

4-2015

# Synthetic Methods of CTS and CZTS Nanocrystals

Rachel R. Bohling

Michael M. Davis

Blake J. Gerold

Ted M. Pappenfus

*University of Minnesota - Morris*

Follow this and additional works at: [http://digitalcommons.morris.umn.edu/urs\\_2015](http://digitalcommons.morris.umn.edu/urs_2015)



Part of the [Materials Chemistry Commons](#)

---

## Recommended Citation

Bohling, Rachel R.; Davis, Michael M.; Gerold, Blake J.; and Pappenfus, Ted M., "Synthetic Methods of CTS and CZTS Nanocrystals" (2015). *Undergraduate Research Symposium 2015*. Book 9.  
[http://digitalcommons.morris.umn.edu/urs\\_2015/9](http://digitalcommons.morris.umn.edu/urs_2015/9)

This Book is brought to you for free and open access by the Undergraduate Research Symposium at University of Minnesota Morris Digital Well. It has been accepted for inclusion in Undergraduate Research Symposium 2015 by an authorized administrator of University of Minnesota Morris Digital Well. For more information, please contact [skulann@morris.umn.edu](mailto:skulann@morris.umn.edu).

# Synthetic Methods of CTS and CZTS Nanocrystals

UNIVERSITY OF MINNESOTA  
**MORRIS**

Rachel R. Bohling, Michael M. Davis, Blake J. Gerold, Ted M. Pappenfus  
Division of Science and Mathematics, University of Minnesota, Morris

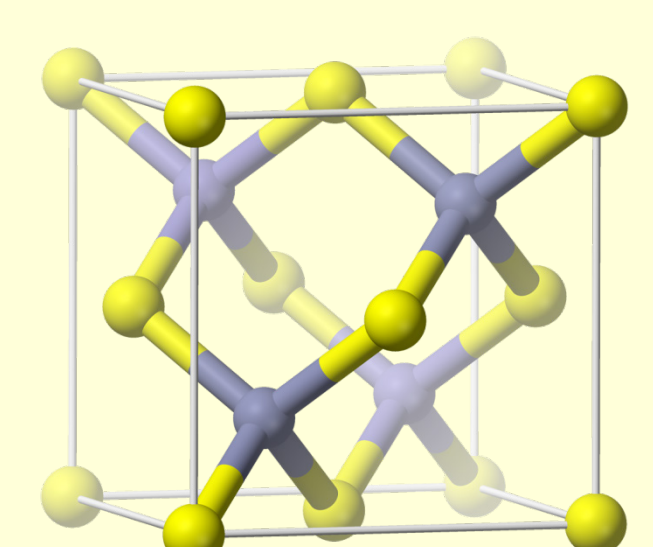
UNIVERSITY OF MINNESOTA  
**MORRIS**

## Introduction

- One of the vital components in a solar cell is the semiconductor
- Most semiconductors in circulation are made from silicon which is difficult to process and environmentally harmful to make
- Current research into semiconductors involves nanocrystals which are made up of earth abundant materials
- Our objective was to find energy efficient, low cost, and effective synthetic methods of CTS and CZTS nanocrystals
- We altered reaction time, solvent ratios, and heating methods in three different reactions and compared the results of each to narrow down the most effective method

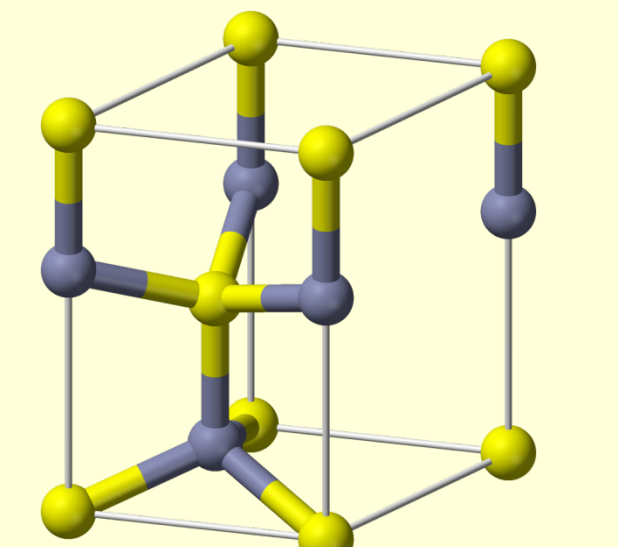
## Nanocrystal Structures

Zincblende Structure



The body-centered cubic structure of zincblende nanocrystals. Yellow atoms represent sulfur and blue atoms represent either copper, zinc, or tin.

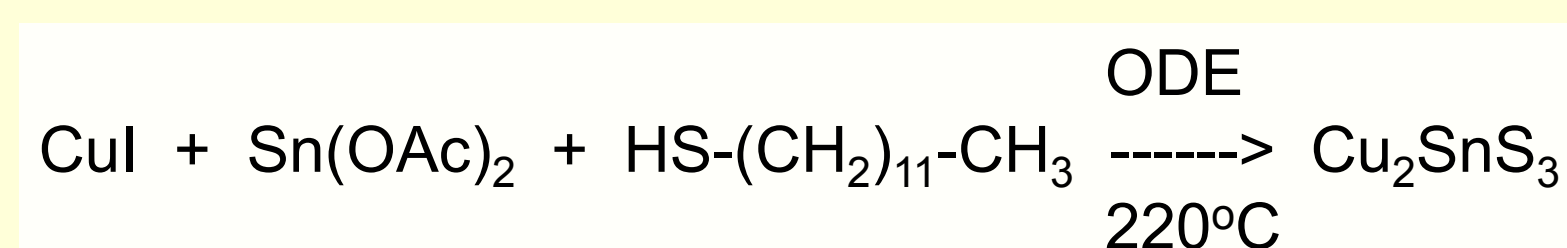
Wurtzite Structure



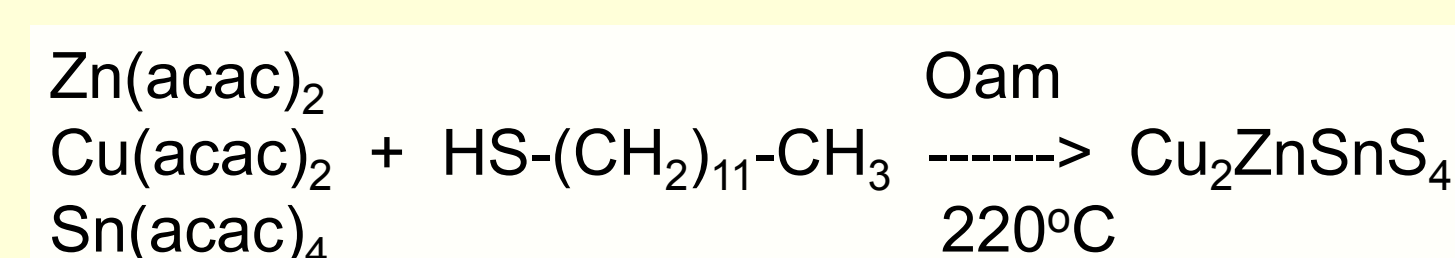
The hexagonal structure of Wurtzite nanocrystals. Yellow atoms represent sulfur and blue atoms represent either copper, zinc, or tin.

## Methods

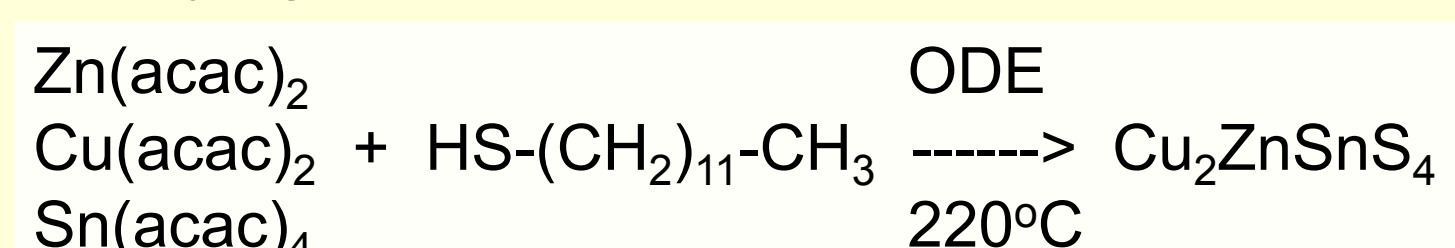
- Reaction 1: Synthesis of CTS zincblende nanocrystals
  - Copper iodide, tin acetate, and 1-octadecene (ODE) were heated to 100°C under an inert atmosphere. 1-docanethiol (DDT) was added and the reaction was heated to 220°C under an inert atmosphere overnight.



- Reaction 2: Synthesis of CZTS Wurtzite nanocrystals
  - The reagent tin(IV) acetyl acetonate was prepared in lab by dissolving tin(IV) chloride in DI water and 2,4-pentanedione under magnetic stirring for 15 minutes. The product was precipitated with triethylamine and vacuum filtrated with ethanol and water.
  - Tin(IV) acetylacetonate, copper(II) acetylacetonate, zinc acetylacetonate, DDT, and oleylamine (Oam) were heated to 220°C overnight.



- Reaction 3: Synthesis of CZTS zincblende nanocrystals
  - This followed the same procedure as reaction 2, except it used varying amounts of ODE as a solvent.



## Abstract

The synthesis of various morphologies of copper zinc tin sulfide ( $\text{Cu}_2\text{ZnSnS}_4$ ) and copper tin sulfide ( $\text{Cu}_2\text{SnS}_3$ ) nanocrystals were explored to find a more energy efficient synthesis. Reactions were all carried out at 220°C under either inert atmospheres or normal conditions. Variations in synthetic methods included reaction time and solvents used. Products were analyzed with powder X-Ray diffraction and compared to simulated powder patterns of zincblende and wurtzite nanocrystals. The synthesis of CTS nanocrystals required the reaction to be heated to 220°C overnight under an inert atmosphere. The reaction used for the synthesis of CZTS nanocrystals required less energy and only required the reaction to be heated to 220°C for four hours. The effects of solvents were found to be that 1-octadecene (ODE) yielded predominantly a zincblende morphology, oleylamine (OAm) yielded predominantly a Wurtzite morphology, and the use of 1-dodecanethiol (DDT) as the only solvent yielded a mixture of zincblende and Wurtzite nanocrystals. The various nanocrystals produced assisted in achieving our overall goal by narrowing down an energy efficient and effective synthesis of CZTS and CTS nanocrystals using earth-abundant and low cost reagents.

## Summary of Results

### CTS Zincblende Synthesis

	Variation	Percent Yield	XRD Results
Method 1	Combined reagents in 1 step	38.0%	Zincblende with weak peaks
Method 2	Heated for 4 hours	76.0%	Unknown
Method 3	Followed literature	46.8%	Zincblende with strong peaks

### CZTS Zincblende Synthesis

	Variation	Percent Yield	XRD Results
Method 1	Followed literature	72.7%	Wurtzite with strong peaks
Method 2	Followed literature	70.6%	Wurtzite with strong peaks
Method 3	Removed the solvent oleylamine	100%	Mix of zincblende and Wurtzite

### CZTS Wurtzite Synthesis

	Variation	Percent Yield	XRD Results
Method 1	0.5 mL DDT, 4 mL ODE	38.0%	Zincblende with impurities
Method 2	1 mL DDT, 4 mL ODE	76.0%	Zincblende with impurities
Method 3	Followed literature	46.8%	Zincblende with impurities

## Conclusions

- Reaction 1: CTS zincblende synthesis
  - The success of method 1 provides evidence that in this reaction, it is necessary to heat the reagents to 100°C under an inert atmosphere before adding the DDT and heating to 220°C overnight.
  - Heating these reagents for 4 hours achieves no results, and the omission of the intermediate heating step to 100°C decreases yield and nanocrystal strength.
- Reaction 2: CZTS Wurtzite synthesis
  - Methods 1 and 2 produced Wurtzite nanocrystals with high yields in an energy efficient synthesis.
  - The removal of oleylamine in method 3 resulted in an undesired mixture of zincblende and Wurtzite nanocrystals.
- Reaction 3: CZTS zincblende synthesis
  - All three methods suggested that using 1-octadecene as a solvent instead of oleylamine produced the zincblende morphology with some impurities.
  - The solvent ratios could be further adjusted to achieve better results.

## Future Work

- Investigating the possibility of ODE as a solvent to produce zincblende nanocrystals
- It was found that solvents have a strong effect on the types of nanocrystals produced. In the future we would like to further look into the effects of different solvents and how to minimize solvent amounts and achieve the best results
- We would like to continue to vary the reaction time or energy input to achieve the highest yields, while decreasing the amount of unreacted impurities

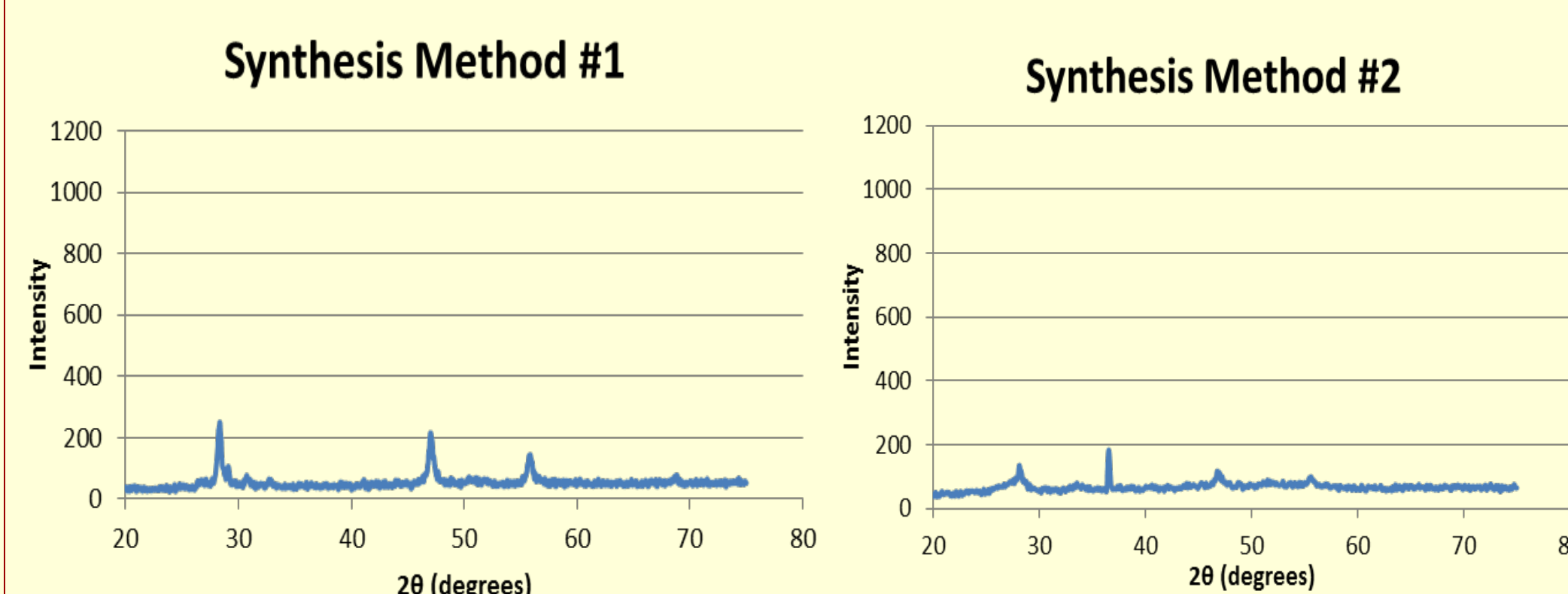
## Acknowledgements

- Dr. Ted Pappenfus and Dr. Nancy Carpenter
- University of Minnesota, Morris Chemistry Discipline
- UMM Division of Science and Mathematics

## References

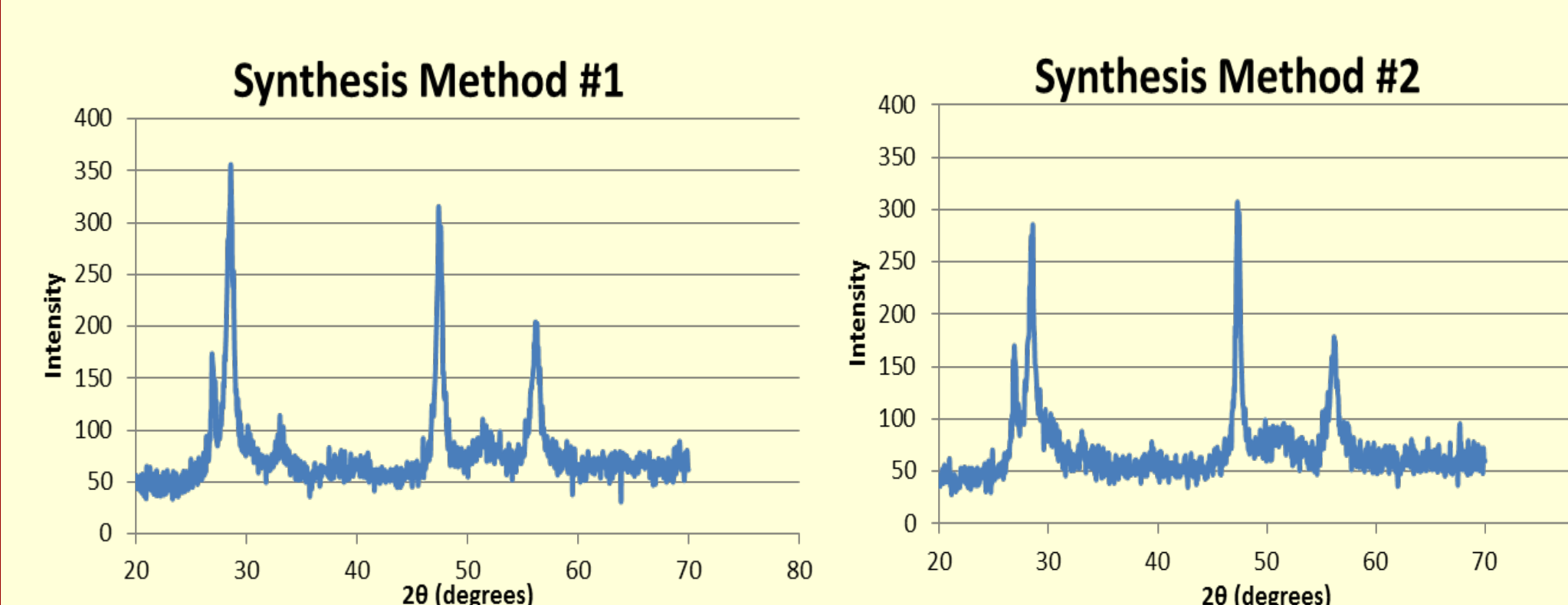
1. U. S. Geological Survey: A Laboratory Manual for X-Ray Diffraction. <http://pub.usgs.gov/of/2001/of01-041/html/doc/xrpd.htm> (accessed Apr 24, 2004)
2. NCPV Home Page. <http://www.nrel.gov/ncpv/> (accessed January 29, 2014).
3. Todorov, T.; Mizzi, D. Shedding light on new frontiers of solar cell semiconductors, 2012. IBM Research.
4. Chang, J.; Wacławik, E. Controlled synthesis of  $\text{CuInS}_2$ ,  $\text{Cu}_2\text{SnS}_3$ , and  $\text{Cu}_2\text{ZnSnS}_4$  nanostructures: insight into the universal phase-selectivity mechanism. *CrystEngComm*. [Online] 2013, 15, 5612-5619. <http://pubs.rsc.org/en/content/articlelanding/2013/cr/c3ce28494a>
5. Li M.; Zhou, W.; Guo, J.; Zhou, Y.; Hou, A.; Jiao, J.; Zhou, Z.; Du, Z.; and Wu, S. Synthesis of Pure Metastable Wurtzite CZTS Nanocrystals by Facile One-Pot Method. *The Journal of Physical Chemistry*, 2012. American Chemical Society
6. The Cambridge Crystallographic Data Centre. <http://www.iucr.org/resources/other-directories/software/vesta-3> (accessed Feb 17, 2014).
7. Images obtained from Wikipedia: [http://en.wikipedia.org/wiki/Zinc\\_sulfide](http://en.wikipedia.org/wiki/Zinc_sulfide)

## CTS Zincblende Synthesis



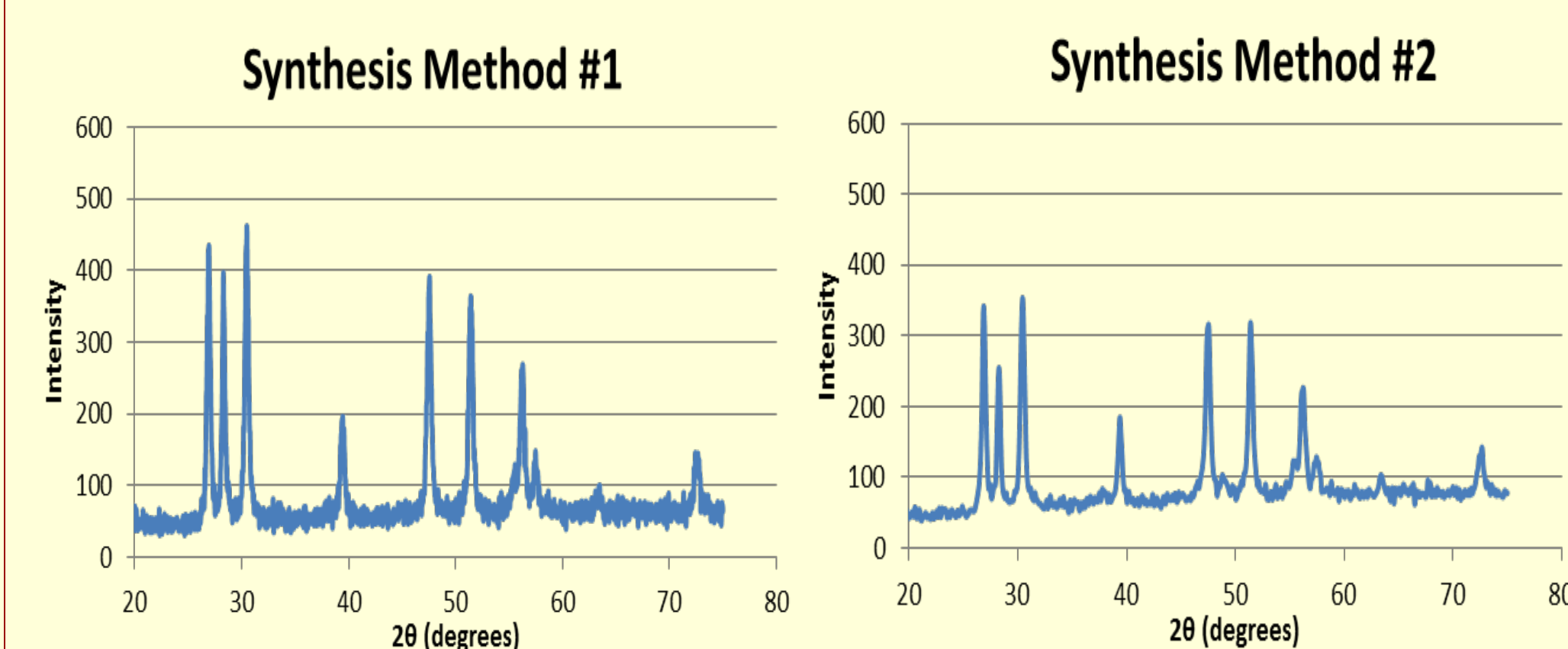
	Reagents
Method 1	0.2 mmol CuI, 0.1 mmol Sn(OAc) <sub>2</sub> , 2.1 mmol DDT heated to 220°C overnight under inert atmosphere
Method 2	0.2 mmol CuI, 0.1 mmol Sn(OAc) <sub>2</sub> , and 4.0 mL DDT heated to 100°C under inert atmosphere. Added 2.1 mmol DDT, heated to 220°C for 4 hours
Method 3	0.2 mmol CuI, 0.1 mmol Sn(OAc) <sub>2</sub> , and 4.0 mL DDT heated to 100°C under inert atmosphere. Added 2.1 mmol DDT, heated to 220°C overnight

## CZTS Zincblende Synthesis



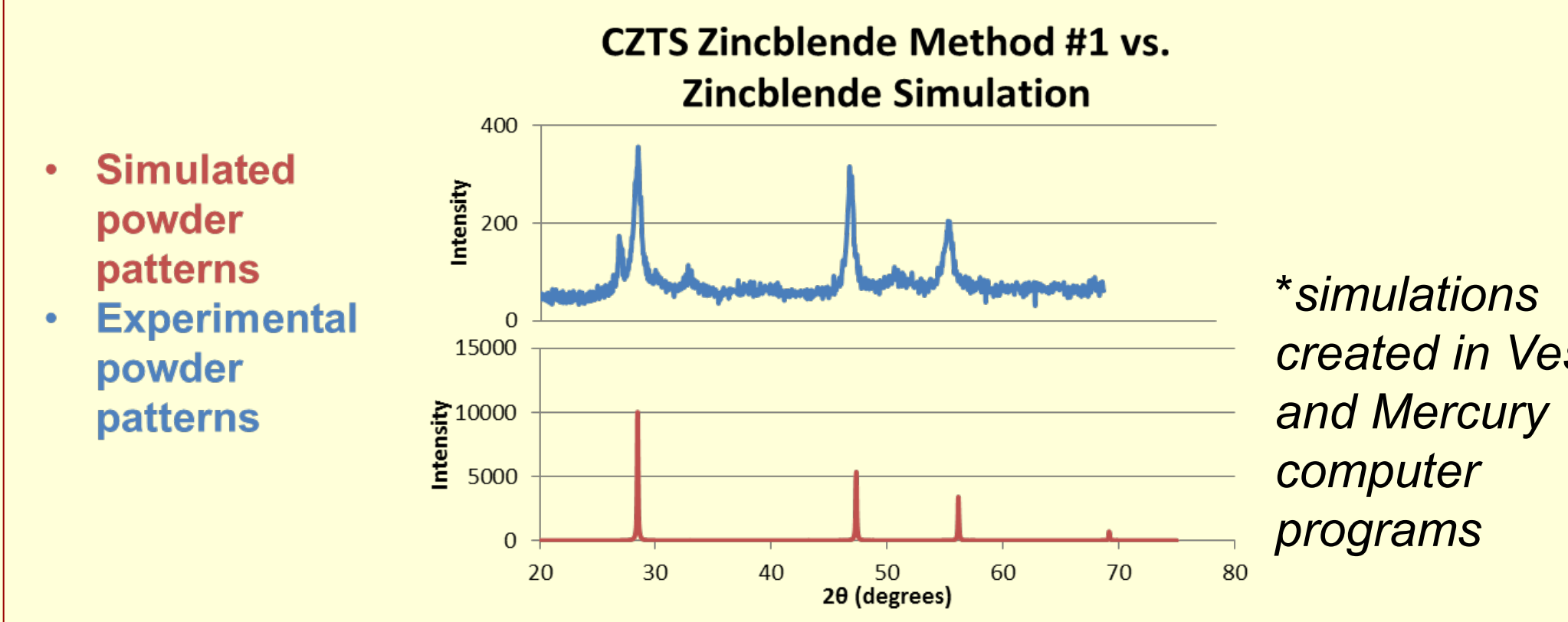
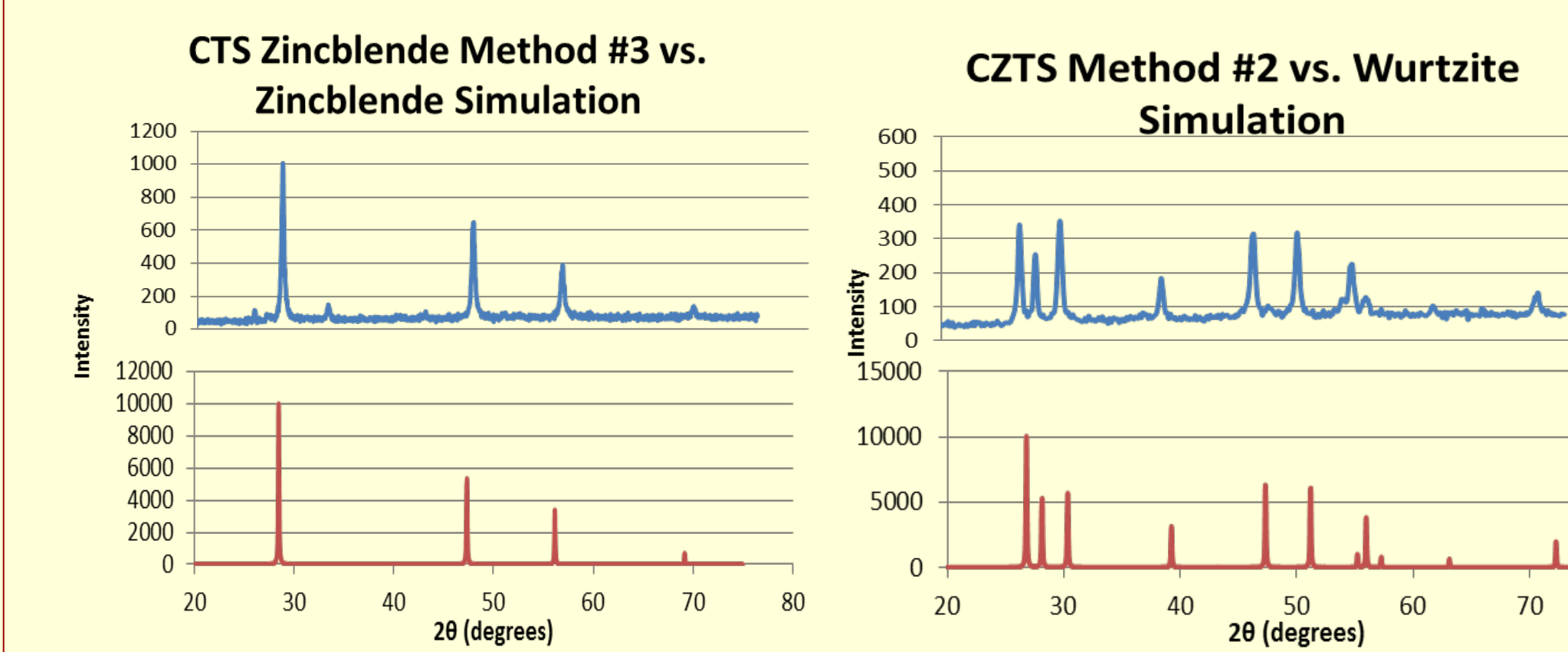
	Reagents
Method 1	0.1 mmol Sn(acac) <sub>2</sub> , 0.2 mmol Cu(acac) <sub>2</sub> , 0.1 mmol Zn(acac) <sub>2</sub> , 2.1 mmol DDT, 0.5 mL ODE heated to 220°C for 4 hours
Method 2	0.1 mmol Sn(acac) <sub>2</sub> , 0.2 mmol Cu(acac) <sub>2</sub> , 0.1 mmol Zn(acac) <sub>2</sub> , 4.2 mmol DDT, 8 mL ODE heated to 220°C for 4 hours
Method 3	0.1 mmol Sn(acac) <sub>2</sub> , 0.2 mmol Cu(acac) <sub>2</sub> , 0.1 mmol Zn(acac) <sub>2</sub> , 2.1 mmol DDT, 8 mL ODE heated to 220°C for 4 hours

## CZTS Wurtzite Synthesis



	Reagents
Methods 1 & 2	0.1 mmol Sn(acac) <sub>2</sub> , 0.2 mmol Cu(acac) <sub>2</sub> , 0.1 mmol Zn(acac) <sub>2</sub> , 41.7 mmol DDT, 0.5 mL OAm heated to 220°C for 4 hours
Method 3	0.1 mmol Sn(acac) <sub>2</sub> , 0.2 mmol Cu(acac) <sub>2</sub> , 0.1 mmol Zn(acac) <sub>2</sub> , 41.7 mmol DDT heated to 220°C for 4 hours

## Comparison to Simulated Data



- Simulated powder patterns
- Experimental powder patterns

\*simulations created in Vesta and Mercury computer programs