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Anomalous coercivity enhancement with temperature and tunable exchange bias in Gd and Ti co-doped BiFeO₃ multiferroics

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Abstract

We have investigated the effects of temperature on the magnetic properties of the $Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO_3$ (x = 0.00-0.20) multiferroic system. Unexpectedly, the coercive fields (H_c) of this multiferroic system increased with increasing temperature. The coercive fields and remanent magnetization were higher over a wide range of temperatures in sample x = 0.10, i.e. in a sample with a composition $Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O_3$ than those of x = 0.00 and 0.20 compositions. Therefore, we carried out temperature-dependent magnetization experiments extensively for sample x = 0.10. The magnetic hysteresis loops at different temperatures exhibit an asymmetric shift towards the magnetic field axes, which indicates the presence of an exchange bias effect in this material system. The hysteresis loops were also carried out at temperatures of 150 K and 250 K by cooling down the sample from 300 K in various cooling magnetic fields (H_{cool}). The exchange bias field (H_{EB}) values increased with H_{cool} and decreased with temperature. The H_{EB} values were tunable by field cooling at temperatures of up to 250 K.

Keywords: magnetism, multiferroics, coercivity, exchange bias

S Online supplementary data available from stacks.iop.org/JPhysD/49/095001/mmedia

(Some figures may appear in colour only in the online journal)

I. Introduction

Multiferroic materials, in which ferromagnetic, ferroelectric and/or ferroelastic orderings coexist, have attracted significant research interest for many years [1-5] due to their potential applications in data storage media, spintronics and ferroelectric random-access memories. The co-existence of 'ferro'-orders in multiferroics allows the possibility that the magnetization can be tuned by an applied electric field, and vice versa. Among the limited choices offered by the multiferroic materials, BiFeO₃ (BFO), one of the single-phase multiferroic materials at room temperature, exhibits the coexistence of ferroelectric ordering with a Curie temperature ($T_{\rm C}$) of 1123 K and antiferromagnetic (AFM) ordering with a Néel temperature ($T_{\rm N}$) of 643 K [6]. In BiFeO₃, the magnetic ordering is of the antiferromagnetic type, having a spiral modulated spin structure (SMSS) with an incommensurate long-wavelength period of 62 nm [6]. This spiral spin structure cancels the macroscopic magnetization and inhibits the



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observation of the linear magnetoelectric effect [7]. These problems ultimately limit the use of bulk BiFeO₃ in functional applications. Recent investigations demonstrated that in order to perturb the SMSS and improve the magnetic properties of BiFeO₃, the partial substitution of Bi by rare-earth ions [8, 9] or alkaline-earth ions [10], and also the substitution of Fe by transition metal ions [11, 12], is an effective route. It is also reported that the simultaneous minor substitution of Bi and Fe in BiFeO₃ by ions such as La and Mn, La and Ti, Nd and Sc etc, respectively [13–15] also enhanced the magnetism and ferroelectricity in BiFeO₃.

Recently, we observed that the simultaneous substitution of Gd and Ti in place of Bi and Fe, respectively in BiFeO₃ multiferroics improved their morphological, dielectric and magnetic properties at room temperature [16]. Later on, another group also observed fascinating magnetic, optical and dielectric properties in this Gd and Ti co-doped BiFeO₃ ceramic system at room temperature [17]. Therefore, in this investigation, we were interested in conducting experiments on the temperature dependence of the magnetic properties of Gd and Ti co-doped $Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO_3$ (x = 0.00–0.20) multiferroic materials. In particular, our interest is in investigating the effects of temperature on the remanent magnetization, coercive fields and exchange bias (EB) fields of these bulk polycrystalline materials. Notably, the EB phenomenon, which manifests itself by a shift of a magnetic hysteresis loop in systems containing ferromagnetic/antiferromagnetic bilayers, has been studied extensively for many years due to its importance in spintronic applications [18]. The EB effect usually occurs when the system is cooled down in an external magnetic field through the magnetic ordering temperatures. Most of the research in this field is focused on specially prepared systems, although recent investigations have reported the presence of the EB effect in perovskite manganites [19], cobaltites [20], Heusler alloys [21] and multiferroics [22]. Although EB has been observed in various bulk materials, the effect in most cases has been limited to far below room temperature (<100 K) [23, 24], thus making the systems less attractive for applications.

In our previous investigation, the magnetization versus magnetic field (*M*–*H*) hysteresis loops indicated the presence of the exchange bias effect in Gd and Ti co-doped $Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO_3$ (x = 0.00-0.20) ceramics at room temperature, although the biasing field was very small [16]. Therefore, in the present investigation, we have explored the exchange bias effect in this material system at different temperatures ranging from 20 K to 300 K. We have also investigated the influence of cooling magnetic fields at temperatures of 150 K and 250 K to observe a tunable exchange bias in a sample composition $Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O_3$ (this composition is referred to as sample x = 0.10 throughout the manuscript).

II. Experimental details

The polycrystalline samples with compositions $Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO_3$ (*x* = 0.00–0.20) were synthesized by

using a standard solid state reaction technique, as described in detail in our previous investigation [16]. The powder materials and ceramic pellets sintered at 1100 K were used for the magnetic characterization. The *M*–*H* hysteresis loops of Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO₃ (x = 0.00-0.20) multiferroic ceramics were carried out at different temperatures using a Superconducting Quantum Interference Device (SQUID) Magnetometer (Quantum Design MPMS-XL7, USA). The temperature-dependent magnetization measurements were carried out both at zero field cooling (ZFC) and field cooling (FC) processes [25]. The magnetic hysteresis loops were also carried out at different temperatures by cooling down the sample from 300 K in various cooling fields (H_{cool}) [25].

III. Results and discussions

III.A. Magnetic characterization

For magnetic characterization, the M-H hysteresis loops of the Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO₃ (x = 0.00-0.20) samples were measured at different temperatures ranging from 20 K to 300 K with an applied magnetic field of up to ± 50 kOe. As a typical example, the *M*-*H* loops of sample x = 0.10 (composition Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃) at different temperatures are presented in figure 1(a). Figures 1(b)-(h) demonstrate an enlarged view of the low-field M-H hysteresis loops of this sample measured at temperatures: (b) 20 K (c) 50 K (d) 100 K (e) 150 K (f) 200 K (g) 250 K and (h) 300 K. The hysteresis loops for the two other compositions are shown in the supplemental figures 1(S1) and 2(S2)³ (stacks.iop.org/JPhysD/49/095001/ mmedia). It should be noted that the M-H hysteresis loops (figure 1, supplemental figures 1(S1) and 2(S2) (stacks.iop. org/JPhysD/49/095001/mmedia)) were carried out initially without applying any cooling magnetic field.

The coercive fields (H_c) and remanent magnetization (M_r) extracted from the hysteresis loops were quantified as: $H_c = (H_{c1} - H_{c2})/2$, where H_{c1} and H_{c2} are the left and right coercive fields [16, 26] and $M_r = |(M_{r1} - M_{r2})|/2$ where M_{r1} and M_{r2} are the magnetization with positive and negative points of intersection with H = 0, respectively [13]. The calculated values of H_c and M_r are plotted as a function of temperature in figures 2(a) and (b), respectively for Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO₃ (x = 0.00-0.20) samples. Both the coercive fields and remanent magnetizations are higher for sample x = 0.10 than those for x = 0.00 and x = 0.20. Therefore, it is clear that the

³ In supplemental figure 1(S1) (a) we show *M*–*H* hysteresis loops of Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO₃ (x = 0.00) sample measured at different temperatures. Figures 1(S1) (b)–(h) demonstrate the enlarged view of the low field hysteresis loops at temperatures: (b) 20 K, (c) 50 K, (d) 100 K, (e) 150 K, (f) 200 K, (g) 250 K and (h) 300 K. Figure 2(S2) (a) shows *M*–*H* hysteresis loops of Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO₃ (x = 0.20) sample at different temperatures. Figures 2(S2) (b)–(h) present the enlarged view of the low field hysteresis loops at temperatures: (b) 20 K, (c) 50 K, (d) 100 K, (e) 150 K, (f) 200 K, (g) 250 K and (h) 300 K. Figures 3(S3) (a)–(e) show the *M*–*H* hysteresis loops at *T* = 150 K carried out at different cooling magnetic fields. The *M*–*H* hysteresis loops at *T* = 250 K for different cooling magnetic fields are shown in figures 4(S4) (a)–(e). The asymmetric shifts toward the field axes are clearly visible from the enlarged views. Table 1 displays the variation of exchange bias fields, *H*_{EB} of Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO₃ (x = 0.00 and x = 0.20) at different temperatures.



Figure 1. (a) The *M*–*H* hysteresis loops of sample x = 0.10 (composition Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃) carried out at different temperatures. (b)–(h) An enlarged view of the low-field *M*–*H* hysteresis loops of sample x = 0.10 obtained at temperatures: (b) 20 K, (c) 50 K, (d) 100 K, (e) 150 K, (f) 200 K, (g) 250 K and (h) 300 K.

substitution of 10% Ti in place of Fe in the Bi_{0.9}Gd_{0.1}FeO₃ compound significantly increased H_c and M_r . However, a further increment of Ti to 20% in place of Fe reduced H_c and M_r , although their net values are still higher than those of the Ti undoped Bi_{0.9}Gd_{0.1}FeO₃ sample. As reported in our previous investigation [16], the larger values of H_c and M_r in sample x = 0.10 are related to the microstructure of the composition, i.e. with a homogeneous small grain size of the material. In the case of the La and Nb co-substituted BiFeO₃ [27] and Pr and Zr co-substituted BiFeO₃ compounds [28], an increase in the coercive field with the substitution was also attributed to the decrease in grain size. The value of H_c in these materials is much higher than that in pure BiFeO₃ [15, 16] and such a high value of coercivity in the Gd and Ti co-substituted BiFeO₃ samples may be related to their magnetic anisotropy [15, 29, 30].

A remarkable feature observed in figure 2(a) is that the coercivity of these ceramic samples increases with temperature. Figure 3 shows, as a typical example for the x = 0.10 sample, that while the coercivity increases on increasing the temperature, the maximum magnetization (M_s) at 50 kOe decreases on increasing the temperature [31]. For all the



Figure 2. The variation of (a) coercivity (H_c) and (b) remanent magnetization (M_r) as a function of temperature in the Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO₃ (x = 0.00-0.20) compounds. Both H_c and M_r are higher over a wide range of temperatures in sample x = 0.10.



Figure 3. The variation of M_s (the maximum magnetization at 50 kOe) and H_c as a function of temperature in sample x = 0.10 (Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃).

studied samples, the coercivity show a strong temperature dependency and the H_c values are significantly higher at room temperature than those at 20 K. For example, the H_c value at room temperature for sample x = 0.10 is three times higher than that at 20 K.

The usual trend in a typical magnetic system is for the coercivity to increase on decreasing the temperature [32-34] since the anisotropy decreases much more sharply than does the magnetization on increasing the temperature [35]. In similar multiferroic material systems, e.g. La-doped BiFeO₃ [29, 30] and LuFe₂O₄ [36], the H_c values were found to increase at a lower temperature than that at room temperature. The



Figure 4. The temperature dependence of magnetization (M-T curves) of the Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ sample measured in ZFC and FC processes in the presence of 500 Oe applied magnetic fields. Both the ZFC and FC curves coincide with each other without showing any bifurcation.

unexpected decreasing trend of H_c at a low temperature as compared with the room temperature values for all the compositions investigated here may be explained by the presence of magnetoelectric coupling in these multiferroic materials [31, 35]. The presence of the magnetoelectric coupling produces an additional contribution to the anisotropy, which actually acts to decrease the effective magnetic anisotropy [31, 35]. If K_u is the uniaxial anisotropy constant in the absence of coupling effects and K'_u is the uniaxial anisotropy constant in the presence of magnetoelectric coupling, then

$$K'_u = K_u - \chi_\perp \frac{(\beta P_z)^2}{2}$$

Here β is the homogeneous magnetoelectric co-efficient that is related to the Dzyaloshinsky Moriya magnetic field, χ_{\perp} is the magnetic susceptibility in the direction perpendicular to the antiferromagnetic vector and P_z is the spontaneous electric polarization [35, 37]. Thus, the temperature variation in H_c is determined by the competition between the magnetic anisotropy and the magnetoelectric coupling [31, 35, 37].

The higher values of H_c and M_r in sample x = 0.10 than those of the x = 0.00 and 0.20 compositions motivated us to investigate further its magnetic properties in detail. Therefore, we carried out the temperature dependence of the magnetization (M-T) of the Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ bulk sample. The *M*–*T* curves measured in ZFC and FC modes in the presence of 500 Oe applied magnetic field is shown in figure 4. In the ZFC process, the sample is initially cooled from 300 K to the lowest achievable temperature and the data were collected while heating in the presence of the applied field. On the other hand, in the FC mode, the data values were collected while cooling in the presence of the magnetic field, which is commonly known as a cooling magnetic field [22]. Here the temperature dependence magnetization measurements demonstrate clearly that both the ZFC and FC curves of the Bi₀ .9Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ ceramic coincide with each other without showing any bifurcation, which indicates the absence of any



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Figure 5. The variation of the exchange bias fields (H_{EB}) as a function of temperature in Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃. The H_{EB} values were calculated from the asymmetric shift of the *M*–*H* hysteresis loops of figures 1(b)–(h). The hysteresis loops were taken without applying a cooling magnetic field.

spin flipping effect [38–40]. In similar multiferroic materials both the ZFC and FC curves were also found to coincide with each other [41, 42].

As shown in figures 1(a)-(h), the room temperature M-H hysteresis loop as well as the loops taken at other temperatures exhibit an asymmetric shift towards the magnetic field axes [25]. This is a signature of the presence of an exchange bias effect in multiferroic $Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O_3$ material [16, 25, 43]. In the present investigation, the hysteresis loops of the Gd and Ti co-doped BiFeO₃ ceramic system are unsaturated even with an applied magnetic field of up to ± 50 kOe, which confirms the basic antiferromagnetic nature of the compounds. Notably, undoped BiFeO₃ possesses a very narrow hysteresis loop with a very small but non-zero remanent magnetization (0.0009 emu g^{-1}) and a coercive field of ~ 110 Oe at room temperature [16]. Compared to undoped BiFeO₃, the centre of the M-Hloops of $Bi_{0.9}Gd_{0.1}Fe_{1-x}Ti_xO_3$ (x = 0.00–0.20) compounds are wider (as shown typically in the enlarged view of sample x = 0.10, figures 1(b)–(h)), which suggests a weak ferromagnetic nature [44] of this co-doped ceramic system. The weak ferromagnetic nature of this material system is also revealed from the temperature-dependent magnetization curves [44]. In this way we anticipate the co-existence of strong-anisotropic ferri/ferromagnetic (FM) and antiferromagnetic domains in this multiferroic material system. As a consequence of the exchange coupling at the interfaces between these multiple magnetic domains, it is expected that the system acts as a natural system for generating an EB effect in Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ multiferroics [26, 32, 34, 45]. The exchange bias field (H_{EB}) from the loop asymmetry along the field axis can be quantified as $H_{\text{EB}} = -(H_{c1} + H_{c2})/2$, where H_{c1} and H_{c2} are the left and right coercive fields, respectively [25, 32]. The variation of $H_{\rm EB}$ as a function of temperature in Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ calculated from the asymmetric shift of the M-H hysteresis loops of figures 1(b)-(h) is shown in figure 5. The temperature dependence of $H_{\rm EB}$ for the two other compositions were





Figure 6. Cooling field dependence of the exchange bias field (H_{EB}) at 150 k and 250 K for the Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ ceramic. The graph also demonstrates the dependency of H_{EB} on temperature.

presented in the supplementary information (supplementary table $1)^4$.

As was mentioned earlier, the EB effect usually occurs when the system is cooled down in an external magnetic field through the Néel temperature (T_N) . It is worth mentioning that in the BiFeO₃ ceramic system the exchange bias effect was observed without any magnetic field annealing process through $T_{\rm N}$ [46], which is an conventional method of inducing unidirectional anisotropy [47]. It has also been observed without using any alloy layers [48], although then the biasing strength of BiFeO₃ is observed to be very weak with $H_{\rm EB} = 36$ Oe [48] at room temperature. The exchange bias fields indicate the strength of the exchange coupling of an exchange bias system. As shown in figure 5, the values of $H_{\rm EB}$ of $Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O_3$ at 150 K and 250 K are higher than those at any other temperatures. The $H_{\rm EB}$ values shown in figure 5 is observed without applying any cooling magnetic field and therefore the biasing strength is weak and random. In the case of a FM/AFM bilayer system, it is well known that the cooling magnetic field plays an important role in establishing a strong unidirectional anisotropy due to the exchange coupling [49]. Hence, in the following experiments, the magnetic hysteresis loops of Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ material were carried out at temperatures of 150 K and 250 K by cooling down the sample from 300 K in various cooling magnetic fields (H_{cool}) ranging from 20 kOe to 60 kOe. In each experiment related to cooling magnetic fields, the measuring magnetic fields were from -30 kOe to 30 kOe. The details of the loop asymmetry at different cooling fields and temperatures can be found in the supplementary figures 3(S3) and $4(S4)^5$ (stacks.iop.org/JPhysD/49/095001/mmedia).

The influence of cooling magnetic fields on the exchange bias effect at temperatures of 150 K and 250 K in the Bi_{0.9}G $d_{0.1}Fe_{0.9}Ti_{0.1}O_3$ multiferroic material is illustrated in figure 6. The *H*_{EB} values increased significantly on the application of cooling magnetic fields. For example, at a temperature of 250 K and a cooling magnetic field of 60 kOe, the biasing field

⁵ See footnote **3**.

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Table 1. The table shows the effect of cooling magnetic fields on
H_c of the Bi _{0.9} Gd _{0.1} Fe _{0.9} Ti _{0.1} O ₃ sample at temperatures of 150 K
and 250 K.

T(k)	H_c (kOe)			
	$\overline{H_{\rm cool} = 0}$ KOe	$H_{\rm cool} = 20$ kOe	$H_{\rm cool} = 40$ kOe	$H_{\rm cool} = 60$ kOe
150 250	4.7 5.6	4.7 5.6	5.0 5.8	5.0 5.8

Note: The effect of temperature on H_c of the Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ sample without applying any cooling magnetic fields was inserted into figure 2.

increased more than twelve times than that for a cooling magnetic field of 20 kOe. During the field cooling experiments, the $H_{\rm EB}$ values reduced on increasing the temperature, see figure 6, which is similar to the results reported in previous investigations [22, 24, 50]. The $H_{\rm EB}$ values are higher than those in related material systems [22, 51], specifically at high temperatures. In the present investigation, the temperature-dependent ZFC and FC measurements (figure 4) demonstrate the absence of any bifurcation from 300 K down to 5 K, and therefore we conducted the field cooling experiments by cooling the sample from 300 K down to 150 K and 250 K. By using the SQUID magnetometer (Quantum Design MPMS-XL7, USA), it was not possible to heat the sample above 300 K; therefore, the field cooling experiments were not possible to conduct by cooling down this sample through T_N , which is around 520 ± 10 K for the Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ ceramic measured from the temperature-dependent dielectric measurements (data not shown here). As was mentioned earlier, the EB has been observed in various bulk materials, although the effect in most cases has been limited to low temperatures [23, 24]. The observation of EB up to room temperature is of interest from the perspective of practical applications. Therefore, in the future we intend to conduct field cooling experiments at room temperature by cooling Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ material through $T_{\rm N}$, which is above the room temperature.

The influence of H_{cool} on coercive fields was also measured at temperatures of 150 K and 250 K and the results are displayed in table 1. Notably, in figures 2 and 3, we show the effect of temperature on H_c without applying any cooling magnetic field. Here, in table 1, we have inserted the effect of a cooling magnetic field on H_c and the measurements were carried out at two different temperatures close to room temperature. The exchange bias fields are strongly affected by the cooling magnetic field, as shown in figure 6, although the H_c values (table 1) are influenced only to a small extent. This is not unusual; in the case of NiFe/Co bilayers a similar effect was previously observed, i.e. the exchange bias field is strongly affected by the cooling magnetic field, whereas the H_c is weakly influenced [49].

In our previous investigation [25], we synthesized nanoparticles of the same composition, i.e. of $Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O_3$ with a mean size of 40–100 nm directly from their bulk powder by using the sonication technique described in [52]. In this specially prepared nanoparticle system, the exchange bias effect was also observed and the magnitude of the exchange bias fields was also found to increase with cooling magnetic fields [25]. Obviously, the cooling field dependence of the H_{EB} values of the Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ bulk system were weaker than those of the specially prepared Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ nanoparticles. For example, in both the bulk and nanoparticle systems the highest H_{EB} values were observed at a temperature of 150 K by applying a 60 kOe cooling magnetic field. At this temperature and cooling magnetic field, the H_{EB} value of the bulk system is 20% less than that of nanoparticles with sizes 40–100 nm. This is worth noting as the preparation of bulk materials is comparatively easy and straightforward considering the multistep process for the preparation of nanoparticles.

IV. Conclusions

We have observed a strong influence of temperature on coercive fields and exchange bias fields of Gd and Ti co-doped BiFeO3 multiferroics. The coercive fields of this multiferroic system were enhanced anomalously on increasing the temperature. The anomalous enhancement of the coercivity on increasing the temperature, and particularly the observation of the high values of H_c near/at room temperature may be of future use in potential applications where a coercivity stability at high temperature is crucially effective. We have also observed the presence of the exchange bias effect due to the interface exchange coupling between the FM and AFM domains of the Gd and Ti co-doped BiFeO₃ material system. The magnitude of the exchange bias fields in bulk Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ were also found to increase with a cooling magnetic field. This magnetically tunable exchange bias obtained in the bulk multiferroic Bi_{0.9}Gd_{0.1}Fe_{0.9}Ti_{0.1}O₃ material up to temperatures of 250 K is promising, as most of the bulk materials show EB only far below room temperature. We anticipate that the presence of both exchange and magnetoelectric coupling in Bi0.9G $d_{0.1}Fe_{0.9}Ti_{0.1}O_3$ multiferroic material might be worthwhile for potential applications in novel multifunctional devices.

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References

- [1] Spaldin N A and Fiebig M 2005 Science 309 5733
- [2] Eerenstein W, Mathur N D and Scott J F 2006 Nature 442 759
- [3] Cheong S W and Mostovoy M 2007 *Nat. Mater.* **6** 13
- [4] Ramesh R 2009 Nature 461 1218
- [5] Wu S M, Cybart S A, Yi D, Parker J M, Ramesh R and Dynes R C 2013 Phys. Rev. Lett. 110 067202

- [6] Fischer P, Polomska M, Sosnowska I and Szymanski M 1980 J. Phys. C: Solid State Phys. 13 1931
- [7] Ederer C and Spaldin N A 2005 *Phys. Rev.* B **71** 060401
 [8] Yuan G L, Wing S, Liu J M and Liu Z G 2006 *Appl. Phys.*
- [6] Tuan G L, whig S, Eld J W and Eld Z G 2000 Appl. Thys. Lett. **89** 052905
- Khomchenko V A, Paixao J A, Costa B F O, Karpinsky D V, Kholkin A L, Troyanchuk I O, Shvartsman V V, Borisov P and Kleeman W 2011 Cryst. Res. Technol. 46 238
- [10] Khomchenko V A, Kiselev D A, Vieira J M, Kholkin A L, Sá M A and Pogorelov Y G 2007 Appl. Phys. Lett. 90 242901
- [11] Xu Q Y, Zai H F, Wu D, Qiu T and Xu M X 2009 Appl. Phys. Lett. 95 112510
- [12] Chang F G, Zhang N, Yang F, Wang S X and Song G L 2007 *J. Phy. D: Appl. Phys.* **40** 7799
- [13] Anjum G, Kumar R, Mollah S, Shukla D K, Kumar S and Lee C G 2010 J. Appl. Phys. **107** 103916
- [14] Reetu, Agarwal A, Sanghi S, Ashima and Ahlawat N 2012 J. Phys. D: Appl. Phys. 45 165001
- [15] Rao T D and Asthana S 2014 J. Appl. Phys. 116 164102
- [16] Basith M A, Kurni O, Alam M S, Sinha B L and Ahmmad B 2014 J. Appl. Phys. 115 024102
- [17] Kumar M, Sati P C and Chhoker S 2014 J. Mater. Sci., Mater. Electron. 25 5366
- [18] Dieny B, Speriosu V S, Parkin S S P, Gurney B A, Wilhoit D R and Mauri D 1991 Phys. Rev. B 43 1297
- [19] Zhang T and Dressel M 2009 *Phys. Rev.* B 80 014435
- [20] Pradheesh R, Nair H S, Sankaranarayanan V and Sethupathi K 2012 Appl. Phys. Lett. 101 142401
- [21] Nayak A K et al 2015 Nat. Mater. 14 679
- [22] Tian Z M, Yuan S L, Zheng X F, Jia L C, Huo S X, Duan H N and Liu L 2010 Appl. Phys. Lett. 96 142516
- [23] Yu P et al 2010 Phys. Rev. Lett. 105 027201
- [24] Ang R, Sun Y P, Luo X, Hao C Y, Zhu X B and Song W H 2008 J. Appl. Phys. 104 023914
- [25] Basith M A, Khan F A, Ahmmad B, Kubota S, Hirose F, Ngo D-T, Tran Q-H and Mølhave K 2015 J. Appl. Phys. 118 023901
- [26] Guo Y, Shi L, Zhou S, Zhao J, Wang C, Liu W and Wei S 2013 J. Phys. D: Appl. Phys. 46 175302
- [27] Zhai L, Shi Y G, Tang S L, Lv L Y and Du Y W 2009 J. Phys. D: Appl. Phys. 42 165004
- [28] Sati P C, Arora M, Chauhan S, Chhoker S and Kumar M 2012 J. Appl. Phys. 112 094102
- [29] Suresh P and Srinath S 2013 J. Alloys Compd. 554 271
- [30] Das S R, Choudhary R N P, Bhattacharya P, Katiyar R S, Dutta P, Manivannan A and Seehra M S 2007 J. Appl. Phys. 101 034104
- [31] Hussain S, Hasanain S K, Jaffari G H, Ali N Z, Siddique M and Shah S I 2015 J. Alloys Compd. 622 8
- [32] Fertman E, Dolya S, Desnenko V, Pozhar L A, Kajnakova M and Feher A 2014 J. Appl. Phys. 115 203906
- [33] Huang X H, Ding J F, Zhang G Q, Hou Y, Yao Y P and Li X G 2008 Phys. Rev. B 78 224408
- [34] Qian J F, Nayak A K, Kreiner G, Schnelle W and Felser C 2014 J. Phys. D: Appl. Phys. 47 305001
- [35] Park T J, Papaefthymiou G C, Viescas A J, Lee Y, Zhou H and Wong S S 2010 Phys. Rev. B 82 024431
- [36] Patankar S, Pandey S K, Reddy V R, Gupta A, Banerjee A and Chaddah P 2010 Europhys. Lett. 90 57007
- [37] Ruette B, Zvyagin S, Pyatakov A P, Bush A, Li J F, Belotelov V I, Zvezdin A K and Viehland D 2004 Phys. Rev. B 69 064114
- [38] Fang L, Liu J, Ju S, Zheng F, Dong W and Shen M 2010 Appl. Phys. Lett. 97 242501
- [39] Singh M K, Prellier W, Singh M P, Katiyar R S and Scott J F 2008 Phys. Rev. B 77 144403
- [40] Rana D S, Kuberkar D G and Malik S K 2006 Phys. Rev. B 73 064407

- [41] Lu J, Günther A, Schrettle F, Mayr F, Krohns S, Lunkenheimer P, Pimenov A, Travkin V D, Mukhin A A and Loid A *Eur. Phys. J.* B 75 451
- [42] Lazenka V V, Zhang G, Vanacken J, Makoed I I, Ravinski A F and Moshchalkov V V 2012 J. Phys. D: Appl. Phys. 45 125002
- [43] Murthy J K and Venimadhav A 2013 Appl. Phys. Lett. 103 252410
- [44] Ramachandran B, Dixit A, Naik R, Lawes G and Ramachandra Rao M S 2012 J. Appl. Phys. 111 023910
- [45] Deng D, Zheng J, Yu D, Wang B, Sun D, Avdeev M, Feng Z, Jing C, Lu B, Ren W, Cao S and Zhang J 2015 Appl. Phys. Lett. 107 102404
- [46] Dho J, Qi X, Kim H, MacManus-Driscoll J L and Blamire M G 2006 Adv. Mater. 18 1445
- [47] Borisov P, Hochstrat A, Chen X, Kleemann W and Binek C 2005 Phys. Rev. Lett. 94 117203
- [48] Yao R, Cao C, Zheng C and Lei Q 2013 RSC Adv. 3 24231
- [49] Ambrosea T and Chien C L 1998 J. Appl. Phys. 83 7222
- [50] Huang S, Shi L R, Sun H G, Zhu C M, Tian Z M and Yuan S L 2014 Appl. Phys. Lett. 105 192904
- [51] Karmakar S, Taran S, Bose E, Chaudhuri B K, Sun C P, Huang C L and Yang H D 2008 Phys. Rev. B 77 144409
- [52] Basith M A, Ngo D-T, Quader A, Rahman M A, Sinha B L, Ahmmad B, Hirose F and Mølhave K 2014 Nanoscale 6 14336