National Institute of Standards and Technology
U.S. Department of Commerce

2019 MRS FALL MEETING & EXHIBIT
December 1–6, 2019 | Boston, Massachusetts

Tutorial EL04: Introduction to Chalcogenide Discovery and Design

Bulk Crystal Growth and Phase Diagrams for Metal Chalcogenides

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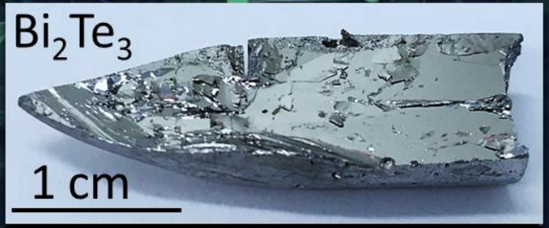
Material Science & Engineering Division



Goal and Outline

- **Metal chalcogenides**: focus on van-der-Waals layered materials
- **Synthesis overview**: thin film and bulk crystal growth
  - Advantages of bulk single crystals
  - Two primary growth methods for bulk: i) melt solidification, ii) vapor transport (CVT)
- **Growth from melt:**
  - Direct solidification (Bridgman-Stockbarger)
  - Solidification from flux
- **Growth from vapor** (CVT)
- **Concluding remarks**

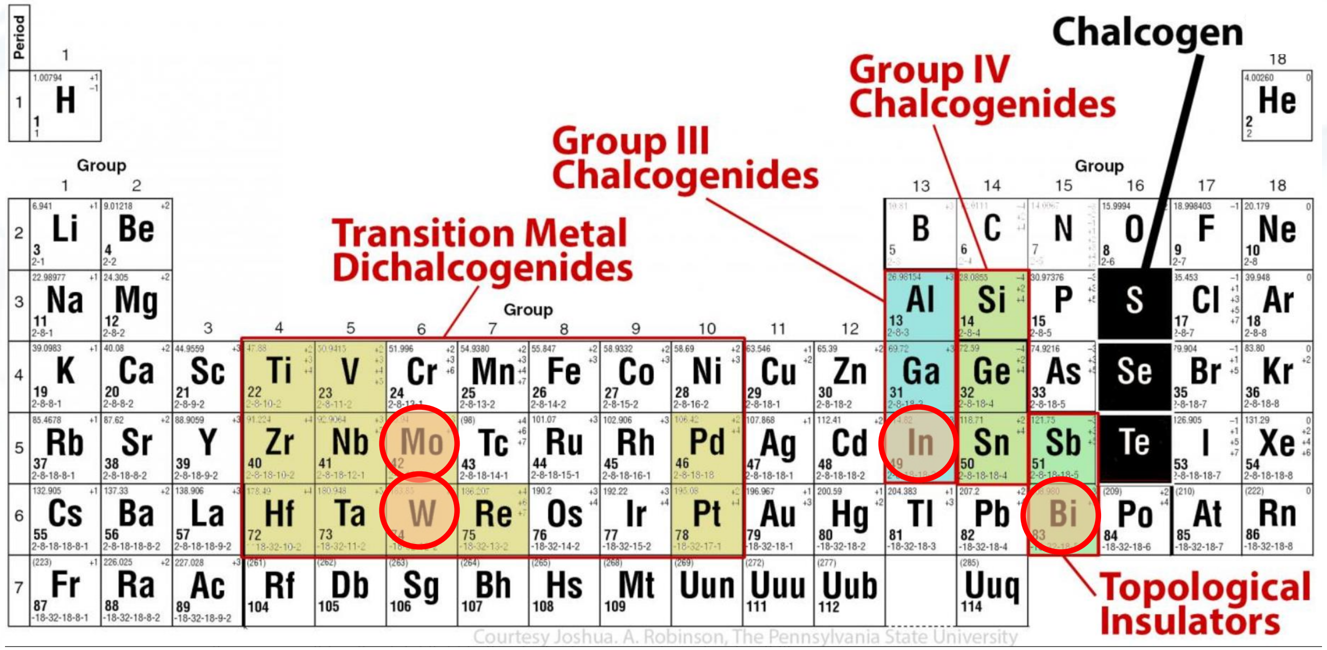
Goal: Design growth of metal chalcogenide single crystals with defined properties.

Take-home message: *"Phase diagram can serve as a map for materials processing"*

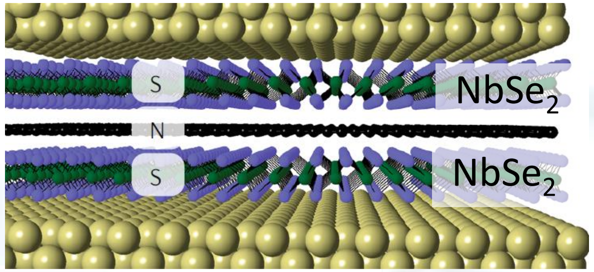
Acknowledgement for crystal growth: Sergiy Krylyuk (MSED, NIST)

Phase diagrams are from ASM Alloy Phase Diagram Database

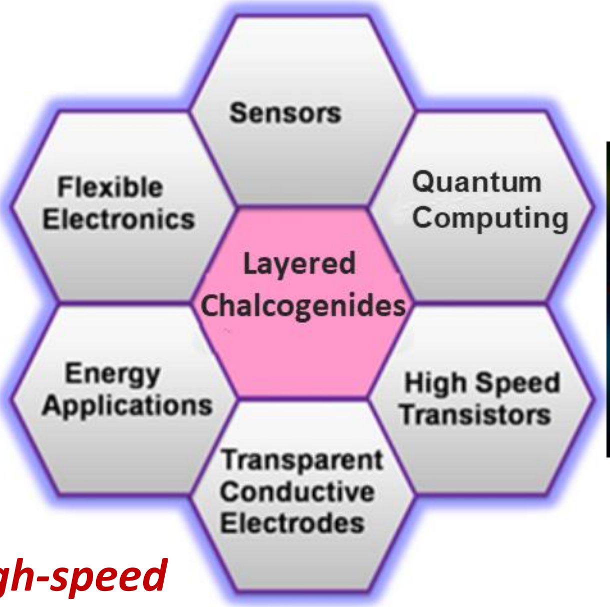
Metal chalcogenides family



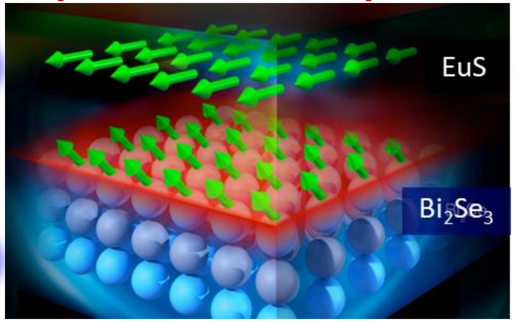
2D Josephson Junction



Liu 2019

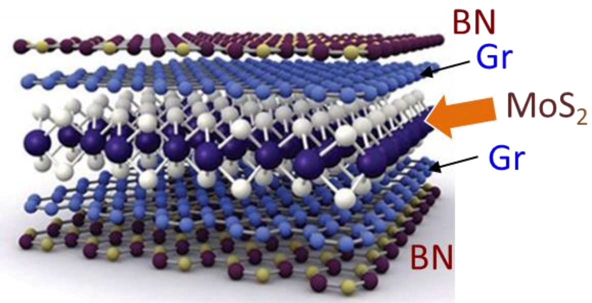


Ferromagnetic TI for spintronics and qubits

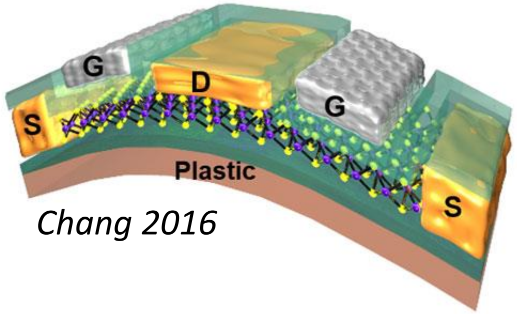


Katmis 2019

Flexible/low-power/high-speed nanoelectronics

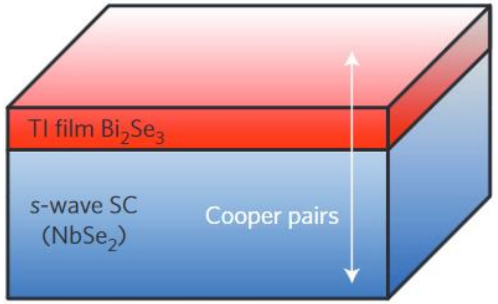


Novoselov 2016



Chang 2016

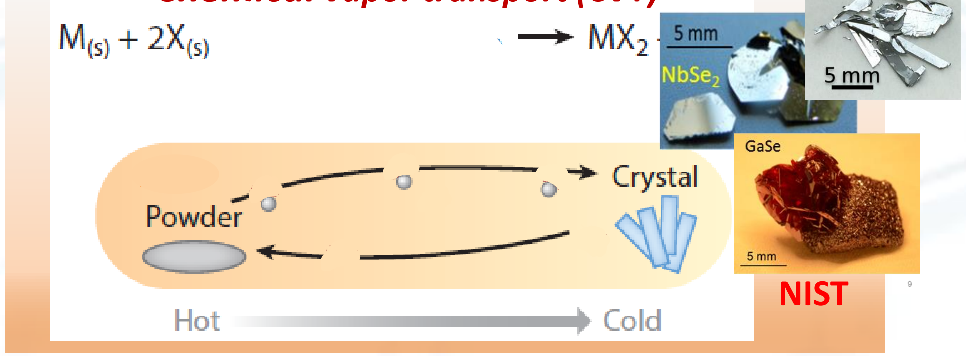
SC/TI proximity topological qubits



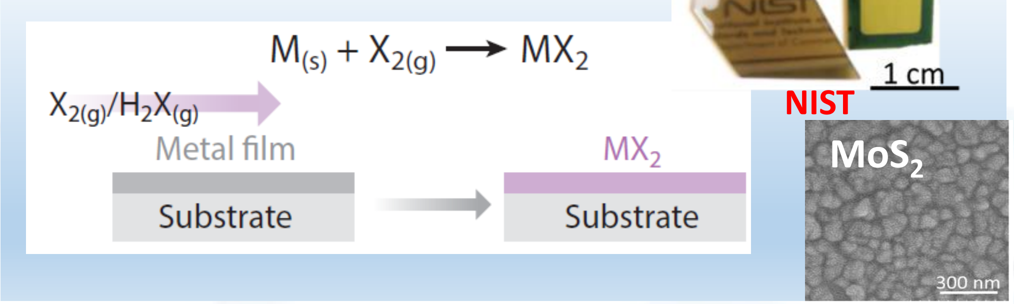
Dai 2017

Growth Methods: from vapor, melt and solutions

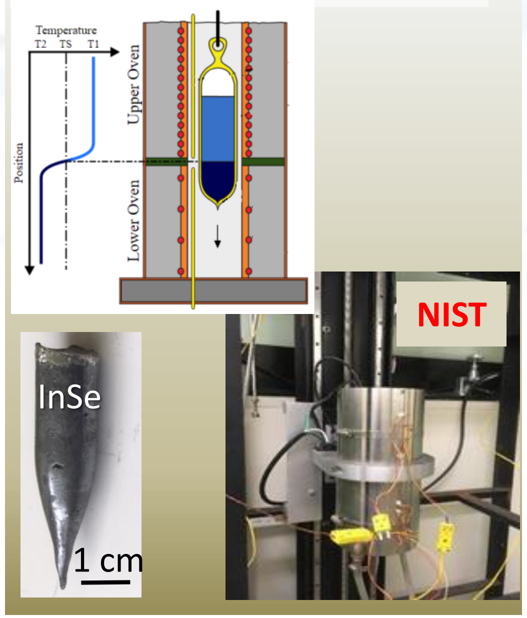
Chemical vapor transport (CVT)



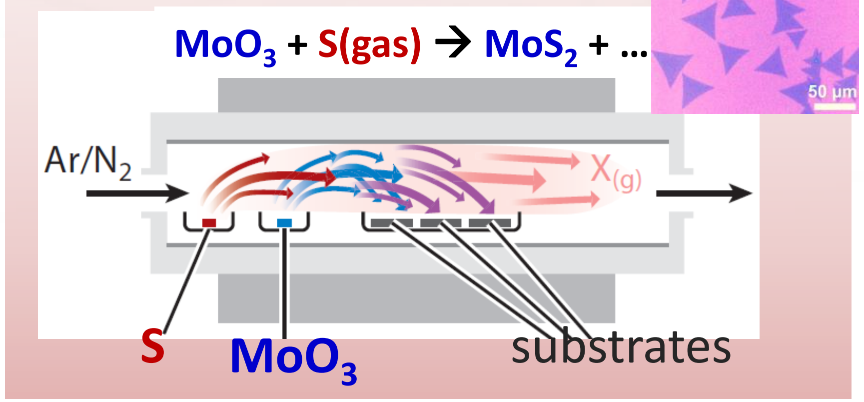
Metal Sulfurization



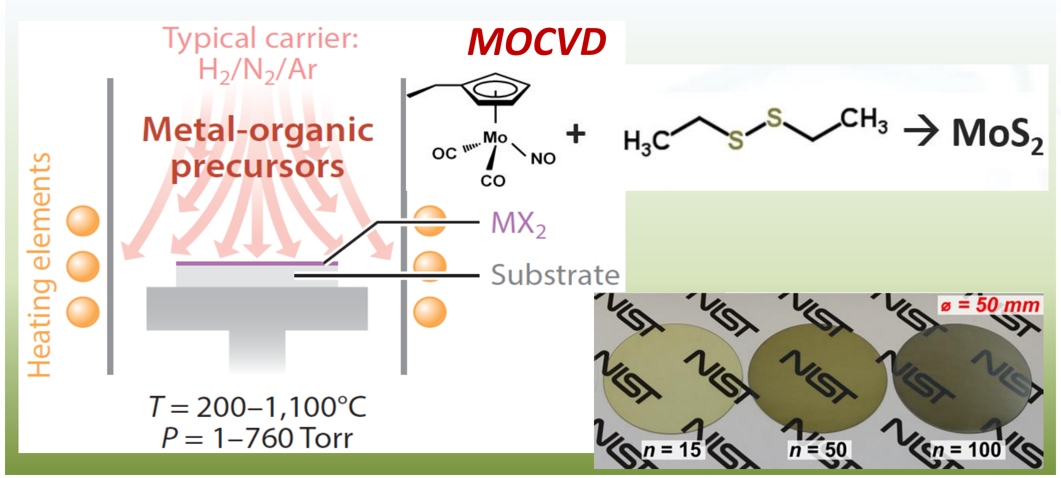
Solidification from melt



Chemical Vapor Deposition (CVD)

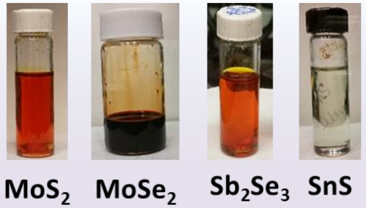


MOCVD

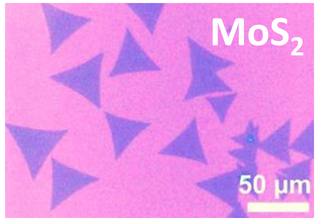


Other methods:

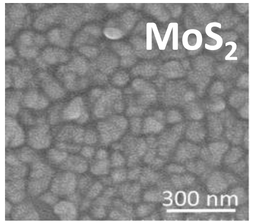
- MBE
- PLD
- Electrochemical synthesis
- **Solution methods (dip-coating + annealing)**



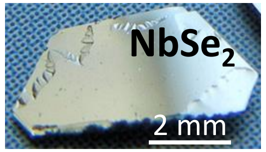
CVD films



Sulfurized films



Bulk crystals



- Focus on bulk crystal growth: CVT and Solidification

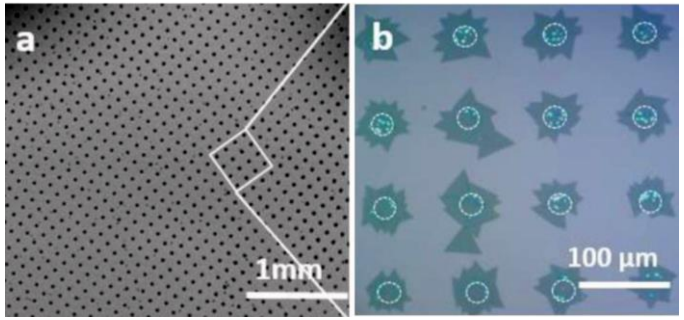
NIST

Advantages of single crystals vs. thin films

- Large crystals to measure basic properties: structural, optical, electrical
- Nearly-perfect state of material: purity, no grain boundaries, less structural defects, stress, etc.
- Tunability of bulk properties: control of phase stoichiometry, doping level, alloy composition
- Exfoliation and stacking of heterostructures (“twistronics”, optoelectronics) at ~room temperature

Key Disadvantage – manufacturability issue

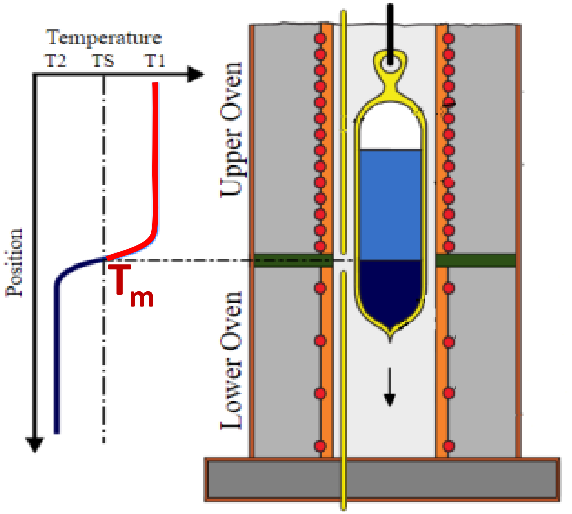
- *Ex situ* fabrication of device layers => inter-layer contamination possible
- Limited scalability (however: site-specific exfoliation and 3D printing under development)

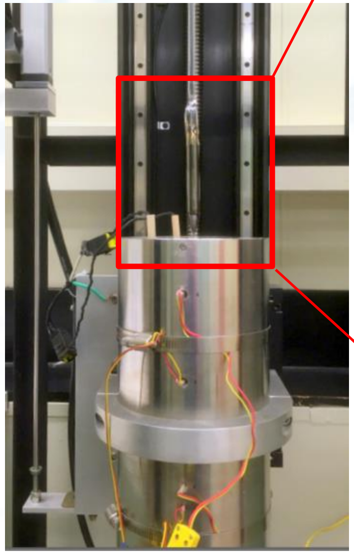


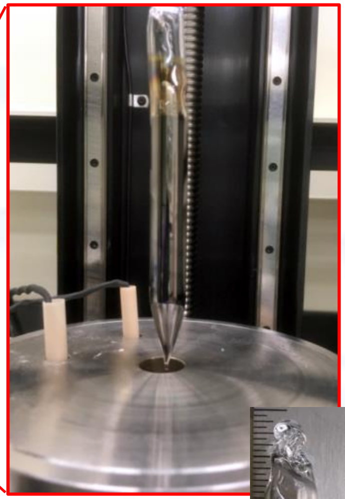
Wang 2017

Melt Solidification

Bridgman-Stockbarger method







Materials:

1) Quartz tubing, ceramic crucibles
2) metal, chalcogen ≥3 9's purity
3) Vacuum system (few mTorr) w/ backfill Ar-gas and O_2/C_3H_8 torch
4) Two-zone vertical furnace w/ motor (speed ~ 0.5 mm/h; temp. gradient ~ 50 C/cm)

*p.s. For further details, see APS 2019 comprehensive tutorial on crystal growth by **Michael McGuire** (ORNL)*

What to know:

1) T_m , melting point

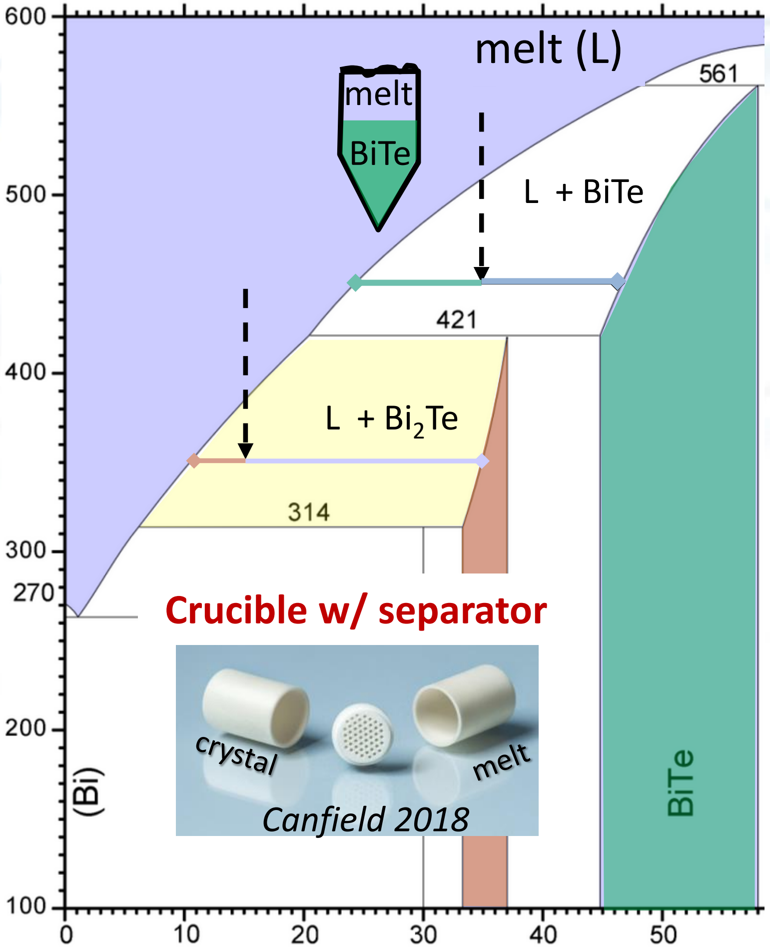
2) are compositions of solid and melt the same at T_m?

yes → Direct solidification

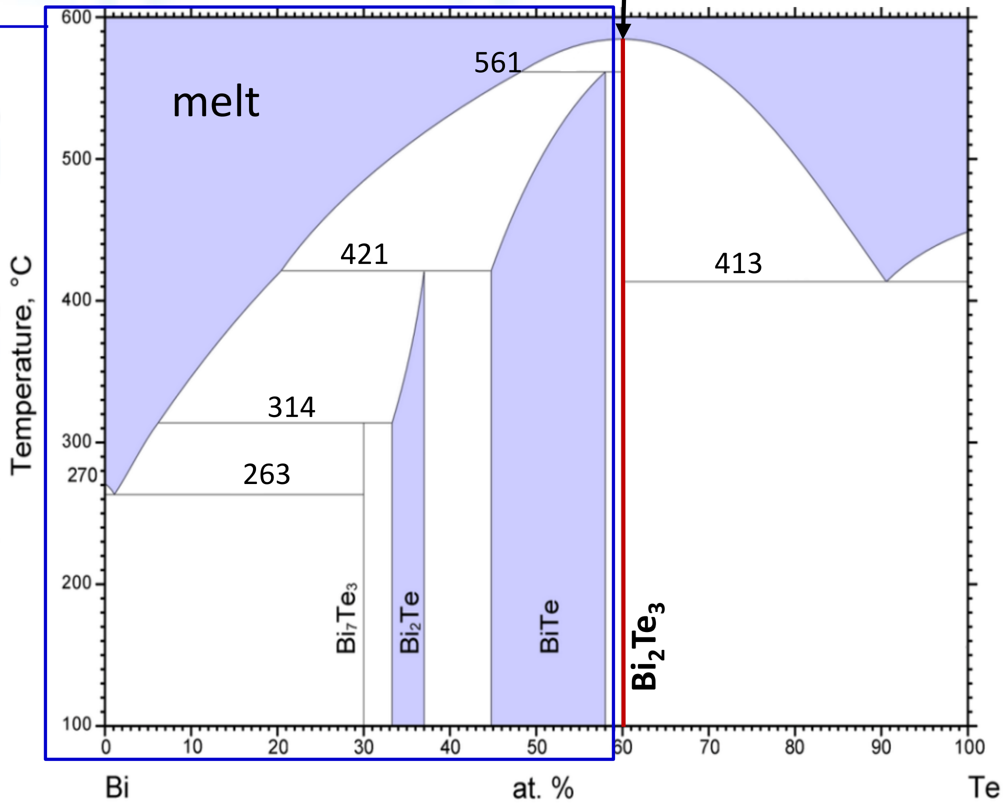
no → Growth from flux or Not suitable

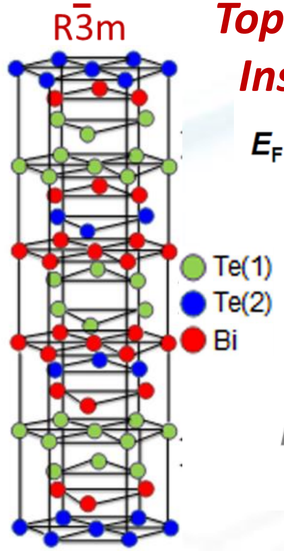
Phase diagram needed

Growth of *congruently melting* phase vs. Flux-growth

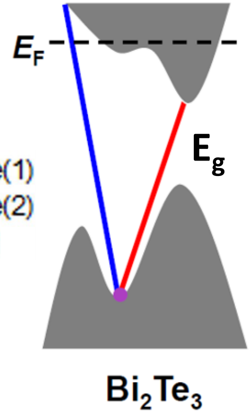


T-x Phase Diagram

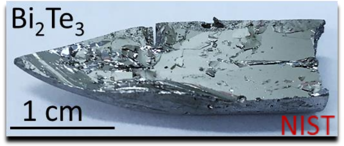




Topological Insulator



Bi_2Te_3 single crystal

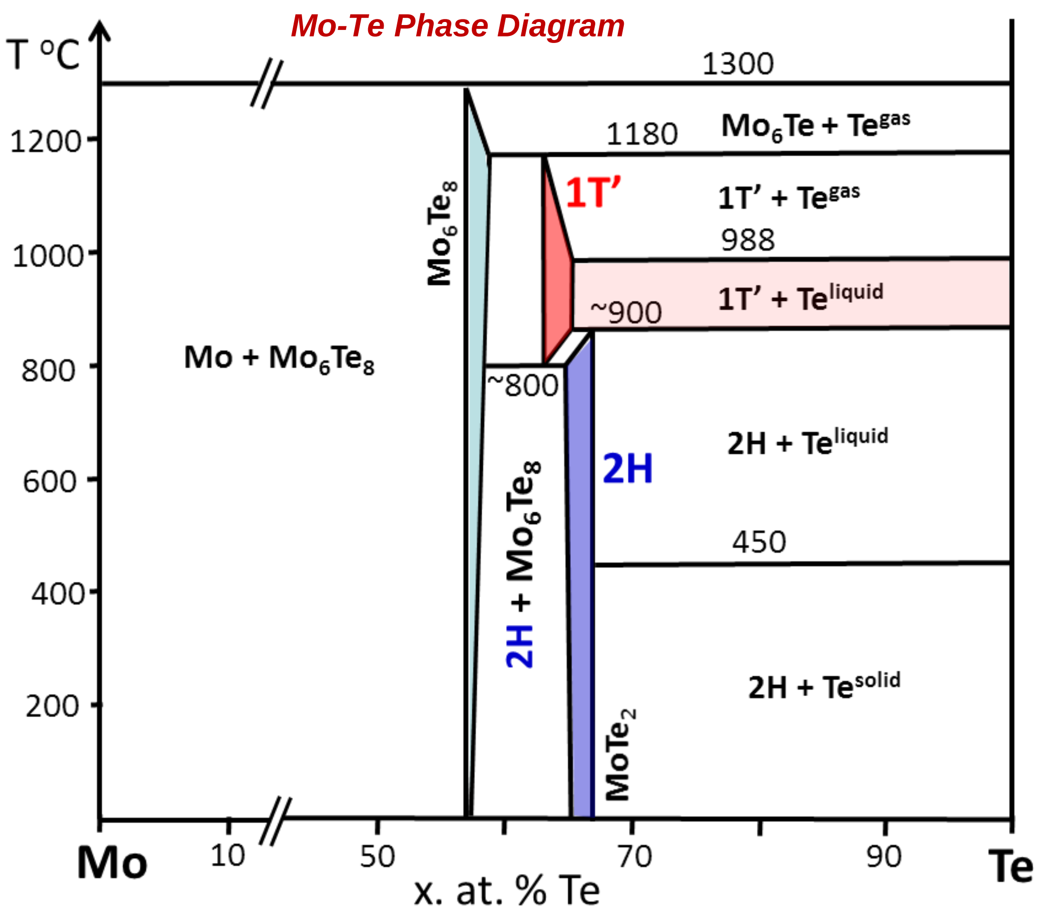


- Congruent melting point: T_m^{congr} = 584 °C ($x_{melt} = x_{solid}$ = 60 at. % Te) => growth from stoichiometric composition
- Other single crystals with congruent melting point, grown in our lab: Bi_2Se_3, GaSe, InSe

What if phase does not melt congruently? e.g., $Bi_2Te \overset{T_m^{incongr} = 421°C}{=} BiTe + L$

=> **Flux growth** window: x ≈10-20 at.% Te and T= 314 – 421°C

Flux growth of 1T'-$MoTe_2$ from Te-rich melt

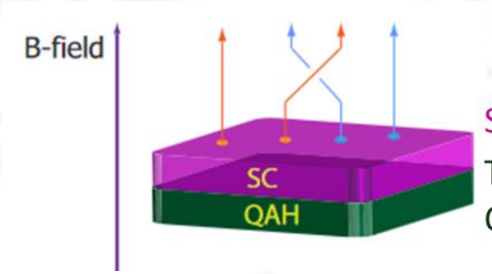


From <u>Rhodes (J. Hone's group) 2019</u> :

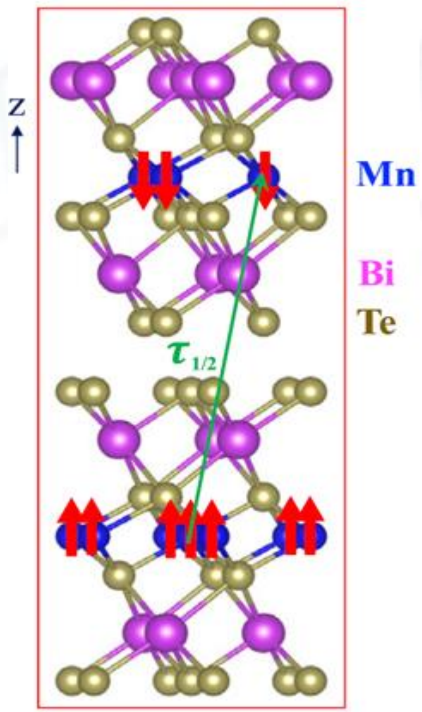
- *Placed powders of Mo:Te=1:20 (95% Te) in evacuated ampoule*
- *Heated to 1100 ℃ for 24 h*
- ***Cooled to 880 ℃ and held for 17 days***
- *Decanted melt from $MoTe_2$ crystals*
- *Annealed $MoTe_2$ at 425 ℃ for 24 h to remove residual Te*

Growth of $MnBi_2Te_4$, magnetic topological insulator (TI)

Qubits in superconductor/TI junction

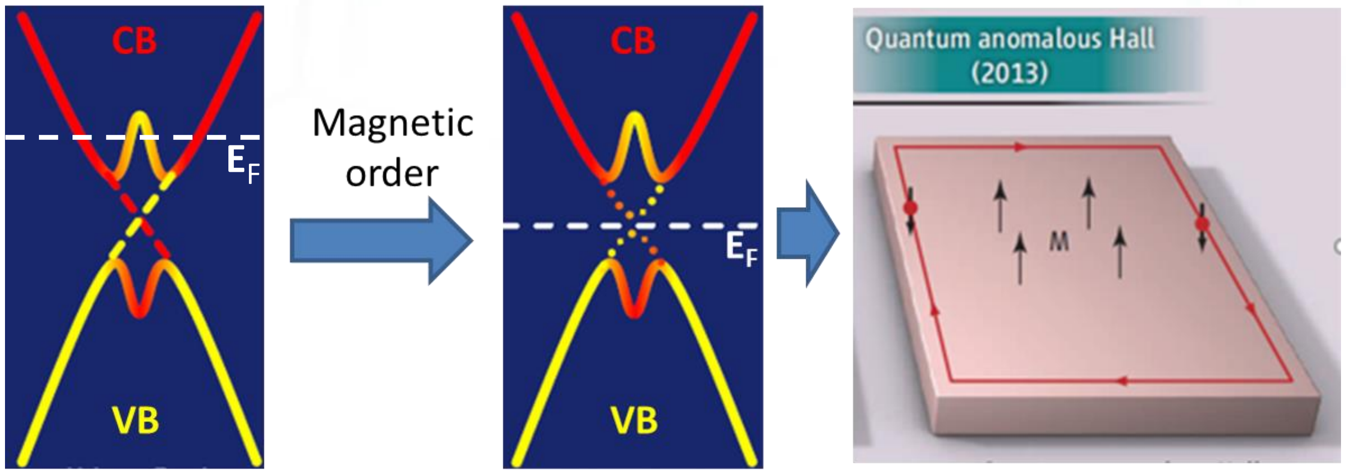


$MnBi_2Te_4$



Zhang 2019

TI ***FM/AFM TI***

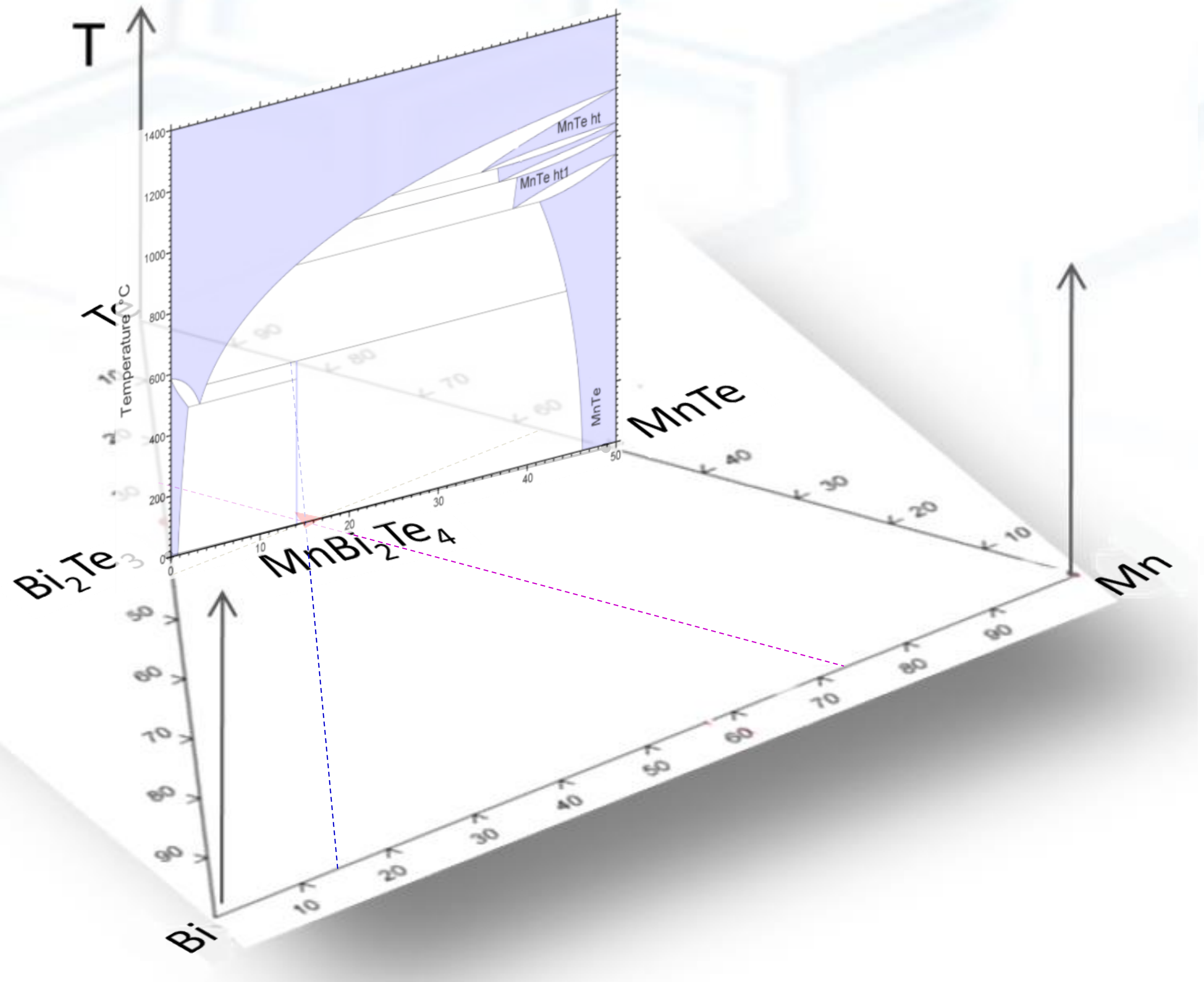


Bi_2Te_3 Cr-doped $(Bi,Sb)_2Te_3$

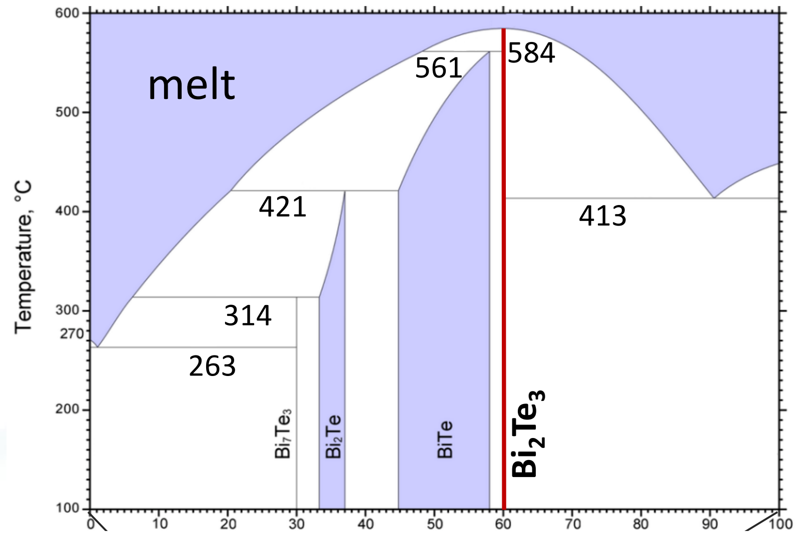
- **Needed:** (anti)ferromagnetism at higher temperatures and larger bandgap
- **Candidates:** $Mn(Bi,Sb)_2(Se,Te)_4$ family

Cont.: Growth of $MnBi_2Te_4$ from melt

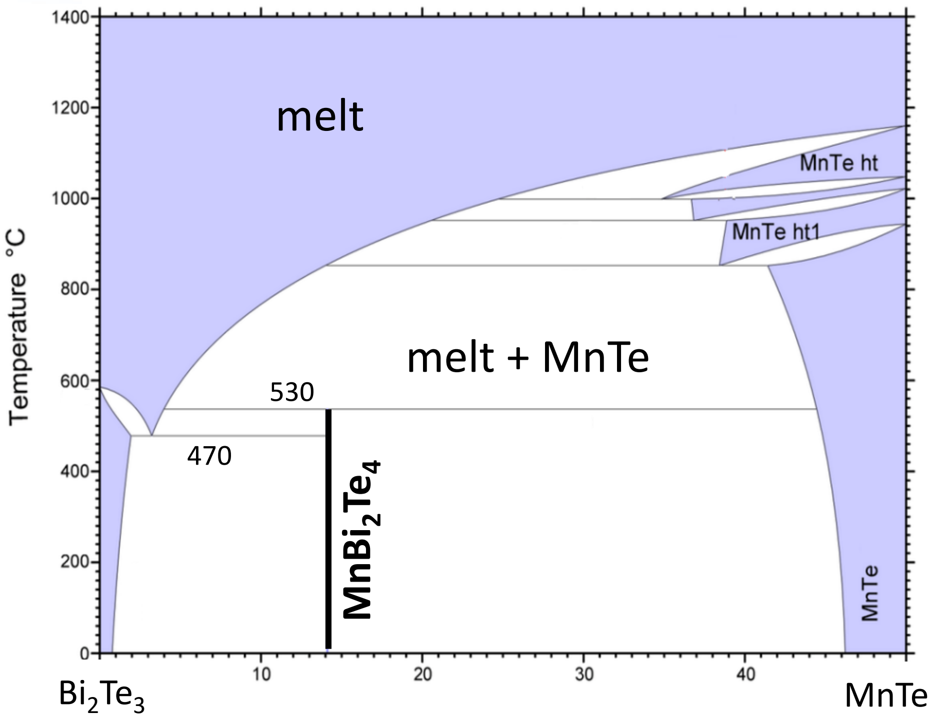
(T-x-y)- Phase Diagram for Mn-Bi-Te system



(T-x)- Diagram for Bi-Te



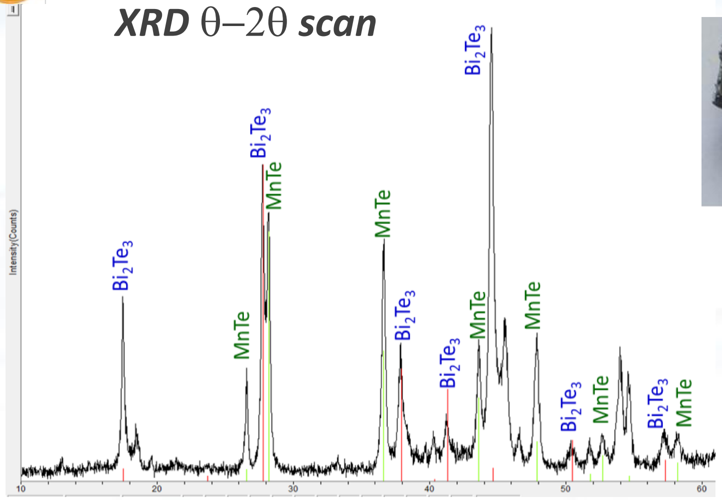
(T-x)- Section Bi_2Te_3 - MnTe

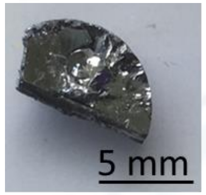


$MnBi_2Te_4$ Mn:Bi:Te = 1:2:4 = 14.3 : 28.6 : 57.1 at. %

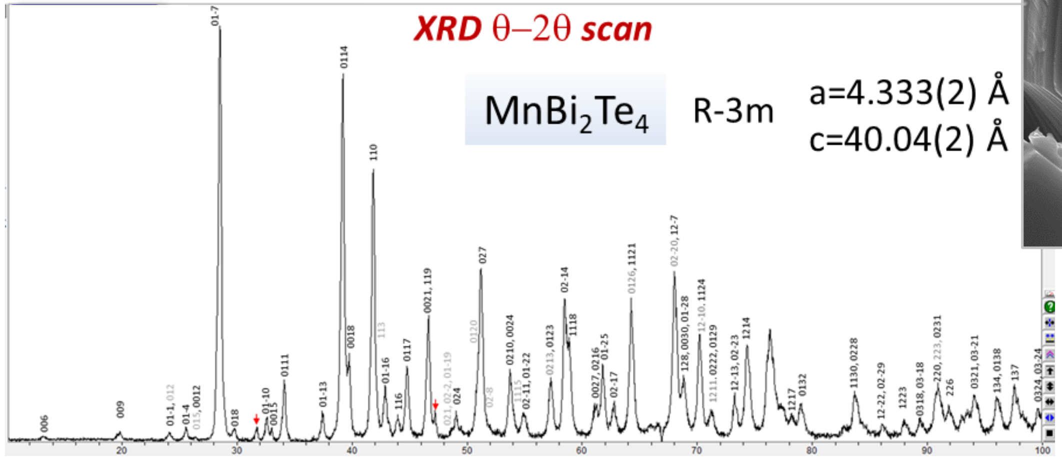
Cont.: Growth of $MnBi_2Te_4$ from melt

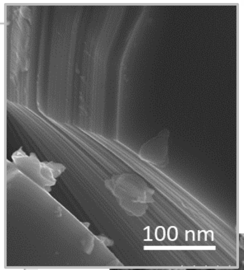
Attempt #1: follow published recipe and “ignore” phase diagram

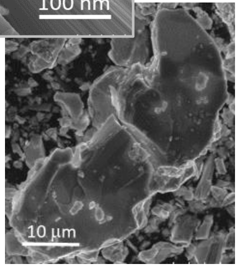


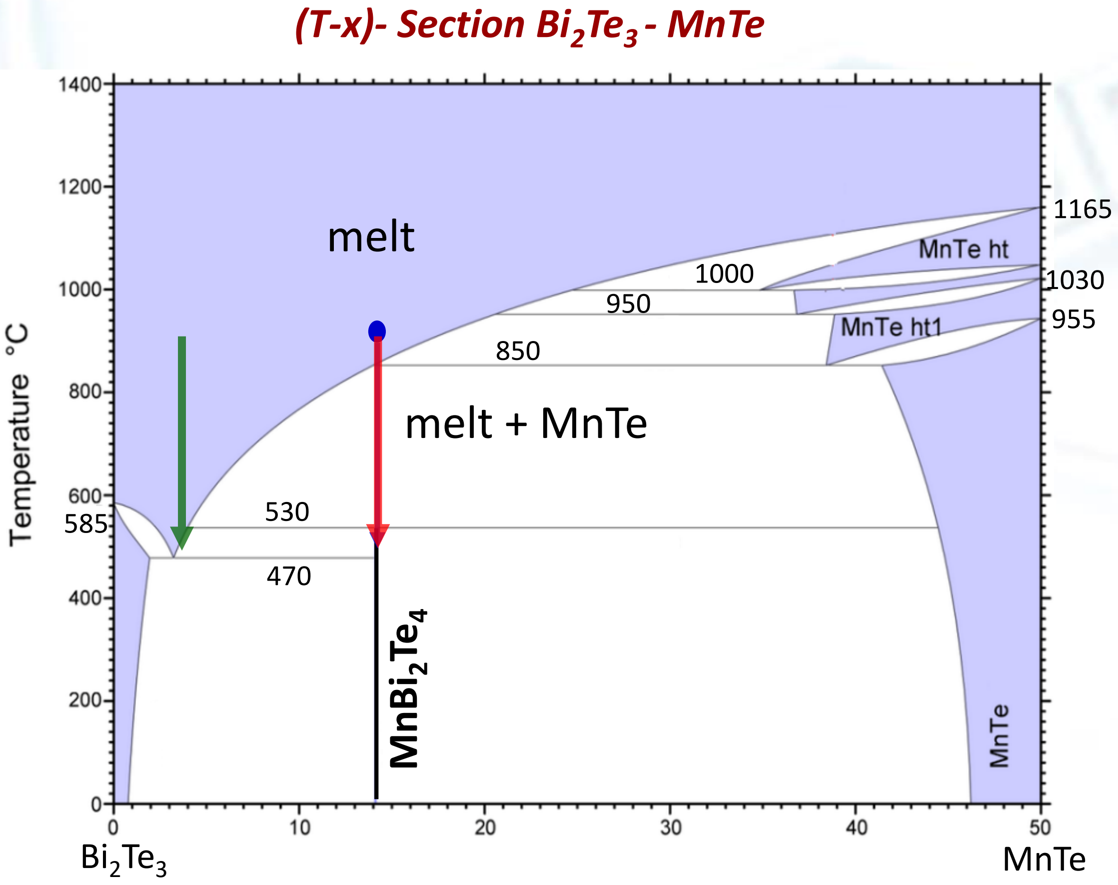


Attempt #2: ignore published recipe, but “cheat” on phase diagram









Attempt #3 (in-progress): use Bi_2Te_3-rich flux: Bi_2Te_3 : MnTe ≈ 5:1 @ T ≈ 530 °C

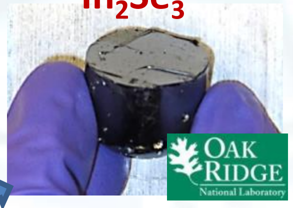
Summary: Congruent melting => Bridgman growth

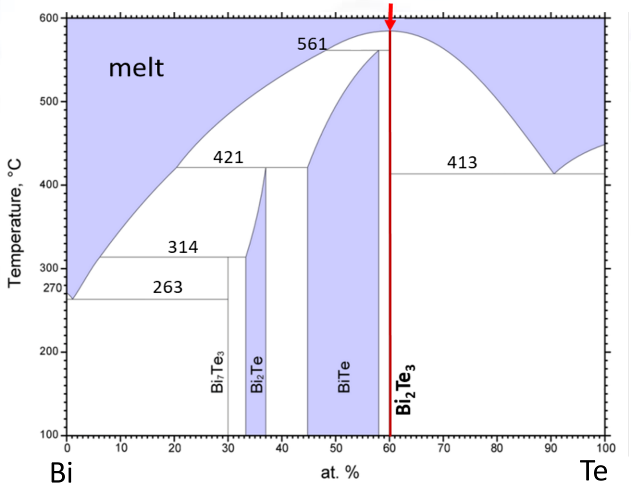
Bi_2Te_3

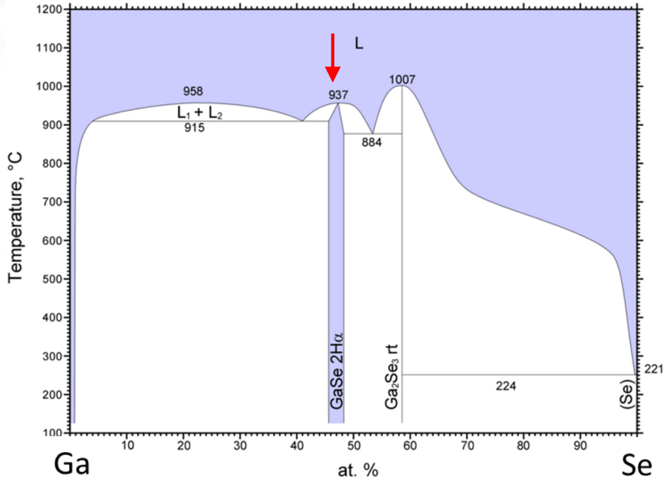
GaSe

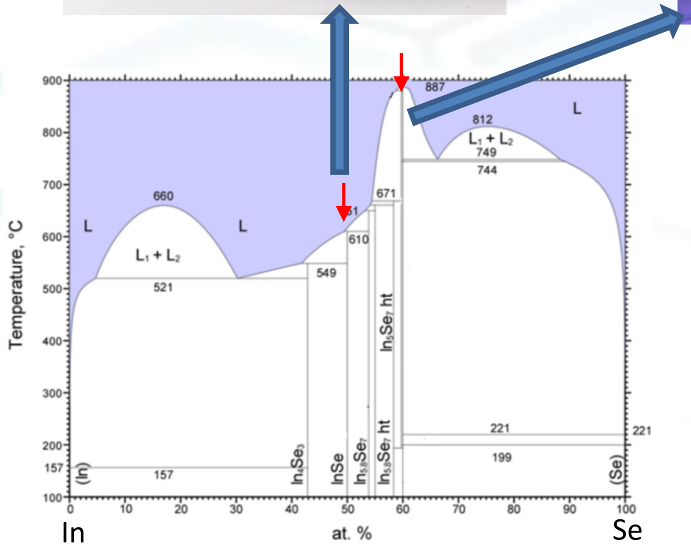
InSe

In_2Se_3





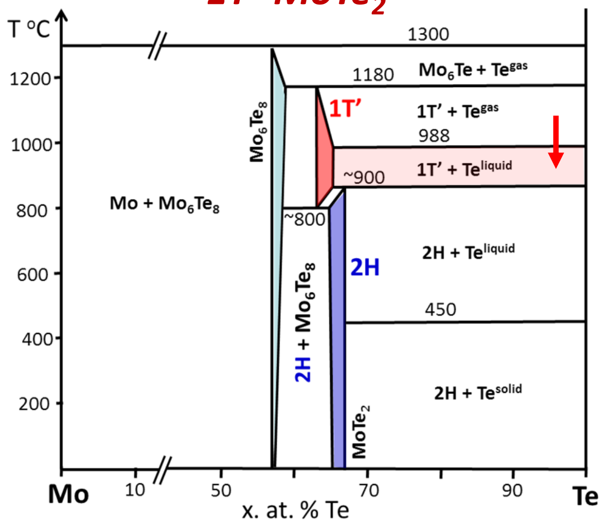




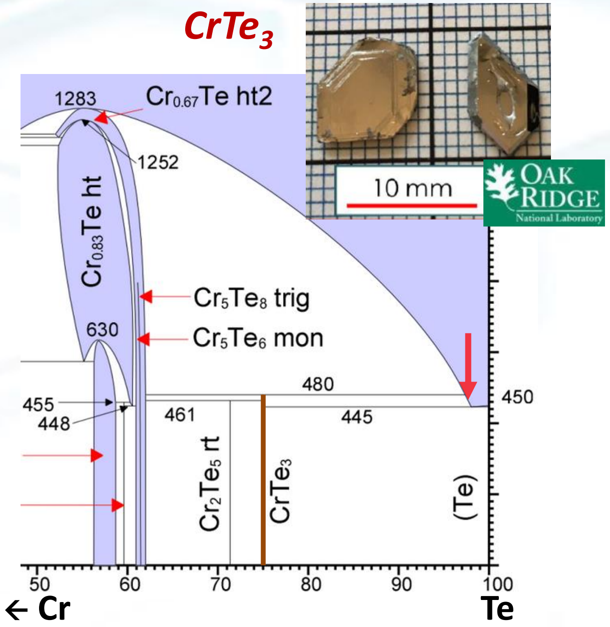
- Congruent melting => bulk crystal growth possible for other layered chalcogenides :
  $SnSe_2$ (647°C), SnS_2 (865°C), MoO_3 (795°C); ZrS_2 (1450 °C), VS_2 (≈1750°C), VSe_2*(≈1700°C), WS_2 (1800°C)

Summary: Incongruent melting => Flux Growth

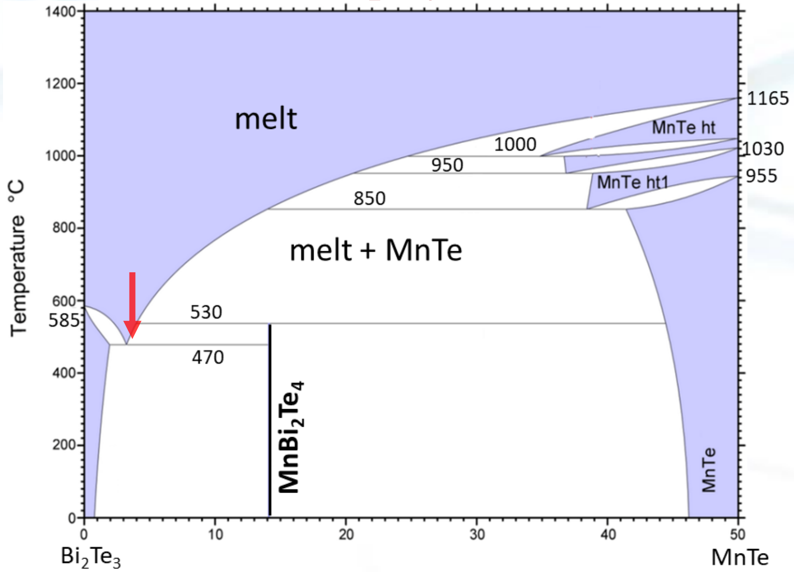
1T'-$MoTe_2$



$CrTe_3$

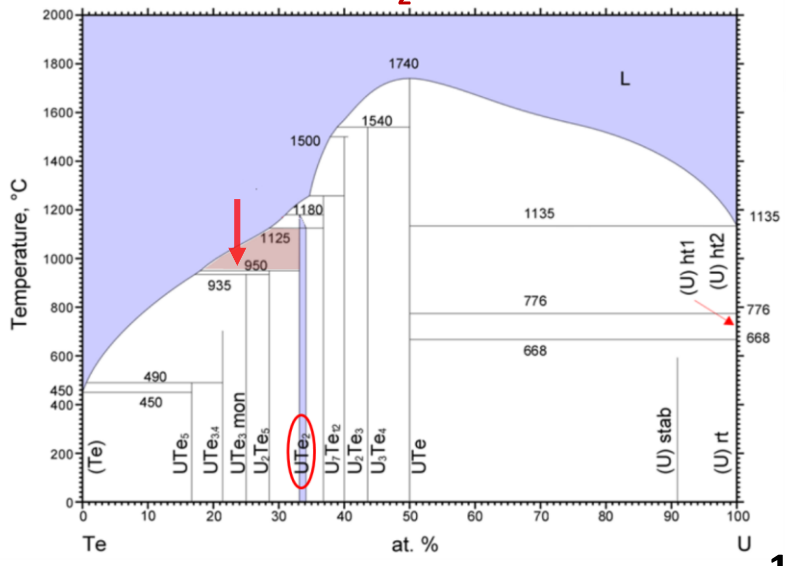


$MnBi_2Te_4$



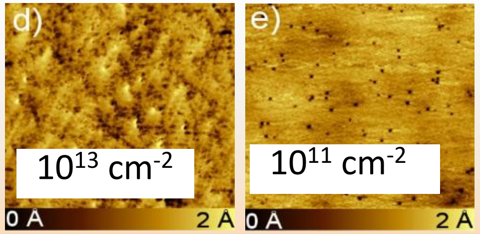
- **Incongruent** or **high melting temperature** =>
  bulk crystal growth demonstrated: $SnSe_2$, $MoSe_2$, WSe_2, Fe_3GeTe_2, $Cr_2Ge_2Te_6$

UTe_2



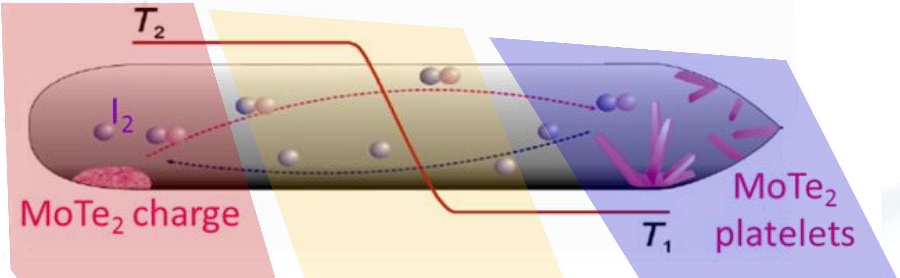
- Flux growth 'heals' chalcogen vacancies and other point defects:

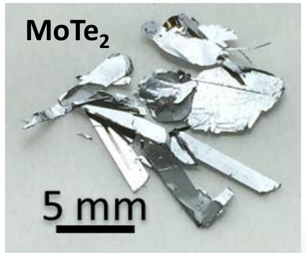
WSe_2 by CVT *WSe_2 by flux*

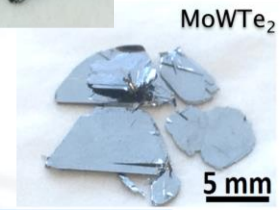


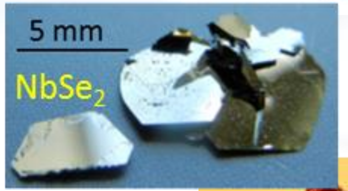
Edelberg 2018

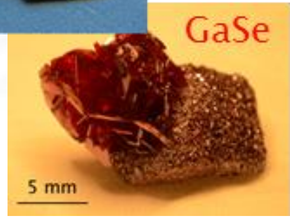
Growth from vapor: Chemical Vapor Transport (CVT)



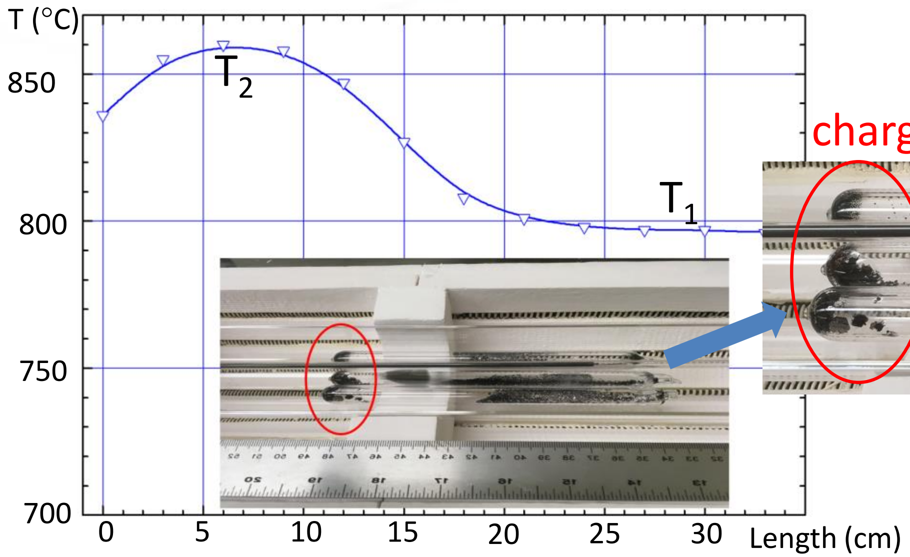


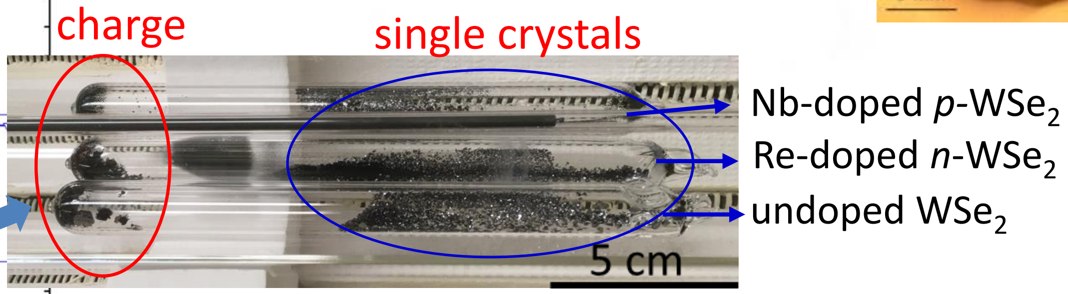






- Simplified version: physical vapor transport: GeSe(s) = GeSe(g) → GeSe (single crystals)
- CVT with transport agent (I_2, Br_2, $TeCl_4$, etc.): TiS_2(s) + I_2(g) = TiI_4(g)+ S_2(g) → TiS_2 (single crystals)





NIST single crystal library: $NbSe_2$, WSe_2, $MoTe_2$, $Mo_{1-x}W_xTe_2$, WTe_2, $W_{1-x}Nb_xSe_2$, $WSe_{2(1-x)}Te_{2x}$, GaSe, GeSe

Important issues in CVT:

- Choice of transport agent affects electrical properties
- Composition of charge ≠ composition of crystals
- Vapor-solid growth => P-T-x diagrams define stability limits

Transport Agents (TA) in CVT

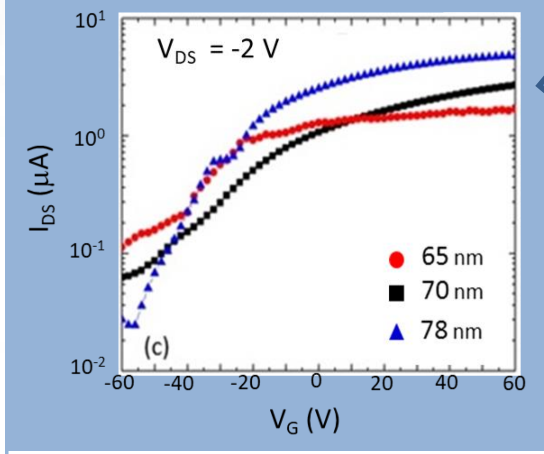
- Usual Transport Agents: I_2, Br_2 ($SeBr_4$), Cl_2 ($SeCl_4$, $TeCl_4$)
- TA incorporates into crystal lattice and affects electrical properties (!)

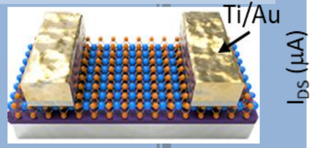
2H-$MoTe_2$ growth using $TeCl_4$ vs. I_2 (our work in progress)

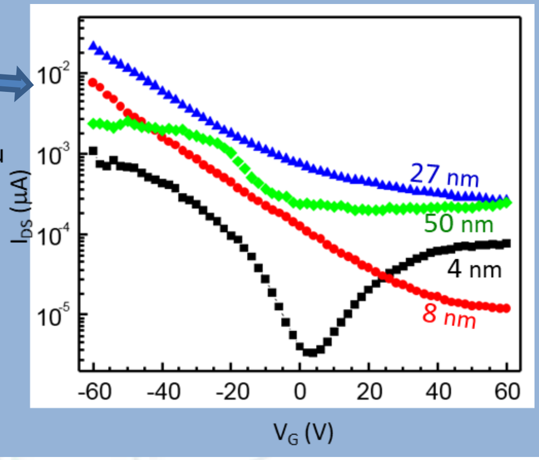
Cl-assisted growth => *n-$MoTe_2$*

I-assisted growth: *p-$MoTe_2$*

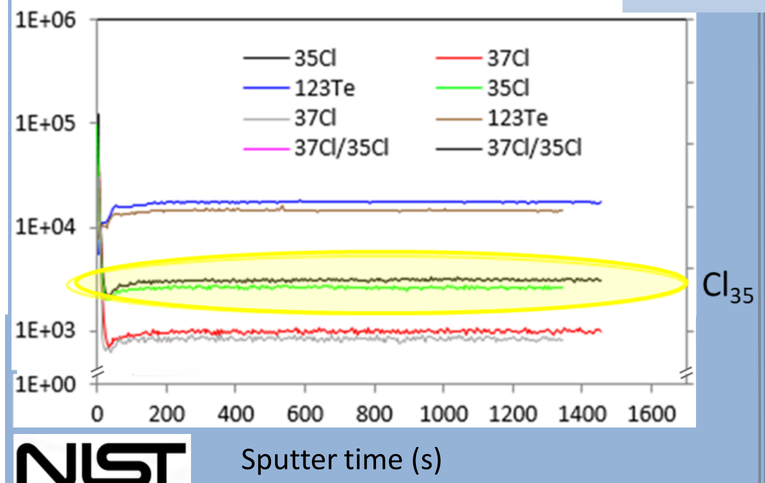
FET transfer characteristics

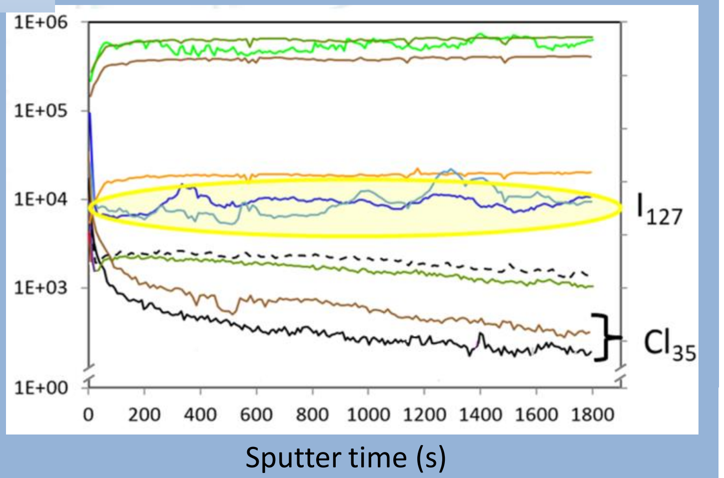




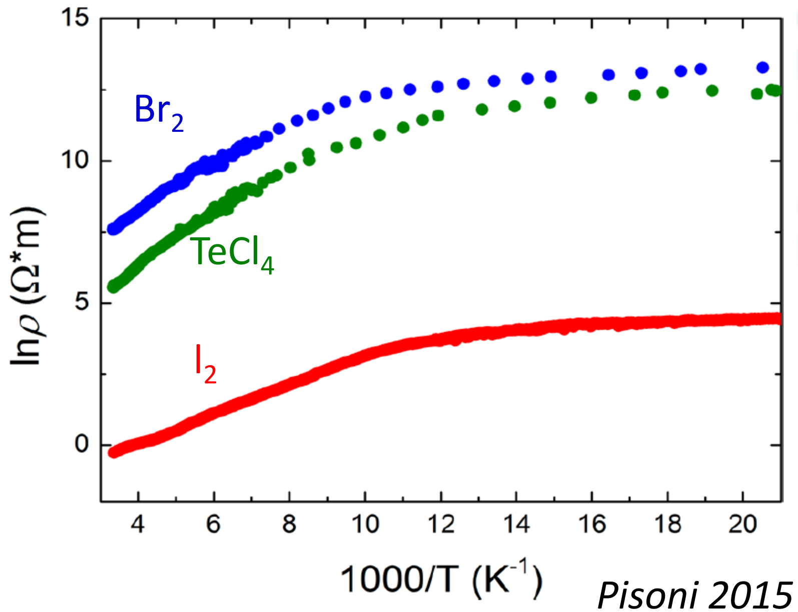


TOF SIMS





MoS_2 growth using $TeCl_4$, Br_2 and I_2



Pisoni 2015

Other references (e.g., *Legna 1993*) also indicate that $MoSe_2$ and WSe2, grown with *Cl-* and *Br-* were **n-doped**, while growth with *I-* resulted in **p-doping.**

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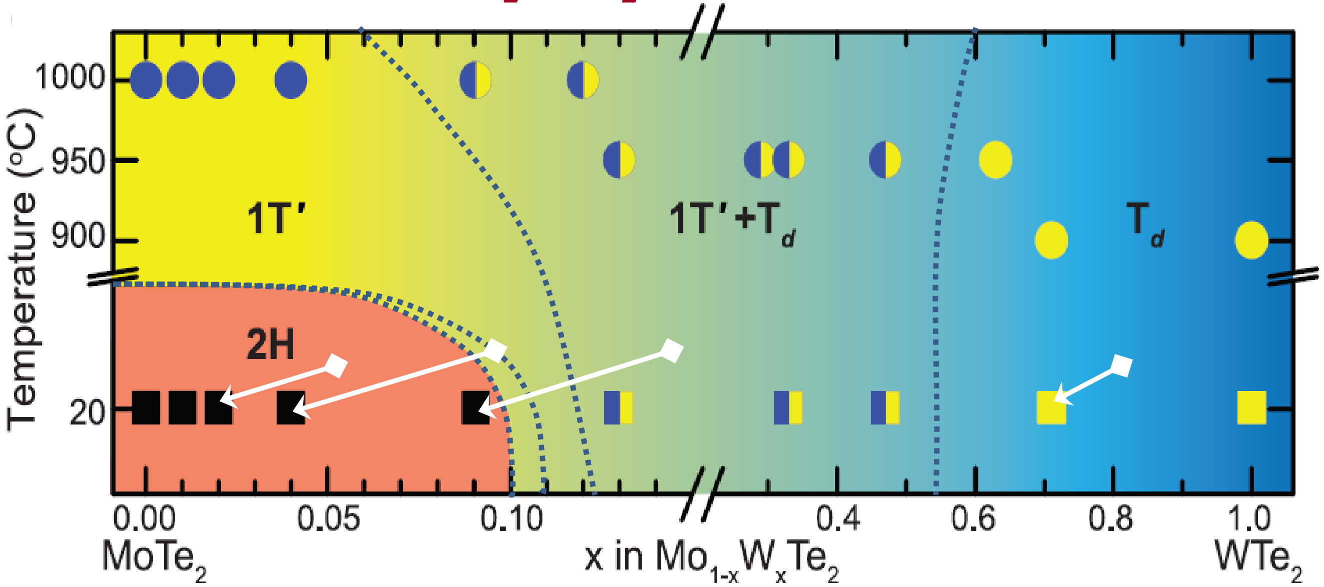
CVT growth: verify the phase and composition!

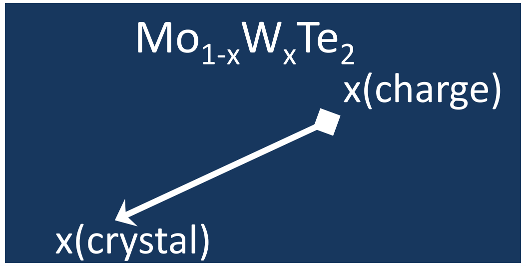
Key point: CVT reactions complicated

- Phases sublime (in)congruently
- Components' partial pressures and transfer rates vary

- 'Wrong' phase can grow: e.g., new *spin-triplet superconductor* **UTe_2** was originally intended to be **U_7Te_{12}**
- We found that doping level can be orders of magnitude lower than prescribed, e.g. in Nb-doped WSe_2
- Alloy composition is hard to control: e.g., **$Mo_{1-x}W_xTe_2$**, $WSe_{2(1-x)}Te_{2x}$, $W_{1-x}Nb_xSe_2$ and $Mo_{1-x}Nb_xSe_2$

$MoTe_2$-WTe_2 pseudo-binary (T-x)- section

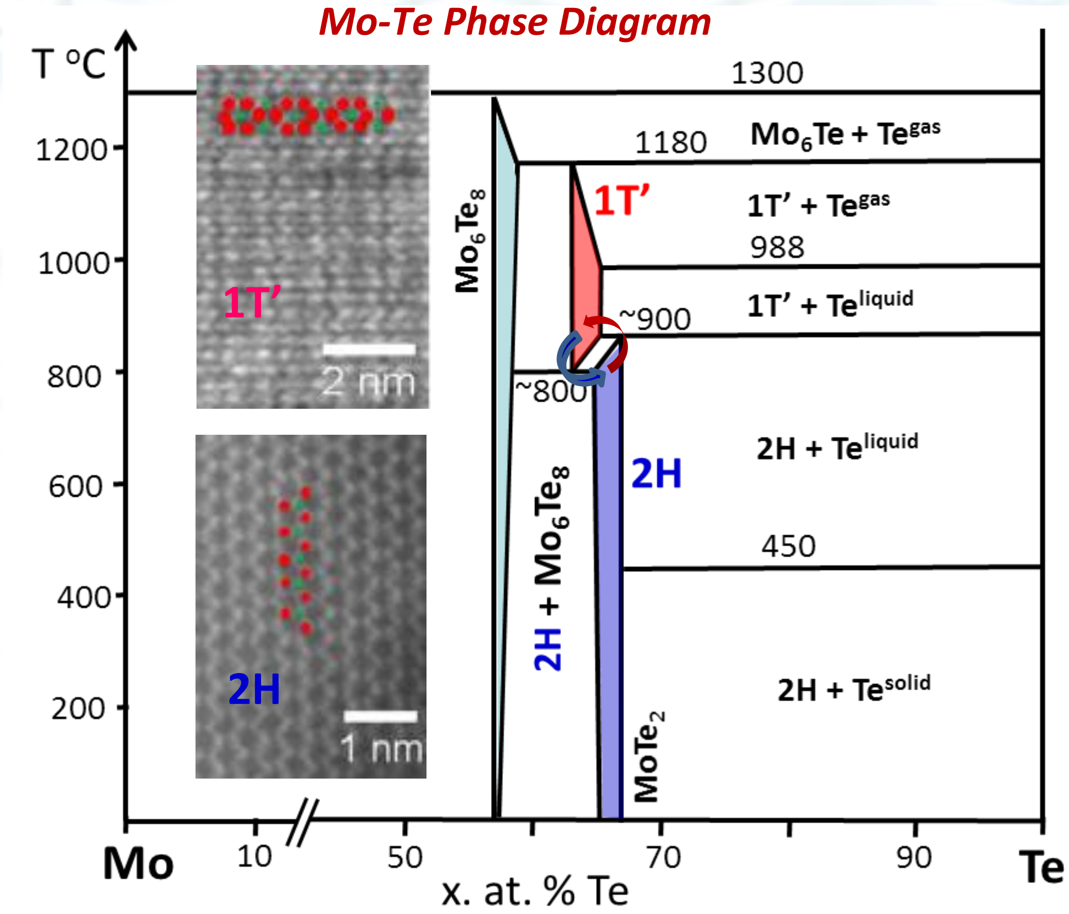


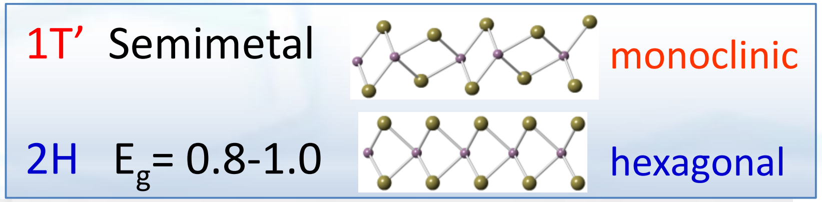


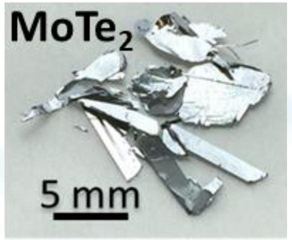
W-content is always less in crystal (~ factor of x2)

Oliver et al., 2D Mater. 4 (2017) 045008

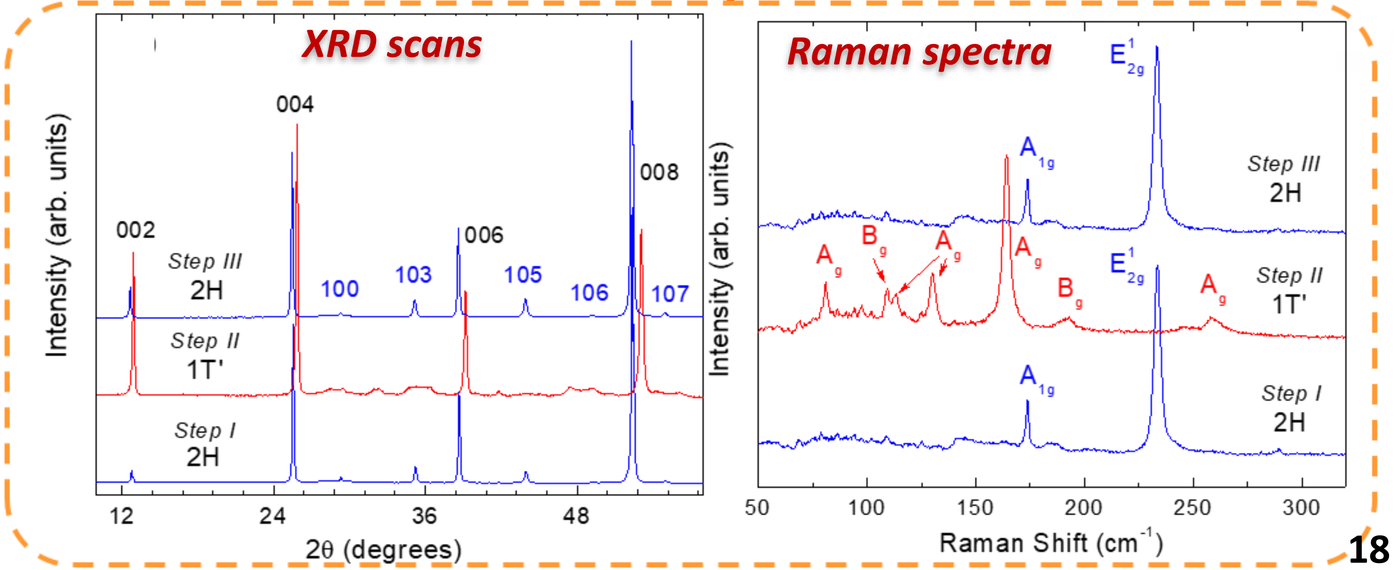
(T-x)- Phase Diagram for CVT growth: Mo-Te case







- 1T' grows at T > 850 °C; 2H grows at T = 750 - 800 °C
- Reversible phase transition 1T' ↔ 2H upon annealing



- Growth is affected by ampoule size
- P_{Te} inside of ampoule is different
- P-T-x diagram maybe useful (in a long run)

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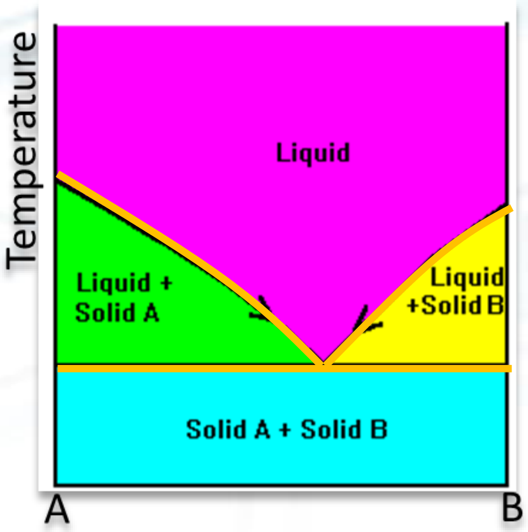
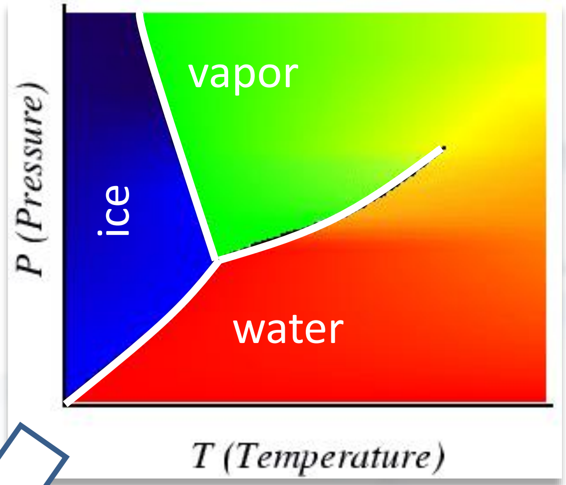
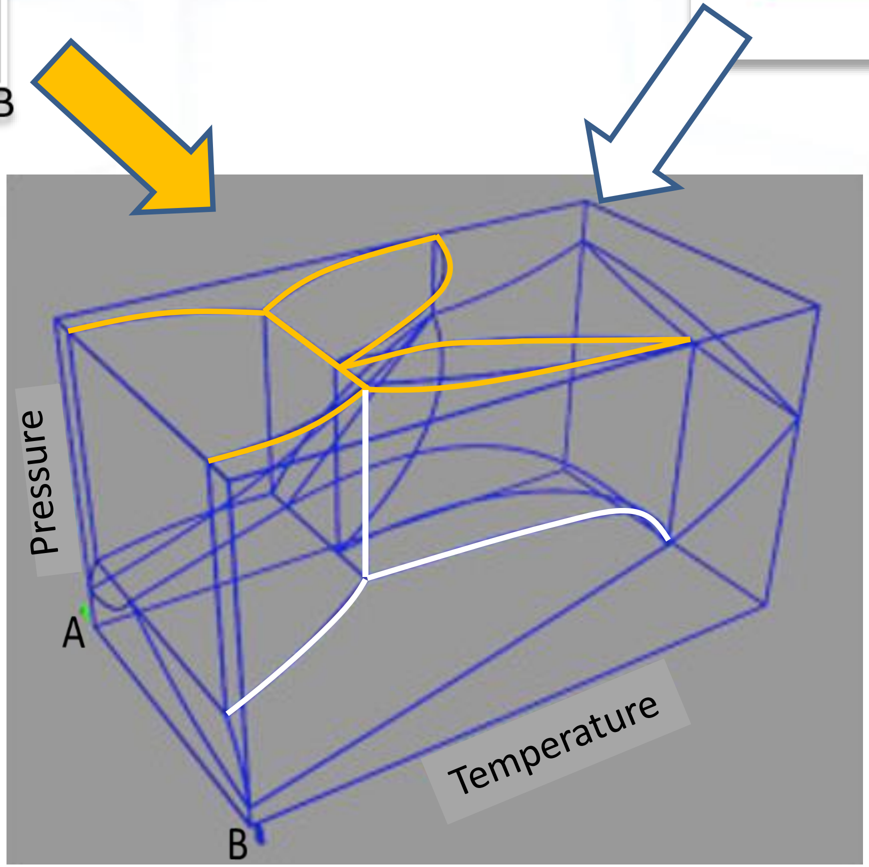
Full phase diagram: P-T-x

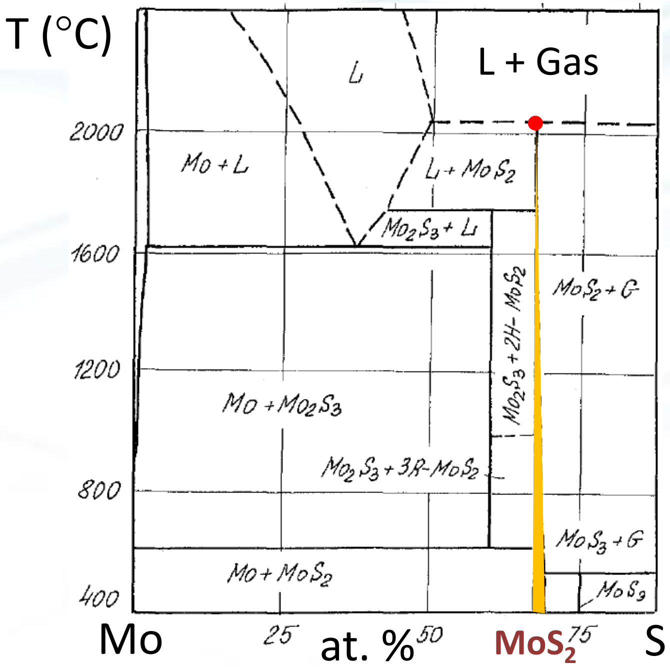




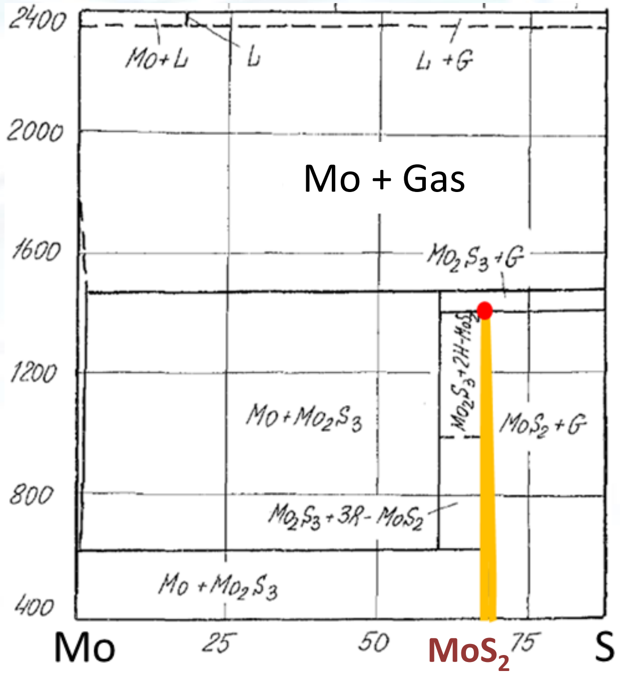


P-T-x Diagram for Mo-S System

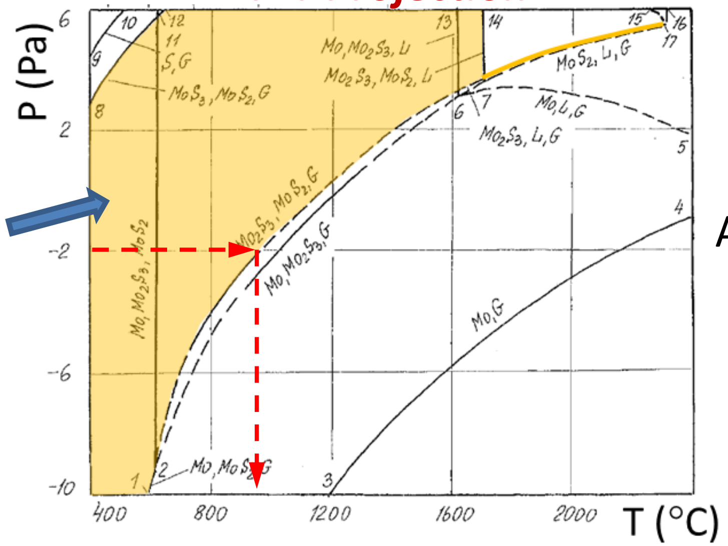
T-x Section at P=10^5 Pa



T-x Section at P=10^2 Pa



P-T Projection

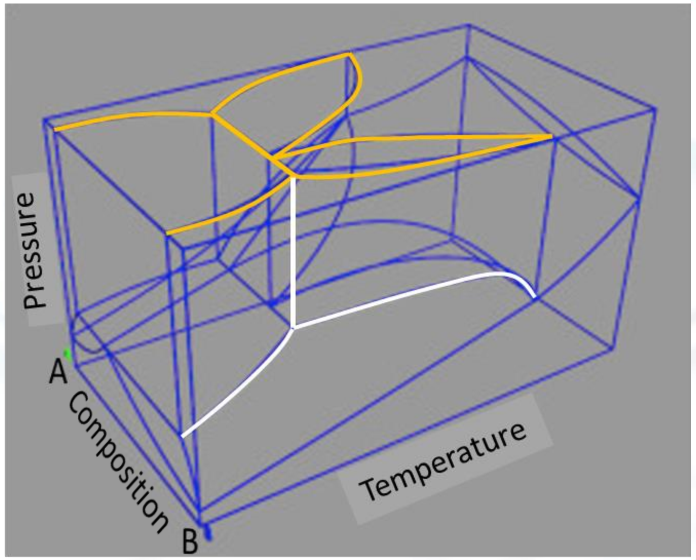


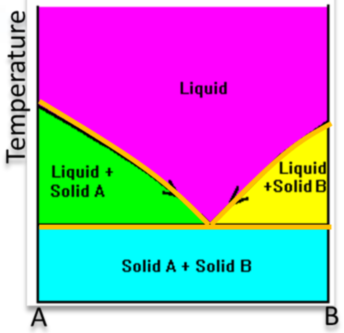
Levinsky, 1997

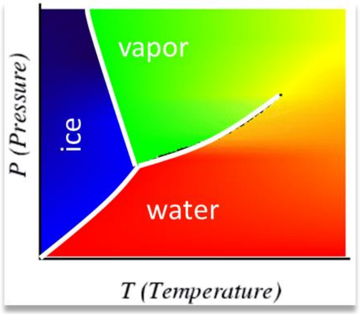
MoS_2 is stable within this yellow-highlighted area

At $P_{S2} = 10^{-2}$ Pa, $T_{decomp} = 1044$ °C

P-T-x diagram of binary system







- Chalcogen partial pressure defines stability of metal chalcogenides

Concluding thoughts

- When planning a crystal growth, see if phase diagram is available:
  - It helps to define growth window & phase stability (in terms of *Pressure-Temperature-composition)*
- *Growth from melt* (Bridgman and flux methods) produces large single crystals
  - Congruently melting phase => use Bridgman growth
  - Otherwise – grow from flux (identify “melt + solid” area on a phase diagram)
- *CVT growth*: complex process with many variables => check identity and composition of the phases

Further reading – next slide, courtesy of Michael McQuire (ORNL)

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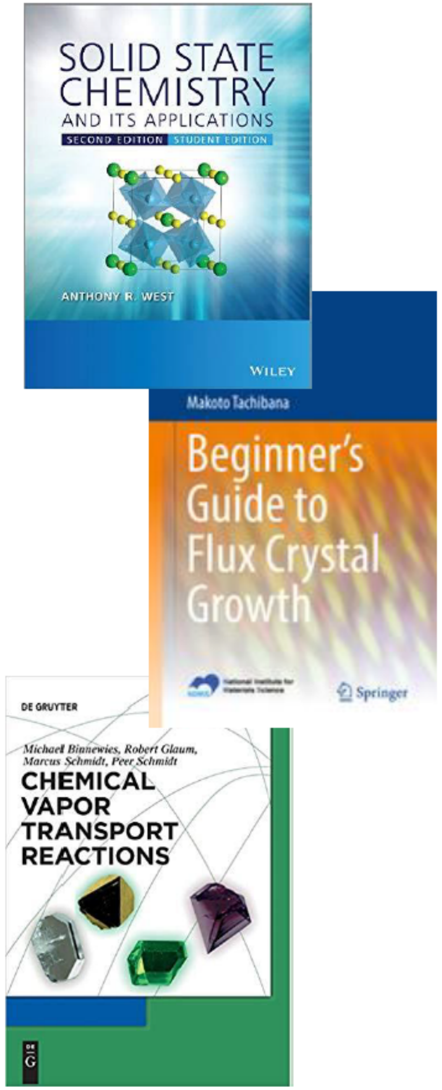
Further reading, courtesy of Michael A. McQuire (ORNL)

Additional resources

- General synthesis, phase diagrams
  - A.R. West, *Basic Solid State Chemistry* and *Solid State Chemistry and its Applications*
  - P. Hagenmuller (ed.), *Preparative Methods in Solid State Chemistry*
  - A. Brown and J.H. Westbrook, "Formation Techniques", in *Intermetallic Compounds*, (J.H. Westbrook, ed.) [container material selection in particular]
  - FactSage FTSalt phase diagrams: http://www.crct.polymtl.ca/fact/documentation/FTsalt/FTsalt_Figs.htm
  - ASM Alloy Phase Diagram Database https://matdata.asminternational.org/apd/
- Flux growth
  - Kanatzidis, Pöttgen, Jeitschko "The metal flux: A preparative tool for the exploration of intermetallic compounds" *Angew. Chem. Int. Ed.* 44, 6996 (2005). Canfield and Fisk "Growth of single crystals from metallic fluxes" *Phil. Mag. B* 65, 1117 (1992).
  - M. Tachibana "Beginner's Guide to Flux Crystal Growth"
- Vapor transport reactions
  - H. Schäfer "Chemical transport as a preparative procedure", in *Preparative Methods in Solid State Chemistry* (P. Hagenmuller, ed.)
  - Binnewies, Glaum, Schmidt, Schmidt, *Chemical Vapor Transport Reactions*



OAK RIDGE National Laboratory

Acknowledgements

- Sergiy Krylyuk – CVT growth Jim Maslar – CVD growth
- Huairuo Zhang, Alina Bruma, Leo Bendersky – TEM
- Gheorghe Stan – AFM, KPF
- Berc Kalanyan, Stephen McDonnell – XPS
- Irina Kalish – XRD
- Shinichiro Muramoto, Joe Bennett, Greg Gillen – SIMS
- Angela Hight Walker, Heather Hill, Amber McCreary,
  Sean Oliver, Patrick Vora, Ryan Beams – Raman
- Ben Burton – ab-initio modeling
- Asha Rani, Kyle DiCamillo, Ratan Debnath, Zheng Sun – FET fabrication & measurements