Tunable Perovskites: From Cuprate Superconductors to Versatile Organic-Inorganic Optoelectronics

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Outline:
1. Perovskites and high-$T_c$ SC → Some history…
2. Lead/tin-based O-I hybrid perovskites… Tunable semiconductors
3. Conclusions / Future directions

AharonFest, Stanford Univ.
Sept. 15, 2018
What are perovskites?

**pe·rovsk·ite:** ˌpərəˈvəskit,-ˈrəfs/- noun
1. a yellow, brown, or black mineral consisting largely of calcium titanate (CaTiO₃);
2. Named for Lev Aleksevich von Perovski (1792-1856)
3. any of a group of related minerals and ceramics having same crystal structure as this.

Examples: SrTiO₃, CsSnBr₃, CH₃NH₃SnI₃, ...

**Ferroelectrics**
- BaTiO₃
- PbTiO₃
- KNbO₃
- NaTaO₃

**Ferromagnets**
- BiMnO₃
- LaMnO₃
- Sr(Cr₀.₅Mo₀.₅)O₃
- Ba(Fe₀.₅Re₀.₅)O₃
- Ca(Cr₀.₅Re₀.₅)O₃

**Superconductors**
- (Ba,K)BiO₃ (30 K)
- Ba(Pb,Bi)O₃ (12 K)
- Ba(Pb,Sb)O₃ (3.5 K)
- SrTiO₃ (0.25 K)

“organic-inorganic” or “hybrid”
Layered inorganic perovskites?

Ruddlesden–Popper (RP) Phases

\[ A_2BO_4 \]

\[ A_3B_2O_7 \]

Shift of adjacent layers by \((\frac{1}{2}, \frac{1}{2})\)

D. Lee et. al. *Materials* 10, 368 (2017)
My intro to perovskites?

Possible High $T_c$ Superconductivity in the Ba–La–Cu–O System

J.G. Bednorz and K.A. Müller
IBM Zürich Research Laboratory, Rüschlikon, Switzerland
Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba–La–Cu–O system, with the composition $\text{Ba}_x\text{La}_{2-x}\text{Cu}_y\text{O}_{3+y/2}$, have been prepared in polycrystalline form. Samples with $x=1$ and $0.75$, $y>0$, annealed below 900 °C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, but possibly also from 2D superconducting fluctuations of double perovskite layers of one of the phases present.

I. Introduction

“On the extreme forefront of research in superconductivity is the empirical search for new materials” [1]. Transition-metal alloy compounds of $A_15$ (Nb$_5$Sn) and $B1$ (NbN) structure have so far shown the highest superconducting transition temperatures. Among many $A_15$ compounds, careful optimization of Nb–Ge thin films near the stoichiometric composition of Nb$_5$Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest $T_c = 23.3$ K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high $T_c$’s [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li–Ti–O system with oxides as high as 13.7 K, was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high $T_c$ [5]. Other oxides like perovskites exhibit superconductivity despite their [6]. This large electron-phonon coupling allows a $T_c$ of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound BaPb$_{1-x}$Sr$_x$O$_3$ by Slichter et al., also a decade ago [8]. The highest $T_c$ in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries $n=2.4 \times 10^{21}$ cm$^{-3}$ [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm$^{-1}$ whose intensity is proportional to $T_c$, exist [10]. This last example indicates that within the BCS mechanism, one may find still higher $T_c$’s in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A

Propose $K_2NiF_4$ structure


Fig. 3. Low-temperature resistivity of a sample with $x$(Ba)=0.75, recorded for different current densities
“On the basis of the existing data, it appears that the high-temperature superconductivity above 77 K reported here occurs only in compound systems consisting of a phase or phases in addition to or other than the K₂NiF₄ phase.”
Layered perovskites?

Oxygen-deficient perovskites and lower-dimensionality…
Layered perovskites? 1987

"Woodstock of physics"

https://www.youtube.com/watch?v=pQMHPHclUWo
Layered perovskites?

https://en.wikipedia.org/wiki/Superconductivity

Bork to replace Powell on Court

WASHINGTON — President Reagan will nominate federal appellate Judge Robert Bork to the Supreme Court by the middle of the week, subject to checks with Senate leaders of both parties by White House chief of staff Howard Baker Jr. and Attorney General Edwin Meese III, administration sources said Monday.

The tentative decision was made at a 32-minute meeting Monday of Reagan, Baker, Meese, White House counsel A.B. Culvahouse and Assistant Attorney General William Bradford Reynolds, Meese’s counsel. Two senior White House officials called Bork the leading candidate.

One senior official said Bork would be given the nomination unless “there’s a major obstacle on the Hill that you can’t overcome.” He said that Patrick Higginbotham, a federal appeals court judge in Dallas, and two others remained under consideration if any problems developed during a preliminary background investigation and the discussions with key senators.

Bork, 60, is regarded as an unbending conservative. Unlike retiring Justice Lewis Powell, he is not regarded as a legal scholar. Powell is a moderate, and his judicial scholarship demonstrated during five years on the U.S. Circuit Court of Appeals here, as solicitor general and as a law professor at Yale.

In filling Powell’s vacancy, the president has the historic opportunity of shaping the ideological balance of the Supreme Court by giving it a majority of conservatives.

Mad dash to higher $T_c$ ...
Science and Beyond...

1987-1988

International Centre for Theoretical Physics... Trieste, Italy

Thanks Aharon!
My intro to perovskites… Going more complex

\[ \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \]

Understanding the physics requires understanding the chemistry!
Anomalous Spectral Weight Transfer at the Superconducting Transition of Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$

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Stanford Electronics Laboratories, Stanford University, Stanford, California 94305
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(Received 4 October 1990)

Anomalous spectral weight transfer at the superconducting transition of single-crystalline Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ was observed by high-resolution angle-resolved photoemission spectroscopy. As the sample goes superconducting, not only is there spectral weight transfer from the gap region to the p(3c) peak as in BCS theory, but there is also a decrease (increase) in higher (lower) binding energies in the p(3c) region. This spectral weight transfer is also observed in Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$, Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{8+δ}$, and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{8+δ}$ samples.

PACS numbers: 74.65.+x, 71.20.

Observation of a Commensurate Array of Flux Chains in Tilted Flux Lattices in Bi-Sr-Ca-Cu-O Single Crystals

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D. B. Mitzi and A. Kapitulnik
Stanford University, Stanford, California 94305
(Received 22 October 1990)

We report the observation of a novel flux-lattice structure, a commensurate array of flux-line chains. Our experiments consist of the magnetic decoration of the flux lattices in single crystals of Bi-Sr-Ca-Cu-O where the magnetic field is applied at an angle with respect to the conducting planes. For a narrow range of angles, the equilibrium structure is one with uniformly spaced chains with a higher line density of vortices than the background lattice. Our observations are in qualitative agreement with theories which suggest that in strongly anisotropic materials, the vortexes develop an attractive interaction in tilted magnetic fields.

PACS numbers: 74.60.Gf, 74.70.Vy

Flux lattices in the high-$T_c$ superconductors have proven to be a rich and interesting area for research. Strong anisotropies and the importance of thermal fluctuations have combined to produce new structures and regimes not previously seen in flux lattices in conventional superconductors. Oval vortices, hexatics, liquids, solidification process, are typically in the form of thin sheets with basal-plane dimensions of up to several cm and thicknesses up to 100 μm. The lattice constants, $a_0 = 5.413(2)$ Å, $b_0 = 5.411(3)$ Å, and $c_0 = 30.911(1)$ Å, were determined using a four-circle x-ray diffractometer. As is typical in these materials, an incommensurate
My intro to perovskites… *Modulated Structures* 1990


Can we replace the inorganic mushy layer with an organic layer?

→ Move to IBM…
O-I perovskite: Inorganic $\rightarrow$ organic modulation layer

\[(\text{R-NH}_3)_2\text{MX}_4 \quad \text{"Staggered"} \]

\[(\text{NH}_3\text{-R-NH}_3)_2\text{MX}_4 \quad \text{"Eclipsed"} \]
O-I perovskite: Inorganic $\rightarrow$ organic modulation layer

$M^{2+} = Cu, Cd, Mn, Ge, Sn, Pb...; X^- = Cl, Br, I$

(R-NH$_3$)$_2$MX$_4$  
"Staggered"

(NH$_3$-R-NH$_3$)$_2$MX$_4$  
"Eclipsed"

Can we make them conducting?
Varying inorganic layer thickness...

\[ A'^2A_{n-1}M_nX_{3n+1} : <100> \text{ series} \]
\[ M = \text{Ge, Sn, Pb}; X = \text{Cl, Br, I} \]

\[ (C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Sn_{n}I_{3n+1} \]  
\[ (n=3) \]

Semiconductor \(\rightarrow\) Metal

Tunable and Solution Processable Semiconductor...

\[ \text{A'}_2\text{A}_{n-1}\text{M}_n\text{X}_{3n+1}: <100> \text{ series} \]
\[ \text{M} = \text{Ge, Sn, Pb}; \text{X} = \text{Cl, Br, I} \]

\[ (\text{CH}_3\text{NH}_3)_{1-x}(\text{NH}_2\text{CH}=\text{NH}_2)_x\text{SnI}_3 \]

\[ a_{x=0} = 6.242(1) \text{ Å} \]
\[ a_{x=1} = 6.316(1) \text{ Å} \]

Semiconductor \( \rightarrow \) Metal

Spin Coated PEA$_2$SnI$_4$ Channel

- $\mu < 1.4 \text{ cm}^2/\text{V-sec}$ in saturation regime
- Current density $> 400 \text{ A/cm}^2$
- $I_{on}/I_{off} = 10^6$

Organic-Inorganic LED

\[ \text{Ag (1200 Å)} \]
\[ \text{Mg}_{20}\text{Ag (600 Å)} \]
\[ \text{OXD7 (200 Å)} \]
\[ (\text{AE4T})\text{PbCl}_4 (3000 Å) \]
\[ \text{SiO}_2 (1300 Å) \]

\( \lambda_{\text{peak}} = 530 \text{ nm} \)

Organic-Inorganic Electronics:

Organic–inorganic hybrid materials enable the integration of useful organic and inorganic characteristics within a single molecular-scale composite. Unique electronic and optical properties have been observed, and many others can be envisioned for this promising class of materials. In this paper, we review the crystal structures and physical properties of one family of crystalline, self-assembling, organic-inorganic hybrids based on the layered perovskite framework. In addition to exhibiting a number of potentially useful properties, the hybrids can be deposited as thin films using simple and inexpensive techniques, such as spin coating or single-source thermal ablation. The relatively new field of “organic–inorganic electronics” offers a variety of exciting technological opportunities. Several recent demonstrations of electronic and optical devices based on organic–inorganic perovskites indicate the potential for significant improvements in brightness, and resolution, the depth and weight of CRTs render them inappropriate for portable applications. Ultimately, organic liquid crystals, which share useful properties of crystalline solids and liquids, have provided the basis for most flat panels found in current portable units [2], including laptop and palmtop computers.

Recently, other organic materials have received considerable attention as potential replacements for their inorganic counterparts in flat-panel-display driver circuitry and light-emitting elements. Organic materials have the key advantage of simple and low-temperature thin-film processing through inexpensive techniques such as spin coating, ink-jet printing, or stamping. In addition, the flexibility of organic chemistry enables the formation of organic molecules with useful luminescent and conducting properties. Since the first consideration of organic electroluminescence (EL) devices more than 30 years ago [3], organic light-emitting devices (OLEDs) have been widely pursued, and near-commercial dot-matrix displays have recently been demonstrated [4]. Luminous efficiency, brightness, and operating voltages are high in OLEDs [1, 5, 6]. In addition to


$M^{2+}$ Component: An important example... APbX$_3$

Perovskite PV Evolution


>20% efficiency achieved in 6 yr!

→ Very low $V_{oc}^{def} = E_g/q - V_{oc} \approx 0.4V$

For GaAs: $V_{oc}^{def} \sim 0.3V$ (eff. = 28.8%)

M. A. Green et. al., Prog. Photovoltaics 26, 3 (2018).

CH$_3$NH$_3$, NH$_2$CH=NH$_2$, Cs PbI$_3$

(Organic-Inorganic or “Hybrid” Perovskite)

(CH$_3$NH$_3$, NH$_2$CH=NH$_2$, Cs) PbI$_3$


$V_{oc} = 1.144 \text{ V}$

$J_{sc} = 24.92 \text{ mA/cm}^2$

FF = 79.6%

PCE = 22.7%

Killer apps?

Organic-Inorganic Hybrid Materials as Semiconducting Channels in Thin-Film Field-Effect Transistors


Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency†

Michael Saliba,†a,b Tsaiuke Matsui,†a Ji-Youn Seo,† Konrad Domanski,†a,†b Juan-Pablo Correa-Baena,† Mohammad Khaja Nazeeruddin,a,†b Shaik M. Zakeeruddin,a,†b Wolfgang Tress,a Antonio Abate,a Anders Hagfeldt,a and Michael Grätzel,a

Bright light-emitting diodes based on organometal halide perovskite


Solid-state light-emitting devices based on direct-bandgap semiconductors have, over the past two decades, been utilized as energy-efficient sources of lighting. However, fabrication of these devices typically relies on expensive high-temperature and high-vacuum processes. Render these uneconomical for organometal halides. All electrics measured in air at 37 °C.

In our infrared three-law

Efficient luminescent solar cells based on tailored mixed-cation perovskites

Dongqin Bi, Wolfgang Tress, M. Ibrahim Dar, Peng Gao, Jingshan Luo, Clémentine Renvoise, Kurt Schenk, Antonio Abate, Fabrizio Giordano, Juan-Pablo Correa Baena, Jean-David Decoppet, Shaik Mohammed Zakeeruddin, Mohammad Khaja Nazeeruddin, Michael Grätzel, Anders Hagfeldt

We report on a new metal halide perovskite photovoltaic cell that exhibits both very high solar-to-electric power conversion efficiency and intense electroluminescence. We produce the perovskite films in a single step from a solution containing a mixture of FAI, PbI2, MABr, and PbBr2 (where FA stands for formamidinium cations and MA stands for methylammonium cations). Using mesoporous TiO2 and Spiro-OMeTAD as electron- and hole-specific contacts, respectively, we fabricate perovskite solar cells that achieve a maximum power conversion efficiency of 20.8% for a 3-cm2 active area.
What is special about 3D Pb/Sn-based Perovskites?

- Direct 1.5 eV band gap and \( p - p \) transition (\( I \) \( p \) to Pb \( p \)) → Ultrahigh absorption… Enables ultrathin absorbers.

- \( s-p \) coupling enhances dispersion of the upper VB… Small effective masses for \( e^-/e^+ \)… high mobilities and long \( L_d \)

- Rashba Splitting: SOC and inversion symmetry breaking… Long minority carrier lifetimes

- Effective photogeneration/collection of \( e^-/e^+ \)

- Dominant shallow point defects…

- Intrinsically benign grain boundaries

- Relatively high dielectric constant

- Low recombination & high \( V_{oc} \)

\( \text{Pb} \ 6s^2 \) lone pair & ionic nature

\( \text{Pb}^{2+} \rightarrow [\text{Xe}]4f^{14}5d^{10}6s^2 \)


Other examples of structural/electronic tunability…
Control over inorganic layer orientation...

(a) \[ \text{<100>-oriented} \]

(b) \[ \text{<110>-oriented} \]

(c) \[ \text{<111>-oriented} \]

\[ \text{(RNH}_3\text{)}^2\text{A}_{n-1}\text{M}_n\text{X}_{3n+1} \ (n=2) \]

\[ \text{(RNH}_3\text{)}^2\text{A}_m\text{M}_m\text{X}_{3m+2} \ (m=2) \]

\[ \text{(RNH}_3\text{)}^2\text{A}_{q-1}\text{M}_q\text{X}_{3q+3} \ (q=2) \]

Varying Orientation of Inorganic Layers…

\[
H_2N-C≡N + HI \rightarrow H_2N-C(I)=NH
\]

iodoformamidinium

\[
H_2N\text{C(I)}=N\text{H}_2^+ + HI \rightarrow H_2N\text{C(I)}=N\text{H}_2^+
\]

(e.g., iodoformamidinium)

\[
[NH_2C(I)=NH_2]_2(CH_3NH_3)_nM_nX_{3n+2}
\]

(e.g., alkylammonium)

\[
(RNH_3)_2(CH_3NH_3)_{n-1}M_nX_{3n+1}
\]

Control over inorganic layer orientation…

Selection of organic cation $\rightarrow$ optoelectronic properties…

Acene alkylammonium lead halide family (organic cation templating)…

Can vary:
- Length of alkylammonium tethering group
- Number of benzene rings

This study: $(\text{RH})_2\text{PbX}_4$  $X = \text{Cl, Br, I}$ and $R=$

How does structure impact properties in this family?

Acene alkylammonium lead halide family…


Acene alkylammonium lead halide family…

In-plane Distortion (Sn-I-Sn bond angle < 180°):  

- Loss of antibonding interactions between Sn 5s and I p_x/p_y orbitals → Lowers top of valence band.  
- Bottom of the conduction band largely non-bonding in undistorted structure; distortion induces orbital mixing among Sn 5p + I s/p orbitals → Raises conduction band bottom.  
- Band gap may be tuned by as much as 1 eV using the steric impact of the organic cation on the inorganic framework.
Thermal properties of HOIP films?… (R-NH$_3$)$_2$SnI$_4$ example

Do the hybrids melt?
→ SnI$_2$ / PbI$_2$ melts at 320$^\circ$C / 402$^\circ$C …

TGA/DSC…

a) structural transition
b) melting transition
c) decomposition

→ Organic cation has large effect on melting properties

## Influence of Organic Cation on Thermal Properties

<table>
<thead>
<tr>
<th>Hybrid perovskite</th>
<th>Organic molecule</th>
<th>$T_s$ [°C]</th>
<th>$T_m$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4-BrPEA)$_2$SnI$_4$</td>
<td>4-bromophenethylamine</td>
<td>–</td>
<td>270(1) [a]</td>
</tr>
<tr>
<td>(4-CIPEA)$_2$SnI$_4$</td>
<td>4-chlorophenethylamine</td>
<td>–</td>
<td>262(1) [a]</td>
</tr>
<tr>
<td>(5FPEA)$_2$SnI$_4$</td>
<td>2,3,4,5,6-pentafluorophenethylamine</td>
<td>227.0(8)</td>
<td>253(1) [a]</td>
</tr>
<tr>
<td>(3-CIPEA)$_2$SnI$_4$</td>
<td>3-chlorophenethylamine</td>
<td>197.0(3)/204.3(2)[b]</td>
<td>241.8(6)</td>
</tr>
<tr>
<td>(NEA)$_2$SnI$_4$</td>
<td>2-naphthaleneethylamine</td>
<td>–</td>
<td>240.6(8)</td>
</tr>
<tr>
<td>(4-FPEA)$_2$SnI$_4$</td>
<td>4-fluorophenethylamine</td>
<td>–</td>
<td>234.2(8) [a]</td>
</tr>
<tr>
<td>(3-FPEA)$_2$SnI$_4$</td>
<td>3-fluorophenethylamine</td>
<td>209.2(4)</td>
<td>233.0(8)</td>
</tr>
<tr>
<td>(2,4-CIPEA)$_2$SnI$_4$</td>
<td>2,4-dichlorophenethylamine</td>
<td>163.4(4)</td>
<td>231.3(6) [a]</td>
</tr>
<tr>
<td>(2-BrPEA)$_2$SnI$_4$</td>
<td>2-bromophenethylamine</td>
<td>208.6(2)</td>
<td>221.9(8)</td>
</tr>
<tr>
<td>(2-CIPEA)$_2$SnI$_4$</td>
<td>2-chlorophenethylamine</td>
<td>202.7(4)</td>
<td>221.1(8)</td>
</tr>
<tr>
<td>(PEA)$_2$SnI$_4$</td>
<td>phenethylamine</td>
<td>191.9(3)/208.2(5)[b]</td>
<td>213.4(8)</td>
</tr>
<tr>
<td>(4-MeOPEA)$_2$SnI$_4$</td>
<td>4-methoxyphenethylamine</td>
<td>–</td>
<td>210.1(6)</td>
</tr>
<tr>
<td>(3-MeOPEA)$_2$SnI$_4$</td>
<td>3-methoxyphenethylamine</td>
<td>125.7(3)</td>
<td>208.4(6)</td>
</tr>
<tr>
<td>(2-FPEA)$_2$SnI$_4$</td>
<td>2-fluorophenethylamine</td>
<td>174.0(3)</td>
<td>200.8(8)</td>
</tr>
<tr>
<td>($\beta$-MePEA)$_2$SnI$_4$</td>
<td>$\beta$-methylphenethylamine (racemic)</td>
<td>137.1(4)</td>
<td>170(1)</td>
</tr>
<tr>
<td>($S\beta$-MePEA)$_2$SnI$_4$</td>
<td>($S$)-$\beta$-methylphenethylamine</td>
<td>154.1(4)</td>
<td>173(1)</td>
</tr>
<tr>
<td>($R\beta$-MePEA)$_2$SnI$_4$</td>
<td>($R$)-$\beta$-methylphenethylamine</td>
<td>153.9(5)</td>
<td>170(1)</td>
</tr>
</tbody>
</table>

[a] With decomposition. [b] Two structural transitions are noted before melting.

The why of the melting temperature trend?

Various bonding configurations will determine melting properties…
More steric hindrance around NH$_3^+$ anchoring group $\rightarrow$ lower $T_m$
Melt-Processed Organic-Inorganic FET (OIFET)

\[ \mu_{\text{sat}} = 2.6 \text{ cm}^2/\text{V-sec} \]
\[ \mu_{\text{lin}} = 1.7 \text{ cm}^2/\text{V-sec} \]
\[ \frac{I_{\text{on}}}{I_{\text{off}}} \approx 10^6 \]

(>2x better than spin-coated!)

Recently with Pb-based systems also

2-D perovskites: More functional organic cations…

More complex cations…

(AE4T)PbX₄

AE4T = aminoethylquaterthiophene

X = Cl

X = I

PL

PLE


Tailoring of Energy Levels in Hybrid Perovskites…


Heyd-Scuseria-Ernzerhof (HSE06) hybrid density functional plus perturbative spin-orbit coupling
Tailoring of Energy Levels in Hybrid Perovskites…

Heyd-Scuseria-Ernzerhof (HSE06) hybrid density functional plus perturbative spin-orbit coupling

Tailoring of Energy Levels in Hybrid Perovskites…

Can account for PL quenching…

“bandgap engineering”

Multilayer quantum well structures

Some Other Interesting Structural Motifs…

Polymerization

\[(\text{HOOC-CH=CH-CH=CH}_2\text{NH}_3)_2\text{CdCl}_4\]

Intercalation

\[(\text{C}_6\text{F}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4 \cdot (\text{C}_6\text{H}_6)\]

\[(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4 \cdot (\text{C}_6\text{F}_6)\]

Some Other Interesting Structural Motifs…

**Intercalation w/ reaction**

(a) \((\text{BYA})_2\text{PbBr}_4\)  
(b) \((\text{BYA-}I_2)_2\text{PbBr}_4\)

\((\text{BYA} = \text{but-3-yn-1-ammonium})\)

Double perovskites: $+1/+3$ metals vs $+2$

$\text{(n=2) (BA)}_2\text{Cs(AgBi)Br}_7$  
$\text{(n=1) (BA)}_4\text{(AgBi)Br}_8$

Conclusions and Future Directions Hybrid Perovskites

- Halide and hybrid perovskites offer great opportunity for tunability…
- Structural templating among organic & inorganic components
- Organic component can impact optical/electrical/thermal properties
- Complex organic cations → analogy with multilayer QW structures

Key challenge: Harnessing potential of both organic/inorganic realms

Few interesting recent observations / questions:

1. Large Rashba splitting energy (40 meV) and parameter (1.6 eV·Å)…

   ![Graphs showing Rashba splitting](image)

   How can we control this and make use of it?

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2. Long spin coherence time of $\sim$1ns (at 4K), despite large SOC…

Understanding the origins?

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Key challenge: Harnessing potential of both organic/inorganic realms

Few interesting recent observations / questions:

1. Large Rashba splitting energy (40 meV) and parameter (1.6 eV·Å)
2. Long spin coherence time of ~1ns (at 4K), despite large SOC
3. Slow hot carrier thermalization (100s of ps)... Efficient hot-phonon bottleneck slows down hot carrier cooling above critical injection density of ~5 × 10^{17} cm⁻³

Overall: There is still a vast range of unexplored space for HOIPs ... for new structural chemistry and interesting physics!
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Happy Birthday Aharon!