Hybrid Semiconductors Perform Under Pressure

Materials with cage-like octahedral structures (perovskites) have highly tunable electronic properties. The crystal structure depicted on the left is a hybrid (organic–inorganic) perovskite-like analog. The inorganic component—pairs of edge-sharing tin iodide octahedra—form a framework able to fit a relatively large organic molecule—N,N’-dimethylpyrazinium (dmpz)—in its interstitial cavities. Compressing the material raises the level of the framework’s valence band (bucket analogy, right) to lie closer to the dmpz empty orbitals, which can then accept electrons from the framework.

**Halide perovskite solutions**

Tunable semiconductor materials containing organic compounds can be synthesized from solution using scalable, inexpensive methods. The resulting hybrid (organic–inorganic) compounds belong to a class of materials known as perovskites, named after the mineral in which their distinctive octahedral structures were first identified. The structures are stable, yet flexible enough to allow for variations to produce desired material properties.

In halide perovskites, metal ions (e.g., lead or tin) are enclosed in octahedral cages defined by halide ions (e.g., bromide or iodide). Such materials offer useful optoelectronic properties, including tunable band gaps and strong optical absorption. Accordingly, they are of great interest for use in applications such as light-emitting diodes (LEDs), lasers, and solar cells. In the latter case, lead iodide in particular has shown remarkable improvements in photovoltaic efficiency.

However, there are still fundamental challenges in need of solutions. For example, a greater understanding of how to control electronic transport properties in these materials via doping is needed to improve their performance as semiconductors and open up new possibilities.

**Elbow room for doping**

As with other semiconductors, doping in halide perovskites has mainly relied on the introduction of defects and impurities. However, these strategies are hindered by the formation of compensating defects in these self-assembling materials. To avoid this, a team led by researchers from Stanford University sought to incorporate redox-active (electron-accepting or -donating) molecules into the organic component of the perovskite.

Previously, the group had successfully synthesized a series of expanded halide perovskites, with cavities large enough to accommodate organic molecules with six-membered aromatic rings. In this work, the researchers synthesized an expanded perovskite analog using tin iodide for the inorganic framework and N,N’-dimethylpyrazinium (dmpz) as organic electron donor.
acceptors. The band gap of this material is set by the energy difference between the empty low-lying orbitals of the dmpz and the filled orbitals of the tin iodide framework. However, the lowest levels of the dmpz were too high in energy to accept electrons from the valence-band maximum of the tin iodide. The researchers hypothesized that squeezing the material would affect the energy levels of the dmpz and tin iodide framework differently, decreasing the gap and allowing charge transfer.

Please squeeze the charges

The material’s pressure-induced structural changes were tracked using powder x-ray diffraction (up to 60 GPa) at ALS Beamline 12.2.2. Optical and transport properties were also characterized at both ambient and high pressures. The ALS measurements revealed that the material is highly compressible, nicely explaining its response to increasing pressure: the band gap nearly closed, and conductivity increased by five orders of magnitude—considerably exceeding the values achieved by related perovskites at similar pressures.

Contact: Hemamala Karunadasa (hemamala@stanford.edu)


Researchers: R. Matheu and N.R. Wolf (Stanford University); F. Ke, A. Breidenbach, Y. Lee, and H.I. Karunadasa (SLAC National Accelerator Laboratory and Stanford University); Z. Liu (University of Illinois at Chicago); L. Leppert (University of Twente, The Netherlands); and Y. Lin (SLAC National Accelerator Laboratory).

Funding: U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) program; DOE National Nuclear Security Administration; National Science Foundation; and Stanford University. Operation of the ALS is supported by DOE BES.