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SYNTHESIS AND CHARACTERIZATION OF CuInSSe ABSORBENT MATERIALS SYNTHESIZED VIA MICROWAVE RADIATION

P. VALENCIA-GÁLVEZ[a*], A. GALDÁMEZ[a], V. MANRÍQUEZ[a],
G. GONZÁLEZ[a,b]
[a]*Facultad de Ciencias, Universidad de Chile, Santiago, Chile.*
[b]*Center for the Development of Nanoscience and Nanotechnology, CEDENNA, Santiago, Chile.*

In this paper, the results of the synthesis, structural, vibrational and optical characterization of the CuInSSe *pseudo-quaternary* compound (CISS) obtained via the assistance of microwave radiation and the conventional ceramic method are compared. The synthesis was performed in vacuum sealed quartz ampoules and exposed to microwave radiation at 2, 3 and 4 minutes for 3 days. The structural characterization indicates that the products are single phases with crystal structure Chalcopyrite-type. The average particle sizes were estimated through the use of Scherrer's formula, and the results showed that there is a correlation between the duration of exposure to radiation and the particle size obtained. The SEM-EDS analysis confirms the chemical compositions expected. The Raman analysis confirmed the formation of the pseudo-quaternary phase presenting the characteristic peaks and displacement for these compounds. Finally, the measurement of diffuse reflectance show band-gap values E_g between 1.21 and 1.29 eV allowing us to conclude that the microwave-assisted synthesis leads to the obtaining of the CISS phase, which are presented as good candidates to be used as absorbing material in solar cells.

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1. Introduction

The compounds of the I-III-VI_2 family stand out for having a crystal structure of chalcopyrite-type and these compounds have been used optoelectronic devices and photovoltaic systems[1]–[3]. One of their main features is related to their direct band gaps, with values between 1.00 and 3.50 eV. However, despite these attractive features, ternary compounds generally have relatively low conversion efficiencies[4].

Studies on "*pseudo-quaternary*" alloys formed by chemical substitutions of another element from the III and /or VI group, lead to the obtaining of phases with independent control of the lattice parameter and the energy gap[5]–[8]. This feature allows these materials to achieve a better coupling in thin film devices, a situation that is virtually impossible in the ternary phases because of the direct correlation between these two parameters.

The $CuIn(S_{1-X},Se_X)_2$ (CISS) are pseudo-quaternary semiconductor materials which have shown excellent potential as absorbers in solar cells. Among the features of the CISS that have stood out, there are a high absorption coefficient of the order of 10^5 cm^{-1}[9] and a direct band gap of 1.2 eV[10]–[12]. However, the efficiency of these materials has been limited by high rates of recombination[13]. We have focused our objectives in this aspect in order to synthesize the compounds with high purity and small particle sizes in a quick and simple way, which would help reduce the rate of recombination.

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[*] Corresponding autor: p.valencia.galvez@gmail.com

Due to the attractive features of the CISS, these have been synthesized through various methods, such as the horizontal Bridgman[14], chemical spray pyrolysis[15], thermal diffusion of S and/or Se[16], electrodeposition[17], plus various solution methods[18], solvothermal[19], colloidal[11] among others. However, these methods are expensive and require long working hours. Therefore, this brings to the need for more efficient methods of synthesis, which allow to decrease energy consumption and response times. The microwave radiation (*MW*) proved to be a highly viable alternative offering numerous advantages over conventional methods of synthesis including selective, uniform and volumetric heating, fast power supply and high reaction yields just to name a few[20]–[22].

In this paper we compare the results of the syntheses in solid state assisted by the microwave radiation for durations of 2, 3 and 4 minutes with the results of the conventional ceramic method for the CuInSSe compound. Furthermore, the structural and vibrational characterizations plus the optical properties of these phases were carried out in order to be used as energy absorbers in solar cells.

2. Experimental Section

2.1 Synthesis

The synthesis of CuInSSe was performed on solid state by direct combination of the pure elements in stoichiometric ratios, Cu: In: S: Se is 1: 1: 1: 1. The reagents used were powders of: copper (Cu), indium (In), sulfur (S) and selenium (Se), ALDRICH with purities of 99.99%. The elements were placed in quartz ampoules sealed under vacuum. Two preparation methodologies were used:

a) Ceramic method where the ampoule was subjected to a temperature of 950° C in a tube furnace with temperature control for a 72-hour reaction (sample *CM*).

b) The microwave assisted syntheses were carried out with a microwave oven (HL25G, Howland) of frequency 2.45 GHz and a power of 850 Watt, with working times of 2, 3 and 4 minutes of exposure (samples *MW2*, *MW3* y *MW4* respectively)

2.2 Powder x-ray diffraction measurements

Powder X-ray diffraction patterns were collected, at room temperature, on Bruker D8 Advance powder diffractometer, with CuK$_\alpha$radiation (λ = 1.54098 Å) and in the range 5º < 2θ< 80º. The equipment operates at 40 kV and 25 mA. XRD patterns were refined by the Rietveld method using the MAUD software[23]. Standard LaB$_6$ sample was used for measuring the instrumental profile.

2.3 SEM-EDS analysis

The chemical compositions of the samples were determined by scanning electron microscopy (SEM) using a Vega 3 Tescan with Bruker Quantax 400 energy dispersive X-ray spectroscopy (EDS) detectors. Analyses were carried out by chemical mapping.

2.4 Raman Scattering measurements

The Raman scattering measurements of CISS were made using a RM1000 Renishaw micro-Raman spectrometer with detectors CCD (Chargue-Coupled Device) in combination with a microscope Leica LM/PM using excitation of wave length 514nm. The spectrometer was calibrated using a reference single crystal Si sample (Raman peak at 520.7 cm^{-1}). The spectra data was collected at room temperature in back scattering configuration in the spectral range100 – 500 cm^{-1}, with a laser spot on the sample of about ~1 μm and a laser power ~2mW.

2.5 Diffuse reflectance measurements

Diffuse reflectance spectra were recorded on a Perkin Elmer UV-visible spectrophotometer, model lambda 35. The measurements were carried out on microcrystalline samples, which were dispersed between two polyethylene films supported on a BaSO$_{4.}$

3. Results and Discussion

3.1 Compositional characterization and X-ray powder diffraction

The chemical compositions of the reaction products were determined using the EDS analysis on compressed powder samples. The backscatter image and EDS analysis (chemical maps on several areas) revealed that the samples were uniform throughout of the material. Table 1 summarizes the chemical composition of the synthesized samples.

Figure 1 shows Powder x-rays diffraction patterns at different reaction times. In order to make a better structural characterization of the compounds obtained, the Rietveld refinement was performed using the standard data reported for the $CuIn(S,Se)_2$ phase (ICSD # 656272)[10]. Figure 2 shows the result of the refinement performed on the sample *MW4*, in which a good fit is observed, since the difference between the calculated profile generated by the structural starting model, and the experimental or observed diffraction profile is virtually a straight line. These results allow us to confirm that all samples crystallize with Tetragonal Chalcopyrite structure (space group $I\bar{4}2d$). The goodness of fit obtained from the refinement, the structural parameters and the ratio between c/a, in addition to the distortion of the lattice via the parameter δ, for all samples are summarized in Table 2.

Table 1. Chemical compositions of the samples determined by EDS

Samples	Atom (%)			
	Cu	In	S	Se
CM	26.36	22.26	22.29	29.08
MW2	27.10	23.06	21.52	28.32
MW3	27.78	21.78	21.73	29.70
MW4	27.69	21.63	22.84	27.85

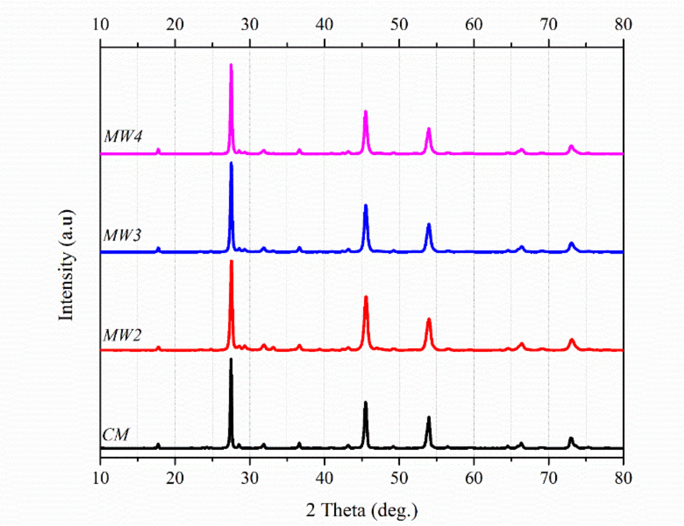

Fig. 1. XRD powder pattern of the product from ceramic method (CM) and microwave synthesis (MW2, MW3, MW4).

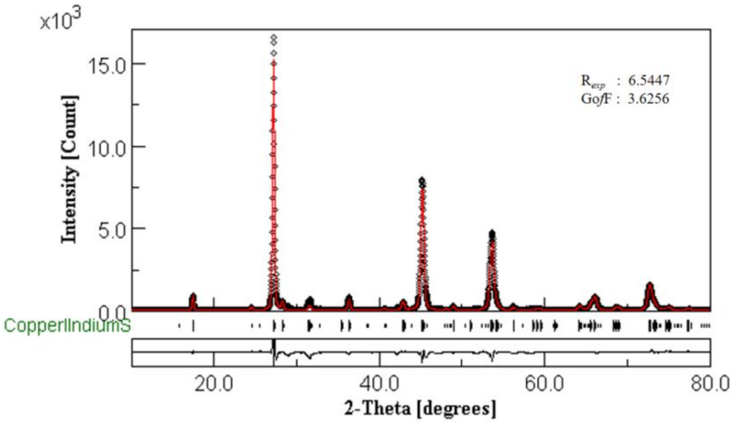

Fig. 2. Rietveld refinement plot of MW4. Observed (open circles), calculated (line) and difference profile of X-ray diffraction are plotted.

Table 2. Lattice parameters, tetragonal distortions experimental with to data reported of CISS and Rietveld refinement data.

Samples	Lattice parameters				Refinement data		
	a (Å)	c (Å)	c/a	δ*	R_{wp}	R_b	R_{exp}
[10]	5.625	11.353	2.018	-0.018	---	---	---
[21]	5.633	11.338	2.013	-0.013	---	---	---
CM	5.646	11.363	2.013	-0.013	18.4609	26.4956	6.9409
MW2	5.649	11.361	2.011	-0.011	27.8738	32.8479	7.6407
MW3	5.647	11.371	2.014	-0.014	24.4674	28.0757	6.9822
MW4	5.653	11.377	2.013	-0.013	23.7286	27.7338	6.5447

*δ =2-c/a

Another factor that helps to identify the CISS obtained via microwave radiation have crystallized chalcopyrite type structures (Figure 3), it is through the tetragonal distortion, defined as δ = 2- c/a. If the value of δ is zero, the structure can be considered as zinc blende superstructure. However, when the ratio c/a is other than 2, a distortion is generated in the tetragonal lattice[24]. Our results are slightly greater than 2, indicating that the unit cell is distorted by an elongation along the axis c. This confirms that synthesis via microwave allows obtaining compounds identical to those obtained by other synthesis techniques [13]. Table 3 presents a comparison of the distance between the interplane distances d. The results confirm that the products obtained via microwave radiation are identical to that obtained by the ceramic method as previously reported[10], [25].

Table 3. Comparison of d spacing of CISS with those reported by Barron et al[21], [25]

hkl	*d* spacing (Å)				
	CM	*MW2*	*MW3*	*MW4*	[21], [25]
112	3.27	3.26	3.27	3.27	3.29
121	2.46	2.46	2.46	2.47	2.47
024	2.00	2.00	2.00	2.00	2.01
116	1.71	1.71	1.71	1.71	1.71
008	1.42	___	1.42	1.42	1.42
332	1.30	1.28	1.30	1.30	1.30

On the other hand, the average values of the "D" grain sizes were obtained using Scherrer's formula:

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

Where k is a dimensionless form factor, with a value of 0.9; λ is the wavelength of the radiation used (λ_{Cu}= 1.54098 Å); β is the full width at half maximum (FWHM) of the diffraction peak of the sample and θ is the diffraction peak position.

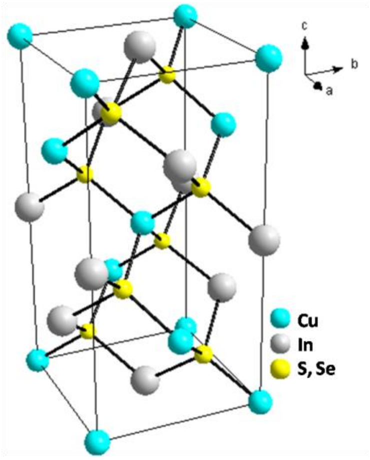

Fig. 3. The unit cell of the chalcopyrite compounds[26].

The average grain sizes determined for the samples *MW2*; *MW3*; *MW4* and *CM* were: 28.8; 33.1; 38.5 and 59.1 nm respectively. These results indicate that the syntheses via microwave radiation favors a reduction in the particle size of the product obtained and also that the sizes achieved depend on the duration of the radiation exposure.

3.2Raman analysis

The irreducible representation obtained from the application of the group theory for compounds with Chalcopyrite type of structure is determined by space group symmetry and the presence of two molecular formulas in each unit cell, which are distributed according to their symmetry as it follows: $\Gamma opt = A1 \oplus 2A2 \oplus 3B1 \oplus 3B2 \oplus 6E$[17], [26].

The Raman spectra of the CuInSSe phases synthesized via the ceramic method and microwave radiation (Figure 4) show a combination of the signals found for the ternary $CuInS_2$ and $CuInSe_2$ phases. In order to perform a better analysis of the spectra obtained, an adjustment for all samples with Lorentzian curves was performed. Figure 5 shows the spectra and the phase settings for *CM* and *MW2* respectively.

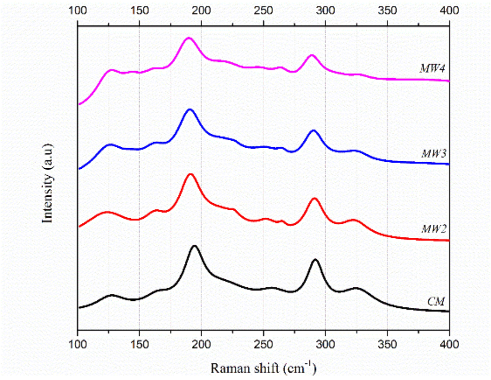

Fig. 4. Comparison of the Raman spectrum of the product from ceramic method (CM) and microwave synthesis (MW2, MW3, MW4).

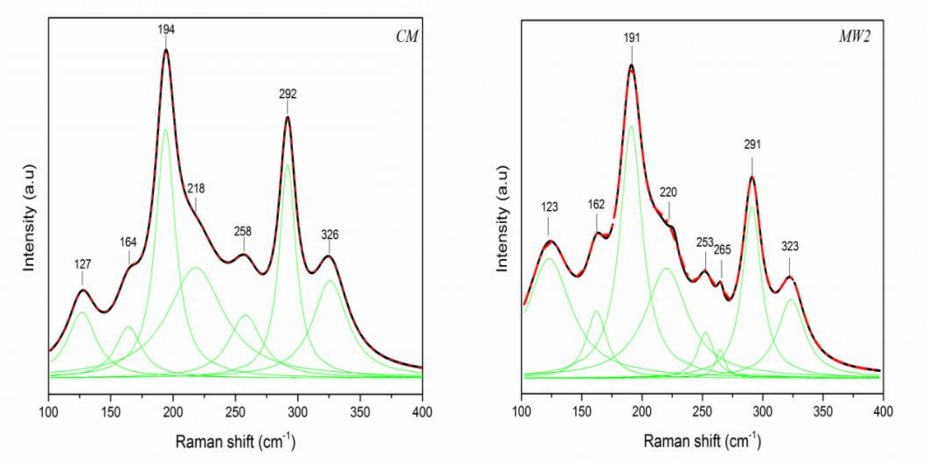

Fig. 5. Raman spectrum of samples CM and MW2 with the different contributions as deduced from the fitting of the different peaks with Lorentzian functions (Green lines).

The spectra have two dominant peaks at 190 and 290 cm^{-1} approximately, attributed to the vibrational mode *A* which is characteristic to chalcopyrite-type crystal structure. This mode corresponds to an anti-phase vibration of the anions (Se-Se and S-S) in the lattice following the crystallographic directions X-Y of the crystal, while the cations (Cu, In) remain at rest[17], [27], [28].

In particular, the *A* mode to *pseudo-quaternary* compounds with Chalcopyrite structure is extremely sensitive to the chemical variations, so the S content in the compound CISS influences the position and the intensity of the peak corresponding to the vibration Se-Se[27]. For all our samples, we observed a shift in the peak corresponding to the vibration Se-Se about 20 cm^{-1} with respect to the $CuInSe_2$ (173 cm^{-1}) phase (see Table 4); this result along with the data previously reported[28] allow us to confirm the obtaining of compounds CISS via microwave radiation with a composition S: Se in a close relationship of 1: 1.

Table 4. Frequency and proposed mode assignment of Raman peaks from solid solutions CISS compared with experimental data reported.

Samples CISS				Symmetry	References
CM	*MW2*	*MW3*	*MW4*		
127	123	126	125	B_1	[26]
164	162	160	161	B_1	[26]
194	191	190	189	A_1	[17], [27], [28]
218	220	220	219	B_2, E	[27]
258	253	252	246	E	[26], [29]
-----	265	265	264	E	[26], [29]
292	291	290	289	A_1	[17], [28]
326	323	323	319	B_2, E	[27]

The remaining peaks at 125, 160, 220, 255, 265 and 326 cm^{-1} were assigned to the following modes of vibration. The peaks around 125 and 160 cm^{-}1correspond to the *B* mode, and are attributed to the vibration phase of the atoms Cu and In[26]. For the peaks around 220 and 323 cm^{-1}, a similar behavior to the one observed in the *A* mode occurs; these peaks have been assigned to the *E* and *B2* modes, whose transverse components are observed in the intermediates (CISS), while the longitudinal counterpart of this mode has been detected only for the extreme compounds ($CuInS_2$ and $CuInSe_2$)[27] .With respect to the peak at about 255 cm^{-1} and the peak at 265 cm^{-1} for the CISS phases synthesized via microwave (Figure 4, *MW2*), two interpretations have been reported. Zaretskaya et. al.[30] and Ishii et. al[31] attribute these peaks to the more intense modes for the CuS and CuSe compounds respectively, meanwhile Rincon et al.[26] and Tverjanovich et al.[29] attribute these peaks to the *E* mode in the Chalcopyrite.

3.3 Diffuse reflectance analysis

In order to determine the band gap width of the synthesized CuInSSe phases, the reflectance diffuse was measured using a UV-Vis spectrometer. The optical gap of the compounds was calculated using the Tauc model[32], which can be described by equation 2:

$$\alpha \mathrm{h\nu} = \mathrm{A}\,(\mathrm{h\nu} - E_g)^{\mathrm{n}} \qquad (2)$$

In this expression α is the linear absorption coefficient of the material; A is a proportionality constant; hν is the photon energy; E_g is the band gap; n = 1/2 is a characteristic value for semiconductors that have transitions from the valence band to the direct conduction band type. To determine the gap by this method, it is plotted $(\alpha h\nu)^2$ against hν, being the value of the energy gap E_g the intersection point of straight line of the graph.

Figure 6 shows the plot and the linear-fit zone for all compounds. The extrapolation allowed to determine the experimental gap with values between 1.21 and 1.29 eV which is consistent with gaps reported for the $CuIn(S,Se)_2$ phase obtained by other methods of synthesis[10]–[12] and with an intermediate value in respect to their ternary $CuInSe_2$ and $CuInS_2$

phases at 1.00 and 1.45 eV, respectively[13], [33], [34]. We highlight that the correlation coefficients obtained from the adjustments are considered within an excellent range for the technique used.

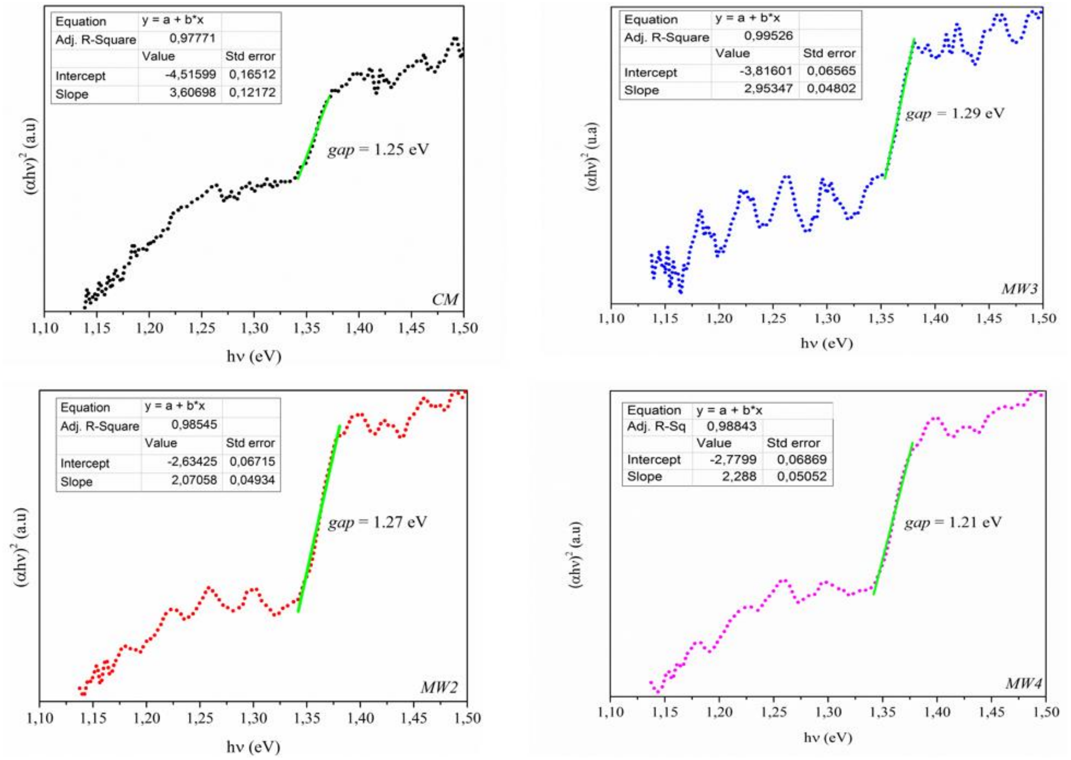

Fig. 6. Plot of (αhν)^2 against photon energy (hν) for samples CM, MW2, MW3 and MW4.

These results suggest that we have obtained products with semiconductor quality, making the synthesized CISS via microwave be a candidate to be used as absorbents in photovoltaic solar cells [21].

4. Conclusion

This paper presented a comparison of the vibrational and optical characterization of the CuInSSe compound synthesized through the microwave radiation (in a reaction of minutes) and ceramic method (in a reaction of days). Furthermore contrasting with the conventional method, the particle size is regulable with the time of microwave radiation method.

The experimental results confirm that the products obtained via microwave radiation present physical and chemical characteristics similar to those obtained by the conventional method. Thus, the X-ray diffraction shows that the compounds obtained belonging to Chalcopyrite-type, crystallized in the space group $I\bar{4}2d$. The Raman spectra allowed us to confirm that we are in the presence of the pseudo-quaternary phase showing the characteristic peaks and displacements for this type of structure and not the mechanical mix of their ternary phases. Regarding the diffuse reflectance spectra, we confirmed that the compounds obtained via microwave radiation have an average band gap of 1.25 eV. The latter is a promising result because previous studies indicated that the obtained products did not have the quality of a semiconductor.

Finally, we highlight that the synthesis via microwave radiation is a successful method for growing CuInSSe polycrystalline by accelerating the reaction in a factor of 10^3 with respect to the ceramic method.

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