





# **EARLY CAREER SCHOLARS IN MATERIALS SCIENCE 2022**

# Developing new antiferroelectric and ferroelectric oxides and chalcogenides within the A<sub>2</sub>BX<sub>3</sub> family

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Received: 31 May 2021; accepted: 4 October 2021

Here, we employ first-principles methods to expand the set of functional materials known as ferroelectrics and antiferroelectrics. We use known compounds, whose properties have previously been overlooked, as the springboard for new materials. We first develop methodology to search for polar instabilities in known nonpolar and antipolar compounds and then use this technique to identify new members of the  $A_2BX_3$  family. This methodology identities new Pb-free oxides and chalcogenides, with a wide range of band gaps, to be used as solid-state photovoltaics. Finally, we perform a cursory evaluation of how compositional tuning of oxide materials can adjust the difference in energy between ground and metastable states, to assess the likelihood of polarization switching. In total, we report on a targeted sets of new materials to synthesize and design routes to obtain ferroelectrics and antiferroelectrics with energetic barriers amenable to switching with an electric field.



Joseph W. Bennett joined the University of Maryland Baltimore County (UMBC) in 2019 as a pre-faculty fellow through the College of Natural and Mathematical Sciences and was promoted to Assistant Professor in 2021. Bennett has built a research group in the Department of Chemistry & Biochemistry where he trains students to investigate problems related to human health, energy, and the environment using first-principles density functional theory. His interest in devising new routes to join experimental findings and atomistic calculations to create new materials began at the University of Pennsylvania, where he obtained a PhD in Chemistry in 2009. Since then, his work has combined crystallographic and thermodynamic database mining, inorganic chemistry, and first-principles methods to explore structure-property relationships across a wide range of bulk materials and their surfaces. This methodology led Bennett and coworkers to uncover new families of intermetallic ferroelectrics and antiferroelectrics while he was as a postdoctoral scholar in the Department of Physics & Astronomy at Rutgers University. Later, Bennett and coworkers created new models to explain the thermodynamics of surface

transformations for solid oxide cathode materials in contact with water. These collaborative efforts took place while he was as a member of the Center for Sustainable Nanotechnology, during his tenure as a research specialist at the University of Iowa. His current research activities are focused on the discovery of new chalcogenide-based functional materials for energy applications, the dissolution of oxide scales in water delivery systems, and understanding how computational surface science could assist in art conservation.

# Introduction

To augment experimental endeavors, computational investigations of a variety of materials have provided atomistic insights into a wealth of new compounds that display switchable polarizations, specifically solid-state ferroelectrics (FEs) and antiferroelectrics (AFEs) [1–10]. FE materials demonstrate a switchable polarization, most times driven by an applied electric field, and through a higher-symmetry nonpolar paraelectric



intermediate state. FEs also have a ground state that can be classified in crystallographic space groups that allow for polarization, so they are found within the ten polar crystal classes 6 *mm*, 6, 3 *mm*, 3, 4 *mm*, 4, *mm*2, *m*, 2, and 1 [11, 12]. AFEs, though similar in composition, are different; they have an antipolar ground state that is close in energy to a metastable FE state and can exhibit multiple polarization states [13]. The excitement in finding new examples of these types of functional materials is apparent in the last decade of research which has demonstrated that FEs are capable of energy production [14–16], and AFEs are capable of energy storage [17–20].

A few common examples of solid-state FEs include the perovskites [21–27], Ruddlesden-Popper phases [28, 29], Aurivillius and Dion Jacobson compounds [30–34], boracites [35, 36], tellurides [37, 38], and K<sub>2</sub>SeO<sub>4</sub>-type materials [39, 40]. Solidstate AFEs also include the perovskites [41–46], as well as sulfoaluminates [47], ZrO<sub>2</sub>, and HfO<sub>2</sub> [48, 49], orthorhombic *ABC* semiconductors [2, 7], Bi<sub>2</sub>SiO<sub>5</sub> [50, 51], and tungsten bronzes [52]. There are a preponderance of example FEs and AFEs that include oxides, sulfides, and selenides, and multiple examples where a variety of experimental techniques such as doping, film growth, strain engineering, confinement, and compositional tuning has resulted in the stabilization of new phases and resulted in enhanced material performance [17, 18, 43, 49, 53].

To complement both experimental techniques and the re-examination and development of new ferroic phase transitions theories [13, 54, 55], we focus on new example families of potentially functional materials to investigate as candidate

FEs and AFEs. In prior work, we combined density functional theory (DFT) and crystallographic database mining to establish a family of known compounds as materials whose functional properties have previously gone overlooked [56]. This family has a general chemical formula of  $A_2BX_3$  where A is a 1+ cation (Li, Na, K, Rb, Cs, Cu, Ag), B is a 4+ cation (Ti, Zr, C, Si, Ge, Sn, Pb), and X is a 2- anion (O, S, Se). While the compositions contain similar elements to conventional perovskite oxides and the other examples listed in the previous paragraph (K, Cs, Ti, Zr, O, S, etc.), the  $A_2BX_3$  family of materials has markedly different coordination environments. For example, the B-site is within a fivefold coordinate square pyramid, where the  $BX_5$  pyramids are edge-sharing units in a 1D network. The rotation of these units aligned or anti-aligned creates either polar or antipolar states, as depicted in Fig. 1. The structures in Fig. 1 are classified in crystallographic space groups Cmcm (#63), Pnma (#62), and  $Cmc2_1$  (#36), which we define as being nonpolar, antipolar, and polar, respectively. Compositions such as K<sub>2</sub>PbO<sub>3</sub> and Rb<sub>2</sub>PbO<sub>3</sub> were reported in space groups Pnma and Cmc2, [57-59], while Cs<sub>2</sub>PbO<sub>3</sub> was reported in space groups Cmcm and Cmc2<sub>1</sub> [59, 60]. When members of a materials family are reported in multiple space groups, this is a strong indication that the energetic barriers between nonpolar, antipolar, and polar states might be low. If so, then the family serves as an ideal model system for analysis from a computational materials design perspective.

Prior to our initial investigation, there were few reports of how any of the known structures might be related to each other [61–63] and to the best of our knowledge none that described



**Figure 1:** Shown here are the 3 primary structure types of the orthorhombic  $A_2BX_3$  investigated here. The antipolar (lower left-hand side) and polar (lower right-hand side) structural variants are symmetry related to a nonpolar parent structure. Each A-site is depicted as a solid black sphere, and each *B*-site is depicted as a light blue sphere inside of a  $BX_5$  square pyramid composed, whereas the *X*-sites are depicted as red spheres.



any member of the family as a candidate FE or AFE. Here, we more fully map out the potential energy landscape of  $A_2BX_3$ family of materials and further develop their novel structure–property relationships. First, we develop symmetry-based methodology to search for polar instabilities in nonpolar and antipolar compounds and then use these techniques to examine potentially new structure types of stoichiometry  $A_2BX_3$ . Second, we use DFT to identify new examples of oxide and chalcogenide materials with a wide range of band gaps using this method, and finally, we perform a cursory evaluation of how compositional tuning of known materials can adjust  $\Delta E$ , the difference in energy between ground and metastable states. In total, we (i) report on targeted sets of new materials to synthesize, (ii) design routes to obtain polar and antipolar ground-state structures, and (iii) better understand their spectrum of (meta)stable states.

# **Results and discussion**

Our prior work predicts that the  $A_2BX_3$  family of materials contain AFE and FE members whose properties have previously been overlooked. The AFEs have a computed antipolar ground state, that is within < 10 meV/fu of a polar metastable state, and are the previously synthesized compounds K<sub>2</sub>SnO<sub>3</sub>, K<sub>2</sub>PbO<sub>3</sub>, Rb<sub>2</sub>PbO<sub>3</sub>, K<sub>2</sub>TiO<sub>3</sub>, K<sub>2</sub>ZrO<sub>3</sub>, and K<sub>2</sub>TiS<sub>3</sub>. One composition, predicted to be FE, Cs<sub>2</sub>PbO<sub>3</sub>, has a polar ground state that is within < 10 meV/fu of an antipolar metastable state [56]. The barrier to switch between the polar and antipolar states is approximated as  $\Delta E_1$ , which here is the DFT-computed difference in total energy between antipolar and polar structures, or the AFE to FE switching barrier. Another metric of use is the computed FE barrier to switch between polar and nonpolar states, which here is labeled  $\Delta E_2$ . A depiction of the relationships between nonpolar, antipolar, and polar  $A_2BX_3$  structures and their energetics is shown in Fig. 1. The values of  $\Delta E_1$  are used to assess the likelihood of switching between polar and antipolar states, and the values of  $\Delta E_2$  are used to assess the likelihood of switching between polar and nonpolar states. To compare to known FE oxides, the DFT-computed  $\Delta E_2$  would be ~ 20 and 200 meV/f.u. for BaTiO<sub>3</sub> and PbTiO<sub>3</sub>, respectively [21]. The larger value of 200 ~ meV/f.u. has been considered the upper limit of FE switching in prior DFT studies [1, 64].

The displacement patterns of cations and anions in the antipolar and polar structures relative to the high symmetry nonpolar parent structure, as shown in Fig. 1, can be illustrated using irreducible representations (irreps) of the *D2h* point group. The antipolar distortion can be described using the amplitude of the  $Y^{2-}$  irrep and the polar distortion can be described using the amplitude of the  $\Gamma^{2-}$  irrep. Each of the displacement patterns is characterized primarily as a series of tilts within the 1D network of edge-sharing square-pyramidal  $BX_5$ 

units, while the *A*-sites remain almost stationary with respect to the parent structure. Also of importance is that the polar and antipolar structures are related by a 1<sup>st</sup> order phase (discontinuous) transition, where only 1/2 of the  $BX_5$  square pyramids are tilted in the same direction in either structure. In Fig. 1 these are the  $BX_5$  square pyramids with a black *A*-site depicted in front of them. The other  $BX_5$  square pyramids are in an opposing orientation so  $\Delta E_1$  is a measure of the energy required to orient all  $BX_5$  square pyramids in the same direction.

It should be noted that the polar distortions in this work do not result in the known Na<sub>2</sub>SiO<sub>3</sub> structure type, but a yet to be reported structure type in the same crystallographic space group. The *B*-site in the Na<sub>2</sub>SiO<sub>3</sub> structure type are fourfold coordinate and this difference in structure types is explored in Ref. [56]. The present study serves to identify (a) a complete set of polar metastable states for a proposed set of AFEs, (b) new semiconductive members of this family that are yet to be reported, and (c) compositionally tuned structural variants where  $\Delta E$  values changes as a function of atomistic identity.

#### Identifying metastable polar states

Inspired by recent investigations into the interplay between AFEs and improper FEs [65] we aim to develop a systematic route to search for new examples of FEs and improper FEs from AFEs. We start with harvesting known nonpolar and antipolar  $A_2BX_3$  structure types from the ICSD and (i) create polar displacements in 1 Cartesian direction, resulting in 1 ungerade irrep, or (ii) couple polar displacements in 2 Cartesian directions, resulting in 2 ungerade irreps. The series of polar space groups that result from applying this procedure to select  $A_2BX_3$ structures is shown in Fig. 2. Not depicted are the nonpolar modes that could result in a trilinear coupling scheme as observed in improper FEs. For example, polar displacements in both Cartesian x and z directions from the Cmcm structure would result in a structure of Cc (#9) symmetry, while another route to obtain Cc symmetry would be to couple polar mode  $\Gamma^{2-}$  to nonpolar mode  $\Gamma^{4+}$ , allowing for a polar mode  $\Gamma^{3-}$  to condense in after full-cell relaxation. This is what occurred for Cs<sub>2</sub>PbO<sub>3</sub> in Ref. [56]. Here we would induce both polar irreps simultaneously and then let the structure fully relax. This search strategy is not based on the specific symmetry considerations of specific structure types, but a generalizable procedure that can be implemented for any nonpolar or antipolar structure type. The results of this procedure on a test set of related compounds can also yield insights into the complete set of polar distortions one might observe in experiment for ternary or quaternary tuned compositions.

Our test set includes 3 oxide compounds that we predict to have an antipolar ground state, as well as a DFT-predicted





Figure 2: The sets of polar displacements made to the nonpolar Cmcm parent (left-hand side) and antipolar Pnma subgroup (right-hand side) result in structures that can be classified in the orthorhombic and monoclinic polar space groups listed. Polar irreps are depicted in purple.

metastable polar state close in energy. K2TiO3, K2PbO3, and Rb<sub>2</sub>PbO<sub>3</sub> and were chosen to observe how sets of polar distortions would behave when the electronic state of the *B*-sites  $(d^0)$ vs. main group cations) and size of the A-site (as K and Rb) vary. We selectively induce polar displacements in both the nonpolar parent structure and antipolar ground state to obtain the set of potential polar distortions that could be engineered using experimental parameters such as strain, compositional tuning, and epitaxial growth to stabilize a FE state. Here we do not include displacements from the  $A_2BX_3$  structure types found in C2/c symmetry, previously investigated in Ref. [56], as this nonpolar structure type was rarely found to be close in energy to the antipolar ground state or metastable polar state. The complete set of irreps that result from the induced atomic displacements is illustrated in Fig. 2. If polar displacements are made along one direction this results in a polar orthorhombic structure (Amm2, Cmc2<sub>1</sub>, Pna2<sub>1</sub>, etc.) and if polar displacements are made along two directions this results in polar monoclinic structures (Cc, *Pc*, *Pm*, etc.) The resulting structures are then used as the input for our DFT relaxations to see if any polar distortions are stable (or metastable) in our test set.

We find for K<sub>2</sub>TiO<sub>3</sub>, K<sub>2</sub>PbO<sub>3</sub>, Rb<sub>2</sub>PbO<sub>3</sub> that only 1 polar displacement pattern, described using the irrep  $\Gamma^{2-}$ , does not relax back to high symmetry space group *Cmcm*. This is the polar phase depicted in Fig. 1 when displacements are made along the *z*-axis. For our test cases we find that the resulting structure can be classified in crystallographic space group *Cmc2*<sub>1</sub> and is representative of a new polar structure type. This polar structure is only 1, 3, and 3 meV/fu higher in energy than the predicted antipolar ground states of K<sub>2</sub>TiO<sub>3</sub>, K<sub>2</sub>PbO<sub>3</sub>, and Rb<sub>2</sub>PbO<sub>3</sub>, respectively. This small  $\Delta E_1$  could explain why the structures of K<sub>2</sub>PbO<sub>3</sub> and Rb<sub>2</sub>PbO<sub>3</sub> were previously assigned to both polar and antipolar structure types [57–59]. The % change in volume corresponding to a transition between antipolar and polar phases is 0.18, 0.41, and 0.39% for K<sub>2</sub>TiO<sub>3</sub>, K<sub>2</sub>PbO<sub>3</sub>, and

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 $Rb_2PbO_3$ , respectively, and the orientation of the edge-sharing  $BX_5$  square pyramids in the polar phase can be easily switched relative to the high symmetry nonpolar parent structure (*Cmcm* symmetry).

We believe that the metastable polar structures of the test set are FE, making the antipolar ground state an AFE. All polar displacements from antipolar space group *Pnma* relax back to *Pnma*, indicating that the for the test set the antipolar irrep  $Y^{2-}$  does not couple to any polar displacements. While the compositions K<sub>2</sub>TiO<sub>3</sub>, K<sub>2</sub>PbO<sub>3</sub>, and Rb<sub>2</sub>PbO<sub>3</sub> display only 1 metastable polar state (classified in space group *Cmc2*<sub>1</sub>) this procedure can be used to map out the potential energy landscape of new members of the  $A_2BX_3$  family and be incorporated into future high-throughput studies.

#### Creating new members of the family

The electronic band structures of the antipolar ground-state compounds investigated in the previous subsection, the previously synthesized oxides K2TiO3, K2PbO3, and Rb2PbO3, are plotted in Fig. 3, next to a projected density of states (PDOS) for each compound. It should be noted that semi-local GGA methods tend to underestimate  $E_{gap}$  values, and here we use the computed Egap values as a qualitative guide to better understand how atomistic composition affects the electronic structure. The band gap  $(E_{gap})$  of K<sub>2</sub>TiO<sub>3</sub> in Fig. 3a is 3.66 eV, much larger than for K<sub>2</sub>PbO<sub>3</sub> and Rb<sub>2</sub>PbO<sub>3</sub>, which are 1.48 and 1.50 eV, respectively, as shown in Fig. 3b and c. A comparative analysis of the PDOS shows that this large difference in  $E_{gap}$  is primarily caused by the structures with B = Pb having a band centered at approximately 2.5 eV. This character of this band is mostly composed of contributions from the Pb 6s-orbital and O 2p-orbital. The overlap of the Pb 6s and O 2p orbitals suggest that this band comes from the bonding interaction of the Pb and O, since they are in close contact in square-pyramidal geometry. Notably, this





(a) K<sub>2</sub>TiO<sub>3</sub>



(b) K<sub>2</sub>PbO<sub>3</sub>



(c)  $Rb_2PbO_3$ 

Figure 3: Compared here are the electronic band structures and corresponding PDOS for (a) K<sub>2</sub>TiO<sub>3</sub>, (b) K<sub>2</sub>PbO<sub>3</sub>, and (c) Rb<sub>2</sub>PbO<sub>3</sub>, all of which have an antipolar ground-state structure of *Pnma* symmetry.

band structure feature is nearly identical to the lowest unoccupied orbital (LUMO) of  $K_2 TiO_3$ , but closer to the Fermi level ( $E_p$  set to 0 here). This demonstrates that substitutions of Pb for Ti can lower the band energy in select compositions by adjust the electronic states in a qualitative sense of having a *B*-site with either empty (Ti) or filled (Pb) *d*-states. As expected, the occupied states of all 3 structures have predominantly O 2p character. This is because O is highly electronegative, and therefore electrons are pulled toward the O atoms within the structure, as observed in oxides found in the perovskite and delafossite families.

While K<sub>2</sub>PbO<sub>3</sub> and Rb<sub>2</sub>PbO<sub>3</sub> have band gaps of 1.48 and 1.50 eV, respectively,  $K_2 TiO_3$  has  $E_{gap}$  of 3.66 eV, just out of the range of semiconductors. To examine Pb-free materials and decrease the  $E_{gap}$  of materials in this family with K and Ti, we can switch our focus from the effects of changing A and *B*-site cations to the effects of changing the anion *X* from oxygen to sulfur and selenium. S and Se are less electronegative than O, form more covalent/less ionic bonds than O and tend to decrease  $E_{gap}$ . DFT examples where S and Se anion substitutions for O can decrease  $E_{gap}$  include BaZrS<sub>3</sub> [66], BaZrSe<sub>3</sub> [67], CaZrS<sub>3</sub> [68], PbTiO<sub>3-x</sub>S<sub>x</sub> [69] and the sets of materials identified in Ref. [70]. The  $E_{gap}$  values presented in Ref. [70] also include materials that have been experimentally prepared (CaZrS<sub>3</sub>, BaZrS<sub>3</sub>, Ba<sub>3</sub>ZrS<sub>7</sub>, etc.) with  $E_{gap}$  lower than their oxide counterparts, qualitatively consistent with original DFT reports.

Crystallographic database mining shows that  $K_2TiO_3$  [62],  $K_2TiS_3$  [71],  $K_2ZrO_3$  [72],  $Cs_2ZrO_3$  [73], and  $Cs_2ZrSe_3$  [61] compounds are known, but combinations with Rb are not yet reported, nor are select S and Se compositions. Here we use the procedures outlined in the previous subsection to map out the potential energy landscape of yet to be synthesized compositions that contain O, S, and Se. The set of new compounds evaluated here are  $K_2TiSe_3$ ,  $K_2ZrS_3$ ,  $K_2ZrSe_3$ ,  $Rb_2ZrO_3$ ,  $Rb_2ZrS_3$ ,  $Rb_2ZrSe_3$ , and  $Cs_2ZrS_3$ . We find that for these compounds the ground-state structures can be described as either antipolar (combinations with A = K or Rb) or nonpolar (combinations with A = Cs), in agreement with the conclusions of Ref. [56].

Table 1 contains the DFT-computed ground-state space group, complete with relaxed lattice parameters and volume. Next is the PBE-GGA computed band gap ( $E_{gap}$ ), and finally the difference in energy between the ground state and metastable polar state(s) for the  $A_2BX_3$  series where A = K, Rb, Cs and X = O, S, Se for select compositions with B = Ti or Zr. As X increases in size from O to S to Se, the relaxed volume of the ground-state structure increases, as do the  $\Delta E_1$  values to the first metastable polar state. For the B = Zr series, the increase in  $\Delta E_1$  is largest for K<sub>2</sub>ZrSe<sub>3</sub> and smallest for Cs<sub>2</sub>ZrO<sub>3</sub> indicating that the computed switching barrier is dependent upon periodic trends such as atomic size and electronegativity. These factors also determine the variations in computed  $E_{gap}$ , where the values are highest for oxides (3.66–4.04) and decrease for sulfides (1.28-1.88) and selenides (1.53-1.57). We predict that the chalcogenide members of the  $A_2BX_3$ 



$A_2BX_3$	GS	a (Å)	b (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	$E_{\rm gap}$ (eV)	$\Delta E_1$ (meV)	PS1	<i>P</i> (C/m <sup>2</sup> )	ΔV (Å <sup>3</sup> )	∆ <i>V/V</i> (%)
K <sub>2</sub> TiO <sub>3</sub>	Pnma	10.068	6.868	5.450	376.890	3.66	1	Cmc2 <sub>1</sub>	0.047	+0.68	+0.18
K <sub>2</sub> TiS <sub>3</sub>	Pnma	11.748	8.227	6.446	633.992	1.28	7	Cmc2 <sub>1</sub>	0.092	- 1.29	- 0.21
K <sub>2</sub> TiSe <sub>3</sub>	Pnma	12.149	8.496	6.835	705.555	1.53	18	Cmc2 <sub>1</sub>	0.029	- 0.41	- 0.06
K <sub>2</sub> ZrO <sub>3</sub>	Pnma	10.415	6.925	5.867	423.123	3.96	6	Cmc2 <sub>1</sub>	0.110	+0.92	+0.22
$K_2ZrS_3$	Pnma	12.182	8.124	6.839	676.821	1.86	30	Cmc2 <sub>1</sub>	0.070	+6.33	+0.94
$K_2ZrSe_3$	Pnma	12.545	8.423	7.157	756.290	1.57	35	Cmc2 <sub>1</sub>	0.067	+5.34	+0.71
Rb <sub>2</sub> ZrO <sub>3</sub>	Pnma	10.729	7.305	5.891	461.709	3.84	1	Cmc2 <sub>1</sub>	0.060	+0.51	+0.11
$Rb_2ZrS_3$	Pnma	12.428	8.582	6.841	729.641	1.88	12	Cmc2 <sub>1</sub>	0.030	- 0.04	- 0.00
$Rb_2ZrSe_3$	Pnma	12.992	8.745	7.090	805.530	1.53	5	Cmc2 <sub>1</sub>	0.042	+1.16	+0.14
Cs <sub>2</sub> ZrO <sub>3</sub>	Стст	11.206	7.617	5.914	504.796	4.04	0	-	-	-	-
Cs <sub>2</sub> ZrS <sub>3</sub>	Стст	12.707	9.058	6.798	782.450	1.84	0	-	-	-	-
Cs <sub>2</sub> ZrSe <sub>3</sub>	Стст	13.008	9.371	7.084	863.456	1.54	2	Cmc2 <sub>1</sub>	0.001	- 3.23	- 0.37

**TABLE 1:** For each of the  $A_2BX_3$  compositions tabulated here, we report first the space group of the ground state (GS), lattice parameters *a*, *b*, *c* in units of Angstroms (Å), and the volume in units of Å<sup>3</sup>.

Next we report the computed band gap  $E_{gap}$  in units of eV, followed by  $\Delta E_1$ , the space ground of the first polar metastable state (PS1), its polarization, P, in units of C/m<sup>2</sup>, and finally  $\Delta V$  and  $\Delta V/V$ , given in units of Å<sup>3</sup> and as a %, respectively. A dash (–) for entries with A = Cs indicates that no metastable polar states exists for these compounds using our search methods.

family, with A = K or Rb and B = Ti or Zr will be both semiconducting and AFE, given that the computed values of  $\Delta E_1$ are all below 40 meV/fu.

An important consideration when proposing new AFEs is the change in volume that results from 1st order phase transition between the antipolar ground state and polar metastable stable. Reported in Table 1 are the change in volume relative to the ground state and also the % change. To compare to known AFE oxides, the largest absolute value of  $\Delta V/V$  for DFT-computed metastable polar phases of PbZrO<sub>3</sub> is 1.3% [3] and similar values are obtained for ZrO<sub>2</sub> [48].

Additional criteria in assessing the formability of new structures, and their dynamic stability, is to investigate quantities such as their formation enthalpy and vibrational spectra. These are both presented in the supplemental materials, where the DFT GGA formation enthalpy with respect to elements in their standard state is given in Sect. 1 of the supplemental materials. Section 2 of the supplemental materials contains a representative phonon band structure, of the new compound K<sub>2</sub>ZrS<sub>3</sub>, while the phonon modes at  $\Gamma$  of the antipolar ground state and metastable polar state of new AFE compounds K<sub>2</sub>ZrS<sub>3</sub>, Rb<sub>2</sub>ZrO<sub>3</sub>, and Rb<sub>2</sub>ZrS<sub>3</sub> are detailed in Sect. 3 of the supplemental materials. We find that for the 3 new AFE compounds there are no unstable vibrational modes at  $\Gamma$  in either the antipolar or polar states, and that all 3 have formation enthalpies below ~ – 9 eV/f.u. (or – 1.5 eV/atom), increasing their likelihood as candidate targets for synthesis.

Our overall assessment is that the compounds  $K_2$ TiSe<sub>3</sub>,  $K_2$ ZrS<sub>3</sub>,  $K_2$ ZrSe<sub>3</sub>,  $Rb_2$ ZrO<sub>3</sub>,  $Rb_2$ ZrS<sub>3</sub>, and  $Rb_2$ ZrSe<sub>3</sub> are 6 new functional materials that are potentially AFE, joining known members ( $K_2$ TiO<sub>3</sub>,  $K_2$ ZrO<sub>3</sub>, etc.) of the family previously suggested to also be AFEs. Figure 4 is a pictorial representation of

how changing either the size of the *A*-site (top) or *X*-site affects  $\Delta E_1$  (green) and  $\Delta E_2$  (purple). DFT calculations demonstrate that increasing the size of the *A*-site from K to Rb to Cs leads to a decrease in  $\Delta E_1$  and  $\Delta E_2$  for  $A_2$ ZrO<sub>3</sub> compounds, with Cs<sub>2</sub>ZrO<sub>3</sub> showing no (meta)stable polar or antipolar structures. This suggests that further compositional tuning of  $A_2$ ZrO<sub>3</sub> materials, to adjust  $\Delta E_1$  and  $\Delta E_2$  values, should focus on compositions with mixed K and Rb. Another route to investigate how compositional tuning could affect the energy barriers of phase transitions would be to compare the changes in  $\Delta E_1$  and  $\Delta E_2$  values as the *X* anion is changed in the K<sub>2</sub>ZrX<sub>3</sub> series. Our DFT results indicate that increasing the size of *X* from to O to S to Se tends to increase  $\Delta E_1$  and decrease  $\Delta E_2$ , though these differences are still all below 40 meV/f.u.

One benefit of creating new chalcogenide or mixed chalcogenide systems using this data as a starting point is that most combinations are ensured to have decreased  $E_{gap}$  values when compared to their pure oxide analogs. Table 1 highlights that the primary advantage of proposing new compositions such as K<sub>2</sub>ZrS<sub>3</sub> and Rb<sub>2</sub>ZrSe<sub>3</sub> (or mixed variants) is that they display a decreased  $E_{gap}$  when compared to their oxide counterparts, in line with the perovskite and Ruddlesden-Popper compositions presented in Ref. [70]. Moreover, Fig. 4 shows that for specific compositions additional polar phases are potentially metastable. We find for compositions with  $X = \text{Se}(\text{K}_2\text{ZrSe}_3, \text{Rb}_2\text{ZrSe}_3)$  a polar monoclinic phase Cc is present in the energy landscape, in agreement with prior DFT investigation on Cs<sub>2</sub>ZrSe<sub>3</sub> [56], and contains multiple polar modes, reminiscent of the conditions required for some types of hybrid improper FEs.



# Article



**Figure 4:** For compositions with B = Zr, increasing the size of the *A*-site (a, top) in the oxides series decreases  $\Delta E_1$  (green values, given in meV) and  $\Delta E_2$  (purple values, given in meV). For combinations with A = K and B = Zr, increasing the size of the anion *X* (b, bottom) increases  $\Delta E_1$ , while  $\Delta E_2$  values remain relatively the same.

#### Compositional tuning to adjust energy barriers

The prior two subsections focused on methodology to map out the potential energy landscape of pure  $A_2BX_3$  compounds, and then using this methodology to discover new compounds in the family that are as yet to be reported. Here we focus on an abbreviated approach to understanding how mixed cation systems could behave if synthesized. We are unaware of any prior studies of compositional tuning for any antipolar members of the  $A_2BX_3$  family and are using this opportunity to probe if a response in  $\Delta E_1$  and P will even occur with changes in A and B-site composition and ordering. Therefore, we limit ourselves to two types of cation ordering for each example. For this analysis, two known compounds of the  $A_2BX_3$  family are used as end members in multiple compositional tuning schemes: K<sub>2</sub>PbO<sub>3</sub> and Rb<sub>2</sub>PbO<sub>3</sub>. We map out the energetics of compositional tuning to assess how  $\Delta E_1$  and  $\Delta E_2$  change as a function of fractional cation replacement. Our first example contains mixed B-sites (1:1 mix of Sn/Pb) and our second example contains mixed A-sites (1:1 mix of Na/K and K/Rb). To create our multiple configurations, we substituted half of the cation sites of the 4 major structure types of the A<sub>2</sub>BX<sub>3</sub> family, found in crystallographic space groups Cmcm, *Pnma*,  $Cmc2_1$ , and C2/c [56] and let them fully relax. Unlike the examples in the previous subsections, we do not create any additional polar displacements in these mixed cation systems. This is because our findings in Results & Discussion sections (a) & (b) indicated that polarization along the *z*-direction, found in space groups  $Cmc2_1$  or its subgroup Cc were the only (meta)stable polar structural variants. All DFT-computed formation enthalpies of the series are presented in Sect. 1 of the Supplemental Materials.

In the first example we investigate 2 configurations, where Configuration 1 has the same B-sites within 1 horizontal chain of edge-sharing BX<sub>5</sub> square pyramids and Configuration 2 has alternating B-sites within each horizontal chain. The resulting structures of Rb<sub>2</sub>(Sn<sub>1/2</sub>Pb<sub>1/2</sub>)O<sub>3</sub> are depicted in Fig. 5, along with their fully relaxed crystallographic space groups. Substituting 1/2 of the Pb with Sn to create horizontal chain of edge-sharing BX<sub>5</sub> square pyramids where the B-sites are the same, Configuration 1 in Fig. 5 transforms the crystallographic space groups of  $A_2BX_3$  in the following ways:  $Cmcm \longrightarrow Pmma$ ,  $Pnma \longrightarrow$  $Pca2_1$ ,  $Cmc2_1 \longrightarrow Pc$ , and  $C2/c \longrightarrow P2/c$ . It is important to note here that while some space groups in the series could allow for a polarization to be present (Pca21, Amm2, etc.), our DFT calculations show that these contributions are either zero or orders of magnitude smaller when compared to the Pc or Cm examples. Berry phase polarization values for all 3 Cartesian directions for each structure are reported in Table 2.

The ground state of Configuration 1 is the structure classified in space group  $Pca2_1$ , with antipolar  $BX_5$  displacement patterns, and the lowest energy metastable state is the structure classified in space group Pc, with polar  $BX_5$  displacement patterns. This metastable structure is 3 meV/fu higher in total energy and has  $P_z = 0.120 \text{ C/m}^2$ , an order of magnitude larger than observed for the  $Pca2_1$  structure with antipolar tilts. The volume change in going from the ground state to the first metastable state is 0.51 Ang.<sup>3</sup> or 0.11%, in line with the values reported previously in Table 1.





**Figure 5:** Shown on the left-hand side is a side view of each  $Rb_2(Sn_{1/2}Pb_{1/2})O_3$  configuration, and then to the right are each of the 4 structures and their resulting crystallographic space groups. The Rb atoms are depicted as yellow spheres, and the  $SnO_5$  and  $PbO_5$  square pyramids are light and dark blue, respectively. In this series, the structures can be thought of as generally nonpolar, antipolar, polar, and nonpolar going left to right, though there are some examples where a small nonzero polarization is present in the Cartesian *y*-direction due to cation ordering effects. Polarization values for each structure are tabulated in Table 2.

**TABLE 2:** Tabulated for each Configuration of mixed *B*-sites are the resultant crystallographic space group, lattice parameters (in units of Å), and the  $\Delta E$  from the ground-state structure. Next is the polarization (*P*) in each Cartesian direction, given in units of C/m<sup>2</sup>.

SG	a (Å)	b (Å)	<i>c</i> (Å)	β	Δ <i>E</i> (meV)	$P_x$ (C/m <sup>2</sup> )	$P_y$ (C/m <sup>2</sup> )	$P_z$ (C/m <sup>2</sup> )
Sn/Pb Conf	iguration 1							
Pmma	10.735	7.451	5.917	90.00	29	0	0	0
$Pca2_1$	10.829	7.322	5.959	90.00	0	0	0	0.015
Рс	10.860	7.327	5.945	89.98	3	0	0	0.120
P2/c	10.747	7.449	5.922	93.02	28	0	0	0
Sn/Pb Conf	iguration 2							
Amm2	10.719	7.452	5.924	90.00	27	0	0.017	0
Pmn2 <sub>1</sub>	10.808	7.325	5.971	90.00	0	0	0.013	0
Ст	11.077	7.483	6.046	89.89	3	0	0.014	0.124
C2	10.759	7.417	5.950	93.37	27	0	0.015	0

Substituting 1/2 of the Pb with Sn to create horizontal chain of edge-sharing  $BX_5$  square pyramids where the *B*-sites *alternate*, Configuration 2 in Fig. 5, transforms the crystallographic space groups of  $A_2BX_3$  in the following ways:  $Cmcm \longrightarrow Amm2$ , Pnma $\longrightarrow Pmn2_1$ ,  $Cmc2_1 \longrightarrow Cm$ , and  $C2/c \longrightarrow C2$ . The ground state of Configuration 2 is the structure classified in space group  $Pmn2_1$ , with antipolar  $BX_5$  displacement patterns, and the lowest energy metastable state is the structure classified in space group Cm, with polar  $BX_5$  displacement patterns. This metastable structure is also 3 meV/fu higher in total energy and has  $P_z = 0.124 \text{ C/m}^2$ . The volume change in going from the ground state to the first metastable state is 28.36 Ang.<sup>3</sup> or 6.00%, much larger than observed in Configuration 1 and the compounds reported in Table 1. Of note here is that all 4 of the structures in

Configuration 2 have a small nonzero *P* along the *y*-direction, but this is an order of magnitude smaller than the  $P_z$  of the *Pc* structure. Switching between these 2 lowest energy structures should result in a large change in  $P_z$ . In this first example we find that *B*-site substitutions lead to a range of structures where  $\Delta E$  values are within 30 meV/f.u., comparable to the range of values for known oxides presented in Ref. [3] (strained PbZrO<sub>3</sub>) and [48] (ZrO<sub>2</sub>).

In the second example we investigate 2 configurations, where 1/2 of the *A*-sites in K<sub>2</sub>PbO<sub>3</sub> are substituted with either Na or Rb. Configuration 1 has its *A*-sites ordered in the vertical direction to create alternating *pillars* of *A*-sites and Configuration 2 has its *A*-sites ordered in the horizontal direction to create alternating *rows* of *A*-sites. The resultant configurations of





**Figure 6:** Depicted on the left-hand side is a side view of each  $(A,K)PbO_3$  configuration, and then to the right are each of the 4 structures and their resulting crystallographic space groups. K is depicted as green sphere, dopant A-sites as yellow spheres, and the  $PbO_5$  square pyramids as dark blue. In this series, the structures can be thought of generally as nonpolar, antipolar, polar, and nonpolar, though there are some examples where a small nonzero polarization is present in the x direction due to cation ordering effects. Polarization values for each structure are tabulated in Table 3.

(K,Na)PbO<sub>3</sub> and (K,Rb)PbO<sub>3</sub> are illustrated in Fig. 6, along with their fully relaxed crystallographic space groups.

*x* direction and not *y*, and it is smaller by almost an order of magnitude when compared to the values in Table 3. Of note here is that in each configuration only 1 structure has a sizable *P* comparable to BaTiO<sub>3</sub>, and that the  $\Delta$ E to access this state

Much like the previous  $Rb_2(Sn_{1/2}Pb_{1/2})O_3$  example the structures exhibit a small nonzero *P*, though here it is in the

**TABLE 3:** Tabulated for each Configuration of mixed *A*-sites are the resultant crystallographic space group (SG), lattice parameters (in units of Å), and the  $\Delta E$  from the ground-state structure. Next is the polarization (*P*) in each Cartesian direction, given in units of C/m<sup>2</sup>.

SG	a (Å)	b (Å)	c (Å)	β	Δ <i>E</i> (meV)	$P_x$ (C/m <sup>2</sup> )	$P_y$ (C/m <sup>2</sup> )	$P_z$ (C/m <sup>2</sup> )	
Na/K Configuration 1									
Ama2	10.242	6.847	6.002	90.00	365	0.006	0	0	
Pna2 <sub>1</sub>	10.081	6.769	5.890	90.00	8	0.007	0	0	
Сс	10.148	6.696	5.898	90.03	0	0.010	0	0.198	
Pc	10.082	6.769	5.891	90.00	8	0.007	0	0	
Na/K Configuration 2									
Amm2	10.196	6.922	6.001	90.00	263	0	0.012	0	
Pmn2 <sub>1</sub>	10.294	6.603	5.922	90.00	23	0	0.016	0	
Ст	10.323	6.609	5.916	91.86	0	0	0.015	0.225	
Pm	10.295	6.602	5.923	89.99	23	0	0.015	0	
Rb/K Configuration 1									
Ama2	10.663	7.324	6.050	90.00	103	0.004	0	0	
Pna2 <sub>1</sub>	10.726	7.182	6.052	90.00	0	0	0	0	
Сс	10.775	7.197	6.042	88.86	3	0.004	0	0.151	
Pc*	10.725	7.182	6.052	89.99	0	0.005	0	0	
Rb/K Configuration 2									
Amm2	10.669	7.320	6.049	90.00	89	0	0.006	0	
Pmn2 <sub>1</sub>	10.794	7.100	6.070	90.00	0	0	0.002	0	
Cm	10.824	7.148	6.058	89.60	3	0	0	0.163	
Pm*	10.793	7.101	6.069	89.99	0	0	0.002	0	





Figure 7: Plotted from left to right are the structures and energetics of Configurations 1 and 2 for (K,Na)PbO<sub>3</sub>, K<sub>2</sub>PbO<sub>3</sub>, and (K,Rb)PbO<sub>3</sub>. (K,Na)PbO<sub>3</sub> has a polar ground state (denoted as p), while K<sub>2</sub>PbO3 and (K,Rb)PbO<sub>3</sub> have an antipolar ground state (denoted as ap).

is 3 meV for the 2 K/Rb test cases presented. Surprisingly, we find that adding Na to  $K_2PbO_3$  changes the preferred ground state to one with polar displacements, and that this was the case for both Configuration 1 and 2. Configurations 1 and 2 have ground states with P = 0.198 and 0.225 C/m<sup>2</sup>, respectively, as shown in Table 3. This did not happen with (K,Rb)PbO<sub>3</sub>, where the ground state maintained its antipolar PbO<sub>5</sub> tilt system.

Compositional tuning of K<sub>2</sub>PbO<sub>3</sub> can change the preferred ground-state structure and adjust the switching barriers  $\Delta E_1$ and  $\Delta E_2$ , and this is illustrated in Fig. 7. Adding a larger cation, such as Rb, to K<sub>2</sub>PbO<sub>3</sub> does not change the computed barrier to switch from an antipolar to polar state (it stays 3 meV), but it does decrease the barrier to switch between the polar to nonpolar structures. This is one route to reduce the energy of a FE phase transition. Adding a smaller cation, such as Na, to K<sub>2</sub>PbO<sub>3</sub> changes the nature of the ground state and increases the computed barrier to switch between them. In our example the difference to switch between polar and antipolar states increases from 3 to either 8 or 23 meV, depending upon the ordering of the A-sites. It also increases the difference in energy between the polar and nonpolar structures, from 127 to 357 or 245 meV, depending upon the ordering of the A-sites. While our studies here limited to a 50:50 mix, we can interpolate from Fig. 7 that compositions with 0 < x < 0.5 can be further investigated through experiment to determine the range of x that leads to a FE ground state. Moreover, this analysis of multiple configurations for different mixed compositions can serve as a template for future high-throughput studies of more complex compositional tuning schemes.

# Conclusions

In this manuscript, we use DFT methods to expand the number of functional materials with general formula  $A_2BX_3$  by developing a series of new compounds that are related to known materials. The known materials (K<sub>2</sub>PbO<sub>3</sub>, Rb<sub>2</sub>PbO<sub>3</sub>, K<sub>2</sub>TiS<sub>3</sub>, Cs<sub>2</sub>ZrSe<sub>3</sub>, etc.) are oxides, sulfides, and selenides that have already been synthesized and characterized using a variety of methods that include molten hydroxide fluxes [62], high-temperature ampule reactions [61], solid-state calcination [74], hydrothermal growth [75], and sol-gel reactions [73], and whose functional properties as FE and AFE materials has previously gone overlooked. The main goals of this study are to (a) develop methodology for future high-throughput studies, (b) more fully map out the potential energy landscape of antipolar and polar  $A_2BX_3$  compositions, (c) predict new semiconductive AFE and FE materials that are yet to be synthesized, and (d) investigate the effects of compositional tuning on known structures.

We developed a symmetry-based procedure amenable to high-throughput investigations to search for (meta)stable polar displacements and then showed that for a test set of known oxides, only a few polar displacement patterns are (meta)stable. Journal of Materials Research 💻 2021 💻 www.mrs.org/jmr



These polar displacements are then used to map out the potential energy landscape of compositions that are as yet to be synthesized. This led to 6 new example AFEs, where select member such as  $K_2ZrS_3$  and  $Rb_2ZrSe_3$  demonstrate a reduced  $E_{gap}$  compared to their oxide analogs while maintaining the same relative ground-state and metastable structures. Our analyses indicate that these new example AFEs, as well as the known materials on which they are based, are prime targets for DFT calculations that should include (i) nudged elastic band pathways to evaluate multiple switching pathways and their associated barriers, (ii) complete phonon spectra for all ground and metastable state structures, and (iii) PBE0- or GW-type calculations to compute  $E_{gap}$  values beyond the semi-local GGA values reported here in our preliminary assessments.

Once these materials are synthesized, structurally characterized, and their functional properties are mapped out, they could also be used as end members in compositional tuning schemes. The compositional tuning schemes presented here can be used as a guide for experiment: we predict that adding Na to  $K_2PbO_3$ changes the preferred ground state from antipolar to polar, while adding Rb to  $K_2PbO_3$  can decrease the barrier for FE switching of metastable states. Much like the new chalcogenides listed in the previous paragraph, these mixed oxides could serve as templates for phonon calculations to assess how composition affects vibrational frequency, in line with landmark studies on perovskite oxides that explored how to understand and control the soft modes that lead to FE instabilities.

Future studies using previously synthesized Pb-free compounds not explored here (K<sub>2</sub>SnO<sub>3</sub>, K<sub>2</sub>ZrO<sub>3</sub>, K<sub>2</sub>TiS<sub>3</sub>, etc.) could also expand upon these points and examine further the optimized properties that could result from mixing both *A*- and *B*-sites. Delving further, this would result in designed materials with more than 1 dominant metastable polar state with adjustable  $\Delta E_1$  and  $\Delta E_2$  values and open new lines of research into applications that could employ hybrid improper FEs with multiple tunable switching barriers. In total, this work has resulted in new examples of FE and AFE oxides, sulfides, and selenides, some of which have a  $E_{gap}$  amenable to photovoltaic applications, while others appear to be more useful as solid-state materials for energy storage.

#### **Materials and methods**

The ground-state calculations presented here employ periodic DFT methods [76, 77] and are carried out using ABINIT, an open-source software package [78, 79]. All atoms are represented using optimized norm-conserving Vanderbilt (ONCV) pseudo-potentials [80–82] and a plane-wave cutoff of 50 Ry. Bulk structural relaxations use a  $6 \times 6 \times 6$  k-point grid [83] and the energy convergence criteria for self-consistent relaxations

was  $5 \times 10^{-6}$  eV. This stringent criteria allows for  $\Delta E$  comparisons down to atleast 1 meV and also results in relaxed structures with maximum residual forces of 1–5 meV/Å per atom per Cartesian direction. Wherever applicable, we report polarization using the Berry phase approach [84, 85]. All calculations are performed at the GGA level using the Wu-Cohen (WC) modified PBE-GGA exchange correlation function for solids [86, 87]. We choose the WC-modified PBE-GGA because of its (i) improved agreement with experimental structures for a wide range of semiconductors, including oxides and chalcogenides [88], (ii) ability to match well the properties of known FEs PbTiO<sub>3</sub> and BaTiO<sub>3</sub> [87], and (iii) utility in investigating phase transitions of FEs [89], even when compared to meta-GGA functionals [90].

The DFT-computed formation enthalpy presented in Sect. 1 of the Supplemental Materials employ crystal structures of the ground-state atoms and molecules, calculated using known crystal structures of Na, K, Rb, Ti, Zr, Cs, S, and Se that were found in the ICSD, consistent with the methods outlined in Ref [91]. For a cursory evaluation of the dynamic stability of the new compounds Rb<sub>2</sub>ZrO<sub>3</sub>, K<sub>2</sub>ZrS<sub>3</sub>, and Rb<sub>2</sub>ZrS<sub>3</sub>, we use ABINIT to compute the vibration modes of the antipolar ground state (Pnma) and the first metastable polar state  $(Cmc2_1)$ . These calculations are performed at the  $\Gamma$  point using a 6 × 6x6 k grid using DFPT methods Refs. [92, 93] for these 24 atom cells. The vibrational modes are reported in Sect. 3 of the Supplemental Materials and are accompanied by the mode effective charges and contributions to the dielectric constant, as detailed in Refs. [94, 95]. A representative phonon band structure for the new compound K2ZrS3 is presented in Sect. 2 of the Supplemental Materials.

To more fully map out the potential energy landscape of the  $A_2BX_3$  family of materials, we employ a symmetry-guided approach using the ISOTROPY software suite [96]. Our first step is to create polar displacements in both the high symmetry nonpolar parent structure (in space group Cmcm) and antipolar subgroup structure (in space group Pnma). These displacement patterns are created by adding 0.02 to 0.05 reduced coordinates to the cation coordinates and subtracting 0.02 to 0.05 reduced coordinates from the anion coordinates, in one or more Cartesian directions. The polar displacements are also accompanied by an increase in 0.4 to 0.8 Ang. of the lattice constant in that direction, depending upon the size of the cation A-sites (e.g.,  $r_{\rm Rb} > r_{\rm K}$ ) and anion X-sites (e.g.,  $r_{\rm Se} > r_{\rm S} > r_{\rm O}$ ). The set of structures with polar displacements are then used as the input for our DFT calculations, where we employ FINDSYM [97, 98] to obtain the crystallographic space group, and then use ISODISTORT [99, 100] to obtain the sets of irreducible representations (irreps) that describe the induced polar displacements before the structures are let to fully relax. The polar irreps from this pre-relaxation analysis are depicted in Fig. 2.



# Acknowledgments

JWB acknowledges resources provided by the College of Natural and Mathematical Sciences and the Department of Chemistry and Biochemistry at the University of Maryland, Baltimore County. This work used the Extreme Science and Engineering Discovery Environment (XSEDE, [101]), which is supported by National Science Foundation Grant number ACI-1548562 through start up allocation ID TG-CHE190075 and renewal allocation TG-CHE200108. The hardware used in some of the computational studies is part of the UMBC High-Performance Computing Facility (HPCF). The facility is supported by the US National Science Foundation through the MRI program (Grant nos. CNS-0821258, CNS-1228778, and OAC-1726023) and the SCREMS program (Grant no. DMS-0821311), with additional substantial support from the University of Maryland, Baltimore County (UMBC).

## **Data availability**

Data will be made available on reasonable request.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

## **Supplementary Information**

The online version contains supplementary material available at https://doi.org/10.1557/s43578-021-00410-3.

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#### References

 J.W. Bennett, K.F. Garrity, K.M. Rabe, D. Vanderbilt, Phys. Rev. Lett. 109, 167602 (2012)

- J.W. Bennett, K.F. Garrity, K.M. Rabe, D. Vanderbilt, Phys. Rev. Lett. 110, 017603 (2013)
- 3. S.E. Reyes-Lillo, K.M. Rabe, Phys. Rev. B. 88, 180102 (2013)
- 4. N.A. Benedek, C.J. Fennie, J. Phys. Chem. 117, 13339 (2013)
- 5. N.A. Benedek, T. Birol, J. Mater. Chem. C 4, 4000 (2016)
- R. Zhang, B.M. Abbett, G. Read, F. Lang, T. Lancaster, T.T. Tran, P.S. Halasyamani, S.J. Blundell, N.A. Benedek, M.A. Hayward, Inorg. Chem. 55, 8951 (2016)
- B. Monserrat, J.W. Bennett, K.M. Rabe, D. Vanderbilt, Phys. Rev. Lett. **119**, 036802 (2017)
- T. Zhu, G. Khalsa, D.M. Havas, A.S. Gibbs, W. Zhang, P.S. Halasyamani, N.A. Benedek, M.A. Hayward, Chem. Mater. 30, 8915 (2018)
- 9. J. Young, J.M. Rondinelli, Phys. Rev. Mater. 2, 065406 (2018)
- Z. Fei, W. Zhao, T.A. Palomaki, B. Sun, M.K. Miller, Z. Zhao, J. Yan, X. Xu, D.H. Cobden, Nature 560, 336 (2018)
- 11. J.W. Bennett, K.M. Rabe, J. Solid State Chem. 195, 21 (2012)
- 12. J.W. Bennett, J. Solid State Chem. 281, 121045 (2020)
- K.M. Rabe, Antiferroelectricity in Oxides: A Reexamination (Wiley, New York, 2013)
- I. Grinberg, D.V. West, M. Torres, G. Gou, D.M. Stein, L. Wu, G. Chen, E.M. Gallo, A.R. Akbashev, P.K. Davies, J.E. Spanier, A.M. Rappe, Nature 503, 509 (2013)
- K.T. Butler, J.M. Frost, A. Walsh, Energy Environ. Sci. 8, 838 (2015)
- Z. Xiao, Y. Yuan, Y. Shao, Q. Wang, Q. Dong, C. Bi, P. Sharma, A. Gruverman, J. Huang, Nat. Mater. 14, 193 (2015)
- S.E. Young, J.Y. Zhang, W. Hong, X. Tan, J. Appl. Phys. 113, 054101 (2013)
- C.W. Ahn, G. Amarsanaa, S.S. Won, S.A. Chae, D.S. Lee, I.W. Kim, ACS Appl. Mater. Interfaces 7, 26381 (2015)
- M. Zhou, R. Liang, Z. Zhou, S. Yan, X. Dong, ACS Sustain. Chem. Eng. 6, 12755 (2018)
- L. Yang, X. Kong, F. Li, H. Hao, Z. Cheng, H. Liu, J.F. Li, S. Zhang, Progr. Mater. Sci. **102**, 72 (2019)
- 21. R.E. Cohen, Nature 358, 136 (1992)
- N. Sicron, B. Ravel, Y. Yacoby, E.A. Stern, F. Dogan, J.J. Rehr, Phys. Rev. B 50(18), 13168 (1994)
- J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale,
  B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V.
  Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, R. Ramesh,
  Science 299, 1719 (2003)
- 24. J.M. Rondinelli, N.A. Spaldin, Adv. Mater. 23, 3363 (2011)
- J.W. Bennett, I. Grinberg, A.M. Rappe, J. Am. Chem. Soc. 130, 17409 (2008)
- 26. K. Takae, H. Tanaka, P. N. A. S. 115, 9917 (2019)
- P.F. Li, W.Q. Liao, Y.Y. Tang, H.Y. Ye, Y. Zhang, R.G. Xiong, J. Am. Chem. Soc. 139, 8752 (2017)
- 28. N.A. Benedek, C.J. Fennie, Phys. Rev. Lett. 106, 107204 (2011)
- S. Yoshida, K. Fujita, H. Akamatsu, O. Hernandez, A.S. Gupta,
  F.G. Brown, H. Padmanabhan, A.S. Gibbs, T. Kuge, R. Tsuji,



S. Murai, J.M. Rondinelli, V. Gopalan, K. Tanaka, Adv. Funct. Mater. **28**, 1801856 (2018)

- H. Djani, E.E. McCabe, W. Zhang, P.S. Halasyamani, A. Feteira, J. Bieder, E. Bousquet, P. Ghosez, Phys. Rev. B. 101, 134113 (2020)
- N.A. Benedek, J.M. Rondinelli, N. Djani, P. Ghosez, P. Lightfoot, Dalton Trans. 44, 10543 (2015)
- P. Boullay, J. Tellier, D. Mercurio, M. Manier, F.J. Zuniga, J.M. Perez-Mato, Solid State Sci. 14, 1367 (2012)
- J.B. Li, Y.P. Huang, G.H. Rao, G.Y. Liu, J. Luo, J.R. Chen, J.K. Liang, Appl. Phys. Lett. 96, 222903 (2010)
- A. Snedden, C.H. Hervoches, P. Lightfoot, Phys. Rev. B. 67, 092102 (2003)
- 35. M. Clin, J.P. Rivera, H. Schmid, Ferroelectrics 108, 207 (1990)
- 36. H. Schmid, Ferroelectrics 162, 317 (1994)
- 37. B.J. Kooi, B. Noheda, Science 353, 221 (2016)
- W. Wan, C. Liu, W. Xiao, Y. Yao, Appl. Phys. Lett. 111, 132904 (2017)
- 39. M.S. Haque, J.R. Hardy, Phys. Rev. B. 21, 245 (1980)
- 40. J.M. Perez-Mato, F. Gaztelua, G. Madariaga, M.J. Tello, J. Phys. C **19**, 1923 (1986)
- E. Sawaguchi, H. Maniwa, S. Hoshino, Phys. Rev. 83, 1078 (1951)
- 42. D.J. Singh, Phys. Rev. B 52, 12559 (1995)
- L. Zhao, Q. Liu, J. Gao, S. Zhang, J.F. Li, Adv. Mater. 29, 1701824 (2017)
- 44. Z. Liu, T. Lu, J. Ye, G. Wang, X. Dong, R. Withers, Y. Liu, Adv. Mater. Technol. **3**, 1800111 (2018)
- S. Han, X. Liu, Y. Liu, Z. Xu, Y. Li, M. Hong, J. Luo, Z. Sun, J. Am. Chem. Soc. 141, 12470 (2019)
- Z. Wu, X. Liu, C. Ji, L. Li, S. Wang, Y. Peng, K. Tao, Z. Sun, M. Hong, J. Luo, J. Am. Chem. Soc. 141, 3812 (2019)
- T. Wakamatsu, G. Kawamura, T. Abe, Y. Nakahira, S. Kawaguchi, C. Moriyoshi, Y. Kuroiwa, I. Terasaki, H. Taniguchi, Inorg. Chem. 58, 15410 (2019)
- S.E. Reyes-Lillo, K.F. Garrity, K.M. Rabe, Phys. Rev. B. 90, 140103 (2014)
- M.H. Park, Y.H. Lee, H.J. Kim, Y.J. Kim, T. Moon, K.D. Kim, J. Muller, A. Kersch, U. Schroeder, T. Mikolajick, C.S. Hwang, Adv. Mater. 27, 1811 (2015)
- A. Girard, H. Taniguchi, S.M. Souliou, M. Stekiel, W. Morgenroth, A. Minelli, A. Kuwabara, A. Bosak, B. Winkler, Phys. Rev. B. 98, 134102 (2018)
- H. Taniguchi, A. Kuwabara, J. Kim, Y. Kim, H. Moriwake, S. Kim, T. Hoshiyama et al., Angew. Chem. Int. Ed. 52, 8088 (2013)
- 52. T. Murata, H. Akamatsu, D. Hirai, F. Oba, S. Hirose, Phys. Rev. Mater. 4, 104419 (2020)
- S.T. Zhang, A.B. Kounga, W. Jo, C. Jamin, K. Seifert, T. Granzow, J. Rodel, D. Damjanovic, Adv. Mater. 21, 4716 (2009)
- 54. C. Kittel, Phys. Rev. 82, 729 (1951)
- 55. P. Toledano, M. Guennou, Phys. Rev. B. 94, 014107 (2016)

- 56. J.W. Bennett, J. Phys. Chem. C. 124, 19413 (2020)
- R. Hoppe, H.J. Roehrborn, H. Walker, Naturwissenschaften 51, 86 (1964)
- R. Hoppe, H.D. Stover, Zeitschrift fuer Anorg. und Allgemeine Chem. 437, 123 (1977)
- H. Stoll, R. Hoppe, Zeitschrift fuer Anorg. und Allgemeine Chem. 551, 151 (1987)
- P. Panek, R. Hoppe, Zeitschrift fuer Anorg. und Allgemeine Chem. 393, 13 (1972)
- 61. K.O. Klepp, A. Kolb, Z. Kristallogr. 213, 694 (1998)
- H.S. Khalsa, M.D. Smith, H.C. zur Loye, *Mater. Res. Bull.* 44, 91 (2009)
- M.R. Harrison, M.G. Francesconi, Coord. Chem. Rev. 255, 451 (2011)
- 64. K.F. Garrity, Phys. Rev. B. 97, 024115 (2018)
- 65. N.V. Ter-Oganessian, V.P. Sakhnenko, J. Phys. 32, 275401 (2020)
- J.W. Bennett, I. Grinberg, A.M. Rappe, Phys. Rev. B. **79**, 235115 (2009)
- M. Ong, D.M. Guzman, Q. Campbell, I. Dabo, R.A. Jishi, J. Appl. Phys. **125**, 235702 (2019)
- J.A. Brehm, J.W. Bennett, M.R. Schoenberg, I. Grinberg, A.M. Rappe, J. Chem. Phys. **140**, 224703 (2014)
- J.A. Brehm, H. Takenaka, C.W. Lee, I. Grinberg, J.W. Bennett, M.R. Schoenberg, A.M. Rappe, Phys. Rev. B. 89, 195202 (2014)
- 70. R. Jaramillo, J. Ravichandran, APL Mater. 7, 100902 (2019)
- 71. K.O. Klepp, Z. Naturforsch 47b, 201 (1992)
- 72. B.M. Gatehouse, D.J. Lloyd, J. Solid State Chem. 2, 410 (1970)
- R. Mishra, M. Ali, S.R. Bharadwaj, D. Das, J. Therm. Anal. Calorim. 66, 779 (2001)
- Y. Masubuchi, R. Miyazaki, H. Kirkuchi, T. Motohashi, S. Kikkawa, Dalton Trans. 43, 13751 (2014)
- R.J. Terry, C.D. McMillen, X. Chen, Y. Wen, L. Zhu, G. Chumanov, J.W. Kolis, J. Cryst. Growth 493, 58 (2018)
- 76. P. Hohenberg, W. Kohn, Phys. Rev. 136, B864 (1964)
- 77. W. Kohn, L.J. Sham, Phys. Rev. 140, A1133 (1965)
- X. Gonze, B. Amadon, P.M. Anglade, J.M. Beuken, F. Bottin, P. Boulanger, F. Bruneval, D. Caliste, R. Caracas, M. Cote et al., Comput. Phys. Commun. 180, 2582 (2009)
- X. Gonze, F. Jollet, F. Abreu-Araujo, D. Adams, B. Amadon, T. Applencourt, C. Audouze, J.M. Beuken, J. Bieder, A. Bokhanchuk, E. Bousquet et al., Comput. Phys. Commun. 205, 106 (2016)
- D.R. Hamann, M. Schluter, C. Chiang, Phys. Rev. Lett. 43, 1494 (1979)
- 81. D. Vanderbilt, Phys. Rev. B 41, 7892 (1990)
- 82. D.R. Hamann, Phys. Rev. B. 88, 085117 (2013)
- 83. H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13, 5188 (1976)
- 84. R.D. King-Smith, D. Vanderbilt, Phys. Rev. B 47, 1651 (1993)
- 85. R. Resta, Rev. Mod. Phys. 66, 899 (1994)



- J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)
- 87. Z. Wu, R.E. Cohen, Phys. Rev. B. 73, 235116 (2006)
- F. Tran, R. Laskowski, P. Blaha, K. Schwarz, Phys. Rev. B. 75, 115131 (2007)
- 89. P. Ganesh, R.E. Cohen, J. Phys. 21, 064225 (2009)
- A. Paul, J. Sun, J.P. Perdew, U.V. Waghmare, Phys. Rev. B. 95, 054111 (2017)
- J.W. Bennett, D.T. Jones, B.G. Hudson, J. Melendez-Rivera, R.J. Hamers, S.E. Mason, Environ. Sci. Nano 7, 1642 (2020)
- 92. X. Gonze, C. Lee, Phys. Rev. B. 55, 10355 (1997)
- 93. X. Gonze, Phys. Rev. A. 52, 1096 (1995)
- 94. E. Cockayne, J. Eur. Ceram. Soc. 23, 2375 (2003)

 J.W. Bennett, I. Grinberg, A.M. Rappe, Phys. Rev. B. 73, 180102R (2006)

Article

- 96. H.T. Stokes, D.M. Hatch, B.J. Campbell, http://iso.byu.edu
- 97. H.T. Stokes, D.M. Hatch, Phys. Rev. B. 30, 4962 (1984)
- 98. H.T. Stokes, D.M. Hatch, J. Appl. Cryst. 38, 237 (2005)
- B.J. Campbell, H.T. Stokes, D.E. Tanner, D.M. Hatch, J. Appl. Cryst. 39, 607 (2006)
- 100. S. Kerman, B.J. Campbell, K.K. Satyavarapu, H.T. Stokes, F. Perselli, J.S.O. Evans, Acta Cryst. **A68**, 222 (2012)
- 101. J. Towns, T. Cockerill, M. Dahan, I. Foster, K. Gaither, A. Grimshaw, V. Hazlewood, S. Lanthrop, D. Lifka, G.D. Peterson, R. Roskies, J.R. Scott, N. Wilkins-Diehr, Comput. Sci. Eng. 16, 62 (2014)