Diverging Expressions of Anharmonicity in Halide Perovskites

Adi Cohen, Thomas M. Brenner, Johan Klarbring, Rituraj Sharma, Douglas H. Fabini, Roman Korobko, Pabitra K. Nayak, Olle Hellman, and Omer Yaffe*

1. Introduction

Hybrid and all-inorganic lead-based halide perovskite crystals have been intensively studied in the last decade due to their promising optoelectronic properties for a wide range of applications. As research progressed, it became increasingly clear that the lead-based perovskites form a unique class of semiconductors that exhibit a unique combination of optoelectronic and structural properties. For example, they exhibit many structural defects that can be readily observed under a simple light microscope. Yet, these defects are electronically benign. We and others have argued that this special combination can exist due to strongly anharmonic structural dynamics of the lead-based halide perovskites.

Raman, neutron, and inelastic X-ray scattering measurements indicate that the thermal fluctuations in the lead-based halide perovskites are strongly anharmonic. In a recent effort to develop lead-free halide perovskites, Cs2AgBiBr6 has emerged as a promising material despite having an indirect bandgap of \( \approx 2 \) eV. However, extensive investigations so far showed that Cs2AgBiBr6 does not share the unique set of electronic properties of the lead-based perovskites that are needed for solar cells. It appears to have low mobility and deep-level defects compared to the lead-based perovskites. Therefore, it is of interest to compare the structural dynamics of Cs2AgBiBr6 to that of lead-based perovskites. This comparison will allow us to explore how anharmonic lattice dynamics are expressed in lead-free halide perovskites and investigate whether strong anharmonicity is related to the lead-based halide's excellent optoelectronic properties.

In this work, we utilize Raman scattering, specific heat, and dielectric spectroscopy measurements to investigate the evolution with temperature of the structural dynamics of Cs2AgBiBr6 in comparison to that of its lead-based analog—CsPbBr3. We show that despite the apparent similarities between these...
compounds, the evolution with temperature of their structural dynamics is markedly different. Specifically, we show that Cs₂AgBiBr₆ and CsPbBr₃ exhibit diverging types of anharmonic expressions. While the lead-based perovskite shows broad Raman scattering that does not coincide with the existence of well-defined normal modes, the anharmonicity in Cs₂AgBiBr₆ is expressed by a soft mode, similar to that of SrTiO₃, an archetypical oxide perovskite. We conclude that the octahedral tilting instability evolves differently with temperature in each material, leading to the breakdown of the normal-mode picture in CsPbBr₃ but not in Cs₂AgBiBr₆. Finally, we discuss the consequences of the normal-mode breakdown on the optoelectronic properties.

2. Results and Discussion

2.1. Symmetry-Based Analysis of the Raman Spectra

Cs₂AgBiBr₆ has one reported cubic-to-tetragonal (Fm 3m to I4/m) phase transition at 122 K. The top panels of Figure 1 present the unpolarized Raman spectra of Cs₂AgBiBr₆ in its cubic (at room temperature) (a) and tetragonal (40 K) (b) phases. Microscopy images of the measured crystal are presented in Figure S1, Supporting Information. Factor group analysis predicts four Raman active modes in the cubic phase (A₁g + E₉ + 2T₂g), and nine Raman active modes in the tetragonal phase (3A₉ + 3B₉ + 3E₉). Indeed, four clear peaks are observed in the cubic phase (at 43, 74, 135, and 178 cm⁻¹), and nine peaks are observed in the tetragonal phase (17, 27, 39, 44, 72, 75, 138, 139, and 180 cm⁻¹).

To verify the agreement between the experimental results and the symmetry-based factor group analysis we performed polarization orientation (PO) Raman measurements. In this measurement, we use linearly polarized light to excite a single crystal. The scattered light is filtered by another polarizer (analyzer) to collect light in a parallel or perpendicular orientation with respect to the incoming light. The incoming light polarization is rotated stepwise, and parallel and perpendicular measurements are taken at each step. Figure 1 shows image plots of the raw PO data for a Cs₂AgBiBr₆ single crystal in its cubic (Figure 1a) and tetragonal (Figure 1b) phases, in parallel (middle panels) and perpendicular (bottom panels) configurations. These color plots show the fluctuations of the Raman signal intensity as a function of the angle between the incident light polarization and an arbitrary axis in the plane perpendicular to the direction of light incidence. The white dashed lines divide the tetragonal phase PO panel (Figure 1b) into segments with different intensity scales due to large intensity variations between the peaks.

The mode assignments resulting from a factor-group-based analysis procedure are shown in Figure 1 next to each peak. In this fitting procedure, the PO dependence of each mode is described by its Raman tensor[37–39] related to the peak intensity fluctuations by

\[ I(\theta) \propto |c_i(\theta) R e_s(\theta)|^2 \]  

where I is the integrated intensity of the peak, \( \theta \) is the angle between the polarized incoming light and an arbitrary axes on the surface plane, \( e_i \) and \( e_s \) are the polarization vectors of the incident and scattered light, respectively, and \( R \) is the modes’ Raman tensor. In our analysis, \( e_i \) and \( e_s \) are defined for the

![Figure 1](image-url)
[111] crystal growth direction of the cubic phase as confirmed by an X-ray measurement (Figure S1, Supporting Information). (Raman tensors are given in the Supporting Information).

The intensity of all the peaks in the cubic phase is PO independent (Figure 1a). Typically, intensity fluctuations are observed for single crystals. However, our analysis shows that no fluctuations are expected for the [111] crystal orientation of \textit{Fm\textit{3}m} space group (see analysis in Section S1, Supporting Information). We also note that our results are reproducible for different samples in multiple spots and that the PO response at the same spot in the tetragonal phase (Figure 1b) does exhibit intensity fluctuations. Thus, confirming we detected a single crystal. Our mode assignments for the cubic phase agree with previous studies. The PO data for the tetragonal phase also agree with factor group analysis predictions (see Supporting Information for more details). Furthermore, our results are in agreement with the ab-initio-computed static phonon dispersion relation (Figure S2, Supporting Information).

The excellent agreement between the measurements and factor group analysis predictions yields an important insight about the nature of the material. Factor group analysis assumes the atoms oscillate about equilibrium positions defined by the crystal structure. The collective motion of the atoms can then be described by normal-modes whose frequency is determined by an effective harmonic potential centered at these positions. The success of the factor group analysis indicates that both the cubic and tetragonal phases of Cs$_2$AgBiBr$_6$ can be described by an effective harmonic potential at any temperature excluding those close to the phase transition. Nonetheless, as will be discussed below, the evolution from the tetragonal to the cubic structure requires strong anharmonicity to be at work.

2.2. Detection of an Unreported Low-Temperature Phase Transition

Our Raman measurements at low temperatures also revealed a second, unreported phase transition at \(\approx 37\) K. Figure 2a shows an image plot of the low-frequency Raman spectra as a function of temperature ranging from 10 to 130 K (which captures both phase transitions). It is clear that just below 37 K (marked with a white, horizontal line) there is an abrupt change in the Raman spectra where twelve new peaks appear. The appearance of the new peaks is indicative of a phase transition. To explore this further, we conducted temperature-dependent dielectric spectroscopy (top panel in Figure 2b), specific heat measurements (middle panel Figure 2b), and PO Raman measurements at 10 K (Figure S3, Supporting Information). The dielectric measurements show a nearly temperature-independent response with no peak at the transition, ruling out the possibility of a polar ground state. The specific heat measurements confirm the subtle phase transition at \(\approx 37\) K, evident in the first derivative of the specific heat as a function of temperature (bottom panel of Figure 2b, marked with a gray line). We tentatively find this unreported transition to be weakly first-order due to the sudden appearance of the new peaks in the Raman spectrum below 37 K (Figure 2a).

We find this phase transition an extremely small perturbation of the intermediate-temperature one, based on the low

![Figure 2](image-url). a) Normalized intensity map of Cs$_2$AgBiBr$_6$ low-frequency Raman spectra as a function of temperature. The intensity scale is logarithmic. There are two phase transitions (marked with white horizontal lines): an unreported low-temperature-phase-to-tetragonal transition at \(\approx 37\) K, and another tetragonal-to-cubic at \(\approx 122\) K. The tetragonal-to-cubic transition is displacive, displaying two soft modes (marked with white arrows) which shift to 0 cm$^{-1}$ as the phase-transition temperature is approached and disappear above the transition. b) Top: Static dielectric constant of Cs$_2$AgBiBr$_6$ from capacitance-loss measurements (20 kHz). No changes or peaks are observed at either of the phase transitions. Middle: Measured specific heat of Cs$_2$AgBiBr$_6$. The two colors indicate two different passes in differing temperature regions. The tetragonal-to-cubic phase transition at 122 K shows a clear peak in the heat capacity measurement. The unreported phase transition at \(\approx 37\) K is only apparent in the first derivative, shown in the bottom panel. Phase transitions are indicated by gray lines.
intensity of the new Raman peaks and the subtle effect on specific heat. We note that during the manuscript revision, a pre-print appeared in ArXiv that validates our findings with X-ray diffraction and neutron scattering.[45]

2.3. Soft-Mode Driven Phase Transition

We now discuss the mechanism of the tetragonal-to-cubic phase transition at \( \approx 122 \) K. The \( I_4/m \) tetragonal phase is observed in our Raman data between 40 and 120 K, between the two white horizontal lines in Figure 2a. The most notable spectral features are the two peaks that are marked with white arrows. We identify these peaks as “soft modes.”

A soft mode is a lattice normal mode whose frequency decreases anomalously toward the structural phase-transition temperature.[46,47] Such modes drive displacive phase transitions. The collective atomic displacements of the soft mode freeze out at the phase transition as the mode reaches zero frequency, giving rise to a change in the crystal symmetry.[48,49] Soft modes appear in many oxide perovskites[47] and other elpasolites.[50–52] Among them, SrTiO\(_3\) is considered to be a canonical example for a soft-mode driven displacive phase transition.[53,54]

It is instructive to compare our Raman measurements of the Cs\(_2\)AgBiBr\(_6\) soft modes to those of SrTiO\(_3\) to confirm the displacive nature of the phase transition. The phase sequence and Raman temperature-dependence of Cs\(_2\)AgBiBr\(_6\) was discussed in detail in the preceding text. Regarding CsPbBr\(_3\), it involves a cubic (\( Pm\_3m \)) to tetragonal (\( P4/mmb \)) phase transition at 404 K, and an additional phase transition from tetragonal to orthorhombic (\( Pnma \)) at 360 K.[43,44] Our Raman PO measurements confirm the symmetry of the tetragonal-phase soft modes, and the temperature dependence shows they exhibit the expected softening. The soft modes vanish in the cubic phase as expected by their selection rules in that phase. Thus we can confirm the displacive nature of the phase transition. Indeed, the occurrence of a displacive phase transition in Cs\(_2\)AgBiBr\(_6\) is in agreement with the prediction some of us made in a previous publication.[58]

2.4. Comparison of Anharmonic Expressions in Cs\(_2\)AgBiBr\(_6\) and CsPbBr\(_3\)

In SrTiO\(_3\), this instability corresponds to a triply degenerate, Raman-inactive phonon with symmetry of \( T_{2u} \) at the R point of the Brillouin zone in the cubic phase. This mode softens and splits into two zone-center Raman-active phonons with symmetry \( E_g \) and \( A_{1g} \) in the tetragonal phase.[43,44] In Cs\(_2\)AgBiBr\(_6\), the tilting instability corresponds to a triply degenerate Raman-inactive mode at the \( T \) point (\( T_{1g} \)) in the cubic phase. This mode splits into two Raman active \( E_g \) and \( A_{1g} \) modes in the tetragonal phase, as we concluded from comparison to other elpasolites with the same phase sequence.[51,52,56,57] Our Raman PO measurements confirm the symmetry of the tetragonal-phase soft modes, and the temperature dependence shows they exhibit the expected softening. The soft modes vanish in the cubic phase as expected by their selection rules in that phase. Thus we can confirm the displacive nature of the phase transition. Indeed, the occurrence of a displacive phase transition in Cs\(_2\)AgBiBr\(_6\) is in agreement with the prediction some of us made in a previous publication.[58]

Figure 3 presents the temperature-dependent Raman spectra of Cs\(_2\)AgBiBr\(_6\) (Figure 3a) and CsPbBr\(_3\) (Figure 3b) in a temperature range that includes the entire phase sequence of both compounds (the temperatures of the phase transitions were taken from XRD data reported in the literature[43,44] and are labeled in the figure). It is immediately apparent that there are stark differences in the Raman progression despite the many structural and chemical similarities of the two compounds.

The phase sequence and Raman temperature-dependence of Cs\(_2\)AgBiBr\(_6\) was discussed in detail in the preceding text. Regarding CsPbBr\(_3\), it involves a cubic (\( Pm\_3m \)) to tetragonal (\( P4/mmb \)) phase transition at 404 K, and an additional phase transition from tetragonal to orthorhombic (\( Pnma \)) at 360 K.[43,44] The orthorhombic phase at 80 K shows several pronounced peaks. As temperature increases, all the peaks soften, broaden and merge. However, unlike in Cs\(_2\)AgBiBr\(_6\), there are no distinguishable soft modes.
To fully appreciate these differences, it is important to note that the calculated phonon dispersion (at 0 K) of the cubic phase of both CsPbBr$_3$ and Cs$_2$AgBiBr$_6$ has imaginary frequency modes.$^{[58,59]}$ These imaginary frequency modes correspond to octahedral tilting instabilities associated with “multi-well” potentials.$^{[60]}$ Importantly, our measurements show that the same octahedral tilting instability evolves differently with temperature in the two crystals and by phonon–phonon interactions (i.e., anharmonic structural dynamics)$^{[68]}$ stabilize the cubic phases at nonzero temperatures.

The difference between the two crystals is most apparent when considering their cubic phases (but is pronounced throughout the phase sequence). In its cubic phase, CsPbBr$_3$ should be Raman inactive according to factor group analysis. Yet, it exhibits very strong Raman activity, which resembles the activity in the tetragonal phase. This means that the effective harmonic approximation does not hold and cannot describe the dynamics of CsPbBr$_3$ at elevated temperatures. Instead, the dynamics of CsPbBr$_3$ can be described by an anharmonic multi-well potential that is being populated as temperature increases. Its minima correspond to a variety of configurations involving octahedral tilting coupled to Cs distortions.$^{[7,59–63]}$ As temperature increases, hopping between the wells (i.e., large amplitude octahedral tilting and deformations) becomes possible$^{[21,60,64]}$ and phase transitions take place.

This means that the equilibrium positions do not coincide with the average cubic structure positions, which is a dynamically averaged structure. The Raman activity of the cubic phase arises due to the hopping between these minima, which breaks the symmetry of the crystal and relaxes the selection rules for Raman scattering.

This is in clear contrast to Cs$_2$AgBiBr$_6$ that, despite being anharmonic, exhibits a Raman spectrum in accordance to what is predicted by factor group analysis. In other words, Cs$_2$AgBiBr$_6$ has well-defined normal modes throughout the measured temperature range, and CsPbBr$_3$ exhibits a complete breakdown of the normal-mode picture at elevated temperatures. This type of behavior has also been observed for hybrid lead-based halide perovskites$^{[6,7]}$ as well as for tin- and germanium-based perovskites which also contain divalent group I metal cations with lone pair electron configurations.$^{[63]}$

2.5. Relationship between Anharmonicity and Optoelectronic Properties

Electronic properties of crystals (e.g., carrier mobility) are derived from their calculated electronic band structure which is based on the average structure of the crystal. This means that thermal fluctuations are implicitly assumed to introduce a small perturbation to the average structure. As discussed in the previous section, our work suggests that the perturbative treatment holds for Cs$_2$AgBiBr$_6$ but not for CsPbBr$_3$, even though both crystals are strongly anharmonic. Therefore, the failure/ success of factor group analysis to predict the Raman spectrum of a material is a useful criterion to determine whether the average crystal structure, as extracted from diffraction experiments, can adequately describe the electronic properties of the crystal. Specifically, in CsPbBr$_3$, the breakdown of the normal-mode picture dictates that the actual electronic structure is more localized than what is predicted from band structure calculations of the static average structure.$^{[65]}$ This may explain the much lower measured carrier mobility compared to the expected value.$^{[3,66–68]}$

Moreover, in a previous series of studies, we showed that the type of anharmonic behavior in lead-based perovskites (including CsPbBr$_3$ that is reported here) also leads to local polar fluctuations.$^{[7,62,63]}$ These polar fluctuations may screen defects and minimize their capture cross-section, leading to the long lifetimes of excited carriers demonstrated in lead-based perovskites.$^{[5,16,19,69]}$ Since our measurements show that the normal-mode picture holds for Cs$_2$AgBiBr$_6$, we conclude that this material has no local polar fluctuations. The absence of local polar fluctuations may explain why Cs$_2$AgBiBr$_6$ has more electronically active defects compared to the lead-based perovskites.$^{[34,35,70]}

3. Conclusions

We have compared the evolution with temperature of the Raman spectra of two halide perovskite crystals: Cs$_2$AgBiBr$_6$ and CsPbBr$_3$. We show that both crystals exhibit strong anharmonic effects related to octahedral tilting instabilities. However, the tilting instability evolves differently in each material, leading to dramatically different structural dynamics in the cubic phases of the two materials. The Raman spectra Cs$_2$AgBiBr$_6$ show a soft mode but retain the normal-mode picture at any temperature. In contrast, the Raman spectra of CsPbBr$_3$ deviate strongly from what is predicted by symmetry-based analysis of the average crystal structure (as extracted from diffraction experiments). The most obvious deviation is in the cubic phase, which is expected to be Raman inactive but instead shows strong Raman activity. Based on these findings, we suggest that the validity of the symmetry-based analysis to describe the Raman spectra is a criterion to determine if the average crystal structure is a proper starting point to predict and understand the electronic properties of the crystal at finite temperatures.

4. Experimental Section

Synthesis: Cs$_2$AgBiBr$_6$ crystals for the Raman measurement were taken from the same batch as reported by Schade et al.$^{[36]}$ which provided the details regarding synthesis and characterization of the crystal. Briefly, AgBr (2 mmol), CsBr (4 mmol), and BiBr$_3$ (2 mmol) were dissolved in 4 mL of DMSO to get a clear solution of the salts. Acetone was added to the above-mentioned solution to precipitate polycrystalline powders. 1 g of the dried polycrystalline powder was dissolved in 10 mL of 9 m HBr by heating the solution at 110 °C in an oven. The HBr solution was then cooled to room temperature at a rate of 0.5 °C h$^{-1}$ to get 1 mm size single crystals which were later characterized by X-ray diffractions methods which have been reported by Schade et al.$^{[36]}$ The crystals (0.5–2 mm) for the heat capacity and dielectric measurements were synthesized by slow evaporation of a concentrated aqueous HBr solution of AgBr and BiBr$_3$, with Cs$_2$CO$_3$ as the Cs$^+$ source. AgBr was prepared by precipitation from an aqueous solution of AgNO$_3$ and KBr, and BiBr$_3$ was prepared by reacting Bi$_2$O$_3$ with concentrated aqueous HBr. Phase purity was confirmed by powder X-ray diffraction of crushed...
crystals, and composition was confirmed by energy-dispersive X-ray spectroscopy. The synthesis procedure with the characterization of CsPbBr₃ crystals is given in ref. [71]. The crystal was grown by Yevgeny Rakita.

Raman Scattering: Raman scattering measurements were taken in a home-built back-scattering system. 1.57 eV CW diode laser (Toptica Inc., USA) and 1.16 eV CW solid-state laser (Coherent Inc.) was used to measure Cs₂AgBiBr₆ and CsPbBr₃, respectively. The beam was focused on the sample with a 50X objective (Zeiss, USA). The Rayleigh scattering was filtered by notch filters (Ondax Inc., USA). Finally, the scattered light was focused into a 1 m spectrometer (FHR 1000, Horiba) with a 1800 g mm⁻¹ grating for Cs₂AgBiBr₆ and 600 g mm⁻¹ for CsPbBr₃, and detected by a CCD and InGaAs detectors, respectively. For the polarization measurements the beam was passed through two polarizers (Thorlabs, USA), one linearly polarized the incoming light, and the other filter the scattered light in a parallel or perpendicular polarization to the incoming light (analyzer). The polarization of the light was rotated by a half-wave plate (Thorlabs, USA). Each Raman spectrum that appears in the image plot of Figure 2 and in Figure 3a was a sum of Raman spectra in two or three polarization angles, respectively, that captures all the features. The Raman spectra of Figure 3b were taken in one polarization angle. For the temperature-dependent measurements, the samples were placed inside a Janis cryostat ST-500 controlled by Lakeshore model 335. The sample was cooled with liquid helium to reach 10 K.

Specific Heat: Specific heat was measured by relaxation calorimetry in a Quantum Design PPMS. A single crystal was mounted on the sapphire stage with Apiezon N grease, and the heat capacity of these addenda (measured separately) was subtracted.

Dielectric Spectroscopy: Flat-plate capacitors were prepared by pressing polycrystalline Cs₂AgBiBr₆ (from ground crystals) to 2 t in a 6 mm diameter cylindrical die (typical thickness, 0.5 to 1.2 mm). DuPont silver paste was applied and cured at 55 °C to form the electrodes. 6 mm diameter cylindrical die (typical thickness, 0.5 to 1.2 mm). DuPont pressing polycrystalline Cs₂AgBiBr₆ (from ground crystals) to 2 t in a cylindrical die (typical thickness, 0.5 to 1.2 mm). DuPont silver paste was applied and cured at 55 °C to form the electrodes.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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