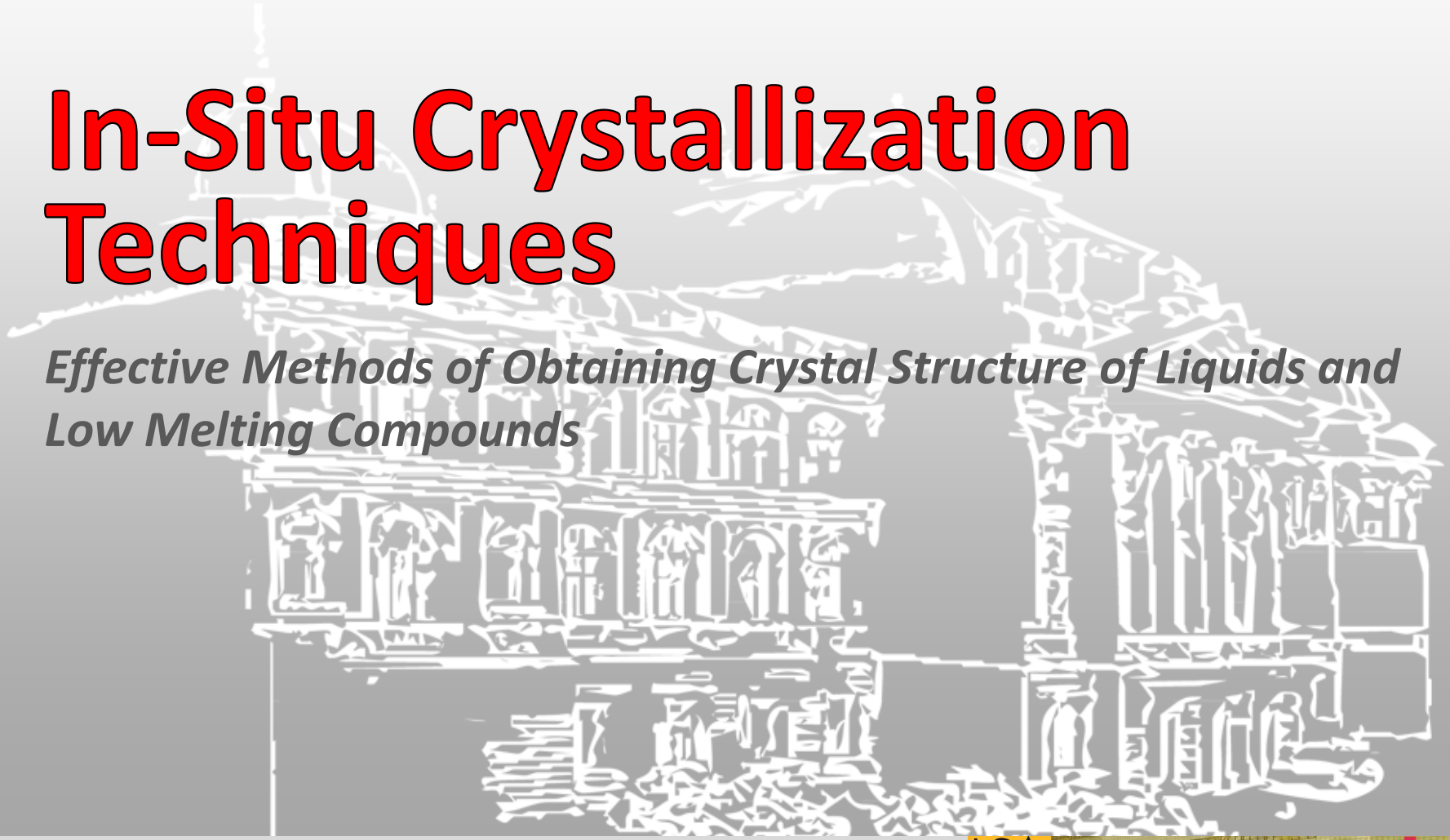
In-Situ Crystallization Techniques

Effective Methods of Obtaining Crystal Structure of Liquids and Low Melting Compounds



In-Situ Crystallization

Crystallization of a sample in a capillary while on the diffractometer

Advantages:

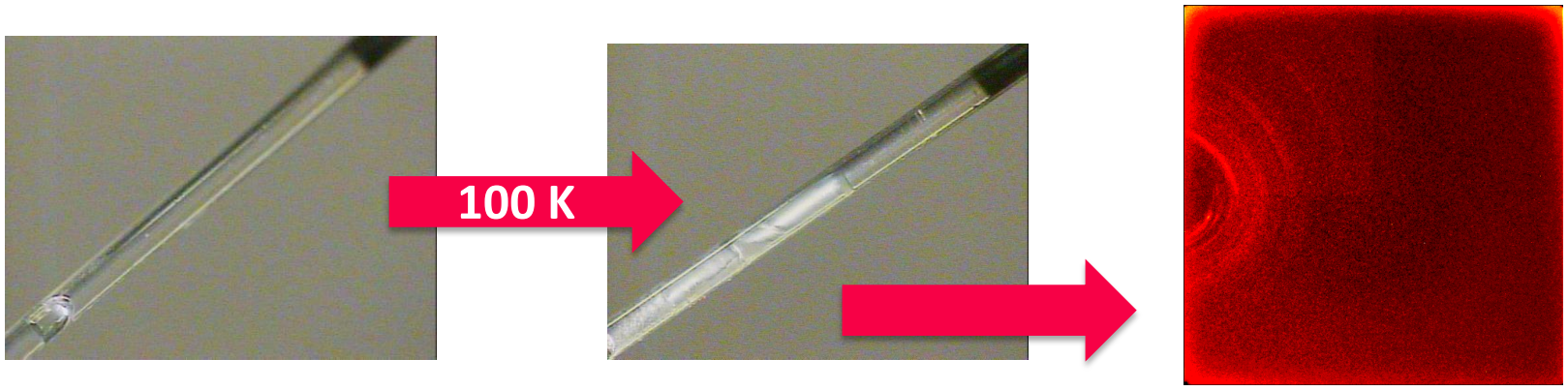
- Crystallization control
- No sample degradation from transferring unto machine
- Crystallization of liquids, low melting compounds, and compounds with phase transitions

Requirements:

- Pure sample (void of solvents)
- An idea of a freezing point range
- Stable enough to transfer to a capillary
- Heating method is necessary

Heating the Sample

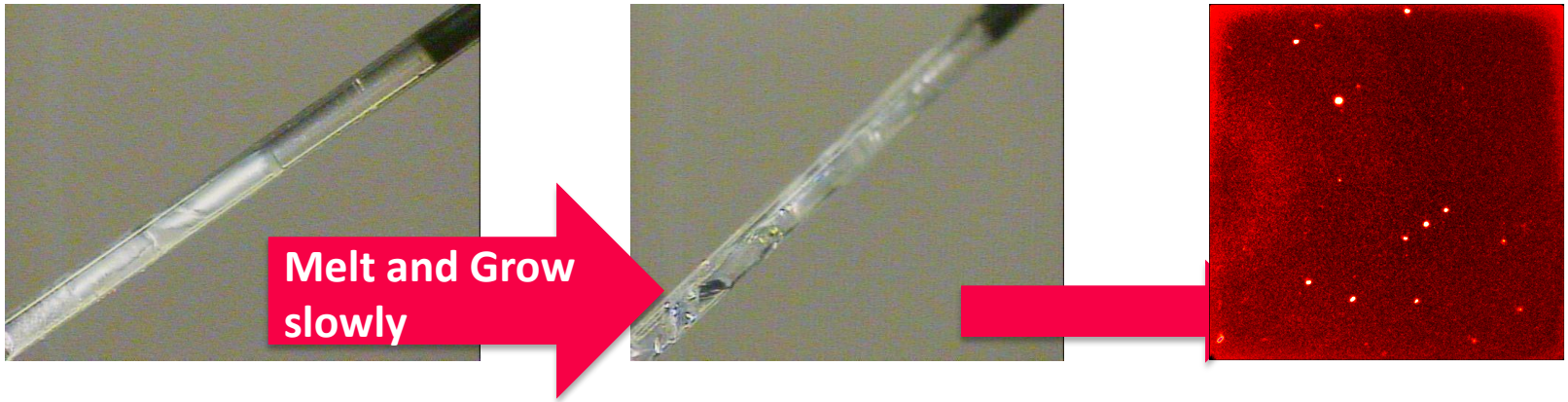
When the capillary is placed in a cold stream (100 K) – it freezes!!



- Supercooling and “glass formation” leads to no diffraction

Heating the Sample

When the capillary is placed in a cold stream (100 K) – it freezes!!



- Heating is necessary to melt the sample and slowly grow crystal
- Metastable region is below the melting point
- Crystal nucleation occurs slowly and uniformly (crystal growth control)

Heating - Manual Technique

Heating the sample

Modify the LT temperature:

The LT device can be used to expose the capillary to different temperatures (heating and cooling) in the range of 100 – 293 K

Capillary position:

Capillary can be moved in and out of the cold stream in order to induce melting

Heating device:

A metal rod (heating device) can be used to manipulate the sample.

Manual Technique - Procedure

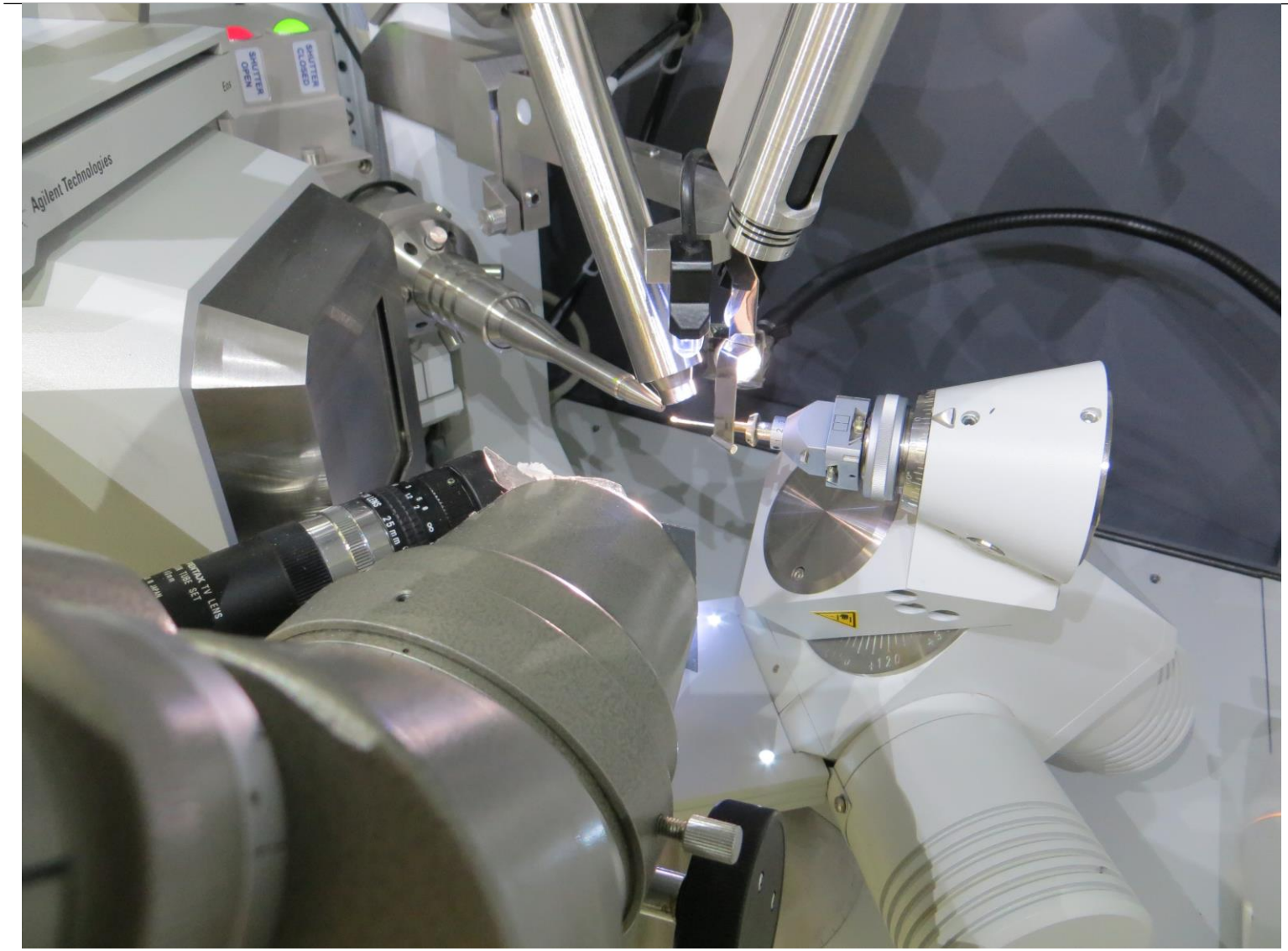
Heating the sample

- Sample is prepared and mounted on goniometer
- Goniometer is placed on the cold stream or a temperature which is known the sample will be solid at
- Alternatively, to avoid supercooling, liquid nitrogen can be used to freeze the sample
- Increase the temperature of the nitrogen stream until the sample starts to melt (monitor through a microscope)
- Using the heating rod and changing the position of the capillary in the cold stream, leave a seed crystal in the capillary
- Program the LT to cool down the cold stream at a very slow rate to induce slow crystallization (within tenths of a degree)

Crystals grow best several degrees below the melting point!!

Instrumentation

Instrumentation



Instrumentation

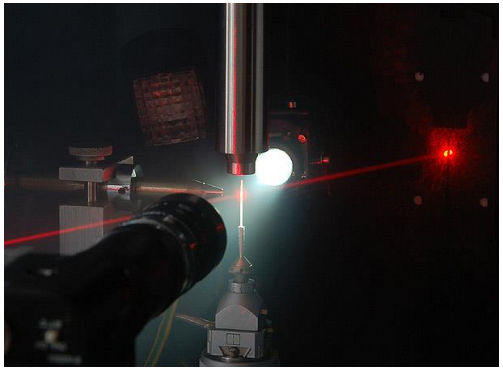
Heating - OHCD Laser

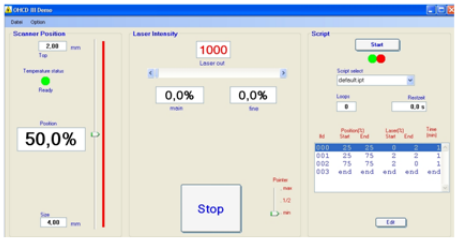
Crystal growth method developed by Prof. Roland Boese (U. Duisburg-Essen)

Heating is performed by exposing the capillary to a focused IR laser

Laser is programmed to scan different regions of the crystal

Temperature gradients are applied for slow crystallization





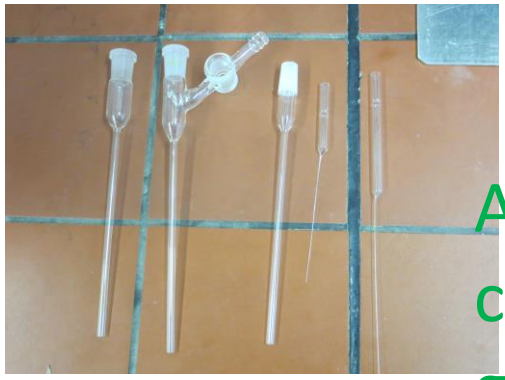
Sample Preparation

Air stable

- Simply fill a capillary
- Seal with glue or in a flame (!)
- Affix to the copper rod
  - Glue or molding clay

Air sensitive – The hard way

- Condense the sample using a vacuum line into a capillary



Add picture of condensation glassware

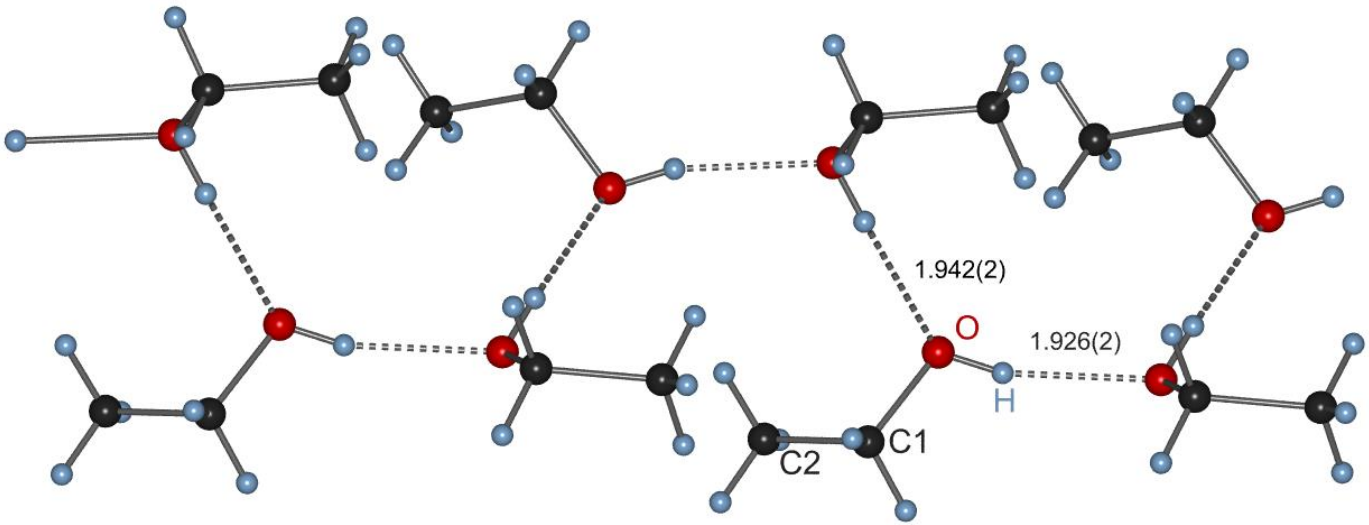
Sample Preparation

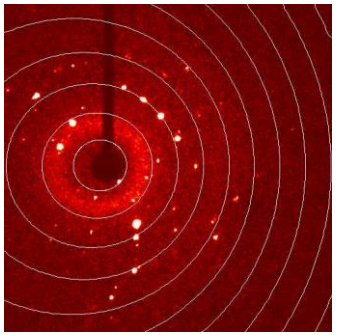
Air stable
- Simply fill a capillary
- Seal with glue or in a flame (!)
- Affix to the copper rod
  - Glue or molding clay

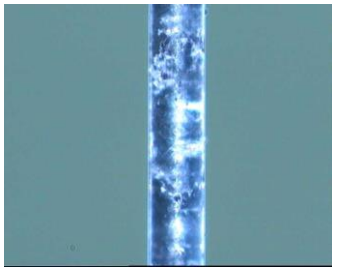
Air sensitive – The easy way
- Prepare in drybox
- Seal with teflon or silicone grease
- Seal with glue once outside of drybox
- Affix to the copper rod
  - Glue or molding clay

Results - Ethanol

Melting Point = 159 K





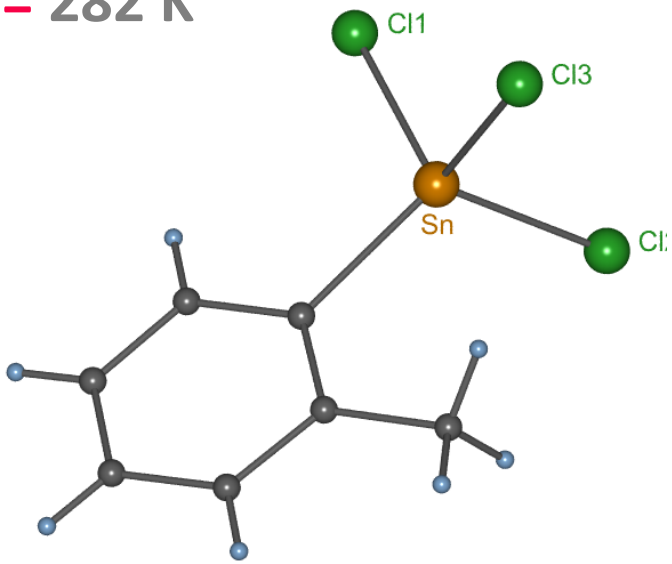


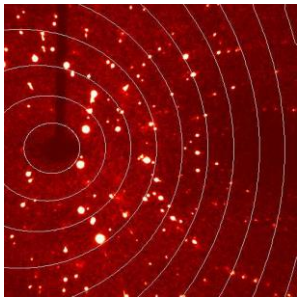
Space Group, Pc
Crystallization at ~156 K
Collected at 87 K
OH-H 1.931(4) Å

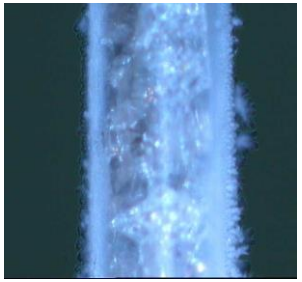
Space Group, Pc
Crystallization at 158.2 K
Collected at 145.3 K
OH-H 1.934(2) Å

Results – *o*-tolylSnCl$_3$

Melting Point = 282 K





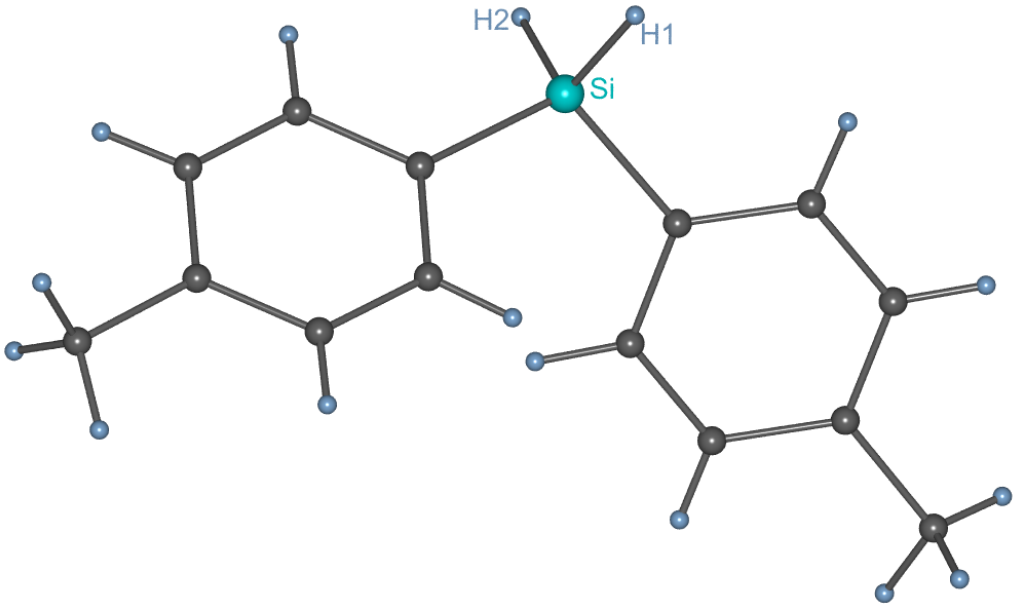


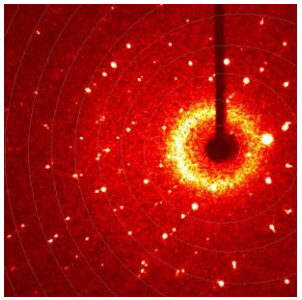
TU - Single Crystal
Space Group, P-1
Crystallization 277.15
Collected at 100 K
Missed twinning
Completeness issues

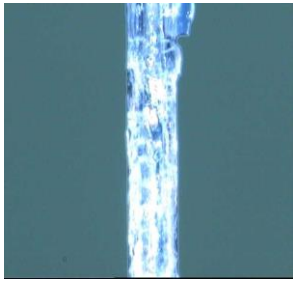
Capillary
Space Group, P-1
Crystallization at 281.8 K
Collected at 100 K
Twinning issues resolved
100 % completeness

Results – *p*-tolyl$_2$SiH$_2$

Melting Point = 289.9 K





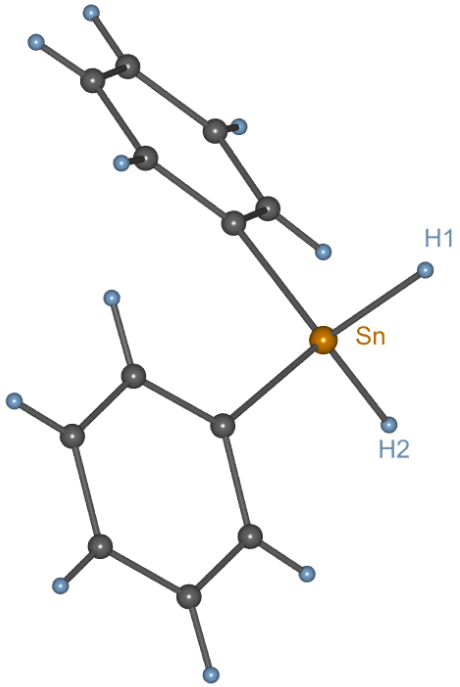


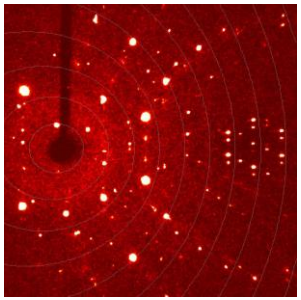
Capillary
Space Group, $P2_12_12_1$
Crystallization at 289.2 K
Collected at 100 K

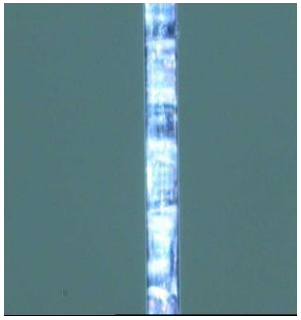
H atoms on found positions!
Si—H1 = 1.415(2)
Si—H2 = 1.409(2)
No twinning!!

Results – Ph_2SnH_2

Melting Point = 248.1 K



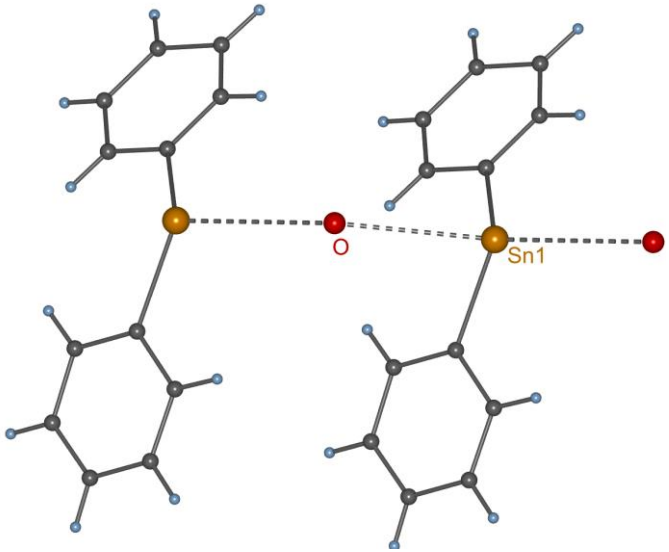


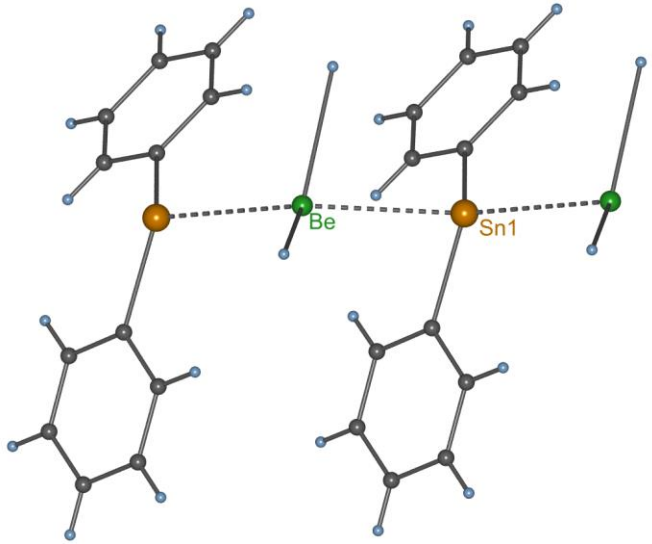


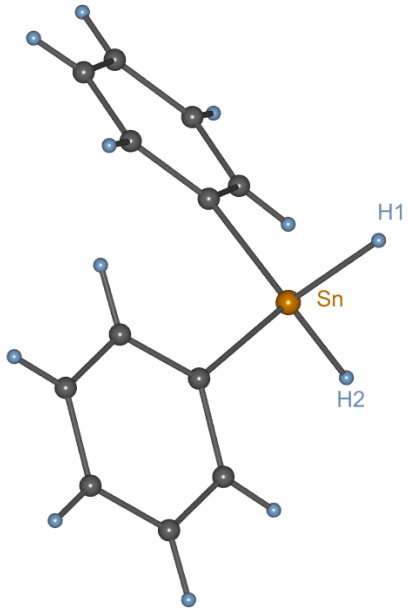
Capillary
Space Group, $P2_1$
Crystallization at 246.8 K
Collected at 100 K

H atoms on found positions!
Si—H1 = 1.54(2)
Si—H2 = 1.76(2)
Merohedral twinning

Results – Ph_2SiH_2







Collection temp = 248 K
R1 = 4.75%

Collection temp = 100 K
R1 = 2.35%

Twin Refinement
R1 = 1.75%

Results

Benzyl$_2$SiH$_2$ and *o*-tolyl$_2$SiH$_2$

- No Diffraction
  - At -80 ° C, sample was viscous and oil like
  - Manual Techniques or OHCD Laser did not result in crystal formation
  - Impurities????

In- Situ Crystallization - Considerations

It works really well!!!!

Sample

- Sample should be pure and devoid of solvent
- Prior knowledge of Freezing Point range is necessary
  - Supercooling can be tedious

Patience

- Melting Point range can be difficult to determine
- Crystals will take time to grow (fast = bad)
- Good quality crystal growth might not be achieved

Careful

- Break the capillary
  - Exposing to high laser power
  - Cracking by freezing with liquid nitrogen
  - Breaking with the heating rod

In- Situ Crystallization - Considerations

Oligocrystallization

- One single crystal is hard to achieve
  - Twin refinement is usually required

Publication

- Crystal size
- Absorption Corrections
- Sample preparation and collection methods have to be addressed

Acknowledgements

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