

FERROELECTRICITY

Perovskite ferroelectrics go metal free

Metal-free perovskites exhibit ferroelectric properties rivaling those of BaTiO₃

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Ferroelectric materials, which have spontaneous electric polarization that can be switched with an external electric field, have applications as capacitors, sensors, and data-storage devices (1). Since the discovery of high-performance BaTiO₃ and LiNbO₃, ferroelectric perovskite oxides have dominated industrial applications (2). However, these ceramics are expensive to produce as high-quality thin films, and they often contain heavy metals such as Pb²⁺, which raises health and environmental concerns. Replacing heavy metals with organic components in the perovskite lattice was

Many hybrid organic–inorganic perovskites have been synthesized by replacing the single atomic X site with bitopic organic linkers such as formate and dicynamide groups (8).

Can this strategy extend to the B site? The perovskite framework is constructed via coordination bonding in oxides and hybrid systems. Formation of coordination bonds requires that a ligand donate lone-pair electrons to the orbitals of transition metals. Likewise, for forming hydrogen (H) bonds, electronegative atoms with lone-pair electrons are needed as acceptors. In this sense, these two different bonding interactions exhibit some geometrical similarity. As the B site requires spherical symmetry to bond

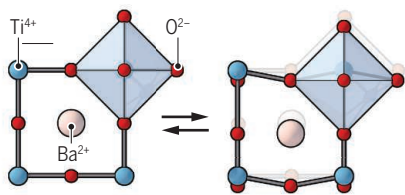
should enable wide potential applications in environments where conventional oxide materials dominate. In addition, their multiple polarization directions enable facile rotation through electrical-field manipulation, which should make the poling process easier (10).

The substantial organic content of the metal-free perovskites makes these compounds soft, so they respond to stress differently compared with oxides and hybrid perovskites, in which stronger ionic and coordination bonding forces exist. This facilitates facile growth of high-quality thin films that are critical for managing electric dipoles through strain engineering. These new metal-free perovskite ferroelectrics are simple to synthesize, low cost, and lightweight.

The marriage between symmetry and H bonding in these metal-free compounds extends the fields of perovskites and ferroelectrics to a new realm. However, some exciting aspects need further exploration. Bonding interactions between NH₄⁺ and halides extend beyond H bonding, and their electronic nature needs to be further unveiled. Some of the transitions in these metal-free perovskites are strongly first-order and ferroelastic, which leads to substantial shear strains and distinctive twin-wall dynamics (11). Ferroelastic twin walls show exotic physical properties beyond the bulk material (12), so knowledge of the twin-wall nature in these metal-free perovskites would enrich their potential for high-density memory devices (13). Finally, the existence of chirality in these molecular perovskites complicates the alignment of electric dipoles in their crystal lattices, so understanding its coupling with ferroelectric ordering could lead to unexpected properties at the bulk and nanoscale levels (14). ■

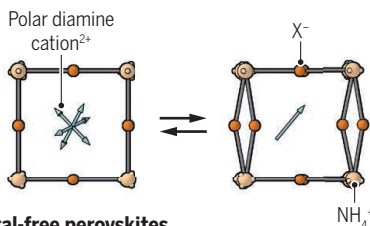
Ferroelectric origins in perovskites

Ferroelectricity in perovskites is induced by discrete structural changes that occur at phase transitions.



Perovskite oxides

Ferroelectricity primarily arises from the displacement of the Ti⁴⁺ ion from the center of the TiO₆ octahedron in BaTiO₃.



Metal-free perovskites

Ferroelectricity in the materials of Ye *et al.* primarily stems from the order-disorder of the polar diamine cation.

considered an alternative (3), but hybrid organic–inorganic perovskites have not shown comparable ferroelectricity and stability (4). On page 151 of this issue, Ye *et al.* (5) report metal-free perovskites that can compete with ferroelectric oxides (see the figure).

Perovskites have a general formula ABX₃, where A and B are large and small metal cations, respectively, and X is a bitopic anion (for example, O²⁻) that coordinates to B. The structural topology can be maintained if the A- and X-site ions are replaced with organic molecules within certain size ranges (6). The obvious starting point would be substituting the large A-site metal cation, and the successful structural characterizations of MAPbX₃ (where MA is methylammonium, and X is Cl, Br, or I) opened up such possibilities (7).

with six neighboring X sites for forming an octahedron, replacing it with a molecular cation that requires an octahedral H-bonding mode to bind with appropriate X-site acceptors could result in metal-free perovskite compounds. Indeed, the first metal-free perovskite, (piperazinium)(NH₄Cl₃)·H₂O, was synthesized by assembling the NH₄⁺ with chlorides through H-bond interactions (9).

Guided by these molecular design principles, Ye *et al.* have designed a new class of ferroelectric metal-free perovskites. The inclusion of noncentrosymmetric or chiral organic amine cations imposed the polar symmetry that rendered the desired ferroelectric ordering in the perovskite lattice. The prototypical compound MDABCO-NH₄I₃ (MDABCO, *bis-N*-methyl-*N'*-diazabicyclo[2.2.2]octanone) exhibits a high Curie temperature (*T*_c of 448 K) and substantial spontaneous polarization (*P*_s of 22 μC/cm²), which compare well with the properties of commercial BaTiO₃. Such notable *T*_c and *P*_s values of MDABCO-NH₄I₃

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ACKNOWLEDGMENTS

We acknowledge funding from the National Natural Science Foundation of China (no. 21571072).

10.1126/science.aat5729

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Science **361** (6398), 132.

DOI: 10.1126/science.aat5729

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