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Synthesis and performance optimisation of spray coated $\text{Cu}_2\text{ZnSnS}_4$ absorbing layers from single-source xanthate precursors

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Abstract

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a promising non-toxic and cheap absorber layer for the use in photovoltaic cells. In this work copper, zinc and tin xanthates were synthesised and deposited using a single-source spray coating technique to produce CZTS thin films, to investigate how the ratio of these precursors can alter the performance of the device. It was determined that using a tin rich xanthate precursor mix resulted in the thin film with the chemical composition closest to CZTS, with few contaminating phases (i.e. Cu_{2-x}S , Cu_2SnS_3 and ZnS). To explain this observation, isothermal thermal gravimetric analysis was used to determine rate constants for the decomposition of these xanthate precursors. The rate constants of copper xanthate and zinc xanthate align very well (1.26 and 1.24 s^{-1} respectively). However, the rate constant for tin xanthate differs significantly (1.09 s^{-1}). Therefore, to form the appropriate ratio in the final product, a tin rich precursor mixture is required. This tin rich xanthate sample was shown to have a band gap of

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1.73 eV and a power conversion efficiency of 0.15 %.

Keywords: Copper zinc tin sulfide; Xanthate; Spray deposition; Thin Film Solar Cells

1. Introduction

CZTS solar cells refer to a thin film of $\text{Cu}_2\text{ZnSnS}_4$, a semiconducting material consisting of only abundant, cheap and non-toxic materials, and a band gap of roughly 1.5 eV [1–7]. Solar cells utilising CZTS absorber layers have been shown to display Power Conversion Efficiencies (PCEs) exceeding 10 %, and are predicted to continually rise [3, 6]. Therefore, CZTS based solar cells have attracted much interest in recent years.

In an effort to try and prepare these devices, many different deposition methods have been investigated to optimise the performance of CZTS films, including electrochemical deposition [8–10], magnetron sputtering [5, 11–15], inkjet printing [16], spray pyrolysis [17, 18], and spin coating [3]. However, these prevalent methods deposit CZTS as a two-step process, requiring additional sulfurisation steps [10, 14, 15, 17–20]. Using a two-step method adds additional costs and scale-up issues when looking for the future industrialisation of the technique. On the other hand, by developing a single-step deposition technique that could effectively deposit CZTS, the future industrialisation of this technique could be greatly enhanced. It has been reported that spray coating is an effective single-step deposition technique [21]. Due to the inherent simplicity of this technique, high speed fabrication of devices is possible for laboratory applications, while also allowing for easy scale-up to commercialisation [21]. Though, this would require the use of an appropriate single-source precursor, to enable the deposition of a metal sulfide without the need for an additional sulfur source.

Therefore, it is highly beneficial to select an appropriate precursor for the single-step deposition of CZTS active layers, while also utilising a highly scalable process. Furthermore, the selected precursor should preferably function as a low temperature precursor, as it has been well reported that high temperatures can result in the loss of volatile components (such as SnS and S) damaging the stoichiometry of the CZTS active layer [18, 20, 22–24].

Metal xanthates have been used as a low temperature single-source precursor to form metal sulfides, with the general formula $[\text{M}(\text{S}_2\text{COR})_n]$, where R is an alkyl group, and have been shown to be viable precursors for $\text{Cu}_2\text{ZnSnS}_4$

59 Therefore it is of great significance to address how the chemical composition
60 of the precursor mix alters the device.

61 This work focuses on the synthesis and spray coating of four metal xan-
62 thate precursors (Cadmium Ethyl Xanthate, Copper (I) Ethyl Xanthate, Zinc
63 Ethyl Xanthate and Tin (IV) Ethyl Xanthate). These samples were deposited
64 using spray coating, a previously utilised technique with high versatility and
65 low cost [7, 31, 32]. The chemical composition of the single-source precursor
66 was altered to investigate how this impacts the performance of deposited
67 devices. Isothermal Thermal Gravimetric Analysis (TGA) was conducted in
68 order to determine the rate constants for decomposition for the metal xan-
69 thate precursors, allowing for key issues and results to be highlighted for
70 fabricating a CZTS based solar cell using a single-source precursor process.

71 2. Methodology

72 2.1. Metal Xanthate Synthesis

73 Each procedure of xanthate synthesis followed a similar synthetic route
74 proposed by Agrawal et al [33].

75 2.1.1. Cadmium Ethyl Xanthate (*CdXan*) synthesis

76 3.5 g of potassium ethyl xanthate dissolved in 20 ml of de-ionized water
77 and added drop wise to 1 g of cadmium chloride dissolved in 20 ml of de-
78 ionized water. This aqueous solution was then stirred for 24 hours, revealing a
79 pale yellow precipitate. Finally, the prepared precipitate was filtered, washed
80 with de-ionized water and dried at 50 °C.

81 ^1H NMR (300 MHz, CDCl_3): $\delta = 4.43$ (q, 4H), 1.32 (t, 6H) ppm.

82 Calc. for $\text{C}_6\text{H}_{10}\text{O}_2\text{S}_4\text{Cd}$ (%): C 20.3, S 36.1, Cd 31.7; found: C 20.0, S
83 36.2, Cd 32.2.

84 2.1.2. Copper (I) Ethyl Xanthate (*CuXan*) synthesis

85 Copper(II) chloride dihydrate (0.9 g) was dissolved in 20 ml of de-ionized
86 water. Then, an aqueous solution of potassium ethyl xanthate (3.5 g dissolved
87 in 20 ml of de-ionized water) was gradually added drop wise to the copper
88 dichloride solution under gentle stirring. The reaction was allowed to stir
89 for 24 hours. The orange precipitate was filtered off, washed in ethanol and
90 dried under vacuum to obtain CuXan as a yellow powder. It is important
91 to note that, despite the use of copper (II) chloride as a reagent in the
92 synthesis of CuXan, the product is noted to be copper (I) xanthate. This is

93 a well-established phenomena and is attributed to the reduction of the formed
94 copper (II) xanthate to copper (I) xanthate via a self-redox reaction, with
95 metal-free xanthate dimers ((S₂COR)₂) remaining as a byproduct [3, 34].

96 ¹H NMR (300 MHz, CDCl₃): δ = 4.69 (q, 2H), 1.43 (d, 3H) ppm.

97 Calc. for C₃H₅OS₂Cu (%): C 19.5, S 34.7, Cu 34.4; found: C 19.8, S
98 35.5, Cu 34.2.

99 2.1.3. Tin (IV) Ethyl Xanthate (SnXan) synthesis

100 3.5 g of potassium ethyl xanthate was dissolved in 20 ml of de-ionized
101 water and added drop wise to a solution of tin(IV) chloride pentahydrate
102 (1.4 g) dissolved in 20 ml of de-ionized water. This solution was then stirred
103 for 24 hours. The resulting orange paste was then dried at 40 °C, resulting in
104 a dark cream powder. It is worth noting that this precursor is very thermally
105 unstable and will decompose gradually over a period of a week after synthesis.

106 ¹H NMR (300 MHz, CDCl₃): δ = 4.55 (q, 8H), 1.49 (t, 12H) ppm.

107 Calc. for C₁₂H₂₀O₄S₈Sn (%): C 23.9, S 42.5, Sn 19.7; found: C 22.7, S
108 42.3, Sn 20.2.

109 2.1.4. Zinc Ethyl Xanthate (ZnXan) synthesis

110 Zinc(II) chloride (0.7 g) was dissolved in 20 ml of de-ionized water, and
111 3.5 g of potassium ethyl xanthate was dissolved in 20 ml of de-ionized water.
112 Then, the zinc chloride solution was added drop wise to the the potassium
113 xanthate solution, and the resulting solution was stirred for 24 hours. The
114 white precipitate was filtered off, rinsed with de-ionized water, and dried
115 under vacuum at 50 °C revealing a a white powder.

116 ¹H NMR (300 MHz, CDCl₃): δ = 4.59 (q, 4H), 1.49 (t, 6H) ppm.

117 Calc. for C₆H₁₀O₂S₄Zn (%): C 23.4, S 41.7, Zn 21.2; found: C 23.6, S
118 41.5, Zn 21.4.

119 2.2. Substrate Pre-treatment

120 Prior to deposition, each substrate was ultra-sonically cleaned in ethanol
121 for 10 minutes. After cleaning, the substrates were dried and an inert gas
122 was blown onto the films to ensure no remaining dirt was trapped.

123 2.3. CZTS Deposition

124 Metal xanthates were dissolved into a solution of 5 ml pyridine and 1 ml
125 1,2-dichlorobenzene. The solution was then stirred for roughly 10 minutes,
126 allowing for the precursors to dissolve. Once dissolved, these solutions were

127 loaded into the spray coater and deposited onto Indium Tin Oxide (ITO)
128 coated glass for 10 seconds. The spray distance and orientation remained
129 constant for each iteration, a horizontal distance of 10 cm. These samples
130 were then heated to 160 °C for 30 minutes to allow for complete decom-
131 position of the xanthates into their respective metal sulfides. 160 °C was
132 selected as it was shown to be the lowest temperature at which full CuXan
133 decomposition was noted.

134 *2.4. Device Fabrication*

135 After CZTS deposition occurred, CdS was spin coated (using an EZ6
136 Schwan technology spin coater) onto the active layer in order to create a
137 photovoltaic device. A CdXan precursor was utilised to form the CdS accep-
138 tor layer. The precursor was deposited on the CZTS coated substrate and
139 spun for 30 seconds at 1000 rpm. This was then decomposed at 160 °C for
140 30 minutes. Then, 50 nm of gold was sputtered on the CdS layer to function
141 as an electrode.

142 *2.5. Characterisation techniques*

143 NMR resonance ^1H NMR spectra were recorded on a Bruker Ultrashield
144 300, using CDCl_3 solutions at 300 MHz to the singlet of CDCl_3 at 7.26 ppm.

145 Elemental analysis was carried out using Perkin Elmer Series II CHNS/O
146 Analyzer for carbon and sulfur and a Perkin Elmer NexION 300X for copper,
147 tin and zinc.

148 TGA data was collected on SII 6300 EXSTAR in an air atmosphere be-
149 tween 50-300 °C, increasing by 5 °C/minute.

150 The thickness of active layer surfaces were characterised in air using Veeco
151 3100 scanning probe microscope (SPM).

152 Optical characteristics of the samples were measured at room temperature
153 using a Cary 5000 UV-vis absorption spectrometer at a rate of 400 nm/s,
154 between 350–750 nm. One cycle was taken for each sample.

155 A Zeiss Σ IGMA Scanning Electron Microscopy (SEM) operating at 5.0
156 kV was used to determine the morphology, size of the deposited films, while
157 the composition was analysed by Energy Dispersive Spectroscopy (EDS) on
158 an X-Act (Oxford Instrument) coupled with the previously mentioned SEM
159 device.

160 Crystal structures were determined using X-ray diffraction (XRD). XRD
161 patterns were collected using a D8 Advance diffractometer (Bruker) equipped

162 with a copper anode (Cu-K α radiation $\lambda = 0.154$ nm) over the angular range
163 of $10^\circ < 2\theta < 90^\circ$ with a step size of 0.01° at 40 kV and 35 mA.

164 Current-voltage measurements were made using a CHI600E electrochemi-
165 cal workstation under illumination at AM1.5 G (100 mW cm^{-2}) light intensity.

166 3. Results and Discussion

167 3.1. Precursor Characterisation

168 TGA was initially utilised, with a scanning temperature range of 50-300
169 $^\circ\text{C}$ at a ramping temperature of $5 \text{ }^\circ\text{C}/\text{min}$, to determine the decomposition
170 behaviour of the metal xanthates into their respective metal sulfides, see
171 **Figure 2**.

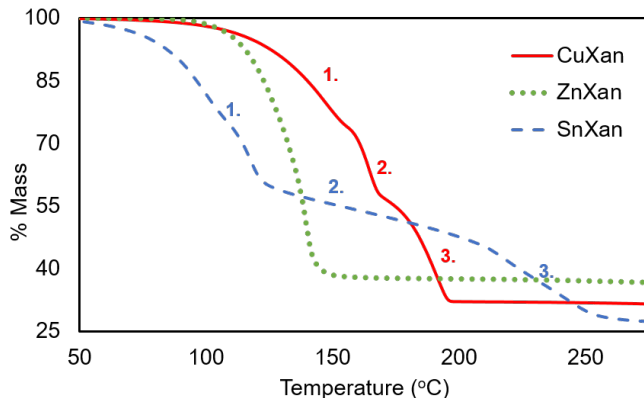


Figure 2: TGA of precursors used in deposition, from 50-300 $^\circ\text{C}$ at a ramping temperature of $5 \text{ }^\circ\text{C}/\text{min}$. Red and blue numbers are shown on the profiles for CuXan and SnXan respectively, to emphasise the three stages of decomposition as shown in **Figure 1**.

172 All xanthate precursors show the expected decomposition behaviour be-
173 low $160 \text{ }^\circ\text{C}$, however, their initial decomposition temperatures vary, as does
174 the steepness of the decomposition curves (as shown in **Figure 2**). Both
175 CuXan and ZnXan start initial decomposition at roughly $115 \text{ }^\circ\text{C}$, though,
176 their decomposition profiles are rather different. ZnXan shows a quite steep
177 one step profile, while CuXan displays a shallower decomposition profile re-
178 vealing three distinct steps (shown by red numbers on **Figure 2**), coinciding
179 with the elimination stages in the Chuagaev elimination reaction (as num-
180 bered in **Figure 1**) [30]. SnXan also shows a similar three step decomposition
181 as CuXan (as shown by blue numbers in **Figure 2**). It can also be seen that

182 despite SnXan having the lowest thermal stability, the presence of a long,
 183 shallow intermediate step suggests a slow rate of decomposition, as steeper
 184 gradients relate to faster rates of decomposition.

185 Despite the variation in decomposition profiles, all xanthates were shown
 186 to have observed percentage mass losses that align closely with the theoretical
 187 values calculated (see **Table 1**).

Table 1: The experimental mass losses of the used precursors at 300 °C and the theoretical percentage mass loss of the precursors after xanthate decomposition.

Precursor	Observed Mass Loss	Theoretical Mass Loss
CuXan	31.74 %	31.25 %
ZnXan	36.56 %	31.66 %
SnXan	27.52 %	30.29 %

188 This correlation shown in **Table 1** suggests the appropriate decomposi-
 189 tion pathway to the metal sulfide, providing evidence for these metal xan-
 190 thates to be viable precursor materials for the deposition of their respective
 191 metal sulfides.

192 3.2. CZTS Thin Film Characterisation

193 The investigation into the fabrication of CZTS solar cells via xanthate
 194 precursors looked into alterations of the xanthate ratios. This can help to
 195 determine the effect that the chemical composition had on the active layers
 196 and therefore the devices. **Table 2** shows the name used to identify the seven
 197 different compositions investigated, as well as the amount of each xanthate
 198 used in the precursor mix and their recorded thicknesses from AFM analysis.

199 These samples were then investigated using SEM/EDS (**Figure 3** and
 200 **4**), XRD (**Figure 5** and **6**) and UV-vis (**Figure 7**).

201 As shown in **Figure 3 a**), CZT displays a very granular layer, with few
 202 crystals evenly blended throughout the material. For all variations from CZT,
 203 these crystalline areas are noted to be more prevalent, with CZ2T and CZT2
 204 (shown in **Figure 3 c**) and **e**) respectively) displaying large patches of this
 205 crystalline phase. EDS analysis was conducted on these sites to colourise
 206 the images depending on the element. Cu is shown in red, Zn in green,
 207 and Sn in blue. From this analysis (see **Figure 3 d**) as an example) it

Table 2: Labels and descriptions of the investigated compositions of CZTS devices deposited.

Label	CuXan(g)	ZnXan(g)	SnXan(g)	Thickness
CZT	0.33	0.34	0.22	1.53 μm
C2ZT	0.66	0.34	0.22	1.65 μm
CZ2T	0.33	0.68	0.22	1.62 μm
CZT2	0.33	0.34	0.44	1.69 μm
C0.5ZT	0.165	0.34	0.22	1.48 μm
CZ0.5T	0.33	0.17	0.22	1.43 μm
CZT0.5	0.33	0.34	0.11	1.35 μm

208 was determined that these crystalline phases displayed a strong green colour,
 209 attributing these phases to Zn.

210 This corresponds with previous observations made in the literature show-
 211 ing that ZnS phases can often form within the CZTS layer [35]. This reduces
 212 the stoichiometric accuracy of CZTS within the active layer and increases
 213 the length of charge transfer, which in turn reduces exciton generation and
 214 increases recombination of excitons. Therefore this ZnS phase can be stated
 215 as a detrimental feature of the active layer. This detrimental feature was
 216 noted in all devices except CZ0.5T (see **Figure 3 g**), and **4**), the zinc poor
 217 sample, which appears the most crystalline out of the samples.

218 **Figure 4 b**) shows that these crystal phases appear to be a blend of Cu-
 219 rich and Sn-rich areas, suggesting further detrimental phases to be present
 220 within the device. These detrimental phases are likely to be copper sulfide
 221 (Cu_{2-x}S) and copper tin sulfide (Cu_2SnS_3), as these have also been previously
 222 noted in CZTS active layers [32, 35, 36].

223 To confirm the presence of these additional phases XRD was conducted
 224 on the deposited samples. **Figure 5** shows the XRD diffractogram for CZT,
 225 with the position of each phase noted on the pattern. **Figure 6** shows a
 226 comparison for samples with varying Cu, Zn and Sn compositions.

227 In **Figure 5** characteristic kesterite ($\text{Cu}_2\text{ZnSnS}_4$) [36], (JSCPDs No. 26-
 228 0575) could be seen at roughly $2\theta = 18, 23, 28, 33, 44, 47$ and 56° . This
 229 shows a good alignment between the material and expected diffractogram,
 230 providing evidence of successful deposition. However, it is important to note
 231 that other crystal phases are likely to also be present. It has also been

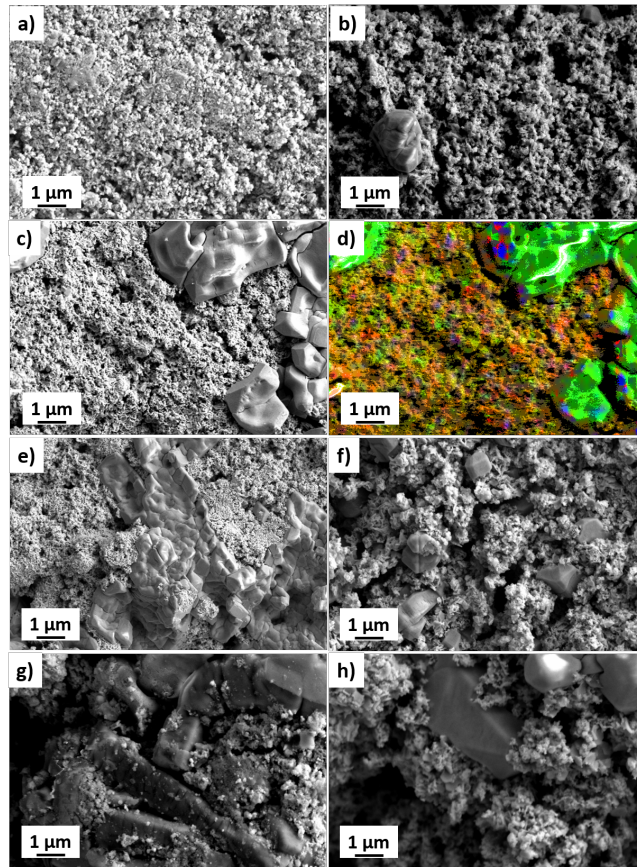


Figure 3: SEM images of a) CZT, b) C2ZT, c) CZ2T, e) CZT2, f) C0.5ZT, g) CZ0.5T and h) CZT0.5. d) shows an EDS mapping image of c) CZ2T, to function as an example for the observed features. For the EDS image Cu is shown in red, Zn in green and Sn in blue.

232 reported that Cu_{2-x}S (JCPDS No. 47-1748), Cu_2SnS_3 (JCPDS No. 27-0198)
 233 and ZnS (JCPDS No. 79-2204) crystal phases have been detected in CZTS
 234 thin films [32, 36]. Cu_{2-x}S has expected diffraction peaks at $2\theta=23, 26, 30, 32,$
 235 $37, 39, 43, 45, 48, 51$ and 56° . Cu_2SnS_3 diffraction peaks could be located at
 236 roughly $2\theta= 16, 18, 21, 24, 28, 31, 34, 38, 42, 48$ and 51° . Diffraction peaks
 237 located at $27, 28, 30, 40, 56$ and 63° (2θ) could also suggest the presence of
 238 ZnS crystal phases within the analysed samples. As the diffraction peaks of
 239 these crystal structures often align, the comparison of multiple peaks is vital
 240 to determine the variation in crystal phase.

241 From **Figure 6 a)**, it is apparent that there are two significant variations

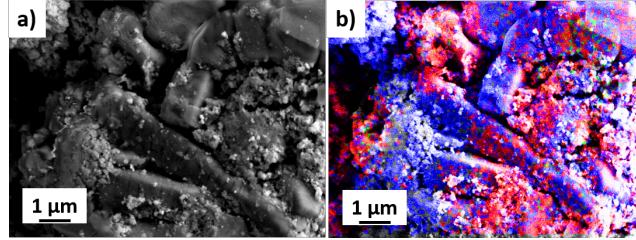


Figure 4: SEM image of a) CZ0.5T. b) shows an EDS mapping image of a) CZ0.5T. For the EDS image Cu is shown in red, Zn in green and Sn in blue.

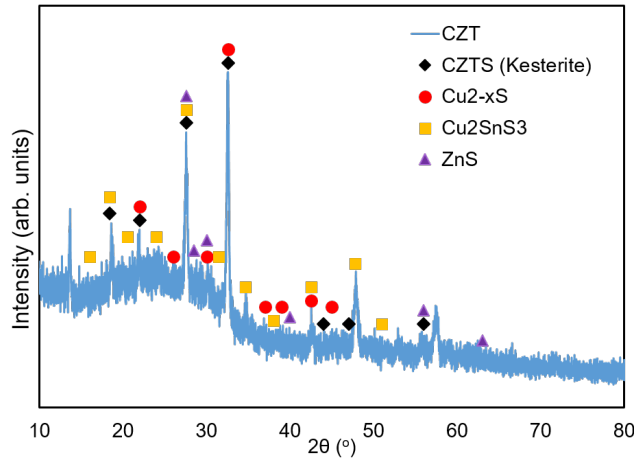


Figure 5: XRD analysis of CZTS using the xanthate mix CZT. All expected peaks for expected phases are shown on the diffractogram.

242 in the diffractograms when altering the amount of CuXan in the precursor
 243 mix. These peaks occur at roughly $2\theta = 16$ and 21° , and suggest the presence
 244 of Cu_2SnS_3 . It can be said that the higher CuXan load within the precursor
 245 mix results in increased intensity for these peaks. Therefore, the increase in
 246 CuXan within the material causes the additional phase of Cu_2SnS_3 to become
 247 more prevalent, which could act as a barrier for carrier transport [36].

248 **Figure 6 b)** displays the variation between the diffractograms with alter-
 249 ing ZnXan load in the precursor. The presence of two additional phases can
 250 be seen with increasing ZnXan load. The increased presence of an additional
 251 ZnS phase can be deduced from the increasing intensity of peaks seen at $2\theta =$
 252 30 and 56° . More intense peaks at $2\theta = 25$ and 31° suggest an additional
 253 layer of Cu_2SnS_3 , while the reduced intensity of $2\theta = 28^\circ$ could suggest a

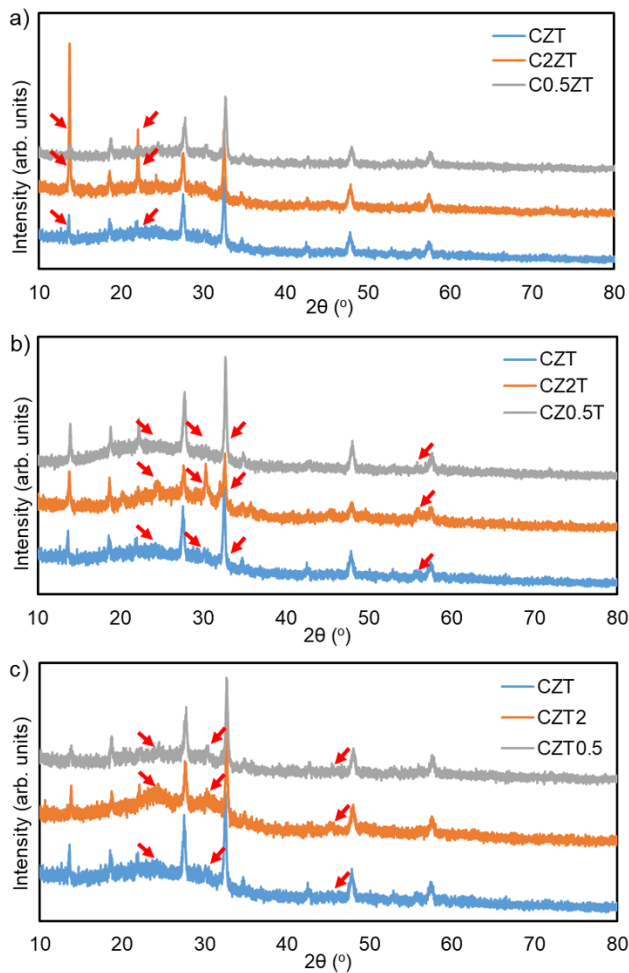


Figure 6: XRD analysis of CZTS xanthate mixes. **a)** presents peaks for CZT, C2ZT and C0.5ZT with key peaks at $2\theta= 16$ and 21° highlighted by red arrows; **b)** reports the peaks for CZT, CZ2T and CZ0.5T with key peaks at $2\theta= 25, 30, 31$ and 56° highlighted by red arrows; and **c)** shows peaks for CZT, CZT2 and CZT0.5 with two bumps noted at $2\theta= 25$ and 30° and a key peak seen at at $2\theta= 44^\circ$ highlighted by red arrows.

254 lower amount of CZTS. It is also worth noting that there is less variation
 255 between the intensity of the peaks seen in the diffractogram for CZ2T. This
 256 could suggest that the sample is highly polycrystalline, resulting in reduced
 257 charge transport and increased recombination of excitons [36, 37]. The low
 258 ZnXan load also displays an increase in intensity for $2\theta= 31^\circ$, suggesting the
 259 presence of Cu_2SnS_3 , this is an expected result due to the lower availability

260 of ZnS to form CZTS.

261 As seen in **Figure 6 c**), after the increase in SnXan load the sample
262 appears to become more amorphous, displaying two bumps at $2\theta=25$ and
263 30° . This suggests the presence of a polycrystalline structure of Cu_{2-x}S with
264 small crystals. An additional small peak can also be seen at $2\theta=44^\circ$, which
265 also correlates to the presence of CZTS, leading to the presumption that the
266 CZT2 layer produces the most stoichiometric sample. For the low SnXan
267 sample it can also be seen that there is a decrease in the peak seen at $2\theta=$
268 16° , this is likely due to the reduced quantity of Cu_2SnS_3 able to be formed.

269 From the XRD analysis, it can be stated that all variations from CZT
270 either causes the addition of further crystal phases or the reduction of the
271 CZTS crystal phase, lowering the quantity of CZTS and increasing the length
272 of the charge transport route for generated excitons, resulting in less gener-
273 ation and more recombination of excitons. However, the CZT2 sample
274 revealed an additional kerestite peak (as seen in **Figure 6**), which could
275 suggest a higher quality CZTS precursor mix.

276 To further understand the potential these active layers have as photo-
277 voltaic devices, optical investigations into the chemical compositions were
278 undertaken. Absorbance spectra were collected for each sample, to study the
279 optical properties of the active layers (see **Figure 7**).

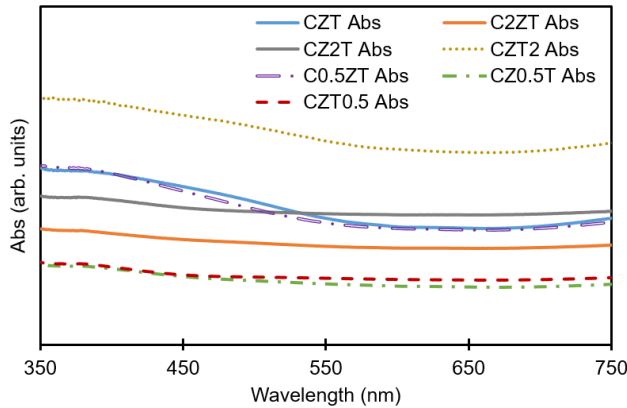


Figure 7: UV-vis absorbance spectra of deposited CZTS active layer

280 The first key observation seen in **Figure 7** relates to the varying inten-
281 sity in absorbance between the active layers. While it can be stated that
282 the absorbance intensity is affected by the thickness (see **Table 2**) of the
283 active layer, as the thickest layer (CZT2) has the highest absorbance and the

284 two thinnest layers (CZ0.5T and CZT0.5) have the lowest absorbance, this
285 does not fit as a description for all profiles. While it can be said that the
286 thickest layer is the most absorbing, it is only $0.04 \mu\text{m}$ thicker than the CZT
287 layer, which is the third least absorbing layer. Furthermore, the difference
288 in thickness between C0.5ZT and CZT is $0.05 \mu\text{m}$ (a similar difference seen
289 between CZT and CZT2), yet their absorbance profiles appear at a simi-
290 lar level across the spectra. Therefore, secondary phases that appear in the
291 active layers are likely to have a more significant effect on their absorbance
292 profiles.

293 It can be seen from **Figure 7** that only three samples (CZT, CZT2 and
294 C0.5ZT) show significant change in absorbance across the spectra, increasing
295 in absorbance between 350-550 nm. From the XRD analysis (**Figure 6a**)
296 and **6c**) it can be stated that these three samples have fewer additional
297 crystal phases, with a crystal structure that more closely resembles that of
298 CZTS. Furthermore, visually these three samples (CZT, CZT2 and C0.5ZT)
299 look similar, as confirmed by SEM images (**Figure 3 a), e) and f**).

300 It is suggested that the observed UV-vis absorbance profile is due to the
301 increased presence of the CZTS crystal phase, as the spectra match previously
302 obtained spectra of CZTS [32]. Tauc plots were then generated to calculate
303 the band gap of each active layer, extrapolating the band gaps from the
304 straight lines seen in **Figure 8**.

305 The value of the band gaps calculated for CZT, CZT2 and CZ2T all fit
306 within the same region of roughly 1.93 eV, while CZT2 exhibits the lowest
307 value of 1.73 eV (see **Figure 8 a**). This has previously been attributed
308 to the fewer impurities within the active layers, especially the formation of
309 Cu_{2-x}S [17, 32]. This would also mean that the two bumps, seen at at $2\theta=$
310 25 and 30° on the CZT2 diffraction pattern (**Figure 6 c**) can also be
311 attributed to CZTS kesterite peaks that appear in similar areas.

312 **Figure 8 b)** shows that the band gap becomes larger as precursor loads
313 are reduced. As discussed for **Figure 8 a)**, these increases in band gap energy
314 could be attributed to the presence of extra phases and contaminants, such
315 as Cu_{2-x}S , Cu_2SnS_3 and ZnS .

316 From this analysis, it can be assumed that a stoichiometric mixture of
317 xanthate precursors does not result in a stoichiometric product. Instead,
318 additional SnXan is required to yield results similar to that expected for
319 CZTS. Therefore, it can be deduced that the composition of these films will
320 still be affected by the rate in which these components decompose.

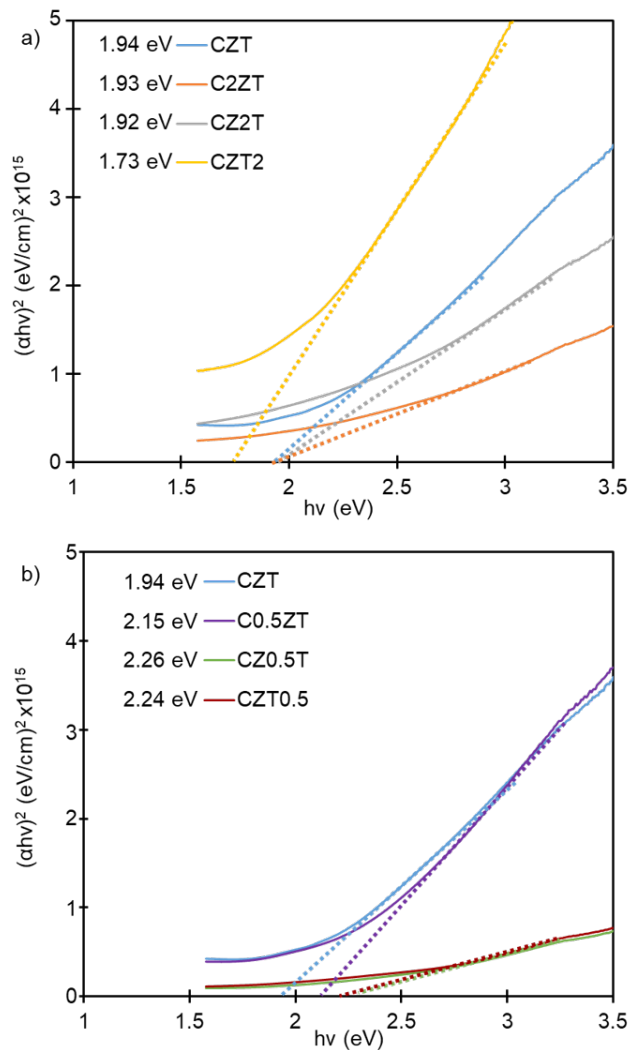


Figure 8: Tauc plots of **a)** increased metal load for CZTS solar cells and **b)** decreased metal load for CZTS solar cells. Band gap values are given in the legend.

321 *3.3. Kinetic analysis of decomposition*

322 In order to work out the rate constants for the decomposition for each
 323 of these precursors, and therefore make a comparison based from this ki-
 324 netic component, isothermal TGA measurements were taken at 160 °C (the
 325 deposition temperature used in the previous depositions) for each precursor.

326 The first step towards making these calculations is to plot a graph of β

327 against time. β is dependant on weight loss and is calculated by:

$$\beta = \frac{wi - wt}{wi - wf} \quad (1)$$

328 where wi is the initial weight, wt the weight at each time and wf the final
329 weight.

330 These isothermal scans then require additional analysis to yield insight
331 into the mechanism of thermal degradation. It is generally seen that materials
332 follow [38]:

$$\frac{\delta\beta}{\delta t} = k(T)(1 - \beta)^n \quad (2)$$

333 where t is time, $k(T)$ the kinetic rate constant at the analysed temperature
334 and n the order of reaction.

335 It is important to note that this rate term is temperature dependant and
336 is expressed by $k(T)$ [39]. In order to extract useful data from the graph it
337 needs to be linearised, to achieve this the kinetic standard method was used,
338 using the following equation [38]:

$$\ln \frac{\delta\beta}{\delta t} = \ln[k(T)] + n \ln(1 - \beta) \quad (3)$$

339 A plot of $\ln(\delta\beta/\delta t)$ vs $\ln(1 - \beta)$ results in a gradient of n (giving the units
340 for k) and an intercept that allows for the calculation of k . This is shown
341 graphically in **Figure 9**.

342 Following this approach it was shown that the rate constants of CuXan
343 and ZnXan align very well, at 1.26 and 1.24 s⁻¹ respectively. This would
344 suggest that the rates at which these two xanthates decompose are very
345 similar, with ZnXan decomposing faster. This mirrors results from **Figure**
346 **2**, showing similar initial decomposition temperatures and ZnXan showing a
347 steeper decomposition curve. However, the rate constant for SnXan differs
348 significantly. Despite having the lowest initial decomposition temperature,
349 it has the smallest rate constant (1.09 s⁻¹) suggesting the slowest reaction.
350 This is reflected in the decomposition profile of SnXan, by the long, gradual
351 intermediate decomposition peak. Therefore, it was noted that additional
352 SnXan is required due to the small rate constant of decomposition. As the
353 other two xanthates decompose faster, more SnXan would need to be added
354 to allow for the correct chemical composition. However, this is not an effective

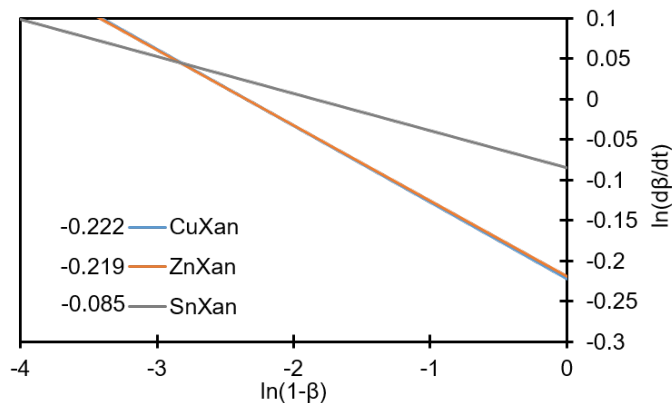


Figure 9: A plot of $\ln(\delta\beta/\delta t)$ vs $\ln(1 - \beta)$. The intercept values are written in the legend and allow for the calculation of k . In this figure CuXan and ZnXan appear almost identically, masking the appearance of CuXan

355 solution and to better address this problem one, or a combination, of three
 356 key ways could be implemented:

- 357 1. As the rate constant is temperature dependent, an investigation into
 358 how the rate constants vary with temperature could help to align them.
- 359 2. The decomposition of these metal xanthates is initiated by a syn-
 360 elimination, of a beta-hydrogen, via a 6-membered cyclic transition
 361 state to form an alkene (as shown in **Figure 1**) [30]. Therefore, in-
 362 creasing the number of beta-hydrogens on the 'R' group of the metal
 363 xanthate precursors would increase the rate of the reaction. Imple-
 364 menting this for SnXan could align the rate constants of the xanthate
 365 precursors. However, SnXan is already very thermally unstable and
 366 this would potentially further reduce the thermal stability, making the
 367 precursor difficult to effectively implement.
- 368 3. Using the same idea as point 2, the amount of beta-hydrogens for
 369 CuXan and ZnXan could be reduced, thereby allowing the reactions
 370 to be slowed down and match that of SnXan. However, this would
 371 increase the thermal stability of the precursors and might result in the
 372 need for higher temperatures for decomposition.

373 From these descriptions, it is assumed that CZT2 produces the most
 374 pure CZTS layers, and is hypothesised to function as the most effective pho-
 375 tovoltaic solar cell.

376 *3.4. Photovoltaic device performance*

377 To determine how these materials function as photovoltaic devices, current-
378 voltage (I–V) curves (shown in **Figure 10**) were collected from the prepared
379 samples, to establish the influence of the abovementioned chemical and op-
380 tical differences on key photovoltaic parameters.

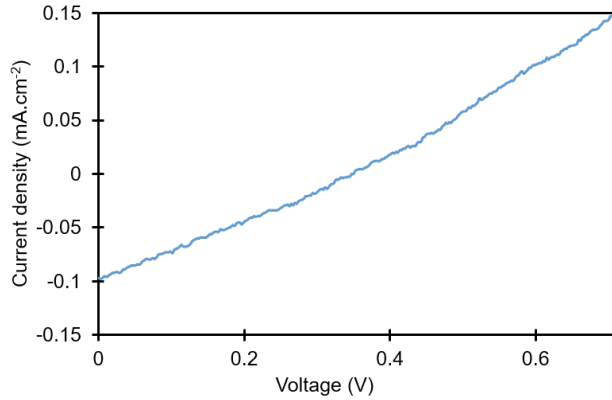


Figure 10: Current-voltage curves of CZT2 under illumination with an intensity of 100 mW.cm⁻².

381 It was noted that only one precursor mixture (CZT2) resulted in a func-
382 tional photovoltaic device (as shown in **Figure 10**). CZT2 had an open
383 circuit potential (Voc) of 0.347 V, similar to that previously reported for
384 a non-stoichiometric CZTS device [7]. The short circuit current (Jsc) and
385 Fill Factor (FF) were calculated to be 1.55 mA.cm⁻², and 0.27 respectively,
386 resulting in a PCE efficiency of 0.15 %. It is important to note Voc, Jsc and
387 PCE outperform the previously reported CZTS photovoltaic devices made
388 from metal xanthate precursors (with a Voc of 0.2 V, a Jsc of 1.3 mA.cm⁻²,
389 and a PCE of 0.11 %), although the FF is reduced from 0.37 to 0.27 [3].

390 Despite performing well, compared to previously reported CZTS photo-
391 voltaic devices deposited using metal xanthate precursors, the PCE is quite
392 low compared to other CZTS photovoltaic devices [4, 6]. This can be at-
393 tributed to the product of low Jsc and FF values. The lower Jsc can be
394 ascribed to the influence of resistance between different components of the
395 device. This could potentially be dramatically improved through various
396 methods, such as energy level optimisation via introducing layers to enhance
397 carrier mobility and current collection or altering the chemistry and crystal

398 of current layers through the introduction of additional dopants or post-
399 treatments [7, 40–42]. The low FF value is likely due to high recombination
400 within the device. As recombination occurs at grain boundaries [37], the
401 polycrystalline bumps (at $2\theta = 25$ and 30° in **Figure 6 c**) would suggest
402 smaller crystal sizes and therefore more recombination sites, leading to a
403 lower FF. It is possible to improve this by increasing the decomposition tem-
404 perature used, or adding an additional annealing step, as this has previously
405 been shown to increase crystallinity [3, 43].

406 Furthermore, it is important to point out that the performance of typical
407 CZTS devices are also limited by a Voc deficit, dominated by heterojunction
408 interface recombination [15]. Therefore, it is important to further optimise
409 the design of these devices and reduce detrimental secondary phases.

410 4. Conclusions

411 This investigation looked into the use of metal xanthate precursors in
412 the deposition of CZTS thin films via spray coating, helping to promote this
413 manufacturing route for possible future commercial viability.

414 SEM-EDS analysis of zinc rich and copper poor precursor mixtures showed
415 significant areas of ZnS crystallisation, a detrimental feature for the devices
416 as it reduces the quantity of CZTS and increases the length of the charge
417 transport route for generated excitons, resulting in less generation and more
418 recombination of excitons. XRD analysis confirmed these findings and fur-
419 ther showed the presence of Cu_{2-x}S , Cu_2SnS_3 , and ZnS contaminating phases
420 in almost all thin films. The tin rich sample (CZT2) was shown to contain
421 the least contamination and therefore, the most accurate overlap with the
422 CZTS crystal structure. A tin rich precursor mixture was required due to
423 the slower decomposition of SnXan compared to that of CuXan and ZnXan,
424 reflected in the rate constants for decomposition as 1.09, 1.26 and 1.24 s^{-1}
425 respectively. Thus requiring more SnXan to be added to form the required
426 stoichiometry. This finding was confirmed through UV-vis analysis and the
427 derived Tauc plots, showing that CZT2 had a band gap closer to the expected
428 band gap of 1.5 eV. Photovoltaic devices were made from all CZTS samples
429 described in **Table 2**, with only CZT2 showing significant photoactivity.
430 The produced device displayed an improved Power Conversion Efficiency for
431 a CZTS based metal xanthate deposited photovoltaic device, with a Power
432 Conversion Efficiency of 0.15 %. These findings provide evidence for the need

433 of further developing this under investigated deposition pathway to develop
434 devices with comparable efficiency and reduced toxicity.

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