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To my family
Abstract

Methylammonium lead (II) iodide has recently attracted considerable interest which may lead to substantial developments of efficient and inexpensive industrial photovoltaics. The application of this material as a light-absorbing layer in solid-state solar cells leads to impressive efficiency of over 22% in laboratory devices. However, for industrial applications, fundamental issues regarding their thermal and moisture stability need to be addressed. MAPbI$_3$ belongs to the perovskite family of materials with the general formula ABX$_3$, where is the organic cation (methylammonium) which is reported to be a major source of instability. In this work, a variety of alkyammonium lead (II) iodide materials have been synthesized by changing the organic cation, to study the relationship between the structural and physical properties of these materials. Methylammonium, ethylammonium and propylammonium were used for the [(A)PbI$_3$] series. In another set of experiments, butyldiammonium, hexyldiammonium, and octyldiammonium cations were studied as (A)PbI$_4$ perovskite materials. Various dimensionalities for the structures of these materials were found; three dimensional (3D) networks (MAPbI$_3$, MAPbBr$_3$), two dimensional (2D) layered systems (BdAPbI$_4$, HdAPbI$_4$, OdAPbI$_4$), and one dimensional (1D) columns (EAPbI$_3$, PAPbI$_3$, EAPb$_2$I$_6$). Several new lower dimensional materials (2D and 1D) were investigated and reported for the first time. X-ray single crystallography was used to obtain the detailed structures of the products. Bulk structures were confirmed by comparison of the X-ray diffraction patterns with single crystal data. [PbI$_6$] octahedral structural units were repeated through the material network depending on the dimensionality and connectivity of the materials. Where a bulkier cation was introduced, the crystallographic unit cell increased in size which resulted in lower symmetry crystals. The connectivity of the unit cells along the material networks was found to be based on corner-sharing and face-sharing. Lower dimensionality resulted in larger bandgaps and lower photoconductivity, and hence a lower light conversion efficiency for the related solar cells. The thermal and moisture stability was greater in the 1D and 2D materials with bulkier organic cations than with
methylammonium. The electronic structure of the new 2D layered perovskites was investigated by X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and X-ray emission spectroscopy. Density functional theory was applied to calculate band structures, densities of states and partial densities of states. These findings were in agreement with the experimental part, indicating that the valence band is composed mainly of iodine orbitals, while lead orbitals predominate in the conduction band. The iodide/lead ratio obtained from surface analysis of the material deposited on the TiO$_2$ films matched the proposed general formula from single crystal data.

In total, an overview is provided of the relationship between the chemical dimensionality and physical properties of the organic-inorganic lead halide materials with focus on the solar cell application. Keywords: Perovskite, Solar cells, Organic-inorganic lead halide, Dimensionality, Bandgap, X-ray diffraction, X-ray spectroscopy.
Svenska sammandrag:

Metylammoniumbly(II)jodid har under de senaste åren genererat ett stort intresse som ett möjligt material för utveckling av effektiva och på industriell skala billiga solceller. Detta material har använts som ljusabsorberande skikt i fasta solceller med imponerande omvandlingseffektiviteter på över 22% för solceller i laboratorieskala. För att denna nya typ av solceller ska bli intressanta för produktion på industriell skala, så behöver grundläggande frågeställningar kring materialens stabilitet avseende högre temperaturer och fukt klargöras. MAPbI₃ har formellt perovskitstruktur med den allmänna formeln ABX₃, där A utgörs av den organiska katjonen (metyammoniumjonen) och som kan kopplas till materialets instabilitet. I denna avhandling har olika alkylammoniumbly(II)jodidmaterial syntetiserats där den organiska katjonen modifierats med syftet att studera växelverkan mellan struktur och fysikaliska egenskaper hos de resulterande materialen. Material av olika dimensionalitet erhölls; tredimensionella (3D) nätverk (MAPbI₃, MAPbBr₃), tvådimensionella (2D) skiktade strukturer (BdAPbI₄, HdAPbI₄, OdAPbI₄), och endimensionella (1D) kedjestrukturer (EAPbI₅, PAPbI₃, EAPb₂I₆). Flera nya lågdimensionella material (2D och 1D) tillverkats och karaktäriserats för första gången. Enkristalldiffraktometri har använts för att erhålla materialens atomära struktur. Strukturen hos material tillverkade i större mängder konfirmerades genom jämförelse mellan resultat från pulverdiffraktion och enkristalldiffraction. Den oktaedriska strukturenheten [PbI₆] utgör ett återkommande tema i materialen sammankopplade till olika dimensioner. Då större organiska katjoner används karakteriseras i regel strukturerna av större enhetsceller och lägre symmetri. De lågdimensionella materialen ger typiskt större elektroniskt bandgap, lägre fotoinducerad ledningsförmåga och därför sämre omvandlingseffektiviteter då de används i solceller. De lågdimensionella materialna (1D och 2D) som baseras på de större organiska katjonerna uppvisar bättre stabilitet med avseende på högre temperaturer och fukt. De tvådimensionella materialens elektroniska struktur har karakteriseras med hjälp av röntgenfotolektronspektroskopi, liksom röntgenabsorptions- och
emissionsspektroskopi. Resultat från teoretiska beräkningar stämmer väl överens med de experimentella resultaten, och de visar att materialens valensband huvudsakligen består av bidrag från atomorbitaler hos jod, medan atomorbitaler från bly främst bidrar till edningsbandet.

Sammantaget erbjuder avhandlingen en översikt av sambandet mellan kemisk dimensionalitet och fysikaliska egenskaper hos ett antal organiska/oorganiska blyhalogenidmaterial med fokus på tillämpning i solceller.
Abbreviations

Mtoe  Million tonnes of oil equivalent
W    Watt
TW   TeraWatt
AM   Air Mass
AMG  Air Mass Global
t   Tolerance Factor
LHE  Light Harvesting Efficiency
\( \eta \)  Power Conversion Efficiency
\( P_{\text{max}} \)  maximum output Power
\( P_{\text{in}} \)  Power of Incident Light
CIGS  Copper Indium Gallium Selenide
CZTS  Copper Zinc Tin Sulfide/Selenide
CdTe  Cadmium telluride
OSC  Organic Solar Cells
DSSC  Dye-Sensitized Solar Cells
ISC  Inorganic Solar Cells
DFT  Density Functional Theory
XRD  X-ray Diffraction
PXRD  Powder X-ray Diffraction
SXRD  Single X-ray Diffraction
OIH  Organic-Inorganic Hybrid
LED  Light Emitting Diode
3D  Three Dimensional
2D  Two Dimensional
1D  One Dimensional
AMI  Alkylammonium Iodide
LCA  Life Cycle Assessment
DMF  Dimethylformamide
GBL  Gamma-Butyrolactone
HI  Hydroiodic acid
MAI  Methylammonium Iodide
EAI  Ethylammonium Iodide
PAI  Propylammonium Iodide
BdAI\(_2\)  Butyl di-ammonium Iodide
HdAI\(_2\)  Hexyl di-ammonium Iodide
OdAI\(_2\)  Octyl di-ammonium Iodide
MAPbI\(_3\)  Methylammonium Lead (II) Iodide
MAPbBr\(_3\)  Methylammonium Lead (II) Bromide
EAPbI\(_3\)  Ethylammonium Lead (II) Iodide
PAPbI\(_3\)  Propylammonium Lead (II) Iodide
AdAPbI\(_4\)  Alkyl di-ammonium Lead (II) Iodide
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>BdAPbI₄</td>
<td>Butyl-1,4-di-ammonium Lead (II) Iodide</td>
</tr>
<tr>
<td>HdAPbI₄</td>
<td>Hexyl-1,6-di-ammonium Lead (II) Iodide</td>
</tr>
<tr>
<td>OdAPbI₄</td>
<td>Octyl-1,8-di-ammonium Lead (II) Iodide</td>
</tr>
<tr>
<td>HAXPES</td>
<td>Hard X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>HERFD-XANES</td>
<td>High Energy Resolution Fluorescence Detection-X-Ray Absorption Spectroscopy (Near Edge)</td>
</tr>
<tr>
<td>RIXS</td>
<td>Resonant Inelastic X-ray Scattering</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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</table>
List of Publications

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:

I. **Structure and function relationships in alkylammonium lead (II) iodide solar cells.**
   
   **Majid Safdari,** Andreas Fischer, Bo Xu, Lars Kloo, and James M. Gardner
   
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II. **Layered 2D Alkyldiammonium Pb^{2+} Iodide Perovskites: Synthesis, Characterization, and Use in Solar Cells**

   **Majid Safdari,** Per H. Svensson, Minh Tam Hoang, Ilwhan Oh, Lars Kloo, and James M. Gardner.
   
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III. **Spectroscopic Material Characterization of Organic Lead Halide Perovskite Materials**

   **Majid Safdari,** Andreas Fischer, Sergey V. Dvinskikh, István Furó, Lars Kloo, and James M. Gardner
   
   Manuscript

IV. **Impact of Synthetic Route on Structural and Physical Properties of Butyl-1,4-Diammonium Lead Iodide Semiconductors**

   **Majid Safdari,** Dibya Phuyal, Bertrand Philippe, Per H Svensson, Sergei M. Butorin, Kristina O. Kvashnina, Håkan Rensmo, Lars Kloo, and James M. Gardner
   
   Decision of Journal of Material Chemistry A

   Revision

V. **Electronic structure of 2D Lead (II) Iodide Perovskite. An Experimental and Theoretical Study**
Majid Safdari, Dibya Phuyal, Peng Liu, Bertrand Philippe, Kristina O. Kvashnina, Sergei M. Butorin, Håkan Rensmo, Olof Karis, Lars Kloo and James M. Gardner

Manuscript

The author’s contribution in the papers is as follows:

Paper I, II, and III, I initiated the project and performed most of the experiments, analysis of data and wrote the first draft of the manuscript.

Paper IV, I initiated the project and performed most of the experiments (except X-ray single crystallography, X-ray spectroscopy), analysis of data and wrote the first draft of the manuscript.

Paper V, I initiated the project and contributed to the experiments, analysis of data, and writing the first draft of the manuscript.
Papers not included in this thesis:

VI. A quasi-liquid polymer-based cobalt redox mediator electrolyte for dye-sensitized solar cells
Muthuraaman Bhagavathi Achari, Viswanathan Elumalai, Nick Vlachopoulos, Majid Safdari, Jiajia Gao, James M. Gardner, and Lars Kloo

VII. 1,1,2,2-Tetrachloroethane (TeCA) as a Solvent Additive for Organic Hole Transport Materials and Its Application in Highly Efficient Solid-State Dye-Sensitized Solar Cells
Bo Xu, Erik Gabrielsson, Majid Safdari, Ming Cheng, Yong Hua, Haining Tian, James M. Gardner, Lars Kloo, and Licheng Sun

VIII. Investigation of cobalt redox mediators and effects of TiO2 film topology in dye-sensitized solar cells
Majid Safdari, Peter W. Lohse, Leif Häggman, Sara Frykstrand, Daniel Högberg, Mark William Rutland, Rubén Álvarez Asencio, James Michael Gardner, Lars Kloo, Anders Hagfeldt, and Gerrit Boschloo
RSC Adv., 2016, 6, 56580-56588

IX. NMR longitudinal relaxation enhancement in metal halides by heteronuclear polarization exchange during magic-angle spinning
Anna A. Shmyreva, Majid Safdari, István Furó, and Sergey V. Dvinskikh
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1. Introduction

1.1. Energy Demands and Solar Energy
Energy (difference in distribution of energy) drives the universe. It can be defined as the “ability to make a change”. We use energy in every possible aspect of our lives. Energy moves our cars, trains, boats. It grows and bakes our foods, etc.

There are different forms of energy which can be categorized into two major classes: Potential energy and Kinetic energy.

Different sources of energy can be classified as Non-renewable and Renewable energy sources. Non-renewable sources include fossil fuels, coal, uranium, etc. while renewable sources include solar, wind, biomass etc.

All living creatures have used energy—in some form—for thousands of years. Nowadays the energy consumption is increasing and it plays a vital role in development of the human society. The population of the world is increasing and so is the demand for energy. More than 80% of the world population is living in developing countries, and they are trying to boost their living standards, and this results in a higher energy consumption. Figure 1.1 shows that the energy consumption is not evenly distributed over the world. Based on these facts energy demand is expanding. According to the statistics in the “Global Energy Statistical Yearbook 2016” the world’s total energy consumption has increased by over 2% during the last 15 years and it is expected to increase in the near future.

The extensive use of limited sources of energy like fossil fuels generates problems such as pollution, global warming, etc. Hence, the search for new sustainable energy sources is inevitable and crucial.
Solar power is a strong candidate alternative as an energy source due to its nature of being free, clean, highly abundant, renewable and environment-friendly.

The sun is constantly radiating light to Earth with energy of $4 \times 10^{24}$ W.\(^5\)

The practical solar energy potential on the Earth’s surface is 600 TW. Using 10% efficient solar panels, we can utilize 60TW which would be more than double the energy demand projected in 2050.\(^6\)–\(^9\)

Sunlight reaching the surface of the Earth covers a wavelength range from ultraviolet to infrared. Solar irradiation is influenced by atmospheric absorption, the position of the sun and the pathway of the photons. A standardized version of this spectral irradiation is the Air Mass 1.5 Global spectrum (AM1.5G) presented in figure 1.2.\(^10\)

**Figure 1.1.** Geographical distribution of energy consumption in 2015.\(^1\) Energy consumption unit is reported as Mtoe and is “Million Tonnes of Oil Equivalent”.

**Figure 1.2.** Solar irradiance spectra at the top level of the atmosphere (AM0) and at sea level (AM1.5G)\(^10\). The spectra include the global tilting angle.
The Air Mass is the path length for photons through the atmosphere; AIR mass 1.5 is 150% of the standard AIR Mass. AM1.5G corresponds to an irradiation with an integrated power density of 1000 W/m² (100 mW/cm²). This is the most commonly used spectrum and represents the terrestrial solar spectral irradiance on a clear day with the recipient surface plane tilted at an angle of 37° with respect to the sun.

1.2. Organic-Inorganic Hybrid Materials

Organic-inorganic hybrid (OIH) materials are an enormous family of materials with a large variety of structures. The diversity of the materials based on inorganic and organic components, opens up a window for the interesting scientific exploration of new functional materials which can potentially be applied in technological advancement. Pure organic materials are easily accessible as thin films originating from low-cost processing methods such as spin coating, and their interesting conductive and light-emitting properties have led to a great advancement in their application in electronic devices, but, the low stability (thermal and mechanical) of organic materials reduces the life time of their devices. OIH materials, however, allow the merging of useful properties of organic and inorganic materials. The synthesis of these materials makes it possible to enhance the chemical, physical and/or structural properties with respect to the organic or inorganic part alone. The bonding interaction between these units can range from strong interactions (e.g. covalent, ionic bonding) to weak interactions (e.g. Van der Waals or hydrogen bonding). The structural network of these materials consists of sequentially repeating units of organic and inorganic parts. Within these networks, the inorganic part can show high conductivity and this can be added to the possible light interaction of the organic part. During recent years, a large number of these materials have been structurally and/or physically investigated. Several alternative metals have been used as the core metals for these materials such as triply charged metals: bismuth (Bi)\textsuperscript{12-14}, antimony (Sb)\textsuperscript{13, 15} and doubly charged metals, of which are the most common examples are copper (Cu),\textsuperscript{16} manganese (Mn)\textsuperscript{17}, germanium (Ge),\textsuperscript{18} tin (Sn)\textsuperscript{19-22} and lead (Pb)\textsuperscript{23-26}. The ease of structural modification of these materials by
altering the dimensionality of the inorganic frame or the functionality of the organic part leads to unique impressive photo-electrochemical properties, and these materials have shown advanced physical properties such as a band-gap range leading to a broad spectrum of light absorption and luminescence, high electron and charge conductivity, and potential thermal stability.\textsuperscript{11, 26} These characteristics are the main inspirations for the application of these materials in modern optoelectronic devices e.g. solar cells, light-emitting diodes (LEDs), etc.\textsuperscript{27, 28} Although some of these materials have amorphous structures, most of them are crystalline materials.\textsuperscript{11, 29} Their high degree of crystallinity means that they can be structurally investigated by methods such as X-ray diffraction. This thesis focuses on the relationships between the chemical structures of these materials and their possible functionality.

Perovskite structure is one of the important families of large organic-inorganic hybrid materials. This structure was first found in a purely inorganic material, calcium titanium oxide (CaTiO$_3$) by Gustav Rose and it was named perovskite after the Russian mineralogist Lev Perovski.\textsuperscript{30} The structure has the general formula ABX$_3$, where B is a metal cation and X is an anion either singly charged like a halide, Cl\textsuperscript{-}, Br\textsuperscript{-}, I\textsuperscript{-} or doubly charged like O\textsuperscript{2-}, S\textsuperscript{2-}, etc.\textsuperscript{31} The cation can be either organic or inorganic. The unit cell is a BX$_6$ octahedron where B is at the center surrounded by six bonded Xs. The network is built through the repeating of unit cells by corner connection. The A cations are placed in the 12 coordinated holes between the consecutive unit cells (See Figure 1.3).

\textbf{Figure 1.3.} The basic unit cell for ABX$_3$ perovskite showing the cubic structure in the ideal form.
In the ideal cubic structure the B-X-B angle is 180° but depending on the conditions, several adjustments may happen to the octahedral units resulting in a tilted angle and lower symmetry. The structure of these materials is extremely dependent on the size of the cation and on the functionality between the cation and the metal. Furthermore, the connectivity of the octahedral units can be affected by these factors leading to corner-sharing, face-sharing, or edge-sharing. The two latter cases (face-sharing and edge-sharing), lead to non-perovskite networks.

Through the connectivity of these structural octahedral units, several different structural networks can be formed: if the connectivity is along all three axes, a three-dimensional (3D) perovskite network is created, but if the connectivity is lost in one or two axes, the structure becomes two-dimensional (2D) or one-dimensional (1D), respectively. The general formula for 2D materials can be A$_2$MX$_4$ or A$^{2+}$MX$_4$, etc, while that for the 1D material is A$^{3+}$MX$_5$ or A$_3$MX$_5$ etc.
Figure 1.4. Schematic diagram of the building of structural units from octahedral unit cells. Three unit cells were added in each axis leading to 3-units 1D rods, 3×3 2D structural planes, and 3×3×3 3D networks respectively. The connectivity of the unit cells is through corner-sharing. For the sake of simplicity the A cation is not shown.

Doubly charged cations can also be used to replace two singly charged A cations, for example in 2D-A$_2$MX$_4$ or 1D-A$_2$M$_2$X$_6$. Several examples of new structures based on the doubly charged cations have been introduced and investigated in this work.

In many cases, structural distortions have been observed in the perovskite structure. The reason for existence of these lower symmetry structures is that A and/or B ions are not fitted to the size that is provided by the remaining components.\textsuperscript{31} A tolerance factor (t) is determined by the atomic radii of the three components and is calculated as

\[
t = \frac{(R_A + R_X)}{\sqrt{2}(R_X + R_B)} \quad (1.1)
\]

where \(R_A\), \(R_B\), and \(R_X\) are the atomic radii of the three components in the perovskite structure. To maintain a perfect cubic three-dimensional structure, \(t\) should be in the range of 0.813<\(t\)< 1.107.\textsuperscript{31-33}

The structural dimensionality is also highly dependent on the ratio between the metal and the anions, the solvent reactivity and the temperature and pressure of reaction. The synthetic route is crucial, as it can lead to different structural and physical properties. Some of the findings in the present studies cover these facts (see section 3.4).

1.3 Solar Cells
A solar cell or photovoltaic device is a device that absorbs sunlight and converts it to electricity. The efficiency of this device is the absorbed light divided by the total illumination, and power conversion efficiency (\(\eta\)) of a solar cell is the maximum output power (\(P_{\text{max}}\)) divided by the input power (\(P_{\text{in}}\)).

There are different types of solar cells which can be divided into three different classes or generations of solar cells. They differ in both their light-harvesting material component and their mechanism of conversion of light into charge carriers. The first generation of solar
cells was based mainly on crystalline silicon, which dominated in technological applications of photovoltaics because of its high efficiency and stability. The second generation was based on amorphous silicon, copper indium gallium selenide (CIGS), or cadmium telluride (CdTe). They had a lower conversion efficiency than the first generation but were cheaper. In the third generation, solar cells are based on the organic materials and were intended to break the Shockley-Queisser limit, although none actually have achieved this breakthrough. A wide range of materials can be sensitized for applications in these solar cells,\(^{34,35}\) giving several benefits such as the potential for absorption of a larger fraction of sunlight, cheaper materials, fabrication simplicity, etc.\(^6\) Organic solar cells (OSC), and dye-sensitized solar cells (DSSC) are examples of these devices. The working principle of inorganic solar cells (ISC) and DSSC is summarized in Figure 1.5. The charge separation in junction solar cells is governed by an electric field generated at the p-n contact intersection.\(^{36}\) In the dye-sensitized solar cells, light absorption and charge injection are decoupled from the charge diffusion processes that occur in the semiconductor.\(^6\)

**Figure 1.5.** The basic working principle of the generation of exciton in a. Junction (inorganic and organic) solar cell and b. Dye-sensitized solar cell.\(^6,36\)

1.3.1 Thin Film Solar cells
This family of solar cells also known as second generation solar cells, which includes amorphous silicon, cadmium telluride (CdTe), cadmium sulfide(CdS), copper-indium-gallium-selenide (CIGS) and copper-zinc-tin-sulfide/selenide (CZTS).\(^{34}\) These solar cells have an inorganic light-absorbing layer with a high extinction coefficient so that a thin film is
enough for light absorption. Therefore they are called thin film solar cells.

The greatest efficiency for crystalline silicon solar cells is reported to be 25.6%\textsuperscript{37} but their high production cost is the main disadvantage of these solar cells in close competition with other solar cell technology. Solar cells with a much lower production cost, based on a chalcopyrite (copper, indium, gallium, selenide) absorbing layer are the main competitor for silicon solar cells.

1.3.1.1 CIGS solar cells
From the first report in 1974\textsuperscript{38} till now the growing interest in CIGS solar cells resulted in the record efficiency of 21.0%\textsuperscript{37} on a glass substrate and over 18% on a flexible substrate.\textsuperscript{39,41} To make a typical CIGS solar cell, a glass substrate is covered by a back contact molybdenum layer followed by a copper, (indium, gallium) selenide (sulfur) light-absorbing layer. A cadmium sulfide buffer layer is then deposited. Finally, solar cell is completed by a layer of zinc oxide (ZnO) and/or zinc oxide-aluminum on the front surface.\textsuperscript{39,42,43} Vacuum-based techniques are used to make this type of solar cells. The CIGS absorbing layer is produced through two processes. In the one-step method, all materials (CIGS) are deposited in a single step by using various evaporation processes. In the two-step process, the Copper, Indium and Gallium are first deposited, and the sulfurization or selenization sulfur(S) or selenide (Se) process then follows.

1.3.2.2 CdTe/CdS Solar Cells
Solar cells based on a CdTe layer have reached an efficiency of 21.0 % on a glass substrate.\textsuperscript{37} Through a vacuum-based method, the conductive glass substrate is covered by an n-layer of CdS and then a p-layer of CdTe. The final layer is a back contact, usually aluminium (Al).\textsuperscript{44} The structural simplicity of these solar cell means that they are easy to make and therefore a competitive candidate in solar cells technology.\textsuperscript{45, 46} In addition, the band gap for the CdTe is 1.5 eV, very close to the optimum band gap for the p-n junction solar cells due to their black body limit.\textsuperscript{47}
1.3.2. Dye Sensitized Solar Cells (DSSCs)

The manufacture of the efficient solar cells discussed so far requires specific techniques (such as high vacuum and temperature) and high purity materials in a clean environment. This leads to the consumption of a large amount of energy in the production process. DSSCs and perovskite solar cells (PSC-section 1.3.3) are however usually processed in solution resulting in a lower potential production cost.

A dye-sensitized solar cell consists of a sensitized photo-anode, cathode and electrolyte (in liquid DSSC) or a solid state hole transport layer (in solid state DSSC). The anode is based on a metal-oxide high band-gap semiconductor (e.g. titanium dioxide: TiO$_2$, zinc oxide: ZnO$_2$, etc) chemically bound to a dye molecule through a sensitization process. The redox couple (in liquid DSSC) or hole transport layer (in solid state DSSC) acts as a charge transport bridge between the anode and cathode. Conventional liquid DSSC uses platinum cathode, and solid state DSSC has silver as cathode.$^{6,48-50}$

As it was presented in Figure 1.5.b, the exciton is produced after light absorption by the dye molecule. Charge separation occurs first by electron injection into the conduction band of the oxide semiconductor /TiO$_2$. Then the oxidized dye is regenerated by either a redox couple or a hole transport layer. Since the discovery of dye-sensitization by Moser in the late 19th century$^{51}$ great efforts have been made to increase our knowledge and to boost the efficiency of these solar cells, but the milestone was in 1991, when O’Regan and Grätzel reported a 7% efficiency for liquid dye sensitized solar cells.$^{50}$ the current world record for these solar cells is over 14% $^{52}$ for liquid DSSC and 7.7% $^{53}$ for solid state DSSC.

1.3.3 Perovskite Solar Cells (PSCs)

A perovskite solar cell is defined as a solar cell which uses mainly organic-inorganic halide perovskite as light-absorbing component and in some cases as a hole transporting material.$^{54,55}$ Perovskite materials have been known for many years (Section 1.2) but their application in solar cells started only recently. Methylammonium lead (II) iodide [(MA)PbI$_3$] is the most famous material for this application. The cubic
structure of (MA)PbI$_3$ was first reported by Weber in 1978. The cubic structure is stable at temperatures above 56 °C and at lower temperatures it transforms to a structural phase with a tetragonal and orthorhombic structure. This phase transition is due to the molecular motion of the methylammonium cation along the C–N axis. Due to the unique properties of this material such as a medium direct band gap of 1.5eV, relatively high absorption coefficient, and high carrier mobility, it is a strong candidate for solar cell application. In addition, the fact that they are processable in solution and maintain high crystallinity with few defects in the mesoscopic semiconductor films strengthens their utilization in solar cells. The solution-based synthesis is one of the cheapest ways to achieve for efficient crystalline films for these materials, in contrast to high-vacuum-based synthetic routes which have a high energy consumption. The high-vacuum-based synthetic routes are still applicable for some types of thin solar cells e.g. CIGS and CdTe solar cells. The use of (MA)PbI$_3$ in solar cells started in 2009 by Kojima et al. where they used it as light-absorbing material in liquid dye-sensitized solar cells. The fabricated solar cells had 3.8% conversion efficiency but very poor stability due to the solubility of the organic cation of the perovskite in the electrolyte solution. The novelty of the work was nevertheless noticed 2-3 years later and led to the development of perovskite solar cells. The key turning point was changing from liquid solar cells to solid state solar cells using a hole transport material. This leads to a very rapid development in conversion efficiency starting from 9%. The conventional solid state hole transport material is a p-type organic semiconductor named Spiro-OMeTAD (2,2’,7,7’-tetrakis-(N,N-di-p-methoxy-phenl-amine)9,9’-spirobiofluorene) which is still used in the most efficient perovskite solar cells. Several modifications have been made to the composition and procedure for solar cells. Mixed halide perovskite with the composition (MA)PbI$_{3-x}$Cl$_x$ has gained attention since Lee et al first used it in solar cells. Previously reported data have shown that most of the chlorine evaporates during the annealing step, but a very small portion of the chlorine (depending on the
concentration of chlorine reagents) remains in the structure of the materials. A higher crystallinity was reported for the chlorine-containing perovskite which led to longer charge carrier diffusion lengths but a band-gap similar to that of the pure iodine perovskite. The effect of changing the halide composition has been investigated in several reports mainly leading to band gap changes. The halide moiety affects the electronic structure rather than the chemical structure, resulting in a variety of band-gap values while maintaining the 3D perovskite structure. This observations mainly led to obtaining a higher open circuit voltage for solar cells or band-gap tuning for possible application of the materials in tandem solar cells. A boost in the efficiency of these solar cells was achieved when the perovskite film properties were improved by using mixed halide composition, mixed cation composition, and/or solvent engineering, reaching a current efficiency of 22.1%. Currently the most efficient solar cells are based on a complex light-absorbing layer composed of triple cation (methylammonium, formamidinium, and cesium) lead iodide/bromide. Some of the major advances in perovskite solar cell efficiency are summarized in Figure 1.6.

**Figure 1.6.** Development of Perovskite Solar Cells.

Due to this rapid advance in the efficiency of the solar cells, there is an urgent need to work on the industrialization of these types of solar cells.
However, there are many fundamental questions that need to be addressed regarding the material itself and the structure of the solar cell. A crucial question is the instability of the material layer under ambient conditions.\textsuperscript{76, 77} The methylammonium cation is soluble in the water sorbed from moisture in the air, resulting in the degradation of the (MA)PbI\textsubscript{3} layer into lead iodide (PbI\textsubscript{2}). Reported study on ZnO/(MA)PbI\textsubscript{3} interface showed proton-transfer reaction as the origin of instability. Moreover, hole transport layer has a severe effect on the degradation process.\textsuperscript{78, 79} On the other hand, most of the interesting physical properties of the perovskite originate from the chemical structure and high crystallinity of the film deposited on the substrate. Any instability or deviation in the structure drastically changes the physical properties. Hence, almost all of the laboratory-efficient solar cells have been fabricated in an inert atmosphere e.g. nitrogen (N) or argon (Ar) inside a glove box. Several attempts have been made to modify the solar cell fabrication process to improve the long-term stability.\textsuperscript{77, 80} However, it is still urgent to introduce new materials with similar properties and higher stability. Because of the instability in the chemical composition of MAPbI\textsubscript{3}, a few examples of new materials where the methylammonium moiety is replaced by a more stable cation have been reported.\textsuperscript{81-83} There are also environmental concerns about the material due to the toxicity of lead and pollution by methylammonium iodide. According to the life cycle assessment (LCA) of the perovskite solar cells by Espinosa et al\textsuperscript{84}, lead has a high human toxicity cancer effect and methylammonium iodide surprisingly dominates the freshwater ecotoxicity issue.

Despite great efforts to boost the efficiency of the solar cells, few reports have addressed the fundamental aspects of the unprecedented functionality of these materials. Change in the chemical composition of these materials have a major effect on physical properties such as light absorption or conductivity.\textsuperscript{85} Thus, understanding the fundamental structural properties and relating them to the physical properties of the
material is a crucial step to meet the challenge of making new materials.
1.4. The aim of thesis
Organic-inorganic halide (OIH) materials are a family of materials that have attracted a lot of interest in several fields, from fundamental studies to their possible technological applications. Among the OIH materials, methylammonium lead (II) iodide perovskite has contributed enormously to the advancement of solar cell research, but some fundamental question regarding the properties of these materials need to be addressed. Their poor stability toward heat and moisture is one of the main questions. The methylammonium moiety shows very low stability and dissolves in water from moisture in the air or evaporates at high temperature, and this leaves PbI₂ with completely different chemical and physical properties. In the present work, attempts have been made to produce new materials with new chemical structures. Several new OIH lead (II) halide materials have been synthesized and characterized. The new materials were based on varying the cation moiety in the methylammonium lead(II) halide perovskite. These materials showed very high stability compare to methylammonium based material. Detailed structural information was obtained by single crystal X-ray characterization, followed by X-ray powder diffraction and in some cases Raman spectroscopy, showing whether these materials crystalized in three-dimensions networks, two-dimensional planes, or one-dimensional columns. Examples of perovskite and non-perovskite structures were obtained. The stability of the new materials was assessed and compared with that of methylammonium lead(II) iodide. Change in the structure has effect on the physical properties of these materials and investigation of these properties is one of the main aims of this work. Several methods were used to investigate physical properties such as conductivity, and light absorption. Higher bandgaps and lower conductivities were obtained for the lower dimensional structures. This originates from the limited atomic connection for these material compare to convention three dimensional methylammonium lead(II) iodide. Several X-ray spectroscopy techniques have been used to investigate the electronic structure of these materials and track the changes due to changes in the chemical structure. The electronic structures of new materials were thoroughly investigated near both
valence bands and conduction bands, and the electronic structures were related to their chemical structures, to show the effect of bonding environment and local coordination in the valence band and conduction band compositions.

The functionality of these materials in the solar cells has finally been investigated. The efficiency of the fabricated solar cells was up to 1.1%. Despite rather high band-gap values for these materials, the recorded efficiencies were impressive. As a first step, the solar cells were prepared based on the optimized condition for the conventional perovskite solar cells. Further improvement can be expected with device engineering.

In total, the main aim of this thesis is to present a comprehensive database for the structural and physical properties of these materials, and to relate the functionality of the materials in the solar cells to these properties.
2. Experimental Methods & Characterization Techniques

2.1. Material Synthesis and Crystal growth

Solution techniques are the most feasible methods for the synthesis and crystal growth of the OIH materials. Hence, a feasible way to make OIH lead-based perovskite materials is to mix lead halide with the salt of an organic halide in a suitable solvent. Based on the solubility of the organic and inorganic components, dimethylformamide (DMF), gamma-Butyrolactone (GBL), and water (H2O) have been used. The important physical properties of these solvents for the synthesis of OIH materials are presented in table 2.1. Hydriodic acid (HI) has also been used as additive to some of aqueous solutions.

Table 2.1. Properties of solvents used for the synthesis of OIH materials.\cite{56, 87}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling point (°C)</th>
<th>Vapor pressure (mmHg) at 20 °C</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>153</td>
<td>2.7</td>
<td>0.92</td>
</tr>
<tr>
<td>GBL</td>
<td>204</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td>H2O</td>
<td>100</td>
<td>17.5</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Depending on the activities of the components and the products, different stoichiometries of starting materials were chosen to initiate the synthesis. Optimization of the temperature and time is necessary for completion of the reaction in the solvent. Figure 2.1 illustrates the synthetic routes which have been used in this work.

![Figure 2.1. Schematic diagram of the synthesis of OIH lead halide materials.](image)
Chemicals were purchased from Sigma-Aldrich unless otherwise stated. Hydriodic acid was purchased from Alfa Aesar. For the synthesis of the mono-ammonium iodide salt, the 1:1 mole equivalent stoichiometry of the HI (57% w/w in water with 1.5% hypophosphorous acid as stabilizer) was mixed with the relevant alkyamine. For methylammonium iodide (MAI), ethylammonium iodide (EAI), and propylammonium iodide (PAI), 15 mL of HI was mixed with 13.9 mL of methyl amine (40% w/w in methanol), 10.8 mL of ethylamine (70% in water), or 11.2 mL of propylamine (>99%). For methylammonium bromide, hydrobromic acid (15.3 mL of 48 wt. % in water) was mixed with methylamine (14.1 mL of 40% methyl amine in methanol). The solutions were stirred at 0°C for two hours, and the alkylammonium halide salts were recovered by evaporation of the solvent at 50°C using a rotary evaporator. Products were washed three times with diethylether (>99.0%), followed by drying at 60°C overnight:

\[
\text{[A]X} \quad \text{(2.1)}
\]

The same procedure was used for the preparation of methyl ammonium bromide, where 15.3 mL hydrobromic acid (48 wt. % in water) was mixed with the 14.1 mL methylamine (40% in methanol).

For the preparation of diammonium iodide salts, 1 mole equivalent of the relevant alkyldiamine was mixed with 2 mole equivalents of hydriodic acid. For the preparation of butyldiammonium iodide (BdAI₂), hexyldiammonium iodide (HdAI₂), and octyldiammonium iodide (OdAI₂), 3.18 g of 1,4-diaminobutane (99%), 4.22 g of 1,6-diaminohexane (98%), or 5.30 g of 1,8-diaminoctane (98%) were mixed with 13.4 g of HI (57% w/w in water with 1.5% hypophosphorous acid as stabilizer). The solutions were stirred at 0°C
for two hours. After evaporation of solvent, the recovered products were washed with diethyl ether and dried at 60 °C overnight:

\[
\text{di-alkylamine} + 2\text{HI} \rightarrow \text{di-alkylammonium iodide} \quad (2.2)
\]

Note: Extra alkylamine or alkyldiamine (~12 w%) was added to the reaction mixture to avoid any residual HI in the products. The remaining alkylamine or alkyldiamine were washed away from the minor residual solution during the evaporation of solvent and washing with diethyl ether after the reaction.

For materials synthesis, a mixture of the relevant alkyl (di)ammonium iodide salt and lead iodide salt was stirred in a suitable solvent. The details of the experimental conditions are given below.

For alkylammonium lead iodide [(A)PbI\(_3\)], a 1:1 equivalent molar ratio of alkylammonium iodide and lead iodide (99.999%) (PbI\(_2\)) were dissolved in dimethylformamide (anhydrous, 99.8%, DMF). For the syntheses of methylammonium lead iodide, ethylammonium lead iodide [(EA)PbI\(_3\)], and propylammonium lead iodide [(PA)PbI\(_3\)], 207 mg of MAI, 225 mg EAI, or 243 mg PAI were mixed with 600 mg of lead(II) iodide in 10 ml of DMF. Methylammonium lead bromide [(MA)PbBr\(_3\)], was synthesized through a mixture in 1:1 molar ratio of 145 mg of methylammonium bromide mixed with 477 mg of lead(II) bromide (PbBr\(_2\)) (99.999%) in 10ml DMF.

The solutions were stirred at 60°C overnight, and any precipitate was filtered with a 0.45 µm PTFE syringe filter. The powder products were recovered by evaporation of the DMF and drying under vacuum overnight:

\[
PbI_2 + (A)X \xrightarrow{1) \text{Adding GBL, stir overnight at 60 °C}} APbX_3 \quad (2.3)
\]

1) Stirring at 0 °C for 2 hours
2) Product recovery by solvent evaporation
3) Washing with diethylether and drying
The procedure for crystal growth of the (A)PbI₃ materials has been reported elsewhere.²⁴ Solutions of (A)PbI₃ in GBL with a concentration of 400 mg mL⁻¹ were heated to 100 °C. After 30 minutes, the solutions were slowly cooled at a rate of 3 °C per hour. Crystals started growing at ~70 °C. For (MA)PbI₃ crystals were obtained at a temperature above 55°C due to the phase transition at this temperature, but (PA)PbI₃ crystals were picked from the solution at room temperature.

For synthesis of one-dimensional butyldiammonium lead iodide ([NH₃(CH₂)₄NH₃]Pb₂I₆, (BdA)Pb₂I₆), BdAI₂ and Pbl₂ with a mole ratio of 1:2 were mixed in DMF. 0.739 g of BdAI₂ with 1.982g Pbl₂ were dissolved in 5ml of DMF, stirred at 60 °C overnight. 1 ml of the solution was used for crystal growth. When the solvent was evaporated from the remaining part, a yellow powder remained. The product was washed with diethyl ether three times, and finally dried under vacuum overnight:

\[
PbI₂ + (1/2)(BdA)I \rightarrow BdAPb₂I₆ \quad (2.4)
\]

For the synthesis of two-dimensional alkyldiammonium lead(II) iodide [(AdA)PbI₄] perovskites, a solution in HI of 1 mole equivalent of dAI₂ mixed with a solution in HI of 2 mole equivalents of Pbl₂. For the synthesis of two-dimensional butyldiammonium lead(II) iodide [(BdA)PbI₄], heptyldiammonium lead(II) iodide [(had)PbI₄], Octyldiammonium lead(II) iodide [(OdA]PbI₄], 0.5157g of BdAI₂, 0.5577g HdAI₂, or 0.5997g OdAI₂ was dissolved in 3ml of HI. Each of these solutions was mixed with a solution of 1.383 g Pbl₂ in 4 ml HI and stirred at 90 °C for 1 hour. After evaporation of half (or slightly more than half) of the solvent, the magnetic stir bar was taken out and the solution was cooled slowly at a rate of 3-5°C per hour. The cooling process was continued to -10°C in order to grow single crystals with a size suitable for crystallography. After removal of some of the applicable crystals, the remaining precipitate was washed with diethyl ether and dried under vacuum overnight.
Note: To recover powders of the products during evaporation of the solvent, a small portion of the solution was kept, the precipitate was filtered and washed with diethyl ether followed by drying under vacuum.
2.2. Chemical Structure Characterization

2.2.1 X-ray Diffraction (XRD)

X-ray powder diffraction of a crystalline material leads to a unique characteristic. This method is normally used to identify the detailed spatial arrangement of the atoms in a material, provided that the material is crystalline. If the material is amorphous, X-ray analysis can still provide information about the local structure. XRD patterns can also be used to identify already known phases by comparison with database information. There are different structural factors that can be identified by XRD, for example, unit cell’s shape and size and atomic spacing. The radiation from the X-ray source hits the sample and is diffracted in all directions. The regular pattern for the atomic arrangements in a crystalline material is obtained due to interference of rays diffracted from different crystalline planes. Constructive interference occurs when the path lengths of rays diffracted from different planes differ by a multiple of the wavelength.

![Figure 2.2](image)

Figure 2.2. Two parallel incident X-rays reflected from crystalline planes separated by a distance d.

Bragg's Law (equation 2.6) explains how a diffraction peak is produced. Constructive interference occurs when condition of Bragg’s law is obtained:

\[ n\lambda = 2d \sin \theta \]  

(2.6)

where \( \lambda \) is the wavelength of the irradiation, \( \theta \) is angle of the scattering, and \( d \) is the distance between the structural planes. Unit cells in the samples are randomly oriented, so by doing the experiment in the 2θ range all of the directions for the diffractions are involved in the obtained patterns.\(^{89,90}\)
Powder X-ray diffraction (PXRD)
A PANalytical- X'Pert PRO diffractometer equipped with an X-ray tube for Cu-Kα radiation has been used. Homogenized fine powder samples were prepared by grinding in a mortar. For the thin film samples, a fixed angle for the X-ray radiation was chosen. Diffraction patterns were obtained over a 2θ range of 5-80° or 5-40°. Depending on the important peaks, the appropriate 2θ range was chosen for presentation of the data.

Single Crystal X-ray Diffraction (SXRD)
With this non-destructive technique, detailed information about the crystalline sample can be obtained, including types of atoms, unit cell parameters, bond lengths and angles, lattice ordering, etc. During the analysis, the interaction between X-ray irradiation and the electrons of the atoms in the single crystal results in an image pattern and a structural report is prepared based on the data collection after solving and refining the structure.

Two instruments were used for the single crystallography of the samples. For characterization of (A)PbI₃ and (MA)PbBr₃, data were collected on a Bruker-Nonius KappaCCD diffractometer in the Applied Physical Chemistry Division at KTH. Corrections of the absorption based on multiple scans (SADABS) were applied. The structures were resolved using direct methods, and these structures were refined on F₂ with anisotropic thermal parameters for all non-hydrogen atoms.

For single crystallography of the (BdA)Pb₂I₆ and (AdA)PbI₄ series, a Bruker APEXII diffractometer (MoKα radiation) with a CCD detector at SP Process Development, Södertälje was used. Data collection was carried at 200K. Crystals were placed on a cryoloop using low-temperature immersion oil and placed in a N₂ cold stream. Data were recorded by ω-scans and φ-scans and integrated with the Bruker SAINT software. A function of the empirical transmission surface was
used for fitting and correcting the absorption (Bruker SADABS). To solve and refine the structures, SHELXS and SHELX were used. A direct method was used to resolve the structure, resulting in positioning of the non-hydrogen atoms, after which the positions of the hydrogen atoms were calculated. Using the anisotropic thermal parameters, final refinements were achieved for all non-hydrogen atoms.

2.2.2. Raman Spectroscopy
Raman Spectroscopy is based on the inelastic interaction of light with molecular energy levels. The samples are illuminated by radiation from a strong light source and a detector collects the scattered light. The interactions between the incident light and the samples lead to changes in the frequency of the incident light monitored by the detector. The scattered light with frequencies different from that of the incident light is presented as a Raman spectrum. Raman spectra are presented as intensity vs Raman shift in cm\(^{-1}\). Although most of the scattered light has the frequency of the incident light (elastic scattering), a small part has a different frequency and is used to construct the Raman spectrum. Scattered light with a frequency less than that of the incident light (energy has been absorbed by systems in predominantly the ground state) represents Stokes lines. On the other hand, recorded scattered light having a frequency higher than that of the incident light is considered as anti-Stokes (energy has been emitted by the systems in predominantly excited states). The Stokes bands represents transitions from lower to higher excited vibrational levels; hence, they have higher intensities measured in conventional Raman spectroscopy (there are simply more systems in the ground state than in excited states). Figure 2.3 shows the different Raman shifts.
For doing the Raman characterization, a BioRad FTS 6000 spectrometer was used, equipped with a quartz beamsplitter and a nitrogen-cooled Ge detector. A resolution of 4 cm\(^{-1}\) was used. Powder samples were ground prior to the experiment to give a fine powder well packed in the experimental tube-sample holder.

2.3. Physical Characterization

2.3.1. Steady state (UV-Visible) Absorption Spectroscopy

Many molecules or materials absorb ultraviolet (UV) or visible (Vis) light of specific wavelengths. This is the basis of absorption spectroscopy which can be used for qualitative or quantitative analysis. The absorption of light passing through a solution is described by the Beer-Lambert Law:

\[
A = log_{10} \frac{I_0}{I} = \varepsilon \cdot b \cdot c \quad (2.7)
\]

where \(I_0\) is the intensity of the incident light and \(I\) is the intensity of the transmitted light, \(\varepsilon\) (M\(^{-1}\)cm\(^{-1}\)) is the absorption coefficient, b (cm) is the length of the light path, and c (M) is the concentration of the solution. This formula can be used to compare different species, but absorption spectroscopy can also be used to study solid samples. Electronic transitions from lower to higher energy levels can be studied by applying this technique. Depending on the quantized energy levels of the molecules/materials, energy is needed for electronic transition to occur. In the molecules, this transition typically takes place from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This is the lowest energy transition, but many higher energy transitions can take place. In semiconducting materials, light absorption causes electronic transition from the valence band (VB) to the conduction band (CB).\(^93\)\(^94\) This value corresponds to the band-gap. A Cary 300 spectrophotometer was used in this work to record the absorption spectra. For all the materials, an absorption edge in the
visible region was observed. For the band-gap calculation the Tauc equation was used.  

\[(\alpha h\nu)^{1/n} = A (h\nu - E_g) \]

where \(\alpha\) is the absorption coefficient, \(h\) is Planck constant, \(\nu\) is the frequency in eV, \(E_g\) (eV) is the bandgap and \(A\) is normalization constant. \(n\) is equal to ½ and 2 for indirect and direct band-gap semiconductors respectively.

2.3.2. Conductivity measurements

Electrical conductivity is an important property of materials for solar cell applications. For semiconducting films, such as the materials used in this work, the dimensionality of the materials, the orbital overlap between different atoms, and the crystallinity of the films affect the conductivity. The conductivity measurements were made with a two probe device.

![Figure 2.4](image)

**Figure 2.4.** Schematic diagram of the devices used for the conductivity measurement. The conductivity value was reported as the average of the values obtained from the different illustrated measurements.

For preparation of the device, a defined thickness of mesoporous TiO\(_2\) layer was coated on a non-conducting glass, followed by spin coating a layer of the DMF solution of the hybrid materials on top of the TiO\(_2\) film. A crystalline film was created by annealing, and a 200nm thick layer of silver (Ag) was thermally evaporated as the final step. A bias voltage in the range of -1V to 1V was applied across the two electrodes, and the photocurrent response was recorded (See Figure 2.4). The slope of the current-voltage curve was determined as the reverse of resistance (\(R\)) and the conductivity (S.cm\(^{-1}\)) was calculated as

\[\sigma = \frac{W}{RLd} \]

(2.9)
where $W$ is the distance between two neighboring Ag contacts, $L$ (cm) is the length of the Ag contact and $d$ (cm) is the thickness of the film of TiO$_2$ and hybrid material (Figure 2.2). The thickness was corrected for the porosity of the TiO$_2$ film by multiplying the thickness of TiO$_2$ by a factor of 0.6. The thickness of top layer of the material (if any) was considered in the calculations.$^{96,97}$

2.3.3. DFT Calculation

Data based on Density Functional Theory (DFT) were obtained through collaboration and the author did not personally perform the calculations. DFT calculations were applied to obtain the band structure of the two-dimensional materials in paper V. Density of states (DOS) and partial density of states (PDOS) near the valence band (VB) and conduction band (CB) edge were obtained. This data support the X-ray spectroscopic data obtained on the VB and CB and have been used to create the electronic structure of these materials.

CRYS\textsc{tal} 09 code was used to perform the theoretical calculations.$^{98}$ To correct for the exchange-correlation interaction, the Perdew-Burke-Ernzerhof function was applied.$^{99}$ Effective core potentials (ECP) of the Stuttgart-Dresden type$^{[3]}$ were used for the lead and iodine atoms and the 6-3111G basis sets were used for carbon, nitrogen and hydrogen atoms.$^{100}$ To calculate the density of states (DOSs), a k-point mesh was chosen using Monkhorst–Pack net and a 6×6 shrinking factor was also used.$^{101}$

2.3.4. X-ray Spectroscopy

Three techniques based on X-ray illumination have been used in the work described in papers IV and V. The author has not made these characterizations. The electronic structure of the materials was investigated using Hard X-ray Photoelectron Spectroscopy (HAXPES), High Energy Resolution Fluorescence Detection X-Ray Absorption Spectroscopy (HERFD-XANES), and Resonant Inelastic X-ray Scattering (RIXS). Valence band of the OIH samples were investigated and minor shifts of the VB edges are detected. Occupied
and unoccupied states of the iodine were characterized indicating the iodine orbital contribution in VB and CB.

**HAXPES**

HAXPES was performed at BESSY II (Helmholtz Zentrum Berlin) at the KMC-1 beamline using the HIKE end-station. The photon energy was fixed at 4000 eV. A Model R4000 analyzer (Scienta) optimized for high kinetic energies was used to record the photoelectron kinetic energies (KE).

**HERFD-XANES and RIXS**

The HERFD-XANES and RIXS experiments were performed at beamline ID26 at the European Synchrotron Radiation Facility. RIXS spectra and XANES in the high-energy resolution fluorescence detection (HERFD) mode were measured using an X-ray emission spectrometer.

2.3.5. Nuclear Magnetic Resonance (NMR) Spectroscopy

Solid-state NMR Spectroscopy data have been obtained through scientific collaborations. A Bruker Avance-HD 500 MHz spectrometer equipped with a 4 mm CP-MAS probe was used. To record the $^{14}$N spectra, a resonance frequency of 21.7 MHz was applied. The $^{14}$N NMR characterizations were performed on a Bruker Avance-II 300 MHz spectrometer equipped with a 4 mm CP-MAS probe. Corresponding signals of TMS (for $^1$H and $^{13}$C) and NH$_4$Cl (for $^{14}$N) were set to 0ppm to reference the chemical shifts. In the $^{207}$Pb spectra, the chemical shift was referenced by setting the signal of $^{207}$PbSO$_4$ to -3611 ppm.

2.4. Photovoltaic Characterization

For solar cell characterization, Current Voltage (IV) and Incident Photon-to-Current Conversion Efficiency (IPCE) measurements were made under simulated solar radiation and monochromatic light, respectively.
2.4.1. Current Voltage (IV) Characterization

IV measurement is the most common and essential measurement for solar cells, where the short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and power conversation efficiency (PCE or $\eta$) are investigated.

The source is simulated based on the similarity of the emitted spectrum to the solar AM1.5G spectrum. The intensity of the spectrum is normally calibrated to 1 Sun corresponding to 1000 Wcm$^{-2}$ light intensity. The efficiency of a solar cell ($\eta$) is given by the ratio of the maximum output power ($P_{max}$) to the power of the input light ($P_{in}$).

$$\eta = \frac{P_{max}}{P_{in}} \quad (2.10)$$

The measurement is performed by applying a voltage at a desirable range and recording the photocurrent response. Measuring the voltage in open circuit conditions gives $V_{oc}$, and this defines the range of applied bias voltage between the $V_{oc}$ and zero for the IV measurement. The highest possible current density under short circuit condition is measured as $J_{sc}$. The theoretical power is defined as $P_T = J_{sc}V_{oc}$. FF is an quality factor in the solar cells that is represented by the shape of the IV-curve of the solar cell and is defined as the ratio between $P_{max}$ and the product of $J_{sc}$ and $V_{oc}$:

$$FF = \frac{P_{max}}{P_T} = \frac{J_{max}V_{max}}{J_{sc}V_{oc}} \quad (2.11)$$

and the efficiency of the solar cell can thus be defined as:

$$\eta = \frac{J_{sc}V_{oc}.FF}{P_{in}} \quad (2.12)$$

In this work, after an external potential bias had been applied, the generated photocurrent was recorded with a Keithley model 2400 digital source meter. A 300 W collimated xenon lamp (Newport) was used as illumination lamp, and this was calibrated with a certified silicon solar cell (Fraunhofer ISE) at a light intensity of 100 mW·cm$^{-2}$ under AM1.5G solar light conditions. A mask with an area of 0.126 cm$^2$ was used during the measurement to expose the solar cells to the illumination.
2.4.2. Incident Photon-to-Current Conversion Efficiency (IPCE)

The IPCE of a solar cell is a wavelength-dependent measure that describes how many incoming photons are converted to photocurrent. The solar cell is illuminated by monochromatic light, and the generated photocurrent is recorded. This photocurrent is dependent on various processes in the solar cells; the amount of light absorbed ($\eta_{abs}$), the proportion of the generated electrons that are injected from the light-absorbing layer to the electron transport layer ($\eta_{inj}$), and the efficiency of the device in charge collection ($\eta_{coll}$). The IPCE value is defined as the product of these three efficiencies.

\[ IPCE = \eta_{abs} \cdot \eta_{inj} \cdot \eta_{coll} \]  \hspace{1cm} (2.13)

The absorbed photon-to-current conversion efficiency (APCE) is another term used to compare the photovoltaic performances of the materials. APCE reflects the $\eta_{inj}$ and $\eta_{coll}$ and corrects for the $\eta_{abs}$ from IPCE data.

\[ APCE = \frac{IPCE}{\eta_{abs}} \]  \hspace{1cm} (2.14)

Since the materials used in this thesis have shown varying band-gap and absorption properties, the APCE values were calculated (or estimated) to compare their charge injection and charge collection efficiencies. By choosing a wavelength lower than the wavelengths corresponding to the band-gaps of the materials (e.g. 450nm), APCE values were calculated from IPCE values.

IPCE spectra were recorded on a computer-controlled unit equipped with a xenon lamp (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110) and a Keithley digital multimeter (Model 2700). A certified silicon solar cell (Fraunhofer ISE) was used to calibrate the source.
3. Result and Discussion

3.1. Structural characterizations and effect of Dimensionality

3.1.1 Introduction
Recent substantial advances in the conversion efficiency of perovskite solar cells have led to an increased interest in the fundamental properties of these materials. Structural studies can give useful information about the atomic positions of the material components and their arrangement in the structure. Such information may address some of the fundamental questions about the properties of the materials. In this section, structural studies on the OIH lead-based materials are presented. Lead-based metal halide materials have shown different structural properties with very broad dimensionalities. In the present work, single crystals obtained by wet methods have been characterized. 3D networks, layered 2D systems, and 1D columns were obtained by altering the organic cations. X-ray powder diffraction patterns were obtained for the materials as complementary data for comparison between the single crystal data and the bulk materials. When the data were found to be well-matched, single crystallography results were used as reliable representatives of the bulk materials. The structural properties of these materials were discussed in relation to the physical properties (section 3.2.) Several articles have reported the importance of the solvent in the crystallization of perovskite materials on a TiO₂ film. Differences in crystallization affect the film density and uniformity and this affect the light absorption and more importantly the conductivity. The effect of the solvent on the crystallization of some of the products has been examined.
3.1.2 Three-Dimensional Network
As was briefly mentioned in the introduction, the basic perovskite structure is a systematic repeat of corner-sharing octahedral unit cells of BX$_6$ and A cations imbedded in a cuboctahedral hole surrounded by 12 X atoms. Among the materials here characterized by X-ray single crystallography, methylammonium lead (II) iodide [(MA)PbI$_3$] and methylammonium lead (II) bromide [(MA)PbBr$_3$] have three-dimensional perovskite structures. The structures of these materials were first investigated in the 1970s and 1980s$^{23, 56}$, but after their application in solar cells, these structures have been more extensively investigated in recent years.

For (MA)PbI$_3$ (at 60°C) and (MA)PbBr$_3$ (at room temperature) cubic structures with a space group of $Pm3m$ were found in agreement with previous reports$^{23, 24}$. Detailed structural data including lattice parameters for the two structures are presented in Table 3.1. The structural details are similar except for some small differences due to the smaller atomic radius for bromide than for iodide. The distance between lead atoms is 6.284Å in (MA)PbI$_3$ and 5.913Å in (MA)PbBr$_3$. The Pb-X-Pb angle in both structures is 180° and X-Pb-X angle is 90°.

<table>
<thead>
<tr>
<th>Space group</th>
<th>(MA)PbI$_3$</th>
<th>(MA)PbBr$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P m -3 m</td>
<td>P m -3 m</td>
</tr>
<tr>
<td></td>
<td>a 6.284</td>
<td>a 5.913</td>
</tr>
<tr>
<td>Cell lengths (Å)</td>
<td>b 6.284</td>
<td>b 5.913</td>
</tr>
<tr>
<td></td>
<td>c 6.284</td>
<td>c 5.913</td>
</tr>
<tr>
<td></td>
<td>a 90.00</td>
<td>a 90.00</td>
</tr>
<tr>
<td>Cell angles</td>
<td>β 90.00</td>
<td>β 90.00</td>
</tr>
<tr>
<td></td>
<td>γ 90.00</td>
<td>γ 90.00</td>
</tr>
<tr>
<td>Cell volume (Å$^3$)</td>
<td>248.15</td>
<td>206.74</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

A phase transition of (MA)PbI$_3$ occurs at a temperature below 56°C resulting in a tetragonal structure with $I4/mcm$ space group$^{24, 25}$ and according to our findings (in agreement with previous reports$^{23}$), (MA)PbBr$_3$ showed a cubic structure at room temperature. These findings were confirmed by the X-ray powder diffraction patterns.
Figure 3.1. Crystal structure of cubic (MA)PbI₃ and (MA)PbBr₃ obtained by crystallography. The ball-and-stick model was used for simplicity and a 50% probability level was used. The same structure was obtained in all three dimensions.

X-ray powder diffraction (XRD) of the (MA)PbBr₃ are presented in Figure 3.2 and compared with the calculated patterns from single crystal data.

Figure 3.2. Powder diffraction pattern obtained using Cu-Kα radiation --- comparing with the calculated pattern --- using the single crystal data for (MA)PbBr₃. The Miller indices are obtained from the single crystal data.

The XRD pattern for the (MA)PbI₃ powder sample was obtained at room temperature, and is presented in figure 3.3, compared with the predicted pattern for cubic (MA)PbI₃ calculated from single crystal data. The pattern shows different peaks indicating that there is a phase transition in the powder sample at room temperature. The Miller indices for the tetragonal phase at room temperature are taken from a previous report.²⁴
Figure 3.3. XRD recorded pattern for (MA)PbI$_3$ powder at room temperature --- indicating a tetragonal phase, compared with the calculated powder pattern --- of a cubic (MA)PbI$_3$ perovskite. The calculated pattern was obtained from single crystal data using Mercury 3.3 software.

The patterns obtained for (MA)PbI$_3$ and (MA)PbBr$_3$ indicate that the samples are poly-crystalline and a single phase.

3.1.3 Layered Two-Dimensional (2D) Systems

One of the main issues related to the commercialization of perovskite solar cell technology is their stability. Previous investigations of the stability of perovskite have reported that they are unstable under ambient conditions. One explanation of this instability is the dissolution of the methyl ammonium cation in water absorbed from the air. Another explanation is the degradation of the (MA)PbI$_3$ layer at higher temperature.\textsuperscript{76, 78, 79, 109, 110}

Perovskite materials have been applied in tandem cells. The band-gap of 1.55eV for the (MA)PbI$_3$ makes it inappropriately large for use in a single junction solar cell. On the other hand, it is smaller than the optimum value for use as top layer in a tandem cell. In the latter case, it can be coupled with the best known solar cell technology to increase the light conversion efficiency.\textsuperscript{111-113} For these reasons, researchers are interested in layered perovskite materials which originate from the synthesis based on mixed cations. These efforts have led to more stable solar cells with an efficiency of 12.5%.\textsuperscript{81-83, 114, 115} In this section, the structural properties of the three pure two dimensional materials are
discussed. Layered 2D systems were synthesized by the reaction of alkyl di-ammonium iodide salt with lead iodide, and thoroughly discussed in paper II. Butyldiammonium lead (II) iodide [(BdA)PbI₄], hexyldiammonium lead (II) iodide [(HdA)PbI₄], and octyldiammonium lead (II) iodide [(OdA)PbI₄] were characterized by X-ray single crystallography, and were shown to have two-dimensional structures with inorganic lead iodide planes separated by organic cations. High quality single crystals of (HdA)PbI₄ and (OdA)PbI₄ were picked and characterized. Despite the best efforts and repeating the characterization, a disorder effect was found for (BdA)PbI₄ in the single crystal data and the data obtained were reported as a model. However, X-ray powder diffraction patterns for all three 2D samples matched the calculated patterns from single crystal data, indicating that the selected crystals are reliable representatives of the bulk materials. The structure of the (HdA)PbI₄ is presented in Figure 3.4. Similar two-dimensional structures were found for the other two materials in this series. The structures obtained consist of inorganic structural planes of corner-sharing octahedral [PbI₆] units, separated by the organic cations.

![Figure 3.4. Crystal structure of (HdA)PbI₄ along three axes illustrating the two-dimensional nature of the chemical structure. Bal-and-stick model was chosen and hydrogen atoms and bonds are omitted for simplicity.](image)

(BdA)PbI₄ crystalized in a triclinic structure with a space symmetry group of P1. The lattice parameters were recorded as a = 8.4815(14) Å, b = 8.8472(14) Å, and c = 11.2028(17) Å. Similar structures and symmetry groups were found for the other two materials. (HdA)PbI₄ and (OdA)PbI₄ have shown monoclinic systems with the P2₁/c symmetry group. The unit cell diameters for (HdA)PbI₄
were \( a = 11.8055(6) \) Å, \( b = 8.4509(4) \) Å, and \( c = 9.0262(5) \) Å, and for \((\text{OdA})\text{PbI}_4\) were \( a = 13.7343(10) \) Å, \( b = 8.3435(5) \) Å, and \( c = 9.0041(6) \) Å. The cell volume for \((\text{OdA})\text{PbI}_4\) is the largest of the series, because it has the largest cation in the unit cell. Although similar structures were found for the materials, a major difference was observed. The role of the organic cation is to link the structural planes together. Since the length of the organic cation increases from butyldiammonium to octyl diammonium, the distance between the layers are expected to increase. In \((\text{BdA})\text{PbI}_4\), the inorganic components of the structure are confined in the (001) planes, but in \((\text{HdA})\text{PbI}_4\) and \((\text{OdA})\text{PbI}_4\) the inorganic planes are in the (200) direction.

Table 3.2. Crystallographic data for the two-dimensional materials.

<table>
<thead>
<tr>
<th></th>
<th>(BdA)\text{PbI}_4</th>
<th>(HdA)\text{PbI}_4</th>
<th>(OdA)\text{PbI}_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>( P 1 ) (triclinic)</td>
<td>( P 2_1/c ) (Monoclinic)</td>
<td>( P 2_1/c ) (Monoclinic)</td>
</tr>
<tr>
<td>Cell lengths (Å)</td>
<td>( a = 8.4815(14) )</td>
<td>( a = 11.8055(6) )</td>
<td>( a = 13.7343(10) )</td>
</tr>
<tr>
<td></td>
<td>( b = 8.8472(14) )</td>
<td>( b = 8.4509(4) )</td>
<td>( b = 8.3435(5) )</td>
</tr>
<tr>
<td></td>
<td>( c = 11.2028(17) )</td>
<td>( c = 9.0262(5) )</td>
<td>( c = 9.0041(6) )</td>
</tr>
<tr>
<td>Cell angles</td>
<td>( \alpha = 76.83 ) (7)</td>
<td>( \alpha = 90.00 )</td>
<td>( \alpha = 90.00 )</td>
</tr>
<tr>
<td></td>
<td>( \beta = 69.67 ) (7)</td>
<td>( \beta = 107.073(2) )</td>
<td>( \beta = 106.577(4) )</td>
</tr>
<tr>
<td></td>
<td>( \gamma = 89.46 ) (9)</td>
<td>( \gamma = 90.00 )</td>
<td>( \gamma = 90.00 )</td>
</tr>
<tr>
<td>Cell volume (Å³)</td>
<td>765.28</td>
<td>860.833</td>
<td>988.915</td>
</tr>
<tr>
<td>( Z )</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

The distance between the planes is defined as the lead-to-lead distance between two adjacent planes. This distance was 10.4Å for \((\text{BdA})\text{PbI}_4\), but for \((\text{HdA})\text{PbI}_4\) and \((\text{OdA})\text{PbI}_4\) it was 11.8Å and 13.7 respectively. This increase in the interplanar distance is a reason for the decreasing relationship between the layers, and this may be important for the physical properties of the materials. The same increasing trend was found in the interlayer iodide distances of 4.25 Å, 6.06 Å, and 8.29 Å for \((\text{BdA})\text{PbI}_4\), \((\text{HdA})\text{PbI}_4\), and \((\text{OdA})\text{PbI}_4\) respectively.
Figure 3.5. Illustrated structural planes with different distances in the three two-dimensional materials a. (BdA)PbI₄ b. (HdA)PbI₄, and c. (OdA)PbI₄. The increasing trend is evident from left to right.

The lead-to-lead distance between two adjacent octahedral units in one structural plane can also be compared. These distances were found to be 6.1 Å, 6.16 Å, and 6.14 Å for (BdA)PbI₄, (HdA)PbI₄, and (OdA)PbI₄ respectively, which distances can be compared with 6.28 Å for (MA)PbI₃ and 5.91 Å for (MA)PbBr₃.

Another important feature of these two-dimensional structures is the structural organization of the octahedral units in the planes. The Pb-I-Pb angles were found to be 150°, 148°, and 147° for (BdA)PbI₄, (HdA)PbI₄, and (OdA)PbI₄ respectively. By comparing these angles with the 180° for cubic (MA)PbI₃ and (MA)PbBr₃, it can be concluded that there is less ordered structural arrangement in the repeating unit cells in these 2D systems than in the cubic 3D networks.

Bulk powder X-ray diffraction patterns were obtained at room temperature and compared with the calculated powder XRD pattern from single crystal data. The matched patterns in figure 3.6 imply that the chosen crystals are reliable representative for the bulk of the material. Hence, structural properties can confidently be used in discussions of the relationships between structural and physical properties.
3.1.4 One-Dimensional Rod

In organic-inorganic metal halide materials, one-dimensional structures consist of metal halide units along chains with organic cations between the chains. The structural order in these materials is usually less than that in the 2D and 3D systems and the distance between the inorganic units is greater.

X-ray single crystallography was performed on the two 1D materials, propylammonium lead iodide [(PA)PbI$_3$] and 1D-butyrolactone lead iodide [(BdA)Pb$_2$I$_6$]. No suitable single crystal of ethylammonium lead iodide [(EA)PbI$_3$] was obtained and literature data were used to discuss its structure.$^{85}$

Single crystallography of (PA)PbI$_3$ showed the incorporation of a single $\gamma$-butyrolactone molecule in the unit cell of the crystalline material. A monoclinic structure with a space group of $Cc$ was recorded with X-ray single crystal experiment. While Park et al$^{85}$ reported an orthorhombic structure in the space group of $Pmmn$ for (EA)PbI$_3$. Comparing these structures with the findings for (MA)PbI$_3$ reveals that the addition of one or two [CH$_2$] groups to the organic cation has a significant impact on the structural properties of this type of OIH material. The incorporation of a bulkier cation in the space between the octahedral [PbI$_6$] in (EA)PbI$_3$ and (PA)PbI$_3$ units leads to a reduction in the symmetry compared to that of (MA)PbI$_3$. One-dimensional chains were
obtained for (PA)PbI₃ and (EA)PbI₃ with face-sharing repeating octahedral [PbI₆] units. The structures can be compared as the distances between the lead atoms in a single structural column or between two columns. Lead-to-lead distances along the chains of (EA)PbI₃ were found to be in the range of 3.648 Å to 4.499 Å, and for (PA)PbI₃ they were 4.036 Å. The closest lead-to-lead distances between the chains were 8.804 Å and 10.829 Å for (EA)PbI₃ and (PA)PbI₃ respectively. The crystal structure of (PA)PbI₃ in all three dimensions is presented in Figure 3.7.

![Illustrated ball and stick crystal structure of (PA)PbI₃. The structure is depicted in three axes showing connections between the [PbI₆] octahedral along the C axis. Hydrogen atoms are not shown.](image)

Figure 3.7. It is also of interest to compare the I–Pb–I angles. In (EA)PbI₃, they are between 172.0° and 178.8°, while for (PA)PbI₃, they are from 175.88° to 178.4°. The Pb-I-Pb angles varied from 72.2° to 85.9° in (EA)PbI₃ and from 77.0° to 77.8° in (PA)PbI₃. Bond lengths of Pb—I were recorded from 6.050 Å to 6.858 Å and from 6.423 Å to 6.479 Å for (EA)PbI₃ and (PA)PbI₃ respectively. The structural details of (EA)PbI₃ and (PA)PbI₃ are compared in table 3.3. In paper I, where three alkylammonium lead iodide materials [(MA)PbI₃, (EA)PbI₃, and (PA)PbI₃] were discussed, these values were compared with those of three dimensional (MA)PbI₃. For all the structural aspects, including the lead-to-lead distances, angles and bond lengths, considerable differences were observed indicating the significant impact of introducing a bulkier cation into the structure.
Table 3.3. Structural information of one-dimensional solvated (PA)PbI₃ and (EA)PbI₃.

<table>
<thead>
<tr>
<th></th>
<th>(EA)PbI₃[^85]</th>
<th>(PA)PbI₃ (+C₄H₆O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Pmmn</td>
<td>C c</td>
</tr>
<tr>
<td>Cell lengths (Å)</td>
<td>a 8.742</td>
<td>a 17.770</td>
</tr>
<tr>
<td></td>
<td>b 8.147</td>
<td>b 12.380</td>
</tr>
<tr>
<td></td>
<td>c 30.310</td>
<td>c  8.071</td>
</tr>
<tr>
<td>Cell angles</td>
<td>α 90.00</td>
<td>α 90.00</td>
</tr>
<tr>
<td></td>
<td>β 90.00</td>
<td>β 116.77</td>
</tr>
<tr>
<td></td>
<td>γ 90.00</td>
<td>γ 90.00</td>
</tr>
<tr>
<td>Cell volume (Å³)</td>
<td>2158.78</td>
<td>1585.26</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns for well-ground powder samples of (EA)PbI₃ and (PA)PbI₃ are presented in Figure 3.8. They show sharp peaks indicating that the samples are poly-crystalline. The indices given for (EA)PbI₃ are taken from literature[^85] and for (PA)PbI₃ from single crystal data. The differences between the patterns calculated from single crystal data and the recorded patterns for these 1D materials indicates an orientation bias for the crystalline materials in the powder.

![X-ray diffraction patterns](image)

Figure 3.8. X-ray powder diffraction patterns of --- (EA)PbI₃ and --- (PA)PbI₃.

(BdA)Pb₂I₆ has shown a one-dimensional structure with inorganic lead iodide structural columns and organic butyldiammonium cations intercalated between the columns. Solvent molecules are incorporated in the structure of the (BdA)Pb₂I₆. Due to the large size of the butyldiammonium cation a large hole is created between the structural rods and this facilitate the incorporation of a solvent with high
coordination affinity such as dimethylformamide. The inorganic chains consist of face-sharing [PbI₆] octahedral units with lead-to-lead distances between the chains varying from 10.21 Å to 13.04 Å. Some of these distances are shown in figure 3.9 which present the (BdA)Pb₂I₆ crystal structure in three axes. The solvated structure of (BdA)Pb₂I₆ was crystallized in the p1 space group. The characteristics of the unit cells were recorded as 8.08Å, 14.56Å, and 17.53Å for a, b, and c unit cell diameters respectively. The angles of the unit cells were obtained as 99.13, 102.41, and 96.35 degrees for α, β, and γ respectively.

![Figure 3.9. Refined crystal structure of one-dimensional (BdA)Pb₂I₆. Ball-and-stick model was used and hydrogen atoms are omitted for simplicity.](image)

Figure 3.10 presents X-ray powder diffraction spectra of (BdA)Pb₂I₆ with high peaks in the low angles indicating a large volume unit cell for the crystals. High crystallinity of the bulk sample can be concluded from the recorded pattern.

### Table 3.4. Structural information of one dimensional solvated (BdA)Pb₂I₆.

<table>
<thead>
<tr>
<th></th>
<th>(BdA)Pb₂I₆</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space group</strong></td>
<td>P1</td>
</tr>
<tr>
<td><strong>Cell lengths (Å)</strong></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>8.0827(4)</td>
</tr>
<tr>
<td>b</td>
<td>14.566 (8)</td>
</tr>
<tr>
<td>c</td>
<td>17.536(9)</td>
</tr>
<tr>
<td><strong>Cell angles</strong></td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>99.131(3)</td>
</tr>
<tr>
<td>β</td>
<td>102.409 (3)</td>
</tr>
<tr>
<td>γ</td>
<td>96.351(3)</td>
</tr>
<tr>
<td><strong>Cell volume (Å³)</strong></td>
<td>1968.27</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
</tbody>
</table>
The lead iodide bonds increase in length from 3.177 Å to 3.283 Å. Lead-to-lead distances in a single structural chain are between 4.00 Å and 4.07 Å. The Pb-I-Pb angles vary from 76.6 to 78.2 degrees. From these structural data, it can be concluded that decreasing the dimensionality to a one-dimension chain results in compact units along the structural chain.

Figure 3.10. XRD pattern of well ground powder samples of one-dimensional butyldiammonium lead iodide [(BdA)PbI₆].

3.1.5 Raman spectroscopy
Raman spectroscopy was used in paper I to investigate the structure of (A)PbI₃, and also in paper IV where (MA)PbI₃ and (MA)PbBr₃ were studied. The Raman spectra obtained are presented in Figure 3.11.

Figure 3.11. Recorded Raman spectra of --- (MA)PbI₃, --- (MA)PbBr₃, --- (EA)PbI₃, --- (PA)PbI₃. A ND-YAG laser with excitation wavelength of 1064 nm was used.
The obtained peak at \( \sim 120 \text{ cm}^{-1} \) was attributed to the vibration of Pb-I bond where in the case of (MA)PbBr\(_3\), Pb-Br vibration mode was observed at higher Raman wavenumbers. This is expected due to the shorter bond length for Pb-Br interactions as compared to that of Pb-I. Considering the (MA)PbI\(_3\) and (MA)PbBr\(_3\) compounds, which crystallize in three dimensional structures, the strongest peak can be attributed to the triply degenerate symmetric breathing stretch mode of X-Pb-X (or Pb-X-Pb) which extend along the three crystallographic directions. This peak was observed at 130 cm\(^{-1}\) and at 143 cm\(^{-1}\) for (MA)PbI\(_3\) and (MA)PbBr\(_3\) respectively. However, the corresponding peak is instead observed at the lower wavenumbers of 113 cm\(^{-1}\) and 115 cm\(^{-1}\) for (EA)PbI\(_3\) and (PA)PbI\(_3\), respectively. The observed structural changes match these findings well, since the I-Pb-I angle is less than 90 degrees in both (EA)PbI\(_3\) and (PA)PbI\(_3\). The Pb-I bond lengths in these materials are reported from single crystallography to 3.246 Å (on average) for (EA)PbI\(_3\) , and 3.228 Å (on average) for (PA)PbI\(_3\). Comparing that to 3.14 Å for (MA)PbI\(_3\) one should expect the related Raman peaks at lower wavenumbers.

Some of Raman peaks of the DMF solvent (highlighted with red arrows in figure 3.11) were observed in the recorded spectra of (PA)PbI\(_3\). This supports the crystallographic results for this material where the packing of the cations and anions obviously allows the inclusion of solvent molecules in the chemical structure.

The detected peaks at higher wavenumbers (at 900 cm\(^{-1}\) and above) can be attributed to the organic moiety. Comparable features were obtained for the samples, where the peaks at \( \sim 1400 \text{ cm}^{-1} \) were attributed to bending mode of -CH\(_3\) entities. While a similar mode originating from -CH\(_2\) units in (EA)PbI\(_3\) and (PA)PbI\(_3\) was observed at slightly higher wavenumbers. Comparable peaks were obtained for the related alkylammonium halide salt.
3.1.6 Summary
The synthesized materials were successfully investigated representing three different structural dimensionalities including 3D, 2D, and 1D. The connectivity of the inorganic network is highly dependent on the choice of organic cations. Three-dimensional networks were obtained for (MA)PbI$_3$ and (MA)PbBr$_3$, in accordance with previous findings. Two-dimensional structures were found for (BdA)PbI$_4$, (HdA)PbI$_4$, and (OdA)PbI$_4$. These two-dimensional structures differ with respect to the distances between their structural planes. The inorganic structural plane consists of a lead iodide system and the organic cations are embedded between them. (PA)PbI$_3$ and (BdA)Pb$_2$I$_6$ formed one-dimensional systems, with inorganic lead iodide columns with organic cations between them.

The lead-to-lead distances were the same along all three axes in the 3D systems, while in the lower dimensional structures it increased in one or two directions. The longer distances between the structural units in the lower dimensional systems allow the incorporation of e.g. solvent between the unit cells in these directions. The X-ray powder diffraction patterns of the bulk samples matched the single crystal data. Raman spectroscopy data confirmed the various structural differences between the chemical bonds and angles of the different samples.

The detailed structural database obtained has been used in the next section to discuss the differences in the physical properties of these materials.
3.2. Dimensionality impact on Physical Properties

3.2.1. Introduction
After the synthesis and structural characterization of the organic-inorganic hybrid materials, it was important to determine their physical properties. Through these experiments, it is possible to relate the physical properties to the chemical structure of the materials as a step towards the possible industrial application of these materials. The conductivity and light absorption were investigated as two key properties. Furthermore, the electronic structure was investigated to see how changes in the chemical bonding through the structural systems affected the valence band and conduction band edges.

3.2.2. Absorption Spectroscopy and Band-gap
For all of the samples [(MA)PbI₃, (MA)PbI₃, (EA)PbI₃, (PA)PbI₃, (BdA)PbI₄, (HdA)PbI₄, (OdA)PbI₄, and (BdA)Pb₂I₆] the optical properties were investigated by UV-Visible absorption spectroscopy. In the absorption spectra, absorption edges were recorded in the near-IR and visible regions representing the related energy gaps between the valence band and conduction band. Figure 3.11 shows the absorption spectra of thin films of the different materials.

![Absorption Spectra](image)

Figure 3.11. UV-Visible absorption spectra of monoammounium and diammonium (right) OIH films on mesoporous TiO₂.

The band-gap values (previously described) have been estimated using the Tauc equation⁹⁵:

\[(\alpha h\nu)^{1/n} = A (h\nu - E_g) \quad (3.1)\]
where $h$ is the Plank's constant, $\nu$ (eV) is the frequency, $\alpha$ is the absorption coefficient, $E_g$ (eV) is the energy gap, and $A$ is a normalizing constant. The value of $n$ is dependent on whether the electronic transition between the valence band and conduction band is direct or indirect. For a direct band-gap, $n$ is equal to 2 and for an indirect band-gap $n$ is $\frac{1}{2}$. The product $(\alpha h \nu)^{1/n}$ was plotted vs $h \nu$ for all of materials considering both direct and indirect values. The direct plot showed a greater slop in the band edge indicating that all of the materials have a direct band-gap.

Table 3.5. The estimated band-gaps of the organic-inorganic lead halide materials using their absorption spectra and Tauc equation.

<table>
<thead>
<tr>
<th>OIH materials</th>
<th>Bandgap(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MA)PbI$_3$</td>
<td>1.56</td>
</tr>
<tr>
<td>(MA)PbBr$_3$</td>
<td>2.24</td>
</tr>
<tr>
<td>(EA)PbI$_3$</td>
<td>2.18</td>
</tr>
<tr>
<td>(PA)PbI$_3$</td>
<td>2.38</td>
</tr>
<tr>
<td>(BdA)PbI$_4$</td>
<td>2.37</td>
</tr>
<tr>
<td>(HdA)PbI$_4$</td>
<td>2.44</td>
</tr>
<tr>
<td>(OdA)PbI$_4$</td>
<td>2.55</td>
</tr>
<tr>
<td>(BdA)Pb$_2$I$_6$</td>
<td>2.28</td>
</tr>
</tbody>
</table>

Table 3.5 shows that incorporation of organic cations with different sizes drastically changes the band-gap values. A similar effect was observed when the halide anion was changed from iodide to bromide. In (MA)PbI$_3$, (EA)PbI$_3$, and (PA)PbI$_3$ when one or two \([\text{CH}_2]\) groups were added to the organic cations, the band-gap values were 1.56 eV, 2.18 eV, and 2.38 eV respectively. It was confirmed by structural studies that an increase in the distance between the octahedral structural units leads to a severe decrease in the orbital overlaps and finally to a lower absorption.

In (BdA)PbI$_4$, (HdA)PbI$_4$, and (OdA)PbI$_4$, the band-gap values were 2.37 eV, 2.44 eV, and 2.55 eV respectively. Although the chemical structure has the same dimensionality, the distance between the inorganic structural planes increased, leading to a decrease in the overlap between the orbitals and finally to a lower absorption in the visible region. The absorption coefficient also decreased when a bulkier
cation was introduced into the two-dimensional structure. In the case of three-dimensional lead perovskite materials, it has been reported that the absorption properties of the thin film are affected by the crystal size of the material.\textsuperscript{116,117} If the same effect is assumed for the 2D materials, the larger volume of the unit cells of the materials with bulkier cations may lead to larger crystal sizes and, hence, a lower absorption coefficient.

For (MA)PbBr\textsubscript{3} a band-gap of 2.24 eV was obtained, which is comparable with the previous report.\textsuperscript{67,69} Comparing this value to 1.56 eV for the (MA)PbI\textsubscript{3} band-gap, the lower absorption by (MA)PbBr\textsubscript{3} can be attributed to the smaller atomic radius of bromide compared to that of iodide, which leads to lower orbital overlap between lead and halide and a lower absorption.

The band-gap of 2.28 eV for (BdA)Pb\textsubscript{2}I\textsubscript{6} and the lower absorption coefficient compare to that of (BdA)PbI\textsubscript{4}, may be due to the different structural orientations and the lower crystalline order in (BdA)Pb\textsubscript{2}I\textsubscript{6}.

3.2.3. Conductivity Data

Conductivity measurements were performed on all the organic-inorganic lead iodide materials discussed in papers I, II, and IV. The values obtained are presented in table 3.6.

<table>
<thead>
<tr>
<th>OIH material</th>
<th>Conductivity (Scm\textsuperscript{-1})</th>
<th>Dimensionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MA)PbI\textsubscript{3}</td>
<td>1.3×10\textsuperscript{-4}</td>
<td>3D</td>
</tr>
<tr>
<td>(EA)PbI\textsubscript{3}</td>
<td>1.3×10\textsuperscript{-6}</td>
<td>1D</td>
</tr>
<tr>
<td>(PA)PbI\textsubscript{3}</td>
<td>9.4×10\textsuperscript{-7}</td>
<td>1D</td>
</tr>
<tr>
<td>(BdA)PbI\textsubscript{4}</td>
<td>1.3×10\textsuperscript{-5}</td>
<td>2D</td>
</tr>
<tr>
<td>(HdA)PbI\textsubscript{4}</td>
<td>1.2×10\textsuperscript{-5}</td>
<td>2D</td>
</tr>
<tr>
<td>(OdA)PbI\textsubscript{4}</td>
<td>1.2×10\textsuperscript{-5}</td>
<td>2D</td>
</tr>
<tr>
<td>(BdA)Pb\textsubscript{2}I\textsubscript{6}</td>
<td>5.3×10\textsuperscript{-6}</td>
<td>1D</td>
</tr>
</tbody>
</table>

The conductivity of 3D-(MA)PbI\textsubscript{3} was 1.3×10\textsuperscript{-4} Scm\textsuperscript{-1}, but it was one order of magnitude lower in the range of 10\textsuperscript{-5} Scm\textsuperscript{-1} for 2D materials and at 10\textsuperscript{-6} Scm\textsuperscript{-1} for 1D materials. The electronic conductivity is strongly dependent on the chemical connectivity between the structural
units. So that, when the dimensionality decreases, the connectivity is poorer through the crystal lattice, and this leads to lower conductivity.

3.2.4. Electronic Structure DFT Calculation
The DFT calculation was used in paper IV to study the electronic structure of the layered 2D perovskite. The total density of state (DOS), the partial density of state (PDOS), and the band structure of (BdA)PbI₄, (HdA)PbI₄, and (OdA)PbI₄ were investigated. Calculated band structures are presented in Figure 3.12. The shapes of the band structures for the three materials were similar with a slight difference in the band structure of BdAPbI₄ as compared to that of the other two. BdAPbI₄ crystallizes in the triclinic system while the other two are monoclinic, and this is the reason for the different band structures. The calculated band-gap values for these materials were 2.04 eV, 2.09 eV and 2.15 eV for (BdA)PbI₄, (HdA)PbI₄, and (OdA)PbI₄, respectively. The trend in the band-gap is similar to that of the experimental results, although a shift 0.3-0.4 eV to lower values was observed in the calculational results.

![Image of band structures](image-url)

**Figure 3.12.** Calculated band structures of a. (BdA)PbI₄, b. (HdA)PbI₄, and c. (OdA)PbI₄. The estimated band-gaps were 2.04 eV, 2.09 eV, and 2.15 eV respectively.

The atomic contributions of Pb and I in the valence band and conduction band were also estimated from the calculational results, and the results presented in Figure 3.13 indicate that the valence band is dominated by contribution from iodine atomic orbital while lead orbitals dominate in the conduction band.
Figure 3.13. Calculated DOS and PDOS for layered 2D perovskite samples presented on the left (a., b., and c.) for the valence band and on the right (d., e., and f.) for the conduction band.

Similar studies previously reported for the 3D perovskites [(MA)PbI$_3$ and (MA)PbBr$_3$] show similar elemental contributions to the valence band and conduction band where the halide moiety dominates in the VB and lead in the CB.\textsuperscript{118}

3.2.5. X-ray Spectroscopy

Three spectroscopy techniques were used to study the electronic structure of some of the synthesized materials. These X-ray spectroscopy techniques were hard X-ray photoelectron spectroscopy (HAXPES), high-energy resolution fluorescence detected-X-ray absorption near-edge spectroscopy (XANES-XANES), and Resonant Inelastic X-ray Scattering (RIXS). In papers IV and V, combined data analyses of the results obtained for (BdA)Pb$_2$I$_6$, (BdA)PbI$_4$, (HdA)PbI$_4$, \ldots
and (OdA)PbI$_4$ were used to deepen the understanding of the valence and conduction band configurations of these materials. The measured iodine 4d and lead 5d core level intensities orbitals were used to estimate the I/Pb ratio on the surface of each material (Figure 3.14).

![Figure 3.14. PES spectra of the I (4d) and Pb (5d) binding energy levels. The stoichiometry of the materials on the surface has been estimated using the recorded peak intensities in these spectra.](image)

Appropriate ratios obtained for the materials are presented in Table 3.7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>I/Pb</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BdA)PbI$_4$–[NH$_3$(CH$_2$)$_4$NH$_3$]PbI$_4$</td>
<td>3.82</td>
<td>4</td>
</tr>
<tr>
<td>(BdA)Pb$_2$I$_6$–[NH$_3$(CH$_2$)$_4$NH$_3$]Pb$_2$I$_6$</td>
<td>2.65</td>
<td>3</td>
</tr>
<tr>
<td>(HdA)PbI$_4$–[NH$_3$(CH$_2$)$_6$NH$_3$]PbI$_4$</td>
<td>4.09</td>
<td>4</td>
</tr>
<tr>
<td>(OdA)PbI$_4$–[NH$_3$(CH$_2$)$_8$NH$_3$]PbI$_4$</td>
<td>3.85</td>
<td>4</td>
</tr>
<tr>
<td>PbI$_2$</td>
<td>1.78</td>
<td>2</td>
</tr>
</tbody>
</table>

The obtained experimental results matched the expected ratios from the chemical formula reasonably well. The recorded intensities were corrected for the photo-ionization cross-section for each element, using database values. The intensity ratios between different core levels were calculated from the experimental results.$^{119}$

The valence band spectra of the materials on the mesoporous TiO$_2$ substrates are presented in the Figure 3.15. These spectra were calibrated against the Fermi level at zero binding energy. The most
intense peak in each spectrum was used to calibrate the intensity of the spectrum, unless otherwise stated.

Figure 3.15. Valence band spectra for different samples obtained from XPS measurement. A photon energy of 4000 eV was used for spectral measurements.

The overall shapes of the valence band spectra of the materials were similar, although different valence band edges were observed for the different materials. The spectral increase at ~1.7 eV was used to estimate the valence band edges of the samples presented in Table 3.8.

Table 3.8. Estimated valence band offset for different samples via Hard X-ray PES.

<table>
<thead>
<tr>
<th>Sample</th>
<th>VB offset</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BdA)PbI₄</td>
<td>1.46 eV</td>
</tr>
<tr>
<td>(BdA)Pb₂I₆</td>
<td>1.35 eV</td>
</tr>
<tr>
<td>(HdA)PbI₄</td>
<td>1.33 eV</td>
</tr>
<tr>
<td>(OdA)PbI₄</td>
<td>1.31 eV</td>
</tr>
<tr>
<td>PbI₂</td>
<td>1.69 eV</td>
</tr>
</tbody>
</table>

These values for the valence band edges were combined with the estimated bandgap values from absorption studies and were used to draw a schematic diagram of the VB and CB energy levels of these materials. (See Figure 3.16)
Figure 3.16. Diagram illustrating the energy level positions of different materials versus the Fermi level. The relative VB and CB edges are derived from absorption spectra and PES data.

The frontier orbitals of the samples were further investigated by HERFD-XANES and RIXS. The incident flux was used to normalize the intensities. The absorption of the fluorescence radiation between the cryostat and the spectrometer was cooled by a helium-filled bag. For selection of the acquisition time, samples were checked for radiation damage. Multiple spots on the samples were chosen for the measurements in order to avoid the effects of radiation damage. The spectra recorded by HERFD-XANES and RIXS are presented in Figures 3.17a. and b., respectively.

With HERFD-XANES, unoccupied p orbitals of iodine were investigated. Different local geometries in the chemical structures of (BdA)Pb$_2$I$_6$ and (BdA)PbI$_4$ are reflected in the observed changes in the spectra from 5.19 keV to higher energies. In other words, the differences between the bonding environments of the iodine atoms in the one-dimensional and two-dimensional structures lead to different spectral features in the high-energy XANES region.
**Figure 3.17.** a. HERFD-XANES spectra showing the unoccupied states of iodine. b. RIXS spectra showing the occupied states of iodine in the samples.

In the 2D series, small shifts in the absorption edge toward higher energies were clearly observed in the (BdA)PbI$_4$ < (HdA)PbI$_4$ < (OdA)PbI$_4$ series. Hence, the conduction band edge in the 2D series is slightly shifted to higher energies with increasing length of the organic chain. The detected spectra indicate that, although the contribution of the iodine in the conduction band is small, the effect of the iodine can be observed in the shifts. The small contributions of iodine in the conduction bands of the 2D materials were supported by DFT calculations (see Figure 3.13.e).

RIXS spectra characterize the occupied states of Iodine which were taken at the first maximum of the iodine L1 absorption edge. The dipole-allowed transitions from iodine in the 5p orbitals are the origin of the RIXS spectrum, which shows the partial density of states near the valence band edge position.

A shift was observed rise at ca. 5.188 in the RIXS spectra of (BdA)Pb$_2$I$_6$ and (BdA)PbI$_4$. This indicates that the observed valence band shift of these materials is due mainly to the iodine contribution. A small wing was observed at ca. 5.18 keV corresponding to the degree of hybridization between the iodine 5p and lead 6s orbitals. This feature is expected to exhibit only minor changes in the 2D materials due to the small differences in the I-Pb-I bonds and angles.
3.2.6. Nuclear Magnetic Resonance (NMR) Spectroscopy

Through collaboration, NMR spectroscopy was employed in order to characterize MAPbBr\textsubscript{3}. NMR spectroscopy, as an element specific technique, may provide information about the unique local chemical environment. This may give more information about possible defects in the lattice of the materials studied. You may also get information whether the formally equivalent crystal sites in fact also are chemically equivalent. Recorded \textsuperscript{1}H NMR, \textsuperscript{13}C NMR, and \textsuperscript{14}N NMR spectra of crystalline MAPbBr\textsubscript{3} are depicted in Figure 3.18 a., b., and c. respectively. In the \textsuperscript{1}H NMR spectra two signals at \(~3.6\) ppm and at \(~6.6\) ppm are attributed to the CH\textsubscript{3} and NH\textsubscript{3} parts in the methylammonium cation, respectively. Carbon and Nitrogen single peaks in the related NMR spectra are representing the carbon atom in the methyl group and the nitrogen atom in the amine group, respectively. These finding are in agreement with the previous reports.\textsuperscript{120, 121}

![Figure 3.18](image)

**Figure 3.18.** Recoded solid state a. \textsuperscript{1}H NMR b. \textsuperscript{13}C NMR c. \textsuperscript{14}N NMR and d. \textsuperscript{207}Pb NMR spectra of methylammonium powder. In d. spectra recorded under both static (black) and magic angle spinning (red, with 10 kHz spinning rate) conditions are shown.

The \textsuperscript{207}Pb NMR spectra of MAPbBr\textsubscript{3} recorded under static and spinning conditions are illustrated in Figure 3.18. d. Comparing the \textsuperscript{207}Pb NMR spectra of MAPbBr\textsubscript{3} and MAPbI\textsubscript{3} a clear difference in chemical shift is observed (figure 3.19).
The chemical shift of $^{207}$Pb in the iodide compound is higher than that of the bromide one. This indicated a higher local magnetic field and is opposite to what would be expected considering that the Pb-I bond should be considerably more covalent than the Pb-Br one. However, this effect has been observed before and unexpected effects from the relativistic character of these heavy elements should be taken into account.

![Figure 3.19](image.png)

**Figure 3.19.** $^{207}$Pb NMR Spectra of MAPbBr$_3$ --- and MAPbI$_3$ ---.

While conceptually this should allow for atom specific information about coordination environments for Pb, the rapid relaxation times and weak coupling between the heavy neighboring atoms (Pb and I or Pb and Br) produced broad structural features that did not provide detailed structural information.

The $^{207}$Pb peaks are unexpectedly wide, and referring to a recent study it is clear that other factors than mere relaxation are involved. These can either involve unresolved coupling to the quadrupolar halide nuclei caused by the high crystal symmetry or undefined relaxation mechanisms. In general, no new structural insights are provided by the solid state NMR spectra in relation to the X-ray structures. The technique, while exceptional in theory, was unsatisfactory in practice.
3.2.7 Summary
Absorption spectroscopy was successfully applied to obtain the absorption band edge representing the energy difference between the valence band and conduction band. Higher band-gap values were obtained for the lower dimensional materials with the exception of (BdA)Pb$_2$I$_6$. The highest conductivity value was obtained for MAPbI$_3$ with a three-dimensional network and a highly crystalline film. The conductivity of the lower dimensional materials was less than that of 3D materials due to the connectivity loss in one or two directions.

In the case of the diammonium-based materials, detailed electronic structures were presented, providing a comprehensive understanding of the contributions of the different atomic orbitals in the valence band and conduction band of each material. The effect of chemical coordination and bonding environment on the results were discussed.

A strong relationship between the physical properties and the chemical structure of the materials was observed.
3.3. Solar Cell Assembly and Characterization

3.3.1. Solar Cell Architecture

Pilkington TEC15 Fluorine-doped tin-oxide (FTO) coated glass was used as substrate. The substrates were cleaned by sonication for 30 minutes each in 2% detergent solution, ethanol and acetone. One side of the substrate with a 3 mm edge was etched using zinc powder and 2M hydrochloric acid (Figure 3.20.a). A compact blocking layer was deposited by spin coating at 2000 rpm for 30 seconds of a solution of titanium isopropoxide in ethanol and hydrochloric acid (a mixture of 175μL of titanium isopropoxide in 1.25 ml ethanol and 175μL of 2 M HCl in 1.25ml ethanol). This was followed by sintering at 500°C for 30 minutes giving a ca. 100 nm thick compact layer. A TiO$_2$ compact layer was also prepared by another method. The FTO substrates were pre-heated to 500°C for 15 minutes, and a blocking layer was then prepared by spray pyrolysis of a 2M titanium isopropoxide solution in propanol followed by sintering at 500°C for 30 minutes. A solution of 80 mM SpiroOMeTAD, 200 mM 4-tert-butylpyridine (TBP, 99%) and 30 mM bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, 99%, Io-li-tec) in acetonitrile:chlorobenzene(1:9) was used as a solution of hole transport material (HTM). The HTM solution was spin coated at 2000 rpm for 30 seconds, and the final layer was deposited by thermal evaporation of 200 nm silver or 80 nm gold. The solar cells were in all cases fabricated in ambient air at ambient temperature, except for the thermal evaporation of the back contact. The humidity varied a lot in our laboratory and it changed from 33% to 56.7% depending on the season.
3.3.2. Photovoltaic Characterization

Since the performance of a solar cell is highly dependent on the TiO$_2$ film thickness, the type of back contact (Gold or Silver), and the ambient conditions (especially for (MA)PbI$_3$-based solar cells), the solar cell characterization results were discussed in papers I, II, and IV with respect to the preparation conditions. In these three papers, the current-voltage characterization was carried out at 10mV/s scan rate for the bias voltage in order to reduce the risk of hysteresis.\textsuperscript{123}

In paper I, the solar cells were based on alkyammonium lead iodide [(A)PbI$_3$] with changes in the organic cations by adding one [CH$_2$]. Based on (MA)PbI$_3$-(CH$_3$NH$_3$)PbI$_3$, (EA)PbI$_3$-(CH$_3$CH$_2$NH$_3$)PbI$_3$, and (PA)PbI$_3$-(CH$_3$CH$_2$CH$_2$NH$_3$)PbI$_3$ as light-absorbing layer, solar cells were prepared and characterized. In this series, 600 nm thick TiO$_2$ films were used as electron conductor layer, Spiro-OMeTAD was used as the HTM, and a 200 nm layer of silver was used as back contact. The recorded data are presented in table 3.9 and figure 3.21.
The best efficiency was recorded as 7.4% (average of 5 devices) for (MA)PbI₃-based solar cells with a short circuit current density ($J_{sc}$) of 16.29 mAcm⁻², an open circuit voltage ($V_{oc}$) of 0.784 V, and a fill factor (FF) of 0.580. The solar cell efficiency was drastically reduced to 0.26% for (EA)PbI₃ and to 0.016% for (PA)PbI₃. For (MA)PbI₃, a relatively low band-gap of 1.56 eV and conductivity of $1.1 \times 10^{-4}$ Scm⁻¹ were obtained. The high performance of the (MA)PbI₃ solar cells can be attributed to their efficient light-harvesting property based on the low band-gap and rather high extinction coefficient, and to the efficient charge collection originating from the promoted conductivity. IPCE curves for the solar cells (see Figure 3.21.c) showed much higher values for the (MA)PbI₃-based solar cells.
Table 3.9. Average values (of 5 devices) of IV characteristics of alkylammonium lead iodide based solar cells.

<table>
<thead>
<tr>
<th></th>
<th>(MA)PbI$_3$</th>
<th>(EA)PbI$_3$</th>
<th>(PA)PbI$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jsc (mAcm$^{-2}$)</td>
<td>16.29±1.69</td>
<td>0.77±0.14</td>
<td>0.075±0.021</td>
</tr>
<tr>
<td>Voc (V)</td>
<td>0.784±0.026</td>
<td>0.662±0.040</td>
<td>0.564±0.034</td>
</tr>
<tr>
<td>FF</td>
<td>0.580±0.011</td>
<td>0.521±0.051</td>
<td>0.372±0.034</td>
</tr>
<tr>
<td>$\eta$ (%)</td>
<td>7.4±0.59</td>
<td>0.26±0.025</td>
<td>0.016±0.004</td>
</tr>
<tr>
<td>APCE</td>
<td>78.35</td>
<td>2.83</td>
<td>0.18</td>
</tr>
<tr>
<td>Band-gap(eV)</td>
<td>1.56</td>
<td>2.18</td>
<td>2.38</td>
</tr>
<tr>
<td>Conductivity (Scm$^{-1}$)</td>
<td>1.1×10$^{-4}$</td>
<td>1.3×10$^{-6}$</td>
<td>9.4×10$^{-7}$</td>
</tr>
</tbody>
</table>

Solar cells with (EA)PbI$_3$ and (PA)PbI$_3$ as light-absorbing layer were made under conditions similar to those for the (MA)PbI$_3$-based solar cells. Much lower solar cell efficiencies were recorded for (EA)PbI$_3$ as 0.26% and (PA)PbI$_3$ as 0.016%. This drop in efficiency originated mainly from the lower short circuit current than in the (MA)PbI$_3$-based cells.

An increase in the estimated bad-gap was obtained from 1.56eV for (MA)PbI$_3$, to 2.18eV and 2.38eV for (EA)PbI$_3$ and (PA)PbI$_3$ respectively. This can be one of the reasons for the drop in efficiency. The conductivity values are also a determining factor in the solar cells, recorded as 1.3×10$^{-6}$ Scm$^{-1}$ for (EA)PbI$_3$ and 9.4×10$^{-7}$ Scm$^{-1}$ for (PA)PbI$_3$. The structure of (MA)PbI$_3$ was 3D, but 1D for (EA)PbI$_3$ and (PA)PbI$_3$. The lower connectivity in the chemical structures of the 1D materials has a significant impact on the electronic conductivity through the lattice network. The absorbed photon-to-current conversion efficiency (APCE) values for the fabricated solar cells was 78% for (MA)PbI$_3$ cells, 3% for (EA)PbI$_3$ cells, and 0.2% for (PA)PbI$_3$ cells. Hence, in addition to the large band-gap, another key factor affecting the efficiency is the deficiency in charge collection or charge injection in the 1D solar cells. A low conductivity value results in a longer charge transport time and a much greater risk of recombination of the electrons from the conduction band of the 1D materials. IPCE curves show an onset trend confirming the estimated band-gap values based on the absorption spectra. The very low IPCE for (PA)PbI$_3$ cells, are attributed
to the high band-gap, and low conductivity of this material compared to (EA)PbI₃ and (MA)PbI₃.

In paper II, the two dimensional materials were used as light-absorbing layer in the solid state solar cells, and for comparison, (MA)PbI₃-based solar cells were prepared under similar conditions. Table 3.10 presents the characteristics of these solar cells.

<table>
<thead>
<tr>
<th></th>
<th>(BdA)PbI₄</th>
<th>(HdA)PbI₄</th>
<th>(OdA)PbI₄</th>
<th>(MA)PbI₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eff (%)</td>
<td>1.08</td>
<td>0.59</td>
<td>0.012</td>
<td>2.11</td>
</tr>
<tr>
<td>Voc (V)</td>
<td>0.870</td>
<td>0.725</td>
<td>0.730</td>
<td>0.805</td>
</tr>
<tr>
<td>Jsc (mAcm⁻²)</td>
<td>2.894</td>
<td>1.735</td>
<td>0.047</td>
<td>5.858</td>
</tr>
<tr>
<td>FF</td>
<td>0.430</td>
<td>0.471</td>
<td>0.340</td>
<td>0.449</td>
</tr>
<tr>
<td>APCE (%)</td>
<td>24.2</td>
<td>8.1</td>
<td>0.23</td>
<td>31.2</td>
</tr>
<tr>
<td>Bandgap (eV)</td>
<td>2.37</td>
<td>2.44</td>
<td>2.55</td>
<td>1.56</td>
</tr>
<tr>
<td>Conductivity (Scm⁻¹)</td>
<td>1.3×10⁻⁵</td>
<td>1.2×10⁻⁵</td>
<td>1.2×10⁻⁵</td>
<td>1.3×10⁻⁴</td>
</tr>
</tbody>
</table>

The (BdA)PbI₄ cells showed an efficiency of 1.082% with 0.870 V, 2.894 mAcm⁻², and 0.430 as open circuit voltage, short circuit current density, and fill factor respectively. To my knowledge, this is the highest reported efficiency for a solar cell based on a pure 2D perovskite light-absorbing layer. For the (HdA)PbI₄ and (OdA)PbI₄ the cell conversion efficiency was 0.592% and 0.012% respectively.

**Figure 3.22.** a. IV, b. IPCE curves for (BdA)PbI₄ ——, (HdA)PbI₄ ——, (OdA)PbI₄ —— and (MA)PbI₃ ——. Solar cells were fabricated under the same conditions. Mesoporous TiO₂ films were used as substrate and the IV curves were recorded under 1sun AM1.5G illumination.
The open circuit voltage was 0.870 V for (BdA)PbI₄, 0.725 V for (HdA)PbI₄, and 0.732 V for (OdA)PbI₄ compared to 0.805 V for (MA)PbI₃ cells. For the (HdA)PbI₄ and (OdA)PbI₄ cells, a lower V_{oc} was recorded than for the 3D perovskite cells. A large recombination loss for (HdA)PbI₄ and (OdA)PbI₄ cells can originate from exciton trapping between the layers of the 2D systems. This reduces the difference in quasi-Fermi levels for TiO₂ and Spiro-OMeTAD, and finally reduces the V_{oc}.¹²⁴

The band-gap values for these materials were estimated to be 2.37 eV for (BdA)PbI₄, 2.44 eV for (HdA)PbI₄, and 2.55 eV for (OdA)PbI₄. Considering the relatively large band-gap for (BdA)PbI₄ and the lost portion of sunlight, an impressive efficiency of 1.08% was obtained for the related solar cell. Despite small changes in the band-gap values and the similar conductivities of the three 2D materials, their conversion efficiency was very low. The low extinction coefficient for the (OdA)PbI₄ could be one explanation for the efficiency drop. Furthermore, due to the relatively large interplanar distances and larger volume for the unit cell, crystalline (OdA)PbI₄ may not be compatible with the small pore size of the TiO₂ substrate. XRD patterns of the three 2D materials after deposition on the mesoporous TiO₂, show some level of mismatch for (OdA)PbI₄ but the match is better for the other 2D materials (see Figure 3.23).

![Figure 3.23](image-url)

**Figure 3.23.** X-ray diffraction patterns of --- powder sample, --- calculated pattern from single crystal data, and --- spin coated sample on mesoporous TiO₂ for a. (BdA)PbI₄, b. (HdA)PbI₄ and c. (OdA)PbI₄.

The much greater moisture stability of the 2D materials than of the (MA)PbI₃ was a notable property for the solar cell assembly under...
ambient conditions. These solar cells were fabricated in a humidity of 55.6% and a temperature of 23.4°C (measured by an AMPROBE TH-3 hygrometer on a typical summer day in Stockholm, Sweden). As mentioned in the experimental section, these solar cells were prepared from pure iodide solution by one step deposition method. Since an efficiency of just over 9% has been reported with a similar solution and deposition method in a glovebox-controlled atmosphere, the efficiency of 2.11% found here can be attributed to the very low stability of the (MA)PbI₃ in the presence of moisture. (MA)PbI₃ solar cells died after only 4 days at ambient environment but the (BdA)PbI₄ solar cells were rather stable after 4 days in similar condition. These data have been discussed in paper II. Comparable results have been reported by Cao et al. The X-ray diffraction pattern of the (MA)PbI₃ showed PbI₂ peaks indicating the instability of (MA)PbI₃ in a humid environment. One of the largest sources of instability is the high solubility of the methylammonium salt in water absorbed from the air and the PbI₂ remaining on the substrate.

Figure 3.24. XRD patterns of (MA)PbI₃. A tetragonal phase powder sample at room temperature --- , the calculated powder pattern from cubic single crystal data, and a spin coated sample under humid atmosphere on mesoporous TiO₂.

IPCE curves showed an onset in accordance with the UV-Visible spectra. Because of differences in the band-gap, the APCE values were used to provide a better comparison for the charge-collection or charge-injection efficiencies in these solar cells. In the (BdA)PbI₄ cell, an impressive APCE value of 24.1% was recorded in comparison with 31.2% for the (MA)PbI₃ cell. This result indicates that, despite high
band-gap values, the (BdA)PbI$_4$ cells have an efficient charge collection and charge injection. APCE values of 8.1% and 0.23% were obtained for the (HdA)PbI$_4$ and (OdA)PbI$_4$ cells respectively. Using a perovskite solar cell in combination with another type of solar cell in a tandem cell is a novel and interesting idea. Despite the importance of the idea and previous reports$^{112, 125, 126}$ a band-gap of 1.56 eV for (MA)PbI$_3$ is not in the best range for coupling to other types of solar cells. It is lower than the optimal value for use as top layer. For coupling to silicon with a band-gap of 1.1 eV, a top layer of 1.8 eV is needed. This combined tandem cell can reach a theoretical efficiency of 42%.$^{127}$ The band-gap obtained for these 2D perovskite (2.2-2.5 eV) indicates that it is more appropriate to couple them with for instance CdTe with a 1.5 eV band-gap. This tandem cell has a theoretical efficiency of 35%.$^{127}$ Since solar cells based on (BdA)PbI$_4$ showed a promising efficiency, considering their energy diagram, there is sufficient driving force for electron injection from the conduction band. Their high thermal and moisture stability can make these materials more competitive candidates for use in a tandem cell.

In paper IV, one-dimensional (BdA)Pb$_2$I$_6$ solar cells were studied and compared with the two-dimensional (BdA)PbI$_4$ solar cells. New set of solar cells were fabricated based on these two materials with only minor changes in the fabrication process. Compared with the solar cells previously described, a thinner mesoporous TiO$_2$ layer (~200nm) was employed with a back contact of gold (Au) instead of silver (Ag). The detailed structural configuration is presented in the cross-sectional SEM pictures in Figure 3.25. The recorded characteristic data are presented in Table 3.11.
(BdA)PbI4-based solar cells showed an efficiency of 1.146% with 925 mV as $V_{oc}$, 2.73 mAcm$^{-2}$ as $J_{sc}$, and 0.453 as FF. For the (BdA)Pb$_2$I$_6$-based solar cell, an almost identical efficiency of 1.144% was recorded, but with a lower $V_{oc}$ of 850 mV, and a slightly higher $J_{sc}$ of 2.91 mAcm$^{-2}$, and 0.463 as FF. The lower Voc of 75 mV for (BdA)Pb$_2$I$_6$ can be attributed to the higher valence band position for (BdA)Pb$_2$I$_6$, which lowers the maximum possible open circuit voltage. A greater risk of recombination can be expected in one-dimensional than in two-dimensional systems, due to their less structural connectivity and lower conductivity.
Table 3.11. IV data for the fabricated solar cells, 1 sun AM1.5G light illumination was used for the measurements.

<table>
<thead>
<tr>
<th></th>
<th>Eff (%)</th>
<th>Voc (mV)</th>
<th>Jsc (mACm⁻²)</th>
<th>FF</th>
<th>APCE (%)</th>
<th>Band gap (eV)</th>
<th>Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BdA)PbI₄</td>
<td>1.14</td>
<td>925</td>
<td>2.73</td>
<td>0.453</td>
<td>36.1</td>
<td>2.37</td>
<td>1.3 × 10⁻⁵</td>
</tr>
<tr>
<td>(BdA)Pb₂I₆</td>
<td>1.15</td>
<td>850</td>
<td>2.91</td>
<td>0.463</td>
<td>35.3</td>
<td>2.28</td>
<td>5.3 × 10⁻⁶</td>
</tr>
</tbody>
</table>

The slightly higher Jsc for (BdA)Pb₂I₆ (~0.2 mAcm⁻²) can be due to the small shift in band-gap of (BdA)Pb₂I₆ (2.28 eV) compared to that of (BdA)PbI₄ (2.37 eV). This shift can increase the possibility of light harvesting by the solar cells and can lead to a higher current density. The IPCE curves show the band-gap shift. The recorded IPCE onsets agree well with the band edges obtained from the absorption spectra (figure 3.11). The good crystallinity and uniformity of the thin films of both materials on the TiO₂ substrate may result in high charge collection and charge-injection efficiencies. As a result, rather high and similar APCE values (~36%, table 3.9) were obtained for both the solar cells.
3.3.3. Summary
As an initial application, the new materials were used in solar cells and characterized. MAPbI$_3$-based solar cells were prepared in each step for comparison. In a high humidity, stable solar cells based on (BdA)PbI$_4$ and (BdA)Pb$_2$I$_6$ materials showed 1.1% efficiency, compared with the 2.1% efficient MAPbI$_3$ solar cell which showed very low stability under ambient condition. IPCE spectra were in agreement with the recorded absorption spectra (presented in previous chapter).
4. Concluding remarks

Overall, the work presented in this thesis has focused on the synthesis of new OIH materials, understanding their properties, and examining their functionality in solar cells. It provides an insight into the main structural properties of the characterized materials and relates their physical properties to these structures, with an emphasis on solar cell applications.

The chemical structure of the synthesized materials was first characterized by X-ray techniques leading to the identification of the specific chemical coordination and bonding environments of the different components in each material. The materials have been designed to give a diverse range of dimensionalities. Different groups of 3D perovskites, 2D perovskites, and 1D non-perovskites were investigated. The detailed structural properties of these materials were compared and their differences were discussed. Different bond lengths and angles were obtained depending on the structural design of the crystalline network of each material. This led to unique physical properties for each material.

The introduction of a bulkier cation than methylammonium into the structure has substantially increased the stability of the material towards moisture and heat.

A band-gap range from 1.55 eV to 2.55 eV was obtained for the different materials, indicating a great versatility of the OIH materials for band-gap engineering. Conductivity measurement confirmed that when moving from a 3D network to a 2D plane, the conductivity dropped one order of magnitude. The values were even lower for 1D materials. This decrease in conductivity was attributed to the loss of connectivity in one and two crystallographic directions in the 2D and 1D systems.

X-ray spectroscopy characterization of the di-ammonium based materials showed detailed differences in the electronic structures of the materials. The valence band edge and conduction band edge were investigated and showed the dominant contribution of the iodine orbital in the VB edge and of the lead orbital in the CB edge value. A
schematic energy band diagram was presented based on the XPS and UV-Vis absorption data, and this can be used to identify further possible applications of these materials in various device architectures. Characterization of solar cells based on the different materials showed that methylammonium lead iodide has the highest light conversion efficiency, but solar cells based on the new di-ammonium materials have shown up to 1.1% light-conversion efficiency with a substantially higher stability. The bandgap values of these materials (2.2-2.4 eV), show that they are suitable for use as top layers in tandem devices. They can for example be combined with CdTe in a tandem cell to obtain 35% theoretical efficiency.\textsuperscript{128}
5. Future outlook

To the best of my knowledge, some of the materials presented in this thesis have here been structurally characterized for the first time. In addition, most of the lower dimensional materials were subjected to physical characterization and applied in solar cells for the first time. The relationship shown between the structure and the function of the materials can be utilized in the further development of new materials. New materials can be oriented toward lead-free systems, as this seems to be an urgent matter in the perovskite research community. In another approach, one can focus on the improvement of the light-absorption properties of these materials in order to improve the efficiency of these types of solar cells.

The synthesized materials have shown a greater stability, and their band-gap values make them suitable for use as top layer in tandem devices.

Significant improvements in the efficiency of the solar cells based on the conventional perovskite have been achieved by choosing mixed halide compositions for the perovskite. This approach may help to improve the solar cell efficiency of the materials presented in this thesis.
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