Large polarons in lead halide perovskites

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Lead halide perovskites show marked defect tolerance responsible for their excellent optoelectronic properties. These properties might be explained by the formation of large polarons, but how they are formed and whether organic cations are essential remain open questions. We provide a direct time domain view of large polaron formation in single-crystal lead bromide perovskites CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$. We found that large polaron forms predominantly from the deformation of the PbBr$_3^–$ frameworks, irrespective of the cation type. The difference lies in the polaron formation time, which, in CH$_3$NH$_3$PbBr$_3$ (0.3 ps), is less than half of that in CsPbBr$_3$ (0.7 ps). First-principles calculations confirm large polaron formation, identify the Pb-Br-Pb deformation modes as responsible, and explain quantitatively the rate difference between CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$. The findings reveal the general advantage of the soft [PbX$_3^+$] sublattice in charge carrier protection and suggest that there is likely no mechanistic limitations in using all-inorganic or mixed-cation lead halide perovskites to overcome instability problems and to tune the balance between charge carrier protection and mobility.

INTRODUCTION

The exceptional rise in research activities on hybrid organic-inorganic lead halide perovskites (HOIPs) is a direct result of their marked optoelectronic properties that resemble defect-free semiconductors, despite static and dynamic disorder (1–3). Even with modest mobilities (4–8), they show long carrier lifetimes and diffusion lengths that are key to their successes in optoelectronic devices (9–11). An HOIP crystal consists of a lead halide sublattice (PbX$_3^+$), which determines the band structure (12), and a disordered organic cation sublattice (A$^+$), which modulates the electronic properties (13–17). This unique APbX$_3$ structure and associated dielectric responses (17, 18) have led to the large polaron proposal (19, 20) in which the dynamically screened coulomb potential minimizes charge carrier scattering with defects, with other charges, and with longitudinal optical (LO) phonons. Although this proposal may explain some of the carrier properties of HOIPs, there has been no direct observation or confirmation of (large) polaron formation. Whether A-site organic cations are essential (13–16, 21) or not (22–25) also remains an open question. Here, we provide a direct time domain view of phonon dynamics in the CH$_3$NH$_3$PbBr$_3$ HOIP in comparison to its all-inorganic counterpart, CsPbBr$_3$, using time-resolved optical Kerr effect (TR-OKE) spectroscopy (26, 27) in conjunction with hybrid density functional theory (DFT) calculations. We show the dominance of coupling between PbBr$_3^+$ lattice motions to across-bandgap electronic transitions in both perovskites, but different polaron formation time constants of 0.3 and 0.7 ps for CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$, respectively. DFT calculations reveal the major role of a subset of coupled Pb-Br stretching and Pb-Br-Pb bending modes in large polaron formation. Our calculations also suggest that the coupled motions of the organic cations to the PbBr$_3^+$ lattice are responsible for faster polaron formation in CH$_3$NH$_3$PbBr$_3$ than that in its all-inorganic counterpart.

RESULTS AND DISCUSSION

We synthesized optically flat, single-crystal CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$ samples (see Materials and Methods and fig. S1 for details) (6), with effective bandgaps of $E_g = 2.28$ and 2.35 eV, respectively (see fig. S2). In TR-OKE, the electric field of a linearly polarized pump laser pulse creates transient anisotropy, and the resulting birefringence is detected by the polarization rotation of a probe pulse, which allows us to measure the system’s response in a wide time range (femtosecond to nanosecond). We implement heterodyne-detected TR-OKE using homebuilt two-color pump-probe systems (see fig. S3). The photon energy of the pump was tunable ($h\nu_1 = 1.85$ to 2.45 eV), and that of the probe was fixed ($h\nu_2 = 1.55$ or 1.65 eV).

We examine structural flexibility and dynamic disorder in CH$_3$NH$_3$PbBr$_3$ coupled to carriers by varying the pump photon energy from nonresonant (1.85 eV) to preresonant (2.10 eV) regimes (Fig. 1A). We see that the broad and featureless nuclear response is distinctively different from that of a typical solid, where impulsively stimulated Raman excitation should appear as oscillatory features (28), and is instead characteristic of liquids (26, 27). The absence of oscillatory features suggests that we detect predominantly overdamped phonon modes that can be attributed to strong anharmonicity and dynamic disorder (29, 30). As $h\nu_1$ moves closer (2.03 to 2.18 eV) to $E_g$, we find enhanced slow responses ($\geq 1$ ps). This is attributed to the resonant Raman mechanism, where nuclear motions are coupled to electronic transitions (31). As seen in Fourier spectra of the OKE transients (Fig. 1B), approaching the $E_g$ resonance enhances low-frequency (<100 cm$^{-1}$) motions corresponding to those of the PbBr$_3^+$-lattice (32), particularly the coupled Pb-Br stretching and Pb-Br-Pb bending motions, as shown by the calculated phonon spectrum at the top of Fig. 1B.

By tuning $h\nu_1$ to 2.30 eV ($\geq E_g$), we directly probe the OKE response upon charge injection (topmost transient in Fig. 1A). We observe qualitatively different structural dynamics: a subpicosecond component with a time constant of $\tau_1 = 0.29 \pm 0.04$ ps and longer-lived anisotropy that decays with $\tau_2 = 3.4 \pm 0.5$ ps. These features are absent in OKE transients for $h\nu_1 < E_g$ and are thus associated with the dynamic response of nuclei to the photoinjection of carriers, that is, formation of (large) polarons. We show, at the top of Fig. 1B, projections (sticks) of the displacement vector following a positive charge injection onto the calculated normal modes and find that a subset of stretching and bending...
modes of the inorganic sublattice is mainly responsible for this structural relaxation, as detailed later.

We compare the OKE responses in CH₃NH₃PbBr₃ with those in a fully inorganic CsPbBr₃ single crystal (Fig. 2). When \( h\nu_1 = 1.83 \) or 2.00 eV is far below \( E_g \), the OKE signal consists of two responses: a broad feature within \( \sim 0.3 \) ps and an oscillatory response distributed over a few picoseconds (Fig. 2A); the former is liquid-like (26, 27), whereas the latter is Raman-active vibrations typical of solids (28). The corresponding Fourier spectra in Fig. 2B for \( h\nu_1 = 1.83 \) and 2.00 eV show a broad low-frequency peak (<100 cm⁻¹) in the region of coupled lead halide stretching and bending vibrations (see calculated frequencies in Fig. 2B and fig. S4). A few partially resolved phonon peaks are also present in the Fourier spectrum for \( h\nu_1 = 2.00 \) eV. The broad low-frequency peak, which agrees with the Raman spectra of Yaffe et al. (30), reflects the structural softness of CsPbBr₃, whose Young’s modulus is similar to that of CH₃NH₃PbBr₃; both are 10 times lower than those of Si and GaAs (33). As we increase \( h\nu_1 \) to the preresonant regime (2.21 to 2.25 eV), we see the resonance enhancement of slower picosecond-scale responses in CsPbBr₃. This is similar to the results from CH₃NH₃PbBr₃ and can again be attributed to PbBr₃⁻ motions. There is one important distinction: In CsPbBr₃, we see particularly long-lived oscillations, as well as a broad overdamped feature, whereas in CH₃NH₃PbBr₃ only the overdamped feature is observed. On the basis of the calculated vibrational frequencies, we assign the particularly prominent peaks at \( \sim 50 \) and \( \sim 85 \) cm⁻¹ to Pb-Br-Pb bending modes coupled with Pb-Br stretchings (see fig. S4) and the peak at \( \sim 130 \) cm⁻¹ to the pure Pb-Br stretching modes. When \( h\nu_1 = 2.43 \) eV exceeds \( E_g \), the TR-OKE response changes completely. All oscillatory features disappear upon carrier injection, suggesting that a large number of low-frequency modes could couple to photogenerated charge carriers and that there could be increased overdamping of the phonon oscillation due to their coulomb interaction with the charge carriers. Instead of oscillations, we see a subpicosecond component with a time constant of \( t_1 = 0.7 \pm 0.1 \) ps and longer-lived anisotropy that decays with \( t_2 = 6.5 \pm 0.3 \) ps. Notably, the phonon dynamics upon charge injection are similar in both CsPbBr₃ and CH₃NH₃PbBr₃, albeit the time constants are longer by about two times in the former. In CH₃NH₃PbBr₃, although there is negligible contribution of the high-frequency organic cation vibrations to polaron formation (see fig. S5), reorientational motions of these cations within the lead halide cage could couple to Pb-Br-Pb phonon modes, leading to faster polaron formation in CH₃NH₃PbBr₃ than that in CsPbBr₃, as we confirm below in first-principles calculations.

The TR-OKE experiments with \( h\nu_1 \geq E_g \) probe the injected charge dynamics from the phonon perspective. We now probe the same dynamics from the electronic degrees of freedom side using femtosecond transient reflectance. Figure 3A shows a two-dimensional pseudocolor plot of transient absorption coefficient (\( \Delta\alpha \)) of CH₃NH₃PbBr₃ as a function of probe photon energy and pump-probe delay (\( \Delta t \)) following the excitation at time 0 by \( h\nu_1 = 2.92 \) eV. Here, \( \alpha \) is obtained by a Kramers-Kronig transformation from time-dependent reflectance, \( AR/R \) (see Materials and Methods and fig. S6 for details) (34). At \( \Delta t > 1 \) ps, the band-edge spectral region corresponds to simple bleaching of the excitonic resonance, but at shorter times, the spectrum features a derivative shape that corresponds to a red shift in the absorption peak. The red-shifted feature is attributed to band renormalization due to many-body coulomb interaction among photoexcited carriers, as is well known in inorganic semiconductors (35). Because the nanosecond lifetime of charge carriers (23) means that carrier population remains constant on the subpicosecond time scale, the disappearance of the red shift can thus be attributed to the reduction of the many-body coulomb potential, consistent with the dynamic screening of initially excited free carriers in polaron formation. A similar transient red shift has also been observed for CsPbBr₃ (fig. S6). The red shifts disappear with time constants of 0.28 ± 0.04 ps and 0.6 ± 0.1 ps for CH₃NH₃PbBr₃ and CsPbBr₃, respectively (Fig. 3B). These time constants agree with those of the ultrafast screening time in TR-OKE response at \( h\nu_1 \geq E_g \) (Fig. 3C), where faster TR-OKE responses yield time constants of \( t_1 = 0.28 \pm 0.04 \) ps and 0.7 ± 0.2 ps for CH₃NH₃PbBr₃ and CsPbBr₃, respectively. The long time constants (\( t_2 = 3.4 \pm 0.5 \) ps and 6.5 ± 0.3 ps) in TR-OKE are not seen in transient reflectance, suggesting that the ultrafast screening and polaron formation processes are already completed on the subpicosecond time scale of \( t_1 \). The longer time scales can be attributed to further depolarization due to the polaron motion possibly coupled to the slower dynamics of the A-site cations.

Although the TR-OKE responses appear different between CH₃NH₃PbBr₃ and CsPbBr₃ when the pump photon energy is below the bandgap, as the Raman-active phonon modes are partially resolved (oscillatory features in the time domain) in the latter but not in the former, the responses become very similar for across-bandgap excitation (charge injection regime). To understand the seemingly similar origins of polaron formation in CH₃NH₃PbBr₃ and CsPbBr₃, and to reveal possible distinctive atomistic features underlying the different time
with 163° is calculated (Fig. 4D); the opposite holds for the negative charge, in both cases by only a few millielectron volts. For CH$_3$NH$_3$PbBr$_3$, (1.83 and 2.00 eV), preresonant regime (2.21 and 2.25 eV), and carrier injection regime (3.8 and 4.0 eV), respectively, whereas the negative charge is stabilized in the absence and presence of positive/negative added charges using 2 × 2 × 1 crystals (corresponding to the room temperature stable phases) of density associated with the added hole away from a center of maximum distortion (Fig. 5B). This is the signature of the large polaron distortion, which slowly decays away from the point of maximally localized charge (set at the center) and approaching saturation for a radius of $r_0 \sim 2.5$ nm. This polaron dimension is likely a lower bound approximation to the actual value due to the finite size of the used supercell. We are not able to similarly estimate the polaron size for an added electron due to the much smaller structural distortion requiring larger supercell sizes to observe a saturation behavior. However, our calculation suggests that the electron and the hole are localized in spatially distinct regions. By varying the Pb–Br distances in different crystal regions, we are able to localize the excess positive (negative) charge in regions of shorter (longer) Pb–Br distances (Fig. S9). A similar behavior is observed when we modulate the octahedra tilting (Fig. S10), with the positive charge mainly localized in the untitled region characterized by shorter Pb–Br bonds. The opposite structural distortion accompanying positive and negative excess charges suggests a spatially separated distribution of photogenerated excess charges.
electrons (more delocalized) and holes (more localized), consistent with a barrier to electron-hole recombination (42).

We point out that the present calculation focuses on PbBr$_3^-$ lattice phonons that are most strongly coupled to the electronic degrees of freedom in APbBr$_3$. It may be necessary to use a much larger supercell, possibly coupled to long-time scale molecular dynamics simulations, to account for the reorientational motion of the CH$_3$NH$_3^+$ cations in further localization. This approach is computationally beyond reach for the type of first-principles calculations used here but could be feasible with more approximate methods. By sampling randomly generated configurations of the CH$_3$NH$_3^+$ cations in CH$_3$NH$_3$PbI$_3$, Ma and Wang (15) found localization of conduction and valence bands to spatially separate regions with radii of $r_e \sim 8.3$ nm and $r_h \sim 5.6$ nm for electrons and holes, with estimated stabilization energies as large as 100 meV. The larger screening exerted by the dipolar organic cations, as illustrated by Ma and Wang (15), may also explain the different polaron stabilization energies between CH$_3$NH$_3$PbBr$_3$ (60 meV) and CsPbBr$_3$ (140 meV) in our calculation. This was verified in separate calculations in which we removed the A-cations and recalculated the stabilization energy, considering the geometries for the full system. In this case, we calculate a similar positive charge relaxation energy of $\sim 0.09$ eV in both CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$ (fig. S11), pointing to the A-cations as being responsible for the difference between the two perovskites beyond the different phases.

Our calculations not only reveal the essential role of the PbBr$_3^-$ sub-lattice in polaron formation but also explain quantitatively the different polaron formation rates between CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$. The projections of the displacement vector on the normal modes upon large polaron formation (black sticks in Figs. 1B and 2B) give mean frequencies of $\langle v \rangle = 92.4$ and 40.8 cm$^{-1}$ in CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$, respectively. These mean frequencies correspond to time constants of 0.36 and 0.82 ps, in excellent agreement with the corresponding time constants of $\tau_p = 0.3$ and 0.7 ps in CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$, respectively, observed in TR-OKE measurements. This difference can be attributed to the different coupling of cation motions to PbBr$_3^-$ lattice phonon modes; the faster motion of CH$_3$NH$_3^+$ (reorientation) than that of the heavier Cs$^+$ (displacement) can account for the different $\langle v \rangle$ or $\tau_p$ between CH$_3$NH$_3$PbBr$_3$ and CsPbBr$_3$.
We can estimate charge carrier mobilities and large polaron sizes based on the formulism of Fröhlich (43) and Feynman (44). Because the low-frequency phonon modes (≤150 cm⁻¹; Figs. 1B and 2B) mainly responsible for polaron formation in CH₃NH₃PbBr₃ and CsPbBr₃ are highly populated at room temperature, the more general formulism of Osaka is more appropriate (45). The strength of electron-LO phonon coupling is represented by the unitless Fröhlich coupling constant, αe-phonon, which can be calculated from the LO phonon frequency, carrier band mass, and dielectric constants (Fig. S12 and table S2). On the basis of our calculated LO phonon frequencies, we obtain αe-phonon = 1.54 and 2.76 for the electron and the hole, respectively. The corresponding values in CsPbBr₃ are αe-phonon = 2.64 and 4.91 for the electron and the hole, respectively (see Materials and Methods and table S3). The weaker e-phonon coupling in CH₃NH₃PbBr₃ than that in CsPbBr₃ and the weaker e-phonon coupling for the electron than that for the hole both agree with the first-principles results in Fig. 4. These coupling constants are a bit smaller than those in the conventional inorganic perovskite materials, for example, αe-phonon = 3 to 4 in SrTiO₃ (46). We obtain from the Feynman-Osaka formula (44, 45) electron and hole polarizations of μe = 149.8 cm² V⁻¹ s⁻¹ and μh = 79.2 cm² V⁻¹ s⁻¹ with corresponding polaron radii of ρe = 4.18 nm and ρh = 3.13 nm in CH₃NH₃PbBr₃. The corresponding values in CsPbBr₃ are μe = 48.2 cm² V⁻¹ s⁻¹, μh = 41.3 cm² V⁻¹ s⁻¹, ρe = 2.67 nm, and ρh = 2.49 nm (see Materials and Methods and table S3). The calculated ρe in CsPbBr₃ agrees with the estimation value from the first-principles calculation (Fig. 5). Our results also agree with similar treatments by Sendner et al. (47), who estimated an average electron/hole polaron mobility in CH₃NH₃PbBr₃ of μe,h ~ 158 cm² V⁻¹ s⁻¹ for a polaron radius of 4.3 nm and by Frost (48) who calculated electron and hole polaron mobilities in CH₃NH₃PbI₃ of 136 and 94 cm² V⁻¹ s⁻¹, respectively. These estimated polaron mobilities agree with the upper bounds in the range of experimental values from single crystals at room temperature (5, 6, 8, 23, 49, 50): 10 to 115 cm² V⁻¹ s⁻¹ for CH₃NH₃PbBr₃, 24 to 164 cm² V⁻¹ s⁻¹ for CH₃NH₃PbI₃, and 38 cm² V⁻¹ s⁻¹ for CsPbBr₃. Thus, it is mainly optical, not acoustic, phonons that limit the charge carrier mobility in lead halide perovskites. Note that although the experimentally determined temperature dependences in charge carrier mobility (42, 50, 51) agree with the μ ∝ T⁻¹.⁵ scaling law predicted from acoustic phonon scattering in nonpolar semiconductors (52), analysis based on this mechanism yields charge carrier mobilities of the order of 10⁵ cm² V⁻¹ s⁻¹ (53–56), which is one order of magnitude higher than the experimental values (5, 6, 8, 23, 49, 50). Note also that the weakly bound large polarons obtained here are responsible for coherent transport (19), in contrast to the more tightly bound small polarons that may function as minority trapped charges (57).

In summary, we provide a time domain experimental view and first-principles verification of large polaron formation in CH₃NH₃PbBr₃ and CsPbBr₃. The combined experiment and calculation establish the deformation of the PbBr₃₋ sublattice as mainly responsible for the large polaron formation in both crystals. The large polaron model predicts modest charge carrier mobilities that agree with the experimental measurements. The lower frequencies of the PbBr₃₋ sublattice motions (coupled to A-cation motion) in CsPbBr₃ than those in CH₃NH₃PbBr₃ also explain quantitatively the experimentally observed large polaron formation time constants. The difference in large polaron formation rate accounts for its competitiveness with hot carrier cooling in CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ (20, 58), not in CsPbBr₃ (20), but the large polarons may otherwise show similar properties due to common deformations of the lead halide sublattice. The latter suggests a similar mechanism for the protection of band-edge carriers in HOIPs and their all-inorganic counterparts, thus accounting for similar solar cell performance and similar band-edge carrier properties obtained with purely organic, inorganic, and mixed-cation perovskites (22–25). Alloying different organic and inorganic A-cations, which was shown to be an effective strategy toward high-efficiency devices (59), could be a way of tuning the extent of polaron stabilization to balance charge carrier protection (screening) and mobility.

**MATERIALS AND METHODS**

**Synthesis and structural characterizations of APbBr₃ (A = CH₃NH₃ or Cs) crystals**

Millimeter-scale single-crystal samples of CH₃NH₃PbBr₃ and CsPbBr₃ were prepared under ambient conditions via a vapor diffusion method.
in which the vapor of an antisolvent slowly diffuses into a perovskite precursor solution (6).CH$_3$NH$_3$PbBr$_3$ crystals were grown by the slow diffusion of dichloromethane into a solution of PbBr$_2$ and CH$_3$NH$_3$Br (1:2 molar ratio, 0.5 M and 1.0 M) in N,N-dimethylformamide.

CsPbBr$_3$ crystals were grown by a modified vapor diffusion method in which a solution of PbBr$_2$ and CsBr (1:1 molar ratio, 0.4 M) in dimethyl sulfoxide was prepared. This solution was then titrated with MeOH. Once the saturation point was reached, the solution was left to stir for 24 hours. The resulting supernatant was filtered and used as the precursor solution for a similar vapor diffusion process. The antisolvent was MeOH (60).

The single-crystalline nature of the perovskite samples was confirmed by single-crystal x-ray diffraction. Optical images and reconstructed precession images are shown in fig. S1. Data were collected on an Agilent SuperNova single-crystal x-ray diffractometer at room temperature. The lattice constants are given in table S1. These were confirmed by single-crystal x-ray diffraction. Optical images and reconstructions for CH$_3$NH$_3$PbBr$_3$ and the orthorhombic phase for CsPbBr$_3$ (1.83 to 2.48 eV) to gain higher-energy pulses, and its fundamental third harmonic of a Yb-doped fiber laser (Clark-MXR Impulse) operated at 10 kHz were used as tunable pump pulses synchronized with the modulation of the pump beam intensity by a large-area amplified PIN photodiode (100A, Thorlabs), with 700-2° away from the homodyne orientation which gave the principal integral. We use Eq. 2 to calculate the change of absorption coefficient is then calculated by

$$\Delta \alpha(\hbar \omega) = \frac{4 \Delta \kappa(\hbar \omega)}{\lambda}$$

where $n(\hbar \omega)$ was adapted from Yang et al. (63).

The Kramers-Kronig relations are given by

$$Re[\tilde{n}(\omega)] = \frac{2}{\pi} \int_0^{\infty} \frac{Re[\tilde{\kappa}(\omega')]}{\omega'^2 - \omega^2} d\omega'$$

$$Im[\tilde{n}(\omega)] = \frac{-2\omega}{\pi} \int_0^{\infty} \frac{Re[\tilde{\kappa}(\omega')]}{\omega'^2 - \omega^2} d\omega'$$

$$\Delta \kappa(\hbar \omega) = \frac{4 \Delta \kappa(\hbar \omega)}{\lambda}$$

where $Pf$ is the Cauty’s principal integral. We use Eq. 2 to calculate $\Delta n(\hbar \omega)$ and plug this value into Eq. 3 to calculate the change of imaginary part, $\Delta \kappa(\hbar \omega)$. The change of absorption coefficient is then calculated by

$$\Delta \alpha(\hbar \omega) = \frac{4 \Delta \kappa(\hbar \omega)}{\lambda}$$

### Theoretical calculations

DFT calculations were performed on the tetragonal phases of MAPbI$_3$ and MAPbBr$_3$ (48 atoms in unit cells) and on the orthorhombic phase of CsPbBr$_3$ (20 atoms in the unit cell), corresponding to four formula units in all cases. We used the experimental cell parameters throughout the work. We relaxed the geometries of both the neutral and positive and negative (+1 and −1 charge) systems in periodic boundary conditions.

The single-crystalline nature of the perovskite samples was confirmed by single-crystal x-ray diffraction. Optical images and reconstructed precession images are shown in fig. S1. Data were collected on an Agilent SuperNova single-crystal x-ray diffractometer at room temperature. The lattice constants are given in table S1. These were consistent with literature values and reflected the pseudocubic phase for CH$_3$NH$_3$PbBr$_3$ and the orthorhombic phase for CsPbBr$_3$ (61, 62).

### TR-OKE measurements

We carried out femtosecond TR-OKE measurements using a homebuilt two-color pump-probe system described below. The outputs from two noncollinear optical parametric amplifiers (NOPAs) served as pump and probe laser pulse for the measurements for CH$_3$NH$_3$PbBr$_3$, except the one at h$_V$ = 2.3 eV. The NOPAs were pumped by the second and third harmonic of a Yb-doped fiber laser (Clark-MXR Impulse) operated at 500 kHz. The center wavelengths of the visible pump and near-infrared probe pulses were in the range of 1.85 to 2.25 eV (tunable) and 1.61 to 1.66 eV, respectively. The bandwidths for both pulses were ~0.10 eV (FWHM). Pulse energies were 4 and 0.3 nJ for the pump and probe pulses with its spot sizes of about 600 and 120 μm, respectively. The pulses were focused on the sample with polarizations set to 45° with respect to each other, whereas a delay line was used to control the time delay between the pulses. The probe polarization was along the [110] crystal direction for CH$_3$NH$_3$PbBr$_3$ and along the [100] direction for CsPbBr$_3$ to minimize the polarization rotation from intrinsic anisotropy. The pump beam was blocked after the sample, whereas the probe beam was routed through a second polarizer, which was set at the crossed polarization against the first polarizer in front of the sample. To achieve heterodyne detection, a local oscillator was introduced by rotating the second polarizer by 2° away from the homodyne orientation which gave maximum extinction of the probe beam. The Kerr signal was detected by a large-area amplified PIN photodiode (100A, Thorlabs), with 700-nm longpass filter to eliminate a scattered pump beam, and was recorded by a lock-in amplifier (SR830, Stanford Research Systems), synchronized with the modulation of the pump beam intensity by a mechanical chopper at 5 kHz. For the measurements for a CH$_3$NH$_3$PbBr$_3$ crystal at h$_V$ = 2.30 eV and all the OKE measurements for a CsPbBr$_3$ crystal, the output pulses from NOPA pumped by the second harmonic of a Ti:sapphire laser (Wyvern1000-50, KMLabs) operated at 10 kHz were used as tunable pump pulses (1.83 to 2.48 eV) to gain higher-energy pulses, and its fundamental pulses (1.55 to 1.57 eV) were used as probe. Pulse energies were 100 and 3 nJ for the pump and probe pulses, respectively. The Kerr signal was detected by a homebuilt spectrometer equipped with a high-speed linear array detector (AVIV E4M, EV71YEM4CL1014-BA9, e2v) synchronized with the modulation of the pump beam intensity by a mechanical chopper at 5 kHz for shot-to-shot detection. Data collection was carried out via a homebuilt program based on LabVIEW. The typical temporal response measured by the cross-correlation between the pump and probe pulses from a 1-mm-thick glass plate was 70 ± 5 fs (FWHM).

### Time-resolved reflectance measurements and Kramers-Kronig analysis

Transient reflection measurements made use of a 1-mJ Ti:sapphire femtosecond regenerative amplifier operating at a repetition rate of 1 kHz (Newport Spectra-Physics). The pump laser light (~100-fs pulse width) came from an optical parametric amplifier (TOPAS). The probe, a white-light supercontinuum (450 to 900 nm), was focused onto the sample with a small overlapped angle to the pump. The reflected probe light from a perovskite crystal was collected by a mirror and lenses. The detection consisted of a pair of high-resolution multichannel detector arrays coupled to a high-speed data acquisition system (Ultrafast Systems). We used a heat filter in the probe beam before the sample to remove the residual fundamental laser beam; the probe power over the entire spectrum was a few hundred nanowatts. The sample was mounted inside a quartz window cell containing inert gas to avoid sample degradation by absorbing oxygen and moisture. The complex refractive index is given by

$$\tilde{n} = n + ik$$

(1)

Here, the real part $n$ is the refractive index, and the imaginary part $k$ is the extinction coefficient.

The change of refractive index can be calculated from transient reflectance signal as (63)

$$\Delta R (\hbar \omega) = \frac{4 \Delta n(\hbar \omega)}{n(\hbar \omega)^2 - 1}$$

(2)
conditions by generalized gradient approximation (GGA)–DFT. This
procedure is representative of the crystals being investigated at low
temperature, where dynamic fluctuations due to thermal energy can be
neglected. Thus, the results refer to the perfect crystals at zero temperature,
although the phases are those corresponding to the room temperature
stable phases for each system. The displacement vector was extracted
as the difference of the geometrical coordinates in the neutral and
charged states. This defines a global configurational coordinate that
drives the system across the two minima, defined by the neutral and
charged systems. Next, the energy was calculated as a function of the
displacement along the identified distortion pathway, by performing
both GGA (PBE) (64) and hybrid (PBE0) (36) DFT calculations. To
quantify the displacement on the same scale for all the investigated
systems, we calculated the mean square displacement of all atoms in
the cell along the pathway, as well as the variations of the Pb-Br
distances and of the Pb-Br-Pb angles.

Frequency calculations were performed by GGA-DFT at the exper-
imental cell parameters for consistency with the relaxation and
projection procedures. A 4 × 4 × 4 k-point mesh was used, which
ensured converged results [see the study of Quarti et al. (21)].

PBE calculations (structural relaxations and phonon calculations)
were performed by using ultrasoft pseudopotentials with a cutoff on
the wavefunction of 25 Ry (200 Ry on the charge density) and uniform
4 × 4 × 4 grid of k-points in the Brillouin zone. Single-point PBE0
calculations were performed using norm-conserving pseudopotentials
with a cutoff on the wavefunctions of 40 Ry and the same k-point
grids used for the PBE calculations. The convergence of the cutoff in
hybrid calculations, as well as the reliability of our approach in the
determination of the minima and the relaxation energies of the charged
systems, was checked by performing full PBE0 relaxation calculations
on the charged and neutral orthorhombic phase of CsPbBr3 with a cutoff of 70 Ry on the wavefunctions. The same setup
was used to optimize the 2 × 2 × 8 CsPbBr3 pseudocubic supercell.
Relaxation of ions for the neutral and positive and negative charged
systems showed relaxed geometries and relaxation energies in excel-

### Estimation of Fröhlich coupling and mobility

The behavior of polarons was analyzed by Fröhlich model, where a
charge in polar medium was coupled to harmonic optical phonons. The
strength of electron-phonon coupling is characterized by the
so-called Fröhlich coupling, \( \alpha_{\text{e-ph}} \), defined by

\[
\alpha_{\text{e-ph}} = \frac{e^2}{\hbar} \frac{1}{4\pi \epsilon_0} \left( \frac{1}{\epsilon_{\infty} - \epsilon_0} \right) \sqrt{\frac{m}{2\hbar \omega}}
\]

where \( e \) is the charge of carrier; \( 2\pi\hbar \) is the Planck’s constant; \( \epsilon \) is the
dielectric constant of vacuum; \( \epsilon_{\infty} \) and \( \epsilon_0 \) are optical and static dielectric
constants, respectively; \( m \) is the effective mass of bare electron band; and
\( \omega \) is the angular frequency of a characteristic LO phonon mode.

Parameters for the calculation of \( \alpha_{\text{e-ph}} \) are shown in table S2. We estimated \( \omega \) from the calculated \( \text{Im}[1/e(\omega)] \) spectra in far-infrared
region (see fig. S12). We figured out that the polaron in \( \text{CH}_3\text{NH}_2\text{PbBr}_3 \) and \( \text{CsPbBr}_3 \) was
in the large-intermediate regime (\( \alpha_{\text{e-ph}} = 1 \) to 3). The most successful
model for describing the polaron in the regime at finite temperature is
provided by Ōsaka based on the path integral calculation demonstrated
by Feynman. In the model, the self free energy of polaron, \( F \), with \( \alpha_{\text{e-ph}} \)
under the phonon occupation factor \( \beta = \hbar \omega/k_B T \) (where \( k_B \) is the
Boltzman constant and \( T \) is the temperature) is calculated with two free
parameters \( \nu \) and \( w \) (44, 45). To obtain the ground state of the polaron,
we numerically find \( \nu \) and \( w \) that give the minimum \( F = - (A + B + C) \),
where

\[
A = \frac{3}{\beta} \left[ \ln \left( \frac{w}{\nu} \right) - \ln(2\pi\beta) - \frac{1}{2} - \ln \left( \frac{\sinh(\frac{\beta}{2})}{\sinh(\frac{\nu}{2})} \right) \right]
\]

\[
B = \frac{\alpha \nu}{\sqrt{\pi} \left( \exp(\beta) - 1 \right)} \int_0^{\frac{\beta}{\nu}} \left[ \exp(-x) + \exp(\nu x) \right] \frac{\nu^2 x (1 - \frac{x}{\beta}) + \frac{\nu}{x}(\nu^2 - w^2)}{w^2 x (1 - \frac{x}{\beta}) + \frac{\nu}{x}(\nu^2 - w^2)} \, dx
\]

\[
Y(x) = \frac{1}{1 - \exp(-\nu \beta)} \left[ 1 + \exp(-\nu \beta) - \exp(-\nu x) - \exp(\nu (x - \beta)) \right]
\]

\[
C = \frac{3(\nu^2 - w^2)}{4\nu \beta} \left( \coth \left( \frac{\beta}{w^2} \right) - \frac{2}{\nu \beta} \right)
\]

\( \nu \) and \( w \) have a unit of \( \omega \), and, in particular, \( \nu \) is the frequency of relative
motion between a charge and a coupled LO phonon. We can calculate
the reduced mass \( (m_{\text{red}}) \) of the relative motion and the expectation
value of the squared distance between the charge and the phonon,
which defines Feynman large-polaron radius \( (\rho) \), as below (66)

\[
m_{\text{red}} = \frac{\nu^2 - w^2}{\nu^2}
\]

\[
\rho = \sqrt{\frac{3\hbar}{2m_{\text{red}} \nu^2 \times 2\pi \omega}}
\]

In the theory, mobility \( \mu \) is described by (67, 68)

\[
\mu = \frac{3\sqrt{\pi}e}{2\pi m \alpha_{\text{e-ph}}} \sinh(\beta/2) \frac{w^4 1}{\nu^{3/2} K}
\]

\[
K = \int_0^{\frac{\beta}{\nu}} \frac{\cos(u)}{(u^2 + a^2 - b \cos(v + u))^{3/2}} \, du
\]

\[
a^2 = \left( \frac{\beta}{2} \right)^2 + \left( \frac{\nu^2 - w^2}{w^2 \nu} \right)^2 \beta \coth \left( \frac{\beta}{2} \right)
\]

\[
b = \left( \frac{\nu^2 - w^2}{w^2 \nu} \right) \beta \coth \left( \frac{\beta}{2} \right)
\]

The calculated parameters for the polarons—Fröhlich coupling
constants \( (\alpha_{\text{e-ph}}) \), phonon occupation factors \( (\beta) \), parameters at the
lowest energy polaron in the Feynman-Ōsaka formula \( (\nu \text{ and } w) \),
Feynman polaron radii \( (\rho) \), and mobilities \( (\mu) \) —are tabulated in table
S3. Carrier effective masses of CsPbBr3 for the calculations are taken
from Yettapu et al. (69).
SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/8/e1701217/DC1

fig. S1. Optical images of single-crystalline CH3NH3PbBr3 and CsPbBr3.

fig. S2. The spectra of pump pulses in the TR-OKE measurement.

fig. S3. A schematic diagram of TR-OKE measurement and polarization-dependent OKE traces on the CH3NH3PbBr3 crystal.

fig. S4. Calculated IR spectrum and the coefficients of the displacement vector associated with Miyata

fig. S5. Calculated IR spectrum and the coefficients of the displacement vector associated with a positive charge injection in CsPbBr3 projected to the normal modes.

fig. S6. Details in transient reflectance measurements.

fig. S7. Hybrid DFT calculations of the relaxed structures of CH3NH3PbI3.

fig. S8. Potential energy surface for the neutral and positive charged 2 × 2 × 8 cubic CsPbBr3 supercells.

fig. S9. Pseudocubic 2 × 2 × 8 CsPbBr3 model with elongated (shortened) Pb–Br bonds in the left (right) halves of the supercell.

fig. S10. Localization of the positive charge as a function of the octahedral tilting in 2 × 2 × 8 cubic CsPbBr3 supercells.

fig. S11. Hybrid DFT calculations of stabilization energy of CH3NH3PbBr3 and CsPbBr3 with and without cations.

fig. S12. Calculated dielectric functions of CsPbBr3 and MAPbBr3.

table S1. Lattice constants for MAPbI3 and CsPbI3 single crystals.

table S2. The list of input parameters for the polaron calculations.

table S3. The list of the results of polaron calculations under the Feynman-Osaka model.

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