Perovskites: crystal structure, important compounds and properties

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GMF Group Meeting
12,04,2016
To start

• We have to solve the energy problem.

• Any technology that has good potential to cut carbon emissions by > 10% needs to be explored aggressively.

• Researchers should not be deterred by the struggles some companies are having.

• Someone needs to invest in scaling up promising solar cell technologies.
Origin And History of Perovskite compounds

Perovskite is **calcium titanium oxide or calcium titanate**, with the chemical formula **CaTiO₃**. The mineral was discovered by Gustav Rose in 1839 and is named after Russian mineralogist **Count Lev Alekseevich Perovski** (1792–1856)."

All materials with the same crystal structure as CaTiO₃, namely **ABX₃**, are termed perovskites:
Origin And History of Perovskite compounds

- Very stable structure, large number of compounds, variety of properties, many practical applications.
- Key role of the BO$_6$ octahedra in ferromagnetism and ferroelectricity.
- Extensive formation of solid solutions $\rightarrow$ material optimization by composition control and phase transition engineering.

Ideal cubic perovskite structure (ABO$_3$)
Classification of Perovskite System

- **Perovskite Systems**
  - Inorganic Oxide Perovskites
    - Intrinsic Perovskites
    - Doped Perovskites
  - Halide Perovskites
    - Alkali-halide Perovskites $A_2\text{Cl}(\text{LaNb}_2\text{O}_7)$
    - Organo-Metal Halide Perovskites

Structure deduced

1959:

Kongelige Danske Videnskabernes Selskab, Matematisk-Fysikke
Meddelelser (1959) 32,
p1-p17

Author:

Moller, C.K.

Title: The structure of cesium plumbo iodide CsPbl$_3$
<table>
<thead>
<tr>
<th>Reference compound</th>
<th>Properties</th>
<th>Existing and potential applications</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BaTiO$_3$</strong></td>
<td>Ferroelectricity, piezoelectricity, high dielectric constant</td>
<td>Multilayer ceramic capacitors (MLCCs), PTCR resistors, embedded capacitance</td>
<td>Most widely used dielectric ceramic $T_C = 125^\circ$ C</td>
</tr>
<tr>
<td>(Ba, Sr)$_2$TiO$_3$</td>
<td>Non-linear dielectric properties</td>
<td>Tunable microwave devices</td>
<td>Used in the paraelectric state</td>
</tr>
<tr>
<td><strong>Pb(Zr, Ti)O$_3$</strong></td>
<td>Ferroelectricity, piezoelectricity</td>
<td>Piezoelectric transducers and actuators, ferroelectric memories (FERAMs)</td>
<td>PZT: most successful piezoelectric material</td>
</tr>
<tr>
<td><strong>Bi$_4$Ti$<em>3$O$</em>{12}$</strong></td>
<td>Ferroelectric with high Curie temperature</td>
<td>High-temperature actuators, FerAMs</td>
<td>Aurivillius compound $T_C = 675^\circ$ C</td>
</tr>
<tr>
<td>(K$<em>{0.5}$Na$</em>{0.5}$)$_2$NbO$_3$, Na$<em>0.5$Bi$</em>{0.5}$TiO$_3$</td>
<td>Ferroelectricity, piezoelectricity</td>
<td>Lead-free piezoceramics</td>
<td>Performances not yet comparable to PZT but rapid progress</td>
</tr>
<tr>
<td><strong>(Pb, La)(Ti, Zr)O$_3$</strong></td>
<td>Transparent ferroelectric</td>
<td>Optoelectronic devices</td>
<td>First transparent ferroelectric ceramic</td>
</tr>
<tr>
<td><strong>BiFeO$_3$</strong></td>
<td>Magnetolectric coupling, high Curie temperature</td>
<td>Magnetic field detectors, memories</td>
<td>Most investigated multiferroic compound, $T_C = 850^\circ$ C</td>
</tr>
<tr>
<td><strong>PbMg$<em>{1/3}$Nb$</em>{2/3}$O$_3$</strong></td>
<td>Relaxor ferroelectric</td>
<td>Capacitors, actuators</td>
<td>High permittivity, large electrostrictive coefficients, frequency-dependent properties</td>
</tr>
<tr>
<td><strong>SrRuO$_3$</strong></td>
<td>Ferromagnetism</td>
<td>Electrode material for epitaxial ferroelectric thin films</td>
<td></td>
</tr>
<tr>
<td>(La, A)MnO$_3$, A = Ca, Sr, Ba</td>
<td>Ferromagnetism, giant magnetoresistance, spin-polarized electrons</td>
<td>Magnetic field sensors, spin electronic devices</td>
<td></td>
</tr>
<tr>
<td><strong>SrTiO$_3$</strong></td>
<td>Incipient ferroelectricity, thermoelectric power, metallic electronic conduction when n-doped, mixed conduction when p-doped, photocatalyst</td>
<td>Alternative gate dielectric material, barrier layer capacitors, substrate for epitaxial growth, photoassisted water splitting</td>
<td>Multifunctional material</td>
</tr>
<tr>
<td><strong>LaGaO$_3$, BaIn$_2$O$_5$</strong></td>
<td>Oxide-ion conduction</td>
<td>Electrolyte in solid oxide fuel cells (SOFCs)</td>
<td>BaIn$_2$O$_5$ is an oxygen deficient perovskite with brownmillerite structure.</td>
</tr>
<tr>
<td><strong>BaCeO$_2$, BaZrO$_2$</strong></td>
<td>Proton conduction</td>
<td>Electrolyte in protonic solid oxide fuel cells (P-SOFCs)</td>
<td>High protonic conduction at 500-700$^\circ$ C</td>
</tr>
<tr>
<td>(La, Sr)BO$_3$, (B = Mn, Fe, Co)</td>
<td>Mixed conduction, catalyst</td>
<td>Cathode material in SOFCs, oxygen separation membranes, membrane reactors, controlled oxidation of hydrocarbons,</td>
<td>Used for SOFC cathodes</td>
</tr>
<tr>
<td><strong>LaAlO$_3$, YAlO$_3$</strong></td>
<td>Host materials for rare-earth luminescent ions, lasers</td>
<td>Substrates for epitaxial film deposition</td>
<td></td>
</tr>
</tbody>
</table>
Early publications on lead halide perovskites

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

\[
\text{CH}_2\text{NH}_2\text{PbX}_3, \text{ a Pb(II)-System with Cubic Perovskite Structure}
\]

Dieter Weber
Institut für Anorganische Chemie der Universität Stuttgart

Synthesis, X-ray

\[
\text{CH}_3\text{NH}_2\text{PbX}_3 (X = \text{Cl}, \text{Br}, \text{I}) \text{ has the cubic perovskite structure with the unit cell parameters } a = 5.68 \text{ Å} (X = \text{Cl}), a = 5.92 \text{ Å} (X = \text{Br}) \text{ and } a = 6.27 \text{ Å} (X = \text{I}). \text{ With exception of } \text{CH}_3\text{NH}_2\text{PbCl}_3 \text{ the compounds show intense colour, but there is no significant conductivity under normal conditions. The properties of the system are explained by a “p-resonance-bonding”. The synthesis is described.}
\]

\[
\text{CH}_3\text{NH}_2\text{SnBr}_2\text{I}_{0.5} \ (x = 0–3), \text{ ein Sn(II)-System mit kubischer Perowskitstruktur}
\]

\[
\text{CH}_3\text{NH}_2\text{SnBr}_2\text{I}_{0.5} (x = 0–3), \text{ a Sn(II)-System with Cubic Perovskite Structure}
\]

Dieter Weber
Institut für Anorganische Chemie der Universität Stuttgart
Z. Naturforsch. 33b, 862–865 (1978); eingegangen am 5. Mai 1978

Synthesis, X-ray, Mössbauer Spectra

\[
\text{CH}_3\text{NH}_2\text{SnBr}_2\text{I}_{0.5} (x = 0–3) \text{ has the cubic perovskite structure with the unit cell parameters } a = 5.89 \text{ Å} (x = 3), a = 6.01 \text{ Å} (x = 2) \text{ and } a = 6.24 \text{ Å} (x = 0) \text{ and } Z = 1. \text{ The compounds show intense colour and conducting property. The } ^{119}\text{Sn Mössbauer data are consistent with the high symmetry environment of the Sn(II)-ion. A bonding model, using a “p-resonance-bonding”, can explain the properties of the cubic system. The synthesis is described.}
\]
Lead-halide perovskite compounds ($\text{CH}_3\text{NH}_2\text{PbBr}_3$) are known to construct self-organized semiconductor crystal structure (Fig. 1). The perovskite compounds are expected to be constructed in nano-porous structures of TiO$_2$ electrode. In this study, we attempted to form the self-organized perovskite type crystal structure in the TiO$_2$ nano-porous structure and discussed about possibility to apply for visible-light sensitized photo electrochemical cells.


**Table 1. Photovoltaic performance of the cell sensitized by lead-halide perovskite compound**

<table>
<thead>
<tr>
<th>Intensity (mW/cm$^2$)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.64</td>
<td>0.64</td>
<td>0.53</td>
<td>2.19</td>
</tr>
<tr>
<td>12.2</td>
<td>0.68</td>
<td>0.54</td>
<td>0.58</td>
<td>1.73</td>
</tr>
</tbody>
</table>

**Fig. 1** Current-voltage characteristics of polyethylene based solid-state photocells using CH$_3$NH$_2$PbBr$_3$ (line) and CH$_3$NH$_3$PbI$_3$ (dot-line) as sensitizer for TiO$_2$ electrode.
### Solid-State DSC

#### DSSC using redox electrolyte
- Glass substrate
- Platinum-coated FTO cathode
- Redox electrolyte
- Dye
- FTO Anode
- TiO₂

#### DSSC using hole transport material
- Semitransparent metallic cathode
- Solid hole conductor PCE
- light harvester dye or pigment film
- TiO₂ underlayer
- FTO anode
- Glass substrate
Evolution of device structures

Various device fabrication methods
‘Anti-solvent’ the key to optimum morphology


Perovskite vs silicon technology
Production of silicon and silicon wafers

Expensive, high-energy process, generating high levels of waste material
Production of perovskite cell

Simpler, lower cost, lower embodied energy, massively reduced environmental impact

from salts \(\rightarrow\) perovskite

\[\text{Yellow precursor salt} + \text{White precursor salt} + \text{Organic solvent} = \text{Perovskite liquid formulation}\]

from perovskite liquid \(\rightarrow\) perovskite solar panel

Incoming coated glass \(\rightarrow\) Deposit titanium dioxide \(\rightarrow\) Deposit perovskite \(\rightarrow\) Deposit hole transport layer \(\rightarrow\) Finished panel with back contact
<table>
<thead>
<tr>
<th>Characteristics</th>
<th>CdTe</th>
<th>CIGS</th>
<th>c-Si</th>
<th>Perovskite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials cost</td>
<td>Low</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Finished material cost</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Fabrication cost</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Energy payback period</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>LCOE</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Efficiency</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Toxicity</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Abundance</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>
# Low Bandgap – $q \cdot V_{oc}$ Loss in Perovskite Solar Cells

<table>
<thead>
<tr>
<th>Material</th>
<th>Bandgap (eV)</th>
<th>$q \cdot V_{oc}$ (eV)</th>
<th>Energy loss (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>1.43</td>
<td>1.12</td>
<td>0.31</td>
</tr>
<tr>
<td>Silicon</td>
<td>1.12</td>
<td>0.75</td>
<td>0.37</td>
</tr>
<tr>
<td>CIGS</td>
<td>~1.15</td>
<td>0.74</td>
<td>0.41</td>
</tr>
<tr>
<td><strong>Perovskite</strong></td>
<td><strong>1.55</strong></td>
<td><strong>1.07</strong></td>
<td><strong>0.48</strong></td>
</tr>
<tr>
<td><strong>(CH$_3$NH$_3$PbI$_3$)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CdTe</td>
<td>1.49</td>
<td>0.90</td>
<td>0.59</td>
</tr>
<tr>
<td>a-Silicon</td>
<td>1.55</td>
<td>0.89</td>
<td>0.66</td>
</tr>
</tbody>
</table>

M. Green et al. Solar cell efficiency tables (version 42) July 2013
The hybrid Perovskite is a Strongly-Absorbing Direct Band Gap Semiconductor
The Perovskite Bandgap can be tuned by Chemical Substitution

The band gap can be tuned from 1.57 eV to 2.23 eV by substituting bromine for iodine in CH$_3$NH$_3$Pb(Br$_x$I$_{1-x}$)$_3$

But the morphology is not stable!
Lead-free: $\text{CH}_3\text{NH}_3\text{SnI}_3$ Perovskite

$a=b=8.7912 \text{ Å} \text{ and } c=4.4770 \text{ Å}$

Tuning the structure of perovskites from 3D to 2D

• When will a 3D perovskite form?
• When the A, B and X components fit together neatly in the crystal lattice.
• Assuming ionic radii of $R_A$ etc, For a close packed cubic perovskite the structure is possible, provided:

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

Where $t$ is a non defined tolerance factor, typically $0.8 < t < 1$, which relates to how much strain the lattice can tolerate before it will no longer form.
Low dimensional perovskite with more possibilities

Conducting Layered Organic-inorganic Halides Containing \(<110>\)-Oriented Perovskite Sheets


IBM T. J. Watson Research Center, Post Office Box 218, Yorktown Heights, NY 10598, USA. Department of Chemistry and Texas Center for Superconductivity, University of Houston, Houston, TX 77204-5641, USA.

Science 10 March 1995:
Vol. 267 no. 5203 pp. 1473-1476
DOI: 10.1126/science.267.5203.1473

Abstract

Single crystals of the layered organic-inorganic perovskites, \([NH_2C(I=NH_2)_2(CH_3NH_3)_m Sn_mI_{3m+2}\), were prepared by an aqueous solution growth technique. In contrast to the recently discovered family, \((C_4H_9NH_3)_2(CH_3NH_3)n-1Sn_nI_{3n+1}\), which consists of \((100)\)-terminated perovskite layers, structure determination reveals an unusual structural class with sets of \(m \ <110>\)-oriented \(CH_3NH_3SnI_3\) perovskite sheets separated by iodoformamidinium cations. Whereas the \(m = 2\) compound is semiconducting with a band gap of \(0.33 \pm 0.05\) electron volt, increasing \(m\) leads to more metallic character. The ability to control perovskite sheet orientation through the choice of organic cation demonstrates the flexibility provided by organic-inorganic perovskites and adds an important handle for tailoring and understanding lower dimensional transport in layered perovskites.
The basic structures of 2D organic–inorganic perovskite with bilayer and single layer intercalated organic molecules
Schematic representations of hydrogen-bond styles between NH$_3^+$ heads with an inorganic framework
<110> oriented 2D organic-inorganic hybrid perovskite

<110>-oriented \((C_6H_{13}N_3)\text{PbBr}_4\) (API-PbBr\(_4\)) that is prepared by reacting N-(3-amino-propyl)imidazole (API) with PbBr\(_2\) in hydrobromic acid.
5,5’-bis(2-aminoethyl)-2,2’:5’,2’:5’,2’-quaterthiophene (AEQT) based 2D organic-inorganic hybrid perovskite

Room temperature photoluminescence excitation ($\lambda_{em} = 540$ nm) and emission ($\lambda_{ex} = 370$ nm) spectra for thermally ablated thin films of (AEQT)PbX$_4$ with (a) $X = $ Cl and (b) $X = $ I.
Polymerization within the organic layer of perovskite structures

6-amino-2,4-trans,trans-hexadienoic acid, within a cadmium (II) chloride perovskite framework, polymerizes under ultraviolet (UV) irradiation.

More rigid and stable perovskite structure!

Ni(bipy)$_3$ as cations for 2D perovskite as hybrid magnetic semiconductor
Take home message

• Being toxic and instable, Lead-Halide perovskite is an excellent ‘MODLE’ material for electronic application.

• 3D type, Lead-Halide perovskite has found prevailing application in PV field.

• 3D type, Lead-Halide perovskite can be strong competitor to silicon PV

• 2D or 1D type perovskite provide more possibility for more broad applications.
References

1. Band alignment of the hybrid halide perovskites CH3NH3PbCl3, CH3NH3PbBr3 and CH3NH3PbI3
2. Keith T. Butler, Jarvist M. Frost and Aron Walsh
3. Recent progress in efficient hybrid lead halide perovskite solar cells – Jin Cui, Hualiang Yuan, Hong Lin et;al.
5. Perovskite Solar cells: An emerging photovoltaic technology Nam-Gyu Park (SKKU)
Thank you for your attention!