# Effect of impurities on the morphology on electrical properties of multifunctional TAS Crystals: $Tl_3AsSe_3$

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This project is an undergraduate research project of Teja Nagaradona

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## Outlines

- Objectives
- Background
- Purification and synthesis
- Crystal growth
  - Vertical Bridgman
- Fabrication and Characterization
  - Dielectric measurements (focus for this talk)
  - Acousto-Optic (AO) parameters
  - Nonlinear Optical (NLO) characteristics
  - Radiation detection characteristics
- Summary

TAS is an excellent Acousto-Optic, NLO and Radiation detection material

# Multifunctionality of TAS Crystals: $Tl_3AsSe_3$

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**Objectives:**

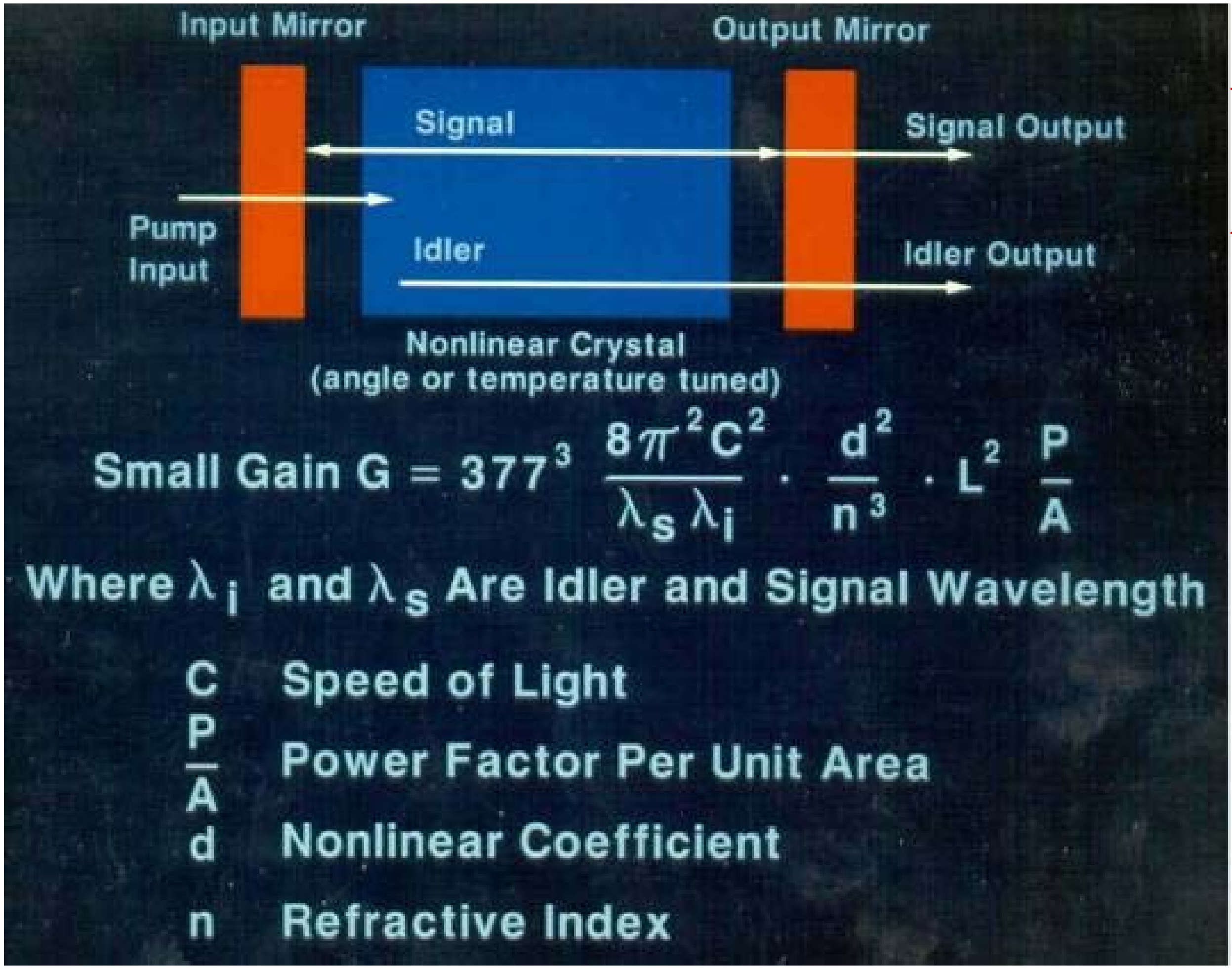
Effect of impurity on the properties of multifunctional ternary chalcogenide crystal for sensors

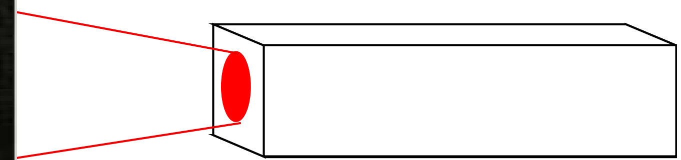
**Approach:**

Develop large single crystal of multifunctional materials. Demonstration of TAS will meet goals for:

- Dielectric constant and resistivity
- NLO (frequency conversion) harmonic generator
- Acousto-Optic Tunable Filter (AOTF) for MWIR and LWIR hyperspectral imaging
- Radiation sensor: $\gamma$-ray sensors
- Etalon and prism based MWIR and LWIR imagers
- A pathway for quaternary selenide semiconductors

# Great need for materials for direct pumping by 1.06 μm laser for MWIR and LWIR



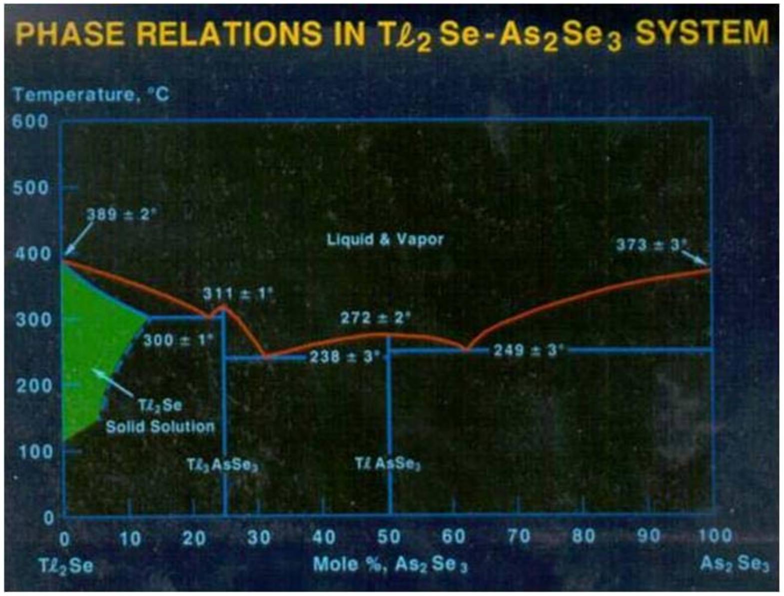
**Birefringent Materials and Required characteristics**

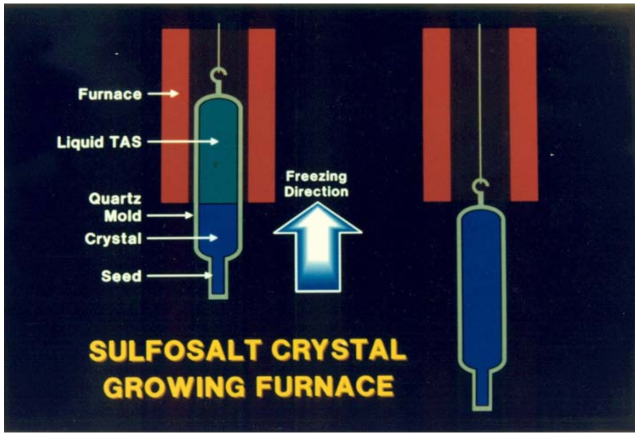
- **Damage T-hold > 3 J/cm$^2$**
- **Small Walk-off**
- **High $d^2/n^3$ (180)**
- **Low cost**
- **Adhering coatings**
- **Transparency 1.0 to 18 μm**

TAS is an excellent material for NLO applications. Transparency range of TAS can be designed by sulfur and Selenium TAS transmits up to 16 micrometer

# TAS phase diagram shows a congruent compound

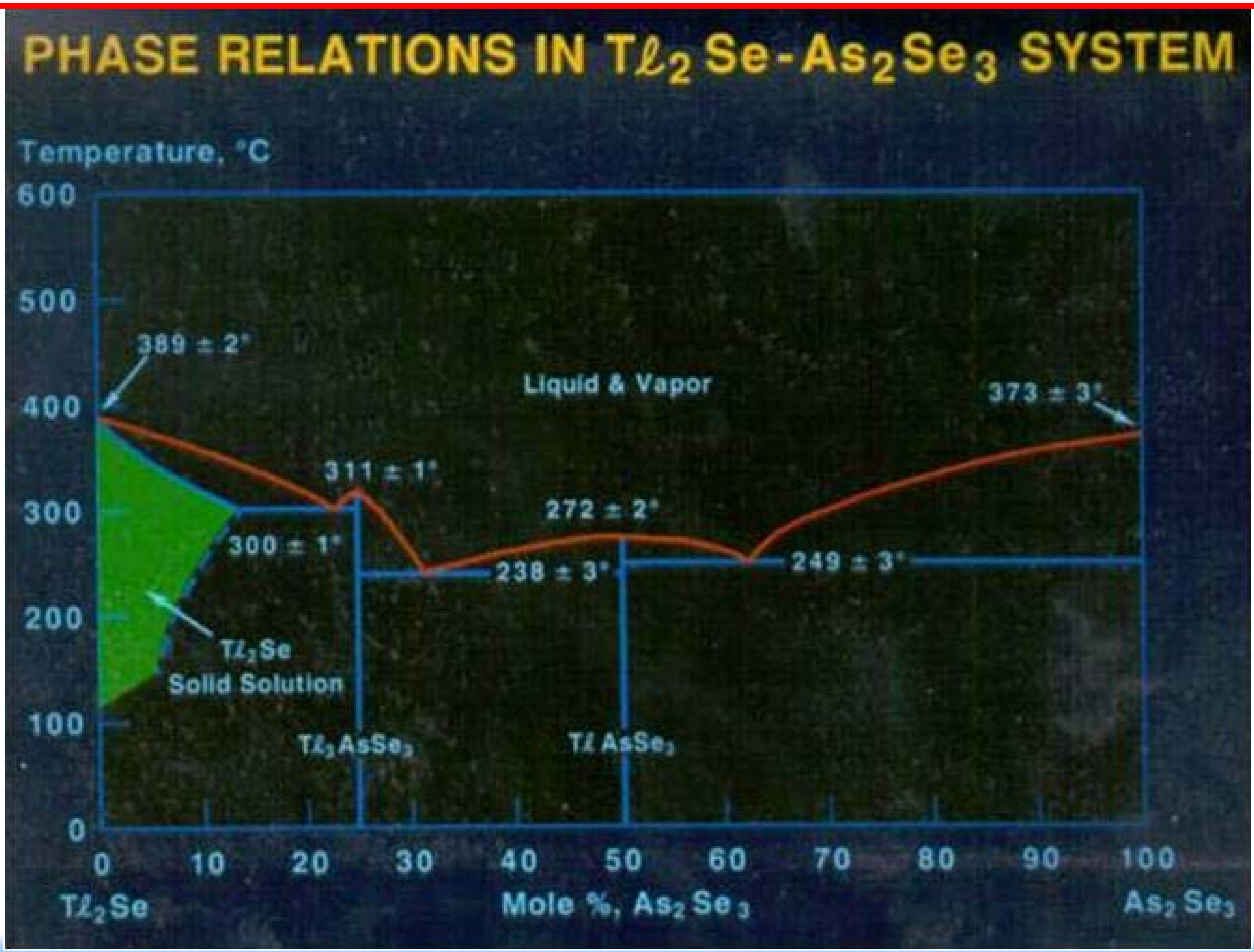
- $Tl_3AsSe_3$ is a congruent compound
- The melting point is 311.5C
- Stoichiometric compound is prepared by reacting Tl, As and Se in stoichiometric ratio.
- Crystals were grown in Bridgman geometry




**• $Tl_3AsSe_3$ is an excellent Acousto-optic and nonlinear crystal**

# To avoid the cleaving and improve fabrication we developed $Tl_3AsSe_3$ compound




**We have demonstrated growth and fabrication capabilities**

# Growth of Thallium Arsenic selenide: $Tl_3AsSe_3$

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## Purification and preparation of stoichiometric source material

**Purification of as-supplied materials:**

Tl: Melt-freeze method (99.999%)

As: 99.9999%

Se: Directional solidification (99.999%)

**Preparation of compounds:**

3Tl + As + 3Se

3x204.38+ 74.92 + 3x78.98 Molecular weight

612.84 + 74.92+ 236.94

1 + 0.1223 + 0.387

*Our approach was to use elements for preparing stoichiometric compounds*

# Growth of Thallium Arsenic selenide: $Tl_3AsSe_3$

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## Reaction Scheme

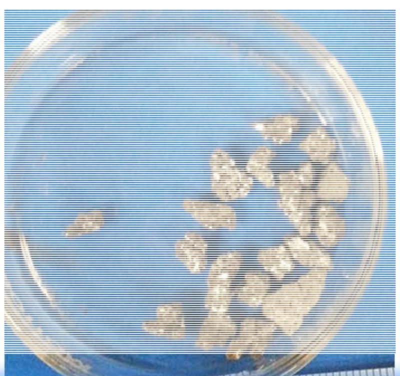
- Horizontal cylindrical furnace was used
- Temperature was raised in steps
- Highest temperature was 420C
- Melt was kept several hours for completing the reaction

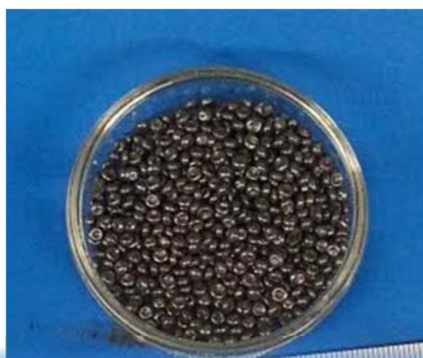

**Horizontal cylindrical furnace used for reaction**

*Great care was taken to avoid explosion since reaction of Tl+As+Se is exothermic*

# Oxidized surface of 99.999% pure Thalliumn was purified


**Purification steps of as supplied Thallium and purified thallium**





**As supplied arsenic and selenium**

*Our approach could not eliminate carbon and oxygen impurities*

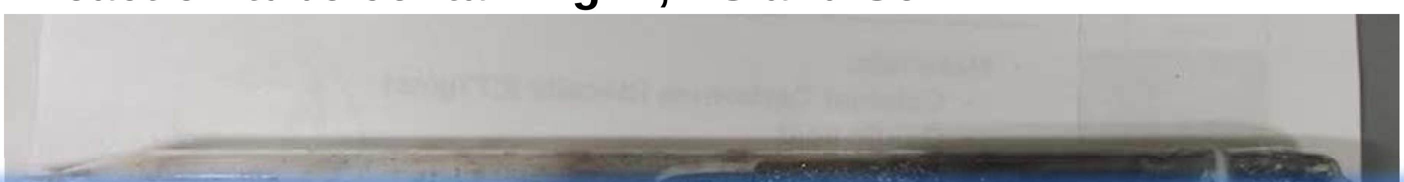
# Tl, As and Se in reaction tube

**Reaction tube with Tl, As and Se and reaction furnace**

**Reaction furnace**

**Reaction tube containing Tl, AS and Se**

**Reacted mixture**



*Care was taken to provide enough volume to avoid rupture (reaction is exothermic)*

# Morphology of the free surface of TAS after reaction

Cm size long needles consisted of rectangular particles at the surface of reacted TAS Charge

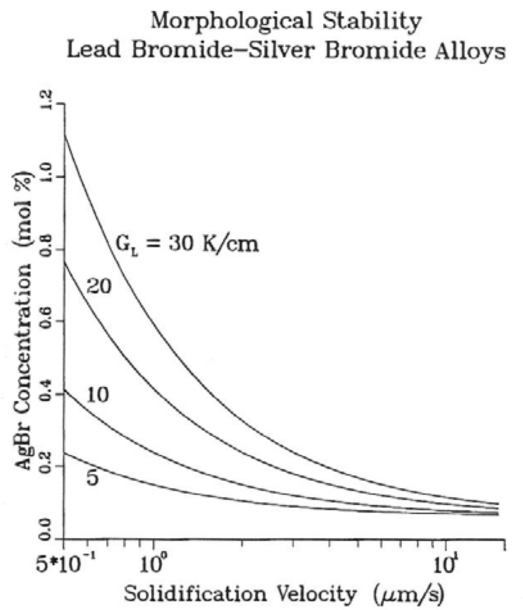
*Long needles consisted of nano cubes are not well understood*

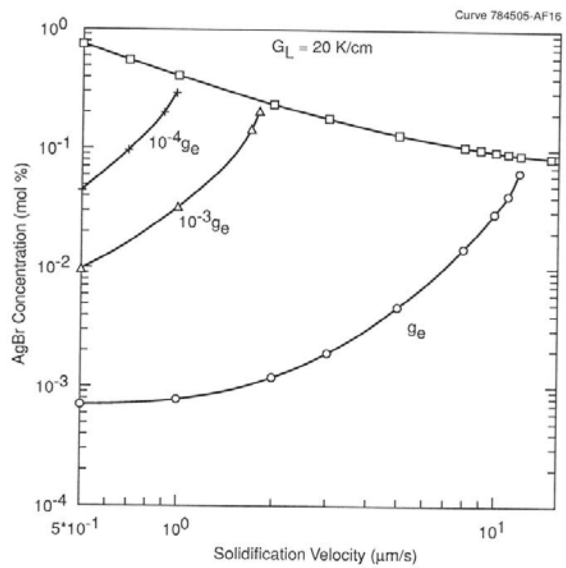
# Arrays of nano, microcubes were showing indication of formation of nanowires

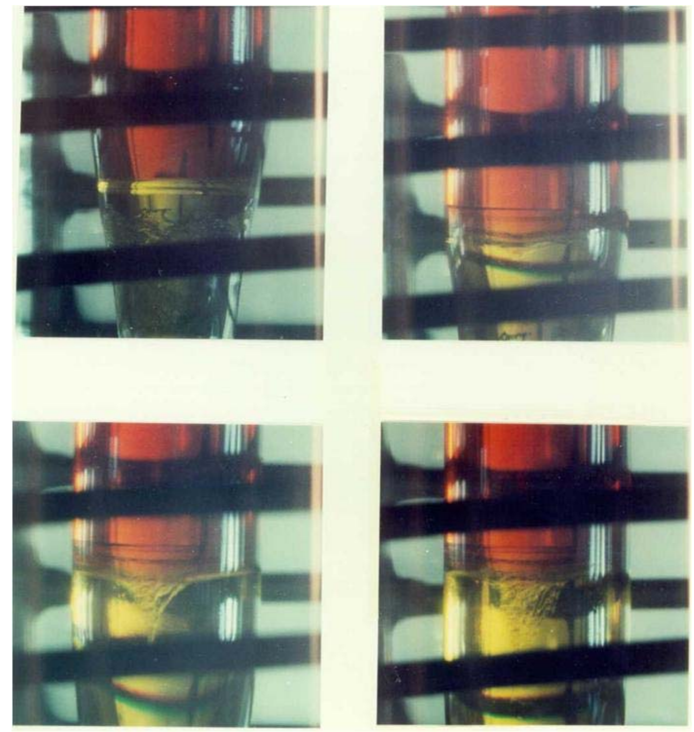
First indication of nanowire formations from particles as reported in N. B Singh, S. R Coriell, Matthew King, Brian Wagner, David Kahler, David Knuteson, Andre Berghman and Sean McLaughlin, Growth Mechanism and Characteristics of Semiconductor Nanowires for Photonic Devices", Journal of Nanoscience and Technology, 1 (2) 1-8 (2014).

Although we did not controlled cooling, this micrograph shows an indicatior that in case of faceted nano/micro wires Nano/micro cubes are building bloc

**Modeling was performed to evaluate growth velocity for different thermal gradients for planar interfaces**



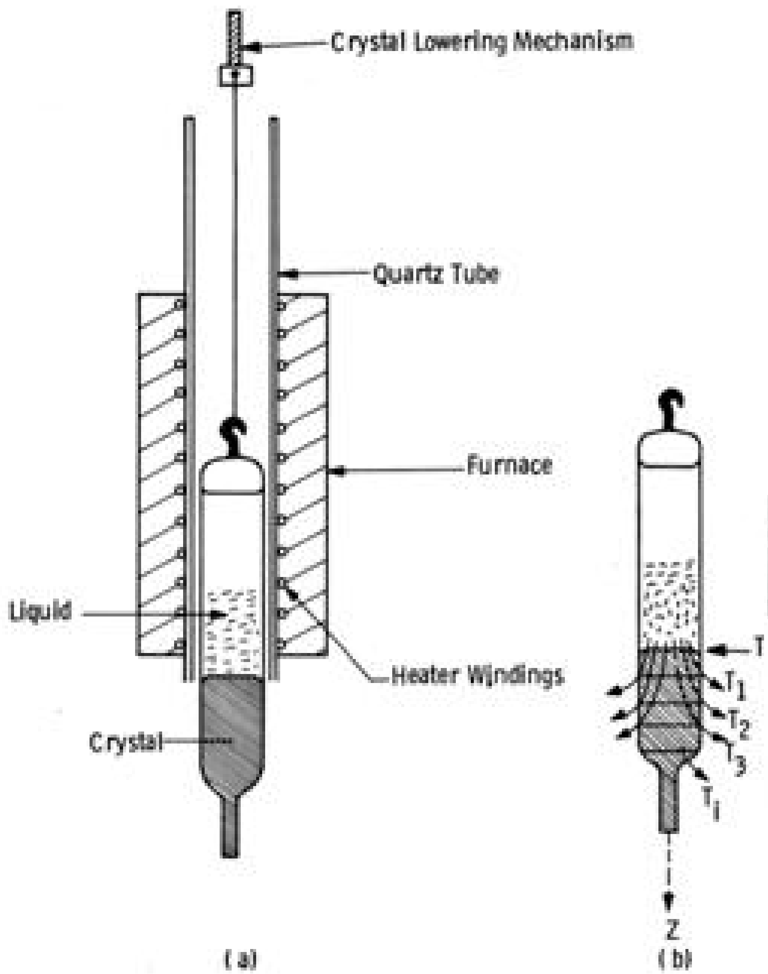



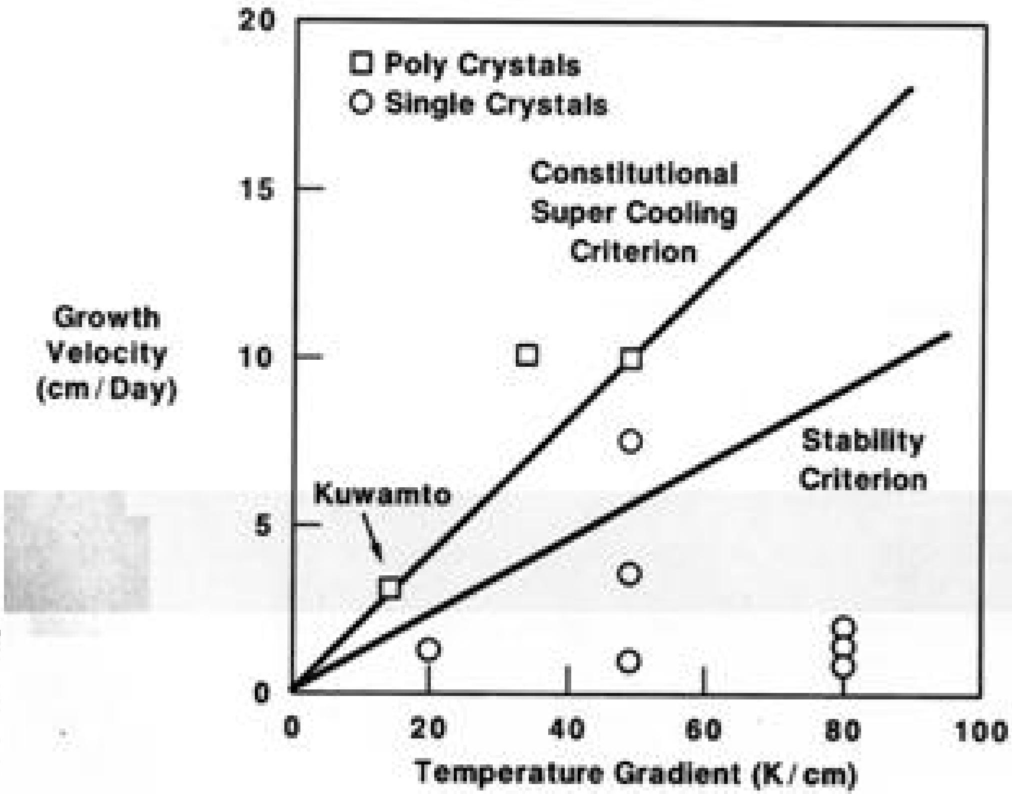



Morphologcal stability limit was determined for Solidification velocity and concentration of dopant

**Morphological stability and convective stability were studied for different growth velocities**

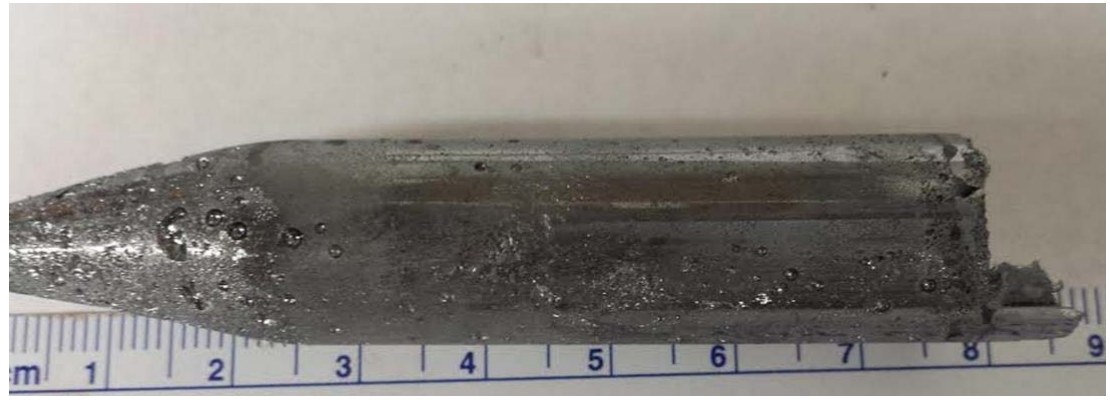
# Temperature and thermal gradient was kept high (>30K/cm) enough to avoid constitutional supercooling




Temperature in hot zone was 450C and cold zone in the range of 200C
The growth speed was 2-3cm/day and thermal gradient >30K/cm

# TAS single crystals were taken out of quartz





**Vertical Bridgman furnace and as grown TAS crystals**

TAS crystal had some bubbles and voids on surface. We expected this since quartz tube was not coated. Fab and quality evaluation is progressing

# Existing growth and characterization facilities


High temperature furnace

Blue M furnace for high temp synthesis

Bulk synthesis and crystal growth

wth

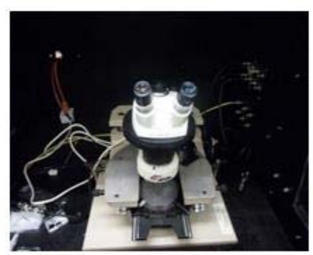
Custom Bridgman growth furnace

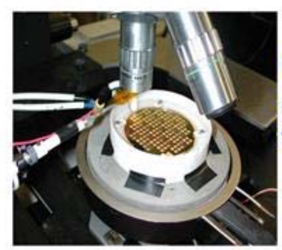
Three zone CVD growth furnace

Thin Film and nano crystal growth

Solution crystallizer

Optical and SEM microscopes





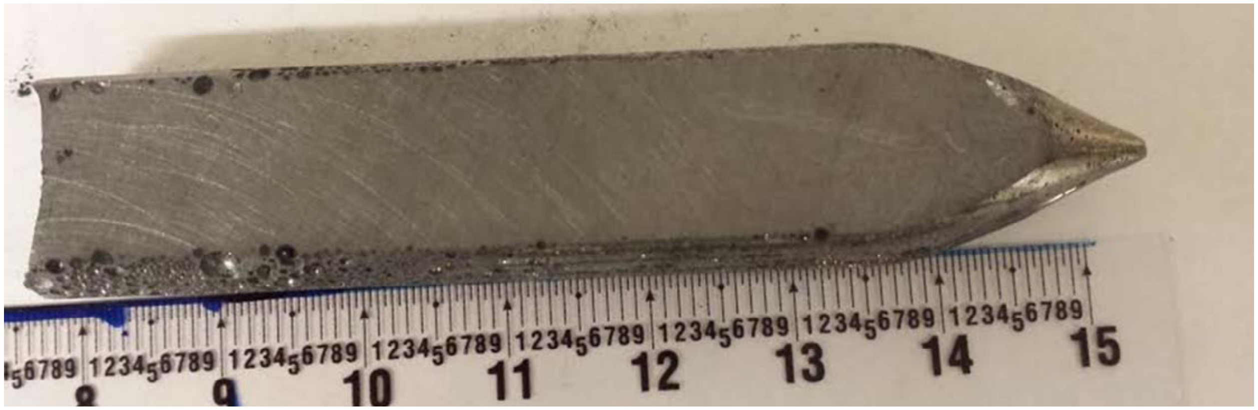
Characterization and device fabrication

Probe facilities for materials and device characterization

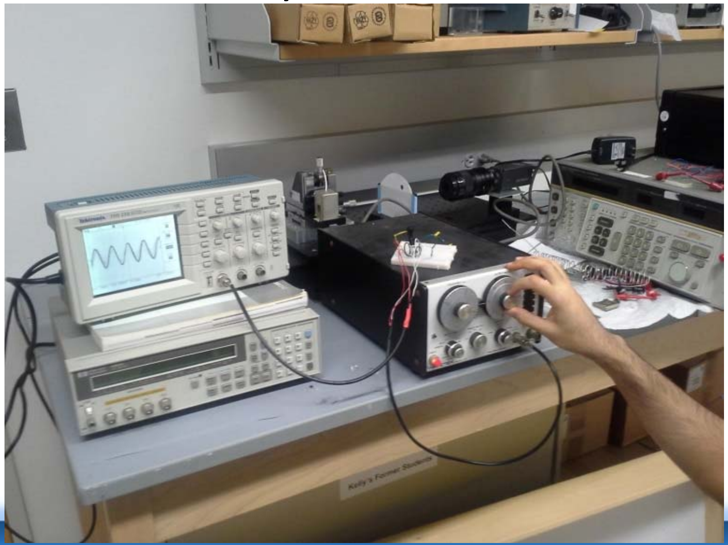
*In addition, we have real time Laue, XRD, SEM and TEM facilities at UMBC*

# As grown crystals were fabricated

Polishing was performed by using  ethylene glycol for polishing slabs

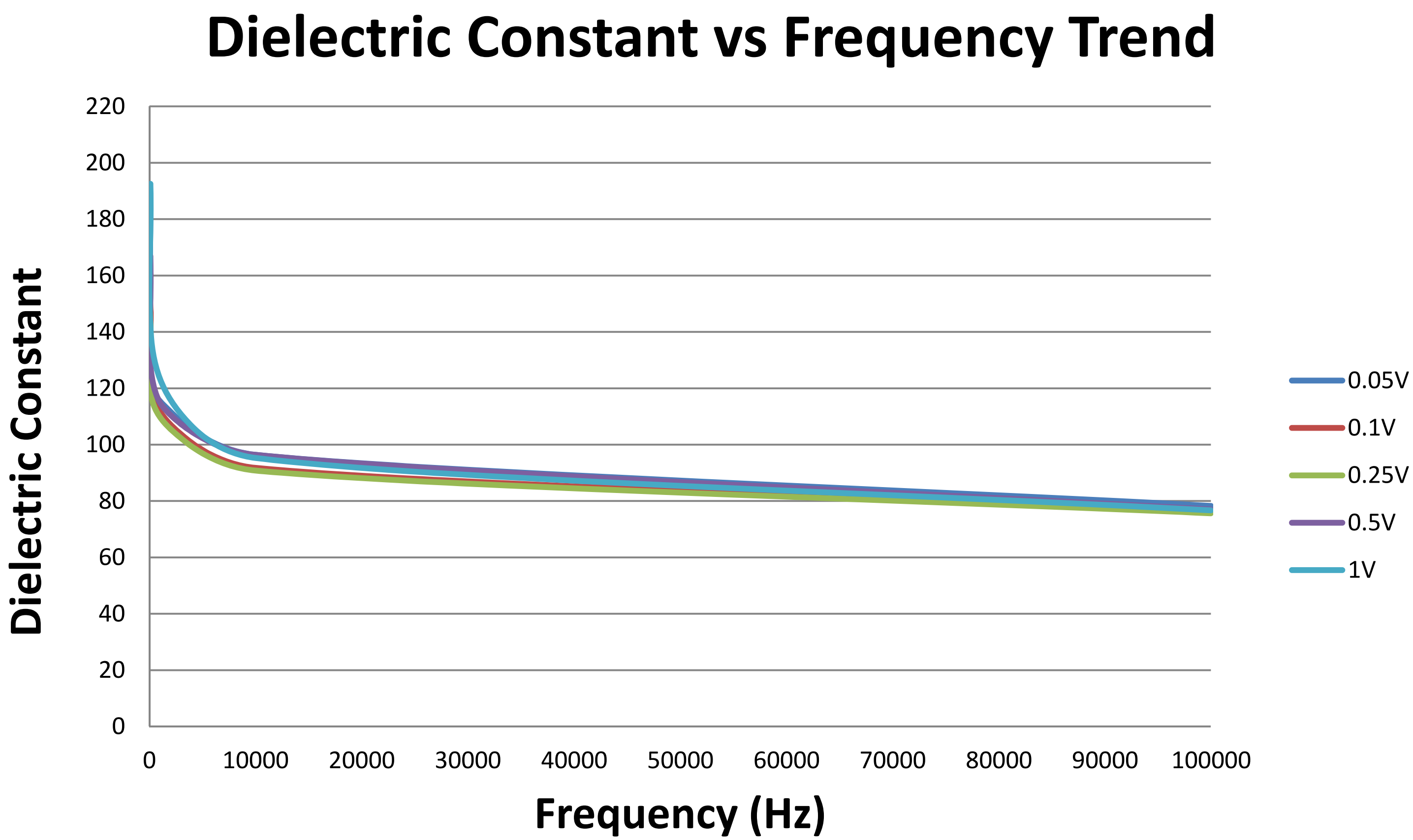



Equipment used for determining dielectric constant and resistivity



- *Dielectric constant and resistivity were measured using small fabricated slabs*

# We focused on dielectric and resistivity measurements




- The dielectric showed the typical pattern as the function of frequency.
- For high purity samples dielectric constant at 9.6GHz was measured to be 26 and loss tan delta= 0.022 at Northrop Grumman Corporation

- *The observed dielectric constant was almost constant in high frequency region*

# Resistivity of as grown crystals as the function of frequency

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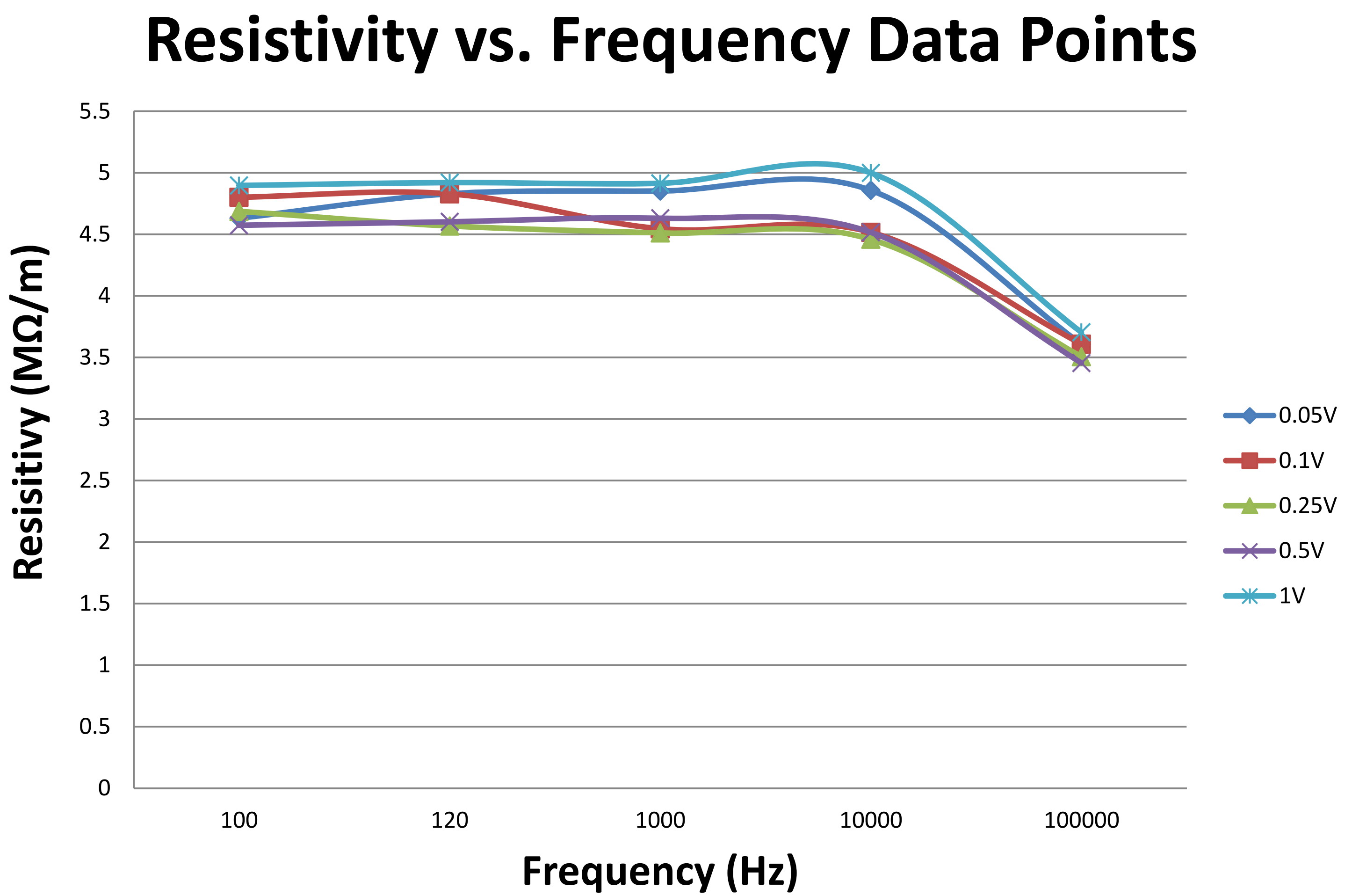
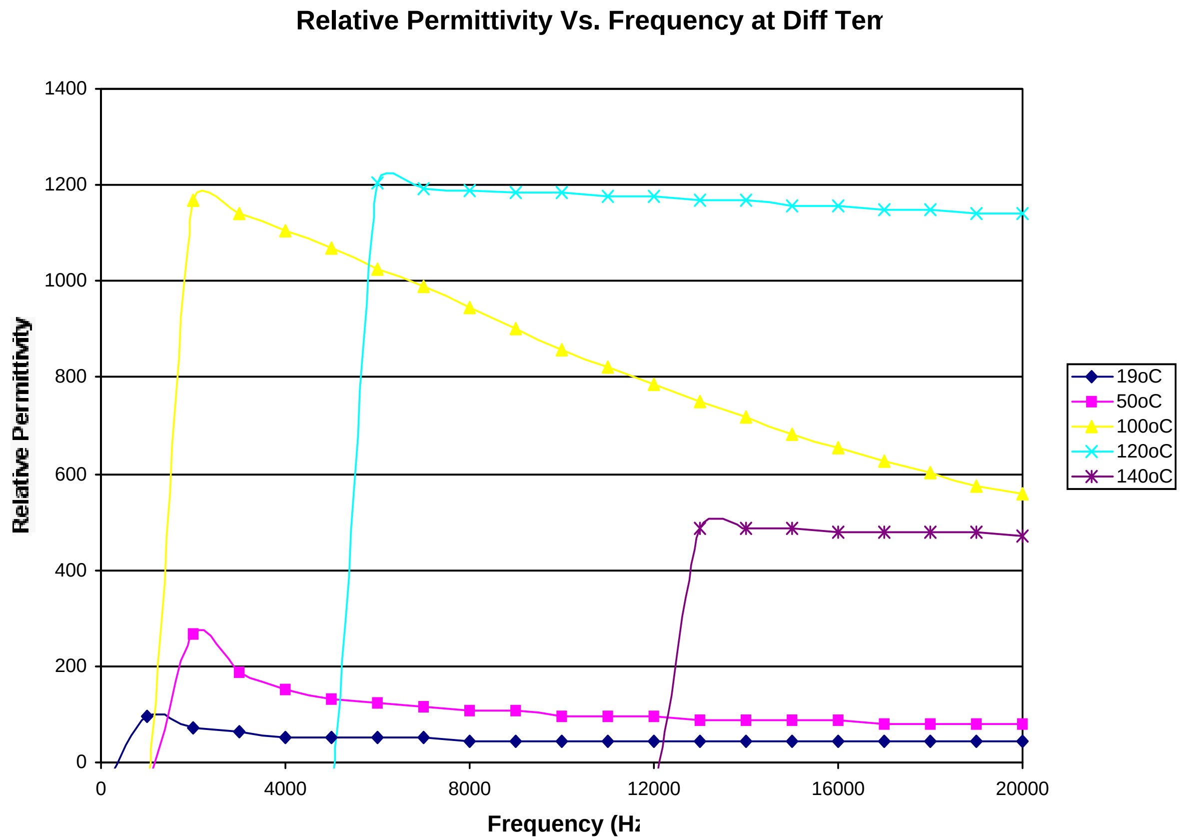



- *Resistivity was higher than previously measured crystals*

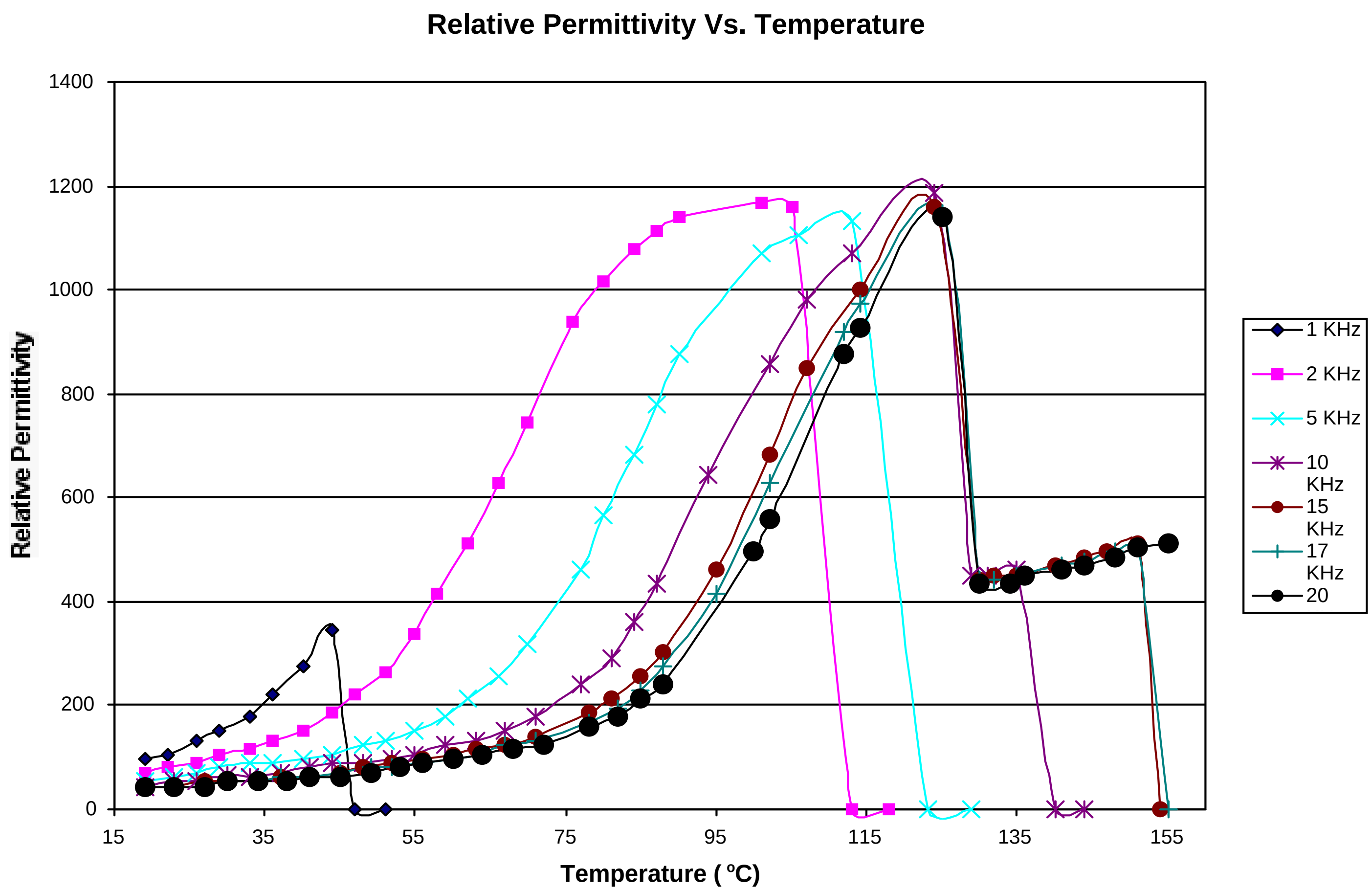
# Effect of Frequency and Temperature on Relative Permittivity (K) of TAS Crystals




**Effect of frequency and temperature on relative permittivity (K) of Tl3AsSe3 Crystal**

- *This is previous data by Prof. Raj Singh for very high purity TAS*

# Effect of temperature and frequency on relative permittivity (K) for Tl3AsSe$_3$ Crystal




- *There was no pattern on dielectric constant in high purity TAS for increasing temperature*

# Properties of TAS in TH range

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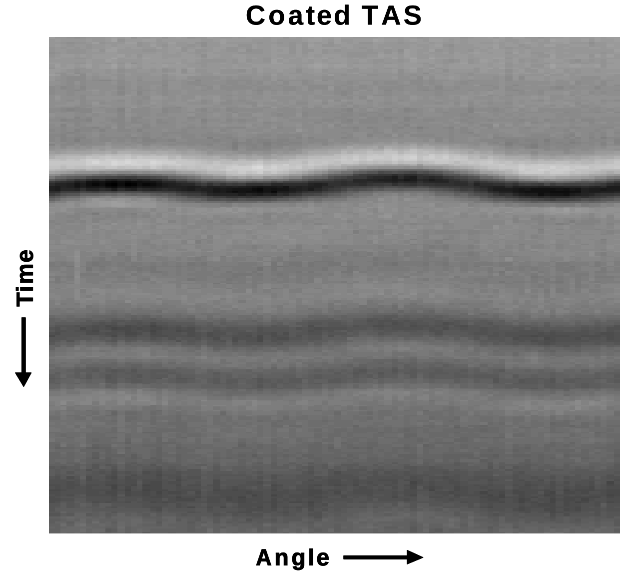
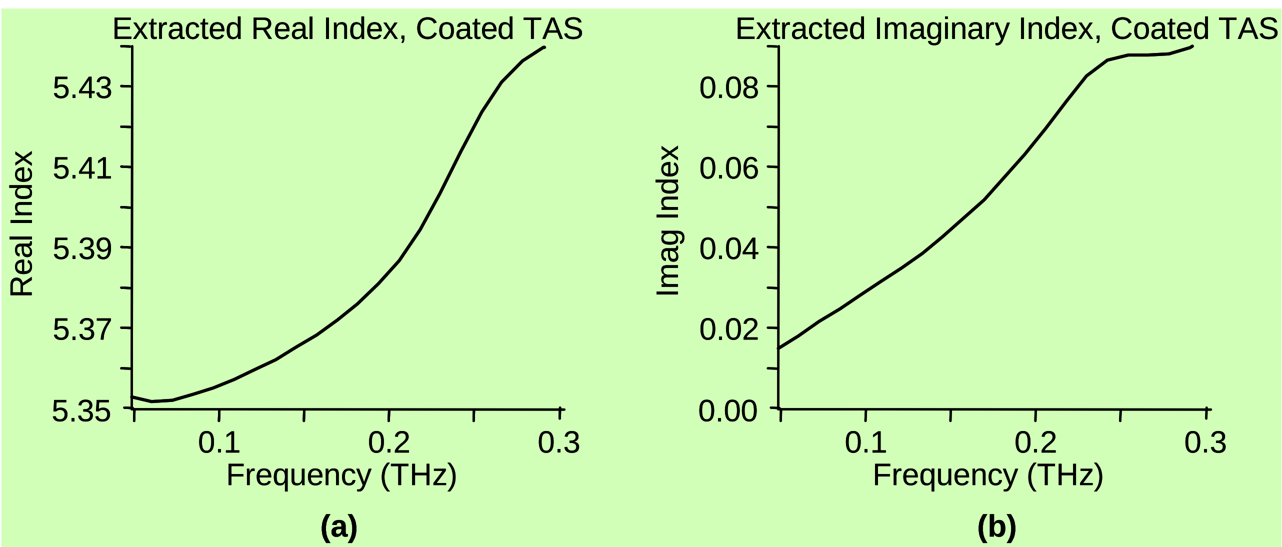



**Wavefield plot of the transmitted terahertz through the coated TAS sample.**




**Refractive index of AR coated $Tl_3AsSe_3$. (a) Real part and (b) imaginary part. The y-scales of both the real and imaginary indices span a range of 0.09.**

*Ref. Singh et al*, J. Optical Engineering, 45(9), 094002-1 (2006)

# Summary: Future research with controlled ppm impurity is required

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- Single crystals of thallium arsenic selenide ($Tl_3AsSe_3$) were successfully grown.
- Arrays of nanocubes were observed on the surface during purification
- Dielectric constant and resistivity were measured by fabricating small slabs
- $Tl_3AsSe_3$ clearly higher resistivity compared to high purity single crystals
- For high purity sample of Northrop Grumman, the absorption coefficient is over 3 $cm^{-1}$ at 0.3 THz, increasing steadily with frequency. This is 4 order magnitude higher than observed in IR range

*Oxygen and carbon Impurities increased the resistivity of TAS crystals*

*Thank you very much for your attention*