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Phys. Rev. B **92**, 235122 — Published 11 December 2015

DOI: [10.1103/PhysRevB.92.235122](https://doi.org/10.1103/PhysRevB.92.235122)

# New class of planar ferroelectric Mott insulators via first principles design

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The bulk photovoltaic effect requires a low electronic band gap (i.e.  $\approx 1\text{-}2\text{ eV}$ ) and large electronic polarization, which is not common in known materials. Here we use first-principles calculations to design layered double perovskite oxides  $AA'BB'O_6$  which achieve the aforementioned properties in the context of Mott insulators. In our design rules, the gap is dictated by B/B' electronegativity difference in a Mott state, while the polarization is obtained via nominal  $d_0$  filling on the B-site, A-type cations bearing lone-pair electrons, and  $A \neq A'$  size mismatch. Successful execution is demonstrated in  $BaBiCuVO_6$ ,  $BaBiNiVO_6$ ,  $BaLaCuVO_6$ , and  $PbLaCuVO_6$ .

PACS numbers: 88.40.fh, 81.05.Zx, 73.20.At, 78.20.Bh

The bulk photovoltaic effect (BPE), which separates photo-excited electron-hole pairs via the internal electric field in an intrinsically polar material<sup>1</sup>, has great potential to harness sunlight with enhanced efficiency. Ferroelectric oxides are a prime class of materials to realize the BPE<sup>2-7</sup>, though there are typically two major deficiencies; large electronic band gap (i.e.  $\geq 3\text{ eV}$ ) and extremely low photo-current<sup>7</sup>. Fortunately, the recent application of shift current theory has provided significant insight into the latter phenomenon, and it is apparent that strong polarization and covalency are necessary ingredients for enhancing the photocurrent<sup>8,9</sup>. While hybrid perovskite materials can satisfy the general requirements of the BPE<sup>8,10-14</sup>, their instability against water due to weak halide bonding and environmental issues associated with lead are still very serious problems<sup>13</sup>. Therefore, satisfying the BPE criteria in transition metal oxides is a very important open problem in materials physics.

Designing a lower band gap in oxide<sup>15,16</sup> and ferroelectric oxides<sup>2-4,17,18</sup> has drawn a large degree of attention. One possible route to smaller band gaps is to utilize Mott or charge-transfer insulators, as in the well-known case of  $BiFeO_3$  where an optical gap edge of  $2.2\text{ eV}$  is realized<sup>19,20</sup>. While the gap is still excessive in this case, this is a promising direction that can be further exploited in the context of the perovskites. Recent studies have expanded to Mott, or Slater-Mott, physics in more complex double perovskites, demonstrating success in achieving lower bandgaps though the polarization is small in these systems<sup>2,4,21</sup>.

In this letter, we design a new class of materials where we leverage the complexity of doubly ordered perovskite  $AA'BB'O_6$ <sup>22-24</sup> to harness all of the existing mechanisms satisfying the aforementioned requirements of the BPE.  $B' \neq B$  is chosen to achieve a nominally empty  $d$ -shell on the B-site (i.e.  $d_0$ ) and a Mott susceptible filling on the B'-site, yielding a low band gap based on electronegativity differences and electronic correlations<sup>25-27</sup>, while the Pseudo Jahn-Teller Effect (PJTE) on the nominal  $d_0$  B-site results in a large ferroelectric polarization. In or-

der to achieve larger polarization, we further exploit A cations bearing lone-pair electrons while  $A'$  does not and has nontrivial size mismatch<sup>21,28,29</sup>. Layered ordering of  $AA'$  and  $BB'$  ions is a final condition we utilize. Experimental exploration of  $BB'$  rock salt ordered  $A_2MWO_6$  ( $M=\text{Ni, Mn, Cu}$ )<sup>30-33</sup> demonstrated no polarization associated with  $d_0$  W, and it was suggested that rock salt ordering was responsible<sup>34</sup>. Therefore, it is desirable to pursue layered ordering of  $BB'$ . Furthermore, octahedral tilting competes with the second order Jahn-Teller distortion associated with the  $d_0$  site<sup>35</sup>, and having a layered ordering of  $AA'$  with large size mismatch can frustrate octahedral tilting<sup>36</sup>. Also, layered  $BB'$  ordering and suppressed octahedral tilting have been found to yield lower band gaps<sup>37</sup>. Layered ordering allows for spontaneously broken symmetry within the plane, resulting in planar ferroelectricity with reasonable energy barriers. For these reasons, we restrict this study to layered ordering of  $AA'$  and  $BB'$  ions, which is conducive to layer-by-layer growth, such as molecular beam epitaxy and pulsed laser deposition.

Here we utilize the above mechanisms to deduce a specific set of materials. We employ  $Bi^{3+}$  or  $Pb^{2+}$  as A-type ions bearing lone pair electrons. In order to maximize  $AA'$  size mismatch, the  $A'$  ion is chosen to have a different valence than the A-type. In particular,  $Bi^{3+}$  is paired with  $Ba^{2+}$  while  $Pb^{2+}$  is paired with  $La^{3+}$ , where the selection was dictated by maximizing the size of the A-type ion in the respective valence state. Given our  $AA'$  selections, nominal valence counting dictates  $(BB')^{+7}$ , and one of these ions should be  $d_0$  which requires sufficient charge transfer. Therefore, we select vanadium as the  $d_0$  ion, which must exist in the  $5^+$  valence, in conjunction with various B ions in the  $2^+$  valence. Vanadium is chosen over, for example,  $Ti^{4+}$  or  $Nb^{5+}$  for several reasons. First,  $V^{5+}$  is smaller than  $Nb^{5+}$  and  $Ti^{4+}$ <sup>38</sup>, which will lead to a larger polarization. Second, having a  $d_0$   $B'^{5+}$  ion dictates a nominal  $B^{2+}$ -type ion that is more susceptible to being a Mott insulator for the later transition metals, which are necessary in order to ensure full charge transfer (i.e. sufficient electronegativity differences). There-

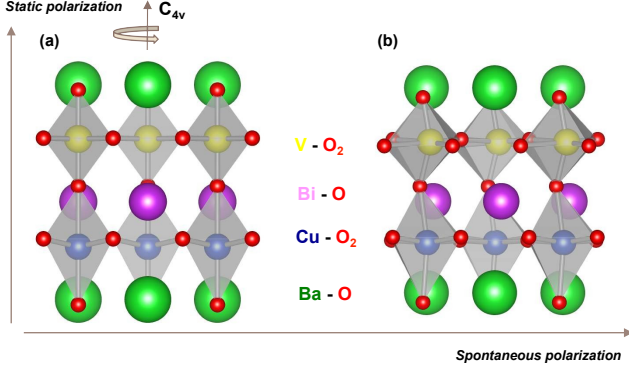


FIG. 1. (a) Reference structure  $R_o$ , where the atoms have been placed on an ideal perovskite lattice and subsequently relaxed only in the  $z$ -direction. As illustrated, this structure retains  $C_{4v}$  symmetry, though it is unstable. (b) Reference structure  $R_{\mathbf{q}=\pi,\pi,0}$ , which allows for full relaxation of all  $\mathbf{q} = (\pi, \pi, 0)$  distortions and lattice strains.

fore, for B-type ions we choose  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . These physically motivated choices are permuted to search for optimal properties, and we additionally explore the validity of these underlying rules. We begin with a detailed exploration of  $\text{BaBiCuVO}_6$ , and then generalize to other possible permutations.

In order to elucidate the origin and nature of the ferroelectric polarization in layered  $\text{BaBiCuVO}_6$ , we consider three reference structures. The first reference structure, referred to as  $R_o$ , consists of placing the atoms on the ideal perovskite lattice and then allowing full relaxations of the lattice parameters while only relaxing the atoms in the  $z$ -direction (space group  $Cmm2$ , see figure 1a). The second reference structure,  $R_{\mathbf{q}=0}$ , corresponds to fully relaxing  $R_o$  with respect to lattice parameters and all internal coordinates within the unit cell (space group  $Cm$ , not pictured). The third reference structure,  $R_{\mathbf{q}=\pi,\pi,0}$ , corresponds to creating a supercell with lattice vectors  $(1/\sqrt{2}, 1/\sqrt{2}, 0)$ ,  $(1/\sqrt{2}, -1/\sqrt{2}, 0)$  and  $(0, 0, 1)$  in terms of  $R_o$ , and then fully relaxing lattice parameters and all internal coordinates (space group  $Pc$ , see figure 1b). These structures allow one to determine the role of  $\mathbf{q} = 0$  relaxations and octahedral rotations. It should be noted that even the highest symmetry reference  $R_o$  contains a static polarization in the  $z$ -direction, though an in-plane ferroelectric polarization can still be formed by spontaneously breaking  $C_{4v}$  symmetry via the destruction of a mirror plane upon degenerating to  $R_{\mathbf{q}=0}$  or  $R_{\mathbf{q}=\pi,\pi,0}$ .

We begin by examining the  $R_o$  structure for  $\text{BaBiCuVO}_6$  (see figure 1). In this case, we observe a large structural relaxation of both the Ba and Bi towards the  $\text{Cu-O}_2$  layer, presumably due to the large nominal

$5+$  charge associated with the V ion. This strong distortion will be seen in all subsequent structures, irrespective of octahedral rotations and other further symmetry breaking. While there is a polarization in the  $z$ -direction associated with this A/A' ordering and the subsequent  $z$ -direction distortion, this is not relevant for our interests as this ordering is static and could not practically be switched. The main question is therefore how symmetry is spontaneously broken relative to this reference.

In figure 2, we have computed phonon spectra for the three reference structures of  $\text{BaBiCuVO}_6$ <sup>20</sup>. In the  $R_o$  structure there are many soft-modes, including at the  $\Gamma$ -point, reflecting the unstable nature of this highest symmetry structure (see figure 2a). In the  $R_{\mathbf{q}=0}$  structure, all of the  $\Gamma$ -point instabilities have been removed as this structure is a fully relaxed degeneration of the  $R_o$  structure (see figure 2b). This effect is pictorially illustrated in the comparison of the planar projections of figures 2f and 2g. However, there are still strong in-plane instabilities shown in the phonons, which correctly suggests that there is some lower energy tilting pattern of the octahedron. In the  $R_{\mathbf{q}=\pi,\pi,0}$  structure, it is demonstrated that all in-plane instabilities have been removed (see figure 2c), and the resulting structure is illustrated in the planar projections of figure 2h and 2i. However, the  $R_{\mathbf{q}=\pi,\pi,0}$  structure still has a small instability in the  $z$ -direction of reciprocal space. By doubling the unit cell in the  $z$ -direction and allowing for full atomic relaxations, we have determined that this instability only causes a very small structural distortion that does not substantially affect the physics (i.e. the energy gain is  $\approx 1\text{meV}$  per f.u.). Therefore,  $R_{\mathbf{q}=\pi,\pi,0}$  is a sufficient approximation for our ground state structure.

Having established how the symmetry degenerates, we now use the Born effective charges of the  $R_{\mathbf{q}=\pi,\pi,0}$  structure to produce an approximate layer-resolved ferroelectric polarization, referenced by  $R_o$ . The main contribution to the polarization comes from large displacements within the Bi-O and V-O<sub>2</sub> layers, which arise from the second order Jahn-Teller effect associated with the lone-pair electrons and  $d_0$  configuration, respectively. In the  $R_{\mathbf{q}=0}$  structure, a large polarization of  $0.5\text{Cm}^{-2}$  is formed with roughly equal contributions from the Bi-O layer and V-O<sub>2</sub> layer, and this occurs in the absence of any octahedral rotations (see figure 2f and 2g). In the  $R_{\mathbf{q}=\pi,\pi,0}$  structure, the magnitude of the polarization remains similar though the direction changes (see figure 2h and 2i). Therefore, octahedral tilts do perturb the direction of the polarization. It should be noted that the polarization in the Bi-O layer is aligned in the same direction as the polarization in the V-O<sub>2</sub> layer, giving rise to the very large in-plane polarization. The possibility of anti-aligning the Bi-O and V-O<sub>2</sub> layers was explored, but this could not be stabilized in our calculations.

In our system, spontaneous breaking of  $C_{4v}$  symmetry inherently provides disparate paths between symmetry equivalent minima, and we explore the paths defined by the  $R_{\mathbf{q}=\pi,\pi,0}$  structure rotated by  $C_\pi$  and  $C_{\pi/2}$ , respec-

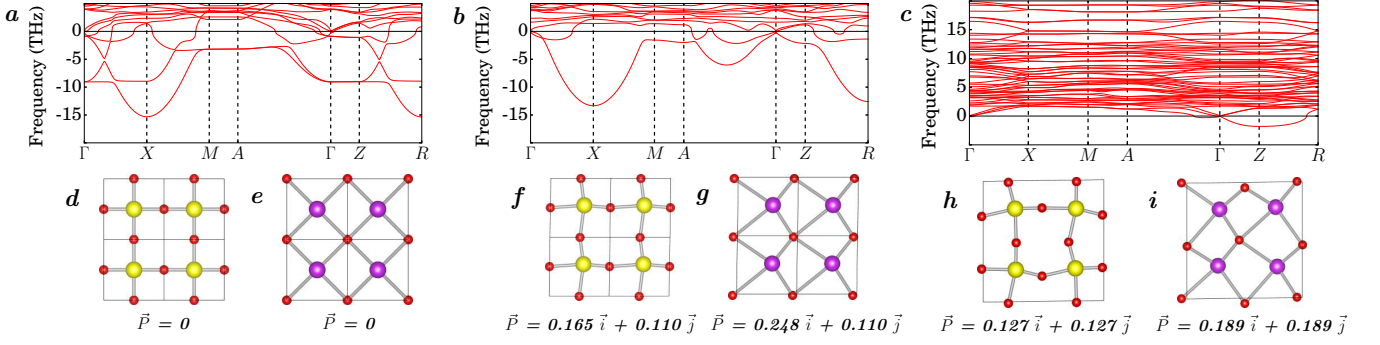


FIG. 2. The phonons of reference structures for BaBiCuVO<sub>6</sub> are presented in panel (a) , (b) , (c) corresponding to  $R_o$ ,  $R_{\mathbf{q}=0}$ , and  $R_{\mathbf{q}=\pi,\pi,0}$ , respectively. Corresponding in-plane projections of the V-O<sub>2</sub> and Bi-O layers are given in panels (d) , (e) for  $R_o$ , panels (f) , (g) for  $R_{\mathbf{q}=0}$ , and panels (h) , (i) for  $R_{\mathbf{q}=\pi,\pi,0}$ .  $\mathbf{P}$  indicates layer-resolved polarization,  $Cm^{-2}$ .

tively. The modern theory of polarization (MTP)<sup>39,40</sup> is utilized to compute the ferroelectric moment in conjunction with the path defined by  $C_\pi$ , yielding  $0.65 Cm^{-220}$ . Additionally, the corresponding energy barrier is calculated to be  $277 meV$  per transition metal ion<sup>20</sup>. Alternatively, the path defined by  $C_{\pi/2}$  results in half of the energy barrier, and this could be beneficial to enhancing switching speeds<sup>41</sup>. These energy barriers for BaBiCuVO<sub>6</sub> are reasonable in the sense that BiFeO<sub>3</sub> has a theoretical energy barrier of  $427 meV/f.u.$  yet the ferroelectric moment is experimentally switchable<sup>42</sup>. Furthermore, this material demonstrates strong hybridization given that using the Born effective charges from a given structure results in a substantial deviation from MTP<sup>20,43</sup>.

In figure 3, we explore the basic electronic structure of BaBiCuVO<sub>6</sub>, which is shown to follow the simple rules outlined in the introduction. More specifically, V nominally donates its sole  $d$ -electron to Cu, analogous to what was observed for Ti in La<sub>2</sub>NiTiO<sub>6</sub><sup>25</sup>. We begin by illustrating this via density functional theory (DFT)+ $U$  calculations, where we use a Hubbard  $U$  of  $5 eV$  on the copper site, consistent with previous studies<sup>44</sup>, and we conservatively use  $U = 0$  on the V site. The standard fully localized limit double counting<sup>45,46</sup> is used, and no on-site exchange is employed given that we are using a spin-dependent density functional<sup>47</sup>. The resulting density of states (DOS) for the ground state antiferromagnetic spin ordering yields a band gap of  $1.1 eV$  (see figure 3a). The atom resolved DOS for V exhibits a strong peak above the gap indicating a complete nominal charge transfer, which is corroborated by zero magnetic moment on the V atom. However, there is a substantial orbital occupation of  $\approx 4$  electrons for the V  $d$ -orbitals due to strong hybridization with the oxygen, as illustrated by the substantial DOS projection of V towards the bottom of the oxygen bands.

The precise value of the on-site Coulomb repulsion  $U$  is still an open problem, and the DFT+ $U$  method is crude in the sense that it is a Hartree approximation to the dynamical mean field theory (DMFT) impurity problem

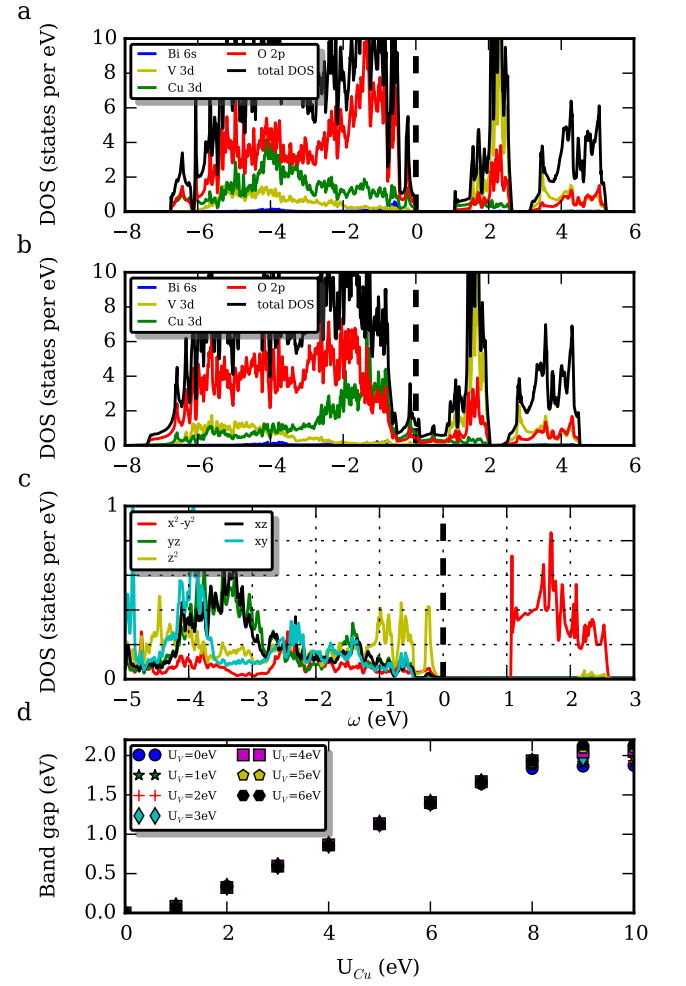


FIG. 3. Atomic resolved density of states of BaBiCuVO<sub>6</sub> in the  $R_{\mathbf{q}=\pi,\pi,0}$  structure for (a)  $U_V = 0$  and  $U_{Cu} = 5 eV$ ; (b)  $U_V = 0$  and  $U_{Cu} = 0$ ; (c) projection onto copper  $d$ -orbitals; Fermi energy is set to be  $0$ ; (d) The band gap as a function of  $U_V$  and  $U_{Cu}$ .

TABLE I. The electronic gap( $E_g$ , eV), energy barrier( $E_B$ ), (layer-resolved) polarization( $P$ ,  $Cm^{-2}$ ), and AA' size difference( $\text{\AA}$ ) based on Shannon radii<sup>38</sup> for AA'BB'O<sub>6</sub> compounds. The energy barrier is normalized per transition metal.  $V_{unit}$  is unit cell volume ( $\text{\AA}^3$ ). The asterisk indicates that  $U$  was increased to  $6.5\text{ eV}$  and  $8.0\text{ eV}$  on Ni and Cu, respectively, in order to ensure a gap was maintained over the entire distortion path, which is a necessary condition for the modern theory of polarization. This change has a negligible effect on the other observables.

AA'BB'O <sub>6</sub>	BaBiCuVO <sub>6</sub>	PbLaCuVO <sub>6</sub>	BaBiNiVO <sub>6</sub>	BaLaCuVO <sub>6</sub>
$E_g$	1.08	1.00	1.05	0.86
$E_B$	287	226	269	214
$P_{tot}$	0.65	0.52*	0.68*	0.41*
$A/A'$	0.25	0.13	0.25	0.26
$V_{unit}$	240.47	229.72	237.41	239.38
$P_{A-O}$	0.04	0.12	0.03	0.03
$P_{A'-O}$	0.28	0.10	0.28	0.08
$P_{B-O}$	0.00	0.00	0.03	0.00
$P_{B'-O}$	0.19	0.23	0.22	0.16

within the DFT+DMFT formalism. Both of these issues warrant a careful exploration of how the results are affected by changes in  $U$ . Therefore, we compute the band gap of the system as a function of  $U$  for vanadium and copper (see figure 3d). The  $U$  of vanadium has very little effect due to the large hybridization with the oxygen. Neglecting exchange, the orbital dependent term within DFT+U that is added to the Kohn-Sham potential has the form  $V_i = U(1/2 - n_i)$ <sup>48</sup>, such that orbitals near half filling will not be substantially perturbed unless  $U$  is sufficiently large relative to the hybridization.

Alternatively, the  $U$  on Cu is essential for driving the Mott physics and is necessary to open a gap (see figure 3a, 3b, and 3c). This scenario is analogous to the cuprates, where there is a substantial crystal field that breaks  $E_g$  symmetry and results in an effective single band Hubbard model which yields an antiferromagnetic Mott insulator. In BaBiCuVO<sub>6</sub>, this is clearly illustrated by the orbitally resolved DOS presented in figure 3c, where  $d_{xy}$  character is seen both above and below the gap while  $d_z^2$  is nearly completely filled. Cu has a magnetic moment of  $0.5\text{ }\mu_B$ , which is substantially reduced from the nominal value of  $1\text{ }\mu_B$ . Increasing the value of  $U$  increases the gap, though the magnitude of the increase is relatively small due to the strong hybridization of Cu and oxygen, and eventually the band gap largely saturates due to the upper band edge being dominated by V and the lower band edge being dominated by oxygen. Even for a relatively large value of  $U = 6\text{ eV}$ , the band gap remains relatively small at  $1.35\text{ eV}$ . This scenario should be contrasted to La<sub>2</sub>TiNiO<sub>6</sub>, where the gap depended strongly on the  $U$  value for Ti<sup>25</sup> due to a relatively smaller electronegativity difference for Ti-Ni and less Ti-O hybridization.

While we have illustrated our design principles in the context of BaBiCuVO<sub>6</sub>, these rules can obviously be

used to generate numerous other compounds with similar properties. For instance, PbLaCuVO<sub>6</sub>, BaBiNiVO<sub>6</sub>, and BaLaCuVO<sub>6</sub> are successfully realized (see table 1). We first consider the case of PbLaCuVO<sub>6</sub>, where we have decreased the A/A' mismatch while retaining one lone-pair cation and kept everything else identical. As expected<sup>28</sup>, the smaller A/A' mismatch results in a smaller polarization within the lone-pair cation layer, though a nontrivial polarization does form in the La-O layer. Nonetheless, the net effect is an overall decrease in polarization and a decrease in the energy barrier, which could be beneficial for ease of electrical switching. Due to the relatively small changes in the Cu-O<sub>2</sub> planes, the band gap changes very little. Another interesting case is to retain the Ba/Bi cations and instead exchange Ni in place of Cu. In this case, Ni will result in a 2+ state, which is susceptible to Mott physics, similar to NiO and the scenario outlined in La<sub>2</sub>TiNiO<sub>6</sub><sup>25</sup>. We find a similar barrier and polarization to BaBiCuVO<sub>6</sub>, which is consistent with the only change being associated with the ion exhibiting Mott physics. Additionally, the band gaps are relatively similar, assuming a reasonable value of  $U = 5\text{ eV}$  for Ni<sup>49</sup>. The final scenario we explore corresponds to the removal of lone-pair cations, which is the case of BaLaCuVO<sub>6</sub>. Here the only nontrivial polarization in the A/A' layers is associated with La-O, which is somewhat similar to what is observed in KNbO<sub>3</sub>-LiNbO<sub>3</sub><sup>50</sup>. The band gap is slightly reduced relative to BaBiCuVO<sub>6</sub> due to diminished tilting in the Cu-O<sub>2</sub> layer.

In conclusion, we have designed a new class of planar ferroelectric Mott insulators with small band gaps and large ferroelectric polarization. These systems satisfy the BPE criteria<sup>8,10</sup> of low band gap, strong ferroelectric polarization, covalent character, oxide-based materials and a large phase space of chemical elements such that properties can be tuned. A planar ferroelectric moment also has potential for application as a light-driven device<sup>5</sup>. Additionally, a sizeable planar ferroelectric moment has been demonstrated to give rise to charged domains walls, which have their own potential device applications<sup>51</sup>. A major experimental challenge will be realizing these materials via layer-by-layer growth.

## ACKNOWLEDGMENTS

We would like to thank D. Vanderbilt and K. Rabe for valuable discussions. The authors acknowledge funding from the FAME, one of six centers of STARnet, a Semiconductor Research Corporation program sponsored by MARCO and DARPA. The research used resources of the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U. S. Department of Energy under Contract No. DE-AC02-05CH11231

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