

PEROVSKITES

Lead halide perovskites: Crystal-liquid duality, phonon glass electron crystals, and large polaron formation

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Lead halide perovskites have been demonstrated as high performance materials in solar cells and light-emitting devices. These materials are characterized by coherent band transport expected from crystalline semiconductors, but dielectric responses and phonon dynamics typical of liquids. This “crystal-liquid” duality implies that lead halide perovskites belong to phonon glass electron crystals, a class of materials believed to make the most efficient thermoelectrics. We show that the crystal-liquid duality and the resulting dielectric response are responsible for large polaron formation and screening of charge carriers, leading to defect tolerance, moderate charge carrier mobility, and radiative recombination properties. Large polaron formation, along with the phonon glass character, may also explain the marked reduction in hot carrier cooling rates in these materials.

INTRODUCTION: THE CRYSTAL-LIQUID DUALITY

Lead halide perovskites have emerged as superstars among materials for photovoltaics and light emission (1–6). A large number of studies have explored the mechanistic origins of their electronic properties, such as long carrier lifetimes, long carrier diffusion lengths, and exceptional defect tolerance (7–11). The unique properties of both hybrid organic-inorganic lead halide perovskites (HOIPs) and their all-inorganic counterparts result from the framework-like structure consisting of a sublattice of corner-sharing PbX_6^{3-} ($X = \text{I}, \text{Br}, \text{or Cl}$) octahedral with overall stoichiometry PbX_3^- and a sublattice of A^+ cations in the cuboctahedral voids, as shown schematically in Fig. 1 (12). Here, $\text{A}^+ = \text{Cs}^+, \text{Rb}^+, \text{CH}_3\text{NH}_3^+$ (MA), or $\text{NH}_2(\text{CH})\text{NH}_2^+$ (FA). The framework structure leads to intrinsic softness and dynamic disorder. The former is shown by their Young’s moduli being approximately $10\times$ lower than those of Si or GaAs (13, 14). The latter is reflected by broadening and anharmonicity in far-infrared (IR) and low-frequency Raman spectra, disorder in nuclear magnetic resonance (NMR) spectra and x-ray or neutron scattering, and liquid-like responses in dielectric function or femto- to picosecond responses (15–26).

For each lead halide perovskite, there are three main structural phases. In the low-temperature orthorhombic phase ($T < 144.5$ K and 370 K for MAPbBr_3 and CsPbBr_3 , respectively), the PbBr_6^{3-} octahedron undergoes Jahn-Teller distortion and the cation motion is restricted (24, 27, 28). For MAPbBr_3 (CsPbBr_3), the perovskite structure transitions to the tetragonal phase at $T = 149.5$ to 237 K (370 to 420 K) and the cubic phase at $T > 237$ K (420 K) (24, 27, 28). Similar phase transitions are present in I- and Cl-based perovskites. These transitions are accompanied by increasing dynamic disorder, particularly the orientational motions of organic cations in HOIPs (26).

The coexistence of a crystalline-like response in coherent band transport of charge carriers and a liquid-like response in phonon activities has prompted Zhu *et al.* (25) to call HOIPs “crystalline liquids” for the cubic and tetragonal phases. We can view the sublattice of organic cations as a confined liquid, with each polar molecular cation confined in a nanoscopic pore; thus, an HOIP in the high-temperature cubic phase is similar to a plastic crystal (29), which refers to a crystalline lattice with long-range translational order but local rotational disorder (30). More precisely, the liquid-like behavior may generally represent the highly disordered and anharmonic motions of the strongly coupled

vibrational modes of both PbX_3^- and A^+ sublattices (31). Here, we discuss three important consequences of the crystal-liquid duality: (i) The contrasting phonon and electron dynamics mean that lead halide perovskites belong to the family of solids called phonon glass electron crystals (PGECs) (32); (ii) the band-like charge transport, coupled with the liquid-like polarizability, means that a charge carrier can effectively form a large polaron (33), whose screened Coulomb potential reduces its scattering with charged defects and with other charge carriers; and (iii) large polaron formation, coupled with the phonon glass characteristics, may explain the much reduced cooling rates of hot carriers in HOIPs (25, 34).

PHONON GLASS ELECTRON CRYSTAL

PGEC refers to a class of solids where charge transport is ballistic and phonon transport is diffusive. This ensures high electric conductivity but low thermal conductivity, the most desirable combination for efficient thermoelectrics. Since the initial proposal by Slack in 1995 (35), the PGEC concept has guided much research in thermoelectrics (32, 36–39). A PGEC typically has large electronic bandwidth for efficient charge transport, whereas the phonon bands are disrupted by efficient scattering with local vibrations. At the limit of phonon disorder when the mean free path for phonon scattering is less than half of the phonon wavelength, we can essentially view nuclear motions in the solid as a collection of local vibrations (32, 39), as is likely the case in HOIPs (31, 40, 41). Thermal transport occurs diffusively from the coupling of these local vibrations to their neighbors via damped oscillations.

The search for PGECs over the past 20 years has focused on semiconductors consisting of crystalline frameworks that determine their electronic band structures, but with pores enclosing weakly bound atoms or ions. A representative PGEC is the so-called type I clathrate compound, whose crystal structure consists of networked cages of tetrakaidecahedrons and dodecahedrons (Fig. 2A), each housing a group 1 or 2 guest atom “rattling” in the cage, as shown in Fig. 2 for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ (32). The motion of a rattling ion with respect to the cage with opposite charge can be represented by a varying dipole moment (Fig. 2B). The rattling in the nanocages introduces efficient scattering for the phonons, particularly acoustic phonons that are mainly responsible for thermal transport.

It is clear from the above definition that a lead halide perovskite crystal belongs to the PGEC material family. Here, the PbX_3^- sublattice

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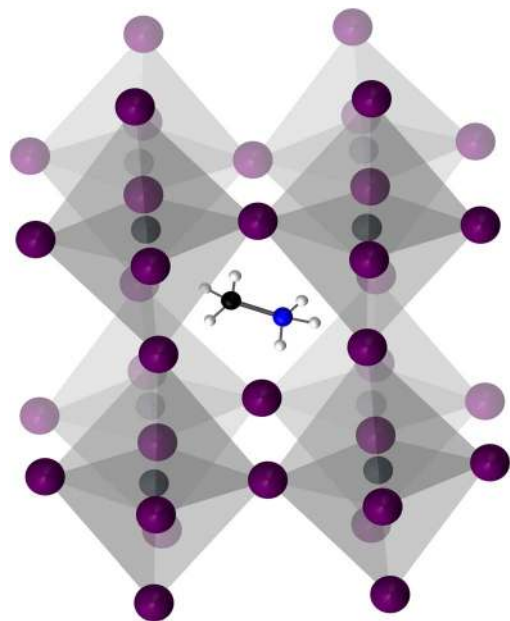


Fig. 1. Structure of $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskite. It consists of a framework of corner-sharing lead (gray) halide (purple) octahedra and the CH_3NH_3^+ cation (black, blue, and white) in the nanocage.

forms the crystalline framework, whereas the A^+ cations “rattle” and/or “rotate” in the cuboctahedral cages (Fig. 1). The “phonon glass” character has come from various spectroscopic studies. Early NMR measurement on $\text{CH}_3\text{NH}_3\text{PbX}_3$ crystals revealed rapid rotational motion of CH_3NH_3^+ cations within the perovskite framework (15). The liquid-like behavior in the tetragonal and cubic phases is particularly apparent from the temperature-dependent dielectric function, which can be well described by the Kirkwood-Fröhlich equation originally developed for polar liquids (16). More recently, direct probe of phonon activities by neutron scattering (17, 19, 20), x-ray scattering (18, 21, 26), far-IR (22), terahertz (THz) (23), Raman (17, 23, 24), two-dimensional IR (42), and time-resolved optical Kerr effect (TR-OKE) (25, 43) spectroscopies all revealed dynamic disorder, large anharmonicity, and overdamped vibrational motions. This dynamic behavior has been confirmed in molecular dynamics simulations (31, 44–46). Here, we show two examples in time and frequency domains, respectively.

As the first example, Fig. 3 compares TR-OKE responses from three single-crystal lead halide perovskites— MAPbBr_3 , FAPbBr_3 , and their all-inorganic counterpart, CsPbBr_3 —at room temperature. Note that at 295 K, both MAPbBr_3 and FAPbBr_3 are in the most disordered cubic phase, whereas CsPbBr_3 is in the most crystalline orthorhombic phase. In a TR-OKE experiment (47, 48), shown schematically in the inset of Fig. 3A, a polarized laser pulse (pump) induces anisotropy in the refractive index and, thus, transient birefringence in the sample. After a controlled time delay, a probe laser pulse measures the decay in transient birefringence based on polarization rotation. This technique has been used in the past to probe liquids, particularly diffusive reorientation dynamics on picosecond time scales (47, 48). In a crystalline solid, the TR-OKE transient is typically dominated by the ultrafast and nearly instantaneous electronic polarization, plus weaker coherent oscillations attributed to impulsively stimulated Raman excitation of phonons (49). The TR-OKE responses in Fig. 3 are more liquid-like than crystalline solid-like. Whereas the transient from CsPbBr_3 is dominated by the

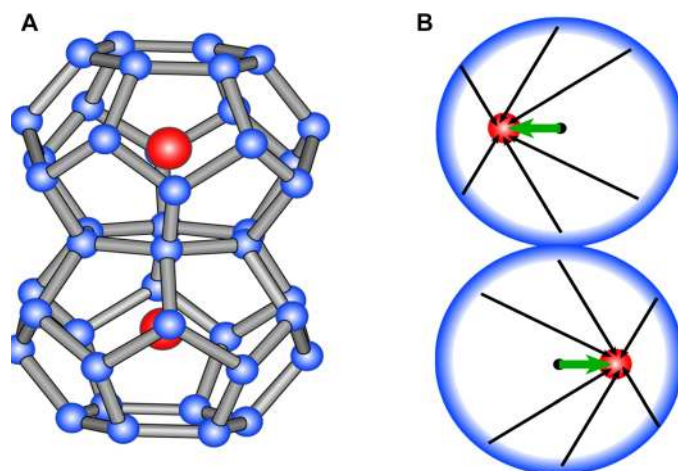


Fig. 2. Structure of a PGEC, $\text{Ba}_9\text{Ga}_{16}\text{Ge}_{30}$. (A) Two tetrakaidecahedron cages along the z direction consisting of anions and guest Ba^{2+} cation rattling against the anionic cage. (B) The cage (outer circles) and the symmetry-broken off-center guest atom compose an effective electric dipole moment (thick arrows), which is the vector sum of each dipole (thin arrows). Reprinted figure with permission from Takabatake *et al.* (32). Copyright 2014 by the American Physical Society.

electronic response (laser cross-correlation) with a tail on the subpicosecond time scale, the transients from MAPbBr_3 and FAPbBr_3 feature broad and picosecond responses typical of diffusive motions in liquids. Note that, in the orthorhombic phase of CsPbBr_3 , the crystalline behavior is revealed by the presence of coherent oscillation in the TR-OKE signal, which is particularly enhanced when the excitation photon energy moves closer to the bandgap (43).

The liquid-like behavior is also evident in the frequency domain, as shown by low-frequency Raman spectra of Yaffe *et al.* (24) for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and CsPbBr_3 crystals across the two phase transitions with increasing temperature (Fig. 4). Although the low-temperature orthorhombic phases (blue) of both crystals feature well-resolved phonon modes ($\leq 100 \text{ cm}^{-1}$), mainly of the lead bromide sublattice, the spectra become very diffuse and are dominated by a central peak in the tetragonal (green) and cubic (red) phases, indicating anharmonic and local polar fluctuations over broad time scales (24). Note that the phase transition temperatures of CsPbBr_3 are much higher than those of $\text{CH}_3\text{NH}_3\text{PbBr}_3$; at room temperature, the former is in the low-temperature orthorhombic phase, whereas the latter is in the high-temperature cubic phase.

The phonon glass characteristics, along with the respectable charge carrier mobilities reported to date, suggest that lead halide perovskites are promising candidates for thermoelectric materials (31, 40, 41, 50–52). Experimental measurements (53–56) and dynamics simulations (31, 41) revealed that thermal conductivities in HOIPs and their all-inorganic counterparts range from 10^{-1} to $10^0 \text{ W m}^{-1} \text{ K}^{-1}$, which are one to two orders of magnitude lower than those in conventional inorganic semiconductors but are rather similar to those of glasses or liquids (57). Kovalsky *et al.* (54) measured the thermal conductivity of MAPbI_3 that is a factor of 1.5 lower than that of CsPbI_3 . The Debye model (that is, phonon gas model) effectively describes the thermal conductivity of both perovskites, consistent with the phonon glass characters, including the greater phonon disorder in MAPbI_3 than that in CsPbI_3 . This phonon glass character and slow acoustic phonon transport may also contribute to the slow cooling of hot carriers, as discussed later.

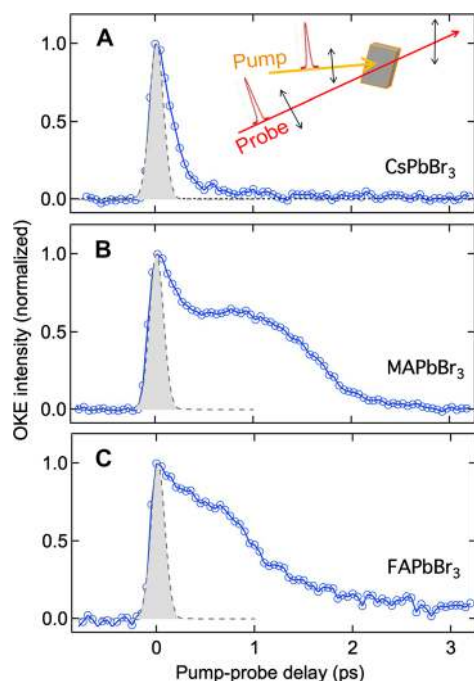


Fig. 3. TR-OKE probes liquid-like motions in lead halide perovskites. TR-OKE transients from single-crystal (A) CsPbBr₃, (B) MAPbBr₃, and (C) FAPbBr₃. The pump-probe cross-correlation is depicted as gray [full width at half-maximum (FWHM), 70 fs]. The inset in (A) illustrates the experimental setup. From Zhu *et al.* (25). Reprinted with permission from AAAS.

DYNAMIC SCREENING AND LARGE POLARON FORMATION

The PGEC “crystal-liquid” duality shown in lead halide perovskites is likely critical to their success as optoelectronic materials through dynamic screening and large polaron formation. Because lead halide perovskite single crystals and thin films are typically grown from solutions at room temperature, a high density of defects is inevitable. However, these materials show exceptional defect tolerance, which leads to low charge carrier trapping and low nonradiative recombination rates (58) that are responsible for long carrier lifetimes and diffusion lengths. Zhu and Podzorov (33) posited that the key to understanding this lies in the realization that charge carriers in lead halide perovskites are not free carriers but are large polarons.

A polaron is an excess electron or hole dressed by polarization of nuclear coordinates in a crystalline lattice and is ubiquitous to polar and polarizable solids (59–63). For lead halide perovskites, we must consider charge formation and transport within the soft and ionic lattice with crystal-liquid duality. Given the exceptionally high polarizability of a soft lattice, a polaron must form for an excess charge. Two fundamental interaction potentials are responsible for polaron formation (63). The first is the long-range Coulomb potential (V^{LR}) between an excess charge and lattice ions, and the second is the short-range deformation potential (V^{SR}) that relates electronic energy to strain. If V^{SR} dominates, the result is a small polaron, with coherence length (L_{coh}) smaller than the unit cell dimension (a). When V^{LR} becomes more significant, L_{coh} is larger than a and the result is a large polaron. A large polaron is delocalized over multiple unit cells and its transport is coherent and band-like, with carrier mobility (μ) decreasing with increasing temperature (T), that is, $d\mu/dT < 0$. In contrast, a small polaron is localized to a unit cell and its transport occurs via thermally activated hopping, that is, $d\mu/dT > 0$.

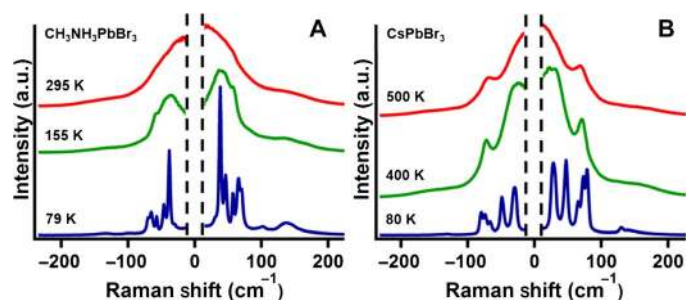


Fig. 4. Low-frequency Raman spectra of hybrid and inorganic lead halide perovskite crystals. MAPbBr₃ (A) and CsPbBr₃ (B) in the orthorhombic phase (blue), tetragonal phase (green), and cubic phase (red). Note that the phase transition temperatures for CsPbBr₃ are much higher than those for MAPbBr₃. The central peak characteristic of dynamic disordered, highly anharmonic, and dissipative vibrations grows with temperature in both materials. a.u., arbitrary units. Reprinted figure with permission from Yaffe *et al.* (24). Copyright 2017 by the American Physical Society.

The polarons in lead halide perovskites must be large polarons, because both transport and spectroscopic measurements showed $d\mu/dT < 0$ in broad temperature windows. Figure 5 shows the temperature-dependent charge carrier mobility obtained from Hall effect measurement on single-crystal CH₃NH₃PbBr₃ (64). In both tetragonal and cubic phases, the observed temperature dependences ($d\mu/dT < 0$) establish coherent transport, but the different scaling laws, $\mu \propto T^{-1.5}$ and $\mu \propto T^{-0.5}$, may suggest the dominance of different scattering mechanisms in the cubic and tetragonal phases, respectively (64). Similar scaling laws have been found from spectroscopic measurements on CH₃NH₃PbI₃ thin films (65–68).

A direct consequence of large polaron formation in lead halide perovskites is the efficient screening of the Coulomb potential. To understand the charge carrier properties, we consider the dielectric functions. Figure 6 shows the calculated dielectric functions for both MAPbBr₃ and CsPbBr₃ in the terahertz range (43). As the frequency decreases from >5 to ~ 1 THz, we see increases in the real part (ϵ_1) of the dielectric function by approximately one order of magnitude due to the activation of PbBr₃[−] longitudinal optical (LO) phonons. The positions of LO phonons are shown by the peaks in $\text{Im}[-1/\epsilon]$. The values of ϵ_1 are further increased in HOIPs by another factor of 2 as the frequency decreases to ~ 0.1 THz, due to the rotational motion of the dipolar methylammonium cations (69, 70). The over one order of magnitude increase of ϵ_1 in lead halide perovskites is in stark contrast to what is known in conventional semiconductors, such as GaAs, where the corresponding increase in ϵ_1 is only $\sim 20\%$ (57). The large increase in ϵ_1 over the terahertz frequency range in HOIPs results in efficient screening of a nascent charge carrier on the subpicosecond time scale. Hence, for the resulting large polaron, all events requiring the Coulomb potential, such as scattering of a charge carrier with charged defects or other charge carriers, are inhibited. Electron-phonon coupling is also reflected in transport as localized shallow state (71–74), in spectroscopy by exciplex emission and polaron-to-free carrier transition in IR absorption (75), and macroscopically by photostriction (76). The coupling of methylammonium cation rotors to charge carriers is suggested by Gong *et al.* (77), who observed decreasing carrier lifetime with increasing moment of inertia when the methylammonium cation is deuterated.

Miyata *et al.* (43) provided a direct time-domain view of large polaron formation in single-crystal MAPbBr₃ and CsPbBr₃ using TR-OKE, with excitation photon energy above bandgap for charge injection (Fig. 7). On

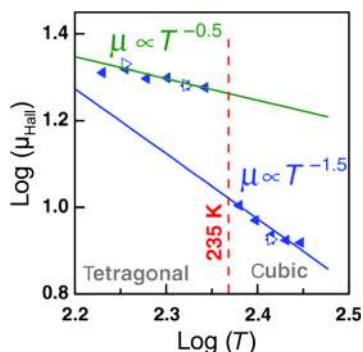


Fig. 5. Temperature dependence of Hall mobility in single-crystal MAPbBr₃. The fits to μ_{Hall} ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) $\propto T$ (K) $^{-\gamma}$ give $\gamma = 0.5$ in the tetragonal phase and $\gamma = 1.5$ in the cubic phase. From Yi *et al.* (64). Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

the basis of the initial time constants for polaron formation, $\tau_{\text{pol}} = 0.3$ ps and 0.7 ps in MAPbBr₃ and CsPbBr₃, respectively, along with first-principles calculations, these authors concluded that large polarons form predominantly from the deformation of the PbBr₃⁻ frameworks, irrespective of the cation type. Although there is more liquid-like disorder in the cubic MAPbBr₃ than in the orthorhombic CsPbBr₃, at room temperature, the intrinsic softness and polarizability of the PbX₃⁻ framework structure enables easy formation of large polarons upon charge injection in both HOIPs and their all-inorganic counterparts. HOIPs and their all-inorganic counterparts show similarly exceptional charge carrier properties for band edge carriers and solar cell performances (78–83).

LONG-LIVED HOT CARRIERS

One of the most striking observations in HOIPs is long-lived energetic carriers at low excitation densities (25, 34). In a conventional polar semiconductor, excess electronic energy above the LO phonon energy is lost on ultrafast time scales of 100s fs due to the ubiquitous Coulomb potential, which governs the scattering of electrons with polar LO phonons (84, 85). In GaAs, the electronic cooling rate $\langle dE/dt \rangle$ is of the order of 1 eV/ps for hot electrons with mean energy $\langle dE^* \rangle > E_{\text{LO}}$, where E_{LO} (=36 meV) is the LO phonon energy; this cooling process is slowed down by three to four orders of magnitude when $\langle dE^* \rangle$ falls below E_{LO} and scattering with acoustic phonons due to the deformation potential becomes dominant (84, 85).

In contrast to GaAs, hot carriers with excess energy above the LO phonon energy are much longer-lived in HOIPs (25, 34). Using time-resolved two-photon photoemission (TR-2PPE) spectroscopy and time-resolved photoluminescence (TR-PL), Zhu and co-workers found long-lived hot carriers in HOIPs at room temperature. The excess electronic energy of the order of 100 meV, which is much higher than E_{LO} , cools down at rates typical of acoustic phonon scattering, as shown in Fig. 8 for polycrystalline MAPbI₃ and single-crystal MAPbBr₃ (25, 34). A comparison of HOIP single crystals with their all-inorganic counterpart at room temperature showed long-lived hot PL in MAPbBr₃ and FAPbBr₃, but not in CsPbBr₃ (25). This correlates well with the more liquid-like responses in MAPbBr₃ and FAPbBr₃ than in CsPbBr₃, as observed in TR-OKE measurements in Fig. 3. TR-2PPE measurement suggests a large polaron formation time of ~0.3 ps in MAPbI₃ (34), in agreement with the TR-OKE measurement for MAPbBr₃ (Fig. 7); this time scale is competitive with the initial LO phonon cooling

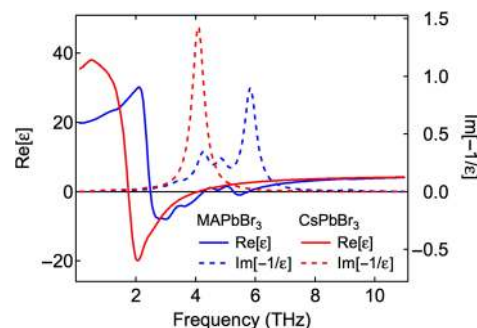


Fig. 6. Calculated dielectric functions of MAPbBr₃ (blue) and CsPbBr₃ (red). The solid and dashed curves show the real, $\text{Re}[\epsilon]$ (left), and imaginary, $\text{Im}[-1/\epsilon]$ (right), parts, respectively. From/adapted from Miyata *et al.* (43). Copyright The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) <http://creativecommons.org/licenses/by-nc/4.0/>.

time, leading to the partial retention of excess electronic energy. Although large polarons form in both MAPbBr₃ and CsPbBr₃ (43), the rate of formation is not competitive with phonon cooling in the latter. More recently, the presence of long-lived hot carriers has also been observed by Guo *et al.* (86) in MAPbI₃ thin films using transient absorption microscopy.

Monahan *et al.* (87) reported the observation of long-lived “warm” carriers (excess energy ~70 meV) on the 10-ps time scale in two-dimensional electronic spectroscopy of MAPbI₃. These authors showed strong coupling of charge carriers to a 0.9-THz phonon mode attributed to PbI₃⁻ lattice distortions (87), in excellent agreement with conclusions of Miyata *et al.* (43) on MAPbBr₃ and CsPbBr₃ from TR-OKE measurements. Monahan *et al.* (87) also observed long-lived coherence on the 10-ps time scale in the 0.9-THz phonon mode. It is possible that the large polaron formed from electron coupling to the PbI₃⁻ LO phonons further isolates the quasi-particle from the phonon glass environment, leading to long-lived coherence in the 0.9-THz mode. This interpretation finds support in a recent far-IR spectroscopy study of Ivanovska *et al.* (88), who observed very narrow absorption features in the terahertz region in photoexcited MAPbI₃. Further support for this idea can be found in the succinct analysis of Frost *et al.* (89), who argued that the transfer of phonon energy from the subset of optical phonons that are in quasi-equilibrium with the hot carrier to the acoustic phonon bath is inefficient due to the low thermal conductivity, a result of the phonon glass character. This analysis also explains the order-of-magnitude higher hot polaron cooling rate in CsPbBr₃ than in MAPbBr₃.

The slowed cooling of energetic carriers due to large polaron formation may be mechanistically different from the conventional phonon bottleneck effect. The latter occurs at high excitation densities when efficient scattering between hot carriers and LO phonons occurs, but the hot LO phonons are not cooled down by acoustic phonons at sufficiently high rate, that is, the bottleneck effect (90, 91). As a result, the hot phonons can reheat the electrons/holes. The phonon bottleneck effect has been observed in MAPbI₃ thin films at high excitation densities ($\geq 10^{18}/\text{cm}^3$) (92–94). A marked difference between the conventional phonon bottleneck and the large polaron mechanism is seen in the excitation density dependences. In the conventional phonon bottleneck at $\rho_{\text{ex}} \geq 10^{18}/\text{cm}^3$ for MAPbI₃, the excess electronic energy at a given time increases with increasing ρ_{ex} (92–94). In contrast, the large polaron mechanism is most important at low excitation densities ($\rho_{\text{ex}} \leq 10^{18}/\text{cm}^3$) and the excess electronic energy decreases with increasing ρ_{ex} (Fig. 9)

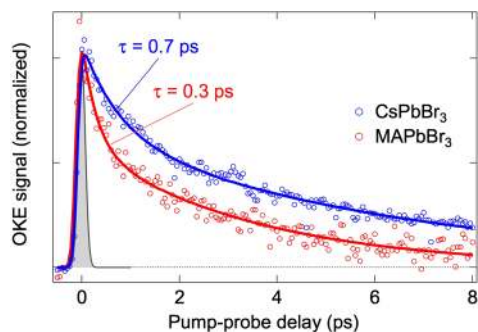


Fig. 7. Phonon dynamics triggered by photo-carrier injection as a function of pump-probe delay observed by TR-OKE with across-gap excitation. The TR-OKE responses for MAPbBr₃ (red circles) and CsPbBr₃ (blue circles) were obtained with excitation photon energies of 2.30 and 2.38 eV, respectively. The lines are double-exponential fits convoluted with a Gaussian function, which describes cross-correlation between the pump and the probe pulse (gray; FWHM, 70 fs). From/adapted from Miyata *et al.* (43). Copyright The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) <http://creativecommons.org/licenses/by-nc/4.0/>.

(34). With increasing excitation density, the mutual repulsive interaction destabilizes the large polarons (63); this is essentially a depolarization effect, leading to the reduction in the magnitude of the Coulomb screening and/or enhancement of the coupling of hot polarons to the phonon glass environment. As pointed out by Frost *et al.* (89), the transition density of $\rho_{\text{ex}} \sim 10^{18}/\text{cm}^3$ is essentially the critical Mott density when the large polarons start to overlap spatially.

The long-lived hot carriers in HOIPs may provide two potential advantages in solar cells. The first is the realization of the so-called hot carrier solar cell, with a theoretical power conversion efficiency (η) as high as 66% (95–97). For comparison, a conventional solar cell harvests carriers only at the band edges and the loss of excess electronic energy (from the absorption of above-bandgap photons) is partially responsible for the Shockley-Queisser limit of $\eta \sim 33\%$ (98). On the basis of the partial retention of hot carrier energy, Niesner *et al.* (34) estimated an upper limit of $\eta \sim 38\%$ from MAPbI₃ when hot carriers are harvested. The second advantage results from the excess kinetic energy. A portion of carriers generated from the absorption of sunlight are hot polarons. The higher kinetic energy of hot polarons may allow for easier transport across energetic barriers at domain boundaries or interfaces, leading to a higher photocurrent seen in HOIP solar cells.

DEFECT TOLERANCE

Efficient screening and large polaron formation in lead halide perovskites are key to the most significant advantage of lead halide perovskite as a semiconductor, that is, defect tolerance (99–102). The defect tolerance leads to long carrier lifetimes and diffusion lengths responsible for their exceptional performance in solar cells and light-emitting devices (1–5, 103–106). Quantitative measurements of PL intensity (79) or photoconductivity (58) as a function of excitation density revealed low first-order nonradiative recombination rates. The latter is illustrated by the scaling of photoconductivity (σ) with excitation density (G , proportional to incident photon flux, F), $\sigma \propto G^\alpha$ or F^α , in the four-probe measurement of Chen *et al.* (58) in either vapor-grown polycrystalline MAPbI₃ thin film or single-crystal MAPbBr₃ (Fig. 10). For excitation density varying over three orders of magnitude, the data can be well

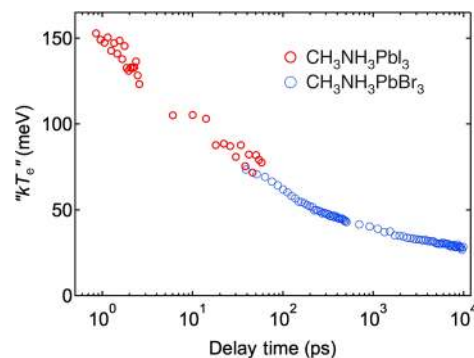


Fig. 8. Slow cooling of hot carriers in HOIPs. The data points are mean hot carrier energies from TR-2PPE of MAPbI₃ thin films (red) (34) and TR-PL of MAPbBr₃ single crystals (blue) (25). In the latter, a background offset due to intrinsic broadening in PL spectra has been subtracted. The excess excitation energy (above bandgap) is 1.0 eV for MAPbI₃ and 0.8 eV for MAPbBr₃.

described by $\alpha = 1/2$ expected for radiative recombination, as opposed to $\alpha = 1$ for trap-mediated nonradiative recombination. The low nonradiative recombination rate exists in both HOIPs and their all-inorganic counterparts; for band edge carriers, the different large polaron formation rates on the picosecond time scales are not expected to affect the properties of band edge carriers with nanosecond to microsecond lifetimes (79).

We can understand the defect tolerance from two perspectives. From a carrier perspective, a free band carrier is rapidly protected on the pico- or subpicosecond time scale to form a large polaron (43), whose screened Coulomb potential drastically reduces its scattering with a charged defect or a trapped charge of opposite sign on an originally neutral defect. The latter scenario means that the well-known Shockley-Read-Hall (SRH) mechanism (107, 108) for nonradiative recombination is diminished. From a defect perspective, the high polarizability in the soft and ionic lattice, including ion mobility on long time scales, can lead to the sufficient screening and compensation of charged defects in a lead halide perovskite lattice (69, 109–111). As a result, the traps are energetically shallow and electrostatically screened (100, 102), thus diminishing the role of these traps in SRH recombination.

The conventional wisdom to reduce defects in semiconductor technology is to achieve perfection, as exemplified by single-crystal silicon with remarkably low defect densities. However, this requirement cannot be met by emerging semiconductors made from molecular, hybrid, or nanocrystalline materials, where room temperature and solution synthesis/processing conditions inevitably result in a high density of defects that are detrimental to their performance. The exceptional defect tolerance in lead halide perovskites suggests that dynamic screening in intrinsically “soft” and polarizable materials provides a design principle to achieve defect tolerance, thus turning imperfection to perfection.

LARGE POLARON TRANSPORT

The “electron crystal” nature of lead halide perovskites is established by the band-like transport of charge carriers, particularly with charge mobility (μ) scaling with temperature (T) by $\mu \propto T^{-1.5}$, as determined directly by Hall effect measurements for MAPbBr₃ in the cubic phase (64), as well as by microwave, gigahertz, and terahertz spectroscopies on polycrystalline MAPbI₃ (65–68). The decreasing mobility with temperature ($d\mu/dT < 0$) unambiguously establishes coherent transport, as expected from large polarons, in stark contrast to thermally activated transport of small polarons (63).

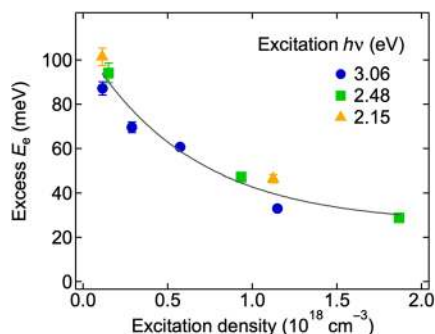


Fig. 9. Excitation density dependence of excess electronic energy in MAPbI₃. The data points are from TR-PL in the initial 0- to 20-ps time window (time resolution) of a vapor-deposited MAPbI₃ thin film. PL at three excitation photon energies, $h\nu = 3.06$ eV (blue), 2.48 eV (green), and 2.15 eV (orange). The gray curve is an exponential fit to the data points. The y axis is excess electronic energy, referenced to the asymptotic value at long times (~ 0.5 ns). Reprinted (adapted) with permission from Niesner *et al.* (34). Copyright (2016) American Chemical Society.

For lead halide perovskites, the valence and conduction bands are determined mainly by the PbX_3^- sublattice, with the A^+ cation sublattice modulating the band structure electrostatically and through electron-phonon coupling. Electronic structure calculations predict large valence and conduction band dispersions that yield low electron/hole masses of 0.1 to 0.15 m_e (112–114). This low band mass is confirmed by magneto optical absorption measurement, which gives the reduced e-h (exciton) mass from the Landau levels (115). Whereas the experimentally determined $\mu \propto T^{-1.5}$ scaling law agrees with prediction from acoustic phonon scattering in nonpolar semiconductors (116), analysis based on acoustic phonon scattering yields charge carrier mobilities (μ) of the order of $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (51, 117–119), only slightly lower than those predicted from band masses and still more than one order of magnitude higher than experimental values.

It has been suggested that scattering with optical phonons is more important than that with acoustic phonons in limiting mobility in HOIPs (120, 121). The scattering of charge carriers with optical phonons has been traditionally treated within the polaron theory of Fröhlich (61), which was subsequently extended by Feynman (62). Here, a unit-less parameter (α_{e-ph}) is introduced to describe the strength of electron LO phonon coupling

$$\alpha_{e-ph} = \frac{1}{2} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \frac{k_e e^2}{\hbar \omega_{LO}} \left(\frac{2m^* \omega_{LO}}{\hbar} \right)^{1/2} \quad (1)$$

where ϵ_∞ and ϵ_0 are the optical and static dielectric constants, respectively; k_e is the Coulomb's law constant; \hbar is the Planck's constant; ω_{LO} is the LO phonon frequency; and m^* is the band mass of electron or hole. To the first-order approximation, the renormalized carrier mass, that is, polaron mass (m_p), is given by

$$m_p \approx m^* (1 + \alpha_{e-ph}/6) \quad (2)$$

On the basis of the mean LO phonon frequencies and the dielectric constants for HOIPs, several groups (22, 45, 58) estimated the electron-phonon coupling constants of $\alpha_{e-ph} = 1.7$ to 2.4, which corresponds to intermediate coupling.

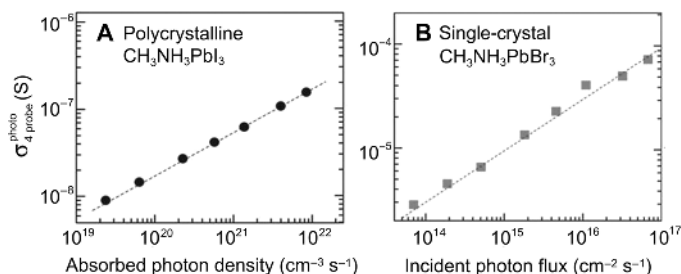


Fig. 10. Excitation density-dependent photoconductivity shows little charge carrier trapping. (A) Photoconductivity measured in a vapor-grown 100-nm-thick polycrystalline $\text{CH}_3\text{NH}_3\text{PbI}_3$ film as a function of absorbed photon density. (B) Photoconductivity measured as a function of incident photon flux in a macroscopic single-crystal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ with a (dark) Hall mobility $\mu_{\text{Hall}} \approx 60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (for holes). Dashed lines are the power law fits with exponent $\alpha = 1/2$: $\sigma \propto G^\alpha$ or F^α . Reprinted with permission from Chen *et al.* (58). Copyright (2016) Nature Commun.

From Eq. 2, we obtain m_p in the range of 1.3 to 1.4 m^* . The corresponding polaron radii, $R_p = \hbar^{1/2}/(2cm^*\omega_{LO})^{1/2}$, are in the range of 3 to 5 nm for HOIPs (22); thus, the diameter of the large polaron is $\sim 10\times$ the unit cell dimension. We estimate the polaron binding energy from the polaron radius to be of the order of 10 to 100 meV, depending on the dielectric constant used (see Fig. 6). The large polarons discussed here are in contrast to the tightly bound small polarons from the computational study of Neukirch *et al.* (122). These small polarons are likely minority trapped charges, not the charge carriers responsible for transport.

The LO phonons are highly populated in HOIPs at room temperature because of their low frequencies (22, 43). Under this condition, it is appropriate to use the general equations of Feynman-Ösaka (62, 123) to calculate electron and hole polaron mobilities. Miyata *et al.* (43) obtained $\mu_e = 149.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_h = 79.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in $\text{CH}_3\text{NH}_3\text{PbBr}_3$; the corresponding values in CsPbBr_3 are $\mu_e = 48.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_h = 41.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Similarly, Sendner *et al.* (22) calculated average electron-hole mobilities of $\mu = 50, 150,$ and $200 \pm 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for MAPbCl_3 , MAPbBr_3 , and MAPbI_3 , respectively, and Frost (124) calculated electron and hole polaron mobilities in MAPbI_3 of 136 and $94 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The calculated mobility values for HOIPs are slightly higher than those reported from experimental studies. For single-crystal MAPbBr_3 and MAPbI_3 at room temperature, the reported μ values are 10 to $115 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 24 to $164 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively (8, 9, 58, 64, 125). Whereas a large polaron is formed mainly from the deformation of the PbX_3^- sublattice, a moving large polaron is further slowed down from dielectric loss to the disordered vibrations at lower frequencies attributed to cation motions. In HOIPs, this additional dielectric loss channel occurs at ~ 0.1 THz, where the rotational motions of the dipolar MA^+ cations are activated, leading to another step increase by $\sim 2\times$ in ϵ_1 (70). This loss process is called “dielectric drag” for ion movement in polar liquids (126). In related work, Anusca *et al.* (70) suggested that the two-tiered dielectric responses led to a “hyperpolaron” as a result of the additional screening of a Fröhlich polaron by the liquid-like MA^+ cation motions.

RADIATIVE RECOMBINATION

The bimolecular radiative recombination rate constants are of the order $k_2 = 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ in both HOIPs and their all-inorganic counterparts (58, 79, 127). There have been arguments that these rate constants are

about five orders of magnitude lower than that predicted from the Langevin model. The Langevin model (128) is typically used to describe bimolecular recombination in low-mobility and disordered systems (129), where the recombination rate can be calculated from the Coulomb capture radius (r_c), that is, the e-h distance for which the Coulomb potential is equal to the thermal energy. However, the Langevin model does not actually apply to lead halide perovskites because of the band-like transport with modest (~ 10 to $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), not low ($< 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), mobilities.

The perceived low values in radiative recombination rate constants that are partially responsible for long carrier lifetime and diffusion length have also led to discussions on the indirect character of bandgap in HOIPs. A particular argument attributes the indirect bandgap character to large Rashba splitting (130–133). Because of strong spin-orbital coupling in the presence of heavy atoms, the conduction band and the valence band may be spin-polarized. In the presence of local electric field resulting from electrostatic ordering (110, 134) and static or dynamic symmetry breaking (130–132), electrons with different spins ($m_s = \pm 1/2$) experience opposite forces from electromagnetic interaction. This leads to the splitting of conduction band and (to a lesser extent) the valence band in momentum space, thus introducing indirect bandgap character. Experimentally, the indirect bandgap is believed to lie at 47 to 75 meV below the direct bandgap in MAPbI₃, as obtained from temperature-dependent PL (65, 135) and pressure-dependent absorption and PL (136). Numerical simulations also addressed the disparate roles of direct and indirect bandgaps in absorption and emission (137).

Here, we present an alternative mechanism to explain the indirect bandgap character. As argued by Chen *et al.* (58), a model more appropriate than the Langevin model to describe radiative recombination in lead halide perovskites is the van Roosbroeck–Shockley theory (138), which obtains the radiative recombination rate from detailed balance under thermal equilibrium in the dark (138, 139). The van Roosbroeck–Shockley theory gives k_2 only approximately one order of magnitude higher than experimental values; this difference can be well accounted for by polaron formation (58). The equilibrium carrier concentration is increased upon polaron formation by the stabilization of a charge carrier and the increased density of states resulting from deviation from parabolic dispersion. These effects decrease k_2 from the van Roosbroeck–Shockley theory by approximately one order of magnitude, leading to good agreement with experimental values (58). For a polaron stabilization energy within 2 to 3 kT at room temperature, there is a dynamic equilibrium between large polarons and free carriers. The electron and hole large polarons are expected to be located in spatially separate regions, due to their opposite effects on the bending of Pb–X–Pb (43), as well as their opposite effects in dipolar polarization (58, 110, 134); in this sense, the indirect character of the bandgap is in real space, not in the momentum space. As a result, the radiative recombination rate from the energetically stabilized large polarons is expected to be much lower than that from free band carriers. This can give rise to thermally activated PL (65, 135). The lower transition strength for the radiative recombination from the e-h polaron states can also appear in absorption due to electron-phonon coupling in the absorption process (136, 140). Besides the large polaron-free carrier equilibrium, there is an equilibrium between carriers and excitons with binding energies of the order of kT at room temperature (5, 10, 69, 141, 142) and the carriers and excitons may be located in spatially separate regions in a heterogeneous environment of a polycrystalline thin film (143). All these effects may contribute to the apparent thermal activation in PL measurements.

SUMMARY AND OUTLOOK

In this perspective, we attempt a unified view of the optoelectronic properties of lead halide perovskites from their unique crystal-liquid duality. We show that lead halide perovskites belong to the PGEC family due to the binary structure consisting of a cage-like PbX_3^- sublattice and a more weakly bound A^+ cation sublattice. This PGEC character gives rise to the remarkable contrast in the transport properties of carrier and phonons. In particular, the thermal transport in lead halide perovskites, particularly HOIPs, is diffusive because of the liquid-like dynamic disorder in the phonon manifold, whereas charge transport is ballistic and band-like in the PbX_3^- sublattice. The partial localization of a band carrier in the PbX_3^- phonon environment leads to the formation of a large polaron, whose screened Coulomb potential reduces its scattering with charged defects and other charge carriers. The effective Coulomb screening can be found in the dielectric function, which, in HOIPs, increases by more than an order of magnitude as frequency decreases from optical to the terahertz region. We can account for the modest mobility of the large polarons by the low frequencies of PbX_3^- LO phonons that are highly populated at room temperature and to additional dielectric loss to the disordered vibrations of the cation sublattice. Large polaron formation and the phonon glass character may also explain the long lifetimes of hot carriers in HOIPs. The understanding presented here suggests a new design principle for high performance and defect-tolerant semiconductors from PGEC type of structures with liquid-like dielectric functions.

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