Single crystal scintillators – preparation technologies

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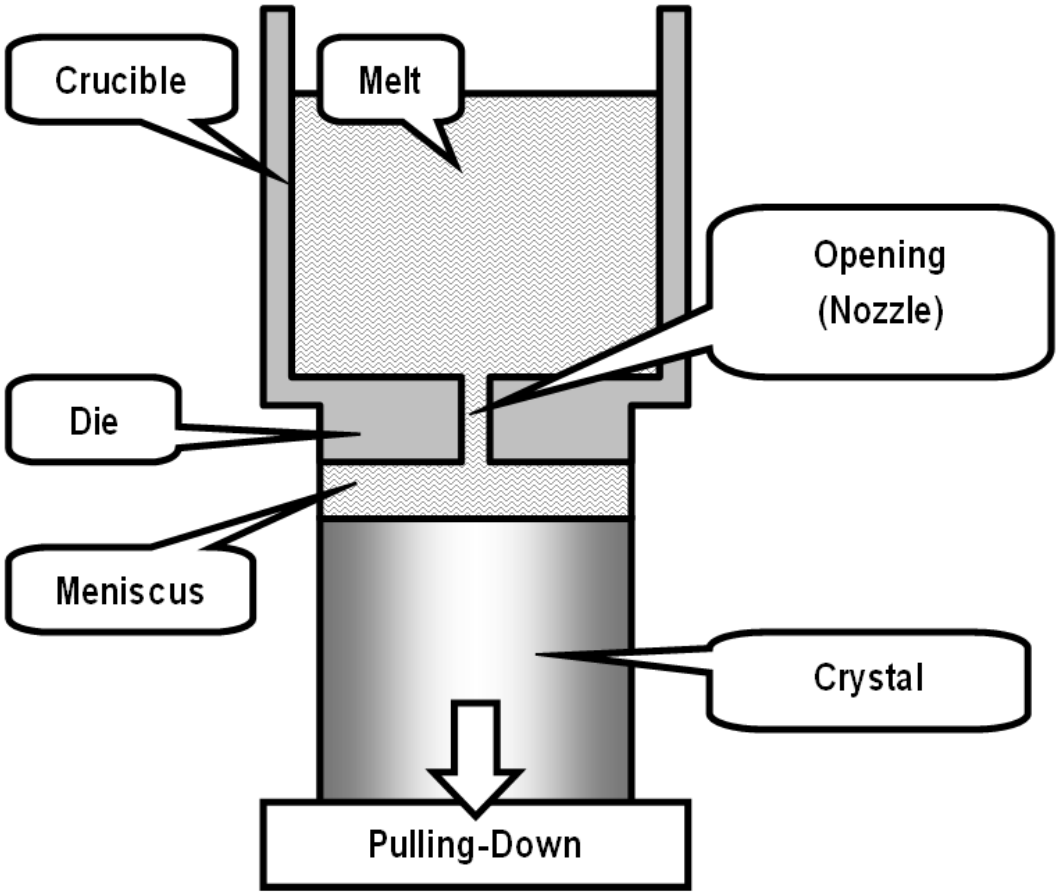
Principle of micro-pulling-down (mPD) method

Growth of small crystals (few mm diameter, few mm-cm length), fast growth rate (0.01-10 mm/min), ideal for material composition screening



Modern mPD setup developed around 1992-1993 in Tohoku University, Sendai, Japan, to grow $LiNbO_3$ and related materials

Micro-capillary for fiber crystal growth + pulling down

Resistive heating, inductive (radiofrequency) heating, possible application of active afterheater

Melt flows out due to gravity, hydrostatic pressure – possibility to grow from non - wetting melts – possibility of shaped crystal growth for wetting melts due to capillary action

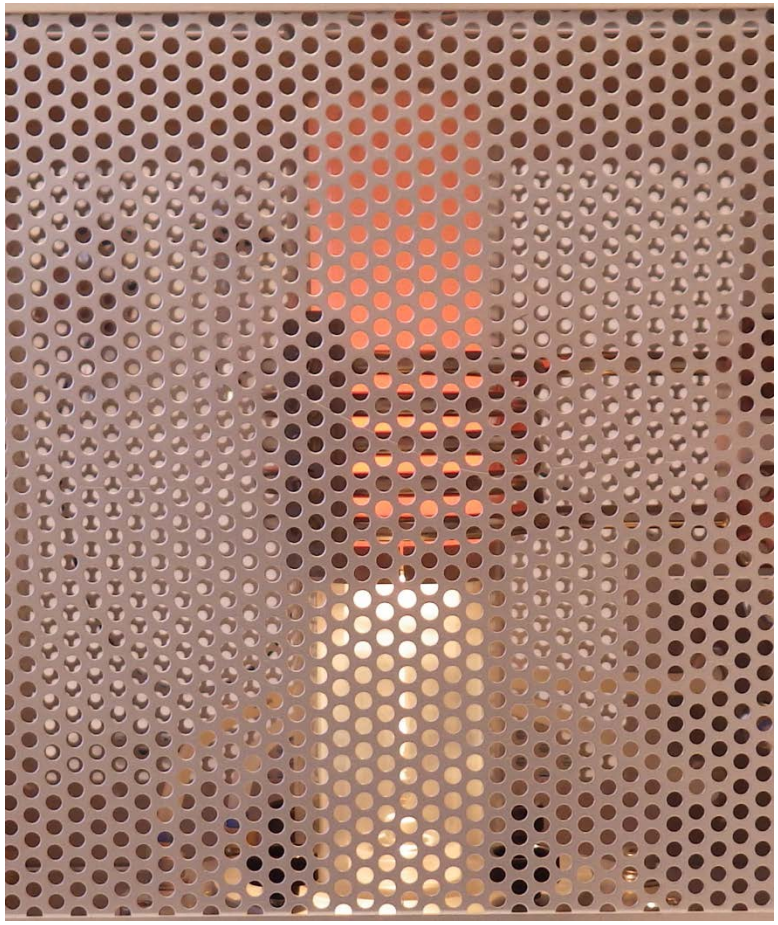
Device-sized crystals, no machining losses

Micro-pulling-down method
Oxide crystals

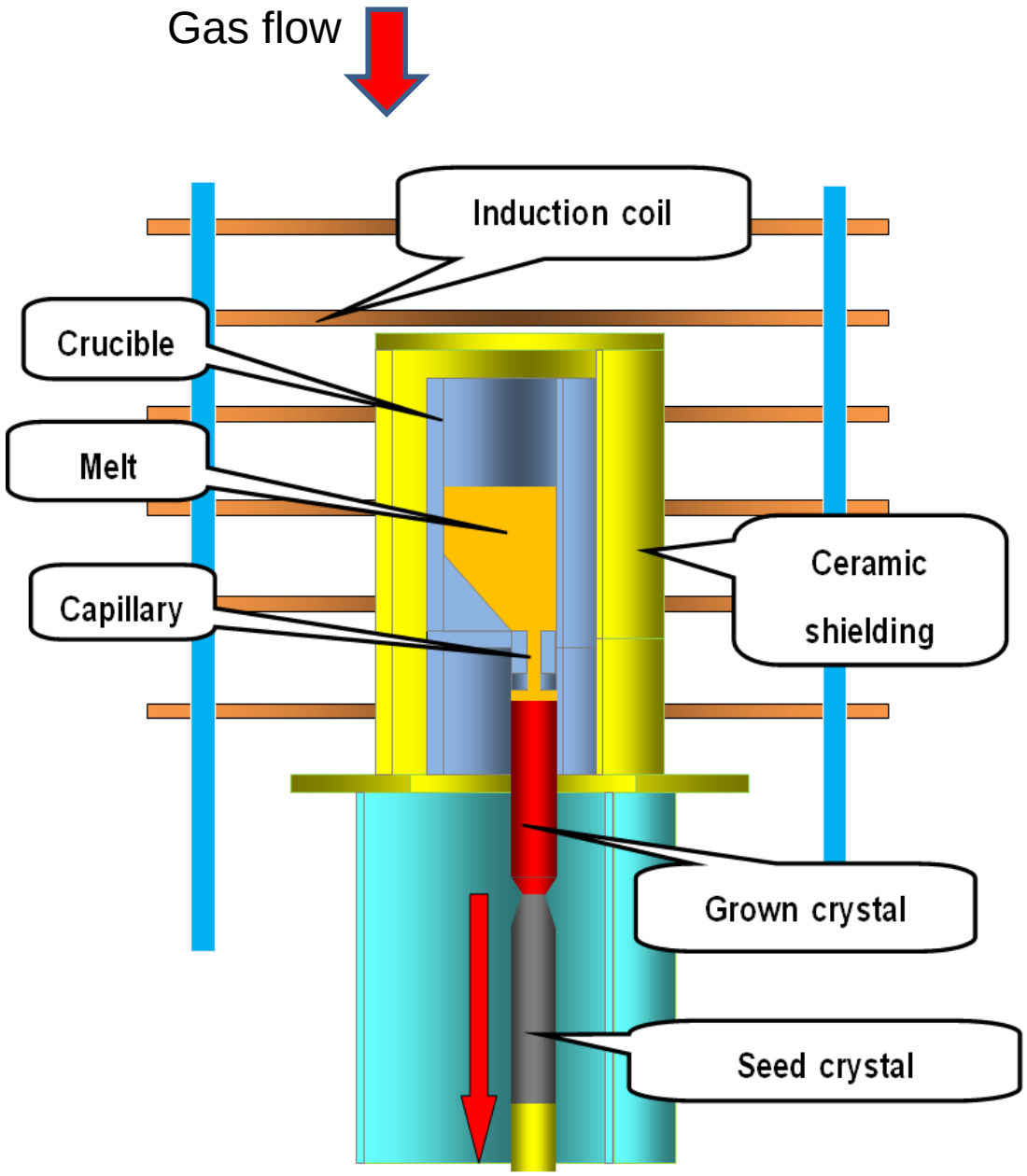
Micro-pulling-down (mPD) setup

Institute of Physics, Czech Academy of Sciences, Prague, Installed in June 2015

Type T-MPD-OX
by Akita Seiko Co., Ltd. Japan



Crystal growth by mPD method



RF heating

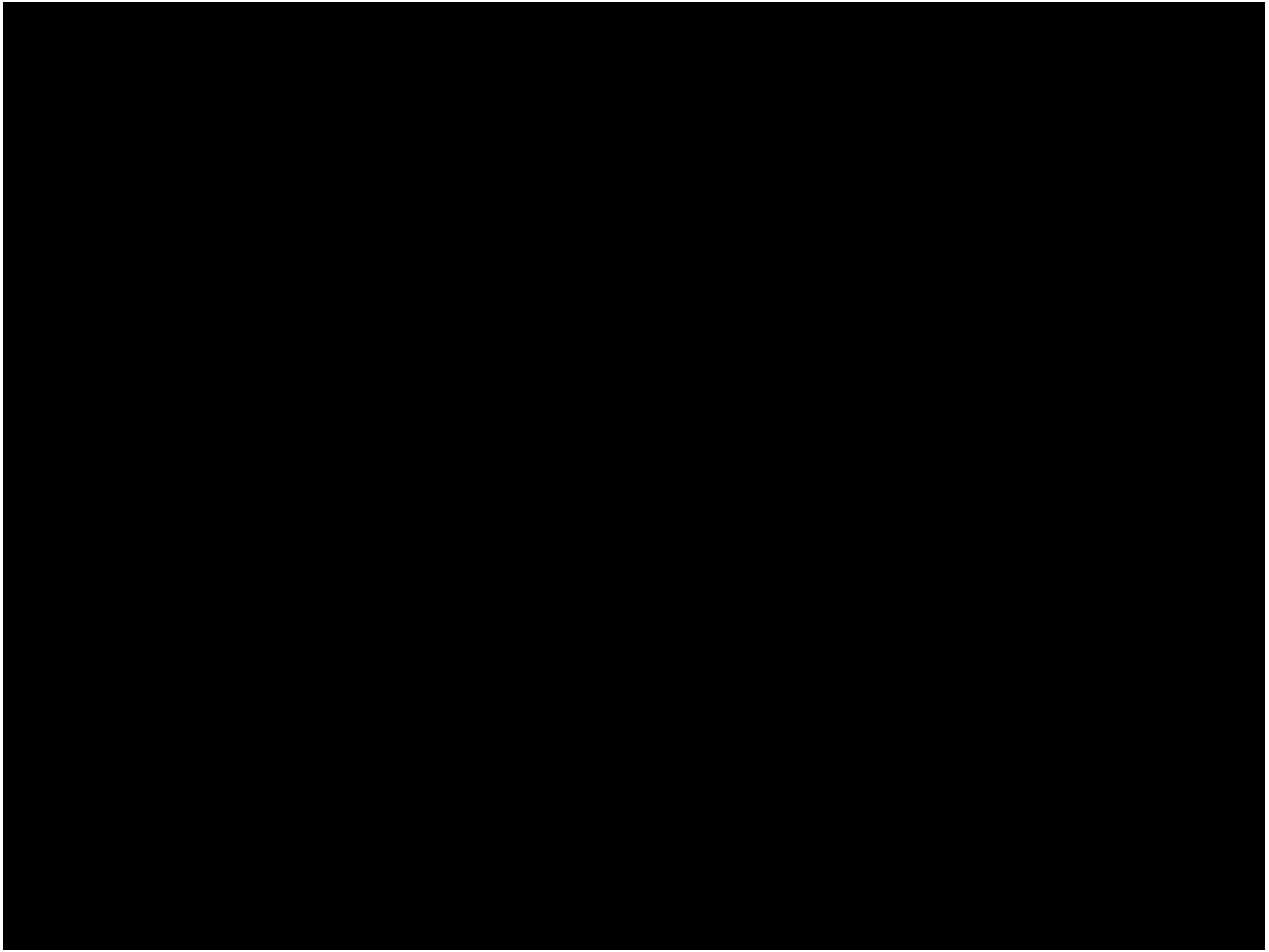
Atmosphere: N_2, Ar
Flow-through system
Flow upwards/downwards (influence on temperature gradient)

Pulling speed: 0.01-1.5 mm/min

Monitoring with a CCD camera through hole in the shielding and afterheater

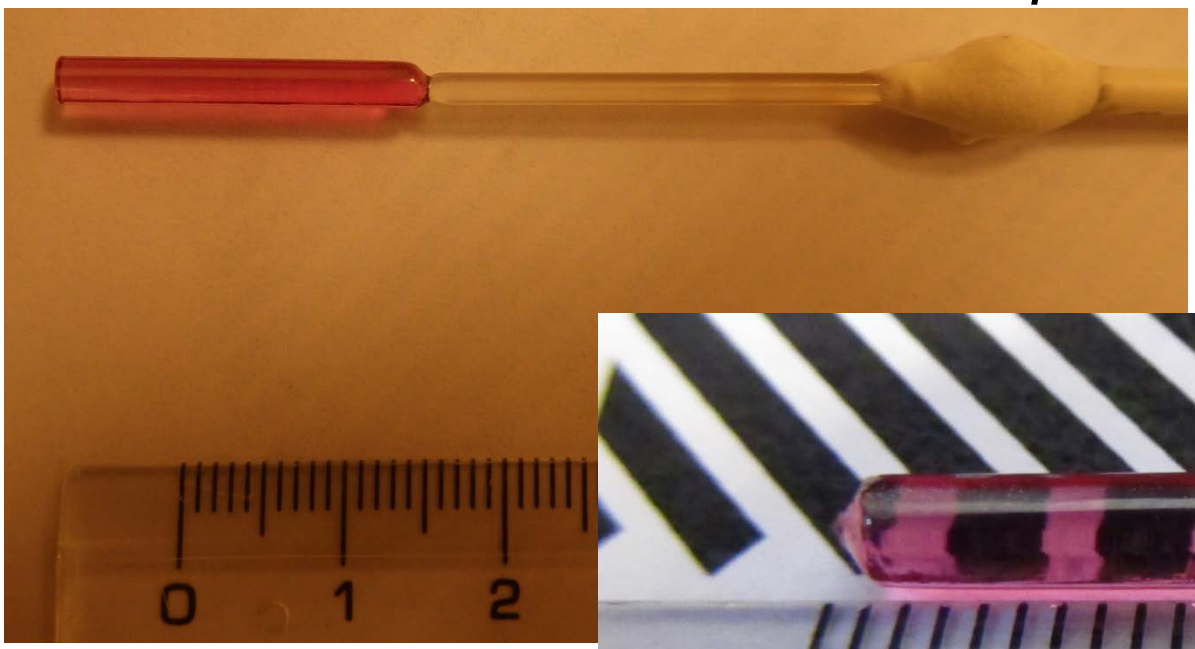
Crystal growth by mPD setup – Al_2O_3:Cr0.1%

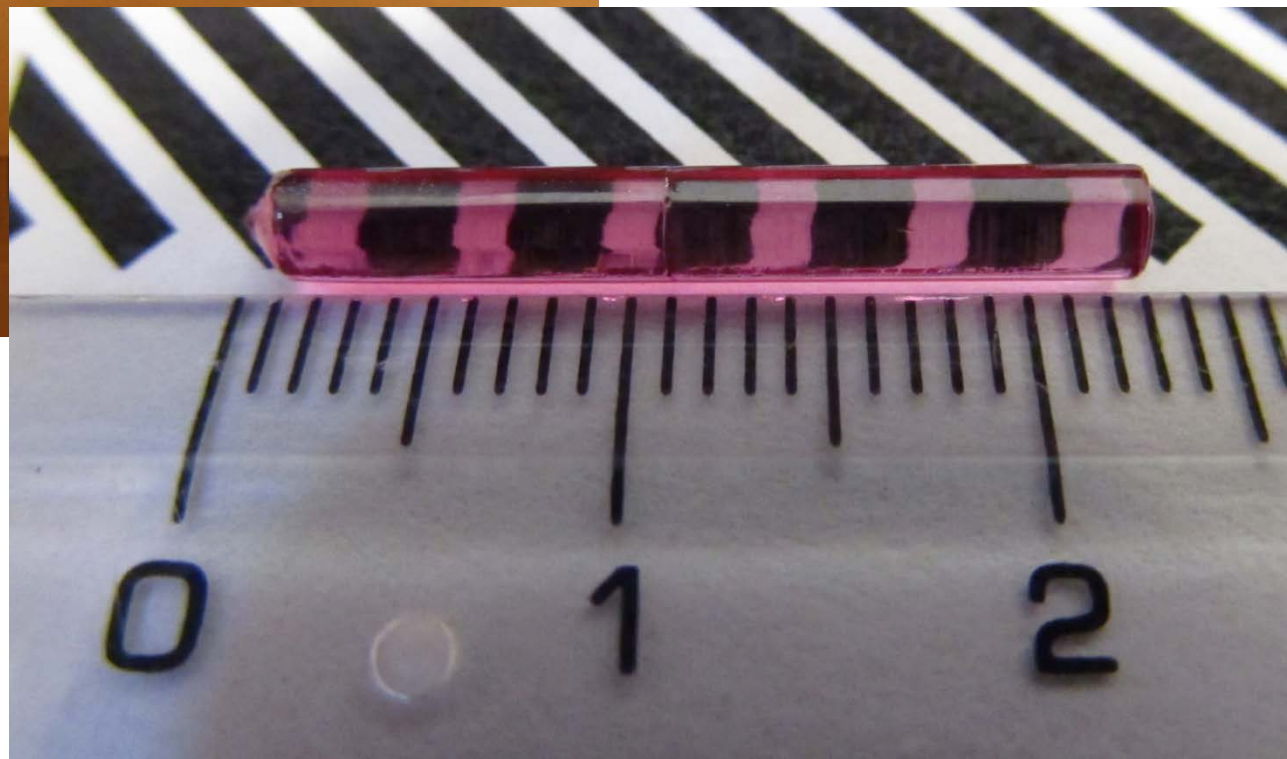
Monitoring by a CCD camera



Crystal growth by mPD setup

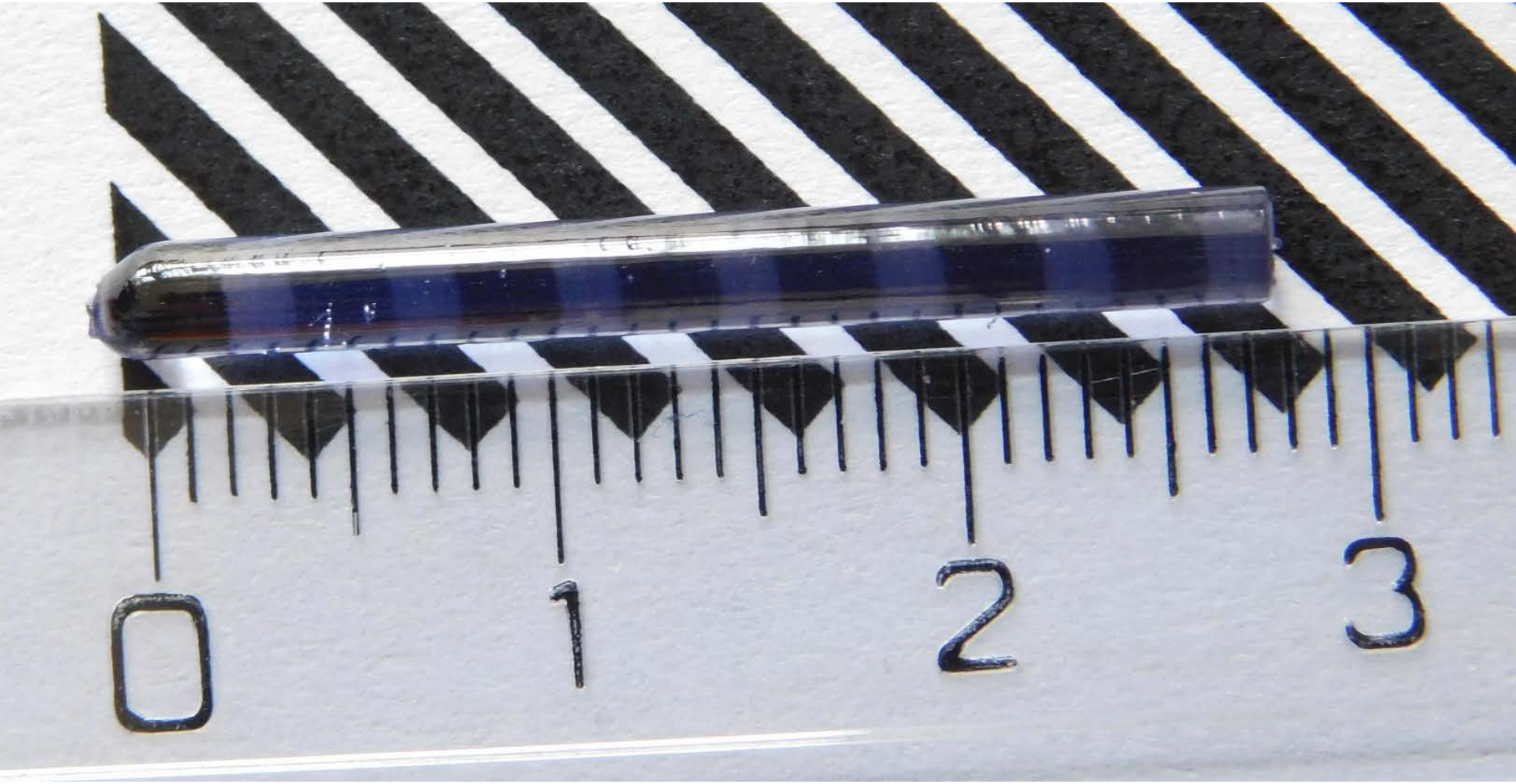
Grown crystals (Al_2O_3:Cr0.1%)
Growth time: 2.5 hours
Total experimental time: cca 7h
Rapid composition screening





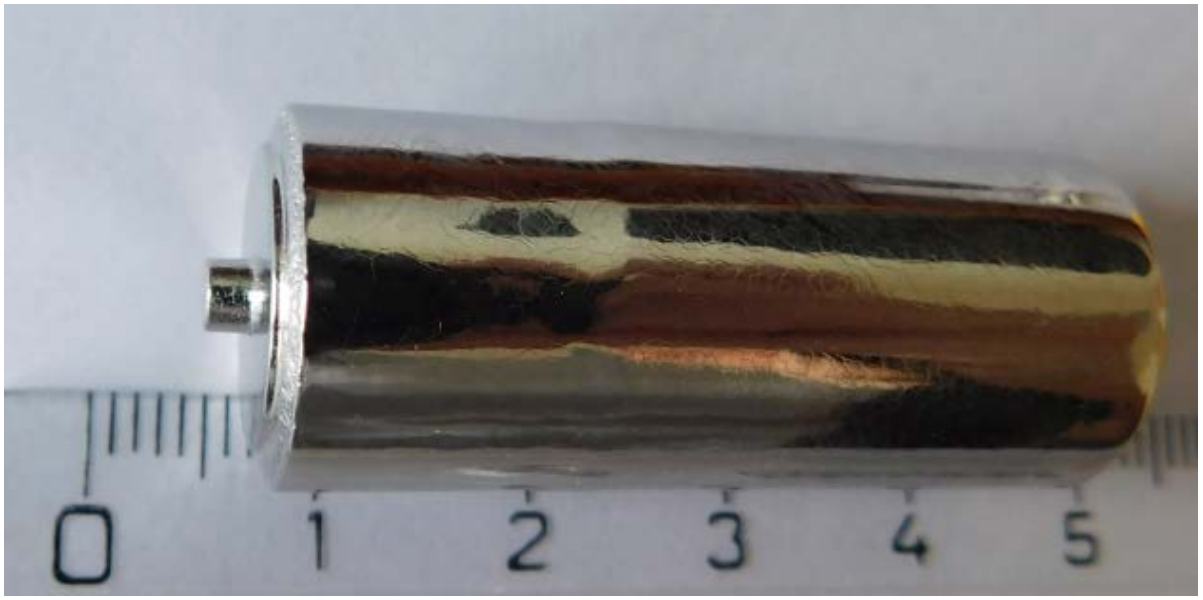
Crystal growth by mPD setup

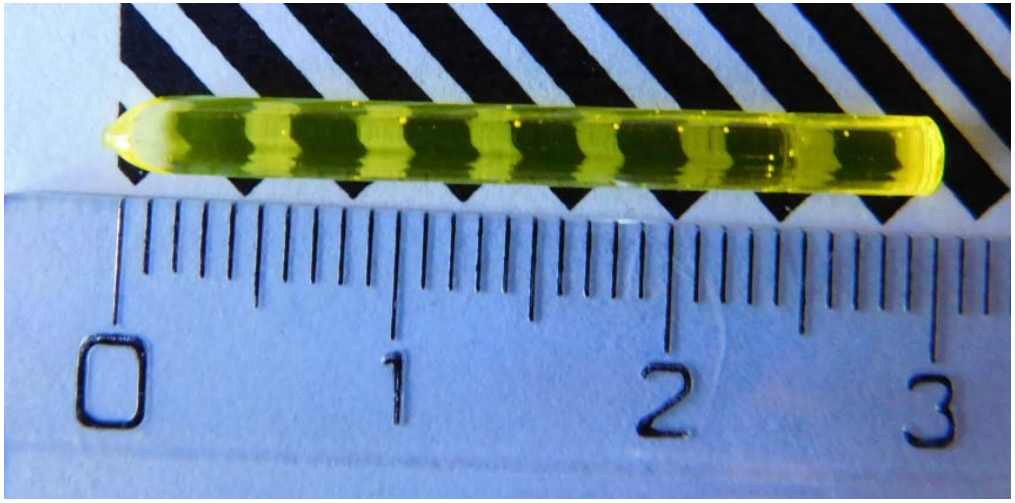
Grown crystals
(Al_2O_3:Fe0.1%Ti0.1%)
Blue sapphire



Crystal growth by mPD setup

Iridium crucible with 3 mm die, 1 capillary

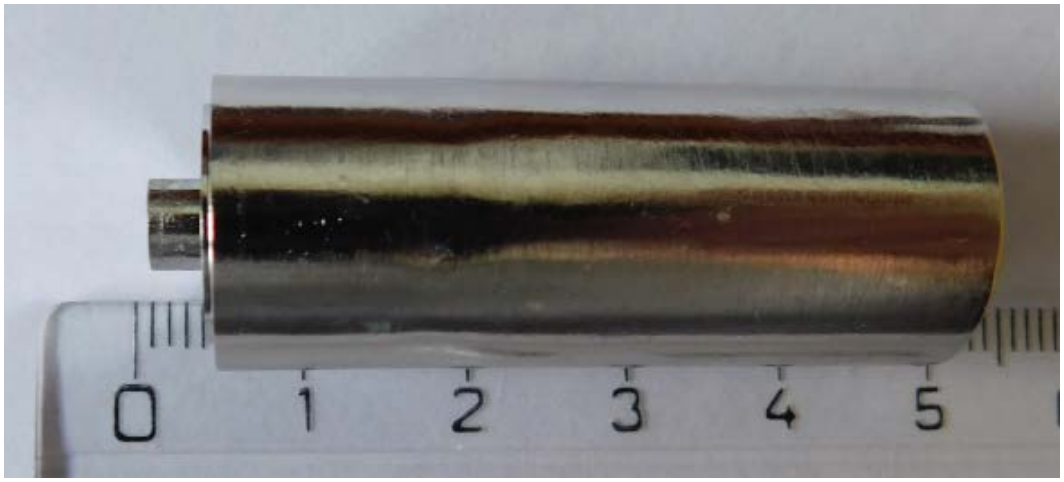


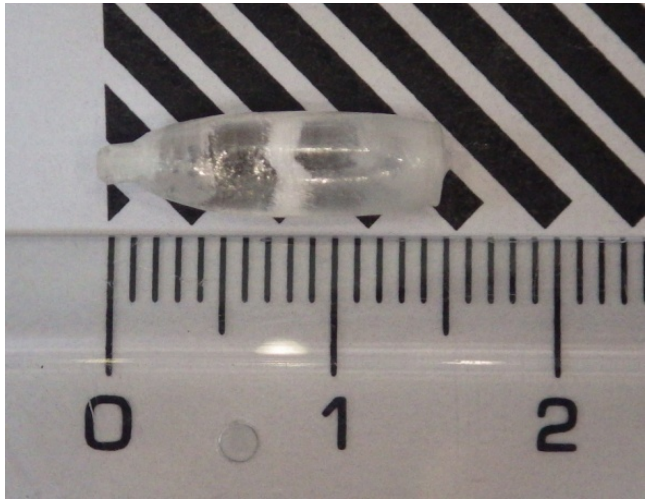


Grown crystal of YAG:Ce

Crystal growth by mPD setup

Iridium crucible with 5 mm die, 5 capillaries

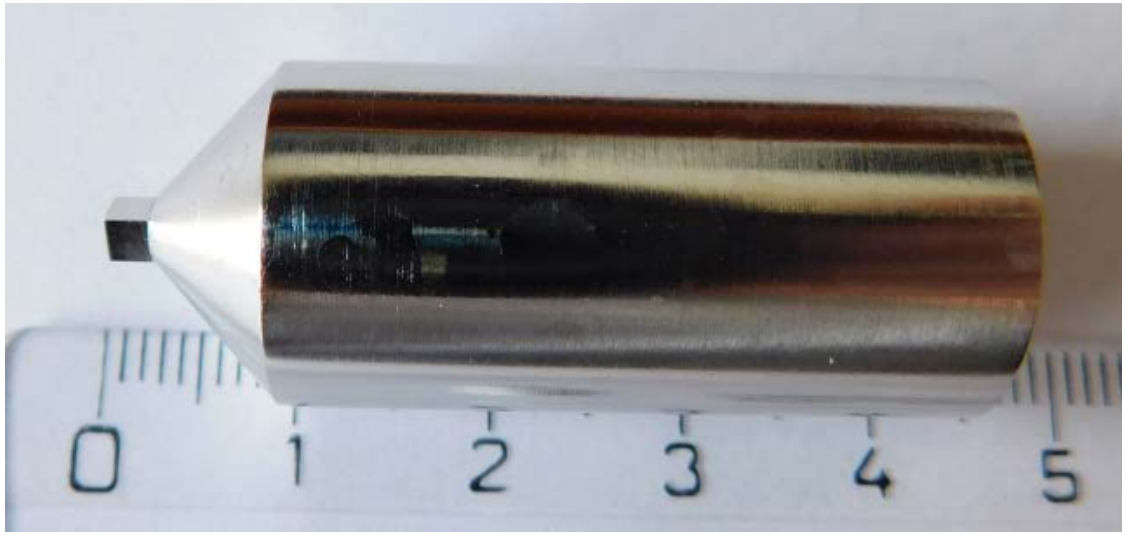


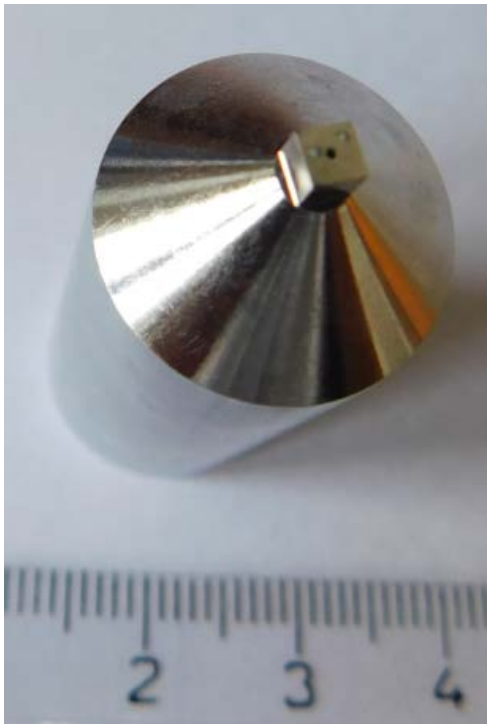


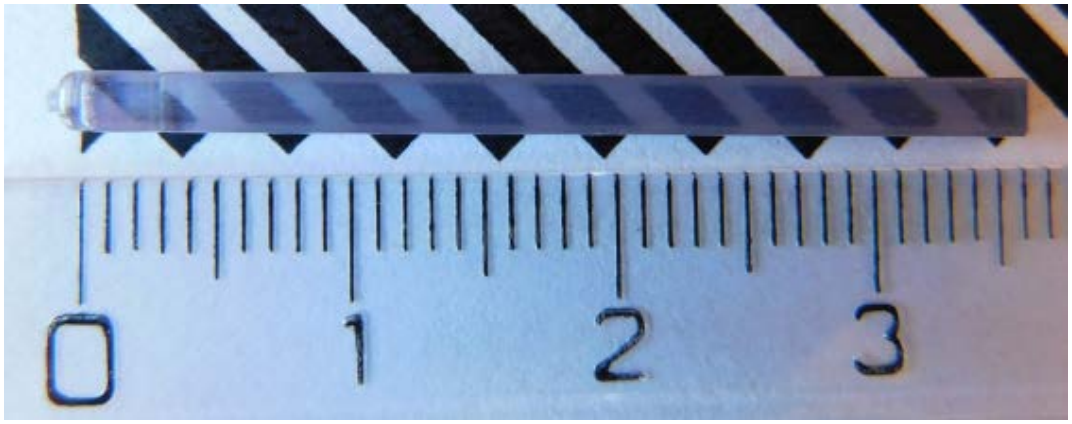
Grown crystal of undoped YAP

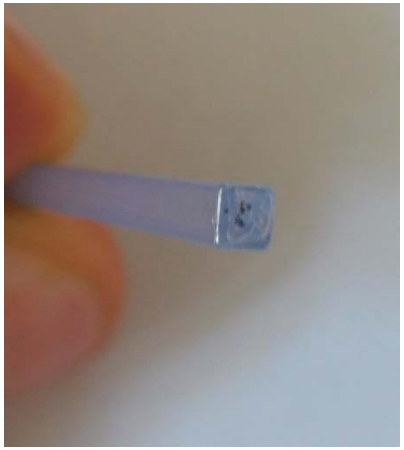
Crystal growth by mPD setup

Iridium crucible with 2x2 mm square die, 1 capillary



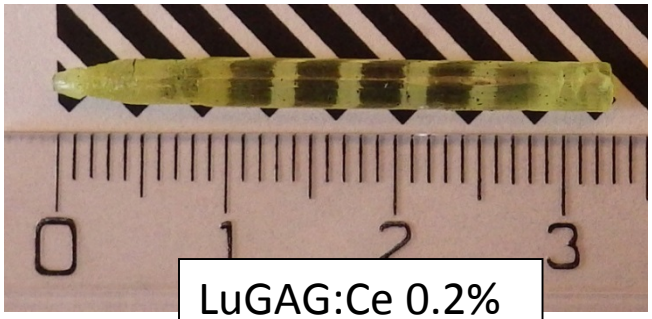




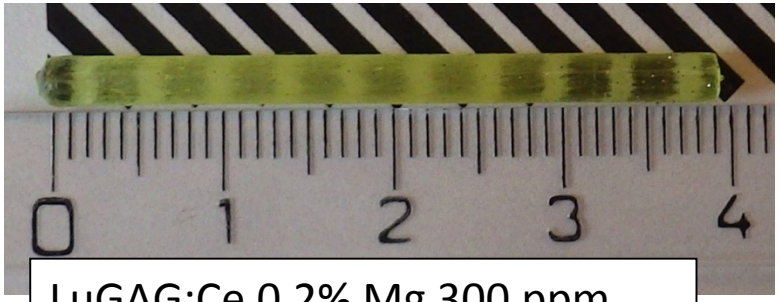


Grown shaped crystal of Al_2O_3:Ti0.1%

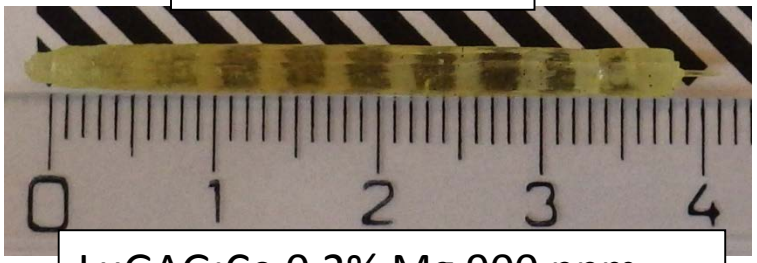
$Lu_3Ga_3Al_2O_{12}$ (LuGAG) - Grown crystals



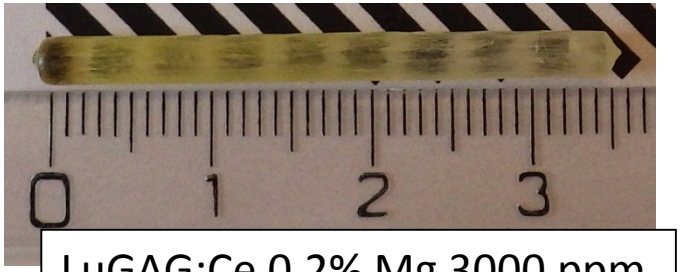
LuGAG:Ce 0.2%



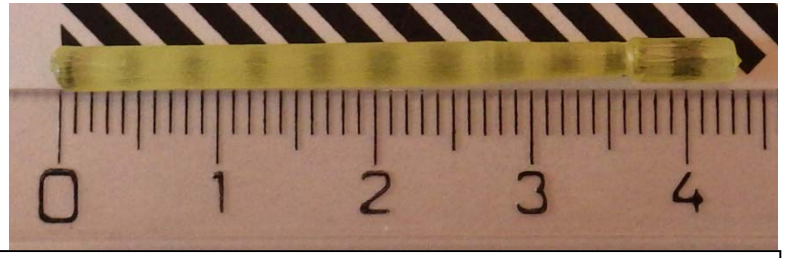
LuGAG:Ce 0.2% Mg 300 ppm



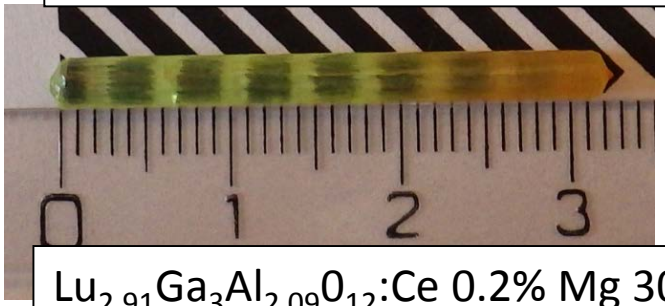
LuGAG:Ce 0.2% Mg 900 ppm



LuGAG:Ce 0.2% Mg 3000 ppm



$Lu_{2.97}Ga_3Al_{2.03}0_{12}$:Ce 0.2% Mg 300 ppm



$Lu_{2.91}Ga_3Al_{2.09}0_{12}$:Ce 0.2% Mg 300 ppm

Atmosphere: Ar+O_2, flow 0.5l/min, **Pulling speed**: 0.07-1 mm/min, **Ir crucible, LuAG <100> seed**

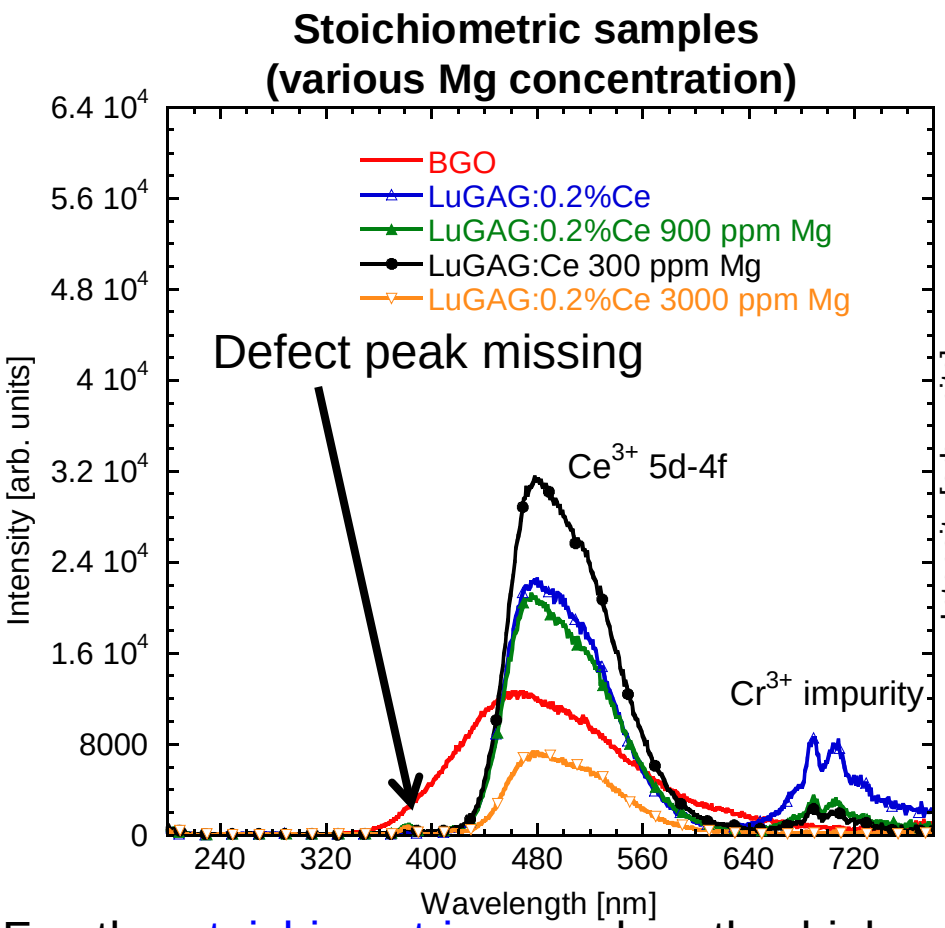
O_2 introduced to suppress Ga evaporation

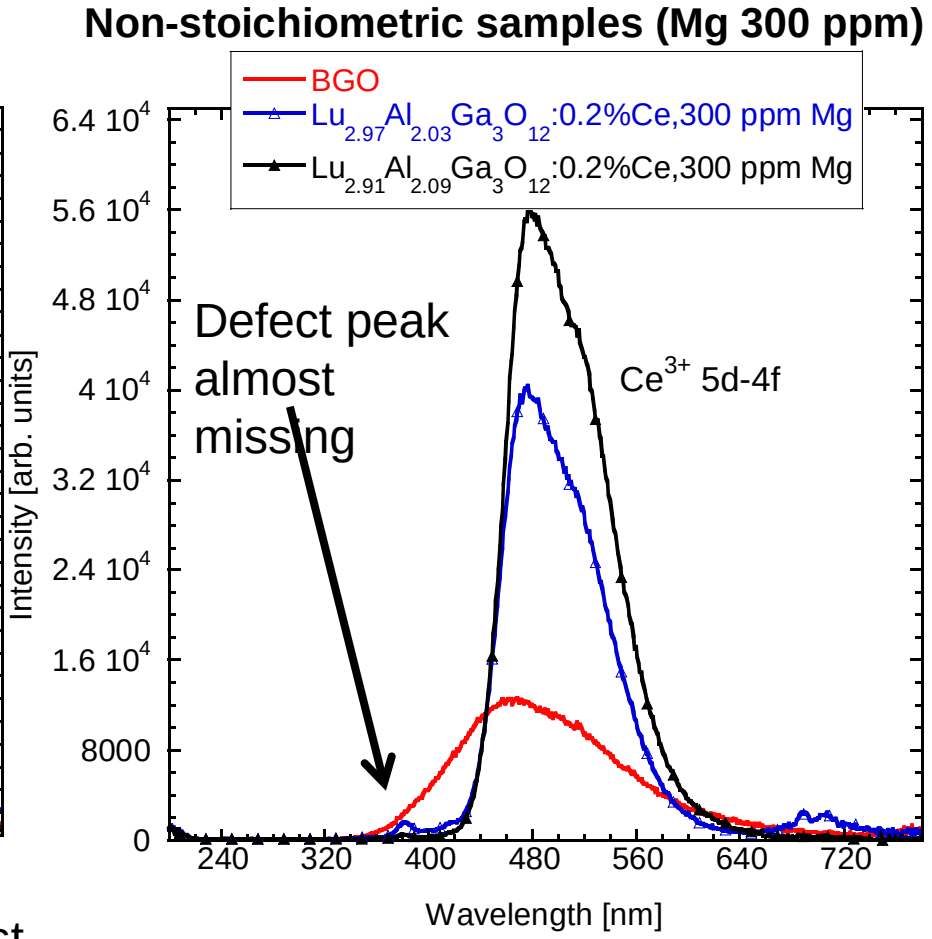
Excess of Ga_2O_3 added to the starting powder mixture to compensate for the Ga evaporation

XRD showed 2-3 different garnet phases of very close compositions.

No annealing performed yet

Radioluminescence(RL) of LuGAG:Ce, Mg (X-ray excitation)





For the stoichiometric samples, the highest intensity is for the Mg 300 ppm. Higher Mg concentration leads to intensity decrease – unlike for the Ga-free counterparts

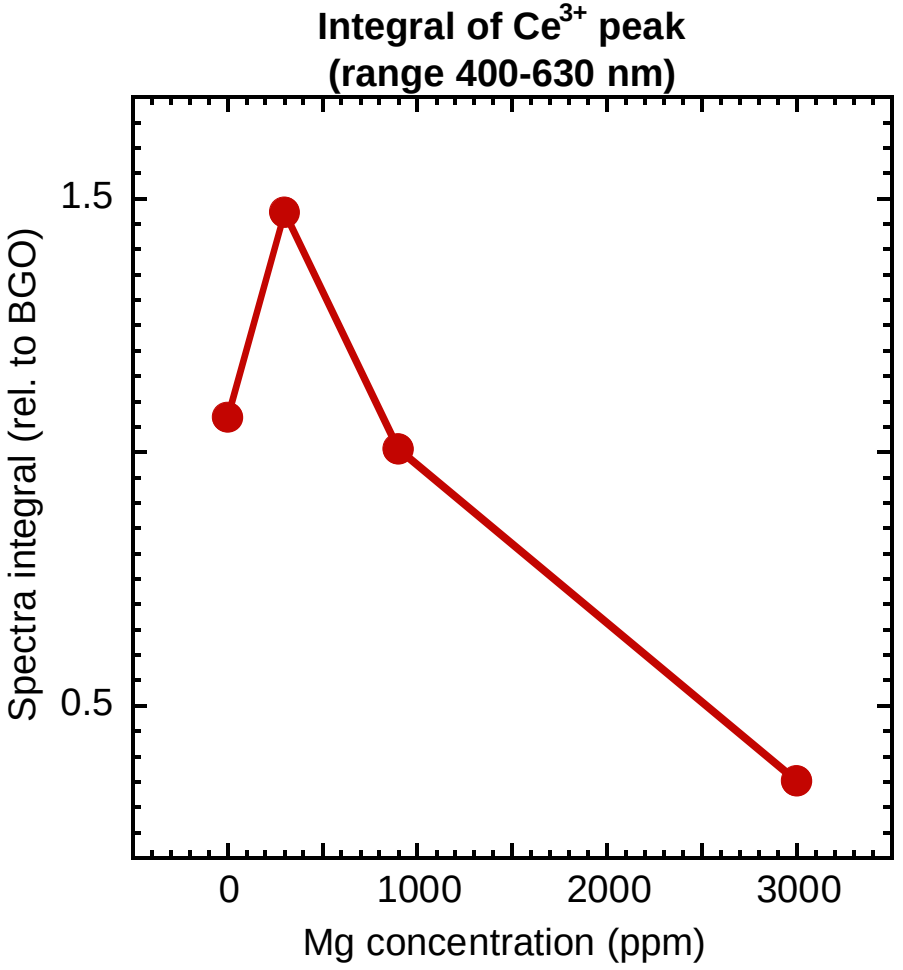
Defect peak completely suppressed!

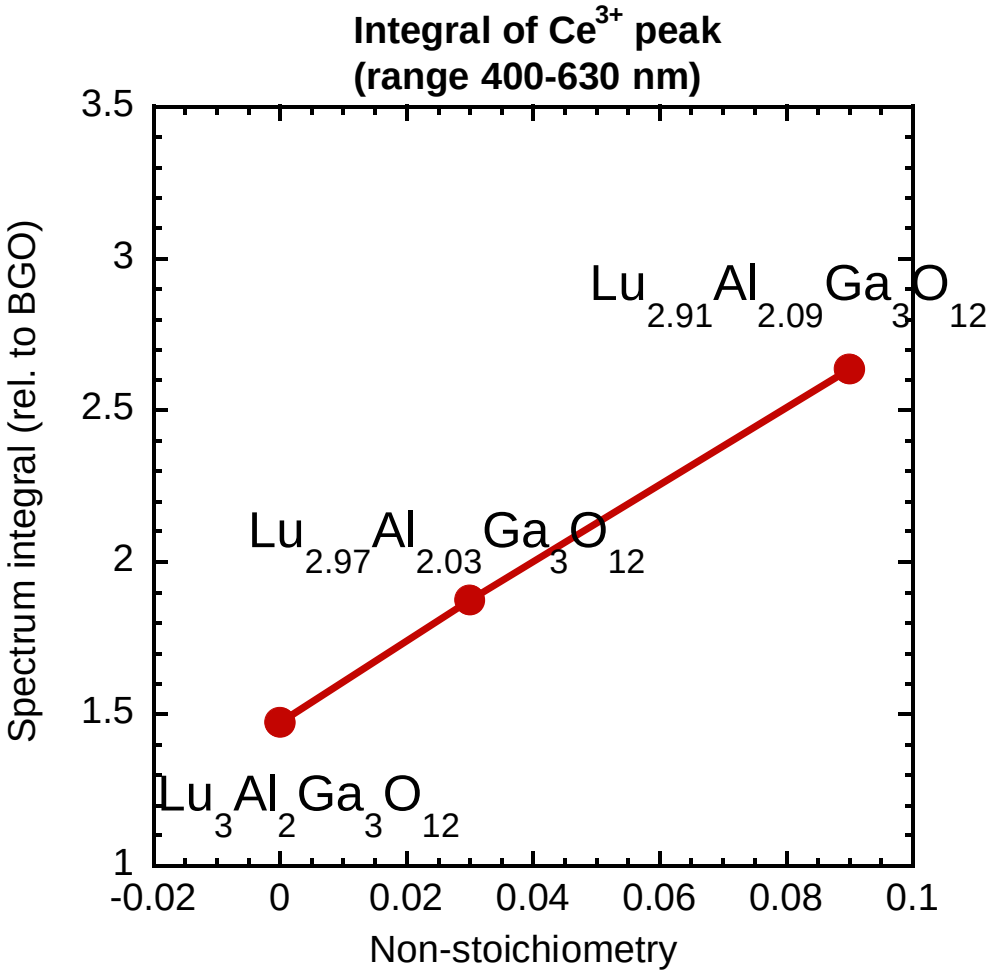
Shift of the emission to shorter wavelength!

Non-stoichiometry again significantly increases the radioluminescence intensity when compared to the stoichiometric samples.

Negligible defect emission observed – caused by the non-stoichiometry?

Radioluminescence of LuGAG:Ce, Mg (general trends)





Stoichiometric samples:

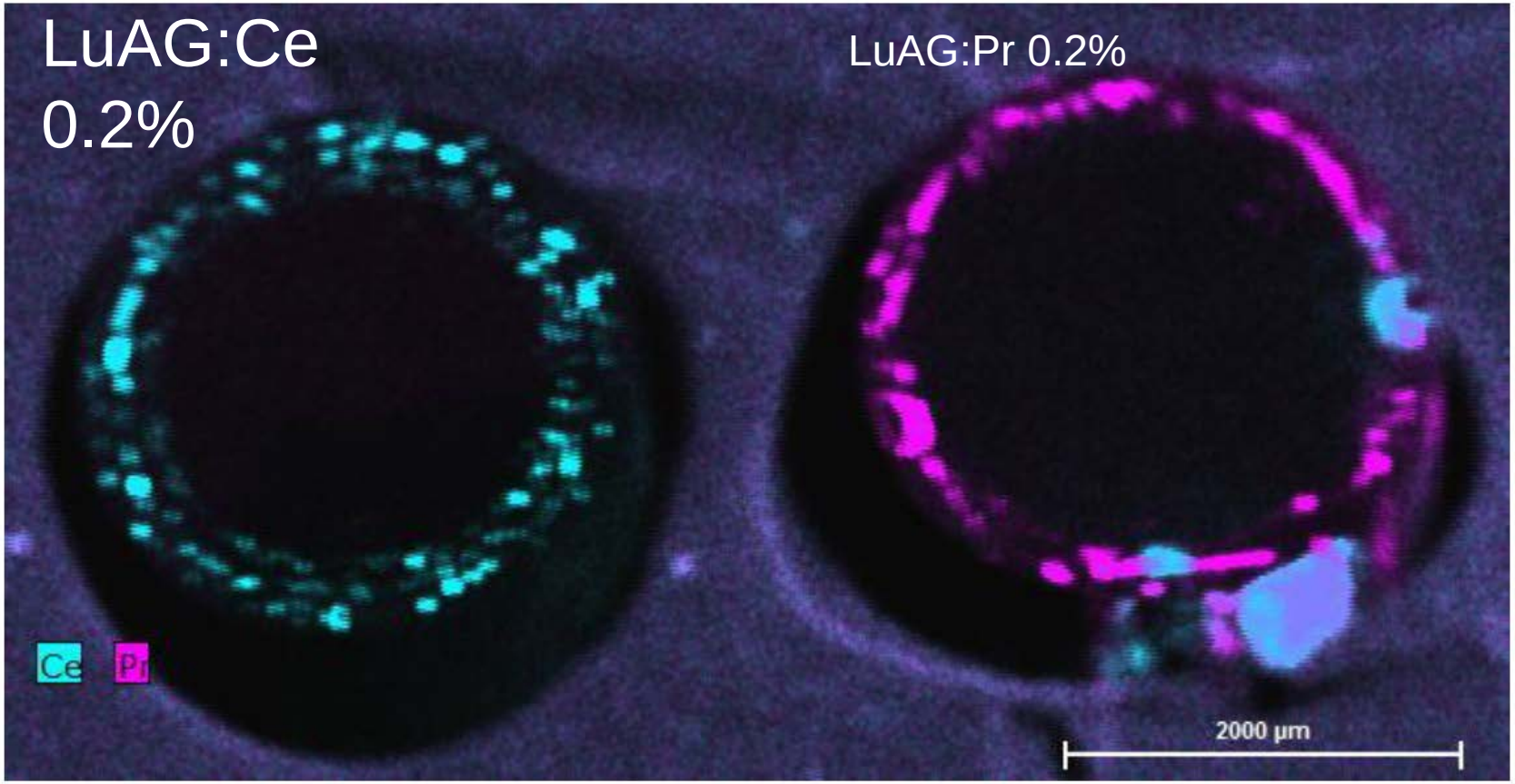
300 ppm Mg – positive effect

Increased Mg concentration leads to decrease of radioluminescence intensity

Non-stoichiometric samples (Mg 300 ppm):

Increased non-stoichiometry leads to significant increase of radioluminescence intensity

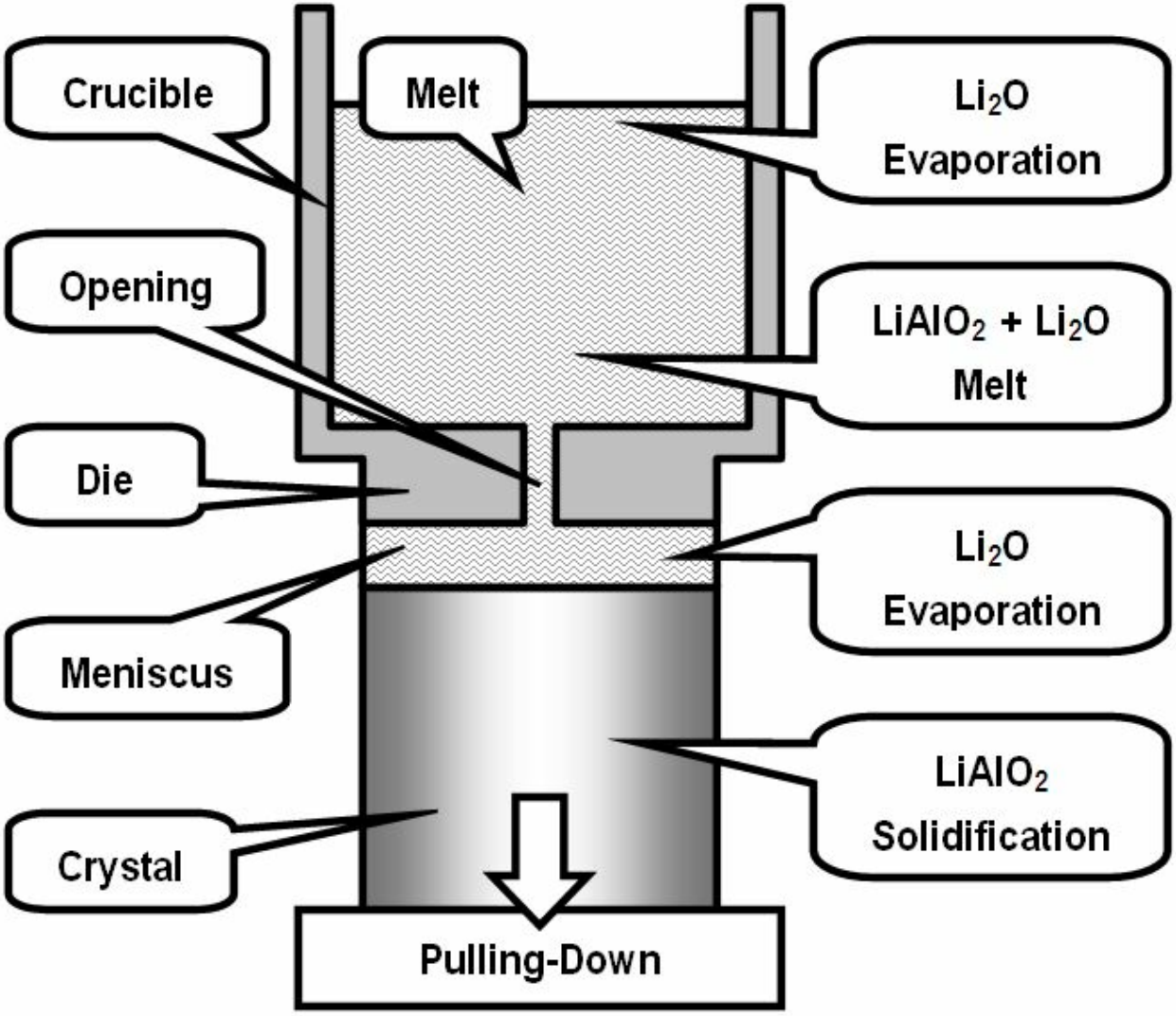
µXRF (micro X-ray fluorescence)



Segregation of Ce (Pr) dopants – rejected to the surface
Similar was observed for LuGAG

Micro-pulling-down method Li-containing oxide crystals

Processes in the crystal growth of $LiAlO_2$



Li_2O excess (6mol%)

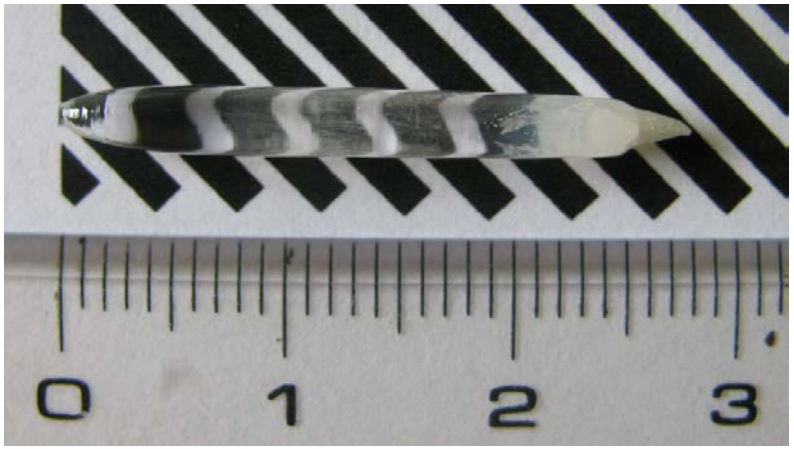
Flux-like growth

Evaporation and crystallization rates kept constant

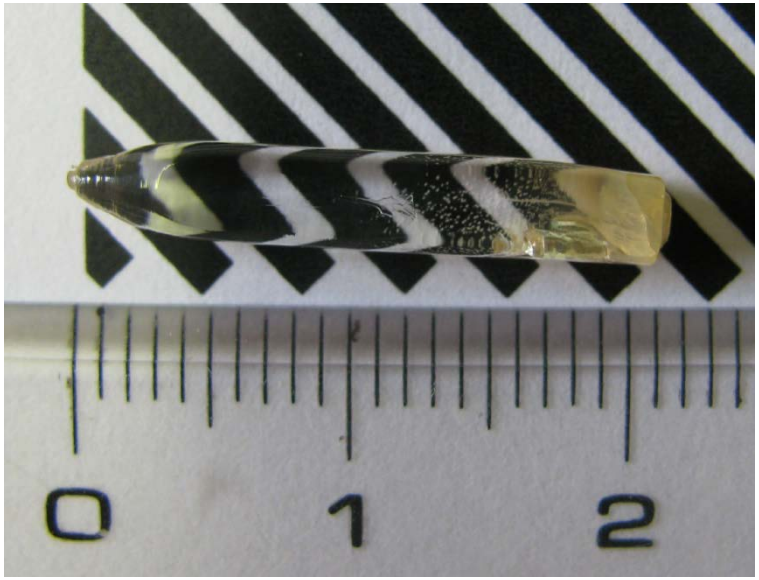
Stable growth (melt composition as well)

$LiAlO_2(melt)/Li_2O(melt) =$
$=LiAlO_2(crystal)/Li_2O(evaporation)=constant$

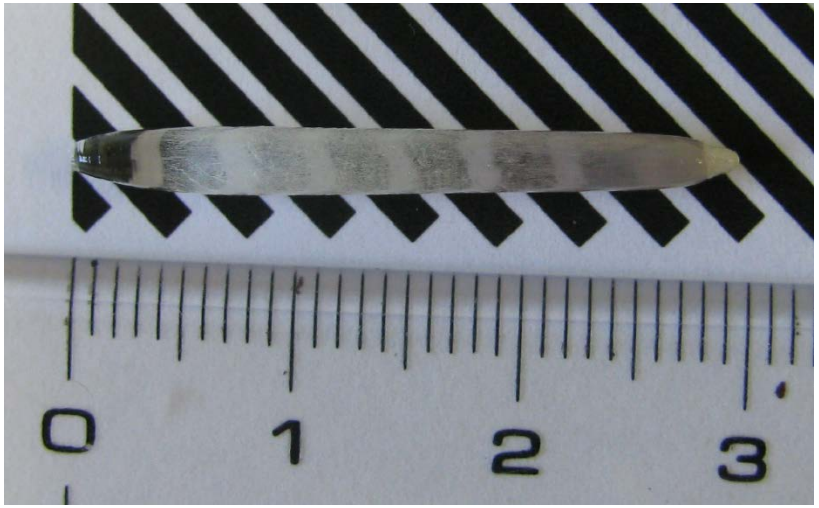
$LiAlO_2$ grown crystals



$LiAlO_2$:Ti0.1%,Mg0.1%



$LiAlO_2$:Fe0.1%
Shaped crystal

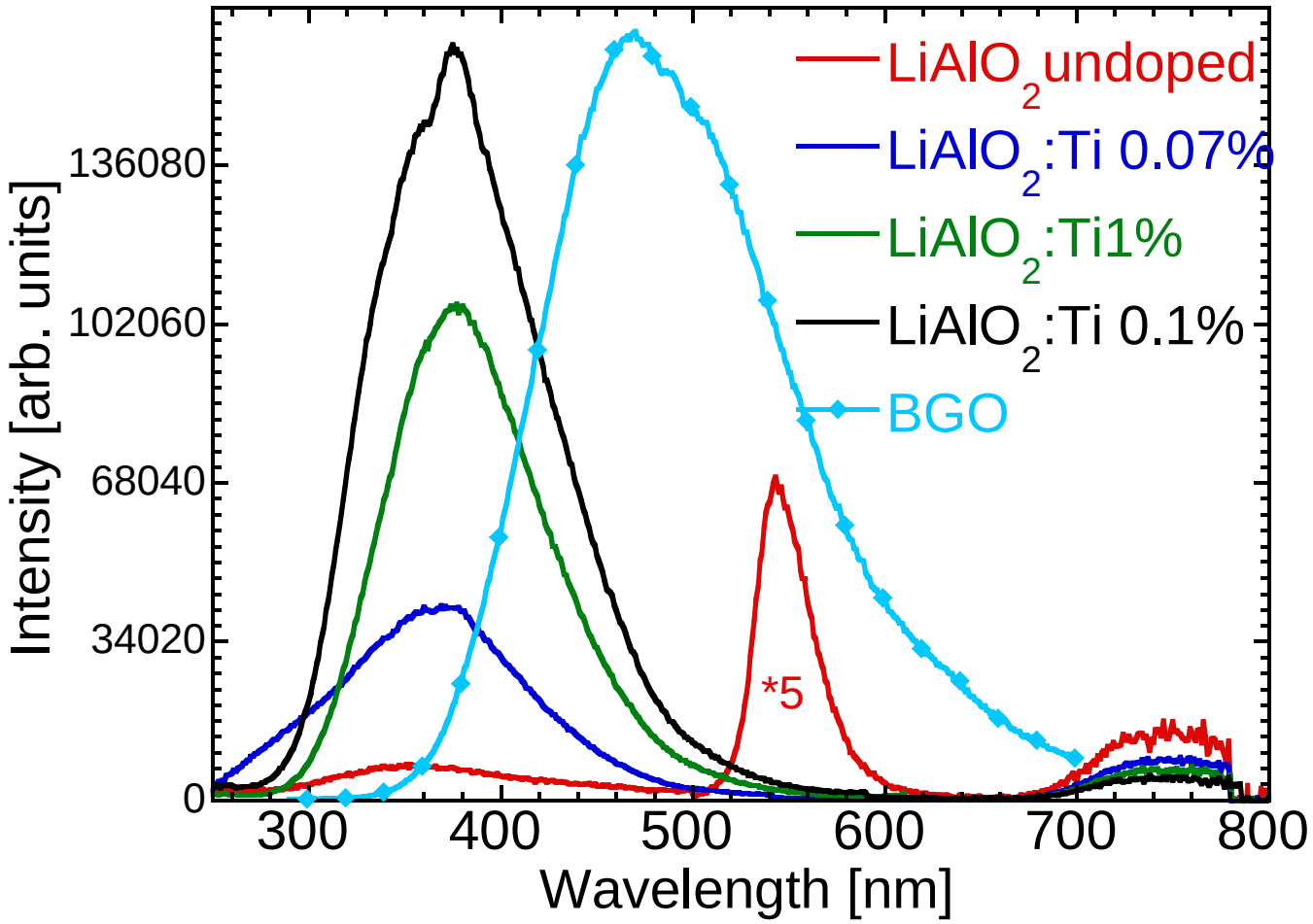


$LiAlO_2$:Ti0.1%

XRD analysis confirmed the $LiAlO_2$ tetragonal γ-phase

$LiAl_5O_8$ or Li_5AlO_4 phases confirmed at the very end of some crystals

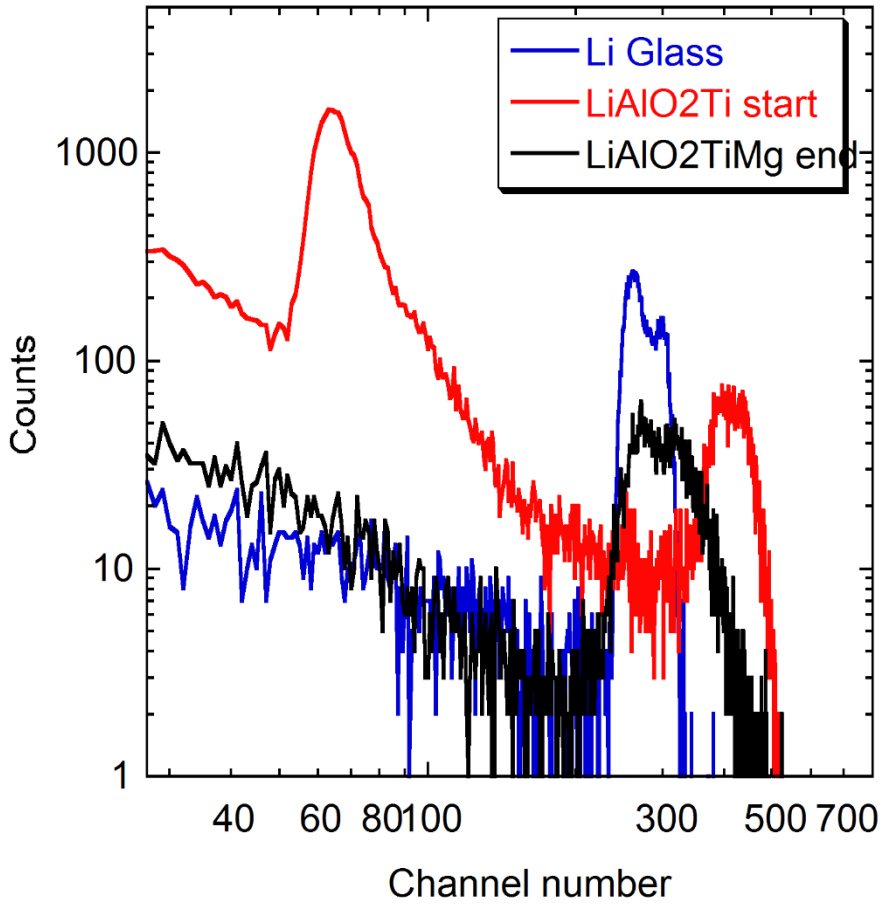
Radioluminescence measurements



Spectra comparable in absolute scale, overall scintillation efficiency of $LiAlO_2$:Ti 0.1% is **100%BGO!!**

Undoped sample – host related emission (present also in the Ti-doped sample)

Neutron response (^{252}Cf)

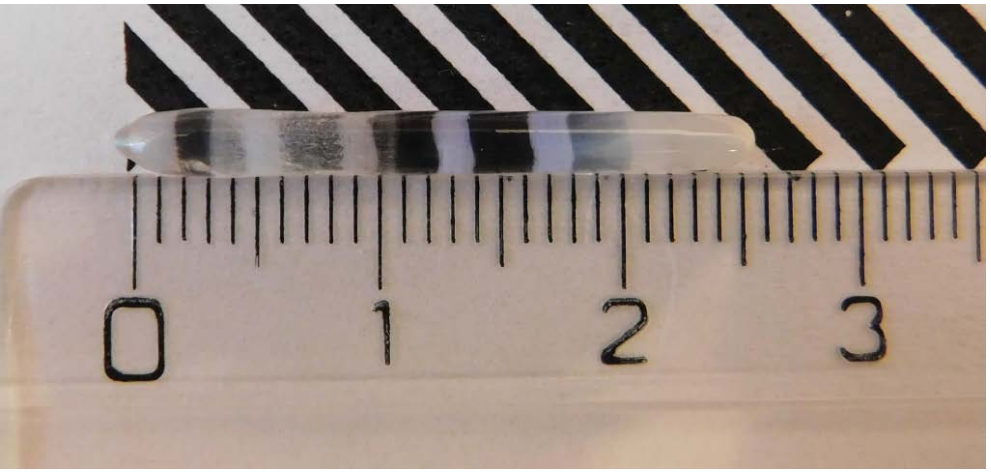


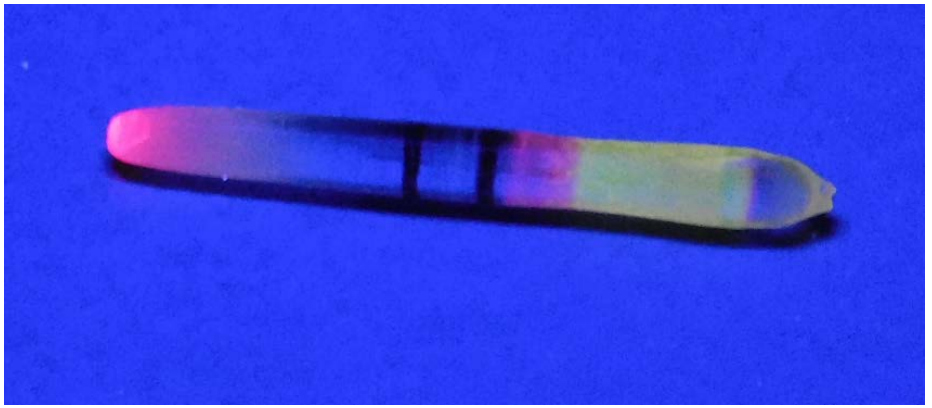
^{252}Cf neutron source used

Data corrected for shaping amplifier gain and photomultiplier spectral sensitivity
Shaping time 10us

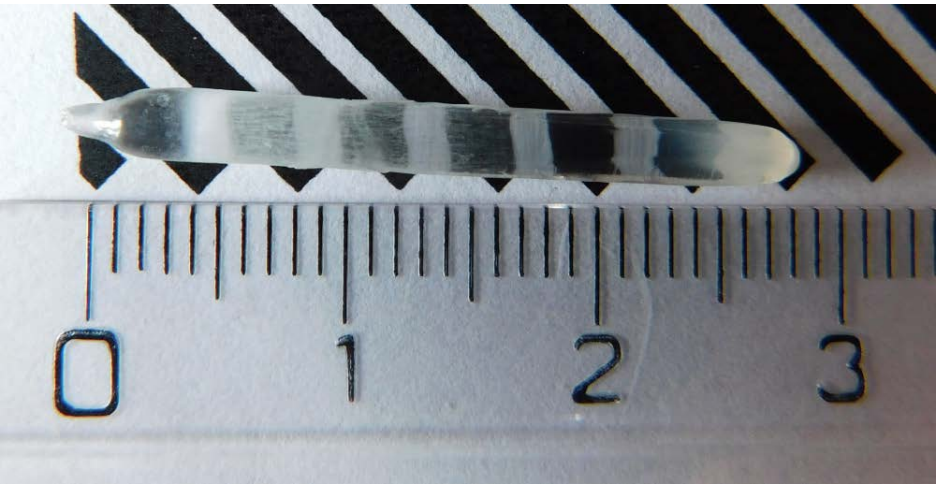
The neutron light yield exceeds that of GS20 Li-glass!
(6000 photons/neutron)

$LiAlO_2$- Grown crystals





$LiAlO_2$:Si0.1%



$LiAlO_2$:Sn1%

Atmosphere: Ar, flow 0.5l/min, **Pulling speed**: 0.07-1 mm/min,
Ir crucible, Ir seed

0.5g of starting material, 0.06g of Li_2CO_3 excess to compensate for Li evaporation

XRD showed tetragonal high-temperature γ-modification

$LiAl_5O_8$ Li-poor phase detected at the end of crystal

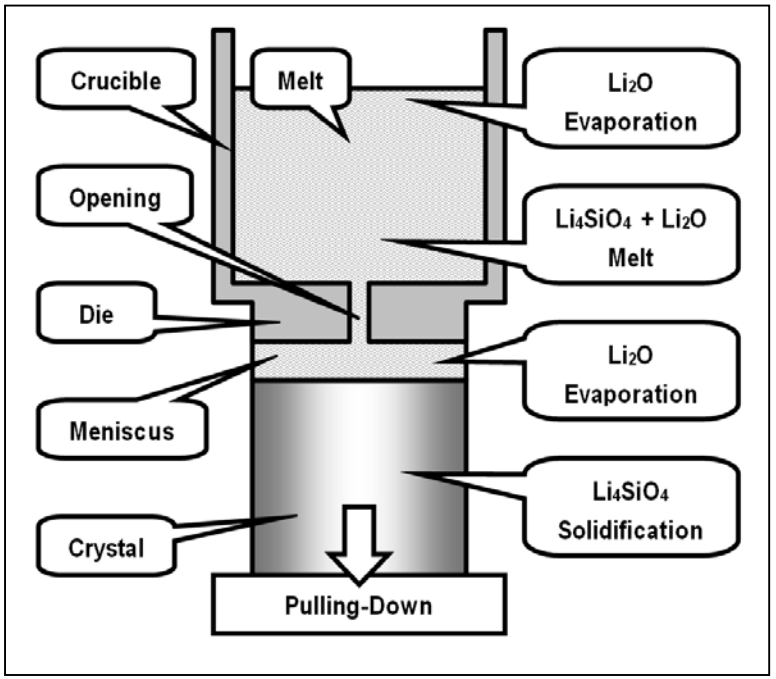
Crystal growth of Li_4SiO_4 by micro-pulling-down method

Flux-like growth

Atmospehere: Ar
Pulling speed: 0.05-0.07 mm/min,
Seed: "spiked" Ir wire

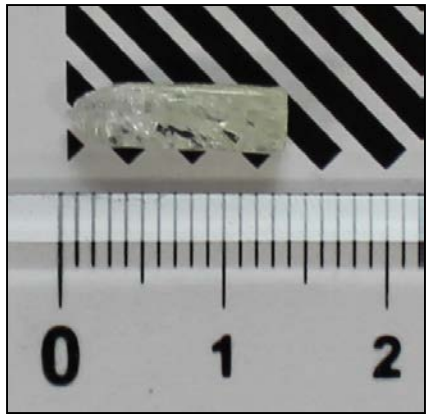
Ir crucible with a die (square or round shape)

Li_2CO_3 excess (5 mol%) added to improve melt properties (wettability) and compensate for Li evaporation



Li_4SiO_4(melt)/Li_2O(melt) = Li_4SiO_4(crystal)/Li_2O(evaporation) = constant

Grown crystal
Many cracks observed



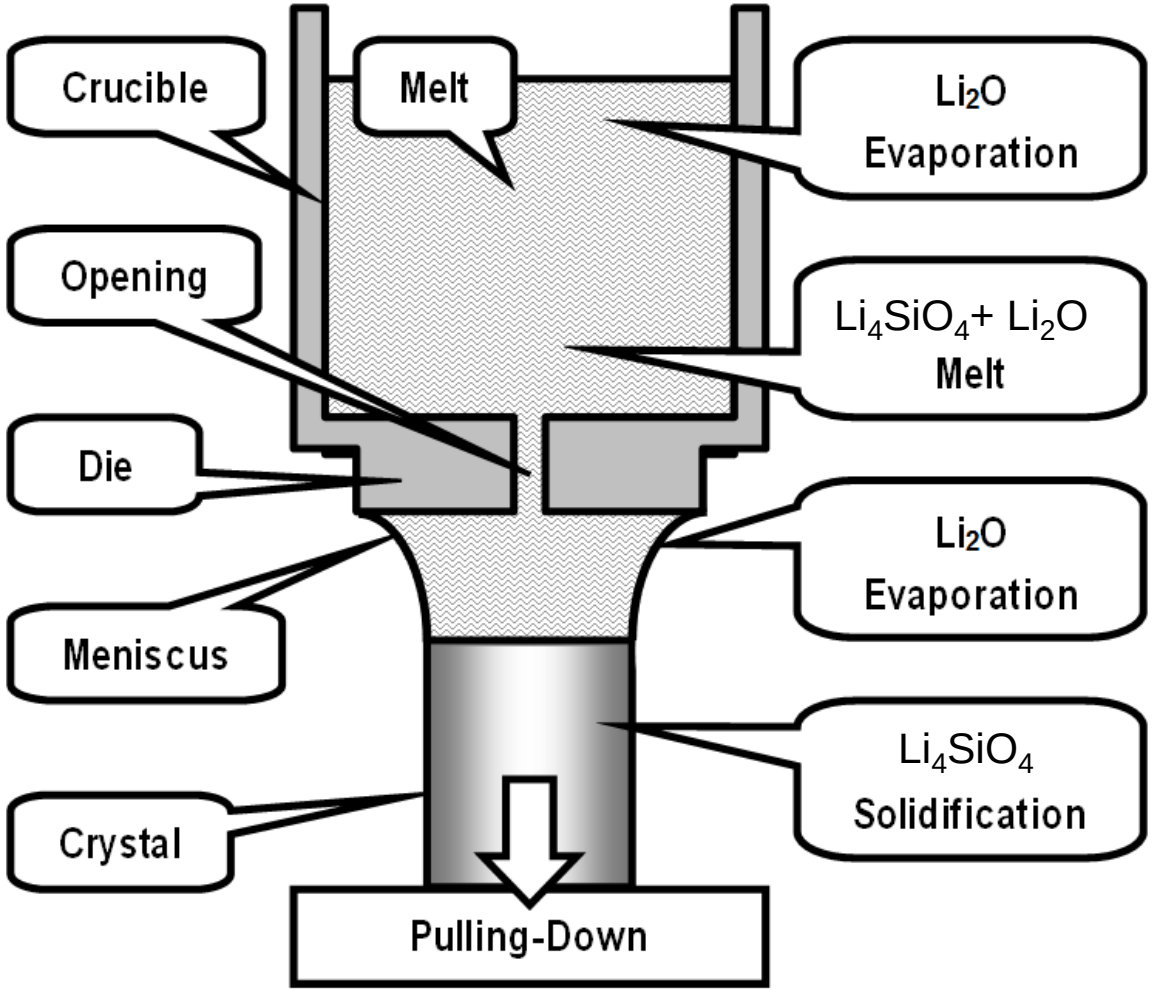
Crystal growth of Li_4SiO_4 by micro-pulling-down method

Optimization of crystal growth conditions:

Increase of the heating power led to increase of meniscus thickness and decrease of crystal diameter.

Increase of mixing and mass exchange at the melt-solid interface

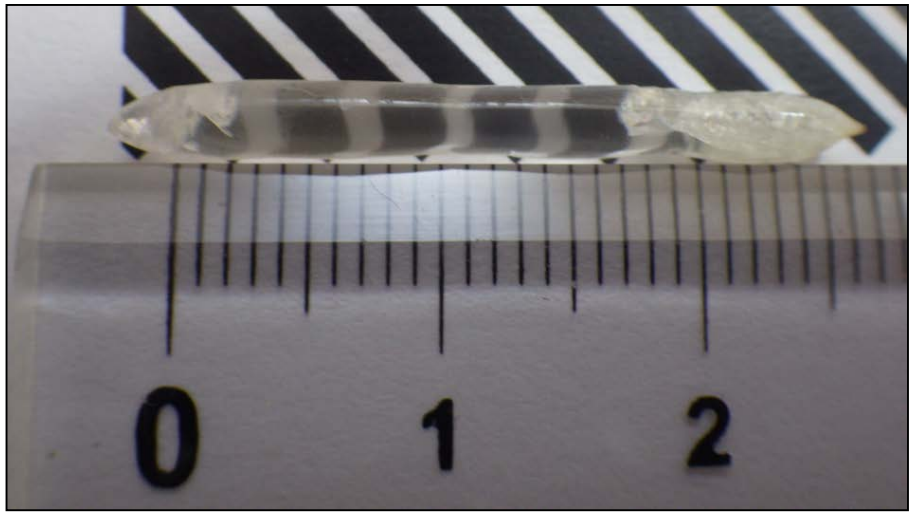
Both the radial and vertical gradient became more shallow and growth of good quality crystals was enabled.



Mass balance of the flux-like crystal growth:

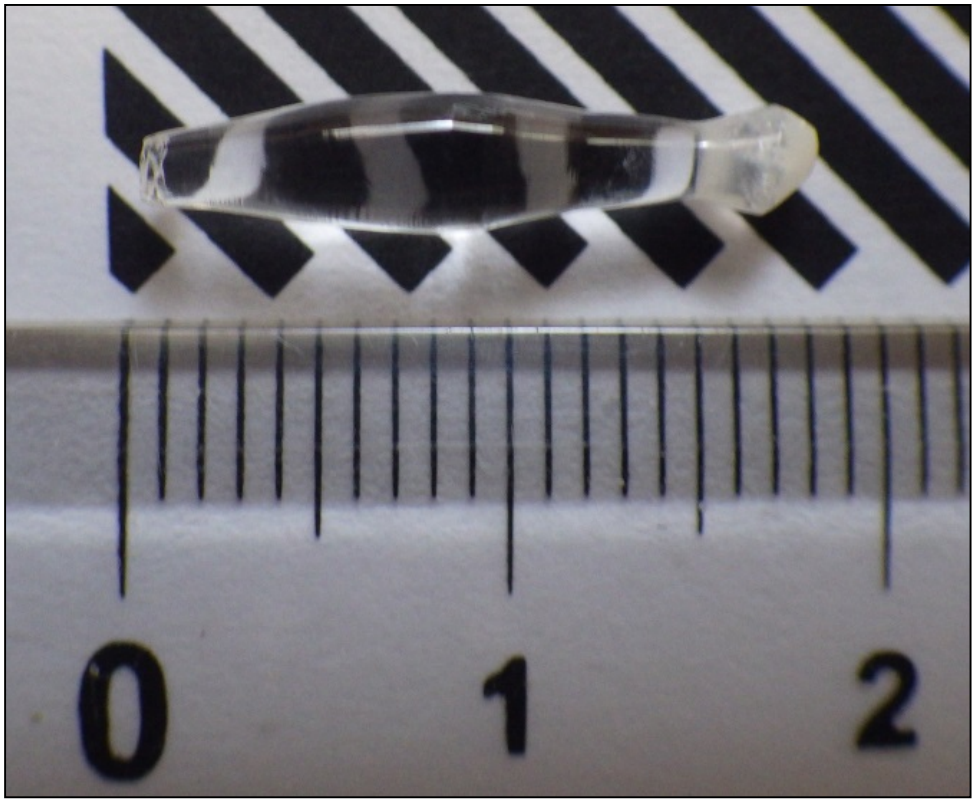
Li_4SiO_4(melt)/Li_2O(melt) = Li_4SiO_4(crystal)/Li_2O(evaporation) = constant

Li_4SiO_4 - grown crystals



Li_4SiO_4 undoped

Reaction with Ir crucible – slightly cracky, brownish color

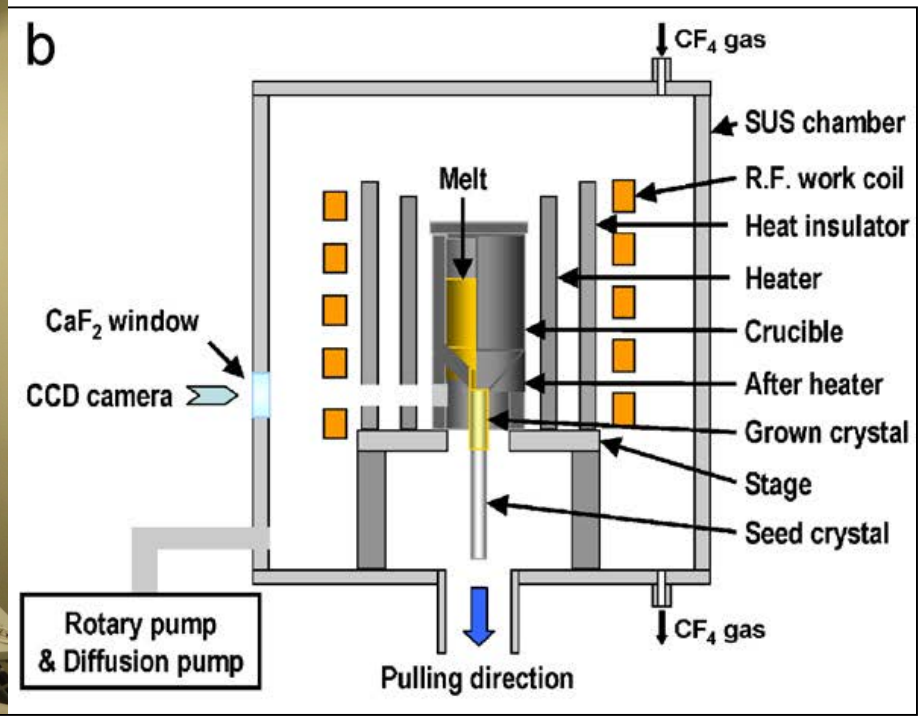


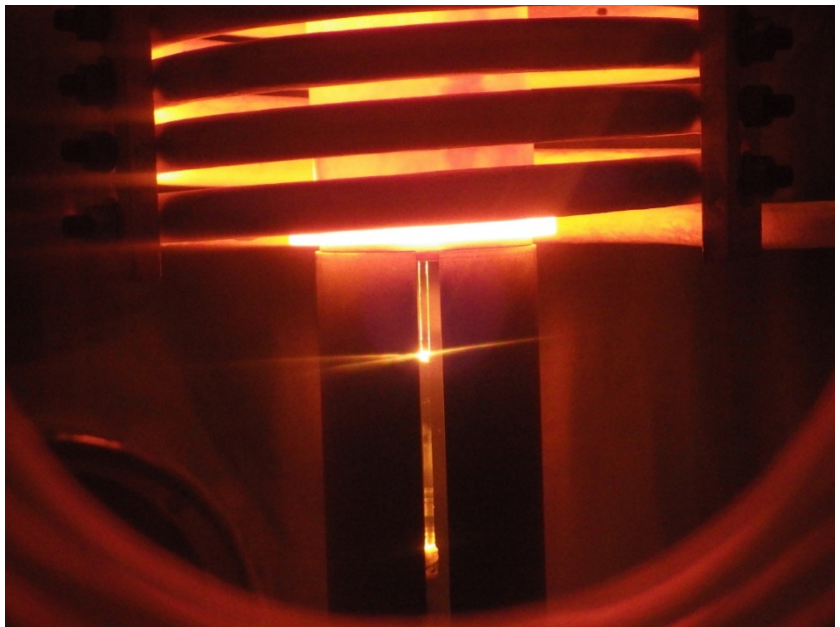
Li_4SiO_4:Ti 0.2%

XRD confirmed Li_4SiO_4 monoclinic phase (PDF#37-1472)

Micro-pulling-down method
Fluoride crystals

Fluoride crystal growth





Growth conditions

Bake out-procedure under high vacuum

Atmosphere:

Ar+10%CF_4 (moisture scavenger!)

Carbon crucible: non-wetting melt

Crystal shape determined by the nozzle shape!

Direct contact of melt and the growing crystal (not separated by a capillary)

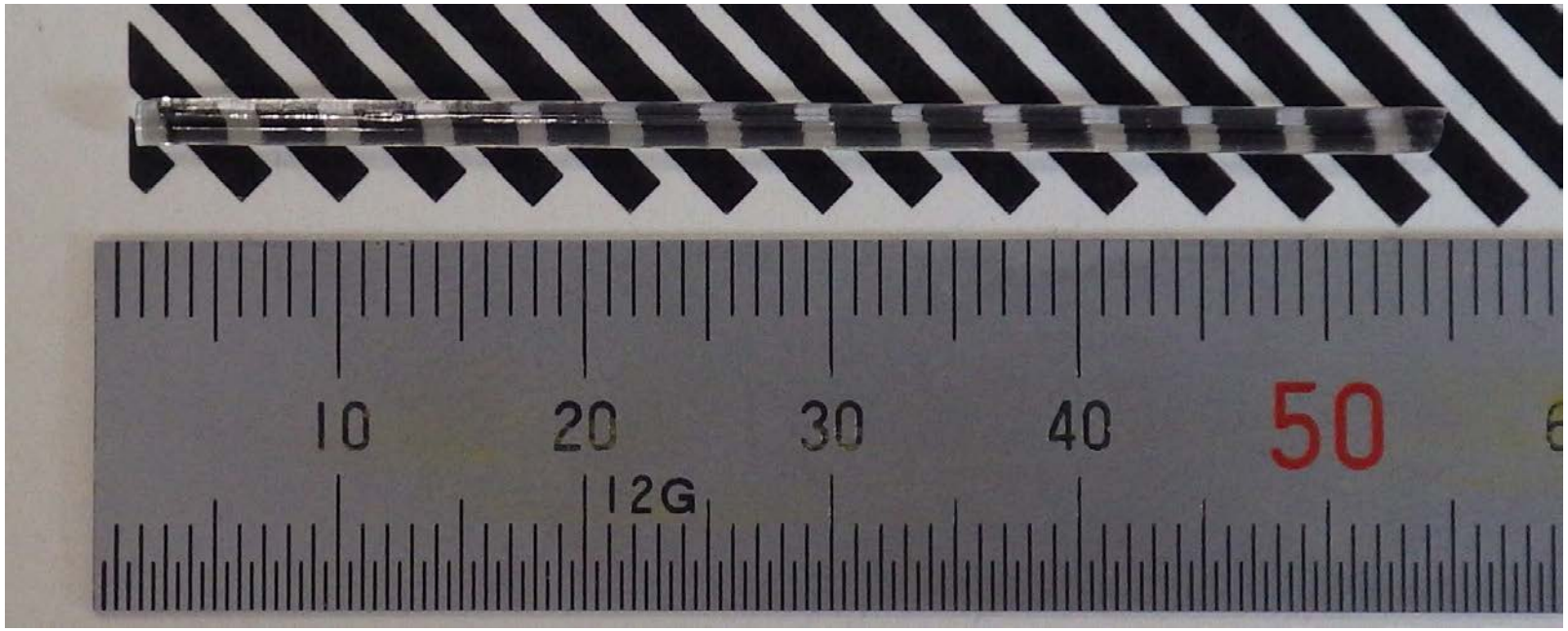
Fluoride micro-pulling-down setup

Carbon crucibles

Micro-pulling-down method for fluorides

Fluoride micro-pulling-down setup

Grown crystal of CaF_2



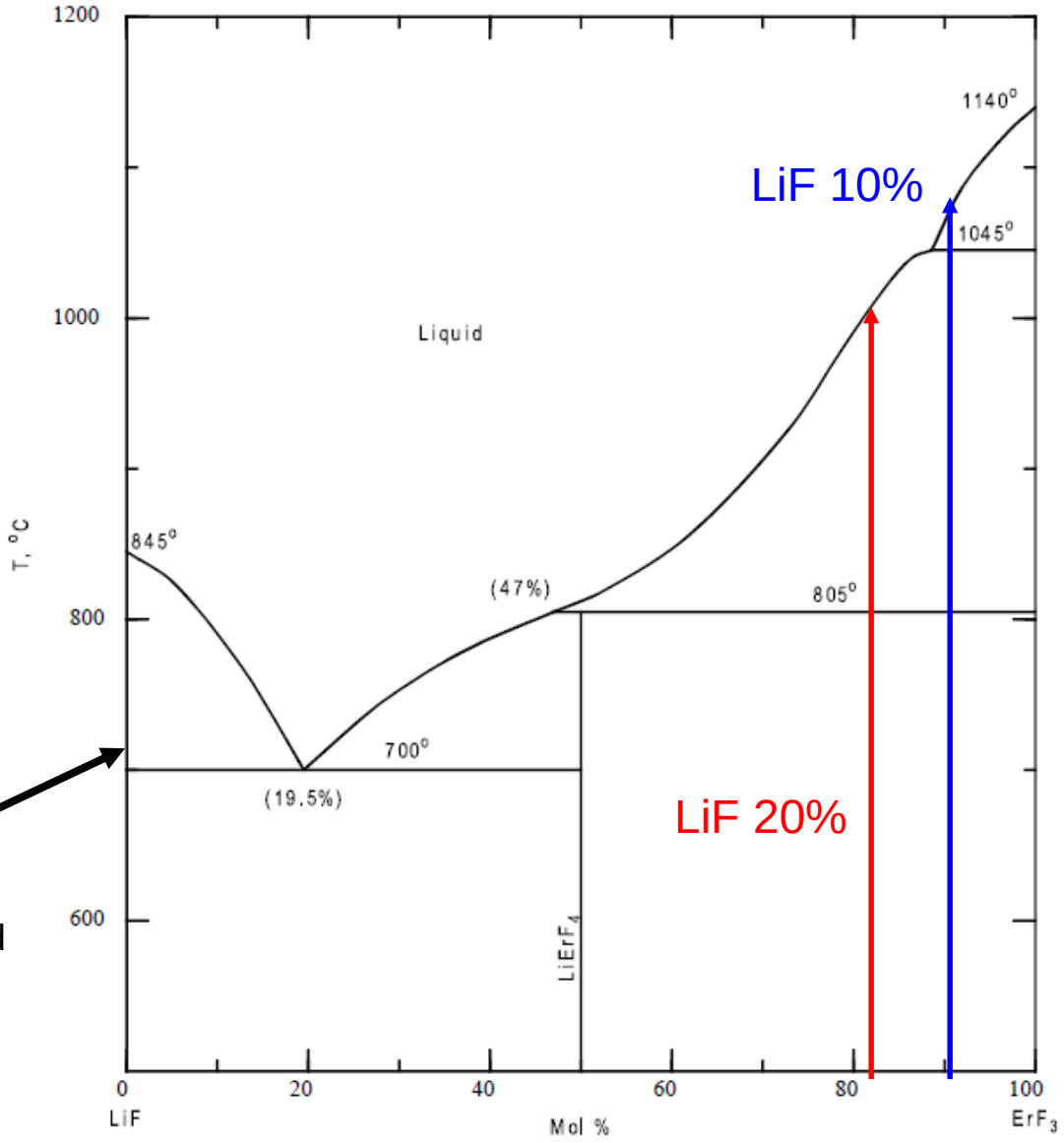
Nd-doped ErF_3

- Energy transfer from Er^{3+} to Nd^{3+}? VUV Analogue to PrF_3:Ce?

  (A. Yoshikawa et al., J. Cryst. Growth 270, 427–432 (2004))

-high density (7.8 g/cm^3) –high gamma ray or X-ray stopping power

-Challenging crystal growth – melting point 1140°C, phase transition (from hexagonal to orthorhombic) at ~1045°C

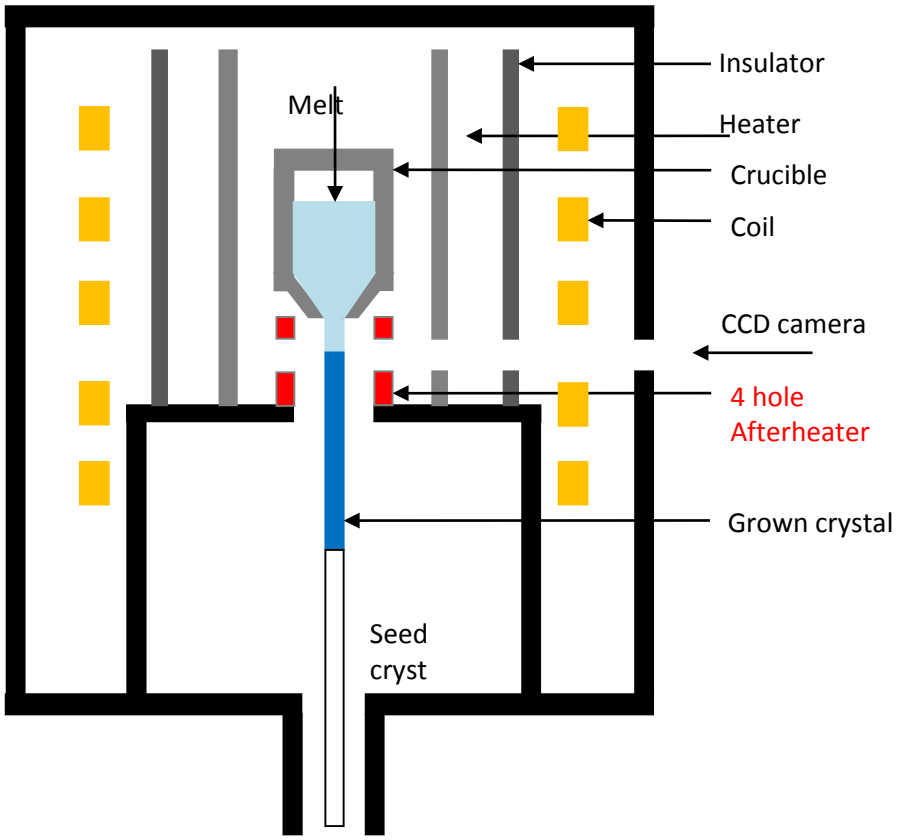


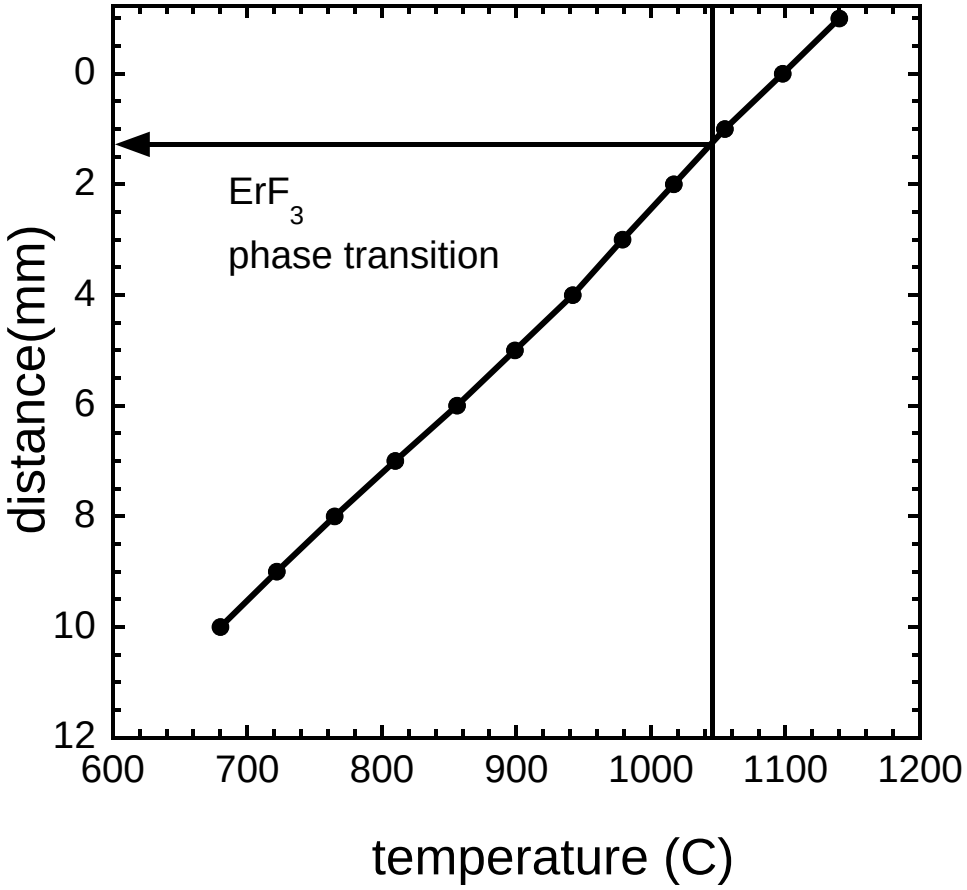
LiF-ErF_3 Phase diagram

According to I. A. Ivanova, M. A. Petrova, and I. G. Podkolzina, Zh. Neorg. Khim., 20 [8] 2292-2293 (1975); Russ. J. Inorg. Chem. (Engl. Transl.), 20 [8] 1273-1274 (1975).

LiF flux growth might be possible

Crystal growth of tetragonal (low temperature) ErF_3 - LiF-flux

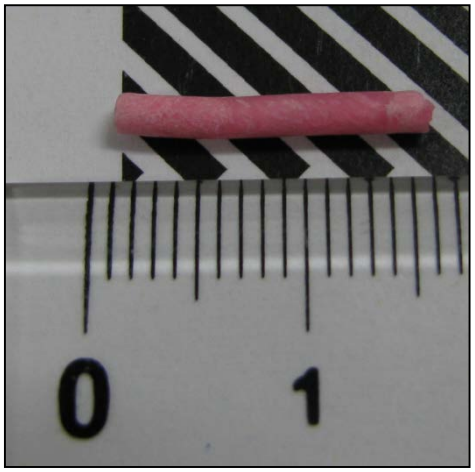




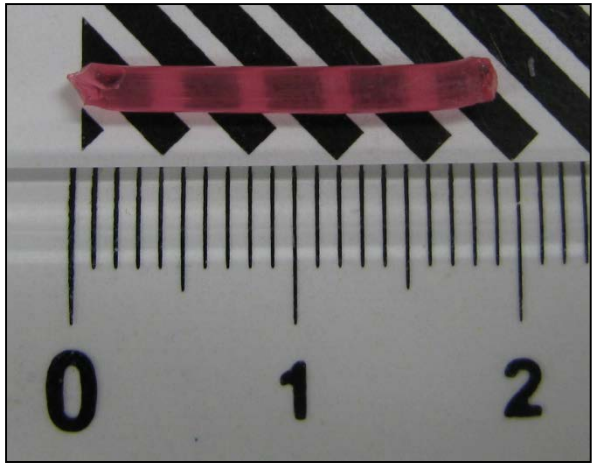
Ir-wire seed, LiF – flux introduced to diminish the melting point. Steep gradient at the crucible nozzle to facilitate melt supercooling

Standard hot zone, 4hole afterheater – makes the temperature gradient steeper

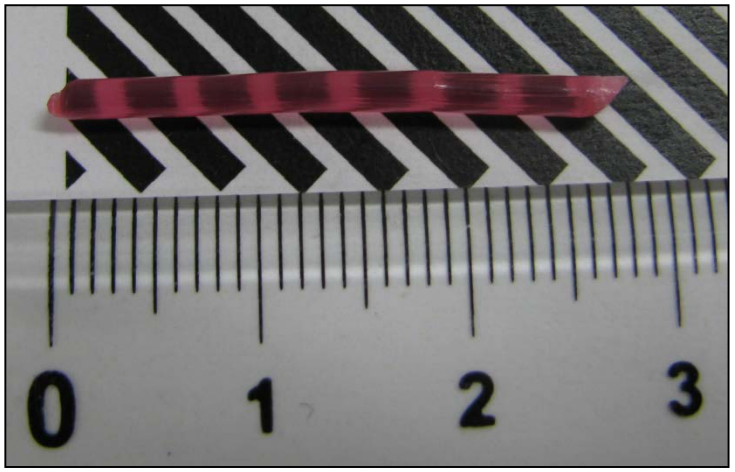
ErF_3, ErF_3:Nd – as grown crystals



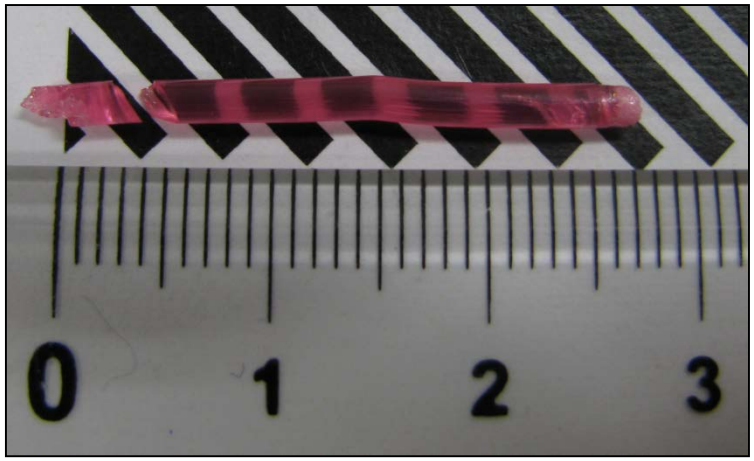
No LiF



LiF 20%



LiF 10%



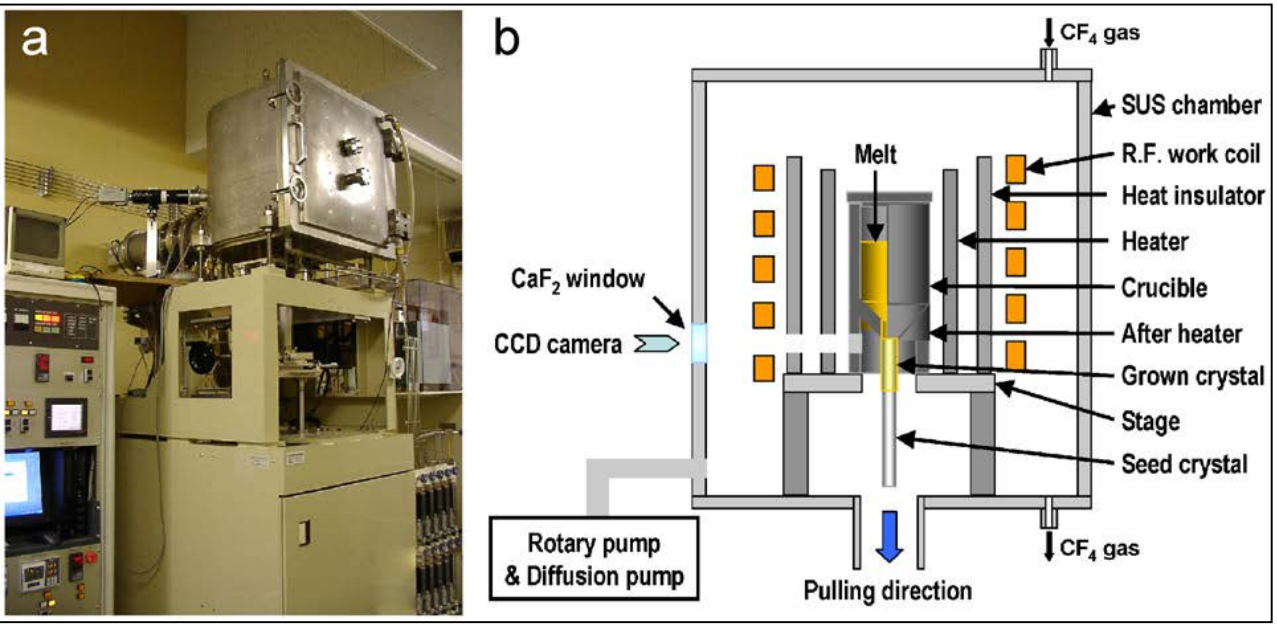
LiF 10%, Nd1% doping
Little cracks

XRD confirmed pure ErF_3 phase

$LiErF_4$ phase confirmed in crucible rest

For LiF 10% excess the composition corresponds to 90.9% ErF_3 and 9.1%LiF – still above the phase transition temperature (peritectic point around 12%LiF) – supercooling takes place

Micro-pulling-down method for LuF_3



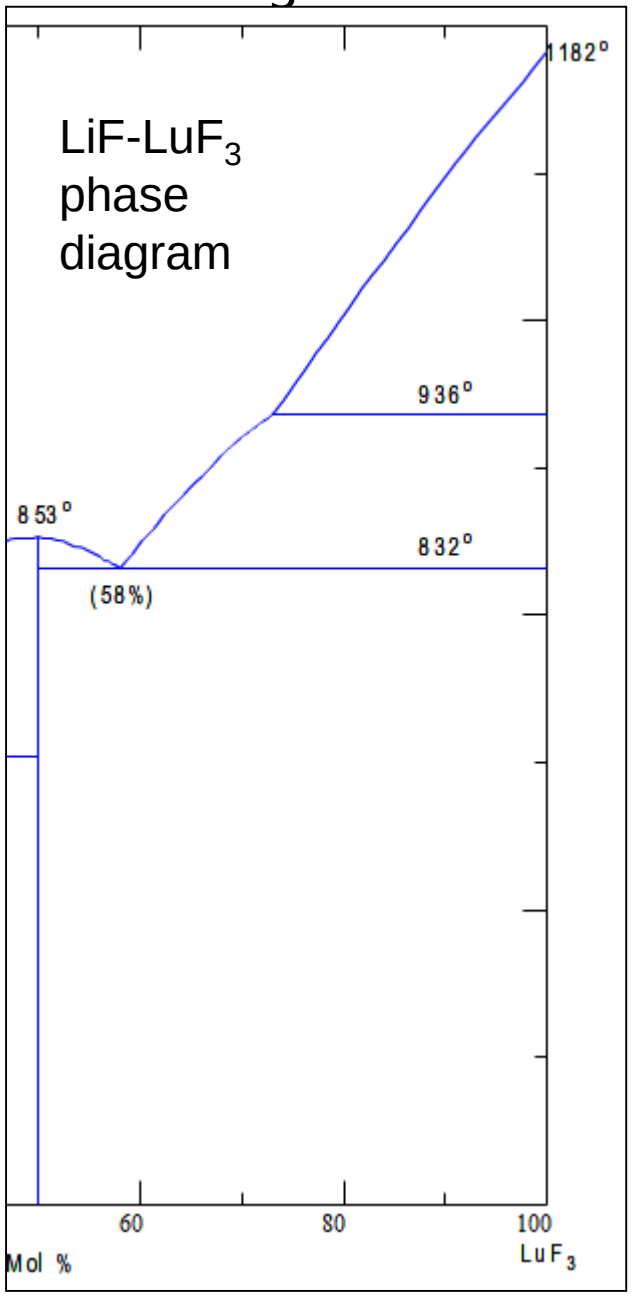
Modification for fluorides:

Graphite crucible, seed, evacuation and baking procedure,

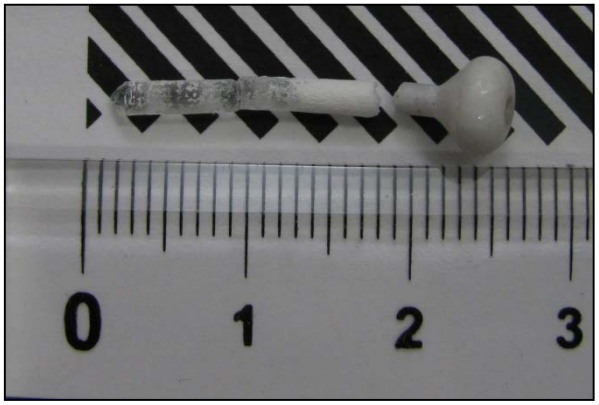
Atmosphere: 90%Ar+10%CF_4 (moisture scavenger gas)

Crucible hole diameter:2 mm

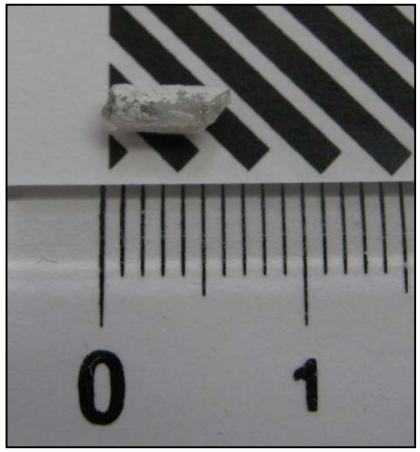
Pulling speed: 0.01mm/min. LiF flux to avoid phase transition (250°C below melting point 1182°), Self-cladding



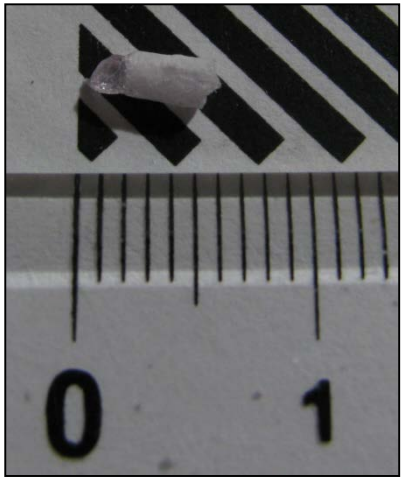
LuF_3-based VUV scintillators – examples of the as-grown crystals



LuF_3
undoped



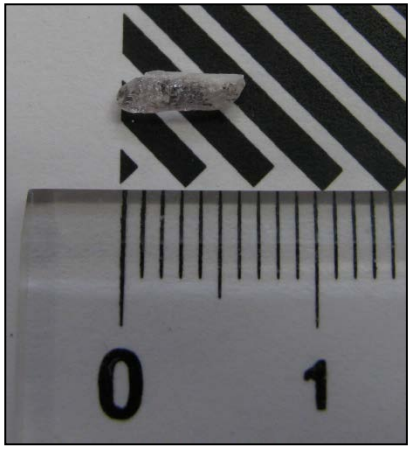
LuF_3:Er1%



LuF_3:Nd1%

LiF flux, Ir-wire seed, pulling speed 0.01 mm/min, LuF_3 phase confirmed by XRD
Self-cladded with $LiLuF_4$

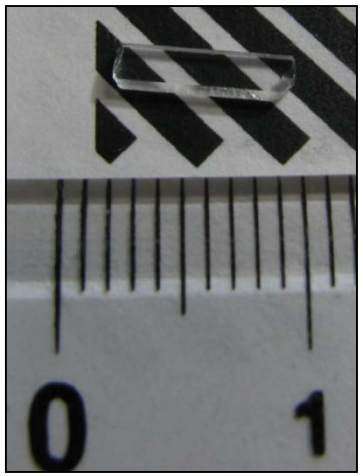
Er codoping – Improvement of energy transfer



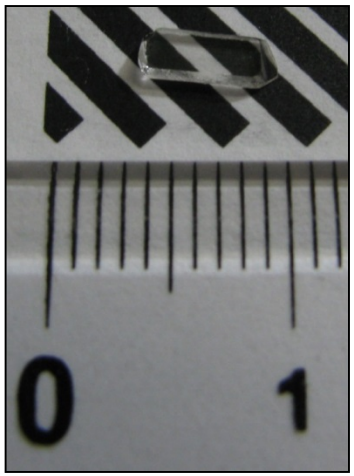
LuF_3:Er1%Nd1%

Studied LuF_3 crystals

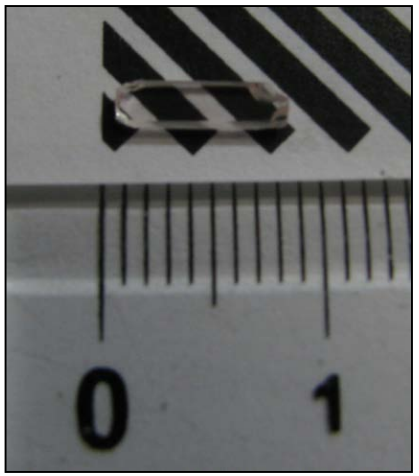
After cutting and polishing



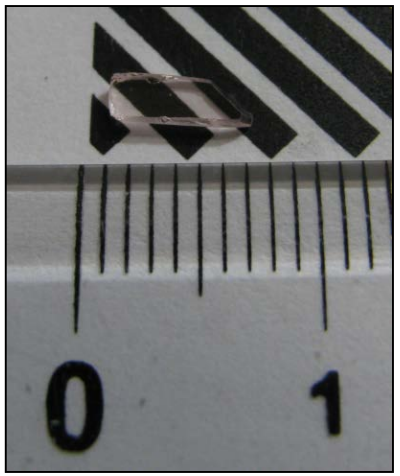
LuF_3 undoped



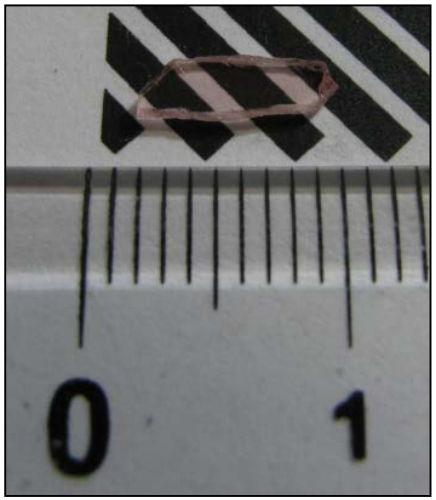
LuF_3:Er1%



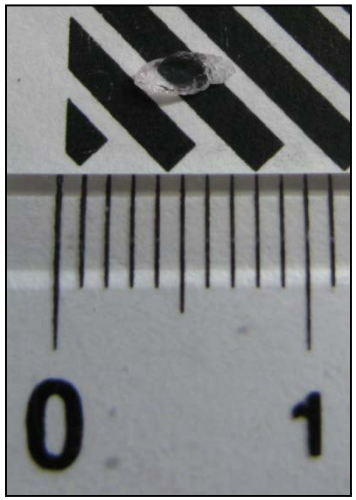
LuF_3:Er3%



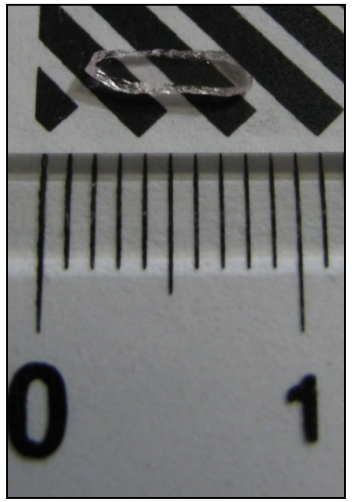
LuF_3:Er5%



LuF_3:Er10%

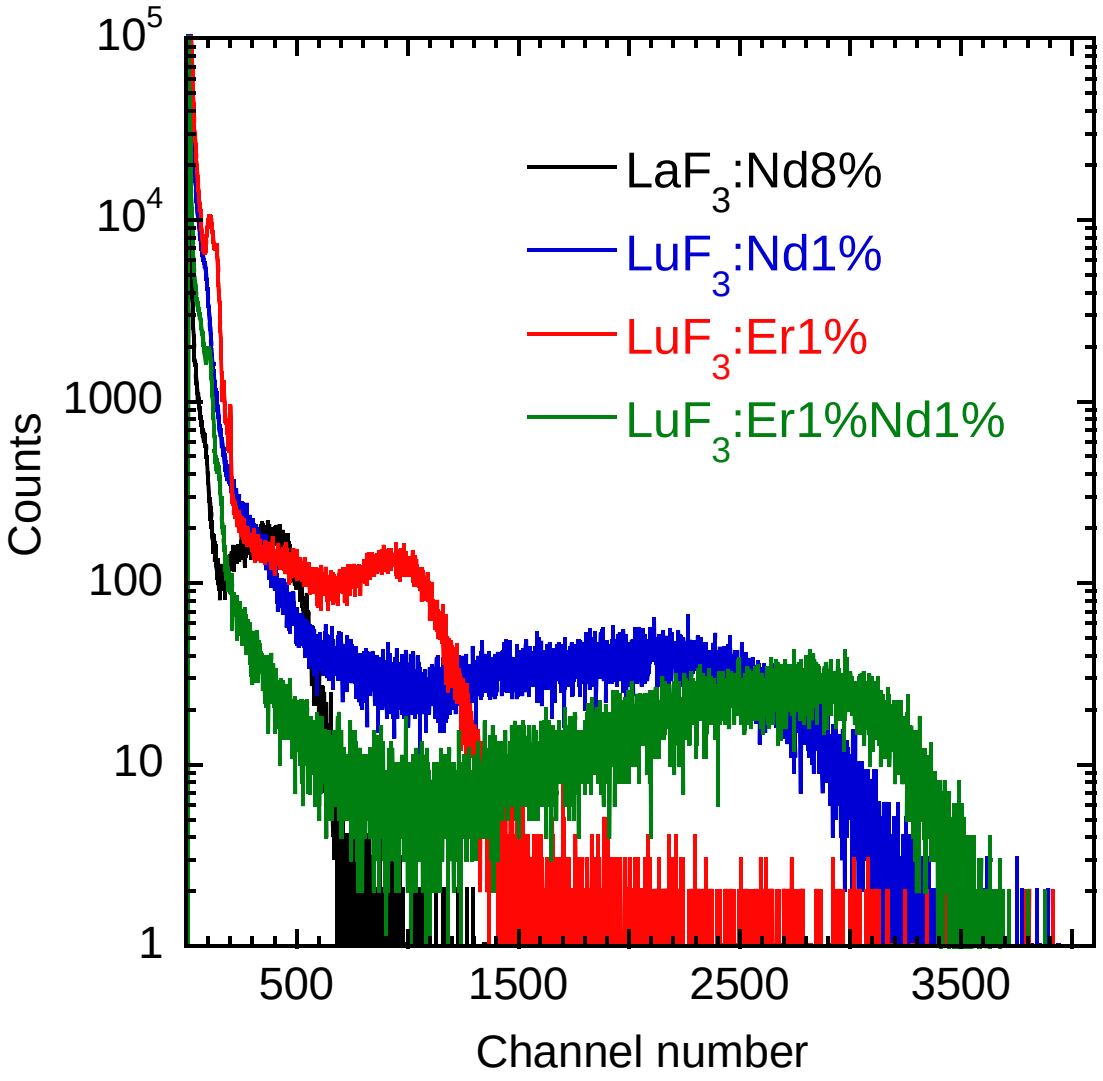


LuF_3:Nd1%



LuF_3:Er1%Nd1%

LuF_3 – Light yield – ^{241}Am alpha-ray excitation
CsI photocathode photomultiplier



Channel numbers:
LaF_3:Nd8% : 250
LuF_3:Er1%: 970
LuF_3:Nd1%: 2350
LuF_3:Er1%Nd1%: 2847

Shaping time: 500ns

Slow HS component of Er^{3+} - decay time of microsecond order – lowered light yield for Er1%-doped sample

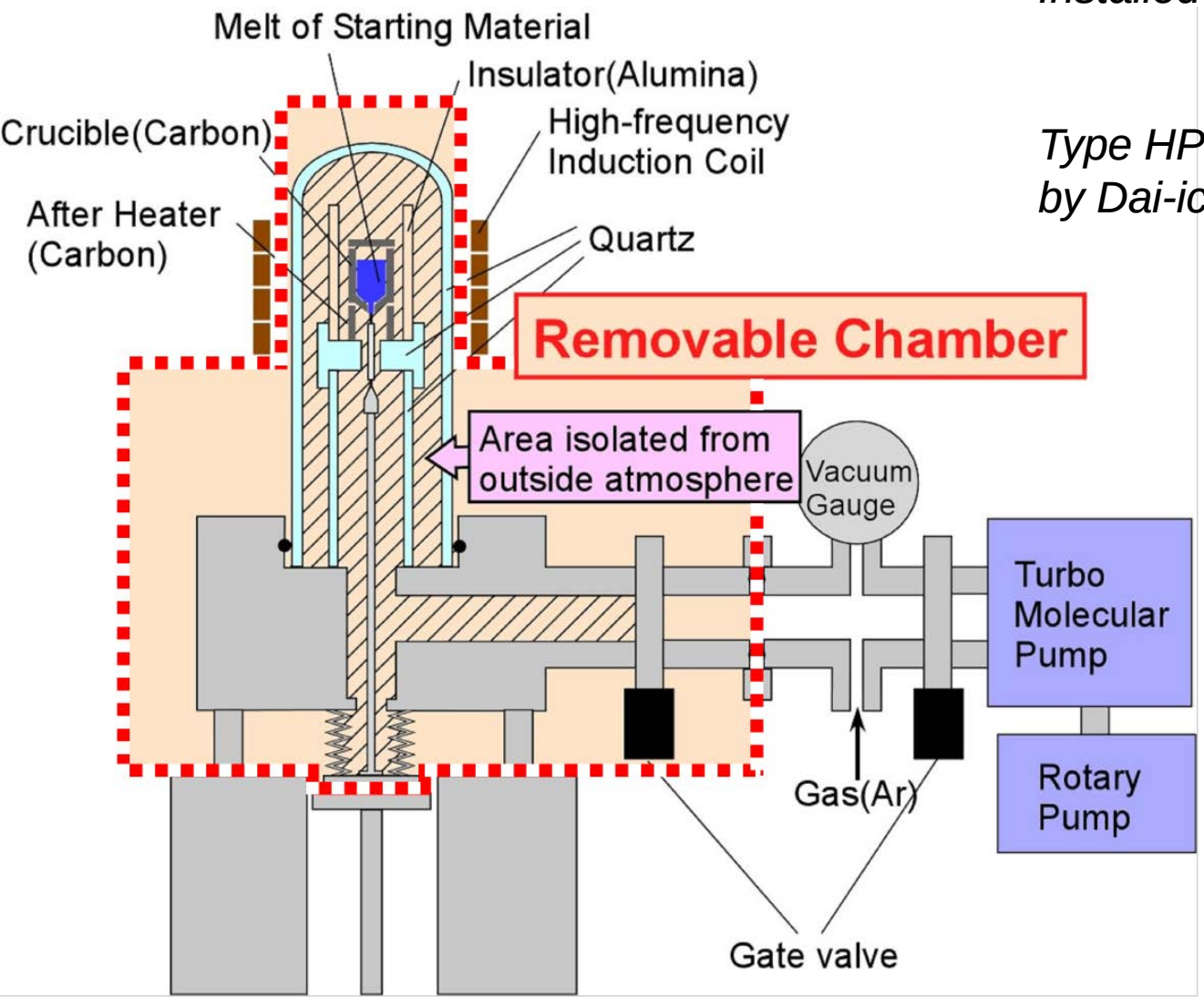
Measurement of dependence of the light yield on shaping time is planned

The Er,Nd doubly-doped sample shows the highest light yield

Micro-pulling-down method
Halide crystals

Halide micro-pulling-down setup

Institute of Physics, Czech Academy of Sciences, Prague, Installed in autumn 2017

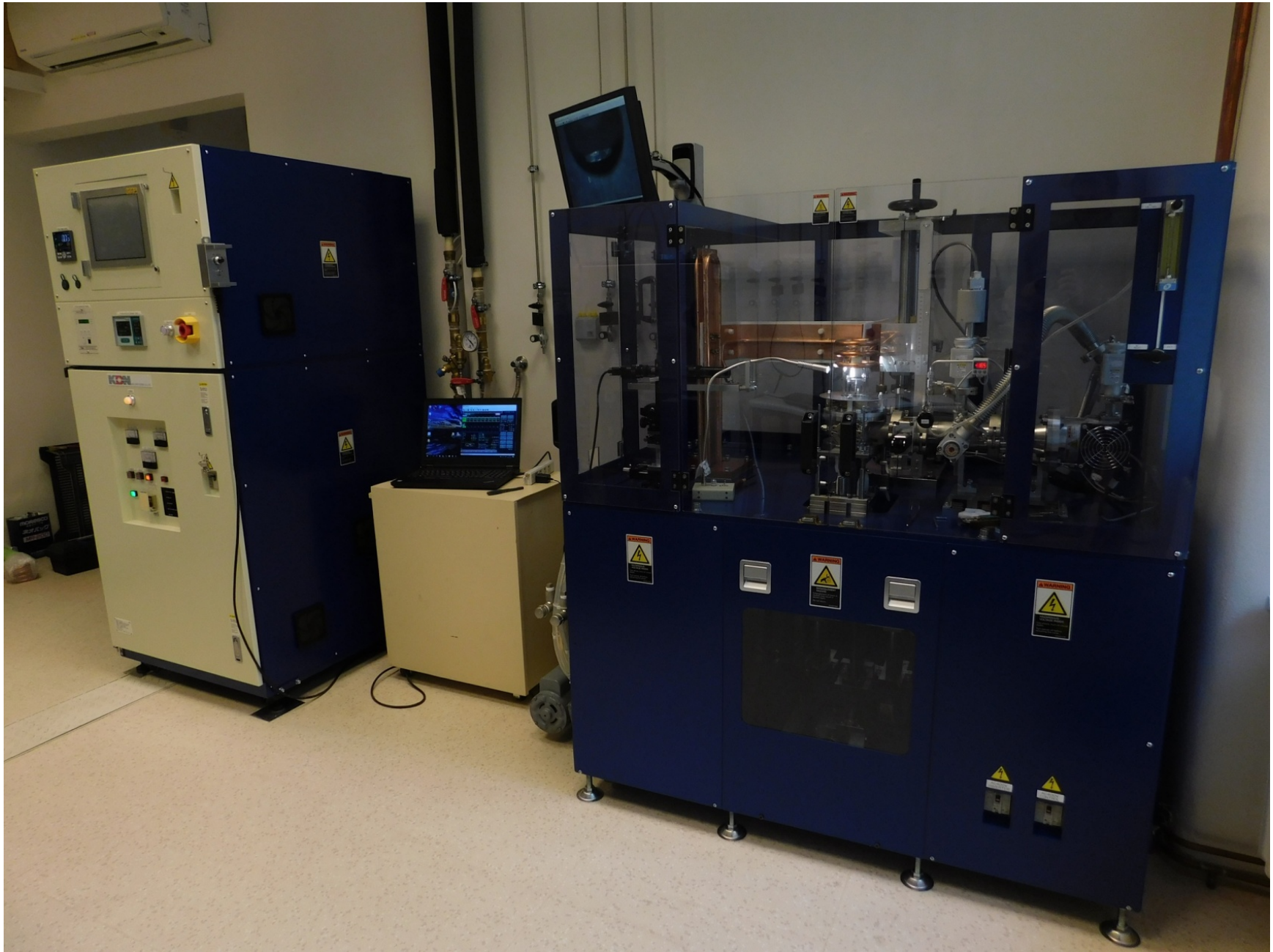


Type HPI-01001
by Dai-ichi Kiden Co., Ltd. Japan

Glove box

Halide micro-pulling-down setup

Type HPI-01001
by Dai-ichi Kiden Co., Ltd. Japan



Halide mPD - parameters

Operation panel (OP):

- Power output
- Pulling rate (remote controller)
- sequences (10 steps)
- max. distance setting

- remote control by NB

Specifications	
RF Power Source	5 kW
Heat. temp.	1000 C (max.)
Removable chamber	YES
pulling rate [mm/min]	0.01-100 (step 0.01)
Coil (Cu)	3 turns (and 4 turns)
CCD Camera	Toshiba TELIBG202C
Crucible	Carbon

Notebook

- ✓ OP con.
- ✓ internet

Table

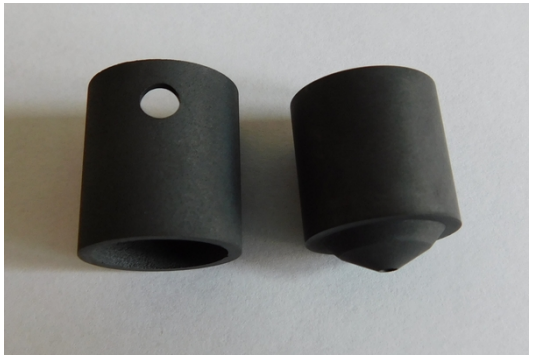
- ✓ Removable chamber
- ✓ CCD cam.
- ✓ pulling mech.
- ✓ VAC – RP, MP
- ✓ transformers

RF source

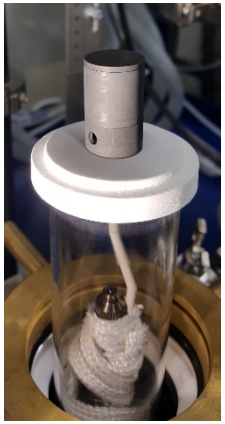
- ✓ OP control
- ✓ manual contr.

Halide micro-pulling-down setup

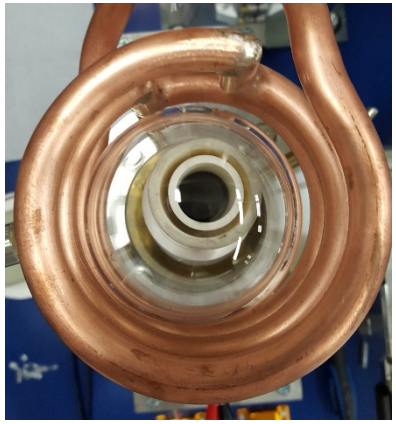
Carbon crucibles



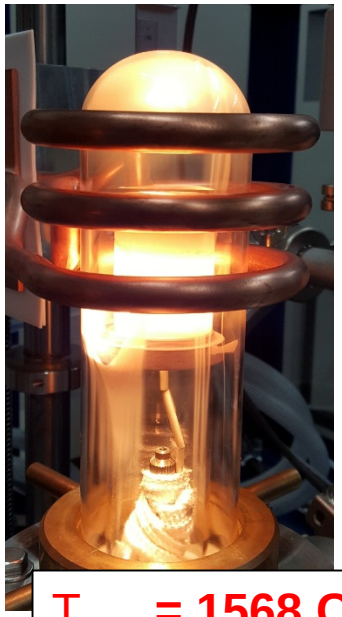
2nd Max. temp. meas.



Al2O3 stage



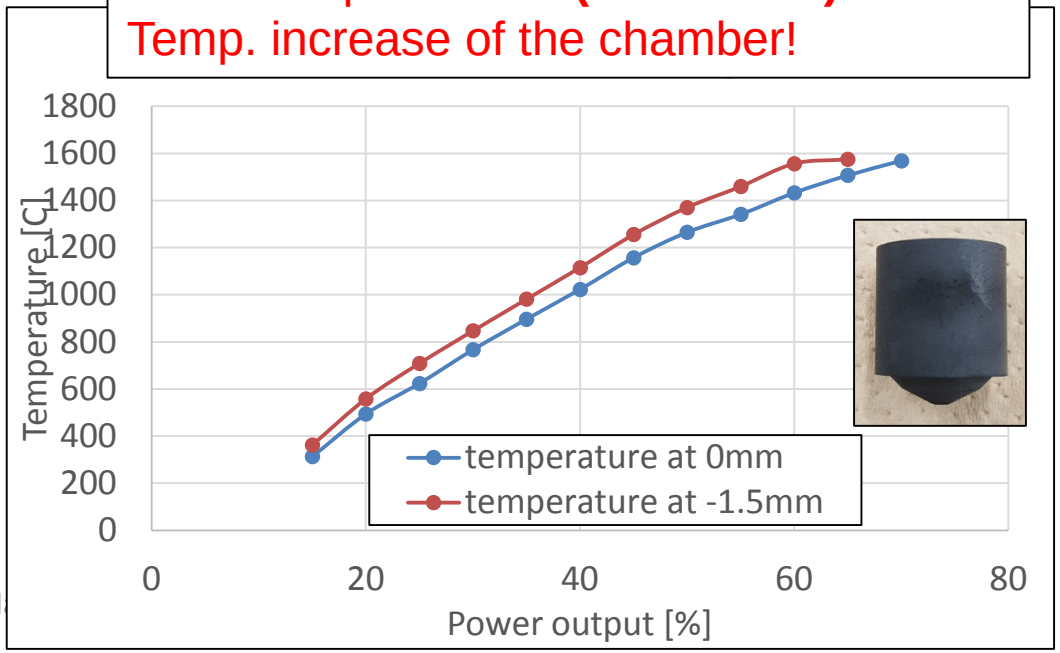
double Al2O3 shield



High carbon evap.

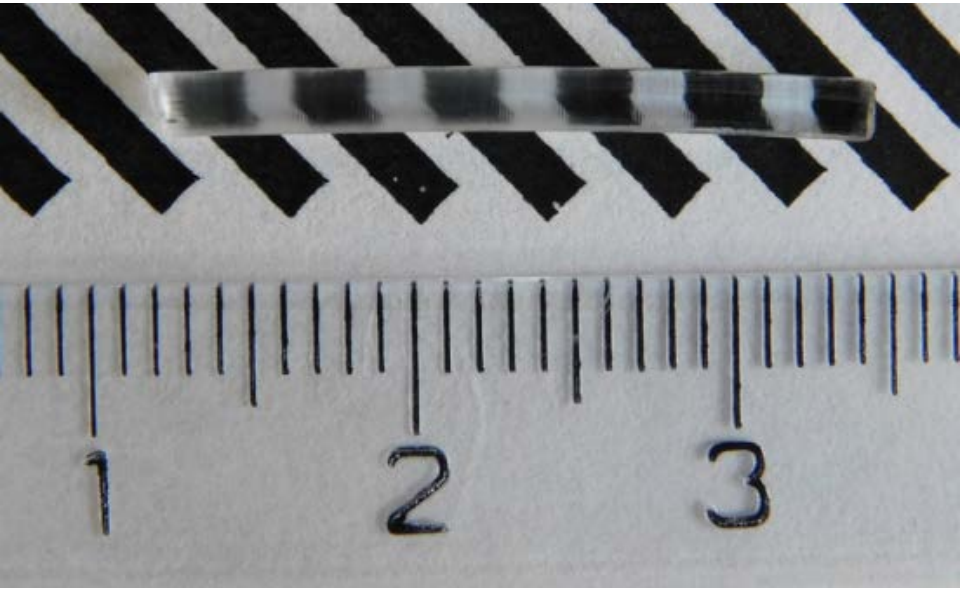
T_{max} = **1568 C (edge)**
T_{max} ~ **1650-1700C (cruc.)**
Power output = **70% (max. 5 kW)**
Temp. increase of the chamber!

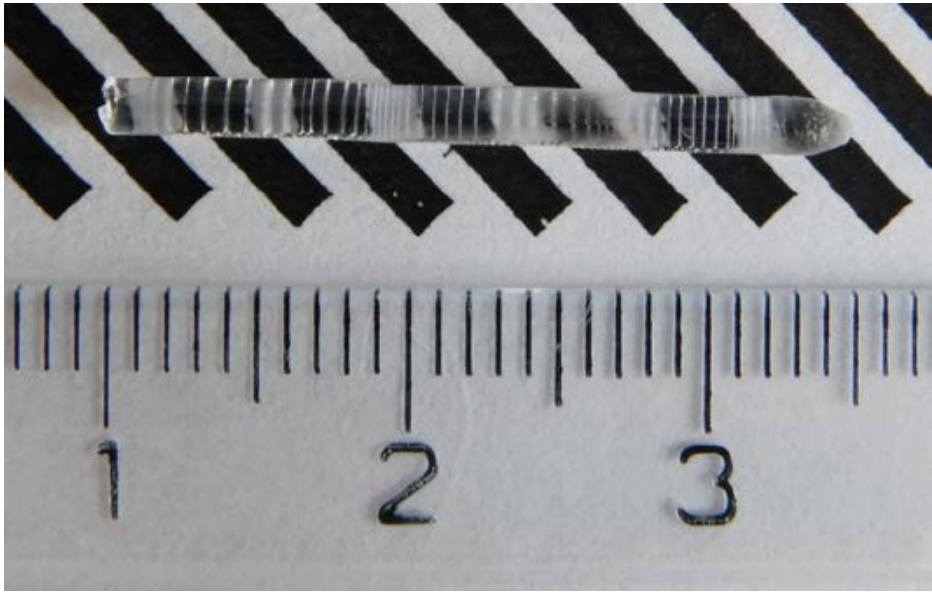
Conditions	
crucible	carbon, hole 2mm (dia.)
afterheater	2x hole, 4 mm (dia.)
2x isolation	Al2O3
Thermocouple	type B, Pt-Rh(6%)/Pt-Rh(30%)
stage	Al2O3
atmosphere	Ar (6N)



Halide micro-pulling-down setup – grown crystals

NaCl





0.1mm/min

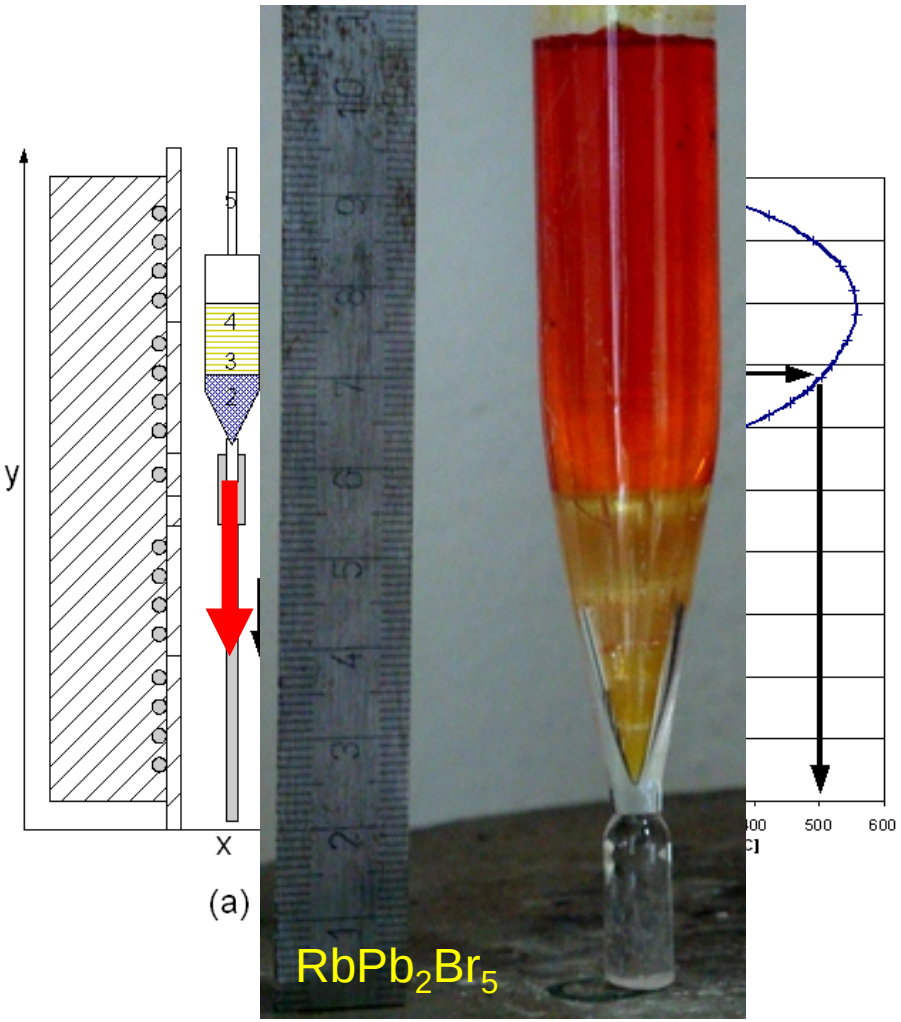
1mm/min

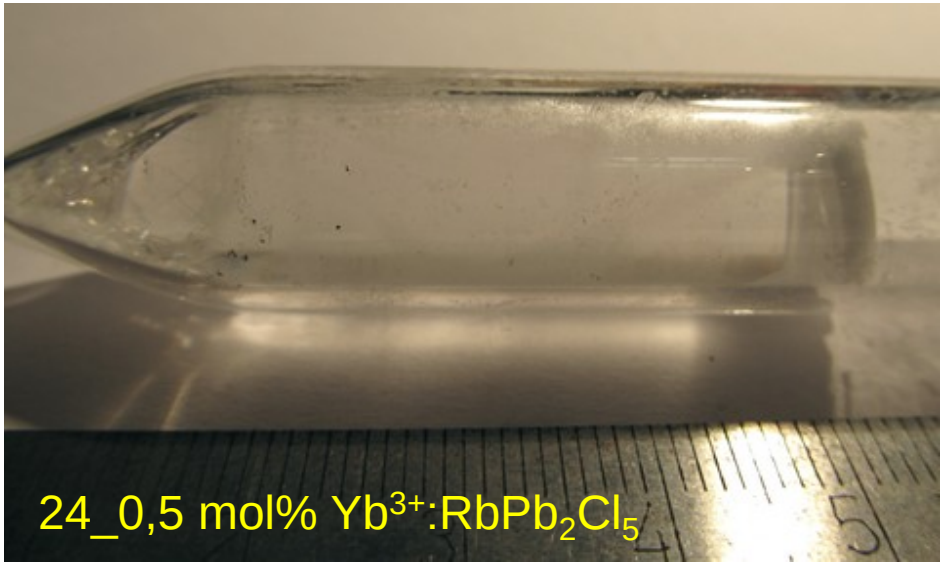
NaCl crystals grown by the new halide micro-pulling-down setup a t a speed of 0.1mm/min (left) and 1mm/min (right)

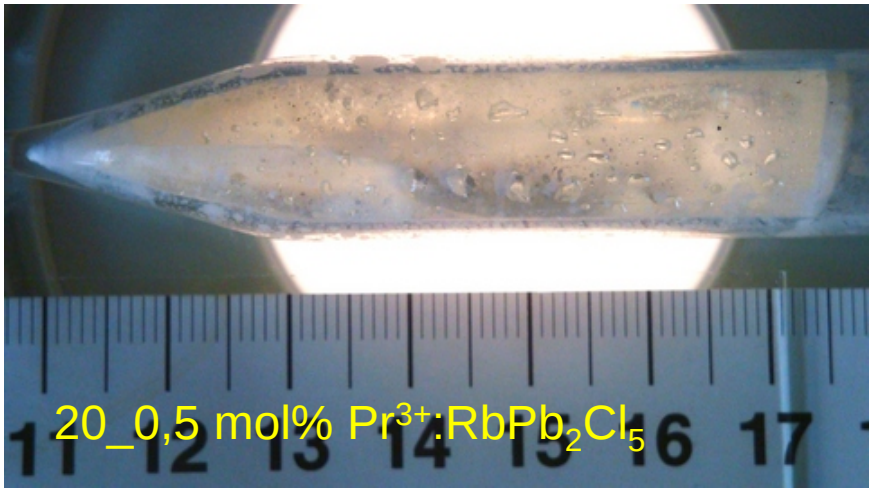
Bridgman method

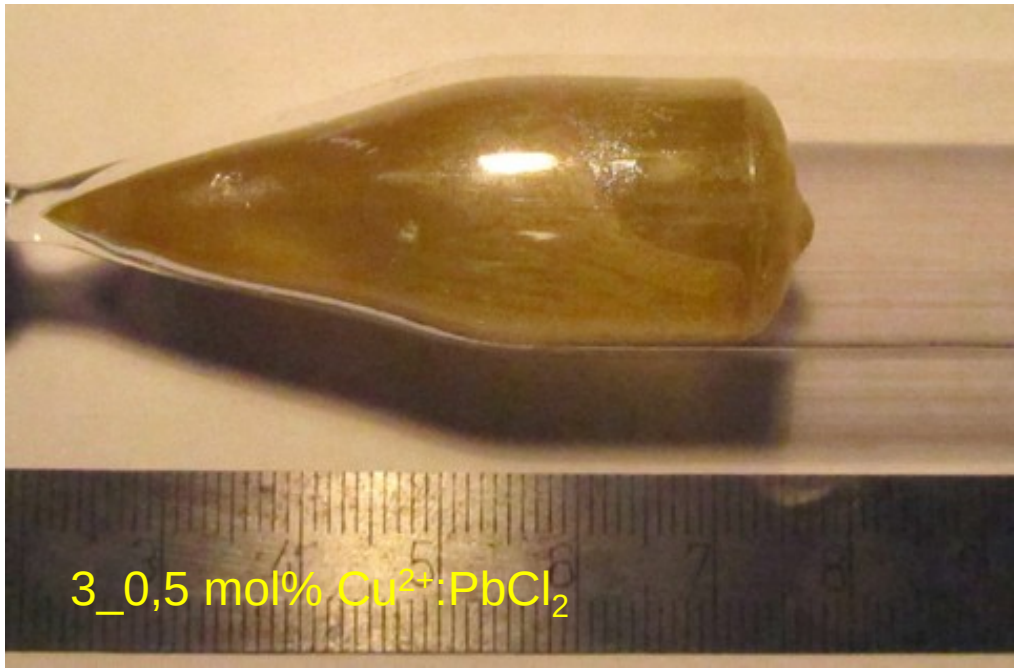
Vertical Bridgman method

- Crystal growth from the melt
- Container = **quartz ampoule**
- Two and more-section resistive furnace
  - top section – ABOVE m.p.
  - bottom section – BELOW m.p.
- Temperature gradient between sections – **10 to 50 K/cm**
- Crystal growth
  - unseeded
  - pulling ampoule down by rate **0,2 to 1,0 mm/h**
  - **10 days**
- RE elements introduced as metals
  - nomin. conc. **0.5 mol% (Yb)** and **5 mol% (Nd, Pr)**




24_0,5 mol% Yb^{3+}:$RbPb_2Cl_5$


20_0,5 mol% Pr^{3+}:$RbPb_2Cl_5$

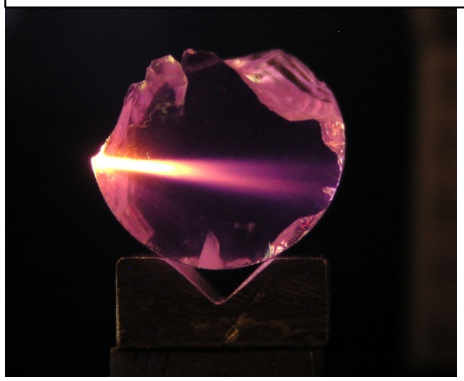

3_0,5 mol% Cu^{2+}:$PbCl_2$

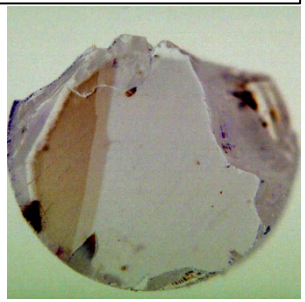
Optical microscopy – crossed polar.

RbPb2Cl5

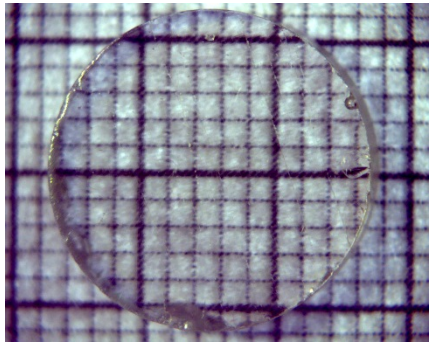
m.p. 423 C, monoclinic structure, a = 8.915 A, b = 7.950 A, c = 12.445 A, beta = 90.14 deg

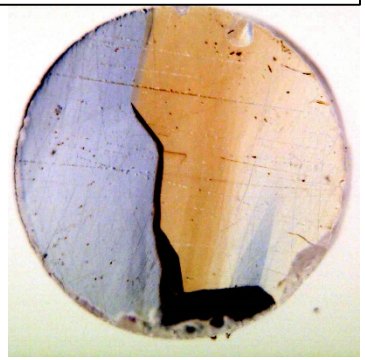
5%Nd:$RbPb_2Cl_5$



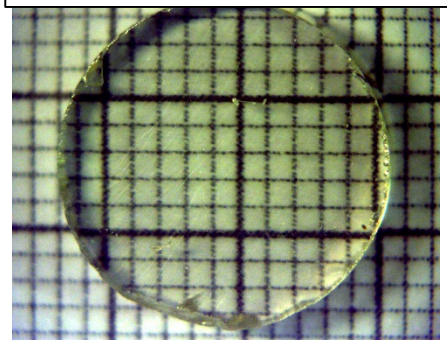


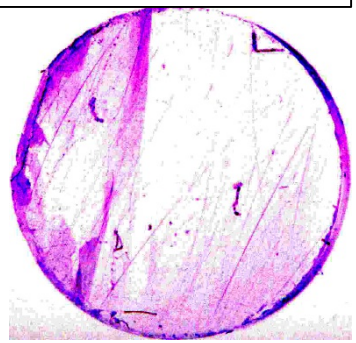
0.5%Yb:$RbPb_2Cl_5$



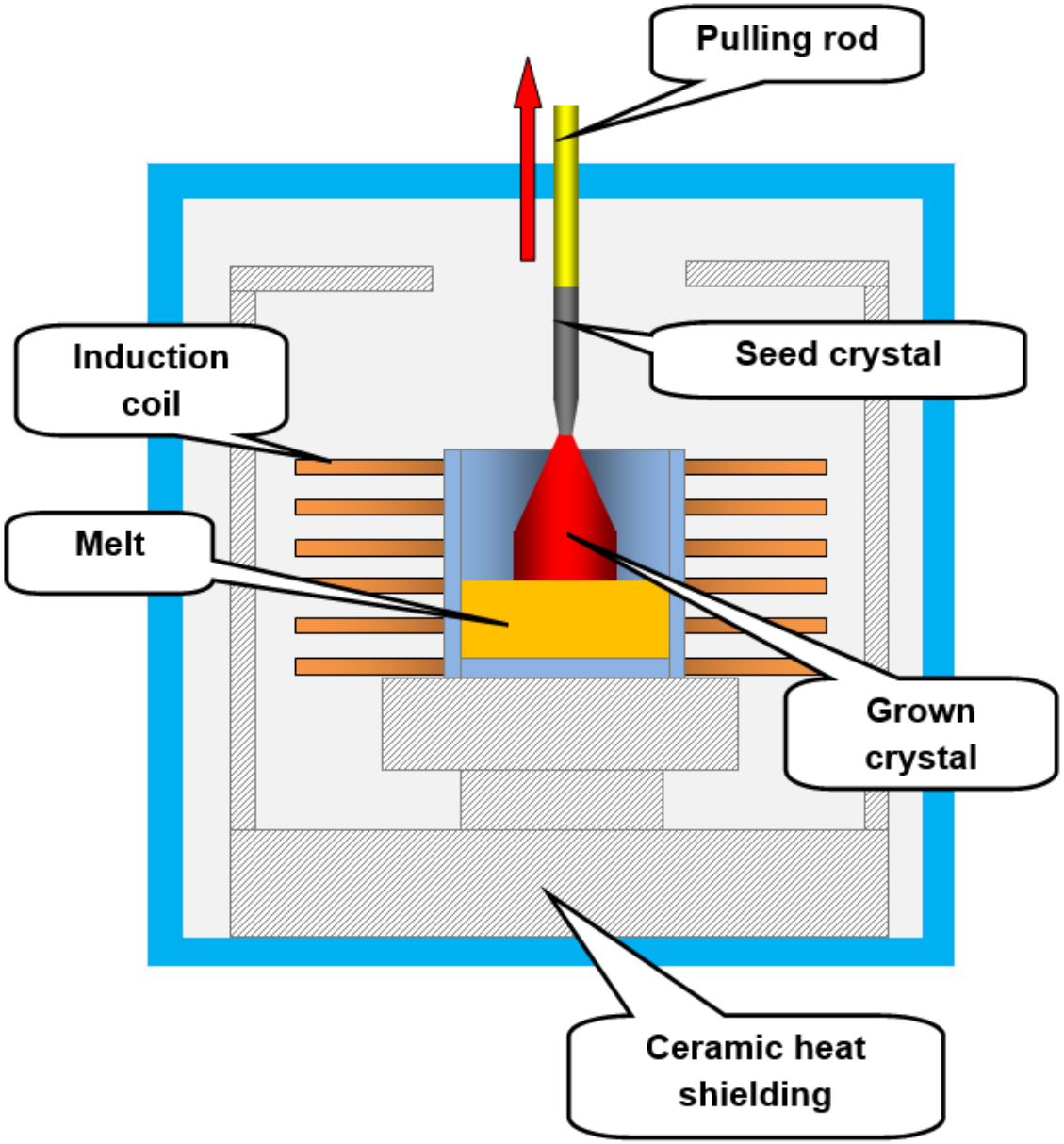


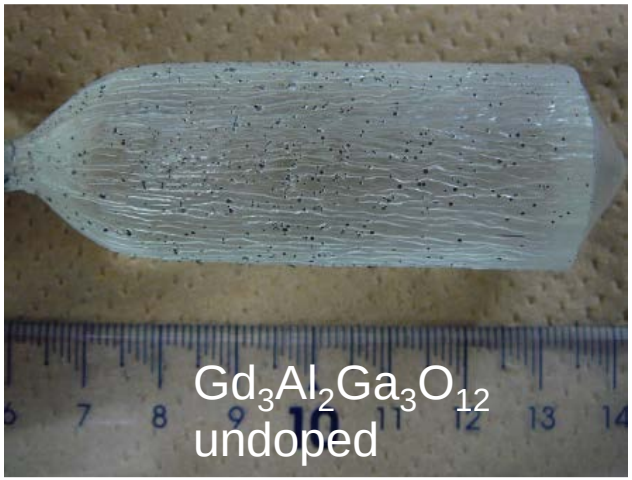
5%Pr:$RbPb_2Cl_5$

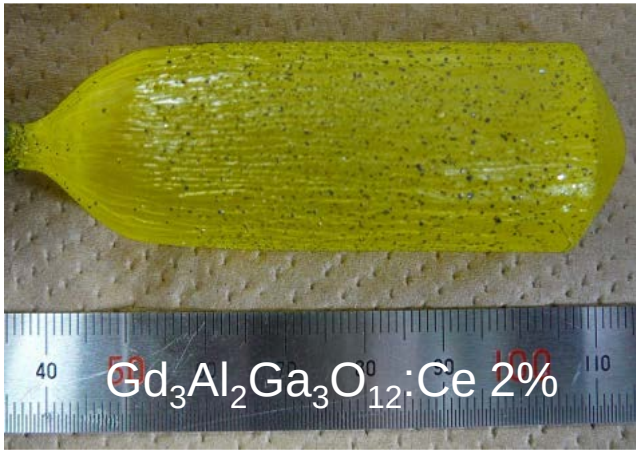




Czochralski method

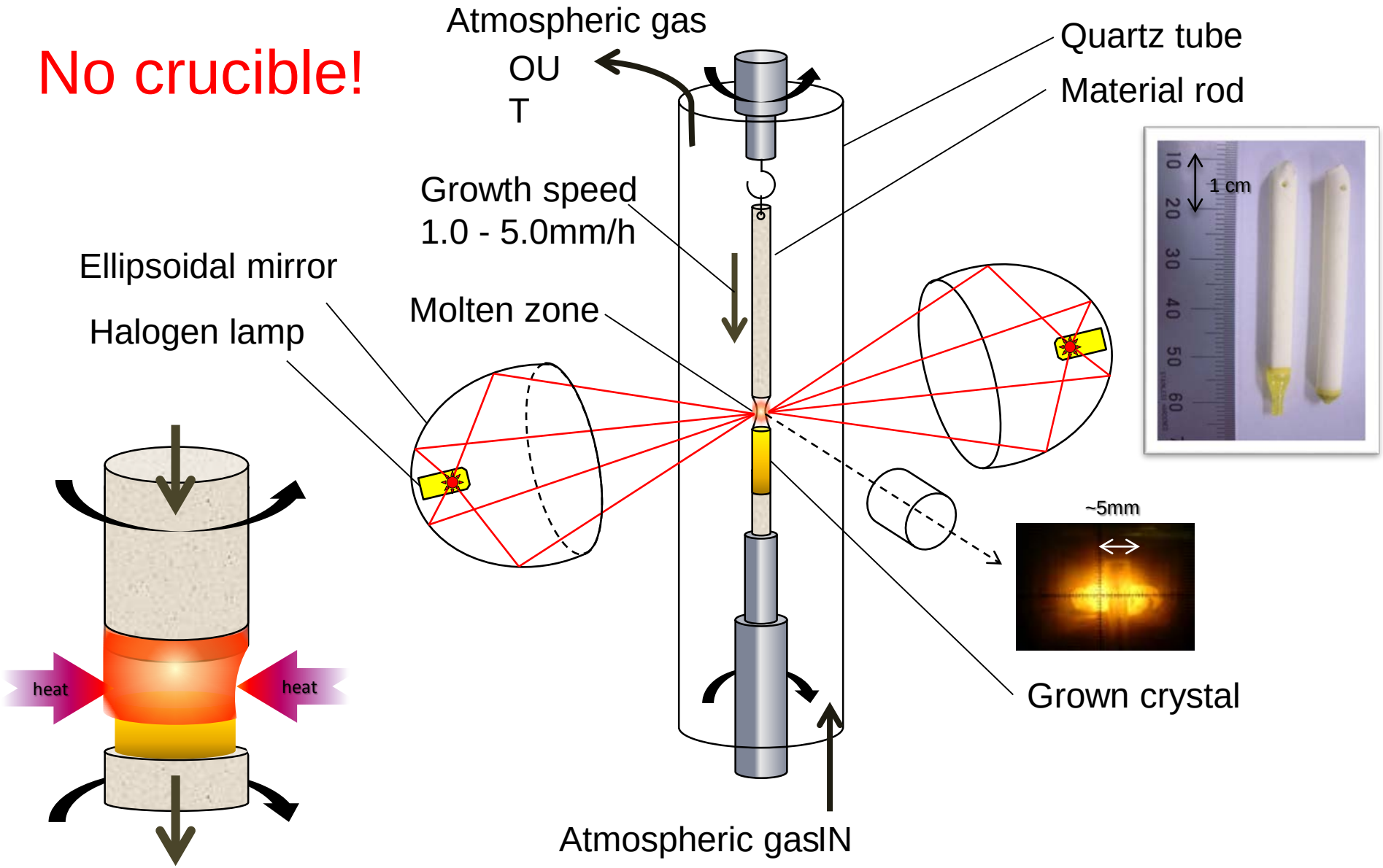




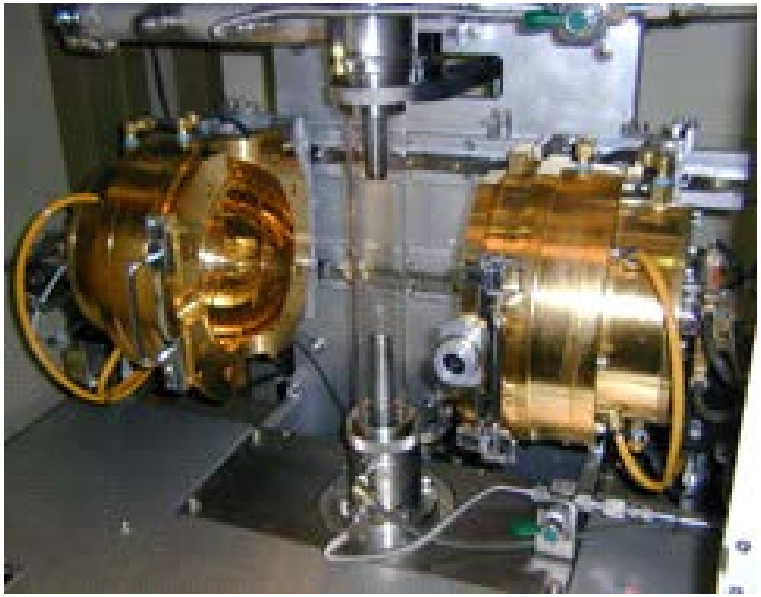


Optical floating-zone (OFZ) method

No crucible!



Optical floating-zone (OFZ) method

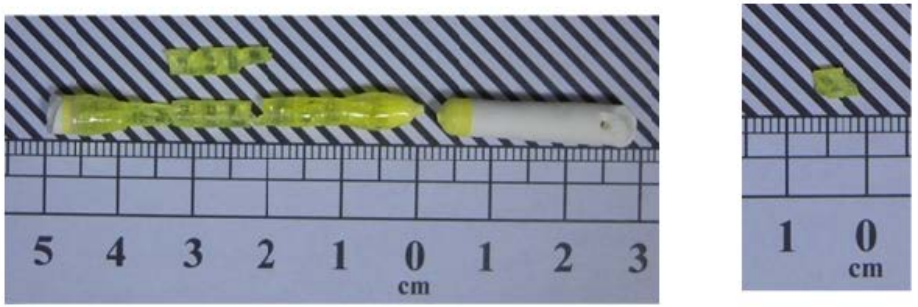


Asgal FZ-SS35WV

As grown crystal

Polished

$Gd_{2.9995}Ce_{00005}Ga_2Al_3O_{12}$ (O_2 20%)



$Gd_{2.9995}Ce_{00005}Ga_2Al_3O_{12}$ (O_2 40%)

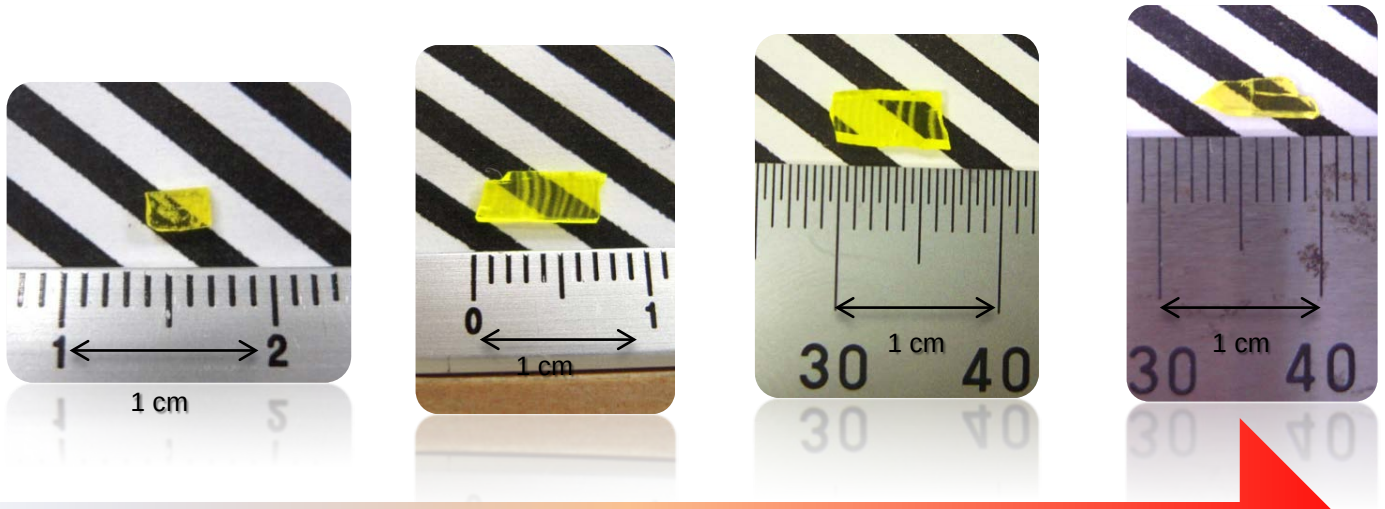
$Gd_{2.9995}Ce_{00005}Ga_2Al_3O_{12}$ (O_2 100%)

Optical floating-zone (OFZ) method

Composition: $(Gd_{0.995}Ce_{0.005})_3Ga_2Al_3O_{12}$

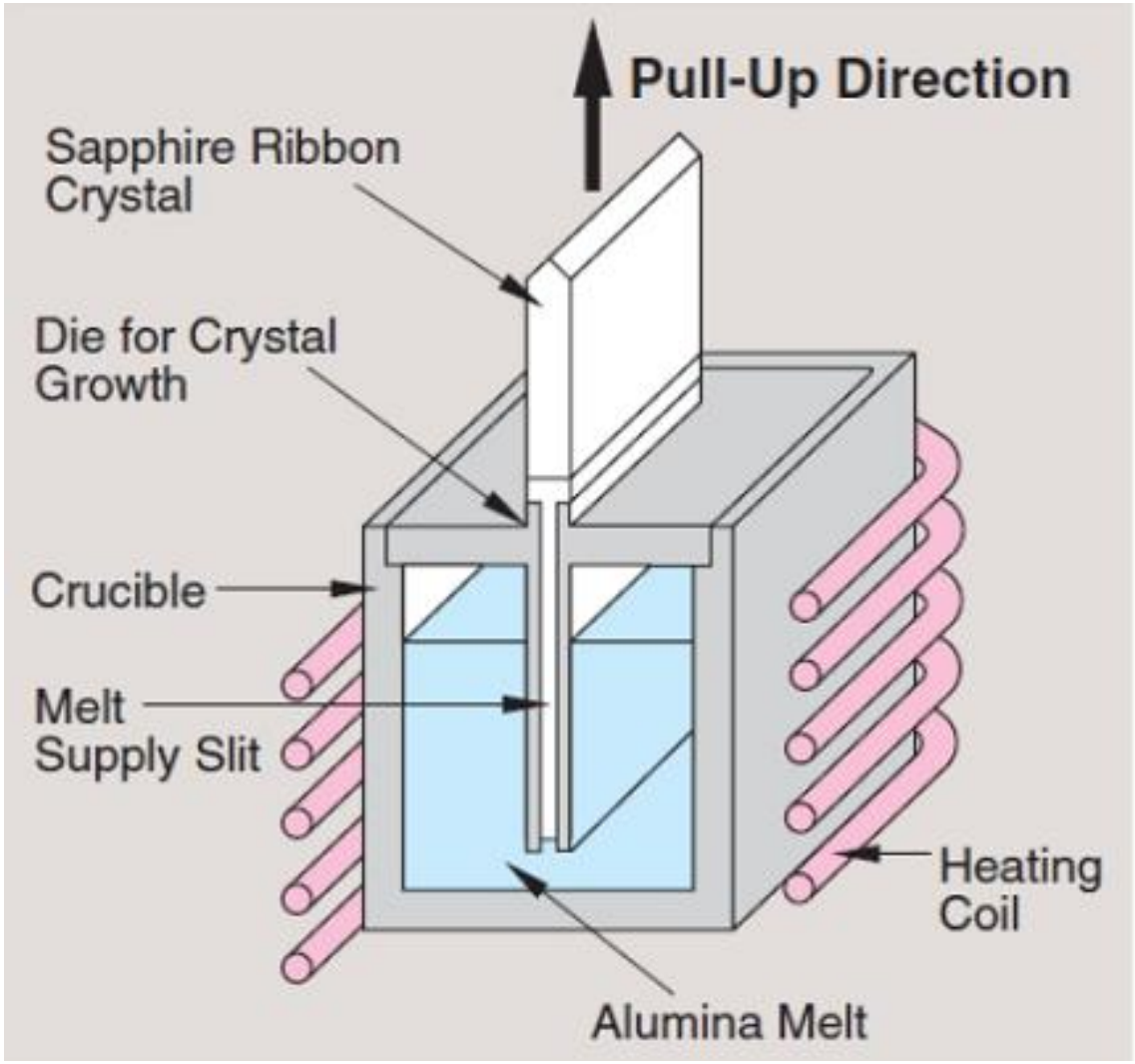
Oxygen gas

① 2 vol%　② 20 vol%　③ 40 vol%　④100 vol%



Ar 100%　**O_2 100%**

Edge-defined film-fed growth (EFG) method



From the webpage of ChinaTungsten corp.

Thank you for your attention!

Micro-pulling-down laboratory

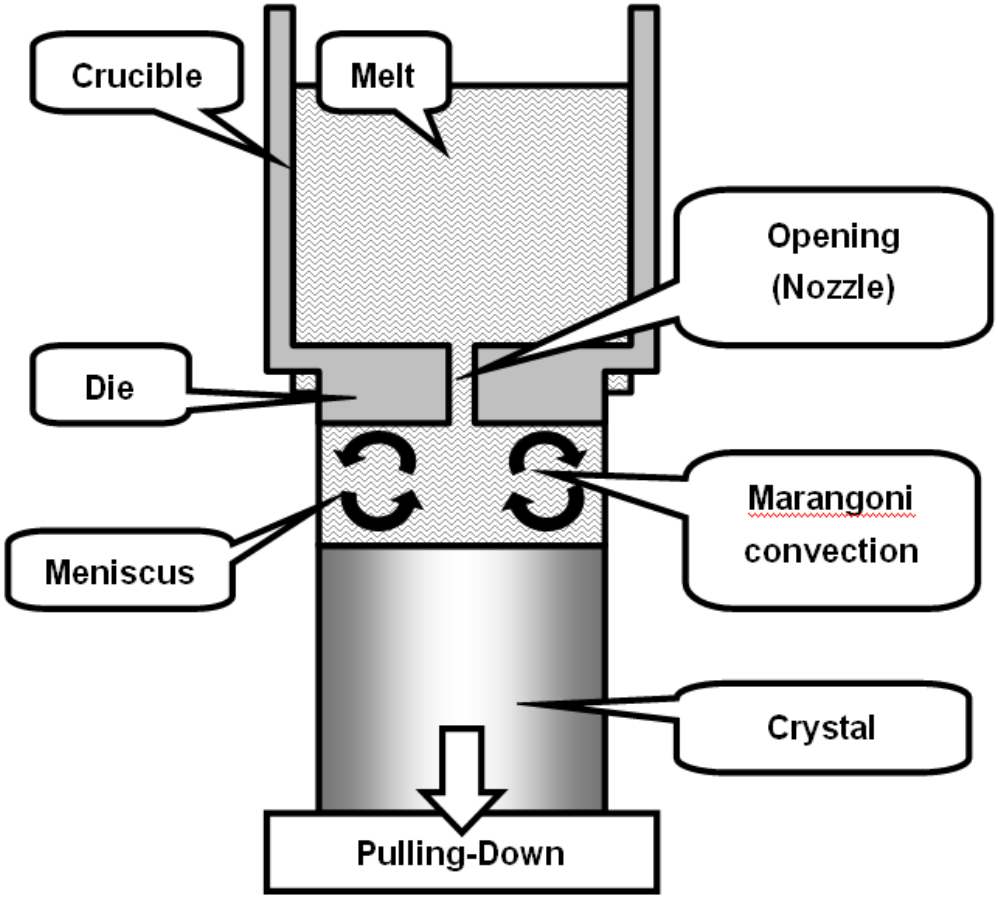
Projects

2015-2017 Czech Science Foundation
Grant for excellent junior scientists 15-18300Y (J. Pejchal)
2018-2020 Czech Science Foundation
Standard grant 18-14789S (J. Pejchal)

2018-2020 Czech Science Foundation
Grant for excellent junior scientists 18-17555Y (R. Král)

Close collaboration with luminescence group (V. Jarý, M. Nikl) and EPR group (V. V. Laguta, M. Buryi)
Strong industrial background (Crytur Ltd., Nuvia Corp.)

Selected phenomena in crystal growth by mPD method



Marangoni convection – more significant than buoyancy, responsible for melt mixing in the meniscus and equilibrium between the melt and growing crystal (difference from EFG)

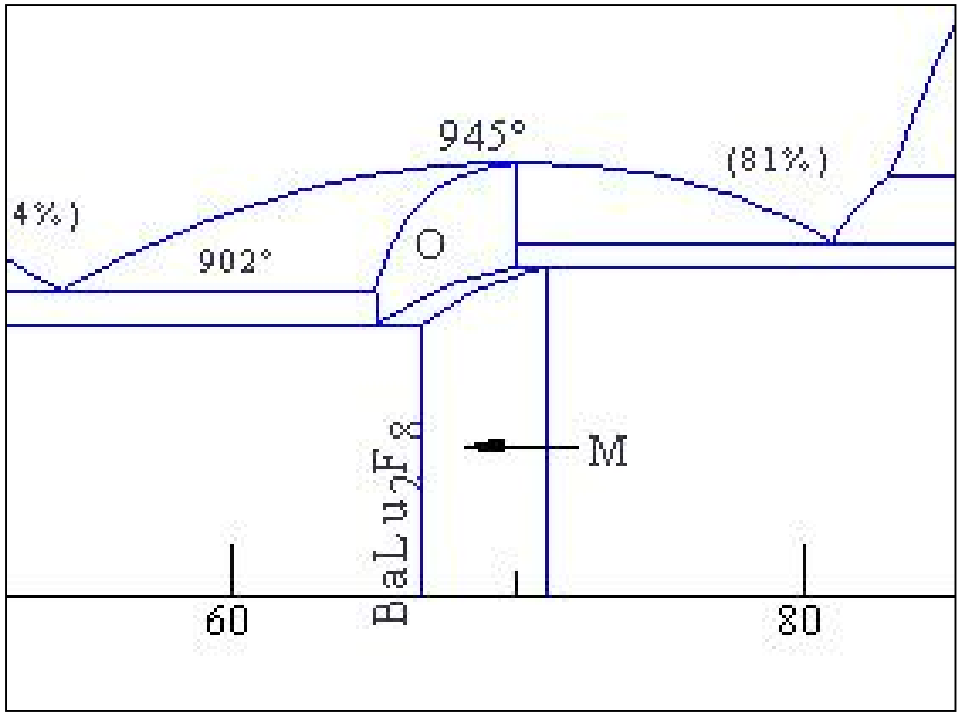
Meniscus thickness – influences Marangoni convection

Crystal/nozzle diameter ratio
– small: mass exchange with the melt in the crucible, segregation, capability of growth incongruently melting compounds
-high: fast transport through capillary, no equilibrium, no segregation, melt composition constant

Growth rate – equilibrium and segregation

Increasing the Lu-concentration: $BaLu_2F_8$ (BaLuF)

- Nd-doped BaLuF - candidate for VUV scintillator
- fast response (14ns decay time)- Nd^{3+} 5d-4f VUV luminescence
- high density (7 g/cm^3) –high gamma ray or X-ray stopping power
- Challenging crystal growth – melting point 945°C, phase transition (from orthorhombic to monoclinic) at ~900°C



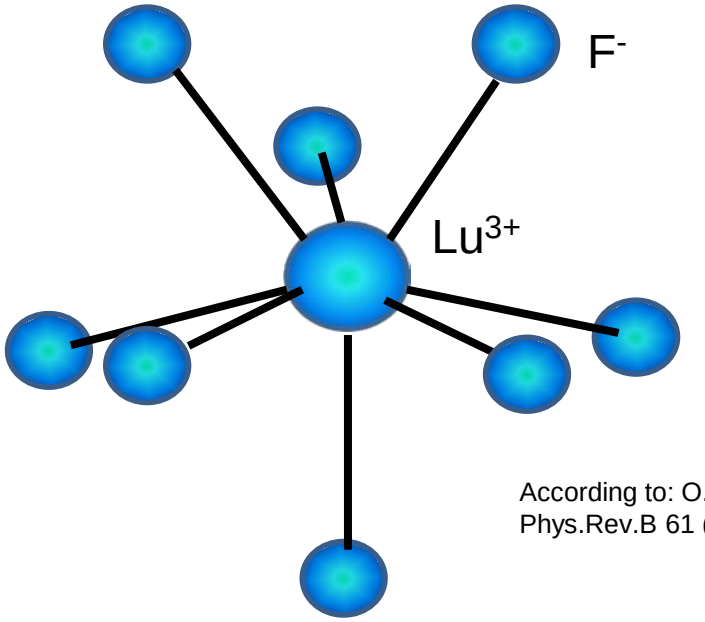
Phase diagram

According to (*B.P. Sobolev, N. L. Tkachenko, Journal of the less common Metals, 85 (1982) 155 - 170*

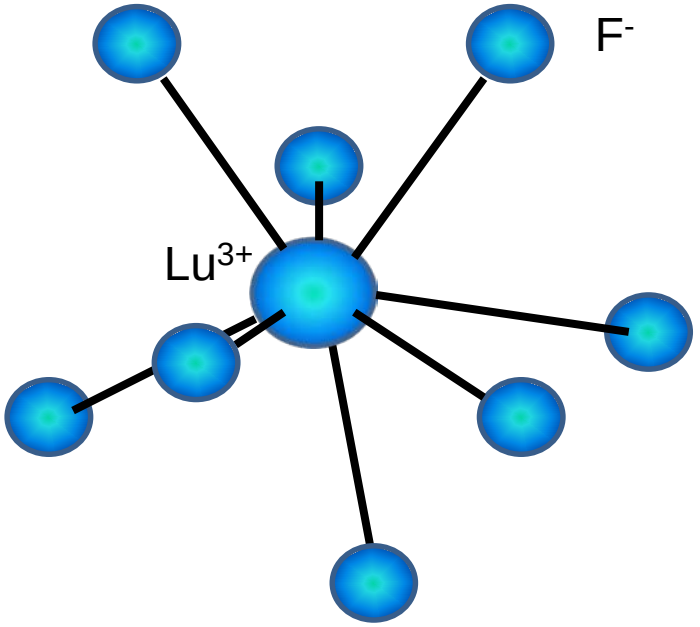
$BaLu_2F_8$ (BaLuF) - structure modifications

Monoclinic (low temperature) structure: C2/m space group, equivalent Lu sites – C_2 symmetry

Orthorhombic (high temperature) structure: Pnma space group, two inequivalent Lu-sites – C_1 symmetry



According to: O.S. Wenger et al.
Phys.Rev.B 61 (2000) 16530



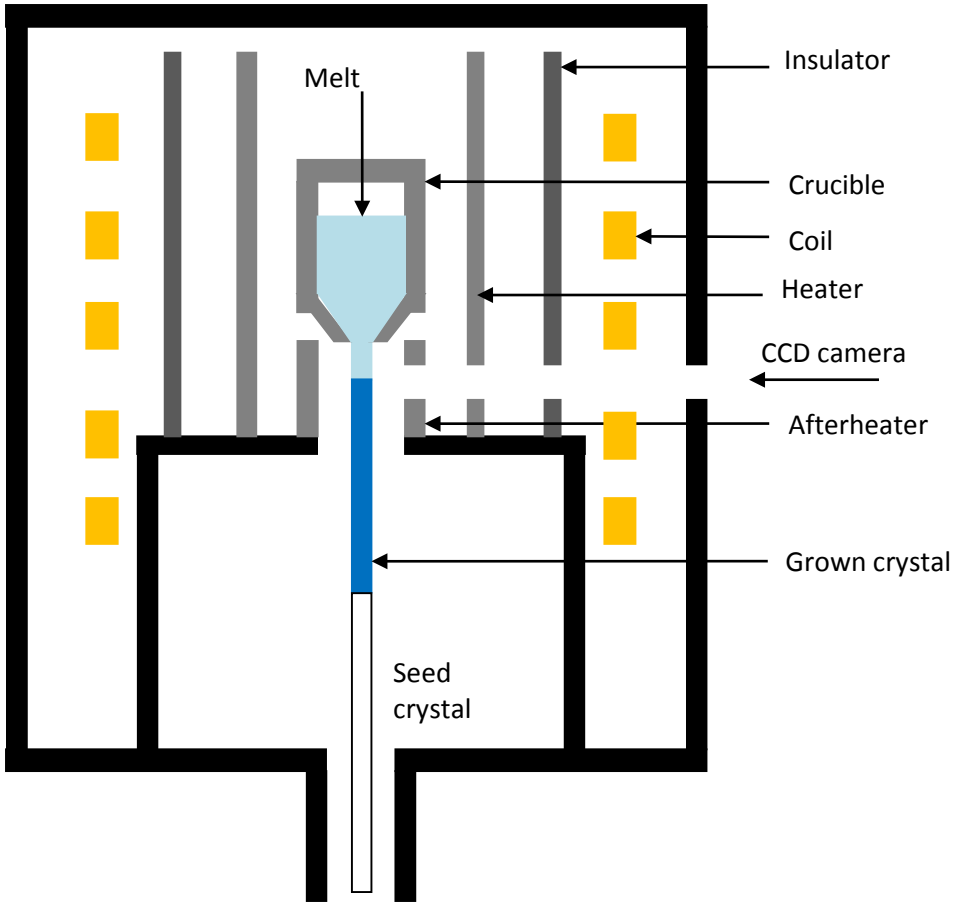
Lu^{3+} site 1 – "spherical"

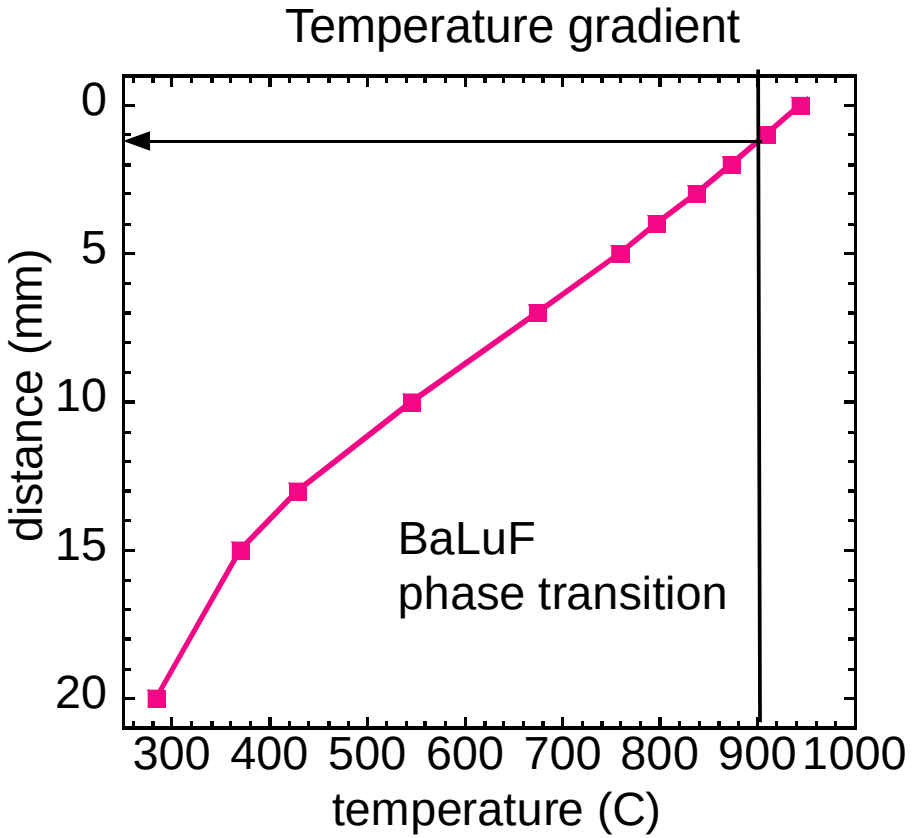
Lu^{3+} site 2 – distorted

Orthorhombic phase – two different sites for doping rare-earth ions

Crystal growth of monoclinic (low temperature) $BaLu_2F_8$

Standard hot-zone, standard crucible

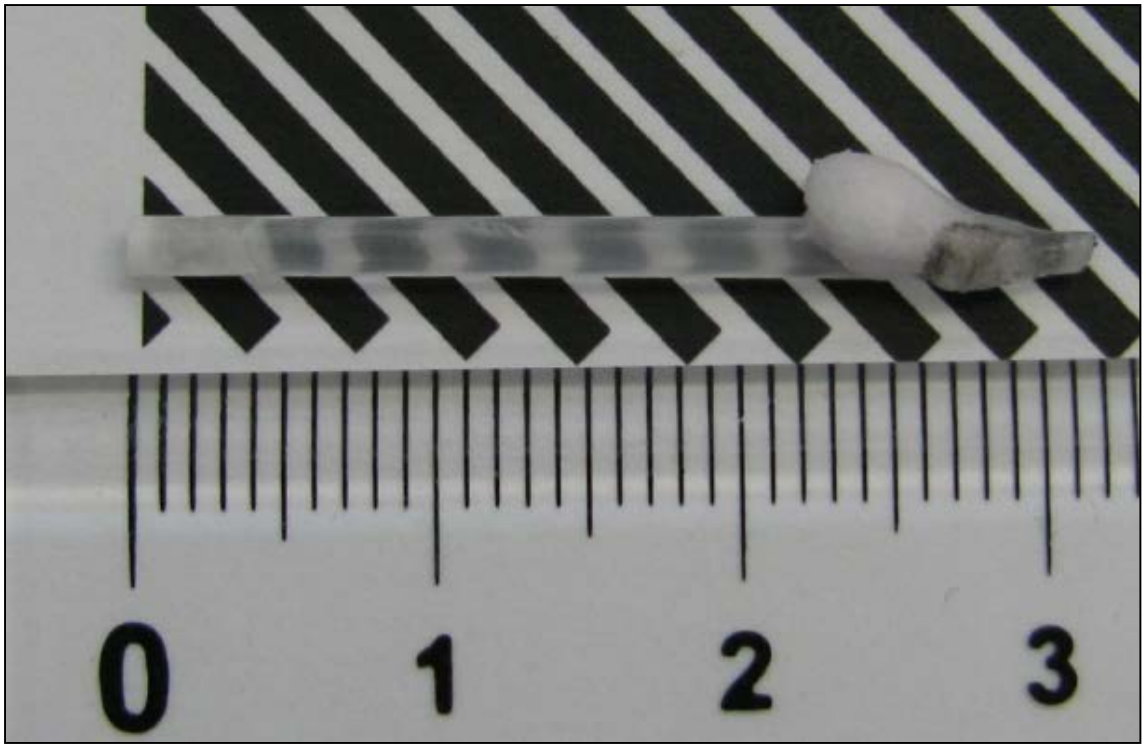




Measurement with Pt-PtRh thermocouple instead of seed, starting from crucible nozzle

Phase transition temperature measured ~1mm below nozzle – cracky crystal → slight melting temperature reduction necessary → LiF flux

Crystal growth of monoclinic $BaLu_2F_8$

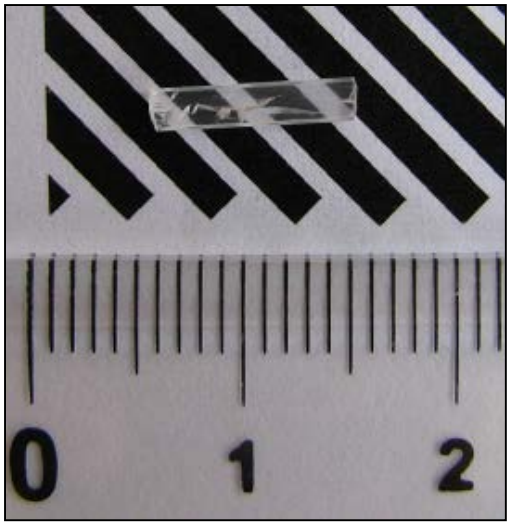


As-grown $BaLu_2F_8$:Nd1%

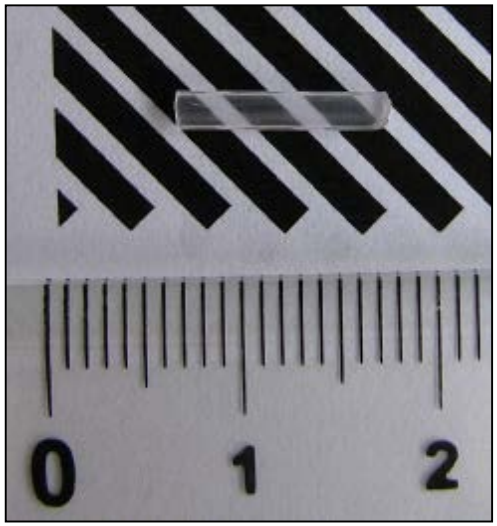
10 mol% LiF flux sufficient to lower the meting point under phase transition.
BaY_2F_8 seed. Monoclinic $BaLu_2F_8$ phase confirmed by XRD.

Samples prepared: **$BaLu_2F_8$** Undoped, Nd1%, Tm1%, codoped Tm1%Nd1% (to test possible $Tm^{3+} \rightarrow Nd^{3+}$ energy transfer)

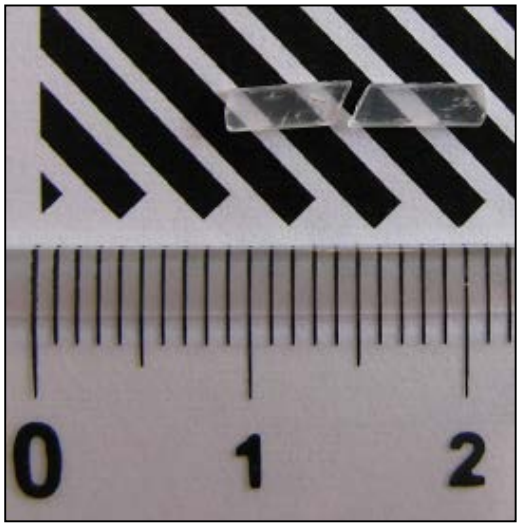
Samples of monoclinic (low temperature) $BaLu_2F_8$ after cutting and polishing



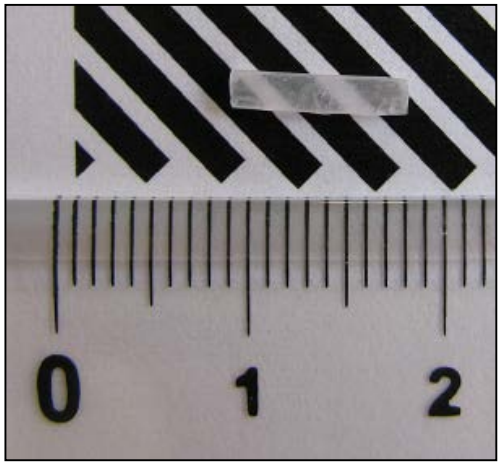
$BaLu_2F_8$ undoped



$BaLu_2F_8$:Nd1%

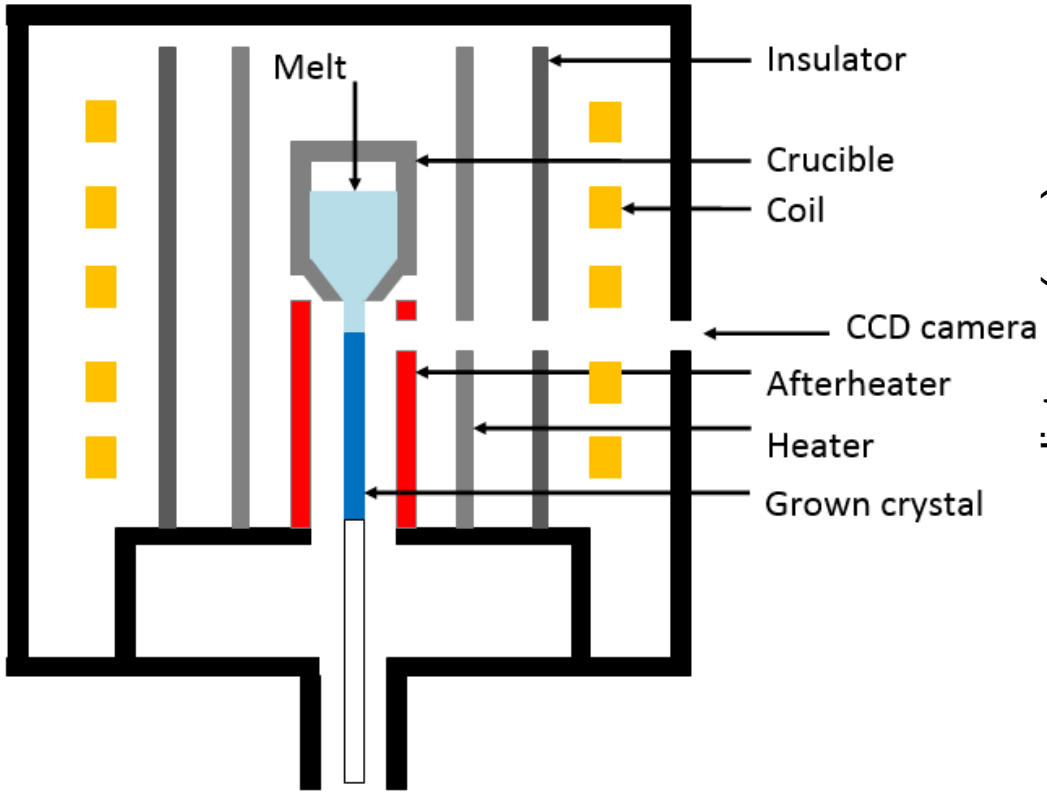


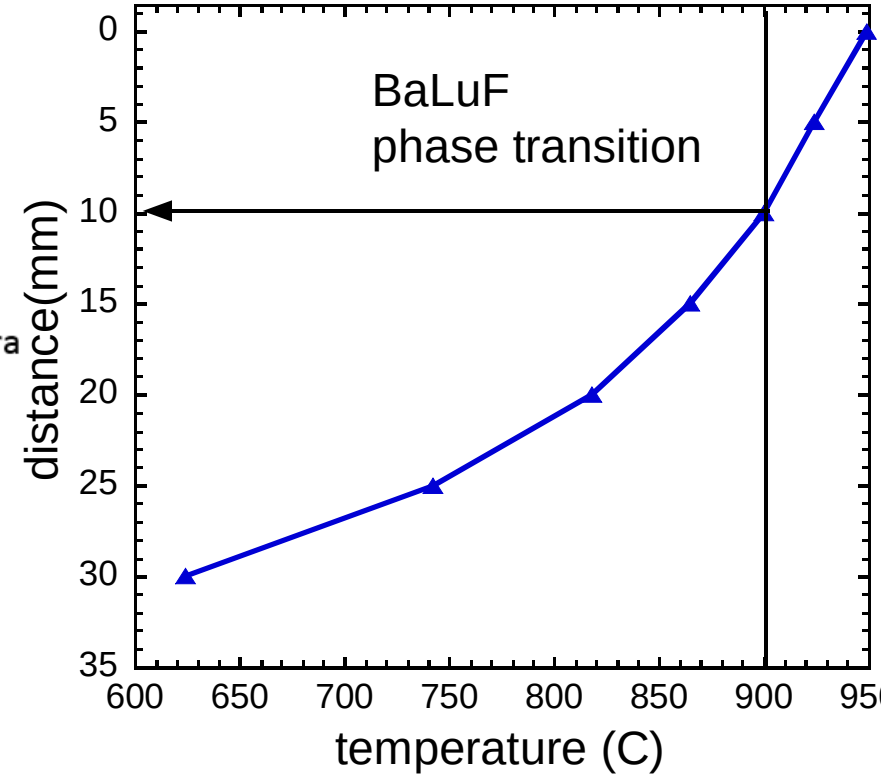
$BaLu_2F_8$:Tm1%

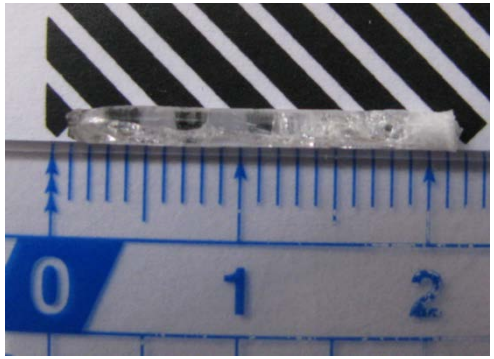


$BaLu_2F_8$:Tm1%Nd1%

Crystal growth of orthorhombic (high temperature) $BaLu_2F_8$
Hot zone search



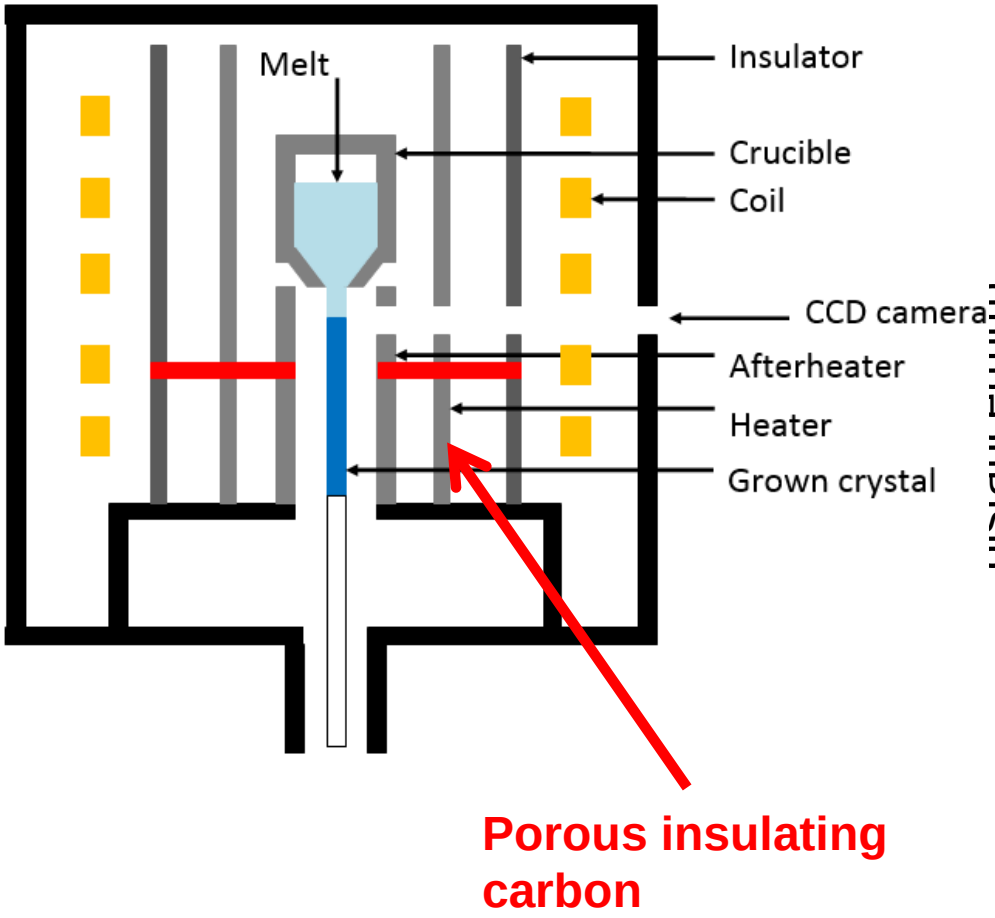


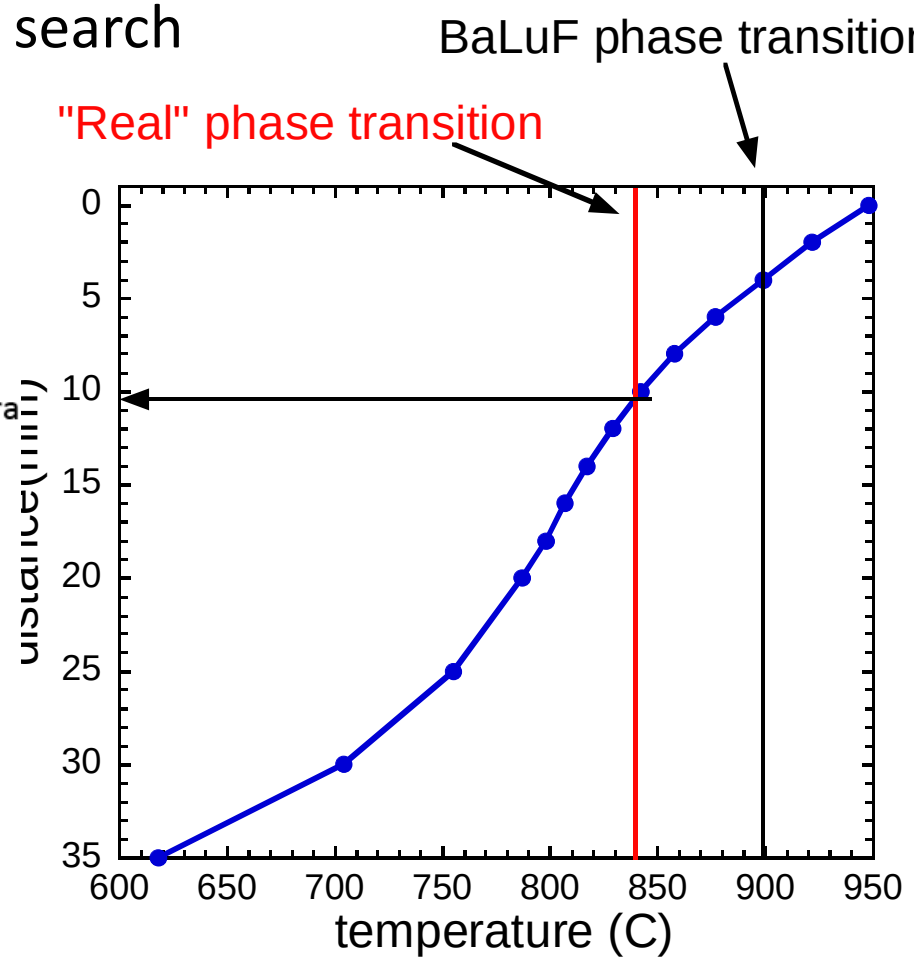


Long hot zone with long 40mm afterheater – not suitable due to high probability of melt drop, quenching process – partial success

Crystal growth of orthorhombic (high temperature) $BaLu_2F_8$

Hot zone search

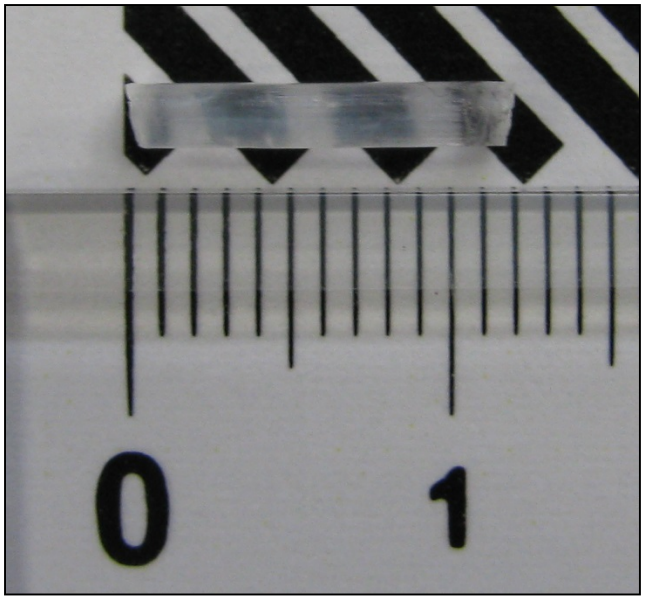




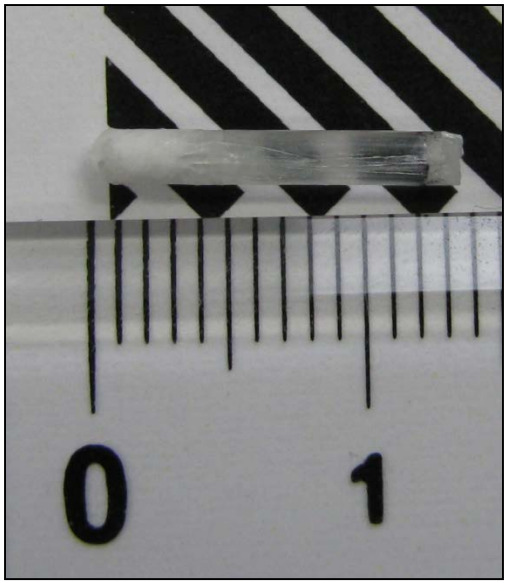
Regular hot zone with **"afterzone"** – suitable to grow around 10-15 mm crystals.

Phase transition occurs at distances higher than expected. Heat conduction through growing crystal significant. Quenching process applied

Crystal growth of orthorhombic BaLuF



As-grown crystal of orthorhombic $BaLu_2F_8$:Nd1%



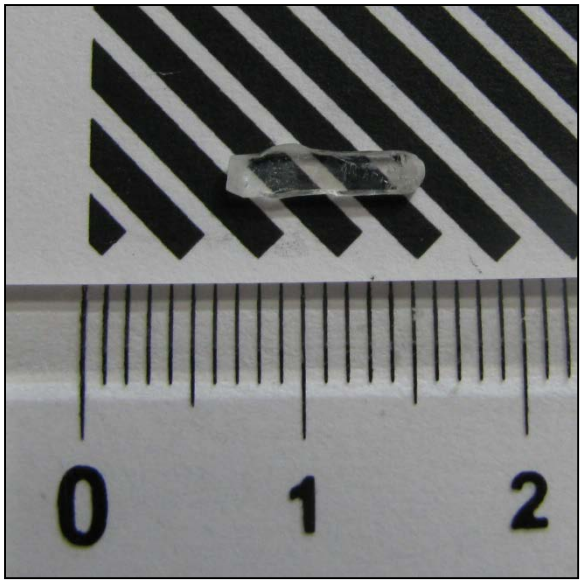
As-grown crystal of orthorhombic $BaLu_2F_8$:Tm1%

Orthorhombic phase confirmed by XRD (signs of monoclinic phase also detected)

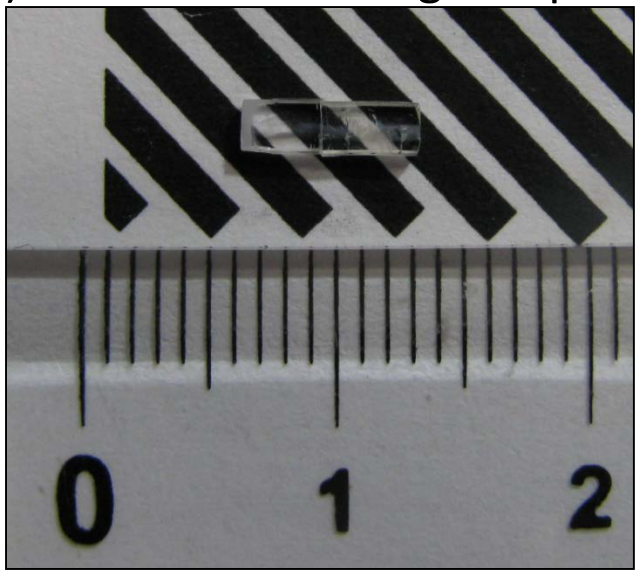
Samples prepared: **$BaLu_2F_8$** Undoped, Nd1%, Tm1%

codoped Tm1%Nd1% (to test possible $Tm^{3+} \rightarrow Nd^{3+}$ energy transfer in the host with inequivalent Lu^{3+} sites)

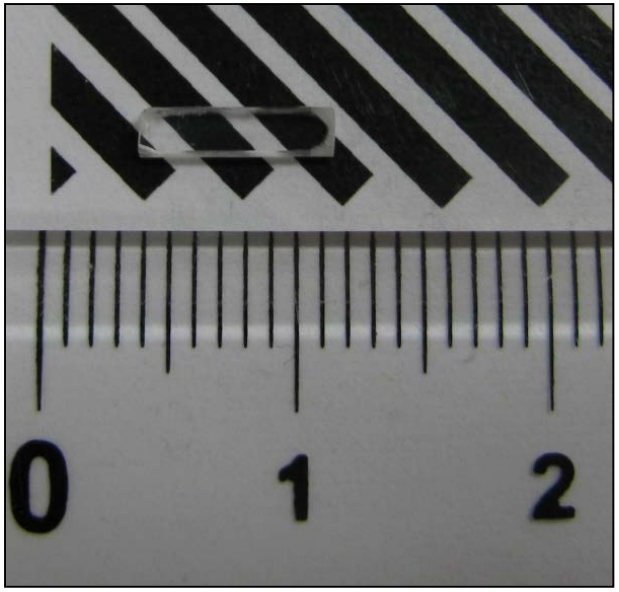
Samples of orthorhombic (high temperature) BaLuF after cutting and polishing



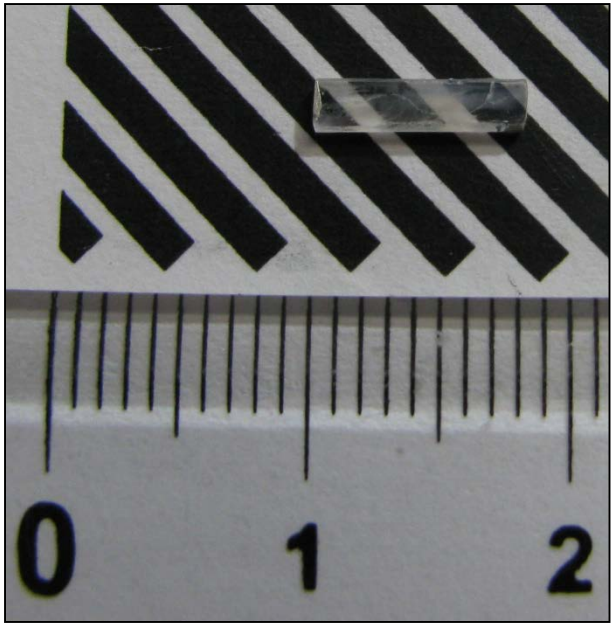
$BaLu_2F_8$ undoped



$BaLu_2F_8$:Nd1%



$BaLu_2F_8$:Tm1%



$BaLu_2F_8$:Tm1%Nd1%