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Structural and electrical properties of $\text{Cu}_2\text{Zn}(\text{Sn}_{1-x}\text{Si}_x)\text{S}_4$ ($x = 0, x = 0.5$) materials for photovoltaic applications

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This work studied the electrical effects of the substitution of tin with silicon on p-type $\text{Cu}_2\text{ZnSnS}_4$ semiconductor compounds. To this purpose, two samples, namely $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSn}_{0.5}\text{Si}_{0.5}\text{S}_4$, were prepared. The samples purities and homogeneities were characterized by both Energy Dispersive X-ray (EDX) spectroscopy and powder X-ray diffraction (PXRD).

We observed that the temperature dependence of the electrical conductivity of materials exhibits a crossover from $T^{-1/4}$ to T^{-1} dependence in the temperature range between 130 and 140 K. The characteristic temperature ($T_{0,\text{Mott}}$), the hopping distance (R_{hop}), the average hopping energy ($\mathcal{A}_{\text{hop}}$), the localization length (ξ) and the density of states ($N(E_F)$), were determined, and their values were discussed within the models describing conductivity in p-type semiconductor.

1. Introduction

Low cost, high efficiency and less environmental pollution have been regarded as the indispensable properties for next generation materials of solar cells [1,2]. The photovoltaic solar cells, which directly convert sunlight into electricity, use semiconductor for light absorption [3,4]. Meeting the requirements of the solar cells, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is one of promising alternative materials which

can be utilized as absorber layers of thin film solar cells [5]. It is characterized by a high absorption coefficient above 10^4 cm^{-1} and a direct band-gap in the range 1.4–1.6 eV [6–9]. Additionally, CZTS shows intrinsic p-type conductivity. Theoretical calculations suggest that this conductivity is due to the easy formation of the Cu_{Zn} antisite defect, generally observed in Cu-poor composition [10]. Defect, in the material, can be induced by partial substitution of some elements. However, recently, a conversion efficiency of 12.6% has been achieved in $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ based solar cells [11]. To improve the conversion efficiency, it is important to study the properties of certain derivatives of semiconductor based on CZTS. In literature, the substitution of sulfur by selenium and Sn by Ge

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[12] are reported but never the Sn element substituted by Si. On other hand, $\text{Cu}_2\text{ZnSiS}_4$ belongs to the family of quaternary chalcogenide and has attracted wide interest for their potential application as solar-cell absorbers [13,14].

For this purpose, we focused our work on preparation of CZTS derivatives with partial substitution of tin by silicon with general formula: $\text{Cu}_2\text{ZnSn}_{1-x}\text{Si}_x\text{S}_4$. Two compounds relative to $x = 0$ (noted A0) and 0.5 (noted A05) were prepared and characterized by both energy dispersive X-ray (EDX) spectroscopy and powder X-ray diffraction (PXRD). Then, we investigated the electrical properties of these compounds by means of impedance spectroscopy and discuss the conduction mechanisms in these materials.

2. Experimental

The studied compounds were synthesized from powders of copper, zinc, tin, silicon and sulfur with a purity of 99.99% following the standard technique described by Bernardini et al. [15].

Prepared samples were characterized, at room temperature, by powder X-ray diffraction (PXRD) using a D8 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) with the $10\text{--}100^\circ 2\theta$ range in the Bragg–Brentano geometry. The analyses of the PXRD patterns were done either through the Rietveld refinement or the Le Bail procedure (full pattern matching) with the help of JANA 2006 software [16].

The chemical compositions of the samples were analyzed using an EDX-equipped scanning electron microscope (JEOL 5800LV). These analyses were performed on polished sections of the products imbedded in epoxy. The elemental percentages were calculated using calibrated internal standards; thus, the results are both accurate and precise.

Impedance spectroscopy measurements were performed using a two electrode configuration. Samples were pressed into pellets with a diameter of 8 mm and thickness of 1.2 mm and 1.45 mm, respectively, for $x = 0$ and $x = 0.5$ by using uniaxial pressure (3 t/cm^2). The samples were sintered for 48 h at 750°C . The real and imaginary parts of the impedance were measured for frequency ranging from 40 Hz to 6 MHz for $x = 0$ and from 40 Hz to 8 MHz for $x = 0.5$, by using an impedance analyzer HP-4192A in a compatible interface with a computer controller. With each sample, temperature was varied from 80 to 300 K .

3. Results and discussion

3.1. Characterization

Fig. 1 shows the refinement results from the PXRD pattern of two compounds. The majority of the peaks can be indexed in the tetragonal system with space group $I-42m$. The obtained lattice parameters are $a = 5.4332(2) \text{ \AA}$, $c = 10.8402(6) \text{ \AA}$ and $a = 5.3766(2) \text{ \AA}$ and $c = 10.6275(5) \text{ \AA}$ for A0 and A05, respectively. The sharpness of the major peaks indicates a good crystallinity [17].

We noted that a very small fraction of ZnS as impurity can be detected in both A0 and A05 samples. It was possible to quantify this impurity in the case of A0 (less than 1%). Unfortunately, it

was not possible to perform such as Rietveld refinements for A05 likely due to a large preferred orientation resulting from the Bragg–Brentano geometry used for the data collection. Nevertheless, the obtained unit cell parameters ($a = 5.3766(2) \text{ \AA}$ and $c = 10.6275(5) \text{ \AA}$) are in very good agreement with their evolution along the solid solution $\text{Cu}_2\text{ZnSn}_{1-x}\text{Si}_x\text{S}_4$ [18].

Fig. 2 shows the morphology of samples, A0 and A05, it is noted that the grain of the sample A0 is larger than those of the sample A05; this is probably due to the effect of the insertion of silicon, since the tin atomic radius is larger than the silicon.

Results of careful EDX analyses for both A0 and A05 samples are presented in Table 1. Taking into account the accuracy of the EDX analyses, the prepared compounds, appear to be roughly stoichiometric.

3.2. Electrical characterization

The temperature dependence of the complex impedance of the samples is shown in Fig. 3. From these curves, we see that the experimental points are located on arcs. The evolution curves $Z'' = f(Z')$ vs. temperature shows the thermal behavior of the material strength. In fact, any increase in temperature is accompanied by a decrease in resistance. To explain the electrical behavior of materials, equivalent electrical circuits are proposed.

3.2.1. Sample A0

The adequate equivalent circuit is made by a series combination of $R_1 + (R_2//L_1) + (R_3//C_1) + (R_4//Q_1)$, where R , L , C and Q are respectively resistance, inductance, capacity and constant phase element.

The real and imaginary components of the whole impedance of this circuit were calculated according to the following expressions:

$$Z' = \frac{R_2(L\omega)^2}{R_2^2 + (L\omega)^2} + \frac{R_3}{1 + (R_3C\omega)^2} + \frac{R_4 + R_4Q\omega^\alpha \cos(\alpha\pi/2)}{(1 + R_4Q\omega^\alpha \cos(\alpha\pi/2))^2 + (R_4Q\omega^\alpha \sin(\alpha\pi/2))^2} \quad (1)$$

$$Z'' = R_1 + \frac{R_2^2L\omega}{R_2^2 + (L\omega)^2} + \frac{R_3^2C\omega}{1 + (R_3C\omega)^2} + \frac{R_4^2Q\omega^\alpha \sin(\alpha\pi/2)}{(1 + R_4Q\omega^\alpha \cos(\alpha\pi/2))^2 + (R_4Q\omega^\alpha \sin(\alpha\pi/2))^2} \quad (2)$$

Both Eqs. (1) and (2) are in the form of three terms corresponding to three relaxations process. The relaxation observed at high frequency and represented by R_1 , R_2 and L are relative to the

Fig. 1. Observed (red circles) and calculated (solid black lines) X-ray diffraction patterns for the two studied samples, A0 (Rietveld refinement) and A05 (full pattern matching). For A0, the phase fraction of ZnS can significantly be extracted from the refinement although it is very low (less than 1%) as exemplified in the inset. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. Scanning Electron Microscopy images of (a) A0 and (b) A05 samples mounted as polished sections.

Table 1

Atomic% composition ratios for metallic elements as measured by EDX.

x	Cu (At%)	Zn (At%)	Sn (At%)	Si (At%)	S (At%)	(Cu)/((Zn) + (Sn) + (Si))	(Zn)/((Sn) + (Si))	(Si)/(Sn + Si)
A0	24.3 ± 2	12.6 ± 3	13.1 ± 1	0	49.9 ± 1	0.94 ± 0.5	0.96 ± 0.7	0
A05	24.7 ± 2	12.1 ± 3	6.4 ± 2	6.4 ± 2	50.4 ± 2	0.99 ± 0.3	0.94 ± 0.8	0.5 ± 0.5

At: Atomic%.

Fig. 3. Nyquist plots ($-Z''$ vs. Z') of impedance data at different temperatures for sample A0 (a) and A05 (b and c).

electrode response [19]. The intercept of the semicircular arcs on the real axis gives the resistances R_3 and R_4 corresponding to relaxation appeared with decreasing frequencies, respectively (Fig. 3a).

C_1 and Q_1 are mounted in parallel, respectively, with R_3 and R_4 referring to capacitance of corresponding relaxation [20]. The simulated values of C_1 and Q_1 are about 10^{-10} Farad (i.e. Table 2)

Table 2

Temperature dependence of fitted circuit parameters for A0.

T	R_1 ($10^4 \Omega$)	R_2 ($10^5 \Omega$)	L_1 (10^{-3} H)	R_3 ($10^4 \Omega$)	C_1 (10^{-10} F)	R_4 ($10^5 \Omega$)	Q_1 (10^{-10} F)	α
80	6.73	1.17	4.00	2.66	2.42	3.37	1.00	0.97
100	4.45	1.00	4.35	6.61	1.25	1.61	1.33	0.99
120	3.70	0.94	4.46	8.08	1.02	1.11	1.90	0.98
130	3.19	0.88	4.47	8.76	0.89	0.77	2.10	0.99
140	2.81	0.87	4.55	8.11	0.89	0.68	2.25	0.99
160	2.28	0.85	4.65	6.37	0.98	0.76	2.07	0.98
180	1.95	0.81	4.67	4.94	1.08	0.89	1.83	0.97
200	1.71	0.76	4.69	3.32	1.33	1.12	2.20	0.99
220	1.59	0.77	4.67	3.14	1.33	1.40	1.73	0.98
240	1.48	0.79	4.81	2.55	1.48	1.39	2.02	0.98
260	1.39	0.75	4.73	2.53	1.48	1.48	2.06	0.98
280	1.38	0.75	4.75	2.40	1.54	1.50	2.24	0.98
300	1.29	0.73	4.81	2.44	1.55	1.56	2.19	0.98

indicating that relaxation observed at low frequency is relative to grain response while the other represent grain boundary effects [21,22].

3.2.2. Sample A05

Simulation of impedance complex data permits us to define two types of adequate equivalent circuits depending on the temperature range. For temperature below 130 K, the first equivalent circuit consists of a series combination of resistor R_s with parallel combination of R_1 - Q_1 and parallel combination of R_2 - Q_2 , Fig. 3b. Expressions of real and imaginary components of the impedance related to the equivalent circuit are:

$$Z' = \frac{R_1^2 Q_1 \omega^\alpha \cos(\alpha\pi/2) + R_1}{(1 + R_1 Q_1 \omega^\alpha \cos(\alpha\pi/2))^2 + (R_1 Q_1 \omega^\alpha \sin(\alpha\pi/2))^2} + \frac{R_2^2 Q_2 \omega^\alpha \cos(\alpha\pi/2) + R_2}{(1 + R_2 Q_2 \omega^\alpha \cos(\alpha\pi/2))^2 + (R_2 Q_2 \omega^\alpha \sin(\alpha\pi/2))^2} \quad (3)$$

$$Z'' = R_s + \frac{R_1^2 Q_1 \omega^\alpha \cos(\alpha\pi/2) + R_1}{(1 + R_1 Q_1 \omega^\alpha \cos(\alpha\pi/2))^2 + (R_1 Q_1 \omega^\alpha \sin(\alpha\pi/2))^2} + \frac{R_2^2 Q_2 \omega^\alpha \sin(\alpha\pi/2)}{(1 + R_2 Q_2 \omega^\alpha \cos(\alpha\pi/2))^2 + (R_2 Q_2 \omega^\alpha \sin(\alpha\pi/2))^2} \quad (4)$$

It has been established in the literature [23] that the higher frequency dispersion corresponds to the grain and the lower to the grain boundary, which normally has a capacitance value in the range of pF and nF, respectively.

For thus, at higher frequencies, the observed shapes correspond to the grain response, are expressed by R_1 - Q_1 parallel circuits while the grain boundary response evidenced at the lower frequencies is modeled by R_2 - Q_2 parallel circuits. Whereas, R_s indicates the contact resistance. The equivalent circuit is given in the inset of Fig. 3b. It is obvious that the capacitance values (Q_1) and (Q_2) are in the ranges of 10^{-10} F and 10^{-8} F, respectively.

The second, optimized between 130 and 300 K, is modeled by a series combination of a resistor in series with parallel R - C , and two parallel combination of R - Q , Fig. 3c. Expressions of correspondents real and imaginary parts of the impedance are:

$$Z' = \frac{R_1}{1 + (\omega R_1 C_1)^2} + \frac{R_2^2 Q_1 \omega^\alpha \cos(\alpha\pi/2) + R_2}{(1 + R_2 Q_2 \omega^\alpha \cos(\alpha\pi/2))^2 + (R_2 Q_2 \omega^\alpha \sin(\alpha\pi/2))^2} + \frac{R_3^2 Q_3 \omega^\alpha \cos(\alpha\pi/2) + R_3}{(1 + R_3 Q_3 \omega^\alpha \cos(\alpha\pi/2))^2 + (R_3 Q_3 \omega^\alpha \sin(\alpha\pi/2))^2} \quad (5)$$

$$Z'' = R_s + \frac{R_1^2 \omega C_1}{1 + (\omega R_1 C_1)^2} + \frac{R_2^2 Q_1 \omega^\alpha \cos(\alpha\pi/2) + R_2}{(1 + R_2 Q_2 \omega^\alpha \cos(\alpha\pi/2))^2 + (R_2 Q_2 \omega^\alpha \sin(\alpha\pi/2))^2} + \frac{R_3^2 Q_3 \omega^\alpha \sin(\alpha\pi/2)}{(1 + R_3 Q_3 \omega^\alpha \cos(\alpha\pi/2))^2 + (R_3 Q_3 \omega^\alpha \sin(\alpha\pi/2))^2} \quad (6)$$

The first response consists of parallel combination of resistance R_1 and capacitance C_1 attributed to the grains, the second of parallel combination of resistance R_2 and a constant phase element Q_2 ascribed of grains boundary. Whereas, the third consists of parallel combination of resistance R_3 and capacitance Q_3 due to the electrode effect, inset in Fig. 3c. The fitted values of different parameters are listed in Table 3.

Nyquist plots reported in Fig. 3 shows a good agreement between the calculated lines and the experimental data. Moreover, experimental and calculated curves of real (Z') and imaginary (Z'') parts vs. frequency for each compound at selected temperature 100 K are superposed, Fig. 4. The continuous line curves are calculated from the corresponding equations defined for equivalent circuit. The good conformity between experimental and calculated curves indicates that the proposed equivalent circuits describe well the behavior of the materials [24]. Bulk conduction of A0 is represented by a constant phase element CPE indicating that charges carriers are dependent. Whereas, for A05, bulk conduction is represented by a pure capacitance for temperature greater than 130 K, indicating the charges carriers are dependent up to 130 K before thus becomes independent [25]. This comportment is related to substitution of tin by silicon.

Knowing the bulk resistance, obtained from equivalents circuit parameters values, and the dimensions of the samples, the conductivity (σ_{dc}) has been calculated at each temperature by means of the relation:

$$\sigma_{dc} = \frac{1}{R} \times \frac{e}{S} \quad (7)$$

where e is the thickness and S is the surface of the sample.

Fig. 5 gives the variations of electrical conductivity with temperature for the samples. Which clearly show two distinct regions presumably corresponding to different conduction mechanisms, at high and low temperatures.

At high temperatures ($T \geq 160$ K for A0 and 140 K for A05; Region I), Fig. 5 shows a liner variation of $\ln\sigma$ vs. $10^3/T$. However, for p-type semiconductors, most of the free holes are recaptured by the acceptors when temperature decreases. Indeed, they not have sufficient thermal energy to be excited from the acceptor levels to the valence band [26]. In this case, the band conduction becomes less important, and holes hop nearest neighbor acceptor

Table 3
Temperature dependence of fitted circuit parameters for A05.

T	$R_s\ (\Omega)$	$R_1\ (\Omega)$	$Q_1\ (10^{-10}\ \text{F})$	α_1	$R_2\ (\Omega)$	$Q_2\ (10^{-7}\ \text{F})$	α_2		
<i>(80–120 K)</i>									
80	13	39481	1.75	0.98	42779	1.10	0.70		
90	14	25230	1.86	0.97	40224	1.32	0.71		
100	16	15494	1.45	1	18346	1.10	0.56		
110	13	11990	2.08	0.97	12228	1.61	0.71		
120	13	9382	2.99	0.95	8432	0.92	0.80		
T	$R_s\ (\Omega)$	$R_1\ (\Omega)$	$C_1\ (10^{-10}\ \text{F})$	$R_2\ (\Omega)$	$Q_2\ (10^{-8}\ \text{F})$	α_2	$R_3\ (\Omega)$	$Q_3\ (10^{-7}\ \text{F})$	α_3
<i>(140–280 K)</i>									
140	6	4505	1.60	4067	10.6	0.88	2885	5.95	0.57
160	8.4	2908	1.55	2250	2.97	1.03	2052	3.72	0.63
180	8.2	2003	1.53	1894	3.93	1.00	1255	2.90	0.67
200	7.5	1440	1.55	1462	4.08	1.00	994	5.16	0.64
220	14.5	1036	1.59	1174	4.33	1.04	782	7.09	0.62
240	13.1	804	1.60	1046	4.83	0.99	541	5.28	0.65
260	12.1	620	1.61	868	4.79	0.98	460	8.17	0.63
280	15.7	466	1.71	732	4.69	1.00	428	15.6	0.57

Fig. 4. Variation of (Z') and ($-Z''$) as a function of the frequency at 100 K for two studied materials.

Fig. 5. Temperature dependence of the conductivity plotted as σT vs. $1000/T$ in a temperature range 80–300 K. The inset figure represents the conductivity plotted as $\sigma T^{1/2}$ vs. $T^{-1/4}$.

states in the impurity band. If the compensation ratio is very high, the Fermi level will be located in the impurity band. Conduction of reported samples, in this case, is realized through NNH of charge carriers with small activation energy directly over impurity states.

Obtained values of activation energy, for both compounds, are approximately 30 meV (i.e. Table 3). The activation energy is low and it can either be due to the conduction from a shallow donor level or due to the predominance of the hopping mechanism [27].

The conductivity in the NNH model is given by Eq. (8) [28]

$$\sigma_{\text{NNH}} = \sigma_0 \exp[-E_{\text{NNH}}/k_B T] \quad (8)$$

and

$$E_{\text{NNH}} = \frac{0.99 \cdot e^2 \cdot N_A^{1/3}}{4 \cdot \pi \cdot \epsilon_0 \cdot \epsilon_r} \quad (9)$$

where σ_0 , E_{NNH} , K_B , N_A and ϵ are respectively: a constant, activation energy, Boltzmann's constant, acceptor concentration and dielectric permittivity.

The critical concentration n_c of the charge carriers for the metal-insulator transition is calculated by the following equation [29]

$$\sigma_{\text{min}} = 0.03 \left(\frac{e^2 \cdot n_c^{1/3}}{\hbar} \right) \quad (10)$$

where e is the electron charge and $\hbar$ is the Planck constant.

Considering NNH mechanism, it is possible to extract some of the above mentioned parameters. This mechanism fit well our data in region I of each compound. Results of fitting are gathered in Table 4. Substitution of tin by silicon induces decrease of conductivity and critical carrier concentration. Whereas, the other parameters remains unchanged. Thus is probably due to decrease of mobility of charge carriers.

At lower temperatures (region II) the conductivity data can be explained in terms of variable-range hopping conduction (VRH), where electron transport in a band of localized states and the carriers move between states via a phonon-assisted tunneling process as predicted by the Davis-Mott model [30].

The conductivity via Mott-VRH mechanism is given by Eq. (11)

$$\sigma_{\text{VRH,Mott}}(T) = \sigma_0 T^{-1/2} \exp \left[\left(-\frac{T_0}{T} \right)^{1/4} \right] \quad (11)$$

σ_0 is given by:

$$\sigma_0 = \frac{3e^2 v}{(8\pi)^{1/2}} \left[\frac{\xi N(E_F)}{K_B} \right]^{1/2} \quad (12)$$

and T_0 is as follows:

$$T_0 = \frac{18}{K_B \xi^3 N(E_F)} \quad (13)$$

where σ_0 is hopping conductivity, v is phonon length, T_0 is characteristic temperature depends on the density state on Fermi level $N(E_F)$ and ξ is localization length. The $T^{1/4}$ Mott's Law has been observed in various classes of semiconductors in particular CZTS [31] and CIGS [32].

For A0 and A05, the plots of $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$ were found to have been linear at lower temperatures, the insets in Fig. 5. This confirmed that the conduction in those compounds is governed by Mott's VRH conductivity. By this way, the characteristic hopping parameters have been obtained. The results of best fits are given in Table 5. The density of states at the Fermi levels $N(E_F)$ and the localization length ξ are obtained from Eqs. (12) and (13), Table 5. The hopping conduction is considered to be valid, if the hopping parameters satisfy the hopping conditions. For the Mott-VRH conduction, the temperature-dependent hopping

distance (R_{hop}) and average hopping energy (Δ_{hop}), gathered in Table 5, are calculated from Eqs. (14) and (15), respectively [30]

$$R_{\text{hop, Mott}}/\xi = \frac{3}{8} (T_{0,\text{Mott}}/T)^{1/4} \quad (14)$$

$$\Delta_{\text{hop, Mott}} = \frac{1}{4} K_B T (T_{0,\text{Mott}}/T)^{1/4} \quad (15)$$

where T is a transition temperature.

The substitution of tin by silicon is accompanied by a slightly decreases of the characteristic temperature $T_{0,\text{Mott}}$. The decrease is reflected in the other hopping parameters as a decrease in both density of states and average hopping energy, and as an increase in the hopping distance. Also the obtained $T_{0,\text{Mott}}$ values are of the same order of magnitude as that found in a variety of CIGS derivatives [32].

These $T_{0,\text{Mott}}$ values are satisfied with the VRH model. The $T_{0,\text{Mott}}$ values are related to the change of homogeneity and density of disorder in samples. $T_{0,\text{Mott}}$ value of the A0 is larger than that of A05, indicating much higher density of disorders presented in the CZTS sample.

Thanks to their low formation energy, copper vacancy (V_{Cu}) and Zn_{Cu} antisite are most important charge carriers in CZTS material [33]. In this case, A0 and A05 are roughly stoichiometric compounds, and present approximately the same copper deficiency. Zinc atoms will occupy the site of copper atoms and thus a copper vacancy (V_{Cu}) and antisite Zn_{Cu} native defects formed in the material. Moreover, the slightly abundance of copper vacancy, the Sn-Si substitutions lead to higher density of V_{Cu} and Zn_{Cu} antisite in A0. In turn, lower conductivity of the CZTSiS (A05) is marked.

The AC conductivity has been calculated from the real (Z') and imaginary (Z'') parts of the impedance data measured over a study range of temperatures using the relation $\sigma_{\text{AC}} = (e/s)[Z'/(Z'^2 + Z''^2)]$, where e and s are the thickness and the area of the pellets.

The angular dependence in the frequency of the alternating current conductivity for both compounds at different temperatures is shown in Fig. 6; it is generally analyzed using equation [34]

$$\sigma_{\text{ac}}(\omega) = \frac{\sigma_s}{1 + \tau^2 \omega^2} + \frac{\sigma_{\infty} \tau^2 \omega^2}{1 + \tau^2 \omega^2} + A \omega^s \quad (16)$$

where σ_s is the conductivity at low frequencies, σ_{∞} is an estimate of conductivity at high frequencies, A is temperature-dependent parameters and s is the power exponent.

For the compound A0, the conductivity increases with increasing angular frequency, as, the conductivity increases with increasing temperature at a certain fixed angular frequency.

AC conductivity of compound A05 shows two plateaus separated by a frequency dispersive region are observed in the pattern. The low-frequency plateau represents the total conductivity whereas the high frequency plateau represents the contribution of grains to the total conductivity [35]. The presence of both high and low frequencies plateaus in conductivity spectra indicates the presence of two processes contribute to the conduction. The above-mentioned equation has been used to fit the AC conductivity data.

In the fitting procedure, A and s values have been varied simultaneously to get the best fits. The obtained values A and s from the fit of AC conductivity at various temperatures are shown in Fig. 7. Both s and A are temperature dependent [36]. It is clear that s and A varies inversely with temperature.

Two conduction patterns are observed in the compound A0, which are organized as follows: before $T = 160$ K, s decrease with increasing temperature, it's vary between $0.63 \leq s \leq 0.67$ indicating that the electrical conduction is insured by the correlated barrier hopping (CBH) model. After $T = 160$ K, s increase with increasing temperature ($0.63 \leq s \leq 0.87$) improving that the

Table 4
Values of the Arrhenius conduction parameters.

x	T (K)	σ_{min} ($\Omega^{-1} \text{cm}^{-1}$)	E_{NNH} (meV)	n_c (cm^{-3})	N_A (cm^{-3})
A0	300–160	0.36	33	11.3×10^{13}	3.73×10^{24}
A05	300–140	0.27	31	4.73×10^{13}	3.09×10^{24}

Table 5

Values of the Mott-VRH conduction parameters.

x	T (K)	$\sigma_{0,Mott}$ ($\Omega^{-1} \text{ cm}^{-1} \text{ K}^{0.5}$)	$T_{0,Mott}$ (K)	ξ (nm)	$N(E_F)$ ($\text{cm}^{-3} \text{ eV}^{-1}$)	R_{hop} (nm)	Δ_{hop} (eV)
A0	160–80	525	3.13×10^5	1.61	1.6×10^{20}	4.15	2.11×10^{-2}
A05	140–80	182	2.44×10^5	5.24	5.9×10^{18}	12.69	1.95×10^{-2}

Fig. 6. Angular frequency dependence of the ac conductivity at different temperatures in top was the spectra of compound A0 and the remaining are those of the compound A05. **Fig. 7.** Variation of A and s as a function of temperature.

electrical conduction is insured by non-overlapping small Polaron tunneling (NSPT) model, Fig. 7a [37]. While for compound A05, three models of conduction are observed, before $T < 120$ K, s increase with increasing temperature, it varies between $0.21 \leq s \leq 0.29$ indicating that the electrical conduction is insured by non-overlapping small Polaron tunneling (NSPT) model. Between $120 \text{ K} \leq T \leq 170 \text{ K}$, s decrease with increasing temperature, it varies between $0.29 \leq s \leq 0.25$ indicating that the electrical conduction is insured by the correlated barrier hopping (CBH) model. After $T > 170$ K, s increase again ($0.25 \leq s \leq 0.40$) the electrical conduction is insured by non-overlapping small Polaron tunneling (NSPT) model again, Fig. 7b [37].

4. Conclusions

Chemical composition and electrical conductivity properties of powder polycrystalline CZTS without and with 50% tin substitution by silicon were investigated. The analysis of the dispersion of the frequency of real and imaginary components of the complex impedance allowed us to determine an equivalent electrical circuit for the CZTS (A0) compound and two different circuits for compound CZTSiS (A05), thus the electrical properties for these compounds have been investigated by temperature-dependent conductivity.

It was found that at temperatures higher than 160 K for (A0) and 140 for (A05) the electrical conductivities of the samples are dominated by band conduction and NNH. However, at lower temperatures, the conductivities of both samples are dominated by "variable range hopping" mechanism. The substitution of Sn with Si decreases the abundance of Zn_{Cu} antisite on A05 which explain the lower conductivity of the material. The AC conductivity showed a variation with frequency and it was found to obey universal power law at different temperatures with s varies between 0.63 and 0.87 for A0 and from 0.21 to 0.4 for A05. In both compounds the ac conductivity is dominated by NSPT and CBH mechanisms.

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