Intrinsic polar metals are rare, especially in oxides, because free electrons screen electric fields in a metal and eliminate the internal dipoles that are needed to break inversion symmetry. Here we use first-principles high-throughput structure screening to predict a new polar metal in bulk and thin film forms. After screening more than 1000 different crystal structures, we find that ordered BiPbTi$_2$O$_6$ can crystallize in three polar and metallic structures, which can be transformed between via pressure or strain. In a heterostructure of layered BiPbTi$_2$O$_6$ and PbTiO$_3$, multiple states with different relative orientations of BiPbTi$_2$O$_6$ polar displacements, and PbTiO$_3$ polarization, can be stabilized. At room temperature, the interfacial coupling enables electric fields to first switch PbTiO$_3$ polarization and subsequently drive 180° change of BiPbTi$_2$O$_6$ polar displacements. At low temperatures, the heterostructure provides a tunable tunnelling barrier and might be used in multi-state memory devices.
Polar metals—analogy of ferroelectrics in metals—are characterized by intrinsic conduction and inversion symmetry breaking. Polar metals are rare (especially in oxides) because mobile electrons screen electric fields in a metal and eliminate internal dipoles that are needed to break inversion symmetry. The discovery of LiOsO$_3$,$^1$ a metal that transforms from a centrosymmetric R$3c$ structure to a polar R$3c$ structure at 140 K, has stimulated an active search for new polar metals in both theory and experiment.$^2$–$^9$

Density-functional-theory-based first-principles calculations have proven accurate in describing crystal structures and have been successfully applied to predict new functional materials, such as ferroelectrics, piezoelectrics and multiferroics.$^{10}$ Since crystal structure is the essential property of polar metals, we need to scrutinize the prediction by not presupposing an a priori favorable crystal structure. First-principles high-throughput crystal structure screening method, which is based on the marriage between first-principles calculations and a multitude of techniques such as particle-swarm optimization algorithm$^{11}$ and evolutionary algorithm$^{12}$, has demonstrated its superior power in effectively searching for the ground state structures and metastable structures of functional materials with only the given knowledge of chemical composition.$^{13}$–$^{15}$

In this work, we use ab initio high-throughput structure screening to predict a new polar metal BiPbTi$_5$O$_{12}$ (BPTO for short). After screening over 1000 different crystal structures, we find that ordered BPTO can crystallize in three different polar metallic structures (post-perovskite Pmm$2$, perovskite Pmn$2$ and perovskite Pmn$2_1$), each of which can be transformed to another via external pressure or epitaxial strain. The mechanism is that 6s lone-pair electrons of Bi and Pb ions tend to favor off-center displacements.$^{10}$ On the other hand, in the perovskite structures, Bi$^{3+}$ and Pb$^{2+}$ enforce a fractional valence on Ti, which leads to conduction; in the post-perovskite structure, strong hybridization between Bi/Pb 6p and O 2p states induces a finite density of states at the Fermi level.

Next we demonstrate potential applications of the new polar metal BPTO by studying a BPTO/PbTiO$_3$ heterostructure. We find that different states in which BPTO polar displacements are parallel, anti-parallel and perpendicular to PbTiO$_3$ polarization can be stabilized in the heterostructure. Also, 180° switching of BPTO polar displacements needs to surmount an energy barrier of about 58 meV per slab. This implies that at room temperature where thermal fluctuations can overcome the switching barrier, the interfacial coupling between the polarization and polar displacements enables an electric field to first switch PbTiO$_3$ polarization and subsequently drive BPTO to change its polar displacements by 180°; at low temperatures where the switching barrier dominates over thermal fluctuations, the BPTO polar displacements can not be switched but the direction of PbTiO$_3$ polarization can be controlled by an electric field. This can stabilize three distinct states with different tunnelling barriers.

Results and discussion
Most stable crystal structures of bulk BPTO. The key question in predicting a new polar metal is to determine its crystal structure. Since ordered BPTO has not been synthesized in experiment, we perform a first-principles high-throughput search for the ground state structure using CALYPSO$^{11,16}$ method, in combination with CrySPY.$^{17}$ In the search, we do not constrain ourselves in any a priori favorable crystal structure. We screen >1000 different crystal structures among which we consider different Bi/Pb ordering in perovskite structure: layered ordering, columnar ordering and rock-salt ordering; and we also consider many non-perovskite structures, including post-perovskite structure and hexagonal structure. The computational details of our first-principles calculations and high-throughput structure screening method are provided in Methods.

Figure 1 shows ten lowest-energy crystal structures of BPTO from our calculations. The details of these ten crystal structures are available in Supplementary Table 1. The lowest energy structure is post-perovskite with a polar symmetry Pmn$2$ (space group No. 25). The crystal structure is explicitly shown in Fig. 1b. The TiO$_6$ octahedra are both corner-sharing and edge-sharing. The lack of inversion symmetry can be appreciated from Ti atoms which have strong polar displacements with respect to neighboring O atoms towards x-axis. The next two lowest-energy crystal
structures are both perovskite with $Pmn_2$ symmetry (space group No. 31) and $Pmmn$ symmetry (space group No. 25). Both $Pmn_2$ and $Pmmn$ are polar. The two perovskite structures have almost the same energy. Figure 1c shows the perovskite $Pmn_2$ crystal structure. Bi and Pb atoms form a rock-salt ordering and their displacements with respect to O atoms in the $xy$ plane make the crystal structure acentric. Figure 1d shows the perovskite $Pmmn$ crystal structure. Bi and Pb atoms have a layered ordering with a stacking direction along $z$-axis. It is clear that Bi, Pb, and Ti atoms all have strong polar displacements with respect to O atoms along $x$-axis, which breaks inversion symmetry.

While post-perovskite oxides are interesting by themselves, perovskite oxides have been widely studied and are more suitable for device applications because many perovskite oxide substrates are available, which makes it feasible to grow perovskite oxide thin films. Therefore, we consider using external pressure or epitaxial strain to transform BPTO among different polar structures. Pressure is widely used in bulk synthesis to isolate metastable phases of matter. Figure 1e shows that both polar structures have almost the same energy. Figure 1c shows the perovskite $Pmn_2$ structure. Bi and Pb atoms have about 0.25 and 0.19 more electrons in the post-perovskite structure. Bi-6 and Pb-6 have about 0.25 and 0.19 more electrons in the post-perovskite structure. Therefore, spin-up and spin-down are not fully empty and thus appear in the DOS of the post-perovskite structure (Fig. 2a), Ti-3d states have negligible contribution around the Fermi level. Instead, Bi-6p and Pb-6p, as well as O-2p states make the largest contribution to the DOS around the Fermi level, which can also be seen in Supplementary Fig. 3 where the electronic states around the Fermi level are zoomed in.

The Bader (static) charge analysis in Table 1 shows that Bi and Pb have about 0.25 and 0.19 more electrons in the post-perovskite structure than in the perovskite structures, which indicates stronger hybridization between Bi/Pb and O atoms in the post-perovskite structure. Therefore in the post-perovskite structure, Bi-6p and Pb-6p states are not fully empty and thus appear around the Fermi level.

Pb and Bi are heavy elements and their spin–orbit interactions (SOI) are not negligible. In the lower panels of Fig. 2, we take into account SOI and show the corresponding densities of states of BPTO of the three polar structures. Similar to the results without SOI, we do not find any magnetization or charge disproportionation in the fully relaxed structures. By comparing the densities of states calculated by DFT without SOI (upper panels of Fig. 2) and DFT with SOI (lower panels of Fig. 2), SOI almost unaffects the electronic structure, similar to previous studies on other polar metals.

While DFT with/without SOI calculations do not find any magnetization or charge disproportionation, correlation effects from Ti-3d orbitals may favor spin ordering and charge ordering.

Table 1 Bader charges for bulk BPTO.
| Structural type | Space group | Bader charges (e) |
|-----------------|-------------|------------------|
| Bi Pb Ti O      |             |                  |
| Post-perovskite | $Pmn_2$     | +1.48 +1.13 +2.19 | −1.16 |
| Perovskite      | $Pmn_2$     | +1.73 +1.32 +2.12 | −1.22 |
| Perovskite      | $Pmmn$      | +1.73 +1.32 +2.06 | −1.19 |

Charges are normalized to per atom.
A long-range magnetic ordering with a charge disproportionation $(\text{Ti}^{3+}+\text{Ti}^{4+})$ can result in an insulating ground state. To test the robustness of our prediction that BiPbTi$_2$O$_6$ is a polar metal, we apply an effective Hubbard $U$ correction on the Ti-3$d$ orbitals and calculate the densities of states for all three low-energy structures. The accurate value of correlation strength of BPTO is not known, but presumably it should not exceed that of Mott insulator LaTiO$_3$, in which Hubbard $U_{\text{Ti}}$ is about 5 eV. Therefore we consider a Hubbard $U_{\text{Ti}}$ ranging from 0 to 5 eV. Within this range of $U_{\text{Ti}}$, we do not find charge disproportionation but find robust metallicity in all the three polar structures of BPTO. Furthermore, in this range of $U_{\text{Ti}}$, we find itinerant ferromagnetism in the perovskite $Pmm2$ structure at $U_{\text{Ti}} \geq 1$ eV and in the perovskite $Pmm2$ structure at $U_{\text{Ti}} \geq 2$ eV (antiferromagnetic ordering is less stable than ferromagnetic ordering). We do not find any magnetism in the post-perovskite $Pmm2$ structure up to $U_{\text{Ti}} = 5$ eV. The magnetic phase diagram for the three polar structures as a function of Hubbard $U_{\text{Ti}}$ is shown in Fig. 3. The origin of itinerant ferromagnetism in BPTO is Stoner instability. In DFT+$U$ calculations, the Stoner criterion to induce itinerant ferromagnetism is:

$$U\rho(E_F) > 1,$$

where $U$ and $\rho(E_F)$ are Hubbard $U$ parameter and density of states at the Fermi level of a non-magnetic state, respectively. The upper panels of Fig. 2 shows that the perovskite $Pmm2$ structure has a large density of state at the Fermi level $\rho(E_F)$ in its non-magnetic state; the perovskite $Pmm2$ structure has a slightly smaller $\rho(E_F)$. Post-perovskite $Pmm2$ structure, on the other hand, has a very small $\rho(E_F)$ (9 times smaller than that of the perovskite $Pmm2$ structure and 15 times smaller than that of the perovskite $Pmm2$ structure). This explains that the critical $U_{\text{Ti}}$ to stabilize itinerant ferromagnetism in the perovskite $Pmm2$ structure is the smallest, while a much larger $U_{\text{Ti}}$ (larger than 5 eV) is needed to induce magnetism in the post-perovskite $Pmm2$ structure.

The role of lone-pair electrons. A local structural instability arising from lone-pair electrons has been reported in ferroelectric insulators and degenerately doped ferroelectrics. However, lone-pair electrons alone are not sufficient to stabilize a polar state in metals or a ferroelectric state in insulators. For example, BiFeO$_3$ is ferroelectric but BiMnO$_3$ is anti-ferroelectric, although lone-pair electrons are present in both of them. Therefore, high-throughput crystal structure prediction is essential in predicting new polar metals and ferroelectric insulators.

![Fig. 3 Phase diagram as a function of Hubbard $U$. The magnetic phase diagram of the post-perovskite $Pmm2$, perovskite $Pmm2$, and perovskite $Pmm2$ structures as a function of Hubbard $U_{\text{Ti}}$. Non-magnetic state and ferromagnetic state are shown by red circle and blue square, respectively.](image)

![Fig. 4 Electron localization function (ELF) and the energy curve from the centrosymmetric structure to the corresponding polar structure. a) The polar structure: post-perovskite $Pmm2$ and d) the centrosymmetric structure: post-perovskite $Pmmm$, b) the polar structure: perovskite $Pmm2$, and e) the centrosymmetric structure: perovskite $Pmm2$; c) The polar structure: perovskite $Pmm2$ and f) the centrosymmetric structure: perovskite $P4/mmm$. The isosurface of ELF is set at a value of ~0.5. g) Transition from the post-perovskite $Pmm2$ structure to the post-perovskite $Pmm2$ structure. h) Transition from the perovskite $Pmm2$ structure to the perovskite $Pmm2$ structure. i) Transition from the perovskite $P4/mmm$ structure to the perovskite $Pmm2$ structure.](image)
Switching barrier of BPTO thin films in a heterostructure.

Next we study BPTO thin films. The Pmm2 perovskite structure of BPTO, which has a layered Bi/Pb ordering, is highly suitable for thin film growth and can be stabilized on a perovskite oxide substrate having a lattice constant of 3.98 Å or larger. The Bi/Pb stacking direction in the Pmm2 perovskite structure is chosen as the z-axis, while the polar displacements are in the xy-plane. In addition, we find that constrained by an in-plane lattice constant of 3.98 Å or larger, ferroelectric PbTiO3 is under tensile strain and favors an in-plane polarization over an out-of-plane polarization (Supplementary Fig. 4). Therefore, we study a BPTO/PbTiO3 heterostructure, in which both BPTO polar displacements and PbTiO3 polarization are parallel to the interface. We will show that different from previously studied ferroelectric/polar-metal states to the parallel state. The energy of anti-parallel state is set as the zero point. The black dashed arrows highlight two energy barriers. The blue circles schematically shown in represent the images on the transition path found in the nudged elastic band calculations. The three energy minima along the transition path are orientations of BiPbTi2O6 polar displacements and PbTiO3 and NdScO3 can provide such a lattice constant. Figure 5a shows the lattice symmetry of doped ferroelectrics ill-defined and correspondingly there is no well-defined continuous structural phase transition at finite temperatures.

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Fig. 5 Switching of polar displacements of BPTO in a BPTO/PbTiO3 heterostructure. a Atomic structure of the BPTO/PbTiO3 heterostructure; “parallel state” (left) and “anti-parallel state” (right). The red (green) arrow refers to PbTiO3 polarization (BPTO polar displacement). b Layer-resolved conduction electrons on each Ti atom in parallel and anti-parallel states. c Layer-resolved polar displacements of metal ions along the x-axis in parallel and anti-parallel states. In a, b and c, the brown dashed lines indicate BPTO/PbTiO3 interface. d Calculated energy barrier along the transition path from the anti-parallel state to the parallel state. The energy of anti-parallel state is set as the zero point. The black dashed arrows highlight two energy barriers. The blue circles represent the images on the transition path found in the nudged elastic band calculations. The three energy minima along the transition path are schematically shown in e: “1” is the anti-parallel state, “3” is the parallel state and “2” is a metastable state with BPTO polar displacements perpendicular to PbTiO3 polarization in the xy plane.
Fig. 6 Multifunctions of the BPTO/PbTiO$_3$ heterostructure. a At high temperature, the energy barrier is easily surmounted by thermal fluctuations and the polar displacements of BPTO can be switched. From the left panel to the right panel, as an electric field switches the polarization of PbTiO$_3$, the BPTO thin film follows the change and switches its polar displacements via the interfacial coupling. b At low temperature, the energy barrier can not be overcome and the polar displacements of BPTO get “stuck”. However, an electric field can switch the polarization of PbTiO$_3$ and stabilize multiple states with different orientation of PbTiO$_3$ polarization relative to the polar displacements of BPTO. Each state has different tunnelling barriers. From the left panel to the right panel, it is “parallel”, “perpendicular”, and “anti-parallel” state. The red arrow refers to the polarization of PbTiO$_3$ thin film. The green arrows refer to the polar displacements of BiPbTi$_2$O$_6$ thin film.

Fig. 7 The comparison between anti-polar and polar phases of BPTO. a The unit cell structure of anti-polar phase Pmma of BPTO. b The two unit cells structure of polar phase Pmm2 of BPTO. The green arrows indicate the polar displacements of the Bi atoms.

Multifunctions of the BPTO/PTO heterostructure. In this section, we discuss potential functions of the BPTO/PTO heterostructure based on the calculated switching barrier in the previous section.

We first discuss room temperature applications. The switching barrier of BPTO is about 58 meV per slab. From transition state theory$^{49}$, at a given temperature $T$, an energy barrier $\Delta E$ with a magnitude of a few $k_B T$ can be easily surmounted (At room temperature, 1 $k_B T \approx 26$ meV). In transition state theory, the probability $P$ of overcoming the energy barrier is proportional to $e^{-\Delta E/k_B T}$, i.e., $P \propto e^{-\Delta E/k_B T}$. The energy barrier ($\Delta E = 58$ meV) is about twice the $k_B T$, hence the probability of overcoming this barrier is around 14%.[3] ($k_B$ is the Boltzmann constant). Room temperature $T = 300$ K is about 26 meV. Our energy barrier is about twice room temperature and therefore room temperature is sufficient to overcome the barrier. This implies that the interfacial coupling at the BPTO/PbTiO$_3$ interface enables an electric field to first switch PbTiO$_3$ polarization and subsequently drive BPTO to 180° change its polar displacements. This realizes an electrically switchable Bi-state in the new polar metal BPTO at room temperature. We note that the transition path chosen in the NEB calculation is only one possibility. The actual transition path could be different from the one in our study and the resulting energy barrier should be even lower, which will make the switching of BPTO polar displacements more feasible. Figure 6a schematically shows how we can use PbTiO$_3$ polarization to control the polar displacements of BPTO at room temperature.

The above switching mechanism is also applicable to multi-layer BPTO thin films. The mechanism is as follows. Our calculations find that bulk BPTO is more stable in the polar $Pmnm$ perovskite structure than the antipolar $Pnma$ perovskite structure by 65 meV f.u.$^{-1}$. The anti-polar $Pnma$ perovskite structure is shown in Fig. 7a. The polar $Pmmm$ perovskite structure is shown in Fig. 7b for comparison. Therefore, for multi-layer BPTO thin films, once the bottom layer of BPTO is 180° switched via the interfacial coupling, the remaining layers of BPTO will be driven by thermodynamics to change their polar displacements in a layer-by-layer manner to avoid an anti-polar state in the film. The above physical picture is computationally confirmed in Supplementary Fig. 9. However, for device applications (e.g. the model device illustrated in Supplementary Fig. 10), BPTO thin films of single-unit-cell thick are most desirable, in analogy to two-dimensional Van der Waals materials.$^9$

Next we discuss low temperature applications. At sufficiently low temperatures where the energy barrier is much larger than $k_B T$, the interfacial coupling can not drive polar metals to change their polar displacements when an electric field switches the polarization of ferroelectrics. However, this has interesting implications: as we use the electric field to change the direction of PbTiO$_3$ polarization, we can individually stabilize multiple configurations in which the BPTO polar displacements are “parallel”, “perpendicular” and “anti-parallel” to the PbTiO$_3$ polarization (shown in Fig. 6b). Each configuration has different tunnelling resistance across ferroelectric insulators, because BPTO polar displacements and PbTiO$_3$ polarization have different relative orientation. As we use an electric field to change the direction of ferroelectric polarization (polar displacements do not follow due to low temperatures), we can tune tunnelling barriers between different states and therefore the BPTO/PbTiO$_3$ heterostructure can be used in multi-state memory devices.

In conclusion, we demonstrate the power of first-principles high-throughput screening in designing new functional materials and in particular predict a new polar metal BPTO by utilizing the Bi/Pb lone-pair electrons. The three lowest-energy structures of BPTO are all polar and metallic (post-perovskite $Pmmm$, perovskite $Pmmm2$ and perovskite $Pnmm$), which can be transformed among each other via pressure or strain. In the perovskite structures, Bi$^{3+}$ and Pb$^{2+}$ enforce a fractional valence 3.5+ on Ti, which leads to conduction. In the post-perovskite structure, strong hybridization between Pb/Bi 6p and O 2p states induces a finite density of states at the Fermi level. In a BPTO/ PbTiO$_3$ heterostructures, at room temperature the interfacial coupling can overcome the switching barrier, which enables an electric field to first switch PbTiO$_3$ polarization and subsequently drive BPTO to 180° flip its polar displacements. This realizes an electrically switchable Bi-state in the new polar metal BPTO. The switching method is applicable to other layered polar metals.$^3$ At low temperature, an electric field can control the direction of perovskite structure.
PbTiO₃ polarization and stabilize multi states in which PbTiO₃ polarization and BPTO polar displacements have different relative orientations, implying different tunnelling resistance. This property can be used in tunable multi-state memory devices. We hope this work will stimulate experimentalists to synthesize the new polar metal in both bulk and thin-film forms.

Methods

**First-principles calculations.** For bulk structures, density functional theory (DFT) calculations are performed using a plane wave basis set and projector-augmented wave method⁵³, as implemented in the Vienna Ab-initio Simulation Package (VASP)³⁴,³⁵. PBEsol, a revised Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation for improving equilibrium properties of densely-packed solids⁵⁶, is used as the exchange correlation functional and has been applied successfully to interpreting the experimental observations of polar metal LiNO₃ in our previous work²⁴. The Brillouin zone integration is performed with a Gaussian smearing of 0.05 eV over a Γ-centered k-mesh up to 12 × 12 × 12 and a 600 eV plane-wave cutoff. The threshold of energy convergence is 10⁻⁶ eV. Hubbard U corrections are also considered in our calculations to model the effects of strong correlation on electronic and magnetic properties. The rotationally invariant approach of Hubbard U proposed by Dudarev et al.⁵⁷ is used in our DFT+U calculations. Spin-orbit coupling (SOC) is also considered to study electronic structure in our DFT+U+SOC calculations⁵⁸.

For the calculations of BPTO/PbTiO₃ structures, a Γ-centered k-mesh of 10 × 10 × 1 is used. The periodic slabs are separated by vacuum of 20 Å thick to diminish the interaction between them. Since asymmetrical interface modelling is used in our calculations, we employ dipole correction to eliminate the artificial electric field in the vacuum⁹⁰,⁹¹. In all the interface calculations, the in-plane lattice constant is fixed to be 4 Å and the bottom layer of PbTiO₃ is fixed to simulate the bulk-like interior that is under tensile strain. All the other atoms are fully relaxed along the three axes. We consider two possible terminations of the heterostructure, i.e., BaO- and BiO-terminated. The former one is less stable than the latter one by ~220 meV per slab. Hence, we only report the BiO-terminated BPTO/PbTiO₃ interface in our study.

The energy barriers between the parallel and anti-parallel states, as well as the saddle points along the transition path are found by the nudged elastic band (NEB) calculations through the climbing image NEB method⁴⁸. In NEB calculations, a set of intermediate states (i.e., images) between the initial state (anti-parallel state) and the final state (parallel state) are generated. They are iteratively adjusted so as to minimize the increase in energy along the transition path.

The electron localization function in our study, which is used to visualize lone–pair electrons in the real space is defined as⁶¹:

\[
ELF = \left( 1 + \frac{D}{D_o} \right)^{-1} \tag{2}
\]

where

\[
D = \frac{1}{2} \sum_i \left| \phi_i^2 - \frac{1}{8} \frac{\left| \nabla \phi_i \right|^2}{\rho} \right| \tag{3}
\]

and

\[
D_o = \frac{3}{10} \left( 3\pi^2 \right)^{2/3} \rho^2 \tag{4}
\]

Here ρ is the electron density and φ are the Kohn–Sham wave functions.

**Crystal structure search.** The crystal structure search for bulk BPTO is carried out using the particle swarm optimization algorithm implemented in CALYPSO code¹¹,¹², with the assistance of CrysPyr¹⁷. More than 1000 structures (50% 10-atom Bi₅Pb₃Ti₄O₁₄ and 50% 20-atom Bi₃Pb₂Ti₃O₁₄) are created in 20 generations. The structural optimization and computation of total energy are performed using VASP. In the first step of high-throughput screening of these 1000 crystal structure, we used non-spin polarized calculations with the exchange-correlation functional of PBEsol. The cutoff energy of 450 eV and the k-mesh grid density is about 2000 per atom. In the second step, the lowest 50 structures are re-calculated by the spin-polarized calculations in which the cutoff energy is increased to 600 eV and the k-mesh grid density is >2500 per atom. We consider ferromagnetic ordering and different types of antiferromagnetic orderings such as A-type, C-type and G-type⁶² to examine possible magnetic properties. The global structure search is performed under 0 GPa. The five lowest energy structures after screening are also studied under pressure. The space groups of the predicted crystal structures are examined by the FINDSYM code⁶³.

**Visualization.** We use software VESTA to show crystal structures and real-space electron localized functions⁶⁴.

Data availability

The authors declare that all the data supporting the findings of this study are available within the paper and its Supplementary Information.

Code availability

The high-throughput crystal structural predictions were carried out using the proprietary code VASP⁵⁴,⁵⁵, with the combination of CALYPSO¹¹,¹² and CrySPY¹⁷. CALYPSO (http://www.calyposo.com/) is freely distributed on academic use under the license of Copyright Protection Center of China (registration No. 2010SP0828020 and classification No. 61000-7500). CrySPY (https://github.com/Tomoki-YAMASHITA/CrySPY) is released under the Massachusetts Institute of Technology (MIT) License and is open source. The electronic structure calculations were all performed using VASP. The thermal properties are calculated by Phonopy⁶⁶. Phonopy (https://github.com/attogpo/phonopy) is released under the BSD-3-Clause License and is open source. The software VESTA⁶⁴ is distributed free of charge for academic users under the VESTA License (http://jp-minerals.org/vesta/sp/download.html).

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**References**

1. Shi, Y. et al. A ferroelectric-like structural transition in a metal. Nat. Mater. 12, 1024–1027 (2013).
2. Zhang, X. I. Origin of polar distortion in LiNO₃-type “ferroelectric” metals: Role of A-site instability and short-range interactions. Phys. Rev. B 90, 094108 (2014).
3. Puggioni, D. & Rondinelli, J. M. Designing a robustly metallic noncentrosymmetric ruthenate oxide with large thermopower anisotropy. Nat. Commun. 5, 3432 (2014).
4. Filippetti, A., Fiorentini, V., Ricci, F., Delugas, P. & Figueiro, J. Prediction of a native ferroelectric metal. Nat. Commun. 7, 11211 (2016).
5. Kim, T. et al. Polar metals by geometric design. Nature 533, 68 (2016).
6. Benedek, N. A. & Birol, T. ‘Ferroelectric’ metals reexamined: fundamental mechanisms and design considerations for new materials. J. Mater. Chem. C 4, 4000–4015 (2016).
7. Luo, W., Xu, K. & Xiang, H. Two-dimensional hyperferroelectric metals: A different route to ferromagnetic-ferroelectric multiferroics. Phys. Rev. B 96, 235415 (2017).
8. Mochizuki, Y., Kumagai, Y., Akamatsu, H. & Oba, F. Polar metal behavior of strained antiperovskites AaNi₄ (A = Mg, Zn, and Cd) from first principles. Phys. Rev. Materials 2, 125004 (2018).
9. Fei, Z. et al. Ferroelectric switching of a two-dimensional metal. Nature 560, 336 (2018).
10. Fang, Y.-W. et al. First-principles studies of multiferroic and magnetoelectric materials. Sci. Bull. 60, 156–181 (2015).
11. Wang, Y., Lv, J., Zhu, L. & Ma, Y. Calypso: a method for crystal structure prediction. Comput. Phys. Commun. 183, 2063–2070 (2012).
12. Glass, C. W., Oganov, A. R. & Hansen, N. USPEX-Evolutionary crystal structure prediction. Comput. Phys. Commun. 175, 713–720 (2006).
13. Wei, Y. et al. A rhombohedral ferroelectric phase in epitaxially strained Hf₀₅₂ Zr₀₅₀ Öz thin films. Nat. Mater. 17, 1095–1100 (2018).
14. He, J., Xia, Y., Naghavi, S. S., Orozini, V. & Wolverton, C. Designing chemical analogs to PbTe with intrinsic high band degeneracy and low lattice thermal conductivity. Nat. Commun. 10, 719 (2019).
15. Zhao, Z. et al. Predicted pressure-induced superconducting transition in electrode LiP. Phys. Rev. Lett. 122, 097002 (2019).
16. Wang, Y., Lv, J., Zhu, L. & Ma, Y. Crystal structure prediction via particle-swarm optimization. Phys. Rev. B 82, 094116 (2010).
17. Yamashita, T. et al. Crystal structure prediction accelerated by bayesian optimization. Phys. Rev. Mater. 2, 013803 (2018).
18. Murakami, M., Hirose, K., Kawamura, K., Sata, N. & Ohiishi, Y. Post-perovskite phase transition in MgSiO₃. Science 304, 855–858 (2004).
19. Ohta, K. et al. The electrical conductivity of post-perovskite in earth’s D° layer. Science 320, 89–91 (2008).
20. Biswas, A., Yang, C.-H., Ramesh, R. & Jeong, Y. H. Atomically flat single terminated oxide substrate surfaces. Prog. Surf. Sci. 92, 117–141 (2017).
21. Zhang, Z. et al. High-pressure bulk synthesis of crystalline Cs₂H₂AsCl₁. a novel Cs₂H₂AsCl₁ graphitic derivative. J. Am. Chem. Soc. 123, 7788–7796 (2001).
22. Klein, R. A. et al. High-pressure synthesis of the BiVO₄ perovskite. Phys. Rev. Mater. 3, 064411 (2019).
23. Korotcenkov, G. Metal Oxide-based Thin Film Structures: Formation, Characterization and Application of Interface-based Phenomena, (Elsevier, 2017).
