Double perovskite Cs$_2$AgBiBr$_6$ radiation sensor: synthesis and characterization of single crystals

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Received: 8 September 2021
Accepted: 24 December 2021
Published online: 16 January 2022
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ABSTRACT

Single crystals of lead-free halide double perovskite Cs$_2$AgBiBr$_6$ sensor material manifest a remarkable potential for application in radiation detection and imaging. In this study, the purity and crystallinity of solution-grown Cs$_2$AgBiBr$_6$ single crystals with cubic $Fm ar{3}m$ symmetry have been corroborated by powder XRD measurements, while the single crystal XRD patterns reveal the dominant {111} lattice planes parallel to the sample surfaces. A wider range of lower resistivity values ($10^6$–$10^9$ Ωcm) was obtained from the $I$-$V$ measurements compared to the $1.55 \times 10^9$–$6.65 \times 10^{10}$ Ωcm values from the van der Pauw method, which is typically higher for the Ag than for the carbon paint electrodes. Charge-carrier mobility values estimated from the SCLC method for the carbon paint-Cs$_2$AgBiBr$_6$ (1.90–4.82 cm$^2$V$^{-1}$s$^{-1}$) and the Ag-Cs$_2$AgBiBr$_6$ (0.58–4.54 cm$^2$V$^{-1}$s$^{-1}$) including the density of trap states ($10^9$–$10^{10}$ cm$^{-3}$) are comparable. Similar values of 1.89 cm$^2$V$^{-1}$s$^{-1}$ and 2.36 cm$^2$V$^{-1}$s$^{-1}$ are derived from the Hall effect measurements for a sample with carbon and Ag electrodes, respectively. The key electrical parameters including the X-ray photoresponse measurements indicate that the Cs$_2$AgBiBr$_6$ samples synthesized in this study satisfy requirements for radiation sensors.

Handling Editor: Kyle Brinkman.

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Introduction

Single crystals of hybrid methylammonium lead halide perovskite MAPbX$_3$ have demonstrated radiation detection capabilities comparable to those of the CdTe and (Cd, Zn)Te radiation sensor materials. The impressive performance of MAPbX$_3$ stems not only from its appreciably high values of resistivity $\rho$ (10$^7$–10$^8$ $\Omega$cm) and mobility-lifetime product $\mu\tau$ (1.2–4.1 $\times$ 10$^{-2}$ cm$^2$V$^{-1}$) but also from low density of trap states $n_{trap}$ (10$^9$–10$^{10}$ cm$^{-3}$) [1–6]. However, radiation sensors with even higher $\rho$ and $\mu\tau$ are required to enhance charge-carrier transport and collection efficiency and in turn achieve lower detection limits and higher sensitivity of devices used in X-ray security screening and medical diagnostics.

Related inorganic semiconductor material Cs$_2$AgBiBr$_6$ with a double perovskite structure has been proposed as a stable alternative radiation sensor due to its improved thermodynamic stability, absence of toxic lead, suppressed ion migration including a higher stopping power attributed to the heavier constituent elements. Compared to the MAPbX$_3$, single crystals of Cs$_2$AgBiBr$_6$ have an indirect bandgap $E_G$ of 2.1 eV, higher $\rho$ (10$^9$–10$^{11}$ $\Omega$cm), similar $n_{trap}$, modest $\mu$ (0.5–12 cm$^2$V$^{-1}$s$^{-1}$), lower $\mu\tau$ of 2.48–5.95 $\times$ 10$^{-3}$ cm$^2$V$^{-1}$s$^{-1}$, and similar sensitivity of 105–1974 $\mu$Gy$_{air}$cm$^{-2}$ and detection limits of 45.7–59.7 nGy$_{air}$s$^{-1}$ [7–12]. These electrical and radiation detection performance parameters reflect beneficial chemical composition and crystal structure of the Cs$_2$AgBiBr$_6$ radiation sensor material.

Cs$_2$AgBiBr$_6$ belongs to the elpasolite class of materials ($A_2B^+B^{3+}X_6$) with the rock-salt arrangement of the $B$-crystallographic site cations in the double perovskite lattice structure described by the cubic space group $Fm\overline{3}m$, which tolerates greater substitutional flexibility than the MAPbX$_3$ [13–15]. The structure is based on a network of corner-sharing [AgBr$_6$]$^{5-}$ and [BiBr$_6$]$^{3-}$ octahedra with the Cs$^+$ cation at the $A$ site (Fig. 1). A weakness in the electrical performance of Cs$_2$AgBiBr$_6$ has its origin in the

![Image](https://example.com/image1.png)

**Figure 1** A unit cell of a single crystal of Cs$_2$AgBiBr$_6$ double perovskite. The network of corner-sharing octahedra, [AgBr$_6$]$^{5-}$ (grey) and [BiBr$_6$]$^{3-}$ (purple), with Cs cations (green) occupying the A-crystallographic sites.
electrical isolation of the two types of octahedra resulting in zero electronic dimensionality and consequently larger effective masses of charge carriers [16]. In addition, owing to the crystal structure and composition, a stronger charge carrier-lattice coupling compared to that in the MAPbX₃ can cause self-trapped charges and inevitably lead to limited μ [17–19]. In contrast, suppressed ion migration arising from the ordered crystal structure, stronger electrostatic interaction between the Cs⁺ and Br⁻ including increased ion migration activation energy (348 meV) and longer ion diffusion barrier of the most mobile defect, V₂Br (0.33 eV), permits application of a larger external bias to collect more efficiently charge carriers [7]. Indeed, enhanced charge-carrier transport is attributed to the high Ag⁺/Bi³⁺ ordering along the (111) lattice planes that are orthogonal to the < 111 > direction, which is coincident with a body diagonal of the cubic lattice with a sequence of …Ag-Cs-Bi-Cs-Ag… ions. Therefore, controlled crystal growth methods are required to synthesize Cs₂AgBiBr₆ single crystals with the dominant (111) crystal planes.

Growth of Cs₂AgBiBr₆ single crystals from supersaturated low-temperature T solutions proceeds via spontaneous nucleation as the T is reduced to room T [7–9, 14, 15]. Both the energy of volume gain and the energy of nucleation growth can overcome the energy of surface increase (energy loss). Growth occurs close to the equilibrium condition and at the solid-nutrient liquid interface via transport of matter and energy. A number of growth stages, which are based on a seed dissolution-regrowth approach, are required to synthesize larger crystals whilst the equilibrium is kept in the solution and outside the nucleation region to prevent secondary nucleation. A regulated cooling crystallisation procedure permits control of the T and growth rate parameters. Development of the (111) planes is enhanced through a slow growth rate, while the (100) and (110) planes are progressively eliminated through a faster growth rate [9]. In the early stage, Cs₂AgBiBr₆ single crystals develop regular octahedron form (111). Later, the growth of the (111), (111) (111), (111), and (111) planes located at the lateral crystal faces is restricted relative to the (111) and (111) planes located at the two opposite crystal faces. The final crystal form is pseudocubo-octahedral with the two largest crystal faces; one triangular face with (111) and the opposite pseudo-hexagonal face with (111), which is consistent with the 3-fold roto-inversion symmetry. Therefore, the size and shape of crystal faces and their angular relationships are determined not only by the shape of the unit crystal cell in the Fm 3m but also by the crystal growth conditions such as T dependent growth rates, direction of flow of solution, and distribution of solutes at different crystal-nutrient liquid interfaces and their frequency of consumption [9].

Theoretical calculations indicate that VAg (acceptor) and A_i (donor) are the most important shallow defects, BiAs (donor) is the most important deep defect, whereas V₂Br is both a deep acceptor and a shallow donor defect [20, 21]. The trap density states present near the crystal surfaces are most likely V₂Br; however, owing to their shallow energy (~80–90 meV) the carrier diffusion lengths exceeding 1 μm are still achievable [23]. Recent research has revealed that a Bi-poor/Br-rich growth condition can produce Cs₂AgBiBr₆ single crystals with suppressed density of deep electron traps BiAs and V₂Br [20], but this non-stoichiometry does not contribute to higher μ values [22].

A few measures have been employed to generate single crystal-based devices with enhanced performances. These include substitution of Cs⁺ cations at the A-crystallographic site (e.g., phenylethylamine bromide) to improve degree of ordering [BiBr₆]³⁻ and [AgBr₆]³⁻ octahedra [9] and post-growth optimisation such as thermal annealing and surface cleaning with isopropanol [7], crystal cleaving [23] and optimisation of metal–semiconductor contact interfaces [24]. Despite demonstrated progress, a number of issues regarding microstructural investigation and electrical characterisation of pristine Cs₂AgBiBr₆ single crystals remain to be addressed.

In particular, publications do not offer insights into microstructural features of single crystals, which reflect the growth stages and progressive advances in growth conditions. They tend to focus on the space-charge-limit current (SCLC) method to derive majority of electrical performance parameters (ρ, trap-filled limit voltage V_TFL and in turn ntrap and μ) except for the μ/7–9, 25). One of the weaknesses is that the studies tend to report only the forward I-V scans, but with an inconsistent range of applied bias voltage. Another weakness is that they are limited to reporting the V_TFL from the intersection between the tangents of the low-voltage regime and the trap-filled-limited TFL regime. This preference overlooks an
alternative calculation from the intersection between the tangent of the space-charge-limited SCL regime and the TFL regime that can yield a more accurate value for the \( n_{trap} \) because the free charge-carrier density becomes larger than the number of traps \([26]\).

Such weaknesses and inclinations in reporting render the correlation of key electrical parameters ambiguous. The common approach to the SCLC method has been recently reviewed and a set of recommendations for performing the \( I-V \) scan measurements based on experimental measurements and on drift–diffusion simulations using the MAPbBr\(_3\) have been suggested \([27]\). We consider these remarks and proposals relevant and present a more comprehensive electrical characterisation approach to acquire the key electrical parameters on the Cs\(_2\)AgBiBr\(_6\) radiation sensor material.

We focus on exploring advances in crystal growth through comparison of microstructural features recorded by crystals synthesised in a preliminary study with those using an advanced growth approach. Both the SCLC method and the Hall effect measurements in van der Pauw geometry are used to derive electrical performance parameters. We account for the similarities and differences in the \( I-V \) curves for the Ag- Cs\(_2\)AgBiBr\(_6\) and carbon paint-Cs\(_2\)AgBiBr\(_6\) contacts that are measured in the forward and reverse direction in the applied bias range \( \pm 100 \, \text{V} \). The bias in the measurements using different Keithley devices is assessed. However, variations in the determined values are clearly inevitable due to the differences in the measurement setup.

The findings of this research provide insights into the growth of red–orange \( 8 \times 10 \times 3 \, \text{mm}^3 \) single crystals of Cs\(_2\)AgBiBr\(_6\) from an assessment of microstructural features. The two opposite crystal faces (a triangular shape and a pseudo-hexagonal shape with \{111\} lattice planes) are consistent with the 3-fold roto-inversion symmetry. They are devoid of trigonal terraces, which are detrimental to charge-carrier transport. A narrower range of \( \mu \) (1.89–2.36 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \)) and higher range of \( \rho \) (1.55 \( \times 10^9 \)–6.65 \( \times 10^{10} \, \Omega \text{cm} \)) are derived from the van der Pauw and Hall effect measurements, respectively, compared to those derived from the \( I-V \) measurements \( (10^6–10^9 \, \Omega \text{cm} \text{ at} 0.58–4.82 \, \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) using either Ag or carbon paint electrodes. Overall, these parameters including the \( n_{trap} \) \( (10^9–10^{10} \, \text{cm}^{-3} \) are in accord with the literature values. The X-ray radiation photoresponse measurements performed on the Exp4 sample suggest suitability of all samples for radiation detection. Our studies contribute to better understanding of impressive potential of this double perovskite material in radiation detection.

Materials and methods

Initial growth of Cs\(_2\)AgBiBr\(_6\) single crystals has in general followed the controlled cooling crystallisation method of Yin et al. \([8]\). Seed crystals were prepared from a boiling 66 mM solution that was cooled down to room T at 0.5 °C/h. Large crystals were grown from a 66 mM solution prepared by dissolving Bi\(_2\)O\(_3\) (1.5184 g, ChemPur), AgBr (1.2735 g, AlfaAesar), CsBr (5.7668 g, Aldrich Chemical) in boiling HBr (100 ml 48 w%, Sigma Aldrich). A small excess of the precursor AgBr was added to suppress formation of the by-product phase Cs\(_3\)Bi\(_2\)Br\(_9\). The solution was heated at 90° for 30 min to dissolve and thus smoothen the very top surfaces of the added seed crystal, and then the solution was cooled down to room T at 0.5 °C/h for 150 h in a closed oven. Successful growth of even larger crystals was achieved by adding sodium acetate NaOAc (1 equivalent, C\(_2\)H\(_3\)NaO\(_2\)) as an additive \([28]\). This growth method yielded higher-quality red–orange, semitransparent Cs\(_2\)AgBiBr\(_6\) single crystals ca. \( 8 \times 10 \times 3 \, \text{mm}^3 \) with a pseudocubo-octahedral form and smoother pseudo-hexagonal crystal faces.

Characterisation techniques

A digital microscope Keyence VHX-5000 and a differential interference contrast microscope Zeiss Axio Imager that operates in reflected light and in transmitted light, respectively, were used to examine microstructures of the synthesized single crystals. The powder X-ray diffraction (PXRD) data were collected using the STOE STADI P transmission diffractometer. This device is equipped with filtered Mo-K\(_{\alpha}\) radiation (\( \lambda \) of 0.7093 Å), curved Ge (111) monochromators, and the MYTHEN 1 K silicon microstrip detector. The setup included the Debye–Scherrer scan mode, a fixed sample, and the detector. The processing of data was performed using the STOE WinXPOW software program.

Single-crystal XRD \( 2\theta \) scan measurements were obtained using the Bruker D8 Discover
dilfractometer. This device features a high-resolution Cu-Kα radiation source (λ of 1.54060 Å Kα1 and λ of 1.54439 Å Kα2), a focusing Goebel mirror as the primary monochromator including an 18 mm anti-scatter slit and a 0.5 mm divergence slit in a fixed mode, and a line focus silicon strip detector LynxEye Xe. The generator was set to 40 mA and 40 kV. The XRD data acquisition and processing were performed using the Bruker Diffrac.EVA software® and the Crystal Impact Match! software.

Electrical characterisation measurements were performed using the Keithley source meter unit (SMU) 2450, an electrometer 6517B model, and a shielded test fixture model 8101 4TRX to minimise electrostatic interferences by shielding and to control leakage current in the cables and connectors by guarding. The purpose of the electrical characterisation was two-fold. The I-V measurements were carried out to determine whether the Ag glue-Cs2AgBiBr6 and Plano® carbon paint-Au electrodes were deposited on the two opposite crystal faces (Supplementary Information Fig. S1a). The area of Ag glue and carbon paint electrodes deposited on a crystal surface was estimated to 0.0227 cm². It was assumed that the contacts do not inject charge carriers at the applied voltages.

In principle, in a low-voltage range, I-V curves follow Ohm’s law (a linear dependence of I on V). In a mid-voltage range, a trap-filled (TFL) regime develops due to the presence of electronic trap states and the I-V curves in a log–log plot have a slope of more than 2 [32]. The ntrap is calculated from the equation:

\[ V_{TFL} = qn_{trap}L^2/\varepsilon_0\varepsilon_r \]

where \( L \) is the thickness, and \( \varepsilon_0 \) and \( \varepsilon_r \) are the vacuum and relative dielectric constants, respectively [33]. In a high-voltage range, a trap-free regime develops due to filling of the traps with the injected free carriers and consequently, the current is limited by the build-up of space-charge. The I-V curves in a log–log plot have a slope of 2 [29]. The current density follows the Mott-Gurney law:

\[ J = (9/8)\mu\varepsilon_0\varepsilon_r(V^2/L^3) \]

where \( V = V_{TFL} \); hence,

\[ \mu = (8/9)JL^3/V_{TFL}^2\varepsilon_0\varepsilon_r \]

Most publications report the \( V_{TFL} \) calculated from the crossing point between the tangent of the Ohmic I-V curve and the TFL I-V curve, which is then used to estimate the value of \( n_{trap} \). However, a more accurate value can be obtained from the \( V_{TFL} \) at the crossing point between the SCLC I-V curve and the TFL I-V curve [26]. From the I-V measurements conducted at different source delay times, it is inferred that the I-V curves measured at 20 s delay...
time is sufficient to reveal the three regimes required to estimate reliable $\rho$, $V_T$, $\mu$, and $n_{tray}$ values using the SCLC method.

For the van der Pauw method, the Ag glue and the carbon paint electrodes were deposited on a hexagonal-shaped crystal face as shown in the Supplementary Information Fig. S1b. The preliminary Hall-effect measurements on the sample Exp4 were performed in van der Pauw geometry by applying a magnetic field $B_z$ of 0.85 T perpendicular to sample’s surface. From these measurements, the $n$ and $p$, $\mu$, and the charge-carrier type were determined. To reduce the effect of biasing and to validate the recorded values, several measurements were performed using the Keithley model 6517B electrometer and the SMU 2450 in different configurations (a voltmeter, an ammeter, and a voltage/current source). All $I-V$, van der Pauw, and Hall effect measurements were repeated at least twice to ensure stability of the Keithley devices and reproducibility of the recorded values, and in turn to increase reliability of calculated values.

The Struer’s GmbH MD-Nap polishing pad, DP-lubricant yellow, and aerosol DP-P spray $1/4$ $\mu$m were used to mechanically remove the Ag glue and carbon paint electrodes from the surfaces of the Cs$_2$AgBiBr$_6$ crystals. The crystals were then washed in isopropanol.

**Results**

**Microstructure**

Initial crystal growth yielded pseudocubo-octahedral single crystals of Cs$_2$AgBiBr$_6$ with an average size of $5 \times 5 \times 1.5$ mm$^3$. All samples have a top crystal face with a triangular shape and the opposite bottom face...
with a pseudo-hexagonal shape (Fig. 2a; Exp0) consistent with a $\bar{3}$-fold roto-inversion symmetry along the $<111>$ growth direction in the cubic lattice ($Fm\overline{3}m$). The triangular face exhibits prominent (111) facets at 120° and off-facet regions that reflect a free growth, but intermittent stages of growth and dissolution (dark grey to black striations) as a consequence of a variable T gradient. In the off-facet regions, trigonal terraces appear in variable intensity and distribution with narrower and wider spaced striations developed due to slower growth rates and faster rates, respectively. These pronounced non-symmetrical features produce not only a rougher crystal surface and a non-uniform sample thickness but evidently, degrade electrical performances. The opposite face with a pseudo-hexagonal shape and $\bar{3}$-fold roto-inversion symmetry is defined by the edges that have been formed through the intersection between alternating opposite and inclined other crystal faces. It has neither facets nor terraces (Fig. 2b; Exp0). Instead, it is riddled with numerous circular and rectangular-shaped impurities (e.g., solvated precursor ions). In general, unstable crystal-solution interfaces cause incorporation of impurities into the growing crystal that can cluster to form precipitates.

**Figure 2** continued.

**Figure 3** PXRD pattern (Mo-$K_{\alpha}$ radiation source) for the Cs$_2$AgBiBr$_6$ powder samples (a) and the XRD patterns (Cu-$K_{\alpha}$ radiation source) for the single crystals Exp1, Exp2, and Exp3 from bottom to top (b).
as a consequence of its growth on the bottom of a growth vessel.

The improved crystal growth produced larger crystals ($8 \times 10 \times 3 \text{ mm}^3$) with flatter and smoother surfaces. Relative to the samples Exp2 and Exp3, the samples Exp1 and Exp4 are more tabular. The two largest and opposite crystal faces are flat and as such desirable for electrical characterisation and X-ray photoresponse measurements. These surfaces are devoid of pronounced trigonal terraces (e.g., Exp2; Fig. 2c–d). However, all samples have strained and fractured overgrowth zones due to stress imparted by a seed (Supplementary Information; e.g., Figure S2a and S2g–h), and some exhibit twin planes (Supplementary Information; e.g., Figure S2e).

### Crystal structure

The phase purity (absence of the precursors and extrinsic dopants) and crystallinity of all Cs$_2$AgBiBr$_6$ samples have been verified from the PXRD data (Fig. 3a). The refined unit-cell parameters $a = b = c = 11.2773$ (7) Å, $\alpha = \beta = \gamma = 90^\circ$ and the unit cell volume of 1434.22 (14) Å$^3$ are consistent with the cubic crystal system and the Fm $3m$. The data are given in Supplementary Information (Table S1). High ordering of Ag$^+$ and Bi$^{3+}$ octahedra cations is apparent from the XRD patterns for single crystals that depict peaks arising solely from the [111] family of planes (Fig. 3b).

Refinement of the single crystal data yielded lattice parameter value of $a = b = c = 11.2548$ (7) Å and the unit cell volume of 1425.6 4(16) Å$^3$, which proves the excellent data quality (Supporting Information; Table S2).
Electrical characterisation

I-V measurements

The I-V scans for the carbon paint-Cs$_2$AgBiBr$_6$ are symmetrical in the low voltage range but fluctuate in the high voltage range (Fig. 4). The overlapping ohmic regimes range from $-11$ to $3$ V for the sample Exp2 with the $\rho$ of $10^8$–$10^7$ $\Omega$cm, to $-50$ V to $17$ V for the Exp3 with the $\rho$ of $5.88$–$9.23 \times 10^8$ $\Omega$cm (Table 1). Also, the maxima levels of the measured current over the whole bias range for the carbon paint-Exp2 and carbon paint-Exp3 contacts (Fig. 4c and e) are unequal and the shape of the I-V curves does not mirror those of the carbon paint-Exp1 and carbon paint-Exp4 contacts (Fig. 4a and g).

In the mid-to high-voltage range, the overlapping ohmic, TFL, and SCLC regimes of the I-V curves for the carbon-Exp1 (Fig. 4b) preclude clear identification of the $V_{TFL}$ and in turn calculation of $\mu$ and $n_{trap}$; hence, the values can be estimated only with reference to other samples (Table 1). The forward I-V scan for the carbon-Exp2 has both the SCLC and TFL regimes (Fig. 4c). The $\mu$ of $160.6$ cm$^2$V$^{-1}$ s$^{-1}$ at $V_{TFL}$ of $9.17$ V is overestimated and the $n_{trap}$ is $4.89 \times 10^9$ cm$^{-3}$ is underestimated. The more realistic values of $27.5$ cm$^2$V$^{-1}$ s$^{-1}$ and $1.76 \times 10^{10}$ cm$^{-3}$ have been calculated at $V_{TFL}$ of $32.9$ V. Only the TFL regimes can be identified in the I-V scans of the carbon-Exp3 (Fig. 4e; Table 1). The TFL and SCLC regimes of the reverse I-V scan for the carbon Exp4 yield $38.1$ cm$^2$V$^{-1}$ s$^{-1}$ and $5.14 \times 10^9$ cm$^{-3}$ at $V_{TFL}$ of $7.94$ V and $28.9$ cm$^2$V$^{-1}$ s$^{-1}$ and $2.47 \times 10^{10}$ cm$^{-3}$ at $V_{TFL}$ of $38.1$ V. The forward scan has the linear and SCLC regimes in the mid-to high-voltage range (Fig. 4h); hence, the $\mu$ and $n_{trap}$ values are estimated (Table 1).

Reasonably symmetrical I-V curves for the Ag-Cs$_2$AgBiBr$_6$ were obtained over the applied bias range in both forward and reverse scan directions (Fig. 5). In the low-voltage range, where the curves overlap, the contacts exhibit the ohmic behavior. The narrowest overlap is from $-10$ to $4$ V for the Exp1 and Exp2 samples with the $\rho$ of $1.02 \times 10^8$–$1.08 \times 10^9$ $\Omega$cm (Fig. 5a and c; Table 2), whereas the widest range is from $-60$ to $10$ V for the Exp3 (Fig. 4e) with the $\rho$ of $1.74$–$2.97 \times 10^9$ $\Omega$cm (Table 2). The maximal values of the measured current for the Ag-Exp2 and Ag-Exp3 contacts (Fig. 5c and e) are neither equal to nor does the shape of the I-V curves mirror those of
Resistivity values are calculated from the most linear segment along the scans overlap. Area of the contacts 0.0227 cm$^2$. Top trigonal crystal face T; Bottom pseudo-hexagonal crystal face B.

| Sample | Contacts | L (mm) | U (V) | $\rho$(Ωcm) | $V_{TFL}$(V) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) | $n_{trap}$(cm$^{-3}$) |
|--------|----------|--------|-------|-------------|-------------|----------------|----------------|
| Exp1   | T + B −  | 4.20   | − 5 to 25 | $4.02 \times 10^8$ | 28.6 | 4.82 | 1.52 $\times 10^{10}$ |
|        | B + T −  |       |         | $4.19 \times 10^8$ | 34.2 | 3.84 | 1.83 $\times 10^{10}$ |
| Exp2   | T + B −  | 3.25   | − 11 to 3 | $1.09 \times 10^7$ | 9.17 | 160.6 | 4.89 $\times 10^9$ |
|        | B + T −  |       |         | $6.93 \times 10^6$ | 3.40 | 1.18 $\times 10^9$ |
| Exp3   | T + B −  | 2.65   | − 50 to 17 | $5.88 \times 10^6$ | 29.5 | 4.50 | 2.37 $\times 10^9$ |
|        | B + T −  |       |         | $9.23 \times 10^6$ | 54.2 | 2.41 | 2.89 $\times 10^9$ |
| Exp4   | T + B −  | 2.95   | − 11 to 7 | $2.73 \times 10^8$ | 75.5 | 1.90 | 5.02 $\times 10^9$ |
|        | B + T −  |       |         | $1.17 \times 10^8$ | 7.94 | 38.1 | 5.14 $\times 10^9$ |

Sample thickness L; Trap filled limit voltage $V_{TFL}$; density of trap states $n_{trap}$; resistivity $\rho$; Ohmic voltage range $U$; permittivity of vacuum $\varepsilon_0$ of $8.85 \times 10^{-14}$ Fcm$^{-1}$; relative permittivity of Cs$_2$AgBiBr$_6$ $\varepsilon_r$ of 51 [7]; elementary charge $q$ of $1.602176 \times 10^{-19}$ C. The resistivity values are calculated from the most linear segment along the I-V curve and where the curves for the forward and the reverse scans overlap. Area of the contacts 0.0227 cm$^2$. Top trigonal crystal face T; Bottom pseudo-hexagonal crystal face B.

Table 1 Calculated $\rho$, $\mu$ and $n_{trap}$ from the I-V curves for the Cs$_2$AgBiBr$_6$ sample using Plano® carbon paint electrodes

The absence of distinctive TFL and SCLC regimes preclude clear definition of the I-V curves for the Cs$_2$AgBiBr$_6$ contacts (Fig. 5a and g). In the mid-to high-voltage range, the I-V curves in both scan directions are characterised by fluctuations. The data scattering is more prominent in case of the carbon-Exp2, Exp3, and Exp4, and the Ag-Exp1 and Ag-Exp2. The carbon-Exp3 and Ag-Exp3 exhibit saturation in current at low values for both scan directions in the negative bias range, while there is a significant mismatch in the current maxima recorded by the Ag-Exp3 for the two scan directions under positive bias range. Both contacts also share a number of key features. The ohmic range is similar, the three segments are absent in the log-log plots of I-V curves for the sample Exp1, while the Exp1 and Exp4 exhibit similar maxima current levels. In general, the Ag-Cs$_2$AgBiBr$_6$ contacts are more resistive than the carbon paint-Cs$_2$AgBiBr$_6$ and yield slightly lower $\mu$, but similar $n_{trap}$.

Van der Pauw method and Hall-effect measurement results

The highest $\rho$ values for both the Ag-Cs$_2$AgBiBr$_6$-Ag and the carbon-Cs$_2$AgBiBr$_6$-carbon configurations are on the order of $10^{10}$ Ωcm, with the maximum value of $6.65 \times 10^{10}$ Ωcm calculated for the Ag-Exp4. These values were determined from the measurements using the 6517B as a voltage source (5 V or 10 V) and an ammeter in combination with the SMU 2450 as a voltmeter and also from the measurements using the SMU 2450 in the constant current mode (1 nA or 2 nA) (Table 3). At higher bias (20 V) and current (10–20 nA) values, the charges are injected at the electrode interfaces and $\rho$ values are reduced to $10^9$ Ωcm. The samples contacted with Ag electrodes demonstrate higher resistivity and, hence, a more efficient electrical performance. The preliminary Hall-effect measurements yielded the $\mu$ and $p$ values of $1.89$ cm$^2$V$^{-1}$s$^{-1}$ and $1.10 \times 10^{10}$ cm$^{-3}$ for the...
carbon-Exp4 and $2.36 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $1.15 \times 10^{10}\text{ cm}^{-3}$ for the Ag-Exp4.

**X-ray photoresponse**

A plot of calibration data is shown in Fig. 6a. An almost linear dependence of the photocurrent density on the dose rate can be observed for the fixed bias of $\pm 2\text{ V}$ and $-10\text{ V}$, with higher values at $-10\text{ V}$ (Fig. 6b). When the detector is biased to $-10\text{ V}$, its maximum sensitivity is $42\text{ \mu CGy}_{\text{air}}^{-1}\text{ cm}^{-2}$ at a dose rate of $75\text{ \mu Gy}^{-1}$. The relationship between the sample photocurrent density and the bias voltage from $-20$ to $20\text{ V}$ has been determined by fixing the X-ray tube current to $5\text{ mA}$ and the sample-to-source distance to $1000\text{ mm}$ (Fig. 6c). The $I-V$ curve is in general symmetrical over the voltage range.

**Discussion**

A number of important differences between the crystals synthesized during a preliminary study and those using a more advanced approach indicate an overall improvement in crystal growth method. Obviously, the crystal size has doubled and surfaces are smoother and flatter. However, the most evident microstructural improvement is the absence of prominent trigonal growth terraces with narrower and wider spaced striations, which reflect slower and faster growth rates, respectively. These features including strained crystal lattice and defects degrade crystal quality and as such have an evident impact on the electrical performance. A regulated crystal growth of Cs$_2$AgBiBr$_6$ single crystals requires controlling the crystal growth parameters and consequently the stability of crystal-nutrient interface. A too high $T$ rate results in a higher concentration of defects, whereas a too low $T$ rate promotes secondary nucleation. A fast growth rate introduces defects and morphological instability due to kinetic processes at the crystal-nutrient interface, whereas a slow growth
rate causes formation of volume defects due to clustering of vacancies/interstitials, dislocations, and plane defects, or formation of precipitates. Further improvements in crystal growth are required to increase the size and reduce density of defects in crystals. The PXRD and the single crystal XRD measurement results are in accord with the literature [7–10, 14, 15].

With regard to electrode type used for contacting purposes, typically Au is evaporated on the opposite crystal faces of a Cs$_2$AgBiBr$_6$ single crystal [7]. The electrode work function $\phi$ and whether it matches the conduction band $E_C$ or the valance band $E_V$ of a semiconductor has an impact on the dominant charge-carrier transport [31]. Hence, Au with $\phi_{Au}$ of 5.10–5.47 eV matches more closely the $E_V$ of the Cs$_2$AgBiBr$_6$ at 5.64 eV [24] and the Au-Cs$_2$AgBiBr$_6$-Au has been reported as a weakly p-type (hole-only devices) [7]. In this study, Ag glue and Plano® carbon paint electrodes were used. The Ag electrode $\phi_{Ag}$ of 4.26 eV matches the $E_C$ of the Cs$_2$AgBiBr$_6$ at 3.64 eV [24], thus, the Ag-Cs$_2$AgBiBr$_6$-Ag is an electron-only device. The carbon paint $\phi_{CP}$ of ca. 4.62 eV matches both the $E_C$ (0.98 eV) and the $E_V$ (1.02 eV) of Cs$_2$AgBiBr$_6$ resulting in a double-carrier carbon paint-Cs$_2$AgBiBr$_6$-carbon paint device. Because the Fermi energy $E_F$ of Ag is close to the $E_F$ of Cs$_2$AgBiBr$_6$, which is at 4.852 eV, injection barrier $q\phi_{inj}$ at the interface can form [30]. However, the effect of $q\phi_{inj}$ on the Ag-Cs$_2$AgBiBr$_6$-Ag and carbon paint-Cs$_2$AgBiBr$_6$-carbon paint devices is considered low, because of the sample thicknesses (2.65–4.2 mm).

The mismatch in the current maxima values of the measured I-V curves for the Exp2 and Exp3 over the whole applied bias range (Fig. 4c and e; Fig. 5c and e) do not imply rectifying contacts, because this feature is characteristic for both the Ag and carbon paint electrodes. There is no unique justification to account for this inconsistency. In terms of the nature of samples, both the Exp2 and Exp3 have thinner rims than the centers, where the seed is located. The overgrowth zones grew as unsymmetrical vertical stairs and developed not only uneven surfaces but also variable defect densities (e.g., twin boundaries, dislocations, inclusions, and impurities). Another possible explanation is a surface-conduction effect. However, the possibility of formation of an injection barrier associated with degradation of the double
Table 2 Calculated values for the $\rho$, $\mu$ and $n_{trap}$ from the I-V curves for the Cs$_2$AgBiBr$_6$ samples using Ag glue electrodes

| Sample | L (mm) | Contacts | $U$ (V) | $\rho$(\Omega cm) | $V_{TFL}$(V) | $\mu$ (cm$^2$V$^{-1}$s$^{-1}$) | $n_{trap}$(cm$^{-3}$) |
|--------|--------|----------|---------|------------------|-------------|-----------------|-----------------|
| Exp1   | 4.20   | T + B –  | -10 to 4 | $8.13 \times 10^8$ | 35.0        | $1.87 \times 10^{10}$ |                 |
|        |        | B + T –  |         | $1.08 \times 10^9$ | 51.0        | $2.72 \times 10^{10}$ |                 |
| Exp2   | 3.25   | T + B –  | -10 to 4 | $1.02 \times 10^8$ | 8.33        | $4.44 \times 10^9$   |                 |
|        |        | B + T –  |         | $1.20 \times 10^8$ | 33.6        | $1.79 \times 10^9$   |                 |
| Exp3   | 2.65   | T + B –  | -60 to 10| $2.97 \times 10^9$ | 67.9        | 0.07             | $3.62 \times 10^9$|
|        |        | B + T –  |         | $1.74 \times 10^9$ | 15.9        | 3.08             | $8.50 \times 10^9$|
| Exp4   | 2.95   | T + B –  | -14 to 10| $8.19 \times 10^8$ | 53.2        | 0.58             | $3.44 \times 10^9$|
|        |        | B + T –  |         | $8.19 \times 10^8$ | 66.5        | 0.64             | $4.31 \times 10^9$|

Sample thickness L; Trap filled limit voltage $V_{TFL}$; density of trap states $n_{trap}$; resistivity $\rho$; Ohmic voltage range $U$; permittivity of vacuum $\varepsilon_0$ of $8.85 \times 10^{-14}$ Fcm$^{-1}$; relative permittivity of Cs$_2$AgBiBr$_6$ $\varepsilon_r$ of 51 [7]; elementary charge $q$ of $1.602176 \times 10^{-19}$ Ce$^{-1}$. The resistivity values are calculated from the most linear segment along the I-V curve and where the curves for the forward and the reverse scans overlap. Area of the contacts 0.0227 cm$^2$. Top trigonal crystal face T; Bottom pseudo-hexagonal crystal face B.

Table 3 $\rho$ values for the Cs$_2$AgBiBr$_6$ samples with Ag glue and carbon paint electrodes

| Setup | Exp1-Ag | Exp2-Ag | Exp3-Ag | Exp4-Ag | Exp1-carb | Exp2-carb | Exp3-carb | Exp4-carb |
|-------|---------|---------|---------|---------|-----------|-----------|-----------|-----------|
| 3a    | $4.88 \times 10^{10}$ | $2.73 \times 10^{10}$ | $4.39 \times 10^{10}$ | $5.40 \times 10^{10}$ | $7.37 \times 10^9$ | $7.50 \times 10^9$ | $5.09 \times 10^9$ | $5.52 \times 10^9$ |
| 3b    | $3.51 \times 10^{10}$ | $2.34 \times 10^{10}$ | $2.67 \times 10^{10}$ | $6.65 \times 10^{10}$ | $3.55 \times 10^{10}$ | $2.34 \times 10^{10}$ | $2.67 \times 10^{10}$ | $6.50 \times 10^{10}$ |
| 2a    | $1.17 \times 10^{10}$ | $1.54 \times 10^{10}$ | $1.22 \times 10^{10}$ | $9.29 \times 10^9$ | $7.09 \times 10^9$ | $2.49 \times 10^9$ | $9.40 \times 10^9$ | $1.96 \times 10^9$ |
| 1a    | $1.05 \times 10^{10}$ | $9.49 \times 10^9$ | $1.11 \times 10^{10}$ | $9.67 \times 10^9$ | $7.21 \times 10^9$ | $1.55 \times 10^9$ | $4.11 \times 10^9$ | $3.12 \times 10^9$ |
| 1b    | $8.48 \times 10^9$ | $4.75 \times 10^9$ | $3.94 \times 10^9$ | $1.04 \times 10^10$ | $8.48 \times 10^9$ | $4.75 \times 10^9$ | $3.94 \times 10^9$ | $1.04 \times 10^10$ |
| 3c    | $8.11 \times 10^9$ | $4.53 \times 10^9$ | $3.76 \times 10^9$ | $5.24 \times 10^9$ | $8.11 \times 10^9$ | $4.53 \times 10^9$ | $3.76 \times 10^9$ | $5.24 \times 10^9$ |
| 2b    | $6.20 \times 10^9$ | $3.58 \times 10^9$ | $2.88 \times 10^9$ | $6.32 \times 10^9$ | $6.33 \times 10^9$ | $3.54 \times 10^9$ | $2.97 \times 10^9$ | $6.32 \times 10^9$ |

Specific resistivity $\rho$ calculated from the van der Pauw method; sample thickness: 0.42 mm Exp 1; 2.35 mm Exp 2; 1.95 mm Exp 3; 2.95 mm Exp 4; setup: (1a; 1b) SMU 2450 in the constant current (1 nA; 2 nA) and measure voltage mode; (2a, 2b) SMU 2450 in the constant voltage (5 V; 10 V) and measure current mode; (3a, 3b, 3c) electrometer 6517B as a voltage source and an ammeter (5 V; 10 V; 20 V) and SMU 2450 as a voltmeter.

Perovskite material in the vicinity of the electrode at 100 V cannot be excluded.

For all samples, the I-V curves in both scan directions are characterised by fluctuations in the mid-to high-voltage range. Several possible explanations for the observed variation in current behavior exist. It can be attributed to drift and diffusion of charge carriers including migration of Br$^-$ anions and their accumulation at an anode and a cathode (saturation current). Other accounts include surface-conductivity effect of the two opposite crystal faces that are characterised by different growth features and defects such as $V_{Br}$ and $Bi_{Ag}$, linear dislocations causing abrupt change in atomic arrangement, twin planes, cracks and inclusions including precipitates. According to these data, we can infer that nature of the samples and electrodes has a strong bearing on the character of the I-V curves.

There are a number of important similarities and differences between the SCLC and Hall-effect measurements. Both measurements are influenced by the type of the electrodes (carbon and Ag) and both have
The limitations in derivation of the \( \mu \). The SCLC method is used to record current flowing between two electrodes deposited on the opposite crystal surfaces as a function of applied bias. Limitation of the SCLC method is in a clear definition of the SCLC regime reached higher voltages. But, the \( I-V \) curves rarely exhibit the three well-defined regimes (the ohmic, trap-filled, and trap-free regimes). Using \( \mu \) value derived in the space-charge-limited regime and the \( \rho \) value derived in the ohmic regime to calculate the charge carrier concentration can be misleading because each regime is characterised by a specific behavior of charge carriers depending on applied bias [29, 30]. On the other hand, the Hall-effect measurements involve measurements of current and voltage across the crystal (between diagonal contacts, for example AC current and DB voltage). Limitation of the Hall effect in van der Pauw geometry is in deflection of charge carriers in a magnetic field and \( \rho \) calculated from the van der Pauw measurements of current and voltage along the edges of a crystal surface (for example, AB current and DC voltage). The preliminary Hall-effect measurements indicate that the Exp4 sample is a p-type semiconductor in case of both Ag and carbon paint electrodes with a narrow range of \( \mu \) values 1.89–2.36 cm\(^2\)V\(^{-1}\)s\(^{-1}\). An improved setup is required to confirm these values and investigate the remaining samples.

In case of the van der Pauw measurements, unsymmetrical growth zones and defects are also the cause of the mismatch in the current and voltage values measured for reversed polarities. Nevertheless, the \( \rho \) values for both the Ag-CS\(_2\)AgBiBr\(_6\)-Ag and the carbon-CS\(_2\)AgBiBr\(_6\)-carbon configurations are on the order of \( 10^{10} \) \( \Omega \)cm, with the maximum value of \( 6.65 \times 10^{10} \) \( \Omega \)cm, are within the range of the published values especially [7] and [8] (Table 4). Although the \( \rho \) data obtained in the SCLC method (carbon \( 10^6-10^8 \) \( \Omega \)cm and Ag \( 10^8-10^9 \) \( \Omega \)cm) and the van der Pauw (carbon \( 10^9 \) \( \Omega \)cm and Ag \( 10^9-10^{10} \) \( \Omega \)cm) were measured using the 2450 Keithley instrument, they differ on the order of \( 10^1 \) \( \Omega \)cm. This rather contradictory result can be explained in terms of the measurement procedure as discussed earlier and nature of the samples. The rims being more resistive along the pseudo-hexagonal crystals face, while the center of a sample, where the seed is located, is more conductive, due to higher density of defects and strained lattice. With respect to \( n_{trapp} \), the current values of \( 10^{10} \) cm\(^{-3}\) are mostly in agreement with the [24] and [25] (Table 4).

The X-ray photoresponse of the sample Exp4 was investigated in terms of the dependence of photocurrent density on the applied bias, the X-ray tube
current, and the source-sample distance. Its calculated maximum sensitivity of 42 μCGy⁻¹ cm⁻² at a dose rate of 75 μGy⁻¹ s⁻¹ and −10 V bias is in good agreement with Pan et al. [7], who reported 50 μCGy⁻¹ cm⁻² at 10 V bias. This study, therefore, indicates that the synthesized Cs₂AgBiBr₆ samples satisfy requirements for radiation sensors.

Further advances in the I-V measurements such as developing an in-house program that controls the measurements are necessary to more accurately assess the importance of source delay time and interval times between scan directions. Thermal annealing and optimisation of metal-semiconductor contacts can in future lead to enhanced performance of the double perovskite-based detector devices. Recently, it has been revealed that the self-trapping process is less severe at room T and can be tuned through electronic dimensionality and composition [19]. Hence, future studies will focus on investigating crystal growth and characterization of 2D layered (BA)₂CsAgBiBr₇ double perovskite material.

Table 4 Key electrical parameters for the Cs₂AgBiBr₆ single crystals derived from the SCLC method including radiation performance parameters

| Electrodes          | ρ(Ω cm) | V_TFL(V) | μ (cm²V⁻¹s⁻¹) | n_trap(cm⁻³) | Sensitivity (μCGy⁻¹ cm⁻²) | Dose rate (nGy⁻¹ s⁻¹) |
|---------------------|---------|----------|--------------|-------------|--------------------------|-----------------------|
| Au/pristine sample [7] | 10⁰     | 3.17     | 4.54 × 10⁹   |             |                          |                       |
| Au/annealed sample [7] | 10¹¹    | 11.81    | 1.74 × 10⁹   | 105         |                          | 59.7                  |
| Ag/pristine sample [24] | 3.48     | 0.49     | 3.58 × 10¹⁰  |             |                          |                       |
| Au/natural cooling sample [8] | 1.51 × 10⁹ | 1.70 | 1974         | 45.7        |                          |                       |
| Au/controlled cooling sample [8] | 1.35 × 10¹⁰ | 10.8 | 6.04 × 10⁹   | 165.5       |                          |                       |
| Au/pristine sample [9] | 5.18     | 2.25     | 1.16 × 10⁹   |             |                          |                       |
| Pristine sample [10] | 5.40 × 10⁹ | 52.4    | 1.44 × 10¹⁰  |             |                          |                       |
| Pristine sample [28] | 8.33 × 10⁹ | 5.02    | 1.16 × 10⁹   | 2772        |                          |                       |
| Au/pristine sample [25] | 5.40 × 10⁹ | 52.4    | 1.44 × 10¹⁰  |             |                          |                       |

Space-charge limit current SCLC method; resistivity ρ; trap-filled limit voltage V_TFL; charge carrier mobility μ; density of trap states n_trap. The charge carrier mobility-lifetime product μτ for a crystal grown using the controlled cooling method is 5.95 × 10⁻³ cm² V⁻¹ s⁻¹ and for a crystal grown using the natural cooling method is 1.36 × 10⁻⁴ cm² V⁻¹ s⁻¹ [8]; μτ of 2.48 × 10⁻³ cm² V⁻¹ s⁻¹ [25].

Conclusion

This work contributes to existing knowledge of Cs₂AgBiBr₆ radiation sensors by providing additional information on the crystal microstructures, electrical characterisation, and X-ray photoresponse measurements. As evidenced from investigation of microstructure, the advanced crystal growth has produced larger single crystals of Cs₂AgBiBr₆ with enhanced crystalline quality and improved electrical performances. The powder XRD measurement has verified the purity and crystallinity of the Cs₂AgBiBr₆ samples with cubic symmetry (Fm 3m). The single-crystal XRD patterns reveal the dominant {111} lattice planes parallel to the sample surface. The van der Pauw ρ values of 1.55 × 10⁹ to 10⁵ Ωcm are typically higher for the Ag electrodes and suggest an improved electrical performance compared to that of the carbon electrodes. The ρ values, the Hall effect, and SCLC estimated nτ values including the n_trap values are comparable with the published data. The key electrical parameters and the initial X-ray photoresponse measurements yielding the maximum sensitivity of 42 μCGy⁻¹ cm⁻² at a dose rate of 75 μGy⁻¹ s⁻¹ and −10 V bias indicate that the Cs₂AgBiBr₆ samples satisfy requirements for radiation sensors.

Acknowledgements

The following academic and research staff are gratefully acknowledged: Prof Andreas Danilewsky (Crystallography Institute) for constructive discussions on crystal growth and microstructure, Dr. Thilo Ludwig (IAAC) for the XRD measurements with the Bruker’s D8 Discover, and Ms. Jiaona Zou (FMF) for the initial assistance with the Zeiss Axio Imager and the Keithley instrument setup.
Author contributions

This study was a part of Ph.D. project undertaken by V. Murgulov. The manuscript was written through contributions of all authors. Data curation, investigation, methodology, formal analysis, validation, electrical characterization, writing original draft, writing review and editing, V. Murgulov; crystal growth, XRD measurements, review and editing, C. Schweinle and M.Daub; X-ray photoresponse measurements and data processing, manuscript review, V. Đedić; project administration, supervision and review, M. Federle, H. Hillebrech, and J. Franc. All authors have given approval to the final version of the manuscript.

Funding

Open Access funding enabled and organized by Projekt DEAL. This research received no external funding. No funding sources and grant/award numbers were allocated to authors.

Declarations

Conflict of interest The authors declare no competing financial interest.

Supplementary Information: The online version contains supplementary material available at http://doi.org/10.1007/s10853-021-06847-5.

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