

# Wide band-gap tuning $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$ single crystals: optical and vibrational properties

E. Garcia-Llamas<sup>a\*</sup>, J. M. Merino<sup>a</sup>, R. Serna<sup>b</sup>, X. Fontané<sup>c</sup>, I. A. Victorov<sup>d</sup>, A. Pérez-Rodríguez<sup>e</sup>, M. León<sup>a</sup>, I. V. Bodnar<sup>f</sup>, V. Izquierdo-Roca<sup>b</sup>, R. Caballero<sup>a\*</sup>

a. Photovoltaic Materials Group, Universidad Autónoma de Madrid, Departamento de Física Aplicada, C/ Francisco Tomás y Valiente 7, 28049 Madrid, Spain

b. Laser Processing Group, Instituto de Óptica, CSIC, C/ Serrano 121, 28006 Madrid, Spain.

c. Catalonia Institute for Energy Research, C/ Jardins de les Dones de Negre 1 2pl., 08930 Sant Adrià del Besòs-Barcelona, Spain

d. Institute of Physics of Solids and Semiconductors, Academy of Sciences of Belarus, 17 P. Brovka Str., 220072, Minsk, Belarus

e. IN2UB, Departament d'Electrònica, Universitat de Barcelona, C/ Martí i Franquès 1, 08028 Barcelona, Spain

f. Belarusian State University of Informatics and Radioelectronics, P. Browski Str., 6, Minsk 220013 Belarus

**Corresponding Author\*** [eduard.garcia@uam.es](mailto:eduard.garcia@uam.es), Tel: +34 914973440, Fax: +34

914973969; [raquel.caballero@uam.es](mailto:raquel.caballero@uam.es), Tel: + 34 914978559

ABSTRACT. The linear optical properties of  $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$  high quality single crystals with a wide range of Ge contents ( $x = 0.1, 0.3, 0.5, 0.7, 0.9$  and 1) have been investigated in the **ultraviolet** and near infrared range using spectroscopic ellipsometry measurements. From the analysis of the complex dielectric function spectra it has been found that the bandgap  $E_0$  increases continuously from 1.49 eV to 2.25 eV with the Ge

1 content. Furthermore, the evolution of the interband transitions  $E_{1A}$  and  $E_{1B}$  has been  
2 also determined. Raman scattering using three different excitation wavelengths and its  
3 analysis have been performed to confirm the absence of secondary phases in the  
4 samples, and to distinguish between stannite, wurtzite, wurzstannite and kesterite  
5 structures. Additionally, the analysis of the high resolution Raman spectra obtained in  
6 samples with different  $[Ge]/([Ge]+[Sn])$  ratios allows describing a bimodal behavior of  
7 the dominant A modes. The understanding of the incorporation of Ge into the  
8  $Cu_2ZnSnS_4$  lattice is fundamental in order to develop efficient bandgap engineering of  
9 these compounds towards the fabrication of kesterite based solar cells with enhanced  
10 performance.  
11  
12  
13  
14  
15  
16  
17  
18  
19

20 **KEYWORDS.**  $Cu_2ZnSn_{1-x}Ge_xS_4$  kesterite; Spectroscopic Ellipsometry; Raman  
21 scattering; Band-gap tuning; Solar cells.  
22  
23  
24

## 25 1. Introduction 26 27 28

29 Nowadays,  $Cu_2ZnSn(S,Se)_4$  (CZTSSe) **compound** is attracting special attention as a  
30 promising light absorber candidate for thin film solar cells because of its appropriated  
31 optical and electronic properties. Moreover, this compound is based on earth abundant  
32 and low toxic elements. However, the last record efficiency reported of 12.6% [1] is still  
33 very far away from the highest performance of  $Cu(In,Ga)Se_2$  (CIGSe) solar cells, 21.7%  
34 [2]. One of the key of the success of CIGSe is the capacity of tuning the absorber band  
35 gap [3]. Recently, it has been shown that this band gap tuning can be also applied on  
36 CZTSSe by partially replacing tin with germanium [4,5]. The role of the Ge/Sn ratio in  
37  $Cu_2ZnSn_{1-x}Ge_x(S,Se)_4$  (CZTGSSe) is analogous to the Ga/In ratio in high efficient  
38 CIGSe solar cells. **Moreover, there is an advantage in terms of reduction of costs by  
39 using the Ge/Sn pair instead Ga/In. Note that due to competition between the  
40 photovoltaic and the semiconductor and optoelectronics industries for the use of In and  
41 Ga resources, the price of the absorber could be very high [6]. Furthermore, the scarcity  
42 of In in the crust of earth might become a limitation in the near future in order to  
43 achieve the production of solar cells to cover the power annual demand by chalcopyrite  
44 thin film technology [7].** Improved efficiency of kesterite thin film solar cells has been  
45 already reported by replacing Sn with Ge, with device efficiencies of 9.4% [8]. In spite  
46 of this promising result for CZTGSSe compounds, there is not much known about their  
47 fundamental properties, and more particularly about the effect on the optical properties  
48 of the atomic ratio  $x = [Ge]/([Ge]+[Sn])$ . So far Morihama et al. [9] have reported  
49 information on structural properties of  $Cu_2ZnSn_{1-x}Ge_xSe_4$  (CZTGSe) **compounds** by X-  
50 ray diffraction and determined the band gap energies by diffuse-reflectance spectra, and  
51 Grossberg et al. [10] have studied the recombination mechanisms of CZTGSe by  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 photoluminescence. In both cases, a linear increase of the bandgap from 0.9 eV to 1.3  
2 eV at room temperature with the Ge content was shown. On another hand, there is even  
3 less information about the fundamental properties of  $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$  (CZTGS)  
4 compounds. A fundamental band gap energy  $E_0 = 2.2$  eV and 2.0 eV for  $\text{Cu}_2\text{ZnGeS}_4$   
5 single crystal and single-crystalline nanowire arrays respectively have been reported in  
6 [11] and [12] respectively. Recently,  $E_0 = 1.59$  and 1.90 eV have been determined for  
7  $\text{Cu}_2\text{ZnSn}_{0.9}\text{Ge}_{0.1}\text{S}_4$  and  $\text{Cu}_2\text{ZnSn}_{0.5}\text{Ge}_{0.5}\text{S}_4$  single crystals respectively by spectroscopic  
8 ellipsometry [5]. The addition of Ge gives the possibility to control the bandgap of the  
9 absorber in a wider region from 1 to 2.3 eV, expanding the range of values available by  
10 varying the anion compositions in CZTSSe [13]. Moreover, it is expected for CZTGS  
11 compounds a linear decrease of the cell parameters when the Ge content increases, like  
12 the linear decrease reported in [9] for CZTGSe, which would control the lattice  
13 parameters depending on the Ge/Sn ratio. These are of main interest for the  
14 development of new multi-junction devices where photovoltaic conversion is optimized  
15 by improving the device efficiency in different spectral regions.

16  
17  
18  
19  
20  
21  
22 The objective of this work is to provide a thorough investigation of the optical,  
23 electronic and vibrational properties of  $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$  (CZTGS) single crystals as a  
24 function of the Ge content for a wide range of compositions,  $x = 0, 0.1, 0.3, 0.5, 0.7, 0.9$   
25 and 1 in a broad energy range from the near infrared to ultraviolet (0.8 eV to 4.6 eV).  
26 The composition of the crystals has been determined by energy dispersive X-ray (EDX)  
27 analysis. The dielectric constants for each selected composition were determined from  
28 variable angle spectroscopic ellipsometry measurements. This data were analysed to  
29 determine the fundamental band gap and the interband transition energies. Moreover,  
30 the near-surface region of every crystal has been studied by Raman spectroscopy.  
31 Raman spectroscopy is a technique based on the evaluation of the inelastic scattering  
32 process of molecules or crystals under monochromatic light. The evaluation of the  
33 energy of inelastic scattered photons in a crystalline material provides information on  
34 the vibrational energy and its density in the lattice (phonons) which is strongly sensitive  
35 to the atomic composition, crystal structure and crystal quality. As a result, Raman  
36 spectroscopy provides direct information of the chemico-physical properties of the  
37 material evaluated. For this reason, this technique is able to give reliable information  
38 about the crystalline structure and inhomogeneity on the surface. In this study three  
39 different wavelengths have been applied on the surface of the single crystals to be able  
40 to distinguish the presence of different secondary phases [14–16]. Additionally, the  
41 Raman characterization allowed evaluating the evolution of the Raman spectra with the  
42  $[\text{Ge}]/([\text{Ge}]+[\text{Sn}])$  ratio. The study of the vibrational properties on chalcogenides solid  
43 solution systems such as  $\text{Cu}(\text{S},\text{Se})$  [17],  $\text{Cu}(\text{In},\text{Al},\text{Ga})(\text{S},\text{Se})_2$  [18–20], and  
44  $\text{Cu}_2(\text{Fe},\text{Zn})\text{Sn}(\text{S},\text{Se})_4$  [15,21,22] has demonstrated a high potential to evaluate the  
45 physical and chemical properties of the material such as the composition, crystal quality  
46 and presence of secondary phases, and opened the possibility of developing  
47 methodologies for non-destructive and high-accuracy compositional assessment.

## 2. Experimental

### 2.1. Synthesis of single crystals

$\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$  single crystals were synthesized by chemical vapor transport (CVT) of the elements [23]. Previously, several bulk kesterite compounds with different Ge/Sn ratios were grown by a modified Bridgman method, using constituents with purities  $\geq 99.999\%$ . The growth was carried out in an evacuated quartz ampoule introduced in a vertical furnace, followed by a heating ramp up to 1173 K avoiding overpressures. While the compound was liquid, a vibration movement was applied to the ampoule to improve the homogenization of the samples. The ampoule was then cooled down and an ulterior homogenization process was applied at 973 K for 7 days. The samples were grinded and used as source materials for the CVT synthesis.

The CVT process was performed in another quartz ampoule filled with the grown compound and adding  $5 \text{ mg cm}^{-3}$  of iodine, located in a furnace with two independent heating zones. Iodine was used as transport agent. The temperature at the crystallization zone was kept at 970 K, around 80 K lower than the temperature at the reaction zone (1050 K), and both were maintained for 8 days [5]. Varying the amount of Ge and Sn, seven  $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$  samples with  $x=0, 0.1$ [5], 0.3, 0.5, 0.7, 0.9 and 1 were grown.

### 2.2. Characterization of $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$ single crystals

The composition of the samples was measured by energy dispersive X-ray (EDX) (Oxford Instruments, model INCAx-sight) inside a Hitachi S-3000N scanning electron microscope. The measurements were performed at 25 kV operating voltage and the Cu-, Zn-, Ge-, S-K lines and Sn-L line were used. Table 1 shows the composition of the investigated samples. The relative error of the concentration values is 1% maximum.

To clarify the presence of secondary phases and to extract structural and vibrational information from the different CZTGS compounds, systematic Raman scattering measurements were carried out. The Raman spectra were obtained with a Horiba Jobin Yvon LabRam HR800-UV matched with an Olympus metallographic microscope. Backscattering measurements were done with three different excitation wavelengths (532, 325, and 785 nm) focusing the laser spot onto the single crystal, and orientating the excitation light polarization along the crystal grown direction. The use of different excitation wavelengths allows the selective enhance of the secondary phases modes and the activation of different CZTGS ones. The laser spot size is of the order of 1-2  $\mu\text{m}$ , but in order to integrate the potential secondary phases, a spot raster facility that extends the analysis to an area of 30  $\mu\text{m}$  x 30  $\mu\text{m}$  has been used. In all Raman measurements, the power density for all excitation wavelengths has been kept below to  $16 \text{ kW/cm}^2$  to avoid thermal effects. All spectra have been calibrated using a Si single crystal as reference and imposing the Raman shift for the main Si band at  $520 \text{ cm}^{-1}$ . Simultaneous fittings of spectra with Lorentzian curves have allowed the identification of the peaks

1 attributed to their optical modes. The position of each Raman peak is presented in Table  
2  
3

4 The measurement of the spectroscopic ellipsometry parameters  $\psi$  and  $\delta$  of the crystals  
5 was carried out using a variable angle spectroscopic ellipsometer (Woollam VASE) at  
6 room temperature at three incidence angles of  $60^\circ$ ,  $65^\circ$  and  $70^\circ$ , to ensure a consistent  
7 and accurate determination of the dielectric function, in the 0.75-4.5 eV photon energy  
8 range, using 0.03 eV steps. In order to obtain reliable data for the optical properties of  
9 the bulk crystals, the preparation of a good quality surface is extremely important to  
10 minimize the surface roughness and oxide formation effects [24,25]. Recently, we have  
11 observed the modification of the values of the effective transitions energies because of  
12 the presence of  $\text{GeO}_2$  on the surface of these compounds [5]. Therefore, the crystal  
13 samples were thoroughly polished using a colloidal silica polishing suspension  
14 (Mastermet) in order to remove the oxides that might form at the surface, and the  
15 ellipsometric parameters  $\psi$  and  $\delta$  were measured immediately after that. The complex  
16 effective dielectric function ( $\epsilon(E) = \epsilon_1(E) + i\epsilon_2(E)$ ) was determined by simulations with the  
17 WVASE ellipsometry analysis software assuming a two-phase (substrate-ambient)  
18 model [24,25]. The second derivative spectra of the real ( $\epsilon_1$ ) and imaginary part ( $\epsilon_2$ ) of  
19 the effective dielectric functions and their extrapolation have been used to determine the  
20 change of the fundamental band gap  $E_0$  [11] as a function of the compositional changes,  
21 and the corresponding interband transitions  $E_{1A}$  and  $E_{1B}$ .

### 30 3. Results

31  
32 CZTSSe-type compound can crystallize in two different structures, the stannite (space  
33 group I-42m) and the kesterite (space group I-4). These two structures are very similar  
34 with the only difference in the distribution of the cations in the tetrahedral sites [26].  
35 This slight difference between these two crystallographic forms increases the difficulty  
36 to distinguish them. It is possible to determine the structure of these compounds by  
37 neutron diffraction experiments [27,28] but Raman spectroscopy measurements are also  
38 a powerful tool to distinguish between stannite and kesterite [15] and the chemicals  
39 inhomogeneity [14,16,17]. In this work, that technique was used to confirm the  
40 presence of a single phase material, so that the optical characterization could be carried  
41 out on the samples accurately.

42  
43 Figure 1(a) shows the Raman spectra (in the region of  $150\text{-}500\text{ cm}^{-1}$  and  $650\text{-}750\text{ cm}^{-1}$ )  
44 obtained for  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS),  $\text{Cu}_2\text{Zn}(\text{Sn}_{0.5}\text{Ge}_{0.5})\text{S}_4$  (CZT<sub>0.5</sub>G<sub>0.5</sub>S), and  $\text{Cu}_2\text{ZnGeS}_4$   
45 (CZGS) single crystals samples. Additionally, figure 1(b) shows the position of the  
46 main bands obtained under different excitation wavelengths, which are the more  
47 sensitive conditions in order to detect secondary phases. The Raman excitation using  
48 different wavelengths allows increasing the Raman cross-section efficiency of different  
49 compounds through the resonance or pre-resonant process. These processes enhanced  
50 several orders of magnitude the Raman contribution of the modes related to the phase  
51 that undergoes the resonant or pre-resonant effect. These processes occur when the  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

energy of the incident laser is coupled with the energy between the electronic ground energy level and other real electronic energy levels of the compound (resonant conditions) or close to this (pre-resonant condition). Applying these conditions is possible to select the proper excitation energy to detect low concentrations of secondary phases. This shows, Raman spectroscopy as a very sensitive technique, as reported for the CZT(S,Se) system [29–31]. Under 325 nm (3.8 eV), 532 nm (2.4 eV) and 785 nm (1.6 eV) excitation wavelengths, the ZnS [29], SnS<sub>2</sub> [32], Sn<sub>2</sub>S<sub>3</sub> [16,33], SnS [16,34], GeS [35] (direct band gaps of 3.7 eV, 2.5 eV, 2 eV, 1.4 eV and 1.6 eV, respectively) present resonant or pre-resonant conditions. Cu<sub>2-x</sub>S [17,36], GeS<sub>2</sub> [37], Cu<sub>2</sub>SnS<sub>3</sub> [32,38,39], and Cu<sub>2</sub>GeS<sub>3</sub> [40] phases do not show a resonant Raman scattering process under these excitation wavelengths because their band gap energies are not coupled with the excitation energy used. Nevertheless, the characteristic peaks of these secondary phases (Cu<sub>2-x</sub>S, GeS<sub>2</sub>, Cu<sub>2</sub>SnS<sub>3</sub>, and Cu<sub>2</sub>Ge) are not overlapped with the main CZTGS peaks, and therefore the detection of these secondary phases is not compromised and could be detected at 532 nm excitation wavelength.

The application of the multiwavelength excitation methodology described by Dimitrievska et al. [41] based on the simultaneous fitting of the Raman spectra obtained under resonant, and non-resonant conditions (325, 532 and 785 nm excitation wavelengths) allows determining the characteristic peaks of CZTS, CZT<sub>0.5</sub>G<sub>0.5</sub>S and CZGS samples. The comparison of the peak positions reported for kesterite [41,42], wurzite [43], and wurtzannite [44] crystal structures allows identifying the structure of the CZTGS system as kesterite type (Table 2). This result is in agreement with CZTS X-Ray diffractogram JCPDS 26-0575 database and the X-Ray diffractogram measured from the CZTS, CZT<sub>0.5</sub>G<sub>0.5</sub>S and CZTGS single crystals powder samples (see Figure 2(a)). Figure 2(b) displays a zoom-in of the 112 peak, showing that all the samples are single phase. Moreover, Figure 1 shows the Raman spectra of the CZTGS compounds with the dominant peaks for each secondary phase. As it can be seen in Figure 1, there is no evidence of the presence of secondary phases in the CZTGS samples.

In order to evaluate the dependence of the dominant Raman contributions (A<sup>1</sup> and A<sup>2</sup> peaks) with the Ge content in the solid solution, Raman spectra of CZTGS single crystals samples with [Ge]/([Ge]+[Sn]) ratios close to 0, 0.3, 0.5, 0.7, 0.9 and 1 under 532 nm excitation wavelength have been measured (see figure 3). All these Raman spectra show the characteristic peaks of the kesterite structure, where A<sup>1</sup>= 359 cm<sup>-1</sup>, A<sup>2</sup>= 296 cm<sup>-1</sup> are the main modes of CZGS, and A<sup>1</sup> = 338 cm<sup>-1</sup>, A<sup>2</sup> = 287 cm<sup>-1</sup> are the main ones for CZTS.

Figure 4 shows the experimental spectral dependence of the dielectric functions of several Cu<sub>2</sub>ZnSn<sub>1-x</sub>Ge<sub>x</sub>S<sub>4</sub> single crystals. The spectra exhibit several clear interband critical points (CP) structures analyzed in terms of standard analytic line shapes:

$$\varepsilon(\omega) = C - A \exp^{i\phi} (\omega - E + i\Gamma)^m \quad (1)$$



1 where  $A$  is the amplitude,  $E$  is the energy threshold,  $\Gamma$  is the broadening, and  $\Phi$  is the  
2 excitonic phase angle [25]. These parameters are determined by fitting the numerically  
3 obtained second derivative spectra  $d^2\varepsilon(E)/dE^2$  of the experimental  $\varepsilon(E)$  to equation (1).  
4 The exponent  $m$  has the value  $-1/2$  for one-dimensional, 0 for two-dimensional, and  $1/2$  for  
5 three-dimensional critical points. From the CPs, information on the energy separation of  
6 valence and conduction bands can be obtained. Previously, calculations based on  
7 different features observed in complex dielectric constants have been reported in CZTS  
8 [45] and CZGS [11] bulk crystals. Here the  $\varepsilon(E)$  spectra show three CPs structures:  $E_0$ ,  
9  $E_{1A}$  and  $E_{1B}$ .  
10

11 To obtain the CP's energies, the  $\varepsilon(E)$  spectra were smoothed by fast Fourier transform  
12 filtering before fitting  $d^2\varepsilon(E)/dE^2$ . Figure 5 exhibits the second derivatives of the real  
13 and imaginary parts of the dielectric functions and their fittings by using equation (1) of  
14 three samples. The fittings have been done taking into account CPs of 3D-type for the  
15 fundamental absorption edge  $E_0=E_g$  and 2D-type for the second,  $E_{1A}$ , and third,  $E_{1B}$ ,  
16 transition energies.  
17  
18  
19  
20  
21

#### 22 4. Discussion

23 Recently, Dhruva et al. [42] have reported the Raman evolution of the CZTGS kesterite  
24 type system. In [42], the reported Raman spectrum of CZTGS sample with a  
25  $[Ge]/([Ge]+[Sn]) \approx 0.5$  shows a clear asymmetric and broad band centered at  $347 \text{ cm}^{-1}$ .  
26 This band has been assigned to pure chalcogenide S-S vibration, and their asymmetry  
27 and high FWHM have been attributed to the presence of the cationic disorder originated  
28 from the solid solution composition. In this work, the Raman spectrum obtained for a  
29 similar  $[Ge]/([Ge]+[Sn])$  ratio (single crystal sample  $CZT_{0.5}G_{0.5}S$ ) shows a splitting of  
30 such broad and asymmetric bands in two resolved contributions centered at  $342$  and  
31  $352 \text{ cm}^{-1}$ . In order to evaluate the interpretation of this band splitting, the evolution of  
32 these two peaks with the  $x=[Ge]/([Ge]+[Sn])$  ratio has been analyzed. Figure 3 shows  
33 the Raman spectra obtained for the different  $x=[Ge]/([Ge]+[Sn])$  compositions from  $275$   
34 to  $380 \text{ cm}^{-1}$  Raman shift. Increasing the Ge content results in a decrease in the intensity  
35 of the higher energy peak (lower Raman shift), while the intensity of the lower energy  
36 peak (higher Raman shift) increases. The Raman shift extrapolation of these two  
37 contributions at  $[Ge]/([Ge]+[Sn])=0$  and 1 allows identifying the lower energy  
38 contribution as Sn-like peak, while the higher contribution one as Ge-like peak [46].  
39 This indicates that as Germanium is incorporated in the CZTGS structure, the A mode  
40 shows a bimodal behavior. A detailed examination of the diffraction peaks for the  
41  $CZT_{0.5}G_{0.5}S$  sample (figure 2 (b)) does not show evidences of asymmetry or splitting of  
42 peaks that could be attributed to presence of mixed CZTGS kesterite compositions. This  
43 suggests that the Raman splitting of the A peak observed in the Raman spectra is  
44 intrinsic to the CZTGS solid solution.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56

57 Table 3 shows the energy threshold of the fundamental absorption edge  $E_0 = 2.25 \text{ eV}$  for  
58  $\text{Cu}_2\text{ZnGeS}_4$  (CZGS), which is in good agreement with the  $2.27 \text{ eV}$  of the kesterite  
59 CZGS theoretical calculations [26] and that obtained experimentally in single crystals  
60  
61  
62  
63  
64  
65

1 by ellipsometry [11]. This  $E_0$  is assigned to the electronic transition at the  $\Gamma(000)$  point,  
2 corresponding to a direct transition from the valence-band maximum (VBM) to the  
3 conduction-band minimum (CBM). For the same compound, the energies of the second  
4 threshold  $E_{1A}$  and the third  $E_{1B}$  are 2.92 eV and 4.24 eV respectively. These energies are  
5 very close to that reported from theoretical band structure studies [26] for the  
6 transitions at the high critical points  $N(A): 2\Pi/a (0.5 0.5 0.5)$ ,  $T(Z): 2\Pi/a (0 0 0.5)$  and  
7  $\Gamma_2:(0 0 0)$  of the first Brillouin zone for the  $E_{1A}$ ,  $E_{1B}$  and  $E_0$  transitions, respectively.  
8  
9

10 The partial substitution of Ge by Sn leads to a decrease of the  $E_0$  values as displayed in  
11 Table 3.  $E_0$  values of 2.20, 1.97, 1.90, 1.69, 1.59 and 1.51 eV were determined for Ge  
12 contents corresponding to  $x$  of 0.9, 0.7, 0.5, 0.3, 0.1 and 0, respectively. Figure 6  
13 displays the variation of the fundamental energy  $E_0$  with the experimental  
14  $[Ge]/([Sn]+[Ge])$  atomic ratio and its linear fitting. The band gap evolution follows  
15 Vegard's law, as already observed for  $Cu_2ZnSn_{1-x}Ge_xSe_4$  [9]. Theoretical works [26]  
16 suggest that Zn does not have an important role in the change of the band gap energy, so  
17 the deviation from a linear increase of  $E_0$  with the Ge content may be related to the  
18 different Cu concentration of the samples. The reason of this deviation may be  
19 originated in the Cu-S p-d coupling that determines the VBM level, and the Cu-poor  
20 samples show higher band gaps due to the decrease in the VBM [26,47,48]. The  
21 phenomena of the "vacancy compound" for Cu-poorer thin films, increasing  $E_0$ , have  
22 been widely used in the chalcopyrite compound to improve their efficiency like in the  
23 case of CISE/CdS interface [49]. The composition of the kesterite plays an important  
24 role because the highest performance obtained for CZTSSe-based solar cells are  
25 obtained for Cu-poor kesterite layers.  
26  
27  
28  
29  
30  
31  
32  
33

34 In the case of  $E_{1A}$  and  $E_{1B}$ , values of  $E_{1A}$  of 3.04, 2.92, 2.82, 2.76 2.75, and 2.69 eV,  
35 and  $E_{1B} = 4.19, 4.20, 4.21, 4.10, 4.09,$  and 4.01 eV were obtained for  $x \approx 0.9, 0.7, 0.5,$   
36  $0.3, 0.1$  and 0 respectively. To our knowledge, at present there are no available band  
37 structure calculations for these pseudo-quaternary compounds; however the same  
38 behavior as for CZTGS could be expected.  
39  
40  
41

42 Following the band gap theoretical calculations [26,50], we can also conclude that our  
43 samples present a kesterite structure due to the fact that the stannite band gap is clearly  
44 smaller than those presented in this work. This result agrees with Raman and XRD  
45 measurements. Furthermore, it has been shown that spectroscopic ellipsometry is an  
46 excellent non-destructive technique to determine the band gap energy and to distinguish  
47 between kesterite and stannite structures. Additionally the presence of the energy band  
48 around 4eV at  $\Gamma$  point for all  $[Ge]/([Ge]+[Sn])$  ratios is in agreement with the presence  
49 of an enhancement of the weaker Raman peaks by resonance process under 325nm (3.8  
50 eV) as reported in [38] for the CZTS compound.  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65



## 5. Conclusions

Cu<sub>2</sub>ZnSn<sub>1-x</sub>Ge<sub>x</sub>S<sub>4</sub> single crystals with different  $x = \text{Ge}/([\text{Ge}]+[\text{Sn}])$  atomic ratios were synthesized by chemical vapor transport. This work presents the wide band-gap tuning of CZTGS, varying  $E_0$  from 2.25 to 1.51 eV when  $x$  changes from 1 to 0, as measured by spectroscopic ellipsometry. Raman scattering experiments have allowed the identification of the crystal structure of the CZTGS system with the kesterite type. Additionally, the Raman experiments performed on single crystals in the entire range of  $[\text{Ge}]/([\text{Ge}]+[\text{Sn}])$  atomic ratios has allowed reporting the evolution of the A<sup>1</sup> and A<sup>2</sup> modes with the Ge incorporation on the CZTGS solid solution and describe the bimodal behavior of the A<sup>1</sup> in CZTGS kesterite solid solution system. This work shows an interesting perspective for the development and characterization of new multi-junction devices based on kesterites where the photovoltaic efficiency will be optimized by improving the device performance in different spectral regions by a suitable design of the absorber film composition.

## 6. Acknowledgements

This work was supported by the Marie Curie-ITN project (KESTCELL, GA: 316488), Marie Curie-IRSES project (PVICOKEST, GA: 269167), AMALIE (TEC2012-38901-C02-01) and **SUNBEAM (ENE2013-49136-C4-3-R)** project funded by the Spanish Ministry of Economy and Competitiveness. RC acknowledges financial support from Spanish MINECO within the Ramón y Cajal program (RYC-2011-08521).

## 7. References

- [1] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency, *Adv. Energy Mater.* (2013) 1–5. doi:10.1002/aenm.201301465.
- [2] ZSW press release, ZSW, *Pv Mag.* (2014). [http://www.pv-magazine.com/news/details/beitrag/zsw-sets-217-thin-film-efficiency-record\\_100016505/#axzz3LKgMy6rd](http://www.pv-magazine.com/news/details/beitrag/zsw-sets-217-thin-film-efficiency-record_100016505/#axzz3LKgMy6rd).
- [3] A.M. Gabor, J.R. Tuttle, D.S. Albin, M.A. Contreras, Noufi, Rommei, High-efficiency CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub> solar cells made from (In<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> precursor films, *Appl. Phys. Lett.* 65 (1994) 198–200.
- [4] G.M. Ford, Q. Guo, R. Agrawal, H.W. Hillhouse, Earth Abundant Element Cu<sub>2</sub>Zn(Sn<sub>1-x</sub>Ge<sub>x</sub>)S<sub>4</sub> Nanocrystals for Tunable Band Gap Solar Cells: 6.8% Efficient Device Fabrication, *Chem. Mater.* 23 (2011) 2626–2629. doi:10.1021/cm2002836.

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65
- [5] R. Caballero, I. Victorov, R. Serna, J.M. Cano-Torres, C. Maffiotte, E. Garcia-Llamas, J.M. Merino, M. Valakh, I. Bodnar, M. León, Band-gap engineering of  $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$  single crystals and influence of the surface properties, *Acta Mater.* 79 (2014) 181–187. doi:10.1016/j.actamat.2014.06.040.
- [6] S. Siebentritt, S. Schorr, Kesterites — a challenging material for solar cells, *Prog. Photovoltaics Res. Appl.* 20 (2012) 512–519. doi:10.1002/pip.2156.
- [7] M.A. Green, Estimates of Te and In Prices from Direc Mining of Known Ores, *Prog. Photovoltaics Res. Appl.* 17 (2009) 347–359. DOI: 10.1002/pip.899.
- [8] C.J. Hages, S. Levenco, C.K. Miskin, J.H. Alsmeyer, D. Abou-Ras, R.G. Wilks, M. Bär, T. Unold, R. Agrawal, Improved performance of Ge-alloyed CZTGeSSe thin-film solar cells through control of elemental losses, *Prog. Photovoltaics Res. Appl.* 23 (2013) 376–384. doi:10.1002/pip.2442.
- [9] M. Morihama, F. Gao, T. Maeda, T. Wada, Crystallographic and optical properties of  $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$  solid solution, *Jpn. J. Appl. Phys.* 53 (2014) 1–6.
- [10] M. Grossberg, K. Timmo, T. Raadik, E. Kärber, V. Mikli, J. Krustok, Study of structural and optoelectronic properties of  $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{Se}_4$  ( $x=0$  to 1) alloy compounds, *Thin Solid Films.* 582 (2014) 176–179. doi:10.1016/j.tsf.2014.10.055.
- [11] M. León, S. Levchenko, R. Serna, G. Gurieva, A. Nateprov, J.M. Merino, E.J. Friedrich, U. Fillat, S. Schorr, E. Arushanov, Optical constants of  $\text{Cu}_2\text{ZnGeS}_4$  bulk crystals, *J. Appl. Phys.* 108 (2010) 1–5. doi:10.1063/1.3500439.
- [12] L. Shi, P. Yin, H. Zhu, Q. Li, Synthesis and Photoelectric Properties of  $\text{Cu}_2\text{ZnGeS}_4$  and  $\text{Cu}_2\text{ZnGeSe}_4$  Single-Crystalline Nanowire Arrays, *Langmuir.* 29 (2013) 8713–8717.
- [13] J. He, L. Sun, S. Chen, Y. Chen, P. Yang, J. Chu, Composition dependence of structure and optical properties of  $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$  solid solutions: An experimental study, *J. Alloys Compd.* 511 (2012) 129–132. doi:10.1016/j.jallcom.2011.08.099.
- [14] X. Fontané, L. Calvo-Barrio, V. Izquierdo-Roca, E. Saucedo, A. Pérez-Rodríguez, J.R. Morante, D.M. Berg, P.J. Dale, S. Siebentritt, In-depth resolved Raman scattering analysis for the identification of secondary phases: Characterization of  $\text{Cu}_2\text{ZnSnS}_4$  layers for solar cell applications, *Appl. Phys. Lett.* 98 (2011) 1–3. doi:10.1063/1.3587614.

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65
- [15] X. Fontané, V. Izquierdo-Roca, E. Saucedo, S. Schorr, V.O. Yukhymchuk, M.Y. Valakh, A. Perez-Rodriguez, J.R. Morante, Vibrational properties of stannite and kesterite type compounds: Raman scattering analysis of  $\text{Cu}_2(\text{Fe,Zn})\text{SnS}_4$ , *J. Alloys Compd.* 539 (2012) 190–194. doi:10.1016/j.jallcom.2012.06.042.
- [16] X. Fontané, Doctoral Thesis, Caracterización por espectroscopia Raman para nuevas tecnologías fotovoltaicas  $\text{Cu}_2\text{ZnSnS}_4$  para nuevas tecnologías fotovoltaicas, Universitat de Barcelona, 2013.
- [17] M. Ishii, K. Shibata, H. Nozaki, Anion Distributions and Phase Transitions in  $\text{CuS}_{1-x}\text{Se}_x$  ( $x = 0-1$ ) Studied by Raman Spectroscopy, *J. Solid State Chem.* 105 (1993) 504–511. doi:http://dx.doi.org/10.1006/jssc.1993.1242.
- [18] V. Izquierdo-Roca, A. Shavel, E. Saucedo, S. Jaime-Ferrer, J. Álvarez-García, A. Cabot, A. Pérez-Rodríguez, V. Bermudez, J.R. Morante, Assessment of absorber composition and nanocrystalline phases in  $\text{CuInS}_2$  based photovoltaic technologies by ex-situ/in-situ resonant Raman scattering measurements, *Sol. Energy Mater. Sol. Cells.* 95 (2011) S83–S88. doi:10.1016/j.solmat.2010.11.014.
- [19] V. Izquierdo-Roca, X. Fontané, E. Saucedo, J.S. Jaime-Ferrer, J. Álvarez-García, A. Pérez-Rodríguez, V. Bermudez, J.R. Morante, Process monitoring of chalcopyrite photovoltaic technologies by Raman spectroscopy: an application to low cost electrodeposition based processes, *New J. Chem.* 35 (2011) 453–460. doi:10.1039/c0nj00794c.
- [20] J. López-García, M. Placidi, X. Fontané, V. Izquierdo-Roca, M. Espindola, E. Saucedo, C. Guillén, J. Herrero, A. Pérez-Rodríguez,  $\text{CuIn}_{1-x}\text{Al}_x\text{Se}_2$  thin film solar cells with depth gradient composition prepared by selenization of evaporated metallic precursors, *Sol. Energy Mater. Sol. Cells.* 132 (2015) 245–251. doi:10.1016/j.solmat.2014.09.003.
- [21] M. Dimitrievska, G. Gurieva, H. Xie, A. Carrete, A. Cabot, E. Saucedo, A. Pérez-Rodríguez, S. Schorr, V. Izquierdo-Roca, Raman scattering quantitative analysis of the anion chemical composition in kesterite  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  solid solutions, *J. Alloys Compd.* 628 (2015) 464–470. doi:10.1016/j.jallcom.2014.12.175.
- [22] M. Dimitrievska, H. Xie, A. Fairbrother, X. Fontané, G. Gurieva, E. Saucedo, A. Pérez-Rodríguez, S. Schorr, V. Izquierdo-Roca, Multiwavelength excitation Raman scattering of  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  ( $0 \leq x \leq 1$ ) polycrystalline thin films: Vibrational properties of sulfoselenide solid solutions, *Appl. Phys. Lett.* 105 (2014) 031913. doi:10.1063/1.4891333.
- [23] I. V. Bodnar, Growth and Properties of  $\text{CuAlS}_{2x}\text{Se}_{2(1-x)}$  Single Crystals, *Inorg. Mater.* 38 (2002) 647–651. doi:10.1023/A:1016271804632.

- 1  
2 [24] J.G. Albornoz, R. Serna, M. León, Optical properties and electronic structure of  
3 polycrystalline  $\text{Ag}_{1-x}\text{Cu}_x\text{InSe}_2$  alloys, *J. Appl. Phys.* 97 (2005) 1–7.  
4 doi:10.1063/1.1899243.  
5  
6  
7 [25] P. Lautenschlager, M. Garriga, S. Logothetidis, M. Cardona, Interband critical  
8 points of GaAs and their temperature dependence, *Phys. Rev. B.* 35 (1987) 9174–  
9 9189. doi:10.1103/PhysRevB.35.9174.  
10  
11  
12 [26] S. Chen, X.G. Gong, A. Walsh, S.H. Wei, Electronic structure and stability of  
13 quaternary chalcogenide semiconductors derived from cation cross-substitution  
14 of II-VI and I-III-VI<sub>2</sub> compounds, *Phys. Rev. B - Condens. Matter Mater. Phys.*  
15 79 (2009) 1–10. doi:10.1103/PhysRevB.79.165211.  
16  
17  
18 [27] S. Schorr, H.-J. Hoebler, M. Tovar, A neutron diffraction study of the stannite-  
19 kesterite solid solution series, *Eur. J. Mineral.* 19 (2007) 65–73.  
20 doi:10.1127/0935-1221/2007/0019-0065.  
21  
22  
23 [28] S. Schorr, The crystal structure of kesterite type compounds: A neutron and X-  
24 ray diffraction study, *Sol. Energy Mater. Sol. Cells.* 95 (2011) 1482–1488.  
25 doi:10.1016/j.solmat.2011.01.002.  
26  
27  
28 [29] A. Fairbrother, V. Izquierdo-Roca, X. Fontané, M. Ibáñez, A. Cabot, E. Saucedo,  
29 A. Pérez-Rodríguez, ZnS grain size effects on near-resonant Raman scattering:  
30 optical non-destructive grain size estimation, *CrystEngComm.* 16 (2014) 4120–  
31 4125. doi:10.1039/c3ce42578a.  
32  
33  
34 [30] A. Fairbrother, E. Garcia-Hemme, V. Izquierdo-Roca, X. Fontané, F.A. Pulgarin-  
35 Agudelo, O. Vigil-Galan, A. Perez-Rodriguez, E. Saucedo, Development of a  
36 Selective Chemical Etch To Improve the Conversion Efficiency of Zn-Rich  
37  $\text{Cu}_2\text{ZnSnS}_4$  Solar Cells, *J. Am. Chem. Soc.* 134 (2012) 8018–8021.  
38  
39  
40 [31] S. López-Marino, Y. Sánchez, M. Placidi, A. Fairbrother, M. Espindola-  
41 Rodríguez, X. Fontané, V. Izquierdo-Roca, J. López-García, L. Calvo-Barrio, A.  
42 Pérez-Rodríguez, E. Saucedo, ZnSe etching of Zn-Rich  $\text{Cu}_2\text{ZnSnSe}_4$ : An  
43 oxidation route for improved solar-cell efficiency, *Chem. - A Eur. J.* 19 (2013)  
44 14814–14822. doi:10.1002/chem.201302589.  
45  
46  
47 [32] C. Julien, H.S. Mavi, K.P. Jain, M. Balkanski, C. Perez-Vicente, J. Morales,  
48 Resonant raman scattering studies of  $\text{SnS}_2$  crystals, *Mater. Sci. Eng. B.* 23 (1994)  
49 98–104. doi:http://dx.doi.org/10.1016/0921-5107(94)90341-7.  
50  
51  
52 [33] H.R. Chandrasekhar, D.G. Mead, Long-wavelength phonons in mixed-valence  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

semiconductor  $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{S}_3$ , Phys. Rev. B. 19 (1979) 932–937.

- [34] H.R. Chandrasekhar, R.G. Humphreys, U. Zwick, M. Cardona, Infrared and Raman spectra of the IV-VI compounds SnS and SnSe, Phys. Rev. B. 15 (1977) 2177–2183.
- [35] J.D. Wiley, W.J. Buckel, R.L. Schmidt, Infrared reflectivity and Raman scattering in GeS, Phys. Rev. B. 13 (1976) 2489–2496.
- [36] P. Kumar, M. Gusain, R. Nagarajan, Supporting Information Synthesis of  $\text{Cu}_{1.8}\text{S}$  and CuS from Copper-Thiourea complexes; anionic ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) influence on the product stoichiometry, Inorg. Chem. 50 (2011) 3065–3070.
- [37] Q. Wang, S.-Z. Kang, X. Li, Y.-W. Yang, L. Qin, J. Mu, A facile preparation of crystalline  $\text{GeS}_2$  nanoplates and their photocatalytic activity, J. Alloys Compd. 631 (2015) 21–25. doi:10.1016/j.jallcom.2014.12.259.
- [38] P.A. Fernandes, P.M.P. Salomé, A.F. da Cunha, Study of polycrystalline  $\text{Cu}_2\text{ZnSnS}_4$  films by Raman scattering, J. Alloys Compd. 509 (2011) 7600–7606. doi:10.1016/j.jallcom.2011.04.097.
- [39] D.M. Berg, R. Djemour, L. Gütay, G. Zoppi, S. Siebentritt, P.J. Dale, Thin film solar cells based on the ternary compound  $\text{Cu}_2\text{SnS}_3$ , Thin Solid Films. 520 (2012) 6291–6294. doi:10.1016/j.tsf.2012.05.085.
- [40] D.B. Khadka, J. Kim, Study of structural and optical properties of kesterite  $\text{Cu}_2\text{ZnGeX}_4$  (X = S, Se) thin films synthesized by chemical spray pyrolysis, CrystEngComm. 15 (2013) 10500–10509. doi:10.1039/c3ce41387j.
- [41] M. Dimitrievska, A. Fairbrother, X. Fontané, T. Jawhari, V. Izquierdo-Roca, E. Saucedo, A. Pérez-Rodríguez, Multiwavelength excitation Raman scattering study of polycrystalline kesterite  $\text{Cu}_2\text{ZnSnS}_4$  thin films, Appl. Phys. Lett. 104 (2014) 1–5. doi:10.1063/1.4861593.
- [42] D.B. Khadka, J. Kim, Band Gap Engineering of Alloyed  $\text{Cu}_2\text{ZnGe}_x\text{Sn}_{1-x}\text{Q}_4$  (Q=S,Se) Films for Solar Cell, J. Phys. Chem. C. 119 (2015) 1706–1713. doi:10.1021/jp510877g.
- [43] Y. Li, W. Ling, Q. Han, W. Shi, Colloidal  $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Ge}_x)\text{S}_4$  nanocrystals: electrical properties and comparison between their wurtzite and kesterite structures, RSC Adv. 4 (2014) 55016–55022. doi:10.1039/C4RA10780B.

- 1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65
- [44] M. Guc, A.P. Litvinchuk, S. Levchenko, V. Izquierdo-Roca, X. Fontané, M.Y. Valakh, E. Arushanov, A. Pérez-Rodríguez, Optical phonons in the wurtzstannite  $\text{Cu}_2\text{ZnGeS}_4$  semiconductor: Polarized Raman spectroscopy and first-principle calculations, *Phys. Rev. B.* 89 (2014) 1–7. doi:10.1103/PhysRevB.89.205205.
- [45] S. Levchenko, G. Gurieva, M. Guc, A. Nateprov, Optical constants of  $\text{Cu}_2\text{ZnSnS}_4$  bulk crystals, *Mold. J. Phys. Sci.* 8 (2009) 173–177.
- [46] R. Caballero, J.M. Cano-Torres, E. Garcia-Llamas, X. Fontané, A. Pérez-Rodríguez, D. Greiner, C. a. Kaufmann, J.M. Merino, I. Victorov, G. Baraldi, M. Valakh, I. Bodnar, V. Izquierdo-Roca, M. León, Towards the growth of  $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$  thin films by a single-stage process: Effect of substrate temperature and composition, *Sol. Energy Mater. Sol. Cells.* 139 (2015) 1–9. doi:10.1016/j.solmat.2015.03.004.
- [47] S.H. Han, A.M. Hermann, F.S. Hasoon, H.A. Al-Thani, D.H. Levi, Effect of Cu deficiency on the optical properties and electronic structure of  $\text{CuInSe}_2$  and  $\text{CuIn}_{0.8}\text{Ga}_{0.2}\text{Se}_2$  determined by spectroscopic ellipsometry, *Appl. Phys. Lett.* 85 (2004) 576–578. doi:10.1063/1.1776616.
- [48] S. Levchenko, M. León, G. Gurieva, R. Serna, J.M. Merino, E.J. Friedrich, E. Arushanov, I. V. Bodnar, Comparative study of tetragonal  $\text{Cu}_2\text{In}_7\text{Se}_{11.5}$  and trigonal  $\text{CuIn}_5\text{Se}_8$  by spectroscopic ellipsometry, *Mater. Chem. Phys.* 125 (2011) 77–81. doi:10.1016/j.matchemphys.2010.08.074.
- [49] D. Schmid, M. Ruckh, F. Grunwald, H.W. Schock, Chalcopyrite/defect chalcopyrite heterojunctions on the basis of  $\text{CuInSe}_2$ , *J. Appl. Phys.* 73 (1993) 2902.
- [50] S. Chen, X.G. Gong, A. Walsh, S.H. Wei, Crystal and electronic band structure of  $\text{Cu}_2\text{ZnSnX}_4$  (X=S and Se) photovoltaic absorbers: First-principles insights, *Appl. Phys. Lett.* 94 (2009) 1–3. doi:10.1063/1.3074499.



Table 1. Composition of the single crystals measured by EDX.

| Sample   | Cu<br>(at%) | Zn<br>(at%) | Sn<br>(at%) | Ge<br>(at%) | S<br>(at%) | Cu/(Zn<br>+IV) | (Cu+Zn)<br>/IV | Ge/IV | S/M  |
|--|-------------|-------------|-------------|-------------|------------|----------------|----------------|-------|------|
| <b>Cu<sub>2</sub>ZnGeS<sub>4</sub></b>                               | 26.95       | 11.38       | --          | 11.08       | 50.59      | 1.20           | 3.45           | 1.00  | 1.02 |
| <b>Cu<sub>2</sub>ZnSn<sub>0.1</sub>Ge<sub>0.9</sub>S<sub>4</sub></b> | 24.81       | 11.78       | 0.85        | 9.80        | 51.32      | 1.09           | 3.43           | 0.92  | 1.08 |
| <b>Cu<sub>2</sub>ZnSn<sub>0.3</sub>Ge<sub>0.7</sub>S<sub>4</sub></b> | 27.18       | 11.90       | 3.39        | 8.48        | 49.05      | 1.14           | 3.29           | 0.71  | 0.96 |
| <b>Cu<sub>2</sub>ZnSn<sub>0.5</sub>Ge<sub>0.5</sub>S<sub>4</sub></b> | 24.62       | 12.07       | 5.63        | 6.77        | 50.91      | 1.01           | 2.96           | 0.55  | 1.04 |
| <b>Cu<sub>2</sub>ZnSn<sub>0.7</sub>Ge<sub>0.3</sub>S<sub>4</sub></b> | 26.49       | 11.78       | 9.17        | 3.55        | 49.00      | 1.08           | 3.01           | 0.28  |      |
| <b>Cu<sub>2</sub>ZnSn<sub>0.9</sub>Ge<sub>0.1</sub>S<sub>4</sub></b> | 24.77       | 13.13       | 11.29       | 1.04        | 49.77      | 0.97           | 3.07           | 0.08  | 0.99 |
| <b>Cu<sub>2</sub>ZnSnS<sub>4</sub></b>                               | 24.48       | 12.13       | 12.71       | --          | 50.68      | 0.98           | 2.88           | --    | 1.02 |

Note: M= Cu + Zn + Sn + Ge; IV = Sn + Ge

Table 2. Frequency (in  $\text{cm}^{-1}$ ) of the clear resolved peaks of Raman spectra measured in the regions  $200\text{-}450\text{ cm}^{-1}$  and  $650\text{-}750\text{ cm}^{-1}$ . These are compared to the experimental Raman shifts reported in CZTGS samples. **In bold are reported the excitation wavelengths (in nm) used in the Lorentzian curve fitting analysis.** Underlined are indicated the bands related to second order Raman scattering process.

| CZTS<br>Kesterite |             | CZTS<br>wurtzite | CZT <sub>0.5</sub> G <sub>0.5</sub> S<br>Kesterite |             | CZT <sub>0.5</sub> G <sub>0.5</sub> S<br>wurtzite | CZGS<br>Kesterite |             | CZGS<br>Wurtzstannite | CZGS<br>wurtzite |
|-------------------|-------------|------------------|--|-------------|---|-------------------|-------------|-----------------------|------------------|
| This work         | <b>[41]</b> | <b>[43]</b>      | This work  | <b>[42]</b> | <b>[43]</b>                                       | This work         | <b>[42]</b> | <b>[44]</b>           | <b>[43]</b>      |
| <b>325,</b>       | <b>325,</b> |                  | <b>325,</b>  |             |   | <b>325,</b>       |             |                       |                  |
| <b>532,</b>       | <b>532,</b> | <b>514</b>       | <b>532,</b>  | <b>532</b>  | <b>514</b>  | <b>532,</b>       | <b>532</b>  | <b>514</b>            | <b>514</b>       |
| <b>785</b>        | <b>785</b>  |                  | <b>785</b>   |             |   | <b>785</b>        |             | <b>785</b>            |                  |
| 166               |             |                  | 153  |             |   | 157               |             | 161                   |                  |
| 251               | 255         |                  | 184  |             |   | 191               |             | 164                   |                  |
| 263               | 263         |                  | 256  |             |   | 262               |             | 178                   |                  |
|                   | 271         |                  | 270  | 270         |   | 274               | 273         | 184                   |                  |
| 287               | 287         |                  | 280  |             |   | 295               | 293         | 273                   |                  |
| 302               | 302         |                  | 292  | 292         |   | 315               | 315         | 277                   |                  |
| 317               | 316         |                  |  | 314         |   | 339               |             | 289                   |                  |
| 320               |             |                  | 331  |             |   | 359               | 357         | 241                   | 354              |
|                   | 332         |                  | 343  |             |   | 382               |             | 314                   |                  |
| 338               | 338         | 332              |  | 347         | 343   | 402               | 403         | 333                   |                  |
| 347               | 347         |                  | 352  |             |   |                   |             | 362                   |                  |
|                   | 353         |                  | 367  |             |   |                   |             | 383                   |                  |
| 367               | 367         |                  | 379  |             |   |                   |             | 386                   |                  |
| 374               | 374         |                  | 391  | 395         |   |                   |             | 407                   |                  |
|                   |             |                  |  |             |   |                   |             | 418                   |                  |
| <b>672</b>        |             |                  | <b>696</b>   |             |   | <b>715</b>        |             |                       |                  |

Table 3. Transition energies  $E_0$ ,  $E_{1A}$  and  $E_{1B}$  values of  $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{S}_4$  ( $x = 0.1, 0.3, 0.5, 0.7, 0.9$  and  $1$ ).

| Sample  | $E_0$<br>( $\pm 0.03$ )<br>(eV) | $E_{1A}$ ( $\pm 0.03$ )<br>(eV) | $E_{1B}$ ( $\pm 0.03$ )<br>(eV) |
|---|---------------------------------|---------------------------------|---------------------------------|
| $\text{Cu}_2\text{ZnGeS}_4$                             | 2.25                            | 2.92                            | 4.24                            |
| $\text{Cu}_2\text{ZnSn}_{0.1}\text{Ge}_{0.9}\text{S}_4$ | 2.20                            | 3.04                            | 4.19                            |
| $\text{Cu}_2\text{ZnSn}_{0.3}\text{Ge}_{0.7}\text{S}_4$ | 1.98                            | 2.92                            | 4.20                            |
| $\text{Cu}_2\text{ZnSn}_{0.5}\text{Ge}_{0.5}\text{S}_4$ | 1.90                            | 2.82                            | 4.21                            |
| $\text{Cu}_2\text{ZnSn}_{0.7}\text{Ge}_{0.3}\text{S}_4$ | 1.69                            | 2.76                            | 4.10                            |
| $\text{Cu}_2\text{ZnSn}_{0.9}\text{Ge}_{0.1}\text{S}_4$ | 1.59                            | 2.75                            | 4.09                            |
| $\text{Cu}_2\text{ZnSnS}_4$                             | 1.51                            | 2.69                            | 4.01                            |

**Figure**  
[Click here to download high resolution image](#)

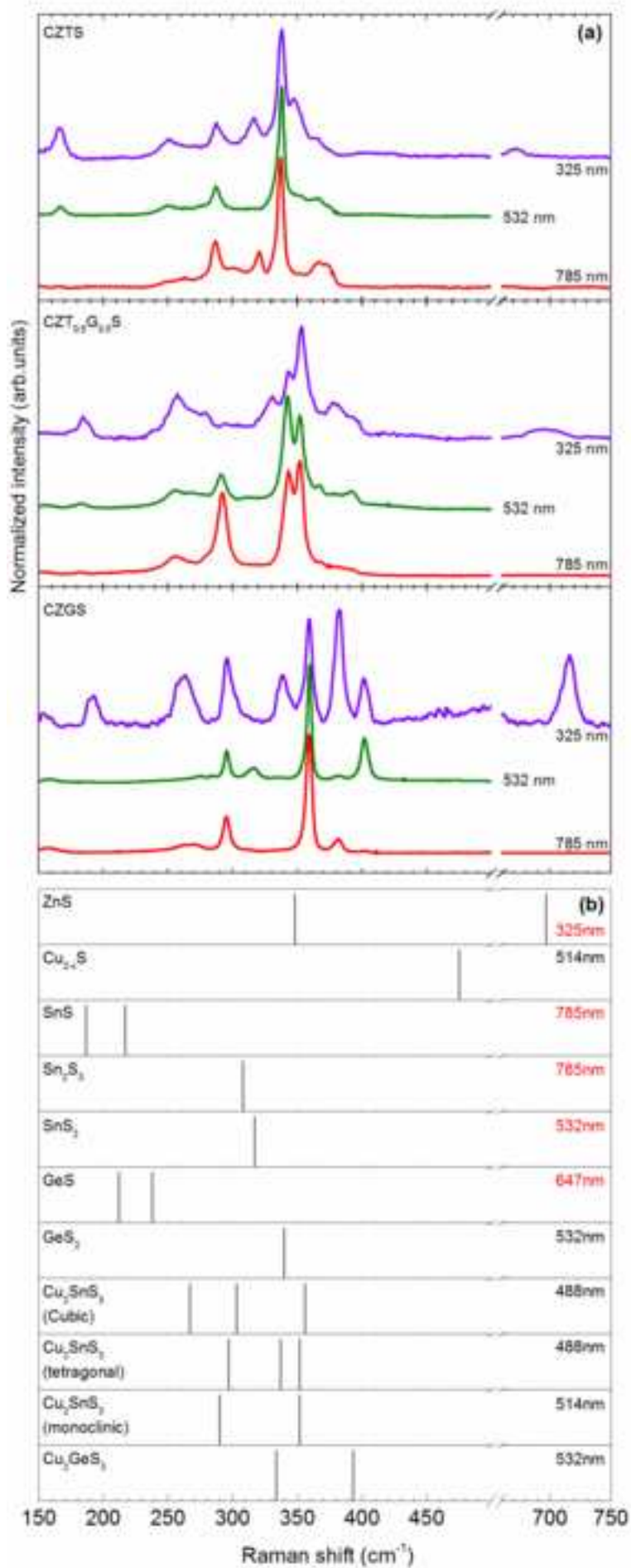


Figure  
[Click here to download high resolution image](#)

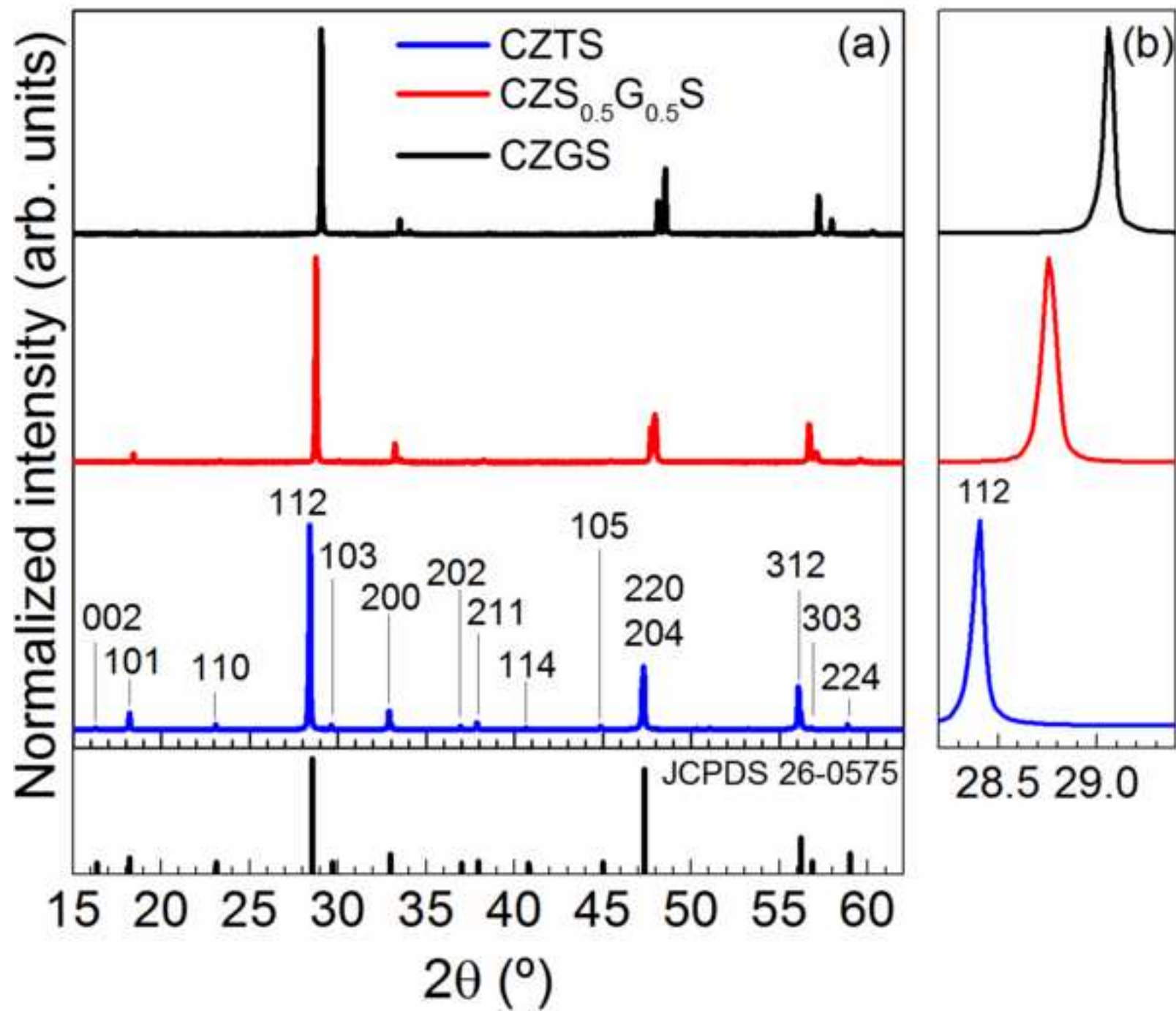


Figure  
[Click here to download high resolution image](#)

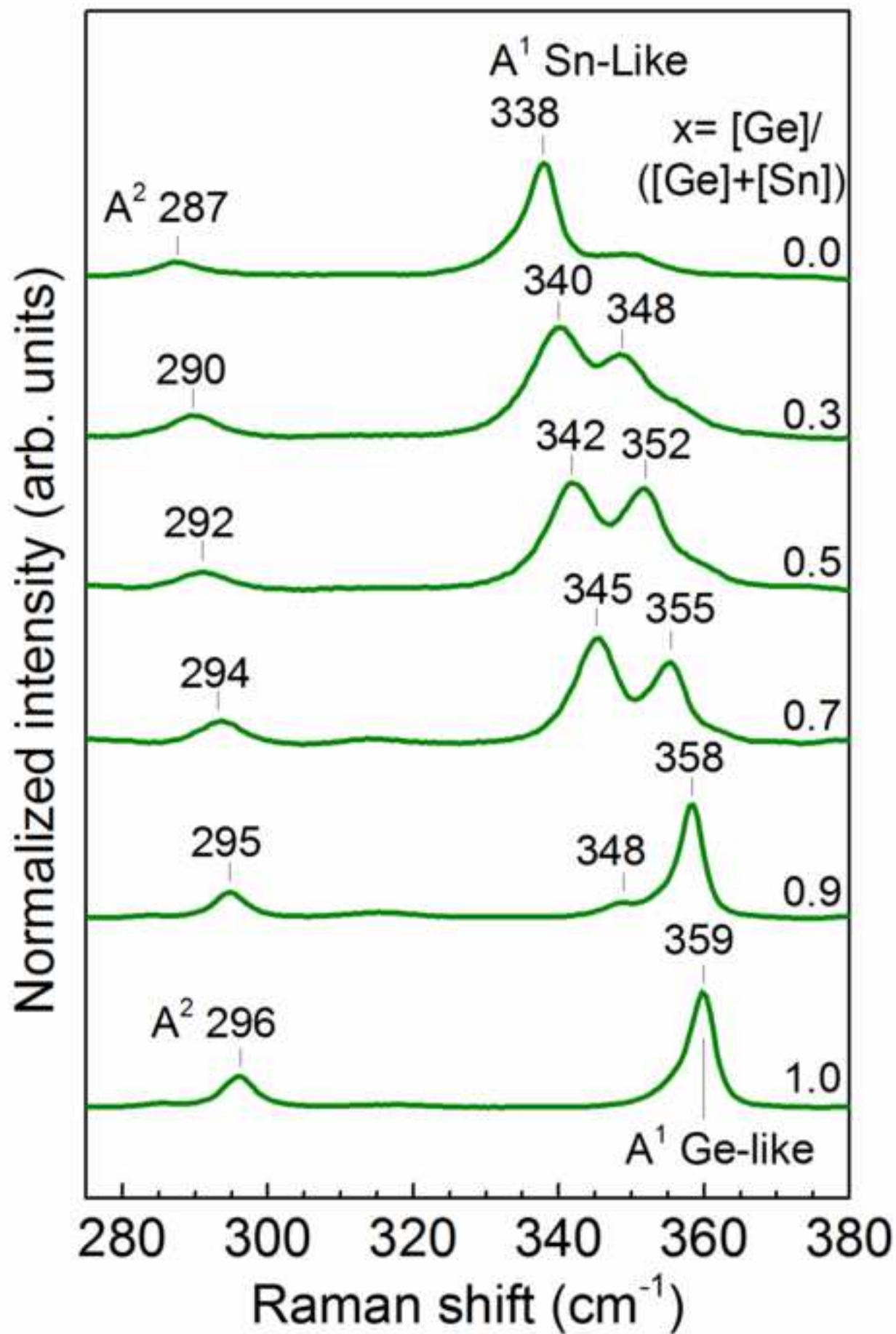
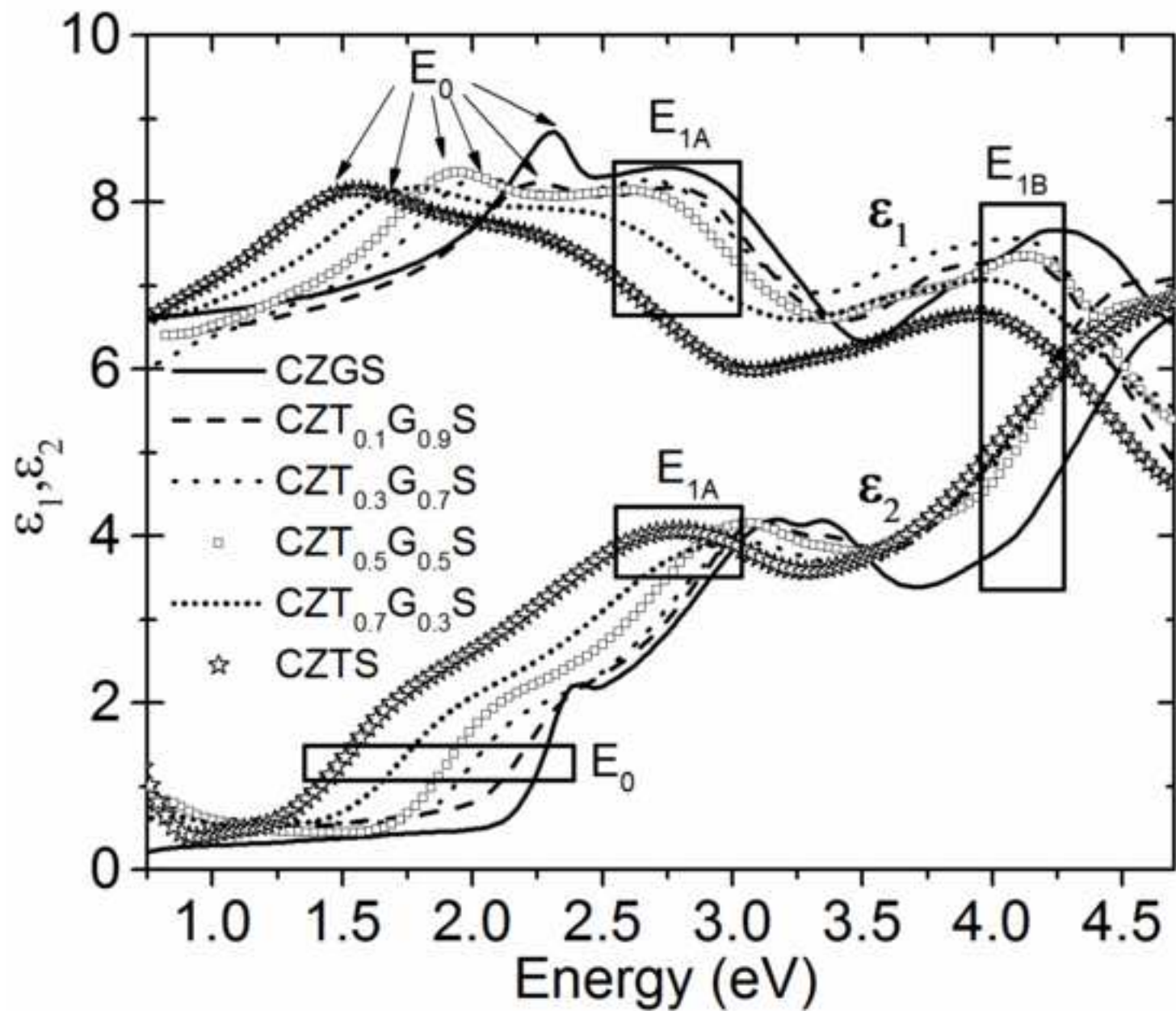




Figure  
[Click here to download high resolution image](#)



Figure

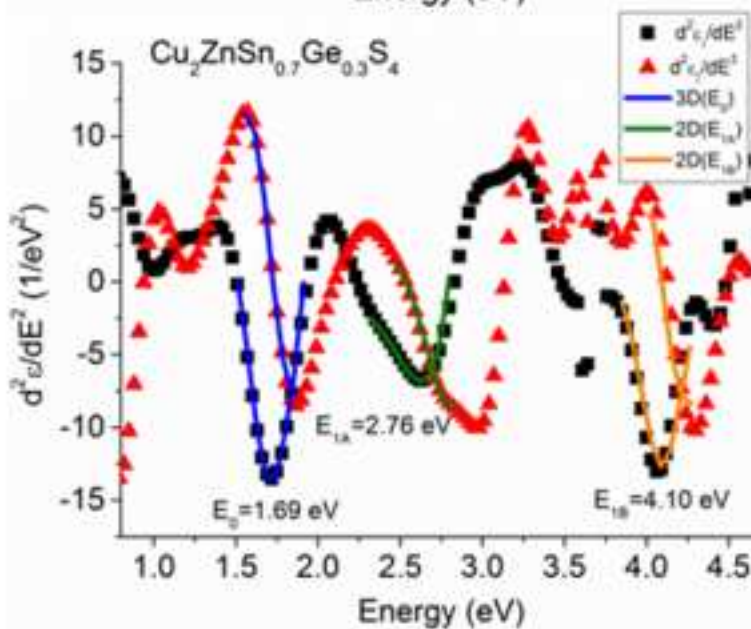
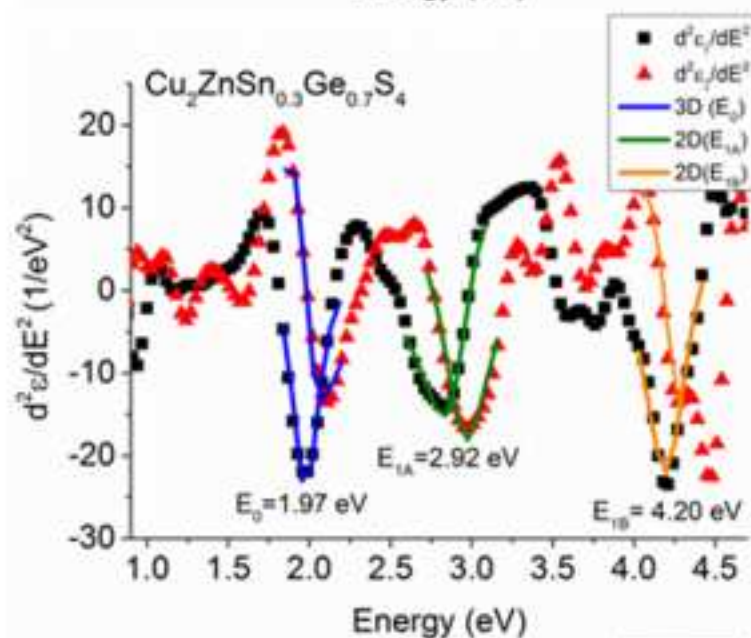
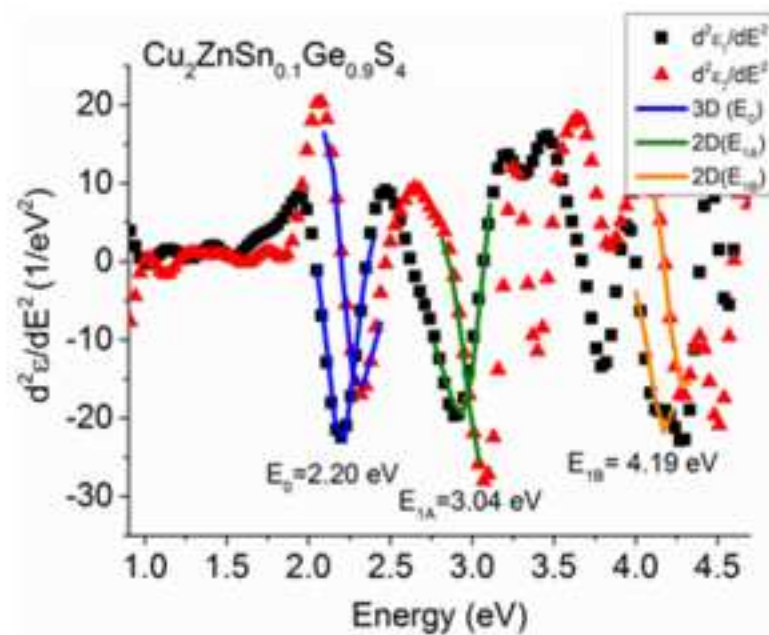
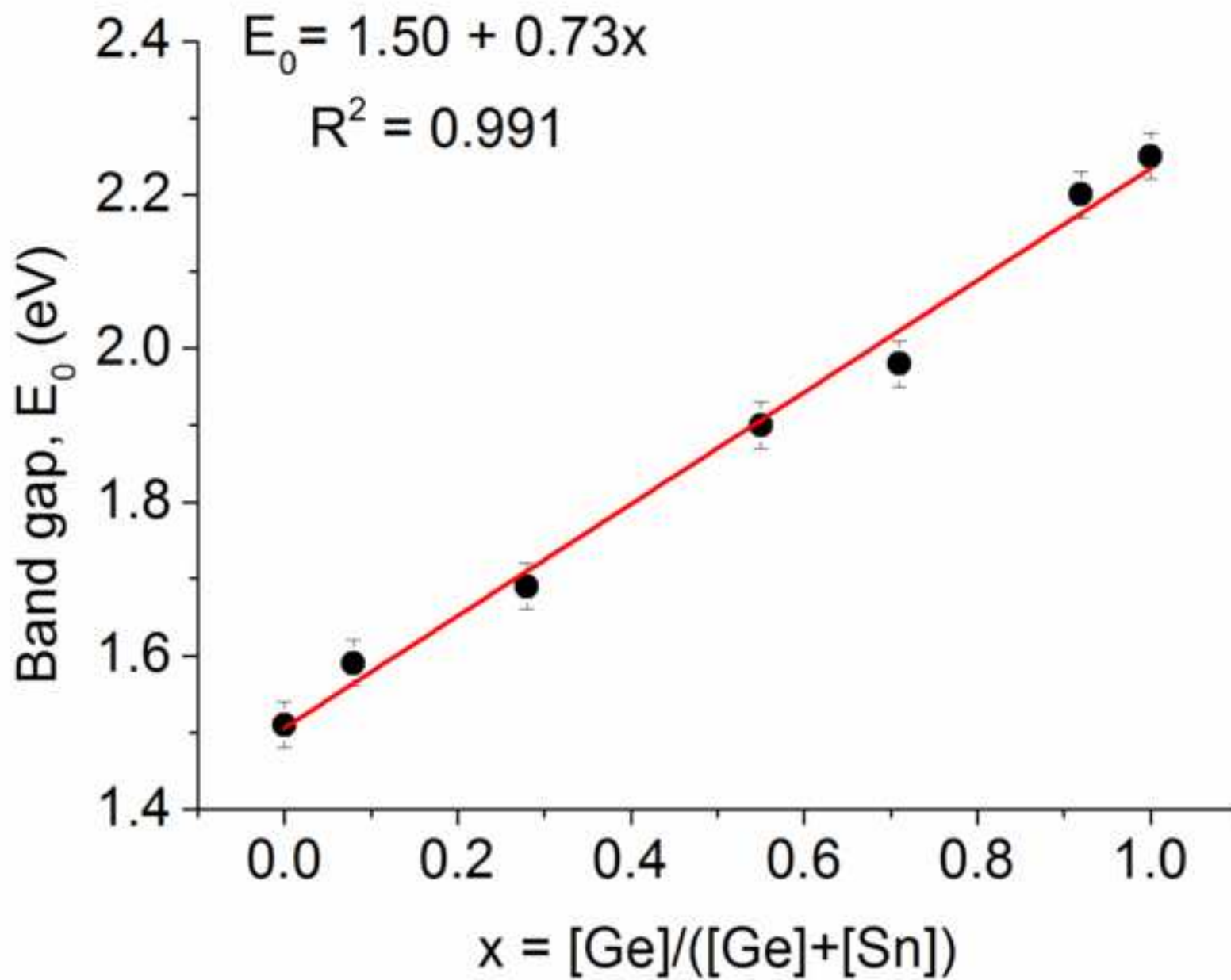
[Click here to download high resolution image](#)

Figure  
[Click here to download high resolution image](#)



## Figure Captions

Figure 1: (a) Raman spectra under 325, 532, and 785 nm excitation wavelengths for CZTS, CZT<sub>0.5</sub>G<sub>0.5</sub>S and CZGS. (b) Summary of the reported main peaks for the possible secondary phases (ZnS [29], Cu<sub>2-x</sub>S [17,36], SnS [16,34], Sn<sub>2</sub>S<sub>3</sub> [16,33], SnS<sub>2</sub> [32], GeS [35], GeS<sub>2</sub> [37], Cubic Cu<sub>2</sub>SnS<sub>3</sub> [38], tetragonal Cu<sub>2</sub>SnS<sub>3</sub> [32,38], monoclinic Cu<sub>2</sub>SnS<sub>3</sub> [39], Cu<sub>2</sub>GeS<sub>3</sub>[40]). The red labels indicate the Raman spectra reported under resonant conditions.

Figure 2: X-Ray diffractogram of CZTS, CZT0.5G0.5S and CZGS single crystals (a), and detail of (112) plane (b).

Figure 3: Raman spectra detail of the A<sup>2</sup> and A<sup>1</sup> region under 532 nm excitation wavelength obtained for different  $x=[\text{Ge}]/([\text{Ge}]+[\text{Sn}])$  compositions

Figure 4. Experimental spectral dependence of dielectric function  $\epsilon(E)=\epsilon_1(E)+i\epsilon_2(E)$  of Cu<sub>2</sub>ZnSn<sub>1-x</sub>Ge<sub>x</sub>S<sub>4</sub> single crystals. The spectra exhibit three CP structures, E<sub>0</sub>, E<sub>1A</sub> and E<sub>1B</sub> for each compound

Figure 5. Second derivative spectra of the experimental real and imaginary dielectric functions and the fitting based on equation (1) of Cu<sub>2</sub>ZnSn<sub>0.3</sub>Ge<sub>0.7</sub>S<sub>4</sub>, Cu<sub>2</sub>ZnSn<sub>0.7</sub>Ge<sub>0.3</sub>S<sub>4</sub> and Cu<sub>2</sub>ZnSn<sub>0.9</sub>Ge<sub>0.1</sub>S<sub>4</sub> single crystals. The transition energies E<sub>0</sub>, E<sub>1A</sub> and E<sub>1B</sub> values are given.

Figure 6. Variation of the fundamental band gap energy with the  $x= [\text{Ge}]/([\text{Sn}]+[\text{Ge}])$  atomic ratio. The solid line represents the linear fit of the experimental data.