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## Cs<sub>2</sub>AgBiBr<sub>6</sub> DOUBLE HALIDE PEROVSKITES AS ADVANCED MATERIALS FOR HIGH-EFFICIENCY SOLAR CELLS

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**Abstract.** Among all double perovskites, Cs<sub>2</sub>AgBiBr<sub>6</sub> has proven to be the most promising and commercially viable. The methods of obtaining of double halide perovskite, such slow crystallization method, solution deposition method, spin-coating method were considered. Results of band gap calculation are presented in the work. The range of it according to different studies includes from 1.6 eV to 2.25 eV depending on calculation method. Valuable review was done in the direction of efficiency, which is dependent on the architecture of solar cell and layers combination. Different solar cells based on Cs<sub>2</sub>AgBiBr<sub>6</sub> were analysed. Optoelectronic properties — absorption, luminescence, photocurrent, luminescence kinetics were considered from different papers. Absorption coefficient of Cs<sub>2</sub>AgBiBr<sub>6</sub> is 10<sup>5</sup>, an absorption spectrum (350-610 nm), charge carrier mobility (1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>), and charge carrier lifetime of 1.4 ms, which is an order of magnitude longer than that in lead-based perovskites. Additionally, they exhibit notable luminescent properties, with a luminescence spectrum in the range of 400-600 nm and decay times up to 600 ns. The performance of solar cells is influenced also by the values of photocurrent and voltage exhibited by the sample. The voltage considered in different works varied from 1.03 V to 1.07 V, and the photocurrent ranged from 0.78 to 1.78 mA·cm<sup>-2</sup>.

**Keywords:** Cs<sub>2</sub>AgBiBr<sub>6</sub>, solar cells, efficiency, band gap, absorption, photocurrent, luminescence, luminescence kinetics



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## **Cs<sub>2</sub>AgBiBr<sub>6</sub> ҚОС ГАЛОИДТЫ ПЕРОВСКИТТЕР: КҮН БАТАРЕЯЛАРЫНА АРНАЛҒАН ТИІМДІЛІГІ ЖОҒАРЫ ЖАҢА ОЗЫҚ МАТЕРИАЛДАРЫ**

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**Аннотация.** Барлық қос перовскиттердің ішінде перспективті және коммерциялық тұрғыдан тиімді материалдардың бірі болып Cs<sub>2</sub>AgBiBr<sub>6</sub> табылады. Соңғы жылдары бұл материал экологиялық қауіпсіздігімен, жоғары тұрақтылығымен және қолайлы оптоэлектрондық қасиеттерімен зерттеушілер назарын ерекше аударуда. Жұмыста қос галоидті перовскитті алу әдістері, мысалы, баяу кристалдану әдісі, ерітіндіні тұндыру әдісі және айналдыру (spin-coating) әдісі қарастырылады. Әрбір тәсіл кристалдардың сапасына, жұқа қабаттардың біртектілігіне және дайын күн элементтерінің сипаттамаларына өзіндік әсер береді. Мақалада жолақ аралығын есептеу нәтижелері ұсынылған. Өртүрлі зерттеулер бойынша оның диапазоны есептеу әдісіне байланысты 1.6 эВ-тен 2.25 эВ-қа дейінгі аралықты қамтиды. Сондай-ақ күн элементі құрылымының тиімділігі мен қабаттар комбинациясын талдауға арналған шолу жүргізілген. Cs<sub>2</sub>AgBiBr<sub>6</sub> негізіндегі өртүрлі күн батареялары да таңдалған. Ғылыми басылымдар деректеріне сүйене отырып, материалдың негізгі оптоэлектрондық қасиеттері — жарықты жұту, люминесценция, фототок және люминесценция кинетикасы талданады. Cs<sub>2</sub>AgBiBr<sub>6</sub> жұтылу коэффициенті 10<sup>5</sup>, жұтылу спектрі 350-610нм аралығында орналасқан. Заряд тасымалдаушылардың қозғалтқыштығы шамамен 1см<sup>2</sup>В<sup>-1</sup>с<sup>-1</sup> және заряд тасымалдаушының қызмет ету мерзімі 1.4мс, бұл қорғасын негізіндегі перовскиттермен салыстырғанда үлкенірек болып келеді. Сонымен қатар, материал айқын люминесценттік қасиеттерге ие: олар 400-600 нм диапазонында люминесценция спектрі және сөну уақыты 600 нм дейін жетеді. Күн батареяларының жұмыс өнімділігіне фототок пен үлгінің кернеу мәндері де әсер

етеді. Өртүрлі зерттеулерде кернеу 1.03 В-тан 1.07 В-қа дейін жетеді, ал фототок 0.78- 1.78 мА·см<sup>2</sup> аралығында болғаны көрсетілген. Бұл көрсеткіш Cs<sub>2</sub>AgBiBr<sub>6</sub> материалын жоғары тиімді және экологиялық таза күн технологияларын дамыту үшін үлкен перспективті негіз ретінде көрсетеді.

**Түйін сөздер:** Cs<sub>2</sub>AgBiBr<sub>6</sub>, күн батареялары, тиімділік, жолақ аралығы, жұту, фототок, люминесценция, люминесценция кинетикасы

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## Cs<sub>2</sub>AgBiBr<sub>6</sub>: ДВОЙНЫЕ ГАЛОИДНЫЕ ПЕРОВСКИТЫ КАК ПЕРЕДОВЫЕ МАТЕРИАЛЫ ДЛЯ ВЫСОКОЭФФЕКТИВНЫХ СОЛНЕЧНЫХ ЭЛЕМЕНТОВ

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**Аннотация.** Среди всех двойных перовскитов одним из наиболее перспективных и коммерчески жизнеспособных материалов признан Cs<sub>2</sub>AgBiBr<sub>6</sub>, который в последние годы привлекает особое внимание исследователей благодаря сочетанию экологической безопасности, стабильности и благоприятных оптоэлектронных характеристик. В работе рассмотрены основные методы получения двойных галоидных перовскитов, такие как метод медленной кристаллизации, осаждение из раствора и метод центрифугирования (spin-coating). Каждый из этих методов обладает своими преимуществами, влияющими на качество кристаллов, однородность плёнок и конечные параметры солнечных элементов. В статье приведены результаты расчётов ширины запрещённой зоны Cs<sub>2</sub>AgBiBr<sub>6</sub>. Согласно различным исследованиям, она варьируется от 1.6 до 2.25 эВ в зависимости от метода расчёта. Проведена обзорная работа по оценке эффективности структуры солнечного элемента и комбинации слоёв. Проанализированы различные солнечные элементы на основе Cs<sub>2</sub>AgBiBr<sub>6</sub>. По данным научных публикаций рассмотрены оптоэлектронные свойства материала: поглощение, люминесценция, фототок и кинетика люминесценции. Коэффициент поглощения Cs<sub>2</sub>AgBiBr<sub>6</sub> составляет 10<sup>5</sup>; диапазон спектра поглощения — 350- 610 нм; подвижность носителей заряда — около 1 см<sup>2</sup>·В<sup>-1</sup>·с<sup>-1</sup>; время жизни носителей — до 1.4 мс, что на порядок выше, чем у свинцовых перовскитов. Материал также обладает выраженными люминесцентными свойствами: спектр

люминесценции лежит в диапазоне 400-600 нм. На эффективность солнечных элементов дополнительно влияют значения фототока и напряжения: в различных исследованиях напряжение варьировалось от 1.07 до 1.30 В, а фототок — от 0.78 до 1.78 мА·см<sup>-2</sup>. Эти показатели подтверждают перспективность Cs<sub>2</sub>AgBiBr<sub>6</sub> в качестве основы для развития высокоэффективных и экологически безопасных солнечных технологий.

**Ключевые слова:** Cs<sub>2</sub>AgBiBr<sub>6</sub>, солнечные батареи, эффективность, ширина запрещенной зоны, поглощение, фототок, люминесценция, кинетика люминесценции

**Introduction.** As photovoltaic elements and materials for solar cells, materials are primarily evaluated based on their band gap properties, absorption coefficient, and stability. The band gap should correspond approximately to the solar spectrum, in the range of about 1.1 eV to 1.7 eV. The absorption coefficient must be sufficiently high to enable the use of extremely thin material layers. On average, this value ranges from 10<sup>2</sup> to 10<sup>5</sup> cm<sup>-1</sup> (Robert L.Z. et al., 2018).

Double halide perovskites are promising candidates as materials for solar energy applications. They are called “double” because, whereas a simple perovskite has the formula ABX<sub>3</sub>, a double perovskite follows the formula A<sub>2</sub>B<sub>1</sub>B<sub>2</sub>X<sub>6</sub>, where B<sub>1</sub> is a monovalent cation and B<sub>2</sub> is a trivalent cation. A 2×2×2 supercell is formed, in which combinations of cations can produce a material with unique physicochemical properties, a large band gap, high absorption coefficient, and long carrier lifetimes (Sirtl Maximilian T. et al., 2022)

For example, when time-resolved photoluminescence was measured, the charge carrier lifetimes in these materials exceeded 100 ns, which is an order of magnitude greater than the required minimum (Slavney A. H. et al., 2016). Another advantage of double perovskites is that they are lead-free and therefore less toxic.

Among all double perovskites, Cs<sub>2</sub>AgBiBr<sub>6</sub> has proven to be the most promising and commercially viable. Substituting Cs<sup>+</sup> cations at the A-site increases the decomposition energy of the perovskite from - 0.111 eV (for MAPbI<sub>3</sub>) to - 0.069 eV (for CsPbI<sub>3</sub>), thereby improving material stability. Toxic lead is replaced with silver (Ag<sup>+</sup>) and bismuth (Bi<sup>3+</sup>) cations. This not only reduces toxicity but also enhances stability by increasing the Coulombic interaction energy (Alkhamash H. I. et al., 2023).

Cs<sub>2</sub>AgBiBr<sub>6</sub> has an optimal crystal structure, long charge carrier lifetimes, and greater stability compared to lead-based analogues (Yang J. et al., 2018). Another notable feature is that Bi<sup>3+</sup> shares the same electronic configuration as Pb<sup>2+</sup>, which is crucial for light absorption and prolonged charge carrier lifetimes (Ji F. et al., 2023).

This review article discusses the structure, synthesis methods, and key optoelectronic properties of Cs<sub>2</sub>AgBiBr<sub>6</sub>, which make it a strong candidate for use in solar cell materials.

**Materials and methods.** The efficiency of a solar cell, the value of the band gap, and the charge carrier lifetime depend on the crystal growth method. Generally, solution deposition, slow crystallization from solution, and spin-coating methods are used.

In the slow crystallization method, the solution is first saturated with CsBr, AgBr,

and  $\text{BiBr}_3$  salts, then cooled to approximately  $4^\circ\text{C}$ , leading to crystal formation. The solvent is  $\text{HBr}$  or another acidic solution. This method is suitable for obtaining single crystals.

For obtaining the purest crystals with good optical properties, the solution deposition method is used. In this method, a mixture of precursors is first placed in solvents such as Isopropyl Alcohol (IPA), Hydroiodic Acid (HI), Dimethyl Sulfoxide (DMSO), or Chlorobenzene (CB) at high temperature. Then the solution is cooled, or the solvents are evaporated, leaving behind crystals.

For film formation, the spin-coating method is suitable. In this method, the dissolved  $\text{Cs}_2\text{AgBiBr}_6$  powder in DMSO (0.5 mol/L) is applied to a substrate using spin-coating, then cured under low pressure (LPA).

Let us consider the various methods used in studies.

In study (Robert L.Z. et al., 2018), a  $\text{Cs}_2\text{AgBiBr}_6$  crystal was grown by the slow crystallization method at low temperature from a saturated solution. The precursors  $\text{CsBr}$ ,  $\text{AgBr}$ , and  $\text{BiBr}_3$  were mixed in  $\text{HBr}$ . After stirring for one hour, the solution was slowly cooled and placed in a refrigerator at  $4^\circ\text{C}$ . Crystals grew over one week using vacuum filtration, followed by immersion in acetone.

In work (Yang J. et al., 2018),  $\text{Cs}_2\text{AgBiBr}_6$  powder was dissolved in DMSO at a concentration of 0.5 mol/L, forming a clear light-yellow solution. A uniform  $\text{Cs}_2\text{AgBiBr}_6$  film was obtained using an optimized LPA method, similar to methods used for the fabrication of organic–inorganic hybrid perovskite films under standard conditions. The solution was deposited onto a glass/ITO substrate using the spin-coating method, after which the film was transferred to a low-pressure chamber for further solidification. Compared to traditional thermal annealing (TA), the LPA method gave a film with higher uniformity and good crystallinity, as confirmed by microscopic images. The lattice constant of the crystal synthesized in this way was  $a = 11.2640(8) \text{ \AA}$ .

The most common method for obtaining crystals is the method of precipitation in solution.  $\text{BiBr}_3$ ,  $\text{CsBr}$ ,  $\text{AgBr}$  are dissolved in isopropanol (IPA, 99.5%), hydroiodic acid (HI, 57% in  $\text{H}_2\text{O}$ , 99.95%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%) and chlorobenzene (CB, 99.8%). The composition of the mixture is thoroughly stirred at a temperature of  $120^\circ\text{C}$ , until the solvents evaporate, leaving behind raspberry-colored crystals. The mixture is then gradually cooled at a rate of  $5^\circ\text{C}$  per hour. The entire set of components is left to stand overnight. After precipitation, the crystals are separated by filtration and washed with ethanol, dried in a vacuum at  $60^\circ\text{C}$ , resulting in  $\text{Cs}_2\text{AgBiBr}_6$ .

**Results and discussion.** *Structure.* Slavney et al. were the first to successfully synthesize the cubic  $\text{Fm}\bar{3}\text{m}$  double perovskite  $\text{Cs}_2\text{AgBiBr}_6$  with an indirect band gap of 1.95 eV (Li Z. et al., 2020), (Savory Ch.N. et al., 2016). The crystal structure is shown in Figure 1.

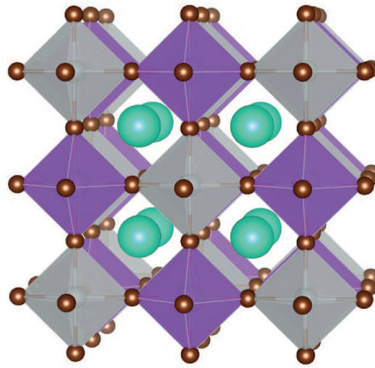


Figure 1. The structure of  $\text{Cs}_2\text{AgBiBr}_6$

The green spheres represent  $\text{Cs}^+$  ions, which occupy the large voids between the octahedra. The grey and violet atoms are  $\text{Ag}^+$  and  $\text{Bi}^{3+}$ , respectively; they alternate within the octahedra formed by Br atoms. The brown Br spheres are located at the vertices of the octahedra, coordinating the silver and bismuth cations. In this structure, both  $\text{Ag}^+$  and  $\text{Bi}^{3+}$  are surrounded by six Br anions.

The conduction band minimum of  $\text{Cs}_2\text{AgBiBr}_6$  originates from antibonding Bi 6p—Br 4p orbitals at the L point, and the valence band maximum from Ag 4d—Br 4p at the X point (Ji F. et al., 2023).

The valence band consists of silver cations and bromide anions, while the conduction band includes silver and bismuth cations.

The band gap width plays an important role for a solar cell material, and it depends both on the method of crystal synthesis and on the method of measurement, whether theoretical or experimental.

In work (Yang J. et al., 2018), the band gap width of the crystal, calculated from the ultraviolet region of the absorption spectrum, is 2.05 eV.

According to HSE06+SOC calculations, the direct and indirect transition energies in the investigated material are 2.45 eV and 1.79 eV, respectively. The conduction band width is calculated to be 0.75 eV, and the Spectroscopic Limited Maximum Efficiency is at the level of 7.92% (Savory Ch.N. et al., 2016).

A range of values has also been obtained for the band gap width of the investigated material: 1.95 eV (Slavney A. H. et al., 2016), 2.19 eV — (Li Z. et al., 2020) 2.25 eV — (Yang J. et al., 2018), 1.95—2.19 eV (McClure E. T. et al., 2016), 1.91 eV (A.Ullah et al., 2024).

According to first-principles calculations, the band gap in the material is indirect and was found to be 1.654 eV. This value is lower than that of  $\text{Cs}_2\text{AgBiCl}_6$  (2.77 eV) and  $\text{Cs}_2\text{AgInCl}_6$  (3.23 eV). - (McClure E. T. et al., 2016).

Band gap engineering of  $\text{Cs}_2\text{AgBiBr}_6$  has been achieved through the introduction of defects and doping with trivalent metals (Yang J. et al., 2018). In order to create a direct band gap material from  $\text{Cs}_2\text{AgBiBr}_6$ , it is necessary to introduce an impurity with valence s-electron states that can occupy the silver site. These can be In or Tl ions. For

example, the addition of 0.075% Tl(I) enabled the formation of a direct band gap of 1.57 eV for  $\text{Cs}_2\text{AgBiBr}_6$  and 1.86 eV for  $\text{Cs}_2\text{Ag}(\text{Bi}_{0.625}\text{Sb}_{2.375})\text{Br}_6$ . However, according to studies, the decomposition energies of such structures were found to be negative, indicating their instability, whereas the decomposition energy of the base material with silver is 0.38 eV, and for  $\text{Cs}_2\text{AgBiCl}_6$  it is 0.57 eV (Savory Ch.N. et al., 2016).

Hydrogenation technology is also applied to tune the band gap width and significantly improve the optoelectronic properties of perovskites. Before plasma treatment for hydrogenation, the  $\text{Cs}_2\text{AgBiBr}_6$  samples were indirect semiconductors with a band gap of 2.18 eV. However, after treatment, a reduction in the band gap to 1.91 eV was observed (Alkhamash H. I. et al., 2023).

In principle, a direct band gap is not a strict requirement for solar cell materials; thicker layers can be selected to ensure effective optical absorption.

Nevertheless, despite the fact that this structure is lead-free and ideal for optoelectronic applications, the challenge in commercialization lies in the fabrication of thin films for use as solar cell components.

#### *Efficiency improvements*

The first solar cell based on  $\text{Cs}_2\text{AgBiBr}_6$  had the following layer structure: FTO/ETL/PAL/HTL/Au. Instead of ETL — AZnO, CdZnS, LBSO, and  $\text{Nb}_2\text{O}_5$ ; HTL — CZTSe, CdTe, PTAA,  $\text{TiO}_2\text{:N}$ ,  $\text{NiCo}_2\text{O}_4$ ,  $\text{Sb}_2\text{S}_3$ , nPB, GaAs, ZnTe, CNTS.

Among previous studies, Alkhamash et al. achieved the highest PCE (21.88%) using the structure FTO/ZnO/ $\text{Cs}_2\text{AgBiBr}_6$ /NiO/Au (Alkhamash H. I. et al., 2023).

At the same time, experimental works using the structures FTO/ $\text{TiO}_2$ / $\text{Cs}_2\text{AgBiBr}_6$ /Spiro-OMeTAD/Au and FTO/ $\text{TiO}_2$ / $\text{Cs}_2\text{AgBiBr}_6$ /Spiro-OMeTAD/ $\text{MoO}_3$ /Ag demonstrated PCEs of 1.66% (E. Greul et al., 2017) and 2,51% (Igbari F. et al., 2019), respectively, which do not meet the expectations of Greul E. et al., 2017, Igbari F. et al., 2019.

However, in the study main, by combining ten different HTLs and four ETLs, an outstanding efficiency of 23.50% was achieved for the proposed structure FTO/AZnO/ $\text{Cs}_2\text{AgBiBr}_6$ /CNTS/Au, which is an exceptional result.

In (Yang J. et al., 2018), the solar cell architecture with the base element was chosen as n-i-p type with ETL —  $\text{SnO}_2$  and HTL — poly(3-hexylthiophene-2,5-diyl) (P3HT). However, this cell demonstrated an efficiency of 1.44% at an annealing temperature of 250 °C. According to experiments, poly(3-hexylthiophene-2,5-diyl) as a hole transport material showed significant instability. In contrast, the architecture without HTL exhibited greater stability.

In (Alkhamash H. I. et al., 2023), a hydrogenated sample of  $\text{Cs}_2\text{AgBiBr}_6$  was used, and hydrogenation through the plasma method, depending on the duration of treatment, increased the degree of hydrogen penetration from the surface to the middle layer. Here, instead of the hole transport material, Spiro-OMeTAD was used, and  $\text{SnO}_2$  served as the ETL. The highest achieved efficiency was 6.37%.

Despite the stability of perovskite solar cells, the exciton binding energy in  $\text{Cs}_2\text{AgBiBr}_6$  is an order of magnitude higher than in the classical  $\text{MAPbI}_3$ , which explains the relatively low efficiency of the former (Yang J. et al., 2018).

In recent years, several experiments have been conducted to improve the characteristics of  $\text{Cs}_2\text{AgBiBr}_6$ :

- Greul and co-authors experimentally studied this material and achieved a PCE of 1.66% (Greul E. et al., 2017).
- Igbari and his team conducted further research and achieved a PCE of 2.51% (Igbari F. et al., 2019).
- Theoretical studies also played an important role. Zhang and Alanazi combined SnO<sub>2</sub> and Spiro-OMeTAD with Cs<sub>2</sub>AgBiBr<sub>6</sub>, achieving PCEs of 6.37% (Zhang Z. et al., 2022) and 14.29% (Alanazi T. I. et al., 2023), respectively.
- Islam and co-authors applied a combination of TiO<sub>2</sub> and Cu<sub>2</sub>O, which resulted in a PCE of 7.25% (Islam M. T. et al., 2020).
- Alkhamash and his group used ZnO and NiO, achieving an impressive PCE of 21.88% (H. I. Alkhamash et al., 2023).
- Chabri and his team also studied Cs<sub>2</sub>AgBiBr<sub>6</sub> and achieved a PCE of 7.16% (I. Chabri et al., 2023).

Thus, further research on Cs<sub>2</sub>AgBiBr<sub>6</sub> is necessary to identify the best material combinations and further enhance its photovoltaic properties in order to unlock the full potential of this perovskite solar cell (PSC).

The benchmark HDP Cs<sub>2</sub>AgBiBr<sub>6</sub> for solar cells was first introduced in 2017 (Greul E. et al., 2017).

The characteristics of solar cells based on Cs<sub>2</sub>AgBiBr<sub>6</sub> with different layer combinations have been analyzed and are shown in Figure 2 (McClure E. T. et al., 2016).

PCE — the efficiency of the solar cell, V<sub>oc</sub>, J<sub>sc</sub>, FF — voltage, current density, and fill factor, i.e., the ratio of maximum power ( $P_m = V_m \times I_m$ ) to the product of V<sub>oc</sub> and J<sub>sc</sub>.

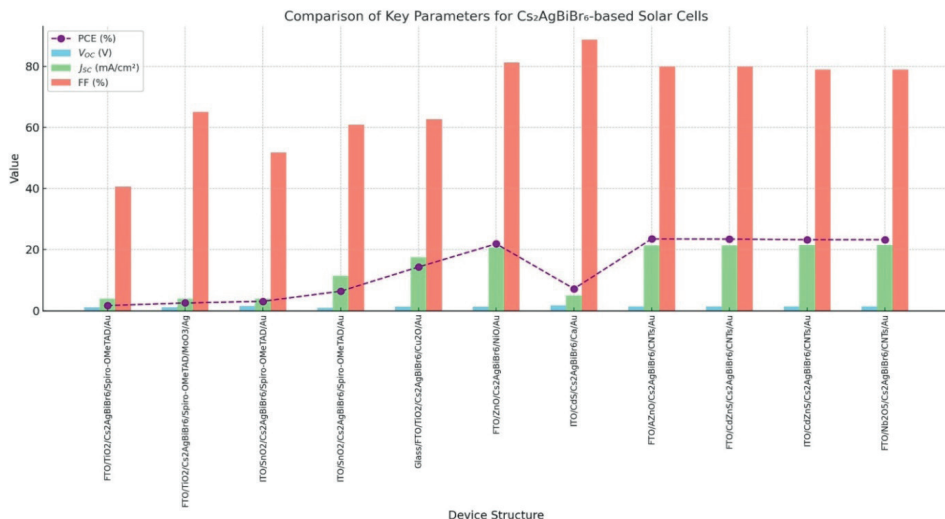


Figure 2. The characteristics of solar cells based on Cs<sub>2</sub>AgBiBr<sub>6</sub>

As can be seen from the figure, the voltage values, in principle, do not vary significantly, unlike the photocurrent density. The combination of layers has a significant effect on



the latter. To provide specific values, for the structure in work 5, the voltage varied from 1.03 V to 1.07 V, and the photocurrent ranged from 0.78 to 1.78 mA·cm<sup>-2</sup>. This was a cell with an n-i-p structure, where the film of the main material was applied to tin oxide (ETL), and poly(3-hexylthiophene-2,5-diyl) (HTL). Hydration improves the transport properties of the material; the hydrated material showed an initial photocurrent of 1.03 mA·cm<sup>-2</sup> and 11.4 mA·cm<sup>-2</sup> after treatment. The voltage increased from 0.88 V to 0.92 V (Alkhamash H. I. et al., 2023).

In work (Ullah A. et al., 2024), photocurrent values of 5.01 mA·cm<sup>-2</sup> and voltage of 0.89 V were obtained. Here, TiO<sub>2</sub> was used as the ETL and Spiro-OMeTAD as the HTL.

The voltage values are directly influenced by the differences in the conduction band energies of the acceptor and the valence band of the donor.

Based on the values of the bandgap and the intensity of the absorption peaks, the photocurrent should lie in the range from 6 to 17 mA·cm<sup>-2</sup>, and the above-shown results generally fall within this predicted range (Tress W. et al., 2022).

The next figure describes the efficiency of Cs<sub>2</sub>AgBiBr<sub>6</sub> solar cells.

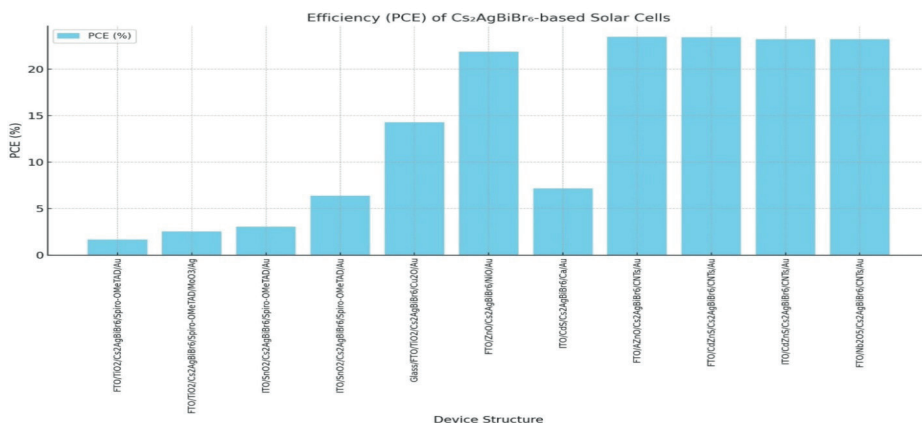


Figure 3. Efficiency of Cs<sub>2</sub>AgBiBr<sub>6</sub> solar cells

### Optoelectronic properties. Absorption

We have reviewed studies on absorption, luminescence parameters, and the obtained values of voltage and current density.

Calculations and measurements of absorption, dielectric function, refractive index, reflectivity, and conductivity play a major role in determining the optoelectronic properties of the samples. In work (Sirtl Maximilian T. et al., 2022), it was concluded that the real and imaginary parts of the dielectric permittivity are high at low photon energies and significantly decrease with increasing photon energy. This value provides information about the speed of light in a dense medium. Dielectric permittivity is more related to the excitation of electrons for intra-band transitions, with its maximum occurring at 6.5 eV. The real part of the refractive index has its maximum value at 2.5 eV, which fully satisfies the requirements for use as a component in solar cells. The value of the refractive index is 2.74 (Ullah A. et al., 2024).

A typical absorption spectrum for  $\text{Cs}_2\text{AgBiBr}_6$  samples is shown in Figure 4, and in many studies, this shape remains consistent, with the peak shift differing by only  $\pm 5$  nm.

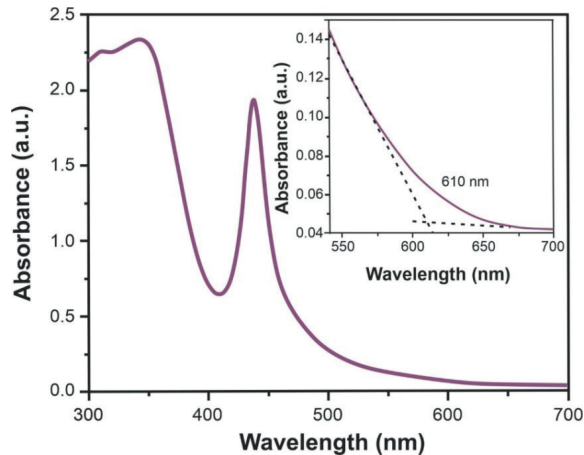


Figure 4. A typical absorption spectrum for  $\text{Cs}_2\text{AgBiBr}_6$  samples (Ji F. et al., 2023)

The absorption consists of three parts. The first is a flat and broad absorption region at wavelengths below 350 nm, associated with absorption due to direct forbidden transitions. This range is close to the value of the bandgap. A characteristic and strong peak around 438-450 nm accounts for more than 20% of the total light absorption in  $\text{Cs}_2\text{AgBiBr}_6$  films. This absorption is related to the optical transition from the ground state  $1S_0$  to the excited state of the triplet  $3P_1$  of the  $\text{Bi}^{3+}$  ion in  $\text{Cs}_2\text{AgBiBr}_6$ . The third region is a weak and broad absorption zone at higher wavelengths with an edge around 610 nm, which arises due to absorption from indirect forbidden transitions (Ji F. et al., 2023).

In study (Robert L.Z. et al., 2018), the absorption peak maximum for the crystal was located at 2 eV. The tails of the absorption spectrum are usually associated with a high degree of disorder, meaning the presence of defects due to silver ions or vacancies caused by cesium.

The maximum absorption intensity is observed at a temperature close to  $100^\circ\text{C}$ , and it decreases as the temperature continues to rise.

In work (Yang J. et al., 2018), the absorption peak is at 438 nm with a weak tail at 610 nm, which corresponds to 2.8 eV and 2 eV, respectively. The first one is attributed to excitonic absorption. The 440 nm peak was also attributed to excitonic absorption in work, while peaks below 400 nm correspond to intra-band transitions.

Samples treated with plasma hydrogenation technology showed an increase in absorption intensity around 496 nm with increasing treatment time up to 1200 s (Alkhamash H. I. et al., 2023). As the degree of hydrogenation increased, the concentration, mobility, and lifetime of charge carriers also increased, which explains the enhanced absorption around 496 nm.

Results from transient absorption spectroscopy showed photoinduced absorption

centered at 2.14 eV. Photoinduced absorption in  $\text{Cs}_2\text{AgBiBr}_6$  decayed with a similar time characteristic to the bleaching of the ground state, which further confirms the slow decay of photocharged particles on a microsecond timescale, as photoinduced absorption can only arise from states formed after excitation.

The absorption coefficient begins at 1.6 eV, and generally, for use in solar cells, a coefficient value at the level of  $10^5$  is sufficient. The maximum measured absorption coefficient is  $22.5 \times 10^5$  at an energy of 14.65 eV. Conductivity in the material begins at 1.85 eV and peaks at 9.71 eV, which corresponds to the low-energy part of the spectrum. This is quite acceptable for optoelectronic applications.

#### *Luminescence*

Photoluminescence (PL) in  $\text{Cs}_2\text{AgBiBr}_6$  exhibits intriguing features due to its electronic structure and defect states. The nature of luminescence in the material is evidently associated either with spatially localized centers of coloration or with intra-band transitions. According to various studies, the peaks are concentrated in the 600–700 nm range, which corresponds to an energy of around 2.0–2.1 eV. This peak is usually attributed to transitions associated with defect states in the material's forbidden band. The position of the peak depends on the method of material preparation, excitation technique, material treatment, and temperature conditions.

Additionally, a significant Stokes shift is observed between the absorption and emission peaks, indicating strong electron-phonon interaction and possible exciton self-localization. Temperature studies show that PL intensity increases as the temperature decreases, which is linked to the suppression of non-radiative recombination processes.

Material processing, such as doping or altering synthesis conditions, can significantly affect the spectral characteristics of PL, allowing for tuning the optical properties of  $\text{Cs}_2\text{AgBiBr}_6$  for potential optoelectronic applications.

In work (Ji F. et al., 2023), thin films were found to have two main peaks: a broad one at 1.87 eV (663 nm) and a narrow one at 1.98 eV (627 nm) at 22,6 K. The forbidden band width for these samples was calculated to be between 1.95–2.19 eV.

In work (Tress W. et al, 2022), photoluminescence was observed at 545 nm. Notably, in these samples, the luminescence was red-shifted compared to the absorption. This large Stokes shift indicates significant electron-phonon interaction, leading to self-localized excitons or emission from coloration centers. While the luminescence between 500–600 nm is characteristic for thin films and single crystals, for nanocrystals, the emission peaks are centered around 460 nm.

In work (Alkhamash H. I. et al., 2023), photoluminescence was observed at 761 nm, and upon applying the hydrogenation technique, the intensity of PL at 761 nm tended to increase. The transitions responsible for PL may involve phonons or be localized at defects. With hydrogenation, due to changes in the band structure (e.g., compression or expansion of the forbidden band), a shift in the PL wavelength may be observed. Additionally, as the degree of hydrogenation increased, the concentration, mobility, and lifetime of charge carriers also increased.

Time-resolved spectroscopy experiments have revealed that luminescence appears after about 1 ns following excitation (Robert L.Z. et al., 2018). The method of time-

resolved absorption spectroscopy allowed for the recording of charge carrier dynamics and their radiative recombination. The carrier lifetime in thin films of the material was recorded at 1.4 ms, which is an order of magnitude longer than in lead-based perovskites. Similar acceptable transport properties were found in larger samples.

It was concluded that most recombinations are non-radiative, while radiative recombinations occur due to defects. To confirm this, Particle Size Distribution (PSD) calculations were made, indicating that the valence band is below the Fermi level, with its maximum at 1.5 eV, suggesting a p-type material. This is due to acceptor impurities, such as silver vacancies or cesium vacancies.

These experiments allowed for the calculation of charge carrier mobility, which was found to be  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , a relatively high value, contributing to the high quantum efficiency of solar cells based on  $\text{Cs}_2\text{AgBiBr}_6$ .

From time-resolved spectroscopy results in work (Yang J. et al., 2018), two photoluminescence quenching times were recorded: 1 ns and 30 ns. The first corresponds to the time of bimolecular recombination, where an electron from the conduction band recombines with a hole from the valence band. The second corresponds to the exciton lifetime.

In work (Ji F. et al., 2023), two luminescence decay times were also recorded: a rapid decay of 50–150 ns, which is emission from traps or temporary states, and a slower decay of up to 600 ns, which is emission from fundamental electron-hole recombination in the material.

According to theoretical predictions, in thin films, photoluminescence should decay relatively slowly, around 200 ns, while in single crystals, it should decay longer than 500 ns.

In work (Sirtl Maximilian T. et al., 2022), results show that density functional theory calculations indicate a derivative nature of the band structure, suggesting low charge carrier mobility due to the relatively large effective mass of the charge carriers.

#### *Photocurrent*

The performance of solar cells is influenced not only by the bandgap width and charge carrier mobility but also by the values of photocurrent and voltage exhibited by the sample. For the structure in work (Yang J. et al., 2018), the voltage varied from 1.03 V to 1.07 V, and the photocurrent ranged from 0.78 to 1.78  $\text{mA}\cdot\text{cm}^{-2}$ . Hydration improved the material's transport properties, and the hydrated material showed an initial photocurrent of 1.03  $\text{mA}\cdot\text{cm}^{-2}$ , which increased to 11.4  $\text{mA}\cdot\text{cm}^{-2}$  after processing. The voltage increased from 0.88 V to 0.92 V (Alkhamash H. I. et al., 2023).

In work (Tress W. et al., 2022), photocurrent values of 5.01  $\text{mA}\cdot\text{cm}^{-2}$  and voltage of 0.89 V were obtained.

Voltage values are directly influenced by the differences in the conduction band energy of the acceptor and the valence band of the donor.

Based on the values of the bandgap width and absorption peak intensity, the photocurrent is expected to fall in the range of 6 to 17  $\text{mA}\cdot\text{cm}^{-2}$ , and the reported results are within this predicted range.

**Conclusion.** Double halide perovskites  $\text{Cs}_2\text{AgBiBr}_6$  represent a new generation of

materials for solar cells due to their outstanding optoelectronic properties. Specifically, these include an optimal bandgap width (1.6 eV — 2.19 eV), an absorption coefficient of  $10^5$ , an absorption spectrum (350 - 610 nm), charge carrier mobility ( $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ), and charge carrier lifetime of 1.4 ms, which is an order of magnitude longer than that in lead-based perovskites. Additionally, they exhibit notable luminescent properties, with a luminescence spectrum in the range of 400-600 nm and decay times up to 600 ns.

Of course, these parameters are strongly dependent on the sample preparation method and fabrication process. Solution crystallization, solution deposition, and spin-coating methods allow the production of high-purity  $\text{Cs}_2\text{AgBiBr}_6$  samples. The bandgap width and its nature (direct or indirect) are influenced by the crystal defect structure and the use of additional technologies.

However, researchers continue to produce various samples and test their optoelectronic properties to improve the stability and efficiency of solar cells. The architecture and layer combinations also play a significant role. As of today, the highest efficiency achieved is 23.5% for the combination of FTO/AZnO/ $\text{Cs}_2\text{AgBiBr}_6$ /CNTS/Au.

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