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ELASTIC CONSTANTS OF TETRAGONAL Cu_2ZnSnS_4 SEMICONDUCTOR: AB-INITIO CALCULATION

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Abstract

In this work, an ab-initio calculation is used to investigate the elastic constants and some other mechanical and thermal parameters of tetragonal Cu_2ZnSnS_4 (CZTS) quaternary semiconducting bulk material in Kesterite (KS) and Stannite (ST) phases. The Quantum Espresso code within the Ultra Soft pseudo potentials (USPP) and the local density approximation (LDA) approach were used in the calculation. Firstly, , studies are started with the prediction of the elastic stiffness constants C_{ij} and the normal and shear anisotropy factors. Then some other mechanical moduli, especially the isotropic bulk modulus B, the shear modulus G, the Young modulus E, the Poisson's ratio v, and the Pugh's criteria (G/B) are delivered. The analysis of the mechanical stability criteria at equilibrium shows that our elastic stiffness constants C_{ij} of CZTS material obey all the stability conditions. Additionally, some other parameters of the CZTS semiconductor, especially: the Vickers hardness H_V, the sound velocity, the Debye temperature θ_D and the melting temperature T_m were also calculated. The obtained values of the elastic constants C_{ij} and other mechanical and thermal parameters agree well with experimental and other theoretical results of the literature. The Debye temperature θ_D of the KS phase was found at around 332.7 K, and that of the stannite phase was found equal to 329.1 K, respectively.

1. Introduction

Photovoltaic conversion systems become actually one of the preferred solutions to produce clean and renewable energy [1]. The production of electricity by photovoltaic conversion systems has reached an industrial stage.

Progress is being made to achieve research and development, cost reductions and performance improvements in PV technologies, and work is being done to characterize the PV technology portfolio. The efficiencies and power outputs of solar panels have improved significantly [2], [3]. While the average module efficiency in 2006 was 13.2% for polycrystalline PV cells and 14.7% for mono-crystalline PV cells, actually, solar cells have an efficiency of up to 20% commercially, and up to 40% on a lab scale [4], [5], [6].

As a motivation element of this study, we can state that it is to produce outputs that will scrutinize what will happen next.

Cu_2ZnSnS_4 semiconducting material is one of the promising absorber layer materials for thin film solar cell application [7], [8], [9]. This semiconductor exhibits a near-optimum direct band gap, which is around 1.5 eV, and it has a large absorption coefficient, which is in the order of 10^4 cm^{-1} [10]. For the CZTS material, three types of crystal structure have been reported: kesterite, stannite, and wurtz-stannite types [11]. Both KS and ST structures consist of CCP array of anions with cation occupying one-half of the tetrahedral voids but assigned different space groups because of the difference in cation distribution in the unit cell [12].

Using X-ray diffraction patterns, and Raman spectroscopy (RS) techniques, Seboui *et al.*[13] studied some physical properties of CZTS thin films deposited by spray pyrolysis technique. They found that all the CZTS films exhibited kesterite structure, possessing band gaps that lie between 1.52 and 1.81 eV. In general, the higher band-gap material has smaller electrical conductivity.

Using first-principles calculations, Gürel *et al.* [14] investigated the vibrational and mechanical properties of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ quaternary compounds in both kesterite and stannite structures, while Gunaicha *et al.* [15] have studied structural, energetic and mechanical properties of $Cu_2ZnSn(S_xSe_{1-x})_4$(x = 1, 0.75, 0.5, 0.25, 0) alloys. They found that all these alloys are mechanically stable at equilibrium. Some other theoretical works [16], [17] studied the elastic constants C_{ij} and some other dynamic properties of CZTS material. However, thermophysical properties such as Debye temperature θ_D and the Grüneisen parameter γ were few reported.

In this paper, the elastic constants C_{ij} and some other mechanical and thermo physical parameters of tetragonal CZTS material in kesterite and stannite phases are determined using the Quantum Espresso (QE) software [18], [19].

2. Theoretical description

Elastic stiffness constants of solid are of interest because they are related to the inter-atomic bonding, the phonon spectra, and some other fundamental solid-state phenomena, they are also linked with the mechanical properties and the microhardness [20]. For many solids, the nonlinearity in the stress–strain curve is quite small so a linear relationship between stress and strain is assumed for most purposes. The elastic stiffness [C] and compliance [S] tensors are defined by the generalized Hooke's law [21]:

$$[\sigma]= [C]x[\varepsilon] \qquad \text{and} \qquad [\varepsilon]= [S]x[\sigma] \tag{1}$$

In Eq.(1), [σ] is the elastic stress tensor, [ε] is the strain tensors. Both the stiffness and compliance tensors [C] and [S] are second-order fourth-rank ones having symmetric 6 × 6 components [21].

The number of elastic constants is reduced due to the symmetry of the crystal [15]. In the case of tetragonal systems, the number of independent elastic constants is related to the space group [21]. For the kesterite phase (with space group $I\bar{4}$), there are seven independent elastic constants [15], which are usually given by the following matrix [C] [21]:

$$[C] = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ C_{12} & C_{11} & C_{12} & 0 & 0 & C_{26} \\ C_{13} & C_{12} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ C_{16} & C_{26} & 0 & 0 & 0 & C_{66} \end{bmatrix} \tag{2}$$

$$C_{16} = -C_{26}$$

For CZTS material, the elastic constant$C_{16} = -C_{26} \approx 0$, so usually the kesterite phase so called stannite-approximated kesterite structure, which has only six independent elastic constants (please see Table 4.3 in Ref [21], page 113).

For the stannite phase (with space group $I\bar{4}2m$), there are six independent elastic constants, which are usually given by the following matrix [C] [21]:

$$[C] = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{13} & C_{12} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \quad (3)$$

Using the elastic constants C_{ij} data of the single crystal, the isotropic bulk B and shear G moduli of the aggregate poly-crystalline material can be computed as $B = (B_V + B_R)/2$ and $G = (G_V + G_R)/2$, which are the arithmetic mean of the bounds on the elastic moduli, found by Voigt and Reuss, respectively [22]. For tetragonal systems (stannite phase, and stannite-approximated kesterite structure), the bulk moduli B_V and B_R of Voigt and Reuss can be defined by [14]:

$$B_V = (2C_{11} + C_{33} + 2C_{12} + 4C_{13})/9 \quad (4\text{-a})$$

$$B_R = [(C_{11} + C_{12})C_{33} - 2C_{13}^2]/[C_{11} + C_{12} + 2C_{33} - 4C_{13}] \quad (4\text{-b})$$

while the shear moduli G_V and G_R are given by [15]:

$$G_V = (2C_{11} + C_{33} - C_{12} - 2C_{13} + 6C_{44} + 3C_{33})/15 \quad (5\text{-a})$$

$$G_R = 15CC_2C_3/\{2C_2C_3(2C_1 + 4C_{13} + C_{33}) + 3C[2C_3 + C_2(C_{44} + 2C_{66})]\} \quad (5\text{-b})$$

With $C = C_{33}(C_{11} + C_{12}) - 2C_{13}^2$, $C_1 = (C_{11} + C_{12})$, $C_2 = (C_{11} - C_{12})$, and $C_3 = C_{44}C_{66}$.

The spherically averaged elastic constants for longitudinal (C_l) and transverse modes (C_t) have an important role, especially in the thermal and carrier transport properties [21]. In the tetragonal stannite-type lattice, these constants are, respectively expressed by [21]:

$$C_l = (8C_{11} + 4C_{13} + 3C_{33} + 8C_{44})/15 \quad (6)$$

$$C_t = (2C_{11} - 4C_{13} + 2C_{33} + 7C_{44})/15 \quad (7)$$

The Debye temperature θ_D is one of the fundamental thermodynamic parameters; it is the characteristic temperature of a solid defined within the framework of the Debye model for the specific heat of solids [23]. The Debye temperature θ_D is usually used to distinguish between low and high temperature regions for a solid [24], [25]. Heat capacity measuring is a technique that allows us to determine the Debye temperature θ_D with high accuracy. At low temperature,

the Debye temperature θ_D can also be predicted from the mean acoustic wave velocity v_m using the following expression [24]:

$$\theta_D = \frac{\hbar}{k_B}\left[\left(\frac{6\pi^2 NKv_m^3}{V}\right)\right]^{1/3} \tag{8}$$

where $\hbar = h/2\pi$, h is the Planck constant; k_B is the Boltzmann constant, N is the number of unit cells in the volume V of the crystal, and K is the number of atoms per unit cell.

For aggregate polycrystalline bulk materials, the arithmetic mean values of different parameters are usually used [22]. The harmonic mean value of the acoustic wave speed v_m is usually given by the following expression [26]:

$$v_m = \left[(1/3)\left((2/v_t^3)+(1/v_l^3)\right)\right]^{-1/3} \tag{9}$$

where v_l and v_t are the longitudinal (compressional) and transverse (shear) sound wave velocities, respectively, which are usually calculated using the following expressions [26]:

$$v_l = \sqrt{(3B+4G)/3\rho}\text{ , and }\ v_t = \sqrt{G/\rho} \tag{10}$$

where B is the bulk modulus B, G is the shear modulus G, and ρ is the mass density, which is given as follows for ideal crystal, $\rho = \left(MZ/NV\right)$, where M is the molecular weight, Z is the number of formula units per unit cell, N is the Avogadro's number, and V is the unit cell volume.

3. Computational method

The modern development in high speed computers and theoretical methodologies allowed scientists and researchers to investigate and predict several physical properties of solids directly from the fundamental equations of quantum mechanics [27]. The Quantum Espresso code [18], [19] is suitable software, which is usually used to predict the elastic stiffness constants C_{ij} and several other physical properties of crystals. It is based on the pseudo-potential (PP) and a plane waves basis set method. In this present work, the local density approximation (LDA) of Perdew-Zunger (PZ) [28] is employed to treat the exchange-correlation term, while the Ultra-Soft pseudopotentials (USPP) form [29] was used to estimate

the term of other interactions. The LDA is efficient in systems with a slowly-varying spatial density but, in general, it overestimates the elastic stiffness constants and the phonon frequencies and underestimates the bond-lengths (structural parameters). In this work, the wave functions were expanded with an energy cut-off equal to 80 Ry for the plane wave basis set, while the charge density cut-off was taken 800 Ry, leading a convergence with an energy threshold of $1x10^{-4}$ Ry. The integration over the Brillouin zone was performed using 4x4x2 k-points Monkhorst-Pack mesh [30].

4. Results and discussion

4. 1. Elasticstiffness constants

The mechanical properties and their related parameters of semiconductors and other materials are very important [31], [32], [33]. Elastic constants of CZTS bulk material have been calculated through second derivative of Helmholtz free energy versus strain as follows [34]:

$$\tilde{C}_{ijkl} = \frac{1}{V}\left(\frac{\partial^2 F}{\partial \epsilon_{ij} \partial \epsilon}\right)_{\epsilon=0} \tag{11}$$

where F is the Helmholtz free energy, which is the sum of DFT total energy and the vibrational free energy, V is the volume of unit cell, ϵ is the strain (for more details, please see the Ref. [34] and references therein).

The obtained values of the elastic constants C_{ij} of the kesterite phase of CZTS material were reported in Table 1, along other theoretical data of the literature [14], [15], [16], [17], while those of the stannite phase were reassembled in Table 2with the values of the Ref. [14], and the Ref. [17]. From Table 1, one can note that our calculated values of the elastic constants C_{ij} are in very good agreement compared to other data of the literature [14], [15], [16], [17]. No experimental data on the second-order elastic constants of CZTS material have been reported until now.

For CZTS material with kesterite phase, we can observe that $C_{16} = -C_{26} = 0.32$ GPa, considerably lower compared to the other elastic constants. C_{16} is also changes very slowly with S content in the $Cu_2ZnSn(S_xSe_{1-x})_4$(x = 1, 0.75, 0.5, 0.25, 0) alloys [15].

For a tetragonal system, the mechanical stability criteria are given by$C_{11} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{66} > 0$, $(C_{11} - C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$, and $\left|2(C_{11} + C_{12}) + C_{33} + 4C_{13}\right| > 0$ [16]. Our values of the elastic constants for the kesterite phase of CZTS semiconducting material obey all these stability conditions.

Table 1. Elastic constants C_{ij} (in GPa) of the kesterite phase for CZTS semiconducting bulk material, along other data of the literature [14], [15], [16], [17].

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	C_{16}	C_{26}
This work	117.65	73.65	74.56	110.84	48.72	46.51	0.32	−0.32
Ref. [14]	115.81	75.50	76.11	117.34	48.33	47.63	-	-
Ref. [15]	114.42	74.51	75.51	115.41	47.30	46.14	0.41	-
Ref. [16]	91.8	55.7	55.8	92.0	41.8	41.2	-	-
Ref. [17]	109.7	71.3	69.2	112.5	45.9	42.6	-	-

Table 2. Elastic constants C_{ij} (in GPa) of the stannite phase for CZTS semiconducting material, along other data of the literature [14], [17].

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	C_{11}/C_{33}	C_{12}/C_{13}	C_{44}/C_{66}
This work	116.10	75.51	74.97	112.21	46.80	48.43	1.03	1.01	0.97
Ref. [14]	117.06	77.45	76.06	122.95	47.22	49.14	0.95	1.02	0.96
Ref. [17]	104.5	68.9	67.9	108.9	43.5	42.4	0.96	1.01	1.03

From Table 2, one can note that our calculated values of the elastic constants C_{ij} of KS phase are also in very good agreement compared to other data of the literature [14], [17]. Our elastic constants C_{ij} obey also the previous conditions of the mechanical stability. From Table 2, one can observe that the ratios of C_{11}/C_{33}, C_{12}/C_{13} and C_{44}/C_{66} are nearly equal to unity, suggesting that the stannite phase of CZTS semiconducting material has pseudo-cubic nature. In addition, in our calculations, $C_{11} \approx C_{33}$, which indicates that the bonding strength along the [100] and [010] direction is as strong as the one of the bonding along the [001] direction [16].

The degree of elastic anisotropy may be characterized by means of the normal and shear anisotropy factors $A_1 = 2C_{66}/(C_{11} - C_{12})$ and $A_2 = 4C_{44}/(C_{11} + C_{33} - 2C_{13})$, respectively [17]. A_1 and A_2 values for KS phase of CZTS are about 2.11 and 2.40, respectively, while those of ST phase are about 2.39 and 2.42, respectively.

4. 2. Elastic moduli and Microhardness

The aggregate Young modulus E and Poisson ratio $v$are usually calculated from B and G as follow: $E = [9BG/(3B+G)]$, and $v = (3B-E)/(6B)$ [22]. The obtained values of the bulk modulus B in this study, the shear modulus G, the Young modulus E and the Poisson ratio $v$of both kesterite and stannite phases of CZTS material were reported in Table 3, along other theoretical data of the literature [15], [16], [17].Our obtained values of B, G,E and v agree very

well with other data of the literature. The obtained value (87.50 GPa) of *B* in this study underestimates the result (88.37GPa) reported by Gunaicha *et al.* [15] by less than 1%, while our predicted result (90.42 GPa) of *E* deviates from the value (88.46GPa) of Ref [15] by around 2.2%.

Another interesting parameter is the ratio between the bulk and the shear modulus *B*/*G*, which has been proposed to predict brittle or ductile behavior of materials. According to the Pugh criterion, a high *B*/*G* value indicates a tendency for ductility. If $B/G > 1.75$, then ductile behavior is predicted, otherwise the material behaves in a brittle manner [16]. The *B*/*G* ratio for the kesterite-type CZTS is 2.57, while that of ST phase is around 2.63, which indicated that both the kesterite-type and the stannite phases of CZTS are more prone to ductile behavior.

Microhardness is one of the most parameters used in the characterization of solids; it is related to the valence electron density, the ionicity, and the bond-length [35]. It can be noted also that the microhardness of real crystal is very strongly affected by the presence of dislocations and other point defects [35].

Although several theoretical works [14], [15], [16], [17] have been published on the elastic constants of the CZTS compound, unfortunately, none of them predicted the microhardness of this material. Theoretically, the Vickers hardness H_V can be calculated from the following empirical expression [24], [35]: $H_V = 0.92\, k^{1.137} G^{0.708}$, where $k = G/B$ is the Pugh's ratio. The microhardness is expressed as a function of the aggregate Young modulus *E* and Poisson ratio *v*as follows [36]: $H = (1-2\nu)E/[6(1+\nu)]$. Our obtained values of H_V and *H*of KS and ST phases of CZTS material were reported also in Table 3.

Table 3. Elastic moduli (B, G, E, H_V and H in GPa, while B/G and v are dimensionless) of KS and ST phases for CZTS material, along other data of the literature [15], [16], [17].

		B	*G*	*B*/*G*	*G*/*B*	*E*	*v*	H_V	*H*
Kesterite	This work	87.50	34.05	2.57	0.39	90.42	0.33	3.82	3.91
	Ref. [15]	88.37	33.18	-	-	88.46	0.33	-	-
	Ref. [16]	67.8	29.7	2.28	-	77.8	0.31	-	-
	Ref. [17]	83.5	32.6	-	-	86.5	0.33	-	-
Stannite	This work	87.60	33.30	2.63	0.38	88.67	0.33	3.66	3.74
	Ref. [17]	80.8	30.8	-	-	81.9	0.33	-	-

The values in this study (3.82 GPa and 3.91 GPa) of the microhardness of CZTS are higher than the estimated value (2.7 GPa) reported by Adachi [21]. Unfortunately, both the

calculated values of microhardness in this study and those reported in Ref [21] are theoretical, so they could not compare with available data due to lack of experimental conformations.

4. 3. Sound wave velocities, Grüneisen parameter and Debye temperature

Previous investigations [37], [38], [39] have shown that the acoustic Grüneisen parameter can be reliably calculated as: $\gamma = 3(1+\nu)/[2(2-3\nu)]$. Our results of acoustic Grüneisen parameter were found equal to 1.97 for KS phase and 1.98 for ST phase, respectively. Our value (1.97) of the Grüneisen parameter of the kesterite-type CZTS is slightly lower than the value 2.28 [16] calculated at 300 K, obtained from the quasi-harmonic Debye model approach, which is assumed that the solid behaves like a harmonic solid at each volume, but the phonon frequencies depend on volume. Unfortunately, to the best of our knowledge, there are other theoretical data or experimental values to make confirmations. It is observed that the Grüneisen parameter decreases usually with increasing pressure, and increases with increasing temperature [40], [41], [42].

The linear thermal expansion coefficient α_{th} is proportional to the specific heat at constant volume C_V, known as Grüneisen's rule [21], [43]:

$$\alpha_{th} = \frac{1}{a}\left(\frac{\partial a}{\partial T}\right)_p = \frac{\gamma C_O C_V}{3V} \Rightarrow \gamma = \frac{3\alpha_{th} V}{C_O C_V} \tag{12}$$

where γ is the averaged Grüneisen parameter, C_O is the isothermal compressibility, and V is the volume of the solid (depending to C_V, usually the molar volume was used) .

Replacing in Eq.(12) the data reported in Ref [21] on the averaged linear thermal expansion coefficient α_{thav}= (2 (8.7×10^{-6}) $+7.4\times10^{-6})/3$ = ~ 8.3×10^{-6} K^{-1}, the isothermal compressibility $C_O = 1/B$ (B is the bulk modulus, B = 86 GPa), the specific heat $C_V \approx C_p$= 23 J mol^{-1} K^{-1} [21](obtained by dividing the original data reported in Ref [44] by eight), and the mean atomic volume, V= 19.96×10^{-30} m^3. The Grüneisen parameter γ of the KS phase was estimated at around 1.13, which is very lower than our acoustic Grüneisen parameter (1.97) and the value 2.28 reported by He and Shen [16].To the best of authors' knowledge, there are no other theoretical data reported in the literature on the Grüneisen parameter γ of CZTS with KS structure. Hope to see experimental measurement on γ for this material soon.

Additionally to the longitudinal (compressional) v_l, and transverse (shear) v_t sound wave velocities, bulk sound wave velocity ($v_B = \sqrt{B/\rho}$) was usually calculated. The obtained values

of the crystal density ρ in this study, compressional, shear and bulk sound wave velocities, and Debye temperature θ_D of the kesterite and stannite phases of CZTS were reported in Table 4.

The value (332.7 K) of the Debye temperature θ_D of the kesterite phase in this study is slightly smaller than the estimated value (400 K) reported by Adachi [21] and slightly higher than the experimental result (301.8 K) of CZTS single crystal reported by Nagaoka *et al.* [44] obtained from analyzing $C_p(T)$ data, using the Debye function.

Table 4. Crystal density ρ (in g/cm^3), compressional v_l, shear v_t, mean v_m and bulk sound wave velocities (in m/s), Debye temperature θ_D (in K), and acoustic Grüneisen parameter γ (is dimensionless) of KS and ST phases for CZTS material.

		ρ	v_l	v_t	v_m	v_B	θ_D	γ
Kesterite	This work	4.819	5252	2658	2980	4261	332.7	1.97
	Ref. [21]	4.564	5300	2700	-	-	400	-
Stannite	This work	4.820	5233	2628	2948	4263	329.1	1.98

The value (332.7 K) in this study is only about 32 K higher than the experimental result (301.8 K) reported by Nagaoka *et al.* [44]. It can be observed also that both the value (332.7 K) of θ_D and the experimental one (301.8 K) reported by Nagaoka *et al.* [44] are strongly higher than the theoretical one (157 K) reported by He and Shen [16], obtained from the quasi-harmonic Debye model approach. Such as the Grüneisen parameter γ, if we multiplied the value 157 K of θ_D by 2, we found 314 K, which is in very good agreement with the experimental value 301.8 K reported by Nagaoka *et al.* [44].

The melting temperature T_m is correlated with structural parameters and is usually determined from the elastic constants [32], [45]. The melting temperature of some Cu_2–II–IV–VI_4 quaternary semiconductors, and the effective cubic lattice constant a_{eff} are related by the following empirical formula $T_m = 4756 – 647a_{eff}$ [21], where T_m is expressed in K, and a_{eff} in Å. Replacing this equation our value (5.33 Å) of a_{eff} of CZTS with KS structure, our calculated value of the melting temperature T_m was found to be around1307 K. Our value (1307 K) of T_m for CZTS with KS phase is slightly higher than the experimental values (1255 K) and (1263 K) reported by Schäfer and Nitsche [46] and Matsushita *et al.* [47], respectively. Our value (1307 K) of T_m deviates from the experimental ones (1255 K) and (1263 K) by only around 4.14% and 3.5%, respectively. To the best of authors' knowledge, there is no theoretical data reported in the literature on T_m of CZTS material.

5. Conclusion

The elastic stiffness constants C_{ij} of tetragonal CZTS semiconducting material in both kesterite and stannite phases are calculated and analyzed using the Ultra Soft pseudopotentials in the framework of the DFT. The main results conclusions concerning this study are:

1. The elastic stiffness constants C_{ij} calculated here for both kesterite and stannite phases are in very good agreement compared to other data in the literature;
2. Due to a similar crystallographic structure, no significant effect of the atomic configuration on the elastic constants C_{ij}, the Debye temperature θ_D and other physical parameters was observed. Our value 332.7 K of θ_D of the kesterite phase deviates from the experimental one (301.8 K) measured at low temperature (T below 7 K) by around 10%;
3. The elastic constants C_{ij} in this study obey the conditions of the mechanical stability, and the ratios of C_{11}/C_{33}, C_{12}/C_{13} and C_{44}/C_{66} are nearly equal to unity, suggesting that both the kesterite and the stannite phases have pseudo-cubic nature;
4. Except for the estimated value (2.7 GPa) of the microhardness H reported by Adachi [21], to the best of our knowledge, there is no other theoretical or experimental data available in the literature on H for Cu_2ZnSnS_4 material to make conformations-such as the methodology used in this study-.
5. This study demonstrates the potential use of Cu_2ZnSnS_4 materials for photovoltaic applications, by contributing to the efforts to reduce the prices and increase the efficiency of PV modules.

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