

# Pressure-driven tuning of bandgap in methylammonium lead iodide

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Hybrid organic-inorganic perovskites of the composition of  $AMX_3$ , where A stands for an organic cation, M is a metal and X is a halide, are promising materials for a wide range of applications, including solar cells, light-emitting devices, photodetectors, and lasers due to low costs and simplicity of preparation, strong light absorption and long diffusion lengths facilitated by long carrier lifetimes and low nonradiative recombination rates.

Hydrostatic pressure can alter bond lengths and valence angles without changing chemical composition, tuning the electronic landscape responsible for basic properties of photovoltaic materials, like the energy bandgap. Moreover, combined with the density functional theory (DFT), it helps recognize structural factors affecting electronic band structure with atomic-level understanding.

In the following, the pressure-generated optical and structural changes of the low-temperature orthorhombic phase (OP) of methylammonium lead iodide were studied experimentally by photoluminescence (PL) and theoretically within DFT. The abnormal bandgap evolution of the OP under pressure with redshift-blueshift-redshift trend observed in both experiment (Figure 1) and theoretical predictions is explained by the competition between Pb-I bond shrinkage and  $PbI_6$  octahedral tilting. Bandgap pressure coefficient within the OP determined from the redshift range of the PL energy is found to be negative and dependent on the temperature ( $\alpha_{40K} = -36.3 \pm 0.1$  meV/GPa,  $\alpha_{80K} = -29.8 \pm 0.1$  meV/GPa,  $\alpha_{120K} = -13.3 \pm 0.1$  meV/GPa). Negative deformation potential results from antibonding character of the bottom of the conduction band and the top of the valence band while dependence on the temperature is related to changes in Pb-I bond length as the atomic configuration approaches temperature-induced phase transition as well as increased transverse acoustic phonon contribution to octahedral tilting at higher temperatures.

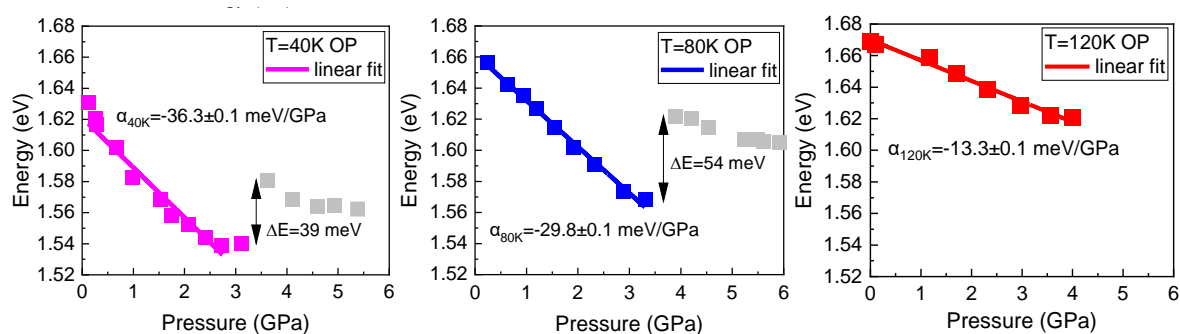


Figure 1. Pressure response of the PL peak positions at (left) 40 K, (middle) 80 K, and (right) 120 K.