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Lead-free double-halide perovskite Cs_3BiBr_6 with well-defined crystal structure and high thermal stability for optoelectronics†

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Halide perovskites have continued to rise as attractive light absorber materials, mainly driven by their potential wide applications in the fields of solar cells, photodetectors, lasers and others. However, the Pb-containing perovskites are posing with serious potential damages to our environment. Thus, there is a strong desire to develop lead-free perovskites as environmentally friendly alternatives. Here, we have shown a successful synthesis of a non-toxic single crystalline perovskite, Cs_3BiBr_6 , and analyzed its structural characteristics for the first time. This perovskite represents a new structure in terms of double-halide perovskites. The crystal structure is featured by an isolated BiBr_6 polyhedra to form a zero-dimensional halide perovskite. The bandgap of this compound is measured to be 2.55 eV. High stability against thermal is also clearly shown in Cs_3BiBr_6 single crystal. Photodetector based on this compound is fabricated and tested, which exhibits a detectivity of 0.8×10^9 Jones and low dark current (0.03 nA) under the 400 nm light illumination. This has demonstrated its potential for applications in optoelectronic devices. Overall, our results show that Cs_3BiBr_6 perovskite as a lead-free perovskite has interesting structures and promising properties for optoelectronic devices.

Introduction

Halide perovskites have been at the forefront of new-emerging energy materials, due to their great potential in design and fabrication of new-generation optoelectronic devices, such as solar cells,¹ photodetectors,²⁻⁵ light-emitting devices,^{6,7} field-effect transistors^{8,9} and lasers.^{10,11} Power conversion efficiency (PCE) of ABX_3 (A = monovalent cation, B = divalent metal, X = halides)-based solar cells has largely increased from 3.8% to 22.6%, which aims towards 30 % in the future.¹²⁻¹⁶ Although they possess unique photo-physical properties such as tunable wavelength, high photoluminescence quantum yield (PLQY), large carrier diffusion length and long carrier lifetime *etc on.*, the current most efficient materials are Pb-containing perovskites. Pb is detrimental to the environment and human body, however, which might cause memory problems and intellectual disability. Therefore, there is a strong desire to replace toxic Pb by a benign element such as Sn, Ge, and Bi *etc.* without drastically reducing the conversion efficiency. However, due to the high-energy-lying of 5s orbitals of Sn^{2+} , its

oxidation into Sn^{4+} would undoubtedly leads to performance reduction drastically.¹⁷⁻¹⁹ As to Ge-based perovskites, the poor

performance makes them lag far behind the other two alternatives.²⁰⁻²²

Among the various alternatives, Bi-based halide perovskites have displayed rapid development. The recently emerged double perovskites, $\text{A}_2\text{BB}'\text{X}_6$, in which B is a monovalent metal and B' is a trivalent metal, have demonstrated to be stable and environmentally friendly. Visible to near-infrared absorption of Cs_2SnI_6 nanocrystals exhibited high mobility after being fabricated into field-effect transistors.²³ Solar cells based on $\text{Cs}_2\text{AgBiBr}_6$ thin films shows a PEC of 2.5 %, which represents the highest efficiency among non-lead perovskites.²⁴ Especially to the double perovskite single crystal, a detectable dose rate in $\text{Cs}_2\text{AgBiBr}_6$ single crystal, $59.7 \text{ nGy}_{\text{air}}\text{S}^{-1}$, was reported to be as low as $\text{CH}_3\text{NH}_3\text{PbBr}_3$ arisen from the suppressed ion migration.²⁵

Except for $\text{A}_2\text{BB}'\text{X}_6$, the development of the series of $\text{A}_3\text{B}_2\text{X}_9$ materials are on par with them. Blue $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{Br}_9$ quantum dots with a high PLQY of 12% were successfully synthesized.²⁶ For the all-inorganic counterparts, a PLQY of 19.4 % was realized in $\text{Cs}_3\text{Bi}_2\text{Br}_9$, exhibiting quite good photostability and moisture stability as well.²⁷ In contrast to the fast development in the optical, electronic and optoelectronic properties of Bi-based perovskites, study on their structures is still in its infancy. For the isostructural compounds, the research mainly relies on the powder X-ray diffraction (XRD) data with comparison to the known phase to refine the atomic

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parameters, where large quantities of simulation and calculation are required. This undoubtedly will give rise to the complexity and inconvenience for researchers. For the unknown phase, for example, researchers have chosen to verify the Cs_3BiBr_6 phase by excluding the solely known phase of $\text{Cs}_3\text{Bi}_2\text{Br}_9$ in the system of Cs-Bi-Br, which is an adventurous and controversial method and needs to be further verified.²⁸ This is because there have also other known chemical formula in this system, such as AB_3X_{10} ,²⁹ ABX_5 ,³⁰ AB_2X_7 .³¹ This might also lead to the loss of the desired materials due to the mismatch with the current database.

In this work, we demonstrate the synthesis and structural analysis of the single crystal of Cs_3BiBr_6 for the first time, which crystallizes in the form of the isolated BiBr_6 octahedra within a three-dimensional (3D) framework. Photodetector based on this perovskite was fabricated, displaying high detectivity of around 0.8×10^9 Jones under ambient conditions. This material has thus successfully substituted Pb^{2+} by Bi^{3+} in the perovskites and could push the toxic issue forward a positive direction. Moreover, it enriches the structural family of non-lead perovskites as well as holds the potential for optoelectronic applications.

Experimental Section

Chemicals

All chemical reagents were at least of analytical grade and used as received without further purification. Bismuth bromide (BiBr_3 , 99%), Cesium bromide (CsBr , 99.9%), Hydrobromic acid (HBr , 48%), N,N-Dimethylformamide (DMF, 99.8%) were all purchased from Sigma-Aldrich.

Synthesis and Crystal Growth of Cs_3BiBr_6

In a typical batch synthesis, BiBr_3 (0.0894g, 0.2 mmol), CsBr (0.1038g, 0.49 mmol) and HBr (2.5 mL) were mixed in a beaker, which was then transferred into an oven at 110 °C for 2 h. Finally, light yellow crystals were obtained. During the synthesis of the single crystal, if the amount of CsBr was much lower than the BiBr_3 , $\text{Cs}_3\text{Bi}_2\text{Br}_9$ was obtained. Therefore, controlling the ratio between the two raw materials is a key factor to obtain the single crystals of Cs_3BiBr_6 .

X-ray Crystallographic Studies

The small crystals of Cs_3BiBr_6 ($\sim 0.1 \text{ mm} \times 0.1 \text{ mm} \times 0.05 \text{ mm}$) were selected and mounted on glassy fibers for single-crystal XRD measurements. Data collections were performed on a Bruker APEX-II CCD diffractometer equipped with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by a multi-scan method.³² The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97.³³ All non-H atoms were refined with anisotropic thermal parameters. The final refined structural parameters were checked by the PLATON program.³⁴ Crystallographic data and structural refinements are summarized in Table S1 in Electronic Supplementary Information (ESI). The final refined atomic

positions and structural parameters are further provided in ESI (Tables S2–S4). Rietveld refinement of the powder XRD was performed by the Fullprof program.

Material characterization

X-ray photodetection spectroscopy (XPS) (Thermo Scientific) was performed to analyze the compositions of samples, with Al- $\text{K}\alpha$ (1486 eV) as the excitation X-ray source. The pressure of the analysis chamber was maintained at 2×10^{-10} mbar during measurements. All characterizations were carried out at room temperature. Scanning electron Microscope (SEM) and Energy dispersive X-ray spectroscopy (EDX) characterizations were carried out on an FEI Quanta FEG 200 ESEM. The absorption behaviours of the samples were studied by the UV-vis spectrometer from Agilent Technologies (Santa Clara, USA). Absorption (α/S) data was converted from diffuse reflectance spectra using the Kubelka–Munk function, $\alpha/S = (1 - R)^2/2R$, where R is the reflectance coefficient and α , S are the absorption and scattering coefficient.³⁵ All the photoelectrochemical characterizations were performed on the Autolab workstation. The phases and purities of all samples were also characterized by powder XRD with Cu $\text{K}\alpha 1$ ($\lambda = 1.5406 \text{ \AA}$) radiation. Thermogravimetric analysis (TGA) was performed in the Mettler Toledo, Star^E System (Columbus, OH, USA) with a GC 100 gas controller in a nitrogen atmosphere at a heating rate of 10 °C/min. It should be noted that all the measurements were performed.

Fabrication of Photodetectors

Prototype optoelectronic devices were prepared in-house. ITO electrodes were prepared by the ultrasonic cleaning in acetone, ethanol, and Milli-Q water successfully. Cs_3BiBr_6 single crystals were dissolved into DMF and then a certain amount of solution was deposited on the device surface by drop-casting, followed by annealing at 100 °C. The working area was 0.004 cm^2 .

Fig. 1 View of structural characteristics for Cs_3BiBr_6 . Bromide-coordination environment for (a) Bi1 and (b) Bi2. (c) 3D framework on the bc plane. Color codes: Cs, green; Bi, purple; Br, brown.

Fig. 2 Chemical and structural relationship among a series of perovskites.

Results and discussion

X-ray analysis indicates clearly that the compound of Cs_3BiBr_6 crystallizes in the orthorhombic system of space group $Pbcm$ with $a = 8.689(2)$ Å, $b = 13.628(1)$ Å, $c = 27.694(9)$ Å (Table S1). There are two Bi atoms, three Cs atoms, and seven Br atoms in an asymmetric unit. Two independent Bi atoms are located at their Wyckoff position of $4c$ and $4d$, respectively. As shown in Fig. 1a and 1b, each Bi atom is coordinated by six Br atoms, forming BiBr_6 octahedra. All of the BiBr_6 octahedra are distorted, as illustrated in the bond lengths and angles in Table S3. The 3D framework of Cs_3BiBr_6 is displayed in Fig. 1c, where all BiBr_6 octahedra are isolated from each other forming 0D perovskite structure. Cs^+ cations filled up the spaces left by the unconnected BiBr_6 octahedra. In particular, Bi1 locates at the mirror plane while Bi1 and Cs3 form a pseudo-triangular tunnel, which are filled up by Cs2 atoms (Fig. S1a). In contrast, Bi1, Bi2 and Cs3 form a square tunnel, where Cs1 atoms are located forming a traditional ABX_3 structure. In order to better understand the structural characteristics of this compound, a relationship among Cs_3BiBr_6 , CsPbBr_3 ,³⁶ $\text{Cs}_2\text{AgBiBr}_6$ and Cs_4PbBr_6 ,³⁷ are discussed, as displayed in Fig. 2. It is known that if one Pb atom is substituted by Ag and the neighbored one is substituted by Bi in CsPbBr_3 , the perovskite $\text{Cs}_2\text{AgBiBr}_6$ forms, where all BiBr_6 are separated by Cs^+ and Ag^+ . This comparison has been generally used to illustrate the relationship between CsPbBr_3 and $\text{Cs}_2\text{AgBiBr}_6$. Despite this, there is a clear statement for the relationship between Cs_3BiBr_6 and $\text{Cs}_2\text{AgBiBr}_6$, where Ag in $\text{Cs}_2\text{AgBiBr}_6$ is substituted by Cs3 atom in Cs_3BiBr_6 . At the same time, the difference comes, which is that after the incorporation of Cs3, the crystallographic symmetry of Cs_3BiBr_6 is lower than that in $\text{Cs}_2\text{AgBiBr}_6$, leading to a distinct structural characteristics in Cs_3BiBr_6 . Meanwhile, we could also clearly observe the

similarity of Cs_3BiBr_6 with that of Cs_4PbBr_6 , where one monovalent Cs^+ and one divalent Pb^{2+} are simultaneously substituted by a trivalent Bi atom. Both structures are a characteristic of isolated MX_6 octahedra, although crystallized in different crystal system. Even compared to its

Fig. 3 (a) Rietveld refinement of the experimental powder XRD pattern of Cs_3BiBr_6 and calculated XRD patterns from single crystal. XPS spectra: (b) survey spectrum; (c) Cs 3d; (d) Bi 4f; (e) Br 3d. (f) Electron micrograph of the microstructure for single crystal Cs_3BiBr_6 . (g-i) EDX mapping of the element distribution: (g) Br, (h) Cs, (i) Bi.

isomers of Cs_3BiCl_6 and Rb_3BiBr_6 (Table S5),³⁸⁻⁴⁰ different crystallographic systems and structures are exhibited. It further reminds us that much more attention is needed for the phase check of a new material if using the known phase as a reference (Fig. S2).

The purity of samples was confirmed by powder X-ray diffraction (Fig. 3a). The dominant diffraction peaks of $2\theta = 13.66^\circ$, 20.09° , 22.06° , 29.19° , 30.08° , 32.22° , 39.08° , 44.98° , 56.43° , could be identified to be the crystal planes of (112),

Fig. 4 Absorption spectrum of Cs_3BiBr_6 . Inset: the Tauc plot showing the bandgap of ca. 2.55 eV.

Fig. 5 (a) Schematic view of the photodetector based on Cs_3BiBr_6 . Periodic photoresponse behavior of Cs_3BiBr_6 under power density of 400 nm wavelength. (b) Photocurrent under various voltages with light density of 25 mW/cm². (c) Photocurrent under various of light intensity and bias of 6 V. (d) I-V characteristics under different power density. (e) Responsivity. (f) Detectivity.

(115), (130), (044) (233), (312), (334), (329) and (367), respectively. Furthermore, we used the Fullprof software to check the purity in detail. The Rietveld refinement results show the good agreement between observed (cross) and fitted (solid lines) diffraction patterns with the resulting χ^2 of 4.40. This consistence between the experimental and simulated XRD patterns confirms the phase purity of the resulting material. Meanwhile, we further confirmed the valence state and element distribution by the XPS measurements (Fig. 3b-3e). From the XPS results, we could observe the signals of Cs ($3d_{5/2}$, $3d_{3/2}$, separated spin-orbitals components $\Delta = 14.02$ eV), Bi ($4f_{7/2}$, $4f_{5/2}$, $\Delta = 5.26$ eV) and Br ($3d_{5/2}$, $3d_{3/2}$, $\Delta = 1.10$ eV), which indicates their valence (+1, +3, -1, respectively) to be consistent with the formula and confirms the existence of all elements in this material (Fig. 3c, 2d, 2e). Besides, the morphology of the as-synthesized single crystal was measured by SEM, where a smooth surface was observed on the single crystal (Fig. 3f). Elemental composition was mapped by Energy dispersive X-ray (EDX) to study the elemental distribution, Fig. 3g-3i. All elements of Cs, Bi, and Br were observed and distributed uniformly on the surface of the single crystal.

To analyze the optical properties of Cs_3BiBr_6 , the UV-vis absorption spectrum was measured. Cs_3BiBr_6 displays an absorption edge at about 485 nm, and the bandgap of the compound is calculated to be 2.55 eV according to the Tauc plot (the inset of Fig. 4). As to the thermal stability, the samples of Cs_3BiBr_6 single crystals are heated under a nitrogen

atmosphere, as shown in the TGA curve in Fig. S3. It can be observed that Cs_3BiBr_6 is stable with increasing temperature up to 425 °C, while the onset of weight loss is observed.^{41,42} As a comparison, the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ was also investigated. For $\text{CH}_3\text{NH}_3\text{PbBr}_3$, the loss in the weight of the sample starts from 285 °C, while a plateau is seen in the temperature range of 420–455 °C. This step was attributed to the loss of $\text{CH}_3\text{NH}_3\text{Br}$. Furthermore, a rapid drop in the weight loss curve is clearly seen above 455 °C, indicating further decomposition of the system. This indicates a higher thermal stability of Cs_3BiBr_6 than in the $\text{CH}_3\text{NH}_3\text{PbBr}_3$.

In order to check the optoelectronic property of the Cs_3BiBr_6 , a photodetector was fabricated on ITO electrodes as illustrated in Fig. 5a. The morphology of the film was examined as displayed in Fig. S4. Fig. 5b shows the I – V characteristics under dark and light illumination at different power density. Obviously, the photocurrent increases with the increase of the light density and voltage. Under 6V bias, ultralow dark current of 0.03 nA was obtained. Fig. 5c shows the dynamic current-time (i-t) curves for the Cs_3BiBr_6 based photodetectors under repeating switching of 400 nm monochromatic illumination with a light density of 25 mW/cm². The amperometric i-t curves demonstrate that the device can repeatedly produce stable photocurrent signals in response to periodical light ON and OFF. Upon illumination, the photocurrent increases to 70 nA/cm² by increasing the voltage up to 8 V. Besides, the photoresponse of the detector versus light power density was

also measured, as shown in Fig. 5d. With the increase of the power density, the photocurrent also increases, reaching to 50 nA/cm² under the light density of 25 mW/cm² at the voltage of 6V. The above results from i-t curves are consistent with our conclusions from the I-V curves. Hereafter, we focus on the investigation of responsivity and detectivity of the photodetector. Fig. 5e and 5f show the responsivity and detectivity of the photodetector versus voltage and light density, respectively. The responsivity (*R*) which can be understood as electrical output per optical input, is calculated by the following equation:⁴³

$$R = (I_{PC} - I_{dark}) / (P_{irra} \cdot S) \quad (1)$$

where *I_{PC}* and *I_{dark}* are currents measured with and without illumination, respectively. *P_{irra}* is the irradiation power density and *S* is the effective working area of the detector. Detectivity (*D**) as a figure merit of evaluating the ability to detect weak light can be calculated using equation (2).

$$D^* = R / (2e \cdot I_{dark})^{1/2} \quad (2)$$

At the voltage of 6 V, the responsivity of this material can reach 25 μA/W at a light density of 4 mW/cm². And their detectivity is calculated to be of around 0.8*10⁹ Jones. External quantum efficiency (EQE) is calculated to be 0.008 % under voltage of 6V and power density of 4 mW/cm² according to the equation of $EQE = R \cdot hc / (e\lambda)$ (Fig. S5). After exposing to 400 nm light illumination, the rise and decay time of the device was extracted to be 50 ms and 60 ms, respectively (Fig. S6). Meanwhile, we also checked the photodetection ability of this material toward white light, as shown in Fig. S7. It is clear that the device behaves similarly with that in 400 nm light, despite a weak responsivity was observed. At a 6 V bias, the responsivity towards white light was only 0.2 μA/W, much lower than that in 400 nm wavelength light.

Conclusions

In summary, we have successfully synthesized a non-toxic single crystal of perovskite, Cs₃BiBr₆. And it is the first time to analyse its crystallography structure, which features as an isolated BiBr₆ polyhedra. Photodetector based on this perovskite is fabricated, exhibiting a good detectivity of 0.8*10⁹ Jones under the 400 nm light illumination, demonstrating the potential for application into optoelectronic devices. Besides, this material displays high stability against thermal and moisture. Finally, this work affords an example of the utilization of non-toxic perovskites for the photodetection. It further facilitates the development of lead-free perovskites toward environment friendly energy conversion devices.

Conflicts of interest

There are no conflicts to declare.

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TOC

Synopsis: A lead-free double halide perovskite with well-defined structure and high thermal stability was synthesized, providing a new candidate material for fabricating non-toxic optoelectronic devices.