

# Studies on nanocrystalline $\text{Ag}_2\text{Se}$



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# Characteristics of Silver selenide

- ⊗ Super ionic conductor
- ⊗ Exhibits polymorphic phase transition
- ⊗ Low temperature beta phase is a N-type semiconductor
- ⊗ High temperature alpha phase is a mixed conductor
- ⊗ Non-stoichiometric form exhibits Magnetoresistance
- ⊗ It is a good thermoelectric material

## *Application of Silver selenide*

Infrared sensors,  
Photolithographic layers,  
Electrochemical storage cells  
Electrochemical potential memory devices  
Magnetic field sensing

# Scheme of Synthesis

## Solution Phase Approach

Se<sup>2-</sup> ion  
source

+

Ag<sup>+</sup> ion  
source



Product

Sodium  
selenosulphate

Silver nitrate

Aquous  
ammoniacal  
medium

Silver selenide  
nanocrystals

## Hydrothermal synthesis

Precursor

+

Solvent cum  
Reducing agent



Product

Silver selenite  
Ag<sub>2</sub>SeO<sub>3</sub>

Dimethyl formamide  
(DMF)

Silver selenide  
Ag<sub>2</sub>Se  
nanocrystals

# Solution Phase synthesis of $\text{Ag}_2\text{Se}$

## Preparation of sodium selenosulphate

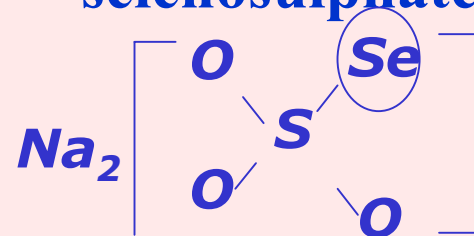
4.83 gm sodium sulphite in 100ml water



2 gm selenium

Refluxed for 10 hours

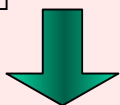
Sodium selenosulphate



1 gm  $\text{AgNO}_3$  in 60 ml water



2 ml Strong  $\text{NH}_4\text{OH}$



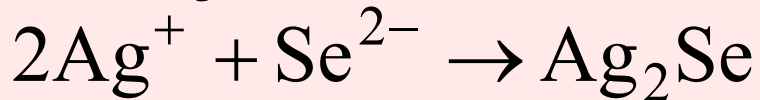
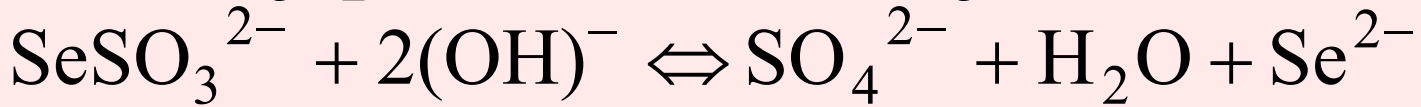
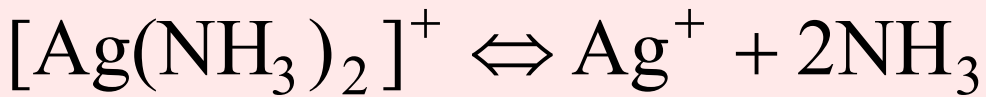
Aqueous ammoniacal solution of  $\text{AgNO}_3$  final pH=11.8

2 ml sodium selenosulphate

Yellow  
Brown  
Dark brown

$\text{Ag}_2\text{Se}$

## Chemical reaction occurs



# Solvothermal synthesis of $\text{Ag}_2\text{Se}$

Selenium dioxide( $\text{SeO}_2$ )  
dissolved in sodium  
hydroxide( $\text{NaOH}$ ) solution



Sodium Selenite  
( $\text{Na}_2\text{SeO}_3$ )

Silver nitrate  
( $\text{AgNO}_3$ ) solution



Sodium selenite  
solution



Silver selenite  
( $\text{Ag}_2\text{SeO}_3$ )

Silver selenite  
( $\text{Ag}_2\text{SeO}_3$ )

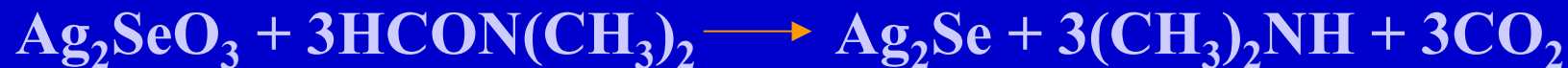


Dimethyl  
formamide  
 $\text{HCON}(\text{CH}_3)_2$

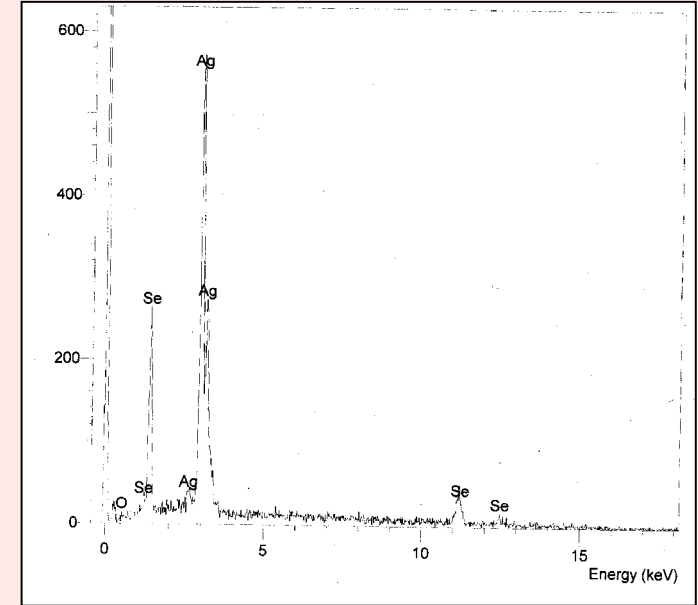
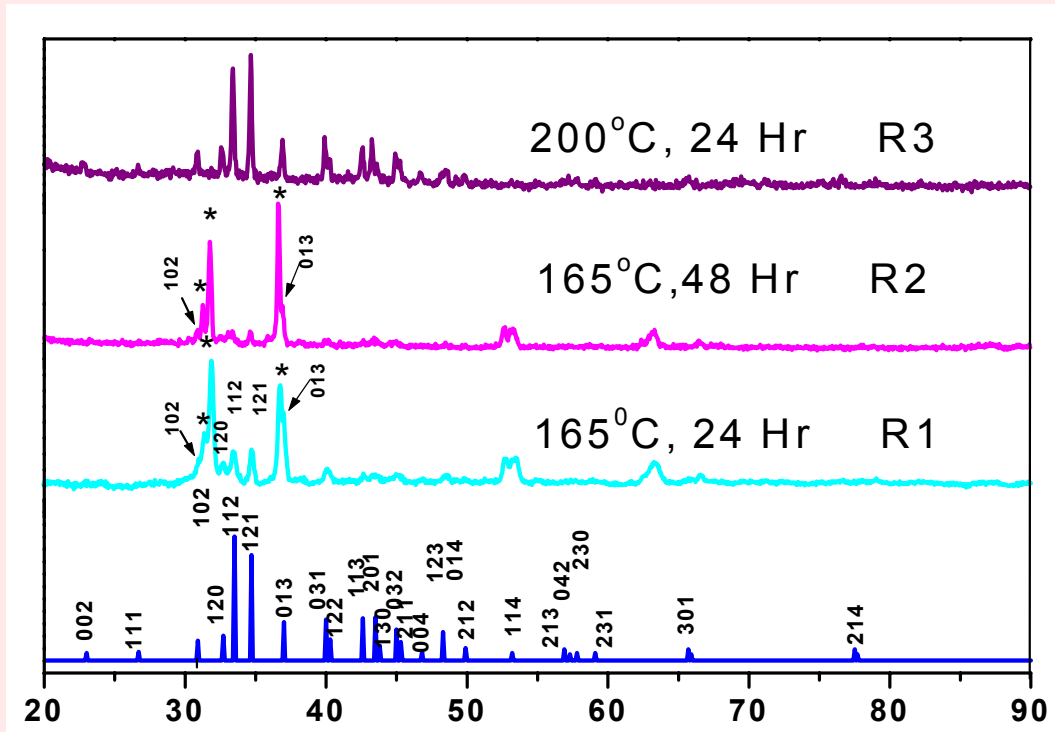
Autoclave  
  
 $200^\circ\text{C}, 24\text{h}$

Silver Selenide  
( $\text{Ag}_2\text{Se}$ )

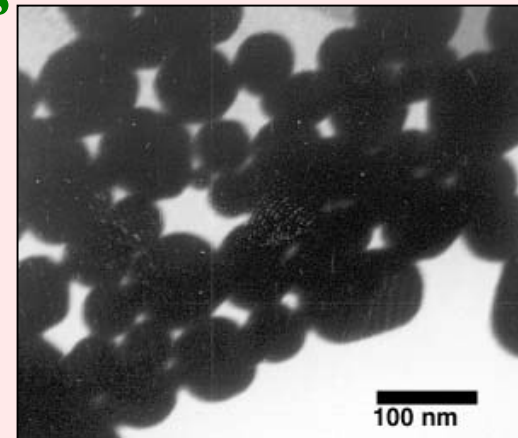
Possible reaction scheme:



# Characterisation



XRD spectrum of  $\text{Ag}_2\text{Se}$  nanocrystals



R3

# EFFECT OF SOLVENT

**Silver  
selenite**



**1:1 (V/V) DMF-  
Alcohol Mixtures**

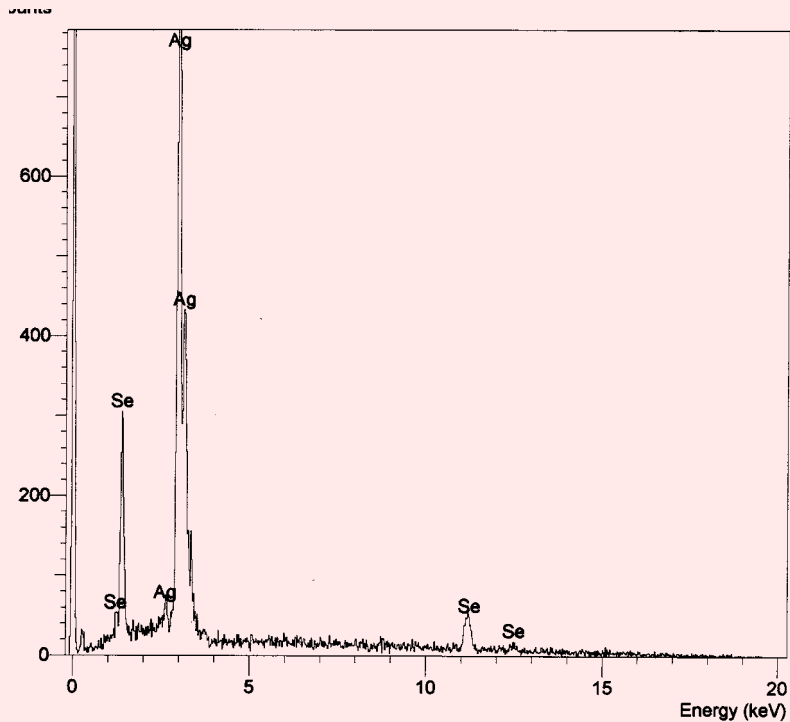
**Autoclave**



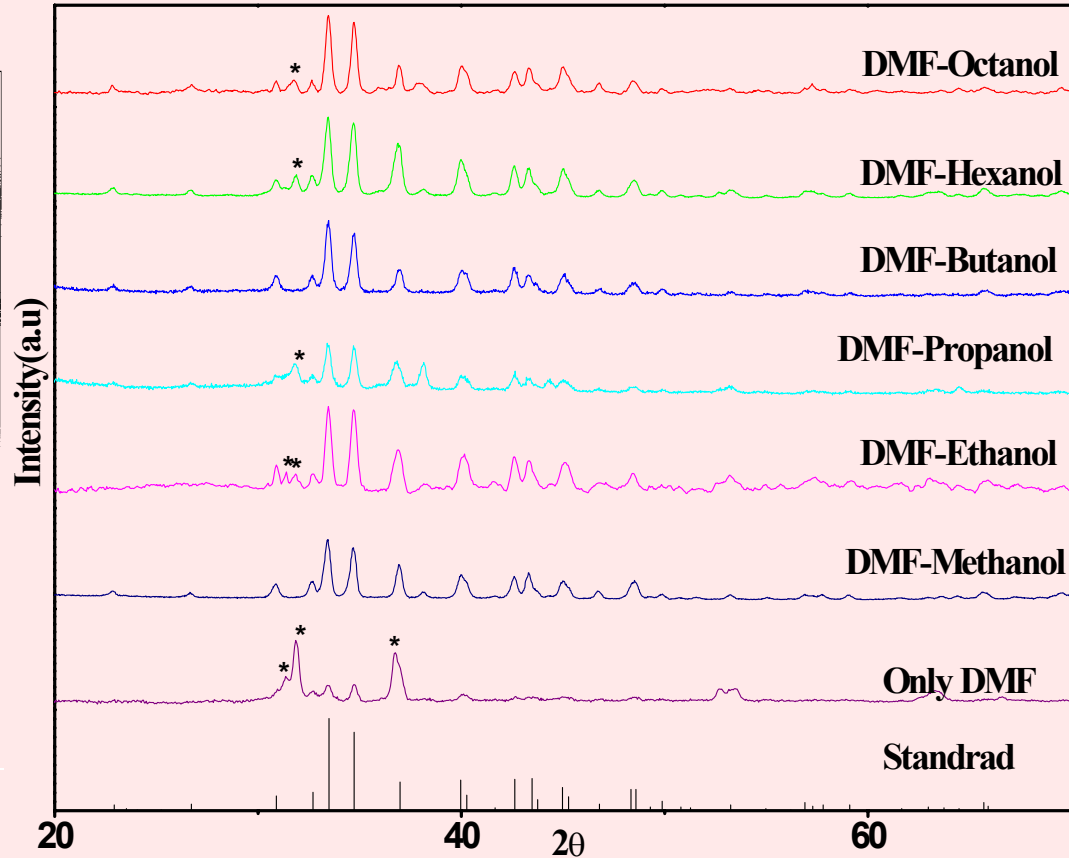
**Microstructured  
Ag<sub>2</sub>Se**

Sample name	Temp	Time	Mixed solvent
R9	165	24	Methanol+DMF
R10	165	24	Ethanol+DMF
R11	165	24	Butanol+DMF
R12	165	24	Hexanol+DMF
R13	165	24	Octanol+DMF

# EDX & XRD SPECTRA

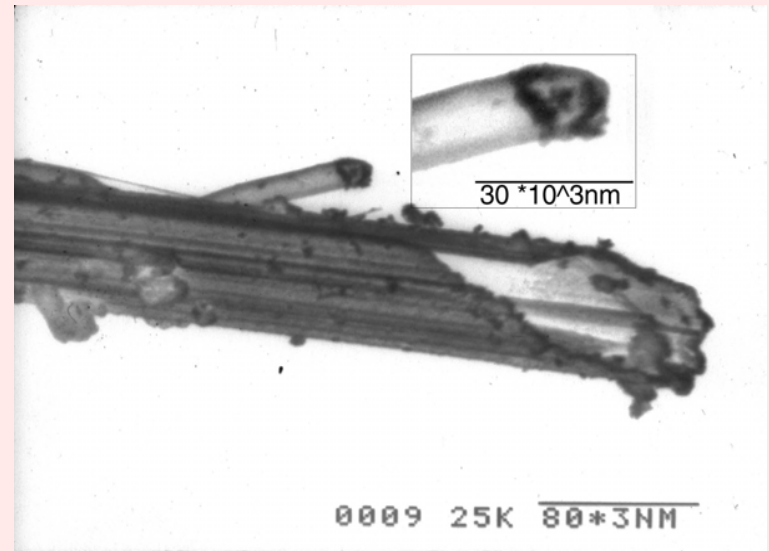
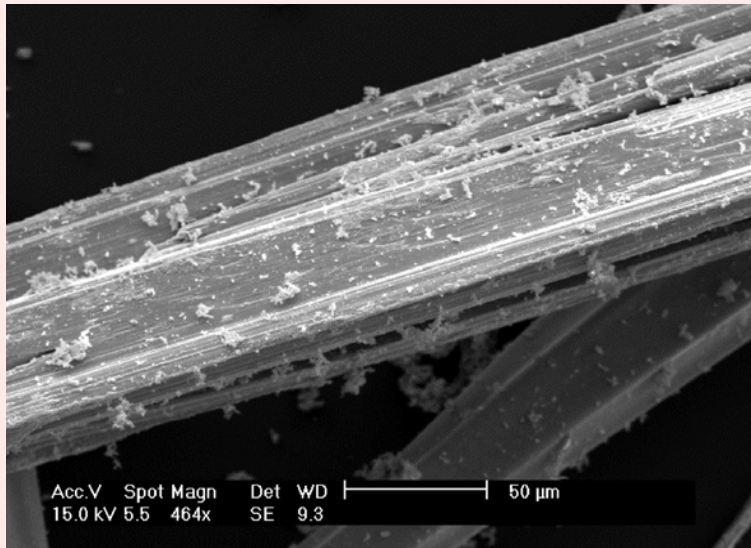
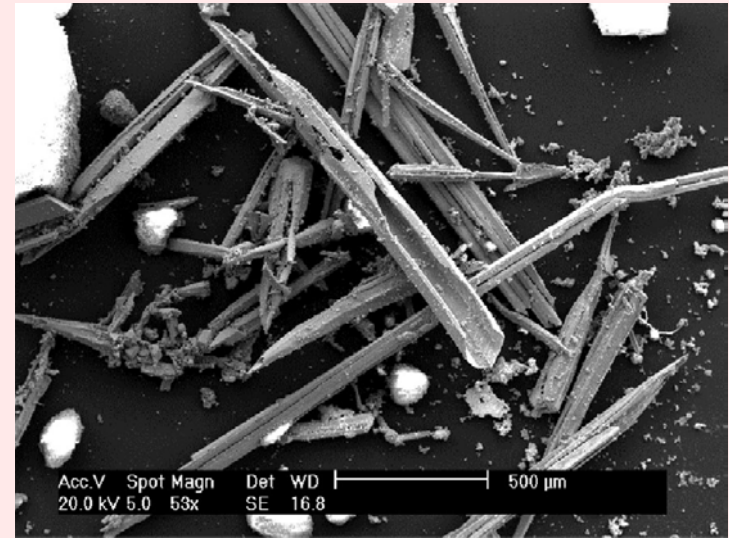
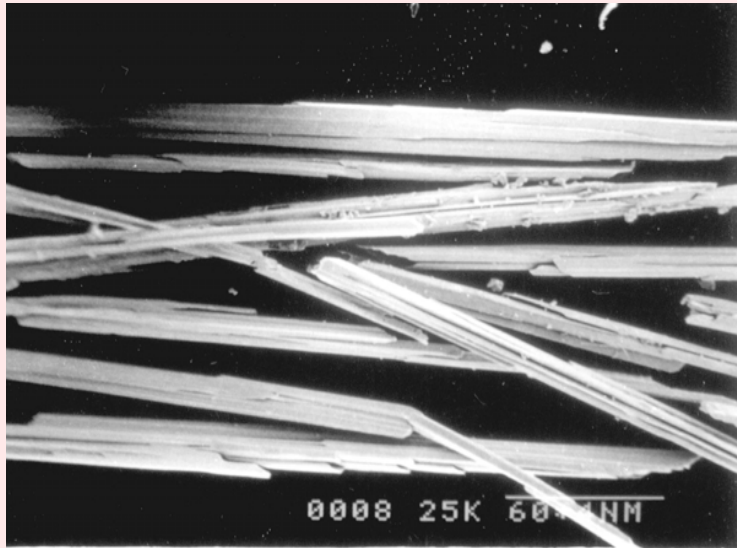


**EDX spectrum of R9**



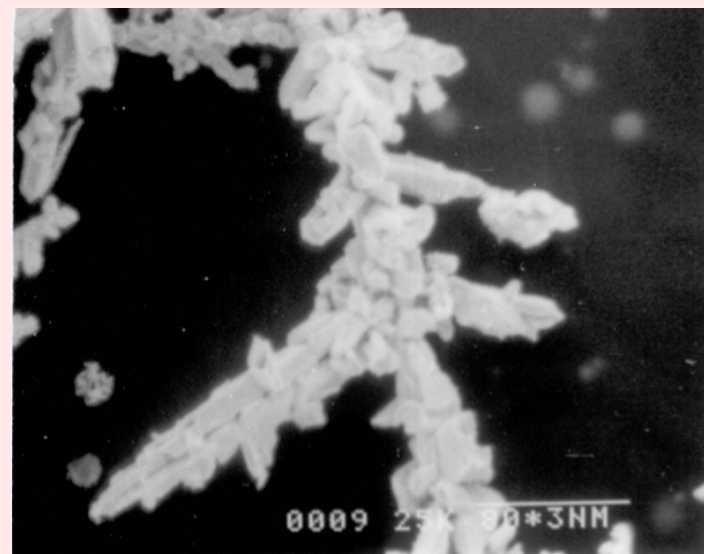
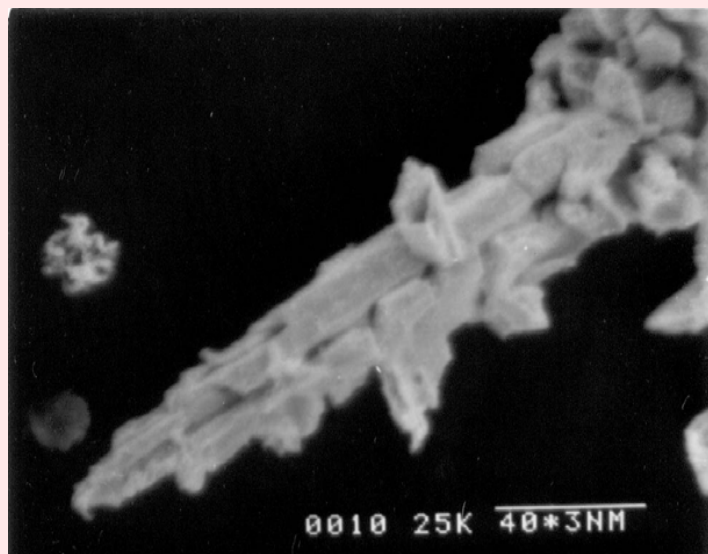
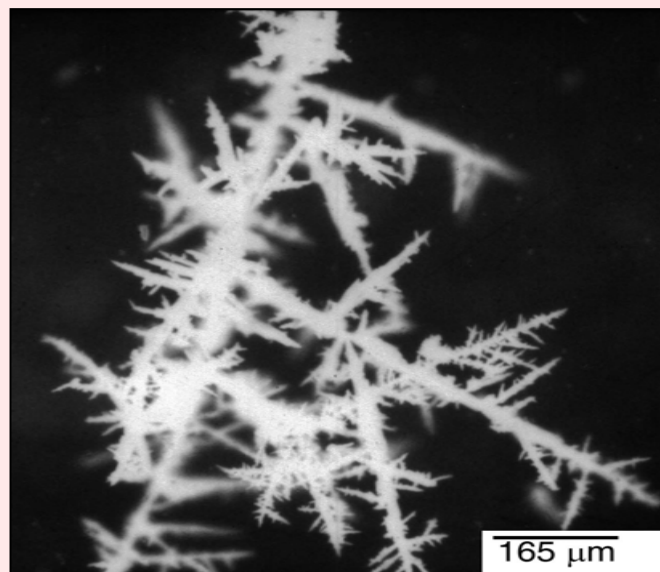
**XRD Spectrum of  $\text{Ag}_2\text{Se}$  synthesised using different mixed solvent**

# OBSERVATIONS

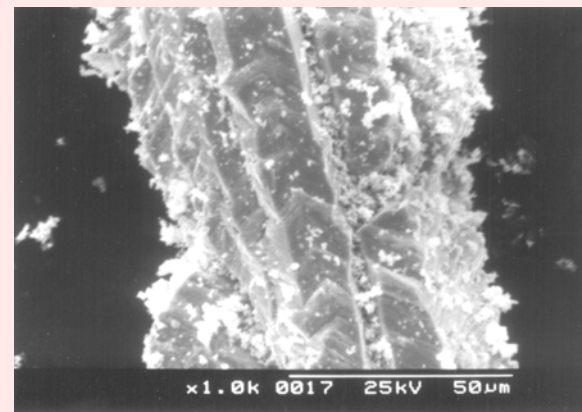
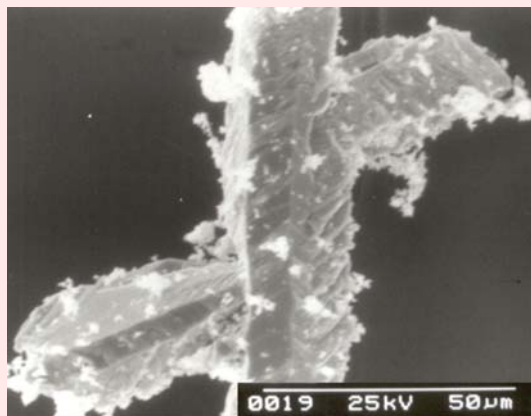
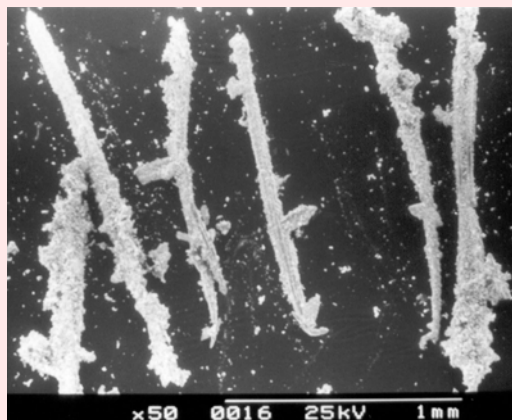


**Tubes like microstructures were formed in case of ethanol-DMF system**

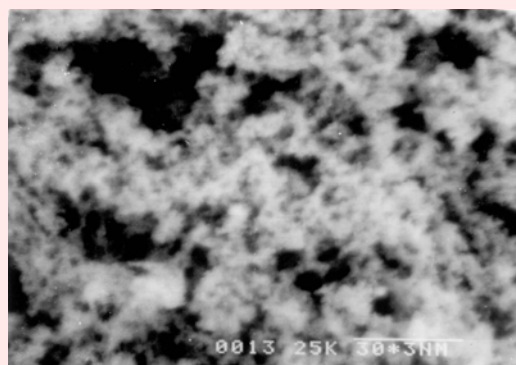
# Fractal like microstructures in methanol-DMF system



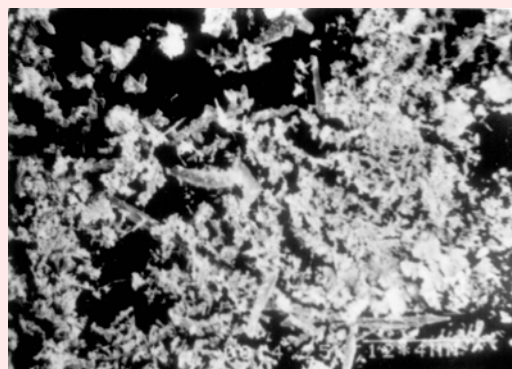
# Micrograph of $\text{Ag}_2\text{Se}$ obtained using different alcohols



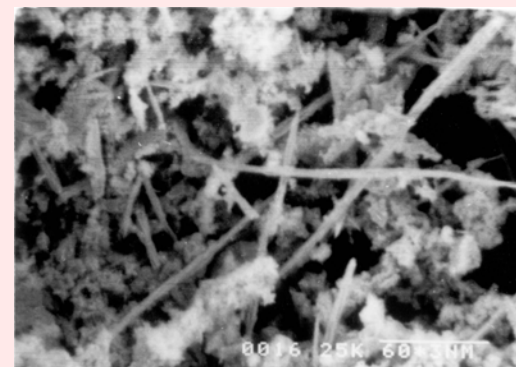
**Propanol**



**Butanol**



**Hexanol**

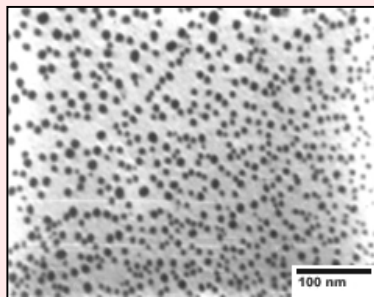


**Octanol**

# Dependence of morphology on the reaction condition

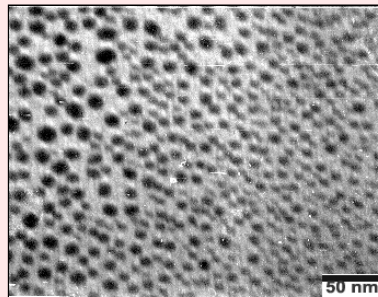
1mM AgNO<sub>3</sub> Aqueous Sol + excess NH<sub>4</sub>OH (final pH 11.8) +  
x mM Se<sup>2-</sup> ion source (Na<sub>2</sub>SO<sub>3</sub>Se)

X=.5



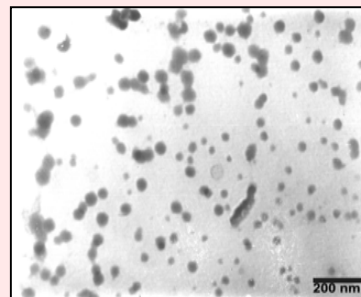
P5

X=.3



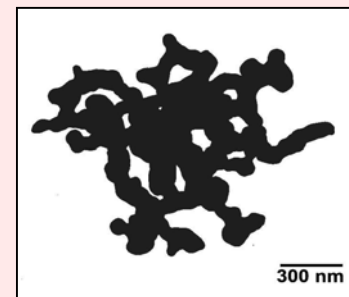
P6

X=.075

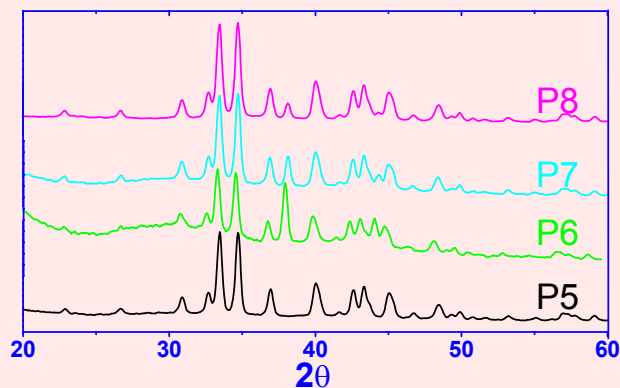


P7

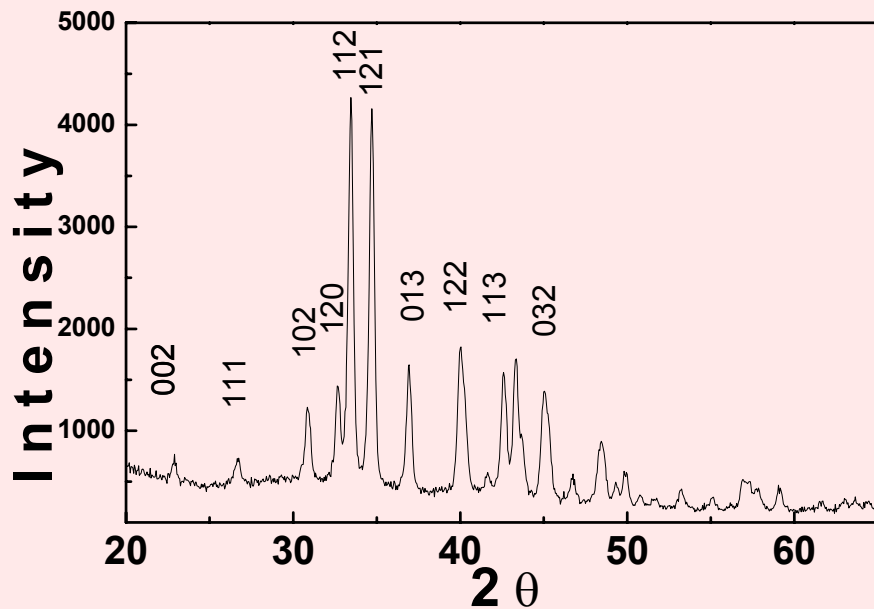
X=.032



P8

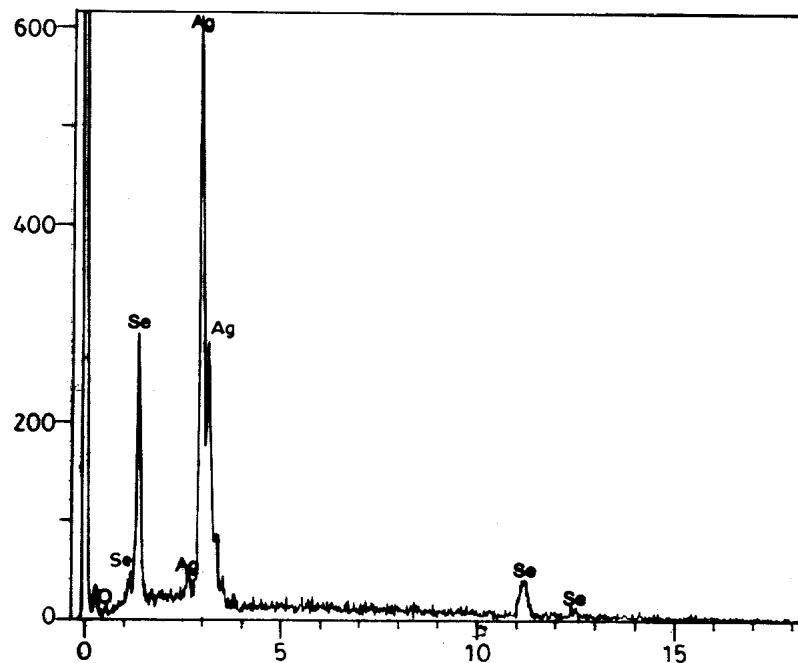


XRD spectra of the samples



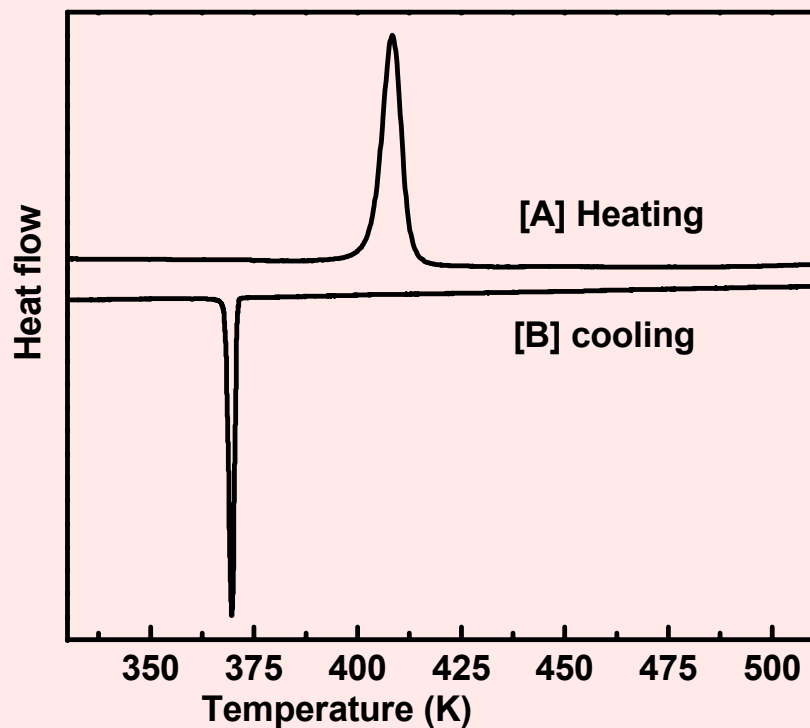
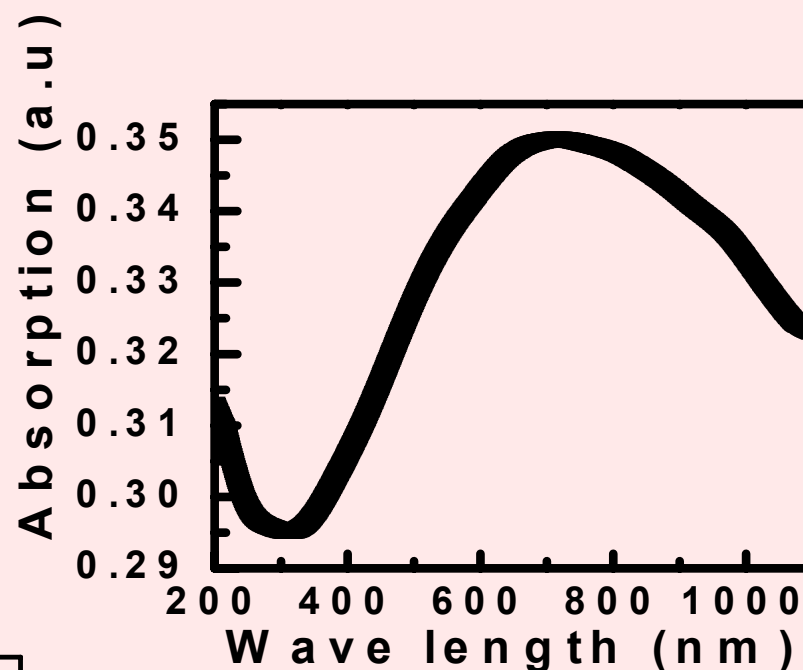
XRD spectra of silver selenide nanocrystals. Peaks are identified according to the JCPDF data sheet

EDXA spectra of Silver selenide nanocrystals



## UV-VIS Absorbance spectra

Maximum at 720 nm.

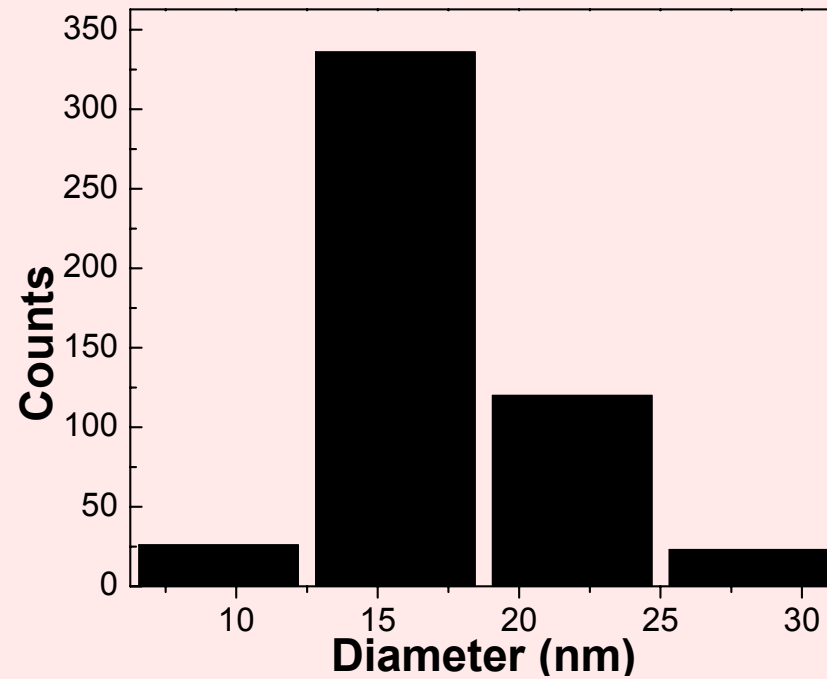
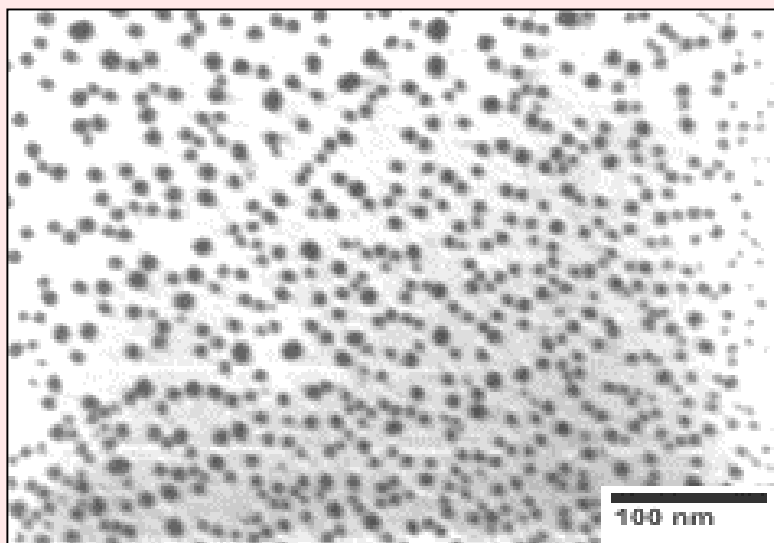


## DSC thermogram

During heating  $T_{\text{transition}} = 406 \text{ K}$

During cooling  $T_{\text{transition}} = 370 \text{ K}$

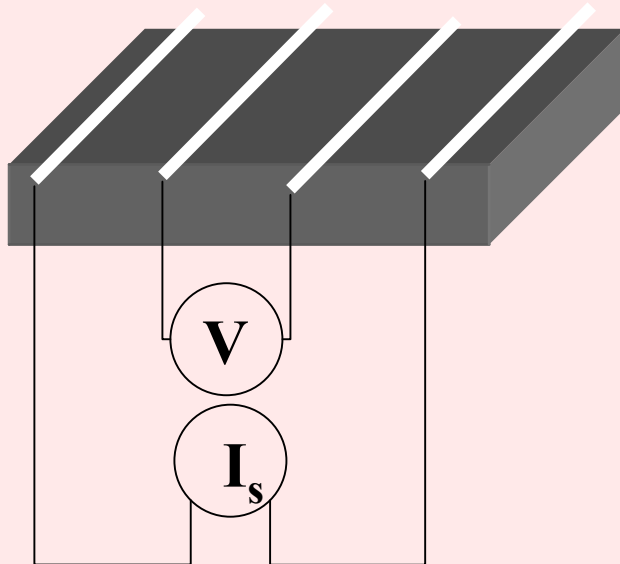
# TEM picture and histogramm



## Electrical characterizations

For electrical characterization a pellet was made by cool pressing the powder samples at 5 ton pressure for 5 minute. A rectangular block was cut from that pellet of dimension 1cm X 0.4cm

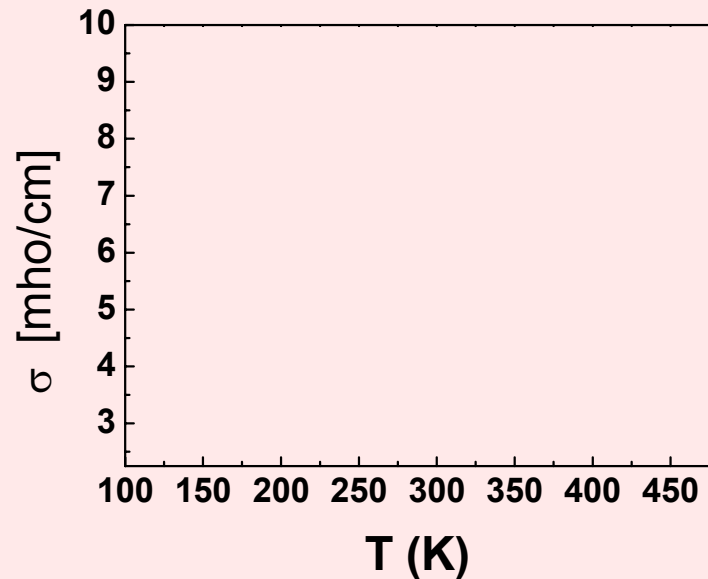
### Conductivity measurement



$I_s = (\pm)20$  mA from a Keithley programmable current source

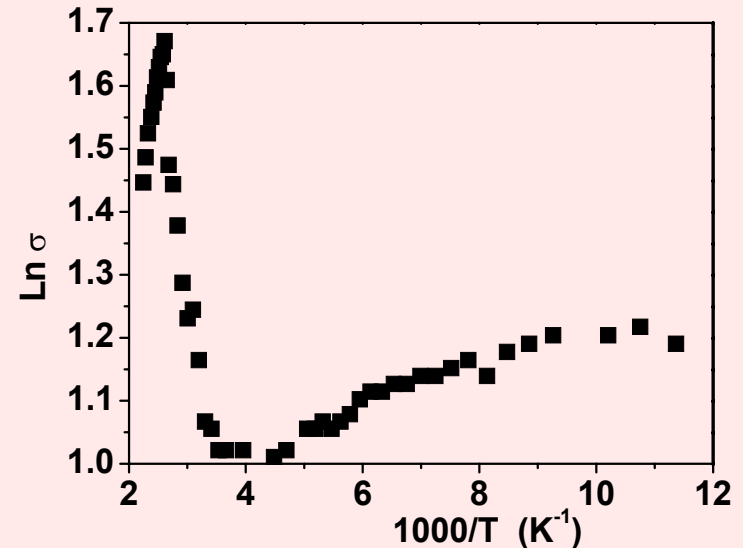
V measured by a Keithley multimeter

# Variation of conductivity with temperature



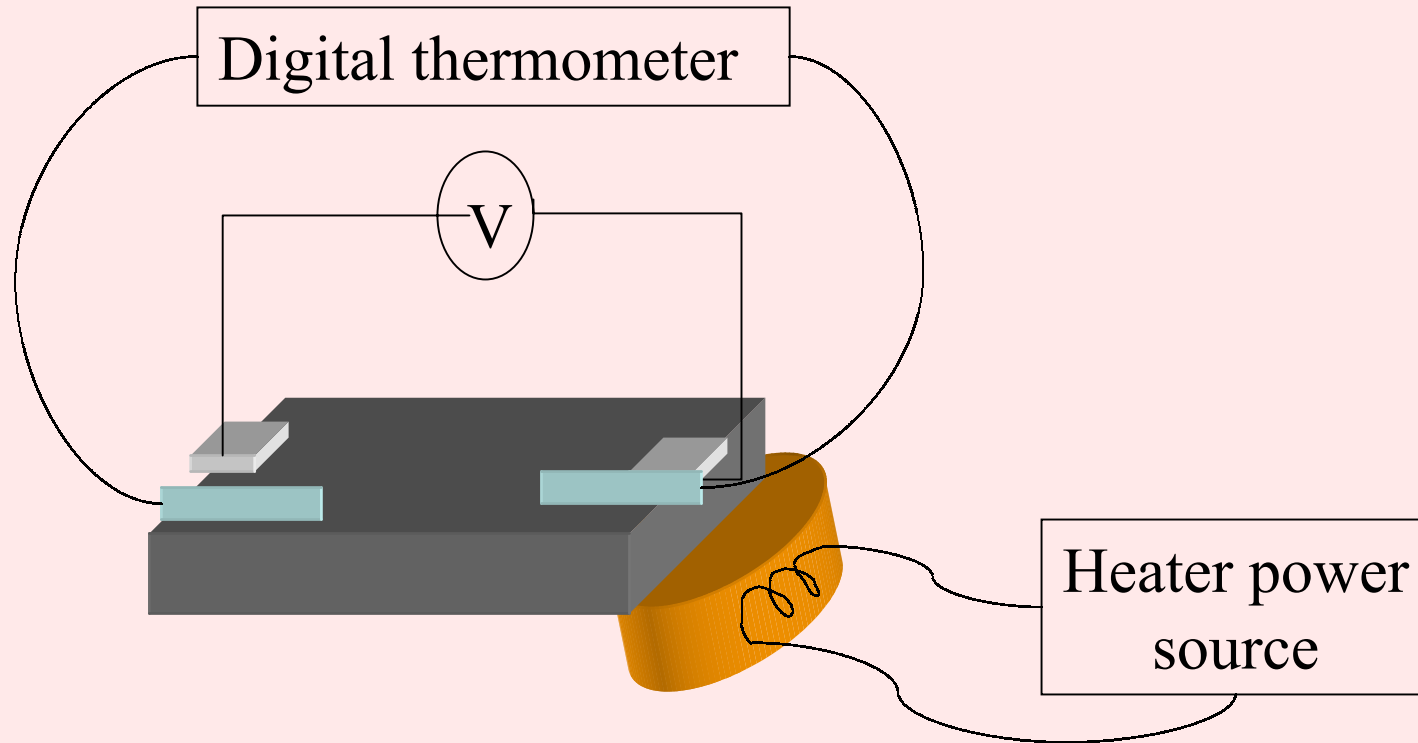
**S increases with T from 250 to 380 after that it decreases with increase of T.**

**The room temperature value of conductivity is  $\sim 3$  mho/cm and it increases to 5.3 mho/cm at the transition temperature 483 K**



**The conduction mechanism is different for three different temperature range**

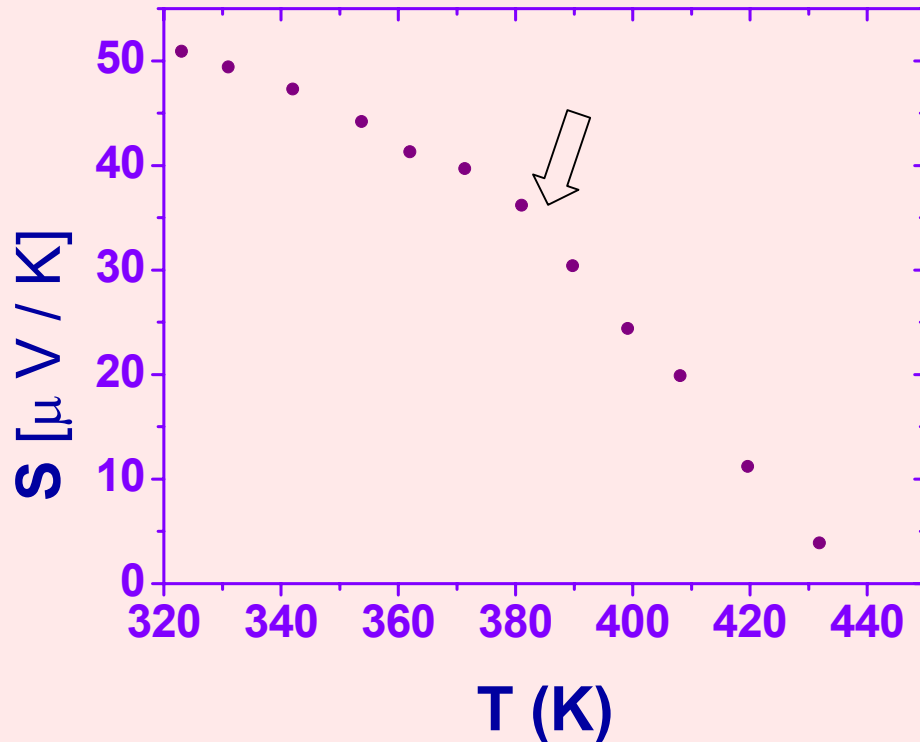
## Thermoelectric Power measurements



**A small temperature difference is maintained at the two ends of the sample by a heater**

**Measuring the potential drop  $\Delta V$  volts in the sample for a temperature gradient  $\Delta T$ , the thermoelectric power  $\theta$  is obtained from the relation  $\theta = (\Delta V/\Delta T)$  volts/ degree.**

# Variation of thermoelectric power with temperature



Two distinct slopes are conspicuous corresponding to two different phases with transition temperature  $\sim 380$  K.

Conn & Taylor as well as Astakhov & Golyshev report slow fall of  $S$  in the temperature range below the room temperature but sharp fall near the transition point and rise above the point in bulk polycrystalline samples.

Shukla et al. report  $S$  is essentially independent of temperature in the low temperature  $\beta$  phase and it slightly decreases with increase of temperature in the high temperature  $\alpha$  phase.

We note that in nano phase, the thermoelectric power decreases with increase in temperature in both  $\alpha$  and  $\beta$  phases but the rate of decrease is higher in alpha phase. In the low temperature phase the rate of fall is nearly  $0.25\mu\text{V} / \text{K}$  but in high temperature phase it is around  $0.6 \mu\text{V} / \text{K}$ .

## Conclusion

- ☀ The nanophasic silver selenide of different morphology was synthesized by different methods.
- ☀ Solution phase synthesis yielded narrow size distribution of the particles.
- ☀ Nano particle obtained by solvothermal synthesis in presence of ethanol or methanol self assembled into novel patterns.
- ☀ Thermoelectric power measurement shows that the electrons are the majority carrier in transport processes .
- ☀ conductivity and thermoelectric power measurements against temperature indicate polymorphic phase transition of the  $\text{Ag}_2\text{Se}$  samples.

# Acknowledgement

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THANK YOU