

Lattice Dynamics and Optoelectronic Properties of Vacancy-Ordered Double Perovskite Cs_2TeX_6 ($\text{X} = \text{Cl}^-$, Br^- , I^-) Single Crystals

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Abstract

The soft, dynamic lattice of inorganic lead halide perovskite CsPbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) leads to the emergence of many interesting photophysical and optoelectronic phenomena. However, probing their lattice dynamics with vibrational spectroscopy remains challenging. The influence of the fundamental octahedral building block in the perovskite lattice can be better resolved in zero-dimensional (0D) vacancy-ordered double perovskites of form A_2BX_6 . Here we study Cs_2TeX_6 ($X = \text{Cl}, \text{Br}, \text{I}$) single crystals to yield detailed insight into the fundamental octahedral building block and to explore the effect that its isolation in the crystal structure has on structural and electronic properties. The isolated $[\text{TeX}_6]^{2-}$ octahedral units serve as the vibrational, absorbing, and emitting centers within the crystal. Serving as the vibrational centers, the isolated octahedra inform the likelihood of a random distribution of 10 octahedral symmetries within the mixed-halide spaces, as well as the presence of strong exciton-phonon coupling and anharmonic lattice dynamics. Serving as the absorbing and emitting centers, the isolated octahedra exhibit compositionally tunable absorption (1.50–3.15 eV) and emission (1.31–2.11 eV) energies. Due to greater molecular orbital overlap between neighboring octahedra with increasing halide anion size, there is a transition from a more molecule-like electronic structure in Cs_2TeCl_6 and Cs_2TeBr_6 – as expected from the effective 0D nature of these single crystals – to a dispersive electronic structure in Cs_2TeI_6 , typical of three-dimensional (3D) bulk single crystals.

Introduction

All-inorganic lead halide perovskites CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have emerged as a promising class of semiconductor materials due to facile, low-cost synthesis methods that yield crystals with excellent optoelectronic properties well-suited for photovoltaic and photonic applications,^{1,2} including tunable bandgap, high absorption coefficients, low defect density, high charge carrier mobility, and long carrier diffusion lengths.³⁻⁶ The emergent photophysical phenomena and optoelectronic properties emergent in these all-inorganic perovskites are largely determined by the soft, dynamic nature of the underlying ionic lattice.⁷ With the three-dimensional (3D) corner-sharing ionic $[\text{PbX}_6]^{4-}$ octahedral network dominating both the electronic and phonon dispersions of these materials,^{8,9} it is important to understand how these octahedra influence the dynamic behavior and anharmonicity of the wider structure. These attributes modulate the dielectric environment in the underlying soft, polar lattice, which give rise to the aforementioned photophysical and optoelectronic phenomena.^{7,9,10} Because symmetry-allowed optical phonon modes directly contribute to this dielectric modulation,¹¹ Raman spectroscopy, by measuring lattice polarizability, naturally serves as an excellent probe of perovskite crystal dynamics, electron-phonon coupling, and lattice anharmonicity.¹² In CsPbX_3 perovskites, understanding the Raman spectra of the high-temperature cubic phase of these materials is complicated by (1) their intrinsic Raman-inactivity that is broken by dynamic disorder (i.e., local symmetry breaking which activates the Raman modes),^{13,14} (2) ultra-low-frequency (ULF, $\omega < 100 \text{ cm}^{-1}$) modes that are strongly thermally smeared into the anharmonic

spectral feature,^{14,15} and (3) an apparent “competition” of detected signals arising from both photoluminescence and Raman scattering in CsPbI₃, which requires either below-bandgap laser excitation or a high-pressure environment to visualize the fundamental modes.^{16,17} These competing factors have allowed the lattice dynamics of mixed-halide CsPbX₃ perovskites to be overlooked, with no known phonon measurements performed on these compositions.

Thus, a detailed analysis of the atomic structure and fluctuations of the octahedral building blocks in perovskites, particularly in the mixed-halide perovskites, is necessary to have a better understanding of the structural, vibrational, and electronic behavior of these systems. The influence of the fundamental octahedral building block can be better resolved in inorganic lead-free vacancy-ordered double perovskites of form A₂BX₆.^{18–20} The A₂BX₆ system is a variation of ordered double perovskites where one of the B-site cations has been replaced by a vacancy.²¹ As this vacancy replacement is systematic, every other octahedron is missing in the crystal structure. As a result, these structures are composed of a network of isolated [BX₆]²⁻ octahedral units²² that are stabilized by the close-packing of the X-site anions and the A-site cations bridging the 12-coordinated cuboctahedral voids created by the octahedra.^{23,24} In contrast to the 3D ABX₃ structure, the A₂BX₆ structure is formed by a network of zero-dimensional (0D) [BX₆]²⁻ octahedra,²⁵ which leads to molecule-like electronic features.²⁶ These isolated [BX₆]²⁻ octahedra are both the electronic and vibrational centers of the A₂BX₆ system, thus allowing the perovskite building block to be directly studied in order to elucidate its fundamental nature.²⁷

In this work, the tellurium-based Cs₂TeX₆ (X = Cl⁻, Br⁻, I⁻) perovskite system is probed at the bulk single crystal-level to investigate the influence that isolating the fundamental building block – the [TeX₆]²⁻ octahedral unit – has on the intrinsic structural and optoelectronic properties of perovskite systems. Pure-halide single crystals Cs₂TeCl₆, Cs₂TeBr₆, and Cs₂TeI₆, as well as

mixed-halide single crystals $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ and $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ of all integer halide ratios ($x = 0-6$), have been synthesized to provide systematically tunable composition spaces. Across these composition spaces, this Cs_2TeX_6 framework assumes the prototypical K_2PtCl_6 -type face-centered cubic (FCC) structure. These isolated $[\text{TeX}_6]^{2-}$ octahedra are the vibrational centers of the Cs_2TeX_6 system, lending each crystal composition a unique set of phonon bands. Probing the vibrational behavior of the Cs_2TeX_6 system proves more powerful than X-ray characterization in determining detailed structural features and in identifying strong exciton-phonon coupling interactions in certain crystal compositions. This strong coupling is in line with the notion of a soft lattice displaying strong anharmonicity. The observed tunable structural properties give rise to tunable absorption and emission, manifesting behavior consistent with the formation of small Frenkel excitons with large binding energies and strong excitonic-lattice dynamics. The electronic features indicate a shift from more molecule-like energy levels in Cs_2TeCl_6 and Cs_2TeBr_6 to more typical dispersive energy bands in Cs_2TeI_6 , coupled with strong exciton-phonon coupling interactions owing to the molecule-like isolated nature of these bulk crystals.

Experimental Methods

Materials. CsCl (>99.999%, Sigma Aldrich), CsBr (99.999%, Sigma Aldrich), CsI (99.999%, Sigma Aldrich), TeCl_4 (99.9%, Alfa Aesar), TeBr_4 (99.9%, Alfa Aesar), TeI_4 (99%, Alfa Aesar), *N,N*-dimethylformamide (DMF, 99.9%, Fisher Scientific), chloroform ($\geq 99.8\%$, Fisher Scientific), and syringe filters (Millex-HN nylon membrane syringe filters, hydrophilic,

0.45 μm pore size, 13 mm diameter) were used as received without further purification or modification.

Synthesis of Cs_2TeX_6 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) Single Crystals. Cs_2TeX_6 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) single crystals were synthesized using the solution-based anti-solvent vapor method.²⁸ The precursor powders CsX and TeX_4 were measured into a 20 mL vial based on the 2:1 stoichiometric ratio for the pure-halide compositions and on the respective stoichiometric ratio for the mixed-halide compositions, and the precursors were dissolved in 6 mL of DMF on a hot plate at 93°C overnight. The supersaturated solutions were filtered into new 20 mL vials, which were placed uncovered into a covered beaker of 14 mL of chloroform (Figure S1). The synthesis was deemed complete when single crystals had visibly precipitated on the walls of the vial. The single crystal precipitations were washed 3 times with absolute ethanol and stored in an inert environment (N_2 box) for future use.

Optical Microscope Imaging. An unpolarized, white-light optical microscope was used to visualize single crystals under either a $20\times$ or a $50\times$ microscope objective. Crystals in the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) alloy space were observed under dark-field imaging, and crystals in the $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 1-6$) alloy space were observed under bright-field imaging. The single crystals were dispersed onto glass for measurement.

Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy. A field-emission SEM (FEI Quanta 3D FEG SEM/FIB) was used to visualize single crystal morphologies and to determine elemental ratios in the single crystals via the EDX detector at the QB3-Berkeley Biomolecular Nanotechnology Center (BNC).

Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) data were collected using a Bruker D8 laboratory diffractometer with a Cu K α ($\lambda_{\text{K}\alpha 1} = 1.5406 \text{ \AA}$, $\lambda_{\text{K}\alpha 2} = 1.54439 \text{ \AA}$) radiation source in ambient condition. Data was collected from $2\theta = 8^\circ - 60^\circ$ with a step size of $0.0181027^\circ/\text{s}$. The single crystals were ground into powders and transferred onto glass for measurements.

Single-Crystal X-ray Diffraction (SCXRD). The SCXRD data were collected at the Small Molecule X-ray Crystallography Facility (CheXray) in the College of Chemistry at UC Berkeley. SCXRD were measured with a Rigaku XtaLAB P200 instrument equipped with a MicroMax-007 HF microfocus rotating anode and a Pilatus 200K hybrid pixel array detector using monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). All crystal datasets were collected at room temperature (293 K). CrysAlisPro²⁹ was used for data collection and data processing, including a multi-scan absorption correction applied using the SCALE3 ABSPACK scaling algorithm within CrysAlisPro. Using Olex2³⁰, the structures were solved with the SHELXT³¹ structure solution program using Intrinsic Phasing and refined with the SHELXL³² refinement package using Least Squares minimization. For the mixed-halide single crystals like Cs₂TeCl₃Br₃, the halogen site was separated into a disorder of Cl and Br with free variables for the occupation.

Raman Spectroscopy. The Raman spectra of the samples were measured by a confocal Raman microscope system (Horiba LabRAM HR800 Evolution). The single crystals were dispersed onto glass microscope slides for measurement. Either a continuous-wave (cw) 632.8 nm laser or a cw 532 nm laser was focused onto a crystal facet at a constant power density set by neutral density filters. The Raman signal from the sample was collected using a microscope

objective in a back-scattering geometry (100×, NA 0.6). High-resolution Raman spectra were measured with a CCD detector equipped with a diffraction grating of 1800 gr/mm and a long pass filter (80 cm^{-1}) to remove the Rayleigh scattering line from the signal. Data were analyzed using the Multipeak Fitting 2 procedure in the Igor Pro software, implementing Lorentzian oscillators.

Ultra-Low-Frequency (ULF) Raman Spectroscopy. The Raman spectra of the samples were measured by a confocal Raman microscope system (Horiba LabRAM HR Evolution) at the Stanford Nano Shared Facilities (SNSF). The single crystals were dispersed onto glass microscope slides for measurement. Either a continuous-wave (cw) 632.8 nm laser or a cw 532 nm laser was focused onto a crystal facet at a constant power density set by neutral density filters. The Raman signal from the sample was collected using a microscope objective in a back-scattering geometry (100×, NA 0.6). High-resolution Raman spectra were measured with an Andor Newton DU970P BVF EMCCD detector equipped with a diffraction grating of 1800 gr/mm and either an ULF filter package (10 cm^{-1}) for the 632.8 nm laser or a band pass filter ($\sim 40\text{-}50\text{ cm}^{-1}$) for the 532 nm laser. Data were analyzed using the Multipeak Fitting 2 procedure in the Igor Pro software, implementing Lorentzian oscillators.

UV-visible Absorption Spectroscopy. The absorption spectra of the samples were measured by a UV-visible spectrophotometer (Shimadzu UV-2600). Data was collected in absorption mode over a wavelength range of 300 nm and 900 nm with a slow scanning rate. The single crystals were ground into a powder and widely dispersed on glass in order to visualize the molecule-like absorption features.

PL Spectroscopy. All photoluminescence-related measurements, including standard PL, PL microscope imaging, and PL quantum yield, were collected with a home-built PL microscope system. The single crystals were either dispersed onto glass or ground into a powder and transferred onto glass for measurement. A continuous-wave solid-state 375 nm laser (Coherent OBIS 375LX) was focused obliquely onto the sample with a constant power density in visible wavelength measurements and infrared wavelength measurements, which was set by neutral density filters. The PL signal from the sample was collected using a microscope objective (50×) coupled to a long-pass filter (390 nm) in visible wavelength measurements and to a long-pass filter (800 nm) in infrared wavelength measurements to remove the laser line from the signal. Visible wavelength PL spectra were collected under a 1 s exposure time with a Si charge-coupled device (CCD) detector cooled to -120°C via liquid nitrogen and equipped with a diffraction grating of 150 gr/mm. Infrared wavelength PL spectra were collected under a 5 s exposure time with a InGaAs CCD detector cooled to -120°C via liquid nitrogen and equipped with a diffraction grating of 150 gr/mm. The PL imaging was taken under bright-field conditions. The PL quantum yield was calculated from integrating sphere measurements.

The cryogenic (4 K) PL measurements were performed in a Janis ST-500 SuperTran continuous flow cryostat system attached to the home-built PL microscope system. Liquid Gallium-Indium eutectic (Ga 75.5%/ In 24.5%, $\geq 99.99\%$ trace metals basis) was used to adhere samples to the cryostat stage, and the cryostat chamber was placed under vacuum with a continuous flow of liquid helium (LHe). A temperature controller was used to monitor the cryostat stage temperature and maintain it at 4 K. No changes were made to the PL microscope system for these measurements other than securing the cryostat, such that the laser was focused

obliquely onto the sample through the cryostat's optical-grade window. All other measurement parameters remained the same as described in the standard PL measurements previously.

Computational Methods for Raman-Active Vibrational Modes of Isolated Octahedra. For each $[\text{TeX}_6]^{2-}$ ($X = \text{Cl}, \text{Br}, \text{I}$) octahedral composition and coordination, density functional theory (DFT) ground-state geometry optimization and lattice vibration frequency calculations were performed for isolated octahedra in a vacuum using the ORCA 3.0.3 software package.³³ The B3LYP hybrid functional³⁴ (20% Hartree-Fock exchange) was used in combination with a polarized valence triple-zeta basis set (def2-TZVP³⁵), and the isolated molecule was left in a negatively charged state (i.e., 2-) with a resultant ground-state multiplicity of 1. Raman modes were simulated by taking the derivatives of the polarizability of the normal modes and visualized using the Avogadro software package³⁶ with the ORCA-supported update. A scaling factor of 1.2 has been used to compare the simulated Raman mode energies with the experimentally derived spectra.

Computational Methods for Electronic Band Structure of Crystal Structures. For generating electronic band structure and electronic density of states (eDOS), density functional theory (DFT) calculations using the Perdew–Burke–Ernzerhof (PBE) functional³⁷ and the projector augmented wave (PAW)³⁸ method, as implemented in the Vienna *ab initio* Simulation Package (VASP).^{39,40} Spin-orbit coupling (SOC) was included for all the compounds, and use was made of PAW potentials (Cs_sv, Te, Cl, Br, and I). The energy cutoff for the plane-wave basis for all compounds was set to 280 eV. Calculations were also performed using the HSE06⁴¹ + SOC functional. The electronic band structure was evaluated along special k-point paths in the Brillouin zone. For eDOS calculations, the tetrahedron method with Blöchl corrections⁴² was

used, and the Brillouin zone was sampled on a k-point mesh of $4 \times 4 \times 4$ for all compositions. The band structure and eDOS plots were generated using the Pymatgen package.⁴³ The effective electron and hole masses were evaluated using the SUMO package.⁴⁴

Results and Discussion

Tunable Composition Space and Crystal Structure of the Cs_2TeX_6 Family.

All bulk single crystals in the composition series of Cs_2TeX_6 ($X = \text{Cl}, \text{Br}, \text{I}$) are octahedral-shaped, with a length scale of 100–400 μm (Figure 1). The crystals vary in color across the series from vibrant yellow Cs_2TeCl_6 crystals to vibrant orange Cs_2TeBr_6 crystals to black Cs_2TeI_6 crystals. The atomic ratio within each crystal composition was confirmed with energy-dispersive X-ray spectroscopy (EDX) (Table S1). This is the first known synthesis of all-inorganic tellurium (Te) mixed-halide crystals of any dimensionality.

Figure 1. Optical microscope images of $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ and $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) single crystals. Dark-field imaging is used for $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) crystals, while bright-field imaging is used for $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 1-6$) crystals. These octahedral-shaped single crystals have triangular facets corresponding to the lowest-energy $\{111\}$ planes in the FCC unit cell. Scale bar: 10 μm .

The triangular facets that create the octahedral-shaped crystals correspond to the close-packed $\{111\}$ planes in the FCC structure. The FCC crystal structure ($\text{Fm}\bar{3}\text{m}$ space group) for the Cs_2TeX_6 system is shown in Figure 2a. Powder X-ray diffraction (PXRD) patterns highlight the expected FCC structure for both the pure- and mixed-halide compositions (Figure 2b).

Across the composition spaces of the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ and $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) alloys, there exists a continuous evolution from larger 2θ values in Cs_2TeCl_6 to smaller 2θ values in Cs_2TeI_6 in all diffraction peaks, indicative of an expansion in the lattice parameter across the composition space. From Bragg's law analysis of the PXRD patterns, the lattice parameter is found to vary from 10.47 Å to 11.69 Å across Cs_2TeCl_6 to Cs_2TeI_6 (Table S2). The continuous expansion of lattice parameter with increasing anion size is consistent with the empirical linear Vegard's law (Figure 2c).⁴⁵

Figure 2. (a) FCC crystal structure of the vacancy-ordered double perovskite Cs_2TeBr_6 (space group $\text{Fm}\bar{3}\text{m}$). (b) Powder X-ray diffraction (PXRD) patterns of $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ and $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) single crystals indicate that all compositions adopt the FCC crystal structure. The corresponding reference patterns for Cs_2TeCl_6 (ICSD 29031), Cs_2TeBr_6 (ICSD 24151), and Cs_2TeI_6 (ICSD 38105) are shown below each respective pattern with a dashed line. (c) Trends in lattice parameter versus alloy composition follow the empirical linear trend of Vegard's Law. There is a unique linear fit for each alloy space.

Single crystal X-ray diffraction (SCXRD) experiments are performed for several Cs_2TeX_6 compositions (Table S3 and Table S4). The pure-halide compositions are confirmed in the FCC structure with determined lattice parameters of 10.4669 Å for Cs_2TeCl_6 , 10.9165 Å for Cs_2TeBr_6 , and 11.6910 Å for Cs_2TeI_6 . A representative mixed-halide composition $\text{Cs}_2\text{TeCl}_3\text{Br}_3$ is also confirmed to be in the $\text{Fm}\bar{3}\text{m}$ space group, existing as a random alloy where the different halide anions are crystallographically equivalent (Figure S2). This suggests that the halide anions do not have a preferential site around the tellurium atom in each isolated octahedron, so it is equally likely that a halide site will be occupied by either chlorine or bromine in the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) alloys and by either bromine or iodine in the $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) alloys. Both the PXRD

and SCXRD only reflect the spatially averaged structure of these mixed-halide compositions, so locally, there could be a distribution of different types of $[\text{TeX}_6]^{2-}$ octahedra.⁴⁶ This aligns well with previous X-ray studies which show that the mixed-halide compositions of CsPbX_3 are constructed of a $[\text{PbX}_6]^{4-}$ octahedral network that is a random distribution of different octahedra types within each alloy.⁴⁷

Probing the Lattice Dynamics Dominated by the Isolated Pure-Halide Octahedra.

With these structural implications, we sought to have a more detailed understanding of the local, atomic-scale structural details and atomic dynamics of the isolated $[\text{TeX}_6]^{2-}$ octahedral units using Raman spectroscopy. Previous Raman studies of the A_2TeCl_6 crystal system **determined** that the vibrational units in the single crystals are the isolated $[\text{TeX}_6]^{2-}$ octahedra.²⁷ By group theory analysis, the O_h symmetry of the isolated octahedra in the pure-halide compositions should result in 3 distinct Raman-active modes. This is confirmed in the Raman spectra of the pure-halide crystals (Figure 3a), using notation (Cs_2TeCl_6 , Cs_2TeBr_6 , Cs_2TeI_6). The highest-frequency modes of (289 cm^{-1} , 176 cm^{-1} , 121 cm^{-1}) can be assigned to the symmetric stretching A_{1g} mode, the middle modes of (246 cm^{-1} , 152 cm^{-1} , 108 cm^{-1}) can be assigned to the asymmetric stretching E_g mode, and the lowest-frequency modes of (140 cm^{-1} , 92 cm^{-1} , 67 cm^{-1}) can be assigned to the bending T_{2g} mode (Figure 3b). The T_{2g} mode of the Cs_2TeI_6 single crystals appears in the ultra-low-frequency (ULF) wavenumber range ($\omega < 100\text{ cm}^{-1}$), as does the translational Cs^+ T_{2g} mode (also known as the lattice band)^{48,49} of all three pure-halide crystals (49 cm^{-1} , 46 cm^{-1} , 38 cm^{-1}) (Figure 3a). The fitted fundamental mode frequencies follow a reduced mass approximation⁵⁰ (Figure 3c), with the reduced mass μ defined by the 6 Te–X bonds in a $[\text{TeX}_6]^{2-}$ octahedron (i.e., $1/\sqrt{\mu} = [(1/m_{\text{Te}}) + (6/m_{\text{X}})]^{1/2}$).⁵¹ The agreeable fit of the fundamental

modes to this reduced mass approximation highlights that there are likely intra-octahedral harmonic bonding potentials in the lattices of the Cs_2TeX_6 family.

By using an excitation energy of 1.96 eV for these Raman measurements, we place the Cs_2TeI_6 crystal under a near-resonant condition (see next section for bandgap determination of Cs_2TeI_6). Due to the coupling of phonon excitation and electron excitation in a resonant condition, the Raman scattering cross-section and thus the measured Raman intensity are increased, leading to the enhancement of Raman modes that have low scattering cross-sections and cannot be observed in non-resonant conditions. This enhancement of mode signals is evident in the spectrum of Cs_2TeI_6 crystals compared to the spectra of Cs_2TeCl_6 and Cs_2TeBr_6 crystals, where Cs_2TeI_6 clearly shows more than just the expected 3 longitudinal-optical (LO) fundamental modes determined by factor group analysis. A band emerges at 84 cm^{-1} that agreeably aligns to a multi-phonon band of the fundamental modes, $A_{1g}-E_g+T_{2g}$ (Figure 3a). Additionally, 2 sets of doublets emerge at (224 cm^{-1} , 238 cm^{-1}) and (329 cm^{-1} , 353 cm^{-1}). These doublet modes are assigned to second- and third-order harmonics of the E_g and A_{1g} fundamental modes, specifically ($2E_g$, $2A_{1g}$) and ($3E_g$, $3A_{1g}$) (Figure 3a). This assignment is supported by the analysis shown in Figure 3d, where the overtone frequencies are relatively close to multiples of the fundamental frequencies.

Figure 3. (a) Raman spectra of the pure-halide single crystals Cs_2TeCl_6 , Cs_2TeBr_6 , and Cs_2TeI_6 ($\lambda_{\text{ex}} = 632.8\text{ nm}$). The pure-halide compositions each show 3 fundamental modes, concomitant with the O_h symmetry of the isolated octahedra within their crystal structures, and 1 Cs^+ cation lattice (translational) mode. Second- and third-order harmonics of the fundamental E_g and A_{1g} modes are observed only in Cs_2TeI_6 crystals. (b) Raman-active vibrational modes in O_h symmetry compositions Cs_2TeCl_6 , Cs_2TeBr_6 , and Cs_2TeI_6 . The vibrational centers are the isolated octahedra within the crystal structures. (c) The

change in frequency position of each fundamental mode with the reduced mass for each pure-halide composition. The shaded region of each linear fit represents the 95% confidence interval. (d) A linear trend emerges between the frequency positions of the fundamental E_g and A_{1g} modes of Cs_2TeI_6 and the observed overtones, thus suggesting that the overtones originate from E_g and A_{1g} , respectively. Error in the fitted mode frequencies is small such that the error bars are not visible on the plot.

The appearance of higher-order harmonics under resonant excitation is a common phenomenon in semiconductor systems by the Franck-Condon principle, representing not only strong exciton-phonon coupling^{12,52} but also a degree of lattice anharmonicity superimposed on harmonic bonding potentials.^{12,53} This degree of lattice anharmonicity likely represents anharmonic inter-octahedral bonding potentials, as observed previously in neutron and X-ray scattering experiments of Cs_2TeI_6 .⁵³ The ratio of the integrated areas under the E_g -based peaks is $E_g : 2E_g : 3E_g = 4 : 2.3 : 1$, and the ratio of the area under the A_{1g} -based peaks is $A_{1g} : 2A_{1g} : 3A_{1g} = 51 : 4.2 : 1$. Thus, with increasing frequency, the overtones become progressively weaker and broader. Large integrated area ratios between a fundamental mode and its respective overtones like those seen here for Cs_2TeI_6 crystals represent strong exciton-phonon coupling in those crystals.⁵² Strong exciton-phonon coupling is important to identify in crystal structures because it is not only indicative of lattice anharmonicity, but it also directly impacts charge carrier mobilities by strongly modulating the dielectric environment that charge carriers experience while moving through the lattice.^{54,55}

The final band that appears in the spectrum of Cs_2TeI_6 due to quasi-resonant conditions is an unknown mode at 140 cm^{-1} (Figure 3a). We observe that this mode emerges in the spectrum over the course of the measurement (see SI Section “Assignment of Cs_2TeI_6 Extra Quasi-Resonant Mode”), indicating that laser irradiation is driving a change in the symmetry of the

crystal. EDX line and map scans over the laser-damaged spot on the crystal surface show a dramatic decrease in iodide content. This iodide deficiency likely represents that as a result of bond breaking under near-resonant excitation conditions, iodide vacancies in the Cs_2TeI_6 crystal⁵⁶ are provided sufficient energy to migrate to the surface, creating a new coordination environment of under-coordinated Te–I units in the Raman probe volume. The anharmonicity observed for this Cs_2TeI_6 lattice also promotes the anionic migration.⁵⁵ The creation of these new coordination units and thus the elimination of O_h -symmetry $[\text{TeI}_6]^{2-}$ units can explain the emergence of this extra mode at the expense of O_h -symmetry intrinsic E_g and T_{2g} modes. Therefore, we can assign this extrinsic mode in Cs_2TeI_6 to a mode brought about by increased Te– V_I (iodide vacancy) bonding in the probe volume, denoted as $\nu_{\text{Te-VI}}$ (Figure 3a).

Understanding the Mixed-Halide Vibrational Properties with a Random Octahedra Distribution.

With the origin of all Raman modes determined in the pure-halide compositions, we turn to understand the Raman spectra of the mixed-halide crystals. These spectra show many broadened, asymmetrical peaks, which suggests that many vibrational modes are thermally smeared together at room temperature (Figure 4a). The appearance of many vibrational modes in Raman spectra could indicate the presence of multiple coordination environments within these mixed-halide single crystals, as opposed to one unique coordination environment. For multiple vibrational centers to exist, there is likely a distribution **of** different isolated octahedra types within each mixed-halide single crystal, which is supported by their random alloy behavior observed in the SCXRD results. Each random alloy can thus be considered as a compound of different octahedra types. Since the isolated octahedra are the vibrational centers, the Raman

spectra of these compounds would be a combination of the vibrational modes contributed by each octahedron type, if no vibrational interactions between the different $[\text{TeX}_6]^{2-}$ octahedra are assumed.⁵⁷ Simulation and statistical analysis were used to elucidate the detailed atomic structure of the mixed-halide crystals.

Within a single mixed-halide space, such as $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$), there are 10 possible $[\text{TeX}_6]^{2-}$ octahedra types that can exist (Figure 4b).^{58,59} Using the method established by Karim et al.,⁵⁷ models of these 10 octahedra types were constructed such that the vibrational behavior of an isolated octahedron of each type could be simulated in vacuum (Figure 4b). As expected from theory, the simulated spectra of the pure-halide octahedra show 3 Raman-active modes (Figure 4a). The degeneracies of the E_g and T_{2g} modes are shown at approximately identical frequencies, respectively, as expected from such a high-symmetry system. The simulated frequencies of the pure-halide octahedra have closely predicted the frequencies of the experimentally observed modes, indicating that simulating the Raman spectrum of an isolated $[\text{TeX}_6]^{2-}$ octahedron in vacuum is a relatively good approximation of the bulk properties.

Figure 4. (a) Experimental Raman spectra (curves) of the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ and $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) alloy single crystals ($\lambda_{\text{ex}} = 632.8$ nm). Large second-order harmonics (indicated by a star) appear in the spectra of the $\text{Cs}_2\text{TeBr}_5\text{I}$, $\text{Cs}_2\text{TeBr}_4\text{I}_2$, $\text{Cs}_2\text{TeBr}_3\text{I}_3$, $\text{Cs}_2\text{TeBr}_2\text{I}_4$, $\text{Cs}_2\text{TeBrI}_5$, and Cs_2TeI_6 single crystals. Simulation results of isolated octahedra under vacuum weighted by a random distribution for each crystal composition are shown as vertical lines. (b) Representations of the 10 possible octahedra types that exist within each alloy space. The experimental Raman spectra highlight the potential of a random distribution of these 10 octahedra being present in each mixed-halide composition.

To understand the distribution of 10 octahedra types within each mixed-halide crystal, a random distribution analysis was performed to determine the probability of each octahedra type within each crystal composition (Figure S8). Under a random distribution, the octahedron type with the greatest population in the crystal corresponds to the stoichiometry of the crystal, and the **populations** of the other octahedra in the crystal average to the greatest-population octahedron type. The distribution results are incorporated by weighting the simulated spectra of each octahedron type by its respective probability in a particular crystal composition. The combination of the weighted spectra creates the summed simulated spectrum of randomly distributed octahedra types within each crystal composition. It is clear by comparing the experimental and full simulated spectra for each crystal that this random octahedra probability model allows all Raman modes in all experimental spectra to be accounted for (Figure 4a). Therefore, given the dynamic nature of these crystals and the ability of Raman spectroscopy to probe local crystal properties, these Raman experiments provide better resolution of the atomic-scale structural details of the mixed-halide crystals than the static SCXRD experiments.

Overtone (both second- and third-order harmonics) can also be visualized in the Raman spectra of the bromide-iodide alloy space $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) due to near-resonant excitation conditions for these crystals. The intensity of these overtones decreases with increasingly bromide-rich (smaller-anion-rich) lattices, until overtones are no longer present in the spectrum of Cs_2TeBr_6 crystals (Figure 4a and Figure S9). The disappearance of overtones does not necessarily mean that these modes are no longer present in the lattice. It could simply indicate that their scattering cross-section has decreased substantially. Given that Cs_2TeBr_6 is far from resonant conditions using an excitation energy of 1.96 eV, this does appear to be the case.

Upon changing to an excitation energy of 2.33 eV, overtones are observed in not only Cs_2TeBr_6 but also most crystals in the chloride-bromide alloy space $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 1-6$) due to near-resonant excitation conditions (Figure S10). The trend observed in overtone intensity in the $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) alloy space under quasi-resonant conditions continues into the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) alloy space, with overtone strength decreasing with increasingly chloride-rich (smaller-anion-rich) lattices. With the excitation energies available, the pure-halide composition Cs_2TeCl_6 could not be placed in resonance or quasi-resonance, so overtones are not observed in its spectrum (Figure S10). Given that overtones are observed in all other crystal compositions when in quasi-resonance, resonance Raman would likely enhance overtones of Cs_2TeCl_6 single crystals to become apparent in the spectrum as well. The presence of overtones in all crystal compositions in the Cs_2TeX_6 family indicates exciton-phonon coupling and lattice anharmonicity in those crystals, and the trend of decreasing overtone intensity with increasing concentrations of small halide anions indicates that the exciton-phonon coupling strength and the degree of lattice anharmonicity decreases in the same direction. The origin of this behavior will be revealed in the next section.

Implications of the Transition from a Molecule-Like to Dispersive Electronic Structure.

The compositional and structural tunability of Cs_2TeX_6 single crystals engenders tunable absorption, due to the absorbing centers and **electronic structure** being determined by the $[\text{TeX}_6]^{2-}$ octahedra.⁸ Tunable absorption across the visible and near-infrared (NIR) wavelength ranges is shown in Figure 5a. In addition to the observed tunability across all compositions, there appear to be distinct spectral features present at the absorption onset for each crystal in the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) composition space, as well as weakly present at the absorption onset of the $\text{Cs}_2\text{TeBr}_3\text{I}$

crystal. Given the presence of octahedral complexes within each crystal structure, it is not unreasonable to think that these spectral features correspond to absorption features characteristic of isolated or electronically-decoupled molecular octahedral complexes.^{60,61} In this case, the appearance of such electronically-decoupled absorption character in only the iodide-poor compositions helps to affirm this hypothesis. Due to the smaller anion size of chloride and bromide, there will be less orbital overlap between halide anions of nearest neighbor octahedra in the crystal structure due to the physical isolation of these octahedra. A direct result of less orbital overlap is a less dispersive, weakly electronically-coupled crystal system for the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) and $\text{Cs}_2\text{TeBr}_5\text{I}$ crystals. In this case, it is likely that the molecule-like energy levels of the isolated octahedra are the dominant contributor to the electronic structure of these crystals. Because these are 3D bulk single crystals, there will still be some level of a dispersive energy band nature, so we can consider these crystals as possessing molecular orbital wavefunctions in an envelope of a dispersive band structure (Figure 5b). As a result, the crystals in the Cs_2TeX_6 system exhibiting absorbance spectral features representative of molecular octahedral complexes can be considered as molecule-like single crystals. Their optical absorption gap (i.e., the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels) varies from 3.15 eV for Cs_2TeCl_6 to 2.59 eV for $\text{Cs}_2\text{TeBr}_5\text{I}$ (Figure S11 and Table S5). This type of molecule-like single crystal behavior due to the physical isolation of octahedra in the crystal structure has been exhibited by other 0D perovskites, namely Cs_4PbX_6 and Cs_4SnX_6 .^{26,62}

Due to the larger anion size of iodide, there will be greater orbital overlap between halide anions of nearest neighbor octahedra. With greater orbital overlap expected in crystals with increasing iodide concentration, we would expect a greater degree of inter-octahedral coupling in

these crystals, which is corroborated by the Raman results via a larger integrated area ratio between fundamental modes and higher-order harmonics of Cs_2TeI_6 compared to that of Cs_2TeBr_6 . A direct result of greater orbital overlap and larger inter-octahedral coupling is a more typical dispersive electronic band structure dominating in the $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 2-6$) crystals. In this case, we no longer have an envelope of a dispersive band structure but rather a true dispersive band structure. This is evidenced by the disappearance of the distinct molecule-like spectral features at the absorption onset starting with the $\text{Cs}_2\text{TeBr}_4\text{I}_2$ crystal, whose absorbance spectrum shows the expected shape of the conduction band density of states in a 3D bulk single crystal. The remainder of the crystals in the $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ space exhibit this same behavior. This is shown schematically in Figure 5b as the traditional picture of energy band formation, with an infinite number of molecular energy levels spaced infinitesimally close. By using indirect bandgap Tauc plots to perform linear fitting to the absorption onset of these dispersive crystals, approximate bandgap values were determined. Indirect bandgap values vary from 1.73 eV for $\text{Cs}_2\text{TeBr}_4\text{I}_2$ to 1.50 eV for Cs_2TeI_6 (Figure S11 and Table S5). To test this hypothesis of a transition from a more molecule-like energy level structure in Cs_2TeCl_6 and Cs_2TeBr_6 to a more typical dispersive band structure in Cs_2TeI_6 , electronic structure calculations were performed and are shown in the next section. This electronic transition from dominant 0D-behavior to dominant 3D-behavior is also apparent in the absorbance spectrum of the isostructural $\text{Cs}_2\text{SnBr}_{6-x}\text{I}_x$ ($x = 0-6$) single crystals,²⁰ but to the authors' knowledge, this is the first report of the mechanism behind this transition in 0D perovskites.

Figure 5. (a) UV-visible absorption spectra of powdered $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ and $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) single crystals recorded at 300 K, showing halide-tunable absorption onset. The broad features at the absorption onset of the iodide-poor compositions correspond to energy levels of the more molecule-like nature of these crystals. (b) Schematic of the evolution in the electronic structure from more molecule-like bulk single crystals in Cs_2TeCl_6 and Cs_2TeBr_6 to more typical dispersive bulk single crystals in Cs_2TeI_6 . The dispersive band structure associated with bulk single crystals is modulated by the molecule-like nature of isolated octahedra with little orbital overlap between neighboring octahedra in Cs_2TeCl_6 and Cs_2TeBr_6 . This is in comparison with the Cs_2TeI_6 composition, which maintains the traditional view of dispersive band structure in bulk single crystals.

Coupled with tunable absorbance, Cs_2TeX_6 single crystals exhibit tunable broad-band emission across the visible and NIR wavelength ranges. Single crystals within the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) composition space emit in the visible wavelength range from 588 nm (bright yellow) for Cs_2TeCl_6 to 670 nm (deep red) for Cs_2TeBr_6 (Figure 6 and Table S6). Emission from these crystals can be visualized upon laser irradiation of the sample at room temperature, particularly from Cs_2TeCl_6 crystals (Figure 6, inset). As a result, a consistent photoluminescence quantum yield (PLQY) of 2.06% is measured for Cs_2TeCl_6 crystals. Despite being able to visualize emission from all crystals in the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) composition space, emission intensity decreases along the composition space, with the highest emission efficiency from Cs_2TeCl_6 single crystals and the lowest emission efficiency from Cs_2TeBr_6 single crystals.⁶³

Figure 6. Photoluminescence (PL) spectra of powdered $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) single crystals recorded at room temperature ($\lambda_{\text{ex}} = 375$ nm), showing halide-tunable visible emission. The inset shows an optical microscope image of bright yellow emission ($\lambda_{\text{em}} = 588$ nm) from a Cs_2TeCl_6 single crystal. A PL quantum yield (PLQY) of 2.06% is measured for this crystal.

The observed photoluminescence (PL) behavior is likely a result of the interplay between the effect of the $5s^2$ lone pair of Te^{4+} , the formation of self-trapped excitons (STEs), and the increase in inter-octahedral coupling between nearest neighbor octahedra from Cs_2TeCl_6 to Cs_2TeBr_6 . When comparing the absorption and emission spectra, the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) space exhibits relatively large Stokes shifts, varying from 1.04 eV in Cs_2TeCl_6 ^{25,64} to 0.90 eV in Cs_2TeBr_6 (Figure S12). This broad-band, strongly Stokes-shifted emission is consistent with the high-symmetry, isolated nature of the $[\text{TeX}_6]^{2-}$ octahedra to form localized Frenkel excitons with large binding energies and to emit via the transition from the degenerate excited state $^3\text{P}_{0,1,2} \rightarrow ^1\text{S}_0$ ground state.^{26,65} This indicates that the likely emission mechanism of the Cs_2TeX_6 system is self-trapped exciton (STE) emission.⁶²

In ns^2 metal cations such as Te^{4+} ($[\text{Kr}]4d^{10}5s^2$), the origin of the large Stokes shift has been attributed to a more stereochemically active ns^2 lone pair leading to stronger excited-state structural relaxations of the isolated octahedra, i.e. the dynamic Jahn-Teller effect.^{65,66} The little to no spectral overlap between excitonic excitation and emission energies resulting from a large Stokes shift creates a non-resonant condition where exciton migration can only occur via the assistance of a phonon.⁶⁴ As a result, there is a much lower probability of exciton migration and thus a much lower probability of excitons to encounter defects and non-radiatively recombine.⁶⁷ Thus, the stereoactivity of the $5s^2$ lone pair of Te^{4+} appears to facilitate the creation of STEs via a dynamic Jahn-Teller effect and to produce a large Stokes shift that hinders the migration of these STEs localized to the isolated octahedra, thus allowing a large population of the generated STEs to radiatively recombine. These phenomena fail to describe why the emission efficiency decreases in crystals from Cs_2TeCl_6 to Cs_2TeBr_6 , but a possible explanation for this observed emission efficiency decrease lies in the strong inter-octahedral coupling that arises in the

compositions with larger halide anions. As shown by the Raman and UV-visible absorption results, crystal compositions with higher concentrations of large halide anions possess strong vibrational and electronic coupling. This strong exciton-phonon coupling leads to a higher probability of STE dissociation. These processes dramatically reduce the probability of excitonic radiative recombination and lead to PL quenching.

On the other hand, single crystals within the first half of the $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 1-3$) composition space emit in the near-infrared (NIR) wavelength range at 4 K (Figure S13 and Table S6). Due to thermal quenching of the PL, these single crystals do not exhibit emission at room temperature.^{62,67} With increasing iodide concentration, single crystals in the second half of the $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 4-6$) composition space experience PL quenching such that no emission is observed, even at 4 K. Similar to the $\text{Cs}_2\text{TeCl}_{6-x}\text{Br}_x$ ($x = 0-6$) composition space, emission intensity continues to decrease non-monotonically along the $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) composition space, with the highest emission efficiency from Cs_2TeBr_6 single crystals and the lowest emission efficiency from Cs_2TeI_6 single crystals. We propose that this behavior is likely the result of the dramatic increase in inter-octahedral coupling between nearest neighbor octahedra with increasing iodide concentration, as suggested by both the Raman and UV-visible absorption results and as calculated for other 0D perovskite systems.^{66,67} The effect of STE dissociation will increase with increasing inter-octahedral coupling,⁶⁶ so it is reasonable that the decrease in emission efficiency with increasing halide anion size and the dramatic PL thermal quenching behavior with high iodide content could be related to the transition from a more molecule-like to a more typical dispersive electronic structure.

A unique behavior that emerges in the emission spectra is that upon incorporation of a single iodide unit into the formula unit (i.e., moving from composition Cs_2TeBr_6 to composition

$\text{Cs}_2\text{TeBr}_5\text{I}$), there is a shift in peak emission wavelength by 164 nm (Figure S13), which is quite a large shift. This behavior continues with the incorporation of a second iodide unit into the formula unit (i.e., moving from composition $\text{Cs}_2\text{TeBr}_5\text{I}$ to composition $\text{Cs}_2\text{TeBr}_4\text{I}_2$), which causes another large shift in peak emission wavelength by 86 nm. However, upon incorporation of a third iodide unit into the formula unit, the shift in peak emission wavelength between compositions becomes more typical, exhibiting a shift of 27 nm in peak emission wavelength when moving from composition $\text{Cs}_2\text{TeBr}_4\text{I}_2$ to composition $\text{Cs}_2\text{TeBr}_3\text{I}_3$. Since the compositions with even higher iodide concentration have no observable emission, this trend of decreasing NIR peak emission wavelength shifting between compositions cannot be confirmed for the entire $\text{Cs}_2\text{TeBr}_{6-x}\text{I}_x$ ($x = 0-6$) composition space. The origin of this shifting trend requires further study.

Understanding the Electronic Structure Transition with DFT Calculations.

To confirm our hypothesis of a transition from a more molecule-like to a more typical dispersive band structure with increasing halide anion size in Cs_2TeX_6 crystals, density functional theory (DFT) calculations were performed for compositions Cs_2TeCl_6 , Cs_2TeBr_6 , and Cs_2TeI_6 using the GGA-PBE functional and including spin-orbit coupling (SOC) effects (PBE+SOC) to determine electronic band structure and electronic density of states (eDOS). A more molecule-like energy level structure in an envelope of a dispersive band structure should appear as nearly flat (small dispersion, or high effective mass due to small curvature) valence and conduction band edges with small bandwidths. On the other hand, a dispersive band structure is characterized by greater curvature of the valence and conduction band edges (i.e., smaller carrier effective mass) and by larger valence and conduction bandwidths (i.e., larger hopping term).

As shown in Figure 7, the calculated electronic band structures display a trend of increasing departure from sharp molecule-like energy levels to a more dispersive nature of bands near the valence band maximum (VBM) and conduction band minimum (CBM) as we move from Cs_2TeCl_6 to Cs_2TeI_6 . As discussed previously, there is expected to be some dispersion in the band structures of all 3 pure-halide compositions, as these crystals are a bulk system. However, for Cs_2TeCl_6 and Cs_2TeBr_6 , the band structures show large swaths of k-space for which the valence band and conduction band are completely or mostly flat (i.e., along the X–W–K direction). On the other hand, the band structure of Cs_2TeI_6 has a typical dispersive nature with significant band curvature. This trend of increasing dispersion is confirmed by comparing the carrier effective masses determined at the VBM and CBM (hole effective mass m_h^i for the valence band and electron effective mass m_e^i for the conduction band) across the 3 compositions (Table 1), as well as by comparing bandwidths of the lowest unoccupied band in the conduction band across the 3 compositions (Table 2). These results were further validated by performing calculations on the same structures using the HSE06 functional that is known to provide bandgaps in better agreement with experimental measurements (Figure S14).

Figure 7. Band structure and corresponding total electronic density of states (eDOS) of bulk (a) Cs_2TeCl_6 , (b) Cs_2TeBr_6 , and (c) Cs_2TeI_6 . Dispersion of the bands increases and the eDOS become more continuous from Cs_2TeCl_6 to Cs_2TeI_6 , highlighting the transition to the more typical dispersive bulk single crystalline nature of Cs_2TeI_6 .

Table 1. Hole effective mass m_h^i at the valence band maximum (VBM) and electron effective mass m_e^i at the conduction band minimum (CBM) for crystals Cs_2TeCl_6 , Cs_2TeBr_6 , and Cs_2TeI_6 .

| Crystal Composition | Hole Effective Mass m_h^i | Electron Effective Mass m_e^i |
|----------------------------|-----------------------------|---------------------------------|
| Cs_2TeCl_6 | $1.70m_0$ | $0.69m_0$ |
| Cs_2TeBr_6 | $1.63m_0$ | $0.48m_0$ |
| Cs_2TeI_6 | $1.00m_0$ | $0.30m_0$ |

Table 2. Bandwidths of the lowest unoccupied band in the conduction band for crystals Cs_2TeCl_6 , Cs_2TeBr_6 , and Cs_2TeI_6 .

| Crystal Composition | Bandwidth of Lowest Unoccupied Conduction Band |
|----------------------------|--|
| Cs_2TeCl_6 | 0.349 eV |
| Cs_2TeBr_6 | 0.459 eV |
| Cs_2TeI_6 | 0.624 eV |

The narrow bandwidth in Cs_2TeCl_6 (Table 2) represents a non-dispersive band nature characteristic of molecule-like energy levels, which supports the notion of weak inter-octahedral coupling strength and ultimately strong radiative recombination at the $[\text{TeCl}_6]^{2-}$ octahedra in the crystal structure. The larger bandwidth in Cs_2TeI_6 represents a more dispersive band nature and a larger hopping term, which supports the notion of strong inter-octahedral electronic and vibrational coupling leading to STE dissociation. The intermediate bandwidth in Cs_2TeBr_6 represents a mixing of molecule-like energy levels and dispersive band structure, which supports the notion of an intermediate coupling strength between neighboring $[\text{TeBr}_6]^{2-}$ octahedra which leads to an energetic competition between radiative recombination and STE dissociation.

The valence band and conduction band character in these pure-halide compositions is expected to be dominated by contributions from hybridized Te-s/X-p orbitals and hybridized Te-p/X-p orbitals, respectively, based on similar molecular orbital contributions in other perovskite systems.⁸ The eDOS calculations confirm this to be the case (Figure 7). The eDOS for Cs_2TeCl_6 shows narrower bands near the VBM and CBM as compared to Cs_2TeI_6 . This

observation can be explained by considering the combination of a more extended nature of X-p orbitals in Cs₂TeI₆ as compared to Cs₂TeCl₆ and Cs₂TeBr₆, resulting in a more dispersive valence band, and of a greater hybridization strength between the Te 5s² lone pair and non-bonding Cl-p orbitals as compared to the Te 5s² lone pair and I-p orbitals. A greater hybridization strength between the Te 5s² lone pair and non-bonding Cl-p orbitals is characterized by a larger energy splitting in the valence band (Figure 7a) and has been shown to result in stronger antibonding character of the top of the valence band.⁶⁷ The decrease in hybridization strength between the Te 5s² lone pair and X-p orbitals from Cs₂TeCl₆ to Cs₂TeBr₆ to Cs₂TeI₆ is also manifested as a relatively lower contribution of Te to the eDOS near the VBM in Cs₂TeBr₆ and Cs₂TeI₆ crystals (Table S7).

Conclusions

In this study, a series of Cs₂TeX₆ (X = Cl⁻, Br⁻, I⁻) single crystals were successfully synthesized through a solution-based method. The isolated octahedral building blocks within the Cs₂TeX₆ crystal structure are at the foundation of its many unique properties. The isolated [TeX₆]²⁻ octahedral units yield a tunable, soft lattice whose dynamics can be easily probed via Raman spectroscopy. Probing these isolated vibrational centers reveal that all mixed-halide crystals in the Cs₂TeX₆ system likely have a lattice constructed of a random distribution of 10 different octahedra types that average to a specific crystal composition. Additionally, the pure-halide compositions Cs₂TeCl₆, Cs₂TeBr₆, and Cs₂TeI₆ crystals exhibit harmonic intra-octahedral bonding potentials and some degree of anharmonic inter-octahedral bonding potentials. Therefore, the Cs₂TeX₆ system exhibits both harmonic and anharmonic lattice behavior. This

degree of anharmonicity increases with increasing halide anion size, which corresponds directly to stronger exciton-phonon coupling in iodide-rich compositions. This stronger inter-octahedral electronic and vibrational coupling leads to the formation of a typical dispersive band structure, to the dissociation of STEs, and to the potential formation of electron and hole polarons in iodide-rich compositions upon photoexcitation. In comparison, chloride-rich lattices with weaker inter-octahedral coupling and stronger ns^2 lone pair effects lead to the formation of more molecule-like energy levels in the band structure and to the higher probability of radiative recombination of STEs. Overall, this study of Cs_2TeX_6 single crystals provides insight into the influence and behavior of the fundamental octahedral building block within perovskite structures.

Associated Content

Supporting Information

The Supporting Information is available free of charge at

Figures S1–S14 and Tables S1–S5 including EDX spectra, SCXRD crystallographic tables, regular and *in-situ* Raman spectra used to identify unknown modes, electronic gap determination, electronic and optical gap trends, and DFT calculations of band structure and quantitative metrics from the band structure.

Accession Code

The crystallographic information file (CIF) has also been deposited in the Inorganic Crystal Structure Database under reference numbers CSD 2092632, 2092633, 2092634, and 2092635. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by emailing data_request@ccdc.cam.ac.uk.

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Notes

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TOC Graphic

