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Electronic structure of $Cu_2ZnGeSe_4$ single crystal: Ab initio FP-LAPW calculations and X-ray spectroscopy measurements

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ABSTRACT

High-quality $Cu_2ZnGeSe_4$ single crystal has been successfully grown by a solution-fusion method and the crystal structure of the compound is refined within tetragonal kesterite-type (space group $I\bar{4}$), with the unit cell parameters $a=5.6112(1)$ Å and $c=11.0473(3)$ Å. X-ray photoelectron core-level and valence-band spectra for pristine and Ar^+-ion irradiated surfaces of the $Cu_2ZnGeSe_4$ crystal are measured. Our X-ray photoelectron spectroscopy (XPS) data indicate that the $Cu_2ZnGeSe_4$ single crystal surface is very rigid with respect to Ar^+ ion-irradiation. The electronic structure of the $Cu_2ZnGeSe_4$ compound has been theoretically studied using first principles calculation employing the full potential linearized augmented plane wave (FP-LAPW) method. Calculations of the total and partial densities of states of atoms constituting $Cu_2ZnGeSe_4$ reveal that the dominant contributors to the valence band of the compound studied are the Cu 3d states, which contribute mainly at the top of the band, while the central portion of the band is composed mainly from the Cu 3d and Se 4p states in almost equal proportion. Additionally, the present FP-LAPW calculations indicate that the bottom of the valence band is dominated by the Zn 3d states, while the bottom of the conduction band is composed mainly from the unoccupied Ge 4s and Se 4p states. The data of the present FP-LAPW calculations are confirmed by comparison on a common energy scale of the X-ray emission bands representing the energy distribution of the valence Cu d, Zn d, Ge p and Se p states and the XPS valence-band spectrum of the $Cu_2ZnGeSe_4$ single crystal.

1. Introduction

Over the past few decades, quaternary diamond-like compounds, with the common formula Cu_2–B^{II}–C^{IV}–X_4 (B^{II}=Zn, Cd, Hg; C^{IV}=Si, Ge, Sn; X=S, Se), have generated increased attention from both scientific and technological points of view due to their stable structures, compositional flexibility and potential applications in photovoltaic cells, optoelectronics and non-linear optical devices [1–6]. The Cu_2–B^{II}–C^{IV}–X_4 compounds are promising materials for thermoelectric applications [7–11] and are explored to be ideal tunable semiconductors because many of their physical and chemical properties (band gap, electrical conductivity, magnetism, etc.) can be adjusted to specific values by changing their compositions [12–17]. Among these compounds, dicopper zinc germanium selenide, $Cu_2ZnGeSe_4$, is of particular interest. The $Cu_2ZnGeSe_4$ compound exhibits p-type conductivity and values of band gap ranging from 1.29 to 1.63 eV as reported in the experimental findings in Refs. [1,18–21]. These band gaps are suitable for optimum conversion efficiency for solar cells (1.2–1.5 eV). The resistivity of the $Cu_2ZnGeSe_4$ compound changes from $2\times10^{-3}\,\Omega$ cm to $4\times10^{-3}\,\Omega$ cm when transitioning from room temperature to liquid nitrogen temperature [1]. Magnetic measurements, made by Guen and Glaunsinger [22], have shown that the magnetic susceptibility, χ_M, of $Cu_2ZnGeSe_4$ is independent of temperature in the range of 77–300 K. Single crystal $Cu_2ZnGeSe_4$ nanowire arrays, prepared recently by Shi et al. [23] via a convenient one-step nanoconfined method, reveal strong optical absorption in the visible region. Furthermore, the $Cu_2ZnGeSe_4$ nanowires are reported to be a very promising material for photovoltaic applications and they are expected to be effectively applied in nanoelectronic devices, such as photoconducting cells and field-effect transistors [23].

It is worth mentioning that most of the Cu_2–B^{II}–C^{IV}–X_4 compounds crystallize either in orthorhombic (space group $Pmn2_1$) or tetragonal (space group $I\bar{4}2m$ or $I\bar{4}$) structures, which are derived

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Fig. 1. Photo of as-grown boule containing $Cu_2ZnGeSe_4$ single crystal used in the present experimental studies.

Table 1
Atomic parameters for $Cu_2ZnGeSe_4$ (space group $I\bar{4}$, $a=5.6112(1)$ and $c=11.0473(3)$ Å).

Atom	Wyckoff position	x/a	y/b	z/c	B (is/eq)
Cu1	2*a*	0	0	0	1.2 (2)
Cu2	2*c*	0	1/2	1/4	1.2 (2)
Zn	2*d*	1/2	0	1/4	1.76 (15)
Ge	2*b*	1/2	1/2	0	1.34 (13)
Se	8*g*	0.747(3)	0.7414(12)	0.8722(3)	0.74 (3)

Table 2
Atomic orbitals used in the present FP-LAPW calculations of the electronic structure of $Cu_2ZnGeSe_4$.

Atom	Core electrons	Semi-core electrons	Valence electrons	Number of electrons involved in the FP-LAPW calculations
Cu	$1s^22s^22p^63s^2$	$3p^6$	$3d^{10}4s^1$	17
Zn	$1s^22s^22p^63s^2$	$3p^6$	$3d^{10}4s^2$	18
Ge	$1s^22s^22p^63s^23p^6$	$3d^{10}4s^2$	$4p^2$	14
Se	$1s^22s^22p^63s^23p^6$	$3d^{10}$	$4s^24p^4$	16

which is isostructural to Cu_2FeSnS_4, with the unit cell parameters $a=5.62$ Å and $c=11.06$ Å. In such a structure of $Cu_2ZnGeSe_4$ with two formula units per cell, Cu, Zn, Ge and Se atoms occupy 4d, 2a, 2b and 8i sites, respectively, and each Se atom is surrounded by two Cu atoms, one Zn atom and one Ge atom, while every cation atom is tetrahedrally coordinated by Se atoms. Matsushita et al. [19] have reported that $Cu_2ZnGeSe_4$ has a congruent type of melting; however, when studying the phase diagram of the Cu_2GeSe_3–ZnSe system [26], it has been established that $Cu_2ZnGeSe_4$ melts incongruently at 1163 K. The latter statement has been confirmed by Differential Thermal Analysis

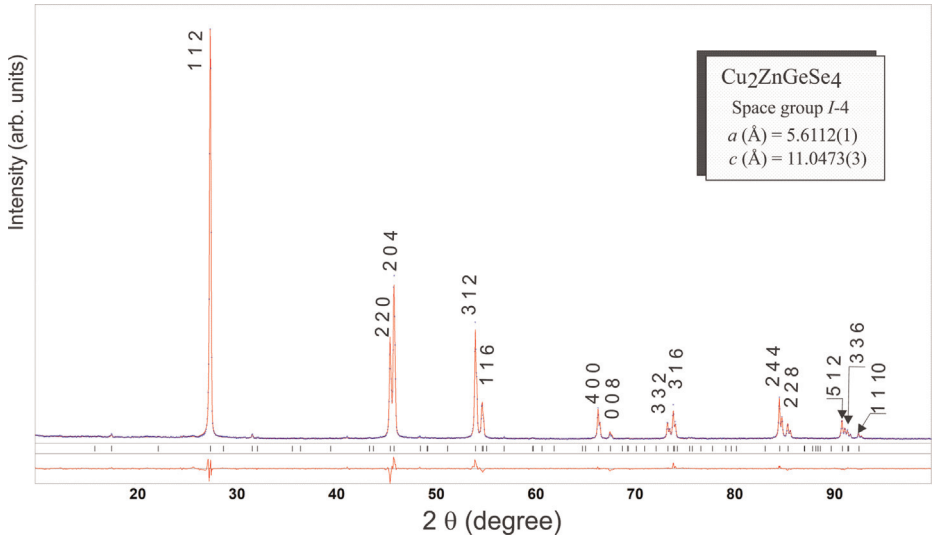

Fig. 2. Experimental (blue) and calculated (red) X-ray diffraction patterns and their difference (the first red line just above the horizontal axis) of the $Cu_2ZnGeSe_4$ compound under study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

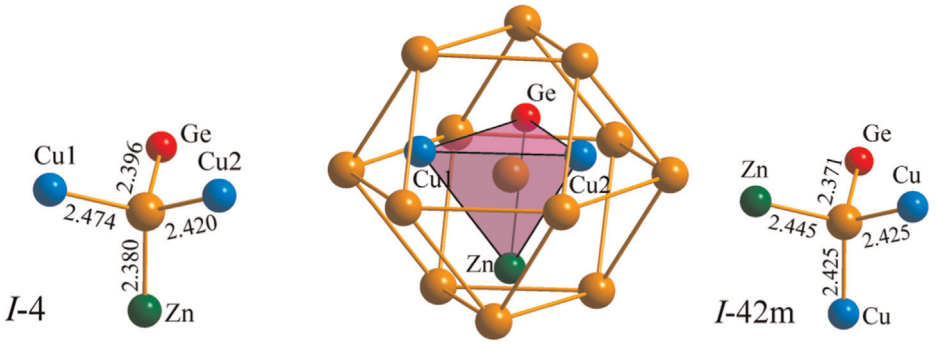

Fig. 3. The first and second coordination surroundings of selenium atoms in the both tetragonal phases ($I\bar{4}2m$ and $I\bar{4}$) of the $Cu_2ZnGeSe_4$ compound.

from the wurzite or zincblende cells, respectively, with an ordering of the metals on the cation sites [2,24]. Hahn and Schulze [25] were the first to suggest that the $Cu_2ZnGeSe_4$ compound crystallizes in the tetragonal stannite-type structure, space group $I\bar{4}2m$, measurements of the $Cu_2ZnGeSe_4$ compound carried out by Caldera et al. [27,28]. The compound undergoes a polymorphous transformation at 1071 K [29].

However, when theoretically exploring the properties of