Grain Size Control of Novel Photoferroic Absorber Bournonite ($CuPbSbS_3$)

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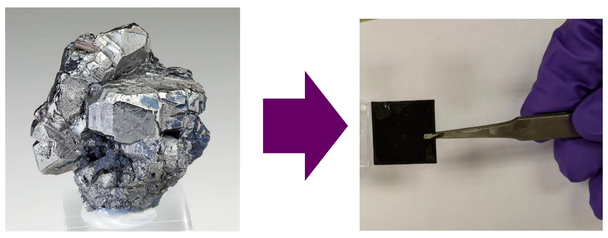
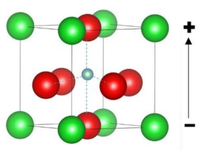
What is bournonite? What are photoferroics?

- Bournonite ($CuPbSbS_3$) is a **mineral** found all over the world, including in the U.K. at Cornwall
- It has **optimal** properties for a **single-junction** PV absorber layer including a **direct** band gap of **1.3eV** and **strong absorption** (~$10^5 cm^{-1}$)
- It has a **polar** space group of $Pmn2_1$. This means it has **photoferroic** properties!



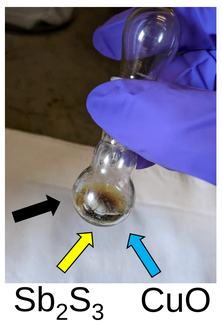


A non-centroymmetric unit cell (seen left in a perovskite structure, ABX_3) leads to electric fields acting across the unit cell due to displaced electron densities

- Photoferroics are materials which are good for PV applications and exhibit **ferroelectric** (FE) properties
- FEs can display macroscopic electric fields which can lead to **an above-bandgap V_{oc}**!
- These **exotic** behaviours suggest a promising research field to **tackle** the trend of **V_{oc} deficits** seen in other emerging thin-films

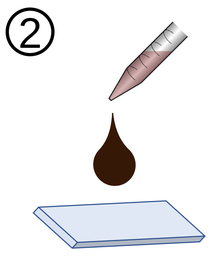
How to make thin-films of $CuPbSbS_3$

① PbO

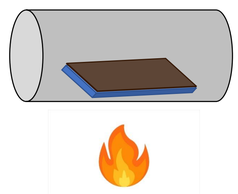


Sb_2S_3 CuO

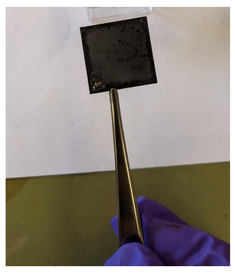
Ethylenediamine dissolves bulk oxides and **ethanedithiol** acts as a **S-source** to build **sulfides** in the stoichiometric ratio for bournonite

② 

Stirring this mixture at **atmospheric pressure** and **room temperature** prepares an ink ready for **spin-coating**

③ 

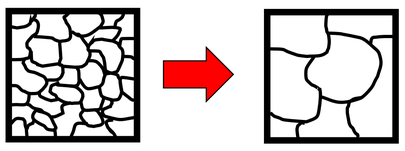
Bournonite is grown through **annealing** in a tube furnace under N_2 flow at temperatures >400°C for 1hr

④ 

Thin-film prepared and ready for analysis! [4]

Why grain size is important and how to make them bigger in $CuPbSbS_3$

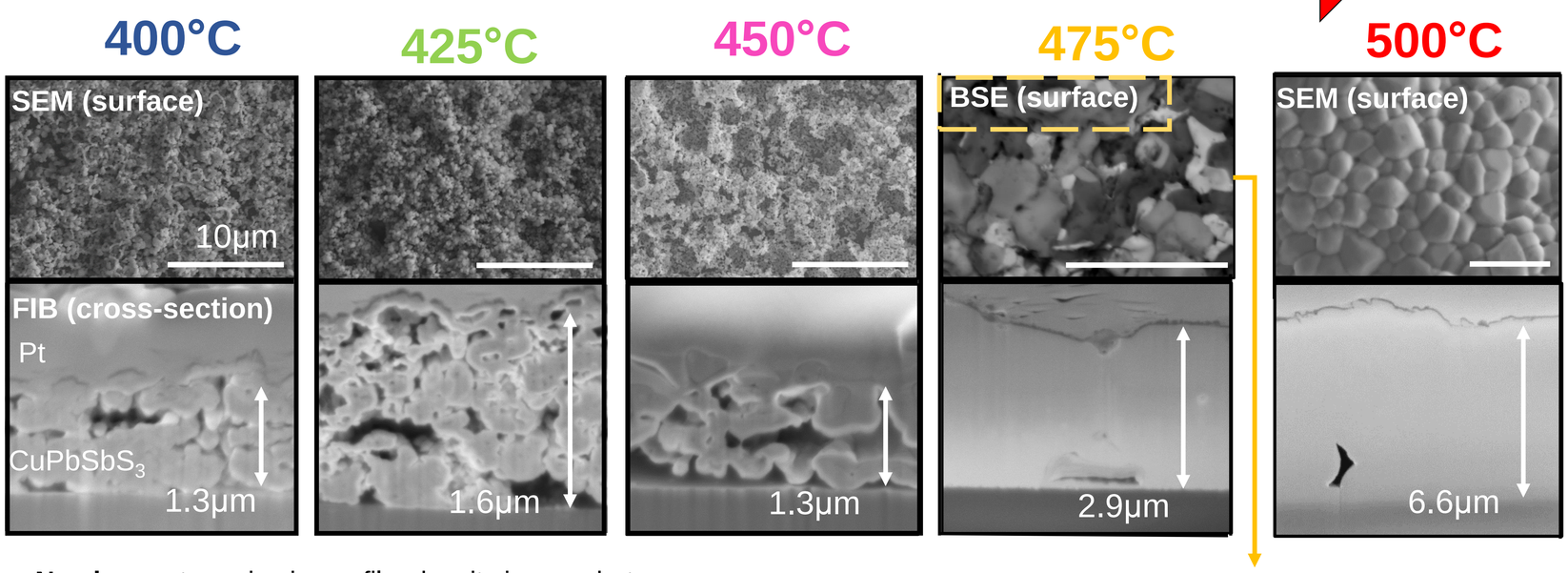
Larger grain sizes ⬇ Fewer grain boundaries ⬇ Better performing devices



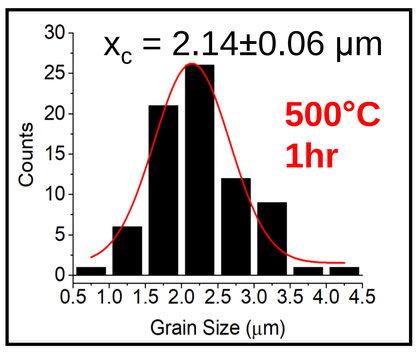
Grain boundaries are sources of **photocarrier recombination**, reducing the number of carriers reaching the device contacts. Controlling grain size is vital to **improving** solar cell performance.

- We are making **bournonite thin-films** and optimising the absorber layer before fabricating devices.
- Currently only one group has made a bournonite solar cell and a **grain size of 0.5µm** limited its power conversion efficiency (PCE) to **2.65%** [2,3]
- The **temperature** at which the films are annealed is key to controlling the absorber morphology (step 3 of synthesis)
- Thin-films were annealed for one hour at temperatures varying from 400°C to 500°C under flowing N_2

Increase in average grain size from 0.4µm to 2.1µm



- **No change** to grain size or film density is seen between 400°C and 450°C. Grains average **0.4±0.1µm** and there are clear **voids** within the material (seen with a cross section prepared with a **focused ion beam**, FIB)
- At 475°C there is a distinct change - material coalesces and forms **thicker** films as islands. This is accompanied by phase **degradation** to PbS and $CuSbS_2$
- At 500°C the phase purity returns along with an average grain size of **2.14±0.06 µm** distributed normally (see right). This is **5*larger** than the grain sizes at lower temperatures. **Grain density** is significantly improved too

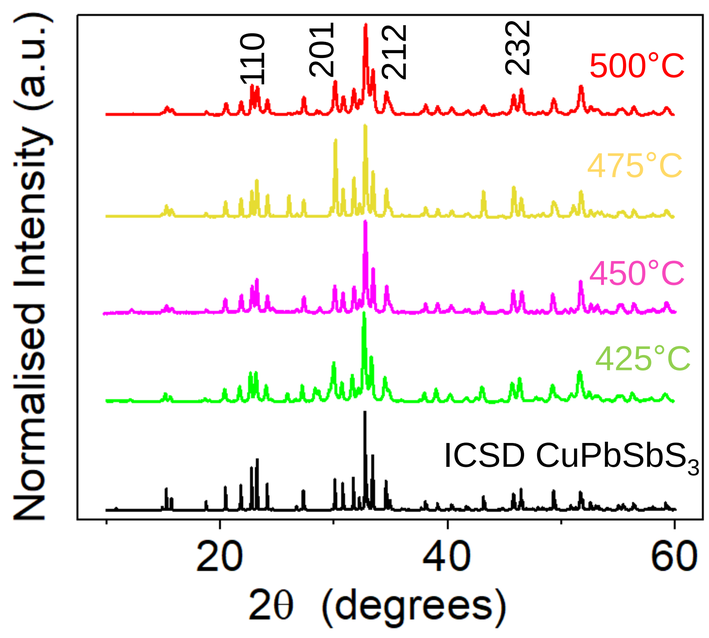


What does BSE mean?

- Backscattered electrons (BSE) can be used to quickly recognise different phases in a material in an SEM
- The intensity of the signal is related to the atomic number, Z. Materials with larger Z give stronger intensity (brighter)

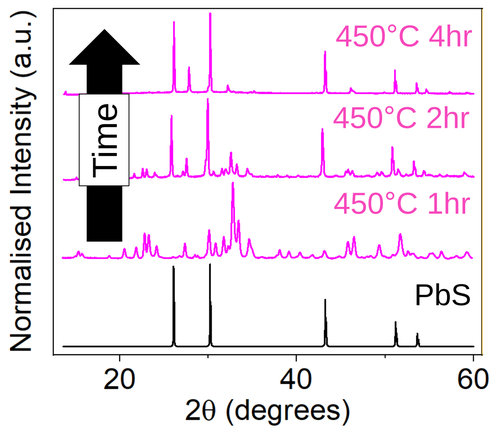
Structural characterisation: are the thin-films phase pure?

- As bournonite is a **quaternary** it is highly **susceptible** to **phase impurities**. Its structure can be derived from inserting PbS into layered $CuSbS_2$.
- It is **challenging** to keep $CuPbSbS_3$ phase pure
- XRD (X-Ray Diffraction) is used to compare a reference from the ICSD to the thin-films synthesised in this work



- All films show **excellent phase purity** except for the 475°C which has PbS defects as a result of **island growth** and nucleation
- Annealing at a higher temperature closer to the melting point of bournonite recovers excellent phase purity

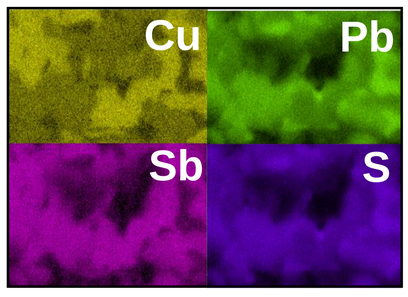
What about a longer anneal at a lower temperature?



- Annealing films at 450°C for longer was done to **try growing larger grains** while avoiding the island growth which starts at 475°C
- Longer anneals however show **decomposition** of $CuPbSbS_3$, mostly into PbS

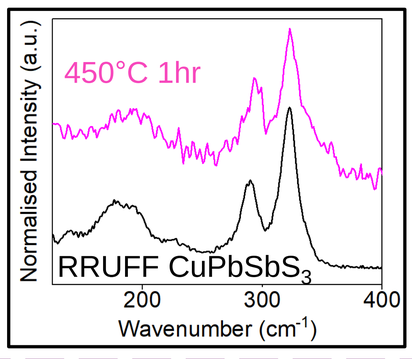
EDX shows 475°C impurities

- X-rays can be measured in an SEM to **spatially resolve** elemental distribution through Energy Dispersive X-ray analysis (EDX)
- EDX of a 475°C sample shows **phase decomposition**, most clearly with Cu and Pb



Raman spectroscopy

- Raman spectroscopy shows **vibrational** modes from bonds excited by a laser
- For $CuPbSbS_3$, the **Sb-S** bonds are **active** modes (at 333cm^{-1} and 294cm^{-1}) and a lattice mode is at 191cm^{-1}
- Raman of these thin-films shows **good agreement** to mineral references



References

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2. Zhang, M. *et al.*, *ACS Applied Materials & Interfaces*, **2021**, 13(11)
3. Liu, Y. *et al.*, *Nano Energy*., **2020**, 104574, 71
4. Koskela, K. *et al., J. American Chemical Soc*, **2020**, 142(13)

Conclusions and future work

- Annealing at 500°C **improves** the grain size of bournonite to **2µm** but with reduced surface coverage and thicker films
- **High phase purity** is achieved with a **thiol-amine dissolution** synthesis, evidenced by a range of experimental techniques
- In the future we look to investigate **diffusion** effects between bournonite and other device layers (e.g. Mo, CdS) deposited through **sputtering** or a **chemical bath** to investigate a **substrate** configuration for a solar cell