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**SYNTHESIS OF FeSb_2 NANORODS AND
NANOPARTICLES BY SOLVOTHERMAL SYNTHESIS
ROUTES (BRIEFING CHARTS)**

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Nonmetallic Materials Division**

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14. ABSTRACT FeSb ₂ has recently been considered as a novel thermoelectric material due to a Seebeck coefficient of ~-45000 μ VK ⁻¹ and a thermoelectric power factor of ~2300 μ WK ⁻² cm ⁻¹ at low temperatures (Bentien, A. et al. 2007 <i>Europhys. Lett.</i> 80 17008). However, its thermoelectric potential is limited by a high thermal conductivity. To lower the thermal conductivity, both nanorods and nanoparticles of FeSb ₂ were synthesized. Nanorods were synthesized following a previously published solvothermal synthesis in ethanol. Nanoparticles were synthesized using a novel sodium naphthalenide reduction in triglyme at ambient pressure. XRD was used to characterize both materials.						
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Synthesis of FeSb₂ Nanorods and Nanoparticles by Solvothermal Synthesis Routes



ACS Central Regional Meeting 2010

Dayton, OH

June 17, 2010

Thermal Sciences and Materials Branch

AFRL/RXBT

Materials and Manufacturing Directorate

Air Force Research Laboratory

Joel Schmidt

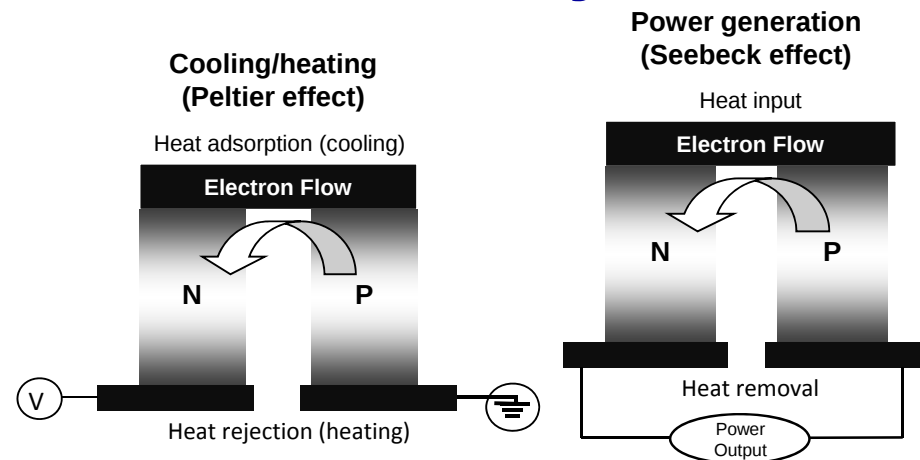


Thermoelectric Materials



- Durable solid state devices which provide cooling, power generation and waste heat harvesting
- Used on deep space probes, sensor cooling and small scale refrigeration
- Current work mostly concentrated on room temperature to high temperature
- Need for low temperature TE's for sensor cooling applications

Theory





Increasing Efficiency



- Figure-of-Merit

$$ZT = \frac{\alpha^2 \sigma T}{\kappa}$$

- ZT drops off at low temperature
- ZT = 1 state of the art at room temperature

**Difficulty of optimizing three
Interrelated parameters**

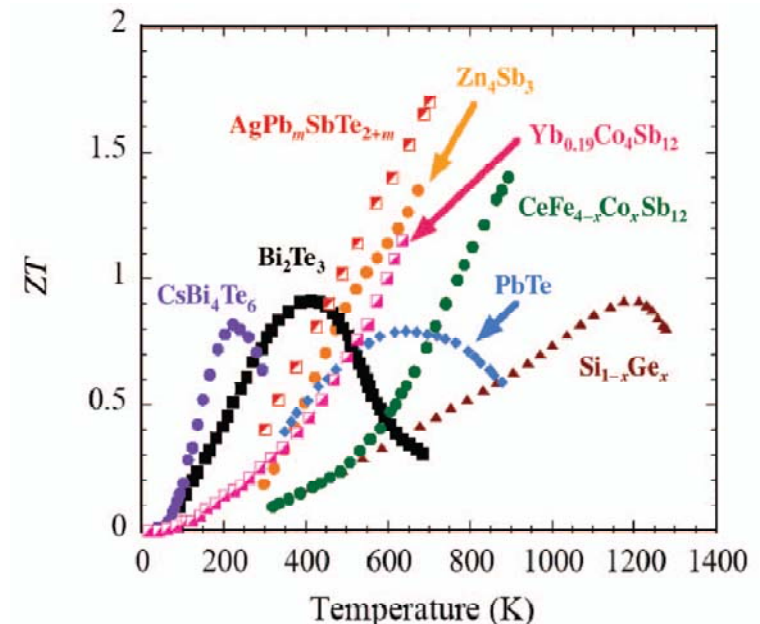
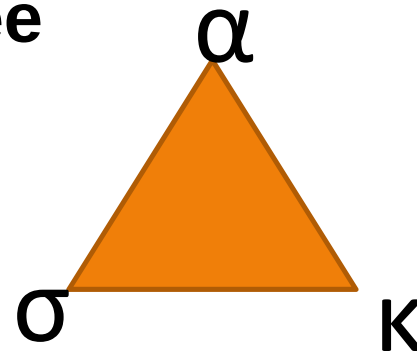


Fig. 1. Figure-of-Merit ZT as a Function of Temperature for Selected TE Materials (from Tritt & Subramanian)

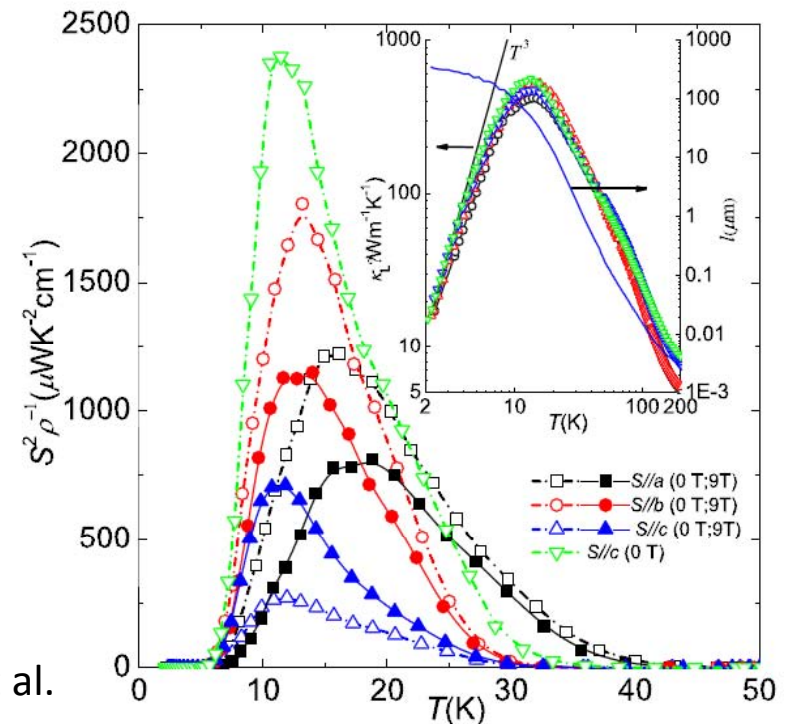




FeSb₂ Thermoelectric Power Factor



- FeSb₂ is narrow gap semiconductor material
- Exhibits a huge Seebeck Coefficient of $\sim -45,000 \mu\text{V/K}$ at 10 K
- Has a record high thermoelectric power factor of $\sim 2300 \mu\text{W/K}^2$ at 12 K
 - 65 times larger than that of Bi₂Te₃
 - Thermal conductivity of $\sim 500 \text{ W/mK}$ leads to a $ZT \sim 0.005$ at 12 K



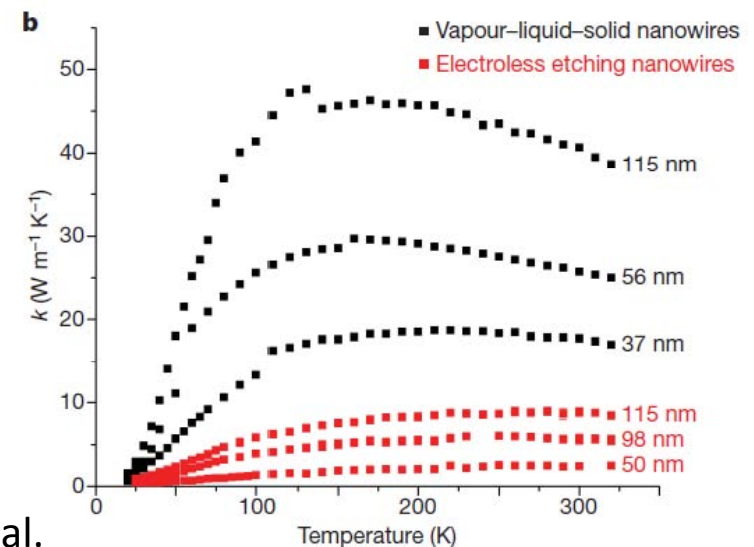
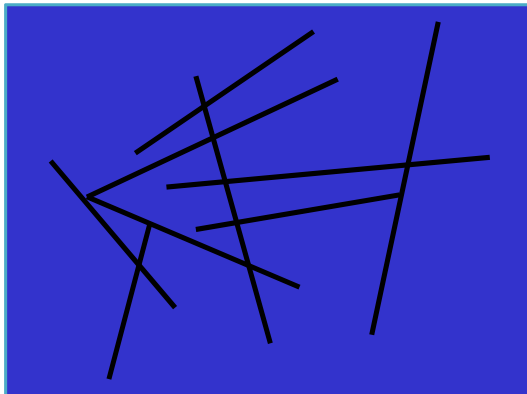
A. Bienten et al.



Thermal Conductivity Reduction



- Bouka et al. and Hochbaum et al. showed it was possible to greatly reduce the κ of silicon by synthesizing nanowires
- Preparing nanostructures with one of more dimension smaller than the mean free path of phonons but larger than the mean free path of electrons and holes can greatly reduce κ without decreasing σ
- Difficulty in preparing nanostructures!



Hochbaum et al.



FeSb₂ Synthesis



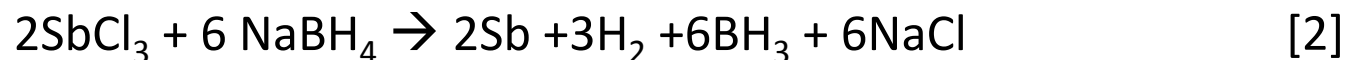
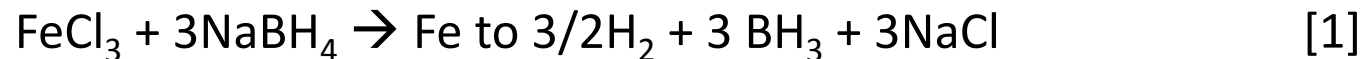
- **Traditional alloying methods:**
 - Heat Fe and Sb to 1070 K for 1 day, crush then temper at 970 K for 7 days, crush then temper at 870 K for 21 days then cool (Gronvold et al.)
 - Melt using high-frequency induced current, anneal at 773 K for 7 days, ball-mill into fine powder (Xie et al., 2003)
- **Problems:**
 - Do not produce nanostructures
 - High temperatures and long synthesis times are impractical for large scale production



Nanowire synthesis



- Reported as a Li-Ion battery anode material
- Procedure (Xie et al., 2006):
 - $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, SbCl_3 , NaBH_4 and anhydrous ethanol were combined in a Parr pressure reactor and heated to 260 °C for 3 days
 - NaBH_4 quickly reduces FeCl_3 and SbCl_3 in the first two reaction so the longer reaction time is needed for the final alloying reaction:

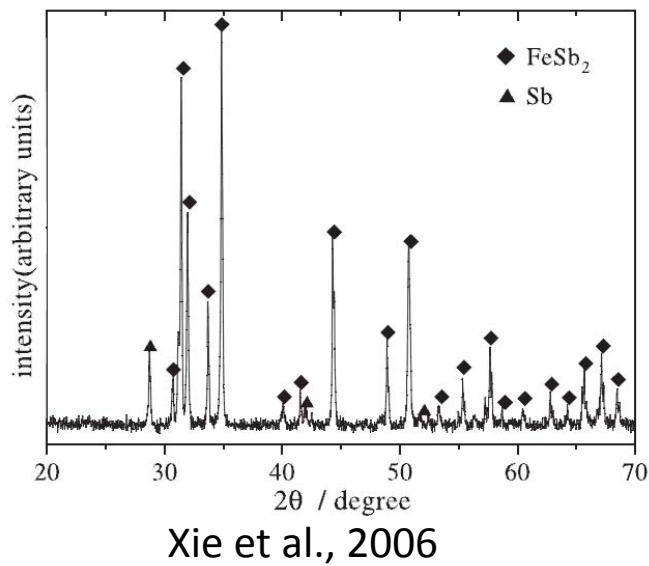




Product Characterization

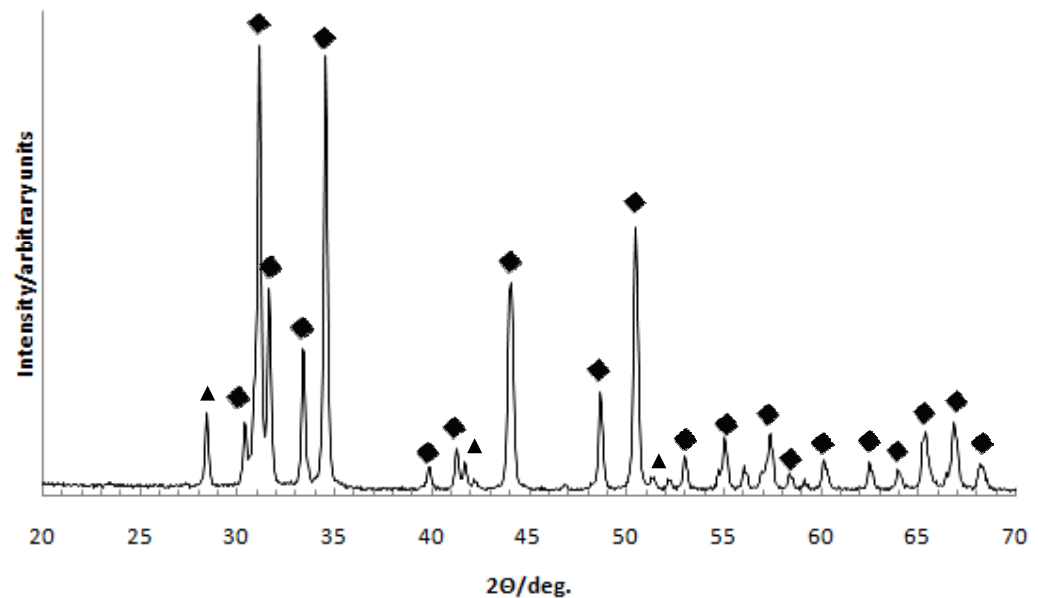


- XRD used for bulk powder characterization



Experimental results

- Literature and experimental preparation compare closely
- Ran for 100 hours, predissolved all reagents





Synthesis Challenges



- **NaBH_4 quickly reduces FeCl_3 and SbCl_3 and the alloying reaction takes place slowly**
- **Silver flakes of antimony metal were visible after the reaction each time it was run**
 - Confirmed by XPS
- **Excess iron metal could not be found**
- **Need to purify the product and remove unreacted antimony**

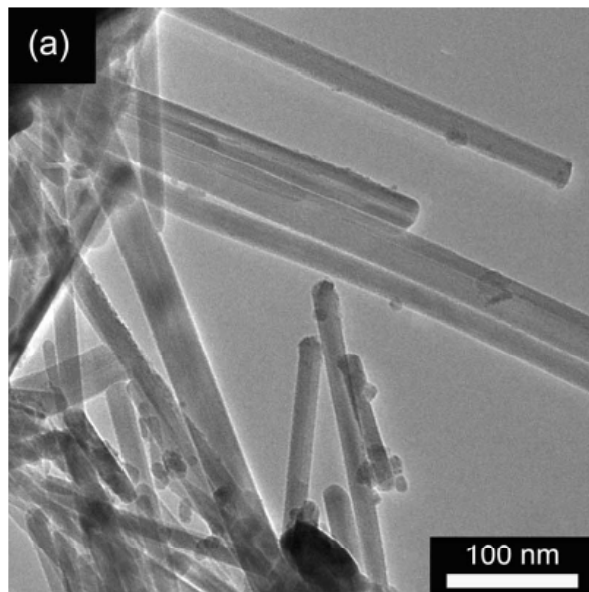


Nanorod characterization



- Characterize nanorods by SEM and TEM

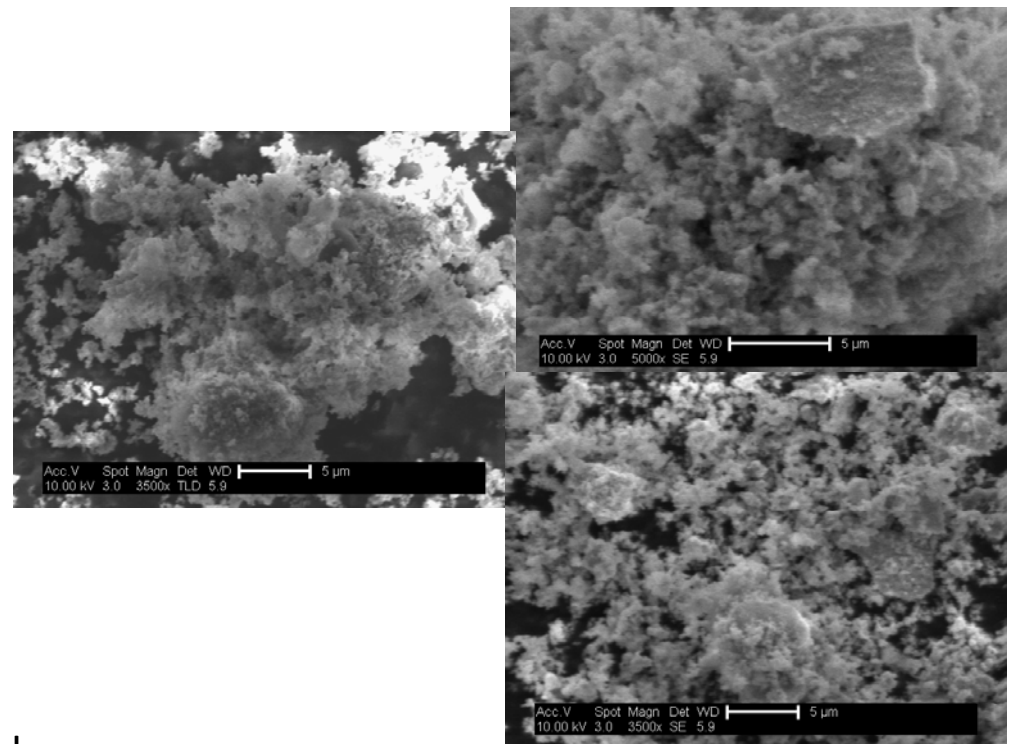
Literature TEM



Nanorod size:

- Large nanorods 200-400 nm in length and 30-40 nm diameter
- Small nanorods 50-200 nm in length and 20-30 nm in diameter (Xie et al.)

Experimental SEM



SEM shows much smaller particle size



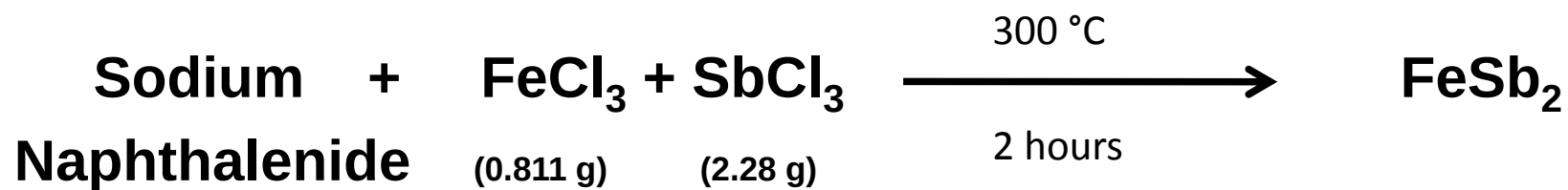
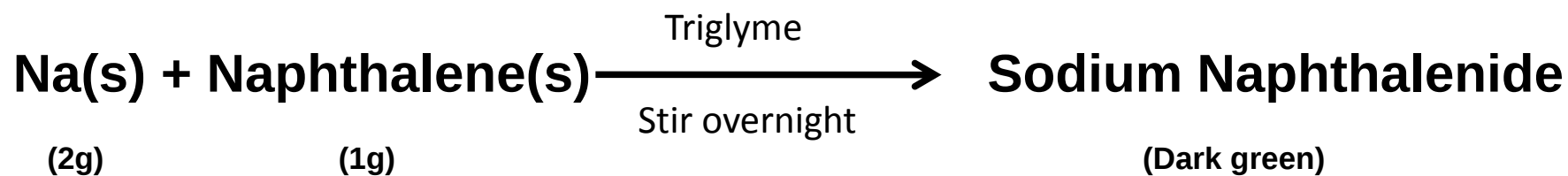
Nanoparticle Synthesis



- **Novel synthesis route using a sodium naphthalenide reduction**
 - Used in literature to prepare compounds such as:
 - PtPb (Alden et al.)
 - InSb (Cho and Lim)
 - GaP (Hwang et al.)
 - Possible reaction difficulties:
 - Rate of reduction needs to be diffusion-limited so that homogeneous particles are formed
 - Choice of solvent so that all materials are soluble
 - This method can be applied to a wide range of systems

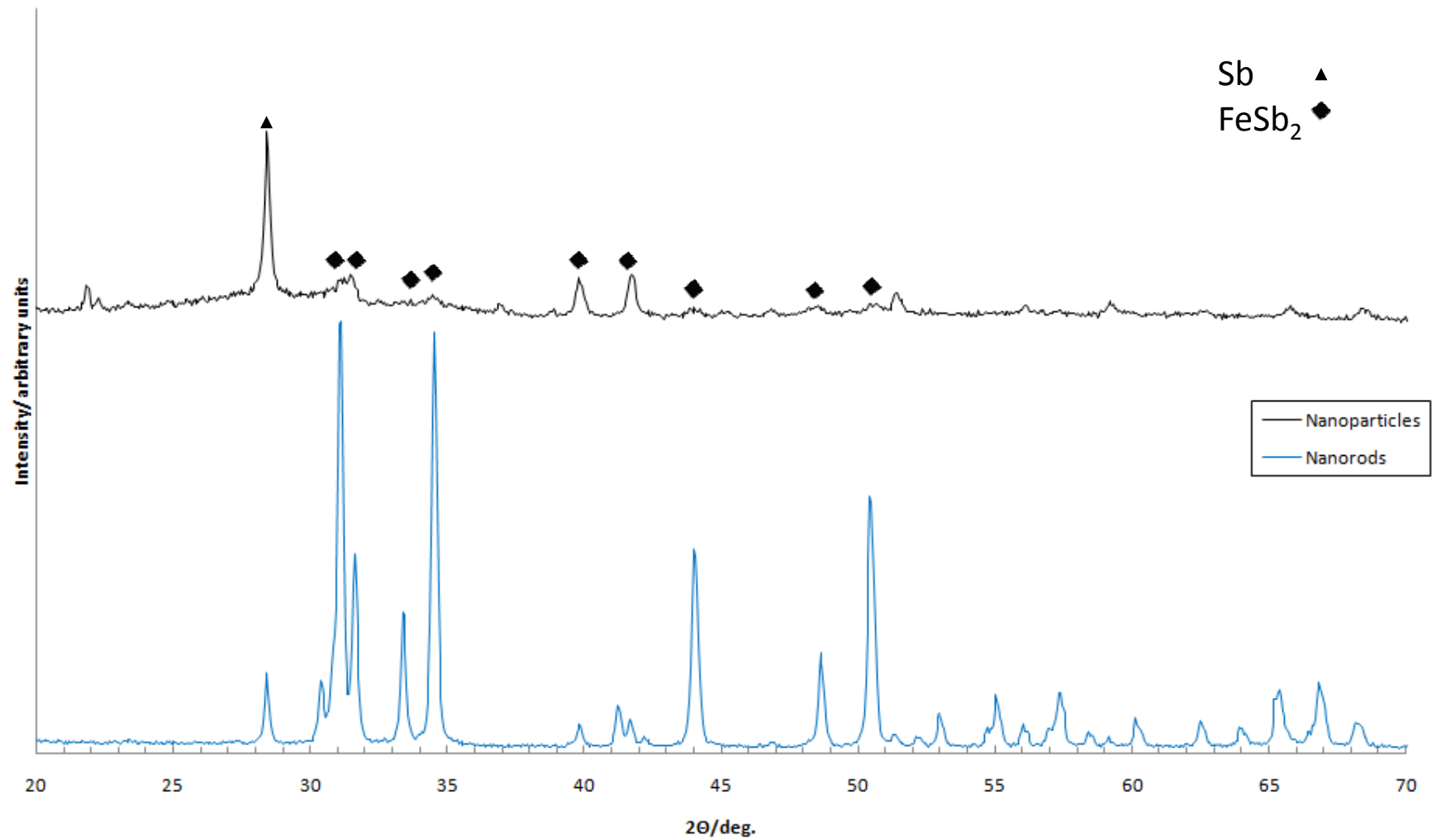


Procedure





XRD Characterization





XRD Conclusions



- Small particle size leads to broader and less well defined peaks
- Presence of antimony metal is easily seen
- Product FeSb_2 is able to be seen in XRD but it has a very weak signal
- Need to perfect the synthesis method in order to get high purity nanoparticles

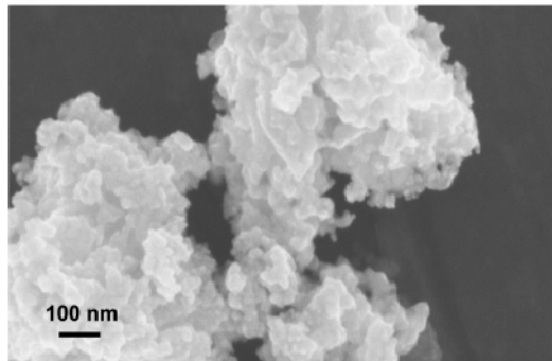
Initial attempts to synthesize do appear to be successful!



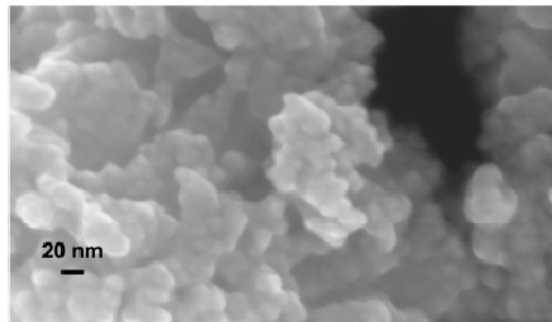
SEM Images



PtPb Nanoparticles

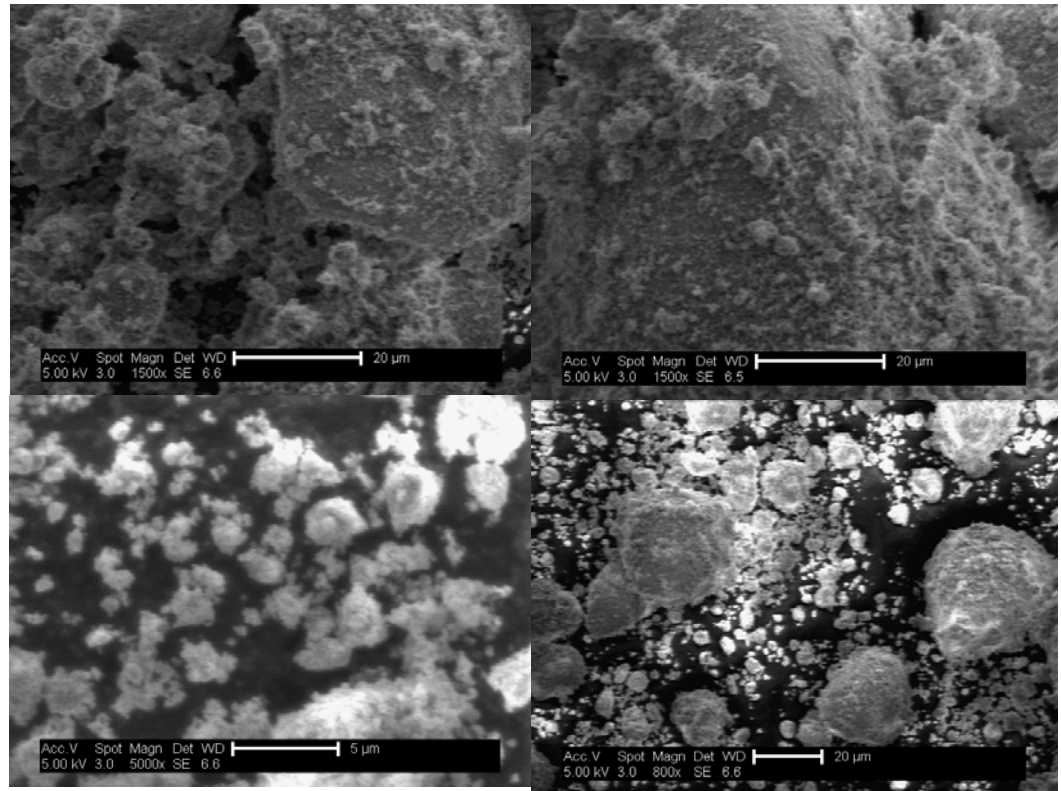


b)



Shown for comparison of particle size and clustering
(Alden et al.)

FeSb Nanoparticles



The image shows the small particle size as well as clustering



Summary of Experimental Results



- **Novel synthesis route utilizing a sodium naphthalenide reduction in triglyme at 300 °C and ambient pressure**
- **XRD shows that product has been formed, however it is contaminated**
- **SEM shows small particle size**
- **Need to optimize method for increased yields and purity**

Synthesis method is ideal for scale up since costly pressure vessels are not required and the reaction is on the order of hours instead of days



Future Work



- **Optimize both synthetic routes**
- **Use of surfactants to control nanorod length and diameter and nanoparticle size**
- **Increase purity and yield of reactions**
- **Scale up**
- **Transport property characterization at cryogenic temperatures**
- **Addition of impurities to increase electrical conductivity and decrease thermal conductivity**



Conclusions



- **Successfully reproduced literature synthesis of FeSb_2 nanorods**
- **Initial characterization shows that a novel synthesis method of FeSb_2 nanoparticles has been developed**
- **Need to increase yields and purity**
- **Characterize cryogenic transport properties**



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