Investigation of single phase Cu$_2$ZnSn$_{1-x}$Sb$_x$S$_4$ compounds processed by mechanochemical synthesis

F. Neves,$^1$* A. Stark,$^2$ N. Schell,$^3$ M. J. Mendes,$^3$ H. Aguas,$^3$ E. Fortunato,$^3$ R. Martins,$^3$ J. B. Correia,$^1$ and A. Joyce$^1$

$^1$LNEG, Laboratório Nacional de Energia e Geologia, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal
$^2$Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Str. 1, D-21502 Geesthacht, Germany
$^3$JN/CENIMAT, Department of Materials Science, Faculty of Science and Technology, Universidade NOVA de Lisboa and CEMOP/UNINOVA, Campus de Caparica, 2829-516 Caparica, Portugal

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The copper zinc tin sulfide (CZTS) compound is a promising candidate as an alternative absorber material for thin-film solar cells. In this study, we investigate the direct formation of Cu$_{1+y}$Zn$_n$Sn$_{1-x}$S$_x$ compounds [CZT(A)S], with $x = 1, 0.85, 0.70,$ and 0.50, via a mechanochemical synthesis (MCS) approach, starting from powders of the corresponding metals, zinc sulfide, and sulfur. The thermal stability of the CZT(A)S compounds was evaluated in detail by in situ synchrotron high-energy x-ray diffraction measurements up to 700 °C. The CZT(A)S compounds prepared via MCS revealed a sphalerite-type crystal structure with strong structural stability over the studied temperature range. The contribution of the MCS to the formation of such a structure at room temperature is analyzed in detail. Additionally, this study provides insights into the MCS of CZTS-based compounds: the possibility of a large-scale substitution of Sn by Sb and the production of single phase CZT(A)S with a Cu-poor/Zn-poor composition. A slight increase in the band gap from 1.45 to 1.49–1.51 eV was observed with the incorporation of Sb, indicating that these novel compounds can be further explored for thin-film solar cells.

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I. INTRODUCTION

According to recent review studies, the production of conventional wafer-based photovoltaic (PV) modules for large-scale application (TW scale) raises questions of sustainability [1,2]. The development of alternative thin-film PV technologies based on abundant and preferably nontoxic elements will alleviate the pressure on all PV technologies in terms of costs and resources [3–5]. The chalcogenide compound Cu$_2$ZnSnS$_4$ (CZTS) is being considered as a very promising absorber material for single junction thin-film solar cells (TFSCs) and for tandem cells due to its numerous advantages [6–8], namely the high abundance and low toxicity of the constituent elements, a suitable direct band gap ($E_g$) ($\sim$1.5 eV), and a high absorption coefficient ($>10^5$ cm$^{-1}$). The current record efficiency of CZTS thin-film solar cells has reached 9.2% [9].

The partial substitution of the cationic elements (e.g., Cu by Ag or Li, Zn by Cd, Fe, or Mn, and Sn by Ge) is seen as one reliable mechanism for tuning the $E_g$ of CZTS and for improving its performance [7,10–12]. A recent theoretical study based on first-principles calculations predicted that doping (i.e., the incorporation of a very small amount of another element) CZTS with antimony (Sb) will result in an increase in the photocurrent and in an improved solar cell efficiency [13]. It was also found that Sb prefers to substitute Sn atomic sites [13]. Furthermore, Sb and Na doping were reported to facilitate the crystallization of the CZTS phase due to the formation of Sb$_2$S$_3$ and NaSb$_2$S$_3$ in thin films produced through a solution-based route [14]. This increase in the degree of crystallization was also linked to preferential interactions of Sb with Sn ions and Na with Cu ions, leading to a decrease in site disorder [14].

Due to its complex chemistry, the production of pure CZTS-based absorbers is always a challenge to researchers. Several processing routes have been investigated, such as sputtering and vacuum evaporation of metals or constituent metal binaries followed by chalcogenization, electrodeposition, a hydrazine solution-based process, and colloidal techniques [15–19]. However, due to some unfavorable features, e.g., the need for high vacuum and the use of highly toxic and unstable solvents, these techniques are not appropriate for large-scale solar cell fabrication. An alternative and potentially more affordable approach is the use of powder technologies, starting from elemental or binary compounds [20–23]. One successful process for the synthesis of CZTS powder is based on the solid-state reaction technique of pure elements in evacuated silica ampoules [20,23]. However, this procedure consists in three steps involving high temperatures (750–820 °C) coupled with long processing times. Due to these characteristics, it was found that the final composition of the sample was not easy to control. More recently, several studies have indicated mechanochemical synthesis (MCS), a solid-state synthesis route using high-energy ball mills, as a suitable and fast way for CZTS powder production [24–30]. In those studies, it is clearly demonstrated that the chemical reactions are activated, near room temperature, by the high levels of the mechanical energy input. This energy results in defects and structural changes that affect the chemical reactivity of the solids being processed [24,31].

As reported in the literature [23,32,33], CZTS compounds can exhibit several crystal structures (Fig. 1): kesterite, staninite, disordered kesterite, PMCA (primitive mixed CuAu-like), and sphalerite. The two main and more stable structure types

*Corresponding author: filipe.neves@lneg.pt
FIG. 1. Crystal structures reported in the literature for CZTS [32]: (a) Kesterite, (b) stannite, (c) disordered kesterite, (d) PMCA (primitive mixed CuAu-like), and (e) sphalerite.

are kesterite and stannite, while sphalerite is considered a high-temperature phase. Experimental studies, using either synchrotron x-ray diffraction or neutron diffraction, have shown that the formation of a kesterite structure with a perfect Cu/Zn ordering is difficult to achieve [23,27,32,33]. Instead, those studies always report the existence of a partial or complete disorder of Cu and Zn on the 2c and 2d positions. The occurrence of this cation disorder gives rise to the disordered kesterite structure [Fig. 1(c)] with Cu and Zn sharing the 4d position. Apparently, the level of disorder depends significantly on the cooling rate after sample synthesis [27,32,33]. Moreover, it was recently shown that, depending on the cation ratio, the 2a site was equally or more disordered than the 2c and 2d sites [32]. Consequently, the model for the fully disordered structure should contemplate Cu-Zn mixing on all sites. Furthermore, the solid-solid phase transition from the disordered kesterite-type structure to the sphalerite-type structure has been suggested to occur in the temperature range of 866–883 °C [23] or 977–1002 °C [32], with this transition temperature being dependent on the composition.

In this study, CZT(A)S compounds were synthesized by MCS, and their thermal stability was characterized by means of in situ synchrotron x-ray-diffraction (XRD) measurements. Complementarily, the CZT(A)S powder particles were also analyzed by electron microscopy, spectrophotometry, laser diffraction, and Raman spectroscopy. We show the feasibility of processing CZT(A)S compounds with a sphalerite-type crystal structure having an $E_g$ ranging between 1.45 and 1.51 eV.

II. EXPERIMENT

Elemental powders of Cu (99.9%, 10 μm), Sn (99.8%, <45 μm), Sb (99.5%, <149 μm), and ZnS powder (99.99%, <50 μm) and S pieces (99.999%, random size) were mixed to the desired composition for the synthesis of Cu$_{1+x}$Zn$_x$Sn$_{1-x}$S$_4$ [CZT(A)S, with $x = 1$, 0.85, 0.70, and 0.50]. For convenience, the following references will be used throughout the text: “CZTS” for $x = 1$, “CZTAS (85/15)” for $x = 0.85$, “CZTAS (70/30)” for $x = 0.70$, and “CZTAS (50/50)” for $x = 0.50$. The molar ratio of Cu(Zn+Sn+Sb) is less than 1, aiming to produce Cu-poor CZTS powders. Afterward, mechanochemical synthesis (MCS) was performed on a high-energy planetary ball mill PM 400 from Retsch. The mixtures were milled during 2 h at 400 rpm with a ball-to-powder ratio (BPR; weight of the balls to the powder) of 20:1, using DIN 1.4034 stainless steel containers (250 mL) and balls (15 mm diam), without any additional fluid medium. The containers were evacuated and back-filled with argon to prevent oxidation during MCS. The
process was interrupted for 5 min, after each 10 min of milling, to cool the containers.

Particle size distributions of the mechanochemical synthesized CZT(A)S powders were evaluated by laser scattering (Cilas 1064 equipment) from a powder suspension in water under mechanical agitation after a 60 s sonication. For each powder mixture, three measurements were carried out to calculate the parameters of the particle size distribution (D10, D50, and D90).

Morphological and microstructural observations were carried out by electron microscopy, in both secondary electron and backscattered configurations, using a Philips XL30 field emission scanning electron microscope (SEM), fitted with a backscattered electron detector (BSE). Local phase composition was determined by making three measurements in three different particles of each powder mixture using energy-dispersive x-ray spectroscopy (EDS), with an EDAX sapphire (SUTW) detector.

Raman spectroscopy experiments were carried out with a Renishaw inVia Qontor confocal Raman microscope, using an excitation wavelength of 532 nm and an 1800 groove/mm grating, yielding a resolution of 0.9 cm⁻¹. The light was focused with a 20 × objective and the laser power on the sample was 0.5 mW, in order to avoid damaging the sample. Spectra were acquired under 30 s of signal collection time and four accumulations [34].

The determination of the optical band-gap energy (E₉) of the CZT(A)S powders was achieved by collecting diffuse reflectance spectra over the spectral range of 350–1300 nm using a Perkin-Elmer Lambda 950 UV/Vis/NIR Spectrophotometer equipped with a 4-in. integrating sphere.

To evaluate the structural stability range of the mechanochemical synthesized CZT(A)S powders, several thermal cycles were carried out on the High Energy Materials Science (HEMS) Beamline P07 (EH1) at PETRA III (DESY, Hamburg). The experimental setup was composed of a high-energy x-ray monochromated incident beam (0.14235 Å) with a cross section of 0.1 mm × 0.7 mm, a heating chamber of a Bähr DIL-805 dilatometer, with beam entrance and exit windows at the beam height, and a two-dimensional (2D) detector consisting of a Perkin-Elmer XRD 1621 Flat Panel (pixel size of 200 μm × 200 μm) placed at a distance of 1500 mm from the sample position. Based on this experimental setup, the angular resolution of the detector was estimated to be 0.008°. For the synchrotron radiation experiments, the synthesized CZT(A)S powders were cold pressed into cylindrical compacts of 3 mm diameter and 5 mm height. To control the temperature, a R-type thermocouple was spot-welded to a Ta foil, which was then placed in direct contact with one of the bases of the cylindrical compacted sample surface in an area that stayed outside the beam. The compact samples were then placed inside quartz tubes, having 4 mm of external diameter and 10 mm height. Quartz wool was placed at the ends of the quartz tubes as a protective measure and to maintain the sample in the right position. All samples were heated to 700 °C at 20 K/min, with a 2 min holding time, followed by quenching. Before each cycle, the heating chamber was evacuated (10⁻⁵ mbar) and back-filled with argon. Throughout each experiment, 2D images were acquired every 13–14 s. The 1D diffractograms were obtained by radial integration of the 2D images. Structural refinements were performed with the PowderCell 2.4 software using a pseudo-Voigt function for fitting the x-ray diffraction peaks [35]. The starting models for the different CZTS crystal structures were based on the data given in Fig. 1. The weighted profile R-factor, R_p, was used as the criterion for refinements. The crystallite size of the mechanochemical synthesized CZT(A)S powders was evaluated using the Scherrer equation.

III. RESULTS AND DISCUSSION

The morphology of the mechanochemical synthesized CZT(A)S powders was studied using SEM. Figure 2 exemplifies the resulting morphologies for the CZTS and CZTAS (50/50) powders [Figs. 2(a) and 2(b) and Figs. 2(e) and 2(f), respectively]. It can be seen that the MCS gave rise to CZT(A)S powder particles with irregular shape having more or less two fraction types—one in the nanometer/submicron scale and another on the order of a few micrometers. These observations were corroborated with laser scattering, where it was found that the particle size distribution curves (Fig. 3) and the obtained D-values (Table 1) range between ~200 nm and ~20 μm.

Figure 3 shows a particle size distribution of the mechanochemical synthesized CZT(A)S powders that is multimodal, typically bimodal for the CZTS powders, and trimodal for the CZTAS powders. Moreover, the median particle size clearly increases with the replacement of Sn by Sb, reaching its maximum in the CZTAS (70/30) powders. The parameters of the particle size distribution (D-values) shown in Table 1 put that effect in evidence with all CZTAS powders showing higher values when compared with those of CZTS powders. The median particle size (D50) increases twofold with the replacement of Sn by Sb. Similar effects are seen for the top and bottom deciles of the distribution (D90, D10). Moreover, Fig. 2 clearly reveals that during the MCS process, the individual nano/submicrparticles have a tendency to aggregate into nano/submicroparticle agglomerates. Similar results were obtained for the morphology of the CZTAS (85/15) and CZTAS (70/30) powders.

The SEM/BSE images of Figs. 2(c) and 2(g) reveal a microstructure having a relatively good level of homogenization. EDS analysis was used to determine the chemical composition of the mechanochemical synthesized CZT(A)S powders. As is exemplified in Figs. 2(d) and 2(h) for, respectively, the CZTS and CZTAS 50/50 samples, EDS analysis confirmed that the synthesized materials were only constituted by CZTS or CZTAS powder particles with no detectable impurities. In turn, the measured Zn/Sn, Zn/(Sn+Sb), Cu/(Zn+Sn), and Cu/(Zn+Sn+Sb) composition ratios indicate that the MCS led to the formation of off-stoichiometry CZTS and CZTAS compounds. All the produced compounds show a Cu-poor/Zn-poor composition. According to a recent cation ratio plot available in the literature [26], the prepared compounds may be associated with the so-called E-type (Cu-poor, Zn-poor region) off-stoichiometric CZTS compounds. Most probably, this unprecedented result can be attributed to the use of the MCS. During this process, the transfer of mechanical energy to the powder particles results in the introduction of strain into the powder, through the generation of dislocations and other
defects that act as fast diffusion paths changing the reactivity of the pristine powders [31].

It is then evident that the synthesis of single phase CZT(A)S powder may be considered a simple task if the MCS experimental conditions described in the present study are used. This is a considerable achievement considering the short duration (2 h) of the MCS process. In fact, in the literature there are no reports showing the direct formation of single phase CZTS powder in such a short time through MCS and starting from mixtures mostly composed by elemental powders [24,25,28–30]. For example, in Refs. [28], [29], and [30], pure phase CZTS powder was only obtained after
FIG. 3. Typical particle size distribution curves of the mechanochemical synthesized CZT(A)S powders. (a) CZTS, (b) CZTAS (85/15), (c) CZTAS (70/30), and (d) CZTAS (50/50).

The thermal stability of the produced CZT(A)S powder was evaluated by in situ x-ray synchrotron radiation measurements. Figure 4(a) shows a sequence of 1D diffractograms obtained between 30 and 700 °C for all mechanochemical synthesized CZT(A)S powders. For the CZTS and CZTAS (50/50) samples, we also show the 1D diffractogram obtained at the end of the heating cycle, i.e., at 30 °C after cooling. The refinements performed on all diffractograms confirmed the absence of secondary phases in the synthesized powders. The best fitting for all the samples, within the tested temperature interval, was obtained with the cubic sphalerite-type structure, with all the other phase structures being ruled out due to poor fitting. The obtained $R_{wp}$ values ranged between 0.123 and 0.136. The indexation of the sphalerite-type structure to all the synthesized CZT(A)S powder mixtures is very interesting, as this phase has only been detected at high temperatures (over 866 °C) and has not been reported under equilibrium conditions [23,32]. It can be seen in Fig. 4(a) that, under the experimental conditions used in this work, the sphalerite-type structure formed with the MCS is stable up to 700 °C and was kept after cooling.

Figure 1(e) puts in evidence that the sphalerite structure is characterized by a fully disordered arrangement in all the cation (Cu, Zn, and Sn) positions. It should be remembered that with MCS the ordered materials get disordered due to the heavy deformation involved in the process [31]. Also, the formation of high-temperature phases with the MCS has already been reported for other alloys and chalcogenide systems [36,37]. Therefore, it is possible that the kesterite phase became disordered during milling, and consequently the disordered cubic phase was formed. Understanding these processes represents one of the fundamental challenges of the MCS.

At this point, it is also important to distinguish between thermal and mechanochemical processes. The MCS is a mechanically activated process that takes place under nonequilibrium conditions, with the chemical reactivity being promoted by unbalanced mechanical forces [31]. Moreover, whereas temperature is an intensive thermodynamic state variable, mechanical deformation occurs on a local basis, being mediated by dislocations and other lattice defects [31]. As a result, it can be expected that in the MCS the mass transport process will be reduced relative to that of high-temperature solid-state diffusion, with a great impact on the chemical and physical behavior of the compounds. Considering that the action of mechanical forces on solid substances frequently leads to polymorphism, this phenomenon may have also occurred in the mechanochemical synthesized CZT(A)S powders.

The partial substitution of Sn by Sb resulted in the shifting of the XRD peaks of the sphalerite-type structure to higher diffraction angles. This can be clearly seen in Fig. 4(b).
where the 1D diffractogram taken at 30 °C for the CZTS sample is compared with that obtained for the CZTAS (50/50) sample. Such a shift was maintained with the increase of the temperature, as also exemplified in Fig. 4(b) for the 1D diffractograms taken at 700 °C. From Fig. 4(c), which shows the lattice parameter \( a \) for the CZTS and CZTAS (50/50) samples, it can be inferred that the XRD peak shift results from the crystal lattice contraction due to substitution of Sn by the smaller ion Sb. Furthermore, Fig. 4(d) puts in evidence the dependence of the lattice parameter with the CZT(A)S compositions. As it can be seen, the lattice parameter of the mechanochemical synthesized CZT(A)S powders changes linearly with composition (it shows a constant and systematic decrease associated with the contraction of the crystal lattice due to the substitution of Sn by Sb) and follows Vegard’s law. That variation was of the order of 0.0032 Å per atomic
percentage of Sb. From Fig. 4(d) it can also be inferred that the differences between the obtained crystallite sizes for all the mechanochemical synthesized samples are not significant as they ranged between a minimum of 11.5 nm and a maximum of 12.3 nm. These two results, the linear decrease of the lattice parameter with Sb and the quite marginal differences between the crystallite sizes, are an indication that Sb is on a substitutional site.

It is important to highlight that the overall results shown in Fig. 4 exclude the hypothetical formation of any secondary phase during the MCS, such as, for example, an amorphous Sb2S3 phase. First, the 1D diffractograms taken at different temperatures [Fig. 4(a)] do not reveal the crystallization of this hypothetical amorphous phase [considering that the crystallization temperature of Sb2S3 is 320 °C [14], the maximum temperature achieved (700 °C) is a temperature high enough for this process to occur]. Secondly, the variation of the lattice parameter [Fig. 4(d)] can be based on Vegard’s law as it shows a linear decrease associated with the contraction of the CZTS lattice due to the substitution of Sn atoms by Sb atoms. If hypothetically the solubility limit of Sb in CZTS was reached, the lattice parameter of CZTS would have remained constant with the increase of Sb and would imply the precipitation of a second phase. However, this was not observed.

Additionally, Fig. 4(c) also reveals a steady increase of the lattice parameter with the temperature. That increase can be fitted to a straight line allowing the calculation of the coefficient of thermal expansion (CTE). The obtained values were about $3 \times 10^{-6} \text{K}^{-1}$ for all the samples, which are in good agreement with values published in the literature for CZTS and CIGS [38,39]. The CTE is an important mechanical property for thin films as many problems can arise from the thermal expansion effect. For example, residual stresses can form due to the mismatch of thermal expansion between the different layers of thin-film solar cells (including between the active layers and the substrate, e.g., the CTE of soda-lime glass is $9 \times 10^{-6} \text{K}^{-1}$, for flexible polyimide substrate it is $20 \times 10^{-6} \text{K}^{-1}$, while for CdS it is $5 \times 10^{-6} \text{K}^{-1}$) [40–42]. It is also worth mentioning that, after the thermal cycle, the obtained values for the lattice parameter were slightly lower when compared to the initial ones. This is again exemplified in Fig. 4(c) for the CZTS and CZTAS (50/50) samples. These results can be associated with an enhancement in crystallinity.

Raman spectroscopy, Fig. 5, is broadly consistent with CZTS modes, which also supports the single-phase hypothesis, in agreement with the results presented above for the EDS analysis and for the XRD measurements. In all mechanochemical synthesized samples, Fig. 5(a), the most intense peak is located at $\sim 332–333 \text{cm}^{-1}$ while minor peaks are located at $\sim 254–258$, $\sim 289–294$, $\sim 315$, and $\sim 372–375 \text{cm}^{-1}$. These values are close to the experimental and theoretical values reported for the most common Raman peak positions of the CZTS modes, which are known to be located at $337 \text{cm}^{-1}$ (A mode), $375 \text{cm}^{-1}$, $287 \text{cm}^{-1}$, and $254 \text{cm}^{-1}$ [43,44]. Relative to these positions, all the obtained Raman peaks show a peak shift and a general peak broadening that can be explained as a direct effect of the MCS and of the formation of CZT(Al)S powders having a sphalerite-type structure. This may be due to the existence of disordered effects in the powders, such as strain, dislocations, and other lattice defects that cause a reduction in the phonon correlation length [25,33,43]. Slightly more narrow Raman peaks were obtained as a result of the heat treatment, as exemplified in Fig. 5(b) for the CZTS sample. This can be interpreted as an improvement in the crystallinity starting from a disordered structure, as reported for CZTS samples with low crystal quality [43].
that a similar effect is present in the disordered sphalerite structure. The strongest Raman peaks in CZTS samples with low crystal quality are also shifted toward lower wave numbers [43]. The Tauc plot for each mechanochemical synthesized powder sample is shown in Fig. 6. The $E_g$ determination procedure from the diffuse reflectance measurements was based on the Kubelka-Munk model and is described in [46]. The obtained $E_g$ values ranged between 1.45 eV, for the CZTS sample, and 1.49–1.51 eV, for the CZT(A)S samples. Although no trend could be established with the Sb content variation, the $E_g$ results indicate a slight increase with the substitution of Sn by Sb. This slight increase opens the possibility of producing CZT(A)S compounds with $E_g$ higher than 1.5 eV, which can be viewed as a very promising result and can facilitate their potential application as an alternative absorber material for the top cell in tandem devices. Moreover, it was reported that the substitution of Sn by Ge leads to an increase of $E_g$ and, consequently, to the improvement of the open-circuit voltage [7,11,12]. It is also important to emphasize that in a recent theoretical study it was suggested that the substitution of Sn atoms by Sb has a lower energy than that by Cu, resulting in fewer Sn atomic sites that can be substituted by Cu [13]. Consequently, they predicted the reduction of antisite defects with benefits for the open-circuit voltage and the solar cell efficiency [13]. Future work will continue to explore the very promising findings reported in the present study.

IV. CONCLUSIONS

The results obtained in the present study show the possibility of performing a substantial substitution of Sn by Sb in CZTS compounds produced by mechanochemical synthesis. In situ synchrotron x-ray diffraction (XRD) measurements revealed the successful preparation of single phase $\text{Cu}_{1.02}\text{ZnSn}_x(\text{Sb}_{1-x})_4$ compounds having a cubic sphalerite-type structure. Furthermore, it was found that this structure was stable up to 700 °C. The formation of such a structure was attributed to several typical phenomena that are connected with the mechanochemical synthesis process. Additionally, EDS analysis showed that the mechanochemical synthesis led to the production of off-stoichiometry CZTS and CZTAS powder compounds with a Cu-poor/Zn-poor composition. The incorporation of Sb leads to a slight increase in $E_g$ from 1.45 to 1.49–1.51 eV. Finally, it can be concluded that CZTAS compounds exhibit promising optical and structural properties for absorber materials in thin film solar cells.

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