High-throughput first principles search for new ferroelectrics

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We use a combination of symmetry analysis and high-throughput density functional theory calculations to search for new ferroelectric materials. We use two search strategies to identify candidate materials. In the first strategy, we start with non-polar materials and look for unrecognized energy-lowering polar distortions. In the second strategy, we consider polar materials and look for related higher symmetry structures. In both cases, if we find new structures with the correct symmetries that are also close in energy to experimentally known structures, then the material is likely to be switchable in an external electric field, making it a candidate ferroelectric. We find sixteen candidate materials, with variety of properties that are rare in typical ferroelectrics, including large polarization, hyperferroelectricity, antiferroelectricity, and multiferroism.

Ferroelectrics, which are materials that have a ground state polar phase that can be switched to a symmetry-equivalent structure by the application of an external electric field, have been studied and used in applications for many years. Much of the attention on ferroelectrics has focused on prototypical examples from the perovskite oxides, like PbTiO$_3$ and BiFeO$_3$. However, in recent years, there has been a renewed theoretical and experimental interest in discovering and understanding the properties of new ferroelectric materials\cite{1}. These new materials have shown a variety of new or rare behaviors, including hybrid improper ferroelectricity, hyperferroelectricity, topological defects/domain walls, etc. In addition, there is interest in and need for ferroelectrics with improved functionality for various applications, including magnetoelectrics, Pb-free piezoelectrics, room temperature multiferroics, solar energy converters, silicon compatible ferroelectrics, ferroelectric catalysts, etc.\cite{15,20}

High-throughput first principles density functional theory (DFT) calculations have been used increasingly in recent years as a tool for materials discovery and screening.\cite{21,20}. DFT calculations using semilocal functionals are generally reliable tools for computing ground state properties and the energy differences between closely related phases, which is the primary screening tool needed to identify ferroelectrics. The main obstacle to finding new ferroelectric materials computationally is identifying the relevant polar and non-polar structures to consider. Any insulator known experimentally to have both a polar and a non-polar phase has likely already been recognized as a potential ferroelectric, necessitating a search for new structures of known compounds. However, systematically searching all insulating compounds for possible new phases is too computationally demanding to attempt systematically.

In this work, we employ two strategies to identify new ferroelectrics, which we apply to a much larger range of materials than related previous searches\cite{11,10,14,27,34}. In the first strategy, aimed at finding proper ferroelectrics, we start with a list of experimentally known non-polar transition metal oxides, nitrides, and sulfides, and we perform a Γ-point phonon calculation, looking for materials with unstable polar modes. In order to reduce the computational cost of this step, we reuse phonon calculations from our earlier study of transition metal thermoelectricity\cite{35}, and we supplement this list with additional calculations of materials with small unit cells. After identifying materials with unstable polar distortions, we proceed to look for the ground state structure, including possible non-polar distortions. If the ground state is polar, then the material is a candidate ferroelectric.

In the second strategy, we begin instead with a list of materials already known to be polar but not known to be switchable in an external electric field. We attempt to identify switchable materials by using a symmetry search algorithm\cite{36} and adjusting the tolerance factor systematically to allow the algorithm to identify possible higher symmetry structures that are related to the polar ground state. Then we calculate the energy of these new structures, and if they are close in energy to the polar structure, the materials are likely to be switchable\cite{1}. An advantage to both of our search strategies is that they are not limited to generating previously observed structure types, allowing us to consider new ferroelectric mechanisms.

In the remainder of this letter, we will detail our search strategy, identify candidate ferroelectrics, and discuss some of their interesting properties. We find materials with unusual chemistry for ferroelectrics, as well as potentially useful properties that include strong polarization, magnetism, hyperferroelectricity, and antiferroelectricity. In addition, we rediscover and identify the missing structures of two materials that were previously studied as ferroelectrics but have not been fully characterized. Full structural details our of candidate materials can be found in the supplementary materials.

We perform first principles DFT calculations\cite{37,38} with a plane-wave basis set as implemented in
We use the PBEsol exchange-correlation functional, which provides more accurate lattice constants and phonon frequencies than other generalized gradient approximation functionals. We perform phonon calculations using DFT perturbation theory, and polarization calculations with the Berry phase method. We use PYMATGEN to manipulate files from the Inorganic Crystal Structure Database (ICSD) to setup the initial structures for relaxation. We relax each structure several times to ensure consistency between the basis set and the final structure, with a force tolerance of 0.001 Ry/Bohr, an energy tolerance of 1 × 10^{-4} Ry, and a stress tolerance of 0.5 Kbar. For phonon calculations, we decrease the force tolerance to 5 × 10^{-5} Ry/Bohr.

To identify ferroelectrics, we look for materials that are a) insulating, b) have a polar ground state, and c) have a higher symmetry reference structure that is close in energy to the polar structure, which we take as an indication the material is likely to be switchable in an external electric field. Some examples of this energy difference for known ferroelectrics include PbTiO_3 (20 meV/atom), Ca_3Ti_2O_7 (40 meV/atom), ZrO_2 (16 meV/atom)\(^{[5,9]}\). Of course, in real ferroelectrics, the switching proceeds via a combination of domain wall nucleation and motion, and does not correspond directly to the first principles energy difference; however, a small energy difference has proven to be a useful indicator of whether a material is likely to be switchable.

In our first search strategy, the initial screening step is to perform a Γ-point phonon calculation, which we did for 267 transition metal oxides, nitrides, and sulfides. We identified 90 compounds with unstable modes at Γ, although some of these distortion were non-polar. After excluding known ferroelectrics and materials with known non-polar distortions, we proceeded to search for the ground state structure. This search consisted of first calculating the phonon dispersion of the material, and then freezing in finite amounts of each unstable phonon eigenvector, as well as pairs of eigenvectors, into supercells that correspond to points in the Brillouin zone with unstable modes. We then relax the resulting structures\(^{[14,16,17]}\). For systems with many unstable modes, which could have ground states consisting of complicated distortion patterns, we supplemented this searching with a random search strategy\(^{[17]}\). To perform a random search, we take a supercell, freeze in small random distortions, and relax. For most materials, we found that after a set of ten random relaxations in a given supercell, the same low energy structures repeated several times, and we terminated the search.

After this search process, if a material has a polar ground state, then the material is a candidate ferroelectric. In addition, if the material has competing polar and antipolar phases, then the material is a candidate antiferroelectric\(^{[2,48]}\). In the top rows of Table I, we present six candidate ferroelectrics discovered with this strategy. We proceed to briefly discuss several of these structures.

First, we note that after doing our analysis, we discovered that BaBi_2Ta_2O_9 and related materials with Sr and Ca have has previously been studied as a ferroelectric\(^{[5]}\). However, only a pseudotetragonal twinned version of the polar structure of BaBi_2Ta_2O_9 had been determined, explaining why it did not show up in our database search as a polar. This material has a layered structure that consists of perovskite-like BaTaO_3 layers separated by BiO layers, and these layers shift relative to each other in-plane, resulting in a relatively large polarization. Re-identifying a known ferroelectric gives us confidence in the utility of our computational methodology.

\[ \text{SrNb}_6O_{16}, \text{ shown in Fig. 1, and the closely related NaNb}_6O_{15}F, \text{ have a variety of notable properties. We will concentrate on SrNb}_6O_{16}, \text{ which has a high symmetry structure consisting of layers of Nb}_6O_{10} \text{ spaced by SrO}_4 \text{ layers. The material has a non-reversible in-plane polarization, but the switchable portion of the polarization consists of out-of-plane buckling in the Nb}_6O_{10} \text{ layers. Because of the large number of atoms in the unit cell,} \]

| Composition | High-sym. space grp. | Polar space grp. | ∆E (meV/atom) | Polariz. (µC/cm²) |
|-------------|---------------------|------------------|---------------|------------------|
| SrNb_6O_{16} | Pnam2 | Cm | 5.5 | 7 |
| NaNb_6O_{15}F | Pnam2 | Cm | 9.5 | 6 |
| RbCa_2Nb_3O_{10} | P4/mmm | Pc | 46.6 | 23 |
| BaBi_2Ta_2O_{9} | I4/mmm | Cmc2_1 | 15.7 | 37 |
| LiScAs_2O_7 | C2 | P1 | 1.6 | 7 |
| YSF | P6_3/mmc | P6_3/mcc | 11.1 | 1.2 |

TABLE I: Data on candidate ferroelectrics, found by starting from high symmetry (top) and low symmetry (bottom) structures. The second and third columns are space groups of the high and low symmetry structures, column four is the energy difference in meV/atom, and the last column is the polarization in µC/cm².
there are a variety of unstable polar and non-polar bucklings. SrNb$_6$O$_{16}$ has anomalously large effective charges in the $z$-direction of 9 to 11 on the Nb atoms and $-7$ to $-9$ on the O atoms. In the $xy$-plane, the effective charges are much lower, and Sr has an effective charge of 2.4. Similar anomalous effective charges are well-known in the perovskite oxides but are not present in many alternative ferroelectrics.

Despite these enormous effective charges, SrNb$_6$O$_{16}$ is actually a candidate hyperferroelectric, a very rare category of proper ferroelectrics with instabilities of both the longitudinal optic (LO) and transverse optic (TO) modes, as shown in table II. These instabilities correspond to unstable polar modes under both zero electric field ($E = 0$) and zero displacement field ($D = 0$) boundary conditions. The polar distortions of normal ferroelectrics are stable under $D = 0$ boundary conditions.

We were initially very surprised to find a hyperferroelectric with large effective charges, as the energetic cost of producing long range electric fields is proportional to $(Z^*)^2/\epsilon$, where $\epsilon$ is the electronic dielectric constant. SrNb$_6$O$_{16}$ avoids this by having three different unstable polar modes that can mix with each other, producing modes that are still polar, but with much smaller mode effective charges under $D = 0$ boundary conditions, as detailed in table II. Hopefully, hyperferroelectric oxides similar to SrNb$_6$O$_{16}$ are more common than previously thought, especially as hyperferroelectrics have potential applications as single layer ferroelectric devices. Further work must be done to understand the $D = 0$ ground state in this material.

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In our second search strategy, we considered a list about 2750 compounds from the ICSD with small unit cells and polar ground states. For each compound, we used the symmetry detection algorithm of pymatgen and varied the tolerance factor from $10^{-6}$ to 3, looking for related structures with higher symmetry with otherwise reasonable structures (e.g. no atoms on top of each other). For compounds where new structures were found, we then relaxed both the experimentally known polar structure and any new structures. In most cases, the new structures were very high energy. For example, in many structures with covalent bonds, the new structures had broken bonds and were unrealistic. In addition, we found a small number of compounds in the opposite situation, where the polar phase relaxed to a non-polar structure. These materials were either misidentified as polar experimentally, or are not well described by the PBEsol functional. However, in addition to those cases, we found ten compounds that have a low but non-zero energy difference between their polar and non-polar structures, making them candidate ferroelectrics. We list them in the second section of table I and we discuss a few interesting cases below.

First, we note that Sb$_2$WO$_6$ is a second example of a previously known (anti-)ferroelectric/ferroelastic that our procedure rediscovered. In this case, the polar structure was previously characterized experimentally, and we have provided new information about the non-polar phase.

The compound CuBiW$_2$O$_8$, as well as the five related materials listed in the ICSD with structure type CuNb$_3$(WO$_4$)$_2\beta$, is listed as having no symmetry in the ICSD. However, according to PBEsol calculations, CuBiW$_2$O$_8$ and the related CuYW$_2$O$_8$ relax to a higher symmetry structure with only inversion symmetry, suggesting that these materials do not have a polar phase. We were surprised to find so many materials possibly misidentified, so we performed LDA calculations to verify our result. We instead found that CuBiW$_2$O$_8$ (but not CuYW$_2$O$_8$) does have polar distortion, with a very small energy difference and polarization, as listed in table I. This functional-dependent behavior is the opposite of the typical behavior of LDA and GGA functionals, where GGA tends to overestimate polar distortions, while LDA underestimates. Further work may be necessary to reveal whether this class of materials is really polar/ferroelectric.

The pair of compounds PbGa$_2$O$_4$ and PbAl$_2$O$_4$ consist of (Al,Ga)O$_4$ tetrahedra separated by Pb atoms, as shown for PbAl$_2$O$_4$ in Fig. 2. Their high symmetry structures have a three-fold rotation axis, and the polar-
ization, which is due to a collective tilting of the tetrahedra, points in one of three equivalent in-plane directions, as shown in Fig. 2. The structure with 180° reversed polarization does not have the same energy, which can be understood by examining the symmetry invariant free energy of the two-dimensional Γ5 distortion up to fourth order:

\[
F = c_2(\Gamma_{5a}^2 + \Gamma_{5b}^2) + c_3(\Gamma_{5a}^3 - 3\Gamma_{5a}\Gamma_{5b}^2) + c_4(\Gamma_{5a}^4 + 2\Gamma_{5a}\Gamma_{5b}^2 + \Gamma_{5b}^4).
\] (1)

In this notation the ground state polar structure corresponds to Γ_{5a} > 0, Γ_{5b} = 0, and the constants c2 and c3 are negative, while c4 is positive. Unlike a typical proper ferroelectric, there is a third-order term, which explains why the structure with reversed polarization is inequivalent. The reversed polarization direction structure is only 9 meV/atom higher in energy than the ground state for PbAl2O4, and represents the transition state between two stable polarization directions. Therefore, it is possible to switch the polarization of PbGa2O4 and PbAl2O4 by rotating it 120° while avoiding the higher energy high-symmetry structure, resulting in a barrier that is eight times lower in energy.

The layered structure of V2MoO8 [58] is interesting for possible applications because it has an enormous polarization of 108 μC/cm², comparable to the largest polarizations in perovskites [59]. As shown in Fig. 3, this material actually has three low energy structures: the high-symmetry phase, the polar phase, and an antipolar phase [60, 61]. This is also seen experimentally and which is 48 meV/atom lower in energy than the polar phase. Because the ground state of V2MoO8 is antipolar with a competing polar phase, this material is better characterized as a candidate antiferroelectric. The very large polarization of the polar phase of this material could make V2MoO8 useful in applications like antiferroelectric energy storage, where a large polarization jump is desirable.

Finally, we note LiV2O5, which consists of layers of V2O5 spaced by Li ions, as shown in Fig. 4 and which has shown experimental evidence of a phase transition [62]. The ferroelectric polarization is driven by the off-centering of Li atoms. According to PBEsol, the material is non-magnetic; however, we also examined various magnetic orderings using DFT+U [63-65], with a U value of 3 eV on the V d-states. These calculations, which we expect to be more accurate for a material with partially occupied 3d orbitals, shows that LiV2O5 is a ferromagnetic insulator with a gap of 0.37 eV in the non-polar phase and 1.00 eV in the polar phase, making LiV2O5 a candidate multiferroic.

In conclusion, we have performed a high-throughput first principles search for new ferroelectric compounds. We use two search strategies: 1) starting with known non-polar structures and looking for polar distortions, and 2) starting with known polar structures and looking for related high-symmetry structures. We discover 16 candidate materials with a variety of interesting properties, including very large polarizations, hyperferroelectricity, antiferroelectricity, and multiferroism. We hope that the particular compounds found in this work, as well as the variety of new chemistries and structures that lead to polar distortions, will be useful in future work understanding and designing ferroelectrics. In addition,
the high-throughout search techniques used in this work should be applicable to future studies of structural phase transitions.

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