A-site size effect in a family of unfilled ferroelectric tetragonal tungsten bronzes: 
$\text{Ba}_4\text{R}_{0.67}\text{Nb}_{10}\text{O}_{30}$ ($\text{R} = \text{La, Nd, Sm, Gd, Dy and Y}$)†

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The effect of A-cation size on the structural and electrical properties in a family of ferroelectric tetragonal tungsten bronzes (TTBs) $\text{Ba}_4\text{R}_{0.67}\square\text{Nb}_{10}\text{O}_{30}$ ($\text{R} = \text{La, Nd, Sm, Gd, Dy and Y}; \square = \text{vacancy}$) was investigated. In each case, the crystal structure, as determined from lab-based ambient powder X-ray diffraction (PXRD), is metrically tetragonal and can be refined in the $P\bar{4}bm$ space group. XRD data show an increased splitting of $hk0 \ 0l$ reflections with decreasing R cation size indicating an increasing tetragonal distortion (measured by tetragonality $c/a$). Dielectric data and ferroelectric measurements indicate that the ferroelectric Curie temperature, $T_C$, increases with decreasing R size and so a direct correlation between $T_C$ and tetragonality/ionic radius of R is demonstrated. Rietveld refinements show that the large A2-site is fully occupied by Ba$^{2+}$ and, in addition to the R cation size, the presence of vacancies at the A1-site (perovskite-like site) is also shown to strongly affect the stability of ferroelectricity in this structure type.

Introduction

Modern applications for ferroelectrics and dielectrics are still dominated by materials with the perovskite structure, largely due to the possibility of structure/property manipulation rationalised via geometrical tolerance factors and tilt systems.1–3 The development/growth of the electronics industry has driven the investigation of other structures in the search for new materials to e.g. replace existing lead-based compounds. Materials with the tetragonal tungsten bronze (TTB) structure were reported to display ferroelectric properties by Goodman in 19534,5 and offer great scope for materials development due to their similar compositional flexibility compared to the closely related perovskite structure.

The TTB structure has general formula $(\text{A1})_2(\text{A2})_4(\text{B1})_2(\text{B2})_8(\text{C})_4(\text{X})_{30}$ (where X = fluorine or more commonly oxygen and A, B, C are metal cations) and consists of square A1-site, perovskite-like, units linked by B1-site BO$_6$ units, which together demarcate a large pentagonal tunnel, the A2-site (Fig. 1).5 A1- and A2-sites are crystallographically distinct but both are occupied by larger cations: alkaline,6 alkaline earth,7 rare earth,8 or lead,5 however, substitutions of heavier cations such as bismuth9 or thorium10 have been reported. Where two (or more) A-cation types are present, the...
larger A2-site is generally preferentially occupied by the larger cations. The B1- and B2-sites are non-equivalent BO6 octahedral sites and usually occupied by small and highly charged cations: Nb, Ti, Ta or W, although minimal amount of doping of first row transition metals and others is possible. The C-site is of sufficient size to only accommodate the smallest cations, e.g. Li+, and consequently is vacant in most reported TTB compounds. When all cation sites are occupied the structure is described as being 'stuffed', while in 'filled' structures A- and B-sites are fully occupied but the C-site is vacant. When vacancies are present within the A-sites, the structure is described as 'unfilled'. Alternative expressions of the general TTB formula are common in the literature. Filled oxide compounds are commonly expressed in the reduced form (A1)(A2)2(B1)(B2)4O15 (A3B5O15) e.g. Ba3.75R0.833Nb10O30 (R = Nd, Sm, Eu, Gd, Y, Ho and Er) based on analysis of powder X-ray diffraction methods, however, did not report lattice parameters. We have produced a series Ba4R0.67Nb10O30 TTB compounds of various R3+ size to examine if size difference and tetragonality concepts are applicable to unfilled systems. Previous reports on both unfilled and filled rare earth-doped TTBs, have indicated that when cations of different sizes occupy the A1- and A2-site, the larger cation preferentially occupies the larger A2-site. In filled rare-earth-doped TTBs of A-site composition Ba4RE2, the size distortion on the ferroelectric properties of this unfilled TTB system to be tested while excluding B-site effects and avoiding mixed A-site cation distribution. The R-cations reported here were specifically selected by two criteria: (i) they only adopt +III valence state and hence avoids the possibility of alternative charge compensation mechanism(s) on doping and (ii) they are of sufficiently large ionic radius to occupy the A-sites only.

It is important to re-emphasise that many TTB compounds adopt larger unit cells due to an orthorhombic distortion and/or incommensurate modulations in the ab-plane. These distortions are frequently subtle and require advanced characterisation techniques such as synchrotron X-ray, neutron or selected area electron diffraction methods. Such techniques, however, are not routinely available and either involve long lead times to access central facilities or are destructive (e.g., SAED of sintered ceramics). The majority of structural variations of the TTB structure, however, involve √2 or 2√2 extension of the a and b lattice parameters, and/or doubling in the c-axis and so can also be described in terms of reduced cell parameters as for perovskites. In many cases such reduced cell
parameters result in a metrically tetragonal representation. Our approach in this study is to utilise this observation allowing widely accessible lab-based PXRD analysis to simply determine tetragonality (without the need for complex techniques or larger units cells) and which can then be empirically correlated with $T_C$ (Table 1).

### Experimental methods

Polycrystalline ceramic samples of $\text{Ba}_4R_0.67\square_1.33\text{Nb}_{10}O_{30}$ ($R = \text{La, Nd, Sm, Gd, Dy, Ho, Er, Yb and Y}$; $\square =$ vacancy), were synthesised using a conventional solid state method. Precursor powders (all >99% purity) of: $\text{BaCO}_3$, $\text{Nb}_2\text{O}_5$, $\text{La}_2\text{O}_3$, $\text{Nd}_2\text{O}_3$, $\text{Sm}_2\text{O}_3$, $\text{Gd}_2\text{O}_3$, $\text{Dy}_2\text{O}_3$, $\text{Ho}_2\text{O}_3$, $\text{Er}_2\text{O}_3$, $\text{Yb}_2\text{O}_3$ and $\text{Y}_2\text{O}_3$ (Aldrich); $\text{Er}_2\text{O}_3$ (Apollo Scientific); and $\text{Yb}_2\text{O}_3$ (Alfa Aesar), were dried prior to use. $\text{BaCO}_3$ and $\text{Nb}_2\text{O}_5$ were dried at 1000 °C, immediately followed by 15 hours at 1250 °C. Samples were air quenched, ground to a powder then milled in ethanol by planetary ball mill for 1 hour (600 r.p.m.). A 10 mm die press was used to form pellets of approximately 2 mm thickness by uniaxial pressing. Pellets were heated in a tube furnace. Polarisation–electric field ($P–E$) measurements were recorded using an AixACCT TF Analyzer 2000, TREK 609E-6 high voltage amplifier, variable temperature (ambient to 473 K) AixACCT piezo sample holder (model TFA 317-7 with sample immersed in Dow Corning 200/100 cs silicone fluid (BDH Ltd)) or closed cycle cryocooler.

### Results and discussion

#### A. Crystal structure

Ceramic samples of $\text{Ba}_4R_0.67\square_1.33\text{Nb}_{10}O_{30}$ ($R = \text{La, Nd, Sm, Gd, Dy, Ho, Er, Yb and Y}$), were prepared as described above and powder X-ray diffraction (PXRD) used to establish the formation of the crystalline TTB structure and ensure the absence of impurity phases. Compositions with $R = \text{La}$ to Dy and also Y, resulted in nominally single phase TTBs. Attempts at producing $R = \text{Ho}$, Er and Yb analogues yielded phase mixtures of a TTB main phase and significant quantities of $\text{BaNb}_2\text{O}_6$ (see ESI†) suggesting that these $R$ cations are too small to be incorporated in these amounts. It is interesting to note that Wakiya et al. also reported that they could not obtain single phase $\text{Ba}_{3.75}\text{Ho}_{0.833}\text{Nb}_{10}O_{30}$, although they reported success for the $\text{Er}$ analogue.$^{28}$ The incorporation of Yb into the TTB structure has been reported but to our knowledge only in minimal concentrations.$^{32,33}$ Based on these observations the smaller rare earth Lu was not investigated.

As mentioned previously, TTB structures can adopt several different symmetries, predominantly in the tetragonal and orthorhombic crystal systems, although distortions are usually sufficiently subtle that it is difficult to distinguish between

#### Table 1: Lattice parameters, tetragonality ($c/a$), unit cell volume and goodness-of-fit statistics, obtained from refinements of ambient temperature PXRD data in space group $P4bmm$, and $T_C$ for $\text{Ba}_4R_0.67\square_1.33\text{Nb}_{10}O_{30}$

<table>
<thead>
<tr>
<th>R</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>Volume ($Å^3$)</th>
<th>$\chi^2$</th>
<th>$R_{wp}$</th>
<th>$R[F^2]$</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>12.45172(14)</td>
<td>3.95503(6)</td>
<td>0.3176</td>
<td>613.209(14)</td>
<td>5.76</td>
<td>0.193</td>
<td>0.23</td>
<td>537</td>
</tr>
<tr>
<td>Dy</td>
<td>12.45845(16)</td>
<td>3.95434(6)</td>
<td>0.3174</td>
<td>613.765(14)</td>
<td>3.81</td>
<td>0.157</td>
<td>0.169</td>
<td>524</td>
</tr>
<tr>
<td>Gd</td>
<td>12.46285(18)</td>
<td>3.95474(7)</td>
<td>0.3173</td>
<td>614.260(17)</td>
<td>4.06</td>
<td>0.159</td>
<td>0.121</td>
<td>491</td>
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<tr>
<td>Sm</td>
<td>12.46758(17)</td>
<td>3.95548(7)</td>
<td>0.3172</td>
<td>614.843(16)</td>
<td>3.80</td>
<td>0.151</td>
<td>0.151</td>
<td>459</td>
</tr>
<tr>
<td>Nd</td>
<td>12.47453(7)</td>
<td>3.95439(4)</td>
<td>0.3170</td>
<td>615.358(7)</td>
<td>3.96</td>
<td>0.148</td>
<td>0.147</td>
<td>406</td>
</tr>
<tr>
<td>La</td>
<td>12.48735(13)</td>
<td>3.95577(5)</td>
<td>0.3168</td>
<td>616.839(12)</td>
<td>2.91</td>
<td>0.145</td>
<td>0.127</td>
<td>297$^b$</td>
</tr>
</tbody>
</table>

$^a$Refined in $P4bmm$ and $P4/nmbm$ with near identical values. $^b$ $T_{in}$ at 1 MHz.
them. Rietveld refinements were carried out on PXRD data using structural models with the non-centrosymmetric $P4bm$ and centrosymmetric $P4/mmbm$ tetragonal space groups. These space groups are commonly reported for the ferroelectric ($P4bm$) and paraelectric ($P4/mmbm$) polymorphs of TTBs. Refinements in both space groups yield near identical lattice parameters, but differing atomic positions. Refinements with other space groups reported for TTBs, notably orthorhombic $Pba2_1$, resulted in poor, divergent or unstable refinements and so, based on the laboratory XRD data obtained, there was no evidence to warrant further lower of symmetry from $P4bm$.

All observed reflections were indexed by the $P4bm$ model, however, a number of calculated peak intensities deviate slightly for data collected on both powder and pellets. These differences may result from preferred orientation associated with the columnar grain morphology (described later), but this was not investigated in detail. Attempts at refining A-cation occupancies both with Ba$^{2+}$ confined to the A2-site and also allowing cross substitution of Ba$^{2+}$ and R$^{3+}$ between the A1- and A2-sites, resulted in unstable, unrealistic, or inferior refinements. Refinements where A-site cation occupancies were consequently fixed such that the A2-site is fully occupied by Ba$^{2+}$ and the two A1-sites partially occupied by 0.67R$^{3+}$ and 1.33□ to achieve the nominal stoichiometry, Ba$_{4}$R$_{0.67}$□$_{1.33}$Nb$_{10}$O$_{30}$ resulted in significantly improved (and stable) fits. (It is important to note that, especially for the early period rare earths, the X-ray scattering factors are not significantly different to Ba.)

The lattice parameters indicate increasing tetragonality, $c/a$, with decreasing size of R-cation which nominally occupies the A1-site, Fig. 2a. The increase in $c/a$ is predominantly driven by decreasing $a$ as the ionic radius of R decreases, whilst the $c$ parameter is comparatively invariant. The resultant decrease in cell volume with decreasing R radius is thus also largely driven by contraction in the $ab$ plane (see ESIf).

Peak splitting of differing magnitude was observed in 4 pairs of $hk0$ reflections in the PXRD data of each compound. This is most clearly evident for the 001 and 310 reflections as shown in Fig. 2b. The magnitude of the splitting increases with decreasing R radius and consequently increasing tetragonality, as expected. This response to changing A-site cation size has previously been reported in both filled and unfilled TTBs. While these trends appear to be consistent, they are comparatively subtle; PXRD patterns for each composition are otherwise visually indistinguishable with the exception of the aforementioned peak splitting.

In addition to the previously described splitting, Ba$_4$La$_{0.67}$□$_{1.33}$Nb$_{10}$O$_{30}$ displays several peaks which exhibit slightly different peak profiles. These peaks do not coincide with known impurity phases and possibly indicate splitting due to lowering of symmetry. However, it was not possible to determine this conclusively given the resolution of the laboratory PXRD data. Nevertheless, the pattern can still be indexed in a tetragonal setting.

SEM micrographs of the thermally etched fracture surfaces of the sintered pellets indicate elongated and relatively uniform sized crystallites in the range of 10–15 µm. Relatively few pores were observed which is consistent with calculated pellet densities (see ESIf).

B. Electrical properties

Polycrystalline ceramics consist of crystalline grains (grain bulk) connected by intergranular material (grain boundaries) and may include a level of porosity, depending on the compound and synthetic conditions. These various electroactive regions typically display differing electrical properties; standard capacitance measurements of polycrystalline samples measure the total, macroscopic sample response and are therefore a convolution of the contributions of these individual electroactive regions within the sample. The electrical properties of a ceramic are typically dominated by the grain bulk and grain boundary responses, however, other contributions such as those from electrodes and surface effects may be observed. The ‘brickwork’ model of discrete grains separated by thin grain boundaries (which therefore are characterised by high capacitances) is not universally observed in all cases as ceramic microstructure is heavily influenced by processing conditions. Dissimilar electrical responses can therefore be observed in nominally identical compositions due to microstructural differences such as grain size, thickness/definition of grain boundary regions, and density.

High temperature immittance spectroscopy was carried out to determine the number of electroactive regions present and to ensure fixed frequency capacitance measurements carried out at lower temperatures represented the bulk response.

All samples display single semi-circular arcs in both impedance, $Z^*$, and modulus, $M^*$, complex plane plots, and single peaks in the $Z''$ and $M''$ spectroscopic plots, Fig. 3(a) and (b). The $Z''$ and $M''$ peaks are spectroscopically coincident, Fig. 3(b), and so belong to the same electroactive component. The magnitude of the capacitance values obtained from the
complex plane plots allow this response to be attributed to the bulk region. Fixed frequency (1 MHz) capacitance measurements can therefore be used as an approximation of the bulk response at all temperatures presented in Fig. 4.

Fixed frequency capacitance sweeps were carried out for all compositions as detailed in the Experimental section. Compositions $R = \text{Nd, Sm, Gd, Dy and Y}$ display single anomalies in the relative permittivity within the temperature range in which data were collected ($50 \text{–} 890 \text{ K}$), Fig. 4. Composition $R = \text{La}$ displays a low temperature frequency dependent relaxor-type peak with maximum, $T_m$ (1 MHz), at 297 K and a frequency independent high temperature peak. This unusual behaviour will be discussed later. Peak maxima for all other compositions display little frequency dependence; $T_C$ differs by less than 5 K over measured frequency range ($10^2 \text{–} 10^7$ Hz). Relaxation in the dielectric loss was observed to occur coincident to the permittivity maxima; all losses ($\tan \delta$) were less than $\sim 10\%$. The diffuse nature of the permittivity peaks in comparison to many perovskite structured ferroelectrics is a common feature of ceramic TTB ferroelectrics and is likely due to the nature of the ferroelectric transition and the intrinsic anisotropy within the TTB structure. It should be noted that despite being multi-phase the Ho and Er samples were also ferroelectric with $T_C$ of ca. 269 and 264 °C, respectively. The lattice parameters of the TTB phase in these samples also have tetragonality ratios which correlate with the observed $T_C$, however as the exact compositions of these phases are unknown and are not likely to contain the same stoichiometric ratios of Ba : $R$ : vacancies we prefer not to include them in the discussion presented here (see ESI† for data regarding $R = \text{Ho and Er}$).

All samples display saturated $P-E$ hysteresis loops with clear associated switching current, Fig. 5, demonstrating that all compositions are ferroelectric up to $T_C$ (or up to the maximum temperature measured, 473 K). Linear lossy dielectric $P-E$
loops above $T_C$ for compositions R = La, Nd and Sm demonstrate the high temperature paraelectric phase, Fig. 5(b) and confirm that the peak maxima in the dielectric data corresponds to a polymorphic phase transition between ferroelectric and paraelectric states and justifies the assignment of the non-centrosymmetric $P4bm$ space group over the centrosymmetric $P4/mnbm$ for ambient PXRD data.

$\text{Ba}_4L_{a0.67}\text{□}_{1.33}\text{Nb}_{10}\text{O}_{30}$ displays two anomalies in the relative permittivity: a frequency dependent relaxor-type peak, $T_m = 297$ K (at 1 MHz) and a high temperature, frequency independent peak, $T_m = 471$ K, Fig. 4(b). Normal ferroelectric $P$–$E$ hysteresis loops are observed at temperatures below the maxima in the relaxor peak and gradually transform into constricted or ‘pinched’ non-ferroelectric loops between the maxima of the dielectric anomalies with (slightly lossy) linear dielectric loops above 473 K, Fig. 5(c–f). Similar dielectric behaviour has been observed in other TTBs although varying rationalisations as to the origin of these observations have been proposed. These
Conclusions

TTB structured materials with varying A1-site cation size, \( \text{Ba}_5R_3\text{Ti}_2\text{Nb}_7\text{O}_{30} \) (\( R = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Y} \)) were produced obtaining nominally single phase ceramics. From lab-based XRD data, these compositions are metrically tetragonal and exhibit an increasing tetragonal distortion as R ionic radius decreases as indicated by refined lattice parameter values and increasing peak splitting of 00l hkl reflections. Compounds \( R = \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Y} \) display single peaks in the relative permittivity with Curie temperatures increasing with decreasing ionic radius and therefore, concurrently with increasing tetragonal distortion. A contraction in the \( ab \) plane drives the structural distortion, with the \( c \)-axis largely invariant. This empirical observation of a correlation between tetragonality and \( T_C \) appears to be universal within A-site (R) doped barium niobate-based TTB compositional series of comparable Ba : R stoichiometric ratio.

The ferroelectric nature of all compositions has been established with \( P-E \) hysteresis measurements. The presence of vacancies at the A1-site are important in inducing the ferroelectric instability in these materials, with ferroelectricity observed for Nd compositions compared to relaxor behaviour...
in corresponding filled analogues. The amount of vacancies incorporated could therefore provide an additional degree of freedom for tuning of properties.

A low temperature relaxor-type peak with strong frequency dispersion and a non-frequency dependent high temperature peak were detected in the relative permittivity of Ba$_{3}$La$_{0.54}$Nb$_{10}$O$_{30}$. Low temperature $P$-$E$ hysteresis loops, indicating ferroelectric behaviour, transform into a ‘pinched’ or antiferroelectric-type loop in the temperature range between the dielectric peaks, and finally to a linear dielectric-type $P$-$E$ response at higher temperature. The precise origins of this behaviour are not yet known.

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References

3 V. M. Goldschmidt, Die Naturwissenschaften, 1926, 4, 477.