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Tang, Yingying; Liang, Mingli; Chang, Bingdong; Sun, Hongyu; Zheng, Kaibo; Pullerits, Tõnu; Chi, Qijin

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Lead-free double-halide perovskite Cs₂BiBr₆ with well-defined crystal structure and high thermal stability for optoelectronics†

Yingying Tang, Mingli Liang, Bingdong Chang, Hongyu Sun, Kaibo Zheng, Tönu Pullerits, Qijin Chi

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, Cs₂BiBr₆, 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 BiBr₆ 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 Cs₂BiBr₆ single crystal. Photodetector based on this compound is fabricated and tested, which exhibits an detectivity of 0.8×10⁹ 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 Cs₂BiBr₆ 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,²⁻⁶ light-emitting devices,⁶⁻¹¹ field-effect transistors¹²⁻¹³ and lasers.¹⁰⁻¹¹ Power conversion efficiency (PCE) of ABX₃ (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 orbital of Sn⁷⁻¹⁰, its oxidation into Sn⁴⁺ 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.¹⁹⁻²²

Among the various alternatives, Bi-based halide perovskites have displayed rapid development. The recently emerged double perovskites, A₂BB’Xₙ, 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 Cs₂SnI₆ nanocrystals exhibited high mobility after being fabricated into field-effect transistors.¹¹ Solar cells based on Cs₂AgBiBr₆ thin films shows a PEC of 2.5 %, which represents the highest efficiency among non-lead perovskites.²³ Especially to the double perovskite single crystal, a detectable dose rate in Cs₂AgBiBr₆ single crystal, 59.7 nGyₚmS⁻¹, was reported to be as low as CH₂NH₃PbBr₃ arisen from the suppressed ion migration.²⁵

Except for A₂BB’Xₙ, the development of the series of A₃B,Xₙ materials are on par with them. Blue (CH₃NH₃)₂Bi₂Br₉ 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 Cs₂Bi₂Br₉, 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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Department of Chemistry, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark
DTU Danchip, Technical University of Denmark, 2800 Kongens Lyngby, Denmark
Department of Micro- and Nanotechnology, Technical University of Denmark, 2800 Kongens Lyngby, Denmark
Department of Chemical Physics and NanoLund, Lund University, Box 124, 22100, Lund, Sweden

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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$_2$BiBr$_6$ phase by excluding the solely known phase of Cs$_3$Bi$_2$Br$_5$ 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$_3$X$_{10}$,\(^{29}\) ABX$_3$,\(^{30}\) AB$_2$X$_7$.\(^{31}\) 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$_2$BiBr$_6$ 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$\times$10$^7$ 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$_2$BiBr$_6$**

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$_3$, Cs$_3$Bi$_2$Br$_5$ was obtained. Therefore, controlling the ratio between the two raw materials is a key factor to obtain the single crystals of Cs$_2$BiBr$_6$.

**X-ray Crystallographic Studies**

The small crystals of Cs$_2$BiBr$_6$ (~0.1 mm × 0.1 mm × 0.05 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 Kα radiation (λ = 0.71073 Å) 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-Kα (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, α/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 Ka1 (λ = 1.5406 Å) radiation. Thermogravimetric analysis (TGA) was performed in the Mettler Toledo, Star$^\text{TM}$ 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$_2$BiBr$_6$ 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$^2$. 

![Diagram](Image317x110 to 539x337)
Fig. 1 View of structural characteristics for Cs$_3$BiBr$_6$. Bromide-coordination environment for (a) Bi1 and (b) Bi2. (c) 3D framework on the bc plane. Color codes: Cs, green; Bi, purple; Br, brown.

![Diagram](image)

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

Results and discussion

X-ray analysis indicates clearly that the compound of Cs$_3$BiBr$_6$ crystallizes in the orthorhombic system of space group Pbcn 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$_3$BiBr$_6$ is displayed in Fig. 1c, where all BiBr$_6$ octahedra are isolated from each other forming 0D perovskite structure. Cs$^+$ cations fills up the spaces left by the unconnected BiBr$_6$ octahedra. In particular, Bi1 located 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$_3$BiCl$_6$, CsPbBr$_3$, Cs$_2$AgBiBr$_6$, and Cs$_3$PbBr$_6$ is 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 Cs$_2$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 Cs$_2$AgBiBr$_6$. Despite this, there is a clear statement for the relationship between Cs$_3$BiBr$_6$ and Cs$_2$AgBiBr$_6$, where Ag in Cs$_2$AgBiBr$_6$ is substituted by Cs3 atom in Cs$_3$BiBr$_6$. At the same time, the difference comes, which is that after the incorporation of Cs3, the crystallographic symmetry of Cs$_3$BiBr$_6$ is lower than that in Cs$_2$AgBiBr$_6$, leading to a distinct structural characteristics in Cs$_3$BiBr$_6$. Meanwhile, we could also clearly observe the similarity of Cs$_3$BiBr$_6$ with that of Cs$_4$PbBr$_6$, 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 isomers of Cs$_3$BiCl$_6$ and Rb$_2$BiBr$_6$ (Table S5), 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 20 = 13.66°, 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), (002), (202), (220), (310), (222), (400), (312), (410), and (510). The diffraction peaks of 20 = 26.34°, 28.30°, 31.11°, 34.33°, 37.44°, could be identified to be the crystal planes of (200), (113), (221), (313), (413), (315), (511), (421), and (611). The Rietvield refinement of the experimental powder XRD pattern of Cs$_3$BiBr$_6$ 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$_3$BiBr$_6$. (g-i) EDX mapping of the element distribution: (g) Br, (h) Cs, (i) Bi.
To analyze the optical properties of Cs$_3$BiBr$_6$, the UV-vis absorption spectrum was measured. Cs$_3$BiBr$_6$ 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$_3$BiBr$_6$ single crystals are heated under a nitrogen atmosphere, as shown in the TGA curve in Fig. S3. It can be observed that Cs$_3$BiBr$_6$ is stable with increasing temperature up to 425 °C, while the onset of weight loss is observed.

As a comparison, the CH$_3$NH$_3$PbBr$_3$ was also investigated. For CH$_3$NH$_3$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 CH$_3$NH$_3$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$_3$BiBr$_6$ than in the CH$_3$NH$_3$PbBr$_3$.

In order to check the optoelectronic property of the Cs$_3$BiBr$_6$, 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 6 V bias, ultralow dark current of 0.03 nA was obtained. Fig. 5c shows the dynamic current-time (i-t) curves for the Cs$_3$BiBr$_6$ based photodetectors under repeating switching of 400 nm monochromatic illumination with a light density of 25 mW/cm$^2$. 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/cm$^2$ by increasing the voltage up to 8 V. Besides, the photoresponse of the detector versus light power density was measured. Periodic photoresponse behavior of Cs$_3$BiBr$_6$ under power density of 400 nm wavelength was observed (Fig. 5d). The amperometric i-t curves for the Cs$_3$BiBr$_6$ based photodetectors under repeating switching of 400 nm monochromatic illumination with a light density of 25 mW/cm$^2$. (c) Photocurrent under various power density of 6 V. (d) I-V characteristics under different power density. (e) Responsivity. (f) Detectivity.

Fig. 4 Absorption spectrum of Cs$_3$BiBr$_6$. Inset: the Tauc plot showing the bandgap of ca. 2.55 eV.

Fig. 5 (a) Schematic view of the photodetector based on Cs$_3$BiBr$_6$. Periodic photoresponse behavior of Cs$_3$BiBr$_6$ under power density of 400 nm wavelength. (b) Photocurrent under various voltages with light density of 25 mW/cm$^2$. (c) Photocurrent under various of light intensity and bias of 6 V. (d) I-V characteristics under different power density. (e) Responsivity. (f) Detectivity.
Conclusions

In summary, we have successfully synthesized a non-toxic perovskite for the utilization of non-toxic perovskites for the photodetection. Besides, this material displays high stability against toxic perovskites for the photodetection. Meanwhile, we also analyzed its crystallography and isolated BiBr polyhedra. Photodetector based on this isolated BiBr polyhedra. Proproceptor based on this isolated BiBr polyhedra. Proproceptor based on this isolated BiBr polyhedra. This work was supported by the Villum Foundation, Inde...


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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.