Invited Lecture

Linking structure and properties in energy materials: intercalation in hybrid perovskites

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Climate change is one of the most pressing problems of the 21st century and in order to reduce our reliance on fossil fuels, new materials for energy conversion and energy storage are required. One family of materials receiving significant interest in this area are hybrid perovskites, also known as organic-inorganic metal halides, which can be used in photovoltaic devices. The archetypal hybrid perovskite is $CH_3NH_3PbI_3$ and the key difference with conventional perovskites is the fact that the A site cation is an organic ammonium cation rather than an inorganic cation. Since first being used in a solar cell in 2009, the power conversion efficiencies (PCE) of $CH_3NH_3PbI_3$ based photovoltaics have increased from 3.8% to 26.1%, whilst tandem solar cells made from silicon and $CH_3NH_3PbI_3$ have achieved a PCE of 33.9 % [1,2]. These materials have a huge degree of compositional flexibility and as a result, they are highly tuneable, as the band gap of these materials can be adjusted by doping on the cation or anion sites of the perovskite. The most common way of tuning the band gap is by halide substitution, whereby a halide anion can be replaced by a different halide. However, work in our group has recently looked at a new method of tuning the band gap, namely halogen molecule intercalation.

Here we show that we can reversibly intercalate Br_2 between the $[PbBr_4]_\infty$ layers in the two dimensional layered perovskite $[H_3N(CH_2)_6NH_3]PbBr_4$ to give $[H_3N(CH_2)_6NH_3]PbBr_4{\cdot}Br_2$ [3]. An in-depth study of the crystal structure shows that upon intercalation, there is an expansion of the *a*-axis of the unit cell, the conformation of the organic cation changes to an all-trans configuration and the interlayer shift between the $[PbBr_4]_\infty$ layers is significantly reduced, changing the structure from a Ruddlesden-Popper-like phase to a Dion-Jacobson-like phase. Together, this results in a decrease in band-gap of 0.85 eV, which is particularly significant as the parent perovskite, $[H_3N(CH_2)_6NH_3]PbBr_4$, only contains a single layer of lead bromide octahedra. Our work is backed up by theoretical studies, which shows that Br_2 intercalation results in a new band in the electronic structure and a decrease in effective masses by around two orders of magnitude. The resistivity also decreases upon intercalation, indicating that $[H_3N(CH_2)_6NH_3]PbBr_4{\cdot}Br_2$ has an increased charge carrier mobility/ carrier concentration when compared to $[H_3N(CH_2)_6NH_3]PbBr_4$. Further examination of the crystal structure and electron density difference maps show that halogen bonding is a key factor for this change in properties. As a result, the halogen bond is another non-covalent interaction which can be exploited in the design of new hybrid perovskites for optoelectronic applications.

[1] Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. (2009). *J. Am. Chem. Soc.* **131**, 6050−6051.

[2] https://www.nrel.gov/pv/cell-efficiency.html (accessed May 6th 2024).

[3] Yang, L., Xuan, X., Webster, D., Krishnan Jagadamma, L., Li, T., Miller, D. N., Cordes, D. B., Slawin, A. M. Z., Turnbull, G. A., Samuel, I. D. W., Chen, H-Y T., Lightfoot P., Dyer, M. S., Payne, J. L. (2023) *Chem. Mater.* **35**, 3801-3814.