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Interface engineering strategies towards Cs₂AgBiBr₆ single-crystalline photodetectors with good Ohmic contact behaviours†

Yangyang Dang, Guoqing Tong, Wentao Song, Zonghao Liu, Longbin Qiu, 
Luis K. Ono  and Yabing Qi *

Lead-free double perovskite materials have attracted much interest for optoelectronic applications due to their nontoxicity and high stability. In this work, centimetre-sized Cs₂AgBiBr₆ single crystals were successfully grown using methylammonium bromide (MABr) as the flux by a top-seeded solution growth (TSSG) method. The low-temperature crystal structure of Cs₂AgBiBr₆ single crystals was determined and refined. To investigate the interface problems between Cs₂AgBiBr₆ single crystals and electrodes, the optical band gap, X-ray photoelectron spectroscopy (XPS), and ultraviolet photoemission spectroscopy (UPS) measurements were performed on Cs₂AgBiBr₆ single crystals. More importantly, we investigated the photodetectors based on Cs₂AgBiBr₆ single crystals with different contact electrodes (Au, Ag, and Al). It is found that a good Ohmic contact with Ag electrodes enables excellent photo-response behaviors. Furthermore, we studied the photodetectors based on Cs₂AgBiBr₆ single crystals using Ag electrodes under room and low temperature conditions, which underwent phase transition. Cs₂AgBiBr₆ single crystal photodetectors show clear differences at room and low temperatures, which is caused by the work function changes of Cs₂AgBiBr₆ single crystals induced by the reversible phase transition. These attractive properties may enable opportunities to apply emerging double perovskite single-crystalline materials for high-performance optoelectronic devices.

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Introduction

Lead (Pb)-based hybrid perovskite materials have attracted tremendous attention owing to their outstanding properties when applied in photovoltaic devices.^{1,2} Power conversion efficiencies (PCEs) as high as 25.2% have been achieved for Pb-based perovskite solar cells.³ However, the toxicity and instability of Pb-based perovskite materials need to be solved. It is imperative to search for alternative perovskite materials containing only non-toxic elements. A strategy is to replace the toxic Pb²⁺ with two different oxidation states Ag⁺ and Bi³⁺ to form double perovskite materials.⁴ Several nontoxic candidates such as Cs₂AgBiX₆ (X = Cl, Br),⁵ (CH₃NH₃)₂AgBiBr₆⁶ and so on have been reported. In particular, Cs₂AgBiBr₆ is considered to be an appealing lead-free semiconducting material due to its promising optoelectronic properties.⁷ Woodward and coworkers

reported the solid-state synthesis and the crystal structure of Cs₂AgBiX₆ (X = Cl, Br) with the cubic system with *Fm* $\bar{3}$ *m* (no. 225) by powder X-ray diffraction (PXRD) experiments and Rietveld refinements.⁵ The computational design and the experimental synthesis of Pb-free halide double perovskites including the band gaps and stability of Cs₂AgBiX₆ (X = Cl, Br) were reported by Giustino and coworkers.^{8–10} Band structure calculations of Cs₂AgBiBr₆ perovskite based on the order–disorder transition by a first principles study were performed in detail by Wei and coworkers.¹¹ Structural analysis and optical properties of Cs₂AgBiBr₆ powder samples below and above the phase transition point were introduced by Schade and coworkers.¹² The authors reported the low-temperature and room-temperature crystal structure parameters on the basis of neutron powder diffraction (NPD), but they did not obtain the single-crystal structure.¹² Zhan and coworkers investigated the application of Cs₂AgBiBr₆ thin films as humidity sensors, which exhibited superfast recovery times as well as high stability.¹³ In many cases, optoelectronic devices, such as solar cells^{14,15} and X-ray detectors,¹⁶ based on double perovskites are in the form of pressed powder (pellets) and thin films.

Single crystals with the absence of grain boundaries and low densities of traps provide an ideal test platform for fundamental

Energy Materials and Surface Sciences Unit (EMSSU), Okinawa Institute of Science and Technology Graduate University (OIST), 1919-1 Tancha, Onna-son, Kunigami-gun, Okinawa 904-0495, Japan. E-mail: Yabing.Qi@OIST.jp

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seed crystal direction to control the shape and size. Thus, we could obtain controllable shape and size, which led to good device reproducibility. It is easier to obtain large size $\text{Cs}_2\text{AgBiBr}_6$ single crystals with MABr as the flux as shown in Fig. S1 (ESI[†]), because MABr can increase the solubility for $\text{Cs}_2\text{AgBiBr}_6$ single crystal growth owing to the enhanced dissolution of $\text{Cs}_2\text{AgBiBr}_6$ materials induced by MABr. $\text{Cs}_2\text{AgBiBr}_6$ single crystals were grown in saturated perovskite precursor solutions. Meanwhile, the crystal structure of $\text{Cs}_2\text{AgBiBr}_6$ at room temperature (Fig. 1c and Table S1, ESI[†]) was determined and refined with the formula $\text{Cs}_4\text{Ag}_2\text{Bi}_2\text{Br}_{12}$, which exhibited the cubic space group of $Fm\bar{3}m$ (no. 225) consistent with a previous report.¹⁸ Based on a previous report on the crystal structure under phase transition from the powder sample,¹² we carried out the low-temperature crystal structure measurements. The crystal structure determinations and refinements at 100 K by single-crystal X-ray diffraction analysis demonstrated that there were two possibilities for the pseudo-polymorphic phase, *i.e.*, tetragonal or cubic space groups (Table S1, ESI[†]). Based on a previous report,¹² $\text{Cs}_2\text{AgBiBr}_6$ single crystals undergo a reversible phase transition (Fig. S2 and Table S1, ESI[†]). The related crystal parameters are listed in Table S1 in the ESI.[†] It is demonstrated that a $\text{Cs}_2\text{AgBiBr}_6$ single crystal at 100 K exhibits the tetragonal space group $I4/m$ (no. 87), which is consistent with the report of Schade *et al.*¹² Based on the single crystal determination, we did not observe MA cations in the low temperature crystal structure. Therefore, it is verified that there exists no MABr in $\text{Cs}_2\text{AgBiBr}_6$ single crystals. Moreover, in Fig. 1d we did not observe redundant peaks for MABr.

Besides, the N 1s peak was not observed according to XPS in Fig. S3 (ESI[†]). The PXRD pattern agrees well with the simulated XRD pattern of $\text{Cs}_2\text{AgBiBr}_6$ single crystals, as shown in Fig. 1d.

XPS was employed to further determine the elemental composition of $\text{Cs}_2\text{AgBiBr}_6$ double perovskites.^{29–31} Although $\text{Cs}_2\text{AgBiBr}_6$ single crystals are stable in ambient atmosphere, to avoid the influence of oxygen and humidity, the surface of each single crystal was first cleaved by a sharp knife in an Ar atmosphere and then polished by abrasive paper and silk textile (Fig. 2a and Fig. S3, S4, ESI[†]). The XPS survey in Fig. S3a (ESI[†]) reveals that these single crystal samples have high percentage of atomic concentrations of Cs, Ag, Bi and Br, and the amount of C and O is negligible. The high-resolution XPS spectra of Cs 3d, Ag 3d, Bi 4f, and Br 3d core levels are shown in Fig. S3c–f (ESI[†]). The peaks at binding energies of 724.6 eV and 738.6 eV are attributed to the Cs 3d_{5/2} and 3d_{3/2} core levels (Fig. S3c, ESI[†]), respectively. The peaks located at binding energies of 368.1 eV and 374.1 eV are attributed to the Ag 3d_{5/2} and 3d_{3/2} core levels (Fig. S3d, ESI[†]), respectively. The peaks located at binding energies of 159.2 eV and 164.6 eV are attributed to Bi 4f_{7/2} and 4f_{5/2} core levels (Fig. S3e, ESI[†]), respectively. The peaks located at binding energies of 68.5 eV and 69.5 eV are attributed to the Br 3d_{5/2} and 3d_{3/2} core levels (Fig. S3f, ESI[†]), respectively. These results are consistent with a previous report on $\text{Cs}_2\text{AgBiBr}_6$ thin films.²⁹ To determine the detailed electronic structure, we performed UPS measurements on the single crystal samples to determine the work function (WF) and valence band maximum (VBM). The UPS survey based on the $\text{Cs}_2\text{AgBiBr}_6$ single crystals is

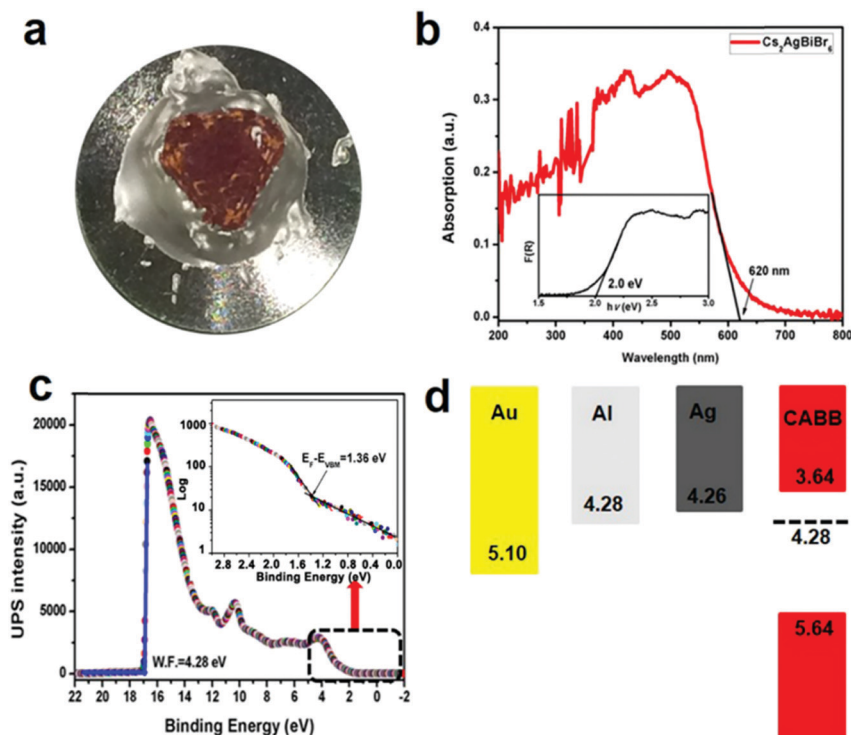


Fig. 2 (a) Photo of the $\text{Cs}_2\text{AgBiBr}_6$ single crystal measured by XPS and UPS; (b) optical band gap of the $\text{Cs}_2\text{AgBiBr}_6$ material; (c) UPS of the $\text{Cs}_2\text{AgBiBr}_6$ single crystal; inset: semi-log scale analysis of Fermi-level versus VBM position, and (d) the energy level diagram of the $\text{Cs}_2\text{AgBiBr}_6$ single crystal and different electrodes (Au, Ag and Al).



shown in Fig. 2c. Based on the secondary electron onset of the UPS spectrum (Fig. 2c), the WF value of Cs₂AgBiBr₆ single crystals is determined to be 4.28 eV, which is smaller than that (5.01 eV) of the Cs₂AgBiBr₆ thin film samples.²⁹ Similarly, in previous reports, the WF value of MAPbBr₃ single crystals was determined to be 4.61 eV,³² while the WF value of MAPbBr₃ thin films was determined to be 5.12 eV.³³ The ionization energy is defined as the energy difference between the vacuum level and VBM. Kahn and coworkers proposed the determination of VBM onsets in perovskites to be conducted in semi-log plots.^{34,35} Accordingly, the ionization energy value is determined to be 5.64 eV (Fig. 2c and d), which is smaller than the previously reported value based on the Cs₂AgBiBr₆ thin films (7.13 eV).²⁹ The differences are possibly caused by the following reasons: (1) different preparation methods can have an influence on the perovskite energy levels^{36a} and (2) single crystals exhibit no grain boundaries and low densities of traps, while polycrystalline thin films have grain boundaries and high densities of electronic traps.^{36b} Combined with the optical band gap (2.0 eV) from Fig. 2b, the conduction band minimum (CBM) is deduced to be at a position of 3.64 eV below the vacuum level in Fig. 2d. It seems that the WF of Cs₂AgBiBr₆ single crystals theoretically matches well with that of the electrodes in the order of Al > Ag > Au according to their energy levels.

The quality of the Cs₂AgBiBr₆ single crystals is verified by evaluating the trap state density, mobility and PL decay lifetime (Fig. S5 and S6, ESI†). The obtained high-quality Cs₂AgBiBr₆ single crystals were cleaved and polished by mechanical processing (Fig. S4, ESI†) before incorporating into a Au/Cs₂AgBiBr₆ thin single crystal/Au vertical device as shown in Fig. S5 (ESI†). The trap state density (n_{trap}) in the Cs₂AgBiBr₆ single crystals was determined by the dark current–voltage (I – V) measurement and analyzing the trap filled limit voltage (V_{TFL}), as shown in Fig. S5a (ESI†). It is found that there exist three regions in the dark J – V curve. With the increase of the applied voltage V , the current increases linearly, which shows the Ohmic behavior ($n = 1$) between the Au electrode and the perovskite when the applied voltage is lower than the first inflection point at ($V = 3.48$ eV).³⁵ A further increase in the applied voltage leads to a fast-nonlinear rise ($n > 3$) in the current. The first inflection point voltage is associated with the trap filling process, and the trap state density and carrier mobility can be computed according to eqn (1) and (2)³⁷

$$V_{\text{TFL}} = \frac{en_{\text{trap}}d^2}{2\epsilon_0\epsilon} \quad (1)$$

$$\mu = \frac{8}{9}(J_{\text{d}}L^3)/(\epsilon_0V^2) \quad (2)$$

where d is the thickness of the Cs₂AgBiBr₆ single crystal in Fig. S5b (ESI†), ϵ is the relative dielectric constant for Cs₂AgBiBr₆ ($\epsilon = 51$),¹⁹ and ϵ_0 is the vacuum permittivity. Steele *et al.* reported the trap density by using the dielectric constant $\epsilon = 5.8$. Therefore, our result based on the extracted trap density from V_{TFL} is one order larger than that reported in a previous report.²⁰ The trap state density n_{trap} and carrier mobility μ are calculated using eqn (1) and (2). The V_{TFL} for Cs₂AgBiBr₆ is 3.48 V, as

shown in Fig. S5a (ESI†), and the corresponding trap state density is $3.58 \times 10^{10} \text{ cm}^{-3}$. The carrier mobility μ is $0.49 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Besides, the average carrier lifetime of Cs₂AgBiBr₆ single crystals is 2.39 ns according to the biexponential fitting formula (Fig. S6, ESI†), which is shorter than those of thin films and powders.⁴⁵ The measured low trap state density verifies the high quality of our Cs₂AgBiBr₆ single crystals.

To obtain high-performance optoelectronic devices, it is important to clarify the impact of the interface between Cs₂AgBiBr₆ single crystals and electrodes. Insertion of interface layers between perovskite crystals and top electrodes has been demonstrated to attain Ohmic contacts by suitable energy matching.^{15,17} For example, Wu and coworkers employed P3HT between the perovskite crystal Cs₂AgBiBr₆ and Au electrode.¹⁵ On the other hand, the search for a viable electrode leading to a good Ohmic contact in Cs₂AgBiBr₆ single-crystal photodetectors is also advantageous considering the simplicity of the device structure. We first investigate the crystal/electrode interface of the Cs₂AgBiBr₆ single crystal photodetectors equipped with different electrodes under illumination at different wavelengths at room temperature in air and vacuum atmospheres. Fig. 3 and Fig. S7 (ESI†) illustrate the photodetectors based on the Cs₂AgBiBr₆ single crystals coated with different electrodes (Au, Ag, and Al), with an electrode area of 1 mm^2 in length and width, channel = $50 \mu\text{m}$, and thickness $\approx 80 \text{ nm}$. For photodetector measurements, a solar simulator is used as the light source and the power density is close to 66.3 mW cm^{-2} . The influence of oxygen and humidity on Cs₂AgBiBr₆ single crystalline photodetectors was investigated employing a probe station that allows vacuum pumping and a controlled atmosphere. We investigated the differences in photo-responses of Cs₂AgBiBr₆ single crystal photodetectors with different electrodes in air and under vacuum conditions. Fig. 3 and Fig. S7 (ESI†) show the I – V curves and photo-responses in air with the light turned on and off for several cycles. In addition, the photodetectors based on Au and Al electrodes under vacuum exhibited current hysteresis phenomena, which is consistent with previous reports based on Au electrodes.^{19,20,22} It is concluded that oxygen and H₂O may reduce current hysteresis phenomena. The work function of the Cs₂AgBiBr₆ single crystal theoretically matches well with that of Al electrodes (Fig. 2d). However, Al tends to react with the Cs₂AgBiBr₆ single crystal, which leads to poor photodetector performance and a hysteresis phenomenon. Similarly, Ahmad and coworkers investigated the interfacial properties of Al and Ag contacts on MAPbBr₃ single crystals, and also found that Al easily reacted with MAPbBr₃ perovskite crystals.³⁸ Interestingly, Cs₂AgBiBr₆ single crystal-based photodetectors using Ag electrodes exhibited excellent photo-response behaviours both in air and under vacuum. In Table S2 (ESI†), the calculated responsivity of Cs₂AgBiBr₆ single crystal devices in air and under vacuum at 293 K is 0.9 and 0.92 mA W^{-1} for the device under 400 nm illumination with a bias of 5 V, respectively. In addition, we assume that the dark current is dominated by the shot noise for estimating detectivity (D^*) (ESI† eqn (S2)).^{46c} The corresponding D^* of the device is calculated to be 1.38×10^9 and 2.66×10^9 Jones (Jones = $\text{cm Hz}^{1/2} \text{ W}^{-1}$), respectively.⁴⁶ The ON/OFF ratio of the device in air and under



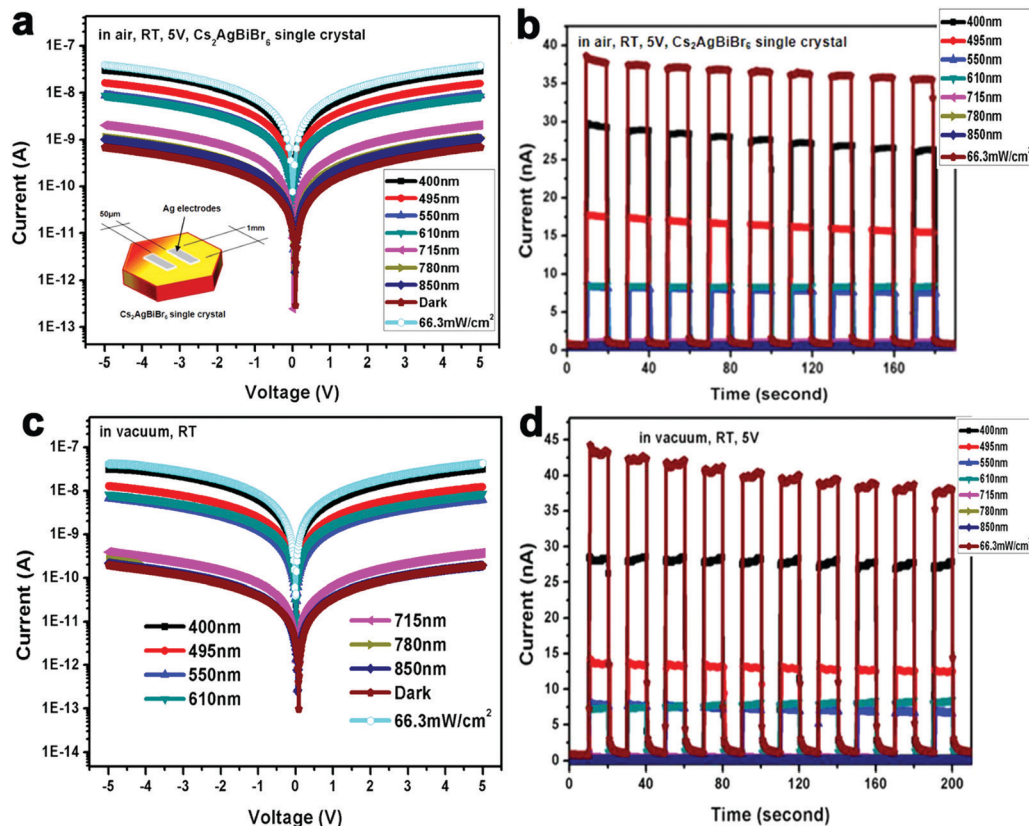


Fig. 3 Comparisons of Cs₂AgBiBr₆ single-crystalline photodetector behaviours based on Ag electrodes at different wavelength under air and vacuum conditions. (a–d) Photodetector data (I - V and I -time curves) of Cs₂AgBiBr₆ single crystals based on Ag electrodes at bias voltage (5 V) when measured (a and b) in air with a relative humidity of 20% and (c and d) under vacuum ($P = 3 \times 10^{-7}$ Torr). All the measurements are performed at room temperature conditions.

vacuum at 293 K is 42 and 153 at a bias of 5 V, respectively, which exhibits better performance than thin film-based photodetectors previously reported by He and coworkers.²⁹ Compared with Au and Al electrodes (Fig. S7d and h, ESI[†]), Cs₂AgBiBr₆ single crystal photodetectors using a Ag electrode exhibit stable photo-response under vacuum at 293 K (Fig. 3b and d). This observation is attributed to the excellent Ohmic contact of Ag with the Cs₂AgBiBr₆ single crystal.

We propose that the superior Ohmic contact of Ag and the Cs₂AgBiBr₆ single crystal *versus* Al and Au is due to the strong interaction of Ag and Cs₂AgBiBr₆. There are two possible explanations about Ohmic contact using Ag electrodes: (1) in Fig. 1c, it is observed that every [AgBr₆]⁵⁻/[BiBr₆]³⁻ octahedron in the crystal structure of Cs₂AgBiBr₆ is surrounded by six [BiBr₆]³⁻/[AgBr₆]⁵⁻ octahedra, because there exist evident differences between the charges of Ag⁺ and Bi³⁺ cations to form a different coordination environment in the crystal structure. Thus, Cs₂AgBiBr₆ exhibits a disordered crystal structure at room temperature, which is consistent with previous reports.^{22,39} Based on the lattice-matching theory and size effect of ionic radius,⁴⁰ Ag atoms can easily permeate into the Cs₂AgBiBr₆ single crystals and balance the charge leading to a better Ohmic contact of the Ag electrode than Au and Al electrodes. (2) Cs₂AgBiBr₆ exhibited the n-type semiconductor properties. According to the energy band

bending theory, when the metal work function is smaller than that of the semiconductors, as shown in Fig. S8 (ESI[†]), there exists no Schottky barrier and the metal-semiconductor contact using Ag electrodes is Ohmic, and *vice versa* based on the devices using Au electrodes in Fig. S8 (ESI[†]).^{41,42} Therefore, Cs₂AgBiBr₆ single crystals exhibit superior Ohmic contact, which can effectively reduce the contact barrier, which helps promote charge carrier transport. It is demonstrated that the electron barrier transports from Ag electrodes to Cs₂AgBiBr₆ perovskite single crystals in the dark to illustrate that the WF of Ag electrodes minus the Cs₂AgBiBr₆ electron affinity helps form the good Ohmic contact. The response time is a key parameter to evaluate the performance of photodetectors. The rise time (t_{rise}) and fall time (t_{fall}) are defined as the increase from 10% to 90% of the maximum value and decrease from 90% to 10% of the maximum value, respectively, in Fig. S9 (ESI[†]). The corresponding rise/fall times of Cs₂AgBiBr₆ single crystal photodetectors in air and under vacuum are 159/85 ms and 75/38 ms, respectively, which are better than those of the Cs₂AgBiBr₆ thin film as seen in Table S3 (ESI[†]). Besides, based on the above energy level and experimental result analysis of electrodes, we observe the dark current decrease of Cs₂AgBiBr₆ single crystal devices based on different wavelengths from Au, Ag and Al in this order in air and vacuum atmospheres at 293 K in Fig. 3 and Fig. S7 (ESI[†]). Cs₂AgBiBr₆



single crystal devices using Au and Al exhibit an obvious hysteresis with an increase in photocurrent like memristor behaviors.⁴³ The photocurrent reduced quicker under vacuum than in air. The possible reason for the photocurrent to reduce more quickly under vacuum than in air is that oxygen and H₂O in air affect the surface of the double perovskite device and have an impact on the photocurrent, compared with the vacuum case.^{47,48} We also measured the stability of Cs₂AgBiBr₆ single crystal photodetectors in air and vacuum atmospheres when exposed to 400 nm light irradiation condition. Cs₂AgBiBr₆ single crystal photodetectors showed relatively good stability in Fig. S10 (ESI[†]). These intriguing results can provide guidance for obtaining high performance lead-free perovskite Cs₂AgBiBr₆ single crystal optoelectronic devices.

Finally, we investigate the Cs₂AgBiBr₆ single crystal photodetector performance at low temperature. Based on a previous

report on the phase transition of Cs₂AgBiBr₆ materials,¹² we found that our Cs₂AgBiBr₆ single crystals also undergo phase transition. As shown in Fig. S2 (ESI[†]), Cs₂AgBiBr₆ single crystals exhibited two different crystal structures above and below the phase transition point (293 K and 100 K), which was consistent with the results previously reported by Schade and coworkers.¹² To investigate the Ohmic contact behaviors at the Cs₂AgBiBr₆/Ag interfaces below and above the phase transition point, we carried out the Cs₂AgBiBr₆ single crystal photodetector measurement using Ag electrodes in a vacuum atmosphere at 293 K and 100 K. We carried out the photodetector measurements in a vacuum atmosphere at 100 K at different applied voltages with a solar simulator (power intensity of 66.3 mW cm⁻²) and at different wavelengths, as shown in Fig. 4 and Fig. S11 (ESI[†]). It was found that Cs₂AgBiBr₆ single crystals did not exhibit Ohmic contact behaviors at a low temperature of 100 K,

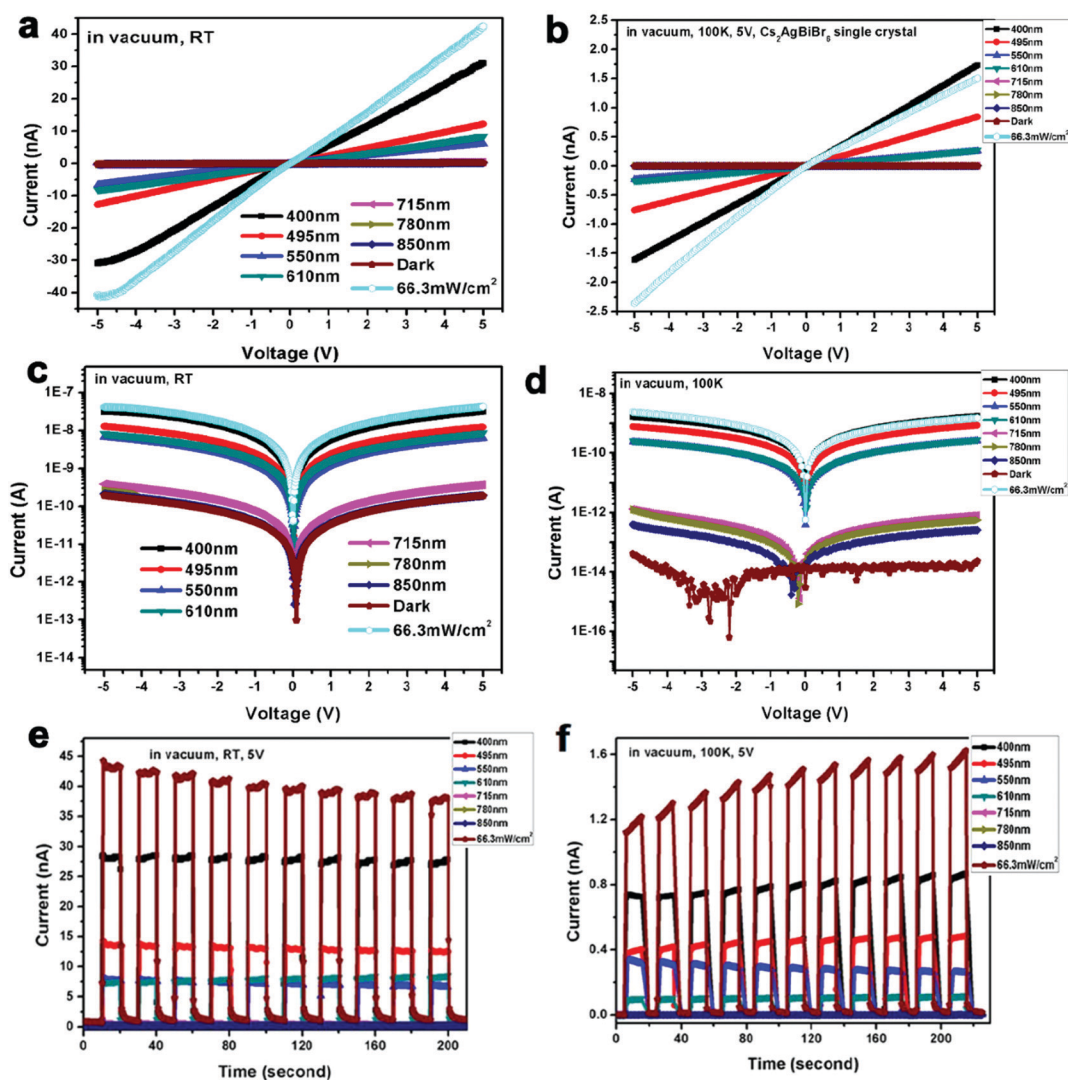


Fig. 4 Comparisons of Cs₂AgBiBr₆ single-crystalline photodetector behaviors based on Ag electrodes at different wavelengths at room and low temperature. (a, c and e) Photodetector data (*I*-*V* and *I*-*t* curves) of Cs₂AgBiBr₆ single crystals based on Ag electrodes at different wavelengths at room temperature; (b, d and f) photodetector data (*I*-*V* and *I*-*t* curves) of Cs₂AgBiBr₆ single crystals based on Ag electrodes at different wavelengths at 100 K. All the measurements are performed under vacuum conditions ($P = 3 \times 10^{-7}$ Torr).



as shown in Fig. 4 and Fig. S11 (ESI†). This observation is different from the above studies at room temperature under vacuum in Fig. 3. In particular, with the light turned on and off for several cycles using different wavelengths, the dark current of Cs₂AgBiBr₆ single crystals was shifted. The formation of a poor Ohmic contact for Cs₂AgBiBr₆/Ag photodetectors at low temperature is possibly caused by the changes in crystal structure arrangements induced by the temperature-dependent phase transition.⁴⁴ Therefore, high-performance optoelectronic devices with good Ohmic contact can be achieved based on the suitable temperature and suitable electrodes for perovskite single crystal materials.

Conclusions

In summary, we obtained large-size Cs₂AgBiBr₆ double perovskite single crystals by means of the addition of MABr as the flux. The optical band gap, XPS and UPS measurements were performed on Cs₂AgBiBr₆ single crystals. Photodetectors based on Cs₂AgBiBr₆ single crystals with different electrodes Au, Ag, and Al under a light source with different wavelength filters were studied. In addition, there is the influence of environment (air and vacuum atmospheres) as well as temperature (293 K and 100 K). It is concluded that photodetectors based on Cs₂AgBiBr₆ single crystals exhibit excellent photo-response by achieving Ohmic contact with Ag electrodes. In addition, photodetectors based on Cs₂AgBiBr₆ single crystals with Ag electrodes under room and low temperature conditions under which phase transition occurred were also systematically investigated. We believe that the present work not only provides an effective way to understand the intrinsic properties of Cs₂AgBiBr₆ single crystals, but also paves the way for high-performance Cs₂AgBiBr₆ single crystal photodetectors.

Experimental

Reagents

All starting reagents including Cs₂CO₃ (97%, Wako), Ag₂CO₃ (99%, Sigma-Aldrich), (BiO)₂CO₃ (80–82.5% Bi basis, Sigma-Aldrich), methylammonium bromide (99%, Dyesol), HBr (48%, Sigma-Aldrich) and H₃PO₂ (50 wt% in H₂O, Sigma-Aldrich) solutions were used without further purifications.

Synthesis and crystal growth

The precursor synthesis of Cs₂CO₃, Ag₂CO₃ and (BiO)₂CO₃ in HBr and H₃PO₂ mixed solution was performed according to the chemical stoichiometric ratios. Cs₂CO₃ (6.5100 g, 0.020 mol), Ag₂CO₃ (2.7500 g, 0.010 mol), (BiO)₂CO₃ (5.0997 g, 0.010 mol) and MABr (2.2400 g, 0.02 mol) were dissolved in 200 ml HI and 20 ml H₃PO₂ mixed solution at 80 °C under constant stirring, forming a yellow transparent solution after three days. Solutions were saturated at 75 °C. Large size Cs₂AgBiBr₆ single crystals were grown by a temperature-lowering method using a top-seeded solution growth (TSSG) method in an ambient atmosphere for about two weeks, as shown in Fig. 1a.

XPS and UPS measurements of Cs₂AgBiBr₆ single crystals

Cs₂AgBiBr₆ single crystals were cleaved and then fixed to the sample holders, as shown in Fig. 2a. The UPS and XPS spectra were measured on an X-ray photoelectron spectrometer (XPS-AXIS Ultra HAS, Kratos) equipped with monochromatic Al-K α (1486.6 eV) and nonmonochromatic He-I (21.22 eV) sources, respectively. All the measurements were carried out in a vacuum atmosphere (<10⁻⁵ Pa).

Photodetector device fabrication and measurements

Single crystal photodetectors with planar-structures were fabricated by depositing \approx 80 nm different electrodes (Au, Ag and Au) with a shadow mask (with a spacing of 1 mm \times 50 μ m) *via* the thermal evaporation method on the surfaces of polished Cs₂AgBiBr₆ single crystals. The photo-response characteristics of the Cs₂AgBiBr₆ photodetectors were collected using Keithley 4200 semiconducting equipment. Monochromatic light was obtained by filtering the white light from a solar simulator with optical filters (400, 495, 550, 610, 715, 780 and 850 nm). The intensities of irradiated light are calibrated using an optical power meter.

CCDC 1919712–1919714 contain the supplementary crystallographic data for this paper.†

Conflicts of interest

There are no conflicts to declare.

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