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Synthetic Methods of CTS and CZTS Nanocrystals

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Abstract
The synthesis of various morphologies of copper zinc tin sulfide (Cu2ZnSnS4) and copper tin sulfide (Cu2SnS3) 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 CTS and CZTS nanocrystals using earth-abundant and low cost reagents.

CZTS Zincblende Synthesis

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Method</th>
<th>Variance</th>
<th>Percent Yield</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction 1: CZTS Zincblende synthesis</td>
<td>Method 1</td>
<td>Combing reagents in 2 drops</td>
<td>98.5</td>
<td>CZTS with weak peaks</td>
</tr>
<tr>
<td>Reaction 2: CZTS Wurtzite synthesis</td>
<td>Method 2</td>
<td>Heated for 4 hours</td>
<td>75.9</td>
<td>Unknown</td>
</tr>
<tr>
<td>Reaction 3: CZTS Zincblende synthesis</td>
<td>Method 3</td>
<td>Energy input</td>
<td>46.8</td>
<td>CZTS with weak peaks</td>
</tr>
</tbody>
</table>

CZTS Wurtzite Synthesis

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Method</th>
<th>Variance</th>
<th>Percent Yield</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction 1: CZTS Zincblende synthesis</td>
<td>Method 1</td>
<td>Followed literature</td>
<td>72.3</td>
<td>CZTS with weak peaks</td>
</tr>
<tr>
<td>Reaction 2: CZTS Wurtzite synthesis</td>
<td>Method 2</td>
<td>Followed literature</td>
<td>70.6</td>
<td>CZTS with weak peaks</td>
</tr>
<tr>
<td>Reaction 3: CZTS Zincblende synthesis</td>
<td>Method 3</td>
<td>Followed literature</td>
<td>46.8</td>
<td>CZTS with weak peaks</td>
</tr>
</tbody>
</table>

Conclusions

• Reaction 1: CZTS 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.

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.

Acknowledgements

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• UMM Division of Science and Mathematics

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

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

The hexagonal structure of Wurtzite nanocrystals. Yellow atoms represent sulfur and blue atoms represent 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-Dodecanethiol (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 (acac) and heating to 220°C under magnetic stirring for 15 minutes. The product was filtered and dried. Copper iodide, zinc 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 overnight. 1-Octadecene (ODE) was added and the reaction was 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.

Comparison to Simulated Data

• Simulations created in Vesta and Mercury Computer programs.

References


5. Figures obtained from Wikipedia: http://en.wikipedia.org/wiki/Zinc_sulfide