Cu_2ZnSnS_4 nanoparticle growth kinetics and mechanisms synthesized utilizing microwave heating

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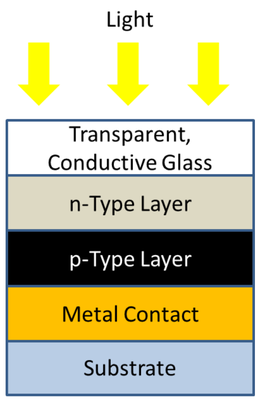
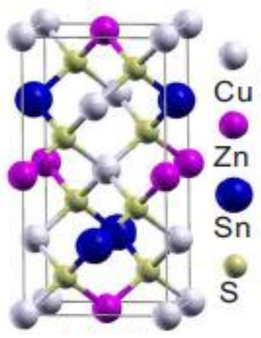
Introduction

The common solar cell has the following general model:



Most common solar cells use materials that are expensive and can be toxic to people and the environment.



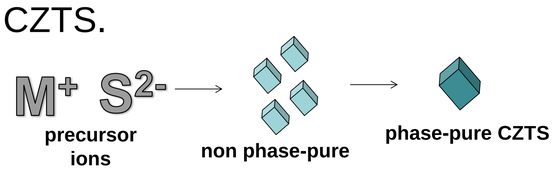
Structure of kesterite CZTS

Copper zinc tin sulfide (CZTS) is a promising material to be used in solar cells:

- Composed of abundant and benign materials
- P-type semiconductor
- Direct band gap of 1.5 eV
- High absorption coefficient

Growth Mechanisms

It is hypothesized that the beginning stages of growth are controlled by the grouping of precursor ions into particles of different phases such as copper tin sulfide. Given time and temperature increases, these particles form into phase-pure CZTS.



After becoming phase-pure, three different growth mechanisms are possible, but it was determined that the CZTS nanoparticles grew following the coarsening mechanism.

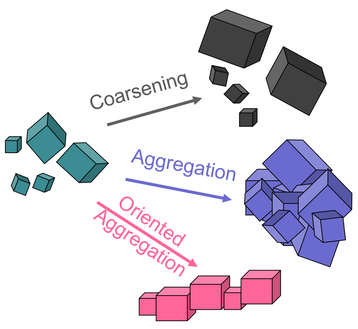


Figure adapted from Lee Penn

This coarsening mechanism can be described by the following equation for Ostwald ripening:

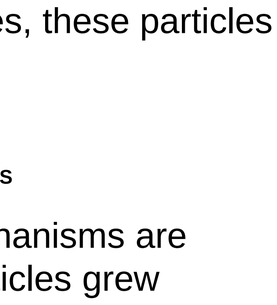
$$D\text{-}D_0=kt^{1/n} \qquad \text{(Equation 1)}$$

Where D is particle size, D_0 is the initial particle size, k is a constant appropriate to the value of the exponent, t is time, and n is 2, 3, or 4, representing whether the growth is controlled by the diffusion of ions along the matrix-particle boundary, the volume diffusion of ions in the matrix, or by dissolution kinetics at the particle-matrix interface.[2]

Materials and Methods

Precursor materials:

- Copper (II) acetate monohydrate
- Zinc (II) acetate dihydrate
- Tin (II) chloride
- Sulfur
- Oleylamine



The solutions were heated using microwave technology and were allowed to react for times between 0 and 12 hours and temperatures between 225 and 300°C.

Acknowledgments

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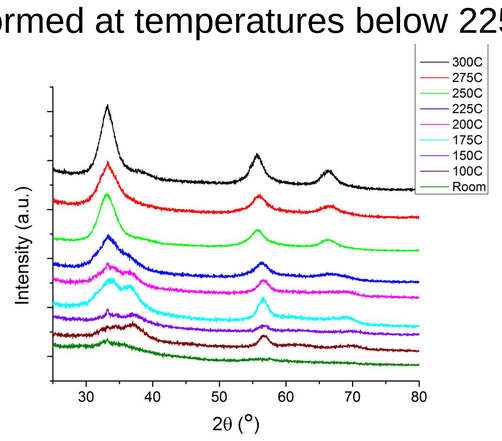
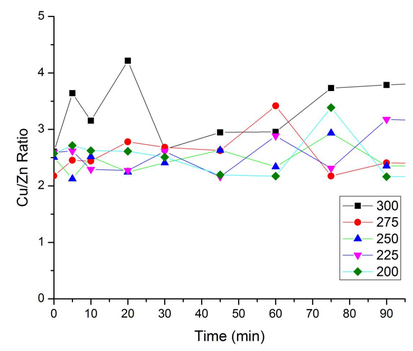
References

1. Huang, F., Zhang, H., & Banfield, J. F. *Nano Letters*, **2003**, *3* (3), pp 373–378
2. Paper in prep

Results[2]

Diffraction data was collected, and it was determined that phase-pure CZTS was not formed at temperatures below 225°C by t=0.





EDS gave further evidence of the pure CZTS product at temperatures 225°C or more, as it gave ratios confirming the Cu_2SnZnS_4 structure.

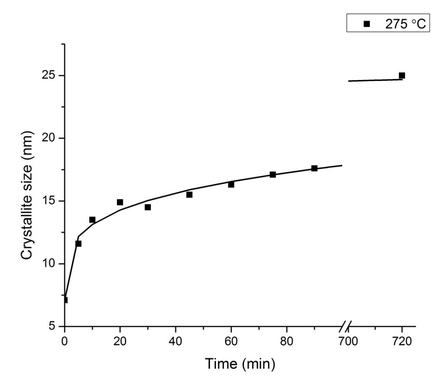
The average crystallite size was calculated using the Scherrer equation:

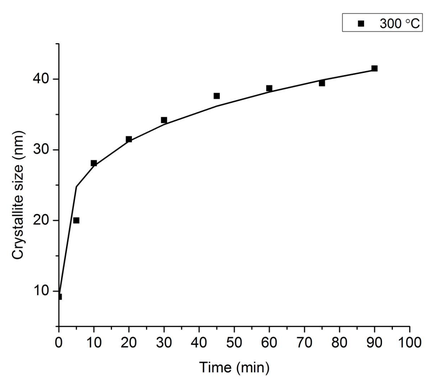
$$\tau = \frac{K\lambda}{\beta cos\theta}$$

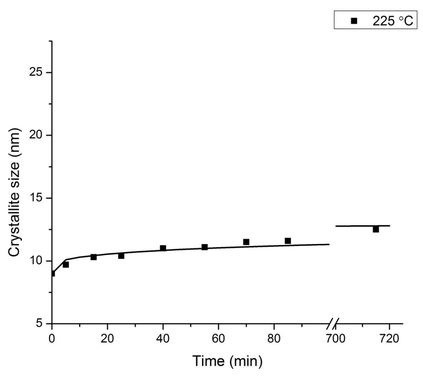
τ is the average size of the particle, K is the shape factor (0.9 here), λ is the X-ray wavelength, β is the line broadening, and θ is the Bragg angle.

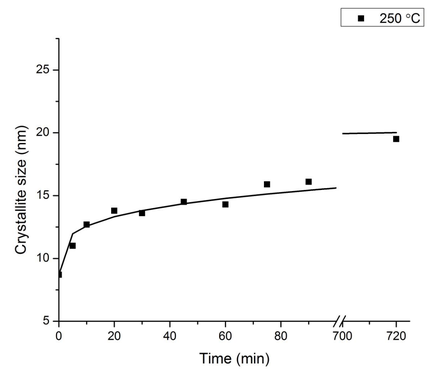
This growth trend was found to fit the following equation (figures shown below):

$$D\text{-}D_0=kt^{1/4}$$





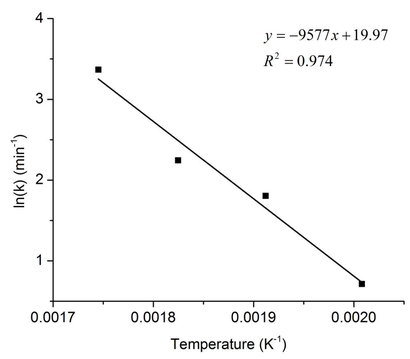




The data gathered resulted with constant, k, which can then be related to the activation energy by the Arrhenius Equation:

$$lnk = \frac{-E_a}{RT} + A_0$$

Using this equation, an Arrhenius plot could be generated for the CZTS:



Conclusions

It was determined that phase-pure kesterite CZTS was synthesized using microwave irradiation at 225-300°C and at times up to 12 hours. Crystallite size was found to increase with temperature and time. The particles grew by an Ostwald Ripening mechanism that followed the kinetic equation as follows:

$$D\text{-}D_0=kt^{1/4}$$

representing that growth is limited by the dissolution kinetics at the particle matrix interface. The activation energy of the particle growth is ?kJ/mol.