

Investigation of single phase $\text{Cu}_2\text{ZnSn}_x\text{Sb}_{1-x}\text{S}_4$ compounds processed by mechanochemical synthesisF. Neves,^{1,*} A. Stark,² N. Schell,² M. J. Mendes,³ H. Aguas,³ E. Fortunato,³ R. Martins,³ J. B. Correia,¹ and A. Joyce¹¹LNEG, Laboratório Nacional de Energia e Geologia, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal²Institute of Materials Research, Helmholtz-Zentrum Geesthacht, Max-Planck-Str. 1, D-21502 Geesthacht, Germany³IN/CENIMAT, Department of Materials Science, Faculty of Science and Technology,

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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 $\text{Cu}_{1.92}\text{ZnSn}_x(\text{Sb}_{1-x})\text{S}_4$ 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 $700^\circ\text{C}.$ 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 $1.49\text{--}1.51$ 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 $\text{Cu}_2\text{ZnSnS}_4$ (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) (~ 1.5 eV), and a high absorption coefficient ($> 10^4$ 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 improvement of 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_2S_3 and NaSb_5S_8 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 ($750\text{--}820^\circ\text{C}$) 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, stannite, disordered kesterite, PMCA (primitive mixed CuAu-like), and sphalerite. The two main and more stable structure types

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