

IODIDE-ION TRANSPORT IN METHYLAMMONIUM LEAD IODIDE PEROVSKITE: SOME SURPRISING ASPECTS

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Methylammonium lead iodide, CH₃NH₃PbI₃ (= MAPbI₃), is a hybrid organic–inorganic perovskite that exhibits excellent photovoltaic properties. In comparison with traditional photovoltaic materials, such as Si or CIGS, MAPbI₃ is evidently characterised by one or more highly mobile constituent ions. In photovoltaic devices based on MAPbI₃, ion mobility is deemed to be responsible for current–voltage hysteresis, a huge low-frequency dielectric response, and long-term instability. Despite enormous interest in ion transport, debate surrounds almost every aspect. This is evident in the excessive scatter in activation enthalpies reported in the literature for ion conduction in MAPbI₃ (see Fig. 1).

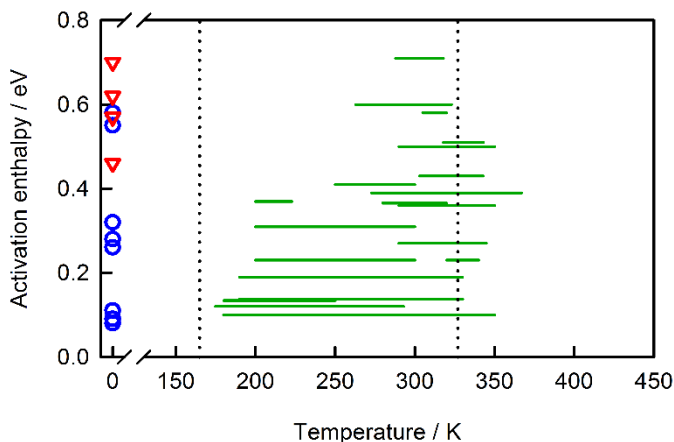


Figure 1 – Activation enthalpies reported in the literature for ion transport in MAPbI₃. Experimental data are shown as green lines, plotted against the temperature range over which the data was acquired. Computational data, referring to migration barriers obtained in static atomistic calculations, are plotted at zero K (red triangles, MA-vacancy migration; blue circles, iodine-vacancy migration). The vertical dotted lines indicate the phase-transition temperatures: orthorhombic–tetragonal and tetragonal–cubic

In a recent study [1], we demonstrated that a single model with one set of parameters could quantitatively explain diverse experimental data related to ion conduction in MAPbI₃. The model combines knowledge of the jump rate of iodine vacancies with the results of defect chemical modelling. A quantitative expression for the vacancy jump rate was obtained by studying iodine tracer diffusion as a function of temperature and iodine-vacancy concentration by means of classical molecular-dynamics (MD) simulations. The defect-chemical model yields acceptor concentrations in experimental samples of 10¹⁵ cm⁻³ and lower, and the enthalpy and entropy of anti-Frenkel disorder. We also demonstrated that the generation of additional iodine vacancies can explain quantitatively the increase in the ionic conductivity under illumination.

In this contribution, I will present our model [1] in detail. I will also draw attention to several surprising aspects regarding ion transport in MAPbI₃ [2,3]. These are (i) the activation enthalpy of iodine-vacancy migration is very low at $\Delta H_{\text{mig,v}} = 80$ meV; (ii) the diffusivity of iodine vacancies would appear to be surprisingly high as a result; (iii) the dominance of anti-Frenkel disorder in the close-packed (perovskite) structure; (iv) the diffusivity of iodine interstitials needs to be lower than that of vacancies; (v) the transport behaviour of point defects in electric fields. Finally I will also make comparisons with the behaviour of the point defects in the oxide perovskite SrTiO₃.

[1] D. Barboni and R. A. De Souza, *Energy Environ. Sci.* 11 (2018) 3266.

[2] R. A. De Souza and D. Barboni, *submitted*.

[3] D. Kemp, D. Barboni and R. A. De Souza, *in preparation*.