**Engineering the thermal transports of hybrid crystals via the manipulation of lattice and polar rotor dynamics**

**Abstract**

This project aims to (1) elucidate the polar rotor phonon scattering mechanisms in organic-inorganic hybrid perovskites and (2) engineer the rotational modes of organic cations in CH3NH3PbI3, H2NCHNH2PbI3, and CH3NH3PbBr3 compounds for desired thermal transport properties. Polar rotors in hybrid perovskites can effectively scatter phonons and directly affect their photovoltaic or thermoelectric energy conversion efficiencies; however, a quantitative microscopic understanding of the scattering mechanisms remains elusive because of the complicated hybrid nature and the limitations of standard research equipment and theoretical methods. A combination of large-scale experimental techniques and advanced theoretical methods will be applied in this project, including quasielastic and inelastic neutron scatterings, thermal transport measurement, and quantum mechanical computations in the electronic and atomistic scales.

The preliminary results of the Principal Investigator (PI) and his team show that the thermal transport in CH3NH3PbI3 is strongly affected by the polar rotational modes of the [CH3NH3]+ cations. The thermal properties of hybrid perovskites are important for a range of engineering applications including thermoelectric and photovoltaic energy conversions. The PI has demonstrated that the less-dispersive four-fold rotational modes of the organic cations in CH3NH3PbI3 strongly scatter not only the acoustic phonons but also the optical ones, which is distinctly different from the similarly less-dispersive rattling modes in skutterudites. Our preliminary results also indicate that the phonon scattering in hybrid perovskites is extremely sensitive and may be effectively tuned via lattice compression or electric field – a hypothesis that will be thoroughly investigated for the first time in this project. To verify this hypothesis, we will further develop our anharmonic lattice dynamics approach and utilize state-of-the-art large-scale neutron research facilities. The development builds upon the PI’s recent work, and it is thus highly feasible.

Strong evidence indicates that the polar rotational modes of organic cations in hybrid perovskites can be engineered via the alternations of chemical compositions. A systematic study of the effects of alloying on polar rotation, phonon scattering, and thermal transport properties will be carried out. Alloying elements will be initially screened via quantum mechanical simulations to provide guidelines for in-depth experimental investigations. Successful implementation of this project will lead to a more complete understanding of the polar rotor phonon scattering mechanisms in hybrid perovskites, and the results will expand our abilities to engineer their thermal transport properties. Moreover, new hybrid perovskite alloys with desired thermal properties will be developed and synthesized for potential applications in the renewable energy industries.

(a) Long-term impact

(1) Deeper insights into the novel polar rotor phonon scattering mechanisms in organic-inorganic hybrid perovskites

Hybrid perovskites exhibit unique optoelectronic and thermal transport properties and have emerged over the past few years as promising materials that have the potential to revolutionize the renewable energy industries. This class of materials are particularly appealing for photovoltaic and thermoelectric energy conversions; e.g., methylammonium lead iodide has a photovoltaic efficiency above 20% and a theoretical thermoelectric figure of merit of 3 at 600 K. Hybrid perovskites usually have low thermal conductivities, which may be ascribed to their low bulk moduli or short phonon lifetimes; nonetheless, a profound understanding of the phonon scattering mechanisms is still missing due to the complicated hybrid nature. The PI’s recent work on methylammonium lead iodide shows that the less-dispersive four-fold rotational modes of the methylammonium cations can strongly scatter both acoustic and optical phonons; this is distinctly different from the similar less-dispersive rattling modes in skutterudites, which scatter mainly the acoustic phonons. Because of the polar rotation of organic cations, novel phonon scattering mechanisms are expected to exist in hybrid perovskites.

A thorough understanding of the polar rotor phonon scattering mechanism is vital to the engineering of the thermal transport properties of hybrid perovskites. Due to the limitations of standard lab equipment and existing theoretical methods, it is difficult to investigate the polar rotor phonon scattering. In this project, we will attempt to tackle this problem by using large-scale neutron scattering facilities and advanced quantum mechanical simulation methods. The PI’s expertise in inelastic neutron scattering and density functional theory has paved the way for the proposed research. Novel and interesting results will be obtained to advance the fundamental knowledge of phonon scattering due to the polar rotation of organic cations.

(2) A pioneering effort to engineer the phonon scattering and thermal transport via the manipulation of the rotational modes of organic cations

Photovoltaic or thermoelectric materials that can directly convert solar energy or waste heat into electricity have attracted much research interest for their potential applications for tackling the global energy crisis. Hybrid perovskites usually have low thermal conductivities, which increase their thermoelectric figures of merit. On the other hand, the low thermal conductivity also benefits their photovoltaic energy conversion efficiencies because it promotes the up-conversion of acoustic-optical phonons and leads to a slow carrier cooling rate. Traditionally, crystalline imperfections such as grain boundaries, dislocations, or point defects are introduced to scatter phonons to minimize thermal transport; however, these lattice defects may be detrimental to the electrical properties due to the additional scattering of charge carriers.

In this project, we focus on the engineering of thermal transport properties of hybrid perovskites via the manipulation of the intrinsic rotational modes of organic cations. The PI’s preliminary results show that the four-fold rotation of the organic cations in methylammonium lead iodide is extremely sensitive, and the polar rotor phonon scattering can be effectively tuned. The effects of pressure and electric field on the different rotational modes of organic cations will be studied to advance current understanding of the intrinsic phonon scattering and thermal transport in hybrid perovskites.

(3) New hybrid perovskite alloys with desired thermal properties for potential industrial energy conversion applications

Hybrid perovskites generally consist of organic cations, metal cations and halide anions. By creating alloys of different hybrid perovskite compounds, the photovoltaic efficiency has increased from 3.8% to 22.1% since 2009. However, thermal property is still one of the major challenges for practical applications. Despite the importance of thermal transport properties, the alloying effects on phonon scattering are still largely unexplored and remain elusive. With the activations of the different rotational modes of organic cations, hybrid perovskites undergo a series of structural phase transitions. Because the corresponding phase transition temperatures vary largely among different hybrid perovskite compounds, it is expected that the polar rotor phonon scattering depends strongly on the chemical compositions and can be effectively tuned via alloying. In this project, a systematic study of the effects of alloying on the different polar rotational modes of organic cations and the thermal transport properties of hybrid perovskites will be carried out. Different alloy systems will be firstly screened from quantum mechanical simulations, and selected alloys will then be experimentally synthesized for in-depth studies. A better understanding of the phonon scattering mechanisms in hybrid perovskite alloys will be obtained, and a novel and practical route to achieve desired thermal properties will be established.

(b) Objectives

1. To elucidate and better understand the fundamental polar rotor phonon scattering mechanisms in organic-inorganic hybrid perovskites.

2. To establish a new approach for effective tuning of thermal transport via the manipulation of polar rotation of organic cations.

3. To develop new hybrid perovskite alloys with desired thermal properties for potential industrial applications in the renewable energy areas.

(a) Background of research

*(i) Work done by others*

Low thermal conductivity materials are of great interest in various engineering fields; e.g., they are extremely attractive for thermal barrier coating and optical phase-change applications [1-3]. Particularly, in the rapidly emerging field of renewable energy, materials with low thermal conductivities have potential applications in the conversion of waste heat and sunlight into electricity. The dimensionless figure of merit of a thermoelectric material is defined as , where , ,, and denote the thermal conductivity, electrical conductivity, Seebeck coefficient, and absolute temperature, respectively [4, 5]. It is seen that the energy conversion efficiency from heat into electricity is inversely proportional to the thermal conductivity [6]; therefore, high-performance thermoelectrics are always low thermal conductivity materials. Furthermore, suppressed thermal transport can also promote the up-conversions of acoustic-optical phonons and decrease the carrier cooling rate. Low thermal conductivity materials facilitate high photovoltaic energy conversion efficiency via the realization of the concept of the hot-carrier solar cell [7].

Thermoelectric and photovoltaic materials are semiconductors, in which the thermal conductions are usually dominated by lattice vibrations [8], also known as phonons. Therefore, phonon scattering represents an effective approach to hinder thermal transport and to achieve low thermal conductivity in materials related to renewable energy applications [9, 10]. Various forms of crystalline imperfections—including vacancies, interstitials, dislocations, and grain boundaries—have traditionally been used to scatter phonons [11]. Particularly, point defects induce mass and strain differences and effectively scatter high-frequency phonons. Differently, dislocations and grain boundaries mainly scatter phonons in the mid- and low-frequency ranges, respectively. Over the past 10-15 years, nanostructuring has been widely applied to maximize grain boundary phonon scattering to achieve low lattice thermal conductivity [12]. Despite the success of crystalline imperfections in lowering thermal transport, they may be detrimental to electrical transport properties because they also scatter carriers in addition to phonons. As can be seen from the above definition of the figure of merit, a high-performance thermoelectric material requires a high electrical conductivity. Additionally, a high carrier mobility is also beneficial for efficient photovoltaic conversion.

**Different from the scatterings of crystalline imperfections, intrinsic phonon-phonon coupling (PPC) can not only realize ultralow thermal conductivity [13, 14], but also maintain high carrier mobility.** Strong PPC represents an emerging paradigm for achieving high thermoelectric performance and realizing the hot-carrier solar cell. It has been reported that lone-pair electrons in IV-VI [15-17] and I-V-VI2 [18, 19], which represent the most studied thermoelectric materials, can induce strong lattice anharmonicity and low thermal conductivity. The lone pair electrons result in marginally stable lattices that tend to go through phase transformations. On the other hand, materials that contain rattling atoms such as skutterudites and clathrates can also exhibit extremely low thermal conductivities [20]. The rattling atoms are loosely bonded to the lattice and have large vibrational amplitudes at elevated temperatures. Acoustic phonons can be strongly scattered by the less dispersive phonon modes related to the rattling atoms [21]. Similarly, the polar rotations of organic cations in hybrid perovskite crystals (see Fig. 1) also induce less dispersive modes, which strongly scatter heat carrying acoustic phonons. Additionally, the study of Li et al. [22] also showed that the polar rotations of organic cations can couple strongly with the optical modes. Therefore, hybrid perovskites show distinctly different phonon coupling mechanisms from skutterudites or clathrates that contain rattling atoms [23].

Organic-inorganic hybrid perovskite crystals have attracted much research interest since 2009 due to their promising photovoltaic and thermoelectric properties [24, 25]; however, the lattice dynamics are still largely unexplored. Understanding the PPC mechanisms in hybrid perovskites is paramount because they not only dominate the thermal transport properties but also strongly affect the carrier mobility; e.g., it is still not clear why there is a large difference in carrier mobility between hybrid perovskites and the corresponding all-inorganic compounds [26]. Well-established method based on density functional theory (DFT) and harmonic approximation unfortunately cannot account for the PPC effects [27], because phonons are regarded as non-interacting quasiparticles. Molecular dynamics (MD) simulation represents a more suitable approach to study the PPC effects; however, reliable interatomic potentials are only available for a few of the most studied hybrid perovskites [28, 29]. On the other hand, experimental study of PPC, including frequency and lifetime across the Brillouin zone, requires large-scale scientific facilities and cannot be carried out using in-house lab equipment.

Despite the difficulties in the quantitative measurements of PPC, recent advances in quasielastic neutron scattering (QENS) and inelastic neutron scattering (INS) techniques have been shown to be extremely successful in the studies of the lattice dynamics of various photovoltaic and thermoelectric materials [30, 31]. For example, Li et al. [22] have investigated the organic cation rotational modes and phonons in CH3NH3PbI3, one of the most studied hybrid perovskites, by carrying out QENS and INS measurements in large-scale neutron facilities. It was found that the ultrafast polar rotation of the organic cations can effectively scatter optical phonons and charge carriers. The lattice dynamics of SnSe, a high-performance thermoelectric material, have also been characterized from INS measurements [13]. The anisotropic thermal conductivity was successfully rationalized, and the strong PPC was found to originate from the condensation of a transverse optical (TO) mode [13]. Additionally, the phonon dynamical structure factors of AgSbTe2, one of the least thermally conductive crystalline compounds, have been mapped across the Brillouin zone. A glass-like phonon scattering mechanism was found to dominate the ultra-low thermal transport [2].

Recent developments of computational methods have paved the way for theoretical studies of PPC in anharmonic crystals. At very low temperatures, harmonic approximation usually suffices in the description of atomic vibrations as phonons can be treated as non-interacting quasiparticles. At elevated temperatures, the effects of thermal expansion on the renormalization of phonon frequency may be accounted for by the quasi harmonic approximation (QHA), whereas this method may fail qualitatively in the case of strong lattice anharmonicity. For example, the phonon frequency of the zone-center TO mode of PbTe increases as temperature rises; however, QHA gave a completely opposite result [32]. More sophisticated theoretical approaches developed in recent years such as the temperature-dependent effective potential method [33] and the self-consistent ab initio lattice dynamical method [34] successfully solved the above problem of QHA for the TO mode of PbTe. These new approaches also allow the computation of phonon lifetime, which is assumed to be infinitely large in the QHA method. **Despite significant successes, these new methods are only applicable to crystals with atoms vibrating near equilibrium positions. The polar rotation of** **organic cations in hybrid perovskites, however, requires treatments beyond the perturbative approach.**

**The aim of this project is to unveil the polar rotor scattering mechanisms in organic-inorganic hybrid perovskites and to engineer their thermal transport properties using state-of-the-art experimental and theoretical approaches.** Three hybrid perovskite crystals—CH3NH3PbI3, H2NCHNH2PbI3, and CH3NH3PbBr3—are chosen as model systems in this project due to their promising photovoltaic and thermoelectric properties [35, 36]; one all-inorganic perovskite compound CsPbBr3 will also be include for comparison studies. It is expected that novel and interesting results will be obtained, which will provide insight into PPC in hybrid perovskites containing rotating organic cations. The successful implementation of this project will also provide important guidelines for developing hot-carrier solar cells and new thermoelectric materials with enhanced energy conversion efficiencies.

*(ii) Work done by the Principal Investigator (PI)*

The PI has an established track record in the research of PPC mechanisms in complex materials using advanced neutron scattering techniques and quantum mechanical computational methods [37-39]. Based on INS measurements, the PI has studied the lattice dynamics of AgCrSe2, which has a layer crystal structure intercalated with Ag atoms [40]. The transverse acoustic (TA) phonon modes of AgCrSe2 were found to be completely suppressed at elevated temperatures, while the longitudinal acoustic (LA) modes are less scattered (see Fig. 2). From DFT calculations, it was revealed that the completely suppressed TA modes originate from the diffusive behavior of the intercalated Ag atoms. It is well known that both TA and LA modes contribute to the thermal transport in solids, but liquids only employ the LA modes. Therefore, the observed features of the lattice dynamics of AgCrSe2 suggest that it has a liquid-like thermal transport behavior, rationalizing its ultra-low thermal conductivity. **This work was recently published in *Nature Materials [41]*.**

Preliminary results of a hybrid perovskite compound CH3NH3PbI3 indicate that the optical phonon modes are strongly scattered by the four-fold rotation of the [CH3NH3]+ cations and the optical phonon spectra are too broad to be determined from INS measurements at elevated temperatures [42]. On the other hand, the acoustic phonons are less affected by the polar rotation and their phonon lifetimes are still measurable, as shown in Fig. 3. Molecular dynamics simulations based on a classical interatomic potential [28] were performed to provide further insight into the experimental observations. The different rotational modes of the [CH3NH3]+ cations and the orthorhombic to tetragonal phase transition of CH3NH3PbI3 were successfully reproduced from MD simulations. The optical phonon spectra were successfully predicted for the first time, showing a dramatic broadening effect induced by the four-fold rotation of the organic cations, in good agreement with the INS measurements. Furthermore, a small hydrostatic pressure of 6 kbar was predicted to suppress the polar rotation of [CH3NH3]+ (see Fig. 4), and alter the phonon lifetime by more than one order of magnitude. These results suggest the possibility of phonon engineering and thermal optimization of hybrid perovskites via the control of polar rotor scattering through external fields.

The PI’s recent work on the PPC of thermoelectric PbTe using combined experimental and theoretical approaches revealed intriguing anharmonic features of the phonons [43]. A new peak was found to emerge from the power spectrum of the TO mode at the Brillouin zone center as temperature rises based on the INS measurements. To better understand the strong lattice anharmonicity, which dominates the low lattice thermal conductivity of PbTe, a theoretical study based on the slave-mode method developed by the PI’s group was carried out. The slave-mode method allows accurate calculations of all the third and fourth order anharmonic terms from DFT, thus enabling one to understand the PPC mechanisms at the deepest level. Additionally, the PI has also performed theoretical studies of lattice dynamics, as shown in Fig. 5, by calculating the phonon self-energy functions from anharmonic force constants. This approach has been applied to graphene and hexagonal boron nitride monolayer to study the PPC and thermal transport behaviors under large strain conditions, although the corresponding experimental measurements are yet to be performed due to the various challenges for two-dimensional systems [44, 45].

In addition to the study of PPC mechanisms, the PI also has extensive experience in performing direct experimental characterizations of thermal transport properties as evidenced from the recent publications on GeTe alloys [46-48], Ag9GaSe6 [49], SnSe [50], and PbTe1-xSex + SrTe [51]. Thermal conductivity () was obtained from , where represents density and denotes the diffusivity coefficient, which was measured using the laser flash method (see Fig. 6). The heat capacity () was obtained from the Dulong-Petit limit assuming that it is independent of temperature. The electronic contribution to the thermal conductivity was analyzed and subtracted from the total value to determine the lattice component. On the other hand, the PI has performed theoretical investigations of thermal transport properties based on the non-equilibrium MD simulations [52, 53], in which a heat source and a heat sink were applied to create a temperature gradient. The thermal conductivity was obtained from , where and represent the heat flux and temperature, respectively. Alternatively, lattice thermal conductivity was also calculated from the Boltzmann equation using the single-mode relaxation time method [45].

It was not realized until recent years that hybrid perovskites are promising materials for various energy related applications; however, the PPC mechanisms that dominate the thermal transport remain elusive. **The PI’s expertise in neutron scattering techniques and quantum mechanical computations is ideal for examining the polar rotor scattering originated from the organic cations.** Such a combination of skills is rare among scientists and offers unique opportunities for the proposed project. The results obtained by the PI so far demonstrate that he has the necessary experimental tools and experience to study the PPC mechanisms in hybrid perovskites and engineer the thermal transport properties. Consequently, the PI proposes a combined experimental and theoretical study as detailed in the following sections.

(b) Research plan and methodology

Polar rotor scattering mechanisms and thermal transport properties of our model systems (CH3NH3PbI3, H2NCHNH2PbI3, and CH3NH3PbBr3) will be investigated using state-of-the-art experimental techniques and quantum mechanical computational approaches. A closely related all-inorganic CsPbBr3 compound will be studied for direct comparisons with the hybrid CH3NH3PbBr3. The anharmonic lattice dynamics method developed by the PI’s group will be further extended to allow the study of the PPC mechanisms in hybrid perovskites with rotating organic cations. Phonon power spectra across the Brillouin zone will be measured from experiments and directly compared with theoretical results for in-depth understanding of the microscopic polar rotor scattering. The effects of external pressure and electric field on the PPC will be studied using ab-initio molecular dynamics (AIMD) simulations made efficient by the orbital transformation (OT) method. The alloying effects will also be systematically studied to engineer the thermal transport properties for enhanced energy conversion efficiency.

*(1) Polar rotor activation and structural phase transformation from* *QENS measurement and AIMD simulation* *(to achieve objective 1)*

Hybrid perovskites are a new class of materials with promising photovoltaic properties. Although they have high photovoltaic energy conversion efficiencies, their carrier mobilities are rather low; e.g., compared with the all-inorganic perovskite compound CsPbBr3, the carrier mobility of the hybrid CH3NH3PbBr3 is almost five times lower [26]. A quantitative microscopic understanding of the polar rotor scattering is not only critical for improving the carrier mobility of hybrid perovskites but also paves the way for thermal transport engineering, which is directly related to the energy efficiency. The PI plans to build on his preliminary results to further investigate the polar rotations of organic cations by carrying out QENS measurements using the large-scale neutron facilities at the Japan Proton Accelerator Research Complex (J-PARC). **The backscattering neutron spectrometer DNA of J-PARC has an ultrahigh energy resolution and will be used to measure the QENS spectra as a function of temperature.** Critical information on the activations of the different rotational modes and the closely related structural phase transitions will be obtained.

To provide further insight into the experimental measurements, the PI will carry out theoretical studies based on accurate AIMD simulations. Different from classical MD, in which atomic forces are calculated from empirical interatomic potentials, AIMD simulations are based on accurate atomic forces obtained from first-principles DFT calculations. Additionally, interatomic potentials are only available for a few of the most studied hybrid perovskites, not to mention their alloying systems. Therefore, AIMD represents the most suitable method for a systematic study of the atomic dynamics of the proposed model hybrid perovskites, given that the Debye temperatures of these model systems are below ~220 K [54]. Nonetheless, AIMD simulation is extremely computationally demanding; even with modern supercomputers, only a few hundred atoms may be readily simulated for a period in the picosecond scale. To accurately account for the atomic dynamics in hybrid perovskites, however, larger systems need to be simulated for longer periods of time. To increase the computational efficiency of AIMD, the PI will apply the recently developed OT method which allows efficient optimization of wave functions and avoids the diagonalization of the Kohn-Sham matrix [55]. The OT method has been successfully implemented in the open-source Quickstep code [56], which greatly eases the burden of this project for method implementation. With existing high-performance computing facilities, the PI has successfully applied the OT method to simulate thousands of atoms for nanoseconds. Based on this combined experimental and theoretical investigation, a more complete understanding of the different rotational modes of the organic cations and the corresponding structural phase transitions of hybrid perovskites is expected to be gained.

*(2) Phonon scattering by rotational organic cations and its effects on the thermal transport properties (to achieve objective 1)*

Building upon the PI’s recent works on the intrinsic phonon coupling mechanisms, he will further develop the anharmonic lattice dynamics approach to study the polar rotor scattering in hybrid perovskites. Phonon power spectra () across the Brillouin zone will be calculated based on the Wiener-Khintchine theorem [57] as a function of temperature using the following equation:

The wave vector and phonon branch are represented by and , respectively; is the number of points; and denote the atomic position and velocity, respectively; and , , and denote the atom type, an atom of a given type, and the displacement, respectively. The phonon eigenvector () will be computed using the finite displacement method [58], which has already been implemented in the open-source Phonopy program [59]. Additionally, INS spectra will be measured at the AMATERAS beamline of J-PARC. The experimental phonon lifetime and frequency will be directly compared with the theoretical values, allowing an in-depth study of the lattice dynamics.

Because the rotations of organic cations are very flat modes, they induce strong scatterings of acoustic phonons. This is analogous to the rattling filler scattering in skutterudites, where less-dispersive modes scatter strongly the acoustic phonons. As acoustic modes carry the majority of the heat, it is expected that polar rotor scattering in hybrid perovskites greatly lowers the lattice thermal conductivity. On the other hand, the PI’s preliminary results also indicate that the polar rotation of the organic cations can scatter the optical phonons intensively, which may result in a further suppression of the thermal transport. To provide further insight into the relation between phonon scattering and thermal transport of hybrid perovskites, non-equilibrium AIMD simulations will be performed in this project, and thermal conductivity will be calculated by dividing the heat flux by the temperature gradient. Based on the proposed combined experimental and theoretical studies, a more complete understanding of the polar rotor scattering of phonons and the corresponding effects on the thermal transport will be obtained, paving the way for further thermal property engineering.

*(3) Manipulating the polar rotor scattering and thermal transport via pressure and electric field* *(to achieve objective 2)*

The PI’s preliminary results show that the polar rotation of the organic cations in CH3NH3PbI3 is very sensitive to compression; a small hydrostatic pressure of 6 kbar can effectively suppress the four-fold rotation of the [CH3NH3]+ cations in the tetragonal phase [42]. Because of the strong polar rotor scattering of phonons and the related structural phase transitions in hybrid perovskites, the manipulation of the rotation of the organic cations is of great significance for engineering the thermal transport properties. Alternatively, due to the polarization of the organic cations, an external electric field may also be applied to tune the polar rotor scattering, analogous to the pressure effects. As the polar organic cations in hybrid perovskites are embedded in inorganic frameworks, it is expected that the energy barrier for activating the rotational modes will be increased once the frameworks are compressed or an electric field is applied to the polar organic cations. However, the corresponding microscopic PPC mechanisms and the thermal transport tuning effects need to be further investigated.

The effects of pressure and electric field on the rotation of organic cations, phonon scattering, and thermal transport of the proposed model hybrid perovskites will be systematically studied based on the nudged elastic band (NEB) method, AIMD simulations, and neutron scattering experiments. Firstly, NEB calculations will be performed to predict the energy barriers for activating the different rotational modes of organic cations under a hydrostatic pressure or an electric field, which can be readily applied using most of the existing implementations of DFT. Particularly, the climbing image method [60] will be used to accurately find the energy saddle point with fewer intermediate images. From the evolution of the energy barrier, one will be able to estimate the magnitude of pressure or electric field that is required to tune the polar rotation. Secondly, efficient AIMD simulations will be performed for further investigation of the effects of pressure and electric field on the lattice dynamics. Because the polar rotation is very sensitive to pressure, corresponding neutron scattering experiments will be performed at J-PARC, which provides a pressure environment up to several gigapascal. Neutron scattering experiments under an electric field may also be performed if the AIMD simulations suggest it is feasible. Lastly, non-equilibrium AIMD simulations will be carried out to study the effects of pressure and electric field on the lattice thermal conductivity. Due to the hybrid nature of the proposed systems, it is expected that the thermal transport properties are highly tunable, which will facilitate the engineering of their energy conversion efficiency.

*(4) Alloying effects on phonon scattering and thermal transport* *(to achieve objective 3)*

Hybrid perovskites can be generally represented by a chemical formula of AMX3, where A denotes an organic cation (e.g., methylammonium [CH3NH3]+ or formamidinium [H2NCHNH2]+); M denotes a metal cation such as Pb2+, Sn2+ or Ge2+; and X represents a halide anion such as Cl-, Br-, or I-. The great tunability of the electronic band gap and the electrical transport properties of hybrid perovskites via alloying facilitates the realization of high photovoltaic efficiency; e.g., the (H2NCHNH2)0.66(CH3NH3)0.33PbI2.5Br0.5 alloy achieved an energy conversion efficiency as high as 20.7% [61]. Despite the importance of thermal properties that are related to the concept of hot-carrier solar cell for ultra-high photovoltaic efficiency and thermoelectric applications, the alloying effects on the polar rotor scattering of phonons and thermal transport remain elusive. From the very different structural phase transition temperatures of hybrid perovskites, which are directly related to the rotational modes of the organic cations, it is expected that alloying will be extremely effective in tuning the polar rotor scattering.

A systematic study of the effects of alloying on the phonon scattering and thermal transport properties of hybrid perovskites will be carried out. To avoid unnecessary trial and error, theoretical investigation will be performed to screen the different combinations of alloying elements at the three different sublattice sites of AMX3. Alloying effects on the activation energy barriers of the different rotational modes of organic cations will be calculated using the NEB method. Ab-initio molecular dynamics simulations will then be performed and the effects of alloying on the polar rotor scattering of phonons will be analyzed at different temperatures. Non-equilibrium AIMD simulations will also be carried out to predict the lattice thermal conductivities of the alloys. Guided by theoretical investigations, selected new hybrid perovskite alloys will be synthesized for further experimental studies. Crystals will be grown using the hydrohalic acid solution method following the steps reported previously [62]. Neutron scattering measurements including QENS and INS will then be performed to study the rotation of organic cations and the microscopic PPC mechanisms. The thermal conductivity will be measured using the Quantum Design Physical Property Measurement System as a function of temperature. The theoretically predicted polar rotation, phonon frequency, phonon lifetime, and lattice thermal conductivity will be compared directly with the experimental results for direct insight into the lattice dynamics and thermal transport.

**In summary**, the PI proposes to carry out combined experimental and theoretical investigations to better understand the polar rotor phonon scattering mechanisms in hybrid perovskites, and to engineer their thermal transport properties via the control of the rotation of organic cations. Promising preliminary results have been obtained. The less-dispersive rotational modes of organic cations in CH3NH3PbI3 were found to scatter strongly both acoustic and optical phonons, which is distinctly different from the conventional rattling filler scattering in skutterudites. The polar rotation of the [CH3NH3]+ cation was found to be extremely sensitive to compression, suggesting the possibility of effective tuning of the phonon scattering and the thermal transport properties. Existing difficulties in the study of polar rotor scattering of phonons in hybrid perovskites demonstrate a need to utilize large-scale neutron research facilities and to further develop current theoretical methods. The successful implementation of this project will lead to deeper insight into the novel polar rotor phonon scattering mechanisms in hybrid perovskites, which will provide guidelines for engineering the thermal transport properties. Furthermore, new hybrid perovskite alloys with desired thermal properties will be developed and synthesized for energy conversion applications.

**Figure 1** (a) Crystal structure of the orthorhombic phase of hybrid perovskite CH3NH3PbI3. (b) Schematic of a unit cell of the orthorhombic phase. (c) The different rotational modes of the organic [CH3NH3]+ cations.

**Figure 2** The PI’s recent work on the inelastic neutron scattering measurements of the dynamic structure factors of AgCrSe2 at 150 K (a) and 520 K (b) [40], showing the suppression of the TA phonon modes. (c) A contour plot of the dynamic structure factor of AgCrSe2.

**Figure 3** Preliminary results showing the dynamic structure factors of hybrid perovskite CH3NH3PbI3 measured from inelastic neutron scattering experiments along the (a) [*hh*0] and (b) [00*l*] directions.

**Figure 4** Our preliminary results showing the activations of the different rotational modes of the [CH3NH3]+ cations in CH3NH3PbI3 from MD simulations at different temperatures and hydrostatic pressures.

**Figure 5** (a) The PI’s recent work on the calculations of phonon spectra of strained graphene at elevated temperatures [43].

**Figure 6** (a) The PI’s recent work [46, 51] on the measurements of thermal conductivity of GeTe-PbSe alloys as a function of temperature using the laser flash technique, and (b) the theoretical investigations of the lattice thermal conductivity of DNTT organic semiconductor using the non-equilibrium MD simulations.

Yue Chen’s research comprises the studies of materials physics for thermal and electrical transports, such as lattice dynamics and electronic structures. In particular, he has been focusing on the phonon-phonon coupling problem in thermoelectric materials using neutron techniques and density functional theory-based methods. He has been studying the intrinsic ultralow thermal conductivities of crystalline solids with giant lattice anharmonicity and the related phonon scattering mechanisms. Lately, he developed an innovative approach for calculating phonon frequencies and lifetimes at elevated temperatures by bridging the computational gap between the electronic and the atomistic scales, named “the slave-mode method”. He has been the Principle Investigator of multiple research projects funded by the Research Grants Council (RGC) of Hong Kong, and the National Natural Science Foundation of China (NSFC).

There are three collaborators in this project: Dr. Yukinobu Kawakita, a neutron scientist at the Japan Proton Accelerator Research Complex (J-PARC), and Prof. Jiaqing He and Prof. Bing Li, established researchers in the fields of thermal transport and lattice dynamics at Southern University of Science and Technology (SUSTech) and Institute of Metal Research, Chinese Academy of Sciences, respectively.

Yukinobu Kawakita will provide technical support to the PI and his team in performing quasi-elastic and inelastic neutron scattering measurements at J-PARC. The collaboration between Yukinobu Kawakita and the PI has been successful; a joint paper entitled ‘Liquid-like thermal conduction in intercalated layered crystalline solids’ was recently published in Nature Materials (v17 (2018) 226).

Jiaqing He will support the PI with his state-of-the-art thermal transport laboratory at SUSTech in Shenzhen, and Bing Li will be collaborating with the PI in the study of lattice dynamics. Because Shenzhen is situated immediately north of Hong Kong, the PI will have convenient access to the equipment. The PI’s highly productive collaborations with Jiaqing He and Bing Li have been demonstrated by recent joint publications in [1] Science, 360 (2018) 778, [2] Energy Environ. Sci., 11 (2018) 2486 (Impact Factor: 30.067), [3] J. Phys. Chem. Lett., 9 (2018) 3029, and [4] Adv. Energy Mater., 7 (2016) 1601450.

The PI will have an overall responsibility for the proposed project, including the execution of all the proposed experimental and theoretical tasks and the analysis of the results. The theoretical work, i.e., method development for polar rotor phonon scattering calculations, AIMD simulations, and thermal transport property computations, will be carried out using the supercomputing facilities of the University of Hong Kong. Experimental tasks, including sample preparation and various in-house characterizations, will also be carried out in Hong Kong. Selected samples will go through further thermal transport and lattice dynamics investigations at SUSTech and J-PARC.