

PEROVSKITES

Peering into pressured perovskites

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Organic lead halide perovskites are exciting organic–inorganic hybrid materials because they are amenable to solar cell and laser applications. Although their structural diversity offers numerous handles with which to tune their properties, this flexibility brings with it issues of instability to ambient environments. Now, a team led by Qihua Xiong show that 2D perovskites are not only tunable synthetically but also by subjecting them to mild pressures. Writing in *Science Advances*, the team find that the 2D perovskite $(\text{PEA})_2\text{PbI}_4$ (where PEA^+ is $\text{Ph}(\text{CH}_2)_2\text{NH}_3^+$) exhibits reversible structural and optical changes through a process that is likely generalizable to a broad range of systems.

While ambient conditions rarely stray far from pressures of 100 kPa,

the pressures in a diamond anvil cell can be on the order of hundreds of gigapascals — conditions under which many ionic compounds can undergo perturbation. Diamonds are transparent to X-rays but absorb some IR light, allowing us to study changes in both electronic and atomic structure as a function of compression. Although previous studies suggested that 3D perovskites exhibit limited electronic tunability before undergoing complex phase changes, Xiong’s team speculated that “2D hybrid perovskites may be more responsive in view of their structural anisotropy.” Indeed, 3D perovskites distribute their electronically active $\{\text{PbI}_6\}$ centres in all dimensions, while 2D perovskites confine these octahedra within planes, thereby affording ‘quantum wells’ separated by organic layers.

When Xiong and his colleagues compressed the 2D perovskite $(\text{PEA})_2\text{PbI}_4$ at 3.5 GPa, they observed a reversible red-shift of the emission spectra, which they ascribed to a decrease in the electronic bandgap. Importantly, this did not come at the expense of quantum yields, which remained near unity. For context, the emission from most semiconductors is blue-shifted upon compression, while photoluminescence from 3D perovskites is typically quenched at pressures above 1.5 GPa. The unusual physical change observed by Xiong and colleagues was studied by in situ synchrotron X-ray diffraction, with increasing pressures causing the intralayer separation to shrink by $\sim 2 \text{ \AA}$ — a large change relative to the lateral deformations (0.39 \AA and 0.47 \AA)

and an effect that accounts for most of the changes in unit cell parameters. This anisotropic shrinkage likely reflects the ‘softer’ organic units at the periphery. First-principles calculations show that the intralayer compression of the organics weakens the quantum confinement effect in the 2D perovskite and lowers its bandgap at higher pressures. Furthermore, the anisotropic deformations result in minimal distortions of the $\{\text{PbI}_6\}$ octahedra, while those in 3D perovskites undergo continuous distortion. Indeed, it appears that the organic cations behave as an elastic buffer for the electronically sensitive inorganic units.

Unlike their 3D counterparts, which show minimal (80 meV) bandgap changes with pressure, the bandgaps of 2D perovskites decrease a lot (320 meV), and this effect should have substantial consequences on their device utilization. However, there still remain fundamental questions. Xiong and colleagues admit “the change of the dielectric confinement and its impact on the excitons need further study.” Although smaller bandgaps enable a wider wavelength of photons to be collected by a photovoltaic, it remains unclear how pressure will impact performance. However, such mild pressures are achievable by proper device engineering, affording another handle to tune material properties.

Adam Weingarten, Associate Editor,
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