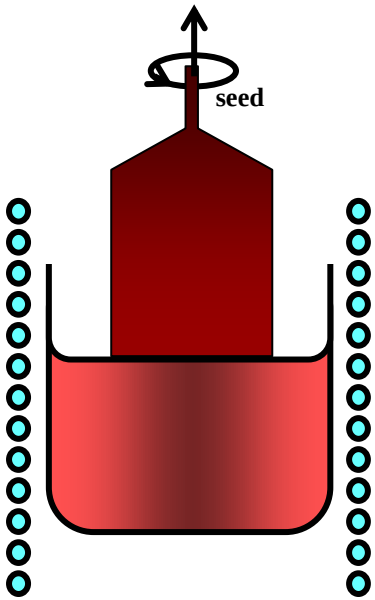
Precursors preparation for growth of low-background scintillation crystals

Laboratory of Crystal Growth, Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk 630090, Russiaa

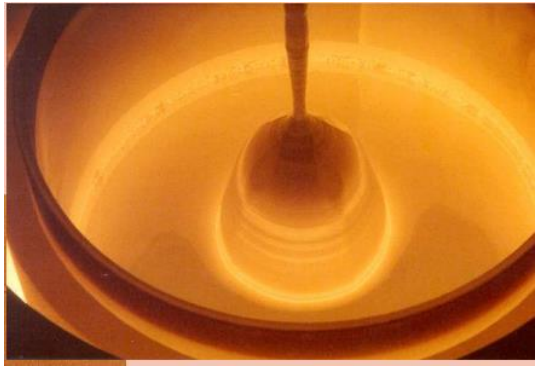
Factors ensuring high quality crystals

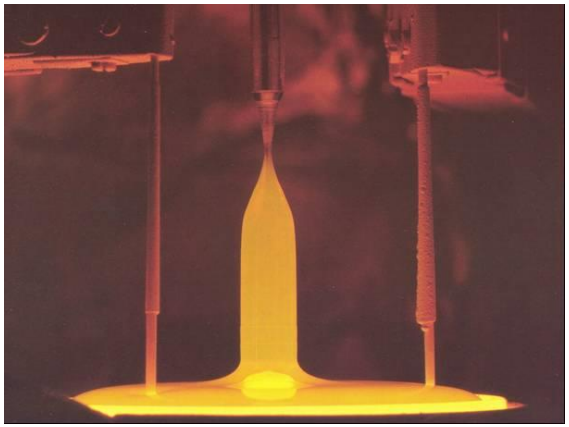
- **First order factor**
  - **Growth technique**
    - methods for synthesis of crystals
    - growth conditions
    - growth mechanism
  - **Initial materials**
    - methods of a synthesis and purification
    - impurity composition

Traditional Czochralski Technique

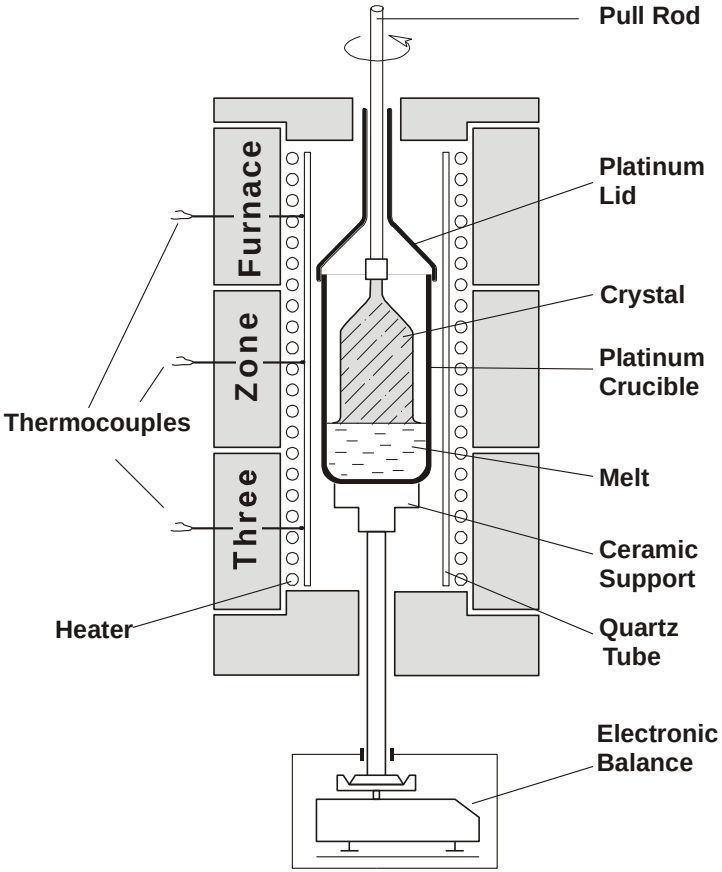


- High temperature gradient ***(10-100 K/cm)***
- Perfect cleavage of CWO, ZWO, NMO thermoelastic stress destroy crystal
- High local superheating of melt up to ***200 K***
- Evaporation and decomposition melt



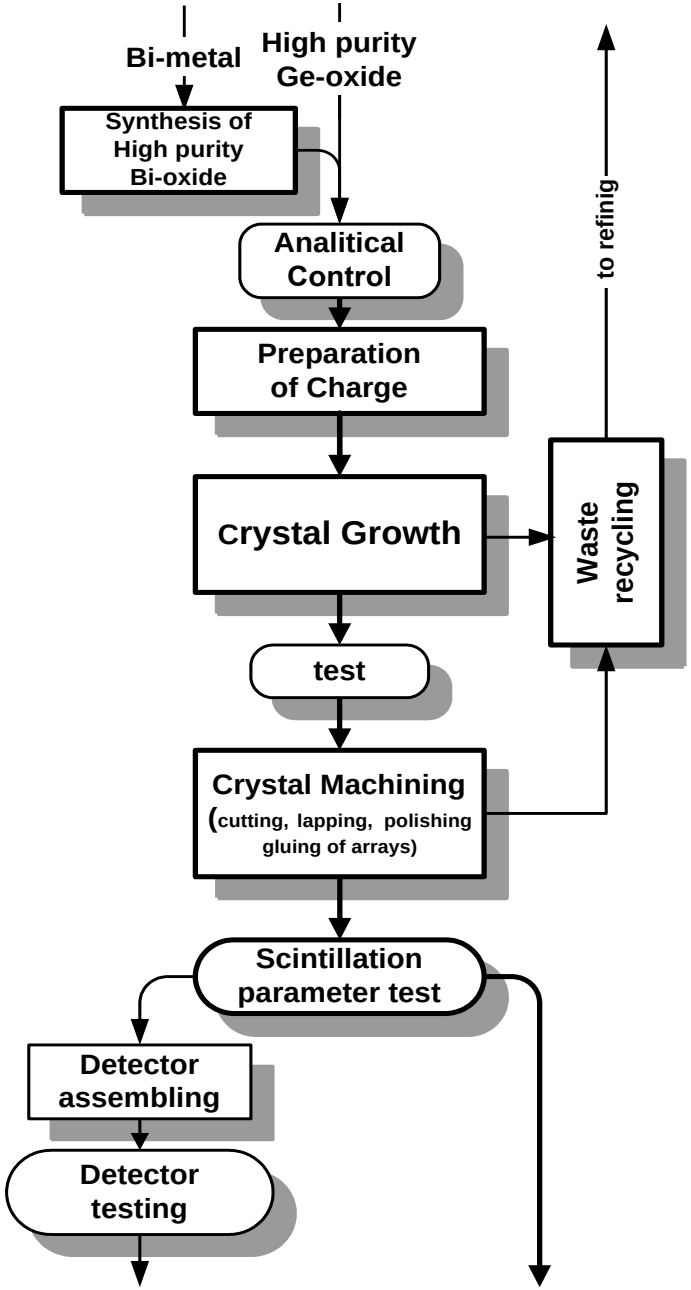


By the contrast ***in The Low Thermal Gradient Czochralski Technique (LTG Cz) the growth conditions are selected in such a way that the temperature gradients become small and the solidification front becomes fully faceted***



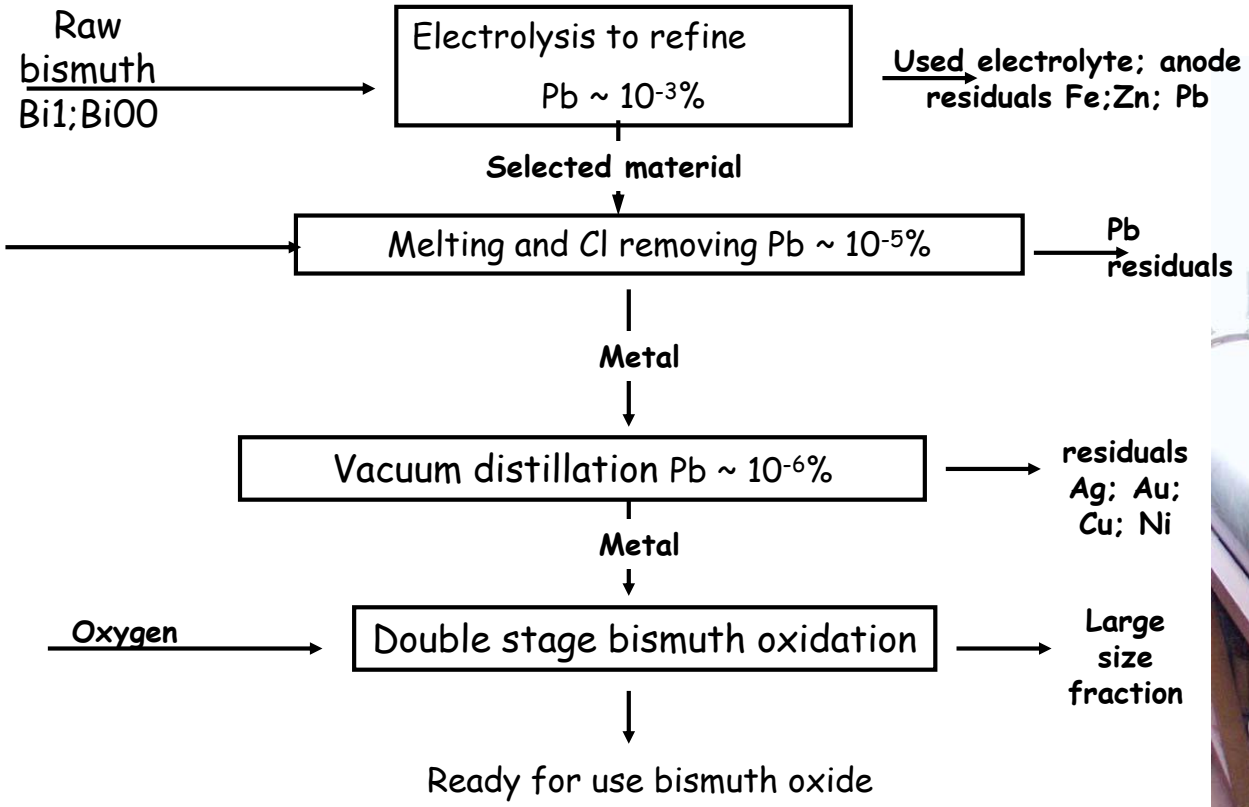
- **During the entire process the grown crystal stays inside the crucible**
- **Temperature gradients within 0.1-1 deg/cm.**
- **Temperature fluctuations in the melt, usually causing crystal inhomogeneities, are not developed**
- **Thermoelastic stresses in crystal are low**
- **Evaporation and decomposition processes are suppressed by the pipe socket, which works as a diffusion barrier**
- **Weighing control at all the stages of the process including the seeding**
- **Crystal dia./crucible dia. ratio up to ~0.8**

Phases of production BGO in NIIC, Novosibirsk



Small R & D sector
plus
off-budget-staff production sector

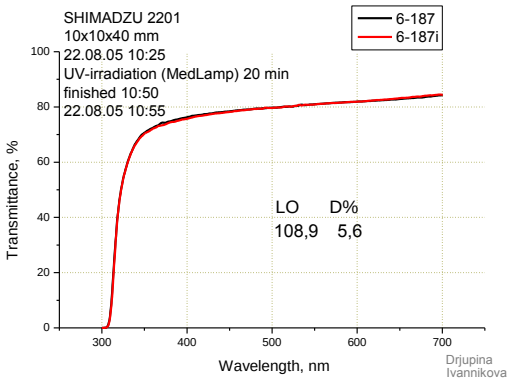
Bi-oxide synthesis and production at NIIC

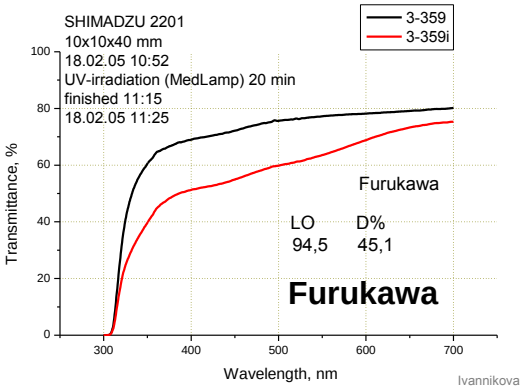


Properties can be drastically differ even for very low level of impurities

`Element % wt	NIIC	NIIC	Furukawa,Japan
	Bi_2O_3 BMO 1-60	Bi_2O_3 BMO 2-118	Bi_2O_3 Lot 04.11.17
C	$\leq 1 \cdot 10^{-3}$	$\leq 3 \cdot 10^{-3}$	$\leq 3 \cdot 10^{-3}$
Na	$7 \cdot 10^{-6}$	n.d.($5 \cdot 10^{-6}$)	n.d.($5 \cdot 10^{-6}$)
Mg	n.d.($5 \cdot 10^{-6}$)	n.d.($5 \cdot 10^{-6}$)	n.d.($5 \cdot 10^{-6}$)
Al	$\leq 3 \cdot 10^{-5}$	$\leq 3 \cdot 10^{-4}$	$\leq 3 \cdot 10^{-4}$
Si	$\leq 2 \cdot 10^{-4}$	$\leq 6 \cdot 10^{-4}$	$\leq 4 \cdot 10^{-4}$
Cl	$9 \cdot 10^{-4}$	$3 \cdot 10^{-3}$	$5 \cdot 10^{-4}$
K	$3 \cdot 10^{-5}$	n.d.($5 \cdot 10^{-6}$)	n.d.($1 \cdot 10^{-5}$)
Ca	$2 \cdot 10^{-5}$	n.d.($5 \cdot 10^{-6}$)	n.d.($1 \cdot 10^{-5}$)
Cr	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)
Mn	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)
Fe	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)
Cu	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)
Zn	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)
Ge	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)
Ag	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	n.d.($1 \cdot 10^{-5}$)
Te	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)	n.d.($1 \cdot 10^{-5}$)
Sb	n.d.($5 \cdot 10^{-6}$)	n.d.($5 \cdot 10^{-6}$)	n.d.($1 \cdot 10^{-5}$)

NIIC 1-60





Polyhedral Crystallization Front of Big Sized BGO Crystal

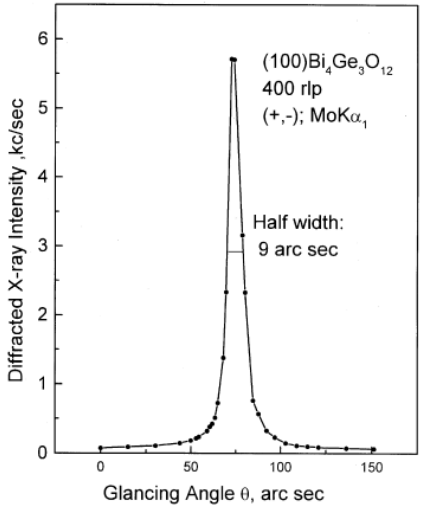
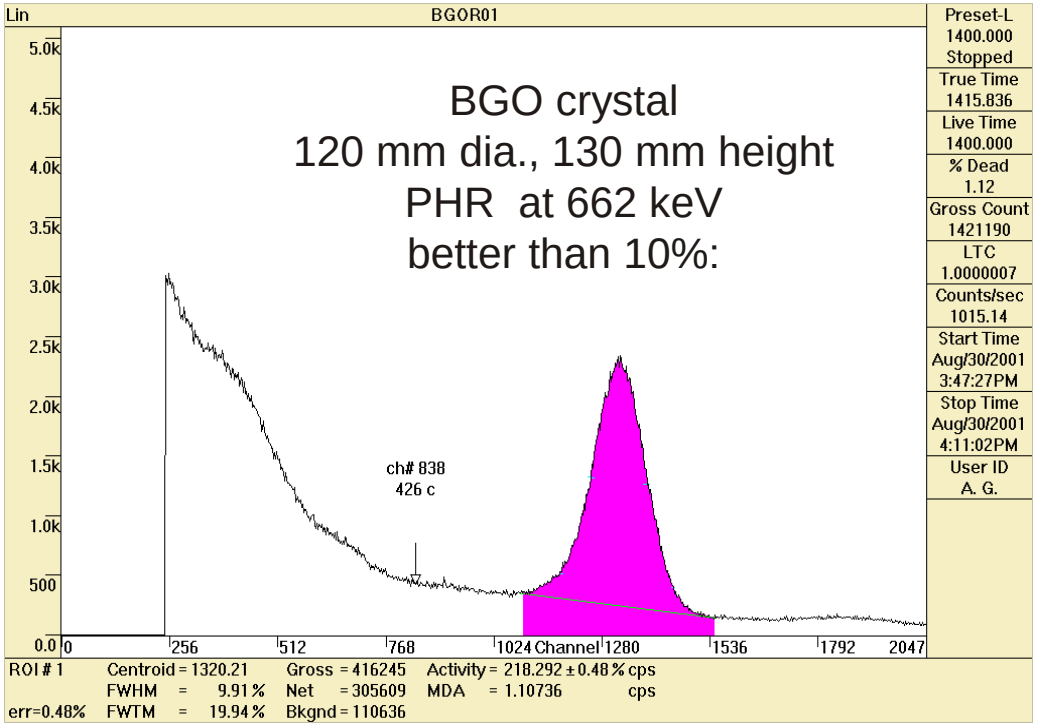


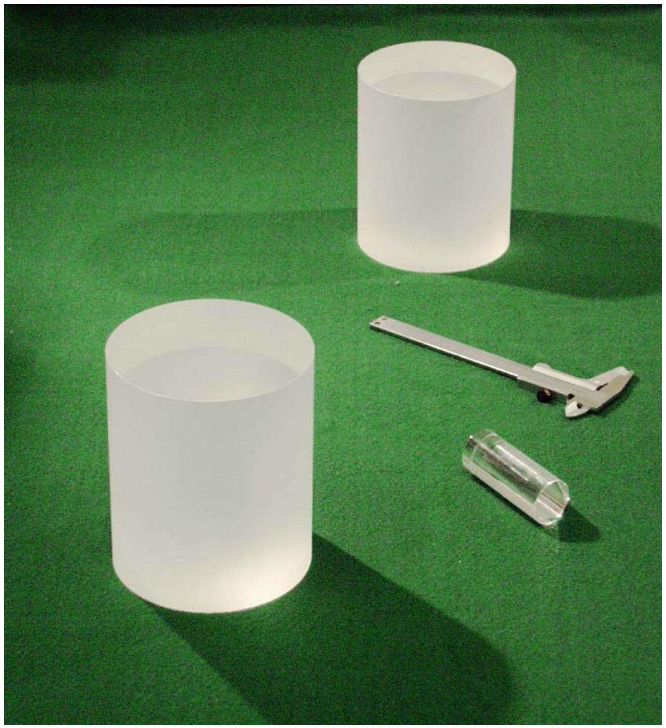
Fig. 5. A typical high-resolution X-ray diffraction curve of a (0 0 1) bismuth germanate single crystal recorded with 400 rlp from the central part of the specimen.

Krishan Lal et al. Journal of Crystal Growth 197 (1999) 865-873

120 mm dia. BGO cylinders

Due to high uniformity of crystals and low light absorption scintillation parameters almost does not worse with increasing of crystal dimensions

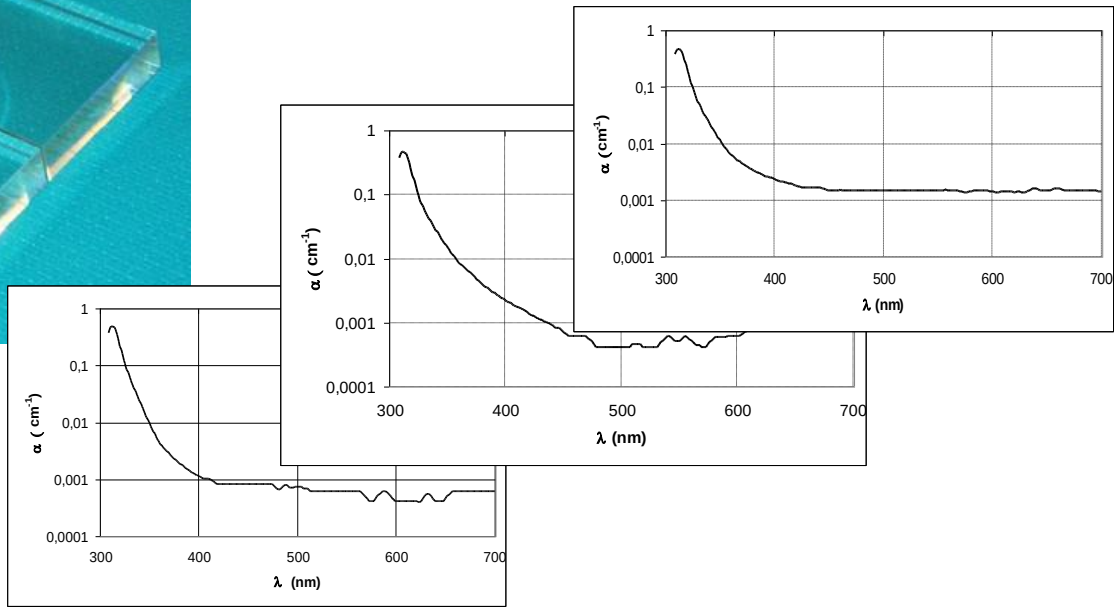




Radiation Hard Crystals for BGO Veto Shield of the Imager IBIS

as one of two main gamma-ray instruments on board of the ESA mission INTEGRAL
(The **Inte**rnational **G**amma-**R**ay **A**strophysics **L**aboratory) launched in Oct 2002

- The area to be shielded is about 8000 cm^2
- Bars dimensions : **20 x 90 x (310-345)** mm^3
- 20 krad radiation environment (induced by ionizing particles) for the lifetime of 5 years
- Due to features of light collection, top-quality transmission properties are needed.
  Attenuation length has to be better than 3 m



BGO crystals for PoGOLite International Project

(A High Sensitivity Balloon-borne Soft Gamma-ray Polarimeter)

Flight: 20013 Total weight of BGO >300 kg

Y. Kanai et al. / Nuclear Instruments and Methods in Physics Research A 570 (2007) 61–71

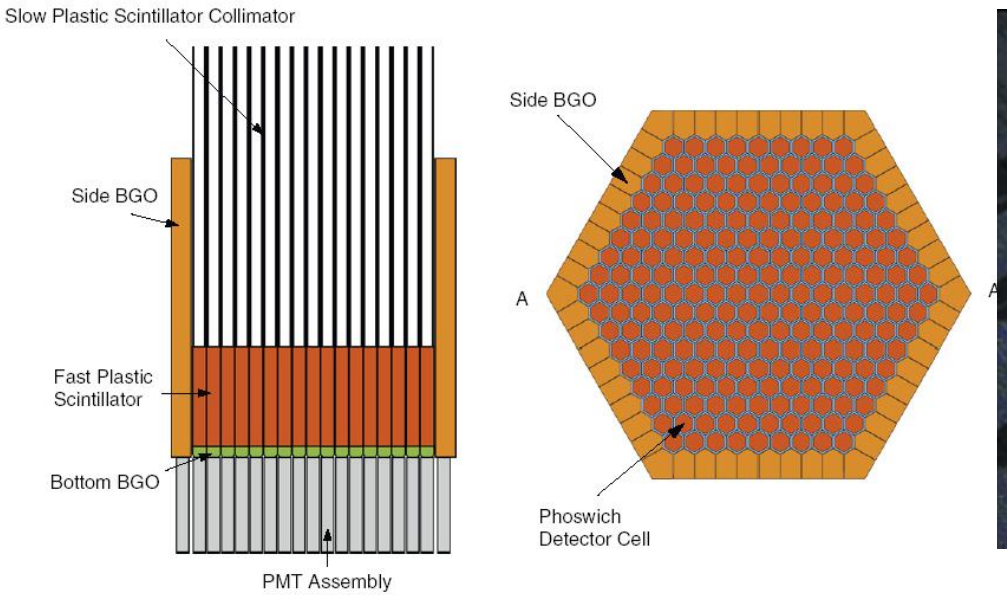
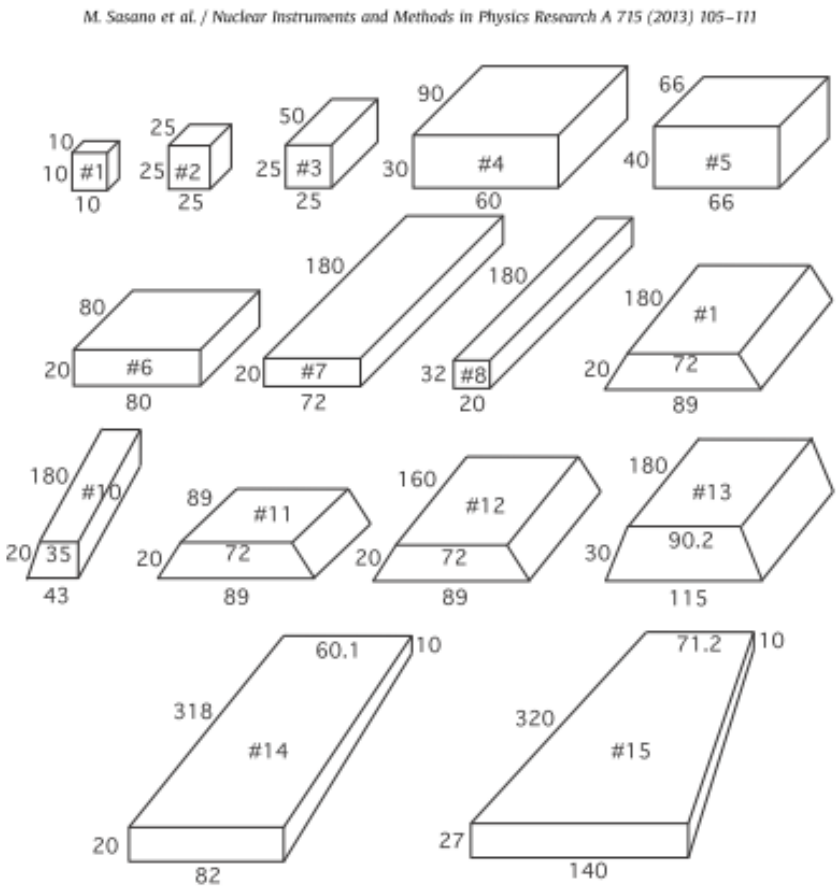


Fig. 1. The PoGOLite detector array. Vertical cross-section AA′ (left) and top view (right).

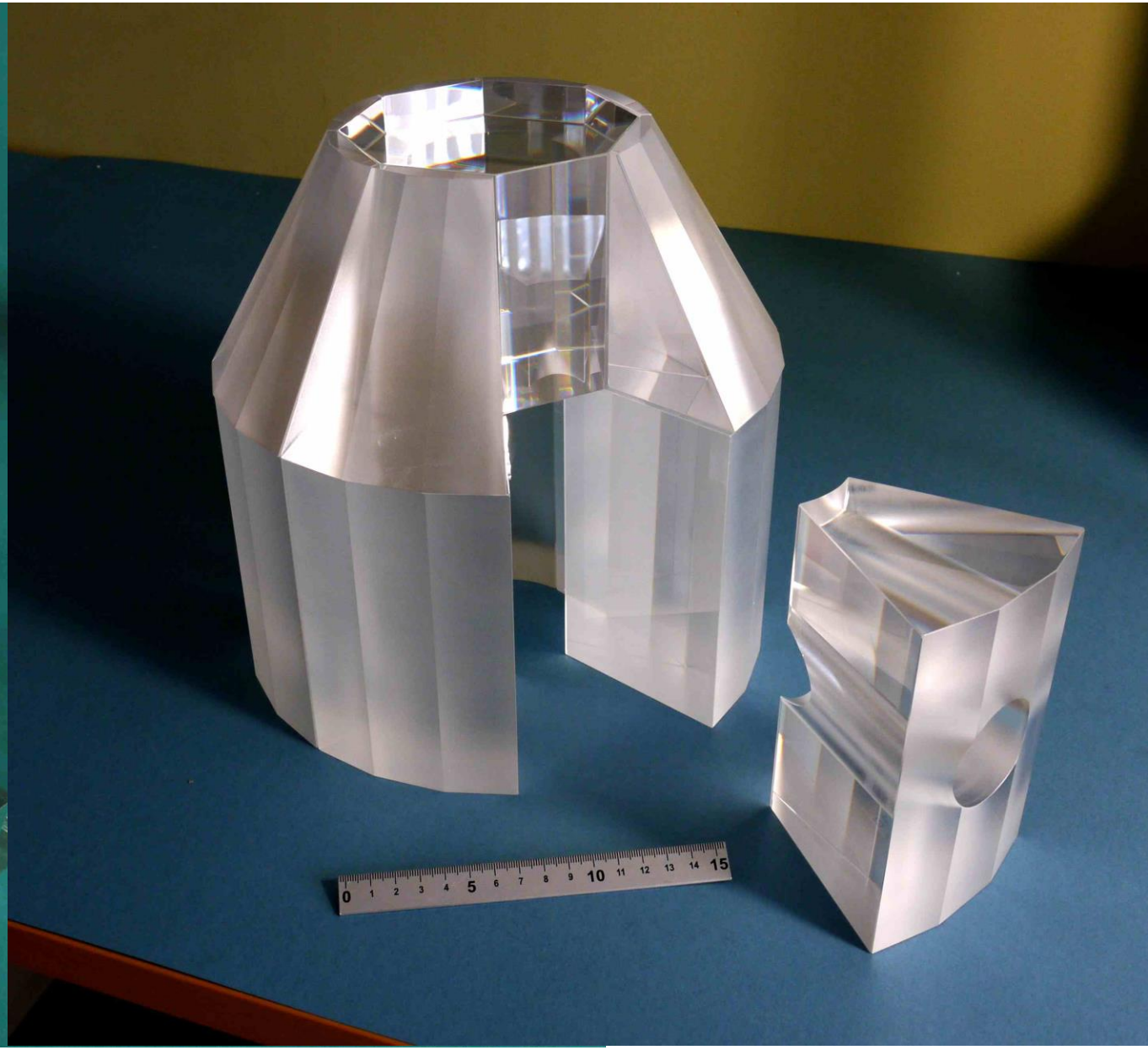
http://www.particle.kth.se/pogolite

Radiation hard BGO

for Hard X-ray Imager and the Soft Gamma-ray Detector, to be onboard the 6th Japanese X-ray Astronomy satellite ASTRO-H



2011-2013: About 15 types, 100 pieces totally


0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

CWO for neutrinoless 2β decay search

Collaboration with *Institute for Nuclear Research, Ukraine*
Max Plank Institute (Germany), INFN (Italy), CNRS (France)

The following advantages of LTG Cz are essential for 2β decay experiments:

- **Good scintillation parameters;**
- **Large maximal crystal size;**
- **High yield of successful growth runs;**
- **High utilization ratio of charge (~0.8)**

2006-2008:	**Evaluation of $CdWO_4$ crystals grown by the LTG Cz as detectors for high sensitivity double beta decay experiments was perfomed.** **CWO Ø 20x20 mm - Ø70x70 mm**

2009:	**Trial Growth of $^{106}CdWO_4$ crystal was performed**
2011:	**Trail growth of $^{116}CdWO_4$ crystals was performed**

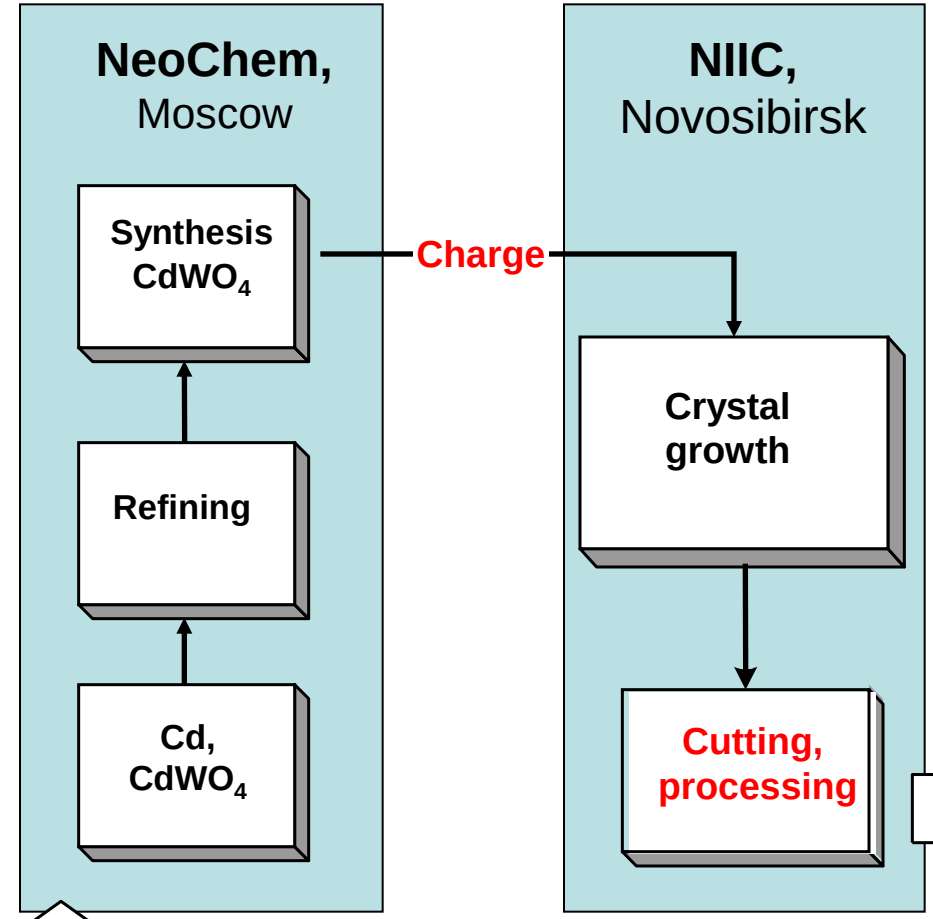
Main problems associated with growth $CdWO_4$, $ZnWO_4$, $ZnMoO_4$, $Na_2Mo_2O_7$ crystals

- **High tendency to crack under the action of thermoelastic stresses associated with the existence of the cleavage plane.**
- **High segregation (distribution) coefficient for iron group ions:**

  1) Re-crystallization does not improve properties;
  2)The residual crystal parts hardly could be utilized
- The volatility of the components of the melt results in changing stoichiometric ratio Me/(W, Mo) in the growth process.
- Deviation from stoichiometry in oxygen does not investigated properly

  $(Zn,Cd)WO_4 \Rightarrow (Zn,Cd)WO_{4-x} + x/2O_2$

Growth of isotopically enriched $^{106}CdWO_4$ and $^{116}CdWO_4$



Crystal, year	$^{106}CdWO_4$ 2009	$^{116}CdWO_4$ 2010
Raw charge:	**265 g**	**2140 g**
isotope content	66,4 %	82 %
Crucible:, mm	Ø40x100	Ø70x190
Growth direction	[100]	[100]
Crystal diameter:	~27 mm	~45 mm
Crystal weight:	**230,5 g**	**1868 г**
Residuals in crucible:	33,7 g	267,7 g
Losses:	0,79 g	2,8 g
Utilization factor:	**87 %**	**87,3 %**

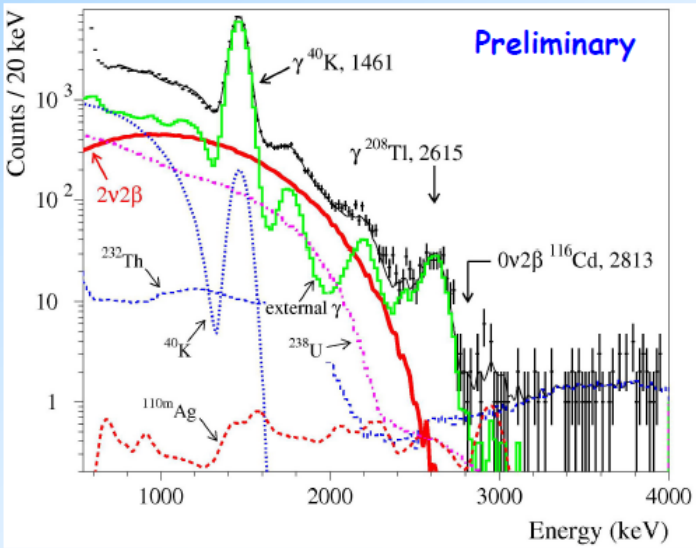
crystals $^{106/116}CdWO_4$

raw material $^{106/116}Cd$

Technology of growing crystals CWO by LTG Cz allows to solve the problem of obtaining crystals for the next stage of a possible experiment with detectors $^{116}CdWO_4$

Radioactive contamination of $^{116}CdWO_4$ crystals

Background $^{116}CdWO_4$ (stage 2)



PSD γ(β), ≈88%

Source	Activity in $^{116}CdWO_4$, mBq/kg			
	No.1	No.2	^{116}CWO [1]	^{106}CWO [2]
^{232}Th	≤ 0.08 [b]	≤ 0.08 [b]	0.053(9) [b]	≤ 0.07 [b]
^{228}Ra	≤ 0.2 [a]	≤ 0.2 [a]	≤ 0.004 [a]	–
^{228}Th	0.041(6) [c]	0.072(8) [c]	0.039(2) [c]	0.042(4) [c]
^{227}Ac	≤ 0.002 [c]	≤ 0.002 [c]	≤ 0.01 [c]	–
$^{238+234}$U	≤ 0.4 [b]	≤ 0.6 [b]	≤ 0.6 [b]	≤ 0.6 [b]
^{230}Th	≤ 0.06 [b]	≤ 0.05 [b]	≤ 0.5 [b]	≤ 0.4 [b]
^{226}Ra	≤ 0.005 [b]	≤ 0.005 [b]	≤ 0.004 [b]	0.012(3) [b]
^{210}Po	≤ 0.4 [b]	≤ 0.6 [b]	≤ 0.4 [b]	≤ 0.2 [b]
Σ α	2.1(2) [b]	2.9(3) [b]	1.4(1) [b]	2.1(2) [b]
^{40}K	≤ 0.9 [a]	≤ 0.9 [a]	0.3(1) [a]	≤ 1.4 [a]
^{90}Sr-^{90}Y	≤ 0.1 [a]	≤ 0.1 [a]	≤ 0.2 [a]	≤ 0.3 [a]
^{110m}Ag	0.12(4) [a]	0.12(4) [a]	–	≤ 0.06 [a]
^{113}Cd	100(10) [d]	100(10) [d]	91(5) [a]	182 [d]
^{113m}Cd	460(20) [d]	460(20) [d]	1.1(1) [a]	116(4)×10^3 [a]
^{137}Cs	≤ 0.3 [a]	≤ 0.05 [a]	0.43(6) [a]	–

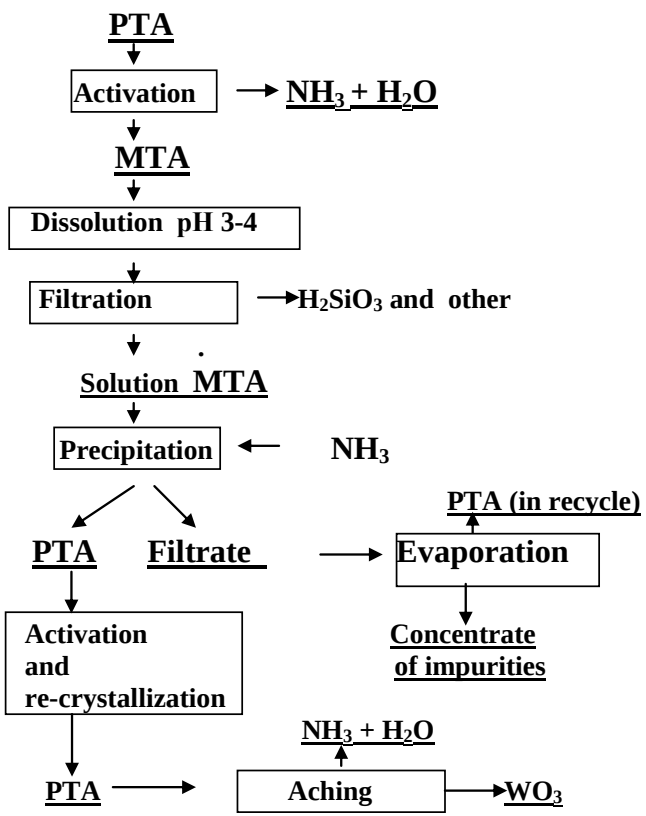
[a] Fit of background spectra; [b] Pulse shape discrimination;
[c] Time-amplitude analysis; [d] ICP-MS analysis

Absolute isotopic composition of the enriched 116Cd

Atomic number	Enriched ^{116}Cd	Natural cadmium [3]
106	0.11 ± 0.01	1.25 ± 0.06
108	0.10 ± 0.01	0.89 ± 0.03
110	1.80 ± 0.05	12.49 ± 0.18
111	2.00 ± 0.05	12.80 ± 0.12
112	4.35 ± 0.04	24.13 ± 0.21
113	2.14 ± 0.06	12.22 ± 0.12
114	7.30 ± 0.06	28.73 ± 0.42
116	82.2 ± 0.1	7.49 ± 0.18

[1] F.A. Danevich et al., PRC 68 (2003) 035501. [2] P. Belli et al., PRC 85 (2012) 044610

Purification and pilot production of WO_3 in NIIC



Element	Initial probe	Probe 5	Probe 6
Ag	n.d.(1×10^{-7})	$4{,}0\times 10^{-7}$	n.d.(1×10^{-7})
Al	5.0×10^{-5}	$\leq 5.0\times10^{-6}$	n.d.(4×10^{-6})
Be	-	n.d.(1×10^{-7})	n.d.(1×10^{-7})
Ba	1.2×10^{-5}	n.d.(1×10^{-5})	n.d.(1×10^{-5})
Ca	1.1×10^{-4}	$1.2\cdot \times10^{-5}$	1.5×10^{-5}
Co	2.0×10^{-5}	n.d.(1×10^{-6})	n.d.(1×10^{-6})
Cr	3.5×10^{-4}	n.d.(1×10^{-6})	n.d.(1×10^{-6})
Cu	1.1×10^{-5}	n.d.(3×10^{-7})	3.6×10^{-7}
Mg	$1.9\times\cdot10^{-5}$	1.4×10^{-5}	1.7×10^{-5}
Mn	3.4×10^{-5}	2.8×10^{-6}	$4.1\times\cdot 10^{-7}$
Ni	8.7×10^{-6}	n.d.(1×10^{-6})	n.d.(1×10^{-6})

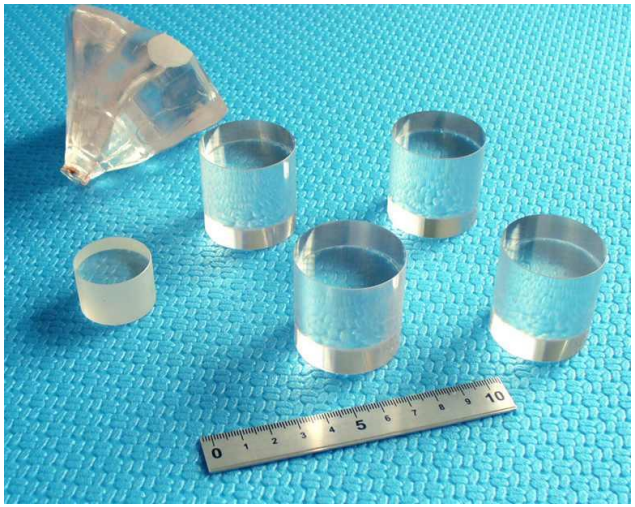
MTA- metatungstenate of ammonium [$(NH_4)_6H_2W_{12}O_{40}$]

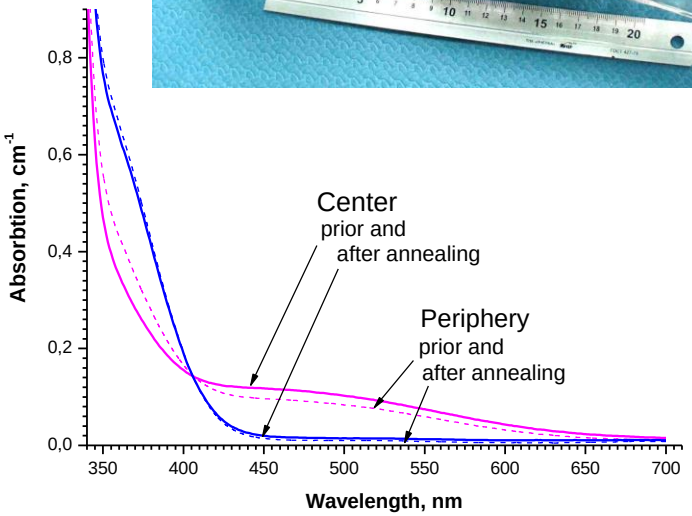
PTA – paratungstenate of ammonium [$(NH_3)_{10}W_{12}O_{41}7H_2O$]

*Inorganic Materials, **44,** No. 12, pp. 1330–1333 (2008).*

2010 : Growth of large size radiopure $ZnWO_4$ crystals

RHR ~10% at gammas 662 keV
for Ø40x40 mm cylinders





Collaboration with

- ***Institute for Nuclear Res., Kyev***
- ***Max Plank Institute (Germany)***
- ***INFN (Italy)***

Проект LUMINEU

Luminescent **U**nderground **M**olybdenum **I**nvestigation for **NEU**trino mass and nature

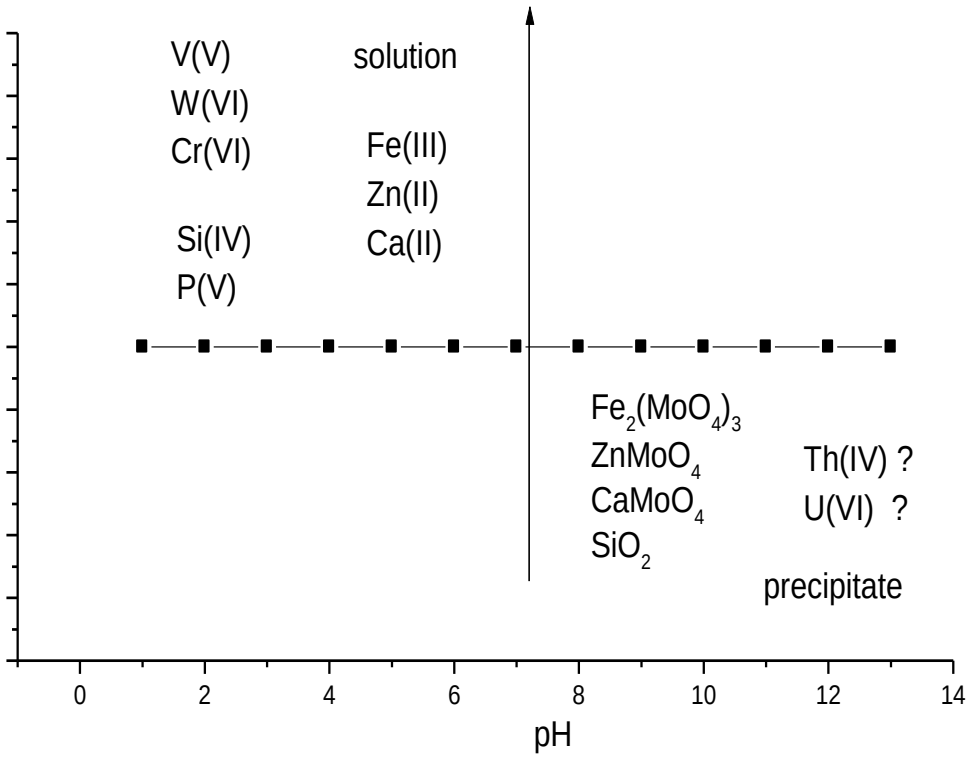
- **ICMCB** (**CNRS**)
- **UNIVERSITE PARIS-SUD** (**CNRS**)
- **CEA, Commissariat à l'énergie atomique et aux énergies alternatives**
- **KINR, Institute for Nuclear Research of the National Academy of Sciences of Ukraine**
- **NIIC**
- **UHEI, Heidelberg University, Seminarst (Germany)**

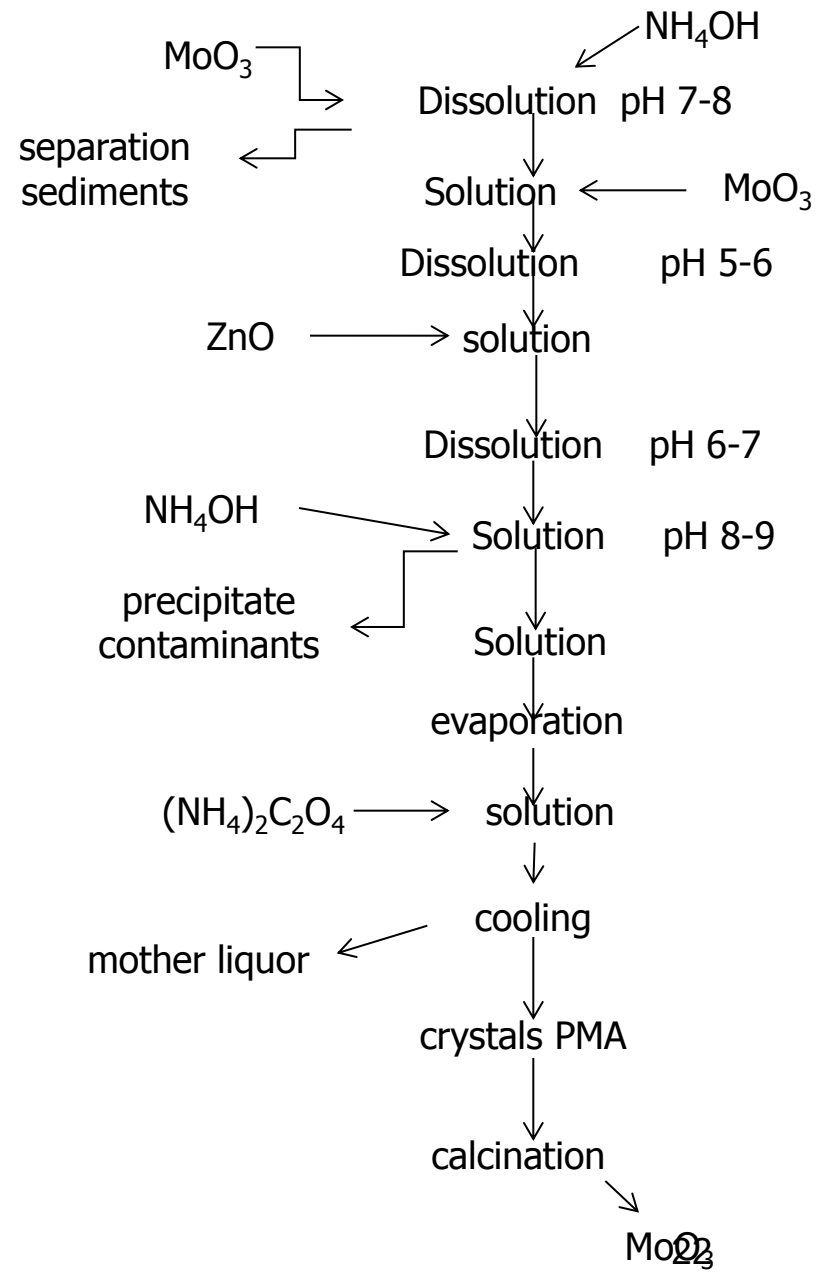
First results growth ZMO crystals

Institute for Scintillation Materials, Kharkov, Ukraina

Prokhorov General Physics Institute, Russian Academy of Sciences

MoO_3 purification scheme



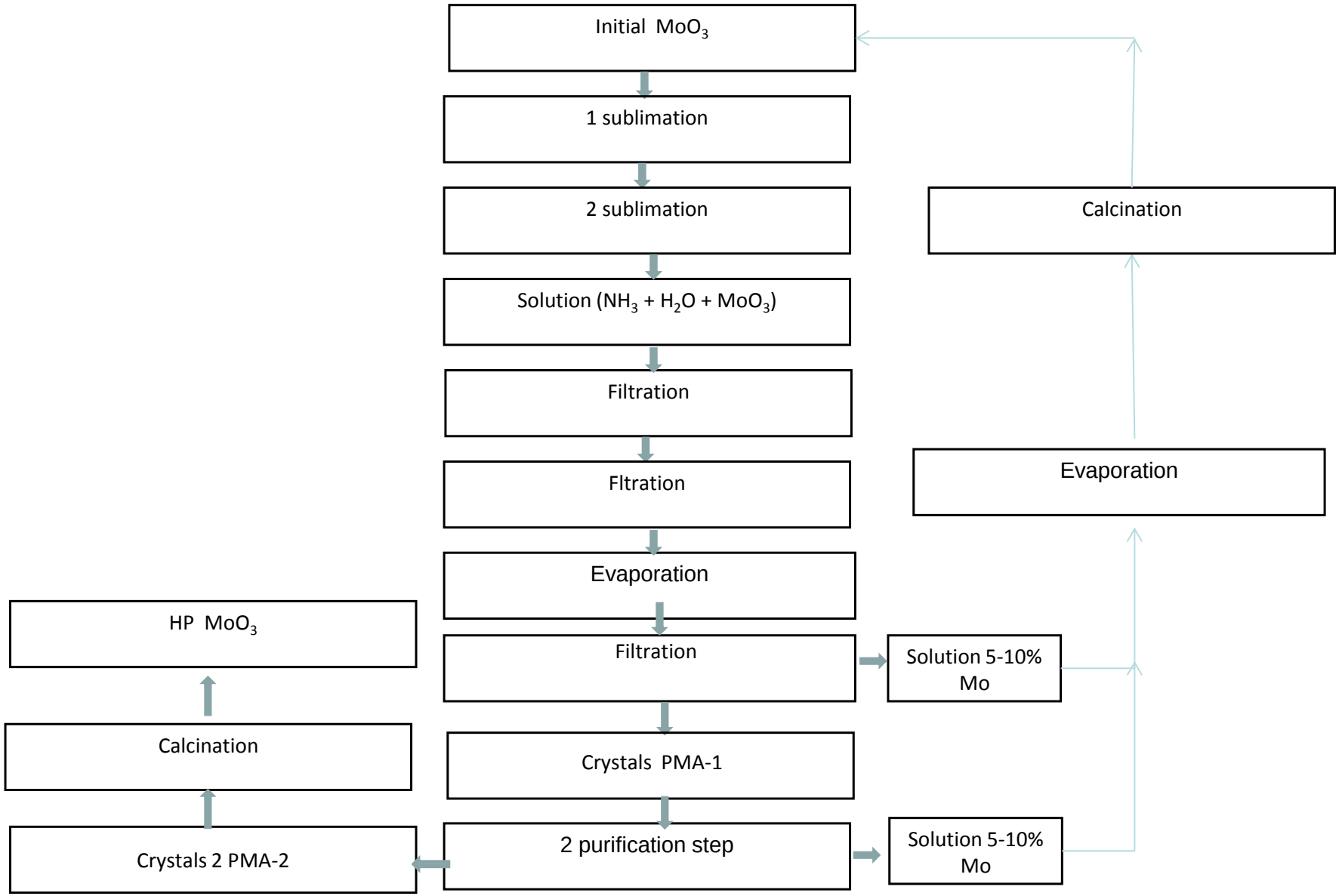


Purification of MoO_3 (sublimation process)

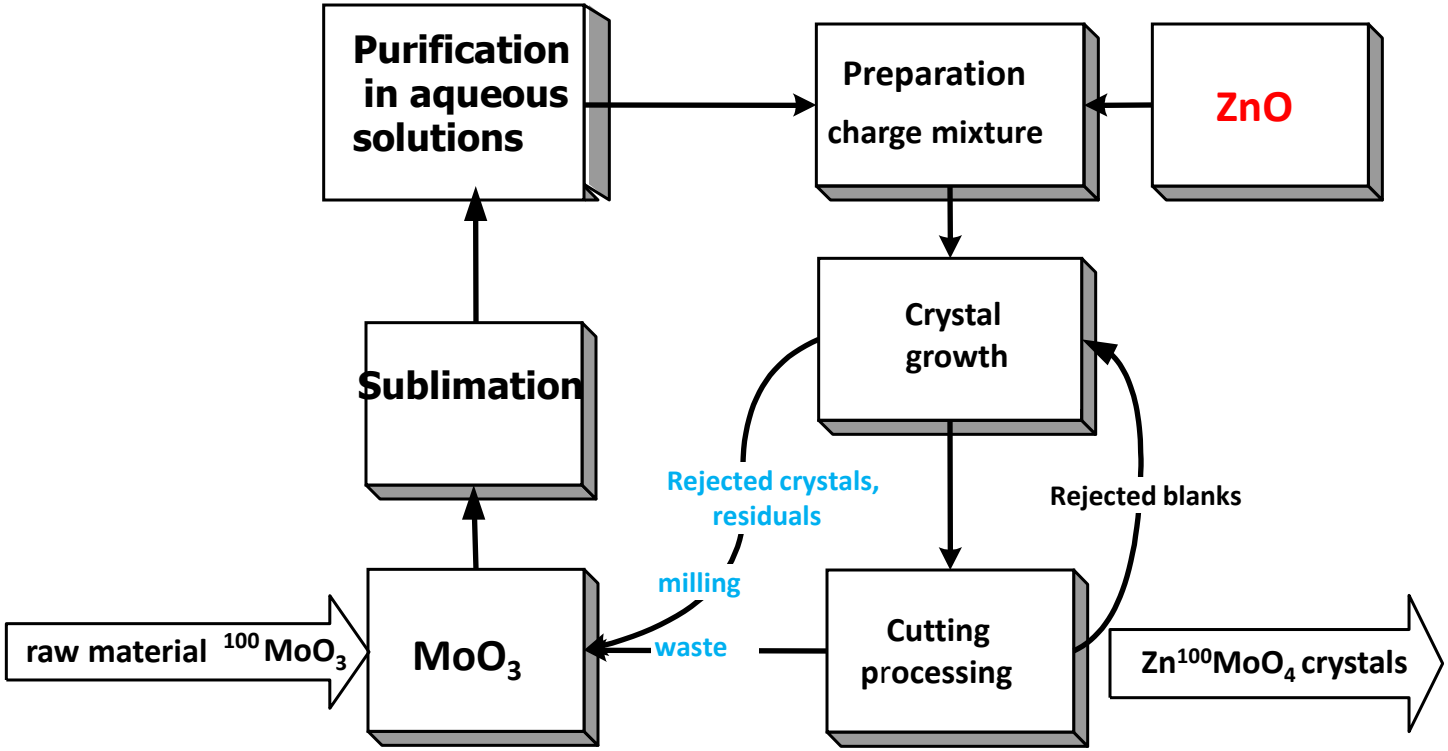
- *The temperature up to 700°C*
- *Pump vacuum*
- *Starting material MoO_3 (metallic impurities 10-100 ppm)*
- *Single entry sublimation reduces the content of: W, Fe, Cr more than one order*
- *Productivity the laboratory setup 1-2 kg/week*

23

Modified MoO_3 purification scheme

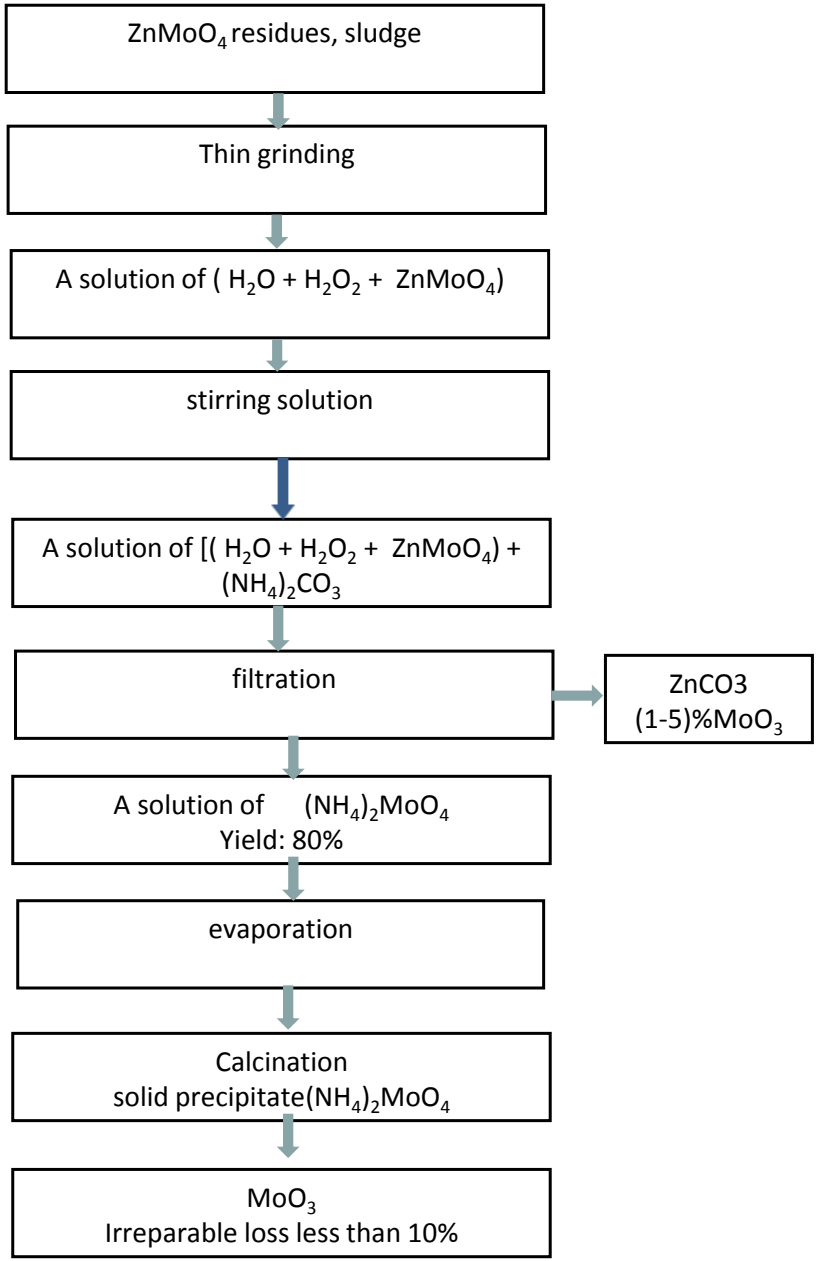


ZMO crystal growth in NIIC



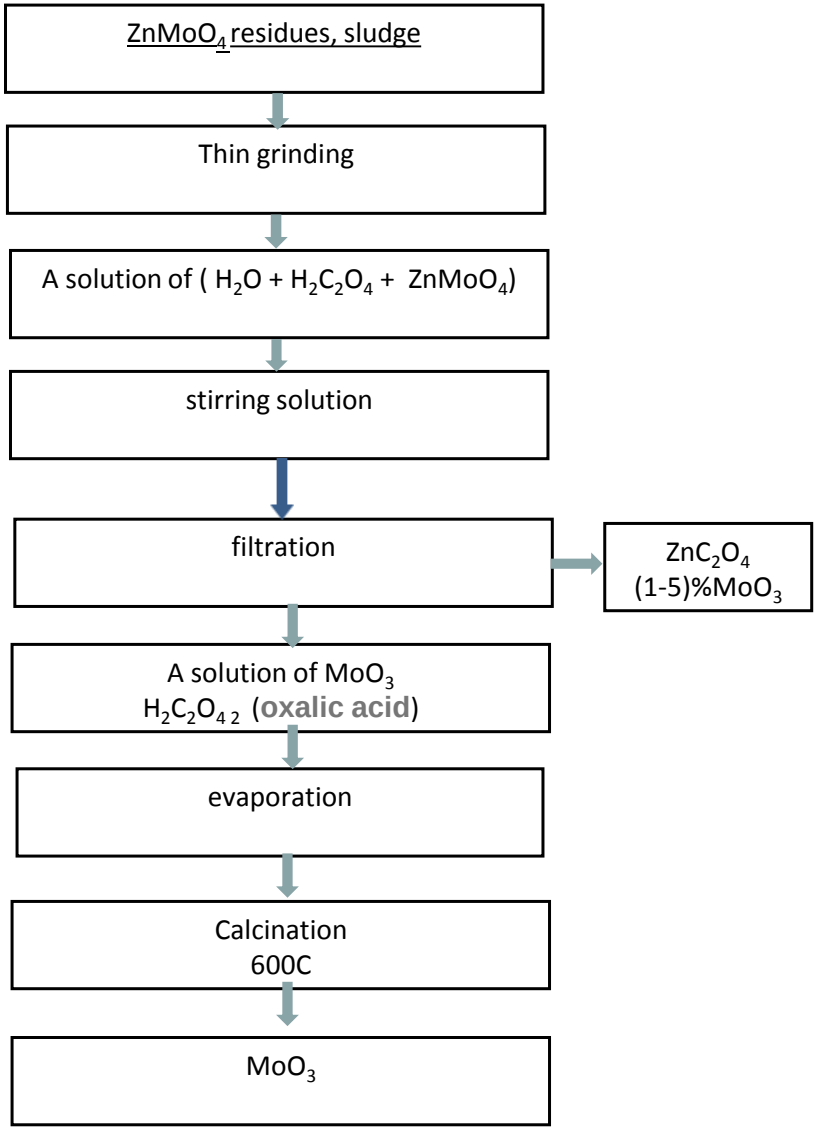
Extraction of MoO_3 from $ZnMoO_4$ residues, sludge

Scheme 1



Extraction of MoO_3 from $ZnMoO_4$ residues, sludge

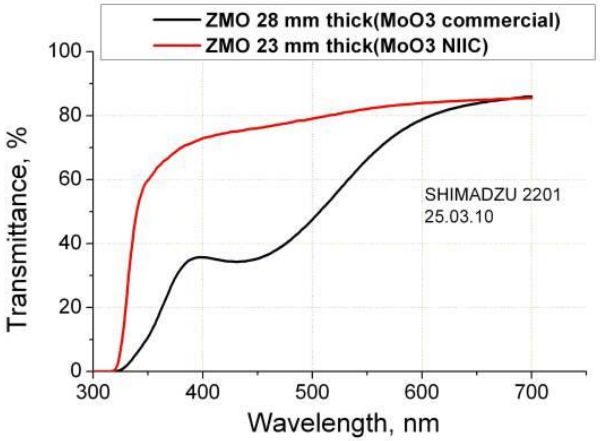
Scheme 2

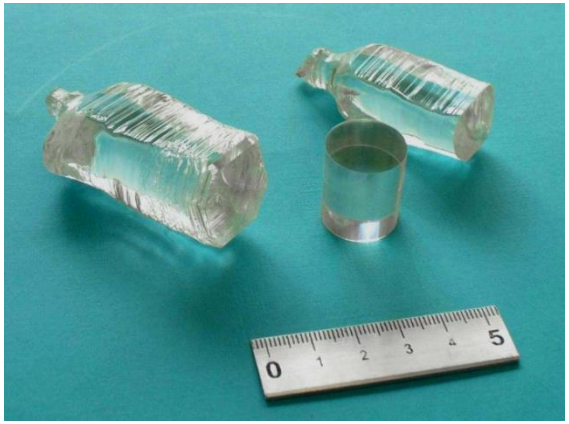


$Zn^{100}MoO_4$: one of the most promising candidate for the search of neutrinoless double-beta decay

Growth of $ZnMoO_4$ along [001] from stoichiometric charge

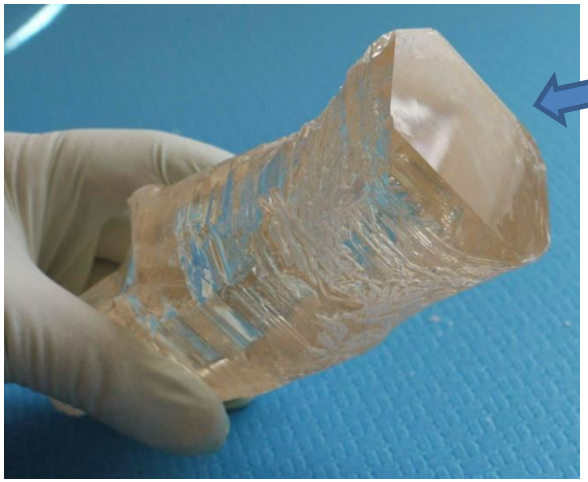
MoO_3 commercial, HP grade
ZnO HP grade produced by UMICORE.





MoO_3 synthesized in the NIIC SB RAS
ZnO HP grade produced by UMICORE.

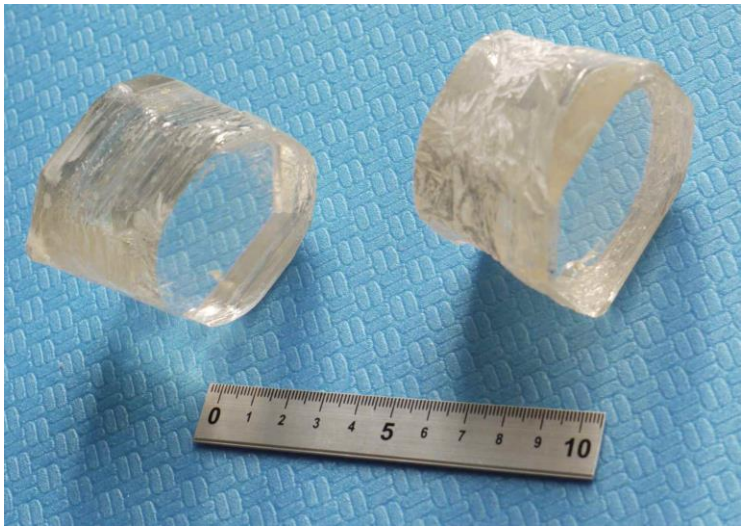
$ZnMO_4$ crystals grown along [001] direction



Growth interface

2012: Project LUMINEU (CNRS, France)

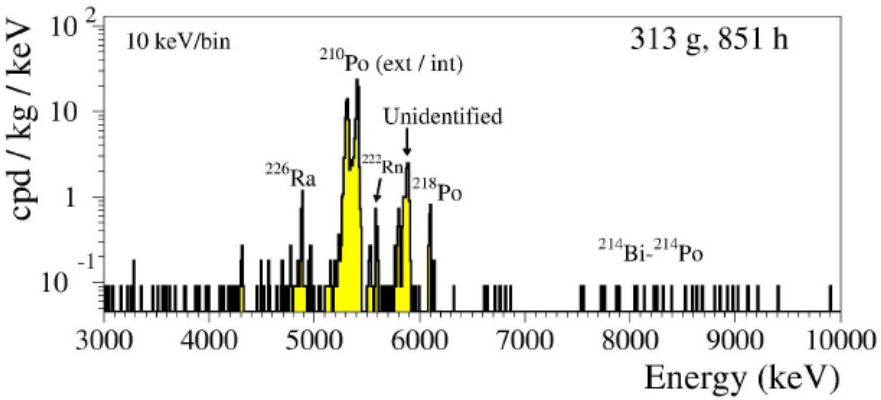
Luminescent **U**nderground **M**olybdenum **I**nvestigation for **NEU**trino mass and nature

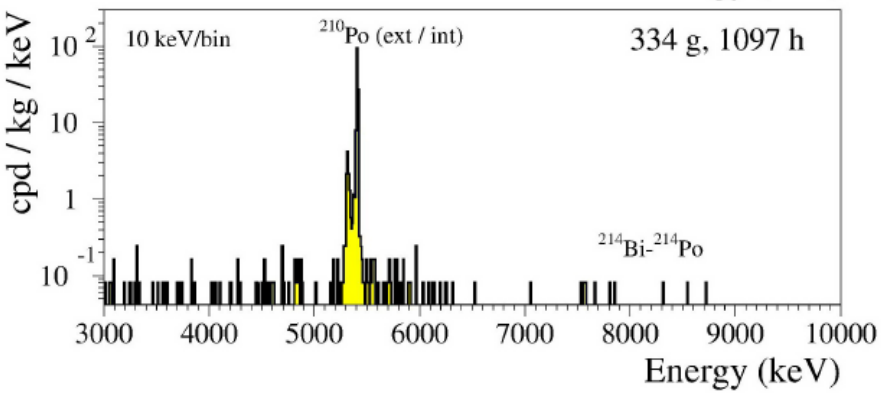


ZMO crystal grown with
the charge utilization factor ~90%

Radiopurity of $ZnMoO_4$ crystals (μBq/kg)

Radiopurity of $ZnMoO_4$ crystal satisfies the LUMINEU requirements





	Advanced ZMO		Precursor ZMO	
	LSM [1]	LSM [1]	LSM [1]	LNGS [2]
	334 g	336 g	313 g	329 g
	1097 h	291 h	851 h	524 h
^{232}Th	≤ 1.4	≤ 10	≤ 5	≤ 8
^{228}Th	≤ 4	≤ 24	10(3)	≤ 6
^{238}U	≤ 4	≤ 8	≤ 8	≤ 6
^{234}U	≤ 4	≤ 22	≤ 14	≤ 11
^{230}Th	≤ 1.4	≤ 13	≤ 9	≤ 6
^{226}Ra	≤ 5	≤ 21	26(5)	27(6)
^{210}Po	1157(49)	939(52)	621(25)	700(30)
^{235}U	≤ 3	≤ 10	≤ 7	–
^{147}Sm	≤ 5	≤ 5	≤ 5	–
^{190}Pt	≤ 4	≤ 5	≤ 3	–
^{65}Zn	164(67)	–	–	–

[1] D.V. Poda, to appear in Proc. ICHEP-2014.
[2] J. Beeman et al., EPJC 72 (2012) 2142.

The results of ZMO crystal growth

The results of LMO crystal growth

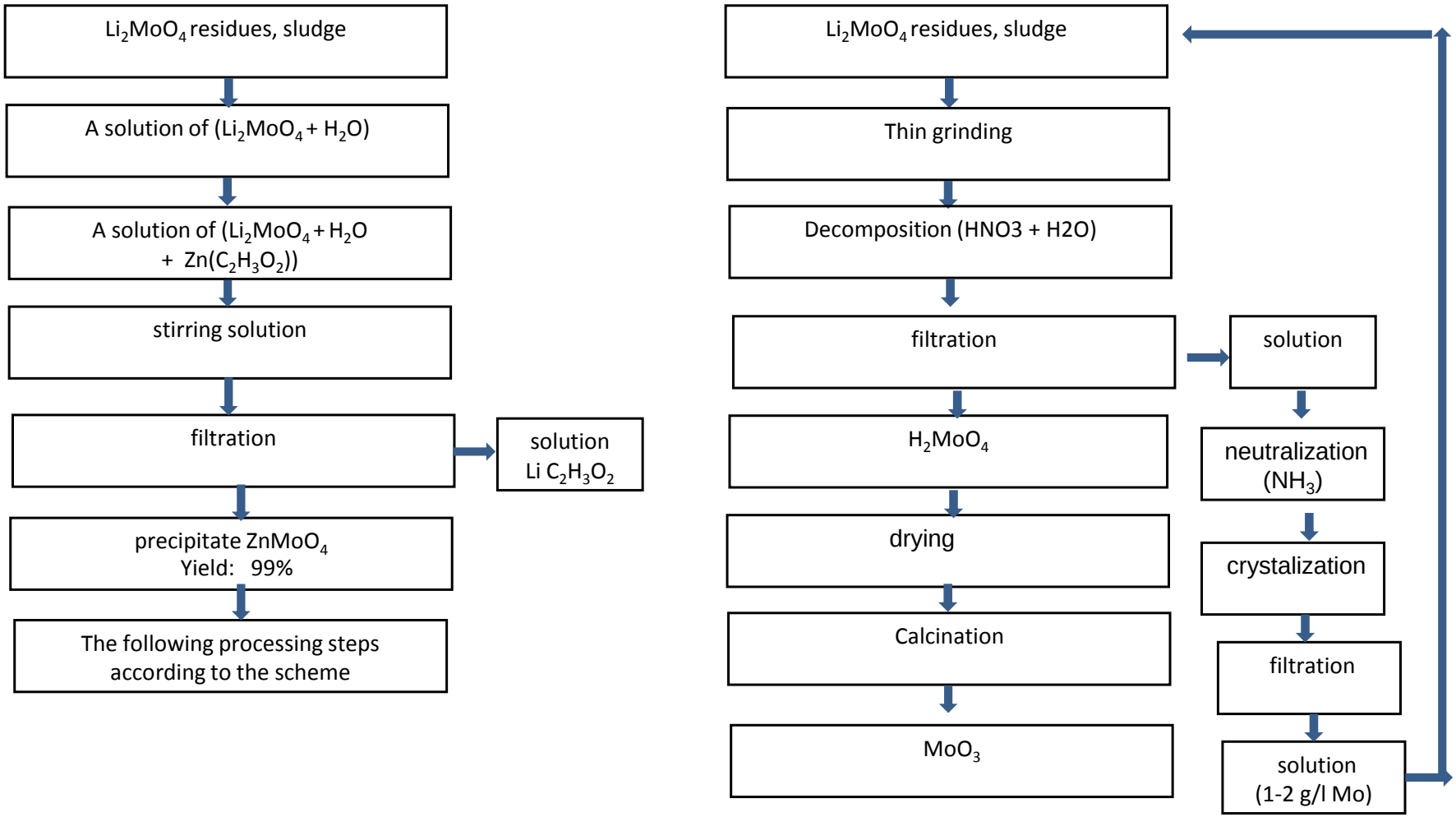
Isotopically enriched $Li_2{}^{100}MoO_4$ crystals

Isotopically enriched crystals
first crystallization

Isotopically enriched crystal
second crystallization

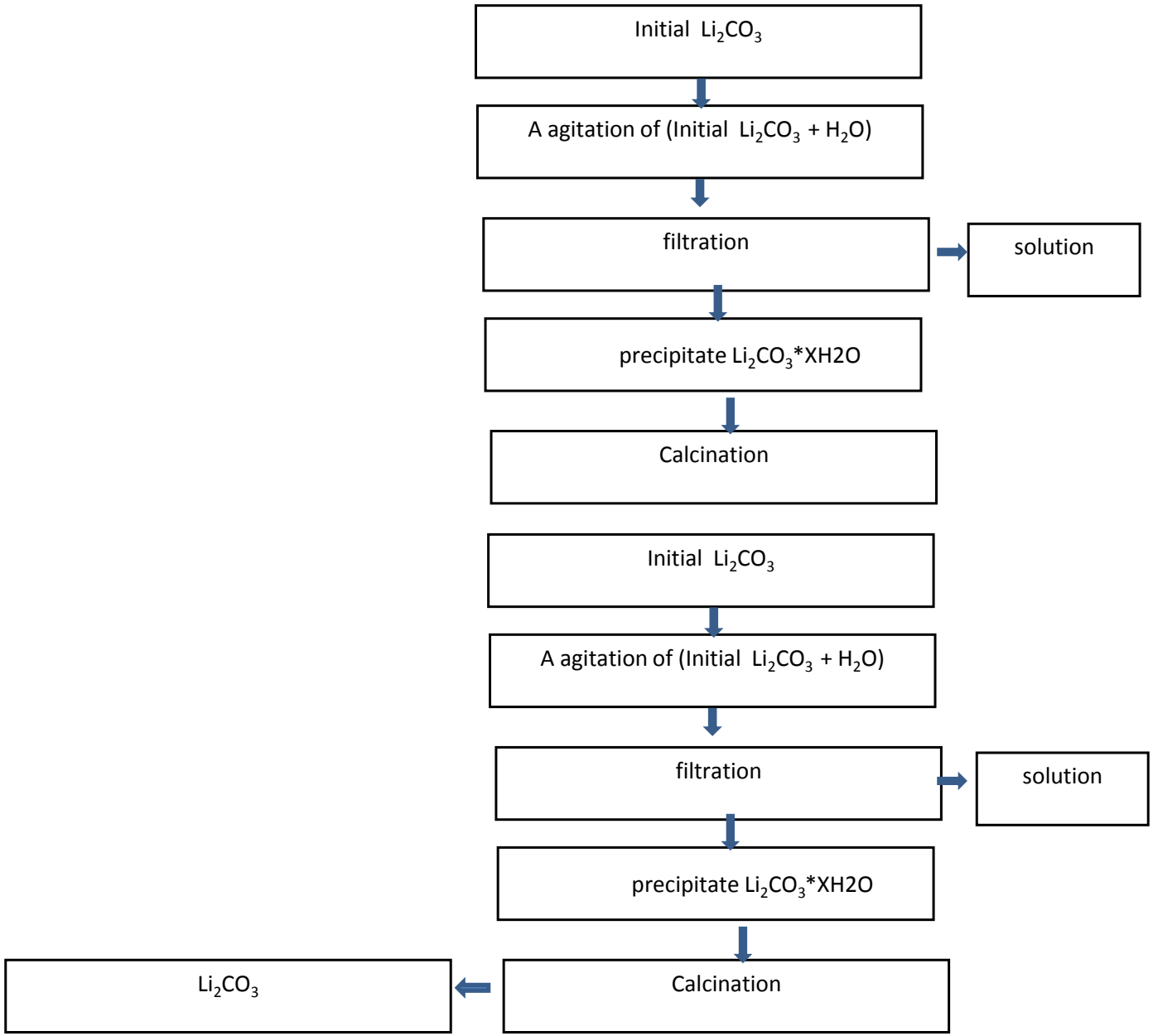
Extraction of MoO_3 from Li_2MoO_4 residues, sludge

Scheme



Synthesis and purification of raw Li_2CO_3

Scheme



Radiopurity ZMO, LMO (μBq/kg)

	$ZnMoO_4$	$ZnMoO_4$	$Zn^{100}MoO_4$	$Zn^{100}MoO_4$	Li_2MoO_4	Li_2MoO_4	$Li_2{}^{100}MoO_4$	$Li_2{}^{100}MoO_4$
^{232}Th	≤ 7.3	≤ 1.4	≤ 8.0	≤ 9.0	≤ 21	≤ 18	≤ 2.7	≤ 11
^{228}Th	≤ 26	≤ 4.6	≤ 8.0	≤ 21	≤ 21	≤ 18	≤ 8.4	≤ 6.2
^{238}U	≤ 13	≤ 2.6	10(4)	39(7)	≤ 37	≤ 48	≤ 4.9	≤ 11
^{234}U	≤ 20	≤ 3.0	11(6)	43(10)	≤ 21	≤ 46	≤ 6.7	≤ 11
^{230}Th	≤ 28	≤ 1.4	≤ 17	≤ 24	≤ 21	≤ 18	≤ 2.7	≤ 11
^{226}Ra	≤ 26	2.8(15)	14(3)	23(4)	≤ 37	130(19)	≤ 6.7	≤ 11
^{210}Po	575(18)	$1.32(3) \times 10^3$	809(32)	$2.39(5) \times 10^3$	195(41)	76(25)	230(20)	60(10)
235U	≤ 19	≤ 2.6	≤ 13	≤ 19	≤ 21	≤ 18	≤ 4.9	≤ 6.2

$Na_2Mo_2O_7$ LTG CZ - first result

Purification of Na_2CO_3

$NaHCO_2$ ← Initial substances → $Na_2CO_3 \bullet 10H_2O$

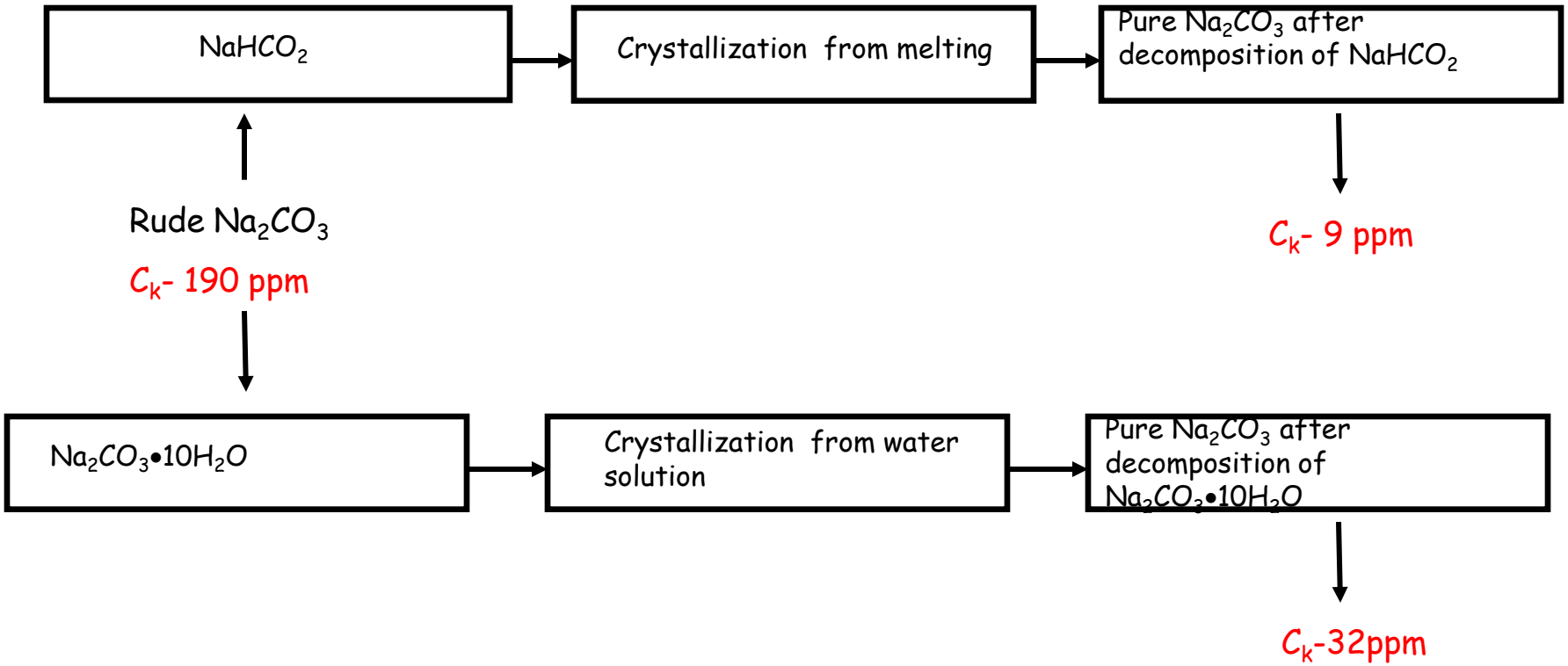
Probable routine simple

$NaHCO_2$ → Crystallization from melting → Pure Na_2CO_3 after decomposition of $NaHCO_2$

$Na_2CO_3 \bullet 10H_2O$ → Crystallization from water solution → Pure Na_2CO_3 after decomposition of $Na_2CO_3 \bullet 10H_2O$

Purification of Na_2CO_3

(first results)



NMO crystals

Conclusion

- **Synthesis und purification of starting materials is an important stage for growth crystals with extremely high characteristics.**
- **A complex variant initial materials purification allows to growth crystals for search rare events**
- **LTG CZ is a good crystal growth technique to search rare events.**