Crystal Structure Features of CsPbBr₃ Perovskite Prepared by Mechanochemical Synthesis

Carlos A. López,* Carmen Abia, María Consuelo Alvarez-Galván, Bo-Kyung Hong, M. Victoria Martínez-Huerta, Federico Serrano-Sánchez, Felix Carrascoso, Andrés Castellanos-Gómez, M. Teresa Fernández-Díaz, and José A. Alonso*

ABSTRACT: We present a mechanochemical procedure, with solvent-free, green-chemistry credentials, to grow all-inorganic CsPbBr₃ perovskite. The crystal structure of this perovskite and its correlations with the physicochemical properties have been studied. Synchrotron X-ray diffraction (SXRD) and neutron powder diffraction (NPD) allowed us to follow the crystallographic behavior from 4 to 773 K. Unreported features like the observed negative thermal expansion of the b unit-cell parameter stem from octahedral distortions in the 4–100 K temperature range. The mechanochemical synthesis was designed to reduce the impact energy during the milling process, leading to a defect-free, well-crystallized sample characterized by a minimum unit-cell volume and octahedral tilting angles in the low-temperature orthorhombic perovskite framework, defined in the Pbnm space group. The UV–vis diffuse reflectance spectrum shows a reduced band gap of 2.22(3) eV, and the photocurrent characterization in a photodetector reveals excellent properties with potential applications of this material in optoelectronic devices.

1. INTRODUCTION

All-inorganic cesium lead halide perovskites (CsPbX₃, X = I, Br, and Cl) have attracted widespread attention because of their improved stability and balanced carrier mobility compared with their hybrid organic–inorganic counterparts. Nevertheless, the electrical and optical properties of these inorganic perovskites are strongly determined by their compositions, morphologies, and crystallographic phases.¹⁻⁴

Among them, the best candidate for photovoltaic applications is CsPbI₃, which shows a low band gap of 1.73 eV when the cubic phase is preserved. However, bulk CsPbI₃ can only maintain the cubic perovskite structure (black phase) above ≈593 K,⁵ and it transforms into an orthorhombic nonperovskite (yellow phase) material at room temperature, losing its photovoltaic property. The addition of bromide to the halide anion makes the black phase at room temperature more stable owing to the increased effective tolerance factor and a lower phase-transition temperature.¹,⁶ However, the larger electronegativity differences between the halogen and lead result in a more ionic bonding character, yielding shorter bond lengths and a larger band gap. This fact limits the short-circuit current (J_SC) of perovskite solar cells (PSCs) but has great potential in tandem and semitransparent photovoltaic applications.

CsPbBr₃ has attracted much interest because it possesses a stable crystalline structure (orthorhombic phase) at room temperature and, depending on its morphology, it can retain high carrier mobility, good optoelectronic properties, large photoluminescence quantum yield, and superior stability under humidity and thermal attacks. These properties make it suitable for applications in various optoelectronic devices such as light-emitting diodes, photovoltaic cells, photodetectors, and lasers.⁶⁻⁹,¹¹,¹²

CsPbBr₃ is usually prepared by reacting equimolar amounts of CsBr and PbBr₂ through conventional wet procedures, while it was described to be prepared through dry methods in only four works. Stoumpos et al.⁷ and Linaburg et al.¹² used solid-state reactions (milling and heating), while Posudievsky et al.¹³ and Pal et al.¹⁴ reported a mechanochemical procedure (without further heating).

In this work, CsPbBr₃ was obtained by a mechanochemical procedure in a planetary ball mill at room temperature. This synthetic process involves simplicity, swiftness, and reproducibility in line with the green chemistry credentials (e.g., solventless solid-state synthesis). The combination of a moderate mechanical energy generated under mild ball-milling conditions and the inherent chemical modification of

Received: December 11, 2019
Accepted: February 3, 2020
Published: March 10, 2020
structures/surfaces makes this methodology extremely promising for greener perovskite syntheses, yielding well-crystallized powders with excellent photovoltaic and optoelectronic properties.

2. EXPERIMENTAL SECTION

CsPbBr₃ was obtained as a microcrystalline powder from mechanosynthesis in a planetary ball mill, from stoichiometric amounts of CsBr (Strem) and PbBr₂ (Alfa Aesar) processed in an N₂ atmosphere. A total of 1.5 g of the reactants was milled using 30 zirconia balls of 5 mm diameter, with a final mass ratio of 8.6:1, for 4 h at 400 rpm in a Retsch PM100 mill. A laboratory X-ray diffraction (XRD) pattern was collected on a Bruker D5 diffractometer with Kα Cu (λ = 1.5418 Å) radiation. To study the crystallographic structure, a neutron powder diffraction (NPD) pattern at room temperature (298 K) was collected using the HRPT diffractometer of the SINQ spallation source (PSI, Paul Scherrer Institute, Villigen, Switzerland) with a wavelength of 1.494 Å. The crystal structure at lower temperatures was investigated from NPD patterns sequentially collected from 100 to 4 K in the D20 instrument (Institute Laue Langevin, Grenoble, France) with a wavelength of 1.540 Å. The sample, contained in a V cylinder, was introduced in a standard "orange" cryostat and measured at 100 K for 1 h, and then cooled down to 4 K while acquiring sequential patterns every 3 min. Finally, a good statistics pattern was collected at 4 K for 30 min. To investigate the high-temperature structural evolution, synchrotron X-ray powder diffraction (SXRD) patterns were collected at RT, 473, 673, and 773 K in the MSPD high-resolution diffractometer at the ALBA facility, Barcelona (Spain), selecting an incident beam with 38 keV energy (λ = 0.3252 Å). The high angular-resolution mode (MAD setup) was selected. The polycrystalline powder was collected in quartz capillaries of 0.7 mm diameter, which were kept rotating during the acquisition time. In both cases, the refinement of the structure was performed by the Rietveld method using the Fullprof software. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The background was interpolated between regions devoid of reflections. The following parameters were refined in the final run: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates, anisotropic displacement factors, and occupancy factors. For the neutron refinements, the coherent scattering lengths for Cs, Pb, and Br were 5.42, 9.405, and 6.795 fm, respectively. The scanning electron microscopy (SEM) images were obtained on a Hitachi instrument, model TM-1000. The optical diffuse reflectance spectrum was measured at room temperature using a UV–vis spectrophotometer Varian Cary 5000. The optoelectronic properties of the CsPbBr₃ crystals were studied by fabricating a photodetector by drop-casting a CsPbBr₃ suspension in dimethyl sulfoxide (ratio perovskite/solvent, 1:4; weight) onto a SiO₂/Si substrate with pre-patterned gold electrodes separated by 10 μm (Ossila). The photoresponse was analyzed by illuminating the device with different light-emitting diode (LED) sources with wavelengths ranging from 420 to 1050 nm (1.18–2.95 eV). The light from the LED sources was focused to form a spot (400 μm in diameter) on the sample, and the intensity was adjusted to achieve a power density of 16 mW/cm².

3. RESULTS AND DISCUSSION

3.1. Initial Characterization. CsPbBr₃ was obtained as a yellowish polycrystalline powder. The initial crystallographic identification of CsPbBr₃ was carried out using laboratory XRPD. A Le Bail refinement, illustrated in Figure 1, shows that CsPbBr₃ is pure and presents the characteristic distortion defined in the orthorhombic symmetry, space group Pbnm. The earliest crystal elucidations were made by XRD and NPD in the 1970s. Recently, several structures have been reported using laboratory and/or synchrotron X-ray diffraction data, but there are no recent measurements from NPD data.

3.2. Room-Temperature Combined Neutron and Synchrotron X-ray Diffraction Characterization. For a precise crystal structure resolution, both NPD and synchrotron SXRD were combined in a joint refinement; hence, both patterns were modeled in the mentioned Pbnm space group. The Cs⁺ and Pb²⁺ cations are located at 4c (x,y,1/4) and 4b (1/2,0,0) Wyckoff sites, while Br1 and Br2 atoms are placed in 4c (x,y,1/4) and 8d (x,y,z) sites. Figure 2 illustrates the quality of the fit for both NPD and SXRD patterns, including anisotropic refinement of the displacement factors for all the atoms. The figure also includes a view of the crystal structure, highlighting the tilting of the PbBr₆ octahedra. Table 1 lists the main crystallographic data. As it is well known, the orthorhombic Pbnm crystal structure in perovskites consists of a three-dimensional (3D) framework of corner-sharing octahedra (PbBr₆), tilted antiphase along the (100) and (010) directions of the pseudocubic cell and in-phase along the (001) direction, which correspond to a a°/b°/Glazer’s notation as derived by Woodward for a simple perovskite. The tilting angles, estimated as α = (180° – θ), where θ = (Pb–Br–Pb), are 7.43 and 11.28° for the antipath and in-phase tilts at RT, respectively. These compare well with the values of 6.8 and 11.35° found by Linaburg et al. for CsPbBr₃ at RT.

3.3. Low-Temperature Neutron Diffraction Characterization. Additional NPD patterns were measured at 100 and 4 K; besides, several patterns were sequentially collected during the cooling process. These data reveal that the orthorhombic unit cell is maintained down to 4 K. Figure 3 shows the a, b, and c unit-cell parameter variation as well as the Rietveld plot at 4 K. It is remarkable that a and c parameters decrease, whereas b increases upon cooling. This conspicuous effect of negative thermal expansion along the b-axis has not been reported before for CsPbBr₃. Normally, negative thermal expansion in Pbnm perovskites is a consequence of magneto-
restrictive effects, concomitant with magnetic ordering, for instance in rare-earth ferrites. In CsPbBr$_3$, it deserves further analysis. Table 2 lists the main crystallographic parameters from the pattern collected at 4 K. The Rietveld refinement and the crystallographic data at 100 K are displayed in Figure S1 and Table S1, respectively. The octahedral tiltings at 4 K are observed close to 4 K. Hence, other structural parameters such as the octahedral distortions that account for the expansion of the Cs−Br bonds, leading to octahedral distortions that account for the expansion of parameter $b$.

### 3.4. High-Temperature Synchrotron X-ray Diffraction Characterization

For the high-temperature analysis, an SXRD experiment was performed at selected temperatures (473, 673, and 773 K). As mentioned above, the RT pattern confirms the already described orthorhombic symmetry; however, at 473 K and above, the structure can be defined in the cubic $Pm3m$ space group. Figure 5 shows a selected angular range that illustrates this phase transition. It is important to remark that between the orthorhombic and cubic phases (RT to 473 K) a transient tetragonal ($P4_{2}2_{1}2_{1}$) phase has been previously reported,$^{7,18}$ which we could not identify.

At 473 K and above, the cubic symmetry is defined in the space group $Pm3m$. Cs atoms are placed at 1c (1/2,1/2,1/2). Wyckoff site, Pb at 1a (0,0,0), and Br at 3d (1/2,0,0). Figure 6 plots the Rietveld refinements at different temperatures, showing an excellent agreement between the observed and the calculated profiles, including an inset with a view of the cubic crystal structure above 473 K. The main crystallographic data are listed in Table 3.

The thermal evolution of the unit-cell parameters is illustrated in Figure 7 as volume/Z versus temperature. On the other hand, the comparison of the unit-cell volume with

---

**Table 1. Crystallographic Data for CsPbBr$_3$ Phase in the Orthorhombic System ($Pbnm$) from Combined NPD and SXRPD at RT$^{46}$**

|   | $x$    | $y$    | $z$    | $U_{eq}$ | occ |
|---|--------|--------|--------|----------|-----|
| Cs | 0.9927(7) | 0.9710(7) | 0.25 | 0.084(4) | 1   |
| Pb | 0.5   | 0      | 0      | 0.026(1) | 1   |
| Br1 | 0.0464(8) | 0.505(1) | 0.25 | 0.086(6) | 1   |
| Br2 | 0.7929(5) | 0.2070(5) | 0.0251(4) | 0.071(4) | 1   |

**Atomic Displacement Parameters (Å$^2$)$^{46}$**

|   | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|----------|----------|----------|----------|----------|----------|
| Cs | 0.089(3) | 0.102(4) | 0.069(3) | 0.022(4) | 0.006(6) | 0.12(3)  |
| Pb | 0.029(3) | 0.026(1) | 0.021(1) | 0.000(2) | −0.002(2) | 0.002(2) |
| Br1 | 0.122(8) | 0.114(6) | 0.021(3) | 0.016(8) | 0.017(2) | 0.009(3) |
| Br2 | 0.059(3) | 0.053(3) | 0.101(5) | −0.034(2) | −0.011(4) | 0.007(4) |

$^{46}$ $a = 8.19154(2)$ Å, $b = 8.24459(2)$ Å, $c = 11.73993(2)$ Å, and $V = 792.87(1)$ Å$^3$. NPD: $R_p = 3.69\%$, $R_{wp} = 4.62\%$, $R_{exp} = 4.29\%$, $\chi^2 = 1.16$, and $R_{w_{avg}} = 8.54\%$. SXRPD: $R_p = 8.41\%$, $R_{wp} = 10.9\%$, $R_{exp} = 9.24\%$, $\chi^2 = 1.39$, and $R_{w_{avg}} = 6.23\%$. 

---

**Figure 2.** Observed (crosses), calculated (black line), and difference (blue line) profiles after the Rietveld refinement in an orthorhombic cubic unit cell for (a) NPD and (b) SXRD. Inset: view of the crystal structure enhancing the tilting of the PbBr$_6$ octahedra and the anisotropic displacement factors.
those reported in the literature reveals significant differences, as illustrated in the inset of Figure 7. The obtained unit-cell volume is subtly lower than those of the previous reports. Additionally, a correlation with the synthesis method can be established. In general, the samples synthesized from the mechanochemical (MC) method (without heating) present a higher unit-cell volume, while those obtained from the solid-state (SS) reaction (with heating) exhibit a smaller unit-cell size. In contrast, our sample obtained by ball-milling exhibits the lowest unit-cell size, which is discussed below.

These subtle changes can be related to the defects in the crystals, since annealing at moderate temperatures may reduce the defects in the sample, producing quality crystals. Moreover, the sample obtained by Stoumpos et al.\textsuperscript{7} in sealed ampoules at 600 °C presents a smaller cell than that obtained by Linaburg et al.\textsuperscript{12} in air at 425 °C for 20 h. In this situation, the unit-cell volume is subtly lower than those of the previous reports.
size of the present sample is in the lower limit of the analyzed samples; this fact suggests that the present milling conditions yield a well-crystallized sample with a minimum number of defects. In the mechanosynthesis technique, the energy transferred to the mixture is a determining factor of the synthetic procedure. It depends on the different characteristics of the milling process, such as the balls/mixture mass ratio, grinding time, and rotation speed. These determine the crystallinity and defective nature of the perovskite structure and thus the lattice parameter and the unit-cell volume. If we compare our milling conditions, ball:mixture mass ratio, milling time, and rpm (8.6:1 mass ratio, 30 balls of 5 mm diameter, for 4 h at 400 rpm) with those described by Posudievsky et al., the latter are by far more energetic than those used in the present work, thus leading to a more defective material. Moreover, this can be quantified by estimating the ball-impact energy ($\Delta E_b$) and weight-normalized cumulative kinetic energy ($E_{\text{cum}}$). For the conditions of the present work, the estimated $\Delta E_b$ and $E_{\text{cum}}$ are 4.1 mJ/impact and 149 kJ/g, respectively. However, for Posudievsky et al., $\Delta E_b$ and $E_{\text{cum}}$ are 20.4 mJ/impact and 826 kJ/g, respectively. The kinetic energy given to the sample per impact is approximately 5 times smaller in the present synthesis; hence, it is possible to infer that such moderate conditions for long times yield a better-crystallized, more defect-free sample. We have prepared, therefore, CsPbBr$_3$ perovskite in mild milling conditions, beyond those typically used in literature.

### 3.5. Microstructure by Scanning Electron Microscopy (SEM)

Figure 8 illustrates some typical views of the as-prepared CsPbBr$_3$ polycrystals. From a mechanosynthesis process, involving the collision of high-energy ZrO$_2$ balls with the specimens, one would expect a highly disaggregated product formed of small particles. However, surprisingly, we can observe a heterogeneous picture where quite large particles (10$^{-20}$ μm) are mixed up with smaller fragments of undefined shapes (Figure 8a). However, in a larger magnification picture (Figure 8b), it is evident that each particle is indeed formed by an agglomeration of much smaller grains of typically 0.5−1 μm diameter.
μm. We assume that these individual grains are monocrystalline, providing a sufficiently large diffraction domain that accounts for the good crystallinity of the sample versus neutron and X-ray synchrotron diffraction techniques. Altogether, this scenario illustrates that the growth of microcrystals is not perturbed by the dynamical motion of the reactants and ZrO2 balls after 4 h of reaction. This morphological evidence is in agreement with that previously deduced from the synthesis conditions in terms of ∆E_b and E_cum energies.

3.6. UV–vis–NIR Spectra. The absorption ability of CsPbBr3 powder was determined by diffuse reflectance UV–vis spectroscopy. Figure 9 depicts the optical absorption coefficient related to the Kubelka–Munk function \( F(R) = \alpha = (1 - R)^{2/3} \), \( R \) is the reflectance) versus the wavelength in electronvolts. The band gap was calculated by extrapolating the linear region to the abscissa. The value obtained for CsPbBr3 (∼2.22(3) eV) is in agreement with data reported in the literature for its band gap at room temperature.6,8,9 Moreover, there is a subtle reduction with respect to the value of 2.27 eV given by Linaburg et al.12 for a sample prepared by solid-state reactions, which is convenient for use in solar cells.

3.7. Optoelectronic Characterization. Figure 10a shows the time evolution of the current flowing through the device (with a bias voltage of 1 V applied between electrodes), while the illumination is switched on and off. This measurement allows one to determine the photocurrent (subtracting the current in the dark to the current upon illumination), as well as the response time of the photodetector device. By employing a wavelength of 420 nm, we obtain a photocurrent of 90 nA with response times of 170 and 90 ms for the rise and decay processes, respectively. In addition, a sizeable overshoot can be clearly seen in this figure, which has already been observed for these materials and has been attributed to a sudden generation of photogenerated charge carriers followed by a slow photocurrent decay toward a steady state when the equilibrium between the charge diffusion rate and its generation rate is achieved.22–24

Figure 8. SEM images of CsPbBr3 samples at 2500× (a) and 7000× (b) magnifications.

Figure 9. Kubelka–Munk (KM) transformed diffuse reflectance spectrum of CsPbBr3. The inset shows an expanded zone of the absorption edge.

Figure 10. (a) Time evolution of the current flowing through the photodetector (bias of 1 V) under alternating dark and light illumination with different wavelengths (power density of 16 mW/cm²). (b) Responsivity of the device as a function of the LED wavelength (bias of 1 V and power density of 16 mW/cm²). The inset shows the device investigated.
To determine the spectral response of our device, we extract the responsivity at different illumination wavelengths. The responsivity is a figure of merit that allows for a direct comparison between different photodetectors. This value is defined as \( R = I_{ph}/P \), where \( I_{ph} \) is the photocurrent and \( P \) the effective power, which is given by \( P = P_{\text{light}}A_{\text{dev}}/A_{\text{pot}} \) where \( P_{\text{light}} \) is the LED power, \( A_{\text{dev}} \) is the area of the material covering the channel of the device and \( A_{\text{pot}} \) is the area of the spot.

Figure 10b exhibits the responsivity as a function of the illumination wavelength. The responsivity increases at shorter wavelengths, reaching a value of 3 A/W at 420 nm, which is higher than that reported, under similar illumination and biasing conditions, for other perovskites like CsPbCl\(_3\) (less than 0.5 A/W) or CsPbI\(_3\) (less than 0.4 A/W).\(^{25,26}\) For CsPbBr\(_3\) photodetectors in the literature, the reported responsivity ranges from \( \sim 0.005 \) to \( \sim 10 \) A/W\(^{27}\) and thus our device is in the upper bound of this range.

4. CONCLUSIONS

We have obtained a well-crystallized CsPbBr\(_3\) perovskite from a mechanochemical method under mild milling conditions. The unit-cell parameters at RT were smaller than those described for samples synthesized by ball milling, but they were similar to those of the specimens previously obtained from conventional solid-state reaction methods. The crystallographic features were analyzed from synchrotron X-ray and neutron powder diffraction in the 4–773 K temperature range. At RT, an orthorhombic superstructure of perovskite, defined in the \( Pbnm \) space group, is observed, which becomes cubic \( Pm\overline{3}m \) above 473 K, in agreement with previous reports. At lower temperatures, the phase remains orthorhombic down to 4 K, and the collapse of the unit cell upon cooling is related to the progressive octahedral tilting; below 8 K, the structure distortion seems to reach a limit in the octahedral rotation. Finally, the optoelectronic properties of our CsPbBr\(_3\) specimen, implemented in a photodetector device, demonstrate a high and selective responsivity of 3 A/W at shorter wavelengths, improving the reported responsivity ranges.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04248.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04248.

AUTHOR INFORMATION

Corresponding Authors
Carlos A. López — Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain; INTEQUIL, (UNSL-CONICET) and Facultad de Química, Bioquímica y Farmacia, UNSL, 5700 San Luis, Argentina; Email: calopez@unsl.edu.ar
José A. Alonso — Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain; orcid.org/0000-0001-5329-1225; Email: ja.alonso@icmm.csic.es

Authors
Carmen Abia — Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain; Institut Laue Langevin, 38042 Grenoble Cedex, France

Maria Consuelo Alvarez-Galván — Instituto de Catálisis y Petrólequímica, CSIC, 28049 Madrid, Spain
Bo-Kyung Hong — Instituto de Ciencia de Materiales de Madrid and Instituto de Catálisis y Petrólequímica, CSIC, 28049 Madrid, Spain
M. Victoria Martínez-Huerta — Instituto de Catálisis y Petrólequímica, CSIC, 28049 Madrid, Spain
Federico Serrano-Sánchez — Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain
Felix Carrascoso — Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain
Andrés Castellanos-Gómez — Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain
M. Teresa Fernández-Díaz — Institut Laue Langevin, 38042 Grenoble Cedex, France

Complete contact information is available at:
https://pubs.acs.org/doi/10.1021/acsomega.9b04248

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support given by the Spanish Ministry of Economy and Competitiveness (ENE2014-21588-C2-1-R project and MAT2017-84496-R) co-founded by FEDER. C.A.L. acknowledges ANPCyT and UNSL for financial support (Projects PICT2017-1842 and PROICO 2-2016), Argentina.

REFERENCES

(1) Deng, J.; Li, J.; Yang, Z.; Wang, M. All-Inorganic Lead Halide Perovskites: A Promising Choice for Photovoltaics and Detectors. J. Mater. Chem. C 2019, 7, 12415–12440.
(2) Gao, Y.; Wu, Y.; Lu, H.; Chen, C.; Liu, Y.; Bai, X.; Yang, L.; Yu, W. W.; Dai, Q.; Zhang, Y. CsPbBr\(_3\) Perovskite Nanoparticles as Additive for Environmentally Stable Perovskite Solar Cells with 20.46% Efficiency. Nano Energy 2019, 59, S17–S26.
(3) Liang, J.; Wang, C.; Wang, Y.; Xu, Z.; Lu, Z.; Ma, Y.; Zhu, H.; Hu, Y.; Xiao, C.; Yi, X.; et al. All-Inorganic Perovskite Solar Cells. J. Am. Chem. Soc. 2016, 138, 15829–15832.
(4) Liang, J.; Han, X.; Yang, J.; Zhang, B.; Fang, Q.; Zhang, J.; Ai, Q.; Ogle, M. M.; Terlilier, T.; Martí, A. A.; et al. Defect-Engineering-Enabled High-Efficiency All-Inorganic Perovskite Solar Cells. Adv. Mater. 2019, 31, No. 1903448.
(5) Dasid, S.; Hawley, C. J.; Dillon, A. D.; Gutierrez-Perez, A. D.; Spanier, J. E.; Fafarman, A. T. Quantitative Phase-Change Thermodynamics and Metastability of Perovskite-Phase Cesium Lead Iodide. J. Phys. Chem. Lett. 2017, 8, 1278–1282.
(6) Sutton, R. J.; Eperon, G. E.; Miranda, L.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.; Hörnert, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; et al. Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. Adv. Energy Mater. 2016, 6, No. 1502458.
(7) Stoumpos, C. C.; Mallikas, C. D.; Peters, J. A.; Liu, Z.; Sebastian, M.; Im, J.; Chasapis, T. C.; Wibowo, A. C.; Chung, D. Y.; Freeman, A. J.; et al. Crystal Growth of the Perovskite Semiconductor CsPbBr\(_3\): A New Material for High-Energy Radiation Detection. Cryst. Growth Des. 2013, 13, 2722–2727.
(8) Li, X.; Tan, Y.; Lai, H.; Li, S.; Chen, Y.; Li, S.; Xu, P.; Yang, J. All-Inorganic CsPbBr\(_3\) Perovskite Solar Cells with 10.45% Efficiency by Evaporation-Assisted Deposition and Setting Intermediate Energy Levels. ACS Appl. Mater. Interfaces 2019, 11, 29746–29752.
(9) Zhang, H.; Liu, X.; Dong, J.; Yu, H.; Zhou, C.; Zhang, B.; Xu, Y.; Jie, W. Centimeter-Sized Inorganic Lead Halide Perovskite CsPbBr\(_3\)
Crystals Grown by an Improved Solution Method. Cryst. Growth Des. 2017, 17, 6426–6431.

(10) Dirin, D. N.; Cherniukh, I.; Yakunin, S.; Shynkarenko, Y.; Kovalenko, M. V. Solution-Grown CsPbBr3 Perovskite Single Crystals for Photon Detection. Chem. Mater. 2016, 28, 8470–8474.

(11) Ramasamy, P.; Lim, D. H.; Kim, B.; Lee, S. H.; Lee, M. S.; Lee, J. S. All-Inorganic CsPbBr3 Lead Halide Perovskite Nanocrystals for Photodetector Applications. Chem. Commun. 2016, 52, 2067–2070.

(12) Limburg, M. R.; McClure, E. T.; Majher, J. D.; Woodward, P. M. Cs1−xRbxPbCl3 and Cs1−xRbxPbBr3 Solid Solutions: Understanding Octahedral Tilting in Lead Halide Perovskites. Chem. Mater. 2017, 29, 3507–3514.

(13) Posudievsky, O. Y.; Konoshchuk, N. V.; Karbivskyy, V. L.; Boiko, O. P.; Koshechko, V. G.; Pokhodenko, V. D. Structural and Spectral Characteristics of Mechanochemically Prepared CsPbBr3. Theor. Exp. Chem. 2017, 53, 235–243.

(14) Pal, P.; Saha, S.; Banik, A.; Sarkar, A.; Biswas, K. All-Solid-State Mechanochemical Synthesis and Post-Synthetic Transformation of Inorganic Perovskite-Type Halides. Chem. – Eur. J. 2018, 24, 1811–1815.

(15) Fauth, F.; Boer, R.; Gil-Ortiz, F.; Popescu, C.; Vallcorba, O.; Peral, I.; Fullà, D.; Benach, J.; Juanhuix, J. The Crystallography Stations at the Alba Synchrotron. Eur. Phys. J. Plus 2015, 130, No. 160.

(16) Rietveld, H. M. A Profile Refinement Method for Nuclear and Magnetic Structures. J. Appl. Crystallogr. 1969, 2, 65–71.

(17) Rodríguez-Carvajal, J. Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction. Phys. B: Condens. Matter 1993, 192, 55–69.

(18) Hirotsu, S.; Harada, J.; Izumi, M.; Gesi, K. Structural Phase Transitions in CsPbBr3. J. Phys. Soc. Jpn. 1974, 37, 1393–1398.

(19) Liu, F.; Wang, F.; Hansen, K. R.; Zhu, X.-Y. Bimodal Bandgaps in Mixed Cesium Methylammonium Lead Bromide Perovskite Single Crystals. J. Phys. Chem. C 2019, 123, 14865–14870.

(20) Glazer, A. M. The Classification of Tilted Octahedra in Perovskites. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1972, 28, 3384–3392.

(21) Woodward, P. M. Octahedral Tilting in Perovskites. I. Geometrical Considerations. Acta Crystallogr., Sect. B: Struct. Sci. 1997, 53, 32–43.

(22) Ding, J.; Du, S.; Zuo, Z.; Zhao, Y.; Cui, H.; Zhan, X. High Detectivity and Rapid Response in Perovskite CsPbBr3 Single-Crystal Photodetector. J. Phys. Chem. C 2017, 121, 4917–4923.

(23) Liu, D.; Hu, Z.; Hu, W.; Wangyang, P.; Yu, K.; Wen, M.; Zuo, Z.; Liu, J.; Wang, M.; Chen, W.; et al. Two-Step Method for Preparing All-Inorganic CsPbBr3 Perovskite Film and Its Photoelectric Detection Application. Mater. Lett. 2017, 186, 243–246.

(24) Cha, J. H.; Han, J. H.; Yin, W.; Park, C.; Park, Y.; Ahn, T. K.; Cho, J. H.; Jung, D. Y. Photosresponse of CsPbBr3 and CsPbBr6 Perovskite Single Crystals. J. Phys. Chem. Lett. 2017, 8, 565–570.

(25) Zhang, J.; Wang, Q.; Zhang, X.; Jiang, J.; Gao, Z.; Jin, Z.; Liu, S. High-Performance Transparent Ultraviolet Photodetectors Based on Inorganic Perovskite CsPbCl3 Nanocrystals. RSC Adv. 2017, 7, 36722–36727.

(26) Zhou, Y.; Luo, J.; Zhao, Y.; Ge, C.; Wang, C.; Gao, L.; Zhang, C.; Hu, M.; Niu, G.; Tang, J. Flexible Linearly Polarized Photodetectors Based on All-Inorganic Perovskite CsPbI3 Nanowires. Adv. Opt. Mater. 2018, 6, No. 1800679.

(27) Liu, X.; Yu, D.; Cao, F.; Li, X.; Ji, J.; Chen, J.; Song, X.; Zeng, H. Low-Voltage Photodetectors with High Responsivity Based on Solution-Processed Micrometer-Scale All-Inorganic Perovskite Nanoplatelets. Small 2017, 13, No. 1700364.