Hybrid Organic-Inorganic Halide Perovskites: Dimensionality vs. Applicability. A Theoretical Standpoint

Giacomo Giorgi
Perovskite, $\text{ABX}_3$ ($\text{CaTiO}_3$)

“A” & “B” ions are both cations with noticeable different radii. “X” is an anion site. Their stability is determined by the Goldschmidt tolerance factor “$t$” which in the case of X being an oxygen anion is given by

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}$$

Piezoelectricity, pyroelectricity, colossal magnetoresistivity, high-T superconductivity, & electrooptic effects and many others….
Although the oxide class represents the most abundant and investigated class of perovskites, halides, sulfides, nitrides, hydrides, oxyhalides, and oxynitrides are similarly known experimentally and have been characterized.

\[
\text{CH}_3\text{NH}_3\text{PbX}_3, \text{ ein Pb(II)-System mit kubischer Perowskitstruktur}
\]

\[
\text{CH}_3\text{NH}_3\text{PbX}_3, \text{ a Pb(II)-System with Cubic Perovskite Structure}
\]

Dieter Weber

Institut für Anorganische Chemie der Universität Stuttgart


Synthesis, X-ray

\[
\text{CH}_3\text{NH}_3\text{PbX}_3 \ (X = \text{Cl, Br, I}) \text{ has the cubic perovskite structure with the unit cell parameters } a = 5.68 \AA \ (X = \text{Cl}), \ a = 5.92 \AA \ (X = \text{Br}) \text{ and } a = 6.27 \AA \ (X = \text{I}). \text{ With exception of CH}_3\text{NH}_3\text{PbCl}_3 \text{ the compounds show intense colour, but there is no significant conductivity under normal conditions. The properties of the system are explained by a “p-resonance-bonding”. The synthesis is described.}
\]

Im System A\text{PbX}_3 \ (A = \text{einwertiges Kation}, X = \text{Cl, Br, I}) \text{ ist die Perowskitstruktur bislang nur bei Hochtemperaturmodifikationen des Typs CsPbX}_3 \ [1, 2] \text{ bekannt. Dagegen kristallisiert das Sn(II)-analoge CsSnBr}_3 \ [3–5] \text{ schon bei Normalbedingungen im kubischen Perowskitgitter. Vermutlich reicht die Größe des Cs+-Kations nicht aus, um in einer Pb(II)-Perowskitstruktur den ihm zur Verfügung stehenden Raum so auszufüllen, daß die Kristallfeldenergie bei Raumtemperatur das Pb(II) in die Oktaeedersymmetrie zwingt. Dementsprechend nimmt die Umwandlungstemperatur von die kubischen Kristalle der Zusammensetzung CH}_3\text{NH}_3\text{PbI}_3 \text{ schwarz sind. Die gemischthalogenierten Verbindungen lassen charakteristische Farbzwischenstufen erkennen. So verursacht die partielle Substitution von Bromid gegen Chlorid eine Farbaufhellung, wie die dunkelgelbe Farbe von CH}_3\text{NH}_3\text{PbBr}_2 \cdot \text{Cl}_0 \cdot \text{7 verdeutlicht. Wird dagegen Bromid durch Iodid ersetzt wie im Fall von CH}_3\text{NH}_3\text{PbBr}_2 \cdot \text{I}_0 \cdot \text{93, so macht sich dies in einer Farbvertiefung nach rotviolett bemerkbar. Das schwarze CH}_3\text{NH}_3\text{PbBr}_0 \cdot \text{45I}_2 \cdot \text{35 unterscheidet sich in der Farbe nicht mehr von CH}_3\text{NH}_3\text{PbI}_3.
\]
What are the organic-inorganic perovskites?

1) 2D crystal hybrid organic/inorganic: potential applications in optoelectronic due to the versatility of the organic part (Mitzi et al., Science 1995)

2) More recently, mixed organic-inorganic perovskite compounds as light harvester (Miyasaka et al., JACS 2009 PCE=3.8%)

NGC2017, Tomsk 20 Sept 2017
- Why are OIHPs so appealing for PV applications?
- How to use them in PV?
- Any possible improvement in their performances?
Perovskite compounds as light harvester (Miyasaka et al., JACS 2009 PCE=3.8%)

- **Snaith et al.** (Science 2012)
  
  “**MSSC**” (Mesosuperstructured solar cells) initially based on ETA concept
  
  Perovskite absorber/mp-TiO₂(n-type)/spiro-OMeTAD (p-type)
  
  - CH₃NH₃PbI₂Cl
  - Insulating Al₂O₃ improves the PCE over mp-TiO₂ (PCE=10.9% @ AM1.5)

- **Grätzel et al.** (Nature Phot., 2013)
  
  (FTO)/TiO₂/perovskite/HTM/Au
  
  - CH₃NH₃PbI₃ has ambipolar character (n-type, p-type conductor)
  
  -HTM: P3HT, PCPDTBT, PCDTBT, PTAA
  
  -Using PTAA leads to PCE=12.0% (standard AM 1.5)

**Sept 2013, Science: Snaith et al.**

(thin film, low T)

- Vapor-deposited: \( J_{sc} = 21.5 \text{ mA cm}^{-2}, \ V_{oc} = 1.07 \text{ V}, \ ff = 0.68, \ PCE = 15.4\% \)

- Solution-processed: \( J_{sc} = 17.6 \text{ mA cm}^{-2}, \ V_{oc} = 0.84 \text{ V}, \ ff = 0.58, \ PCE = 8.6\% \)

**Perovskite solar efficiency: 22.1% (WR)**

2017 July

Ulsan National Institute of Science & Technology (UNIST).

→ **NANOSTRUCTURING PROCESS IS NOT MANDATORY**
Polymorphism of MAPbX$_3$

Table I. Temperature dependent structural data of CH$_3$NH$_3^+$ PbX$_3^-$ (X = Cl, Br, I).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature (K)</th>
<th>Crystal System</th>
<th>Space Group</th>
<th>Lattice (pm)</th>
<th>Volume ($10^6$ pm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CH$_3$NH$_3^+$ PbCl$_3^-$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>&gt; 178.8</td>
<td>cubic</td>
<td>$Pm3m$</td>
<td>$a$ = 567.5</td>
<td>182.8</td>
</tr>
<tr>
<td>$\beta$</td>
<td>172.9–178.8</td>
<td>tetragonal</td>
<td>$P4/mmm$</td>
<td>$a$ = 565.6</td>
<td>180.1</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>&lt;172.9</td>
<td>orthorhombic</td>
<td>$P2_2_1_2_1$</td>
<td>$a$ = 567.3</td>
<td>357.0</td>
</tr>
</tbody>
</table>

| **CH$_3$NH$_3^+$ PbBr$_3^-$** | | | | | |
| $\alpha$ | > 236.9 | cubic | $Pm3m$ | $a$ = 590.1(1) | 206.3 (260 K) |
| $\beta$ | 155.1–236.9 | tetragonal | $I4/mcm$ | $a$ = 832.2(2) | 819.4 |
| $\gamma$ | 149.5–155.1 | tetragonal | $P4/mmm$ | $a$ = 589.4(2) | |
| $\delta$ | <144.5 | orthorhombic | $Pna2_1$ | $a$ = 797.9(1) | 811.1 |

| **CH$_3$NH$_3^+$ PbI$_3^-$** | | | | | |
| $\alpha$ | > 327.4 | cubic | $Pm3m$ | $a$ = 632.85(4) | 253.5 |
| $\beta$ | 162.2–327.4 | tetragonal | $I4/mcm$ | $a$ = 885.5(6) | 992.6 |
| $\gamma$ | <162.2 | orthorhombic | $Pna2_1$ | $a$ = 886.1(2) | 959.5 |

![Diagram of structure]
• **3D bulk analysis**
  • The role of the organic cation:
    • Ambipolar nature of the OIHPs.
    • Alternative, bulky, and less polarizable organic cation (FAPI/GAPI).
    • Aliovalent substitution of Pb metallic cation.
  • Slow hot-hole cooling in lead-iodide perovskite: carrier lifetime from electron–phonon interaction.
  • The effects of the organic–inorganic interactions on the thermal transport properties of MAPI.

• **0D clusters:**
  • Cluster applicability in photovoltaics, light-emitting, and lasing devices. Bulk cut.
  • Structural and electronic features of small hybrid organic–inorganic halide perovskite clusters
• 3D bulk analysis
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• **0D clusters:**
  • Cluster applicability in photovoltaics, light-emitting, and lasing devices. Bulk cut.
  • Structural and electronic features of small hybrid organic–inorganic halide perovskite clusters
- **Ambipolar nature of the OIHPs.**
  (the case of MAPbI$_3$, MAPI)

Bandstructure of the bare fully optimized [PbI$_3$] network (no MA)

- Ideal crystal shows a very sensitive change (*flattening*) of the VBM shape.
  
  **VBM**: 5p orbitals of I atoms.

  Now the Pb 6s ones (mixed with I 5p orbitals) are 0.25 eV below the new VBM.

- **No methylammonium (MA), no ambipolarity**

Macroscopic effects associated to cation removal:

1) Cubic symmetry recovered.

2) Expansion of the cell volume:

MAPbI$_3$ (DFT+SOC)
• Alternative, bulky, and less polarizable organic cation (FAPI/GAPI).

• **Pros:**
  - high compatibility with solution-based processing/good efficiencies (high absorption coefficient);
  - value for the bandgap approaching the optimal value for single-junction solar cells;
  - ambipolar nature of the carriers plus their very long diffusion lengths;
Cons:

Regardless the assembling architecture, a noticeable hysteresis in the J-V curves is always detected.  

**Hysteresis:** slow dynamic reorganization processes & depends on several parameters:
1) scan rate of the measurements  
2) the architecture of the cell  
3) the perovskite deposition rate.

No conclusive explanation of its origin provided so far. Several experimental findings ascribe it to:
1) ionic migration at an applied bias  
2) ferroelectricity (?)  
3) dielectric polarization in the perovskite layer.

Consistently, a *dipole-moment-reduced* cation such as formamidinium (FA) ion is reported to quantitatively reduce the hysteresis from PSCs.
The organic cation role

- Kieslich et al., Chem. Sci., 2014, 5, 4712

Perovskite “classic” tolerance factor (Goldschmidt) extended to OIHP based on classical concept of ionic tolerance factors: prediction of several yet undiscovered hybrid perovskite phases.

\[ \alpha = \frac{(r_A + r_X)}{\sqrt{2(r_B + r_X)}} \]

\[ r_{\text{Aeff}} = r_{\text{mass}} + r_{\text{ion}} \]

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The organic cation role

According to the symmetry of the cation $\rightarrow \mu_{GA} < \mu_{FA} << \mu_{MA}$

While both MAPbI$_3$ and FAPbI$_3$ (the latter characterized by trigonal $P_{3m1}$ sym) are well known and investigated species, very few is known, and mostly at experimental level, about 3D GAPbI$_3$
Top panel: lateral view (a) and top view (b) of the $2 \times 2 \times 2$ optimized supercell of FAPbI$_3$.

Bottom panel: lateral view (c) and top view (d) of the $2 \times 2 \times 2$ optimized supercell of GAPbI$_3$.


- VASP code
- Spin-polarized DFT (PBE) & its revised version for solids (PBESol)
Band structure of FAPbI$_3$, calculated at PBESol/PAW (left) & PBESol/PAW+SOC (right).

Band structure of GAPbI$_3$, calculated at PBESol/PAW (left) and PBESol/PAW+SOC (right).

• Along the A–Γ direction we calculate

\begin{align*}
- m_h^* / m_e^* &= 0.75 \quad \text{FAPbI}_3 \\
- m_h^* / m_e^* &= 1.07 \quad \text{GAPbI}_3
\end{align*}

• GAPbI$_3$ has a more marked ambipolar behavior than FAPbI$_3$, which, still from the comparison, seems to be preferable as hole transport material. (consistency with experimental results, Energy Environ. Sci. 2014, 7, 982.)

Chemical potential ($\mu$) for FAPbI$_3$ & GAPbI$_3$: PAW/PBESol calculated $E_{\text{TOT}}$/unit, we obtain

1) \[ \text{FAPbI}_3 + \frac{1}{3} \text{GAPbI}_3 \rightarrow \text{FA}_{2/3}\text{GA}_{1/3}\text{PbI}_3 + \frac{1}{3} \text{FAPbI}_3 \quad \Delta E_1 = 0.06 \text{ eV} \]

2) \[ \text{FA}_{2/3}\text{GA}_{1/3}\text{PbI}_3 + \frac{1}{3} \text{GAPbI}_3 \rightarrow \text{FA}_{1/3}\text{GA}_{2/3}\text{PbI}_3 + \frac{1}{3} \text{FAPbI}_3 \quad \Delta E_2 = -0.03 \text{ eV} \]

3) \[ \text{FA}_{1/3}\text{GA}_{2/3}\text{PbI}_3 + \frac{1}{3} \text{GAPbI}_3 \rightarrow \text{GAPbI}_3 + \frac{1}{3} \text{FAPbI}_3 \quad \Delta E_3 = -0.03 \text{ eV} \]

Processes 2-3 become exothermic revealing the stability of the intermediate mixed alloys.

NGC2017, Tomsk 20 Sept 2017
The inorganic cation role

- Filip & Giustino, J. Phys. Chem. C 2016, 120, 166

Screening process based on:

1) Thermodynamic factor (the stability of the compound) in a perovskite structure.

2) Electronic factor (band gap, $E_g$).

The process reduces the potential candidate from 248 to 25. 15 of 25 have not yet been proposed as semiconductors for optoelectronics.

$\text{Mg}_x\text{Pb}_{1-x}$ gap is tunable over a range of 0.8 eV.
Aliovalent alloys: Pb-free perovskites

• Sn-based organic-inorganic perovskites potential alternatives to the Pb-based.
  Lower PCEs absorption onset ~ 950 nm (optical gap, 1.3 eV), red shifted compared with the Pb-based. [F. Hao et al., Nature Photonics 2014, 8, 489.]


• Sn-based perovskites easily oxide (Sn$^{2+}$ $\rightarrow$ Sn$^{4+}$): strong p-type character & metallic behavior (doped semiconducting behavior).
• Pb replacement: alternative class of mixed organic-inorganic perovskites, i.e. $\text{MATl}_{0.5}\text{Bi}_{0.5}\text{I}_3$ ($\text{MTBI}$), where pairs of Pb(II) atoms are replaced by Tl(I)/Bi(III) aliwalent units.

$$2\ \text{Pb} (\text{II}) \rightarrow \text{Tl} (\text{I}) + \text{Bi} (\text{III})$$

• Tl similarly to Pb represents an environmental risk. Nevertheless $[\text{Tl}]=0.5*[\text{Pb}]$
Tolerance Factor calculation

- Calculation of the revised tolerance factor ($\alpha$) of hybrid frameworks for “pure” $\text{MATlI}_3$, $\text{MABiI}_3$, respectively comparing the calculated value with that obtained for $\text{MAPbI}_3$ employing the formula

$$\alpha = \frac{(r_{\text{Aeff}} + r_{\text{Xeff}})}{\sqrt{2(r_B + r_{\text{Xeff}})}}$$

(Kieslisch et al., Chem. Sci. 2014, 5, 4712)

- $I^-$ and MA 220 and 217 pm, Shannon ionic radius for the B-site cations

$\alpha = 0.87, 0.80, \text{ and } 0.92$ for $\text{MAPbI}_3$, $\text{MATlI}_3$, and $\text{MABiI}_3$.

- We then considered as $r_B$ for MTBI the averaged value (148.5 pm) of the ionic radius of Bi (117 pm) and Tl (164 pm) obtaining $\alpha = 0.84$.
Three possible structures (top view)

Structure (1) stabilized by a 3D self-passivating mechanism: Bi & Tl as n-/p- centers (DFT/PAW/PBE)

$\Delta E_{2-1} = 0.53 \text{ eV}$

$\Delta E_{3-1} = 1.58 \text{ eV}$

Optimized structures

Table 1. Geometrical parameters of the optimized structures of MAPbI$_3$ and MTBI (lattice parameters bondlengths, Å; Vol, Å$^3$; angles, degrees)

<table>
<thead>
<tr>
<th></th>
<th>MAPbI$_3$</th>
<th>MTBI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = b = 8.92; c = 13.18$</td>
<td>$a = 9.16; b = 8.91; c = 13.32$</td>
<td></td>
</tr>
<tr>
<td>$V = 1048.5$</td>
<td>$V = 1082.9$</td>
<td></td>
</tr>
<tr>
<td>$(979.0^a, 993.8^b, 1037.4^c)$</td>
<td>$\alpha = 91.6; \beta = 85.4; \gamma = 89.6$</td>
<td></td>
</tr>
<tr>
<td>$d_{ap}(\text{Pb–I}) = 3.29, 3.32$</td>
<td>$d_{ap}(\text{Bi–I}) = 3.13, 3.14$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{ap}(\text{Tl–I}) = 3.54, 3.55$</td>
<td></td>
</tr>
<tr>
<td>$d_{eq}(\text{Pb–I}) = 3.21, 3.22, 3.23$, 3.25, 3.27, 3.29</td>
<td>$d_{eq}(\text{Bi–I}) = 3.09, 3.09, 3.10, 3.14$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{eq}(\text{Tl–I}) = 3.41, 3.43, 3.47, 3.48$</td>
<td></td>
</tr>
</tbody>
</table>
The bandgap is direct on \( \Gamma \) point and it is 1.62 eV (0.74 eV) @ PBE/PAW (PBE/PAW/SOC)
\( \mu=0.31 \) (0.20)
\( m^*_e/m^*_h = 0.83 \)

Reduced effective mass
\[
\mu = \frac{(m^*_e \cdot m^*_h)}{(m^*_e + m^*_h)}
\]

MAPbI\(_3\)

MTBI

Bi 6\( p \)

The bandgap is direct on \( \Gamma \) point and it is 1.68 eV (0.84 eV) @ PBE/PAW (PBE/PAW/SOC)
\( \mu=0.33 \)
\( m^*_e/m^*_h = 0.89 \)
TAS analysis [Science 2013, 342, 344–7]: slow hot-hole cooling in MAPbI$_3$

UV–vis absorbance spectrum $\rightarrow$ 2 main absorption peaks:

Peak @ 760 nm: direct VBM $\rightarrow$ CBM excitation.
Peak @ 480 nm? (lifetime $\sim 0.4$ ps, slow hot-hole cooling in the VB?).
Long-lived hot carriers: important for further improvements in PCE.

Xing et al.: the two states (480 & 760 nm) composed of different VB states but same CB state.
Peak @ 480 nm: transition VB2 to CBM. (VB2=VBM-1eV)

Even et al. proposed the optical absorption at 480 nm is composed of multibandgap absorption not only VB2 $\rightarrow$ CBM. Is it slow hot-hole cooling observed?
Electron-phonon interactions by combining density-functional theory (DFT), density-functional perturbation theory (DFPT), and many-body perturbation theory (MBPT).

Here we investigate (a) MAPbI$_3$, (b) CsPbI$_3$, and (c) PbI$_3$.

Phonons & e-ph coupling matrix: DFPT scheme by PHonon code in the PWscf.

(Blue dotted lines) lifetimes with & (red solid lines) lifetimes w/o the imaginary modes. Black crosses: inverse of the DOSs.
• Carrier decay paths: generalized Eliashberg functions of the Fan contribution [first term \(H_1\) of the Taylor expansion of the Hamiltonian \(H_0\)]

• This function defines the contribution of phonons to the carrier relaxation for each electronic state.

→ Vibrational modes coupled with the VBs of CsPbI\(_3\) are ascribed to the motions of I \& Pb, \textit{not} of Cs.

→ The replacement of the perovskite A-site cation has no impact on the mechanism of carrier relaxation.

→ We predict that the slow hot-hole cooling is \textit{universally} observed in APbI\(_3\).
From 3D to 0D: Perovskite Nanoclusters

Three- and low-dimensional inorganic semiconductors
G.C. Papavassiliou
(Prog. Solid State Chem. 1997, 25, 125-270)

- 0D \((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9\) perovskite for optoelectronic applications

(Oz et al. Solar Energy Materials and Solar Cells, 2016)

Solar cells assembled with 0D bismuth based perovskites, with enhanced stability, towards moisture, with respect to 3D lead and tin-based ones.

- Pure \(\text{Cs}_4\text{PbBr}_6\) and its extremely high luminescence. PLQY (PL Quantum Yield) \(\sim 40\%\) (high excitation BE \(\sim 353\) meV)

Color-converting and light emitting applications
(Saidaminov et al., ACS Energy Lett., 2016, 1, 840)

(Protesescu et al., Nano Lett., 2015, 15, 3692.)

Design of highly luminescent perovskite-based colloidal quantum dot materials.

Colloidal nanocubes of \(\text{CsPbX}_3\) (X = halide)

Composition and quantum size-effects: \(E\text{gap} \) & emission spectra tunable over the VIS region.

PL of \(\text{CsPbX}_3\) nanocrystals: narrow emission (very good for blue and green spectral regions)
From 3D to 0D: MAPbI₃ Nanoclusters

Modellization motivated by the lack of experimental and theoretical results about OIHP nanostructures in view of their fundamental property investigations.

(a) PAO/PBE calculated bandstructure and (b) PDOS for t-MAPbI₃. (c) lateral and top view of VBM, and (d) lateral and top view of the CBM of t-MAPbI₃

3 Nanocluster models

- $\text{MA}_{54}\text{Pb}_{27}\text{I}_{108}$, (567 atoms, 1s): regular 3x3x3 grid of 6-fold Pb atoms with 54 MA groups with an organic/inorganic cation ratio of 2.00. Fully MAI-terminated.

- $\text{MA}_{84}\text{Pb}_{45}\text{I}_{174}$: 3x3x5 fully MAI-terminated with an organic/inorganic cation ratio of 1.87 (891 atoms, 60 dangling I atoms, 2i).

- $\text{MA}_{93}\text{Pb}_{60}\text{I}_{213}$ with a final organic/inorganic cation ratio of 1.55. (1017 atoms, 3l) PbI2 (MAI)-terminated along z (xy).

Pb27 & Pb60 (NVE, 3ps, t=0.25fs)
Electronic Properties (DOS)

- DOS of the trajectory at 2.85ps (2.05ps) for the 1s cluster.

- DOS evolution for the 1s cluster along the whole MD run
Angular velocity of MA cation

- As a first approximation, to calculate the angular velocity, we consider the variation of the \(z\)-coordinate of the same C atoms between 2 selected trajectories in the AIMD simulation.

\[
\arcsin (z_C^{I} - z_C^{II}) = d\phi \quad \omega = d\phi / dt.
\]

- 3 different MA cations:
  1. embedded in the network
  2. at the surface, i.e., 1 at the corner; 1 in the middle of the (001) surface.
     3. trajectory (@\~2 ps, 2.0625 ps, 2.125 ps).

For the internal MA of \(\omega = 0.09\) deg/fs, (2.0625 ps-2 ps & 2.125 ps-2 ps).
\(\omega = 0.10\) deg/fs (2.125 ps -2.0625 ps).

- For the external MA cations.
  \(\omega (MA @001\ surface) = 0.26\) deg/fs, 0.28 deg/fs, 0.28 deg/fs
  \(\omega (MA @\ the\ corner) = 0.11\) deg/fs, 0.22 deg/fs, 0.33 deg/fs.

Structural & electronic features of small hybrid OIHP clusters

\[(\text{MA})_j \text{Pb}_k \text{X}_l \ (l=2j+k; \text{MA}=\text{CH}_3\text{NH}_3; \text{X}=\text{halide}) \quad (k=1, 2, 8, 12) \quad \text{Gaussian09 code}\]
## Single octahedron (k=1) @ DFT

### Table: Model Energy

<table>
<thead>
<tr>
<th>Model</th>
<th>Energy</th>
<th>$E_g$</th>
<th>$\varepsilon_r$</th>
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<tr>
<td>1a</td>
<td>+0.3844</td>
<td>4.410</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>+0.2274</td>
<td>4.248</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>+0.0069</td>
<td>4.468</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>—</td>
<td>4.674</td>
<td>2.723</td>
</tr>
<tr>
<td>1d (MA$_4$PbI$_5$Br)</td>
<td>(3.947)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d (MA$_4$PbI$_4$Br$_2$)</td>
<td></td>
<td>4.703</td>
<td>2.664</td>
</tr>
<tr>
<td>1d (MA$_4$PbI$_3$Br$_3$)</td>
<td></td>
<td>4.892</td>
<td>2.546</td>
</tr>
<tr>
<td>1d (MA$_4$PbI$_2$Br$_4$)</td>
<td></td>
<td>4.966</td>
<td>2.503</td>
</tr>
<tr>
<td>1d (MA$_4$PbIBr$_5$)</td>
<td></td>
<td>5.055</td>
<td>2.474</td>
</tr>
<tr>
<td>1d (MA$_4$PbBr$_6$)</td>
<td></td>
<td>5.263</td>
<td>2.426</td>
</tr>
</tbody>
</table>

- As for the bulk, the gap redshift depends on the reduced electronegativity of the halide that enhances the degree of covalency of the Pb-X bond.
- MHF78 instead of MWB78 for Pb

In the nonlinear variation of $E_g$ as function of the composition:

$$E_g[MA_4Pb(I_{1-x}Br_x)_6] = E_g[MA_4PbI_6] - (E_g[MA_4PbBr_6] - b)x + bx^2$$

The parabolic fit that changes the eq. into:

$$E_g(x) = 4.67 + 0.17x + 0.40x^2$$

$b=0.40$, close to the experimental value (0.33 eV) for the bulk case (miscibility originates at the cluster level).

Octamer & dodecamer (k=8, 12)

- Relationship between TOTAL electric dipole moment (EDM) vs FMO wavefunction localization

- EDM described by defining the «center» of the orbital as:

$$\frac{\int d\mathbf{r} |\psi(\mathbf{r})|^2}{\int d\mathbf{r} |\psi(\mathbf{r})|^2}$$

- HOMO/LUMO separation quantified via the overlap integral:

$$S = \int d\mathbf{r} |\psi_{\text{HOMO}}||\psi_{\text{LUMO}}|$$

Octamer & dodecamer ($k=8, 12$)

Relationship between the EDM and the calculated overlap integrals ($S$), in Pb octamers & dodecamers.

Relationship between the EDM and the calculated overlap integrals ($S$), in 12 Pb ($X=Br$).

As the EDM increases the FMO overlap decreases (enhanced separation between HOMO & LUMO)

Acknowledgements

- Prof. Koichi Yamashita
  (The University of Tokyo)

Dr. Hiroki Kawai
Dr. Tomoyuki Hata
Dr. Tomohiro Yoshihara
Some bibliography


