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# Preparation, Crystal Structure, Thermal Analysis, Scanning Electron Microscopy and Optical Band-Gaps of $\text{Cu}_2\text{GeTe}_4$ and $\text{Cu}_2\text{SnTe}_4$ Alloys

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**Authors**

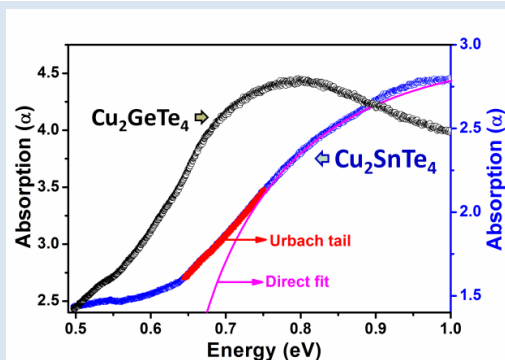
Pedro Grima Gallardo, Ricardo Pena, Luis Nieves, Gustavo Marcano, Miguel Quintero, Ekadink Moreno, Jian-Han Zhang, Jacilynn A. Brant, and Jennifer A. Aitken

PREPARATION, CRYSTAL STRUCTURE, THERMAL ANALYSIS, SCANNING ELECTRON MICROSCOPY AND OPTICAL BAND-GAPS OF  $\text{Cu}_2\text{GeTe}_4$  AND  $\text{Cu}_2\text{SnTe}_4$  ALLOYS

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## ABSTRACT

Polycrystalline samples (weight ~ 1g) of  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$  alloys were prepared by the usual melt and anneal method and the products characterized by X-Ray Diffraction (XRD), Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM) and Optical Diffuse Reflectance UV/VIS/NIR Spectroscopy techniques. It was found that: a)  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$  crystallize in an orthorhombic structure (s.g. Imm2; N° 44) with lattice parameters  $a=5.9281(4)$  Å,  $b=4.2211(6)$  Å,  $c=12.645(5)$  Å and  $a=6.0375(6)$  Å,  $b=4.2706(3)$  Å,  $c=12.844(1)$  Å, respectively; b) both alloys show two thermal transitions: 762 and 636K upon heating and; 700 and 578K upon cooling for  $\text{Cu}_2\text{GeTe}_4$ ; 702 and 636K upon heating and; 650 and 590K upon cooling for  $\text{Cu}_2\text{SnTe}_4$ ; c) both alloys present large deviations of stoichiometry for the cations Cu (~35%), Ge (7.2%) and Sn (26.4%) and minor deviation within the experimental error, for the anion Te; and, d) the measured optical band gaps were 0.63 and 0.53 eV for  $\text{Cu}_2\text{SnTe}_4$  and  $\text{Cu}_2\text{GeTe}_4$ , respectively.

**Keywords:** Semiconductor alloys, X-Ray Diffraction, Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM), Optical Diffuse Reflectance UV/VIS/NIR Spectroscopy,  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$

PREPARACION, ESTRUCTURA CRISTALINA, ANALISIS TERMICO, MICROSCOPIA ELECTRONICA DE BARRIDO Y BRECHA OPTICA DE ENERGIA DE LAS ALEACIONES  $\text{Cu}_2\text{GeTe}_4$  Y  $\text{Cu}_2\text{SnTe}_4$

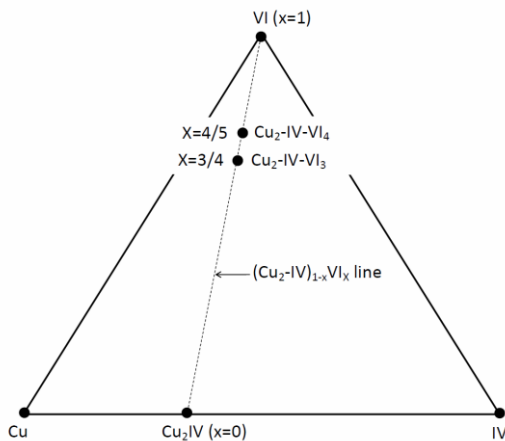
## RESUMEN

Se prepararon muestras policristalinas (peso ~ 1 g) de las aleaciones  $\text{Cu}_2\text{GeTe}_4$  y  $\text{Cu}_2\text{SnTe}_4$  por el método de fusión y recocido y los productos caracterizados por las técnicas de Difracción de Rayos X (DRX), Análisis Térmico Diferencial (ATD), Microscopía Electrónica de Barrido (MEB) y espectroscopía de reflectancia óptica difusa UV / VIS / CIR. Se encontró que: a)  $\text{Cu}_2\text{GeTe}_4$  y  $\text{Cu}_2\text{SnTe}_4$  cristalizan en una estructura ortorrómbica (g.e. Imm2; N° 44) con parámetros de red  $a = 5,9281(4)$  Å,  $b = 4,2211(6)$  Å,  $c = 12,645(5)$  Å y  $a = 6,0375(6)$  Å,  $b = 4,2706(3)$  Å,  $c = 12,844(1)$  Å, respectivamente; b) ambas aleaciones muestran dos transiciones térmicas: 762 y 636K al calentar y; 700 y 578K tras el enfriamiento para  $\text{Cu}_2\text{GeTe}_4$ ; 702 y 636K al calentar y; 650 y 590K tras el enfriamiento para  $\text{Cu}_2\text{SnTe}_4$ ; c) ambas aleaciones presentan importantes desviaciones estequiométricas en sus cationes: Cu (~35%), Ge (7.2%) and Sn (26.4%) y menor que el error experimental para el anión Te; y d) las brechas ópticas de energía medidas fueron 0.63 y 0.53 eV para  $\text{Cu}_2\text{SnTe}_4$  y  $\text{Cu}_2\text{GeTe}_4$ , respectivamente.

**Palabras Claves:** Aleaciones semiconductoras, Difracción de Rayos X (DRX), Análisis Térmico Diferencial (ATD), Microscopía Electrónica de Barrido (MEB), Espectroscopía de Reflectancia Óptica Difusa,  $\text{Cu}_2\text{GeTe}_4$  y  $\text{Cu}_2\text{SnTe}_4$

## 1. INTRODUCTION

The  $\text{Cu}_2\text{-IV-VI}_3$  and  $\text{Cu}_2\text{-IV-VI}_4$  alloys (IV: Ge, Sn; VI: Se, Te) belong to the general Cu-IV-VI system and are located on the  $(\text{Cu}_2\text{IV})_{1-x}\text{VI}_x$  tie line, at  $x=3/4$  and  $x=4/5$ , respectively, as it is showed in Figure 1. These alloys are candidates for applications in solar cells, thermoelectrics conversion and electro-optic devices [1-11].



**Figure 1.** Representation of the Cu-IV-Te alloys system, indicating the localization of  $\text{Cu}_2\text{-IV-VI}_3$  and  $\text{Cu}_2\text{-IV-VI}_4$  alloys.

Recently, our group [12] has investigated the  $\text{Cu}_2(\text{Ge}_{1-x}\text{Sn}_x)\text{Se}_4$  alloys system and determined that  $\text{Cu}_2\text{GeSe}_4$  and  $\text{Cu}_2\text{SnSe}_4$  crystallize in orthorhombic and cubic structures, respectively. The crystal system and lattice parameters of  $\text{Cu}_2\text{GeSe}_4$  coincide with the high-temperature phase of  $\text{Cu}_2\text{GeSe}_3$ , whereas the cubic phase of  $\text{Cu}_2\text{SnSe}_4$  coincides with the room temperature cubic phase of  $\text{Cu}_2\text{SnSe}_3$ . According to the phase diagram of the  $(\text{Cu}_2\text{Ge})_{1-x}(\text{Se})_x$  tie line (Berger et al [13]; also see Figure 8 in [12]) the region in the composition range  $3/4 \leq x \leq 4/5$  is single phase, i.e.  $\text{Cu}_2\text{GeSe}_3$  and  $\text{Cu}_2\text{GeSe}_4$  have the same crystal structure. However, there is a problem with this phase diagram:  $\text{Cu}_2\text{GeSe}_3$  has a solid-to-solid phase transition at high temperature from the tetragonal structure (labeled as  $\tau_1$  in the phase diagram) to an orthorhombic structure (that henceforth we will call  $\tau_2$ ) that has not been taken into account in the diagram.

The analogous tellurium systems have also been studied. The structural properties of the  $\text{Cu}_2\text{GeTe}_3$  alloy have been recently published by Delgado *et al* [14] and Villarreal *et al* [15] with the observation of an orthorhombic crystal structure, crystallizing in

the space group  $\text{Imm}2$  ( $N^\circ 44$ ), with lattice parameters  $a=5.9261(2)\text{\AA}$ ,  $b=4.2115(2)\text{\AA}$ , and  $c=12.641(1)\text{\AA}$ ; on the other hand, the preparation and crystal structure of  $\text{Cu}_2\text{SnTe}_3$  has been published by Delgado *et al* [16] who also reported an orthorhombic crystal structure in the space group  $\text{Imm}2$  ( $N^\circ 44$ ), with lattice parameters  $a=6.043(1)\text{\AA}$ ,  $b=4.274(1)\text{\AA}$ , and  $c=12.833(4)\text{\AA}$ . Previously, Sharma *et al* (1977) [17] reported that  $\text{Cu}_2\text{GeTe}_3$  and  $\text{Cu}_2\text{SnTe}_3$  are two-phases solids with eutectic type microstructure; for  $\text{Cu}_2\text{GeTe}_3$  they found a tetragonal structure with lattice parameters  $a=5.959\text{\AA}$  and  $c=11.858\text{\AA}$  and for  $\text{Cu}_2\text{SnTe}_3$  a cubic disordered structure, with lattice parameter  $a=6.094\text{\AA}$ .

From thermal analysis, Dovletov *et al* [18] reported that no ternary compounds were found in the  $\text{Cu}_2\text{Te-SnTe}$  binary system, but Palatnik *et al* (1961) [19], Rivet *et al* (1963) [20], Averkieva *et al* (1965) [21], Rivet *et al* (1965) [22] and Carcaly *et al* (1975) [23], (1977) [24] affirm the existence of a ternary phase which forms peritectically at 780-785K.

In this work we report the preparation and characterization of polycrystalline samples of  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$ .

## 2. EXPERIMENTAL PART

### 2.1 Preparation

$\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$  were synthesized using the melt and anneal technique. Stoichiometric quantities of Cu, Ge, Sn and Te elements with purity of 99.99% were charged in an evacuated synthetic silica glass ampoule, which was previously subjected to pyrolysis in order to avoid reaction of the starting materials with silica glass. Then, the ampoule was sealed under vacuum ( $\sim 10^{-4}$  Torr) and the fusion process was carried out inside a furnace (vertical position) heated up to 1500K at a rate of 20K/h, with a stop of 48 h at 722.5K (melting temperature of Te) in order to maximize the formation of binary species at low temperature and minimize the presence of unreacted Te at high temperatures. The ampoule was shaken using a mechanical system during all the heating process in order to help the complete mixing of all the elements. The maximum temperature (1500K) was kept for other 48 hours with the mechanical shaking system on. Then, the mechanical shaking system was turning off and the temperature was gradually lowered, at the same rate of 20K/h, until 873K. The

ampoule was held at this temperature for a period of 30 days. Finally, the sample was cooled to room temperature at a rate of 10K/h. The obtained ingots were bright gray in color and homogeneous to the eye.

## 2.2 X-Ray Powder Diffraction

A small amount of each compound was gently ground in an agate mortar and sieved to a grain size of less than 38  $\mu\text{m}$ . Each sample was mounted on a zero-background specimen holder for the respective measurement. X-ray powder diffraction patterns of the samples were recorded using a D8 FOCUS BRUKER diffractometer operating in Bragg-Brentano geometry and equipped with a copper X-ray tube ( $\text{CuK}\alpha$  radiation:  $\lambda=1.5406 \text{ \AA}$ , 40 kV and 40 mA) using a nickel filter and one the dimensional LynxEye detector. A fixed antiscatter slit of 8 mm, receiving slit of 1 mm, soller slits of  $2.5^\circ$  and a detector slit of 3 mm were used for the diffraction optics. Data were collected from  $2$  to  $140^\circ$  ( $2\theta$ ) with a step size of  $0.02^\circ$  ( $2\theta$ ) and a counting time of 0.4 s/step.

## 2.3 Differential Thermal Analysis

Phase transition temperatures were obtained from differential thermal analysis (DTA) measurements, in the temperature range of 300 to 1500K, using a Perkin-Elmer DTA-7. The instrument was calibrated using aluminum and gold as references. The charge was a powdered alloy of approximately 100-mg in weight. Both heating and cooling runs were carried out on each sample, the average rates of these runs were approximately 10 K/min. The error in determining these temperatures is about  $\pm 10\text{K}$ . The temperature values of the thermal transitions were obtained using the intercept of the base line with the beginning of the corresponding peak.

## 2.4 Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS)

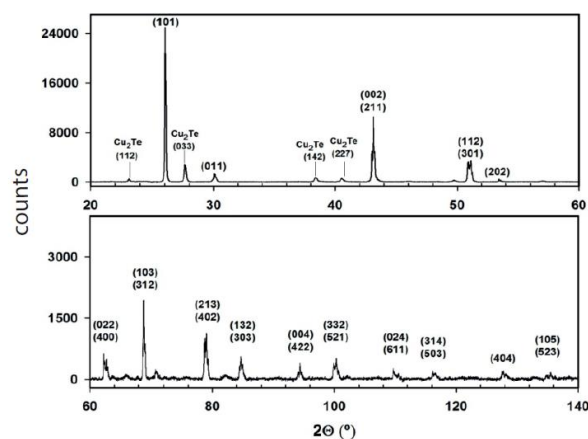
SEM/EDS was performed on a Hitachi S-3400N scanning electron microscope equipped with a Bruker Quantax model 400 energy dispersive spectrometer using an XFlash<sup>®</sup> 5010 EDS detector with a 129 eV resolution. Samples were mounted on double-sided carbon tape affixed to an aluminum specimen holder. EDS spectra were collected using a working distance of 10 mm and an accelerating voltage of 15 kV for 3 min live time.

## 2.5 Optical Diffuse Reflectance UV/VIS/NIR Spectroscopy

Optical diffuse reflectance spectra of the  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$  were obtained using a Varian Cary 5000 UV/VIS/NIR spectrometer equipped with a Harrick Praying Mantis diffuse reflectance accessory that uses elliptical mirrors. Each sample was ground and placed into a sample holder to a depth of 3 mm. Barium sulfate (Fisher, 99.92%) was used as a 100% reflectance standard. Data were collected from 2500 to 200 nm at a scan rate of 600 nm/min. Using the Kubelka-Munk transformation,  $\alpha_{\text{KM}} / s = (1-R)^2 / (2R)$ , the raw reflectance (R) was converted to a relative absorption ( $\alpha_{\text{KM}}$ ) since the scattering coefficient,  $s$ , is unknown [25]. The Urbach energy was also obtained by fitting the optical data to the functional form  $\alpha = A \exp(-E/E_u)$ , where A is a constant, E is the photon energy in eV,  $E_g$  is the band gap energy, and  $E_u$  is the Urbach energy [26].

## 3. RESULTS AND DISCUSSION

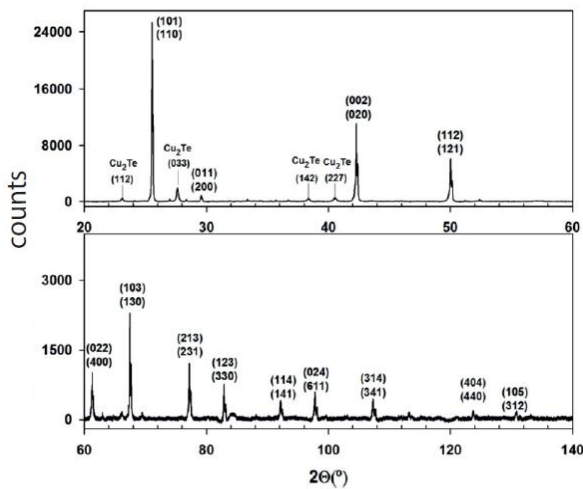
In Figures 2 and 3, the experimental X-ray powder diffraction patterns of  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$  are displayed. Sharp diffraction peaks were observed in the range of  $20$ - $140^\circ$   $2\theta$  indicating good crystallinity and that the samples had reached thermal equilibrium during synthesis.



**Figure 2.** Diffraction pattern of the alloy  $\text{Cu}_2\text{GeTe}_4$ . The hkl-Miller indices are labeled on the top of each peak. A secondary phase, identified as  $\text{Cu}_2\text{Te}$  was also observed.

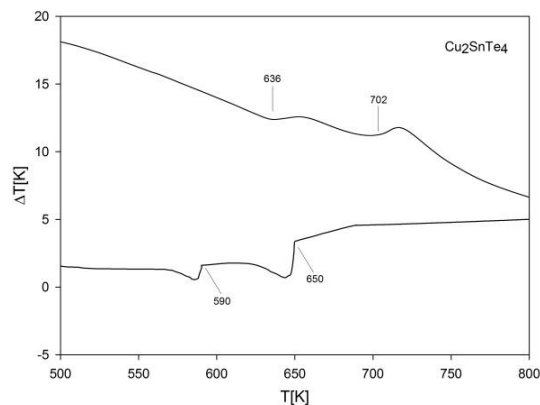
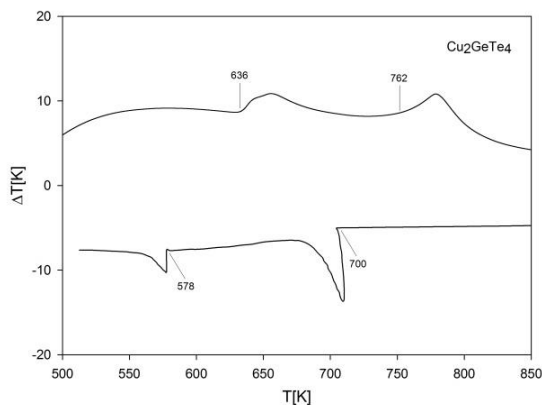
For both alloys, the diffraction patterns can be fully indexed with two phases: one with the orthorhombic crystal structure, space group  $\text{Imm}2$ ,  $N^\circ 44$ ,  $Z=2$ , and a secondary one identified as  $\text{Cu}_2\text{Te}$ . The lattice

parameters (Tables I and II) were calculated using the software Dicvol04 [27]. Those obtained for the orthorhombic phase are very close with those reported previously for the analogous ternaries  $\text{Cu}_2\text{GeTe}_3$  and  $\text{Cu}_2\text{SnTe}_3$  [2-4] (see Table III). With respect to the secondary phase,  $\text{Cu}_2\text{Te}$  does not belong to the  $(\text{Cu}_2\text{Ge})_{1-x}\text{Te}_x$  or  $(\text{Cu}_2\text{Sn})_{1-x}\text{Te}_x$  tie lines, so it is probable that the mechanical shaking during the heating process was not enough to dissolve it.



**Figure 3.** Diffraction pattern of the alloy  $\text{Cu}_2\text{SnTe}_4$ . The hkl-Miller indices are labeled on the top of each peak. A secondary phase, identified as  $\text{Cu}_2\text{Te}$  was also observed.

DTA measurements are showed in Figure 4. Two thermal transitions are observed for both alloys,  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$ . In the case of  $\text{Cu}_2\text{GeTe}_4$ ,



**Figure 4.** DTA curves of  $\text{Cu}_2\text{GeTe}_4$  (left) and  $\text{Cu}_2\text{SnTe}_4$  (right). Top curves: heating cycle; bottom curves: cooling cycle. The labels show the transition temperatures.

the thermogram shows, transitions occurring at 762 and 636K in the heating cycle, and transitions at 700 and 578K in the cooling cycle. Thermal transitions for  $\text{Cu}_2\text{SnTe}_4$  were observed at 702 and 636K upon heating and 650 and 590K upon cooling. It is evident that the overheating (or supercooling) effect produces the positive difference of  $(T_f - T_s)$  where  $T_f$  and  $T_s$  are the fusion and solidification temperatures, respectively.

The first thermal event corresponds to the solid-to-solid transition, i.e. from the room temperature (tetragonal?) to the high temperature phase (orthorhombic?), and the second thermal event correspond to the melting (or solidification) of the solid (liquid) phase. The shape of the peaks in the cooling cycle suggests that the sequence of transitions for  $\text{Cu}_2\text{GeTe}_4$  are liquid-solid<sub>1</sub>-solid<sub>2</sub>, whereas for  $\text{Cu}_2\text{SnTe}_4$  are liquid-solid<sub>1</sub>+liquid-solid<sub>2</sub>.

The well-known Grimm-Sommerfeld condition for semiconductors, states that a compound must have an average of 4 valence electrons per atom. In the case of  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$ , Cu is bivalent ( $\text{Cu}^{+2}$ ), Ge (or Sn) is tetravalent ( $\text{Ge}^{+4}$  or  $\text{Sn}^{+4}$ ) and Te is hexavalent ( $\text{Te}^{+6}$ ). The sum gives 32 electrons in total. However, there are only seven atoms ( $2\text{Cu} + 1\text{Ge} + 4\text{Te}$ ); therefore, it is necessary to have a vacancy in the crystal structure in order to have a total 8 “atoms” for the 32 electrons, giving an average of 4 electrons per atom. Thus, the formula units must be written as  $\square\text{-Cu}_2\text{GeTe}_4$  and  $\square\text{-Cu}_2\text{SnTe}_4$ .

**Table I.** Indexation of  $\text{Cu}_2\text{GeTe}_4$ .

*Orthorhombic, space group Imm2 (N° 44), Z=2*  
*Lattice parameters: a=5.9281(4) Å, b=4.2211(6) Å, c=12.645(5) Å*

$2\Theta_{\text{obs}}(^{\circ})$	$d_{\text{obs}}(\text{Å})$	$I/I_0$	hkl	$2\Theta_{\text{cal}}(^{\circ})$	$d_{\text{cal}}(\text{Å})$	$\Delta 2\Theta(^{\circ})$
25.916	3.43519	100.0	101	25.911	3.43591	0.006
29.933	2.98268	5.5	011	29.929	2.98314	0.005
42.858	2.10839	17.1	002	42.873	2.10772	-0.014
42.983	2.10257	41.1	211	42.980	2.10270	0.003
50.793	1.79606	12.9	112	50.765	1.79700	0.029
50.980	1.78993	14.1	301	50.997	1.78937	-0.017
53.289	1.71768	1.9	202	53.287	1.71774	0.002
62.188	1.49154	2.6	022	62.195	1.49140	-0.006
62.613	1.48245	1.7	400	62.626	1.48216	-0.013
68.593	1.36705	3.7	103	68.585	1.36719	0.008
68.763	1.36409	8.0	312	68.754	1.36424	0.008
78.640	1.21566	4.1	213	78.626	1.21584	0.014
78.861	1.21280	4.4	402	78.895	1.21236	-0.034
84.285	1.14803	1.1	132	84.279	1.14810	0.006
84.526	1.14537	2.0	303	84.550	1.14511	-0.024
93.936	1.05380	0.7	004	93.940	1.05377	-0.004
94.231	1.05128	1.4	422	94.233	1.05126	-0.002
99.805	1.00699	1.4	332	99.815	1.00692	-0.010
100.198	1.00410	2.0	521	100.215	1.00398	-0.017
109.579	0.94280	0.7	024	109.581	0.94278	-0.002
110.436	0.93787	0.6	611	110.425	0.93793	0.011
116.062	0.90801	0.7	314	116.055	0.90805	0.007
116.462	0.90605	0.6	503	116.444	0.90613	0.018
127.496	0.85889	0.7	404	127.519	0.85880	-0.023
134.728	0.83459	0.4	105	134.726	0.83460	0.002
135.389	0.83260	0.8	523	135.379	0.83263	0.010

Figure of Merit:  $M(2\theta)=41.3$ ;  $F(2\theta)=19.0(0.0099, 138)$  [27]

**Table II.** Indexation of  $\text{Cu}_2\text{SnTe}_4$ .

*Orthorhombic, space group Imm2 (N° 44), Z=2*  
*Lattice parameters: a= 6.0375(6) Å, b= 4.2706 (3) Å, c=12.844(1)Å*

$2\Theta_{\text{obs}}(^{\circ})$	$d_{\text{obs}}(\text{Å})$	$I/I_0$	hkl	$2\Theta_{\text{cal}}(^{\circ})$	$d_{\text{cal}}(\text{Å})$	$\Delta 2\Theta(^{\circ})$
25.539	3.48503	100.0	101	25.549	3.48372	-0.010
25.598	3.47719	48.1	110	25.549	3.48372	0.049
29.571	3.01841	3.4	011	29.584	3.01711	-0.013
29.649	3.01063	1.8	200	29.632	3.01234	0.017
42.255	2.13710	43.7	002	42.245	2.13756	0.010
42.364	2.13183	21.3	020	42.357	2.13218	0.007
50.016	1.82214	24.1	112	50.018	1.82206	-0.002
50.149	1.81763	12.1	121	50.092	1.81956	0.057
61.281	1.51142	3.9	022	61.330	1.51034	-0.049
61.438	1.50795	2.1	400	61.438	1.50795	0.000
67.438	1.38764	9.1	103	67.435	1.38768	0.002
67.609	1.38453	4.7	130	67.618	1.38437	-0.009
77.207	1.23460	4.8	213	77.236	1.23420	-0.030
77.428	1.23163	2.5	231	77.390	1.23213	0.038
82.872	1.16398	3.0	123	82.913	1.16350	-0.041
83.113	1.16121	1.3	330	83.093	1.16144	0.020
92.143	1.06956	1.6	004	92.120	1.06976	0.023
92.444	1.06686	0.9	040	92.421	1.06707	0.024
97.768	1.02246	2.4	114	97.736	1.02271	0.032
98.069	1.02012	1.1	141	98.020	1.02050	0.049
107.268	0.95660	1.6	024	107.291	0.95646	-0.023
107.623	0.95443	0.6	611	107.632	0.95438	-0.009
113.250	0.92242	0.6	314	113.265	0.92234	-0.015
113.602	0.92056	0.4	341	113.571	0.92072	0.031
123.898	0.87283	0.3	404	123.897	0.87284	0.001
124.256	0.87139	0.4	440	124.259	0.87137	-0.003
130.695	0.84755	0.5	105	130.690	0.84757	0.005
131.309	0.84548	0.4	150	131.310	0.84548	-0.001

Figure of Merit: M(28)= 29.0; F(28)= 14.9(0.0134, 140) [27]



**Table III.** Comparison of the obtained lattice parameters for the alloys  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$  with  $\text{Cu}_2\text{GeTe}_3$  and  $\text{Cu}_2\text{SnTe}_3$ .

	<i>Lattice parameters</i>	<i>Crystal Structure</i>	<i>References</i>
$\text{Cu}_2\text{GeTe}_4$	a=5.9281(4) Å, b=4.2211(6) Å, c=12.645(5) Å V=316.42 Å <sup>3</sup>	Orthorhombic	This work
$\text{Cu}_2\text{GeTe}_3$	a=5.9261(2) Å, b=4.2115(2) Å, c=12.641(1) Å V=315.49 Å <sup>3</sup>	Orthorhombic	[14-15]
$\text{Cu}_2\text{GeTe}_3$	a=5.959 Å, c=11.858 Å V=421.07 Å <sup>3</sup>	Tetragonal	[17]
$\text{Cu}_2\text{SnTe}_4$	a= 6.0375(6) Å, b= 4.2706 (3) Å, c=12.844(1) Å V=331.17 Å <sup>3</sup>	Orthorhombic	This work
$\text{Cu}_2\text{SnTe}_3$	a= 6.043(1) Å, b= 4.274 (1) Å, c=12.833(4) Å V=331.45 Å <sup>3</sup>	Orthorhombic	[16]
$\text{Cu}_2\text{SnTe}_3$	a=6.094 Å V=226.31 Å <sup>3</sup>	Cubic (disordered)	[17]

**Table IV.** Thermal transition values for  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$

	<i>Heating [K]</i>	<i>Cooling [K]</i>	<i>Remarks</i>
$\text{Cu}_2\text{GeTe}_4$	762 and 636	700 and 578	$\text{Cu}_2\text{GeTe}_3$ M <sub>p</sub> : 800K [14]; 777K[3]
$\text{Cu}_2\text{SnTe}_4$	702 and 636	650 and 590	$\text{Cu}_2\text{SnTe}_3$ : 655K [5]

**Table V.** Comparison of experimental and nominal stoichiometry of the alloys  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$ .

$\text{Cu}_2\text{GeTe}_4$	<i>Nominal [at%]</i>	<i>Experimental [at%]</i>	<i>Deviation [%]</i>	$\text{Cu}_2\text{SnTe}_4$	<i>Nominal [at%]</i>	<i>Experimental [at%]</i>	<i>Deviation [%]</i>
Cu	25.0	34.4	+37.6	Cu	25.0	33.8	+35.2
Ge	12.5	13.4	+7.2	Sn	12.5	15.8	+26.4
Te	50.0	52.2	+4.4	Te	50.0	50.4	+0.8

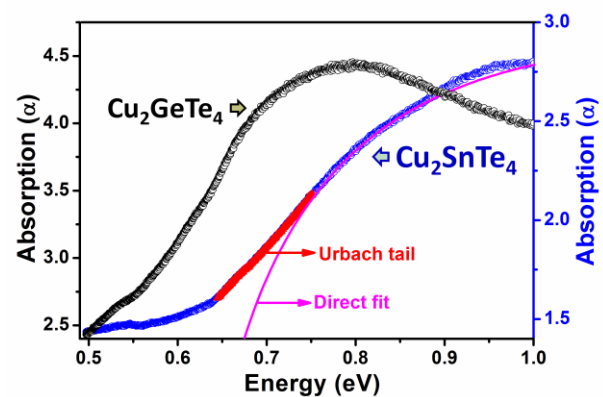
Scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy was used to compare the experimental composition to the nominal stoichiometry. For  $\text{Cu}_2\text{GeTe}_4$ , measurements were performed in three different points of the sample while for  $\text{Cu}_2\text{SnTe}_4$  data were collected on four points. The results are displayed in Table V where the column “experimental” represents the mean value of all measurements for each sample.

We observe stoichiometric deviations that are larger than the experimental error generally accepted for this technique which is  $\sim 10\%$ . Moreover, both alloys show a coincidence of  $\sim 35\%$  excess Cu which discards any experimental error.  $\text{Cu}_2\text{GeTe}_4$  has a Ge-excess of 7.2% whereas  $\text{Cu}_2\text{SnTe}_4$  has a Sn-excess of 26.4%. With respect to Te both alloys have a little deficiency that is less than the experimental error. These deviations from stoichiometry must be studied in relation to a better understanding of the phase diagrams of these alloys, research that is only just now beginning.

Finally, the optical energy gaps were obtained by Optical Diffuse Reflectance UV/VIS/NIR Spectroscopy. Optical diffuse reflectance data were collected for ground samples of  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$ . The spectra exhibit absorption edges indicative of narrow bandgap semiconductors in agreement with their black color, see Figure 5. Tails commonly observed on optical absorption edges originate from defects within the crystal structure that induce defect states in the electronic band structure. These defect states near the valence band maximum and conduction band minimum create a smearing of the band edge that is termed the Urbach tail [28-29]. When estimating the bandgap of a semiconductor it is proper to model the Urbach tail and exclude this region from the fitting of the band edge when determining the bandgap [30]. The Urbach tail appears as a linear region at the low energy region of the absorption edge when the log of the absorption is plotted as a function of energy [26]. Fitting the slope of this linear region yields the Urbach energy, which was determined to be 0.288(1) eV and 0.3795(5) eV for  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$  respectively.

In semiconductor compounds, bandgaps may be of direct or indirect origin, depending on the location(s) of the valence band maximum and the conduction band minimum in k-space. Direct bandgap materials exhibit relatively sharp

absorption edges, while indirect bandgap compounds present a more gradual onset of the absorption edge [28]. In order to determine the nature of the bandgap transition in the compounds presented here, the optical absorption edge data, for energies greater than those determined for the Urbach tail region, were fit to the function for a direct bandgap semiconductor,  $\alpha = A(E-E_g)^{1/2}/E$ , and to the function for an indirect bandgap semiconductor,  $\alpha = A(E-E_g)^2/E$ , where A is a constant, E is the photon energy in eV, and  $E_g$  is the band gap energy [28]. Based on these fits, it was found that the absorption edge of  $\text{Cu}_2\text{SnTe}_4$  showed a larger range of linearity using the direct function rather than the indirect function. Accordingly,  $\text{Cu}_2\text{SnTe}_4$  is assigned a direct bandgap of 0.63 eV, which corresponds to  $\sim 1970$  nm in the near infrared region of the electromagnetic spectrum. We are hesitant to definitely designate the bandgap of  $\text{Cu}_2\text{GeTe}_4$  as direct or indirect, since the band edge lies near the end of the range of our instrument. However,  $\text{Cu}_2\text{GeTe}_4$  appears to have a direct transition and fitting with the function for a direct bandgap yields 0.53 eV, which corresponds to  $\sim 2339$  nm.



**Figure 5.** Diffuse reflectance UV-vis-NIR spectra for  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$ . The data for  $\text{Cu}_2\text{SnTe}_4$  were fit using Tauc's function [34] for a direct-gap semiconductor, while the Urbach tail region (labeled) was excluded from the fitting of the absorption edge. The direct fit is shown with a thin solid curved line.

Telluride compounds in general can be semiconducting or metallic depending upon their composition and structure. The bandgaps reported here are narrower than those of some telluride compounds, such as CdTe,  $E_g \sim 1.5$  eV [28], an ideal value for use in solar cells. On the other hand,

$\text{Cu}_2\text{SnTe}_4$  and  $\text{Cu}_2\text{GeTe}_4$  possess wider bandgaps than some other tellurides such as  $\text{PbTe}$  [28],  $\text{RbHgSbTe}_3$  [31],  $\text{BaBiTe}_3$  [32] and  $\text{Bi}_2\text{Te}_3$  [32], which all have  $E_g < 0.5$  eV.  $\text{CdAgTe}_3$  possess  $E_g = 0.65$  eV [33], which is very close to that of  $\text{Cu}_2\text{SnTe}_4$ .

#### 4. CONCLUSIONS

Polycrystalline samples of  $\text{Cu}_2\text{GeTe}_4$  and  $\text{Cu}_2\text{SnTe}_4$  alloys were prepared by the melt and anneal technique. Both alloys crystallize in an orthorhombic structure together with traces of a  $\text{Cu}_2\text{Te}$  secondary phase. The melting transition of  $\text{Cu}_2\text{GeTe}_4$  was congruent whereas  $\text{Cu}_2\text{SnTe}_4$  melts incongruently. While both alloys present large stoichiometric deviations for the cations Cu, Ge and Sn, the stoichiometry of the anion, Te, is close to the nominal composition. The band-gaps are located in the near-IR region of the electromagnetic spectrum. In view of the results these alloys could have applications as detectors in the near infrared radiation.

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