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Pure raw materials for scintillation detectors of ionizing radiation

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ллдм

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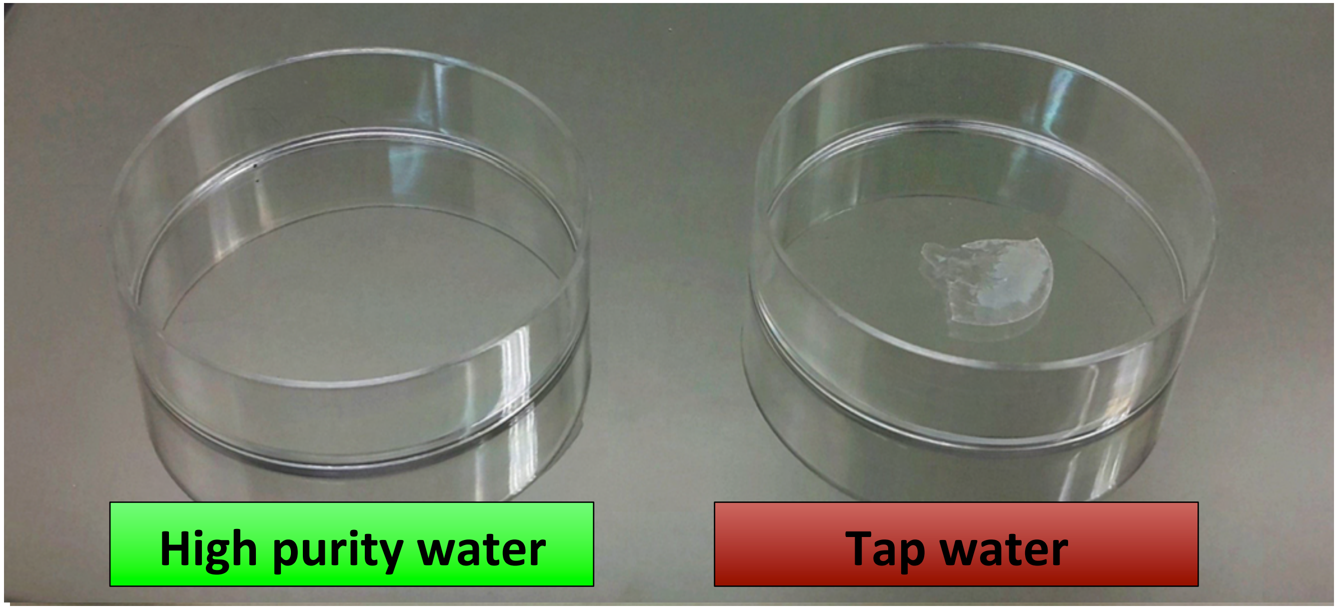
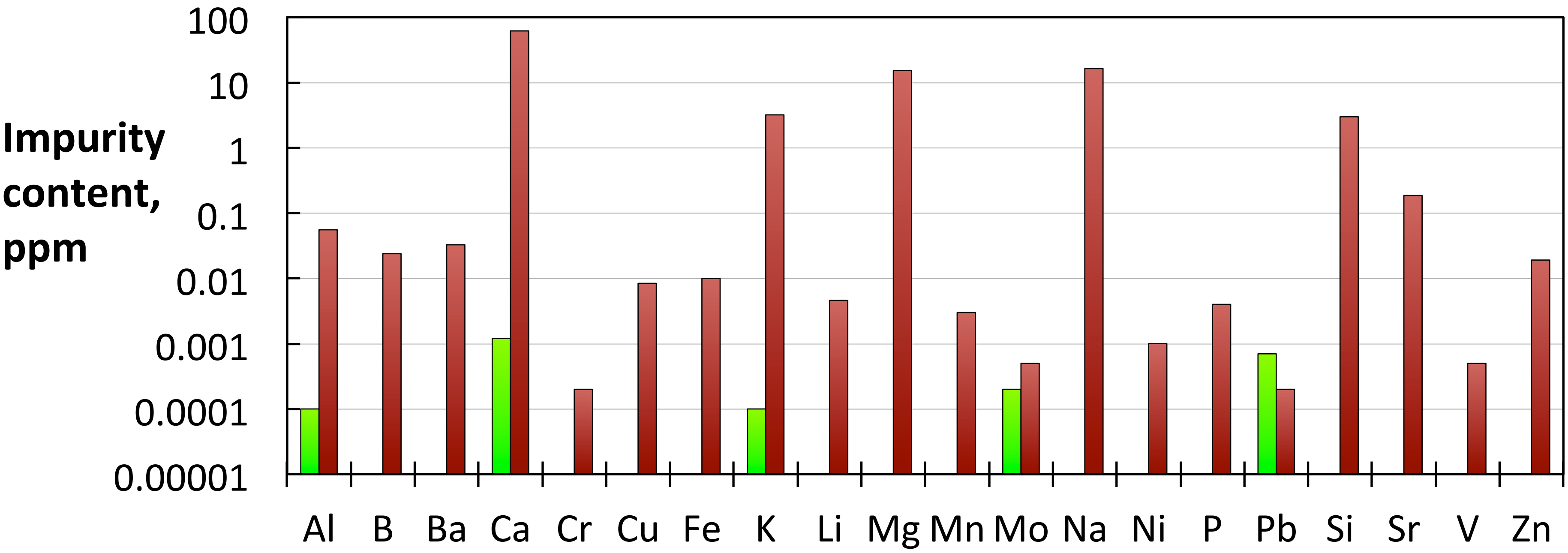
Outline:

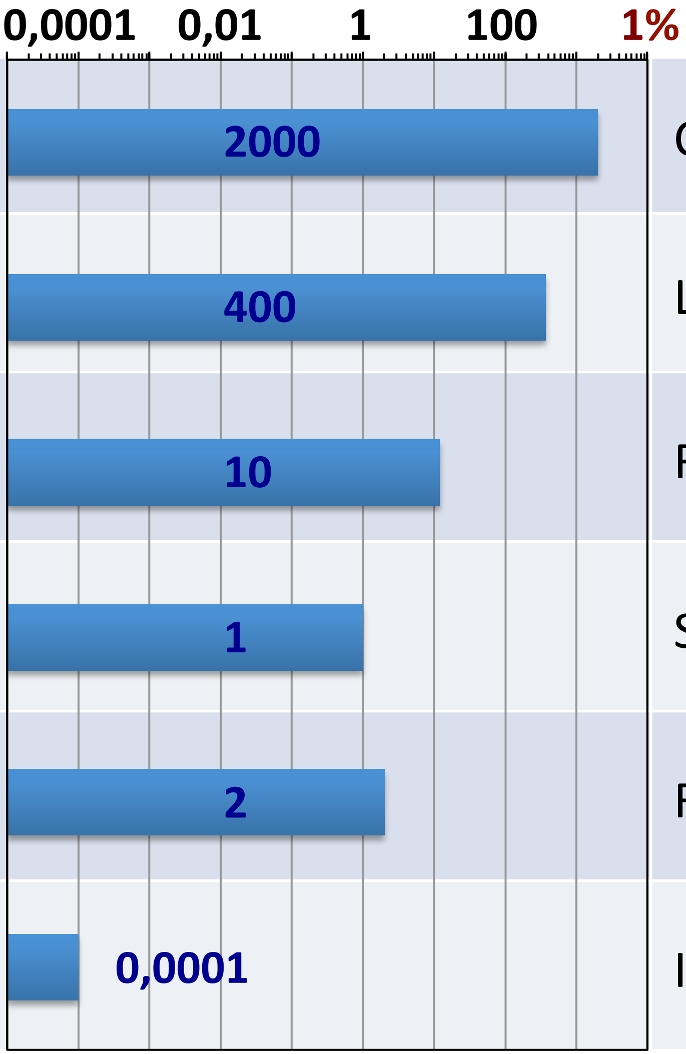
- Impurities, purity, purification and analysis
- Economical considerations:
  production and recycling
- Other factors:
  composition, microstructure and particle size
- Conclusions



1 ppm =
10^{-4} %
1 mg/g
1 g/ton



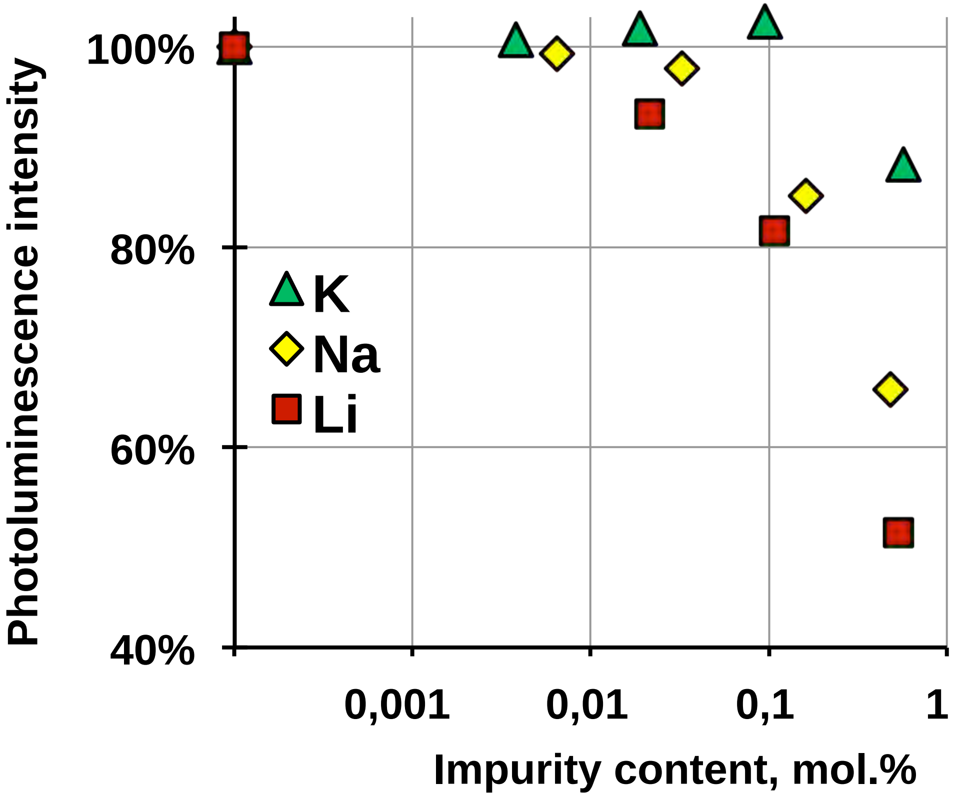
Examples of impurities effects in scintillators



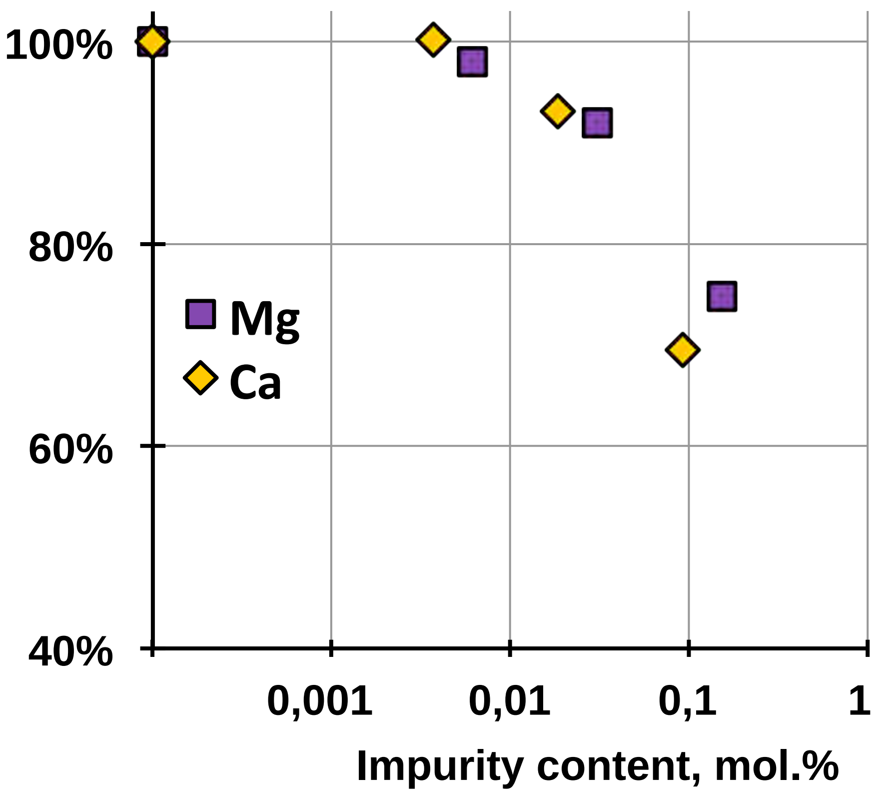
Impurity	Content, ppm	Effect
S in SrI_2	2000	Crystal cracking
Mg in YAG	400	Light yield decrease
Mg in YAG	10	Faster scintillation kinetics
Mo in PWO	1	Slower scintillation kinetics
Fe in PWO	2	Radiation hardness decrease
U,Th in $CaMoO_4$	0,0001	Intrinsic radioactivity background

YAG:Ce photoluminescence – less strict requirements

Alkaline metals



Alkaline earth metals



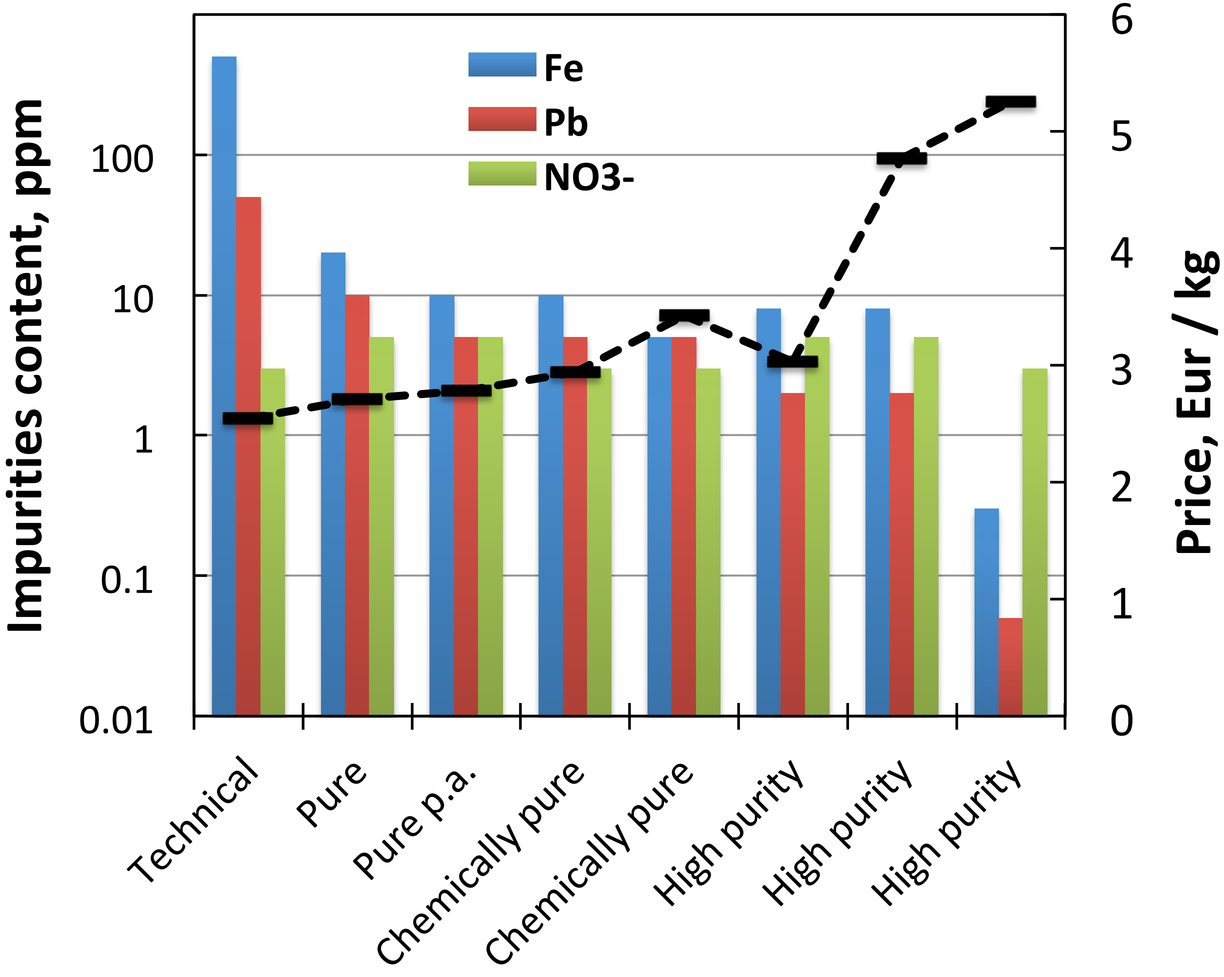
Co-doping – impurity “homeopathy” for scintillation

Grading and pricing – large volume chemicals

Reagent grades

- ACS reagent grade
- Analytical reagent
- Guaranteed reagent
- Reagent
- Chemically pure
- National formulary
- Lab grade (~pure p.a.)
- Purified
- Practical (~pure)
- Technical

Phosphoric acid

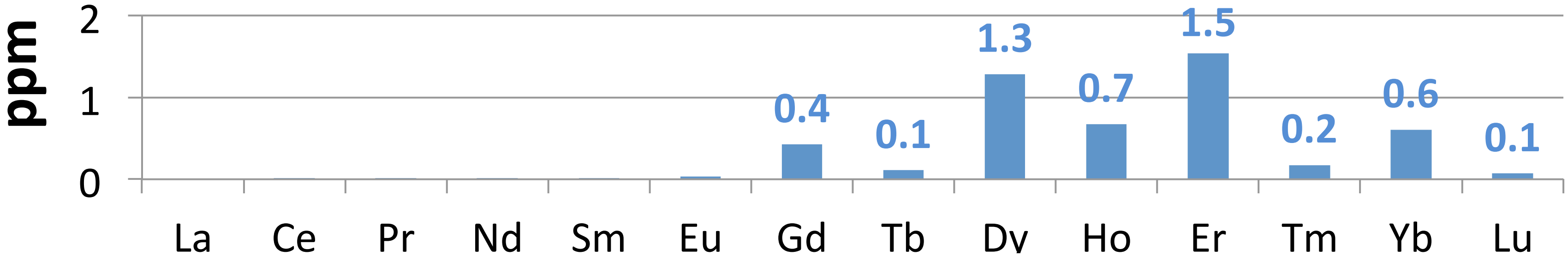


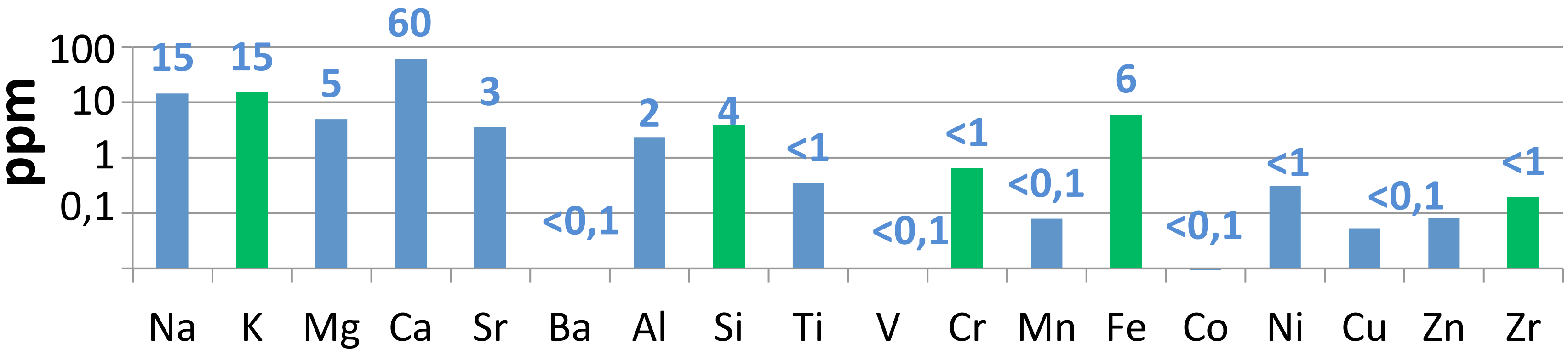
Grading of elements in “nines”

Example: Y_2O_3 99,99%

99,99% = 100% - Σ(All **controlled** impurities)

ICP **mass-spectrometry** + **atomic emission spectrometry**





Product can be either better or worse then graded → Complete specs or direct analysis of impurities could be useful

Classification of impurities

Chemistry:

- cationic / anionic
- rare earth (La-Lu)
- 3-d (Ti-Zn)
- heavy metals (Pb, Bi)

Effect:

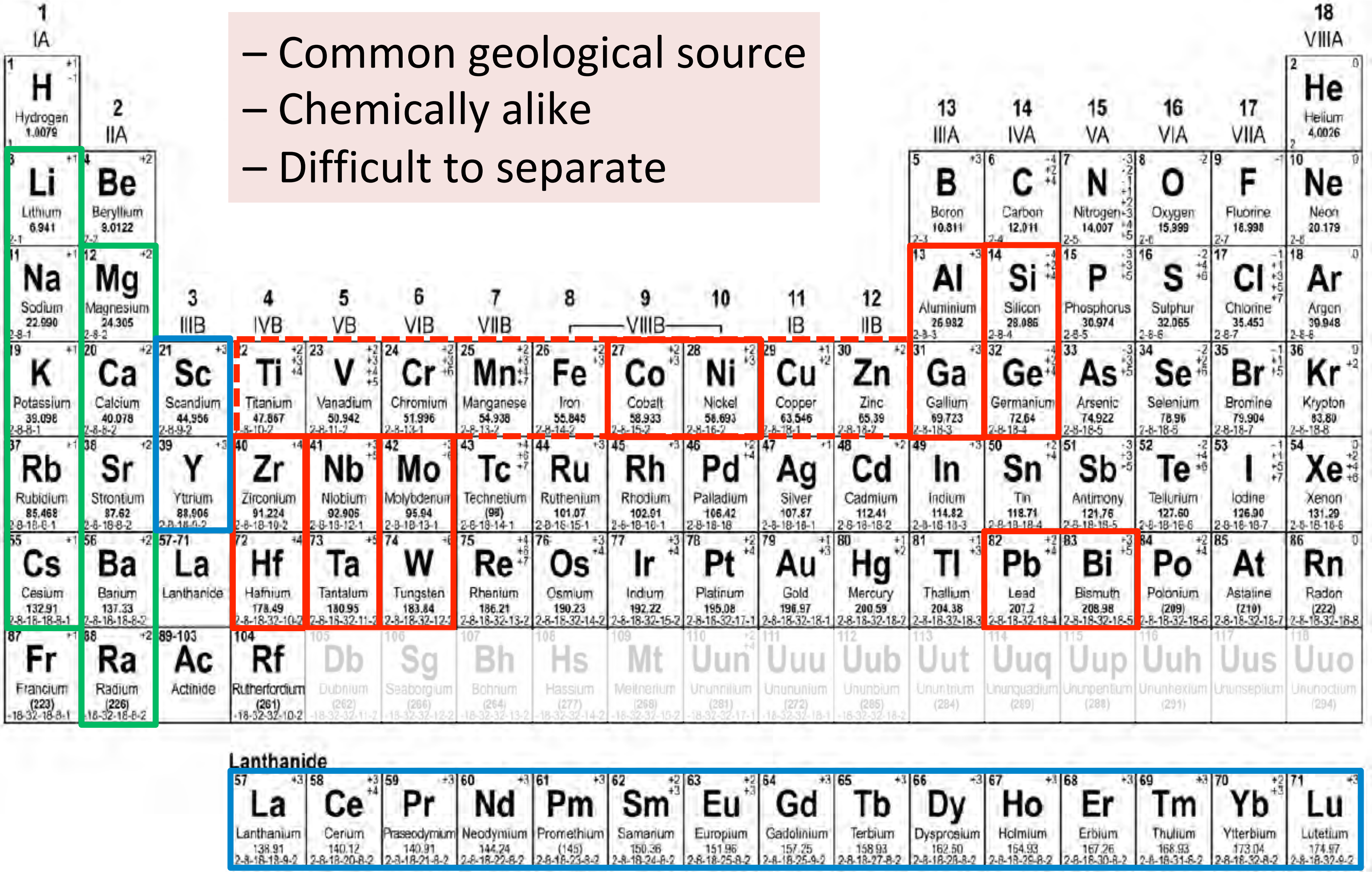
- coloring (Ti, Fe, Co, Ni, Cu)
- Luminescence quenching
- growth
- radioactive (create background)

Source:

- accompanying
- common (Na, K, Mg, Ca, Si, Fe, Al)
- organic carbon

Accompanying impurities

- Common geological source
- Chemically alike
- Difficult to separate



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo

Lanthanide

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Non-metal impurities

Anionic $H_2P_2O_7^{2-}$ in KDP (KH_2PO_4) Growth inhibition
100 ppm causes 1,5 laser damage threshold fall

Usually – crucial for low-temperature growth

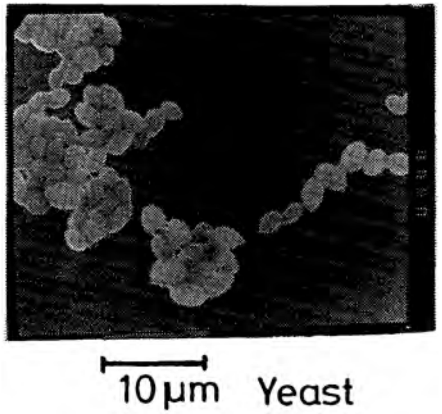
Atmosphere O^{2-} , OH^-, H_2O O^{2-} in BaF_2 causes self-absorption

Usually – difficult to analyze

Organic 10^6 / cm^3 (~ 5 ppm) candida parapsilosis + Al^{3+}, Cr^{3+} in KDP leads to growth defects formation

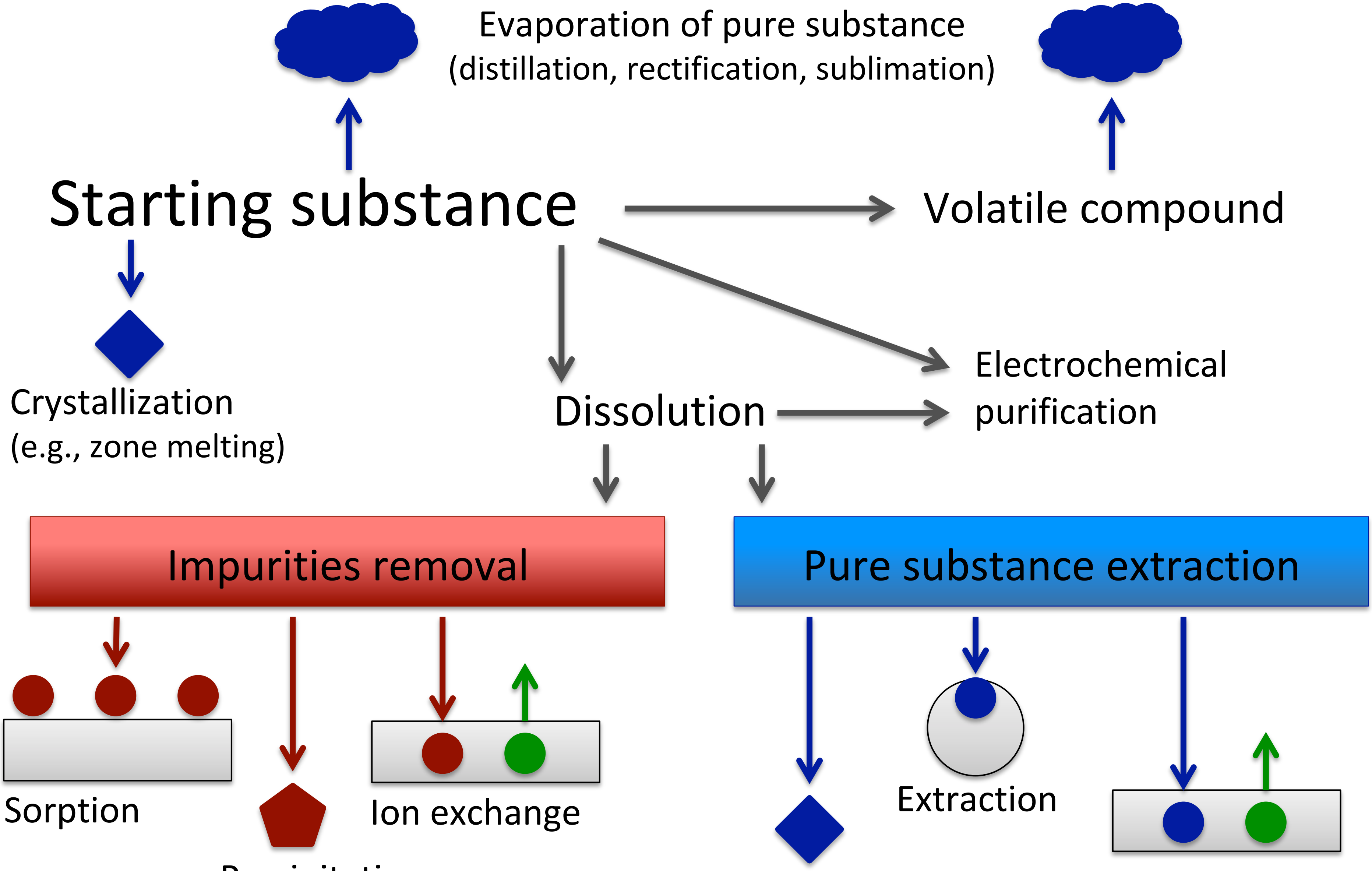
Usually – crucial for low-temperature growth

T. Sasaki et al, Jap. J. Appl. Phys. 1987



Purification

Main principles of purification



Evaporation of pure substance
(distillation, rectification, sublimation)

Starting substance

Volatile compound

Crystallization
(e.g., zone melting)

Dissolution

Electrochemical
purification

Impurities removal

Pure substance extraction

Sorption

Precipitation

Ion exchange

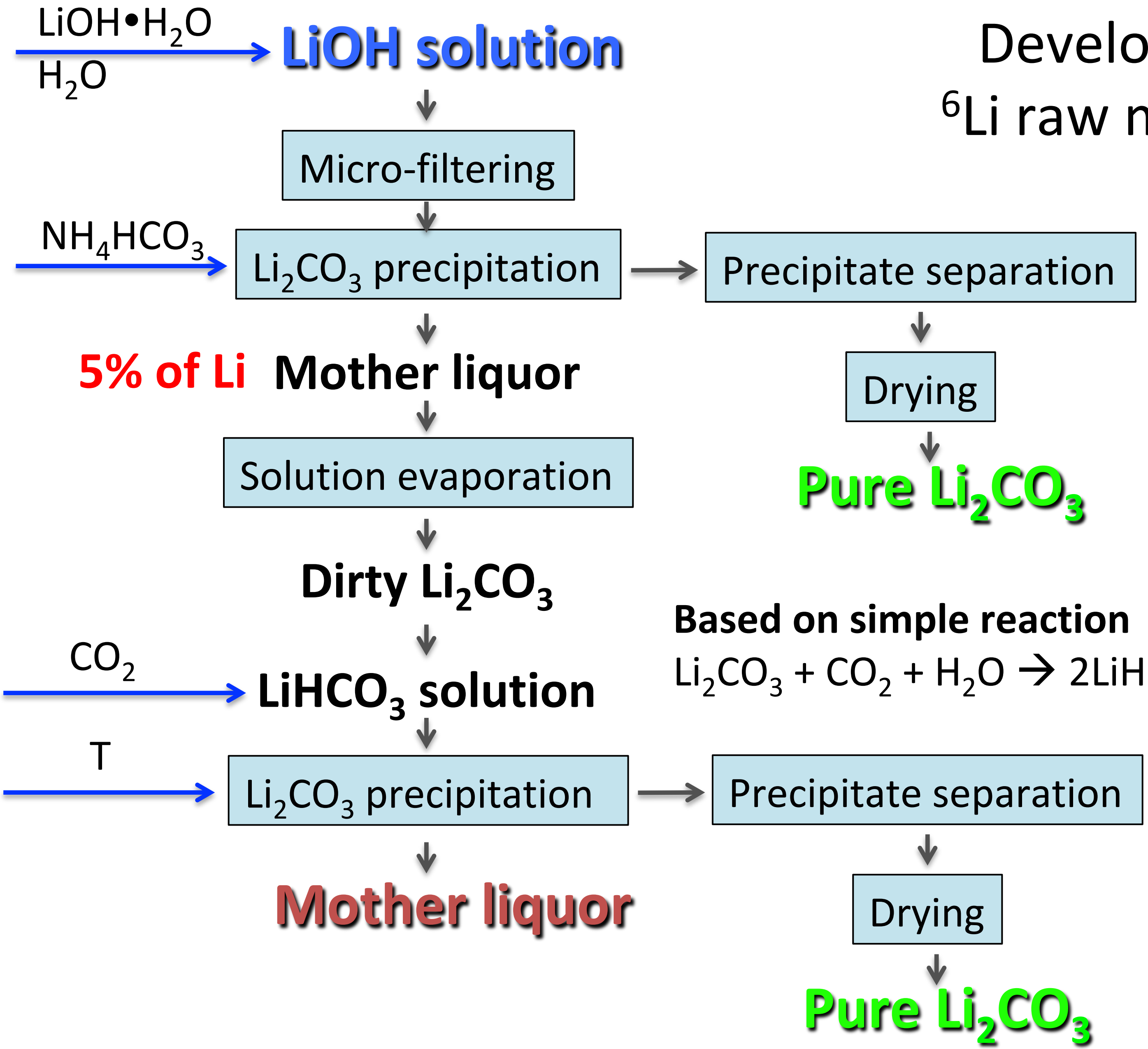
Crystallization

Extraction

Ion exchange

Crystallization purification example

Developed for ^{6}Li raw material



$LiOH \cdot H_2O$

H_2O

LiOH solution

Micro-filtering

NH_4HCO_3

Li_2CO_3 precipitation

Precipitate separation

Drying

Pure Li_2CO_3

5% of Li **Mother liquor**

Solution evaporation

Dirty Li_2CO_3

CO_2

$LiHCO_3$ solution

T

Li_2CO_3 precipitation

Precipitate separation

Drying

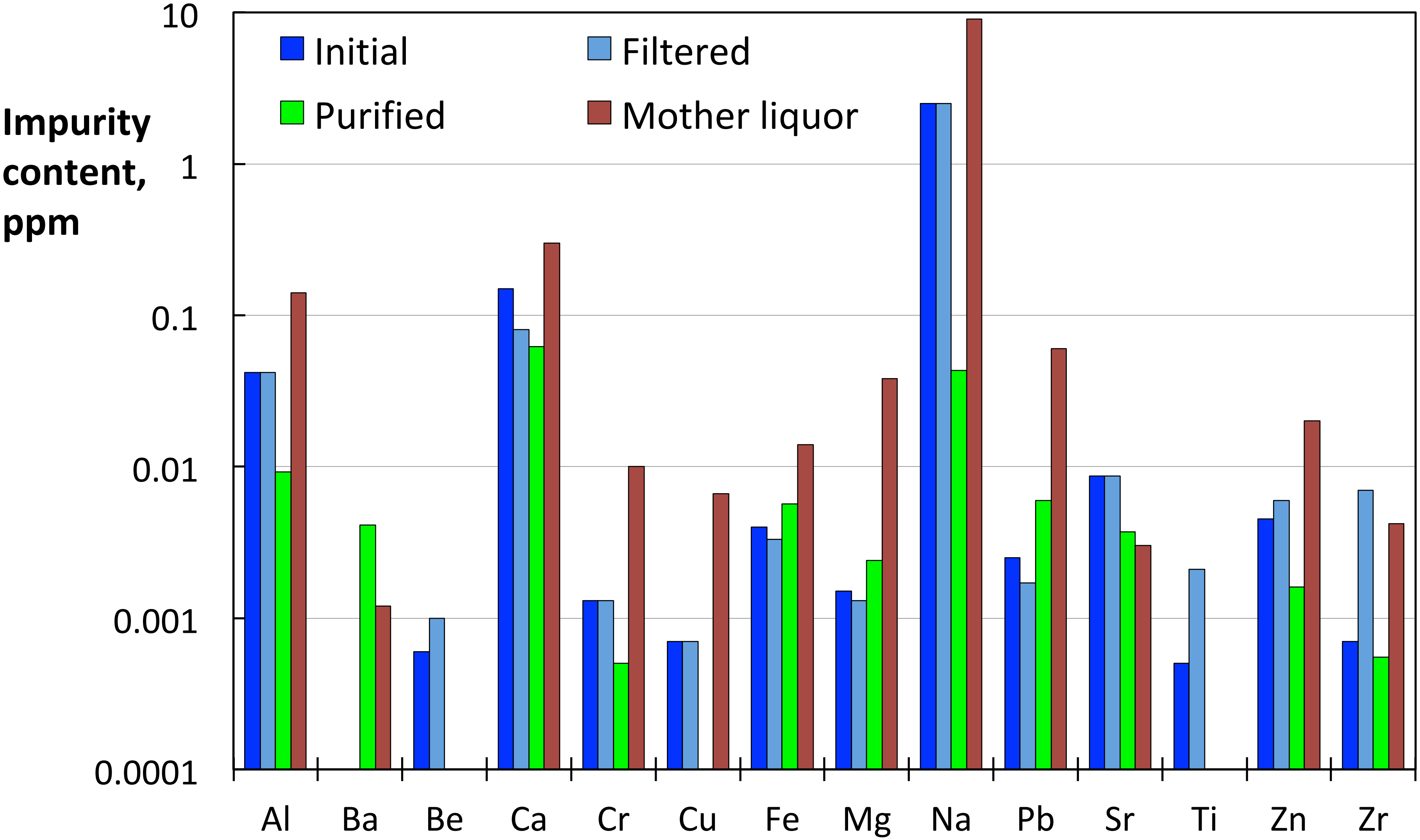
Pure Li_2CO_3

Mother liquor

Based on simple reaction

$Li_2CO_3 + CO_2 + H_2O \rightarrow 2LiHCO_3$

Crystallization purification example



Rare earth elements separation and purification

RE containing ores
0,1 - 5%

→

Rare earth concentrate
70 - 90%

[http://rareearth.ru/ru/
news/20180219/03740.html]

↓ Extraction (50-80 stages)

Rare earth group concentrates
Light (La-Nd), middle-heavy (Sm-Lu + Y)

↓

REE separation

Ion exchange

Extraction
(50-100 stages)

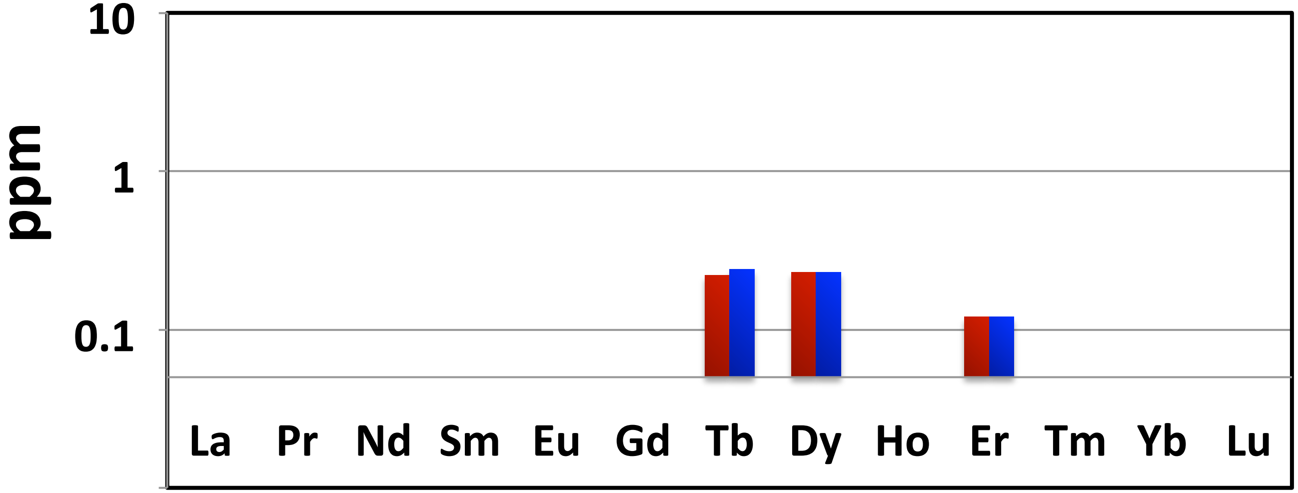
99–99,999% product

↓

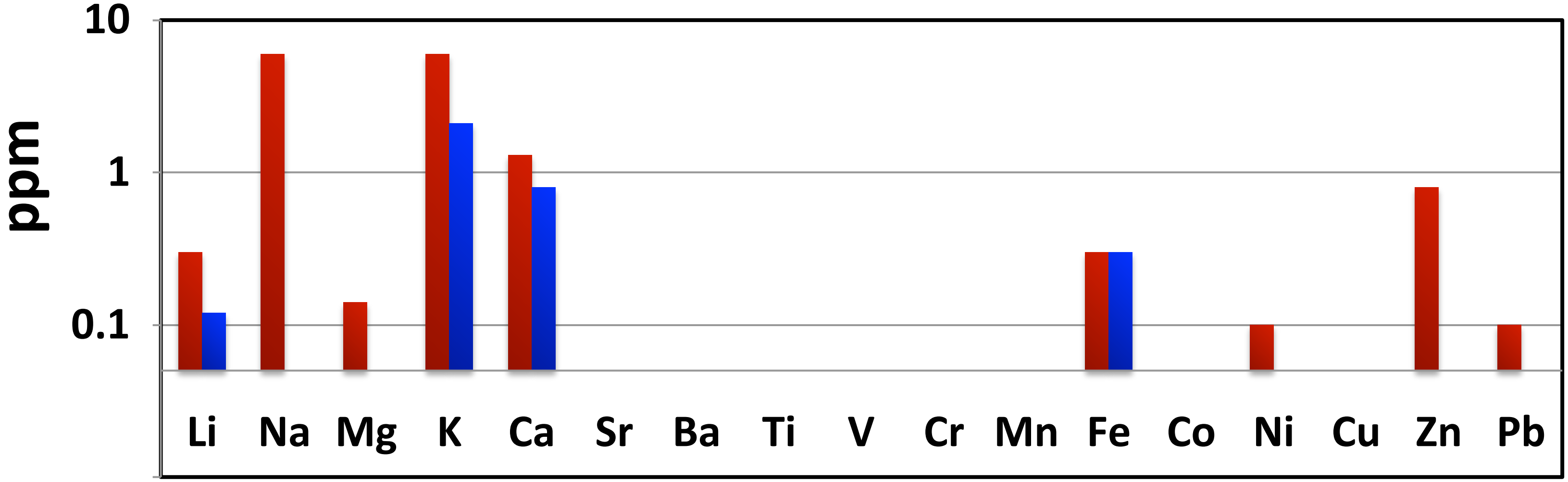
Possible purification from non-RE

Possibility of additional RE purification

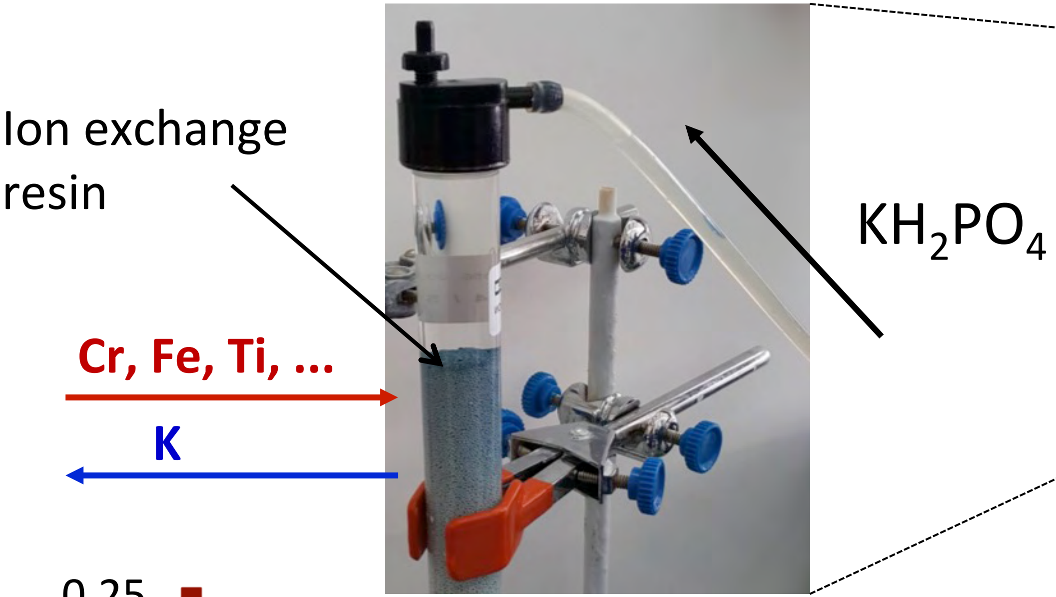
Y_2O_3 (5N) Before crystallization After crystallization

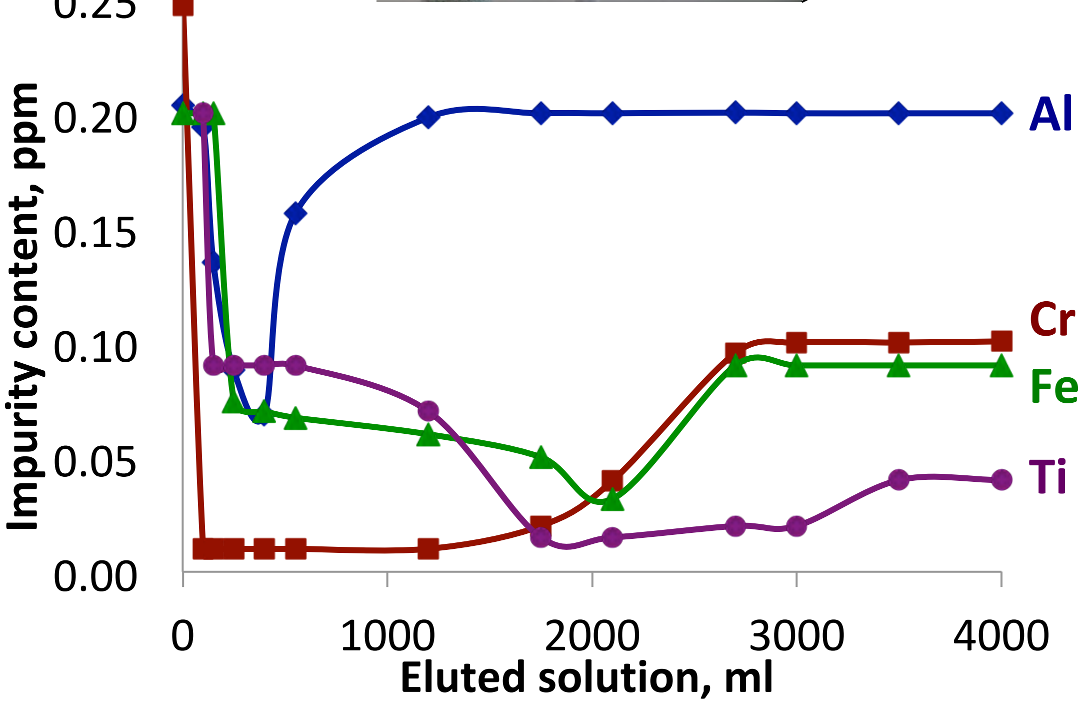


Non-RE impurities are removed, when RE remain in the substance



Purification by ion exchange, example: KDP





Process parameters:

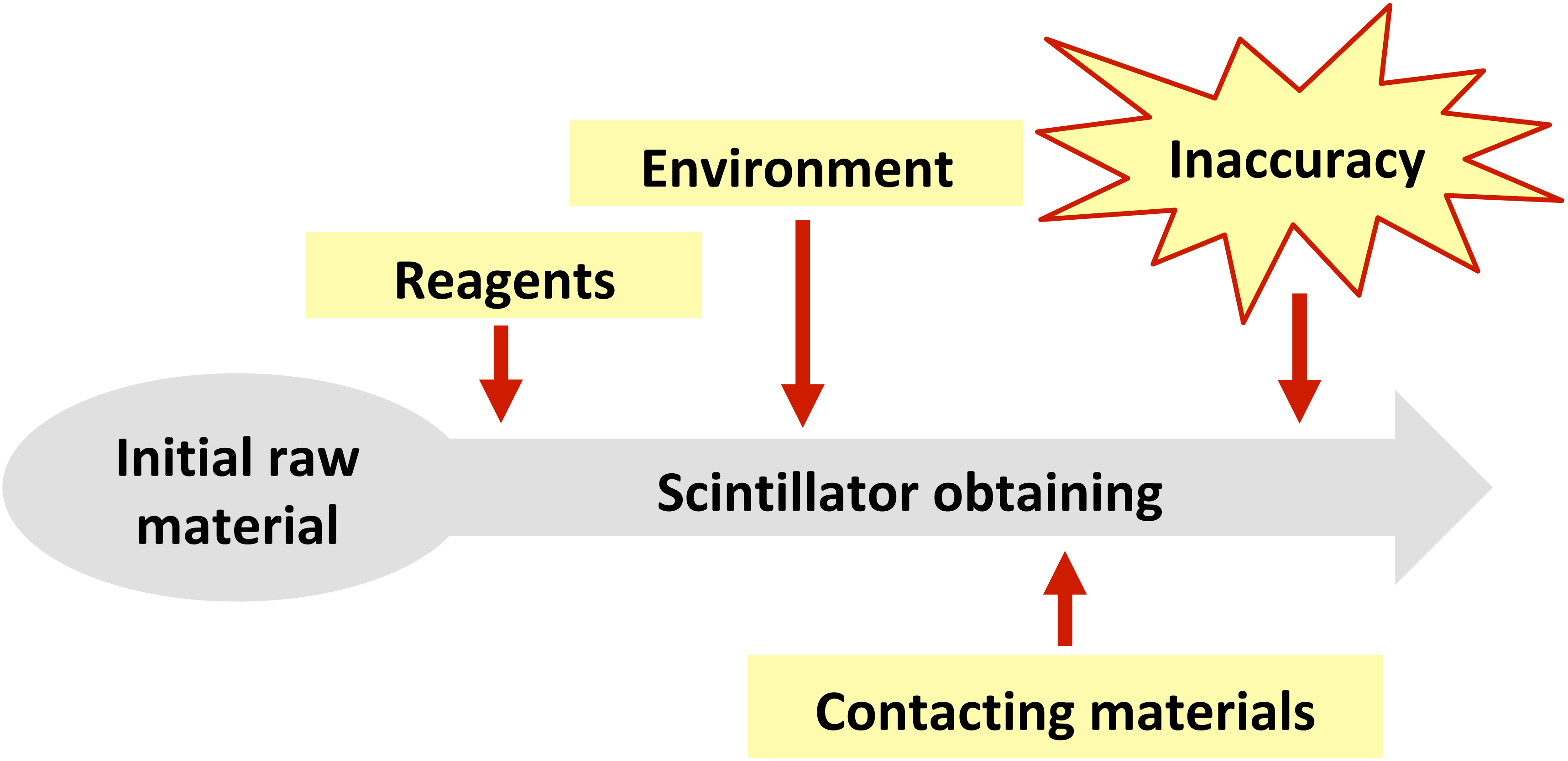
Elution rate

Column geometry

pH

Concentration

Possible sources of impurities



Inaccuracy

Environment

Reagents

Initial raw material

Scintillator obtaining

Contacting materials

e.g. upon glass melting in Al_2O_3 crucible melt could be enriched with up to 2% of Al_2O_3 for (50g sample)

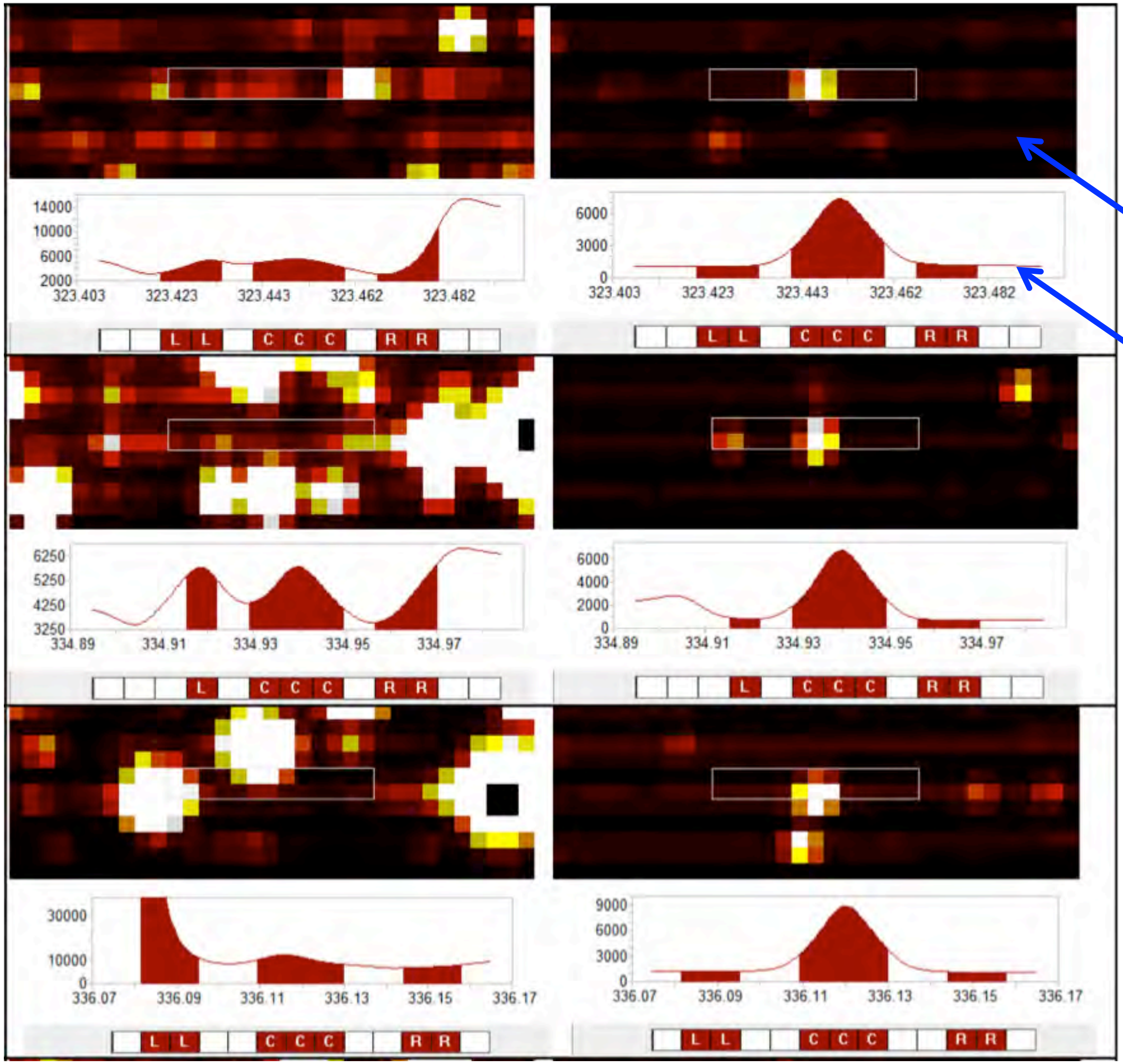
A lot of things could go wrong, so appropriate control should be used

Chemical analysis

Spectral overlaps in atomic emission spectrometry

Equal to 100 ppm Ti in Gd

Gd – 0,1 wt.% **Ti – 10^{-5} wt.%** (solutions)



Line 323,45 nm

Line 334,94 nm

Line 336,12 nm

2D CID detector image

Spectrum representation

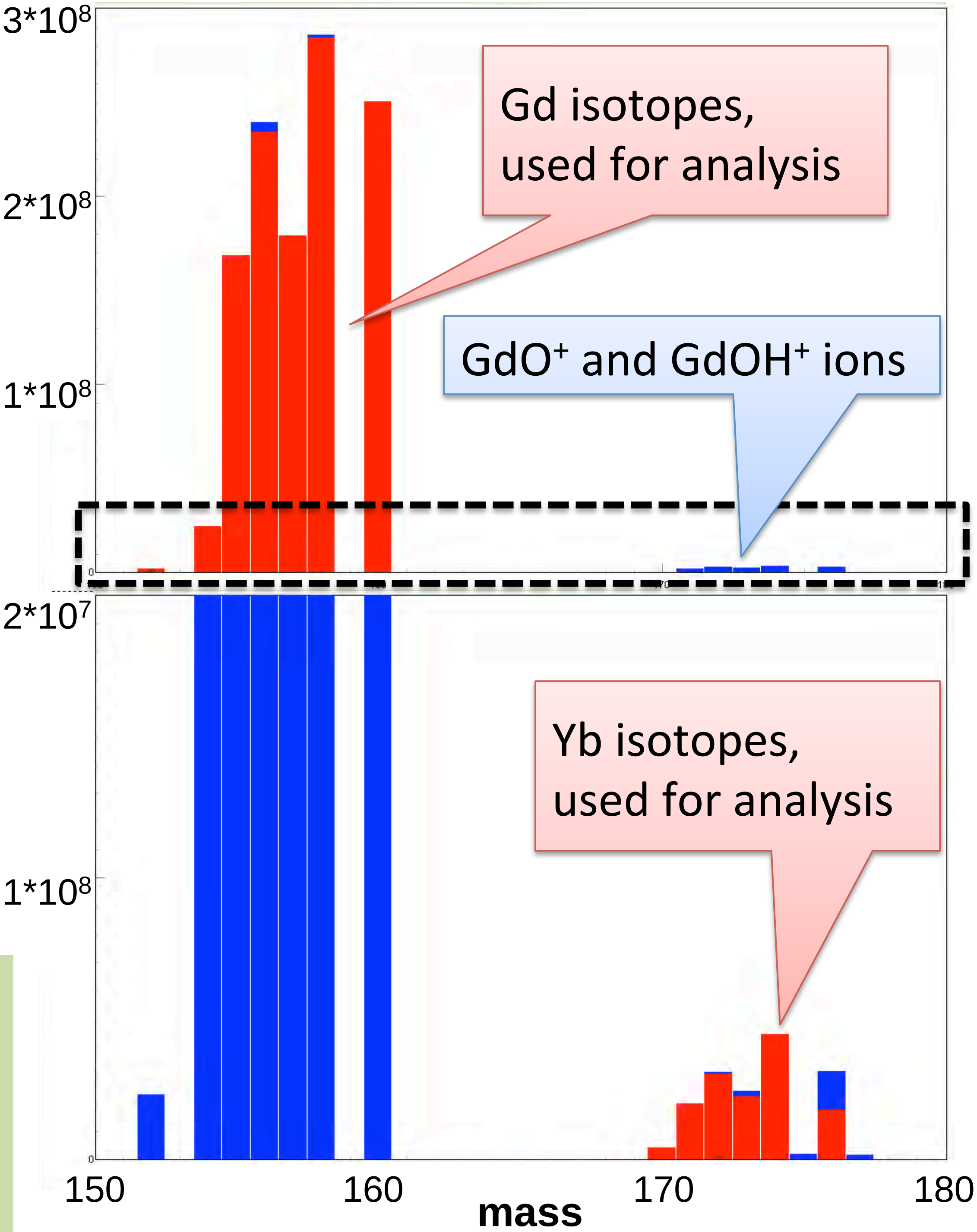
iCAP 6300 Duo spectrometer, Thermo Scientific

Mass spectrometry of Gd_2O_3 5N

All usable **Yb** isotopes are overlapped with **Gd**O^+ and **Gd**OH^+

Tb and **Lu** are also overlapped

“Complicated” compounds require combination of techniques and additional probe preparation



Gd isotopes, used for analysis

GdO^+ and $GdOH^+$ ions

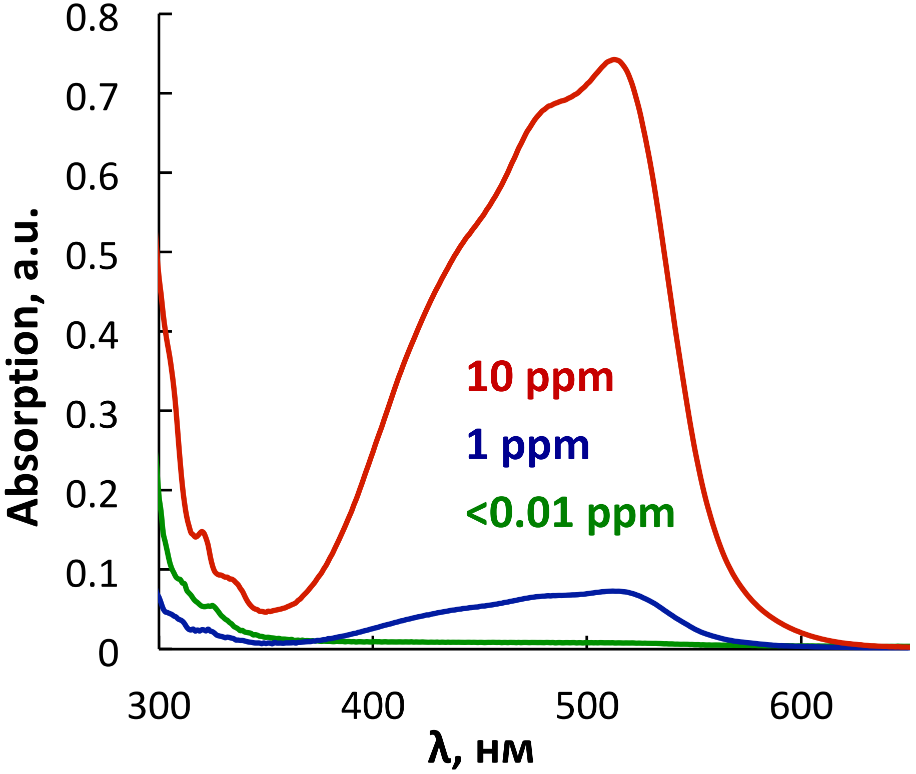
Yb isotopes, used for analysis

Chemical analysis techniques

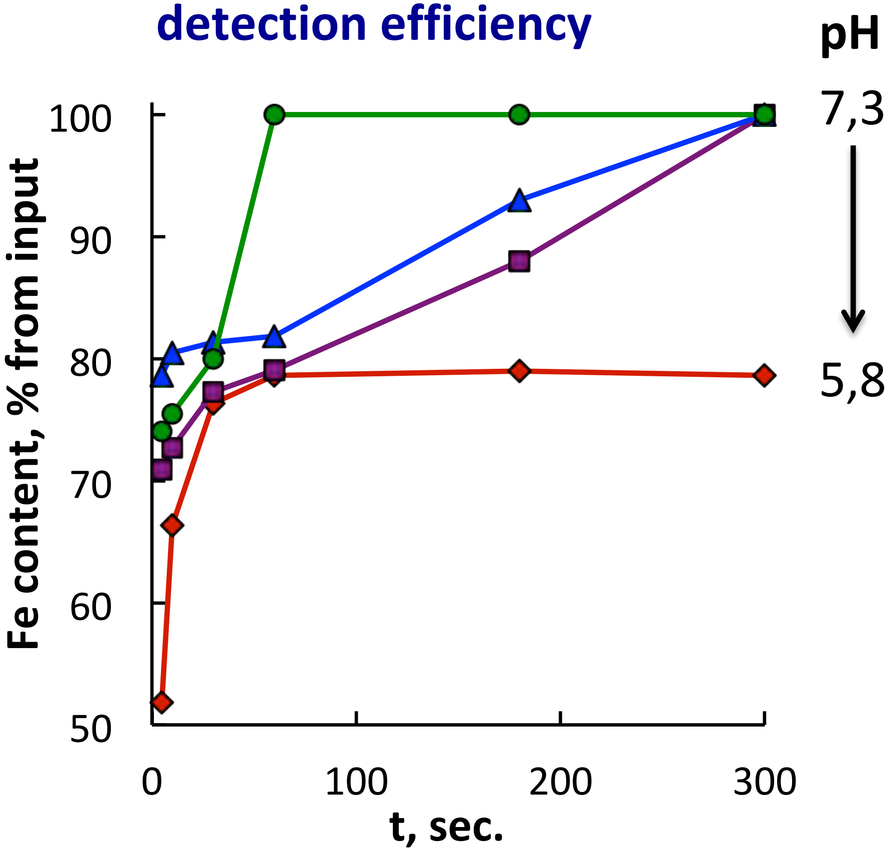
Method	Details	+	-	limit, ppm
Mass-spectrometry (quadrupole)	Solution, ICP (Inductively coupled plasma)	Averaged result, available samples for calibration	Multiple	0,001
Atomic emission spectroscopy		Better precision at higher concentrations	Hardly applicable for elements with rich emission spectra	0,001
MS & AES	Laser ablation	No sample preparation, local	Additional artifacts of probe preparation	
Energy dispersive X-ray analysis	SEM	Local	Depends on probe preparation and other factors	10
	XRF (stand-alone)	Simple and fast	Worse than SEM (Al+ elements)	>10
Wave dispersive X-ray analysis	SEM	Better sensitivity and selectivity compared to EDX	Slow	1

Classical methods – for cross-check or express-check

Example: Colorimetry of solutions for analysis of KDP



Fe-Phen water solutions absorption spectra



0,1 ppm of Fe detection efficiency

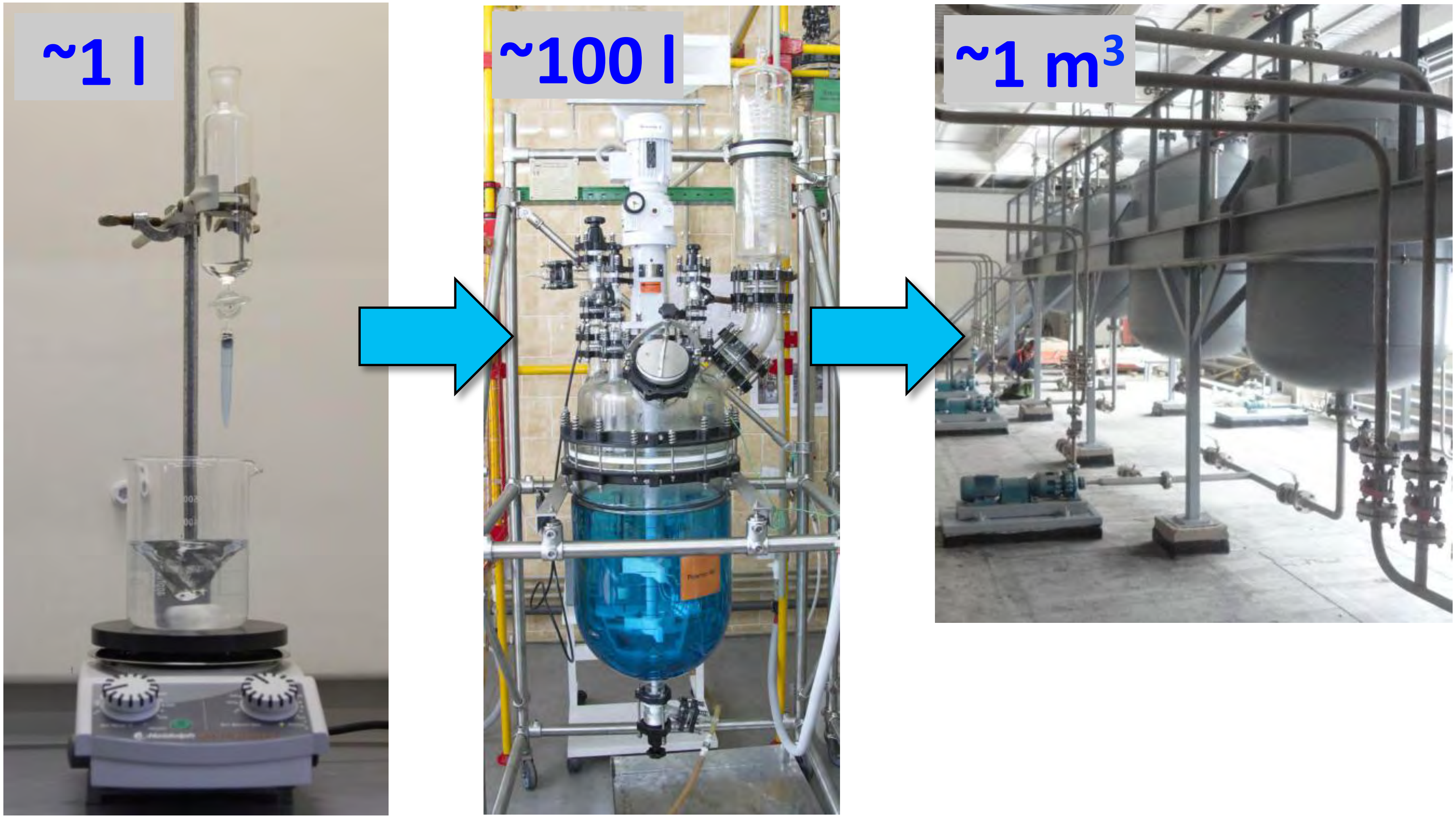
Detection limits:

Fe – down to 0,03 ppm

Cr – down to 0,05 ppm

Economy-driven considerations

Going to production



Lab scale synthesis

~1 l

Small scale production

~100 l

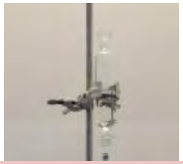
Large scale production

~1 m^3

Technology influences cost

Product per operation (exemplary):

50 g



Environmental note:
Product is pure, wastes are the same

however, lower production volumes and impact can be controlled

5 kg

100 kg

Product price doesn't really matter

Low price at moderate volume

Large investments in equipment are possible

Why high purity substances are expensive?

- Expensive processes
- Expensive equipment
- High qualification of personnel
- More analytical control
- Possible sorting out
- Lower production volumes

Additional factors:

- R&D
- Expensive starting materials
- Special requirements
  (e.g. atmosphere control)
- “Complicated” substances
  (corrosive − e.g. fluorides,
  hygroscopic − e.g. halides)

performance ↔ **cost**

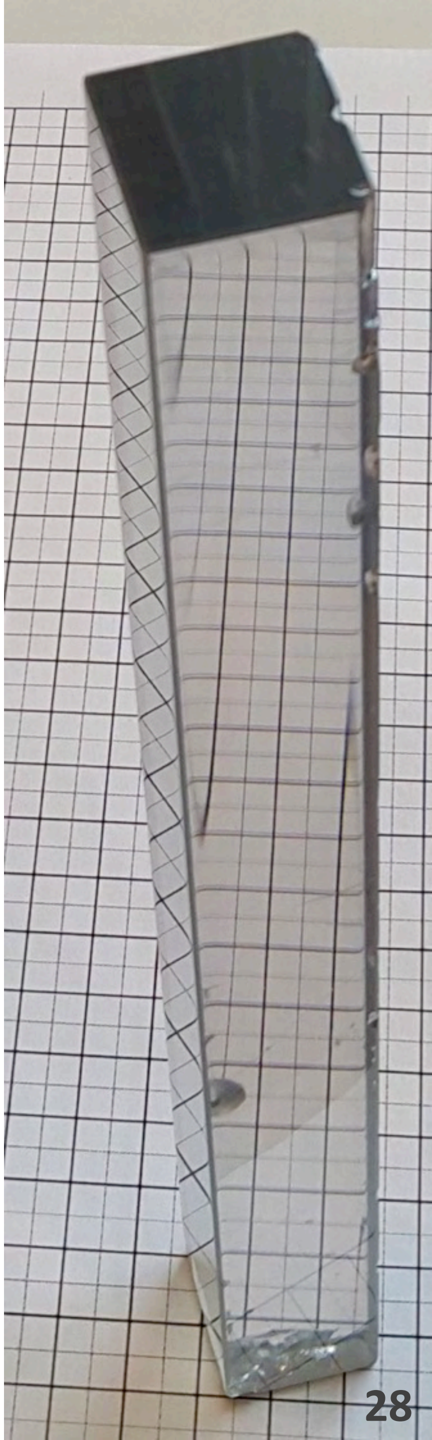
Raw materials specification freezes acceptable ratio

A separate R&D may be needed

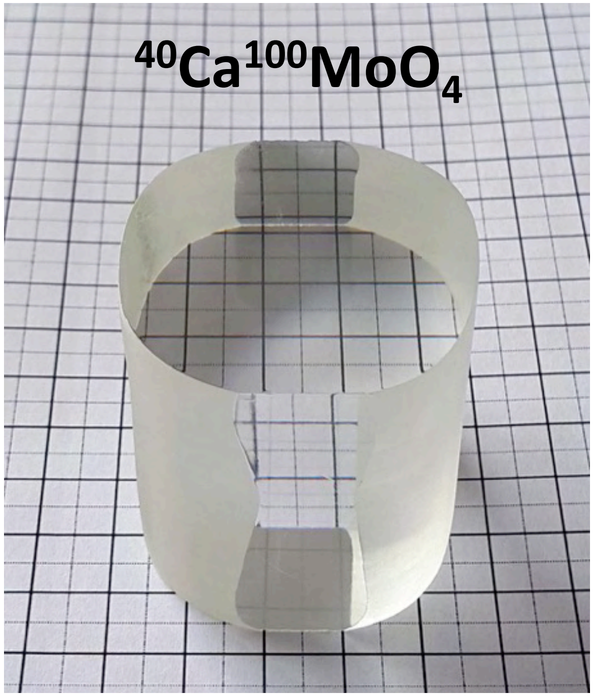
Raw materials for PWO crystals

Developed specifications

Impurity	Limit	Negative influence	Position
Na	5 ppm	Radiation hardness	→Pb
K	2 ppm		
Mg	1 ppm	Scintillation kinetics	→Pb
Ca	5 ppm		
Ba	3 ppm		
Si	5 ppm	Radiation hardness, robustness	→W
3d (Ti-Ni)	0,5ppm	Scintillation kinetics	→W
Fe	2 ppm	Radiation hardness	→W
Cd	5 ppm	Scintillation kinetics	→Pb
Sb	5 ppm		
RE (La-Lu)	Not natural	Radiation hardness, scintillation kinetics	→Pb



Ultra pure raw materials for scintillators for low-background measurements



Grown by FOMOS materials, Moscow

AMoRE experiment – search for neutrinoless double β-decay, Y2L Lab, Korea

Goal specifications for raw materials:

^{226}Ra below 2 mBq/kg (~$5*10^{-15}$ wt.%).

In order to achieve that, U and Th impurities had to be eliminated from the raw material.

Direct element analysis: U < $0.3*10^{-7}$ wt.% (0.3 ppb)
Th < $0.9*10^{-7}$ wt.% (0.9 ppb)

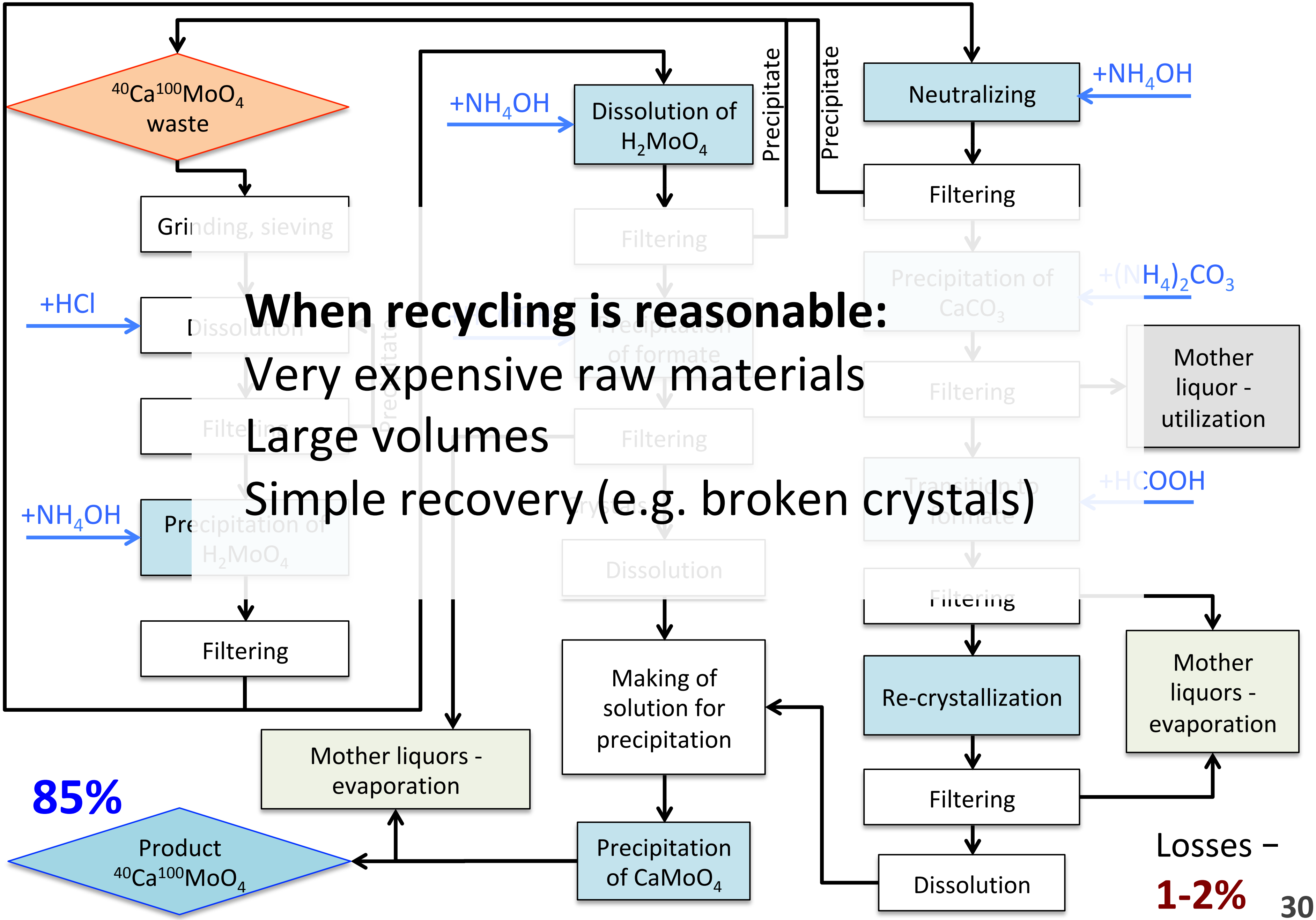
Final check − by low background gamma spectrometry (Baksan Neutrino Observatory, Institute for Nuclear Research, RAS)

- Very expensive raw material
- Special purification process
- Special impurities detection technique

More on that − in [V.V. Alenkov et al, Inorganic Materials 49(12) 2013, 1220-3]

BTW, no glassware could be used in the process!

Recycling could be a complicated process



$^{40}Ca^{100}MoO_4$ waste

Grinding, sieving

+HCl

Dissolution

Filtering

+NH_4OH

Precipitation of H_2MoO_4

Filtering

+NH_4OH

Dissolution of H_2MoO_4

Precipitate

Filtering

Precipitation of formate

Filtering

Dissolution

Making of solution for precipitation

Precipitation of $CaMoO_4$

Mother liquors - evaporation

Product $^{40}Ca^{100}MoO_4$

Precipitate

Neutralizing

+NH_4OH

Filtering

Precipitation of $CaCO_3$

+$(NH_4)_2CO_3$

Filtering

Mother liquor - utilization

Transition to formate

+HCOOH

Filtering

Re-crystallization

Filtering

Dissolution

Mother liquors - evaporation

When recycling is reasonable:

Very expensive raw materials

Large volumes

Simple recovery (e.g. broken crystals)

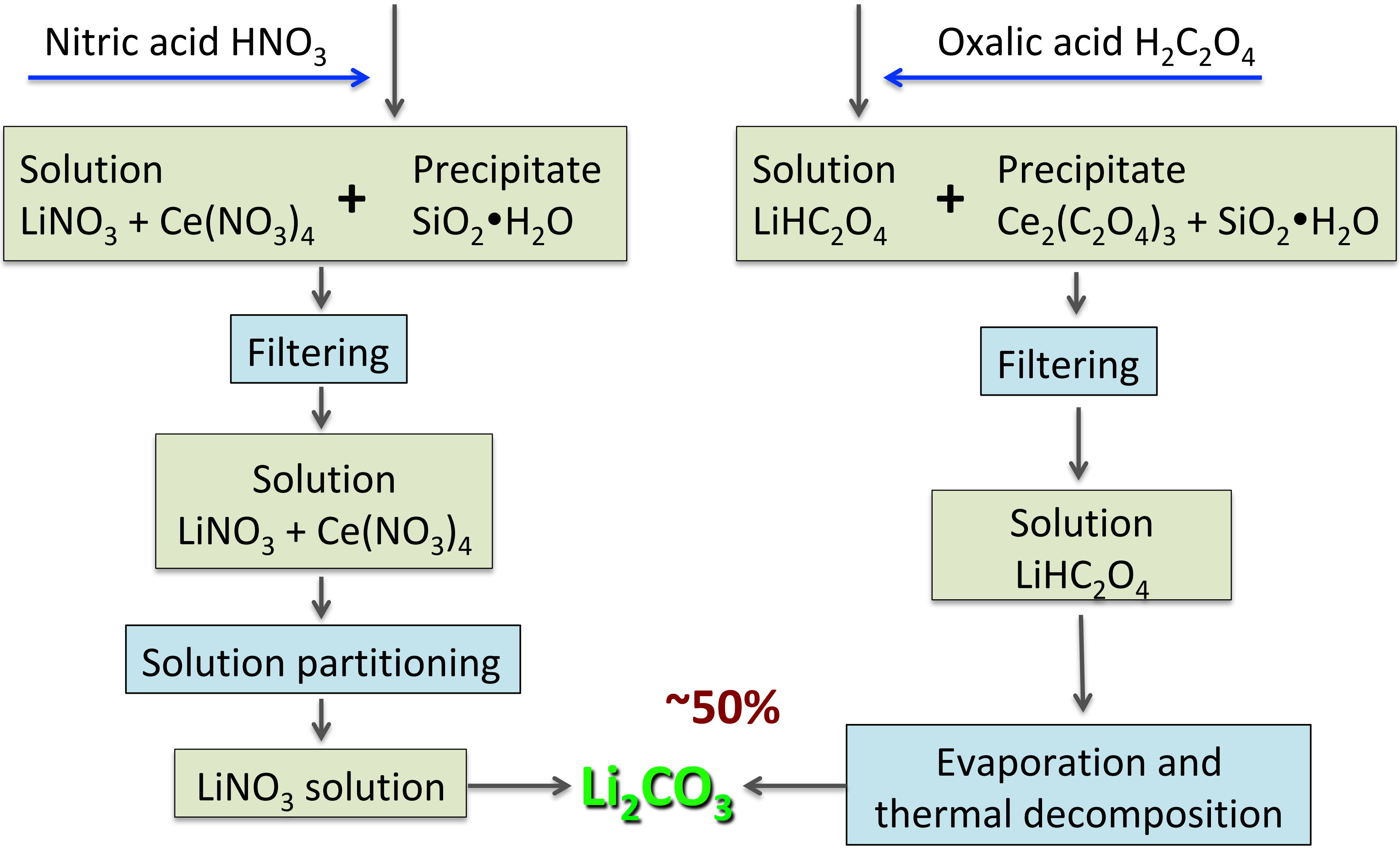
85%

Losses – **1-2%**

Li recovery from glass

Glass:

$Li_2O - SiO_2 - CeO_x$ + other (opt.)



Nitric acid HNO_3

Solution
$LiNO_3 + Ce(NO_3)_4$
+
Precipitate
$SiO_2 \cdot H_2O$

Filtering

Solution
$LiNO_3 + Ce(NO_3)_4$

Solution partitioning

$LiNO_3$ solution

Oxalic acid $H_2C_2O_4$

Solution
$LiHC_2O_4$
+
Precipitate
$Ce_2(C_2O_4)_3 + SiO_2 \cdot H_2O$

Filtering

Solution
$LiHC_2O_4$

Evaporation and thermal decomposition

~50%

Li_2CO_3

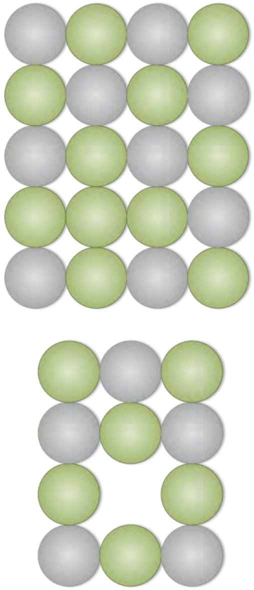
Other requirements for raw materials

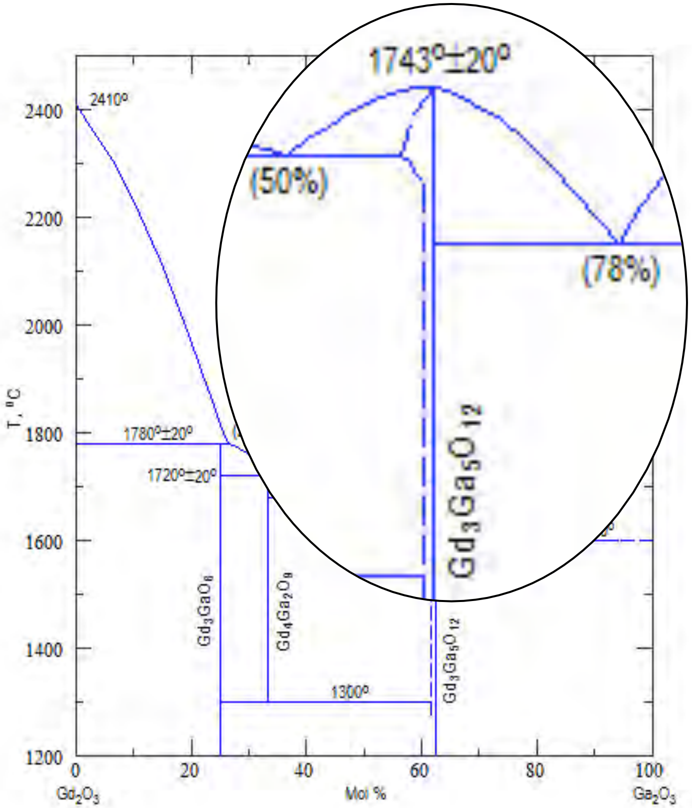
Other requirements for raw materials

Composition – main components

(1% or better)

- non-stoichiometry defects
- heterophase inclusions



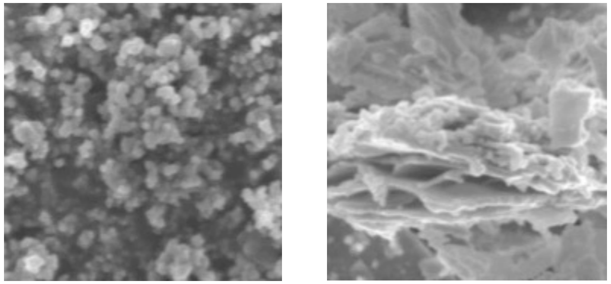


Microstructure

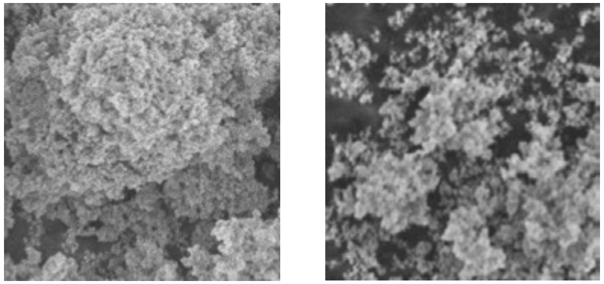
(suitable)

- material formation and properties

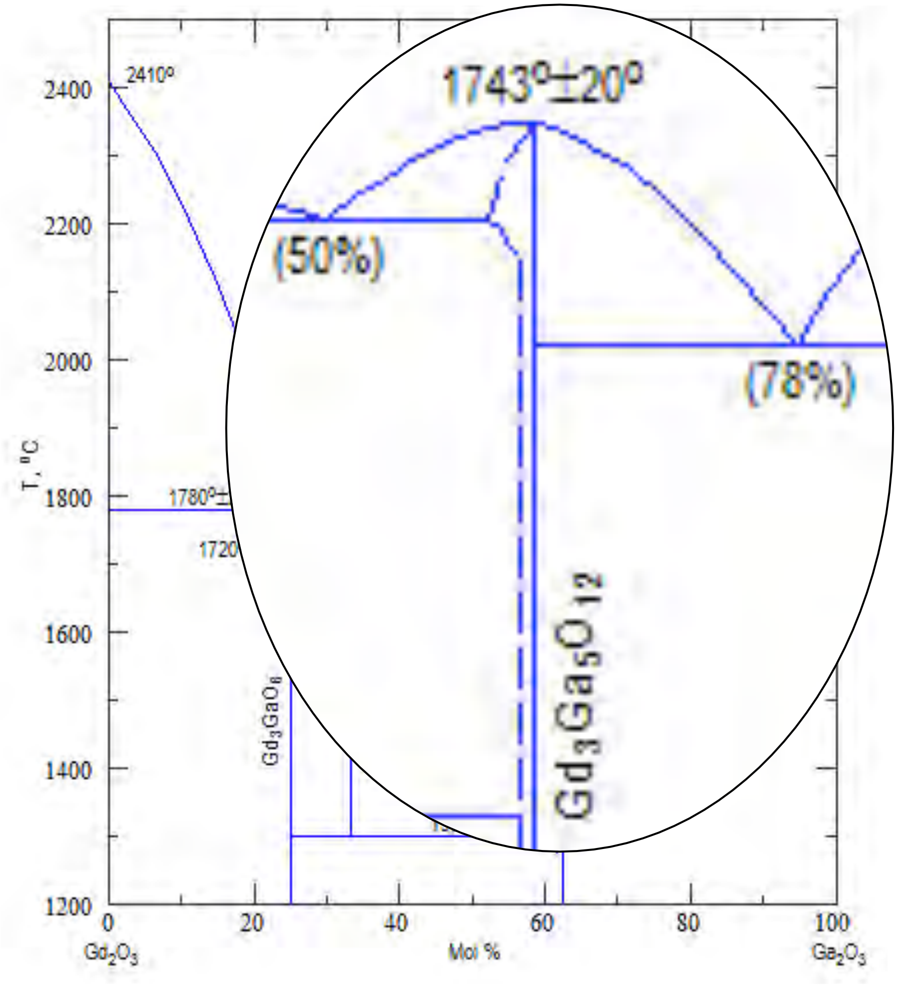
Primary particles size and shape



Agglomerates size and strength

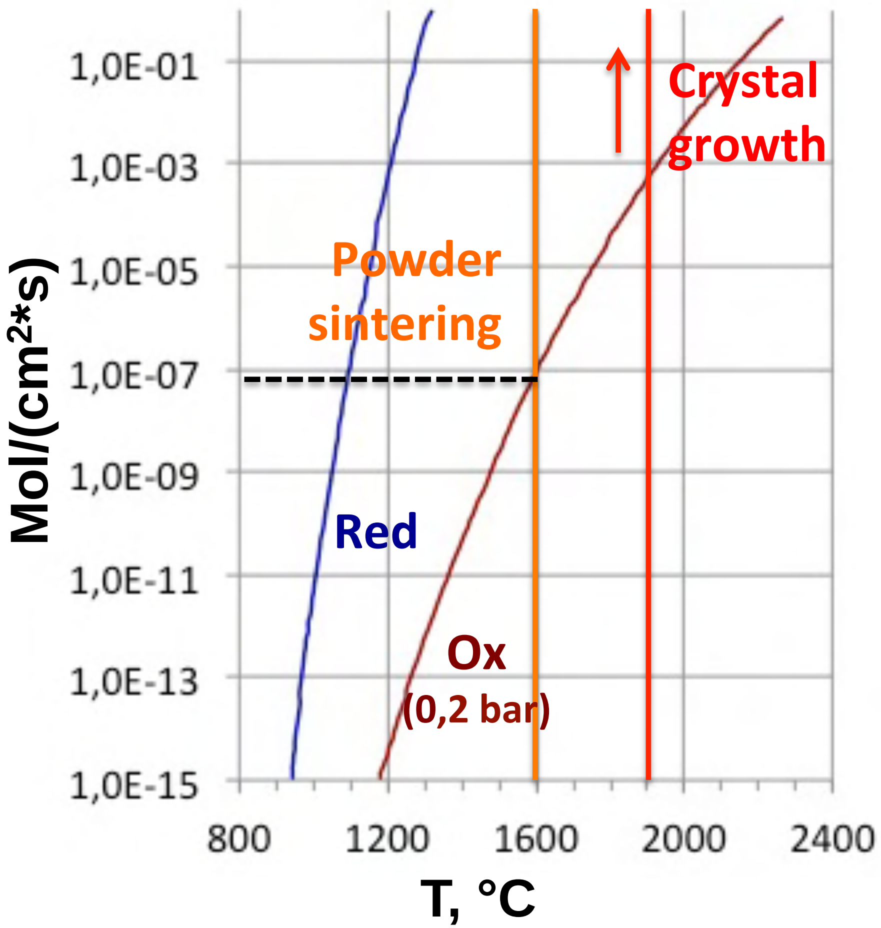


Mixed Gd, Ga containing garnets have wide homogeneity region → risk of defect formation



M. Mizuno and T. Yamada, *Nagoya Kogyo Gijutsu Shikensho Hokoku*, **40** [12] 389-401 (1992).

Ga oxide maximum evaporation rates

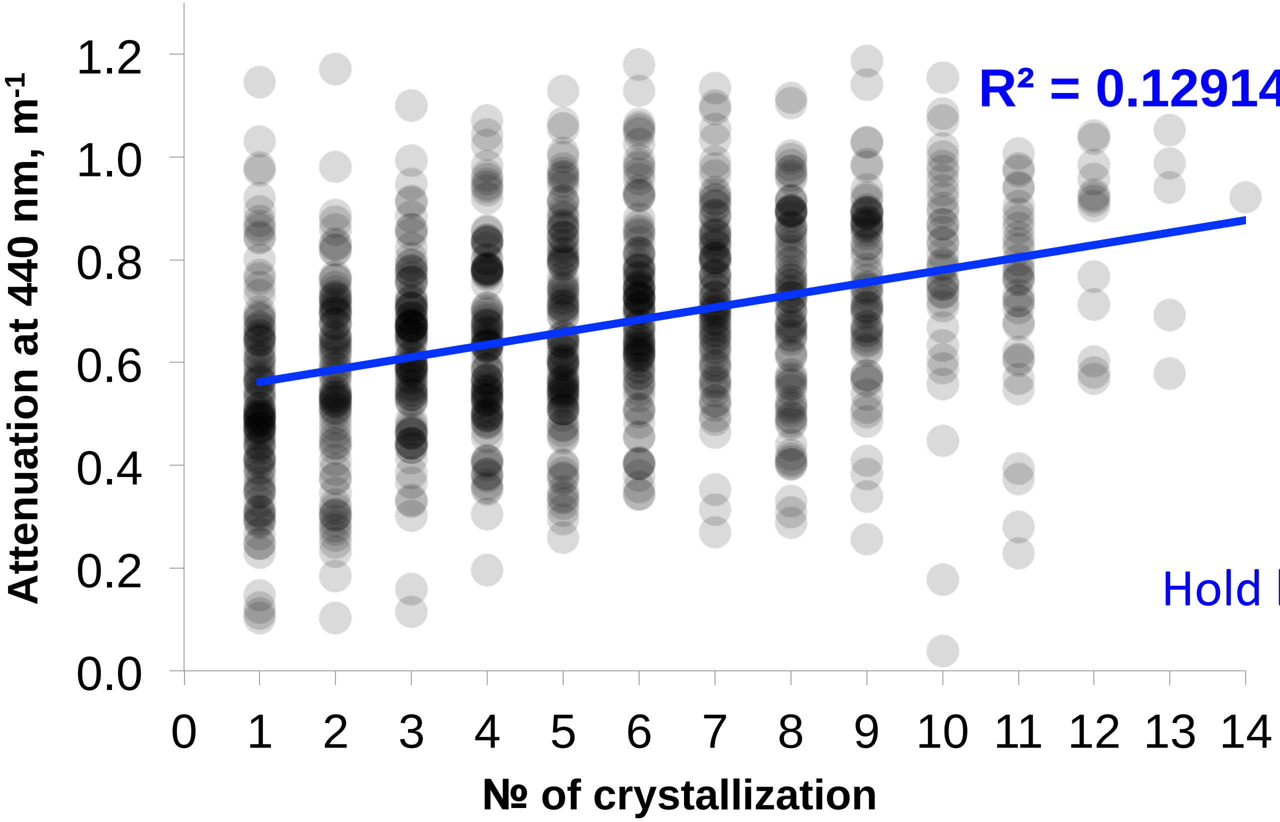


[R.H. Lamoreaux et al, J Phys Chem Ref Data, Vol.16 No.3 1987]

Raw materials composition

In $PbWO_4$ deviation from stoichiometry reduces radiation hardness

PbO : WO_3 evaporate from a melt at rates 60 : 40 → Deviation from stoichiometry accumulates each crystallization



> 900 crystals measurements data from production

Source: ^{60}Co, 10^4 rad/h
Irradiation time: 20 min
Hold before measurement: 8 h

Composition control of initial reagents

Titration

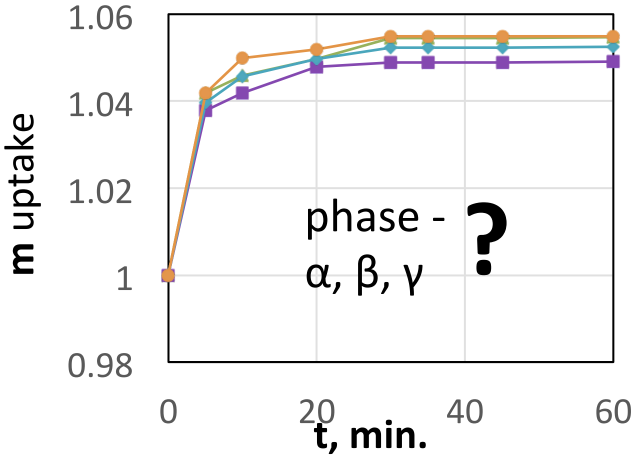
Gravimetric analysis

Known for more then 200 years, but are still the most reliable for quantitative analysis of main components

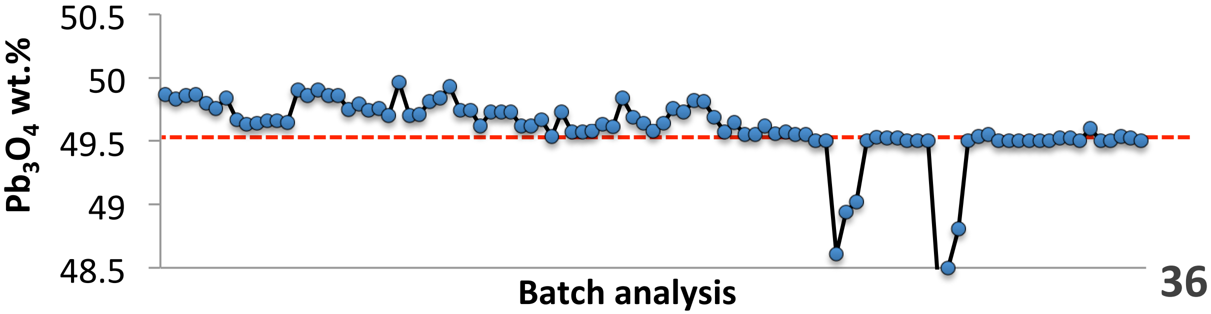
$Al(NO_3)_3$ solution concentration analysis by gravimetry

$Al(NO_3)_3$ or $Al(OH)_3$ thermal treatment ?

T of thermal treatment ?

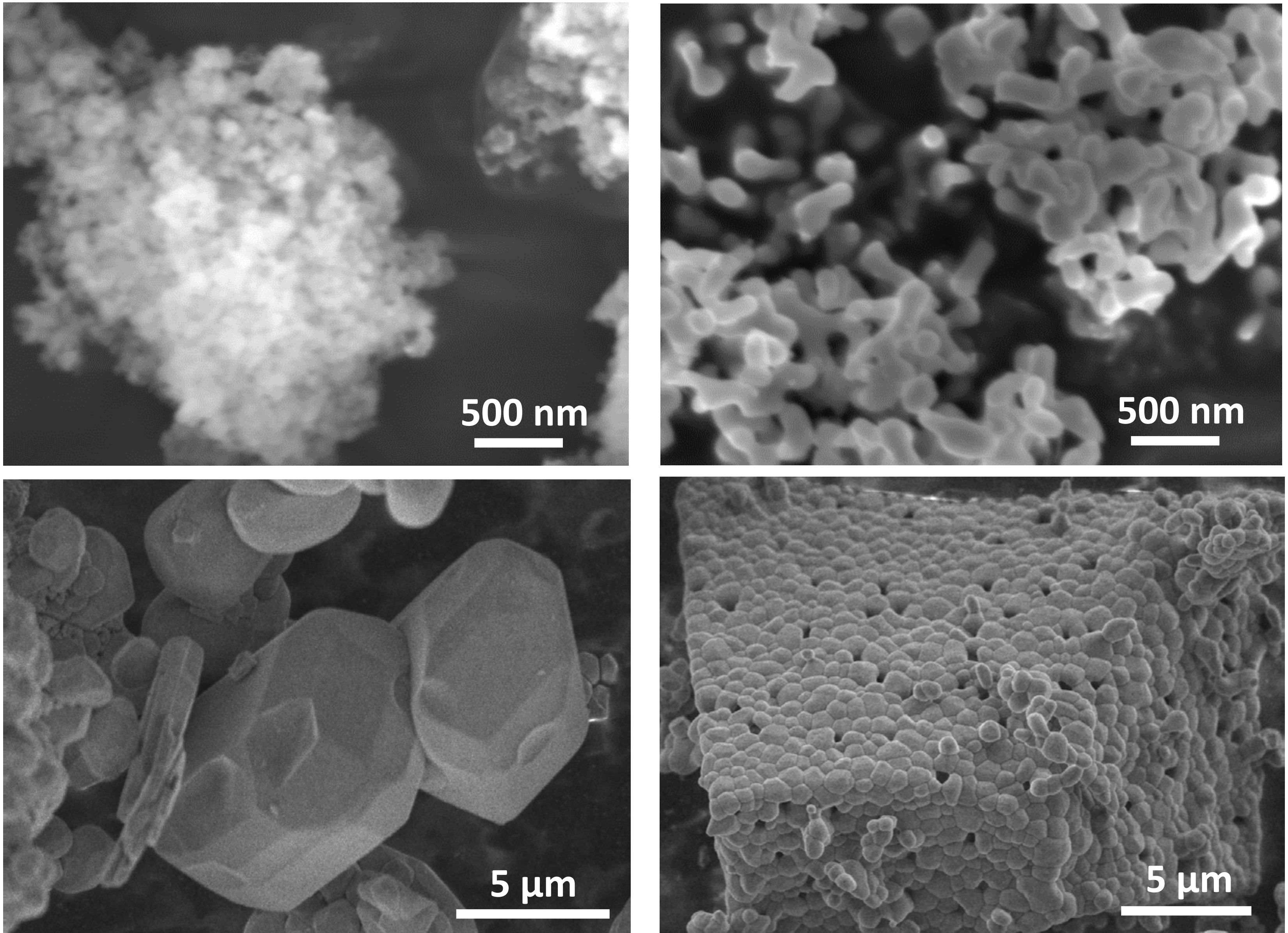


PWO raw material Pb/W ratio control by titration

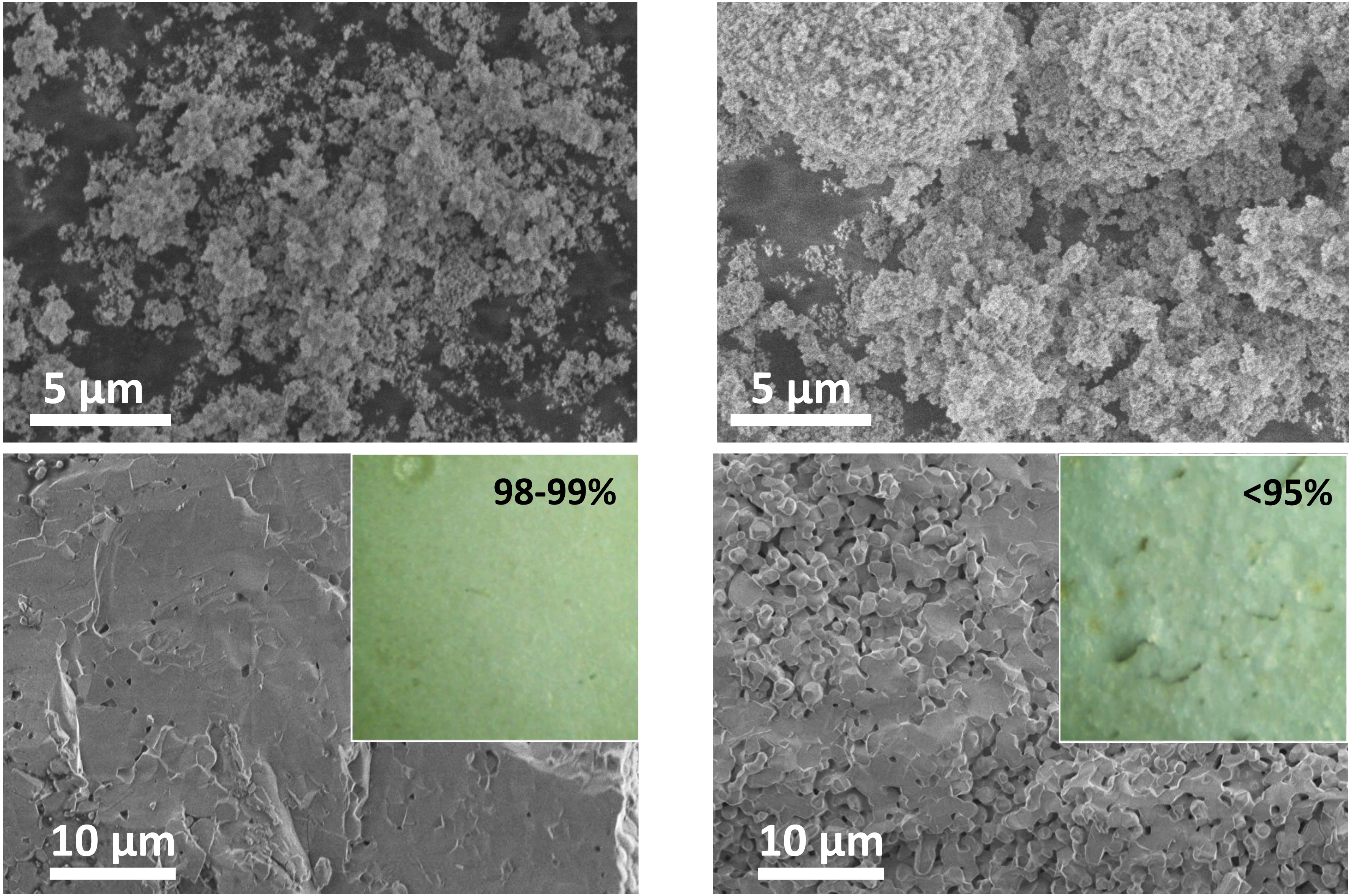


Powder microstructure - primary particles

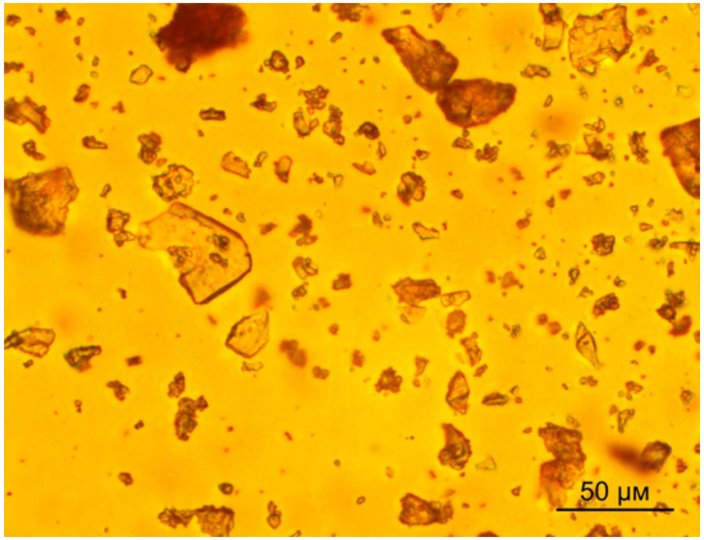
YAG particles obtained with different synthesis routes



Agglomeration in raw material powder (secondary particles) also has effect on ceramics density



Particle (secondary) size distribution



Direct methods

Microscopy of all kinds

+ WYSIWYG (more or less)
+ Some additional details
- Low statistics, could be unrepresentative

Indirect methods

laser diffraction →

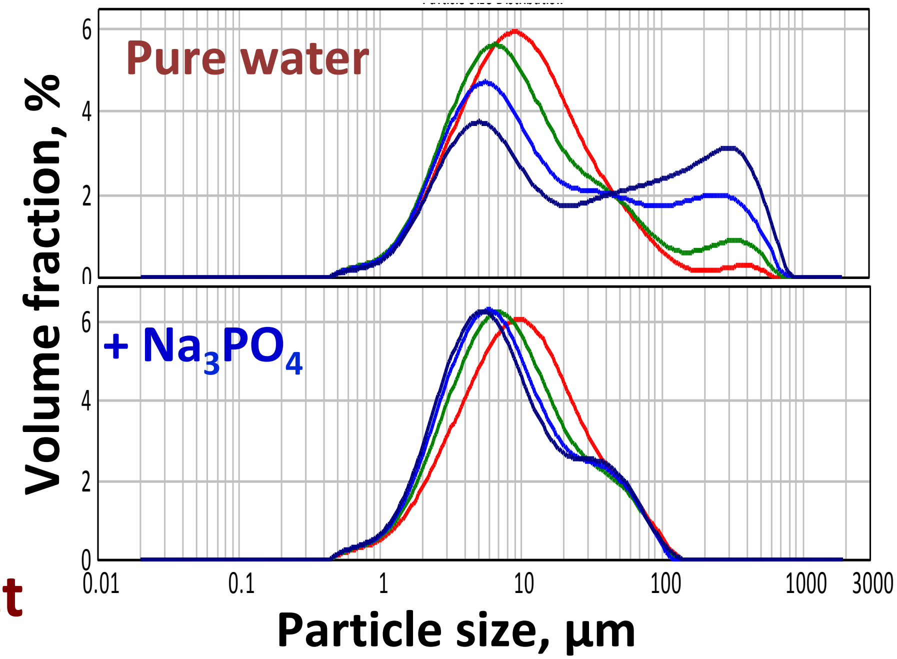
light scattering

surface absorption

sedimentation

+ Express and/or cheap
+ Representative probes
- Needs adjustment for a product

Measurement after 0-2-4-6, min.:



Summarizing notes

- Pure raw materials is a first important step in material development / production
- Other raw materials characteristics are to be considered as well
- If not available on the market, the raw material could be developed on demand
- Raw material development usually requires R&D
- Raw material requirements should consider further process of scintillator obtaining

Thank you for your attention!

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