

Article

Structural and Electronic Properties of Cu_3InSe_4

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Abstract: Single crystals of a new ternary chalcogenide Cu_3InSe_4 were obtained by induction melting, allowing for a complete investigation of the crystal structure by employing high-resolution single-crystal synchrotron X-ray diffraction. Cu_3InSe_4 crystallizes in a cubic structure, space group $P43m$, with lattice constant 5.7504(2) Å and a density of 5.426 g/cm³. There are three unique crystallographic sites in the unit cell, with each cation bonded to four Se atoms in a tetrahedral geometry. Electron localization function calculations were employed in investigating the chemical bonding nature and first-principle electronic structure calculations are also presented. The results are discussed in light of the ongoing interest in exploring the structural and electronic properties of new chalcogenide materials.

Keywords: ternary chalcogenide; crystal structure; electronic structure



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1. Introduction

Multinary metal chalcogenides consisting of primarily earth-abundant, low-cost, and non-toxic constituents exhibit physical properties that can be tuned via composition, specific bonding scheme, lattice defects or disorder, and have been investigated for a variety of different applications of interest including thermoelectrics [1–6], photovoltaics [7–10], superconductivity [11–13], and as potential topological insulators [14,15]. The interest in ternary Cu-based compositions has recently intensified in pursuit of commercially viable solar cells [16–18] and thermoelectrics [19–22]. The ternary Cu-In-Se system is of particular interest [23], with a number of compounds possible along the Cu_2Se – InSe_3 tie-line [24,25] such as CuInSe_2 [26,27], $\text{Cu}_3\text{In}_5\text{Se}_9$ [28], $\text{Cu}_7\text{In}_{19}\text{Se}_{32}$ [23], CuIn_5Se_8 [25], $\text{Cu}_2\text{In}_4\text{Se}_7$ [29] and CuIn_3Se_5 [30]. The crystal structure of CuInSe_2 was reported to be either tetragonal with space group $I4_2m$ [31,32] or cubic, $F43m$ [23,33], where the latter structure can be considered as two interpenetrating face-centered cubic sub-lattices. In the case of Cu_3MSe_4 , where M is V, Ta, Nb or Sb, both cubic [34,35] and tetragonal [36,37] structure types were reported.

To the best of our knowledge, the synthesis and crystal structure of Cu_3InSe_4 has not been previously reported. Wei et al. [38] predicted Cu_3InSe_4 to be metallic, with “holes in the valence band”, however structural information and details of the electronic structure were not reported. Therefore, we have undertaken to synthesize and investigate the crystal structure and electronic properties of Cu_3InSe_4 . We employed high-resolution single crystal synchrotron measurements to determine the structure of this previously unascertained ternary compound. The structural features and bonding were investigated in detail, including analyses of calculated electron localization, and the electronic properties were obtained using density functional theory. Our results are compared to that of other ternary chalcogenides.

2. Materials and Methods

Single crystals of Cu_3InSe_4 were initially obtained in an attempt to prepare $\text{CuFe}_2\text{InSe}_4$, resulting in FeSe as well as the shiny metallic ternary chalcogenide crystals identified as

Cu_3InSe_4 . This procedure was repeated with a stoichiometric ratio of the starting high-purity elements, Cu powder (99.9 % purity, Alfa Aesar, Thermo Fisher Scientific, Ward Hill, MA, USA), In shot (99.99 % purity, Alfa Aesar, Thermo Fisher Scientific, Ward Hill, MA, USA) and Se ingot (99.999 % purity, Alfa Aesar, Thermo Fisher Scientific, Ward Hill, MA, USA) [39]. The elements were placed in a silica ampoule and vacuum-sealed inside a quartz tube, then melted via a water-cooled 3-coil induction (Superior Induction, SI-7KWHF) furnace resulting in an agglomeration of gray Cu_3InSe_4 crystals.

Single-crystal synchrotron measurements were carried out at NSF's ChemMatCARS, Sector 15 of the Advanced Photon Source, Argonne National Laboratory. Data were collected using a Huber 3-circle diffractometer (Huber diffraction, Lancaster, CA, USA) equipped with a Pilatus3X 2M detector (Dectris USA Inc., Philadelphia, PA, USA) using an Oxford Cryojet (American Laboratory Trading, East Lyme, CT, USA). The ω -angle was set at -180° , κ -angle was set at 0° and 30° , with ϕ -angle scanned over the range of 360° using the shutterless mode of the detector. Data integration was performed with the Bruker APEX 3 suite software. The reduction of the data was obtained with the SAINT v.8.38A and SADABS v.2016 programs (Bruker AXS Inc., Madison, WI, USA) that are included in the APEX suite. The structure was solved directly and refined by the full-matrix least-squares method.

Ab initio calculations based on density functional theory, plane-waves basis set, and pseudopotentials were carried out using the Quantum Espresso software package [40]. Projector-augmented waves (PAW) pseudopotentials [41], the generalized gradient approximation of Perdew-Burke-Ernzerhof [42,43] plus Hubbard correction [44] (GGA-PBE + U) exchange-correlation functional were applied. A U parameter of 4 eV for the cations was used based on previous studies on Cu-based chalcogenide materials [45,46] that provide for good agreement between calculated and experimental structure values. For the pseudopotentials, Cu $3d^{10}4s^1$, In $4d^{10}5s^25p^1$ and Se $4s^24p^4$ valence configurations were considered. For self-consistent field (SCF) calculations, a k -point mesh of $6 \times 6 \times 6$ was applied to sample the Brillouin zone. The kinetic energy cutoff for wavefunctions and charge density was set to 70 Ry and 300 Ry, respectively, and an energy convergence threshold of 10^{-7} eV was utilized. The electron localization function (ELF) distribution was analyzed and visualized using VESTA v.3.5.8 software [47].

CCDC 2172956 contains the supplementary crystallographic data. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/search?access=referee&pid=ccdc:2172956&author=ng>, accessed on 10 September 2022, (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

3. Results

The crystallographic data and structural refinement results are shown in Table 1. Cu_3InSe_4 crystallizes in the cubic space group $P\bar{4}3m$ (No. 215) with cell parameter $a = 5.7504(2)$ Å, $Z = 1$ and density = 5.426 g/cm³. The atomic coordinates and equivalent isotropic displacement parameters, U_{eq} , are shown in Table 2. The anisotropic displacement parameters are presented in Table 3. As shown in Figure 1, the structure consists of CuSe_4 (Cu-Se distance of $2.4622(4)$ Å) and InSe_4 (In-Se distance of $2.5775(13)$ Å) tetrahedra connected by corner-sharing Se atoms. Selenium is surrounded by three Cu atoms and by an In atom, as shown in Figure 1a. The CuSe_4 and InSe_4 tetrahedra are illustrated in Figure 1b. The tetrahedron about the In site is a regular tetrahedron with Se-In-Se angles of $109.471(11)^\circ$, while that of Cu is somewhat distorted with Se-Cu-Se angles ranging from $105.63(6)^\circ$ to $111.42(3)^\circ$. The Cu-Se distance ($2.4622(4)$ Å) is similar to that reported for sylvanite and adamantine compounds [36,48,49], while the In-Se distance ($2.5775(13)$ Å) is similar to that for CuInSe_2 (2.591 Å) [49] and LiInSe_2 (2.57 Å) [50]. It is important to note that the structure of Cu_3InSe_4 is related to that of sylvanites Cu_3XQ_4 ($X = \text{V, Nb, Ta}$; $Q = \text{S, Se, Te}$) [19,51,52]; however, the Cu atoms occupy different Wyckoff sites in these two different ternary chalcogenides thus resulting in corner sharing and edge sharing tetrahedra for Cu_3InSe_4 and Cu_3XQ_4 , respectively.

Table 1. Crystal data and structure refinement results.

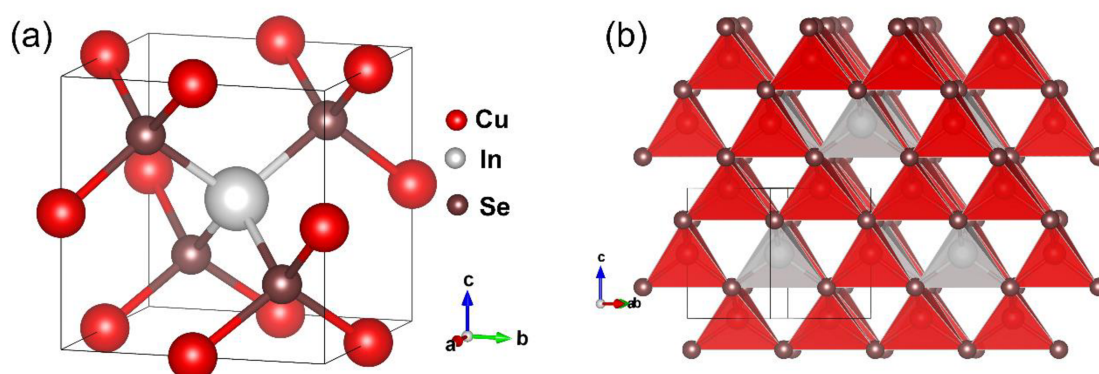
Empirical formula	Cu ₃ InSe ₄
Formula weight	621.32
Temperature	100(2) K
Wavelength	0.49594 Å
Crystal system	Cubic
Space group	$P\bar{4}3m$ (No. 215)
Unit cell dimension	$a = 5.7504(2)$
Volume	$190.15(2) \text{ Å}^3$
Z	1
Density (calculated)	5.426 mg/m^3
Absorption coefficient	11.36 mm^{-1}
Crystal size	$30 \times 20 \times 10 \text{ μm}^3$
Theta range for data collection	2.283 to 26.223°
Reflections collected	2237
Independent reflections	251 [$R(\text{int}) = 0.0945$]
Goodness-of-fit on F^2	1.190
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0375$, $wR2 = 0.0886$
R indices (all data)	$R1 = 0.0403$, $wR2 = 0.0908$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	Site	x	y	z	U_{eq}
In	1b	1/2	1/2	1/2	0.009(1)
Se	4c	0.2412(1)	0.2412(1)	0.2412(1)	0.011(1)
Cu	3d	0	0	1/2	0.007(1)

Table 3. Anisotropic displacement parameters (Å^2). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
In	0.010(1)	0.010(1)	0.010(1)	0	0	0
Se	0.011(1)	0.011(1)	0.011(1)	$-0.002(1)$	$-0.002(1)$	$-0.002(1)$
Cu	0.007(1)	0.007(1)	0.006(1)	0	0	0

**Figure 1.** Schematic illustrating the crystal structure of Cu₃InSe₄ showing the (a) unit cell and (b) stacking of the CuSe₄ (red) and InSe₄ (gray) tetrahedra.

The electron density distribution was investigated by calculating the ELF, revealing the ionic nature of the bonding in Cu₃InSe₄, as shown in Figure 2. Figure 2 shows the calculated ELF along the (110) plane. ELF values of 0.0, 0.5 and 1.0 represent fully delocalized, electron-gas-like pair probability and perfect localization, respectively [53]. The atomic core regions

of the cations have localization domains with ELF values close to unity and low ELF values away from these regions. This suggests electrons transfer from both Cu and In atoms to adjacent Se atoms, indicating ionic bonding. In comparing the Cu_3XSe_4 compounds [54] with Cu_3InSe_4 , the X-Se bonds in the former show a higher degree of covalency as compared with the primarily ionic character for In-Se in Cu_3InSe_4 .

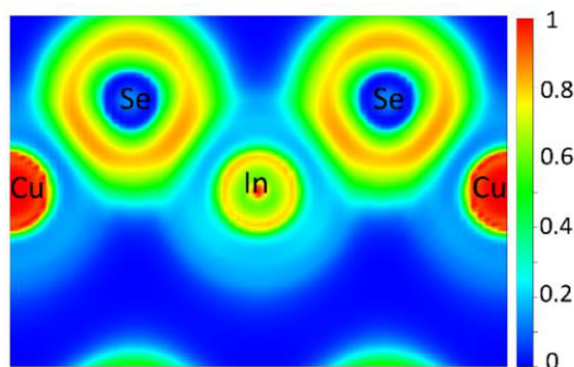


Figure 2. ELF calculated along the (110) plane.

The oxidation states of Cu, In and Se are 1+, 3+ and 2−, respectively, resulting in 30 electrons per formula unit, or two fewer than required for the tetrahedral bonds in Cu_3InSe_4 thus resulting in *p*-type metallic behavior. Our detailed structural analyses allow for an investigation of the electronic structure of Cu_3InSe_4 by calculating the energy band structure and density of states (DOS). As shown in Figure 3, the Fermi level, E_f , crosses the valence band in multiple regions, thus, Cu_3InSe_4 is a *p*-type metal [46,55], confirming the simple charge imbalance argument. This is also in agreement with the early conjecture [38], and corroborated by our room temperature conductivity measurements indicating metallic conduction [56]. The orbital-projected DOS indicates that the valence band maximum has contributions mainly from the Cu 3*d* and Se 4*p* orbitals, while the conduction band maximum is mainly composed of In 5*s* and Se 4*p* and minor contributions from Cu 3*d*4*s*4*p*, In 5*p* and Se 4*s* orbitals. The orbital interactions between the CuSe_4 tetrahedra therefore play a dominant role in the metallic conductivity of Cu_3InSe_4 . It is instructive to compare the electronic structure of Cu_3InSe_4 to that of Cu_3XSe_4 in light of the fact that the crystal structure of Cu_3InSe_4 is not isostructural to that of the later compositions. Specifically, for the case of the Cu_3XSe_4 compositions [19,57,58], an energy gap opens between the valence and conduction bands in these materials. These compositions are therefore semiconductors and are being investigated for thermoelectric [19,20] and photovoltaic [59,60] applications, whereas in the case of Cu_3InSe_4 E_f falls relatively deep in the valence band and will therefore not be of interest for such applications.

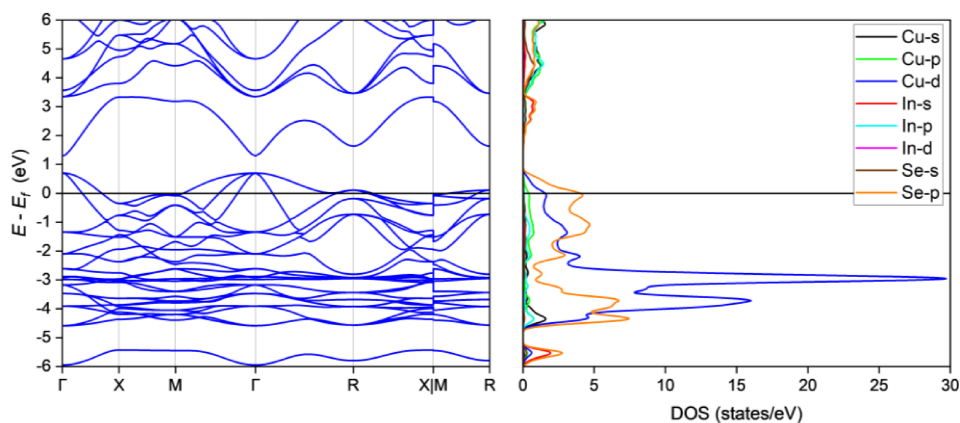


Figure 3. Calculated energy band structure and orbital-projected DOS.

4. Conclusions

Single crystals of a new ternary chalcogenide Cu_3InSe_4 were obtained by induction melting, and the structural and electronic properties are reported for the first time. Cu_3InSe_4 forms in a cubic crystal structure that consists of CuSe_4 and InSe_4 tetrahedra connected by corner sharing Se atoms. Electron localization function analyses indicated partially ionic bonding between the cations and Se atoms, with highly delocalized electrons in the regions between cation and selenium. Electronic structure calculations reveal this ternary chalcogenide to be metallic. Given that ternary chalcogenide compounds are of interest for potential thermoelectric and optoelectronic applications, our findings will be useful for investigations on new materials for applications of interest. The results and analyses in this work add to our understanding of the structural and electronic properties of ternary chalcogenides.

Author Contributions: Conceptualization, G.S.N.; methodology, O.P.O.; data curation, O.P.O., W.W.-N., T.C. and Y.-S.C.; formal analysis, O.P.O., W.W.-N., T.C. and Y.-S.C.; writing—original draft preparation, O.P.O.; writing—review and editing, G.S.N.; visualization, O.P.O.; supervision, G.S.N. All authors have read and agreed to the published version of the manuscript.

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