

Contents lists available at ScienceDirect

Journal of Solid State Chemistry



journal homepage: www.elsevier.com/locate/jssc

Synthesis, crystal structure and physical properties of a novel quaternary selenide Cu_6GeWSe_8



Menghu Zhou^{a,b,*}, Yadong Gu^{b,c}, Binbin Ruan^{a,b}, Qingsong Yang^{b,c}, Genfu Chen^{a,b,c}, Zhian Ren^{a,b,c,**}

^a Songshan Lake Materials Laboratory, Dongguan, Guangdong, 523808, China

^b Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing, 100190, China

^c School of Physical Sciences, University of Chinese Academy of Sciences, Beijing, 100049, China

ARTICLE INFO	A B S T R A C T			
Keywords: Cu_6GeWSe_8 crystal structure semiconductor band gap diamagnetism band structure	Here we report a novel quaternary selenide Cu_6GeWSe_8 synthesized directly from the constituent elements, which forms within the temperature range from 460 to 620 °C. It crystallizes in the space group $P6_3mc$ with two formula units in the cell of dimensions $a = 7.8651$ (5) Å, $c = 12.9275$ (6) Å. In the unit cell composed of MSe_4 ($M = Cu$, Ge and W) tetrahedrons, Cu atoms occupy two sets of 6c Wyckoff positions, Ge and W atoms respectively occupy $2a$ and $2b$ positions, while Se atoms are located at four inequivalent sites, respectively $2b$ (Se1), $6c$ (Se2), $6c$ (Se3) and $2a$ (Se4). The electrical resistivity and Vis-Nir absorption spectrum indicate that the compound exhibits a semiconducting behavior with an optical band gap of 1.586 eV Cu_6GeWSe_8 shows diamagnetism at room tem- perature and the emergence of a Curie-Weiss-like tail at low temperature. The band structure calculation dem- onstrates that the title compound has a direct band gap, and Cu and Se atoms dominantly contribute to the energy bands and density of states. Cu is mostly in $3d^{10}$ state (+1 valence) and Se in $4p^6$ state (-2 valence). On the basis of the experimental and calculation results, it is concluded that Cu_6GeWSe_8 is a diamagnetic direct-gap semiconductor.			

1. Introduction

Transition-metal chalcogenides have recently aroused great interest in both condensed-matter physics and materials science due to their various intriguing electronic properties and potential applications [1-5]. Among these chalcogenides, the multinary ones may be outstanding candidates for thermoelectric, photovoltaic and topological materials [6-10], whereas it is sometimes difficult to prepare them from direct solid-state reaction of the compositional elements. This is because there is a strong inclination to yield impurity or undesirable phase during the fabrication process on account of the lower formation energy of the unintended phase in comparison with that of the target compound. Catamarcaite, a rare quaternary sulfide mineral with an ideal formula Cu₆GeWS₈, was first discovered by H. Putz et al. from Capillitas, Catamarca, Argentina in the year 2006 [11], but it has not caused too much attention since then and its properties remain unidentified. Very recently, the quaternary chalcogenides Cu₆SnWS₈ and Cu₆SnWSe₈ with similar composition to Cu_6GeWS_8 have been prepared in the lab, which exhibit metallic behavior above 30 K [12]. The emergence of an insulator-like tail below about 30 K on the resistivity curve is supposed to be related to the occurrence of a metal-insulator transition [12]. On the other hand, extrinsic factors such as the weak link between grains and the Kondo effect resulted from slight magnetic impurities are also possibly responsible for the transition, which needs further study. A recent band structure calculation on Cu₆SnWS₈ [13] reveals a zero band gap, which also confirms the metallic nature. Cu₆SnWS₈ and Cu₆SnWSe₈ adopt a face-centered cubic structure (space group: F-43m), while Cu₆GeWS₈ crystallizes in a primitive hexagonal structure (space group: $P6_3mc$) [11, 12]. The structural variation may originate from the atomic radius difference between Ge and Sn. In addition, there is very little known about the crystallographic and physical information of the hemusite Cu₆Sn-MoS₈ [14,15] (a homologue of Cu₆SnWS₈) so far. Accordingly, we could speculate that the quaternary chalcogenides with compositions Cu_6ABCh_8 (A = Ge, Sn; B = Mo, W; Ch = S, Se) may bear diverse lattice structures, and exhibit rich electronic structures and multifarious physical properties. However, Cu₆ABS₈ compounds are usually in the form of

** Corresponding author. Songshan Lake Materials Laboratory, Dongguan, Guangdong, 523808, China.

E-mail addresses: zhoumenghu@iphy.ac.cn (M. Zhou), renzhian@iphy.ac.cn (Z. Ren).

https://doi.org/10.1016/j.jssc.2021.122357

Received 18 April 2021; Received in revised form 9 June 2021; Accepted 14 June 2021 Available online 19 June 2021 0022-4596/© 2021 Elsevier Inc. All rights reserved.

^{*} Corresponding author. Songshan Lake Materials Laboratory, Dongguan, Guangdong, 523808, China.



Fig. 1. (a) An SEM image of the polycrystalline bulk Cu_6GeWSe_8 . (b) An enlarged view for the area marked by a red rectangle in (a). (c)–(f) Elemental mappings for the area in (a). The green, blue, yellow and orange ones respectively denote the mapping of Cu, Ge, W and Se. (g) A representative EDS pattern for Cu_6GeWSe_8 . The average atomic contents of Cu, Ge, W and Se in the sample are presented in the inset panel.

rare minerals with small grain size and symbiotic with other minerals, which hinders the in-depth study on their physicochemical properties. And the corresponding selenides have not been reported up to now. Consequently, massive synthesis of pure Cu_6ABCh_8 sample in the lab is essential. This motivates us to synthesize Cu_6GeWS_8 and its analogue Cu_6GeWSe_8 and investigate into their structural and physical properties, which would be of importance to understand the relationship between structures and properties in chalcogenides. Unfortunately, the monophasic sample of Cu_6GeWSe_8 was not obtained. Thus, in this paper we only focus on the selenide Cu_6GeWSe_8 chemically and structurally related to the catamarcaite Cu_6GeWS_8 .

In this contribution, we report the successful synthesis of a new quaternary selenide Cu_6GeWSe_8 with hexagonal symmetry from direct reaction of the component elements. Based on the powder X-ray diffraction data, the crystal structure was solved using the direct-space strategy and refined by the Rietveld method. The electrical and magnetic properties were characterized respectively by electrical resistivity and magnetic susceptibility measurements. The electronic structure was studied through density functional theory calculation.

2. Experimental details

The polycrystalline Cu_6GeWSe_8 sample was prepared by solid-state reaction from stoichiometric amounts of Cu (99.9%, Alfa Aesar), Ge (99.9999%, Alfa Aesar), W (99.95%, Alfa Aesar) and Se (99.999%, Alfa Aesar) powders. The thoroughly mixed ingredient was pelletized and sealed in an evacuated quartz tube with vacuum less than 10^{-6} Torr. The bulk sample for characterization was obtained by sintering at 873 K. The initial heating cycle was performed at 873 K for 3 days and then the sample was furnace-cooled to room temperature. In order to improve the uniformity of the sample, the as-prepared sample was fully ground, pressed into pellets and resealed in an evacuated quartz tube, which was annealed at 873 K for 10 days and finally cooled down to room temperature.

The sample composition was determined from EDS analysis. Scanning electron micrograph (SEM) and energy dispersive X-ray spectroscopy (EDS) for the pristine surface of the bulk specimen were acquired under accelerating voltage of 15 kV on a Phenom ProX scanning electron microscope. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were conducted using a thermal analyzer (Netzsch STA 449 F³ Jupiter®) at a heating rate of 10 °C/min from 40 to 1000 °C under flowing Ar of 60 ml/min. X-ray diffraction (XRD) data were collected at room temperature using a PANalytical X'Pert PRO X-ray diffractometer with CuK_{α} radiation (wavelength $\lambda = 1.5418$ Å). The crystal structure was solved by the direct space method based on the global optimization algorithm (EPCryst package [16]) and refined by the Rietveld method (GSAS-EXPGUI software [17]). The rationality of the crystal structure was examined by the bond-valence theory. The electrical resistivity measurement was performed on a physical property measurement system (Quantum Design, PPMS-9) by using the standard four-probe method. The dc magnetic susceptibility was measured with a vibrating sample magnetometer (Quantum Design, MPMS-VSM) under an applied magnetic field of 1.0 T. The room-temperature optical absorption spectrum for the powder sample was recorded from 620 to 1240 nm on a UV-Vis-Nir spectrophotometer (Shimadzu, UV-3600 Plus). The electronic structure calculation based on the density functional theory (DFT) method was carried out using Cambridge Sequential Total Energy Package (CASTEP) [18,19] integrated in a visualized software BIOVIA Materials Studio 7.0 [20].

3. Results and discussion

The synthesized Cu_6GeWSe_8 is stable at ambient temperature and pressure, and without any detectable degeneration by keeping in the air



Fig. 2. (a) and (b) XRD patterns for the samples synthesized from 460 to 620 °C. (c) XRD pattern for the sample reacted at 450 °C. The reflections indicated by asterisks show relevance to Cu_6GeWSe_8 and the others most probably belong to an unknown phase. (d) XRD pattern of the products obtained by calcinating the synthetic Cu_6GeWSe_8 at 700 °C under vacuum. The diffraction peaks for each component are marked by specified symbol. (e) TG-DTA curve for Cu_6GeWSe_8 from 40 to 1000 °C. (f) A simple thermodynamic temperature-phase composition diagram based on the resultant products in the closed quartz tubes.

for over two years. It mechanically exhibits brittleness due to the rigid tetrahedrons in the crystal structure correlated to the wurtzite structure. Cu₆GeWSe₈ shows dark-grey color with metallic luster, which reveals the metallic or small gap semiconducting character. The microscopic appearance displayed in the SEM image in Fig. 1 (a) manifests the relatively high densification of the sample as a result of a long-period annealing. As shown in Fig. 1 (b), the hexagonal grains indicated by short-dash lines illustrate that Cu₆GeWSe₈ belongs to hexagonal crystal system in line with the result analyzed by XRD, and the grain sizes are between about 1 and 10 µm. No lamellar grains and obvious preferredorientations can be observed, verifying the three-dimensional character of the compound and the absence of layered WSe2 phase. The elemental mappings in Fig. 1 (c)-(f) make clear the even distribution of each element in Cu₆GeWSe₈, indicative of the homogeneity of the sample. The sample composition is analyzed by EDS. A representative EDS pattern is shown in Fig. 1 (g). Taking account of the possible local-inhomogeneity, we selected multiple points to acquire the EDS data and took the average. The average atomic contents within the measurement uncertainties are presented in the inset panel of Fig. 1 (g) and the atomic ratios of Cu, Ge, W and Se are calculated to be 5.97 : 0.99: 1.00 : 8.14 b y normalizing Wstoichiometry to 1.00. Apparently, the stoichiometric ratios are close to the nominal ones, again confirming the sample homogeneity.

Cu₆GeWSe₈ exhibits an intricate thermodynamic phase diagram, since it is found that neither high nor low reaction temperature can generate the title compound during the process of sample preparation. The XRD pattern in Fig. 2 (c) for the sample obtained from reaction at 450 °C for 3 days only shows a faint clue of the formation of the desired substance, instead it is most likely to produce an unknown phase that needs to further study. The specimens prepared between 460 and 620 $^\circ$ C remain monophasic Cu₆GeWSe₈ as revealed in Fig. 2 (a) and (b), which confirms the temperature range for phase formation. This is also verified by TG-DTA below. Above 630 °C, the target compound is not obtained as well, which is supposed to be ascribed to the decomposition of Cu₆GeWSe₈ at high temperatures. To identify the sample change above 630 °C in the evacuated quartz tube which could be regarded as a closed system, the Cu₆GeWSe₈ sample synthesized at 600 °C was portioned and calcined respectively at 630, 640, 650 and 700 °C under vacuum for 3 days, and the products were then examined by XRD. Those heated at 630–650 $^\circ\text{C}$ display similar diffraction patterns, which contain WSe₂, Cu₂Se, Cu_{0.87}Se, Cu₂GeSe₃ and slight Cu₆GeWSe₈. While that calcined at 700 °C completely decomposes into WSe2, Cu1.8Se, CuSe and Cu2GeSe3 (see Fig. 2 (d)). It should be noted that once the stable WSe₂ appears, it cannot react with other constituents to revert to Cu6GeWSe8 upon cooling from 700 °C to room temperature. Furthermore, TG-DTA



Fig. 3. (a) Rietveld refinement plot for Cu_6GeWSe_8 . The observed intensity data, Y_{obs} , are plotted in the upper field as points represented by black cross. The calculated pattern is shown in the same field as an orange solid-line curve. The vertical bars (|) in the middle field indicate the positions of Bragg reflections. The difference, observed minus calculated, is shown in the lower field. (b) A top view of the structure along the *c*-axis direction. (c) A three-dimensional perspective view in a polyhedral representation.

measurement was carried out to evaluate the thermal stability of the compound in flowing argon atmosphere (as an open system). As can be seen from Fig. 2 (e), two distinct endothermic peaks locate respectively at about 688 and 818 °C, the former is close to the aforesaid decomposition-temperature and the latter may be associated with the further decomposition or melting of some components. Weight-loss initially emerges around 663 °C and essentially terminates at about 900 °C. A total loss near 22% may attribute to the volatilization of partial Se. Here TG-DTA only provides qualitative information for physical and chemical changes, the specific evolution of matters in the Cu₆GeWSe₈ system is absent and needs subsequent investigations. The above analysis results are plotted in Fig. 2 (f) as a simple temperature-phase composition diagram based on the resultant products in the closed quartz tubes, which reveals a narrow phase formation temperature range between 460 and 620 °C.

The crystal structure of Cu_6GeWS_8 had been solved by the direct method from single-crystal diffraction [11]. We tried various methods, including the flux technique and chemical vapour transport (CVT), to grow Cu_6GeWSe_8 single crystal, but only binary (CuSe, WSe₂) and ternary (Cu₂GeSe₃) crystals were obtained. This may be because of the narrow temperature window for phase formation and the absence of an appropriate fluxing agent or transport agent. Referencing the structural model of Cu_6GeWS_8 , the crystal structure of Cu_6GeWSe_8 was solved from

powder diffraction data by the direct-space method based on the global optimization algorithm [21] and refined by the Rietveld method [22]. After data reduction and pattern indexing [23,24], five possible space groups (P31c, P-31c, P63mc, P-62c and P63/mmc) were generated for Cu_6GeWSe_8 from the observed reflection conditions (*hhl*: l = 2n; 00l: l =2*n*; *hkl*: l = 2n or h - k = 3n + 1 or h - k = 3n + 2). The structure solution was conducted using the program EPCryst [16]. After several tentative calculations, space group P63mc was chosen because of the best intensity fit with minimum R_{Bragg}. The determined equivalent position combinations show that, in the unit cell, Cu atoms occupy two sets of 6c Wyckoff positions, Ge and W atoms respectively occupy 2a and 2b positions, while Se atoms are located at four inequivalent sites, respectively 2b (Se1), 6c (Se2), 6c (Se3) and 2a (Se4). It is found that Cu₆GeWSe₈ and Cu₆GeWS₈ (catamarcaite) [11] are characterized by the same structural model, namely the two phases are isotypic. Using the above structural model and the approximate positional parameters, we performed Rietveld refinement by the GSAS-EXPGUI software [17]. The observed and calculated XRD patterns are plotted in Fig. 3 (a), and the refined crystallographic parameters are listed in Table 1. Rp and Rwp respectively stand for the profile *R*-factor and the weighted profile *R*-factor, which converge to $R_{\rm p}$ = 2.09%, R_{wp} = 3.50%, revealing the high reliability of the structural model. The molar mass (M_{mol}) of Cu₆GeWSe₈ is 1269.396 g mol⁻¹,

Table 1

Crystallographic data and Rietveld refinement results for Cu_6GeWSe_8 at room temperature.

Formula		Cu ₆ GeWSe ₈ P6 ₃ mc (No.186)							
Space group									
$a = b = 7.8651$ (5) Å, $c = 12.9275$ (6) Å, $V = 692.56$ (5) Å ³ , $Z = 2$, $R_{\rm p} = 2.09\%$, $R_{\rm wp} = 3.50\%$									
Atom	Wyckoff position	x	у	Z	Occ.	U _{iso}			
Cu1	6 <i>c</i>	0.8364	0.1636	0.4339	1	0.035			
Cu2	6c	0.5021 (4)	0.4979 (4)	0.1786 (3)	1	0.025			
Ge	2a	0	0	0.1827	1	0.005			
W	2 <i>b</i>	1/3	2/3	0.0534 (4)	1	0.022			
Se1	2 <i>b</i>	1/3	2/3	0.2385 (4)	1	0.010			
Se2	6c	0.4986 (3)	0.5014 (3)	0.4922 (7)	1	0.017			
Se3	6c	0.8339 (5)	0.1661 (5)	0.2421 (8)	1	0.019			
Se4	2a	0	0	0.00001	1	0.031			

Table 2

Coordination polyhedrons, selected bond lengths and bond angles in $\mathrm{Cu}_6\mathrm{GeWSe}_8.$

Coordination polyhedron	Bond length (Å)		Bond angle (°)	
Cu1(Se2) ₂ (Se3) (Se4) tetrahedron	Cu1–Se2	2.421 (5) (× 2)	Se2–Cu1–Se2	109.9 (3)
	Cu1–Se3	2.479 (7)	Se2–Cu1–Se3	107.8 (3) (× 2)
	Cu1–Se4	2.387 (6)	Se2–Cu1–Se4	109.80 (19) (× 2)
			Se3–Cu1–Se4	111.8 (3)
Cu2(Se1) (Se2) (Se3) ₂	Cu2–Se1	2.426 (5)	Se1–Cu2–Se2	108.4 (2)
tetrahedron	Cu2–Se2	2.409 (6)	Se1–Cu2–Se3	109.00 (18) (× 2)
	Cu2–Se3	2.405 (5) (× 2)	Se2–Cu2–Se3	110.09 (17) (× 2)
			Se3–Cu2–Se3	110.2 (3)
Ge(Se3) ₃ (Se4) tetrahedron	Ge-Se3	2.390 (6) (× 3)	Se3-Ge-Se3	110.16 (18) (× 3)
	Ge-Se4	2.362 (7)	Se3-Ge-Se4	108.77 (18) (× 3)
W(Se1) (Se2) ₃ tetrahedron	W–Se1	2.393 (8)	Se1–W–Se2	109.05 (15) (× 3)
	W–Se2	2.422 (3) (× 3)	Se2–W–Se2	109.89 (15) (× 3)

consequently, the theoretical density (ρ_t) calculated from the formula $\rho_t = ZM_{mol}/N_AV$ (where *Z*, N_A and *V* are respectively the formula units, Avogadro constant and cell volume) is 6.087 g cm⁻³. The measured actual density (ρ_a) of the polycrystalline pellet is 3.872 g cm⁻³. The relative density ($\rho_r = \rho_a/\rho_t$) is thus calculated to be about 0.64, statistically consistent with the microscopic appearance observed in the SEM images (see Fig. 1). The structural rationality of Cu₆GeWSe₈ is verified based on the bond-valence theory formulated by the empirical equation $v_{ij} = \exp [(R_{ij}-d_{ij})/b]$ [25] that elucidates the relation between bond-valence v_{ij} and bond-length d_{ij} , where *b* is commonly taken to be a constant value of 0.37 Å and R_{ij} denotes the bond valence parameter (R_{ij} values are 1.90, 2.35 and 2.51 Å for Cu–Se, Ge–Se and W–Se bonds, respectively) [25,26]. The calculated $v_{Cu1-Se2}$, $v_{Cu1-Se3}$, $v_{Cu2-Se3}$, v_{Ge-Se3} , v_{Ge-Se4} , v_{W-Se1} and v_{W-Se2} are 0.244, 0.209, 0.268,

0.241, 0.252, 0.255, 0.896, 0.967, 1.369 and 1.267, respectively. In terms of the Pauling's electrostatic valence rule [27], the valences of Cu1, Cu2, Ge and W are respectively estimated to be +0.97, +1.00, +3.66, +5.18 and the valences of Se1, Se2, Se3 and Se4 are respectively around -2.09, -2.01, -1.62, -1.77, which are within the reasonable value for each atom and verify the validity of the crystallographic data listed in Table 1. The average chemical valences of Cu and Se are calculated to be +0.98 and -1.84, suggesting a formal valence formula $(Cu^{0.98+})_6 Ge^{3.66+}W^{5.18+}(Se^{1.84-})_8$.

A top view of the structure along the c-axis direction and a threedimensional perspective view in a polyhedral representation are respectively illustrated in Fig. 3 (b) and (c). Fig. 3 (b) intuitively displays the hexagonal symmetry from the 120° cell angle between *a* and *b*-axis and reveals Z = 2 based on the number of W atoms in the unit cell. It has a wurtzite-like structure with tetrahedral coordination between cations and anions. There are two different Cu sites (Cu1 and Cu2) and four distinct Se sites (Se1, Se2, Se3 and Se4) in the structure, in which Cu1, Cu2, Ge and W atoms occupy the (Se2)₂(Se3) (Se4), (Se1) (Se2) (Se3)₂, (Se3)₃(Se4) and (Se1) (Se2)₃ tetrahedral interstices, respectively. The selected bond lengths and bond angles shown in Table 2 demonstrate all tetrahedrons are irregular, since the tetrahedral bond angles deviate from 109°28'. This is possibly because the radius of Cu(I) is slightly larger than the radii of W(VI) and Ge(IV) (The Shannon radii of Cu(I), W(VI) and Ge(IV) under the coordination number of 4, are respectively 0.74, 0.56 and 0.53 Å). The deviation leads to the distorted tetrahedral crystal-field, to some extent, would affect the physical properties. Due to the radius and electronegativity differences between S and Se, the M-S distances (less than 2.335 Å) in Cu₆GeWS₈ [11] are shorter than the *M*-Se distances in Cu₆GeWSe₈, suggesting that the sulfide has stronger *M*-Ch bonds. By comparison, the CuSe₄ tetrahedrons in Cu₆GeWSe₈ are more regular than the CuS₄ tetrahedrons in Cu₆GeWS₈ (S2-Cu1-S2 angle: 104.5°, S3-Cu1-S4 angle: 114.4°, S3-Cu2-S3 angle: 113.5°, S1-Cu2-S2 angle: 104.1°), while the GeSe₄ and WSe₄ tetrahedrons are respectively more irregular than the GeS₄ and WS₄ tetrahedrons (the S-Ge-S and S-W-S angles lie within the range 109.3-109.7°) [11]. In contrast to Cu₆SnWSe₈ with a cubic stacking of double layers along the <111> direction, Cu₆GeWSe₈ consists of a double layer of packets of ABAC type, stacking along the *c*-axis to give a combined *hchc*...sequence. The first layers are composed of Cu1 tetrahedrons and octahedral cavities, and the second layers are composed of Cu2, Ge and W tetrahedrons. In the second layer, the W tetrahedron shares edges with three Cu2 tetrahedrons in the same layer and three Cu1 tetrahedrons in the first layer, while the Ge tetrahedron only shares vertices with three Cu1 tetrahedrons in the first layer and six surrounding Cu2 tetrahedrons in the same layer. Along the <001> direction, a cluster of six Cu tetrahedrons sharing edges with the central W tetrahedron appears as a "supertetrahedron" with Cu tetrahedrons forming each face. In addition, GeSe₄ and WSe₄ tetrahedrons are nonadjacent, while separated by octahedral cavities organized via three Cu tetrahedrons and a Ge tetrahedron.

The electrical properties of the sample were studied by resistivity measurement. The relatively large room-temperature resistivity with a magnitude of about 40 Ω m implies the poor conducting nature of Cu₆GeWSe₈. Upon cooling, the resistivity monotonically increases and is beyond $10^3 \Omega$ m at around 170 K. Further cooling to lower temperatures, the resistance at 110 K exceeds the measurement range of Quantum Design PPMS-9 for the standard four-probe method. Thus we only study the behavior of resistivity over the temperature range 120-380 K. The temperature-dependent resistivity (ρ -T curve) is plotted in Fig. 4 (a), which shows the semiconducting (or insulating) characteristic ($d\rho/dT <$ 0) of the sample. The conductive mechanism of an insulator could be interpreted by the Arrhenius law $\rho = \rho_{\infty} \exp (E_a/2k_BT)$ generally used to model activated-behavior with an activation energy E_a [28] or by the Mott's variable range hopping (VRH) model $\rho = \rho_{\infty} \exp \left[(T_0/T)^{1/4} \right]$ describing the random potential fluctuation induced localization of carriers [28,29]. The former is appropriate to describe the resistivity variation at the high temperature range (280–380 K) by fitting the data using



Fig. 4. (a) Temperature dependent resistivity with temperature ranging from 120 to 380 K. The inset shows the fitted result by the Arrhenius law for the data at high temperature from 280 to 380 K. (b) Temperature dependence of ZFC and FC magnetic susceptibilities under an applied field of 1.0 T and the fitting curve by the Curie-Weiss law. (c) Room-temperature optical absorption spectrum from 620 to 1240 nm. The inset shows the optical absorption spectrum with the abscissa axis in energy (*E*) unit. (d) (*F* (*R*) $h\nu$)² as a function of energy (*E* = $h\nu$).

the relation ln (ρ/ρ_{∞}) $\propto E_a/2k_BT$, deriving an E_a of about 0.309 eV (see the inset panel in Fig. 4 (a)). Due to the low sintering-temperature, the bulk sample used for resistivity measurements contains ~36% of voids. This causes poor grain connectivity and high grain-boundary resistivity, which has a strong influence on the magnitude of electrical resistivity and even on the resistivity-temperature behavior at low temperatures. As a consequence, the rapid increase in resistance in Cu₆GeWSe₈ polycrystal with decreasing temperature and the deviation from the Arrhenius law at low temperatures are confirmed to be ascribed to the grain-boundary barrier that dramatically increases upon cooling.

In Fig. 4 (b), the magnetic susceptibilities under zero-field-cooled (ZFC) and field-cooled (FC) modes both show weak negative signals of an order of 10^{-4} emu·mol⁻¹·Oe⁻¹ and are perfectly coincide with each other in the whole temperature range. The χ -*T* relation exhibits a Curie-Weiss-like behavior and can be formulated by the expression $\chi = \chi_0 + C/(T - \theta_p)$, where χ_0 is a temperature-independent parameter normally composed of three parts: the diamagnetic, Pauli paramagnetic and van Vleck paramagnetic terms, and the first one is dominant here. $C/(T - \theta_p)$ is the Curie-Weiss term, *C* and θ_p are respectively the Curie constant and paramagnetic Curie temperature. The fitted χ_0 , *C* and θ_p are -3.36×10^{-4} emu·mol⁻¹·Oe⁻¹, 8.05×10^{-4} emu·K·mol⁻¹·Oe⁻¹ and -1.67 K, respectively, thus the effective moment μ_{eff} is calculated to be $0.08\mu_B$ per

formula unit by the formula $\mu_{\rm eff} = (8C)^{1/2}\mu_{\rm B}$. The large resistivity stated above reveals the low itinerant-carrier concentration and hence the less Pauli paramagnetic contribution, moreover, formal charge analysis elucidates that the component elements largely possess the fully filled electronic configurations and mainly donate diamagnetism. In short, Cu₆GeWSe₈ overall show diamagnetism, and the upturn tail at low temperature possibly comes from some paramagnetic impurities that can not be detected on the XRD pattern. In terms of the magnitude of the magnetic moments, it can also be categorized as a magnetically disordered substance or a nonmagnetic substance.

To get a more accurate band gap for the granular system, the room temperature Vis-Nir optical absorption spectrum (Absorbance (*A*)-Wavelength (λ) curve) is recorded for the Cu₆GeWSe₈ powder sample from 620 to 1240 nm and drawn in Fig. 4 (c). In the inset of Fig. 4 (c), the abscissa axis is converted into energy (*E*) unit by the relation $E = 1240/\lambda$, where the units of *E* and λ are respectively eV and nm. The Vis-Nir optical absorption spectrum can be interpreted through the Kubelka-Munk model *F* (*R*) = (1-*R*)/2*R* and the relation *A* = -lg*R*, where *R* and *A* are respectively the reflectance and absorbance, and *F* (*R*) is proportional to the extinction coefficient. A modified Kubelka-Munk function (*F* (*R*) μ)² can be established by multiplying *F* (*R*) with $h\nu$ combining with the coefficient *n* = 2 associated with a direct allowed electronic transition from



Fig. 5. (a) Brillouin zone for hexagonal Cu₆GeWSe₈ with special *k*-point paths. (b) The calculated band structure along the special *k*-point paths. The shaded region denotes the band gap. (c) The total density of states (DOS) together with the contributions of Cu, Ge, W and Se atoms.

the valence band to the conduction band. $(F(R)h\nu)^2$ as a function of energy $(E = h\nu)$ is shown in Fig. 4 (d). Therefore, the optical band gap $E_{g,opt}$ of the Cu₆GeWSe₈ semiconductor particles obtained by $(F(R)h\nu)^2 = h\nu - E_{g,opt}$, is estimated to be about 1.586 eV.

In comparison with the metallic Cu₆SnWSe₈ [12] of similar composition, Cu₆GeWSe₈ exhibits semiconducting behavior. The Sn-containing compound adopts a cubic F-43m symmetry while the Ge-containing one crystallizes in a hexagonal $P6_3mc$ symmetry. The different crystallographies of Cu₆SnWSe₈ and Cu₆GeWSe₈ are due to the difference between the *M*Se₄ (M = Sn and Ge) tetrahedrons, mostly, the radius of Sn ion is larger than that of Ge ion [11,30,31]. The structural difference yields the quite distinct electronic band structures and diverse properties. On the other hand, magnetic moment analysis [12] reveals that partial Cu²⁺ ions introduce charge carriers into the host Cu₆SnWSe₈, suggesting a formal valence formula (Cu⁺)_{6-x} (Cu²⁺)_xSnWSe₈ that allows to be considered as a self-doped compound. However, the above bond-valence theory calculation supposes that most of atoms in the semiconducting Cu_6GeWSe_8 may own fully filled shells. As a result, a gap of 1.586 eV opens between the filled and unfilled bands. Compared with Cu_6GeWSe_8 , the stronger bond strength between *M* and *Ch* in Cu_6GeWS_8 as mentioned above implies that the electrons in the sulfide are more localized. This suggests that the sulfide possibly shows a more non-metallic character with a larger band gap.

The electronic structure of Cu₆GeWSe₈ was investigated by the planewave pseudopotential method within the framework of density functional theory. Using the experimental lattice parameters and atomic coordinates in Table 1, we made attempts to perform electronic structure calculations without including the spin-orbit coupling effect. All calculations were carried out within a primitive cell with Monkhorst-Pack *k*point meshes 8 × 8 × 16. An energy cutoff of 880 eV and an SCF (selfconsistent field) tolerance of 5.0×10^{-7} eV/atom were used in our calculations. We tried a variety of exchange-correlation functionals combining with different pseudopotentials to execute the calculations and found that the use of generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional [32] under norm conserving pseudopotential works out a maximum energy gap of 0.868 eV. This calculated gap value is much closer to but still significantly lower than that determined from optical absorption spectrum ($E_{g,opt} \sim 1.586$ eV). This is because that the DFT generally underestimates band gaps of materials substantially, especially for the strongly correlated systems containing transition metals with d and f electrons. Albeit the calculated band gaps using various functionals and pseudopotentials are of significant difference, the band structures are essentially identical. Fig. 5 (a) and (b) respectively show the Brillouin zone for hexagonal Cu₆GeWSe₈ with special k-point paths and the calculated band structure along the special k-point paths. Both the bottom conduction band and the top valence band are at G (Gamma) point, indicative of a direct band gap of 0.868 eV. The valence band edge mainly originated from the hybridization of Cu 3d and Se 4p orbitals and the conduction band edge primarily composed of Cu 3d, Se 4p and W 5d orbitals, are both dispersive. In addition, the calculated band structure suggests a trivial topological-state in Cu₆GeWSe₈ similar to that in Cu₆GeWS₈ [33]. The total density of states (DOS) together with the contributions of Cu, Ge, W and Se atoms are displayed in Fig. 5 (c). On the whole, Cu and Se atoms dominantly contribute to the energy bands and density of states. The deep valence bands (below -10 eV) originate mainly from the contributions of the s-orbitals of Se atoms, the valence bands between -10 and -6 eV are from the dominant contributions of the *s*-orbitals of Ge atoms and the s- and p-orbitals of Se atoms, the valence bands between -6 and -3 eV attribute to the *d*-orbitals of Cu atoms and the *p*-orbitals of Se atoms, the valence bands between -3 and -1 eV ascribe to the *d*-orbitals of Cu atoms. Based on the valence states determined from the bond-valence theory, the DOS just below the Fermi level (the valence band edge) is dominated by Cu (+1 valence) $3d^{10}$ state and Se (-2 valence) $4p^6$ state. Combining the experimental E_g value and the calculated band structure, we conclude that Cu₆GeWSe₈ is a direct band gap semiconductor with an optical band gap of 1.586 eV.

4. Conclusions

A new quaternary selenide Cu_6GeWSe_8 was successfully synthesized in the lab and characterized through SEM, XRD, TG-DTA, electrical resistivity, magnetic susceptibility and optical absorption spectroscopy measurements. Cu_6GeWSe_8 (isostructural with Cu_6GeWS_8) crystallizes in a primitive hexagonal structure of space group $P6_3mc$, which exhibits semiconducting nature and diamagnetism. Analysis on the Vis-Nir absorption spectrum confirms an optical band gap of 1.586 eV. Electronic structure calculations suggest the dominant contributions of Cu and Se atoms to the energy bands and reveal a direct band gap in Cu_6GeWSe_8 . As a consequence, Cu_6GeWSe_8 can be regarded as a diamagnetic direct-gap semiconductor.

CRediT authorship contribution statement

Menghu Zhou: Conceptualization, Investigation, Formal analysis, Writing – original draft. Yadong Gu: Investigation. Binbin Ruan: Investigation. Qingsong Yang: Investigation. Genfu Chen: Resources. Zhian Ren: Resources, Supervision, Writing – review & editing.

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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 11774402 and 12074414), the National Key Research and Development of China (Grant No. 2018YFA0704200 and 2016YFA0300301), and the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB25000000).

References

- [1] Y. Ando, Topological insulator materials, J. Phys. Soc. Jpn. 82 (2013) 102001.
- [2] G.J. Snyder, E.S. Toberer, Complex thermoelectric materials, Nat. Mater. 7 (2008) 105–114.
- [3] Y.X. Shi, C. Sturm, H. Kleinke, Chalcogenides as thermoelectric materials, J. Solid State Chem. 270 (2019) 273–279.
- [4] D. Zhang, H.C. Bai, Z.L. Li, J.L. Wang, G.S. Fu, S.F. Wang, Multinary diamond-like chalcogenides for promising thermoelectric application, Chin. Phys. B 27 (2018), 047206.
- [5] S. Manzeli, D. Ovchinnikov, D. Pasquier, O.V. Yazyev, A. Kis, 2D transition metal dichalcogenides, Nat. Rev. Mater. 2 (2017) 17033.
- [6] M.L. Liu, F.Q. Huang, L.D. Chen, I.W. Chen, A wide-band-gap p-type thermoelectric material based on quaternary chalcogenides of Cu₂ZnSnQ₄ (Q = S, Se), Appl. Phys. Lett. 94 (2009) 202103.
- [7] S.Y. Chen, X.G. Gong, C.G. Duan, Z.Q. Zhu, J.H. Chu, A. Walsh, Y.G. Yao, J. Ma, S.H. Wei, Band structure engineering of multinary chalcogenide topological insulators, Phys. Rev. B 83 (2011) 245202.
- [8] P.D. Matthews, P.D. McNaughter, D.J. Lewis, P. O'Brien, Shining a light on transition metal chalcogenides for sustainable photovoltaics, Chem. Sci. 8 (2017) 4177–4187.
- [9] Y.Y. Sun, M.L. Agiorgousis, P.H. Zhang, S.B. Zhang, Chalcogenide perovskites for photovoltaics, Nano Lett. 15 (2015) 581–585.
- [10] Y.J. Wang, H. Lin, T. Das, M.Z. Hasan, A. Bansil, Topological insulators in the quaternary chalcogenide compounds and ternary famatinite compounds, New J. Phys. 13 (2011), 085017.
- [11] H. Putz, W.H. Paar, D. Topa, E. Makovicky, A.C. Roberts, Catamarcaite, Cu₆GeWS₈, a new germanium sulfide mineral species from Capillitas, Catamarca, Argentina: description, paragenesis and crystal structure, Can. Mineral. 44 (2006) 1481–1497.
- [12] M.H. Zhou, C. Dong, Synthesis, crystal structure and physical properties of kiddcreekite Cu₆WSnS₈ and its congener Cu₆WSnSe₈, J. Solid State Chem. 278 (2019) 120918.
- K. Persson, Materials Data on Cu₆SnWS₈ by Materials Project, 2014, https:// doi.org/10.17188/1717501.
- [14] G.I. Terziev, Hemusite—a complex copper-tin-molybdenum sulfide from the chelopech ore deposit, Bulgaria, Am. Mineral. 56 (1971) 1847–1854.
- [15] M. Shimizu, A. Kato, S. Matsubara, Hemusite and paraguanajuatite from the kawazu mine, shizuoka prefecture, Japan, Mineral. J. 14 (1988) 92–100.
- [16] X.D. Deng, C. Dong, *EPCryst:* a computer program for solving crystal structures from powder diffraction data, J. Appl. Crystallogr. 44 (2011) 230–237.
- [17] B.H. Toby, EXPGUI, a graphical user interface for GSAS, J. Appl. Crystallogr. 34 (2001) 210–213.
- [18] M.D. Segall, P.J.D. Lindan, M.J. Probert, C. J Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, First-principles simulation: ideas, illustrations and the CASTEP code, J. Phys. Condens. Matter 14 (2002) 2717–2744.
- [19] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.I.J. Probert, K. Refson, M.C. Payne, First principles methods using CASTEP, Z. Kristallogr. 220 (2005) 567–570.
- [20] Dassault Systèmes Biovia, Materials Studio 7.0, Dassault Systèmes, San Diego, 2017.
 [21] W.I.F. David, K. Shankland, Structure determination from powder diffraction data,
- Acta Crystallogr. A 64 (2008) 52–64. [22] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures,
- [22] H.M. Kietveld, A profile refinement method for nuclear and magnetic structures, J. Appl. Crystallogr. 2 (1969) 65–71.
- [23] A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, *EXPO2013*: a kit of tools for phasing crystal structures from powder data, J. Appl. Crystallogr. 46 (2013) 1231–1235.
- [24] A. Altomare, G. Campi, C. Cuocci, L. Eriksson, C. Giacovazzo, A. Moliterni, R. Rizzi, P.E. Werner, Advances in powder diffraction pattern indexing: *N-TREOR*09, J. Appl. Crystallogr. 42 (2009) 768–775.
- [25] N.E. Brese, M. O'Keeffe, Bond-valence parameters for solids, Acta Crystallogr. B 47 (1991) 192–197.
- [26] G.P. Shields, P.R. Raithby, F.H. Allen, W.D.S. Motherwell, The assignment and validation of metal oxidation states in the Cambridge Structural Database, Acta Crystallogr. B 56 (2000) 455–465.
- [27] L. Pauling, The principles determining the structure of complex ionic crystals, J. Am. Chem. Soc. 51 (1929) 1010–1026.
- [28] M. Ziese, C. Srinitiwarawong, Polaronic effects on the resistivity of manganite thin films, Phys. Rev. B 58 (1998) 11519–11525.
- [29] Z. Ren, A.A. Taskin, S. Sasaki, K. Segawa, Y. Ando, Large bulk resistivity and surface quantum oscillations in the topological insulator Bi₂Te₂Se, Phys. Rev. B 82 (2010) 241306 (R).
- [30] E. Makovicky, Crystal structures of sulfides and other chalcogenides, Rev. Mineral. Geochem. 61 (2006) 7–125.

M. Zhou et al.

- [31] W.Y. Liu, C. Dong, X.P. Gu, Y. Liu, X.P. Qiu, Y.C. Chen, The crystal structure of kiddcreekite solved using micro X-ray diffraction and the *EPCryst* program, Mineral. Mag. 78 (2014) 1517–1525.
- [32] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868.
 [33] K. Persson, Materials Data on Cu₆GeWS₈ by Materials Project, 2014, https://doi.org/10.17188/1269744.