Electronic Structure and Optical Properties of α-CH₃NH₃PbBr₃ Perovskite Single Crystal

Ji-Sang Park, Sukgeun Choi, Yong Yan, Ye Yang, Joseph M. Luther, Su-Huai Wei, Philip Parilla, and Kai Zhu

National Renewable Energy Laboratory, Golden, Colorado 80401, United States

ABSTRACT: The electronic structure and related optical properties of an emerging thin-film photovoltaic material CH₃NH₃PbBr₃ are studied. A block-shaped α-phase CH₃NH₃PbBr₃ single crystal with the natural ⟨100⟩ surface is synthesized solvothermally. The room-temperature dielectric function ε = ε₁ + iε₂ spectrum of CH₃NH₃PbBr₃ is determined by spectroscopic ellipsometry from 0.73 to 6.45 eV. Data are modeled with a series of Tauc–Lorentz oscillators, which show the absorption edge with a strong excitonic transition at ~2.3 eV and several above-bandgap optical structures associated with the electronic interband transitions. The energy band structure and ε data of CH₃NH₃PbBr₃ for the CH₃NH₃⁺ molecules oriented in the ⟨111⟩ and ⟨100⟩ directions are obtained from first-principles calculations. The overall shape of ε data shows a qualitatively good agreement with experimental results. Electronic origins of major optical structures are discussed.

The organic–inorganic hybrid compounds with the perovskite structure CH₃NH₃PbX₃ (X = Cl, Br, I) are of great interest for their potential applications in high-performance photovoltaic (PV) devices. In less than 2 years of intense studies, the power-conversion efficiency (PCE) of CH₃NH₃PbI₃-based solar cells has already reached as high as 20.1%. Knowledge of optical properties plays a critical role in better understanding a material’s electronic structure and optimizing PV device structures, and therefore further improves the device performance. Despite rapid progress in CH₃NH₃Pb(1−x)Brₓ solar cell technology; however, the material’s fundamental properties are still largely unknown.

Spectroscopic ellipsometry (SE) is recognized as a highly suitable method of determining a material’s optical functions, such as complex dielectric function ε(E) = ε₁(E) + iε₂(E) and complex refractive index N(E) = n(E) + ik(E) over a wide photon-energy range. Therefore, SE has been used to characterize a wide variety of PV materials. For CH₃NH₃Pb(1−x)Brₓ, the ε and N spectra of one end point x = 0.0 (CH₃NH₃PbI₃) have recently been obtained by SE. However, no systematic optical study of the other end point x = 1.0 (CH₃NH₃PbBr₃) has been reported yet.

Here we apply SE to determine the room-temperature ε spectrum of bulk single-crystalline α-phase CH₃NH₃PbBr₃ from 0.73 to 6.45 eV. SE data modeled with the sum of eight Tauc–Lorentz (T–L) oscillators clearly show the absorption edge with a strong excitonic transition at around 2.3 eV and several above-bandgap optical structures associated with the electronic interband transitions. The energy band structure and ε data are obtained for CH₃NH₃PbBr₃ with the CH₃NH₃⁺ molecules oriented in the ⟨111⟩ and ⟨100⟩ directions from the first-principles calculations. Overall, the calculated ε data are in good agreement with the SE-determined spectrum. Electronic origins of the observed major optical structures are discussed based on the results from calculations.

Formation of a single-crystal of CH₃NH₃PbBr₃ is confirmed by an X-ray diffraction (XRD) scan as shown in Figure 1. The 00l (l = 1, 2, 3, and 4) reflections are clearly seen and their angular positions all match well with the results from a simulated XRD curve (not shown), which indicates that the crystal formed in the cubic phase and its surfaces are {001} planes. Details of the XRD analyses are presented in ref 18.

Ellipsometry in its most general form studies the changes of the polarization state of light due to interaction between the light and a material. If the light is neither s- nor p-polarized, then the s- and p-polarizations experience a different attenuation and phase shift upon reflection. The two SE parameters Ψ and Δ are respectively the amplitude component and the phase difference of the complex reflectance ratio ρ. The two parameters are related to ρ by

\[ \rho = \frac{r_p}{r_s} = \tan \Psi \exp[i\Delta] \]  

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where \( r_p \) and \( r_s \) are the complex reflectance coefficients for \( p \)- and \( s \)-polarized light, respectively. The fundamental optical function spectra can be obtained by modeling the two parameters \( \Psi \) and \( \Delta \), and the result with the minimum discrepancy between the model and the experimental data provides accurate optical information on a material.

In this study, the SE data were analyzed with the three-phase model consisting of the ambient, a surface overlayer, and the CH\(_3\)NH\(_3\)PbBr\(_3\) crystal. A surface overlayer is presumably composed of microscopic roughness and native oxides, whose optical response can be represented by the Bruggeman effective medium approximation (BEMA)\(^{19}\) using a 50–50 mix of the underlying material and void. The best result was achieved with a 3.63 nm-thick BEMA layer. As pointed out by Nelson et al.,\(^{20}\) the contributions from microscopic roughness and native oxides to a thin BEMA layer are practically indistinguishable.

The \( \epsilon \) spectrum of CH\(_3\)NH\(_3\)PbBr\(_3\) was constructed by the sum of eight T–L oscillators. The \( \epsilon_2(E) \) of an individual T–L oscillator is expressed by\(^{17}\)

\[
\epsilon_2(E) = \left\{ \begin{array}{ll}
\frac{AE_0C(E - E_0)^3}{(E^2 - E_0^2)^2 + C^2E^2} & (E > E_0) \\
\frac{1}{E_0} & (E \leq E_0)
\end{array} \right.
\]

where \( A \) is the oscillator strength, \( C \) is a broadening parameter, \( E_0 \) is the resonance energy, and \( E_0 \) is the Tauc gap (the onset of absorption). The \( E_0 \) was set to be the same for all T–L oscillators and constrained to be smaller than the \( E_0 \) by definition. The mathematical expression for the corresponding \( \epsilon_1 \) can be calculated by the Kramers–Krönig (K–K) transformation of \( \epsilon_2 \). The two SE parameters \( \Psi \) and \( \Delta \) taken at three incident angles and their best-fit curves are displayed in Figure 2a and Figure 2b, respectively. The experimental data and model are in excellent agreement. The fit-determined parameters \( A, C, \) and \( E_0 \) for all eight T–L oscillators are listed in Table 1. We note that the \( E_0 \) of oscillator no. 8 situates outside the spectral range of our data, which serves mainly as the background correction.

The real (\( \epsilon_1 \)) and imaginary (\( \epsilon_2 \)) parts of the resulting \( \epsilon \) spectrum are shown as solid red and solid blue curves, respectively, in Figure 3. The \( \epsilon_2 \) spectrum exhibits the absorption edge at \( \sim 2.3 \) eV accompanied by a strong exciton peak and several above-bandgap optical structures associated with the electronic interband transitions. For comparison, the \( \epsilon \) spectrum of CH\(_3\)NH\(_3\)PbI\(_3\) obtained from ref 14, are also shown.
the excitons in CH$_3$NH$_3$PbBr$_3$ than that for CH$_3$NH$_3$PbI$_3$, which is clearly seen in Figure 3.

Electronic origin of optical structures observed in the ε spectrum can be identified by comparing the experimental data and the results from the first-principles calculations. In this study, two different geometries of α-phase CH$_3$NH$_3$PbBr$_3$ are considered. The calculations were performed for the CH$_3$NH$_3$+ molecules aligned in the (111) and (100) directions as depicted in Figure 4a and Figure 4b, respectively. Our calculations suggest that CH$_3$NH$_3$+ molecules prefer to align in the (100) direction, although the energy difference between the two configurations is small. The difference in the total energy between the (100) and (111) orientations is estimated to be only 33 meV/unit-cell (12 atoms). A similar conclusion has been drawn from recent density functional theory calculations for CH$_3$NH$_3$PbI$_3$. The absence of a large energy barrier to rotation is likely to result in a labile movement of CH$_3$NH$_3$+ molecules at room temperature. We note that a formation of ferroelectric domain wall has not been considered in our calculations because the energetically favorable domains seem not to change the bandgap much.

The calculated energy band structures of CH$_3$NH$_3$PbBr$_3$ for the two molecular orientations are shown in Figure 5. Charge density analysis shows that the valence band maximum has Pb-s and Br-p antibonding characteristics, while the lowest three conduction band states have Pb-p and Br-s orbital characteristics. The antibonding character of the conduction band state is more clearly observed when the CH$_3$NH$_3$+ molecules are oriented to the (100) direction because Pb-p orbitals become aligned with the bond direction. When the CH$_3$NH$_3$+ molecules are oriented to the (111) direction, Pb-p orbitals rotate with respect to the bond direction, which makes the interaction weaker. Overall, the band structures look similar for both molecular orientations. However, a few small differences are found. While the structure with (111) orientation has a direct bandgap located at the R point of Brillouin zone (BZ), the conduction-band-minimum for the structure with (100) orientation appears at a position that is slightly off the R point toward the Γ point. Thus, CH$_3$NH$_3$PbBr$_3$ exhibits the indirect bandgap characteristic when the CH$_3$NH$_3$+ molecules are aligned in the (100) direction. Our calculations show that the energy difference between the direct and indirect bandgap, ΔE ≡ E$^{\text{dir}}$ − E$^{\text{ind}}$ for the (100) configuration, is 24 meV. A similar result was obtained for CH$_3$NH$_3$PbI$_3$ and the calculated ΔE is 25 meV.

The calculated ε spectra of CH$_3$NH$_3$PbBr$_3$ for the CH$_3$NH$_3$+ molecules oriented in the (111) and (100) directions are displayed in Figure 6a and Figure 6b, respectively. Even though the overall shapes of ε spectra do not show a strong dependence on the molecular orientation, the optical structures in the (111) data appear to be sharper than those in the (100) data. This is because the crystal with the (111) molecular orientation has high symmetry, so there are more degenerate states that lead to sharp peaks in the ε spectra. For the (100) orientation, the lower symmetry leads to band splitting, so the optical spectrum is broadened. However, as discussed earlier, it is unlikely that the SE-determined ε spectrum can be unambiguously matched to either of the calculated ε spectra because the CH$_3$NH$_3$+ molecules could be randomly oriented at room temperature due to the small orientation energy. Therefore, the experimental ε spectrum shown in Figure 3 can be regarded as an average of the two calculated data sets in practice.

To understand the electronic origin of each major optical structure, we resolved the contributions from four high symmetric points of BZ. The ε$_{zz}$ data associated with the M, R, Γ, and X points are shown in colored dashed lines. As shown in the energy band structure diagram (Figure 5a,b), the low-energy structures including the band edge are formed by the transitions at the R point. The transitions occurring at the M and X points have their major peaks at ~3.5 and ~4.0 eV, respectively. The contributions from the Γ point appear at the high-energy region (>5 eV). The major peak spanning from...
∼4.0 to ∼4.5 eV in the experimental spectrum seems to have multiple contributions—transitions at the M, R, and X points, while the shoulder structure at ∼3.5 eV can be attributed mainly to the transition at the M point.

In conclusion, the electronic structure and related optical properties of a bulk single crystal of α-CH$_3$NH$_3$PbBr$_3$ were studied both experimentally and theoretically. Spectroscopic ellipsometry was used to determine the room-temperature dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ spectrum of CH$_3$NH$_3$PbBr$_3$ from 0.73 to 6.45 eV. Data are modeled with a total of eight T=−L oscillators, which show the absorption edge with a strong excitonic transition at ∼2.3 eV and several above-bandgap optical structures associated with the electronic interband transitions. The energy band structure and $\varepsilon$ of CH$_3$NH$_3$PbBr$_3$ for the CH$_3$NH$_3^+$ molecules oriented in the ⟨111⟩ and ⟨100⟩ directions are obtained from first-principles density functional calculations. Results from the calculations suggest that the crystal with the CH$_3$NH$_3^+$ molecules oriented in the ⟨100⟩ direction is energetically more favored than the one in the ⟨111⟩ direction, although the energy difference is rather small at 33 meV/unit-cell. In addition, the ⟨100⟩ molecular orientation makes the crystal become a slightly indirect bandgap material. The energy difference between the indirect and direct bandgap is estimated to be 24 meV. Overall, the shape of calculated $\varepsilon$ data shows a qualitatively good agreement with experimental results. Owing to the small energy barrier between the ⟨111⟩ and ⟨100⟩ molecular orientations, the actual crystal is believed to have CH$_3$NH$_3^+$ molecules in random orientations at room temperature. Electronic origins of major optical structures have been identified.

**EXPERIMENTAL SECTION**

Preparation of CH$_3$NH$_3$PbBr$_3$ Crystalline Perovskite. We dissolved 0.5 mmol PbBr$_2$ (183 mg) and 0.5 mmol CH$_3$NH$_3$Br (56 mg) in 5 mL of dimethylformamide (DMF) solution. This mixed suspension was slightly heated on a hot plate to obtain a transparent solution. The solution was filtered through a compacted Celite column. The filtrate was collected, and 2 mL of this solution was transferred into a 5 mL inner vial (total vial volume). To the outer vial, 5 mL of toluene was added before the transfer of the inner vial. Finally, the outer vial was carefully capped, sealed, and placed in a light-free benchtop. The diffusion of toluene from the outer vial into the inner vial was slow, and the crystallization process was maintained in a dark and undisturbed environment for at least 3 days. An orange, block-shaped (1.4 × 1.4 × 0.7 mm$^3$) single crystal was obtained. Details of the crystal growth are given elsewhere.  

In a separate study, we characterized the structural properties of CH$_3$NH$_3$PbBr$_3$ crystal by single-crystal XRD scans using a Bruker Apex II CCD-based X-ray diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). 

Spectroscopic Ellipsometry. SE measurements were carried out from 0.73 to 6.45 eV with the sample maintained at room temperature using a spectroscopic rotating compensator-type ellipsometer (J.A. Woollam, Inc., M2000-DI model). To accommodate a small-sized sample, the focusing optics unit was employed, which reduces the beam diameter down to a few hundred micrometers. The incident angle varied from 55° to 75° with an increment of 10°. Data were recorded after averaging 2000 cycles of the compensator (2000 revolutions per measurement) to improve the signal-to-noise ratio.

First-Principles Calculations. The electronic structure and related optical properties of CH$_3$NH$_3$PbBr$_3$ for the CH$_3$NH$_3^+$ molecules oriented in the ⟨111⟩ and ⟨100⟩ directions were obtained from first-principles calculations using the generalized gradient approximation (GGA) for the exchange-correlation potential within the density functional theory framework and projector-augmented wave (PAW) potentials as implemented in the Vienna Ab-initio Simulation Package (VASP) code. In the calculations, the lattice parameter is fixed to the experimentally determined value of 5.9312 Å. The internal atomic positions are fully relaxed until the residual forces on the atoms are smaller than 0.05 eV/Å, and a 6 × 6 × 6 k-point grid was used for BZ integration. For the calculation of $\varepsilon_2$, a × 3 × 3 matrix representation of the $\varepsilon_2$ was calculated first, which is given as

$$
\varepsilon_2(\omega) = \left( \frac{4\pi^2 e^2}{\Omega} \right) \lim_{\omega \to 0} \frac{1}{\Omega^2} \sum_{\alpha,\beta} 2\omega_k \delta(\varepsilon_{\alpha,k} - \varepsilon_{\beta,k} - \omega) \times \langle u_{\alpha,k,k+\omega} u_{\beta,k,k}^* \rangle^m
$$

where $\Omega$ is the volume of the primitive cell and $\omega_k$ is the k-point weight. The variable $q$ represents the Block vector, and $\varepsilon_{\alpha(\beta)}$ is the eigenvalue of conduction (valence) band at a given k-point. The cell periodic part of the wave function is denoted as $u$. The vectors $v_{\alpha(\beta)}$ are unit vectors for the three Cartesian directions. Details of the computational method are explained in ref 34. The $\varepsilon_2$ is obtained by averaging the diagonal components. For the calculation of $\varepsilon_2$ data, a denser k-point grid of 10 × 10 × 10 was used. The $\varepsilon_1$ was consequently calculated by the K–K transformation of the $\varepsilon_2$ with a small complex shift of 0.1 eV to make the spectrum smooth for the given k-point meshes. Using the converged charge density, we also performed nonself-consistent-field (NSCF) calculations for subsets of k-points to obtain the contribution from k-points close to one of four high symmetric points of the BZ. In Figure 6, the sum of the contributions is equal to the total $\varepsilon_2$ obtained using all the k-points in the mesh. We note that the GGA functional tends to underestimate the bandgap energy of semiconducting materials, but it describes the bandgap of CH$_3$NH$_3$PbBr$_3$ quite well due to the error cancelation of “exchange-correlation” and “relativistic” effects. However, it will be desirable to use more advanced but also computationally demanding techniques such as the GW method to calculate the electronic structure and related physical properties with higher accuracy.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01699.

Spectra and tabulated data for modeled optical functions, complex refractive index $N = n + ik$, normal-incidence reflectivity $R$, and absorption coefficients $\alpha$, of CH$_3$NH$_3$PbBr$_3$ in the spectral range of 0.74 to 6.40 eV (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*Electronic mail: feelingmn@gmail.com.

Notes

The authors declare no competing financial interest.