Supplementary Information

Influence of crystallisation on structural and optical

properties of lead-free Cs₂AgBiBr₆ perovskite crystals

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Experimental section

Materials and solvents

DMF (99.8 %), DMSO (>99.9 %), CsBr (99.999 %, trace metals basis) were acquired from Sigma-Aldrich. $BiBr_3$ (99.998 %, metals basis) and AgBr (99.998 %, metals basis) were purchased from Alfa Aesar. HBr (48 wt%) was purchased from our in-house chemical supply of the Faculty of Chemistry and Pharmacy of the University Würzburg. All chemicals were used as received and without further purification.

Solubility curves of Cs₂AgBiBr₆

CsBr (2 eq, 47.88 mg, 0.225 mmol), AgBr (1 eq, 21.12 mg, 0.1125 mmol) and BiBr₃ (1 eq, 50.48 mg, 0.1125 mmol) were weighed in stoichiometric amounts into a 4 ml glass vial in a nitrogen filled glovebox with a water and oxygen content below 1 ppm. The solubility curve for the acid-based process was achieved by adding small amounts of HBr (50 μ I) every hour under constant stirring of the solution, until the precursor salts were completely dissolved. This was done for a temperature range from 25 °C to 100 °C, in order to obtain an exact solubility curve for Cs₂AgBiBr₆ in HBr. The error of this process was estimated to be 100 μ I for each precursor solution.

The solubility curves of $Cs_2AgBiBr_6$ in DMF/DMSO (1:2) and pure DMSO were obtained in a similar way: CsBr (2 eq, 301.42 mg, 1.42 mmol), AgBr (1 eq, 132.98 mg, 0.071 mmol) and BiBr₃ (1 eq, 317.75 mg, 0.071 mmol) were weighed in stoichiometric amounts in a nitrogen filled glovebox. By adding either a mixture of DMSO/DMF or pure DMSO under constant stirring, the solubility behaviour was determined for different temperatures. Every hour 50 μ l of the corresponding solvent was added to the solutions, until the precursor salts were completely dissolved. The error of this process was estimated to be 10 g/l.

Cs₂AgBiBr₆ crystal growth from controlled cooling

In order to obtain $Cs_2AgBiBr_6$ crystals from HBr, the commonly known crystal growth protocol was followed:¹ A 0.3 molar solution of CsBr (1.5 mmol, 319.21 mg,2 eq), AgBr (0.75 mmol, 140.83 mg, 1 eq) and BiBr₃ (0.75 mmol, 336.52 mg, 1 eq) was prepared with 10 ml of 48 %wt HBr. The solution was placed on a hotplate, in an oil bath, and heated to 110 °C for 2 h in order to obtain a completely dissolved precursor solution. To promote crystal growth, the solution was cooled down at a rate of 1 °C/h to RT. The crystals were then washed and dried with dichloromethane (DCM) in order to avoid any precursor precipitates remaining on the surface.

Cs₂AgBiBr₆ crystal growth by slow evaporation

A 1.5 molar stoichiometric solution of CsBr, BiBr₃ and AgBr was prepared by weighing 478.82 mg (2.25 mmol, 2 eq) of CsBr, 211.24 mg (1.125 mmol, 1 eq) of AgBr and 504.78 mg (1.125 mmol, 1 eq) of BiBr₃. The precursors were dissolved in 3 ml of a 2:1 DMSO/DMF mixture on a hotplate. After complete dissolving, the solution was filtered using a Poly(1,1,2,2-tetrafluoroethylene) (PTFE) filter with a pore size of 0.20 μ m. The precursor solution was then placed at 146 °C on a hotplate for approximately 72 h until crystallization occurred. The resulting crystals were taken out of the solution and washed with DCM to avoid any precursor precipitates on the surface.

Cs₂AgBiBr₆ thin film synthesis

Thin films were fabricated using the protocol described in our previous work.² A stoichiometric precursor solution was prepared by dissolving CsBr (212.8 mg, 1 mmol, Alfa Aesar, 98.999 % metals basis), BiBr₃ (224.4 mg, 0.5 mmol) acquired from Alfa Aesar (99.9 % , metals basis) and AgBr (93.9 mg, 0.5 mmol), acquired from Alfa Aesar (99.998 % metals basis) in 1 ml of DMSO. The solution was stirred at 130 °C until it was completely dissolved. Afterwards, the thin films were spin-coated dynamically in a nitrogen filled glovebox (Step 1: 1000 rpm for 10 s, Step 2: 5000 rpm for 30 s). 7 s before the end of the second spin coating step, 400 μ l of 2-propanol was dripped quickly onto the substrate. The procedure was followed by annealing the films for 5 min at 275 °C.

EDX measurements

EDX characterization of the crystal surfaces were performed in high vacuum using a scanning electron microscope (SEM) Carl Zeiss Ultra 55+ and an INCAPentaFET-x3 Si(Li) detector to obtain the elemental distribution of Cs, Ag, Bi, and Br. For all

¹ A. H. Slavney, T. Hu, A. M. Lindenberg and H. I. Karunadasa, *Journal of the American Chemical Society*, 2016, **138**, 2138-2141.

² M. T. Sirtl, M. Armer, L. K. Reb, R. Hooijer, P. Dörflinger, M. A. Scheel, K. Tvingstedt, P. Rieder, N. Glück, P. Pandit, S. V. Roth, P. Müller-Buschbaum, V. Dyakonov and T. Bein, Optoelectronic Properties of Cs 2 AgBiBr 6 Thin Films: The Influence of Precursor Stoichiometry, *ACS Appl. Energy Mater.*, 2020, **3**, 11597–11609.

crystals, at least 4 working areas on the crystals were measured. The obtained data were then normalized and averaged to obtain an average stoichiometry and elemental distribution over the whole crystal surface.

X-ray Diffraction and X-ray Fluorescence

Powder and single crystal XRD measurements as well as XRF measurements of the crystal powders were performed using a General Electric XRD 3003 TT with a monochromatic Cu- K_{α} radiation source (V = 40 kV, I = 40 mA) with wavelength λ of 1.5406 Å. Further XRF measurements were recorded with an XR-100T detector from Amptek and an X-ray machine from PHYWE. For the measurements, we applied an unfiltered Mo (Molybdenum)- K_{α} radiation source (V = 35 kV, I = 0.1 mA). All measurements were performed at RT.

Crystal structure analysis

An orange block-like specimen of $Cs_2AgBiBr_6$, approximate dimensions 0.020 mm \cdot 0.020 mm \cdot 0.030 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker D8 Venture TXS system equipped with a multilayer mirror optics monochromator and a Mo K_a rotating-anode X-ray tube ($\lambda = 0.71073$ Å). The measurements were performed at RT.

PLE measurements

Photoluminescence excitation spectra of the crystal surface were measured with a FLS 980 (Edinburgh Instruments). A Xenon lamp with tuneable excitation wavelength was used to excite the samples at energies from 2.0 eV to 3.2eV. The PLE of the surface was collected in reflection geometry with a PMT detector at the corresponding PL maximum of the sample (\approx 1.9 eV) for all excitation wavelengths. All measurements were performed under ambient conditions.

Crystal Transmission

To probe the optical absorption edge of the $Cs_2AgBiBr_6$ crystals, the transmission of the crystals was measured by illuminating the crystals with white light and collecting the transmission with a Princeton Instruments Acton SpectraPro SP-2300 Spectrometer and a PyLoN Silicon CCD Detector, through an aperture. To calculate the absorptance from those measurements, reflection of the crystals was neglected and the transmission calculated by T = $I_{crystal}/I_{lamp}$. The absorptance was then obtained by A = 1-T.

Absorption Coefficient

The absorption coefficient for a thin film and for measurements of crystal transmission was calculated using the equation $A = 1-T = 1-exp(-\alpha d)$, with A being the calculated absorptance of the crystal, d being the thickness of the crystal and α being the absorption coefficient. For PLE the absorption coefficient was obtained by shifting the PLE spectra to the absorption coefficient of the thin film in the energy range of 2.2 eV to 2.4 eV, as the shape of the PLE spectrum aligned perfectly with the shape of the calculated absorption coefficient of the thin film in this energy range. As the absorption coefficient is a thickness independent material property, we therefore find that in the energy range of 2.2 eV to 2.4 eV to 2.4 eV the PLE spectrum must overlap with the absorption coefficient of the thin film.



Figure S1: The solubility curves for methylammonium lead tribromide (MAPbBr₃) in DMF (red) showing the typical retrograde solubility, necessary for growing crystals with ITC.^{3, 4} Other materials such as potassium aluminium sulphate (KAI(SO₄)₂ * 12H₂O) (blue) and sodium acetate (C₂H₃NaO₂) (green) do not show an inverse solubility behaviour in deionized water (H₂O). Here, the solubility of the salts in deionized water (H₂O) increases with increasing temperature and offers the possibility to grow crystals at RT. In contrast, the solubility curve of sodium chloride (NaCl) in H₂O (orange) has a similar shape to the solubility curves of Cs₂AgBiBr₆ dissolved in pure DMSO and in the DMF/DMSO mixture (Fig. 2a). The solubility of NaCl increases only slightly with increasing temperature. As a result, we grew NaCl crystals by slowly evaporating the solvent.

³ M. I. Saidaminov, A. L. Abdelhady, G. Maculan and O. M. Bakr, *Chemical Communications*, 2015, **51**, 17658-17661.

 ⁴ M. I. Saidaminov, A. L. Abdelhady, B. Murali, E. Alarousu, V. M. Burlakov, W. Peng, I. Dursun, L. Wang, Y. He, G. Maculan, A. Goriely, T. Wu, O. F. Mohammed and O. M. Bakr, *Nature Communications*, 2015, **6**, 7586.



Figure S2. Formation of sidephases during crystal growth. The first clear solution turns turbid over time (left) when sidephases $CsAgBr_2$ and AgBr are formed (middle) followed by crystal growth of $Cs_2AgBiBr_6$ (right). For example, at a temperature of 60 °C the turbidity of the solution was observed after approximately 2 h, followed by the formation of the sidephases for about another hour. As a comparison for even lower temperatures like 40 °C the solution turned turbid after 3 h followed by the formation of the sidephases 3h later. This already indicates that the process of crystal growth as well as sidephase formation strongly depends on the chosen temperature.



Figure S3. (a) EDX spectra of the side phases AgBr and CsAgBr₂. (b) Powder XRD pattern of CsAgBr₂ with corresponding fit to evaluate the lattice constant. CsAgBr₂ shows an orthorhombic crystal structure with a = 20.05 Å, b = 5.05 Å, and c = 6.01 Å, which is in good agreement with the values of the β -phase of CsAgBr₂ in the literature⁵.

⁵ S. Hull and P. Berastegui, *Journal of Solid State Chemistry*, 2004, **177**, 3156-3173.

Table S1. Theoretical stoichiometry and experimental data of the side phase AgBr. The exact stoichiometry of $Cs_{0.5}Ag_{48.03}Br_{51.47}$ was obtained using EDX analysis. Only 0.5 at.-% of Cs were found within the side phase, therefore it is safe to assume that some Cs precursor salt can still be found on the AgBr crystals.

Atom Fraction [%]	Theory	Experimental
Cs	0	0.5
Ag	50	48.03
Br	50	51.47
Bi	0	0

Table S2. Theoretical stoichiometry and experimental data of the sidephase $CsAgBr_2$. The exact stoichiometry of $Cs_{23.37}Ag_{21.35}Bi_{0.8}Br_{54.48}$ was obtained using EDX analysis. As the amount of Bi was below 1 at.-%, we conclude that some Bi is found on the crystal surface, while the bulk of the yellow phase follows the stoichiometry of $CsAgBr_2$.

Atom Fraction	Theory	Experimental
[%]		
Cs	25	23.37
Ag	25	21.35
Br	50	54.48
Bi	0	0.80

Table S3. Theoretical stoichiometry and experimental data of $Cs_2AgBiBr_6$ grown by controlled cooling, determined by ICP-MS, ICP-AES and ion chromatography. The exact stoichiometry of $Cs_{19.9}Ag_{10.0}Bi_{10.0}Br_{60.1}$ was found.

Atom Fraction [%]	Theory	Experimental
Cs	20	19.9
Ag	10	10.0
Br	60	60.1
Bi	10	10.0

Table S4. Theoretical stoichiometry and experimental data of $Cs_2AgBiBr_6$ grown by controlled cooling, slow evaporation and fast evaporation of crystal powders, determined by EDX.

Atom Fraction [%]	Theory	Controlled Cooling	Slow Evaporation	Fast Evaporation
Cs	20	22.0	20.1	20.0
Ag	10	10.25	10.8	10.3
Br	60	57.9	59.0	59.8
Bi	10	9.85	10.1	9.9



Figure S4. XRF spectra of $Cs_2AgBiBr_6$ powders, which were recorded with a monochromatic copper radiation source. For the measurements the crystals obtained from controlled cooling and slow evaporation (RT) were crushed into fine powders.



The measurements demonstrate the emission line of the elements Bi, Ag and Cs.

Figure S5. XRF spectra of $Cs_2AgBiBr_6$ crystal powders, obtained from crystals grown by high temperature evaporation (146 °C) and low temperature evaporation (RT). The measurements, which were recorded with an unfiltered molybdenum radiation source, exhibits the X-ray lines of the elements Cs, Bi and Br. *-assigned peaks are due to the sample holder. **Figure S6.** EDX spectra of $Cs_2AgBiBr_6$ crystals, grown by high temperature evaporation and low temperature evaporation, revealing the photon energies of the elements Cs, Ag, Bi and Br.





Figure S7. Powder XRD patterns of $Cs_2AgBiBr_6$, with corresponding fits to evaluate the lattice constant. The XRD measurements for all three crystallization methods agree very well.

Crystal structure analysis

Crystal data for $Cs_2AgBiBr_6$ single crystals obtained by crystal structure analysis, showing the lattice constant and angles for the cubic system.

Crystal data			
Chemical formula	Cs ₂ AgBiBr ₆		
Formula weight	1062.13 g/mol		
Temperature	297(2) К		
Wavelength	0.71073 Å		
Crystal system	cubic		
Space group	F m -3 m		
Unit cell dimensions	a = 11.2727(17) Å α = 90°		
	b = 11.2727(17) Å	β = 90°	
	c = 11.2727(17) Å γ = 90°		
Volume	1432.5(6) Å ³		
Z	4		
Density (calculated)	4.925 g/cm ³		
Absorption coefficient	35.329 mm ⁻¹		
F(000)	1800		

Diffractometer	Bruker D8 Venture TXS		
Radiation Source	Rotating-anode X-ray tube, Mo Kα		
Theta Range for Data collection	3.13 ° – 45.22 °		
Wavelength	0.71073 Å		
Index ranges	-22<= h,k,l <=22		
Reflections collected	18597		
Independent reflections	356 [R(int)=0.0467]		
Refinement method	Full-matrix least-squares on F ²		
Structure solution technique	Direct methods		
Function minimized	$\Sigma w(Fo^2 - Fc^2)^2$		
Weighting scheme	$w=1/[\sigma^{2}(F_{o}^{2})+(0.0291P)^{2}+2.0528P]$ where $P=(F_{o}^{2}+2F_{c}^{2})/3$		
Goodness-of-fit on F ²	1.102		
Data/restraints/parameters	356 / 0 / 7		
Final R indices	340 data; I>2σ(I) R1 = 0.0203, wR2 = 0.0511 all data R1 = 0.0226, wR2 = 0.0527		
R.M.S. deviation from mean	0.155 eÅ ⁻³		
Largest diff. peak and hole	1.232 and -2.575 eÅ-3		
Refinement Program	SHELXT 2014/5 (Sheldrick, 2016)		

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Atomic coordinator and (auivalant icotro	nic stomic dic	nlacomont	naramatara l	A 4 1	
Alonnic coordinales and e	culvalent isotro	DIC ALUITIIC UIS	placement	Darameters i	AI	

U(eq) is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Ag1	0.0	0.5	0.5	0.03027(14)
Bi1	0.5	0.5	0.5	0.02197(9)
Cs1	0.25	0.25	0.25	0.0533(2)
Br1	0.24908(4)	0.5	0.5	0.0565(2)

Anisotropic atomic displacement parameters ($Å^2$) Note that $U_{23}=U_{13}=U_{12}=0$

Note that $U_{23}=U_{13}=U_{12}=0$				
	U ₁₁	U ₂₂	U ₃₃	
Ag1	0.03027(14)	0.03027(14)	0.03027(14)	
Bi1	0.02197(9)	0.02197(9)	0.02197(9)	
Cs1	0.0533(2)	0.0533(2)	0.0533(2)	
Br1	0.0218(2)	0.0739(3)	0.0739(3)	

Bond lengths (Å)

2.8078(6)	Ag1-Br1	2.8078(6)
2.8078(6)	Ag1-Br1	2.8078(6)
2.8078(6)	Ag1-Br1	2.8078(6)
2.8286(6)	Bi1-Br1	2.8286(6)
2.8286(6)	Bi1-Br1	2.8286(6)
2.8286(6)	Bi1-Br1	2.8286(6)
3.9855(6)	Cs1-Br1	3.9855(6)
	2.8078(6) 2.8078(6) 2.8078(6) 2.8286(6) 2.8286(6) 2.8286(6) 3.9855(6) 3.9855(6) 3.9855(6) 3.9855(6) 3.9855(6) 3.9855(6)	2.8078(6) Ag1-Br1 2.8078(6) Ag1-Br1 2.8078(6) Ag1-Br1 2.8078(6) Bi1-Br1 2.8286(6) Bi1-Br1 2.8286(6) Bi1-Br1 3.9855(6) Cs1-Br1 3.9855(6) Cs1-Br1

Bond angles (°)			
Br1-Ag1-Br1	180.0	Br1-Ag1-Br1	90.0
Br1-Ag1-Br1	90.0	Br1-Ag1-Br1	90.0
Br1-Ag1-Br1	90.0	Br1-Ag1-Br1	90.0
Br1-Ag1-Br1	90.0	Br1-Ag1-Br1	90.0
Br1-Ag1-Br1	90.0	Br1-Ag1-Br1	180.0
Br1-Ag1-Br1	90.0	Br1-Ag1-Br1	90.0
Br1-Ag1-Br1	180.0	Br1-Ag1-Br1	90.0
Br1-Ag1-Br1	90.0	Br1-Bi1-Br1	90.0
Br1-Bi1-Br1	180.0	Br1-Bi1-Br1	90.0
Br1-Bi1-Br1	90.0	Br1-Bi1-Br1	90.0
Br1-Bi1-Br1	90.0	Br1-Bi1-Br1	90.0
Br1-Bi1-Br1	90.0	Br1-Bi1-Br1	90.0
Br1-Bi1-Br1	180.0	Br1-Bi1-Br1	90.0
Br1-Bi1-Br1	180.0	Br1-Bi1-Br1	90.0
Br1-Bi1-Br1	90.0	Br1-Bi1-Br1	90.0
Br1-Cs1-Br1	179.701(13)	Br1-Cs1-Br1	59.756(11)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	60.244(11)	Br1-Cs1-Br1	179.701(13)
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	179.701(13)	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	90.0
Br1-Cs1-Br1	90.0	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	90.0
Br1-Cs1-Br1	90.0	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	179.701(13)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	59.756(11)
Br1-Cs1-Br1	60.244(11)	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	90.0	Br1-Cs1-Br1	90.0
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	60.244(11)	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	59.756(11)
Br1-Cs1-Br1	90.0	Br1-Cs1-Br1	90.0
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	179.701(13)	Br1-Cs1-Br1	90.0
Br1-Cs1-Br1	90.0	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	90.0
Br1-Cs1-Br1	90.0	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	120.0
Br1-Cs1-Br1	59.756(11)	Br1-Cs1-Br1	60.244(11)
Br1-Cs1-Br1	120.0	Br1-Cs1-Br1	179.701(13)
Ag1-Br1-Bi1	180.0	Ag1-Br1-Cs1	90.149(6)
Bi1-Br1-Cs1	89.851(7)	Ag1-Br1-Cs1	90.149(6)
Bi1-Br1-Cs1	89.851(6)	Cs1-Br1-Cs1	179.701(13)
Ag1-Br1-Cs1	90.149(6)	Bi1-Br1-Cs1	89.851(6)
Cs1-Br1-Cs1	90.0	Cs1-Br1-Cs1	90.0
Ag1-Br1-Cs1	90.149(6)	Bi1-Br1-Cs1	89.851(6)
Cs1-Br1-Cs1	90.0000(10)	Cs1-Br1-Cs1	90.0



Figure S8. XRD measurement of polycrystalline thin $Cs_2AgBiBr_6$ film with associated fit to evaluate the lattice constant. By fitting the reflections of the pattern, we obtained a simple cubic crystal structure for the film, which is in perfect agreement with the crystal powders.



Figure S9. Rocking scan of the (222) reflection in linear and logarithmic scale performed on the crystal surfaces. (a) The rocking scan of a crystal grown by controlled cooling reveals a perfect crystal quality. (b) The rocking scan of the crystal grown at RT by slow evaporation shows a sharp peak in the linear plot but features small lattice defects, illustrated in the logarithmic plot. For the evaluation of the full width at half maximum, we used the peak shown in the black box.



Figure S10. Transient photoluminescence measurement of $Cs_2AgBiBr_6$ crystals. A clear difference in the decays was found for differently grown crystals. We observed very fast initial decays for crystals grown by fast evaporation compared to crystals grown by slow evaporation and controlled cooling. Additionally, the PL lifetimes of crystals grown by slow evaporation and controlled cooling are increased compared to the PL lifetimes found for crystals grown by fast evaporation. We therefore speculate that trap assisted recombination is more pronounced in crystals grown by fast evaporation.



Figure S11. (a) Probing depths for PLE and transmission measurements on the crystals. The blue arrows show that PLE is only probing the surface of the crystals. Additionally, as PLE is only measured at energies higher than the PL emission, the absorption tail can only be probed at higher energies. The yellow arrows show that transmission can only be detected in the low energy region, as nothing is transmitted at higher energies due to a large absorption coefficient. (b) Scheme of the absorption coefficient for materials with high (black line) and low (blue line) Urbach energies. The red and blue squares demonstrate the regions in which the absorption coefficient are probed by crystal transmission and PLE.