Properties of organic-inorganic hybrids
Kamminga, Machteld Elizabeth

Important note: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document version
Publisher's PDF, also known as Version of record

Publication date:
2018

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
CHAPTER 1

Introduction

This thesis investigates Properties of Organic-Inorganic Hybrids. Organic-inorganic hybrids represent a broad class of materials that consist of both organic and inorganic components that are combined into a single compound. The combination of both components make these materials hybrid. The main interest in hybrid materials arises from the combination of properties coming from the two constituents. This allows for the design of materials that has properties associated with both organic and inorganic compounds, giving the best of both worlds. Inorganic compounds are generally known for their robust electronic and magnetic properties, their wide range of band gaps and bandwidths, and thermal stability. In organic-inorganic hybrids, it is possible to obtain these properties, while maintaining the structural flexibility and easy processing often associated with organic compounds. As the variety of organic and inorganic materials that can be implemented into a hybrid structure is very large, organic-inorganic hybrids represent a large set of materials with very distinct physical properties.

In addition to combining properties of organic and inorganic components, an important characteristic of hybrids is the interplay between the two components. As the two components build up the structure together, changing either of the two has a direct influence on the structure of the other. This means that the physical properties of the inorganic part can be directly controlled by different organic moieties. In other materials, substitutions or doping is often required to achieve this. This simple tuning of the properties makes hybrids unique.

In this chapter, I provide a general introduction to organic-inorganic hybrid materials, their structures and properties. In Section 1.1, I describe the structural diversity of organic-inorganic hybrid materials. In Section 1.2, I highlight the different physical properties that are associated with these structures. The motivation and research aim, and the outline of this thesis are described in Sections 1.3 and 1.4, respectively.
1.1 Crystal Structures of Organic-Inorganic Hybrid Materials

Organic-inorganic hybrids are composites consisting of organic and inorganic components. The most common examples of naturally occurring (bio)organic-inorganic composites are bone and teeth tissue.\cite{1} Inspired by nature, combining the properties of organic and inorganic compounds into a unique material became a challenge that started with the beginning of the industrial era.\cite{2} One of the best-known, commercial man-made examples of an organic-inorganic materials is paint, wherein inorganic pigments (e.g. TiO$_2$) are suspended in organic solvents.\cite{3}

However, hybrid materials are not simply physical mixtures of its constituents. As stated in the beginning of this chapter, the interplay between the organic and inorganic components is an important characteristic of hybrid materials. Therefore, Sanchez and Ribot proposed that hybrids can be classified into two major families, depending on the nature of the chemical interaction between the the constituents:\cite{4} class I covers all hybrid materials that consist of organic and inorganic components that exhibit weak interactions (e.g. hydrogen bonds, van der Waals interaction and ionic bonds), whereas class II covers all hybrid materials in which the two phases are linked together through strong chemical bonds (e.g. covalent or coordination bonds). Note that the interactions between the organic and inorganic components in class II materials do not exclusively have to be strong chemical interactions. The same kind of weak bonds that define class I materials are also possible in addition to the strong interactions.

Examples of class II materials are organic-inorganic hybrid zeolite materials. Zeolites are microporous crystalline silica materials that have molecular-sized confined space in their pore systems.\cite{5,6} Therefore, zeolites can be used as host materials for various composites, providing a wide range of materials with distinct physical properties. The motivation for implementing organic groups is that organic functionalization of zeolites would widen the range of applications. Therefore, Yamamoto et. al.,\cite{7} reported the synthesis of organic-inorganic zeolites containing an organic group as lattice. As a result, they found methylene groups (CH$_2$) to be incorporated into the zeolite framework by substituting lattice oxygen atoms and thereby creating Si–CH$_2$–Si bonds that replace siloxane bonds (Si–O–Si). Other examples of class II hybrid materials are metal-organic frameworks (MOFs). MOFs are compounds consisting of metal ions or clusters that are coordinated to organic linkers.\cite{8} Figure 1.1 shows the schematic structure of a MOF. MOFs can form crystalline one-, two- or three-dimensional (1D, 2D or 3D) structures consisting of covalent bonds between the organic and inorganic parts. As a result, MOFs are often porous materials, similar to zeolites, and their applications are generally related to gas separation, storage and purification, as well as catalysis.\cite{9} The structural diversity of MOFs becomes apparent from the proposed classification by Cheetham et. al.,\cite{8} who classified MOFs based on the dimensionality of the structure with respect to both organic connectivity between metal centers and extended inorganic connectivity.

Examples of class I materials are organic-inorganic hybrid perovskites. Organic-inorganic hybrid perovskites are often referred to as organometal halide perovskites. However, this is an incorrect term as organometallic compounds contain at least one
1.1. CRYSTAL STRUCTURES OF ORGANIC-INORGANIC HYBRID MATERIALS

Figure 1.1: Schematic crystal structure of a metal-organic framework (MOF) compound.

chemical bond between a carbon atom of an organic compound and a metal. These compounds have structures based on the basic building component of the ABX$_3$ perovskite structure. The name ‘perovskite’ originates from the mineral form of CaTiO$_3$, found in nature.\textsuperscript{[10]} The mineral was discovered in 1839 and named after the Russian mineralogist Perovski (1792-1856). The perovskite structure consists of a cubic close-packed AX$_3$ lattice with half of the (6-fold coordinated) octahedral holes filled with B cations. As a result, a 3D network of corner-sharing BX$_6$-octahedra is obtained, where the B atom is typically a metal cation and X is an anion, such as O$^{2-}$ or a halogen. The A cations then fill the 12-fold coordinated holes between the octahedra. Figure 1.2 shows the schematic crystal structure of the perovskite phase. While perovskite structures can have the perfect cubic arrangement as shown in Figure 1.2, perovskites generally have distorted structures. These distortions can originate from cation displacements or octahedral tilts. Such distortions generally lead to interesting physical properties, such as ferroelectricity.

Figure 1.2: Schematic crystal structure of the ABX$_3$ perovskite structure. In organic-inorganic hybrid perovskites, A represents the organic cation, B the divalent metal (e.g. Pb$^{2+}$, Sn$^{2+}$, Mn$^{2+}$, Cu$^{2+}$) and X the halogen (e.g. Cl$^-$, Br$^-$, I$^-$).
In addition to 3D perovskites, layered perovkite structures can also be obtained. These 2D structures are related to the 3D structure by cutting layers from the 3D network, along certain crystallographic directions. The most common layered perovskite structures are based on \( \{110\} \) - and \( \{100\} \)-oriented slabs cut from the 3D perovskite.\(^{[11]}\) This is illustrated in Figure 1.3. The \( \{110\} \)-oriented perovskites generally adopt the formula \( A_nB_mX_{3n+2} \), where A represents a cation, B a metal cation and X an anion. Figure 1.3 shows the structure for \( n = 2 \). An example of such a compound with this structure is \( \text{BaMnF}_4 \) and \( \text{BaZnF}_4 \).\(^{[12,13]}\) Note that \( n = 1 \) compounds do not adopt layered structures, but are 1D compounds consisting of linear chains of \( \text{BX}_6 \)-octahedra, extending along one direction. Furthermore, layered perovskites that are obtained from \( \{100\} \)-oriented slabs are more extensively studied.\(^{[11]}\) The two most common types of these layered structures belong to the Ruddlesden-Popper\(^{[14]}\) and Aurivillius\(^{[15]}\) phases (see Figure 1.3). While Ruddlesden-Popper phases can be thought of as a sliced perovskite structure, the crystal structure can be considered as an intergrowth of perovskite and rock salt (NaCl) structures. The perovskite nature becomes apparent from the slicing of the cubic perovskite structure, as described above, while the rock salt nature becomes apparent from the interface between the slabs. As can be seen in Figure 1.3, cations A and anions X form a rock salt structure at the interface of the perovskite slabs. An example of a \( n = 2 \) Ruddlesden-Popper phase is \( \text{Sr}_3\text{Ti}_2\text{O}_7 \).\(^{[16]}\) Similarly, the Aurivillius phases can be considered as an intergrowth of perovskite slabs with alternating layers of fluorite-like \( \text{Bi}_2\text{O}_2^{2+} \).\(^{[11]}\) This fluorite-like structure becomes apparent at the interface between the perovskite slabs, as can be seen in Figure 1.3. An example of a \( n = 2 \) Aurivillius phase is the ferroelectric \( \text{Ba}_2\text{SrTa}_2\text{O}_9 \) compound.\(^{[17]}\)

\[\begin{align*}
\text{<110> oriented layers} & \quad \text{Cubic perovskite} & \quad \text{<100> oriented layers} \\
\text{A}_n\text{B}_m\text{X}_{3n+2} & \quad \text{A}_{n+1}\text{B}_m\text{X}_{3n+1} & \quad \text{(Bi}_2\text{O}_2\text{)}\text{A}_{n+1}\text{B}_m\text{O}_{3n+1}
\end{align*}\]

**Figure 1.3:** Schematic crystal structures of possible layered structures with different orientations cut from the 3D perovskite structure. The cubic perovskite structure (center) can be cut along either the \( \{110\} \) or \( \{100\} \) crystallographic directions to produce the \( \{110\} \) - and \( \{100\} \)-oriented families of layered perovskites. The thickness of the perovskite sheets depends on the thickness \( n \) of the cut taken from the 3D perovskite structure \( (n = 2 \) is shown in the figure). Both the Ruddlesden-Popper the Aurivillius series are shown for the \( \{100\} \)-oriented family. Figure after Mitzi.\(^{[11]}\)
1.1. CRYSTAL STRUCTURES OF ORGANIC-INORGANIC HYBRID MATERIALS

The so-called organic-inorganic hybrid perovskites date back to more than 100 years ago, even though they were not referred to by this name at the time. To the best of my knowledge, the earliest report on various hybrid perovskite compounds dates back to 1884.[18] As the name suggests, hybrid perovskite have crystal structures closely related to the perovskite structure, see Figure 1.2. The inorganic cation at the A-site is replaced by a small organic cation, that is generally an ammonium cation. A divalent metal, such as Pb\(^{2+}\), Sn\(^{2+}\), Mn\(^{2+}\) or Cu\(^{2+}\) occupies the B-site. The X-site is occupied by a halogen, such as Cl\(^{−}\), Br\(^{−}\) or I\(^{−}\). Therefore, the organic-inorganic perovskite structure consists of metal halide octahedra that share corners and form a 3D network wherein organic cations occupy the 12-fold coordinated holes between the octahedra. There are no covalent bonds between the organic and inorganic part, but the structure is held together by hydrogen bonding between the organic cations and the halides. Thus, the hybrid perovskite compounds belong to class I hybrid materials.[4] Because the 12-fold coordinated A-site is quite small, only small organic molecules are expected to fit in the crystal structure. The size of the void is directly related to the size of the metal cation and the halogen. The Goldschmidt tolerance factor is an indicator for the stability and distortion of crystal structures.[19] The tolerance factor \(t\) is defined as

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

where \(r_A\), \(r_B\) and \(r_X\) represent the ionic radii of A cation, B anion and X cation, respectively. The ideal cubic perovskite structure would have \(t = 1\). However, small mismatches in ionic radii directly result in \(t \neq 1\). When the organic cation is too large to fit at the A-site, i.e. \(t > 1\), the 3D network of the perovskite structure cannot be maintained. As a result, low-dimensional structures, such as the layered structures described above, will form. Most 3D perovskite structures have \(t\) slightly smaller than 1, in the order of 0.8 - 0.9. Note that this allows for distortions in the form of buckling of the BX\(_6\) octahedra. Thus, for a given B cation and X anion, the maximum size of the A cation can be calculated. To illustrate the small size of the A-site, we consider Pb\(^{2+}\) as the metal cation and I\(^{−}\) as the halogen. Given the large size of both ions, this creates one of the largest A-sites. A simple calculation, assuming a perfect cubic perovskite structure (i.e. \(t = 1\)), shows that the radius of the A-site is approximately 2.6 Å. This means that only small molecules of maximum two or three C–C or C–N bonds are expected to fit in the crystal structure.

The structural flexibility of the organic-inorganic hybrids gives rise to a very large family of crystal structures, depending on the choice of its constituents. A variety of small organic cations, such as methylammonium, formamidinium and guanidinium, fit in the 3D perovskite structure. However, incorporating larger organic cations will result in lower-dimensional structures. As stated above, layered perovskites that are obtained from \(\langle 100\rangle\)-oriented slabs are most extensively studied.[11] Characteristic for these Ruddlesden-Popper-type hybrids is that the structure consists of inorganic layers that are separated by bilayers of the organic cation. The individual layers of the organic cations are separated by a van der Waals gap. As these organic cations generally do not have size restrictions, a very large variety of cations can be implemented. Moreover, these organic cations are not limited to simple alkyl groups. For example, aromatic and fluorinated cations can also...
be incorporated, resulting in different physical properties. Additionally, diammonium cations, e.g. $^4$H$_3$N(CH$_2$)$_n$NH$_3^+$, can also be incorporated. These hybrid structures are also layered, but consist of inorganic layers that are separated by a monolayer of the organic dications. Hence, no van der Waals gap between organic cations is formed.

Besides implementing a large variety of organic cations, it is also possible to incorporate a mix of multiple types of organic cations. The implementation of large organic cations, i.e. too large to fit at the A-site in the perovskite structure, generally results in $n = 1$ Ruddlesden-Popper phases. However, higher order organic-inorganic hybrid Ruddlesden-Popper phases (e.g. $n = 2$, $n = 3$, $n = 4$) can be obtained by mixing large organic cations with small organic cations, i.e. cations that do fit at the A-site in the perovskite structure. Subsequently, a layered structure of $n$ layers of perovskite $A'BX_3$ and rock salt $A''X$ will be formed, with $A'$ and $A''$ the long and short organic cations, respectively. Mixing the organic cations in different ratios will give all Ruddlesden-Popper phases ranging from $n = 1$ (solely the large organic cations) to $n = \infty$ (solely the small organic cations). Note that $n = \infty$ represents the 3D perovskite structure.

The choice of the divalent metal has a major influence on the physical properties of the hybrid perovskite. Properties associated with different structures are described in more detail in Section 1.2. The driving force for the variety of structures and properties obtained when incorporating different metals goes beyond the size of the metal cation. For example, incorporation of Jahn-Teller active cations, e.g. Cu$^{2+}$ ($9d$ electrons), results in major structural distortions as well. Jahn-Teller distortions of the metal halide octahedra plays a significant role in the physical properties of the compound, as described in Section 1.2. Besides incorporating divalent metal cations, it is also possible to insert trivalent metal cations, such as Sb$^{3+}$ and Bi$^{3+}$. However, incorporation of trivalent metal cations generally results in hexagonal structures with formula $A_3B_2X_9$, with $A$ the organic cation, $B$ the trivalent metal and $X$ the halogen. As discussed in Chapter 5, the $A_3B_2X_9$ structure is related to the cubic $ABX_3$ perovskite structure (where $B$ represents a divalent metal) and can be described as a hexagonal analogue. Furthermore, it is also possible to mix metal cations into a single compound. However, I found that mixing two divalent metal cations generally gives phase separation. Still, studies have shown that it is possible to mix monovalent with trivalent cations in a 1:1 ratio. Structures of this kind are often referred to as double perovskites. Figure 1.4 shows the schematic crystal structure of a $A_2B'B''X_6$ double perovskite, with $A$ the organic cation, $B$ a monovalent metal (e.g. Ag$^+$), $B'$ a trivalent metal (e.g. Bi$^{3+}$) and $X$ the halogen. Characteristic of the double perovskite structures is that the metal cations order in a rock salt-like manner.

The last branch of organic-inorganic hybrid perovskite structures is based on the choice of the halide. While F$^-$ is generally not used due to its small size, structures consisting of Br$^-$, Cl$^-$ or I$^-$ appear to have different properties as their structures are influenced by the size of the halide. Furthermore, it is also possible to mix halides. Both theory and experiments on thin films have shown that the optical properties can be tuned as a function of the ratio between two halides that were added to the reaction mixture.

To summarize, organic-inorganic hybrids represent a large class of compounds in materials science. Hybrids related to the perovskite structure, so-called hybrid perovskites, represent a large family of organic-inorganic hybrid compounds. I have illustrated the structural diversity of hybrid perovskites by explaining how the organic
and inorganic constituents directly influence the structure. In Section 1.2 I will explain which physical properties are associated with hybrid perovskites. In Chapter 2 I will describe the experimental strategies I have used to synthesize and characterize the crystal structures and physical properties of a variety of organic-inorganic hybrid perovskites. The results are written in succeeding chapters.

1.2 Properties of Organic-Inorganic Hybrid Materials

As described in Section 1.1, organic-inorganic hybrids can adopt a large variety of structures, depending on their constituents. In this section I will explain how this structural variety is reflected by the variety of physical properties found in these compounds. Important to realize here is the connection between the structure and the properties. Different structures have different properties and different structures can be obtained when different (organic and inorganic) constituents are brought together. This implies that the physical properties of hybrid perovskites can be directly tuned by their constituents.

Early interest in organic-inorganic hybrid perovskites has mainly come from their magnetic properties. From early 1970s, long-range magnetic order has been studied in layered hybrid perovskites incorporating $\text{Fe}^{2+}$, $\text{Mn}^{2+}$, $\text{Cu}^{2+}$ and $\text{Cr}^{2+}$ as the metal cation.\cite{37-41} The structure plays a central role in the magnetic properties. Given the perovskite structure, there is no direct linkage between the metal cations. Consequently, the magnetic properties are determined by the magnetic superexchange interactions through the $\text{B–X–B}$ linkages, with $\text{B}$ the metal and $\text{X}$ the halide. Structural parameters, such as bond angles and distances, have a direct influence on the magnetic exchange.
Furthermore, as stated in Section 1.1, incorporation of Jahn-Teller active metal cations has a major influence on the perovskite structure and therefore on the magnetic properties. While Goodenough-Kanamori rules were originally developed for oxide perovskites, they also apply to organic-inorganic hybrid perovskites.\textsuperscript{[42,43]} The Goodenough-Kanamori rules predict that a $\sim 180^\circ$ angle between adjacent B atoms that have partially filled $d$ shells gives rise to a strong antiferromagnetic interaction, while a $\sim 90^\circ$ angle gives rise to a weak ferromagnetic interaction. Layered hybrid perovskites based on Mn$^{2+}$ and Fe$^{2+}$ cations do not exhibit Jahn-Teller distortions, have B–X–B angles of $\sim 180^\circ$ and are therefore antiferromagnetic.\textsuperscript{[37–39]} Cu$^{2+}$ and Cr$^{2+}$, on the other hand, are Jahn-Teller active. These distortions result in the magnetic orbitals of adjacent metal ions being orthogonal to each other. Subsequently, the spins experience ferromagnetic superexchange via a $180^\circ$ pathway.\textsuperscript{[40,41,44]} This is illustrated by the example of ferromagnetic (CH$_3$NH$_3$)$_2$CuCl$_4$ ($T_c = 8.9$ K\textsuperscript{[37,45]}) in Figure 1.5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig1_5.png}
\caption{Polyhedral model of layered (CH$_3$NH$_3$)$_2$CuCl$_4$, projected along the stacking direction of the layers. The Jahn-Teller distortion becomes apparent from the elongated CuCl$_6$-octahedra. The magnetic spin is located in the $d_{x^2-y^2}$ orbital, located at the position indicated by the red ellipsoids. Thus, the orbitals on neighboring copper ions are orthogonal to each other, resulting in ferromagnetic superexchange via a $180^\circ$ Cu–Cl–Cu pathway. Figure obtained from my own single-crystal X-ray diffraction measurements.}
\end{figure}

Similar to oxide perovskites, organic-inorganic hybrids can exhibit ferroelectric properties as well.\textsuperscript{[46,47]} These polar hybrids are of interest for various applications. For example, it is thought that solar cells can benefit from a ferroelectric domain structure, as charge separation is a key aspect of their performance.\textsuperscript{[48,49]} In order to facilitate this, a built-in electric field can enhance the transport of excitons. Furthermore, ferroelectric-gate field-effect transistors (FeFETs) require charge induction, and can benefit from a polar material as the gate electrode: the top electrode changes the resistance by changing the polarization.\textsuperscript{[50]} Application of hybrids in devices such as gate insulators and field-effect transistors is mainly governed by their relatively good dielectric properties.
Moreover, coexisting ferromagnetic and ferroelectric order was also found in CuCl$_4$-based hybrids.\cite{46,51,52} This increased the interest in hybrids in the field of multiferroic materials and their applications. Because organic-inorganic hybrid perovskites are generally easy to process, implementing them in such applications is of interest.

In terms of electrical character, metal halides are predominantly insulating. However, layered hybrid perovskites consisting of Ge, Sn and Pb (group IV metals) are found to be conductive.\cite{53–57} Notably, it was found that the band gap varies with the thickness of the perovskite layer, \textit{i.e.} the band gap decreases as the number of inorganic layers (analogues to the Ruddlesden-Popper type series as described in Section 1.1) is increased. Mitzi was one of the first to demonstrate this behavior in the family of (100)$\parallel$-oriented perovskites ($\text{C}_4\text{H}_9\text{NH}_3)_2$(CH$_3$NH$_3$)$_{n-1}$Sn$_n$I$_{3n+1}$, consisting of $n$ layers of CH$_3$NH$_3$SnI$_3$, separated by bilayers of the butylammonium cations.\cite{54} The largest band gap was found in the $n=1$ compound ($\text{C}_4\text{H}_9\text{NH}_3)_2$SnI$_4$, while the smallest band gap was observed for the $n=\infty$ compound CH$_3$NH$_3$SnI$_3$. While both the earliest and most subsequent studies have mainly focused on tin-based compounds, similar trends in Ge- and Pb-based compounds are observed due to the isoelectronic nature of the metal cations. These examples directly demonstrate the remarkable tunability of the properties of organic-inorganic hybrid perovskites, based on the crystal structure.

Organic-inorganic hybrid perovskites have recently attracted renewed attention as promising candidates for application in optoelectronic devices. Initially used as a sensitizer in dye-solar cells,\cite{58} CH$_3$NH$_3$PbI$_3$ has gained much attention as an efficient absorber material in simplified planar heterojunction solar cell devices.\cite{59–64} Very high power-conversion efficiencies of up to 22.7\% have been reported for lead iodide-based materials.\cite{65} Note that CH$_3$NH$_3$PbI$_3$ is not a new material. As stated in Section 1.1, the first report on organic-inorganic hybrid perovskites dates back to 1884.\cite{18} To the best of my knowledge, CH$_3$NH$_3$PbI$_3$ was first reported in 1978.\cite{66} Thus, while the first report on so-called hybrid perovskite solar cells is less than 10 years old, it is incorrect to say that the hybrid materials are invented by Kojima \textit{et al.}\cite{58} in 2009. The field of hybrid perovskite photovoltaics has just increased the interest and boosted the activity in the field of organic-inorganic hybrids. The main reason why organic-inorganic hybrid perovskites are considered promising candidates for photovoltaic applications is because the device efficiencies have found a steep increase since the first reported cell in 2009. From 2009 to 2017, the efficiency has gone up from 3.8\%\cite{58} to 22.7\%.\cite{65} This means that hybrid perovskites have easily surpassed the efficiency of organic photovoltaics in just a short amount of time. Moreover, they have become serious competitors to silicon solar cells, in terms of efficiency. The benefits of using hybrid perovskites are embedded in their unique optical\cite{67,68} and excitonic\cite{69,70} properties. Furthermore, hybrids are generally easy to synthesize. This means that simplified planar solar cells without any need for nanostructuring can give rise to high efficiencies.\cite{61} In addition to photovoltaic applications, other optoelectronic applications based on organic-inorganic hybrids have also recently emerged. These applications include light-emitting diodes,\cite{71,72} lasers\cite{73,74} and photodetectors.\cite{75}

To summarize, there is a large variety of physical properties associated with organic-inorganic hybrids. These properties include magnetic, ferroelectric, conducting, optical and optoelectronic properties. Subsequently, this diversity allows for the use of hybrid
materials in various applications. In this thesis, I have investigated various fundamental physical properties of different organic-inorganic hybrids. In Section 1.3 I will highlight the motivation and research aims that provide a basis for the research that I have carried out in each subsequent chapter. The outline of the thesis is given Section 1.4.

1.3 Motivation and Research Aim

As described in Section 1.2, a large variety of interesting physical properties have been studied in organic-inorganic hybrid perovskites. However, while several properties have been reported, their origin is not always fully understood. The mechanisms behind the physical phenomena are sometimes yet to be found. It is commonly understood that the physical properties are directly related to the crystal structure, but there is still a lot to gain to come to the point where we fully understand how properties relate to the structure. Questions that arise include: how can we tune the band gap? What is the role of the organic cation? What mechanisms give rise to polar phases? How do properties of single crystals and thin films differ?

The main goal of this thesis is to gain a better fundamental understanding of structure-property relations in organic-inorganic hybrids. Thus, I want to understand how displacements in the crystal structure can change fundamental physical properties in organic-inorganic hybrid compounds. I believe that this understanding could eventually lead to tools that can be used to design materials with desired properties. Furthermore, existing materials can be improved for desired applications.

To achieve this increased understanding, I have synthesized both new and previously reported organic-inorganic hybrid compounds, studied their crystal structure with single-crystal and powder X-ray diffraction, and measured fundamental physical properties. Subsequently, I have investigated structure-property relations and collaborated to test these relations with theory. As a general approach, I have synthesized series of structures that are related to each other, for example by varying the organic cation in lead-based hybrids or by varying the metal cation while keeping the organic cation as a constant. Moreover, I have investigated both crystal structure and physical properties as a function of temperature.

Note that it is incredibly difficult to predict what crystal structure will form based on given starting compounds, i.e. when the organic and inorganic constituents are given. However, synthesizing different series of compounds, investigating their fundamental physical properties and obtaining structure-property relations will give tools to understand how properties depend on the crystal structures. Therefore, I think that these studies will add to the design of materials for desired applications by understanding what structural features are required to obtain certain properties. And the other way around: it will be possible to predict some properties once the crystal structure of a compound is given. Thus, the general research aim of this thesis is to find tools to understand how properties of organic-inorganic hybrids depend on the crystal structure. I have investigated various crystal structures and different fundamental physical properties. Section 1.4 gives the outline of this thesis.
1.4 Outline of this Thesis

As stated in Section 1.3, the research aim of this thesis is to find tools to understand how physical properties of organic-inorganic hybrids depend on the crystal structure. Therefore, I have synthesized and characterized several organic-inorganic hybrids and found ways to relate the properties to their structure. Because I have studied a large variety of compounds, structures and physical properties, each chapter of this thesis can be read individually. I provide a brief summary of each chapter below:

Chapter 2: Various experimental strategies that are of central importance in all research projects carried out in this thesis are highlighted. These experimental strategies include the synthesis methods, patterning techniques and X-ray diffraction data interpretation conducted in the following chapters. This chapter provides an overview of how I have dealt with various research questions, from an experimental perspective based on the synthesis techniques and X-ray diffraction data interpretation.

Chapter 3: Single crystals of both previously studied and new phenylalkylammonium lead iodide organic-inorganic hybrid compounds were synthesized, and characterized by single-crystal X-ray diffraction. Two different type of structures were obtained: layered structures in which the inorganic sheets consist of solely corner-sharing and both corner- and edge-sharing PbI$_6$-octahedra. Density functional theory calculations showed that the face-sharing PbI$_6$-octahedra create a confinement effect leading to effectively one-dimensional behavior, responsible for the observed peak shifts in photoluminescence in the different structures. The results show how the connectivity of the octahedra leads to confinement effects that directly tune the optical band gap.

Chapter 4: The presence of water during synthesis of (C$_6$H$_5$CH$_2$NH$_3$)$_2$PbI$_4$ produced a minority phase with water molecules incorporated in a completely new structure: (C$_6$H$_5$CH$_2$NH$_3$)$_4$Pb$_5$I$_{14}$·2H$_2$O, consisting of ribbons of edge-sharing PbI$_6$-octahedra separated by the organic cations. Density functional theory calculations including spin-orbit coupling showed that edge-sharing PbI$_6$-octahedra cause the band gap to be increased with respect to corner-sharing PbI$_6$-octahedra. To gain systematic insight, the effect of connectivity of PbI$_6$-octahedra on the band gap was modeled in idealized lead iodide perovskite-derived compounds. Notably, it was found that increasing the connectivity from corner-, via edge-, to face-sharing causes a significant increase in the band gap. This provides a new mechanism to tailor the optical properties in organic-inorganic hybrids.

Chapter 5: Single crystals of perovskite-like (CH$_3$NH$_3$)$_3$Bi$_2$I$_9$ hybrids were synthesized, and the results showed how the large dielectric constant is strongly affected by the polar ordering of its constituents. Single-crystal X-ray diffraction studies showed how a well-pronounced, ferrielectric phase transition at 143 K is governed by in-plane ordering of the bismuth lone pair that breaks inversion symmetry and results in a polar phase. The dielectric constant is markedly higher in the centrosymmetric phase above this transition. Here, the bismuth lone pair is disordered in-plane, allowing the polarizability to be...
substantially enhanced. In addition, density functional theory calculations estimated a large ferroelectric polarization and showed that the calculated polarization has almost equal contributions of the methylammonium and Bi\(^{3+}\) lone pair, which are fairly decoupled. The results add to the understanding of possible mechanisms to induce polar phases.

**Chapter 6:** The structural phase transitions of PEA\(_2\)MnCl\(_4\) (PEA = phenethylamine) were studied using temperature dependent single-crystal XRD analysis, including symmetry analysis of the observed space groups. The mechanism responsible for the polar phase transition appeared to be different to previously proposed mechanisms in similar systems. The transition is governed by the opening of a small dihedral angle between the phenyl ring planes of two adjacent PEA molecules, which consequently become crystallographically inequivalent in the polar phase. Notably, the polar axis was found to be out-of-plane with respect to the inorganic sheets. This is in contrast to other layered organic-inorganic hybrids as well as conventional layered perovskites, such as the Aurivillius phases, where in-plane polarization is observed. These findings add to the understanding of possible mechanisms that can induce ferroelectric behavior in layered organic-inorganic hybrids.

**Chapter 7:** Microstructures of two-dimensional (2D), orange-colored (C\(_6\)H\(_5\)CH\(_2\)NH\(_3\))\(_2\)PbI\(_4\) were successfully printed by two different soft lithography techniques. Notably, both techniques yielded microstructures with very high aspect ratios. X-ray diffraction revealed a strong preferential orientation of the crystallites in both patterned structures, compared to nonpatterned, drop-casted thin films. Furthermore, (time-resolved) photoluminescence measurements revealed that the optical properties of (C\(_6\)H\(_5\)CH\(_2\)NH\(_3\))\(_2\)PbI\(_4\) are conserved upon miniaturization. However, it was found that the larger grain sizes of the patterned films with respect to the nonpatterned film gave rise to an enhanced PL lifetime. This demonstrates the possibility to use color-tunable 2D hybrids in optoelectronic devices.

**Chapter 8:** Single crystals of two new compounds were synthesized: 2,5-dimethylaniline tin iodide organic-inorganic hybrids and 2,5-dimethylaniline triiodide. The synthesis routes that drive the growth of the different compounds while starting from 2,5-dimethylaniline and SnI\(_2\) were investigated. Single-crystal X-ray diffraction reveals that the hybrid grows as a rhombohedral structure, consisting of one-dimensional chains of Sn\(_{6}\)-octahedra that share corners and edges to build up a ribbon along the [111] direction. The triiodide salt forms a monoclinic structure consisting of linearly coordinated I\(_3^-\) features, separated by the organic amines. These findings give a better understanding of the role of hypophosphorous acid, H\(_3\)PO\(_2\), on the formation of both compounds.

**Chapter 9:** Spin-singlet formation was observed in a novel organic-inorganic hybrid identified as CH\(_3\)NH\(_3\)Cu\(_2\)Cl\(_5\). The hybrid adopts a layered structure in which Cu\(_2\)Cl\(_5^-\) layers are separated by CH\(_3\)NH\(_3^+\) layers. The inorganic layers consist of corner- and edge-sharing CuCl\(_6\)-octahedra, forming edge-sharing tetramers. Magnetic susceptibility measurements indicate strong antiferromagnetic interactions within the tetramers, whereas the coupling between the tetramers is weak. Low temperature
magnetic susceptibility data suggest a non-magnetic ground state with a large spin gap of $\sim 130$ K, in apparent contradiction with ferromagnetic interactions between nearest-neighbor spins. A novel spin-tetramer model is introduced in which antiferromagnetic next-nearest-neighbor interactions lead to a spin-singlet state.
Bibliography

CHAPTER 1. INTRODUCTION


