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Extraordinarily large intrinsic magnetodielectric coupling of the Tb member within the Haldane spin-chain family R_2BaNiO_5

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The Haldane spin-chain compound Tb_2BaNiO_5 has been known to order antiferromagnetically below ($T_N =$) 63 K. The present magnetic studies on the polycrystals bring out that there is another magnetic transition at a lower temperature ($T_2 =$) 25 K with pronounced magnetic-field-induced metamagnetic and metaelectric behaviors. Multiferroic features are found below T_2 only and not at T_N. The most intriguing observation is that the observed change in dielectric constant ($\Delta\varepsilon'$) is intrinsic and largest (e.g., ∼18% at 15 K) *within this* Haldane spin-chain family R_2BaNiO_5. Taking into account the fact that this trend (that is, the largest value of $\Delta\varepsilon'$ for the Tb case within this family) correlates well with a similar trend in T_N (with the values of T_N being ∼55, 58, 53, and 32 K for Gd, Dy, Ho, and Er cases), we believe that the explanation usually offered for this T_N behavior in rare-earth systems is applicable for this $\Delta\varepsilon'$ behavior as well. That is, single-ion anisotropy following crystal-field splitting is responsible for the extraordinary magnetodielectric effect in this Tb case. This work provides a pathway in the field of multiferroics to promote magnetoelectric coupling.

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I. INTRODUCTION

The area of research exploring the coupling between magnetic and electric degrees of freedom in magnetic insulators continues to be at the center stage in condensed-matter physics, ever since spin-induced ferroelectricity was reported in $TbMnO_3$ by Kimura *et al.* [1], as magnetism and ferroelectricity historically were considered to be mutually exclusive. Besides, this cross coupling bears relevance to applications, e.g., for novel data storage devices for writing electrically and reading magnetically. Various concepts have been proposed to explain the "multiferroic" behavior arising from this cross coupling, mainly in terms of the asymmetric Dzyaloshinskii-Moriya interaction, spin-dependent *p*-*d* hybridization, and exchange striction (see a review article by Dong *et al.* [2]). Despite such an advancement of knowledge, there is a realization for the exploration of new mechanisms, territories [2], and pathways leading to enhanced coupling between magnetic and electric dipoles (also see Refs. [3,4]). In this respect, recent investigations on thin films, heterostructures, and surfaces of certain dilute magnetic semiconductors bring out the role played by magnetocrystalline anisotropy due to preferential orientation of magnetization on the cross coupling as reviewed in Ref. [2]. It is worthwhile to bring out such a role of anisotropy among bulk forms of compounds. It is also necessary to make sure that interference from issues due to other extrinsic contributions, such as leakage current is absent in such materials while interpreting the data, to enable reliable conclusions.

The above scenario prompted us to address the question how single-ion magnetic anisotropy of a given rare-earth (R) ion influences the cross-coupling effects. A comparison of this coupling within a given rare-earth series provides an opportunity to address this question as a change in R^{3+} does not perturb the lattice barring lanthanide contraction. In this respect, the insulating Haldane spin-chain family R_2BaNiO_5 (Ref. [5]) ideally is suited. These compounds, crystallizing in an $Immm$-type orthorhombic structure, have been of special interest in the field of magnetism for over a quarter of a century for anomalies associated with the Haldane spin-chain gap and magnetic ordering of Ni and (magnetic-moment-containing) R ions at the same temperature (see, for instance, Refs. [5–24]). Although this family has been considered to be the prototype for Haldane spin-chain behavior, there was very little focus on understanding the magnetoelectric behavior of these insulators until recently. It may be noted that very high dielectric permittivity at room temperature for nonmagnetic Y_2BaNiO_5 [17] and linear magnetoelectric coupling for the magnetically ordering Ho analog [18] were reported. This family of materials is characterized [6,7] by an infrared allowed optical phonon mode with low frequency, i.e., the existence of a soft phonon mode, which is a clue [25] for exploring magnetoelectric coupling. In light of this, in recent years, we have subjected many members of this family to intense studies to explore the cross-coupling phenomenon and reported [7,19–23] a variety of magnetoelectric anomalies. Although these compounds are found to exhibit multiferroic anomalies and magnetodielectric coupling, the point we would like to stress is that the observed magnitude of magnetodielectric coupling is less than a few percent ($\ll$4%), even at fields as high as 140 kOe in all these compounds investigated until now. Here we attempt to investigate the Tb member for which the Néel temperature ($T_N = T_1 = \sim 63$ K) is the highest within this family. Such a high value within a given R series has been known [26–28] to be a consequence of single-ion anisotropy on magnetism. Naturally, this compound is suited to the aim outlined above.

We have therefore carried out exhaustive magnetic and magnetoelectric studies as a function of temperature (T) and magnetic-field (H) on the title compound. It may be stressed that, barring initial magnetic susceptibility (χ) and neutron diffraction measurements [11,24], reporting onset of antiferromagnetic order, there is no further report in the literature on this compound. The present results reveal the existence of another magnetic transition below ($T_2 =$) 25 K with magnetic-field-induced spin-flop effects in isothermal

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magnetization (M) and magnetodielectric coupling as well as multiferroic behavior. The key observation being stressed is that this compound exhibits the largest intrinsic magnetodielectric effect *within this family* below T_2, e.g., ~18% at 15 K. We therefore suggest that single-ion ($4f$-orbital) anisotropy plays a role in the magnetodielectric properties in this family.

II. EXPERIMENTAL DETAILS

The polycrystalline specimen of Tb_2BaNiO_5 was prepared by a standard solid-state reaction route as described in Ref. [24]. Stoichiometric amounts of NiO (99.995%), $BaCO_3$ (99.997%), and $Tb_2(CO_3)_2{\cdot}nH_2O$ (99.9%) were used as initial precursors. All these starting materials before weighing were dried for 2 h to remove traces of moisture. The pellet of the mixture of these dried starting materials was first heated at 950 °C for 12 h, followed by sintering at 1050, 1150, 1250, and 1350 °C for 12 h each with intermittent grindings. These sinterings were performed in the flow of high-purity Ar because of the instability of Tb^{3+} at high temperatures in air. The formation of the sample was confirmed by a x-ray powder-diffraction using Cu $K\alpha$ radiation at room temperature. The observed diffraction pattern was refined by Rietveld fitting by using the FULLPROF program. The lattice parameters [$a = 3.781(3)$, $b = 5.799\,(2)$, and $c = 11.411\,(4)$ Å] match well with the literature [24]. The homogeneity of the sample was confirmed further by a scanning electron microscope, and the composition (within 2%) was confirmed by energy-dispersive x-ray analysis. Instruments used for measurements of magnetization, heat-capacity (C), and dielectric permittivity as a function of T down to 1.8 K and in magnetic fields have been described in our earlier publications [7,19–23]. Bias electric-field (E) measurements were performed with the help of a Keithley 6517B electrometer. In this case, the sample was cooled to 5 K in the absence of an electric field, and the bias current I_B was measured in the presence of a bias electric field of 2 kV/cm with a heating rate of 2 K/min. Isothermal H dependence of the dielectric constant (ε') was measured at some selected temperatures.

III. RESULTS AND DISCUSSION

A. Evidence for antiferromagnetic transitions at 63 and 25 K

Our dc magnetic susceptibility (χ) data obtained as a function of T are in good agreement with Ref. [24]. There is a kink near 64 K due to the onset of magnetic ordering concurrently from Tb and Ni sublattices [11]. In addition, there is a broad peak at ~40 K [Fig. 1(a)], which usually is attributed to the persistence of the one-dimensional magnetic feature, characteristic of this family of Haldane spin-chain systems. Despite the weakness of the feature at T_N in $\chi(T)$, the heat capacity reveals a prominent anomaly. A distinct jump in the plot of $C(T)$ at 63 K [Fig. 1(b)] could be observed. The fact that the magnetic ordering is of an antiferromagnetic type is confirmed by the observation that the peak gets gradually suppressed, shifting towards the low-temperature range with an increasing dc magnetic field [Fig. 1(b), the inset]. It is worth noting that the observed value of T_N is the highest in this series; for the Gd, Dy, Ho, and Er cases, the respective T_N value is equal to ~55, 58, 53, and 32 K [22,19,18,7]. It was theoretically established long ago [26–28] that the anisotropy of the $4f$ orbital of the crystal-field-split ground state (that is, the sign of some of the crystal-field terms for the Hamiltonian) in general plays a role in such an enhancement of T_N for a heavy member in a given rare-earth family.

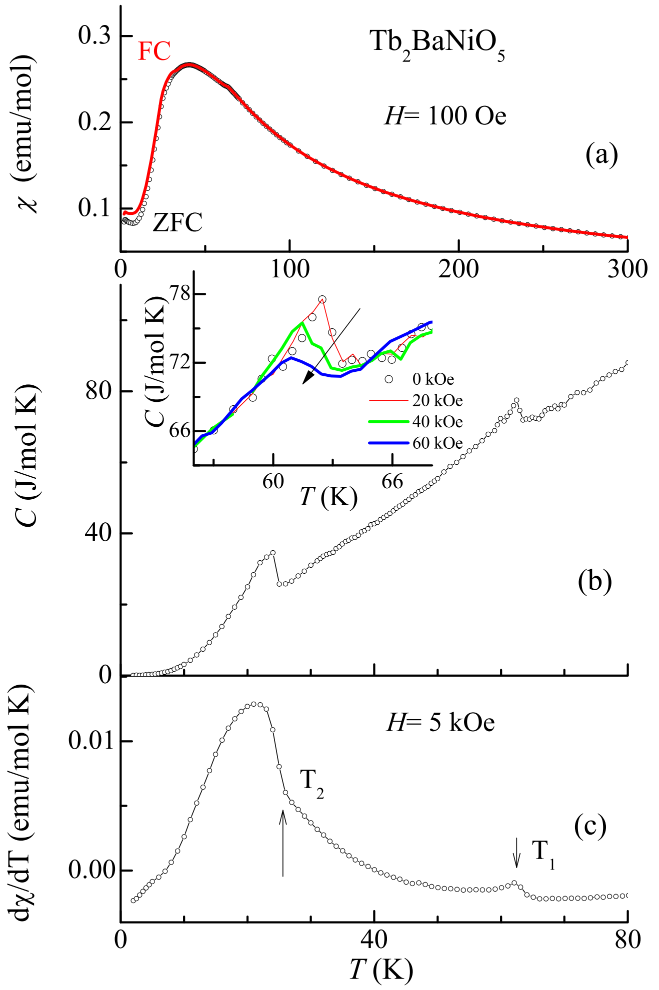

FIG. 1. For Tb_2BaNiO_5, (a) dc magnetic susceptibility (χ) obtained in 100 Oe for the zero-field-cooled (points) and field-cooled (red line) conditions. (b) Heat capacity below 80 K. The inset shows how the peak in the vicinity of T_N shifts with increasing magnetic fields [shown for 0 (points), 20 (red line through the points), 40, and 60 kOe]. (c) The derivative of χ, obtained in 5 kOe. Vertical arrows mark transition temperatures.

In Figs. 1(a) and 1(c), one can see dc χ obtained in a field of 100 Oe for zero-field-cooled (ZFC) and field-cooled (FC) conditions of the specimen and $d\chi/dT$, respectively, for the dc χ data obtained in a field of 5 kOe. There is a distinct increase in $d\chi/dT$ at 25 K as though there is a change in the magnetic character around this temperature. There is no notable bifurcation of ZFC-FC curves near (or below) 25 K, that could characterize this transition as spin-glass freezing. In fact, the heat capacity exhibits a well-defined peak at this temperature (with a jump as much as $10\,\mathrm{J\,mol^{-1}\,K^{-1}}$) [Fig. 1(b)], which renders strong support to the existence of a nonglassy transition at this temperature. The fact that

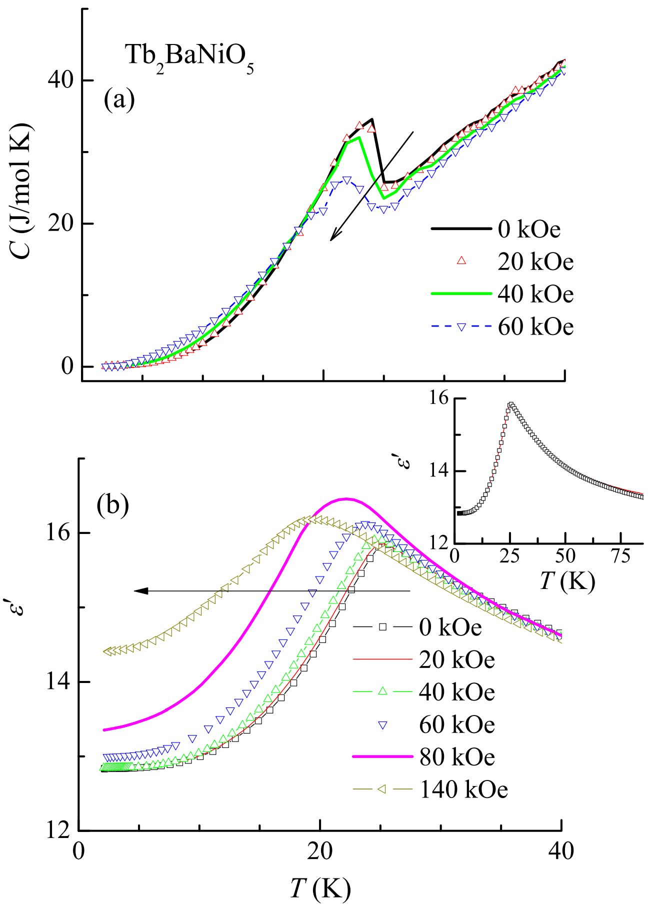

FIG. 2. (a) Heat-capacity behavior and (b) dielectric constant ($\nu = 100$ kHz) below 40 K. In the inset of (b), the data for 1 kHz (line) and 100 kHz (points) in the wider range until 80 K are shown to highlight the absence of ν dependence of the peak and of any feature in the dielectric constant at T_N. In the mainframe, the lines through the data points serve as guides to the eyes; the arrows are drawn to show the direction in which the curves move with increasing magnetic field.

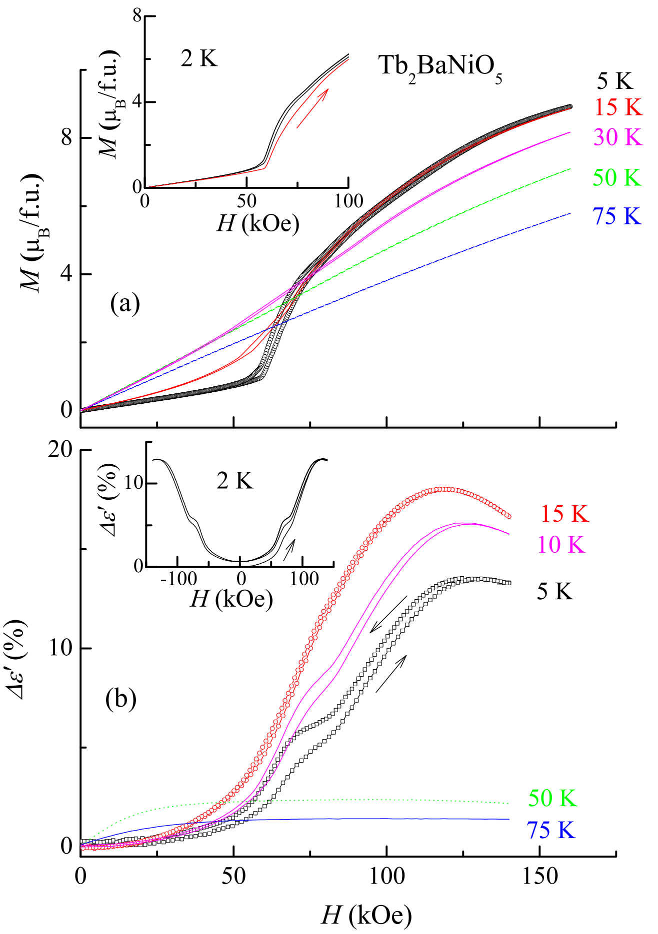

FIG. 3. (a) Isothermal magnetization per formula unit (f.u.) and (b) magnetodielectric behavior. The hysteresis loops at 2 K are shown in respective insets to highlight that the virgin curve (red) lies outside the envelope curve and, for the sake of clarity, the plot is restricted to the first quadrant in the $M(H)$ plot. The lines through the data points serve as guides to the eyes, and the arrows are drawn to show the direction in which the magnetic field was changed.

this $C(T)$ feature also shifts towards lower temperatures with increasing dc magnetic fields [Fig. 2(b)] is consistent with antiferromagnetism.

Many members of this rare-earth family have been shown [7,20–23] to reveal spin-glass characteristics at low temperatures (<10 K) well below the respective T_N. In order to confirm the absence of spin-glass freezing in this case, we performed isothermal remnant magnetization (M_{IRM}) studies at 2, 5, and 20 K. That is, after cooling the specimen in the zero field to the desired temperature, a field of 5 kOe was switched on for 5 min; then M_{IRM} was measured as a function of time after switching off the field. M_{IRM} was found to be negligible immediately after switching off the field, and the slow decay behavior of M_{IRM} expected for spin glasses was found to be absent (not shown here). We also have measured ac χ with various frequencies ($\nu = 1.3$, 13, 133, and 1333 Hz), and all these curves, resembling the dc $\chi(T)$ curve, overlap without any ν dependence of the peak (not shown here). In addition, there is no evidence for any feature in the imaginary part, which further establishes the absence of spin-glass freezing.

In order to support the existence of a magnetic transition around 25 K, we measured isothermal magnetization at various temperatures. We observe [Fig. 3(a)] a distinct upturn in $M(H)$ near ($H_{cr} =$) 60 kOe with a very weak hysteresis for $T \leqslant 15$ K, attributable to the existence of a spin-flop transition. Such a spin-flop transition was not known in the past literature for this compound. However, for 30 and 50 K, this field-induced transition is absent, thereby confirming that there is a difference in the magnetic character as the sample is warmed from 15 to 30 K. At 75 K, no worthwhile feature is seen as expected. The observed field-induced transition seems to be of a disorder-broadened first-order-type transition as the virgin curve lies outside the envelope curve [see the first quadrant of the hysteresis loop for 2 K shown in the inset of Fig. 3(a)].

In short, this second magnetic transition (around 25 K) is reported for this compound. The temperature at which such a second transition appears is the highest for the Tb member as the case for T_N. Garcia-Matres *et al.* [11] claimed, on the basis of neutron-diffraction data, that there is a small moment (1.4 μ_B) on Ni (in addition to that on Tb), making an angle with the c axis at T_N; this Ni moment was proposed to rotate further along the c axis with decreasing temperature; the Tb moment was proposed to align along the c axis below T_N. In view of our present finding, it is worthwhile to reinvestigate this compound across 25 K carefully by neutron diffraction.

B. Dielectric and magnetodielectric behavior

In Fig. 2(b), we show $\varepsilon'(T)$, obtained with an ac bias of 1 V and $\nu = 100$ kHz in various magnetic fields. It is clear that there is no worthwhile feature at T_N. The zero-field and in-field curves look similar, almost overlapping with each other over a wide temperature range above T_2. This means that the magnetodielectric effect is negligible in the vicinity of T_N. This was verified by isothermal magnetodielectric data as well (see below). However, as the temperature is lowered below T_N, a distinct peak appears at T_2. Besides, with increasing H, the peak shifts gradually to a lower temperature, for instance, to ~24, 22, and 19 K for $H = 40$, 80, and 140 kOe, respectively. All these findings establish the existence of magnetodielectric coupling. This H dependence of the peak in ε' resembles that seen for the peak in $C(T)$ [Fig. 2(a)]. We could not resolve any frequency dispersion of the peak in ε' for all H's, thereby ruling out any kind of glassy behavior [see the overlapping curves for 1 and 100 kHz in the inset of Fig. 2(b)]. This finding is in contrast to glassy electric dipole behavior (that is, frequency dispersion) seen for most members of this series [7,20–23] well below T_N. The observed coupling must be intrinsic as the value of the loss factor (tan δ) is insignificant (on the order of 0.0003) in the temperature range of interest.

Further support for magnetodielectric coupling is obtained from isothermal magnetodielectric data, shown in Fig. 3(b). For 5 K, $\Delta\varepsilon'$ [defined as $= \{\varepsilon'(H) - \varepsilon'(0)\}/\varepsilon'(0)$] undergoes a weak increase with H initially, and close to H_{cr}, there is a prominent upturn, supporting the existence of a (broad) metaelectric transition [29]. The field at which this upturn happens decreases with increasing temperature; see, for instance, the curves for 5, 10, and 15 K. The curves are weakly hysteretic in a wider H range around H_{cr}. Besides, the virgin curve lies outside the envelope curve as demonstrated for 2 K [Fig. 3(b), the inset]. No such metaelectriclike feature is observed for the curves well above 25 K [(see the curve for 50 K in Fig. 3(b)], and the values also are found to be $<1\%$. This behavior clearly tracks the features observed in $M(H)$ curves. This one-to-one correspondence between $\Delta\varepsilon'$ and $M(H)$ offers conclusive evidence for the existence of magnetodielectric coupling below T_2. A careful look, however, at the $\Delta\varepsilon'$ curves in the range of 2–10 K reveals that there is a plateau around 70 kOe followed another upturn. This signals the existence of another magnetic-field-induced transition, which is somehow smeared in $M(H)$ curves. We therefore think that there is more than one magnetic-field transition in this Tb material and it is a common feature in this family of materials [19].

We now focus on the most important observation in the magnetodielectric effect. That is, $\Delta\varepsilon'$ (below T_2) attains larger values compared to that in other members of this series. For instance, $\Delta\varepsilon'$ attains a maximum value of about 18% (for about 120 kOe). This is a significant finding for polycrystalline material as extrinsic contributions do not play a role at low temperatures in this compound. This value is more than (or comparable to) that reported for many well-known polycrystalline magnetoelectric oxides, e.g., 7% for $EuTiO_3$ (Ref. [25]), 10% for $TbMnO_3$ (Ref. [1]), 13% at 10 K for hexaferrite $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ (Ref. [30]), and 16% for $CaBaCo_4O_7$ (Ref. [31]). In sharp contrast to this behavior of the Tb compound, we find that the value does not even exceed a few percent for other R members, e.g., Nd, Gd, Dy, and Er members [7,19–23]. The fact that the Tb member alone stands out in this respect rules out any direct role of the Haldane spin chain. It is possible that exchange-striction mechanism and/or magnetic-field-induced spin current (or polarization) due to a change in the angle of the magnetic moment with the c axis [11] is responsible for this large value [32]. Since the magnitude of $\Delta\varepsilon'$ is not that large in other members of this series with similar magnetic structures [11] with the Ni moment making an angle with the c axis, we are tempted to conclude that the anisotropy of the $4f$ orbital of Tb following the crystal-field splitting plays a crucial role in enhancing magnetodielectric coupling, *just as it maximizes* T_N *for this member in this family.* The fact that this enhanced coupling is favored by the magnetic structure below T_2 and not by the one between T_1 and T_2 implies that the magnetic structure also should be favorable for the cross coupling—a fact established in various models for spin-induced multiferroicity [2]. At this juncture, we would like to state that our preliminary x-ray-diffraction experiments at selected temperatures establish the absence of any crystal structure change across 25 K and therefore the anomalies discussed above are magnetic in origin. Incidentally, in the case of the RMn_2O_5 family as well, a similar correlation between T_N and magnetodielectric coupling exists with a maximum for the Dy compound [33,34].

The exact microscopic origin of the role of single-ion anisotropy to enhance cross-coupling features is not clear to us at present. We however like to state that Jia *et al.* [35] proposed a theory more than a decade ago about how bond electric polarization develops due to a noncollinear spin configuration in the limit of strong Hund coupling. Extrapolating this idea, we speculate that the crystal-field-split orbitals following magnetic ordering at low temperatures in these rare-earth systems facilitate the distortion of an electron cloud surrounding the rare-earth ion, resulting in an electronic charge dipole. Such distortions may promote dramatically the exchange-striction effect discussed by us in Ref. [7].

C. Electric polarization behavior

Since there is a well-defined peak in $\varepsilon'(T)$ at T_2, we looked for electric polarization anomalies as well at this temperature. The space-group $Immm$ is centrosymmetric and hence unfavorable for ferroelectricity. However, a small displacement of the atoms around NiO_6 octahedra, following exchange striction, can result [7] in noncentrosymmetric space-group $Imm2$. We therefore searched for ferroelectricity. We followed the protocol suggested in the recent literature [36,37] to look for intrinsic ferroelectric features as stated in the Experimental

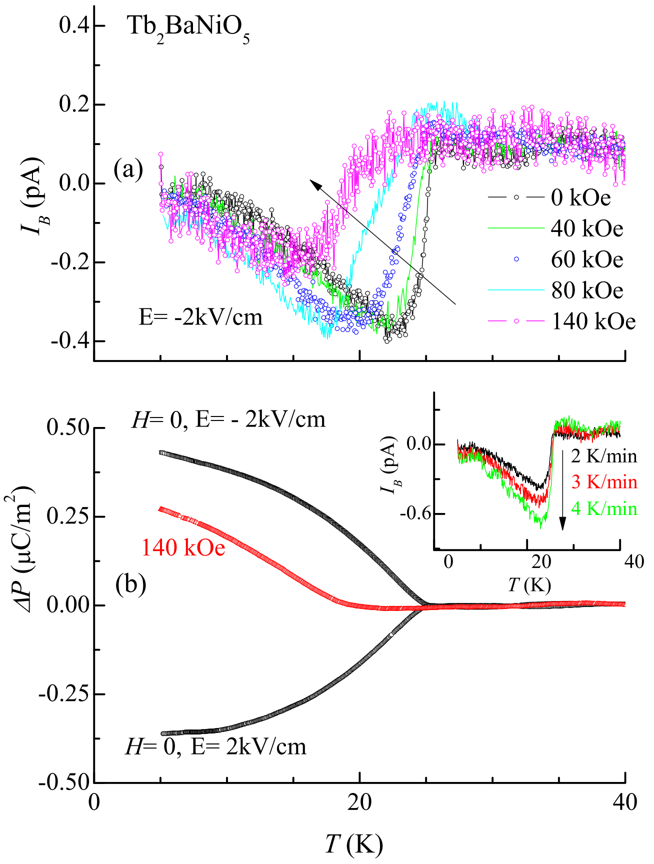

FIG. 4. (a) Variation of dc-biased current (I_B) with temperature (<40 K) obtained with a bias electric field of -2 kV/cm. (b) The change in the electric polarization derived from I_B for opposite polarities of the electric field in the absence of an external magnetic field; the polarization behavior in the presence of a dc magnetic field of 140 kOe also is included. An arrow is drawn in (a) to show the direction in which the curves move with increasing fields. The inset shows the I_B curves for different rates of warming.

Details section. The magnitude of I_B exhibits [Fig. 4(a)] a broad peak around 22 K. The variation of the relative value (ΔP) of electric polarization derived from the I_B data is plotted in Fig. 4(b). The sign of polarization gets reversed with a change in the polarity of E. In addition, there is a pronounced shift of the onset of temperature with increasing dc H [see, for instance, the polarization curve for 140 kOe in Fig. 4(b)]. This trend mimics $C(T)$ and $\varepsilon'(T)$ behaviors [Figs. 2(a) and 2(b)]. We are not able to resolve any shift in the peak temperature or onset temperature for different rates of warming (Fig. 4, the inset), which is consistent with the absence of any other contribution, such as "thermally stimulated depolarization" [38]. These findings suggest the onset of ferroelectricity following the magnetic transition at 25 K (that is, multiferroic behavior below T_2). Possibly, such a transition also can contribute to the $C(T)$ jump.

IV. SUMMARY

We have investigated the polycrystalline Tb-based compound Tb$_2$BaNiO$_5$ by magnetization, heat capacity, dielectric permittivity, and pyrocurrent measurements as a function of temperature and magnetic field. We find that, in addition to long-range antiferromagnetic ordering below 63 K, there is another magnetic ordering at 25 K. The magnetic transition is not of a glassy type—a situation different from that observed in other heavy rare-earth members. Another behavior that makes it different from other heavy rare-earth members is that this compound exhibits magnetoelectric coupling with multiferroic features below 25 K and not at or above T_N. The key observation being stressed is that the observed magnitude (>18%) of magnetodielectric coupling is the largest for this Tb member within this rare-earth family, mimicking the pattern of Néel temperature. This observation offers a clue for the role of the single-ion anisotropy of the Tb ion in promoting magnetodielectric coupling for Tb member in this family.

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