Tuning the Properties in Perovskite Materials for Photovoltaics

Metal halide perovskites are a promising class of materials for high-efficiency solar cells with the potential for low-cost manufacturing via solution processing. In addition, these materials are leading candidates for tandem solar cells because their band gaps can be tuned over a broad range. Band gap tuning is accomplished by altering the chemical formula ABX_3 via compositional substitution in the A-, B-, and/or X-site. While X-site substitution has been the subject of intense study[1,2], the mechanisms of band gap tuning via substitution of the A- and B-sites are not well-understood.

An international research team from Stanford, SSRL, and Hasselt University in Belgium has identified two competing mechanisms through which the A-site cation influences the band gap of metal halide perovskites (Figure 1). In a new study published in the *Journal of the American Chemical Society,* the authors substitute the smaller cesium (Cs) for the larger formamidinium (FA = $HC(NH_2)_2$) in two different perovskite materials and observe opposite effects on the band gap. In formamidinium tin iodide ($FA_{1-x}Cs_xSnI_3$), introduction of Cs in the A-site is seen to decrease the band gap; whereas in formamidinium lead iodide ($FA_{1-x}Cs_xPbI_3$), introduction of Cs is observed to increase the band gap (Figure 2).

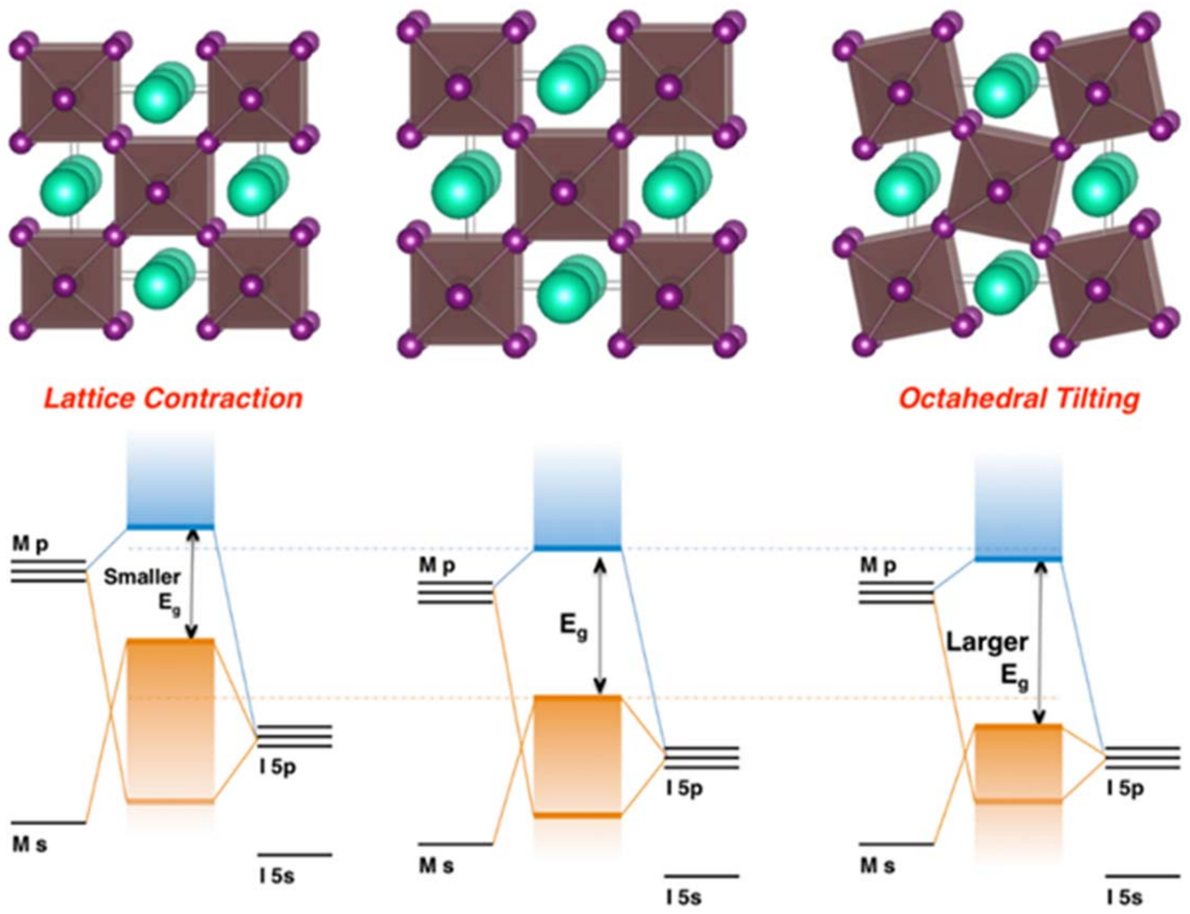

Figure 1. Perovskite lattice diagrams: undistorted cubic (center panel), with lattice contraction (left panel) and with octahedral tilting (right panel). Below each lattice diagram is a schematic energy level diagram, showing how each kind of distortion affects the valence band and band gap.

The authors performed grazing incidence x-ray diffraction (GIXD) measurements at SSRL Beam Line 11-3, revealing that the perovskite crystal structure responds differently to Cs-substitution in these two materials. Upon Cs-substitution, the tin iodide perovskite maintains its cubic crystal structure and the only observed change is isotropic contraction of the lattice. However, in the lead iodide perovskite, additional x-ray diffraction peaks are observed upon Cs-substitution, indicating that the structure experiences tilting of the BX_6 octahedra in addition to lattice contraction.

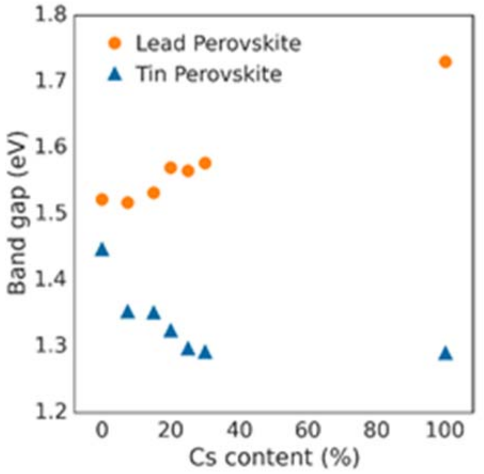

Figure 2. Optical band gap of lead- and tin-based perovskites $FA_{1-x}Cs_x B I_3$ (B = Sn, Pb) as a function of cesium content.

Electronic structure calculations have shown that the valence band maximum (VBM) of these materials is an antibonding hybrid state of the metal s and halide p orbitals, and thus is sensitive to B-X orbital overlap[3]. This explains the different band gap response observed in the tin iodide vs. lead iodide perovskites. In the former, lattice contraction increases orbital overlap, stabilizing the antibonding VBM and decreasing the band gap. In the latter, octahedral tilt decreases orbital overlap, destabilizing the antibonding VBM and causing the band gap to increase (Figure 1). Band energies were directly measured with ultraviolet and x-ray photoelectron spectroscopy (XPS) and the results support this model. The competing effects of octahedral tilt and lattice contraction described in this study provide a new strategy to systematically tune the band gaps of metal halide perovskites.

References

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