



Experimental and theoretical study of crystal structure and bandgap of CdBi_2S_4

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ABSTRACT

In this study, we present a new way of solid state synthesis of single crystals of CdBi_2S_4 . Moreover, we compare the results of both experimental and theoretical studies of crystal structure and energy bandgap of this compound. Obtained single crystals are characterized by X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The presence of single crystals of the title compound is confirmed by the X-ray diffraction studies. The resolved crystal structure agrees with the one already reported for CdBi_2S_4 . SEM images show the compositional homogeneity of obtained crystals and EDX investigation confirms the elemental composition of CdBi_2S_4 . Moreover, the Uspex algorithm is used for crystal structure prediction of this compound to check for potential polymorphs. Results of action of the Uspex algorithm suggest the existence of a new monoclinic phase different than that observed experimentally. *Ab initio* calculations were used to study the band structure of the theoretical crystal structure of CdBi_2S_4 using GGA-PBE and HSE06 approximations. The energy bandgap of bulk CdBi_2S_4 was also studied experimentally with the Tauc method, yielding a value of 1.42 eV, showing the potential of this compound for applications in photovoltaics.

1. Introduction

CdBi_2S_4 is an inorganic compound obtained for the first time in 1983 by Pawar and others in the form of films using the spray pyrolysis technique, for the purpose of solar energy harvesting [1]. Indeed, studies of electrochemical photovoltaic cells using photoanodes made of CdBi_2S_4 films revealed the photovoltaic activity of this material [2,3]. Synthesis of this compound with spray pyrolysis technique has been further studied in the term of influence of substrate temperature on electrical and optical properties of produced films, and in the aspect of reaction of CdS with Bi_2S_3 in solid state [4,5]. Films of CdBi_2S_4 may also be obtained through the electrodeposition process [6].

The first and only so far synthesis of single crystals of CdBi_2S_4 was accomplished by Choe and cooperators using an RbCl/LiCl flux [7]. CdBi_2S_4 adopts a monoclinic structure with space group $C2/m$ that is isostructural with crystal structure of mineral kurdiavite, $(\text{Cd,Pb})\text{Bi}_2\text{S}_4$ [7–9]. There are no reports on other polymorphic structures of CdBi_2S_4 . However, there exists an analog named grumiplucite, HgBi_2S_4 , which has a similar crystal structure and also occurs naturally [10]. Moreover, kurdiavite is an lozenge-like sulfide for which the m plane is repeated with translation of c.a. 4 Å [11]. In lozenge-like structures one of the unit

cell parameters is of about 4 Å which is far less than two others [11]. At the same time, analysis of its crystal structure reveals that it is a member of the pavonite homologous series with the general formula $\text{M}_{n+1}(\text{Bi/Sb})_2\text{Q}_{n+5}$ despite deviation in stoichiometry [9,12]. Recent studies show that pavonites are promising thermoelectric materials due to their extremely low thermal conductivity, crystal structure built of slabs, and possibility for elemental substitution [13,14].

This study presents the solid state synthesis of single crystals of CdBi_2S_4 . Produced single crystals are examined with X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and the Tauc method. Theoretical methods are used to find polymorphic structures of CdBi_2S_4 (based on evolutionary algorithm Uspex) and to determine the energy bandgap of this compound (exploiting DFT and HSE06 calculations). Results of experimental and theoretical studies of crystal structure and bandgap of CdBi_2S_4 are compared and discussed.

2. Material and methods

2.1. Solid state synthesis

The single crystals were obtained in the reaction of elements. 40 mg

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of Cd (granules, 5 N, POCh), 74 mg of Bi (powder, $\geq 99.99\%$, Aldrich Chemistry), and 34 mg of S (powder, pure for analysis, POCh) were placed in a quartz ampoule of 55 mm length and 5 mm inner diameter. Iodine (crystals, pure for analysis, POCh) in the amount of 2 mg was used as an additional transporting agent, however taking into account that the temperature gradient along used ampoule is 5 °C only, no significant vapor transport took place.

The process was carried out in a horizontal tube furnace (Carbolite, EZS 1200) at 600 °C for 14 days. The rate of rising of temperature at the beginning of the process was 1 °C per minute. The cooling down after the reaction was free.

2.2. X-ray diffraction

The procedure and apparatus for both single crystal and powder X-ray diffraction studies are the same as in the investigation performed by Matyszczyk et al. [15–19].

Good-quality black bulk single-crystal with a metallic luster was selected for the X-ray diffraction experiment at room temperature.

CdBi₂S₄ crystallizes in the monoclinic *C2/m* space group. The structure is assumed to be composed of Bi³⁺, Cd²⁺, and S²⁻ ions. The crystallographic data are summarized in Table 1.

Wyckoff positions, atomic coordinates, and atomic displacement parameters are shown in Table S1 in the supplemental material. The values of bond lengths and valence angles are given in Table S2–S3 in the supplemental material.

2.3. Scanning electron microscopy and energy-dispersive X-ray spectroscopy

Scanning electron microscopy observations were carried out by Quanta 200 FEI Microscope equipped with EDAX unit.

2.4. UV–Vis spectrophotometry

The absorbance spectrum needed for preparation of Tauc plots was collected according to procedure used previously by Matyszczyk et al.

Table 1
Crystal data and structure refinement for the investigated compound.

Empirical formula	Bi _{2.02} Cd _{0.98} S ₄
Formula weight	660.77
Temperature/K	296.2(5)
Crystal system	monoclinic
Space group	<i>C2/m</i>
<i>a</i> /Å	13.12051(19)
<i>b</i> /Å	3.98623(4)
<i>c</i> /Å	14.6231(2)
α /°	90
β /°	116.2782(18)
γ /°	90
Volume/Å ³	685.770(19)
<i>Z</i>	4
ρ_{calc} g/cm ³	6.400
μ /mm ⁻¹	55.865
<i>F</i> (000)	1115.0
Crystal size/mm ³	0.177 × 0.086 × 0.077
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	6.21 to 69.938
Index ranges	−20 ≤ <i>h</i> ≤ 20, −6 ≤ <i>k</i> ≤ 6, −23 ≤ <i>l</i> ≤ 23
Reflections collected	12342
Independent reflections	1678 [<i>R</i> _{int} = 0.0563, <i>R</i> _{sigma} = 0.0263]
Data/restraints/parameters	1678/0/48
Goodness-of-fit on <i>F</i> ²	1.165
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0292, <i>wR</i> ₂ = 0.0717
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0723
Largest diff. peak/hole/e Å ⁻³	4.03/−3.85

[15].

2.5. UspeX and *ab initio* calculations

The methodology of crystal structure prediction and *ab initio* calculations was adopted from Matyszczyk et al. study, where experimental crystal structure of Cu₃VSe₄ was predicted by the UspeX algorithm [15, 20,21]. For *ab initio* calculations we used the Vienna Ab Initio Simulation Package VASP.5.4.4 [22].

The GGA-PBE (Perdew–Burke–Ernzerhof) approximation and pseudopotentials of PAW type (projector augmented wave method), which increase the efficiency of simulations, were used for the relaxations of structure obtained by the UspeX algorithm and during its operation [23–25]. These approximations were also used in the band structure calculations, as well as the HSE06 approximation.

3. Results and discussion

The obtained single crystals of CdBi₂S₄ appeared needle-like and black. Scanning electron microscopy image of sample crystal, recorded using backscattered electrons, reveals the compositional homogeneity of it (Fig. 1). The result of the energy-dispersive X-ray spectroscopy investigation of the single crystal presented in Fig. 1 confirms that it is composed of Cd, Bi, and S in ratio 1 : 2 : 4 (the exact ratio Cd:Bi:S is 1 : 2.05 : 4.11).

X-ray diffraction study of synthesized single crystals shows that there are eight atom sites in the asymmetric part of the structure – six non-disordered and two partially occupied by Bi and Cd. These sites are denoted as M1 and M2, where the first one is more occupied by Bi and the latter one by Cd, and both contributions at each site are constrained to sum to 1. Bi, M1, and all S sites lie on an *m* plane, while Cd and M2 have a 2/*m* site symmetry. Wyckoff positions, atomic coordinates, and atomic displacement parameters are shown in Table S1 in the supplemental material.

The crystal structure of CdBi₂S₄ may be represented with edge-sharing BiS₆/BiS₇ and CdS₆ octahedra that are arranged into zig-zag stripes parallel to the *a*-axis, where one stripe contains fully occupied Bi and Cd sites, the other M1 and M2 sites. Between each individual stripe, there appear empty channels along the *b*-axis. The arrangement of atoms within the unit cell and crystal structure packing of CdBi₂S₄ are presented in Figs. 2 and 3. The figures were prepared using the Mercury program [25].

Analyzing the non-disordered sites, Bi–S bond lengths are in the range from 2.599(1) to 2.984(1) Å, however, for simplification of the description and figure-preparation, additionally, interatomic contact between Bi1 and S4 sites of 3.404(2) Å was assumed to be a bond, even though its value is higher than the sum of Bi³⁺ and S²⁻ ionic radii. Cd–S bond lengths are in the range from 2.566(1) to 2.798(1) Å. The values of bond lengths and valence angles are given in Tables S2 and S3 in the supplemental material.

As already indicated by Choe et al., the crystal structure of CdBi₂S₄ is isotopic with HgBi₂S₄ and can be described as a NaCl superstructure with chemical twinning parallel to (113) plane [7]. In Choe's study, the same disorder of Bi and Cd was assumed, however, the final Bi, Cd, M1, and M2 position occupancies were not constrained to sum to 1 [7].

The measured powder diffraction pattern of the obtained product didn't match any phase in the PDF database. However, it is in very good agreement with the simulated powder diffraction pattern based on the crystal structure described above (Fig. 4). This fact further justifies the obtaining of the CdBi₂S₄ phase and additionally proves the crystal structure resolved in this study.

The UspeX algorithm was used to check for the occurrence of potential polymorphic structures of CdBi₂S₄. This algorithm is a very useful tool that many times led to results consistent with experimental data [20,21]. At the same time, it predicted both known and unknown experimentally crystal structures of complex inorganic compounds [27]. In this study, it

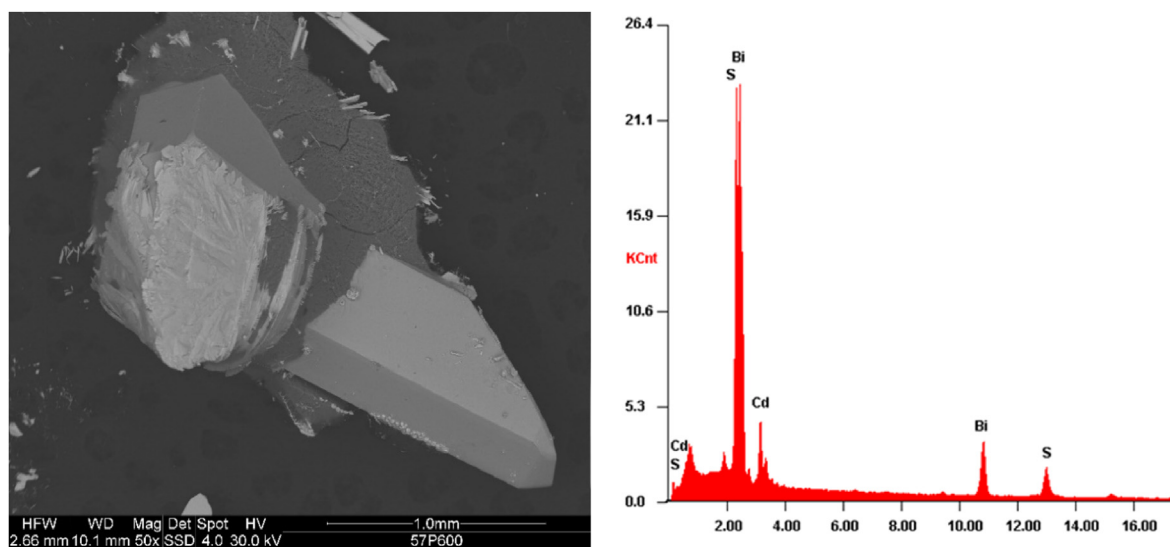


Fig. 1. SEM image and EDX spectrum of crystal of CdBi₂S₄ recorded using the backscattered electrons.

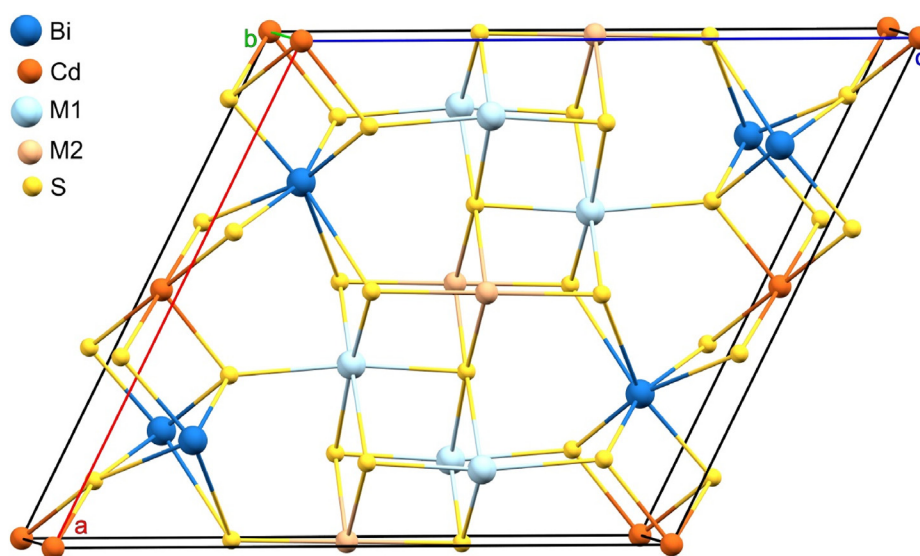


Fig. 2. The unit cell of CdBi₂S₄.

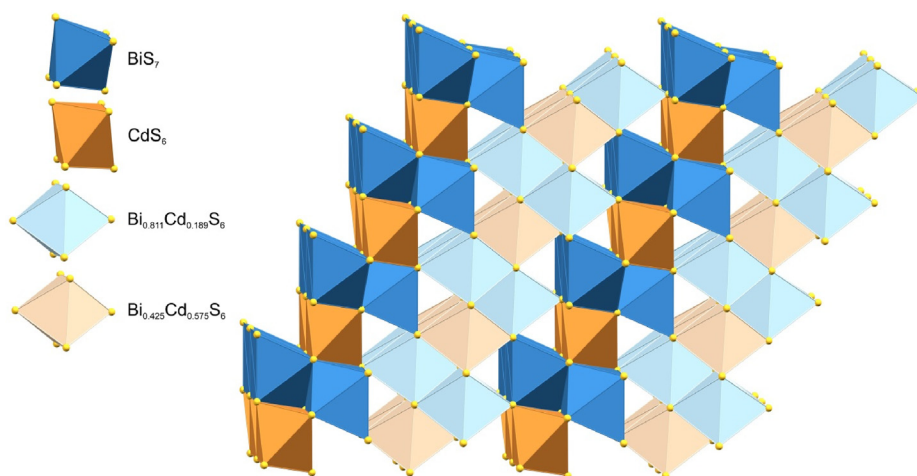


Fig. 3. Crystal structure of CdBi₂S₄.

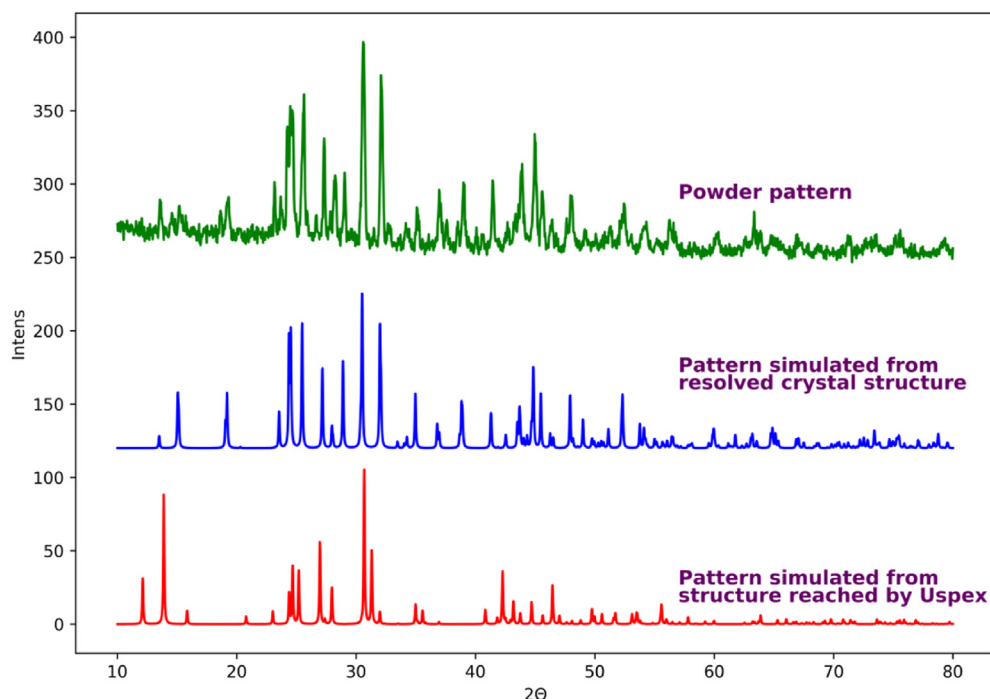


Fig. 4. Comparison of powder patterns: experimental (top), simulated using resolved crystal structure (middle), and simulated using crystal structure determined by Uspex algorithm (bottom). Patterns were simulated using Mercury software [26].

was run 4 times, because of its partially stochastic nature. Each time the algorithm converged just within a dozen generations, which is far below the maximal allowed number of generations. In each run, the Uspex algorithm found only one crystal structure with space group $C2/m$ (no. 12). However, a comparison of simulated powder patterns reveals that this crystal structure is different than experimental one (Fig. 4). To ensure that the Uspex algorithm is not able to reach the real crystal structure in this case, it was run 4 times again but with an additional constraint on symmetry consisting in taking into account structures only with space group $C2/m$. However, the result remained unchanged. Table 2 summarizes structural information on the theoretical structure, while atomic positions are given in Table S4 in the supplemental material.

The difference between the experimental crystal structure and that predicted by the Uspex algorithm is best visible on the view of these structures along the c -axis (Fig. 5). The real crystal structure is denser and more complicated than the theoretical one. The crystal structure reached by the Uspex algorithm appears simple and is composed of layers built from Bi^{3+} and S^{2-} ions separated by Cd^{2+} cations. It looks like the Uspex algorithm is not capable of predicting crystal structures with the structural disorder.

The energy bandgap of bulk CdBi_2S_4 wasn't studied so far. In this study, according to the Tauc method, we have found that bulk CdBi_2S_4 presents a direct energy bandgap of value 1.42 eV. The corresponding Tauc plot is presented in Fig. 6. The indirect transition is not exhibited by CdBi_2S_4 .

The energy bandgap of films of CdBi_2S_4 prepared by spray pyrolysis technique was investigated with the Tauc method, however, the results are contradictory. Pawar et al. showed that such films exhibit a direct energy bandgap of value 2 eV, while Semenov and coauthors reported value slightly above 1.4 eV (also direct) [4,5]. Therefore, there is no doubt that CdBi_2S_4 is a direct bandgap material. After careful comparison of both studies, it turns out that Pawar and coauthors did experimental flaw. Semenov et al. demonstrated that in the spray pyrolysis technique the produced films in the $\text{CdS-Bi}_2\text{S}_3$ system show Bi_2S_3 deficiency of 10 mol % in comparison to the formally equimolar sprayed solution [5]. It is probably caused by the precipitation of some amount of Bi^{3+} ions in the form of poorly soluble complexes [5]. Pawar and coauthors did not

Table 2

Cell parameters of theoretical polymorph of CdBi_2S_4 .

a	b	c	α	β	γ
13.223 Å	4.051 Å	7.565 Å	90.000°	74.589°	90.000°

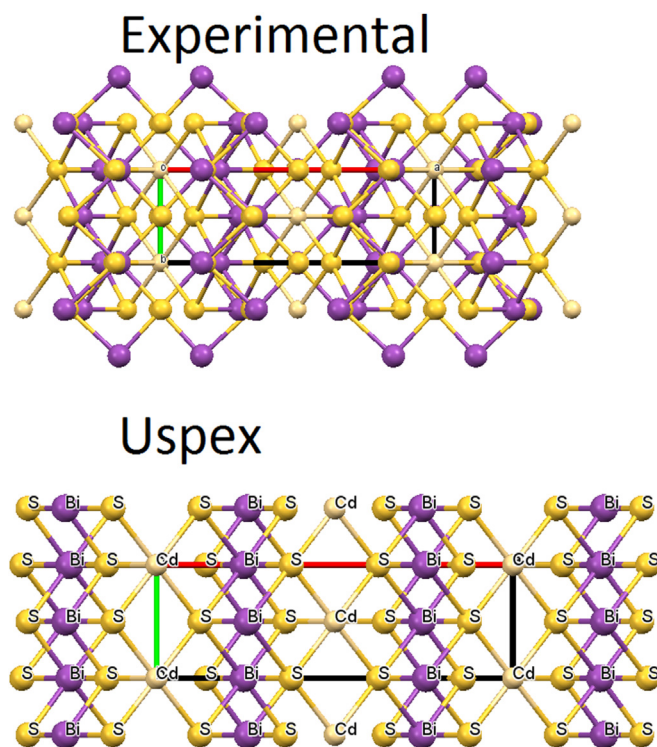


Fig. 5. Comparison of views of experimental and theoretical crystal structures of CdBi_2S_4 along the c axis.

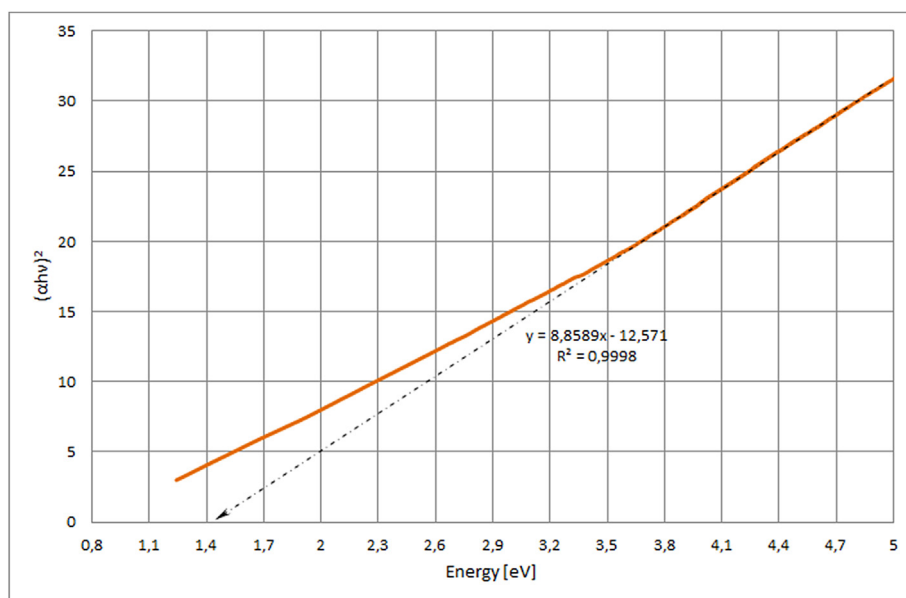


Fig. 6. Tauc plot for suspension of bulk CdBi_2S_4 in ethanol.

check the composition of the resulting film assuming that spraying of an equimolar solution of Cd^{2+} and Bi^{3+} cations will result in CdBi_2S_4 compound [4]. Thus, in fact, Pawar et al. studied film of composition with a greater amount of CdS in comparison to CdBi_2S_4 , what caused the “increase” in energy bandgap to a higher value, closer to that of CdS (which is c.a. 2.4 eV) [4]. Moreover, Semenov's study gave pieces of evidence for the formation of a new compound in the CdS– Bi_2S_3 system (instead of solid solutions or intercalates of CdS in Bi_2S_3) based on X-ray diffraction studies (appearance of additional reflections), change in kind of photo-response, and maxima in density and conductivity near the composition corresponding to CdBi_2S_4 [5]. Our study proves that this compound has an optical energy bandgap of value c.a. 1.4 eV what lies in the optimal range of the Shockley-Queisser limit making CdBi_2S_4 a promising material for applications in solar cells [28].

The electronic band structure along high symmetry points of the

corresponding Brillouin zones for the theoretical structure of CdBi_2S_4 was calculated using two approximations (GGA-PBE and HSE06) to study the bandgap of crystal structure proposed by the Uspex algorithm (Fig. 7).

From Fig. 7 it is seen that the overall profiles of the valence and the conduction bands are very similar in two applied approximations. Calculated electronic band structures reveal the existence of band gaps. The bandgap value calculated with GGA-PBE approximation is 1.50 eV while the application of HSE06 approximation yielded 2.12 eV. In both cases the type of bandgap is indirect. Typically, in the case of complex inorganic sulfides and selenides, the GGA-PBE approximation understates the values of band gaps while the HSE06 approximation gives results that are more reliable [29]. Taking that into account, values calculated here suggest that CdBi_2S_4 with theoretical crystal structure would be less useful in solar cell applications than the one with

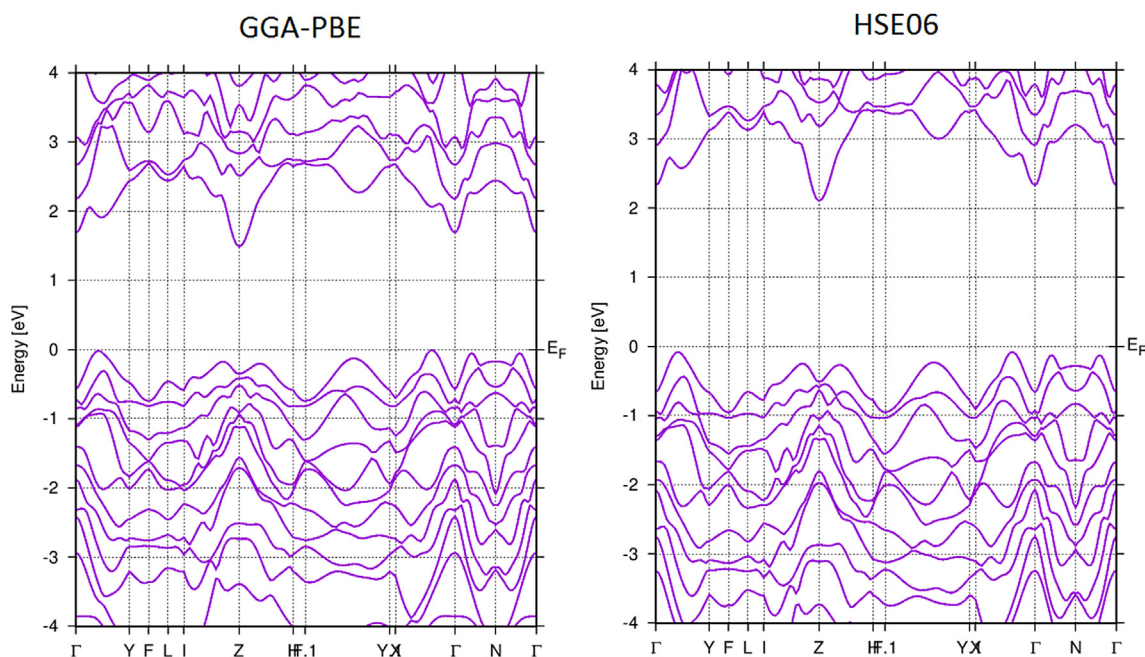


Fig. 7. Electronic band structures of theoretical CdBi_2S_4 structure calculated with GGA-PBE and HSE06 approximations.

experimental, disordered structure.

4. Conclusions

We presented a novel synthesis of CdBi_2S_4 in the solid state reaction. The composition and crystal structure of the product is confirmed by the SEM, EDX, and XRD investigations. The crystal structure of CdBi_2S_4 presented in this study is in agreement with the one presented before in literature. It is monoclinic and exhibiting structural disorder. It should be emphasized that the crystal structure of CdBi_2S_4 synthesized in the solid state reaction is the same as of that obtained using a RbCl/LiCl flux. The genetic algorithm, Uspex, suggests that CdBi_2S_4 theoretically may occur in another monoclinic structure, which doesn't present structural disorder. The *ab initio* investigations of the bandstructure of this new crystal structure reveal that CdBi_2S_4 exhibiting real crystal structure is much more useful for applications in photovoltaics, due to the optimal value of direct energy bandgap (1.42 eV – value lying near the most optimal range in the Shockley-Queisser limit), in contrast to the case of the theoretical structure (1.50–2.12 eV).

CRediT authorship contribution statement

Grzegorz Matyszczyk: Conceptualization, Methodology, Supervision, Writing – original draft, Investigation, Writing – review & editing, Visualization, Formal analysis. **Szymon Sutula:** Investigation, Writing – review & editing, Visualization, Formal analysis. **Krzysztof Krawczyk:** Supervision, Conceptualization. **Krzysztof Woźniak:** Writing – review & editing, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jssc.2021.122695>.

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