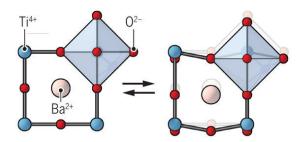


A way to make cleaner metal-free perovskites at low cost

July 13 2018, by Bob Yirka

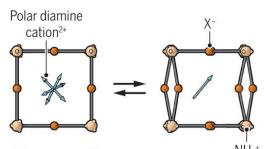
Ferroelectric origins in perovskites

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



Perovskite oxides

Ferroelectricity primarily arises from the displacement of the Ti^{4+} ion from the center of the TiO_6 octahedron in Ba TiO_3 .



Metal-free perovskites

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

Ferroelectricity in perovskites is induced by discrete structural changes that occur at phase transitions. Credit: (c) C. Bickel/ *Science* (2018). DOI: 10.1126/science.aas9330

A team of researchers at Southeast University in China has found a way to make metal-free perovskites in a useable form. In their paper published in the journal *Science*, the group describes their technique and how well it worked. Wei Li and Li-Jun Ji with Nankai University and Huazhong University respectively, offer a Perspective piece on the materials made by the team and explain why it is important, in the same



journal issue.

Ferroelectrics are materials that behave in a useful way—they become polarized when exposed to an electric current and remain in that state even after the electricity is removed. They are important, Li and Ji note, because they can be used as memory devices in electronic gadgets. Currently, most of the useful ones are inorganic perovskites (crystals that have the same structure as calcium titanium oxide). Unfortunately, manufacturing them has proven to be expensive—and because the process involves the use of heavy metals, they are also environmentally toxic. For that reason, scientists have been looking for ways to make perovskites without involving metals, i.e. organic perovskites. In this new effort, the researchers have developed a method to create 23 organic perovskites—one of which appears to be a good candidate to replace one of the most popular inorganic perovskites in use today: barium titanate (BTO).

The researchers report that developing the new technique involved reacting a host of organic reagents with inorganic ammonium compounds and halogen acids. In so doing, they discovered that they were able to make organic perovskites that behaved in similar ways to inorganic perovskites. But perhaps most importantly, they found one, which they have named MDABCO, that has properties very similar to BTO, suggesting it might serve as a viable replacement. Li and Ji note that the organic perovskites are also soft, which means they respond differently to stress than traditional perovskites—a feature that should allow them to be grown in ways that BTO cannot, such as in thin films. This opens the door to new types of products and perhaps improvements in memory used in consumer devices. Additionally, the process also lends itself to lower manufacturing costs since they are so easy to synthesize, and are lighter than conventional ferroelectrics.

More information: H.-Y. Ye el al., "Metal-free three-dimensional



perovskite ferroelectrics," *Science* (2018). science.sciencemag.org/cgi/doi ... 1126/science.aas9330

Abstract

Inorganic perovskite ferroelectrics are widely used in nonvolatile memory elements, capacitors, and sensors because of their excellent ferroelectric and other properties. Organic ferroelectrics are desirable for their mechanical flexibility, low weight, environmentally friendly processing, and low processing temperatures. Although almost a century has passed since the first ferroelectric, Rochelle salt, was discovered, examples of highly desirable organic perovskite ferroelectrics are lacking. We found a family of metal-free organic perovskite ferroelectrics with the characteristic three-dimensional structure, among which MDABCO (N-methyl-

N'-diazabicyclo[2.2.2]octonium)—ammonium triiodide has a spontaneous polarization of 22 microcoulombs per square centimeter [close to that of barium titanate (BTO)], a high phase transition temperature of 448 kelvins (above that of BTO), and eight possible polarization directions. These attributes make it attractive for use in flexible devices, soft robotics, biomedical devices, and other applications.

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