of straintronics$^{28}$, and thus expand the horizon of applications of single-phase-multiferroic/graphene nanocomposite or heterostructure by a great extent.

**3. Conclusion**

In conclusion, the RGO/BFO nanocomposite exhibits a range of interesting properties. The ferromagnetic component of the spin structure weakens while the coercivity exhibits significant enhancement, from $\approx$38 Oe in pure BiFeO$_3$ to $\approx$190 Oe in the composite. Finite negative exchange bias has also been observed in the composite. Most importantly, the ferroelectric remanent polarization as well as the net off-centered displacement of the ions within the unit cell is found to exhibit a nonmonotonic dependence on the applied magnetic field. We show that this remarkable nonmonotonic field dependence of polarization results from field-dependent competition between the negative and positive magnetostriction at the bulk and interface of the composite. This competition yields the field-dependent switch in the variation of the unit cell volume with the magnetic field, from decrease to increase as the field is enhanced across 0–20 kOe. While pure bulk BiFeO$_3$ is known to exhibit negative magnetostriction and hence negative magnetoelectric coupling which results in decrease in ferroelectric polarization under a magnetic field, observation of competition between negative and positive magnetostriction and hence between negative and positive magnetoelectric coupling in the reduced graphene oxide–BiFeO$_3$ nanocomposite reveals the significant role played by the Fe–C bonds. A significant role of Fe–C bonds in the nanocomposite could be further observed in the samples containing different wt% RGO (e.g., 0.5 and 2.5) and hence different concentrations of Fe–C bonds. The magnetic properties were found to change significantly with the change in the Fe–C bond concentration. This reconstruction of the BiFeO$_3$/graphene interface via formation of Fe–C bonds could find many applications in the area of straintronics because of field-driven tuning of compressive and tensile lattice strain. It could also trigger fresh research on atomic scale engineering of the interfaces in the composites or heterostructures for far enhanced functionalities.

**4. Experimental Section**

The RGO/BFO nanocomposite was prepared by the hydrothermal technique. Graphene oxide (GO) was prepared from graphite via the modified Hummers method$^{29}$ in which 70 mL of sulfuric acid ($\text{H}_2\text{SO}_4$, > 98% Merck) was taken within an ice bath (for maintaining the temperature below 2°C) and 1 g of graphite powder (<20 μm from Sigma-Aldrich) and 0.5 g of sodium nitrate (NaNO$_3$, > 97% Sigma-Aldrich) were added to the acid solvent and stirred for a while. After that, 3 g of potassium permanganate (KMnO$_4$, 99% Merck) was added gradually and stirred vigorously. We allowed the bath temperature to stabilize and then removed the ice bath to attain room temperature. The mixed solution was stabilized at room temperature for 2 h and then diluted by adding 5% hydrogen peroxide ($\text{H}_2\text{O}_2$, 30% Merck) solution slowly till the color turned brownish yellow. It confirmed complete oxidation of graphite. Finally, the solution was stirred for 30 min to further exfoliate the as-formed graphite oxide (GO). The GO, thus synthesized, was collected by filtration and washing several times with 1 N hydrochloric acid (HCl, 37% Merck) and deionized water. Synthesized GO and BFO precursors [Bi(NO$_3$)$_3$$\cdot$5H$_2$O, > 98% Sigma-Aldrich] and Fe(NO$_3$)$_3$$\cdot$6H$_2$O, > 98% Sigma-Aldrich] were used for the hydrothermal synthesis$^{10}$ of the composite. The aqueous solution of GO was reduced to form reduced graphene oxide (RGO) using ascorbic acid (>99% Merck) as the reducing agent. The 8 M potassium hydroxide (KOH) and the precursors of BFO were added in stoichiometric ratio. Once homogenized, the as-prepared RGO solution was added to the mixture to maintain 1.50 wt% of RGO in the resulting mixture. The ammonium hydroxide (NH$_4$OH, 28–30% Merck) was added in 1.0 wt% to facilitate the formation of BiFeO$_3$ nanoparticles embedded in the RGO matrix. The solution was stirred for 30 min and put into a preheated autoclave for hydrothermal treatment at 170 °C for 2, 4, 5, 6 h. The sample treated hydrothermally for 6 h turned out to be phase pure and was designated as Com-H. The nanocomposite Com-H was further heated to 550 °C for 20 min. This sample removed the carbon skeleton and left the bare nanoparticles of BiFeO$_3$. This sample was designated as BFO–H. The thermogravimetric analysis was carried out under both air and inert (Ar) atmosphere to track the formation of BFO-H. Other samples with 0.5 and 2.5 wt% of RGO were also prepared following this procedure for examining how variation in covalent bonding in the interface region influenced, for example, the magnetic properties.

All the samples were characterized by powder X-Ray diffraction (XRD), infrared (IR) and Raman spectrometry, scanning and tunneling electron microscopy (SEM and TEM), and X-Ray photoelectron spectroscopy (XPS). The XPS measurements were performed by PHI 5000.
VERSAPROBE II, Physical Electronics System, equipped with a monochromatic Al Kα (1486.7 eV)-focused X-Ray source and a multichanneltron hemispherical electron energy analyzer. All the spectra were collected at an emission angle of 45° with the base vacuum of 5.0 × 10⁻¹⁰ mbar. The binding energies were referenced by measuring C 1s and keeping it at 284.6 eV. The total energy resolution was estimated to be ≈400 meV for monochromatic Al Kα line with pass energy of 11.750 eV. A charge neutralizer was used to compensate the surface charging of the samples. A background was subtracted from the measured raw data. The magnetic hysteresis loops were measured by LakeShore vibrating sample magnetometer (VSM; Model 7407) under ±20 kOe field at room temperature, while the ferroelectric polarization was measured by the Precision LC-II (Radiant Technologies Inc.) ferroelectric loop tester. For preparing the samples for electrical measurements, nanoparticles were dispersed within ethanol and spin coated onto the SiO₂ substrate to form films (supporting information document). Thickness of the film was ≈10 nm, as measured by ellipsometry. Silver dots were used as electrodes. The powder neutron diffraction patterns were recorded at room temperature at the PD-3 beamline of National Facility for Neutron Beam Research (NFNBR), Dhruva Reactor, Mumbai, using a monochromatic beam of wavelength 2.315 Å. The magnetic field was varied across 0–20 kOe.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the Supporting Information of this article.

Keywords
BiFeO₃/multiferroics, nanocomposites, powder neutron diffraction, reduced graphene oxide, X-Ray photoelectron spectroscopy

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