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Structurally frustrated polar nanoregions in BaTaO₂N and the relationship between its high dielectric permittivity and that of BaTiO₃

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This letter presents direct evidence for the existence of the same inherently polar one-dimensional (1D), displacive disorder in BaTaO₂N as occurs in paraelectric BaTiO₃ as well as in doped BaTiO₃ relaxor ferroelectric systems. The inherently polar, off-center and oppositely directed displacements of Ta and neighboring O/N ions along $\langle 001 \rangle$ give rise to 1D polar nanoregions (PNRs) and are responsible for the dielectric properties of BaTaO₂N. A bond valence sum analysis of the underlying crystal chemistry of BaTaO₂N shows clearly that O/N ordering is not directly responsible for inducing the observed 1D PNRs. © 2008 American Institute of Physics. [DOI: 10.1063/1.2890052]

BaTaO₂N of ideal perovskite average structure type¹ is reported to exhibit an extremely high bulk dielectric permittivity (~ 4900 at 300 K),² reminiscent of the values seen in BaTiO₃ near its para to ferroelectric phase transition.³ Unlike BaTiO₃, however, BaTaO₂N does not exhibit a cubic paraelectric to tetragonal ferroelectric phase transition anywhere within a very wide temperature range (its average crystal structure is metrically cubic with a lattice parameter that varies smoothly from 4 K right up to 1200 K)^{1,2} nor the strongly temperature-dependent changes in dielectric permittivity that occur in the vicinity of this transition in the case of BaTiO₃.³ Rather, the extracted bulk dielectric permittivity of BaTaO₂N shows only a relatively moderate temperature dependence (~ 1140 ppm K⁻¹), over the limited temperature range for which the dielectric permittivity has been measured (from 180 up to 300 K).² Again, unlike BaTiO₃, the as measured dielectric constant and dielectric loss of BaTaO₂N are frequency dependent.² This behavior, when coupled with the presence of probable local O²⁻/N³⁻ structural disorder,⁴⁻⁶ is rather more reminiscent of the behavior of relaxor ferroelectrics such as Ba(Ti_{1-x}Sn_x)O₃, $x \geq 0.17$.⁷ While there are severe practical problems associated with the sinterability² of BaTaO₂N, a very high, only moderately temperature dependent, dielectric permittivity is a potentially extremely useful property and its crystal chemical understanding of considerable importance.^{1,2,4-6}

Attention, to date,^{2,4-6} has focused heavily on local O²⁻/N³⁻ ordering and associated induced off-center Ta displacements, giving rise to nanoscale "...polar octahedral units...".² Relaxor ferroelectric behavior has long been attributed to similar polar nanoregions (PNRs).⁸⁻¹¹ First principles calculations on BaTaO₂N (Ref. 4) predicting Ta-N bonds to be shorter on average than Ta-O bonds appear consistent with extended x-ray-absorption fine structure (EXAFS) experiments^{5,6} which find that the nearest neighbor Ta to anion radial distribution function exhibits "...a broad bimodal peak... indicating a low symmetry coordination environment around Ta..."⁶ The problem with linking the dielectric properties of BaTaO₂N directly with off-center Ta shifts induced by local O²⁻/N³⁻ ordering, however, is that

such compositional disorder (and associated polar behavior) is presumably frozen up until high temperature and hence not available to switch sign under the action of an applied electric field. Rather, the PNR's primarily responsible for the dielectric behavior of BaTaO₂N should arise from inherent (i.e., not fundamentally dependent on chemical disorder) cooperative displacive disorder.¹²

We have recently observed direct evidence for such behavior in a range of doped BaTiO₃ relaxor ferroelectric systems^{13,14} in the form of transverse polarized,¹⁵ $\{001\}^*$ sheets of diffuse intensity running through all parent perovskite Bragg reflections **G**. This has prompted the current careful electron diffraction reinvestigation of BaTaO₂N to see if the same behavior might also occur and what this might mean for our understanding of the dielectric properties of BaTaO₂N.

Metrically, cubic BaTaO₂N, $a = 4.1125(4)$ Å, was synthesized by an ammonolysis reaction, as described previously.² Electron diffraction patterns (EDP's) were collected using a Philips EM 430 transmission electron microscope. Figure 1 shows the (a) $\sim [010]$, (b) $\sim [-2, 11, 0]$, and (c) $[-1, 4, 0]$ zone axis EDPs typical of BaTaO₂N. Note that there is a complete absence of diffuse intensity very close to the exact $[010]$ orientation [see Fig. 1(a)]. However, on tilting no more than a few degrees away from the exact $[010]$ orientation keeping an $\langle 001 \rangle^*$ systematic row excited, the presence of quite characteristic, transverse polarized diffuse streaking becomes immediately apparent. This diffuse streaking runs through parent perovskite Bragg reflections **G** perpendicular to the $\langle 001 \rangle$ real space directions forming essentially continuous $\mathbf{G} \pm \{001\}^*$ sheets of diffuse intensity. The transverse polarized¹³⁻¹⁵ nature of this characteristic diffuse distribution is clear from its strong azimuthal intensity variation and shows that the observed $\{001\}^*$ sheets of diffuse intensity necessarily arise from the correlated longitudinal motions of ions along the $\langle 001 \rangle$ real space directions. The absence of diffuse streaking at the exact $\langle 010 \rangle$ zone axis orientations [see Fig. 1(a)] is a characteristic of such systems and arises because of the lack of transverse correlation from one $\langle 001 \rangle$ column to the next (e.g., in the $[010]$ orientation, the neighboring $[001]$ correlated columns of atoms project on top of one another; the average displacements in projec-

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FIG. 1. (Color online) (a) $\sim[010]$, (b) $\sim[-2,11,0]$, (c) $[-1,4,0]$ zone axis EDPs typical of BaTaO_2N and (d) a schematic drawing of the 1D $\langle 001 \rangle$ PNRs of BaTaO_2N required by the observed electron diffraction evidence. The oppositely directed shifts along $\langle 001 \rangle$ of neighboring Ta and O/N ions are labeled by arrows. The Ta and O/N ions are represented by the blue and red balls, respectively.

tion are then zero, and so, there can be no corresponding observed diffuse streaking). Finally, note the characteristic variation in diffuse intensity from one $\mathbf{G} \pm \{001\}^*$ sheet to the next which shows that the individual $\mathbf{q} = \langle 0kl \rangle^*$ modes of distortion responsible for the observed diffuse scattering are inherently polar in nature, e.g., the $h/6 \langle 610 \rangle^* + \gamma \langle 001 \rangle^*$, h odd, diffuse streaking in Fig. 1(b) or the $h/4 \langle 410 \rangle^* + \gamma \langle 001 \rangle^*$, h odd, diffuse streaking in Fig. 1(c) is more intense than the h even diffuse streaking. This characteristic intensity variation requires that the Ta ion at 000 and the disordered O/N anion above it at $\frac{1}{2}, 0, 0$ (along the polar $\langle 100 \rangle$ directions) necessarily shift in opposite directions along $\langle 100 \rangle$ for all $\mathbf{q}$, as shown schematically in Fig. 1(d) (see Refs. 13 and 14 for more details).

Essentially identical, transverse polarized, $\{001\}^*$ sheets of diffuse intensity are characteristic not only of BaTiO_3 -doped relaxor ferroelectrics^{13,14} but, most significantly, also of BaTiO_3 itself,^{16–19} where compositional ordering can have no role to play in the existence of the structured diffuse distribution. This strongly suggests that the correlated polar atomic displacements responsible for the observed structured diffuse in such systems, including BaTaO_2N , must all have an underlying intrinsic crystal chemical origin not primarily related to any compositional ordering of either cations or anions.

The correlation length along the individual 1D chain directions of these polar atomic displacements [see Fig. 1(d)] essentially corresponds to one over the half width at half maximum height of the $\{001\}^*$ sheets of diffuse intensity. This is difficult to measure from electron diffraction data such as that shown in Figs. 1(a)–1(c) but is clearly no less than 3–4 nm along the $\langle 001 \rangle$ direction. While one could, in principle, envisage a minimum of ~ 8 –10 unit cell long–N–Ta–N–strings embedded in even longer–O–Ta–O–strings along a particular $\langle 001 \rangle$ direction which might be compatible with an individual $\mathbf{G} \pm \{001\}^*$ sheet of diffuse intensity,¹⁴ the diffraction evidence also strongly suggests that there is no correlation between different $\langle 001 \rangle$ -type strings (otherwise, one would observe a three-dimensional structured diffuse distribution rather than the observed 1D sheets of diffuse intensity). Thus, the probability of, e.g., a local TaO_6 octahedron, $P(\text{TaO}_6) \sim (\frac{2}{3})^3 = \frac{8}{27}$, $P(\text{TaO}_4\text{N}_2) \sim 3(\frac{2}{3})^2(\frac{1}{3}) = \frac{12}{27}$, etc. From the crystal chemical point of view, such a range of local $\text{Ta}(\text{O},\text{N})_6$ coordination polyhedron would cause enormous local strain and is so unlikely that it can be ruled out as a realistic possibility. Note that this does not mean that local O/N ordering does not occur (indeed, the recently reported neutron PDF study of BaTaO_2N “...favors a *cis* configuration of... (local) ... TaO_4N_2 polyhedra...”), just that it cannot be responsible for the observed structured diffuse distribution. The 1D PNRs cannot therefore be directly related to O/N ordering and associated induced Ta displacements.

What then is the underlying crystal chemical origin of these 1D correlated displacements (1D PNRs) in the case of BaTaO_2N ? If we assume the ideal parent perovskite structure for BaTaO_2N ($Pm-3m$, $a=4.1125$ Å; Ta at 000, Ba at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and O/N at $\frac{1}{2}, 0, 0$) with four O and 2 N surrounding each Ta ion and eight O and 4 N surrounding each Ba ion, then the calculated valence $V_i = \sum_j S_{ij}$ (Refs. 20–23) for the Ba ion is 2.730 valence units (v.u.), for the Ta ion is 4.486 v.u., for the O ion is –2.137 v.u. and for the N ion is –2.942 v.u. using the program EUTAX and the bond valence parameters given in Ref. 23. Given the ideal valences of 2, 5, –2, and –3, respectively, the deviation from the ideal valence ΔV_i is then given by $\Delta V(\text{Ba})=0.730$, $\Delta V(\text{Ta})=-0.514$, $\Delta V(\text{O})=-0.137$, and $\Delta V(\text{N})=0.058$, respectively. [Very similar numbers are characteristic of the cubic paraelectric form of BaTiO_3 suggesting that the similar magnitudes of the bulk dielectric constants of BaTaO_2N (Ref. 2) and BaTiO_3 (Ref. 3) are no accident.] The so-called global instability index,²¹ often used to quantify residual bond strain,^{20–22} is then given by $G_{ii}^2 = 1/N \sum_i \{\Delta(V)_i\}^2 = \frac{1}{5} \{1(0.730)^2 + 1(0.514)^2 + 2(0.137)^2 + 1(0.058)^2\} = 0.1677 = (0.4095)^2$. This rather high value of G_{ii} shows that there is a large amount of chemical strain present. Typically, room temperature structures do not have G_{ii} values higher than 0.2–0.3.^{20–22} A recent comparison of empirical bond valence and first principles energy calculations has shown that G_{ii}^2 scales remarkably well with *ab initio* total energy calculations.²² Empirical experience suggests the same.^{20,21} The question now becomes: Can this residual bond strain be relieved? i.e., how can G_{ii}^2 , or the total energy, be minimized?

Note that the Ba ion is very significantly overbonded and the Ta ion significantly underbonded. By contrast, the O anion is slightly overbonded and the N anions very slightly underbonded. Any displacement of the Ba ion away from the centre of its ideal 12-fold coordination environment can only

increase its already significant overbonding.²¹ Therefore, the Ba ions will strongly resist any such displacement, i.e., it is not possible to significantly reduce G_{ii}^2 by reducing the Ba contribution to it. Of the remaining contributions to G_{ii}^2 , the underbonding of the Ta ion contributes $\sim 87\%$ and it is clear that the reduction of this underbonding is the predominant driving force for the off-center displacement of the Ta ions, the observed diffuse distribution, and the 1D PNRs, not local O/N ordering and associated induced Ta displacements.

The Ta ions can significantly improve their underbonding by moving a distance $\varepsilon_{Ta}a$ directly toward one neighboring anion (whether O or N) along each of the individual $\langle 001 \rangle$ directions [see, e.g., Fig. 1(d)]. Simultaneously, the anion (subscript A in what follows) will move toward the incoming cation a distance $\varepsilon_A a$. (Note that this latter shift will very slightly increase all 12 Ba–O bond distances from $a\sqrt{1/2}$ to $a\sqrt{(1/2 + \varepsilon_A^2)}$ and hence simultaneously very slightly reduce the over bonding of the Ba ions. This, however, is very much a second order effect.) Because the anion toward which the Ta moves is already essentially happily bonded, the Ta ion on the other side of this anion must simultaneously move away from the incoming Ta ion, i.e., the pattern of induced displacements must necessarily be correlated along the $\langle 001 \rangle$ chain directions, i.e., the “modulation” is essentially long range ordered along the $\langle 001 \rangle$ chain directions [see Fig. 1(d)]. Note, however, that there is no requirement from the bond valence point of view for this 1D displacement pattern to be correlated from one chain to the next in the transverse direction, just as is observed experimentally in the form of essentially continuous $\mathbf{G} \pm \{001\}^*$ sheets of diffuse intensity (see Fig. 1).

Given that these chains run along all three $\langle 001 \rangle$ directions simultaneously, the Ta-anion distances then split into two with $r_{1,2} = a\sqrt{[(1/2 \pm (\varepsilon_{Ta} + \varepsilon_O))^2 + 2\varepsilon_{Ta}^2]}$, consistent with the results of the EXAFS experiments which find a “...bimodal peak in the radial distribution function (around Ta)...”⁶ Minimization of G_{ii}^2 suggests that the magnitude of $(\varepsilon_{Ta} + \varepsilon_O)$ should be around 0.036 depending on the ratio of ε_O to ε_A . For $\varepsilon_O/\varepsilon_A = 1$, $G_{ii}^2 (=0.136)$ is minimized for $(\varepsilon_{Ta} + \varepsilon_O) = 0.0365$ corresponding to $r_1 = 2.209$ Å and $r_2 = 1.909$ Å. The relative magnitudes of ε_{Ta} and ε_O , however, cannot really be determined by the present study. The corresponding valence values are then $V(\text{Ba}) = 2.72$ v.u., $V(\text{Ta}) = 4.82$ v.u., $V(\text{O}) = 2.24$ v.u., and $V(\text{N}) = 3.07$ v.u.

The existence of the 1D $\langle 001 \rangle$ PNRs implied by the $\{001\}^*$ sheets of diffuse intensity in BaTaO₂N materials thus are not induced by the local O/N distribution but rather are intrinsic to the fundamental underlying crystal chemistry of the material. Nonetheless, given that O is likely to be slightly more overbonded than N after the addition of the 1D PNRs [see above and Fig. 1(d)], there remains scope for the Ta adjusting their positions within each “octahedra” slightly depending on the type (*cis* or *trans*) and orientation of the local O₄N₂ coordination polyhedra. (The magnitude of any such additional induced Ta shifts, however, is likely to be rather small and hence unlikely to give rise to an observable second type of structured diffuse distribution.) This will give rise to local strain dependent on the exact O/N distribution.

If the O/N ordering does not “induce” the PNRs, then what is the role of the chemical disorder? We suggest^{13,14} that its role is to set up random local strain fields suppressing transverse correlations of the inherent $\langle 001 \rangle$ chain dipoles [see Fig. 1(d)] and the development of a long range ordered ferroelectric state. Theoretical calculations have shown that homogeneous strain distortion plays a critical role in the stabilization of the low temperature ferroelectric phases of BaTiO₃.^{24,25} It would not then be surprising if essentially random local strain distortions induced by the local O/N distribution would suppress the condensation of long wavelength homogeneous strain distortions of the unit cell, thereby suppressing transverse correlations of the $\langle 001 \rangle$ chain dipoles and the development of a long range ordered ferroelectric state.

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- ¹F. Pors, R. Marchand, Y. Laurent, P. Bacher, and G. Roult, *Mater. Res. Bull.* **23**, 1447 (1988).
- ²Y.-I. Kim, P. M. Woodward, K. Z. Baba-Kishi, and C. W. Tai, *Chem. Mater.* **16**, 1267 (2004).
- ³A. R. West, T. B. Adama, F. D. Morrison, and D. C. Sinclair, *J. Eur. Ceram. Soc.* **24**, 1439 (2004).
- ⁴C. M. Fang, G. A. de Wijs, E. Orhan, G. de With, R. A. de Groot, H. T. Hintzen, and R. Marchand, *J. Phys. Chem. Solids* **64**, 281 (2003).
- ⁵B. Ravel, Y.-I. Kim, P. M. Woodward, and C. M. Fang, *Phys. Rev. B* **73**, 184121 (2006).
- ⁶K. Page, M. W. Stolz, Y.-I. Kim, T. Proffen, P. M. Woodward, A. K. Cheetham, and R. Seshadri, *Chem. Mater.* **19**, 4037 (2007).
- ⁷N. Yasuda, H. Ohwa, and S. Asano, *Jpn. J. Appl. Phys., Part 1* **35**, 5099 (1996).
- ⁸G. A. Smolenskii and A. I. Agranovskaya, *Sov. Phys. Solid State* **1**, 1429 (1959).
- ⁹L. E. Cross, *Ferroelectrics* **76**, 241 (1987).
- ¹⁰G. A. Samara, *J. Phys.: Condens. Matter* **15**, R367 (2003).
- ¹¹A. A. Bokov and Z.-G. Ye, *J. Mater. Sci.* **41**, 31 (2006).
- ¹²V. Bovtun, J. Petzelt, V. Porokhonskyy, S. Kamba, and Y. Yakimenko, *J. Eur. Ceram. Soc.* **21**, 1307 (2001).
- ¹³Y. Liu, R. L. Withers, X. Wei, and J. D. Fitz Gerald, *J. Solid State Chem.* **180**, 858 (2007).
- ¹⁴Y. Liu, R. L. Withers, B. Nguyen, and K. Elliott, *Appl. Phys. Lett.* **91**, 152907 (2007).
- ¹⁵R. L. Withers, *Z. Fur Krist* **220**, 1027 (2005).
- ¹⁶J. Harada, M. Watanabe, S. Kodera, and G. Honjo, *J. Phys. Soc. Jpn.* **20**, 630 (1965).
- ¹⁷R. Comes, M. Lambert, and A. Guinier, *Solid State Commun.* **6**, 715 (1968).
- ¹⁸M. Lambert and R. Comes, *Solid State Commun.* **7**, 305 (1969).
- ¹⁹R. Comes, M. Lambert, and A. Guinier, *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* **26**, 244 (1970).
- ²⁰R. L. Withers, J. G. Thompson, and A. D. Rae, *J. Solid State Chem.* **94**, 404 (1991).
- ²¹I. D. Brown, *The Chemical Bond in Inorganic Chemistry. The Bond Valence Method* (Oxford University Press, Oxford, 2002).
- ²²I. Etxebarria, J. M. Perez-Mato, A. Garcia, P. Blaha, K. Schwarz, and J. Rodriguez-Carvajal, *Phys. Rev. B* **72**, 174108 (2005).
- ²³M. O’Keeffe and N. E. Brese, *Acta Crystallogr., Sect. B: Struct. Sci.* **48**, 152 (1992).
- ²⁴Ph. Ghosez, X. Gonze, and J.-P. Michenaud, *Ferroelectrics* **206–207**, 205 (1998).
- ²⁵H. Krakauer, R. Yu, C.-Z. Wang, K. M. Rabe, and U. V. Waghmare, *J. Phys.: Condens. Matter* **11**, 3779 (1999).