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Manipulating the Thermoelectric Properties and Spin Dynamics of 2D- and 3D-Organic-Inorganic Hybrid Perovskites

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14. ABSTRACT
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REPORT

Manipulating the thermoelectric properties and spin dynamics of 2D- and 3D- organic-inorganic hybrid perovskites

Abstract

A key parameter in the development of spintronic and electronic technologies is the assembly of new materials or cleverly engineering interfaces between existing materials. As part of our research efforts, we developed a synthesis approach for the fabrication of magnetic organic-inorganic hybrid perovskites for use in spintronic applications. We also investigated the thermoelectric properties of methylammonium tin iodide ($CH_3NH_3SnI_3$) as a function of morphology, doping, and light stress. During our thermoelectric studies, we faced critical challenges in clearly elucidating how changes in morphology due to different processing conditions affect the thermoelectric properties of $CH_3NH_3SnI_3$. This prompted us to develop an analytical tool which we dubbed mosaicity factor that allows us to accurately determine the degree of orientation of different crystallites within a thin film. By developing this tool, we can then correlate the thermoelectric properties of $CH_3NH_3SnI_3$ to a particular crystallite within the thin film. Last, we investigated the role of hydrogen bonding interactions in organic-inorganic hybrid perovskites when alkyl and π-conjugated crossslinkers are introduced into the structure as a means to impart crystal stability toward light and water degradation.

Research Accomplishments

1. Fabrication of magnetic organic-inorganic hybrid perovskites

Since the discovery of large tunneling magnetoresistance effects in double perovskites (i.e., Sr_2FeMoO_6)[153] and ferromagnetism in cubic perovskite $BaFeO_3$ under small magnetic field, there has been renewed interest in the magnetic properties and electronic properties of magnetic perovskite systems. In particular, materials with an electronically strongly correlated 3d element may allow a tuning of both magnetic and electronic properties via adjustment of interactions like spin-orbit coupling, local magnetic order, and/or structural distortions. Here, we synthesized, structurally characterized, and elucidated the magnetic properties of phenethylammonium manganese chloride $[(C_6H_5CH_2CH_2NH_3)_2MnCl_4]$. We also reported how the incorporation of copper atoms affects the magnetic properties of the hybrid perovskite. **Figure 1A** shows an optical micrograph of a pristine

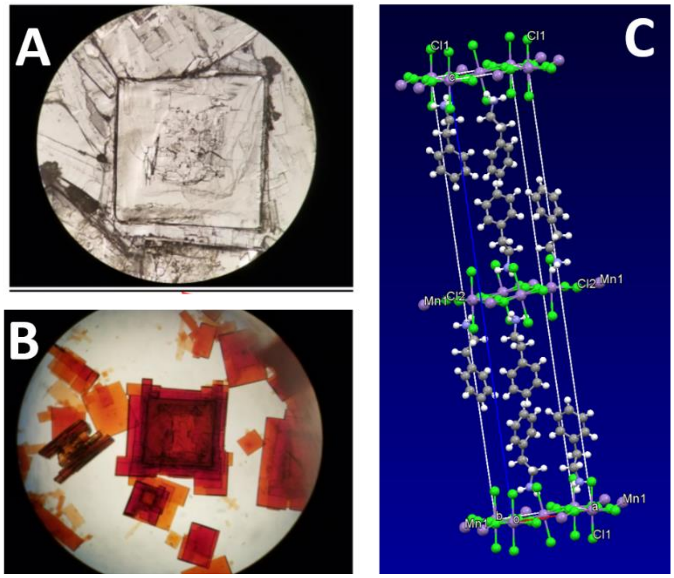

Figure 1. Optical micrographs for a pristine (A) and Mn/Cu (B) $(C_6H_5CH_2CH_2NH_3)_2MnCl_4$ single crystals. C. Crystal structure for the magnetic perovskite.

$(C_6H_5CH_2CH_2NH_3)_2MnCl_4$ single crystal. We can form several Mn/Cu solid solutions by controlling the amount of copper introduced into the $(C_6H_5CH_2CH_2NH_3)_2MnCl_4$ crystal structure. Interestingly, we observe the formation of red crystals when copper is introduced into the crystal structure (**Figure 1B**). Single crystal diffraction data show that both pristine and Mn/Cu solid solutions have the same crystal structure (**Figure 1C**). Moreover, by varying the stoichiometry of $(C_6H_5CH_2CH_2NH_3)_2Mn_{1-x}Cu_xCl_4$ from $x = 0.1$ to 0.5 we can then tune the magnetic properties of the perovskite. We further performed magneto-optic Kerr effect studies as a function of applied magnetic field. The MOKE measurement shows a magnetization loop with significant hysteresis with a Curie point at 247 K. The solid solutions show a magnetization loop with hysteresis at a Curie point as high as 300 K. We are currently using these materials in the assembly of Spin Seebeck devices. *We are currently preparing a manuscript showcasing our findings*.

2. Thermoelectric properties of $CH_3NH_3SnI_3$ thin films

Sn-based hybrid perovskites are metallic conductors over a wide temperature range, although optical absorption studies indicate that these compounds possess a band structure of that of an intrinsic semiconductor. Previous groups have investigated the electronic thermal transport of lead- and tin- based perovskites using *ab initio* electronic structure calculations based on DFT studies. They theoretically demonstrated that these hybrid perovskites possess very large mobilities (1500 cm^2/Vs) and carrier concentrations (10^{17} cm^{-3}) which could be beneficial for thermoelectric applications. These large carrier mobilities might originate from small carrier effective masses, in addition to a relatively weak electron–phonon (and hole–phonon) coupling. Since the investigation of hybrid perovskites for thermoelectrics is a new direction in the field of energy conversion, to the best of our knowledge, there is no precedent in the experimental determination of the electrical conductivity, carrier concentration, and Seebeck coefficient needed for the determination of power factors and hence *ZT* values. We anticipate that the thermoelectric properties of single-crystals and thin films will be different. Therefore, we studies the thermoelectrics properties of $CH_3NH_3SnI_3$ thin films and single crystals as a function of temperature, light exposure, microstructure, orientation, and aging.

Figure 2 depicts the electrical properties of $CH_3NH_3SnI_3$ single-crystals as a function of temperature (sample preparation and measurements are performed inside a glovebox to avoid oxidation of the Sn^{2+} metal center). The Hall hole mobility (the sample is found to have a positive Hall voltage relating to p-type behavior) and carrier concentrations at room temperature are about 300 ± 5 cm^2 V^{-1} s^{-1} and $1.5x10^{19}$ cm^{-3}, respectively. The obtained hole Hall mobility is comparable to those obtained for inorganic semiconductors, such as doped-Silicon and GaAs. These results strongly indicate that the transport properties of $CH_3NH_3SnI_3$ are those of a doped semiconductor. We believe, metal-like carriers are delocalized throughout the entire structure. Also, by using a homemade electrical conductivity/Seebeck setup, we determined a resistivity of $1.5x10^{-3}$ Ωcm for $CH_3NH_3SnI_3$

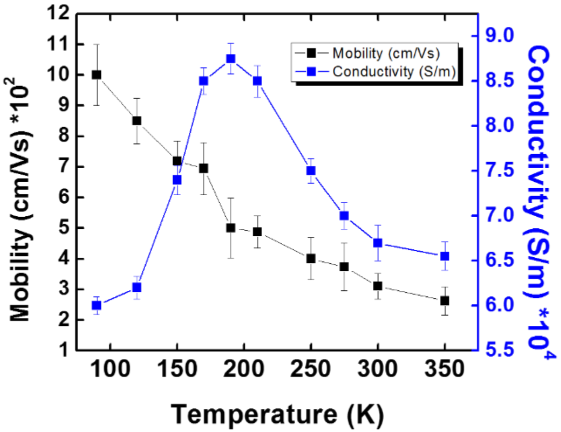

Figure 2. Electron Hall mobility and conductivity properties as a function of temperature for $CH_3NH_3SnI_3$ single-crystals.

single-crystals at room temperature. The obtained resistivity is comparable to most inorganic semiconductors yet we believe we can further decrease sample's resistivity via doping and/or structure engineering (viz., tuning the morphology and orientation). Furthermore, temperature dependence mobilities have been of a $T^{-1.3}$ to $T^{-1.6}$ nature, which suggest polaron dominated transport.

We experimentally determined Seebeck coefficients (**Figure 3**) as a function of temperature for our $CH_3NH_3SnI_3$ single-crystals. We obtained Seebeck values of +195 µV/K at 298 K. Since the Seebeck coefficient is inversely proportional to carrier concentrations, we believe tuning the latter will impact the Seebeck coefficient contribution. We also believe that these large Seebeck coefficient values might stem from multidegenerate conduction and valence bands. Our data point out to the possibility of reaching *ZT* values as high as 0.7 for $CH_3NH_3SnI_3$ single-crystals at room temperature. Although the thermoelectric properties of our $CH_3NH_3SnI_3$ thin films and single-crystals were acquired in a controlled environment, it is not clear to us if these crystals still undergo self-doping of the Sn^{2+} metal center thus turning into a doped semiconductor. In-situ XAFS studies will allow us to elucidate if these materials undergo self-doping upon aging and/or light exposure. *A manuscript for publication is currently under revision*.

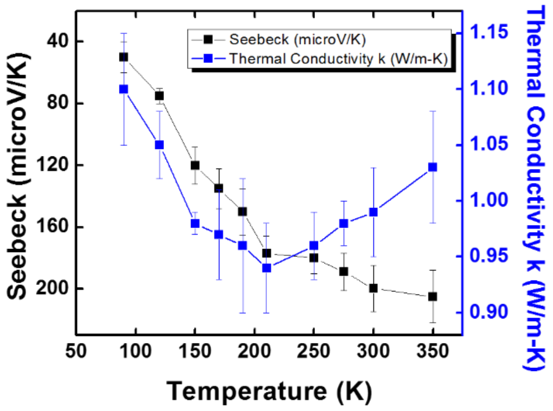

Figure 3. Seebeck coefficients and total thermal conductivity properties as a function of temperature for $CH_3NH_3SnI_3$ single-crystals.

3. Quantifying crystallite orientation and crystal heterogeneities in thin film materials using grazing incidence wide-angle X-ray scattering

Thin film materials have become increasingly more complex in morphological and structural design. When characterizing the structure of these films, a crucial field of study is the role of crystallite orientation, which can give rise to unique electronic properties. It is therefore important to have a comparative tool for understanding differences in crystallite orientation within a thin film, and also the ability to compare the structural orientation between different thin films. Herein we present a new method dubbed the mosaicity factor (MF) to quantify crystallite orientation in thin films using grazing incidence wide-angle X-ray scattering (GIWAXS) data. This method for quantifying orientation of thin films overcomes many limitations inherent in previous approaches such as noise sensitivity, the ability to compare orientation distributions along different axes, and the ability to quantify the orientation of multiple orientations observed within the same miller indices. Following the design of MF, experimental examples are then used to show how the MF approach yields quantitative orientation characterization of various materials assembled on a substrate.

Determining the MF of organic-inorganic hybrid perovskite thin films

It is well documented that the instability of hybrid perovskites towards oxygen and moisture may be improved by reducing their dimensionality from the well-studied three-dimensional system to an up and rising two-dimensional hybrid perovskite system. Ruddlesden-Popper phase perovskites are two-dimensional materials that follow the generic formula $A'_2A_{n-1}B_nX_{3n+1}$ (A' = bulky organic cation spacer; A = small organic or inorganic cation; B = Pb^{2+}, Ge^{2+}, or Sn^{2+}; X = Cl^-, Br^-, I^-; n is

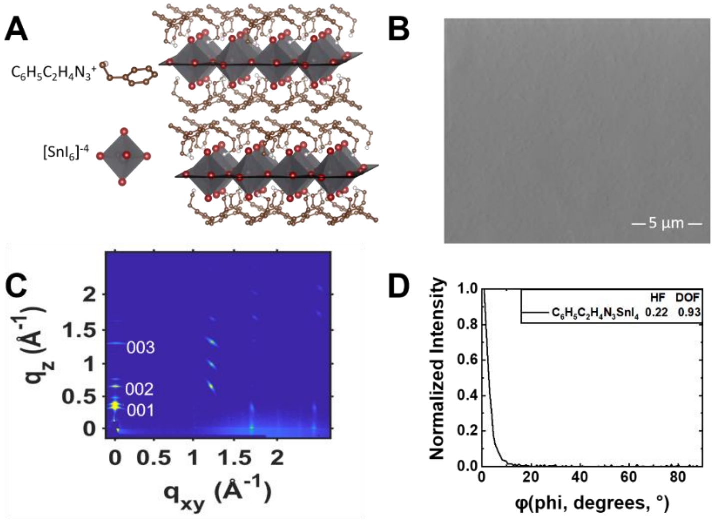

Figure 4. Case study -$(C_6H_5CH_2CH_2NH_3)_2SnI_4$. **(A)** 3D representation of the phenethylammonium tin iodide structure comprised of tin iodide sheets separated by phenethylammonium layers. **(B)** Scanning electron micrograph of a phenethylammonium tin iodide thin film showing a very uniform morphology. **(C)** GIWAXS spectrum of a phenethylammonium tin iodide thin film showing structural orientation with the (00l) indices reflecting along the out-of-plane direction. **(D)** Normalized intensity of the (002) reflection plotted as a function of φ, the azimuthal angle measured from $q_{xy} = 0$. HF and MF values are also listed. In this case, MF shows that the material is very oriented, while the small amount of noise observed along the base of the azimuthally integrated spectrum causes HF to yield an erroneous value.

an integer). Ruddlesden-Popper hybrid perovskites are composed of self-organized building blocks where sheets of corner-shared $[BX_6]^{4-}$ octahedra are stacked along the c-axis, separated by a large organic cation spacer on either side of the inorganic octahedra (**Figure 4A**). The anisotropic structure of the Ruddlesden-Popper hybrid perovskites has a large impact on their in-plane *vs.* out-of-plane charge transport characteristics. The structural orientation of 2D Ruddlesden-Popper hybrid perovskites, with respect to the substrate and upon different processing conditions, will significantly affect their electronic properties. **Figure 4B** shows a scanning electron micrograph for a 2D phenethylammonium tin iodide -$(C_6H_5CH_2CH_2NH_3)_2SnI_4$ (also represented as $(PhEA)_2SnI_4$) thin film. These films were prepared using previously reported methods. **Figure 4C** depicts the GIWAXS spectrum for a 2D $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ thin film. The reflection spots located on the q_z axis at 0.30 and 0.66 A^{-1} are the (001) and (002) crystallographic planes of the $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ crystal structure, respectively. The GIWAXS pattern presented in **Figure 4C** also demonstrates anisotropic intensities around the (001) and (002) crystallographic planes –being both most intense at the meridian ($q_{xy} = 0$). This is an indication that the (*00l*) planes of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ are preferentially oriented parallel to the substrate. **Figure 3D** shows the normalized intensity of the (002) reflection of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ plotted as a function of azimuthal angle (φ). Based on the azimuthal distribution, we can infer that there is very little spectral noise in the data. We can then proceed to determine MF about the (002) reflection of $(C_6H_5CH_2CH_2NH_3)_2SnI_4$ assuming $\varphi = 0^o$ at the meridian. Accordingly, $MF_{(002)}$ can range from 0 to 1 wherein $MF_{(002)} = 1$ indicates perfect alignment of the crystallites parallel to the substrate; $MF_{(002)} = 0$ indicates no preferential alignment of the crystallites. We obtain an $MF_{(002);0^o} = 0.93$, indicating that the film is preferentially oriented parallel to the substrate. On the other hand, the Hermans' orientation factor (the standard method used in the organic electronics community to determine crystal orientation) for the (002) crystallographic plane is 0.22, highlighting how minute amounts of noise within the sample can completely yield misleading orientation values. As such, the weighted amplitude of a signal applied in MF allows for a less errant orientation value when low levels of noise are present.

4. Understanding hydrogen bonding interactions in crosslinked methylammonium lead iodide crystals: towards reducing moisture and light degradation

Several approaches have been developed to unravel the limited stability of organic-inorganic perovskite crystals regarding oxygen, moisture, and UV light exposure. These approaches include modification of the perovskite structure via halide engineering, cation substitution and the addition of dopants, interface engineering, and surface passivation or encapsulation via small molecules or waterproof layers. Studies on mixed–halide perovskites, with the structure $CH_3NH_3PbI_{3-x}Cl_x$ or $CH_3NH_3PbI_{3-x}Br_x$, have been reported to show increased efficiencies and stability in air in contrast to their tri-iodide counterparts. As such, mixed-halide perovskites have become the most frequently used absorber in perovskite solar cell research; however, the increase in stability of the mixed-halide structure is on the order of hours to days under continuous light and moisture exposure, which is far from sufficient for commercial applications. Cation exchange and doping offer another pathway toward solving the short-term stability of metal halide perovskites. Exchanging the organic cation in the perovskite layer for a combination of cesium and methylammonium and/or formamidinium, NH_2CHNH_2, has generated crystals and thin films that are stable for up to 720 hours in a dry environment and up to 4 hours in 90% humidity. While these improvements in both stability and performance are promising, the degradation of the perovskite crystal structure in the presence of moisture levels >60 % remains a challenge. One of the most common procedures used to inhibit the degradation of devices in air relies on encapsulation using an additional protective layer. Notably, small molecules acting as crosslinkers have been shown to bind to the metal halide surface, thus passivating surface defects and preventing moisture infiltration. The use of crystal crosslinking agents is a highly promising area of study, and further investigation could lead to breakthroughs in perovskite solar cell stability; however, little is known about the physicochemical aspects underlying the crosslinking mechanism.

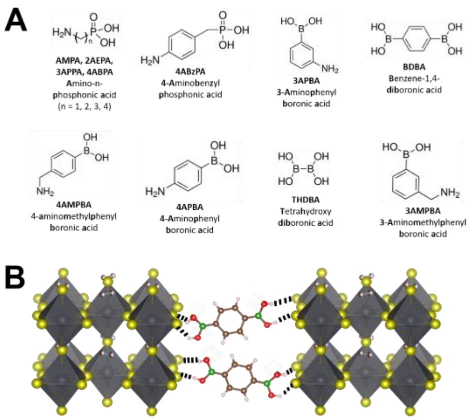

Figure 1. A) Chemical structures of crosslinking phosphonic and boronic acid small molecules used in this study. **B)** Schematic representation of a crosslinker (BDBA) hydrogen bonding two perovskite crystals. The crosslinker hydrogen bonds to the I^- of the $[PbI_6]^{4-}$ octahedra.

One of the major conceptual drawbacks that may be encountered upon introduction of an alkyl crosslinker into the active layer of a solar cell involves its potentially insulating nature. Specifically, it would be expected that an alkyl linker would lack the ability to transfer charges through crystal grain boundaries efficiently. This would introduce charge accumulation and recombination at the crosslinked sites. One possible solution to overcome this hurdle is to replace the alkyl group with a π-conjugated system. We hypothesized that π-conjugated linkers would lead to more efficient charge transfer that would increase the overall power conversion efficiency of the device while retaining the moisture stability benefits demonstrated in previous works. We further hypothesized that more efficient charge transfer between grains would enhance stability under illumination. Prior studies have only considered the stability of crosslinked metal halide perovskites only under dark conditions, and in general little is known about the mechanism and rates of degradation upon light illumination and high moisture levels. Herein, we investigated the effects of alkyl and π-conjugated crosslinking agents on the stability of methylammonium lead halide perovskite crystals under both dark and light conditions as well as under high moisture level exposure (>60 %). To understand the origin of these effects, we further employed X-ray diffraction, infrared spectroscopy, and DFT calculations, to investigate the nature of the interaction of the crosslinker with the perovskite and the mechanism of degradation within the perovskite to better understand how the choice of crosslinker affects stability. *A manuscript for publication is currently under revision*.