Towards novel multiferroic and magnetoelectric materials: dipole stability in tetragonal tungsten bronzes

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We discuss the strategy for development of novel functional materials with the tetragonal tungsten bronze structure. From the starting composition Ba₆GaNb₉O₃₀, the effect of A- and B-site substitutions on the dielectric properties is used to develop an understanding of the origin and stability of the dipolar response in these compounds. Both tetragonal strain induced by large B-site cations and local strain variations created by isovalent A-site substitutions enhance dipole stability but result in a dilute, weakly correlated dipolar response and canonical relaxor behaviour. Decreasing cation size at the perovskite A₂-site increases the dipolar displacements in the surrounding octahedra, but insufficiently to result in dipole ordering. Mechanisms introducing small A-site lanthanide cations and incorporation of A-site vacancies to induce ferroelectricity and magnetism are presented.

1. Introduction

The past decade has seen resurgence in interest of multiferroic materials, particularly materials which exhibit electrical and magnetic ferroic ordering, and specifically those which might exhibit magnetoelectric coupling of the two order parameters [1,2]. The majority of studies (of bulk materials) have focused on materials...
Figure 1. Polyhedral representation of the filled TTB structure showing the three-dimensional corner-sharing network of B1 (light) and B2 (dark) octahedral generating large A1 sites (light spheres) in pentagonal channels and perovskite A2 sites (darker spheres) in square channels. The vacant C-site is located in the trigonal channel. The figure shows $2 \times 2$ unit cells in the $ab$ plane to highlight the connectivity; the short $c$-axis is a single octahedra deep. (Online version in colour.)

Based on the perovskite structure, derived from either the cubic aristotype (including materials such as BiFeO$_3$, the most widely studied material and the only room temperature magnetoelectric antiferromagnetic and ferroelectric oxide known [3]); hexagonal structures such as RMnO$_3$ ($R = Y$, Dy, Ho, Tb, Yb, etc.) [4–6] and $R'$FeO$_3$ ($R' = Y$, Yb, In) [7–9]; ilmenite-based variants, such as LiNbO$_3$, LiTaO$_3$ or FeTiO$_3$ [10–12] or layered intergrowth structures, such as LuFe$_2$O$_4$-type [9], Aurivillius or Ruddlesden–Popper structures. The attractiveness of these structure types is in part their relative ease of synthesis but also the simplicity of the connectivity of the perovskite units which predominantly consist of corner-sharing B-cation polyhedra and the degeneracy of the crystallographic sites on the ‘A’ and ‘B’ cation sublattices. The structural distortions in these perovskite and derived materials are well known with a well-developed set of rules (the so-called perovskite toolbox) which allow us to understand and tune the physical properties.

Another structure type related to perovskite, which a number of ferroelectric and multiferroic materials are known to adopt is the tetragonal tungsten bronze (TTB) structure, general formula $A_{12}A_2B_{12}B_2C_4O_{30}$ (for oxides). As for (pseudo-cubic-based) perovskites, this structure can also be considered in terms of a three-dimensional corner-sharing network of BO$_6$ octahedra (figure 1), but in TTBs the stoichiometry determines that the ratio of octahedral to A-cation sites, $B:A$, is greater than 1 (compared with 1:1 for perovskites and less than 1 for layered structures) and this generates two non-equivalent B-sites (B1 and B2) and also gives rise to three types of ‘channels’ which can be occupied by various other cations. The pentagonal channel generates the large 15-coordinate A1-site, whereas the square (or rhombus) channel creates the 12-coordinate A2-site (note that the connectivity of A2-site and B2 octahedra essentially forms columns of perovskite along the short $c$-axis and which are interconnected by the B1 octahedra). The large A-sites can be occupied by large cations, such as those from the s-block, and early and mid-period f-block; the intermediate B-sites by d-block and late period f-block cations. The small trigonal, 9-coordinate
site can typically only be occupied by small, low-charge species, predominantly Li$^+$. The presence of non-equivalent sites on both A- and B-cation sublattices introduces additional degrees of freedom for compositional tuning if the site occupancy can be controlled. It is also important to note an additional feature of TTBs is that their overall stoichiometry can vary greatly depending on the occupancy of these sites: ‘stuffed’ TTBs have all A-, B- and C-sites fully occupied, e.g. in K$_6$Li$_4$Nb$_{10}$O$_{30}$ [13]; ‘filled’ compositions have fully occupied A- and B-sites but the C-site is vacant, e.g. in Ba$_2$NaNb$_5$O$_{15}$ [14–16]; finally, ‘unfilled’ compositions exist where the A-site is only partly occupied (typically 5/6). The latter category includes the first reported ferroelectric TTB oxides PbNb$_2$O$_6$ and (Sr,Ba)Nb$_2$O$_6$ [17–20]; the other examples cited above are also ferroelectric.

Although ferroelectric TTBs were widely studied in the 1960s and 1970s and are garnering renewed interest, our overall understanding of the general structure–property relationships in this class of materials is not as comprehensive as in perovskite and closely related materials. A few general observations have been reported [21] as well as more quantitative predictive parameters, for example tolerance factor [22] (analogous to perovskites), but the latter includes an additional proviso regarding the electronegativity difference [23] between the cations and anions. While these provide a starting point, they do not seem to be universal for this structure and developing a more complete understanding of structure–property relationships is vital if novel multiferroic materials are to be designed with this structure type. It is in this context that this work was carried out. Our starting point was the filled TTB material, Ba$_6$FeNb$_9$O$_{30}$, which has previously been reported as a magnetic ferroelectric with a ferroelectric Curie temperature of either 133–138 K [24,25] or 570–583 K [26,27]. A systematic doping study was carried out on this material by (i) replacing the Fe$^{3+}$ at the B-site with varying other trivalent cations; (ii) carrying out varying levels of isovalent A-site substitutions using Sr$^{2+}$ and Ca$^{2+}$ instead of Ba$^{2+}$; and (iii) incorporating rare earth cations on the A-site with charge compensation via (1) increased concentrations of trivalent B-site cations and (2) A-site vacancies. The ultimate aim of the study was to investigate the driving force for electrical ordering to produce/enhance ferroelectricity, and eventually to introduce magnetic behaviour.

2. Experimental set-up

All samples were prepared using solid-state reaction and ceramic processing techniques. The starting oxides and carbonates (ACO$_3$ A = Ba, Sr, Ca; Nb$_2$O$_5$; M$_2$O$_3$, M = Fe, Ga, Sc, In; RE$_2$O$_3$, RE = La, Nd, Dy, Ho) were mixed in stoichiometric amounts in an agate mortar and pestle, placed in an alumina boat lined with Pt foil and heated to 1250°C overnight. Calcined powders were then ball-milled at 600 r.p.m. for 1 h, pressed into pellets and sintered overnight in the range of 1300–1400°C to produce coarse-grained ceramics of more than 90% theoretical density; all Ga-containing compounds were heated to 1300°C to avoid melting with the exception of La-containing compositions, which were heated to 1400°C for complete reaction; all other compositions were heated to 1350°C. Single-phase materials were confirmed using X-ray diffraction (XRD, Stoe Stadii P diffractometer). Detailed crystallographic studies were carried out using variable temperature high-resolution powder neutron diffraction (PND) using the HRPD instrument at the ISIS facility, UK, and the D2B instrument at the Institut Laue-Langevin, Grenoble, France. Electrodes for electrical characterization were fabricated using Pt Paste (Gwent Electronics Ltd.) applied to opposing faces of pellets. Dielectric measurements were carried out using Agilent 4294 and HP 4192A impedance analysers in the frequency range of 5 Hz to 10 MHz using an AC excitation of 500 mV and in the temperature range between 50 and 800 K using either a closed system helium cryocooler with DE 202 cold head (A.S. Scientific products Ltd, UK) with a Sumitomo HC-2 compressor or a custom-made sample holder mounted in a Carbolute MTF10/25/130 tube furnace. Ferroelectric hysteresis measurements were performed using an aixACCT TF2000 analyser with a TREK 609E-6 4 kV amplifier and a standard three-train triangular pulse waveform; all measurements were uncompensated. Magnetic measurements were carried out using a Quantum Design Magnetic Property Measurement System (MPMS).
3. Results and discussion

(a) B-cation effects in \( \text{Ba}_6\text{MNb}_9\text{O}_{30}, \text{M}^{3+} = \text{Fe}, \text{Ga}, \text{Sc}, \text{In} \)

XRD confirmed that the compound \( \text{Ba}_6\text{FeNb}_9\text{O}_{30} \) does indeed form the TTB structure with \( a = 12.6043(5) \text{ Å} \) and \( c = 3.9954(2) \text{ Å} \) at 300 K. The XRD data, however, showed no evidence for a polar symmetry and the data were refined in the centrosymmetric space group \( P4/mbm \) (no. 127). Electrical measurements confirmed that the material is indeed not polar at ambient and the materials exhibited a broad, frequency-dependent peak in dielectric permittivity and loss in the range of 100–140 K, consistent with relaxor dielectric behaviour. Magnetic data (figure 2) indicated that this compound is weakly antiferromagnetic with Weiss constant, \( \theta = -16.0 \) to \( -32.1 \text{ K} \) and associated magnetic moment of \( 5.60–5.96 \mu_B \) which is consistent with the expected spin-only value of \( 5.92 \mu_B \) for high-spin \( \text{Fe}^{3+} (d^5) \). The variation in observed values depended on the sintering temperature of the powder/crushed pellet and is likely to arise from small variations in the Fe oxidation state. For this reason, a series of analogues were prepared using fixed \((+\text{III})\) oxidation state cations: \( \text{Ga}^{3+} (d^{10}) \), \( \text{Sc}^{3+} (d^0) \) and \( \text{In}^{3+} (d^{10}) \); these cations were also chosen to investigate the effect of B-cation size on the dielectric properties in an attempt to induce ferroelectric ordering.

All three of the \( \text{Ba}_6\text{MNb}_9\text{O}_{30}, \text{M}^{3+} = \text{Ga, Sc, In} \) analogues adopt the tetragonal TTB structure [28] and display dielectric properties consistent with canonical relaxor dielectrics as characterized by frequency dispersions in the broad maxima of both dielectric permittivity and loss (figure 3). The dielectric curves are displaced to higher temperature with increasing \( \text{M}^{3+} \) cation size (\( r_{\text{Ga}} < r_{\text{Fe}} < r_{\text{Sc}} < r_{\text{In}} \)) indicating an increase in dipole stability. In order to quantify this degree of dipole stabilization, the dipole freezing temperature, \( T_f \), was determined by fitting the dielectric data to two models: the real part (dielectric permittivity) was fitted to the Vogel–Fulcher (VF) expression [29], whereas the imaginary part was modelled according to the two-exponent expression of Jonscher’s Universal Dielectric Response (UDR) [30]. The VF expression, equation (2.1), describes the slowing down of the dipole response on cooling and is essentially a modified Arrhenius expression which includes the critical temperature, \( T_m \), below which the dipoles are not thermally activated, i.e. frozen

\[
f = f_0 \exp \left( -\frac{E_A}{k(T_m - T_f)} \right),
\]

where \( f \) is the frequency of the applied field (Hz), \( T_m \) (K) is the temperature of the maximum in permittivity at frequency \( f \), \( E_A \) is the activation energy for dipole perturbation (J) and \( f_0 \) is the limiting response frequency of the dipole (Hz). The dielectric data of all three analogues are well described by the VF expression (figure 4a) and the fits indicate a near-linear increase in dipole freezing temperature, \( T_f \), with increasing ionic radii.

For the UDR analysis of the imaginary part of the complex permittivity, the dielectric loss fits the data in the frequency domain; the data exhibit a peak in the loss as a function of frequency at some characteristic frequency, \( f_p \). The shape and position of this peak are described by Jonscher’s expression

\[
\varepsilon'' \propto \frac{1}{(f/f_p)^m + (f/f_p)^{1-n}}
\]

where the exponents \( m \) and \( n \) describe the gradient either side of the peak. At dipole freezing, the peak should become infinitely broad and flat on the low-frequency side as characterized by the exponent \( m \) tending to zero. The temperature dependence of \( m \) for all three analogues is shown in figure 4b and the extracted \( T_f \) values are in good agreement with those determined from VF analysis.

In our previous study using temperature-dependent PND, we showed that at the point of dipole freezing these materials exhibit a maximal tetragonal strain as a result of slower thermal contraction in the \( c \)-axis associated with stiffening of the lattice during dipole freezing [31]. These results also indicated that these materials are uniaxial relaxors with dipolar displacements predominantly occurring along the \( c \)-axis. The dipole stability in these materials is therefore...
Figure 2. Magnetic susceptibility data as a function of temperature for Ba$_6$FeNb$_9$O$_{30}$ prepared in flowing oxygen at 1350°C; Curie–Weiss fit (inset) with effective moment, $\mu_{\text{eff}} = 5.96$ $\mu_B$ and Weiss constant, $\theta = -32.1$ K. (Online version in colour.)

controlled by the tetragonality ($c/a$) of the unit cell which can in turn be increased by incorporating larger cations on the B-site [28]. There was no evidence of preferred occupation of the trivalent cation at B1 or B2 sites in any of the compositions studied.

Anisotropic refinements of the B-site thermal displacement parameters, which describe the scattering volume of the B-cations confirm this and show that $c$-axis displacement of the B1 cations is around four times greater than that of the B2 cations (figure 5). When considering the structure this shows that these materials are rather dilute in their dipolar activity which is consistent with the observed canonical relaxor dielectric behaviour as the B1 octahedra are only connected along the $c$-axis and are rather separated in the $ab$-plane (figure 1). In order to induce robust ferroelectric ordering, dipolar activity on the B2 sites would be preferred but the results to date suggest that this is unlikely to result from trivalent B-site substitutions as In$^{3+}$, with an ionic radius of 0.80 Å is the largest trivalent cation which can be fully accommodated in these materials. Attempts to incorporate the next largest trivalent cation, Y$^{3+}$ (radius 0.90 Å), results in phase separation, with the partially substituted TTB main phase still exhibiting relaxor behaviour [28]. In an attempt to induce ferroelectric ordering, the influence of A-site substitution was investigated.

(b) A-cation effects in $A_6$GaNb$_9$O$_{30}$, $A^{2+}$ = Ba, Sr, Ca

Starting from composition Ba$_6$GaNb$_9$O$_{10}$, the A-site Ba$^{2+}$ was substituted to varying degrees with either Sr and/or Ca according to the general formula Ba$_{6-x-y}$Sr$_x$Ca$_y$GaNb$_9$O$_{30}$. The TTB structure forms a significant phase field extending to 75% replacement for Sr-doping alone ($x \leq 4$, $y = 0$), 50% for Ca-doping ($x = 0$, $y \leq 3$) and includes $x = 3$, $y = 2$ and $x = 3$, $y = 1$ for combined doping. XRD showed that these compounds behave as Vegardian solids with the lattice parameters ($a$, $b$, $c$ and unit cell volume) as well as the tetragonality decreasing monotonically with average A-cation size (figure 6a). All the compositions studied exhibit relaxor dielectric behaviour, but with no systematic relationship between the temperature of the maximum in permittivity, $T_m$, and the tetragonality (and therefore average ionic radius; figure 6b) as displayed in the B-site-doped compositions. Instead, the dipole stability appears to show correlation with the degree of local
Figure 3. Dielectric permittivity ($\varepsilon'$) and loss ($\varepsilon''$) as a function of frequency and temperature for (a,b) Ba$_6$GaNb$_9$O$_{30}$; (c,d) Ba$_6$ScNb$_9$O$_{30}$; and (e,f) Ba$_6$InNb$_9$O$_{30}$.

strain (figure 7a) as quantified by the statistical A-site size variance, given by

$$
\sigma^2 = \sum_i y_i r_i^2 - \left( \sum_i y_i r_i \right)^2 = \langle r_A^2 \rangle - \langle r_A \rangle^2,
$$

where $r_i$ is the ionic radius of the $i$th cation at the A-site. This approach has been successfully used by Attfield and colleagues to explain variations in the critical magnetic [32] and ferroelectric [33] phase transition temperatures in perovskite-based oxides. The variance represents a measure of the local structural change, specifically the strain, present owing to the A-site substitution, whereas diffraction techniques probe the long-range, net average of these variations. As shown in figure 6, however, in the compositions described above both the average and local structure are varying. In order to decouple these effects a simple experiment was carried out, the detail of which
Figure 4. Vogel–Fulcher fits of the temperature of maximum permittivity, $T_m$, as a function of frequency, $f$ (a) and frequency exponent, $m$, of dielectric loss (b) for Ba$_6$MNb$_9$O$_{30}$, $M = \text{Ga}$ (circles), Sc (squares) and In (triangles).

Figure 5. B-site octahedra with thermal ellipsoids as determined from PND at 300 K for Ba$_6$ScNb$_9$O$_{30}$ indicating larger $c$-axis displacement of the B1 site. (Online version in colour.)

will be reported elsewhere, but essentially by starting from the composition Ba$_4$Sr$_2$GaNb$_9$O$_{30}$ the Sr$^{2+}$ was systematically replaced by Ba$^{2+}$ and Ca$^{2+}$ in the ratio 0.37 : 0.63 according to Ba$_{4-z}$(Ba$_{0.37}$Ca$_{0.63}$)$_z$GaNb$_9$O$_{30}$, where $z = 0.5, 1.0, 1.5, 2.0$. This approach maintains a constant average A-site ration as $\langle 0.37r_{Ba} + 0.63r_{Ca} \rangle = \langle r_{Sr} \rangle$. XRD data indicate that these compositions have the same average structure (with $a = 12.516$–12.533 Å and $c = 3.952$–3.958 Å) and an invariant tetragonality, $c/a = 0.316$. Fitting of the dielectric data to VF and UDR models as described in §3(a) yields a linear relationship between the dipole ordering temperature, $T_f$, and the size variance, $\sigma^2$ (figure 7b). For comparison, $T_m$ data for these ‘fixed cell’ compositions are included in figure 7a and show good agreement with the compositions where both the average and the local structure were allowed to vary.

Importantly, from Rietveld refinement of PND data the anisotropic thermal displacement parameters of the B-cations again indicate $c$-axis displacements, but unlike in the B-site substituted materials where the B1 displacements were four times larger than that for B2, in these A-site substituted materials the ratio is now closer to 2 : 1, suggesting that the presence of smaller cations on the A-site are ‘switching on’ the B2 displacements. Similar behaviour has been seen in the ferroelectric TTB series Ba$_2$RE$_4$Ti$_2$Nb$_8$O$_{30}$ RE = La, Pr, Nd, Sm, Eu, Gd and Dy) [32,34–37] where with decreasing size there is a cross over from relaxor to ferroelectric behaviour and $T_C$ is increasingly stabilized. Chen and co-workers [38] have suggested that it is not the average size of
the A-cation which is important for ferroelectric ordering, but rather the difference in size of the A-cation species, which appears to be supported by our results where the dipole stability scales not with average size but with the degree of size mismatch (variance). There is evidence in their work and ours that the smaller A-cation has preferred occupancy of the smaller A2 (perovskite) site, which seems rather obvious; it is likely that the presence of the smaller cation at this site relaxes the lattice and drives displacements within the B2 octahedra. In our A-site, isovalent substituted series ferroelectricity is not induced even at the solid–solution limits where the A-cation size is the smallest; Ba3Ca3GaNb9O30 which has both the smallest average size and largest variance is a relaxor with \( T_m \sim 225 \) K (measured at 10 kHz). In order to introduce even smaller cations at the A-site, one must move to the lanthanides which are predominantly trivalent, and therefore need charge compensation in order to be incorporated into the structure.

(c) Combined A- and B-site doping

The simplest mechanism for incorporating RE\(^{3+}\) cations at the A-site while maintaining a ‘filled’ stoichiometry is to charge compensate at the B-site by increasing the amount of trivalent...
species present. This doping mechanism can be described starting from \( \text{Ba}_6 \text{GaNb}_9 \text{O}_{30} \) by the defect reaction

\[
2 \text{RE}_2 \text{O}_3 + \text{Ga}_2 \text{O}_3 \rightarrow 4 \text{RE}^*_{\text{Ba}} + 2 \text{Ga}_{\text{Nb}}'' + 9 \text{O}_O^\times, \tag{3.4}
\]

leading to the general solid–solution formula \( \text{Ba}_{6-2x} \text{RE}_{2x} \text{Ga}_{1+x} \text{Nb}_{9-x} \text{O}_{30} \). We investigated the compositions \( x = 0.5 \) and \( 1.0 \) for \( \text{RE} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy} \) and \( \text{Ho} \), all of which adopt the TTB structure. They are all relaxor dielectrics exhibiting a frequency peak in dielectric permittivity in loss as a function of temperature. With decreasing lanthanide (average A-site) radius, the lattice parameters decrease from La to Sm before increasing (figure 8a). The temperature of the peak in permittivity, \( T_m \), also goes through a maximum at approximately 200 K for Dy (figure 8b). For the Ho analogue, \( T_m \) decreases, suggesting perhaps that some Ho is starting to occupy the B-site (Ho and Y have similar ionic radii), although no secondary phases were observed by XRD. It is important to note that although these are all relaxors and not ferroelectric, and with sub-ambient dipole freezing temperatures, \( T_m \) is increased by almost 180 K by incorporation of small A-site cations.

The second mechanism by which the incorporation of trivalent RE cations at the A-site can be charge compensated is by the presence of A-site vacancies. As mentioned previously, unfilled TTB materials with only 5/6 of the A-site occupied are well known, including those exhibiting robust ferroelectricity, such as \( \text{PbNb}_2 \text{O}_3 \) and \( \text{(Sr,Ba)} \text{Nb}_2 \text{O}_6 \) [20]. In order to maintain the stability induced by the small RE cation at the A-site, we investigated the effect of A-site vacancies starting from a co-doped composition \( (x = 1 \text{ above}) \) and reducing the amount of compensating B-site trivalent cations. This allows a switch from B-site to A-site compensation and can also be considered as Nb-doping of the B-site with formation of compensating A-site vacancies. This mechanism can be described by the defect reaction

\[
\text{Nb}_2 \text{O}_5 \rightarrow 2 \text{Nb}^{**}_\text{Ga} + 2 \text{V}^{**}_\text{Ba} + 5 \text{O}^\times, \tag{3.5}
\]

leading to the general solid–solution formula \( \text{Ba}_{4-y} \text{RE}_2 \text{Ga}_{2-y} \text{Nb}_{8+y} \text{O}_{30} \). For \( \text{RE} = \text{La} \) and \( \text{Nd} \), single-phase TTB materials are formed for \( y = 0.5 \) and \( 1.0 \). In each case, the composition is a relaxor dielectric and the effect of introducing a half and one vacancy per unit cell \( (y = 0.5 \text{ and } 1.0) \) is shown in figure 9. The introduction of vacancies results in an increase in \( T_m \); for La introduction of one vacancy per unit cells stabilizes the dipolar response by \( \text{ca} \) 160 K compared with \( \text{ca} \) 90 K in the case of Nd. In the case of the Dy analogue \( y = 1.0 \), the composition formed was a phase mixture of TTB and \( \text{DyNb}_2 \text{O}_4 \) with trace amounts of \( \text{Ga}_2 \text{O}_3 \). Refinement of PND data suggests the ratios are greater than 74 wt% TTB, approximately 23 wt% \( \text{DyNb}_2 \text{O}_4 \) and less than 3 wt% \( \text{Ga}_2 \text{O}_3 \) and the composition of the main TTB phase is \( \text{Ba}_4 \text{Dy}_{0.87(2)} \text{Nb}_{10} \text{O}_{30} \).
as determined from Rietveld refinement of PND data. This composition with A-site vacancies exhibits a dramatic increase in dipole stability and is in fact a ferroelectric material with $T_C$ of ca. 470 K. Hysteresis loops performed at a range of temperatures are shown in figure 9b. Preliminary magnetic measurements suggest that this material is antiferromagnetic with $T_N \sim 165$ K and undergoes the second magnetic transition at 50 K which results in a small ferromagnetic moment. The nature of this transition is not known and more detailed magnetic analysis of this phase will be reported elsewhere.

The Rietveld refinement of the Dy-sample also indicated that both the Dy and the vacancies occupy the smaller A2 (perovskite) site, and furthermore that the B2 cation displacements now contribute more than the B1 cations to the overall polarization as calculated using the procedure of Shimakawa et al. [39]. This suggests that the presence of the vacancy acts as the ultimate ‘small cation’ at the A2 site, resulting in activation of the B2 cation displacements. This is perhaps a mechanism to be exploited in other TTB systems where the robustness of ferroelectricity may be enhanced by formation of A-site vacancies.

In summary, the TTB structure is incredibly versatile with enormous scope for compositional variation. For filled alkaline earth niobate-based TTBs, we have demonstrated that when the A-site is fully occupied by large Ba cations, the dipole activity is weak and confined predominantly to the B1 site resulting in dilute, relaxor behaviour. The uniaxial (c-axis) nature of the dipolar displacements means that an increase in the tetragonality by extending the c–axis by incorporation of larger B-cations can increase the thermal stability of the dipolar response. For A-site substitutions, the changes in the dielectric response is not simply related to the average cation size but rather to the size mismatch between the A-site cations and can be expressed as the A-site cation size variance. This suggests that the way in which the lattice responds to A-site substitutions is not as simple as in perovskites, and further work is needed to understand the way in which the octahedra tilt and/or distort in response to A-site doping. The data do suggest however that in order to induce sufficiently strong dipolar displacements across all B-cation sites that a sufficiently small effective ionic radius cation at the A2 site is required. This can be difficult to achieve by doping because as the substituting cations become sufficiently small they can either begin to occupy the B-site or are too small to be stabilized in the A-site environment. A mechanism to overcome this is to incorporate a vacancy at the A-site; this has a similar distortive effect as a very small cation and can induce dipole activity at the B2 sites which if sufficiently cooperative can result in ferroelectric ordering.

**Figure 9.** (a) Effect of vacancy concentration on temperature of maximum in permittivity, $T_m$ (measured at 1 MHz) in compositions of general formula $\text{Ba}_{4-y}\text{RE}_x\text{Ga}_{2-y}\text{Nb}_{8+y}\text{O}_{30}$, $\text{RE} = \text{La}, \text{Nd}$ and Dy and (b) polarization-field loops measured at 100 Hz for $\text{Ba}_4\text{Dy}_{0.87(2)}\text{Nb}_{10}\text{O}_{30}$ as a function of temperature indicating ferroelectric switching. (Online version in colour.)
4. Conclusion

We have investigated cation size effects on both A- and B-cation sublattices in a range of barium niobate-based TTB dielectrics. For filled stoichiometry materials where all the A- and B-sites are fully occupied, the materials tend to be uniaxial (c-axis) relaxor dielectrics with dipolar activity predominantly on B1 cations site resulting in dilute behaviour. B-site doping with larger cations expands the c-axis stabilizing the dipole stability, but the one-dimensional connectivity of the B1 octahedra means that the dipolar response remains non-cooperative and dilute. A-site doping with smaller divalent cations introduces local strain which increases the dipole stability and contribution from the B2 perovskite-like octahedra; this effect, however, is not sufficient to induce dipole ordering within the solid–solution limits for stability of the TTB phase. By introducing fewer, smaller lanthanide cations at the A-site and with non-stoichiometry in the form of charge compensating A-site vacancies, it is possible to induce dipole ordering and ferroelectricity. The presence of lanthanide cations with an unfilled 4f shell also introduces magnetic moments and the possibility of multiferroic behaviour. The compositional versatility of the TTB structure makes it an ideal candidate for the investigation of the development of novel multiferroic and magnetoelectric materials.

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