Developing new antiferroelectric and ferroelectric oxides and chalcogenides within the A_2BX_3 family

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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 identifies 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 $6mm$, $6, 3mm$, $3, 4mm$, $4, mm2$, 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_2SeO_4 -type materials [39, 40]. Solid-state AFEs also include the perovskites [41–46], as well as sulfoaluminates [47], ZrO_2 , and HfO_2 [48, 49], orthorhombic ABC semiconductors [2, 7], Bi_2SiO_5 [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_2PbO_3 and Rb_2PbO_3 were reported in space groups $Pnma$ and $Cmc2_1$ [57–59], while Cs_2PbO_3 was reported in space groups $Cmcm$ and $Cmc2_1$ [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 ΔE , 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/f.u. of a polar metastable state, and are the previously synthesized compounds K_2SnO_3 , K_2PbO_3 , Rb_2PbO_3 , K_2TiO_3 , K_2ZrO_3 , and K_2TiS_3 . One composition, predicted to be FE, Cs_2PbO_3 , has a polar ground state that is within < 10 meV/f.u. of an antipolar metastable state [56]. The barrier to switch between the polar and antipolar states is approximated as ΔE_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 ΔE_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 ΔE_1 are used to assess the likelihood of switching between polar and antipolar states, and the values of ΔE_2 are used to assess the likelihood of switching between polar and nonpolar states. To compare to known FE oxides, the DFT-computed ΔE_2 would be ~ 20 and 200 meV/f.u. for $BaTiO_3$ and $PbTiO_3$, respectively [21]. The larger value of $200 \sim$ 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 Γ^{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 1st 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 ΔE_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_2SiO_3 structure type, but a yet to be reported structure type in the same crystallographic space group. The B-site in the Na_2SiO_3 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 ΔE 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 Γ^{2-} to nonpolar mode Γ^{4+} , allowing for a polar mode Γ^{3-} to condense in after full-cell relaxation. This is what occurred for Cs_2PbO_3 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 *Ccm* 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. K_2TiO_3 , K_2PbO_3 , and Rb_2PbO_3 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 $\text{C}2/c$ 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*, *Cmc2₁*, *Pna2₁*, 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_2TiO_3 , K_2PbO_3 , Rb_2PbO_3 that only 1 polar displacement pattern, described using the irrep Γ^{2-} , does not relax back to high symmetry space group *Ccm*. 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 *Cmc2₁* 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_2TiO_3 , K_2PbO_3 , and Rb_2PbO_3 , respectively. This small ΔE_1 could explain why the structures of K_2PbO_3 and Rb_2PbO_3 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_2TiO_3 , K_2PbO_3 , and

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 (*Ccm* 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_2TiO_3 , K_2PbO_3 , and Rb_2PbO_3 display only 1 metastable polar state (classified in space group *Cmc2₁*) 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 K_2TiO_3 , K_2PbO_3 , and Rb_2PbO_3 , 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 E_{gap} values as a qualitative guide to better understand how atomistic composition affects the electronic structure. The band gap (E_{gap}) of K_2TiO_3 in Fig. 3a is 3.66 eV, much larger than for K_2PbO_3 and Rb_2PbO_3 , 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 $B = \text{Pb}$ 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

Figure 3: Compared here are the electronic band structures and corresponding PDOS for (a) K_2TiO_3 , (b) K_2PbO_3 , and (c) Rb_2PbO_3 , 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_2TiO_3 , but closer to the Fermi level (E_F , 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_2PbO_3 and Rb_2PbO_3 have band gaps of 1.48 and 1.50 eV, respectively, K_2TiO_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 $BaZrS_3$ [66], $BaZrSe_3$ [67], $CaZrS_3$ [68], $PbTiO_{3-x}S_x$ [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 ($CaZrS_3$, $BaZrS_3$, Ba_3ZrS_7 , 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 ΔE_1 values to the first metastable polar state. For the $B = Zr$ series, the increase in ΔE_1 is largest for K_2ZrSe_3 and smallest for Cs_2ZrO_3 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

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 Å³.

A_2BX_3	GS	a (Å)	b (Å)	c (Å)	V (Å ³)	E_{gap} (eV)	ΔE_1 (meV)	PS1	P (C/m ²)	ΔV (Å ³)	$\Delta V/V$ (%)
K ₂ TiO ₃	<i>Pnma</i>	10.068	6.868	5.450	376.890	3.66	1	<i>Cmc2₁</i>	0.047	+0.68	+0.18
K ₂ TiS ₃	<i>Pnma</i>	11.748	8.227	6.446	633.992	1.28	7	<i>Cmc2₁</i>	0.092	− 1.29	− 0.21
K ₂ TiSe ₃	<i>Pnma</i>	12.149	8.496	6.835	705.555	1.53	18	<i>Cmc2₁</i>	0.029	− 0.41	− 0.06
K ₂ ZrO ₃	<i>Pnma</i>	10.415	6.925	5.867	423.123	3.96	6	<i>Cmc2₁</i>	0.110	+0.92	+0.22
K ₂ ZrS ₃	<i>Pnma</i>	12.182	8.124	6.839	676.821	1.86	30	<i>Cmc2₁</i>	0.070	+6.33	+0.94
K ₂ ZrSe ₃	<i>Pnma</i>	12.545	8.423	7.157	756.290	1.57	35	<i>Cmc2₁</i>	0.067	+5.34	+0.71
Rb ₂ ZrO ₃	<i>Pnma</i>	10.729	7.305	5.891	461.709	3.84	1	<i>Cmc2₁</i>	0.060	+0.51	+0.11
Rb ₂ ZrS ₃	<i>Pnma</i>	12.428	8.582	6.841	729.641	1.88	12	<i>Cmc2₁</i>	0.030	− 0.04	− 0.00
Rb ₂ ZrSe ₃	<i>Pnma</i>	12.992	8.745	7.090	805.530	1.53	5	<i>Cmc2₁</i>	0.042	+1.16	+0.14
Cs ₂ ZrO ₃	<i>Cmcm</i>	11.206	7.617	5.914	504.796	4.04	0	–	–	–	–
Cs ₂ ZrS ₃	<i>Cmcm</i>	12.707	9.058	6.798	782.450	1.84	0	–	–	–	–
Cs ₂ ZrSe ₃	<i>Cmcm</i>	13.008	9.371	7.084	863.456	1.54	2	<i>Cmc2₁</i>	0.001	− 3.23	− 0.37

Next we report the computed band gap E_{gap} in units of eV, followed by ΔE_1 , the space ground of the first polar metastable state (PS1), its polarization, P , in units of C/m², and finally ΔV and $\Delta V/V$, given in units of Å³ and as a %, respectively. A dash (–) for entries with $A = \text{Cs}$ indicates that no metastable polar states exists for these compounds using our search methods.

family, with $A = \text{K}$ or Rb and $B = \text{Ti}$ or Zr will be both semi-conducting and AFE, given that the computed values of ΔE_1 are all below 40 meV/f.u.

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 PbZrO₃ is 1.3% [3] and similar values are obtained for ZrO₂ [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 K₂ZrS₃, while the phonon modes at Γ of the antipolar ground state and metastable polar state of new AFE compounds K₂ZrS₃, Rb₂ZrO₃, and Rb₂ZrS₃ 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 Γ 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 K₂TiSe₃, K₂ZrS₃, K₂ZrSe₃, Rb₂ZrO₃, Rb₂ZrS₃, and Rb₂ZrSe₃ are 6 new functional materials that are potentially AFE, joining known members (K₂TiO₃, K₂ZrO₃, 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 ΔE_1 (green) and ΔE_2 (purple). DFT calculations demonstrate that increasing the size of the A -site from K to Rb to Cs leads to a decrease in ΔE_1 and ΔE_2 for $A_2\text{ZrO}_3$ compounds, with Cs₂ZrO₃ showing no (meta)stable polar or antipolar structures. This suggests that further compositional tuning of $A_2\text{ZrO}_3$ materials, to adjust ΔE_1 and ΔE_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 ΔE_1 and ΔE_2 values as the X anion is changed in the K₂ZrX₃ series. Our DFT results indicate that increasing the size of X from O to S to Se tends to increase ΔE_1 and decrease ΔE_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 K₂ZrS₃ and Rb₂ZrSe₃ (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 $X = \text{Se}$ (K₂ZrSe₃, Rb₂ZrSe₃) a polar monoclinic phase *Cc* is present in the energy landscape, in agreement with prior DFT investigation on Cs₂ZrSe₃ [56], and contains multiple polar modes, reminiscent of the conditions required for some types of hybrid improper FEs.

(a) Change A-site (K → Rb → Cs)

(b) Change X-site (O → S → Se)

Figure 4: For compositions with $B = \text{Zr}$, increasing the size of the A-site (a, top) in the oxides series decreases ΔE_1 (green values, given in meV) and ΔE_2 (purple values, given in meV). For combinations with $A = \text{K}$ and $B = \text{Zr}$, increasing the size of the anion X (b, bottom) increases ΔE_1 , while ΔE_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 ΔE_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_2PbO_3 and Rb_2PbO_3 . We map out the energetics of compositional tuning to assess how ΔE_1 and ΔE_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_2BX_3 family, found in crystallographic space groups *Cmcm*, *Pnma*, *Cmc2₁*, 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 *Cmc2₁* 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_5 square pyramids and Configuration 2 has alternating B-sites within each horizontal chain. The resulting structures of $\text{Rb}_2(\text{Sn}_{1/2}\text{Pb}_{1/2})\text{O}_3$ 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_5 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* → *Pnma*, *Pnma* → *Pca2₁*, *Cmc2₁* → *Pc*, and *C2/c* → *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*, *Amn2*, 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 *Pca2₁*, 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 *Pca2₁* structure with antipolar tilts. The volume change in going from the ground state to the first metastable state is $0.51 \text{ \AA}^3$ 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 $\text{Rb}_2(\text{Sn}_{1/2}\text{Pb}_{1/2})\text{O}_3$ 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 ΔE from the ground-state structure. Next is the polarization (P) in each Cartesian direction, given in units of C/m^2 .

SG	a (Å)	b (Å)	c (Å)	β	ΔE (meV)	P_x (C/m ²)	P_y (C/m ²)	P_z (C/m ²)
Sn/Pb Configuration 1								
<i>Pmma</i>	10.735	7.451	5.917	90.00	29	0	0	0
<i>Pca2₁</i>	10.829	7.322	5.959	90.00	0	0	0	0.015
<i>Pc</i>	10.860	7.327	5.945	89.98	3	0	0	0.120
<i>P2/c</i>	10.747	7.449	5.922	93.02	28	0	0	0
Sn/Pb Configuration 2								
<i>Amm2</i>	10.719	7.452	5.924	90.00	27	0	0.017	0
<i>Pmn2₁</i>	10.808	7.325	5.971	90.00	0	0	0.013	0
<i>Cm</i>	11.077	7.483	6.046	89.89	3	0	0.014	0.124
<i>C2</i>	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: $\text{Cmcm} \rightarrow \text{Amm2}$, $\text{Pnma} \rightarrow \text{Pmn2}_1$, $\text{Cmc2}_1 \rightarrow \text{Cm}$, and $\text{C2/c} \rightarrow \text{C2}$. 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 Å^3 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 ΔE values are within 30 meV/f.u., comparable to the range of values for known oxides presented in Ref. [3] (strained PbZrO_3) and [48] (ZrO_2).

In the second example we investigate 2 configurations, where 1/2 of the A -sites in K_2PbO_3 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)PbO₃ 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 PbO₃ 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)PbO₃ and (K,Rb)PbO₃ are illustrated in Fig. 6, along with their fully relaxed crystallographic space groups.

Much like the previous Rb₂(Sn_{1/2}Pb_{1/2})O₃ example the structures exhibit a small nonzero *P*, though here it is in the

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 BaTiO₃, and that the Δ*E* to access this state

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 Δ*E* from the ground-state structure. Next is the polarization (*P*) in each Cartesian direction, given in units of C/m².

SG	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β	Δ <i>E</i> (meV)	<i>P_x</i> (C/m ²)	<i>P_y</i> (C/m ²)	<i>P_z</i> (C/m ²)
Na/K Configuration 1								
<i>Ama2</i>	10.242	6.847	6.002	90.00	365	0.006	0	0
<i>Pna2₁</i>	10.081	6.769	5.890	90.00	8	0.007	0	0
<i>Cc</i>	10.148	6.696	5.898	90.03	0	0.010	0	0.198
<i>Pc</i>	10.082	6.769	5.891	90.00	8	0.007	0	0
Na/K Configuration 2								
<i>Amm2</i>	10.196	6.922	6.001	90.00	263	0	0.012	0
<i>Pmn2₁</i>	10.294	6.603	5.922	90.00	23	0	0.016	0
<i>Cm</i>	10.323	6.609	5.916	91.86	0	0	0.015	0.225
<i>Pm</i>	10.295	6.602	5.923	89.99	23	0	0.015	0
Rb/K Configuration 1								
<i>Ama2</i>	10.663	7.324	6.050	90.00	103	0.004	0	0
<i>Pna2₁</i>	10.726	7.182	6.052	90.00	0	0	0	0
<i>Cc</i>	10.775	7.197	6.042	88.86	3	0.004	0	0.151
<i>Pc*</i>	10.725	7.182	6.052	89.99	0	0.005	0	0
Rb/K Configuration 2								
<i>Amm2</i>	10.669	7.320	6.049	90.00	89	0	0.006	0
<i>Pmn2₁</i>	10.794	7.100	6.070	90.00	0	0	0.002	0
<i>Cm</i>	10.824	7.148	6.058	89.60	3	0	0	0.163
<i>Pm*</i>	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)PbO₃, K₂PbO₃, and (K,Rb)PbO₃. (K,Na)PbO₃ has a polar ground state (denoted as p), while K₂PbO₃ and (K,Rb)PbO₃ 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 K₂PbO₃ 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/m², respectively, as shown in Table 3. This did not happen with (K,Rb)PbO₃, where the ground state maintained its antipolar PbO₃ tilt system.

Compositional tuning of K₂PbO₃ can change the preferred ground-state structure and adjust the switching barriers ΔE_1 and ΔE_2 , and this is illustrated in Fig. 7. Adding a larger cation, such as Rb, to K₂PbO₃ 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 non-polar structures. This is one route to reduce the energy of a FE phase transition. Adding a smaller cation, such as Na, to K₂PbO₃ 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 (K₂PbO₃, Rb₂PbO₃, K₂TiS₃, Cs₂ZrSe₃, 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.

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_2SnO_3 , K_2ZrO_3 , K_2TiS_3 , 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 ΔE_1 and ΔE_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 5×10^{-6} eV. This stringent criteria allows for ΔE comparisons down to at least 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_3 and BaTiO_3 [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_2ZrO_3 , K_2ZrS_3 , and Rb_2ZrS_3 , 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 Γ point using a $6 \times 6 \times 6$ 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 K_2ZrS_3 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 Å of the lattice constant in that direction, depending upon the size of the cation A-sites (e.g., $r_{\text{Rb}} > r_{\text{K}}$) and anion X-sites (e.g., $r_{\text{Se}} > r_{\text{S}} > r_{\text{O}}$). 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.

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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

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