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CsPb₂Br₅ Single Crystals: Synthesis and Characterization

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Abstract: CsPb₂Br₅ is a ternary halogen-plumbate material with close characteristics to well-reported halide perovskites. Due to its unconventional two-dimensional structure, CsPb₂Br₅ is being looked at broadly for potential applications in optoelectronics. CsPb₂Br₅ investigations are currently limited to nanostructures and powder forms of the material, which present unclear and conflicting optical properties. In this study, we present the synthesis and characterization of CsPb₂Br₅ bulk single crystals, which enabled us to finally clarify the material's optical features. Our CsPb₂Br₅ crystal has a two-dimensional structure with Pb₂Br₅⁻ layers spaced by Cs⁺ cations, and exhibits a ~3.1 eV indirect bandgap with no emission in the visible spectrum.

The development of solution processed halide perovskite-based semiconductors has flourished in the last five years.^[1] This emergent class of semiconductors, represented with the general formula ABX₃ (A is organic/inorganic cation, B is a lead cation, and X is a halogen anion), exhibits remarkable light absorption and long carriers diffusion length together with tunable bandgaps obtained by tailoring the halogen composition.^[2] Hybrid organic-inorganic lead halogen perovskites of the CH₃NH₃PbX₃-type (X = Cl, Br, and I) represent the most suitable candidates for photovoltaic applications,^[3] while full-inorganic CsPbX₃ perovskites are prime contenders for light emitting devices^[4] and laser applications.^[5] Among inorganic lead halogen perovskites, the recent comeback of low-dimensional perovskite-related structures, with general formula A_nBX_{2+n}, is due to their attractive photoluminescence properties.^[6] Among these compounds, CsPb₂Br₅ represents an inspiring candidate for both light-emitting devices and lasing applications.^[7] CsPb₂Br₅ is often obtained as a secondary product during the syntheses of CsPbBr₃ perovskites,^[8] Cs₄PbBr₆ perovskite-

related structure,^[6a] and/or as a converted product from CsPbBr₃ nanocrystals.^[7a] Pure powders of CsPb₂Br₅ were obtained and characterized initially by Kuznetsova et al.,^[9] and more recently, nanostructures of CsPb₂Br₅ were reported.^[10, 7b, 11] While these works agree on structure and composition of CsPb₂Br₅, they greatly diverge on the interpretation of its intrinsic optical properties, which nowadays is a subject of controversy. For example, reports on CsPb₂Br₅ nanoplatelets and microplates suggest a material with strong green emission and green-lasing properties.^[10, 7b] In stark contrast, studies on CsPb₂Br₅ nanosheets suggest that the material is of an indirect bandgap nature and with no visible photoluminescence.^[11] Thus, to resolve the dispute arisen from the perceived optical properties and to push the field towards controlling the key properties at play in the material, we synthesized bulk CsPb₂Br₅ single crystals as the purest state of the compound – free of any possible ambiguities emanating from structural defects and dimensional properties. Bulk single crystals of CsPb₂Br₅ have yet to be reported, since difficulties in the crystallization process from melt precursors (CsBr and PbBr₂) have only afforded so far CsPbBr₃ and Cs₄PbBr₆ as stable crystals.

In this manuscript, we present for the first time the synthesis and characterization of CsPb₂Br₅ millimetre-sized single crystal. Our crystals are synthesized from solutions of CsBr and PbBr₂ precursors by means of antisolvent vapour crystallization (AVC). Transparent CsPb₂Br₅ crystals were grown with an absorption edge close to 370 nm and without noticeable photoluminescence (PL). DFT calculations agree well with the experimental evidence, by confirming an indirect bandgap of 3.09 eV. From Single-Crystal X-Ray Diffraction (SC-XRD) we resolved the full CsPb₂Br₅ structure, which is composed of two-dimensional layers of Pb₂Br₅⁻ spaced by Cs⁺ cations, in agreement with previously predicted CsPb₂Br₅ structures.^[7, 10, 11]

CsPb₂Br₅ single crystals were obtained from the well-established AVC technique^[12] using CsBr and PbBr₂ as precursors together with dimethyl sulfoxide (DMSO) and methanol (MeOH) as solvent and antisolvent (see details in Experimental Section). Interestingly, the CsPb₂Br₅ crystallization can be divided into two steps (Figure 1a). In the first 48 hours, the diffusion of MeOH in DMSO initiates the nucleation and precipitation of orange crystallites with proper characteristics of CsPbBr₃ (see Figure S1). Subsequently, during the following five weeks, the orange crystallites grow and slowly convert to transparent crystals of CsPb₂Br₅. This process is reminiscent of processes already observed for CsPb₂Br₅ nanocrystals. Indeed, the co-existence of a nanometric dual-phase of CsPbBr₃-CsPb₂Br₅ was first reported by Zhang et al.^[7a] and then supported by Wang et al.^[11] with the conversion of CsPbBr₃ nanocubes to CsPb₂Br₅ nanosheets in the presence of an excess of PbBr₂. In our work, the excess of PbBr₂ is generated by the low solubility of CsBr in DMSO, which continuously decreases during the MeOH antisolvent diffusion. The chemical reactions involved in the crystallization process are shown in Scheme 1.

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Scheme 1. The reaction steps involved in the crystallization process that leads to the formation of CsPb₂Br₅.

In our study, it is necessary to highlight the important role of antisolvent choice. Indeed it was already demonstrated that Cs₄PbBr₆ crystallites could be obtained under similar conditions from AVC using DMSO/diethyl ether (DE) as a solvent and antisolvent pair.^[6b] We believe that the ultimate crystallization products are defined by the miscibility of solvent-antisolvent. Thus, high miscibility (like MeOH in DMSO) produces first CsPbBr₃ and then subsequently CsPb₂Br₅; while low miscibility (like DE in DMSO) directly yields Cs₄PbBr₆.

After five weeks of crystallization, all the crystals in the vial appeared transparent, and no orange CsPbBr₃ crystallites are visible. Scanning Electron Microscopy (SEM) images confirmed the high quality of the CsPb₂Br₅ crystals with a smooth surface and well-defined tetragonal shape (Figure 1b). SC-XRD analysis confirmed that the transparent crystals are CsPb₂Br₅ with tetragonal symmetry and *I*4/*mcm* space group (see Figure 2). The unit cell dimensions $a = b = 8.490 \text{ \AA}$, and $c = 15.197 \text{ \AA}$ are in agreement with what was previously reported for powders (crystal data and structure refinement details can be found in Table S1).^[9] As shown in Figure 2a, CsPb₂Br₅ crystals present a two-dimensional structure composed by Cs⁺ cation sandwiched between Pb₂Br₅⁻ layers. The Pb₂Br₅⁻ layers consist of Pb²⁺ atoms coordinate with eight Br⁻, forming an elongated polyhedron (Figure 2b).^[11] To further validate the absence of any CsPbBr₃

Figure 1. a) Schematic diagram of the CsPb₂Br₅ single crystal growing by AVC method. b) SEM image and c) optical image of the CsPb₂Br₅ single crystal. White and red scale bar: 200 nm.

impurity, we compared the calculated powder spectrum from SC-XRD results with the powder spectrum obtained from

grinded CsPb₂Br₅ crystals (Figure 2c). The reflections of the two patterns are identical; thus we can exclude the presence of any CsPbBr₃ impurity.

Furthermore, to test the chemical composition and homogeneity of our crystals, we performed elemental mapping by means of Energy Dispersive X-Ray Spectroscopy (EDS). CsPb₂Br₅ crystals exhibit the atomic ratio of 1:2:5 (see Figure S2) following the final stoichiometry of the CsPb₂Br₅ crystals.

The optical properties of CsPb₂Br₅ represent an intriguing topic of conflicting interpretations. Strong and narrow green PL stemming from CsPb₂Br₅ nanostructures was described in refs ^[7b, 10]; in contrast Jiang et al. reported CsPb₂Br₅ nanosheets with large indirect bandgap and a PL inactive behavior.^[11] We investigated the PL properties of our crystals by exciting all over the visible and near UV spectrum. We found no detectable emission, which is in agreement with Wang et al.^[11] The absorption spectrum of our crystals exhibits only one edge at 370 nm, from which we deduced a 3.35 eV bandgap (Figure 3a).

Figure 2. a) Crystal structure of the CsPb₂Br₅ single crystal obtained by SC-XRD and detail of the Cs⁺ coordination. b) Pb-Br schematic coordination. c) Powder XRD of the grinded crystal along with the calculated spectrum of tetragonal CsPb₂Br₅.

To gain a better insight into the optical properties of CsPb₂Br₅ crystals, we calculated the electronic band structure and projected density of states with the generalized gradient approximation (GGA)/Perdew-Burke-Ernzerhof (PBE) theory (see the computational details in Supporting Information). As shown in Figure 3b, we obtained an indirect bandgap between X-point (top valence band) and !-point (bottom conduction band) of 3.09 eV and the lowest direct band gap (3.19 eV) at the !-point. The projected densities of states (PDOS) show that the dominant contributions to the valence bands around the Fermi level are from Br-4*p* and the conduction bands are provided by Pb-6*p*; the Cs⁺ cations have no direct contributions to the electronic states in this energy region. In Figure 3c, we also show the charge density distributions of valence band maximum (VBM) and conduction band minimum (CBM) within GGA/PBE, the charge densities of VBM at both !- and X-points are highly localized in the Br atoms, while charge density of CBM at !-point

localizes at the Pb sites. From the calculated optical absorption spectrum by taking into account of electron-hole interaction (using BSE method) as shown in Figure 3a-bottom panel, we observe a sharp increase in the calculated absorption coefficient around 390 nm, which corresponds to the direct optical transitions ($\text{Br-}4p \rightarrow \text{Pb-}6p$) at Γ -point of the band structure.

In light of these results, we conclude that intrinsic CsPb_2Br_5 is an indirect bandgap material, which does not display appreciable intrinsic PL. Our findings suggest that observations^[7b, 10] of emission in this material could be either due to the potential formation of emissive sub-bandgap defects (due the peculiarities of the synthesis procedure) or secondary phases. Indeed, it is very likely that under particular conditions, like those manifested during the synthesis of nanostructures, residual phases or defects induced by the surface strain may give rise to PL. In this sense, a very similar scenario was recently reported for Cs_4PbBr_6 perovskite-related structure, where emissive and non-emissive nanocrystals with the same composition were observed.^[6c, 6d]

Figure 3. a) Experimental absorption spectrum (top panel, orange dots) and calculated absorption coefficient (bottom panel, blue line) of CsPb_2Br_5 . b) Calculated electronic bands and projected density of states (PDOS) of CsPb_2Br_5 at GGA/PBE level. c) Charge density distributions of valence band maximum (VBM) and conduction band minimum (CBM) at Γ -point and VBM at X point.

In summary, we reported the synthesis and characterization of CsPb_2Br_5 bulk single crystals, neither of which has been reported before. Since there are conflicting reports on the optical properties of CsPb_2Br_5 (especially in nanostructure and powder forms), bulk single crystals can clarify the optical features of this ternary halogen-plumbate material. Our crystals exhibit a PL inactive behavior and an indirect bandgap of ~ 3.1 eV as interpreted by DFT calculations. We believe that our results represent a turning point in the classification of the optical properties of this ternary halogen-plumbate material, providing the community with the essential basis for tailoring its properties.

Experimental Section

Synthesis

PbBr_2 (#98%), CsBr (99.9% trace metals basis), MeOH and DMSO were purchased from Sigma-Aldrich and used without further purifications. CsPb_2Br_5 single crystals were obtained from a 0.25 M solution of PbBr_2 and CsBr in DMSO. For AVC, MeOH was used as antisolvent with a 4-to-1 ratio respect to precursors' solution. After one month of undisturbed crystallization, CsPb_2Br_5 crystals were collected and washed with MeOH, prior to stock in a nitrogen atmosphere.

Characterizations

Single-crystal X-ray diffraction data were collected using a Bruker X8 PROSPECTOR APEX2 CCD diffractometer (Cu $K\alpha$, $\lambda = 1.54178$ Å). Powder X-ray diffraction was performed on a Bruker AXS D8 diffractometer using Cu $K\alpha$ radiation. SEM images and EDS characterization were performed with an FEI Quanta 600 microscope. Steady-state absorption spectra were collected from an Edinburg F900 Spectrometer with sample reflectance correction by using BaSO_4 as a reflectance standard. A FluoroMax-4 spectrofluorometer from Horiba Scientific was used to investigate photoluminescence properties. For DFT calculations and SC-XRD details, see the Supporting Information.

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Keywords: halogen perovskites • CsPb_2Br_5 • single crystal • photoluminescence • indirect bandgap

[1] a) H. Tsai, W. Nie, J.-C. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. J. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, L. Pedesseau, J. Even, M. A. Alam, G. Gupta, J. Lou, P. M. Ajayan, M. J. Bedzyk, M. G. Kanatzidis, A. D. Mohite, *Nature* **2016**, *536*, 312-316; b) H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee, *Science* **2015**, *350*, 1222-122; c) X. Y. Chin, D. Cortecchia, J. Yin, A. Bruno, C. Soci, *Nat. Commun.* **2015**, *6*, 7383; d) S. Pathak, N. Sakai, F. Wisnivesky Rocca Rivarola, S. D. Stranks, J. Liu, G. E. Eperon, C. Ducati, K. Wojciechowski, J. T. Griffiths, A. A. Haghghirad, A. Pellaroque, R. H. Friend, H. J. Snaith, *Chem. Mater.* **2015**, *27*, 8066-8075; e) I. Dursun, C. Shen, M. R. Parida, J. Pan, S. P. Sarmah, D. Priante, N. Alyami, J. Liu, M. I. Saidaminov, M. S. Alias, A. L. Abdelhady, T. K. Ng, O. F. Mohammed, B. S. Ooi, O. M. Bakr, *ACS Photonics* **2016**, *3*, 1150-1156; f) U. Bansode, S. Ogale, *J. Appl. Phys.* **2017**, *121*, 133107; g) D. Priante, I. Dursun, M. S. Alias, D. Shi, V. A. Melnikov, T. K. Ng, O. F. Mohammed, O. M. Bakr, B. S. Ooi, *Appl. Phys. Lett.* **2015**, *106*, 081902; h) M. De Bastiani, M. I. Saidaminov, I. Dursun, L. Sinatra, W. Peng, U. Buttner, O. F. Mohammed, O. M. Bakr, *Chem. Mater.* **2017**, *29*, 3367-3370; i) Halder, D. Choudhury, S. Ghosh, A. S. Subbiah, S. K. Sarkar, *J. Phys. Chem. Lett.* **2015**, *6*, 3180-3184; j) S. Subbiah, A. Halder, S. Ghosh, N. Mahuli, G. Hodes, S. K. Sarkar, *J. Phys. Chem. Lett.* **2014**, *5*, 1748-1753; k) Bansode, R. Naphade, O. Game, S. Agarkar, S. Ogale, *J. Phys. Chem. C* **2015**, *119*, 9177-9185; l) F. Lamberti, L. Litti, M. De Bastiani, R. Sorrentino, M. Gandini, M. Meneghetti, A. Petrozza, *Adv. Energy Mater.* **2017**, *7*, 160170; m) Y. Zhang, J. Yin, M. R. Parida, G. H. Ahmed, J. Pan, O. M. Bakr, J.-L. Brédas, O. F. Mohammed, *J. Phys. Chem. Lett.* **2017**, *8*, 3173-3177; n) W. Wang, M. O. Tade, Z. Shao, *Chem. Soc. Rev.* **2015**, *44*, 5371-5408; o) Y. Chen, M. He, J. Peng, Y. Sun, Z. Liang, *Adv. Sci.* **2016**, *3*, 1500392.

[2] a) S. D. Stranks, H. J. Snaith, *Nat Nano* **2015**, *10*, 391-402; b) S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, H. J. Snaith, *Science* **2013**, *342*, 341-344; c) G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaisalkar, T. C. Sum, *Science* **2013**, *342*, 344-347; d) G. Xing, N. Mathews, S. S. Lim, N. Yantara, X. Liu, D. Sabba, M. Grätzel, S. Mhaisalkar, T. C. Sum, *Nat Mater* **2014**, *13*, 476-480.

[3] National Renewable Energy Laboratory (NREL), Best Research-Cell Efficiencies, <http://www.nrel.gov/ncpv/images/efficiency-chart.jpg>, accessed 2017.

[4] a) S. Kumar, J. Jagielski, S. Yakunin, P. Rice, Y.-C. Chiu, M. Wang, G. Nedelcu, Y. Kim, S. Lin, E. J. G. Santos, M. V. Kovalenko, C.-J. Shih, *ACS Nano* **2016**, *10*, 9720-9729; b) S. A. Veldhuis, P. P. Boix, N. Yantara, M. Li, T. C. Sum, N. Mathews, S. G. Mhaisalkar, *Adv. Mater.* **2016**, *28*, 6804-6834; c) N. Yantara, S. Bhaumik, F. Yan, D. Sabba, H. A. Dewi, N. Mathews, P. P. Boix, H. V. Demir, S. Mhaisalkar, *J. of Phys. Chem. Lett.* **2015**, *6*, 4360-4364.

[5] S. Yakunin, L. Protesescu, F. Krieg, M. I. Bodnarchuk, G. Nedelcu, M. Humer, G. De Luca, M. Fiebig, W. Heiss, M. V. Kovalenko, *Nat Commun.* **2015**, *6*, 8056.

[6] a) M. I. Saidaminov, J. Almutlaq, S. Sarmah, I. Dursun, A. A. Zhumekenov, R. Begum, J. Pan, N. Cho, O. F. Mohammed, O. M. Bakr, *ACS Energy Lett.* **2016**, *1*, 840-84; b) D. Chen, Z. Wan, X. Chen, Y. Yuan, J. Zhong, *J. Mater. Chem. C* **2016**, *4*, 10646-10653; c) Y. Zhang, M. I. Saidaminov, I. Dursun, H. Yang, B. Murali, E. Alarousu, E. Yengel, B. A. Alshankiti, O. M. Bakr, O. F. Mohammed, *J. Phys. Chem. Lett.* **2017**, *8*, 961-965; d) Q. A. Akkerman, S. Park, E. Radicchi, F. Nunzi, E. Mosconi, F. De Angelis, R. Brescia, P. Rastogi, M. Prato, L. Manna, *Nano Lett.* **2017**, *17*, 1924-1930; e) L. N. Quan, R. Quintero-Bermudez, O. Voznyy, G. Walters, A. Jain, J. Z. Fan, X. Zheng, Z. Yang, E. H. Sargent, *Adv. Mater.* **2017**, *29*, 1605945.

[7] a) X. Zhang, B. Xu, J. Zhang, Y. Gao, Y. Zheng, K. Wang, X. W. Sun, *Adv. Funct. Mater.* **2016**, *26*, 4595-4600; b) X. Tang, Z. Hu, W. Yuan, W. Hu, H. Shao, D. Han, J. Zheng, J. Hao, Z. Zang, J. Du, Y. Leng, L. Fang, M. Zhou, *Adv. Opt. Mater.* **2017**, *5*, 1600788.

[8] Y. Rakita, N. Kedem, S. Gupta, A. Sadhanala, V. Kalchenko, M. L. Böhm, M. Kulbak, R. H. Friend, D. Cahen, G. Hodes, *Cryst. Growth Des.* **2016**, *16*, 5717-5725.

[9] I.Y. Kuznetsova, I.S. Kovaleva, V.A. Fedorov *Russ. J. Inorg. Chem.* **2001**, *46*, 1900-1905.

[10] K.-H. Wang, L. Wu, L. Li, H.-B. Yao, H.-S. Qian, S.-H. Yu, *Angew. Chem. Int. Ed.* **2016**, *55*, 8328-8332.

[11] G. Li, H. Wang, Z. Zhu, Y. Chang, T. Zhang, Z. Song, Y. Jiang, *Chem. Commun.* **2016**, *52*, 11296-11299.

[12] a) D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, O. M. Bakr, *Science* **2015**, *347*, 519-522; b) W. Peng, L. Wang, B. Murali, K.-T. Ho, A. Bera, N. Cho, C.-F. Kang, V. M. Burlakov, J. Pan, L. Sinatra, C. Ma, W. Xu, D. Shi, E. Alarousu, A. Goriely, J.-H. He, O. F. Mohammed, T. Wu, O. M. Bakr, *Adv. Mater.* **2016**, *28*, 3383-3390; c) Y. Tidhar, E. Edri, H. Weissman, D. Zohar, G. Hodes, D. Cahen, B. Rybtchinski, S. Kirmayer, *J. Am. Chem. Soc.* **2014**, *136*, 13249-13256.

