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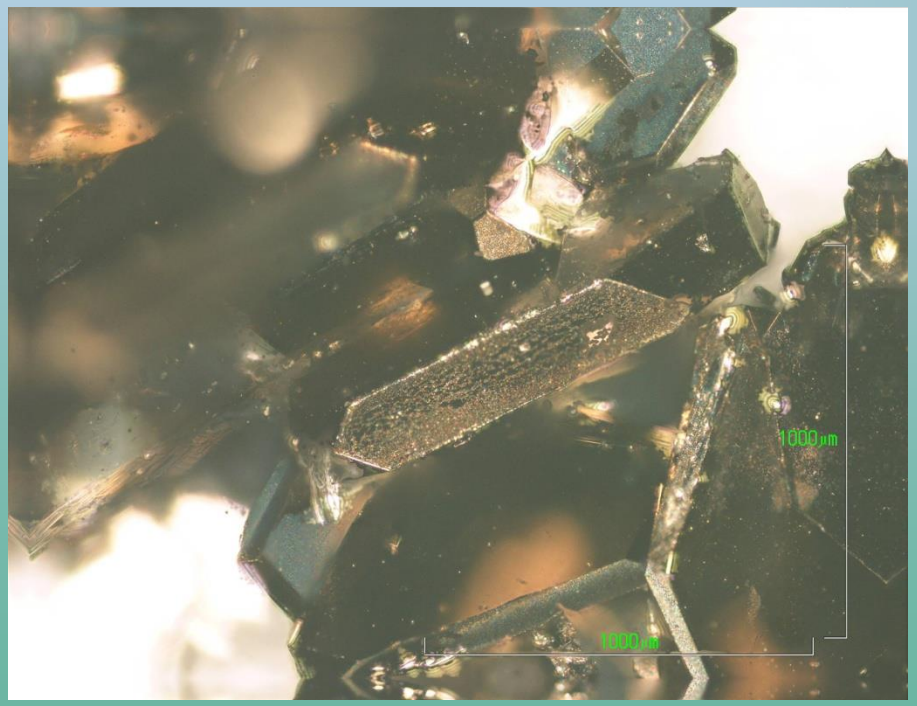
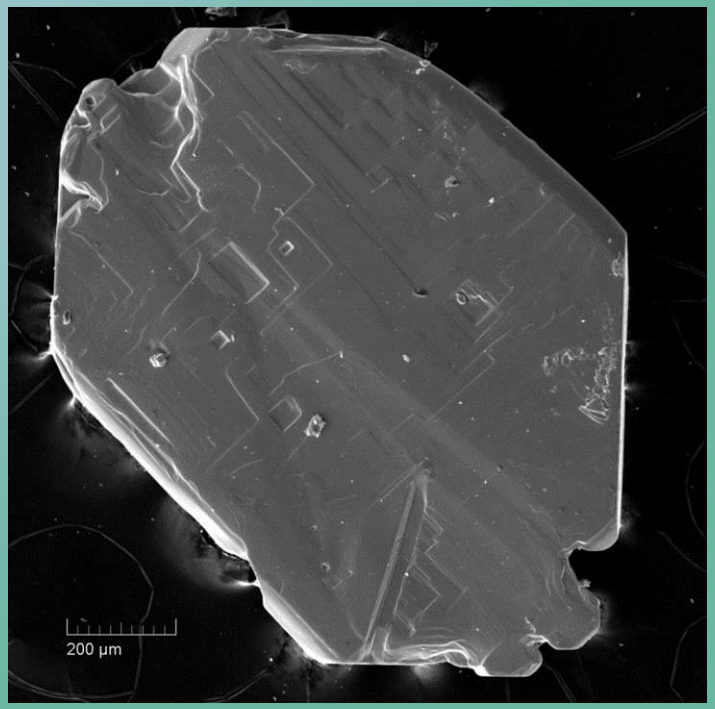
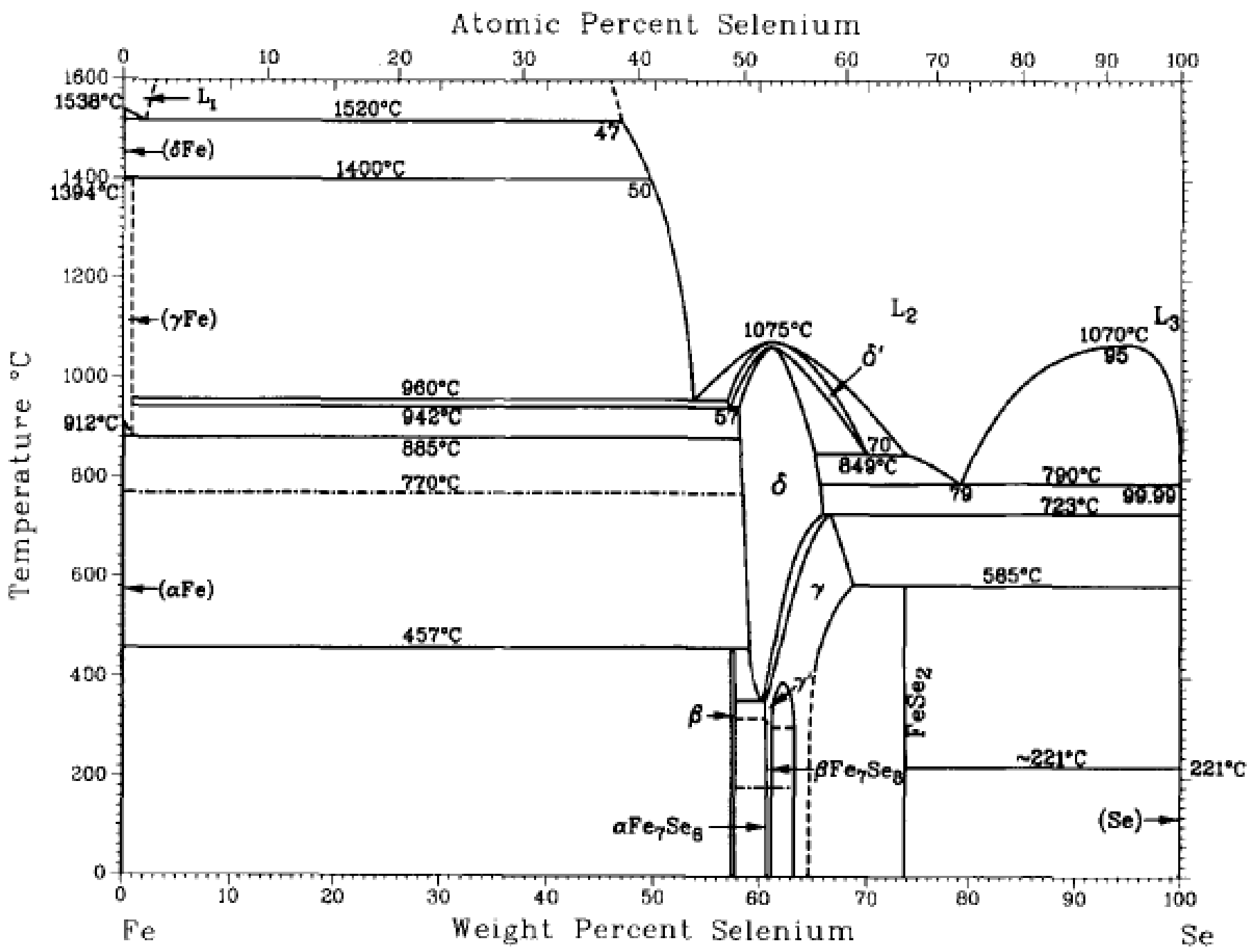
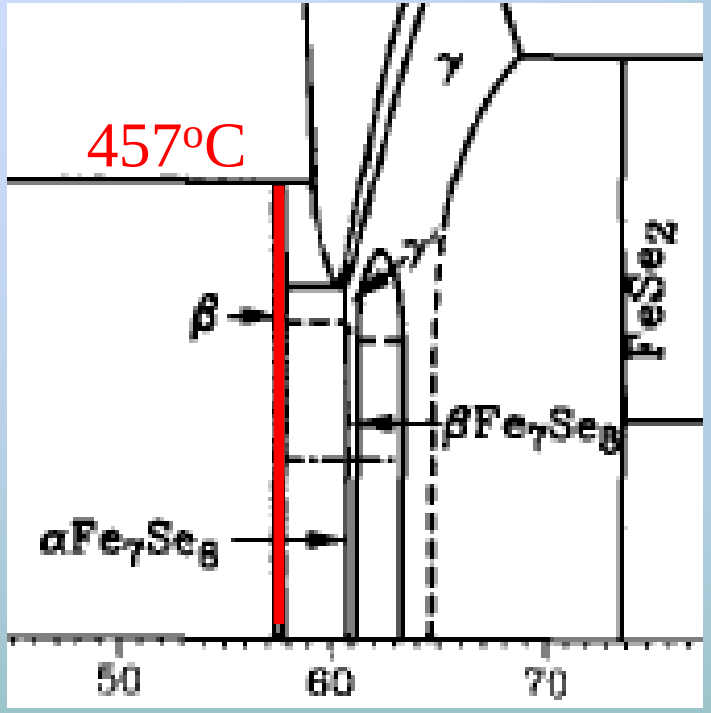
Single crystal growth of tetragonal $FeSe_{1-x}$ superconductors *and other substances*






Atomic Percent Selenium
Weight Percent Selenium
Temperature °C
Fe
Se
1538°C
L1
1520°C
47
(δFe)
1400°C
50
1394°C
(γFe)
1075°C
L2
δ'
1070°C
L3
95
960°C
942°C
57
912°C
885°C
849°C
70
790°C
79
99.99
770°C
δ
723°C
γ
585°C
(αFe)
457°C
β
FeSe2
~221°C
221°C
βFe7Se8
αFe7Se8
(Se)

System Fe-Se



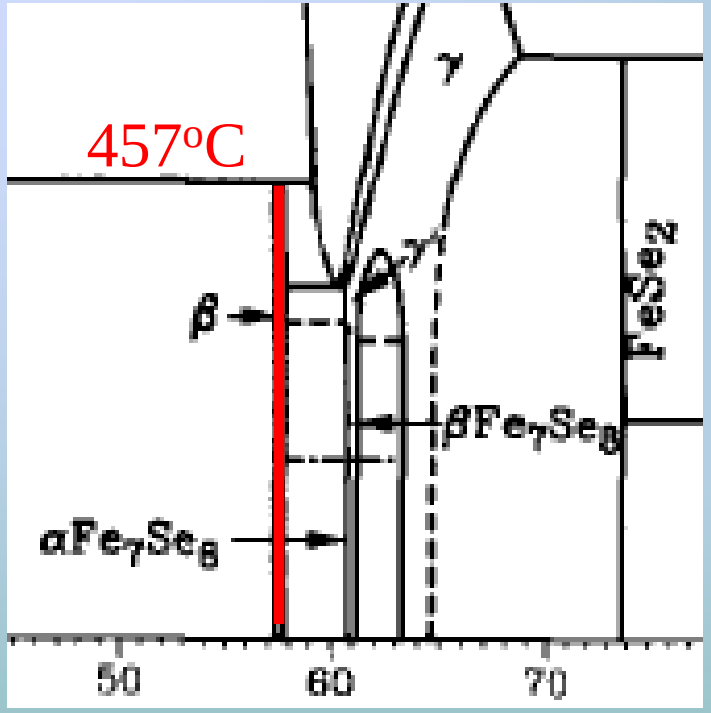
The superconducting tetragonal phase of $FeSe_{1-x}$ exists only **below** 730 K (457°C) in rather **narrow** composition range

Okamoto H., J. of Phase Equilibria, **12**, 383 (1991).

non congruent decomposition of tetragonal $FeSe_{1-x}$ to Fe and hex δ FeSe

~~Liquid → tetragonal $FeSe_{1-x}$~~ ☹

Crystal growth



Cooling of solution Fe and Se in melting salts:

In KCl (m.p. 776° C) in T interval 820 - 770 ° C.

In KCl/NaCl (m.p. 657° C) in T interval 740 - 600 ° C.

Or vapor transport method

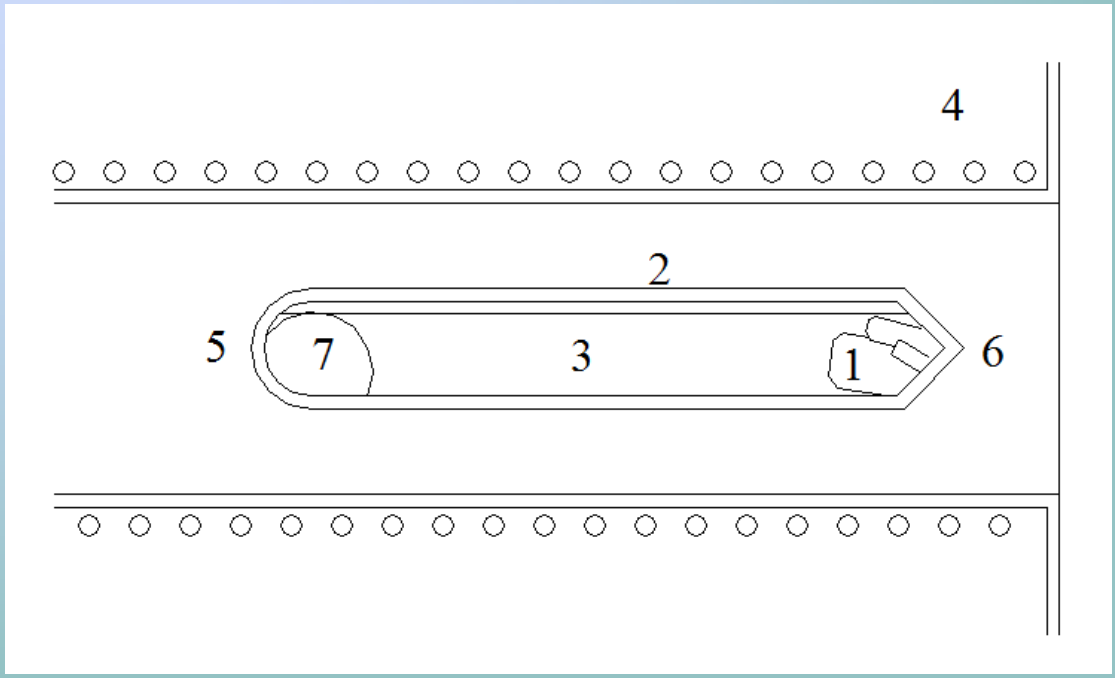
All crystals with hexagonal shape and coexisting of two phases (tetr and hex)

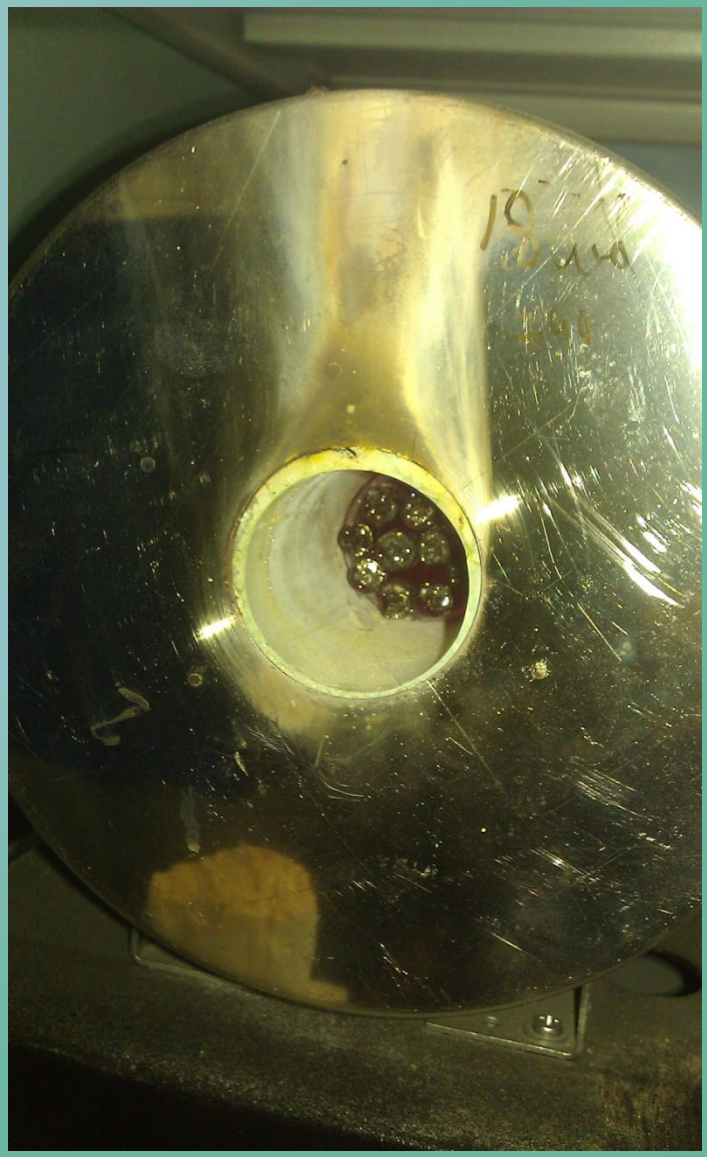
In CsCl/LiCl (m.p. 326° C) in T interval 457 - 300 ° C – correct

Rongwei Hu, Hechang Lei, M. Abeykoon, E. S. Bozin, S. J. L. Billinge, J. B. Warren, T. Siegrist, and C. Petrovic, Phys. Rev. B. **83**, 224502 (2011).

Thereby, to grow tetragonal $FeSe_{1-x}$ single crystals of high quality it is necessary to use eutectic flux which melts at low temperatures (preferably, below 250°C) and arrange synthesis at temperatures below 457°C, providing stable reproducible conditions of growth.

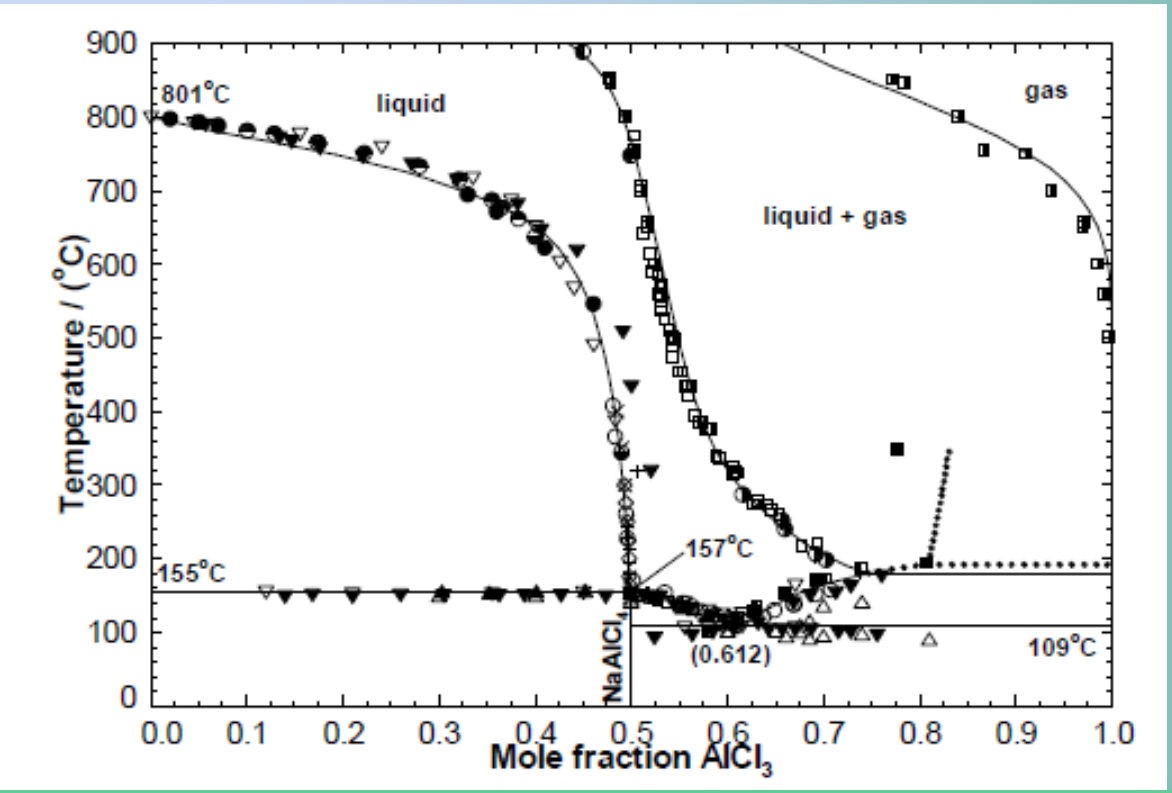
The $FeSe_{1-x}$ single crystals were grown from the flux under permanent gradient of temperature in $KCl/AlCl_3$ flux





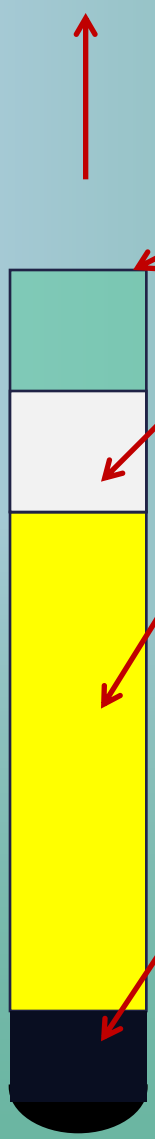
1. Crystals of FeSe
2. quartz ampoule
3. $KCl/AlCl_3$ flux
4. tube furnace
   (edge of tube furnace)
5. Hot end of ampoule 400-427 C
6. Cold end of ampoule ~ 350 C
7. The load ~$Fe_{1.3}Se_1$

$AlCl_3$/KCl phase diagram



Melting point of $AlCl_3$ (66%)+KCl – 109°C

Preparation of crystal growth



to pump

seal

KCl (NaCl/KCl, etc.)
prevent melt and hydrolyzation

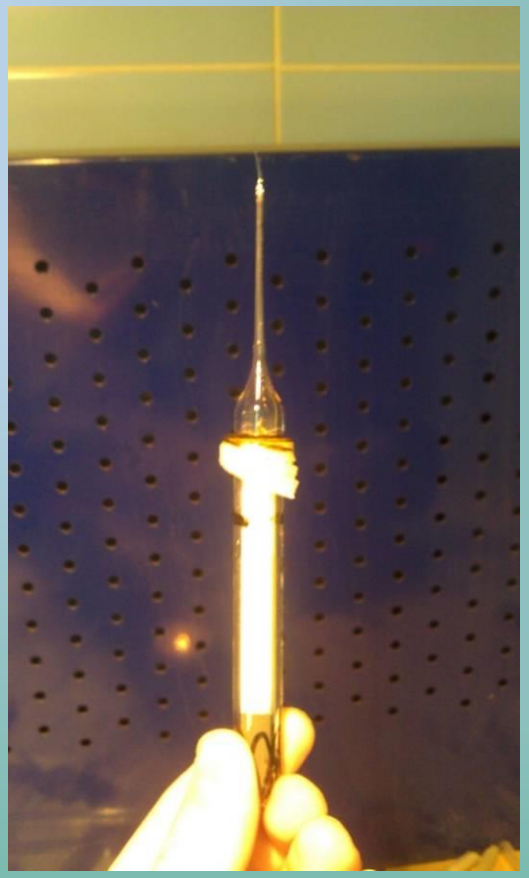
$AlCl_3$ very very very quickly on air
or in glove box

Load (1.3Fe+Se or FeSe+Fe)
~ 0.7 g

quartz ampoule
L 100-120 mm
ID 8-9 mm
ED 10-14 mm

Preparation of crystal growth

amp. during pumping out



amp. after preliminary
closing by oxygen torch

amp. after full
closing by oxygen torch

Preparation of crystal growth

before furnace

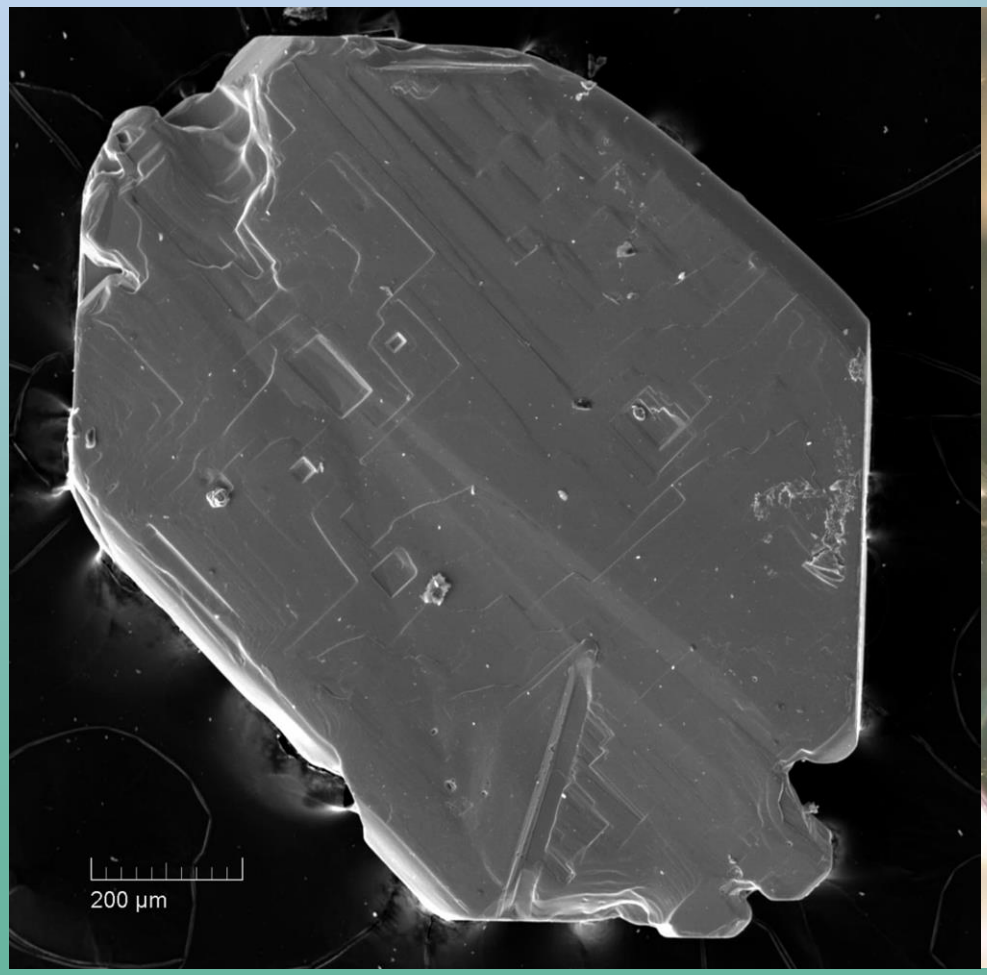
after furnace

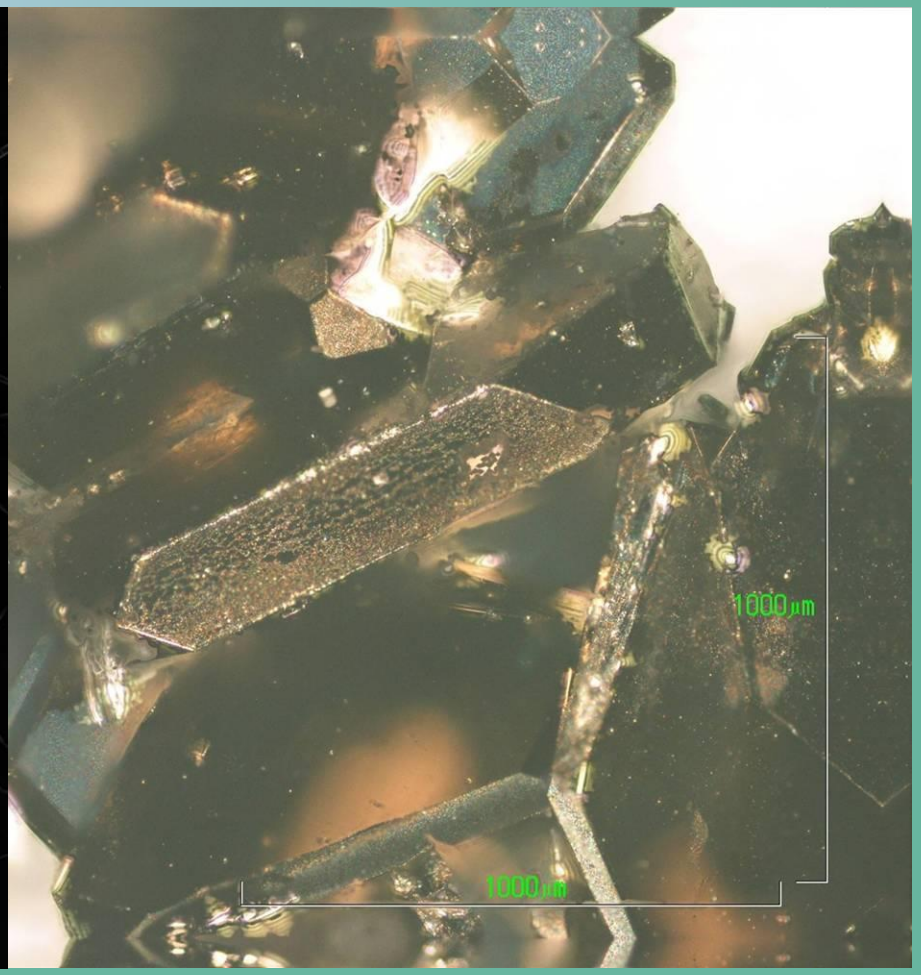
after furnace

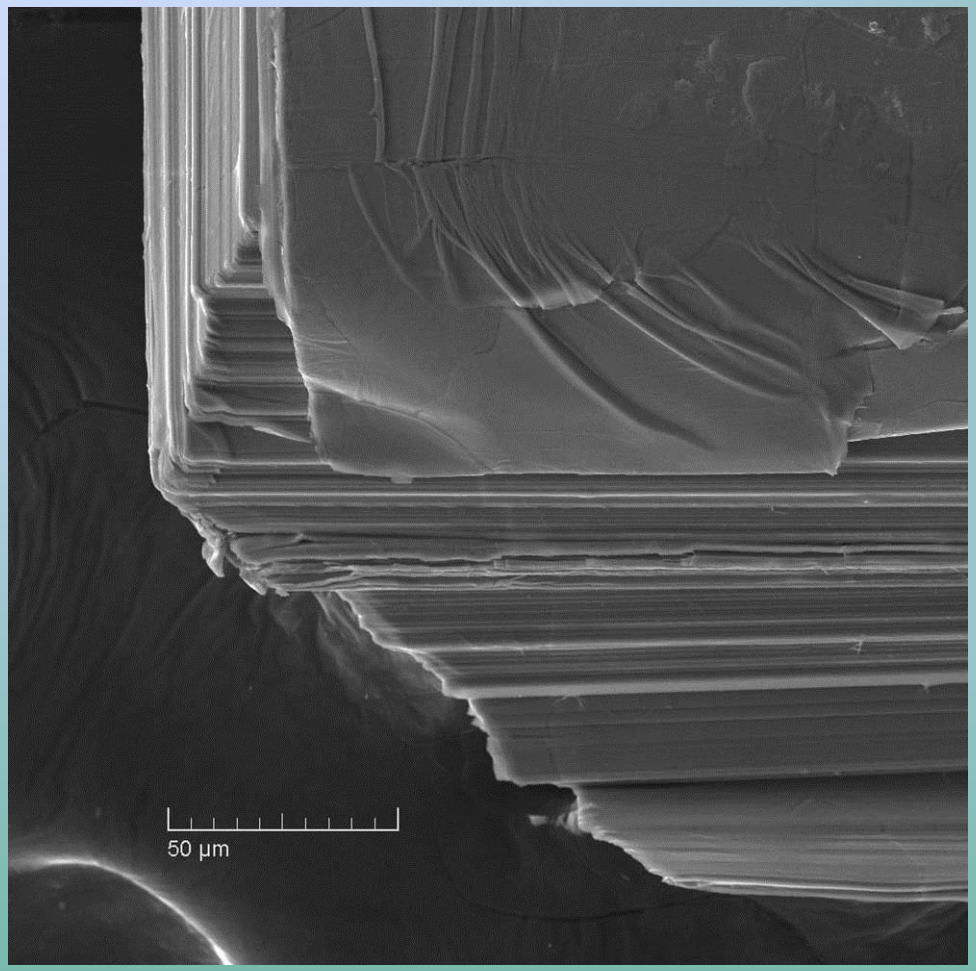
Ampoules after explosion

Extraction of ampules (after 6 – 7 weeks)
Cooling in the air or in water
Cleaning of cold part with
Rinsing in ultrasonic bath two times in water, two times in alcohol and two or three times in acetone.
Heating in a muffle furnace at 70ºC for few minutes. Tetragonal crystals were separation of tetr-FeSe using steel magnetic filling knife
Cleaning the crystals in water and alcohol did not produce any visible oxidation of surface.

The chemical compositions of tetragonal $FeSe_{1-x}$ and hexagonal FeSe were studied by an energy-dispersive X-ray spectroscopy performed on CAMECA SX100 (15 kV) analytical scanning electron microscope



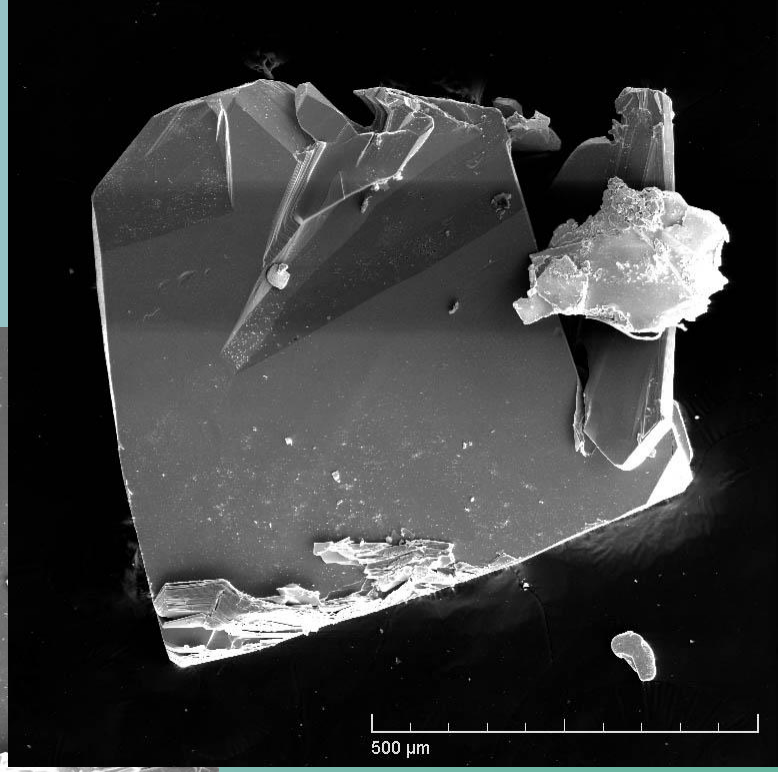


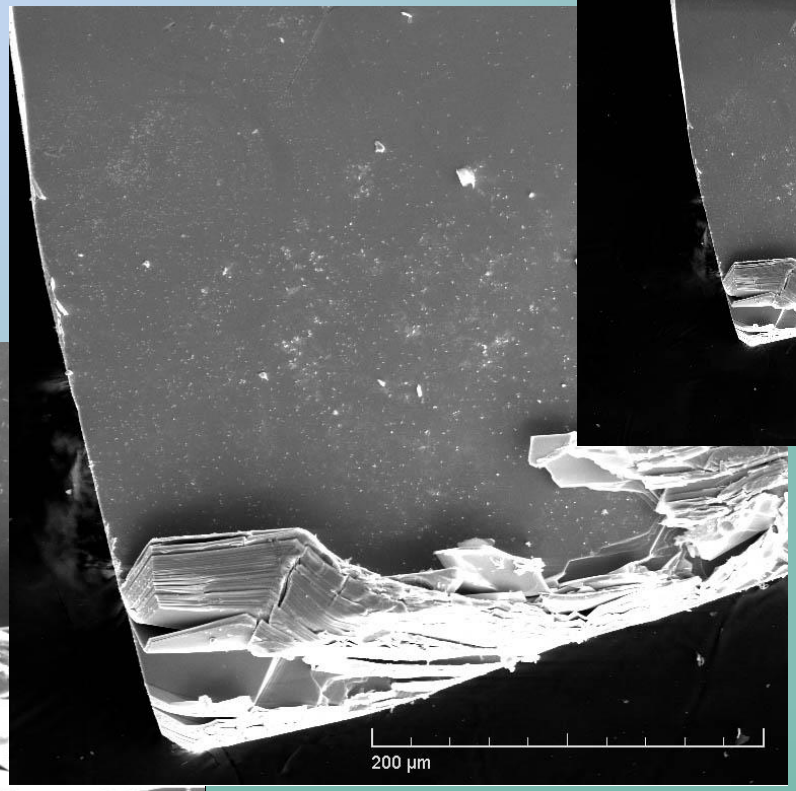


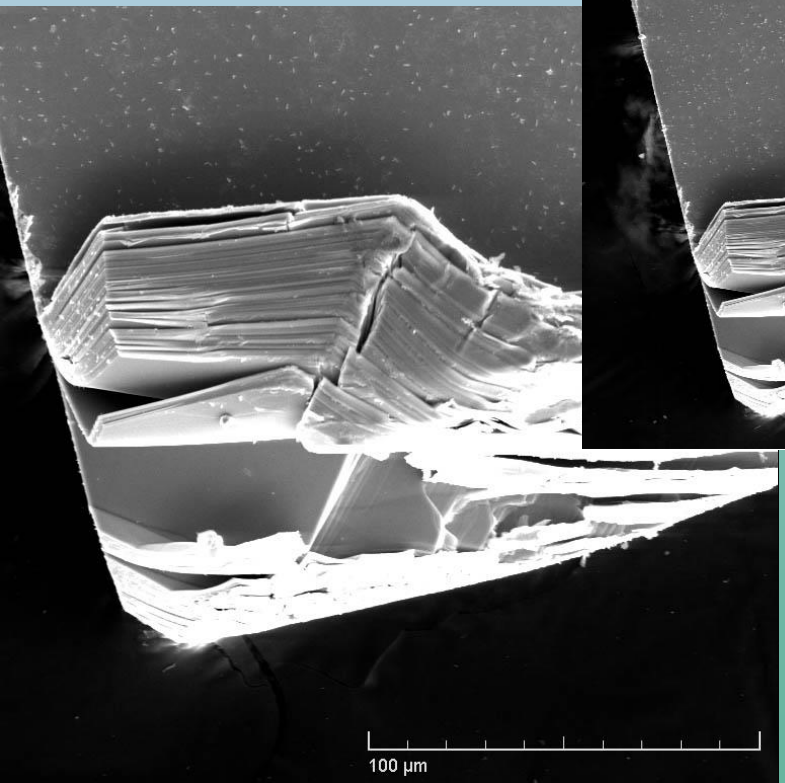
Growth rings of the trees

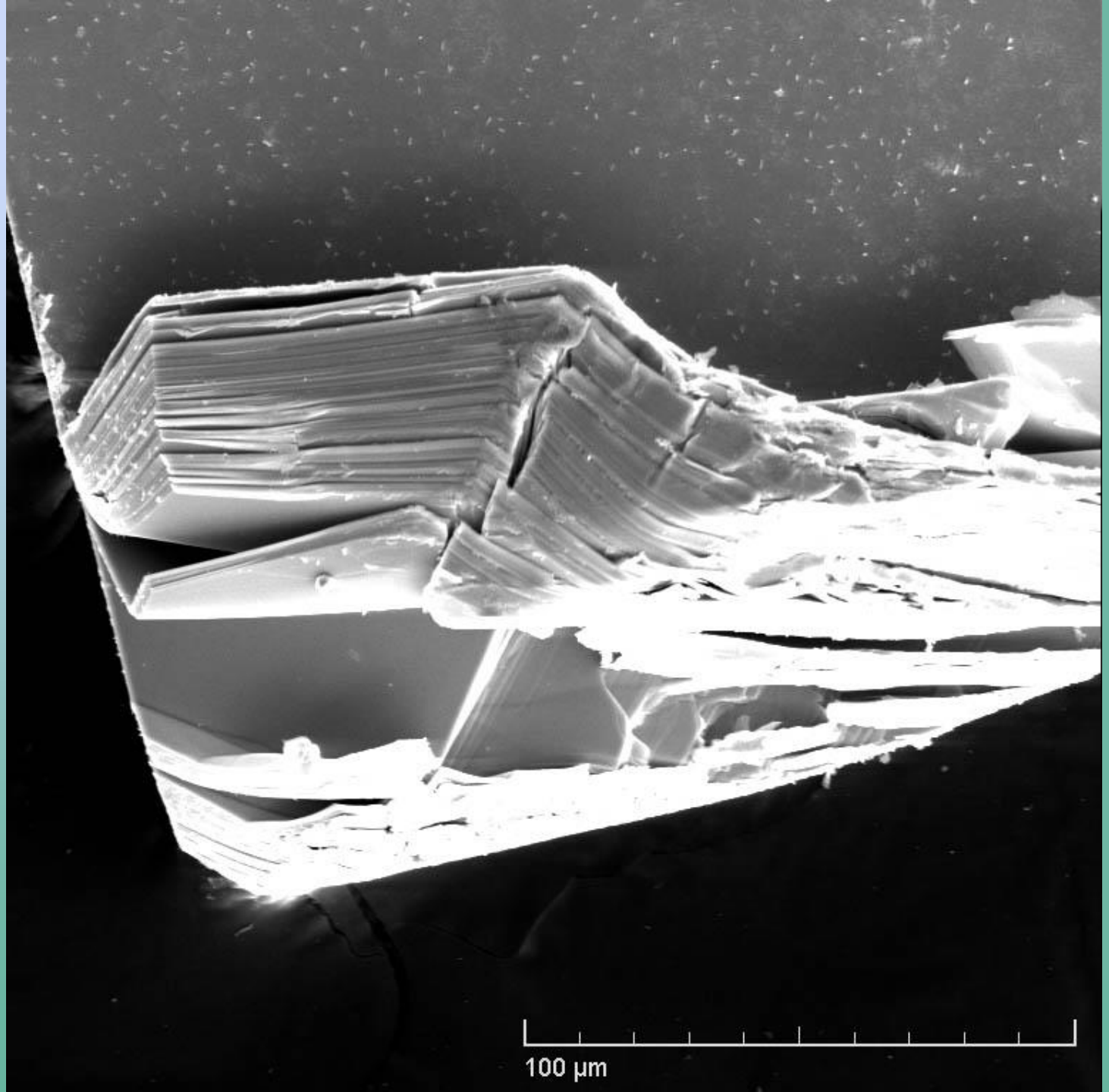
The layered structure of tetragonal $FeSe_{1-x}$ single crystal
Growth layers because of day work of the conditioner (?)

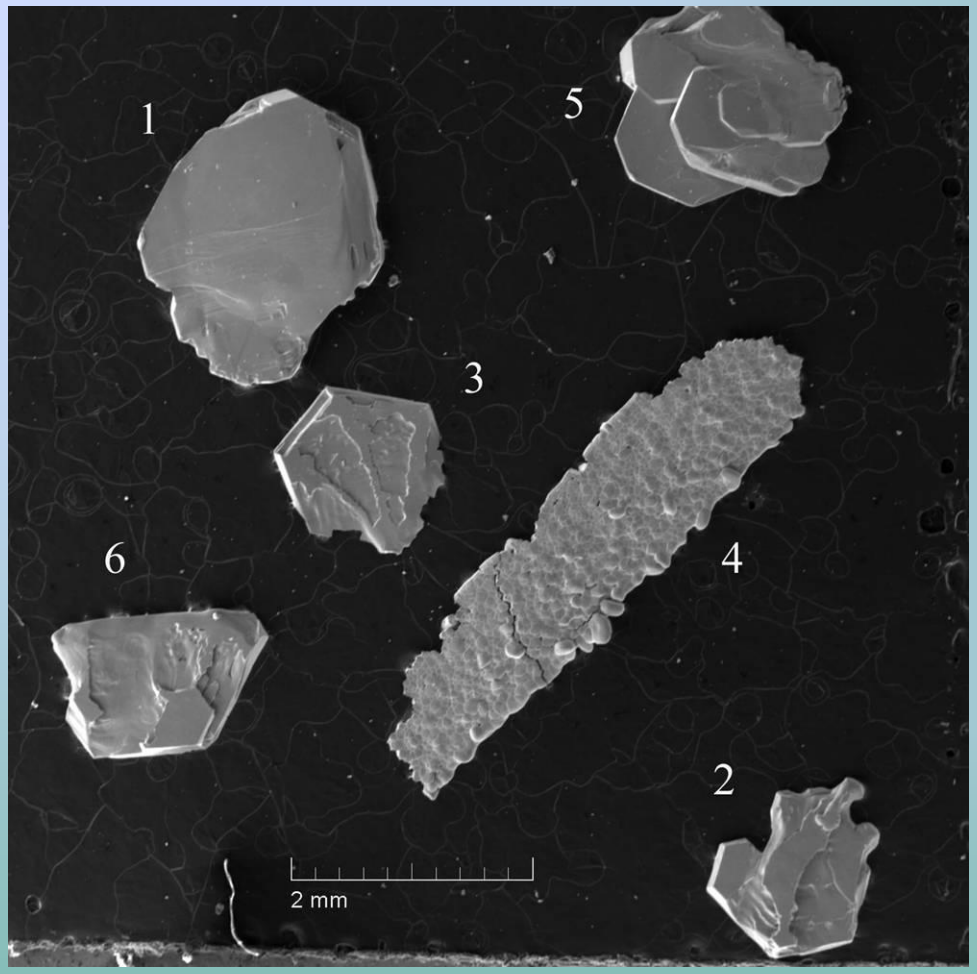
Mechanical deformation showing layered structure



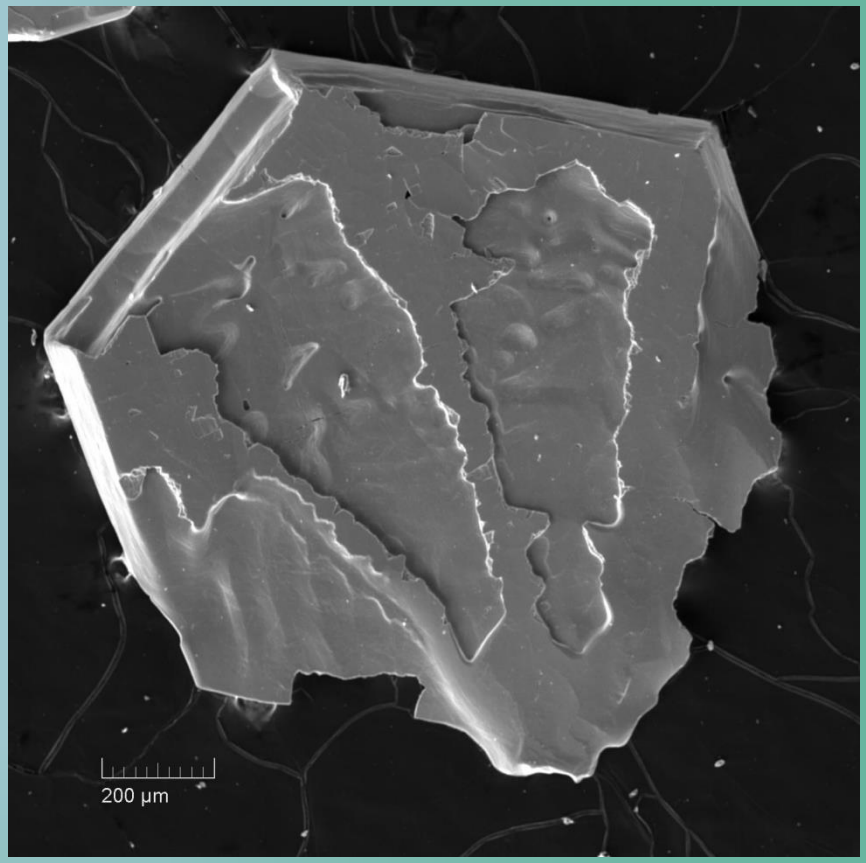




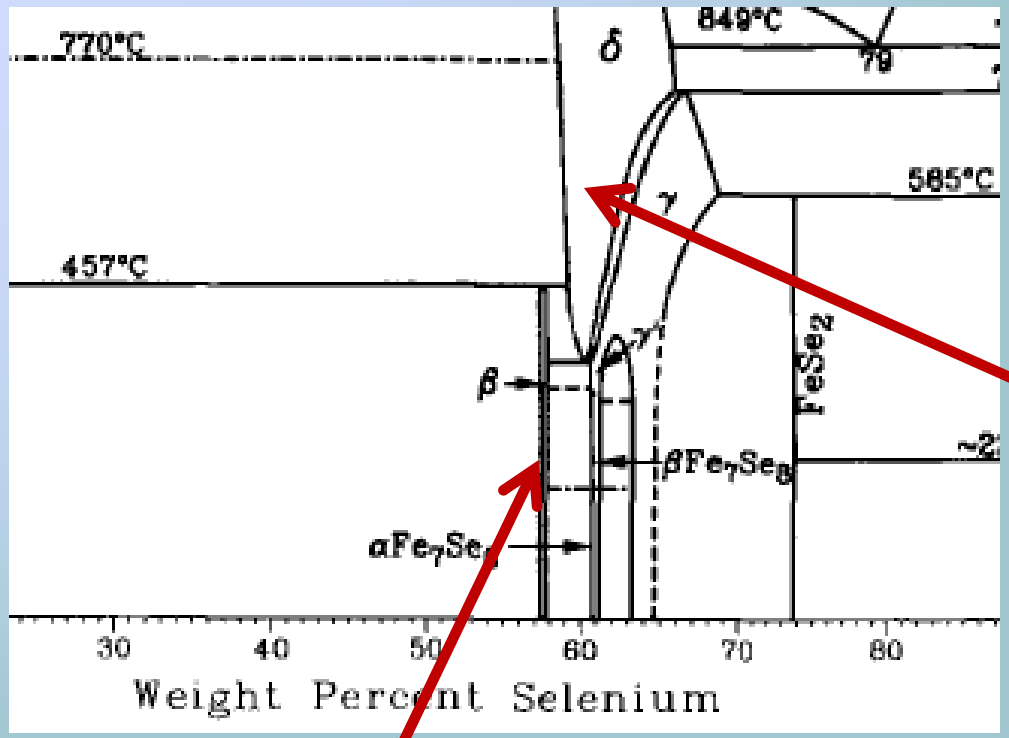

100 µm

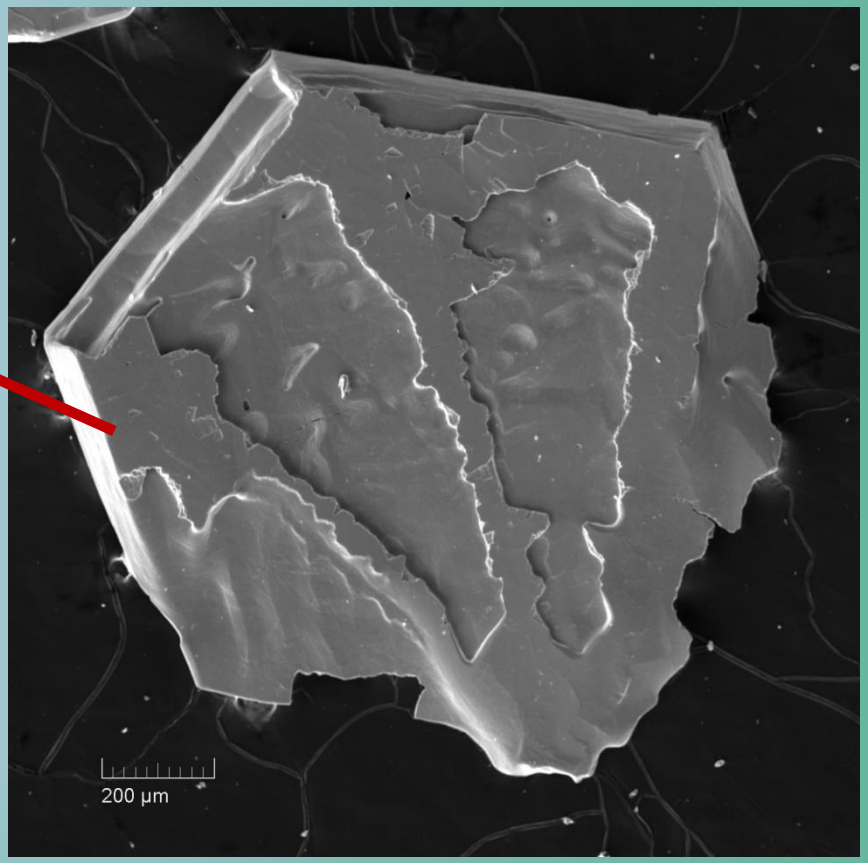


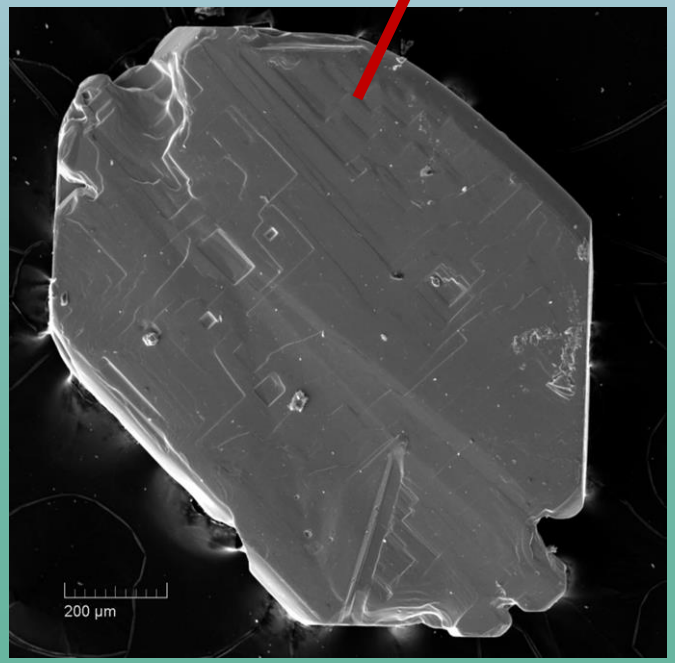
The scanning electron microscope image of products obtained at high temperatures. 1, 2, 3, 6 - hexagonal δ-FeSe crystals, 4 - association of hexagonal δ-FeSe crystals 5 - tetragonal $FeSe_{1-x}$ crystal



The scanning electron microscope image of hexagonal δ-FeSe crystal



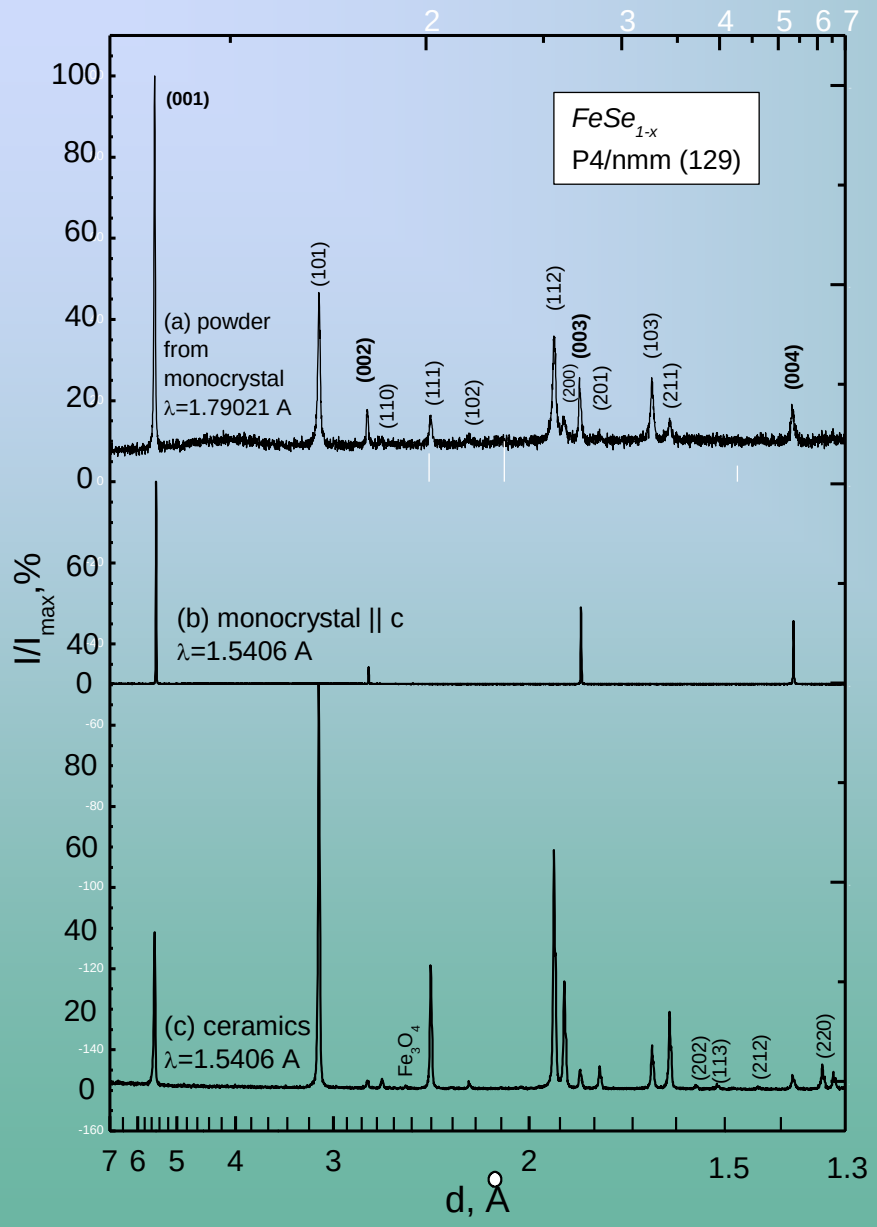




$\delta=\beta+\gamma$

hex FeSe = tetr $FeSe_{1-x}$ + hex Fe_7Se_8

high-T δ hex FeSe – super conductor 90%



The X-Ray diffraction pattern of tetragonal $FeSe_{1-x}$

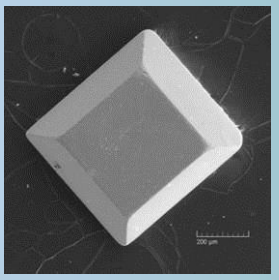
a) The X-Ray diffraction pattern of the grinded in agate mortar single crystals (Co K_{α})

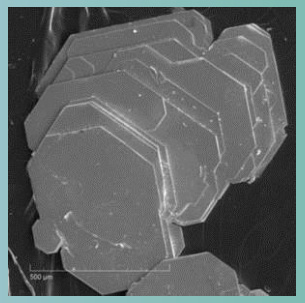
b) The X-Ray diffraction pattern along c axis (Cu $K_{\alpha 1}$)

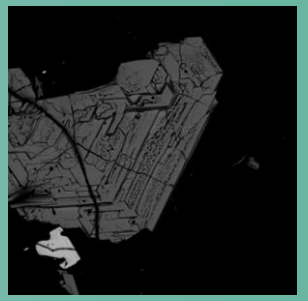
c) The X-Ray diffraction pattern of the polycrystalline sample synthesized for comparison by solid state reaction (Cu $K_{\alpha 1)}$

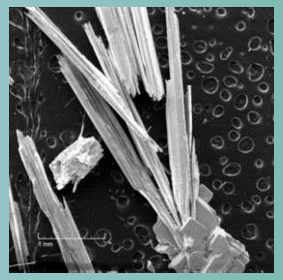
eutectic	application temperature °C	advantages	disadvantages
$AlCl_3$-KCl-(NaCl)	300 - 550	low T	potential of explosion, hydroscopic
$AlBr_3$-$AlCl_3$-….	150 - 400	very low T	potential of explosion, hydroscopic high cost
CsCl-LiCl	400 - 600	low T	amp. demage at crystalization Li reacts with SiO_2 hydroscopic high cost
CsCl-NaCl-(KCl) RbCl-NaCl	500 – 800 500 – 800	medium T nonhydrosc.	amp. demage at crystalization high cost Cs go to crystals (Rb - not)
NaCl-KCl KCl-KBr-KI	700 - 900	low cost nonhydrosc.	high T amp. demage at crystalization

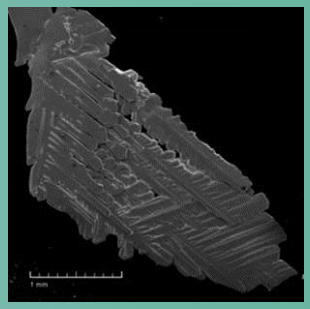
At this moment by means of this method are synthesized single crystals of:











FeSe

$FeSe_{0.8}S_{0.2}$

$FeTe\text{-}FeTe_{0.5}Se_{0.5}$

$FeTe\text{-}FeTe_{0.9}S_{0.1}$

low temp Fe

Fe_7Se_8, $FeSe_2$, $FeTe_2$, FeS, FeS_2

$ZnS\text{-}Fe_{0.56}Zn_{0.44}S$

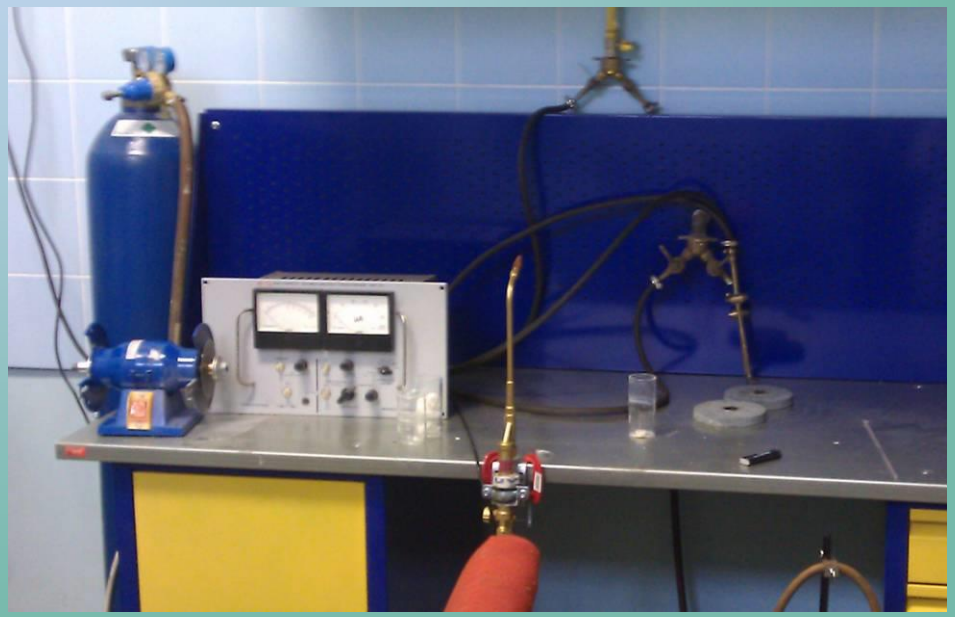
Bi_2Te_3

Bi_2Se_3, $(Bi,Sb)_2Se_3$, $Bi_2(Te,Se)_3$, $Bi_2(Se,S)_3$ small size ☹

CdS, $CsFe_2Se_3$, Cu_2ZnSnS_4

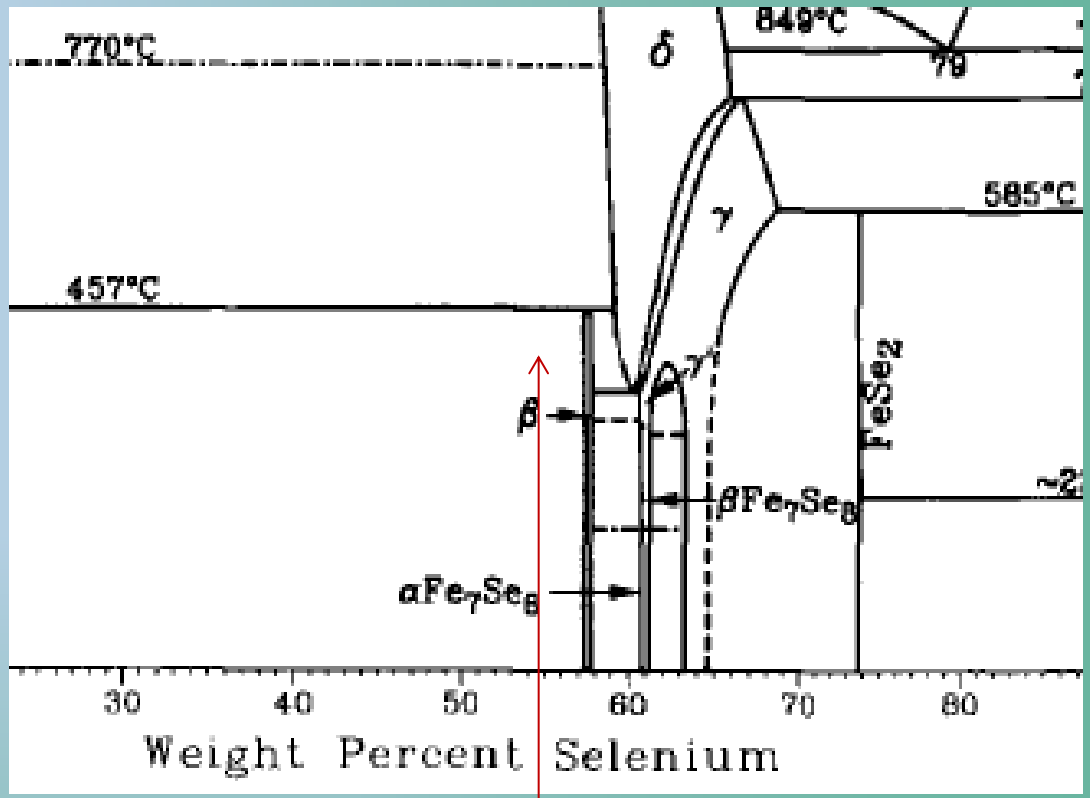
FeAsS


Spasibo
1000µm
1000µm




edding 8400


cd/dvd/bd marker
WORLD'S No.1


770°C
δ
849°C
γ
585°C
457°C
β
αFe7Se8
βFe7Se8
FeSe2
30
40
50
60
70
80
Weight Percent Selenium

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