



The Henryk Niewodniczański
Institute of Nuclear Physics
Polish Academy of Sciences



$\text{LiMgPO}_4:\text{RE}$

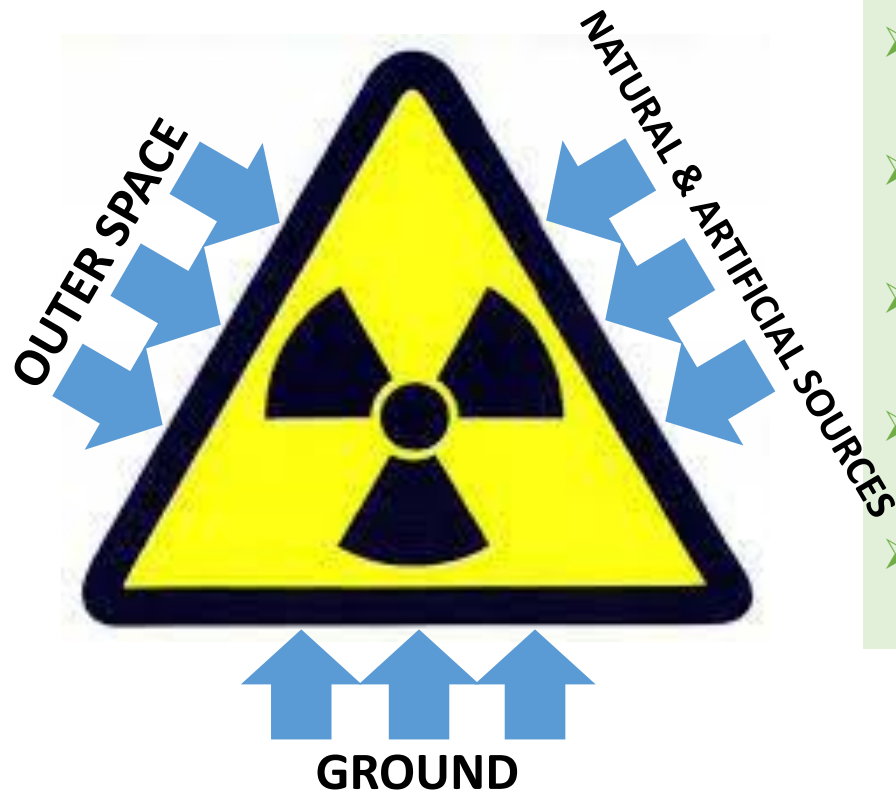
review of the results of 7-years investigations
on new dosimetric crystals

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Ionizing radiation is all around us



Need for dosimetric measurements:

- Personal dosimetry
- Environmental monitoring
- Medical applications
- Industrial applications
- Nuclear physics experiments



Ionizing radiation is all around us



Need for dosimetric measurements

- Personal dosimetry

- Environmental monitoring



How to measure the energy delivered by ionizing radiation

MATERIAL

METHOD

α β γ n



Light detection system



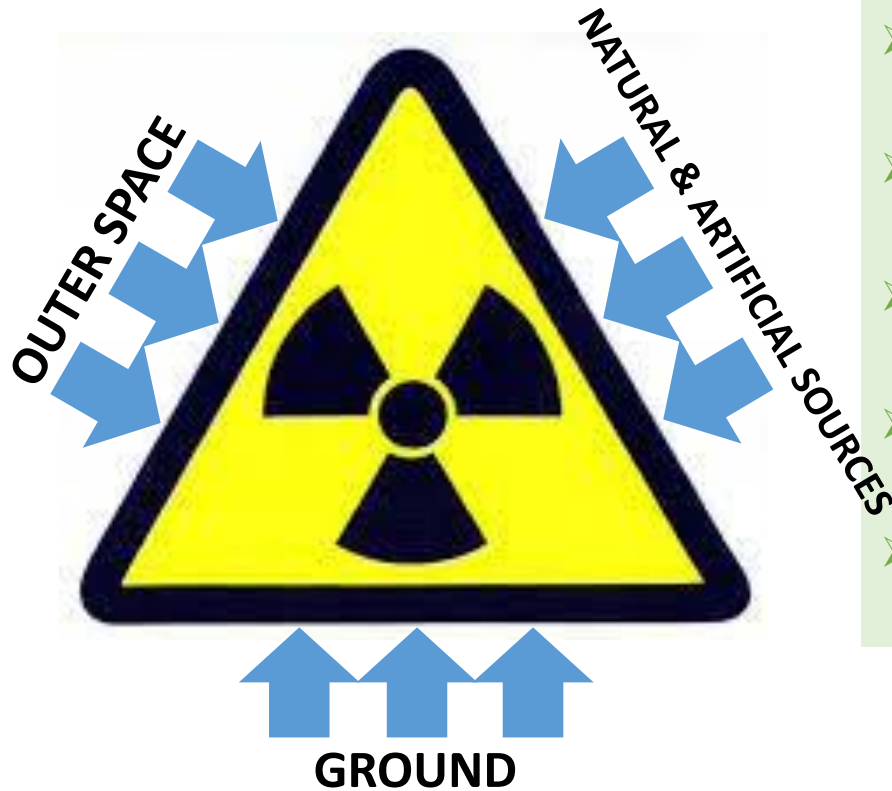
Light emission

Passive radiation detector



Multiplying factor

Ionizing radiation is all around us

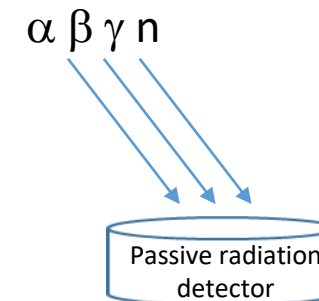


Need for dosimetric measurements

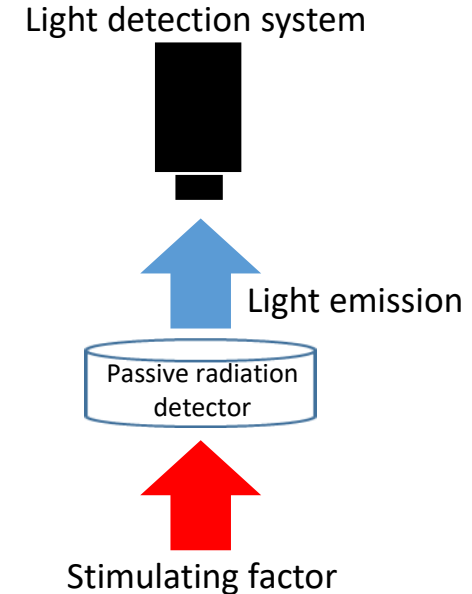
- Personal dosimetry
- Environmental monitoring
- Medical applications
- Industrial applications
- Nuclear physics experiments

How to measure the energy delivered by ionizing radiation

MATERIAL



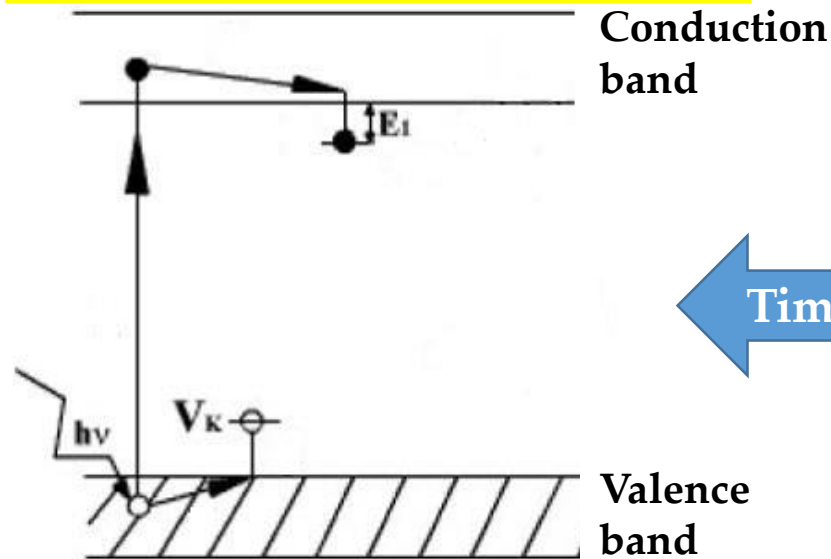
METHOD



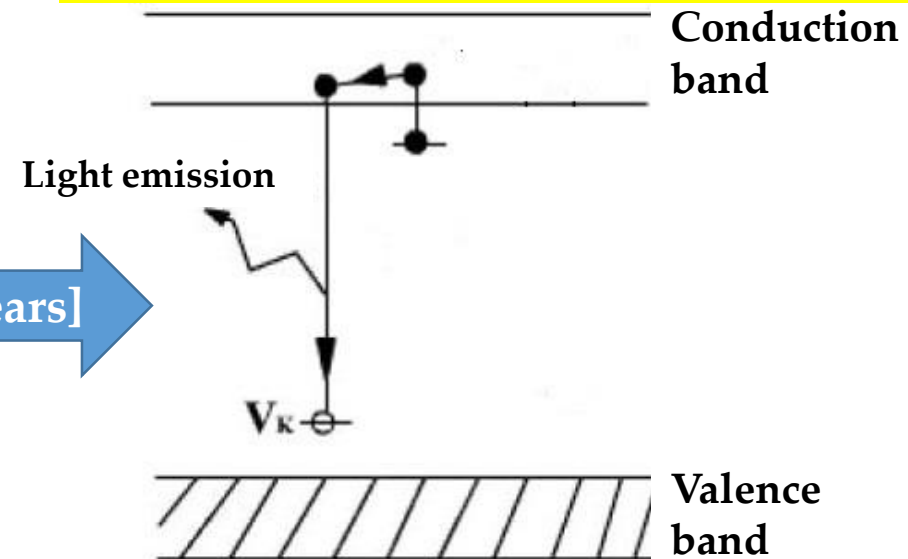
- Thermally Stimulated Luminescence (TSL, TL) – still most popular
- Optically stimulated Luminescence (OSL) – becomes more widely applied measurement technique

Simplified model

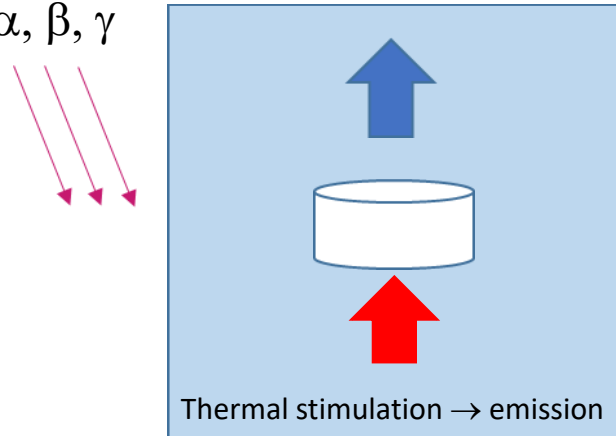
1st stage – absorption of radiation energy



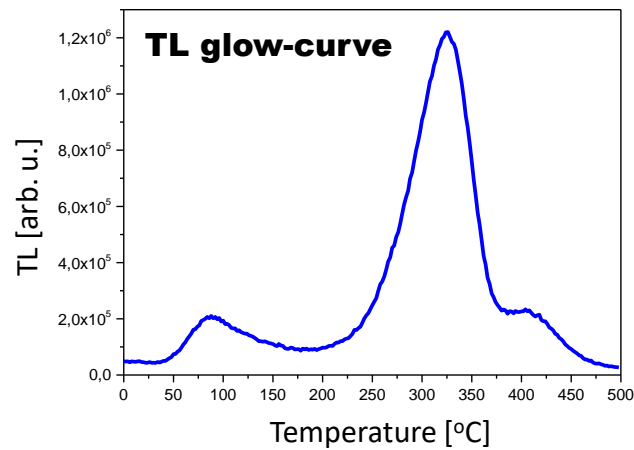
2nd stage – stimulation associated with light emission



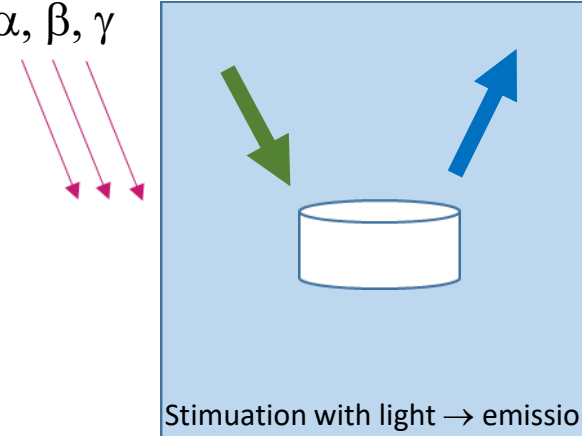
Ionizing radiation (any kind)
 α, β, γ



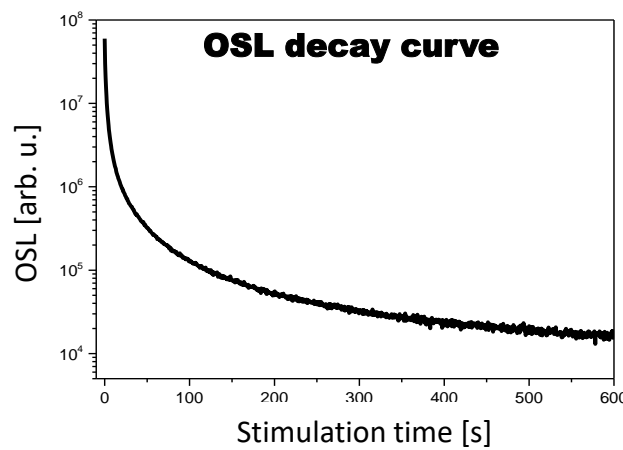
TL



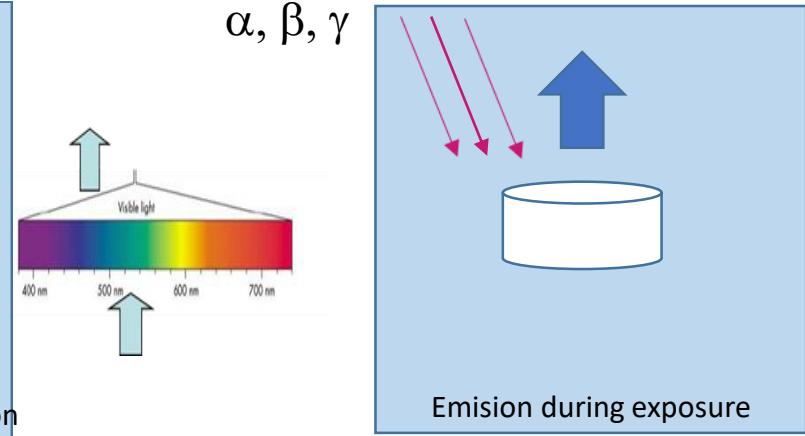
Ionizing radiation (any kind)
 α, β, γ



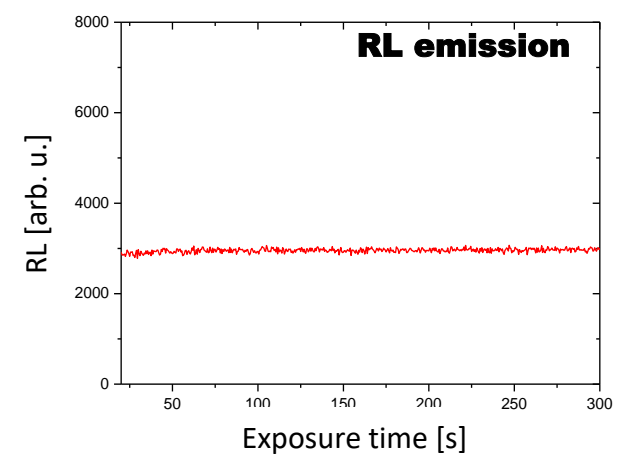
OSL



Ionizing radiation (any kind)
 α, β, γ



RL



Introduction

Widely used TL materials

LiF

CaF₂

CaSO₄

Mg₂SiO₄

Li₂B₄O₇

Al₂O₃

BeO

LiMgPO₄ ???

Thermoluminescent (TL) dosimetry is well developed

Optically Stimulated Luminescence (OSL) becomes very popular

OSL materials

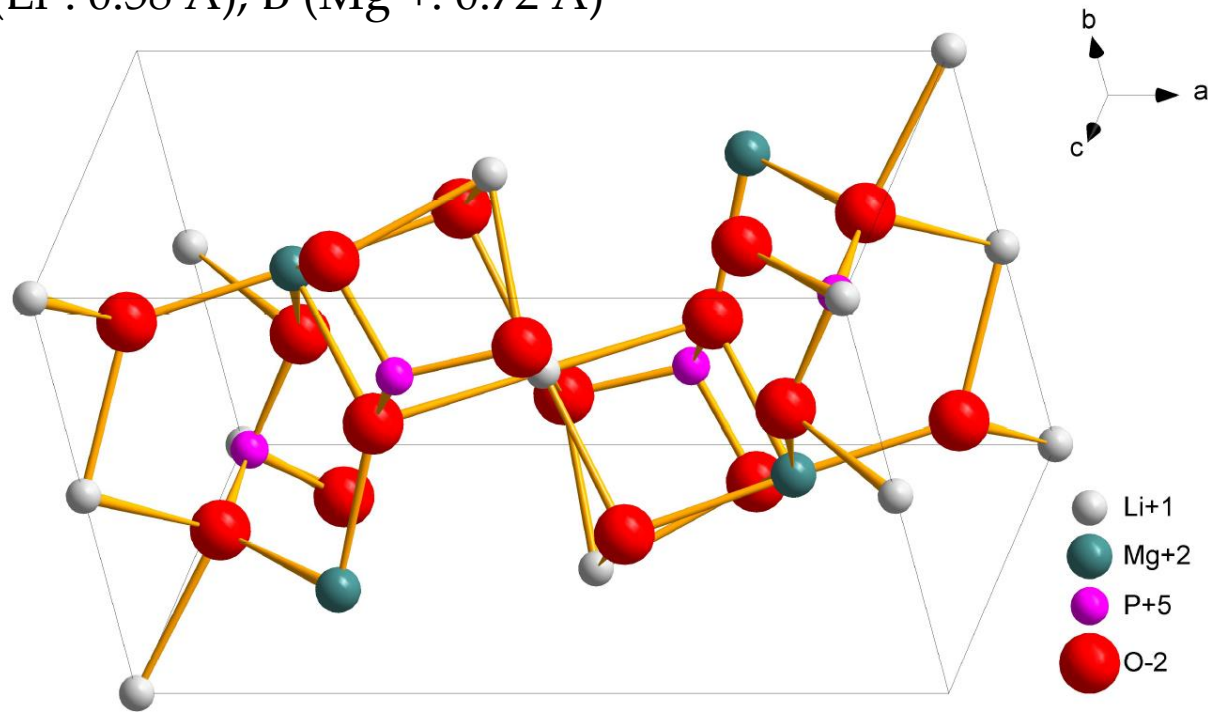
Al₂O₃

BeO

LiMgPO₄ ???

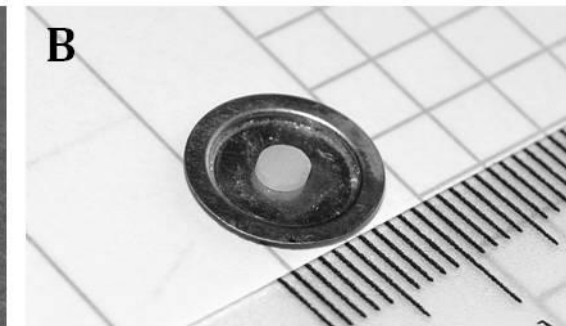
Basic data on LMP compound

Orthophosphate of $ABPO_4$ formula
 A (Li^+ : 0.58 Å), B (Mg^{2+} : 0.72 Å)



3D crystal structure of $LiMgPO_4$ prepared by Diamond 4.1 software using the data from Crystallographic Open Database (COD 1530053)
 View towards the $\langle h,k,l \rangle = \langle 1,1,1 \rangle$ plane

Olivine-type structure stable over a broad temperature range



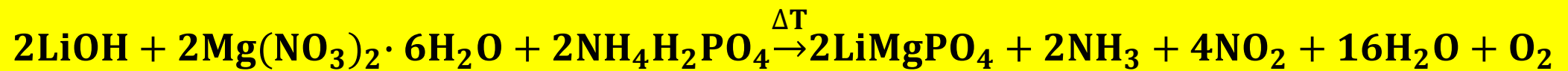
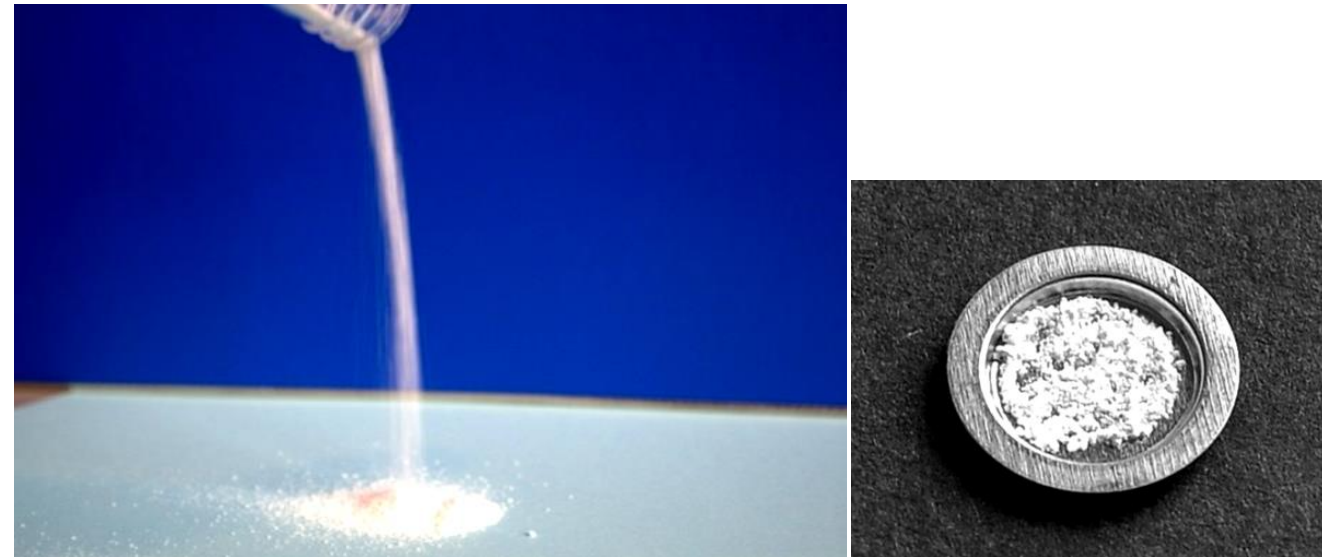
Exemplary LMP crystals placed on stainless-steel cups

Property	Value
Crystallographic system	Orthorhombic
Space group	Pnma
Unit cel parameters	a = $10.147 \cdot 10^{-10}$ m b = $5.909 \cdot 10^{-10}$ m c = $4.692 \cdot 10^{-10}$ m
Unit cel volume	$281.32 \cdot 10^{-30}$ m ³
Molar mass	126.225 g/mol
Density	2.98 g/cm ³
Effective atomic numer (Z_{eff})	11.5
Z_{eff} Al2O3	11.4
Z_{eff} LiF	8.2
Z_{eff} BeO	7.2
Z_{eff} tissue	7.4

Samples preparation techniques (powders)

Solid-state reaction between:

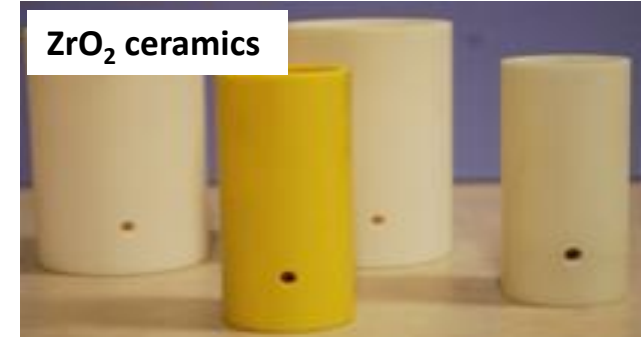
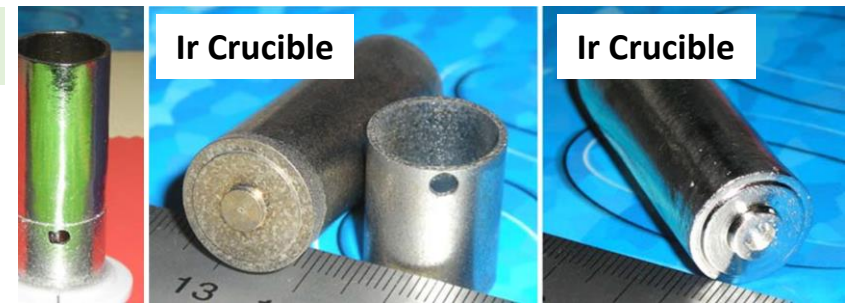
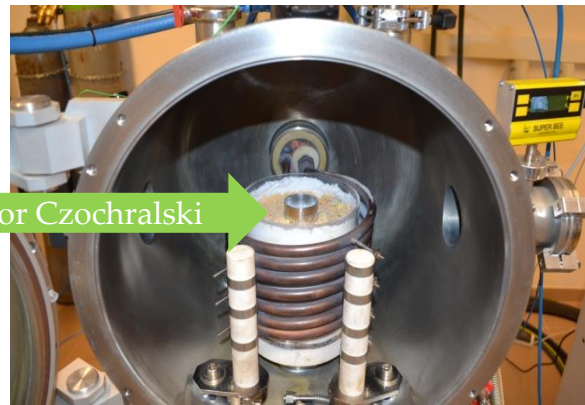
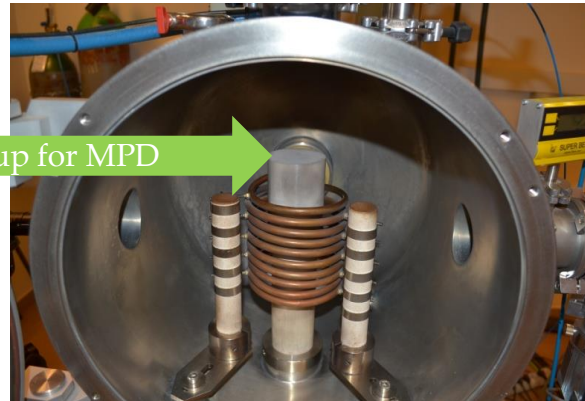
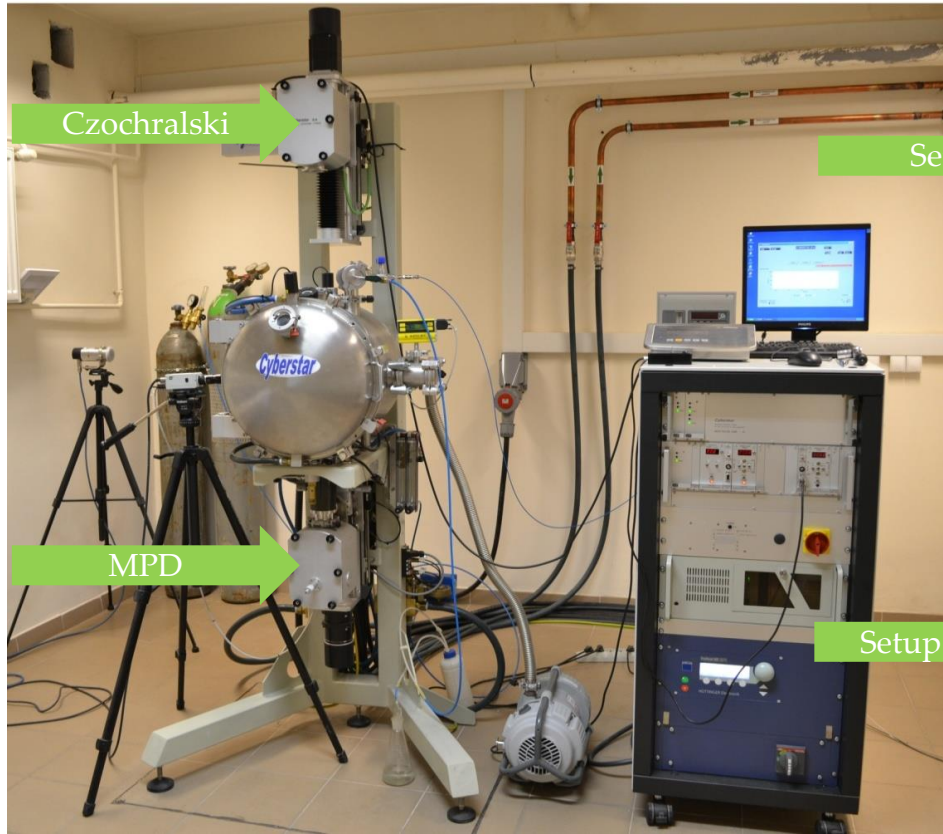
- lithium hydroxide (LiOH)
- hexahydrate magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)
- ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$)



- followed by several annealing cycles at the temperatures ranging from 200 to 750 °C

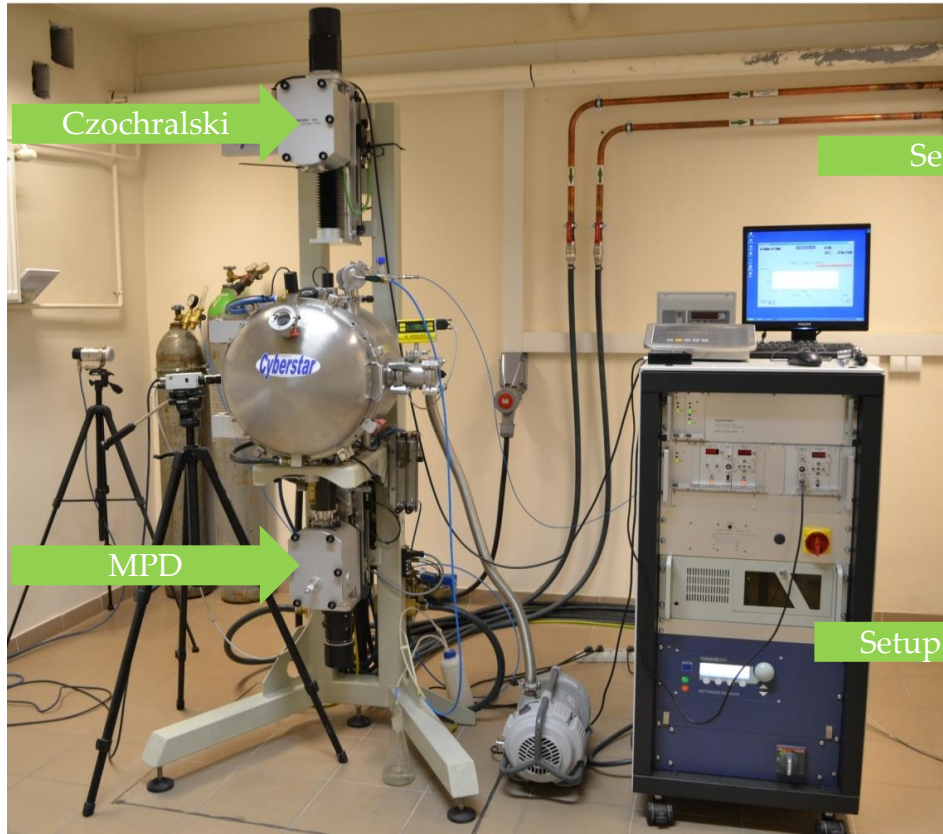
We are probably the first research group that developed and optimized this material in the form of **melt-grown crystals**

Samples preparation techniques (crystals)

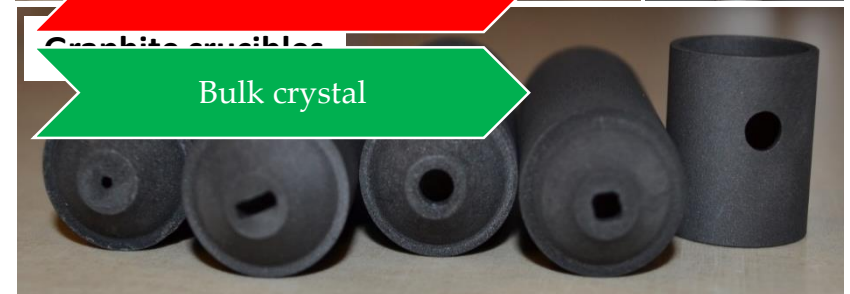
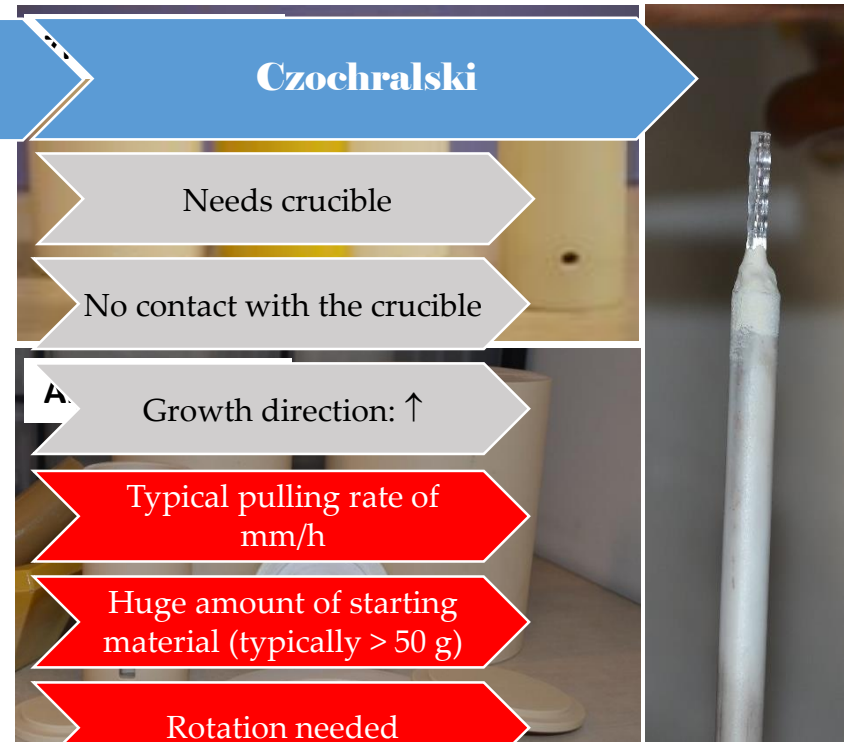
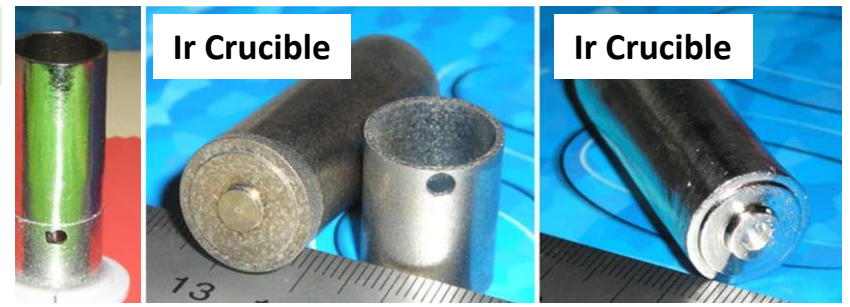
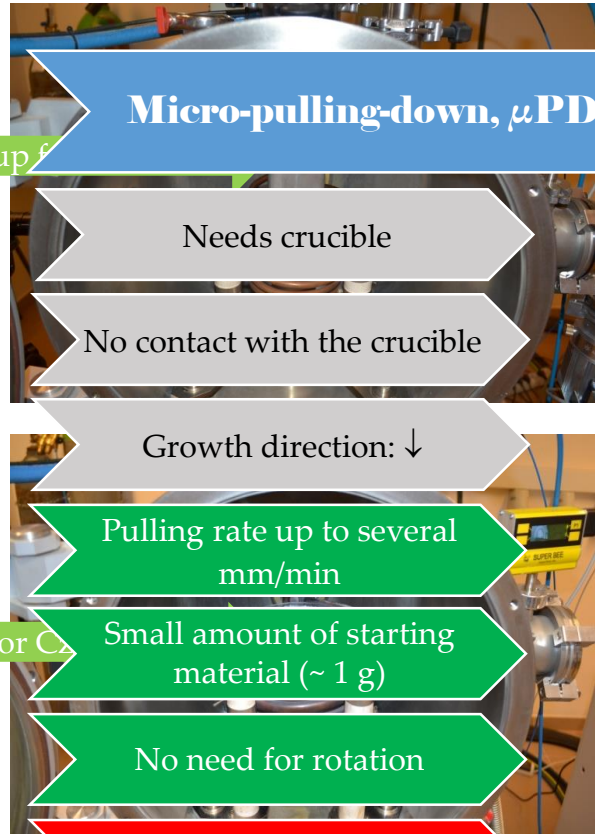


- Inductive furnace made by Cyberstar (France)
- Middle-frequency generator of 20 kW power
- Achievable temperatures above 2000 °C
- Two methods of crystal growth in one device (micro-pulling-down, μ PD and Czochralski)

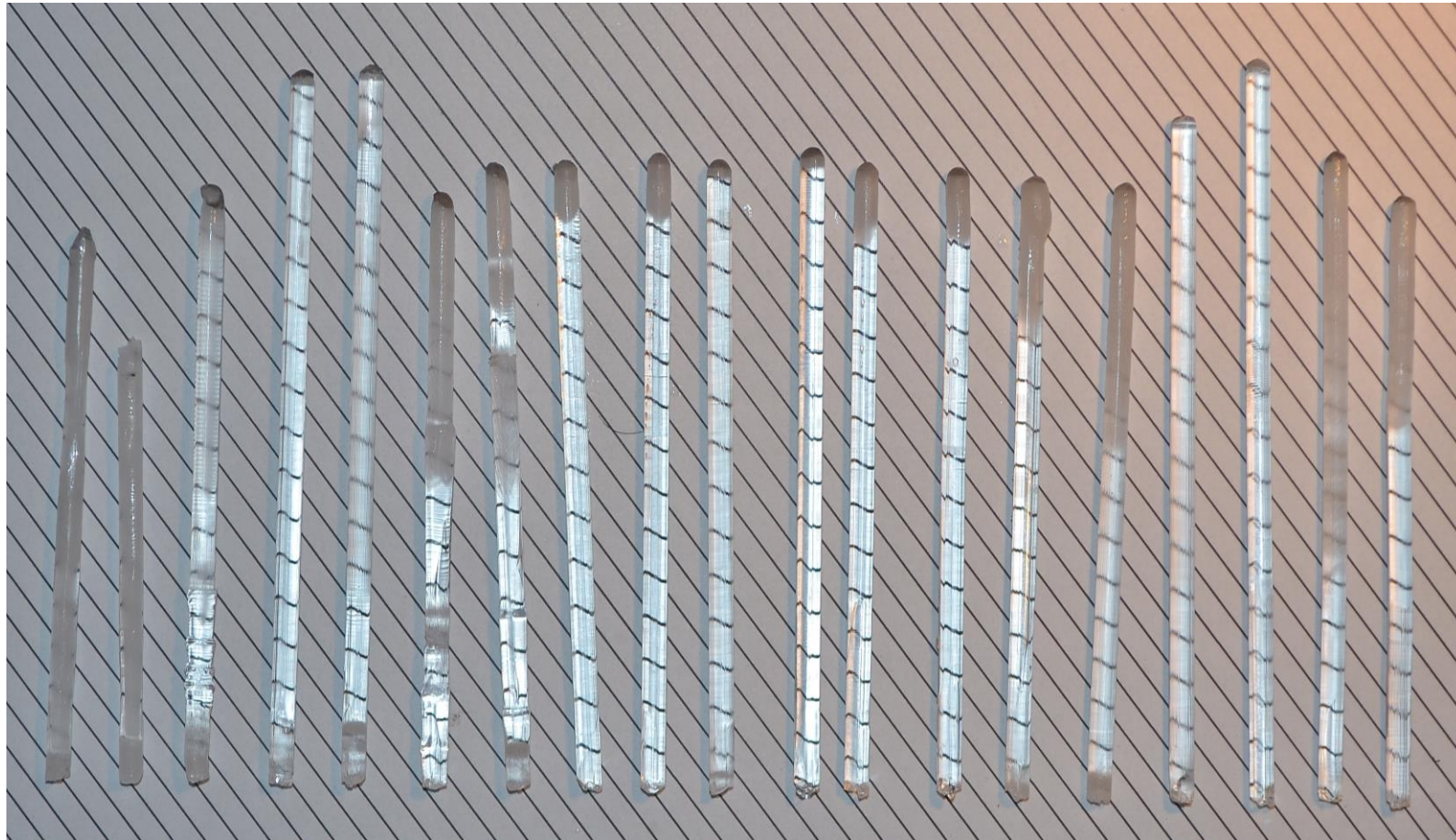
Samples preparation techniques (crystals)



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Samples preparation techniques (crystals)



Series of our LiF crystals obtained by micro-pulling-down method

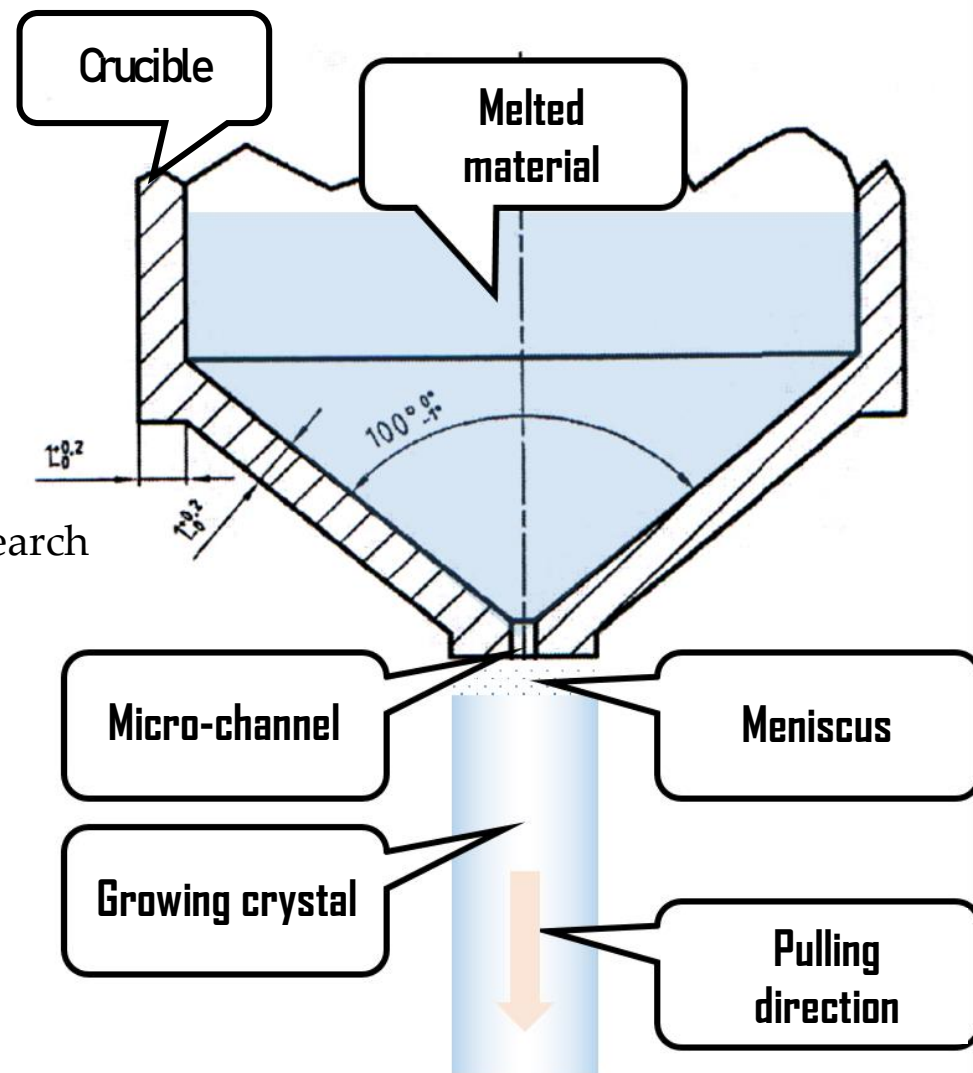
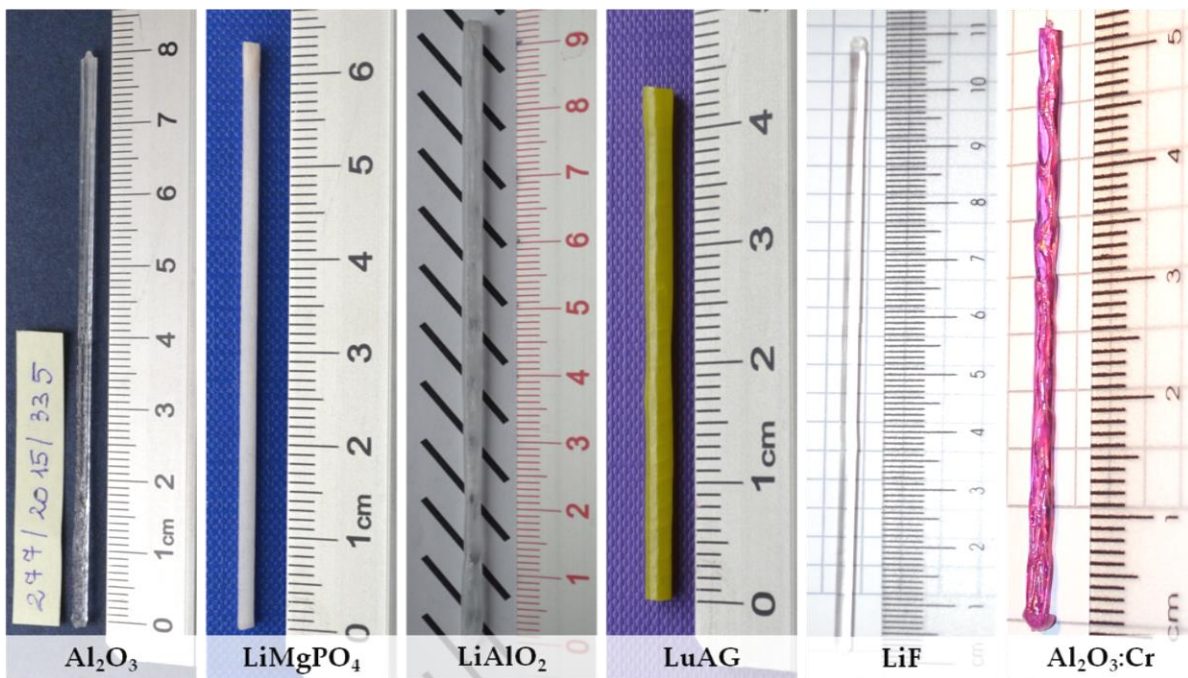


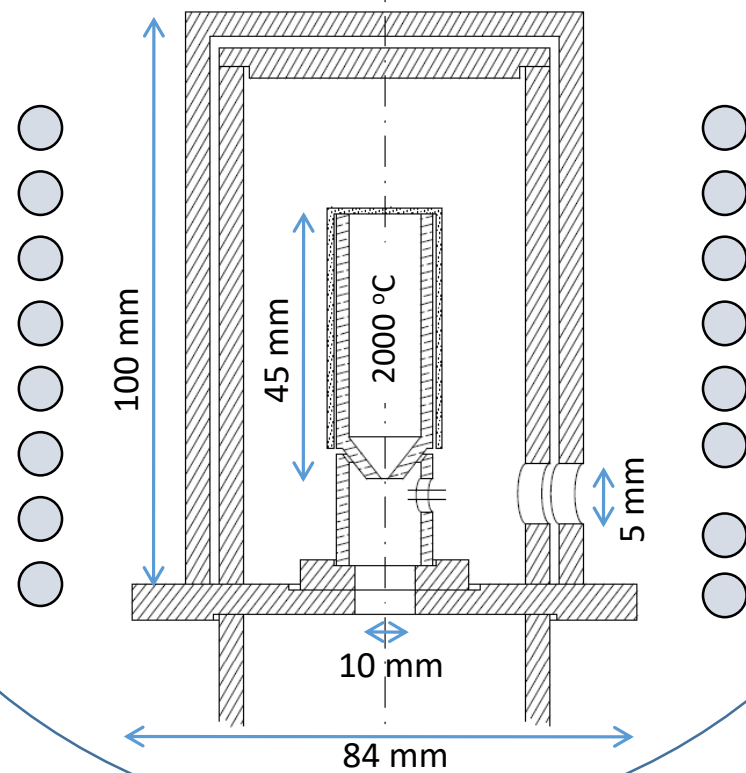
Our LiF crystals obtained by Czochralski method

Samples preparation techniques (crystals)

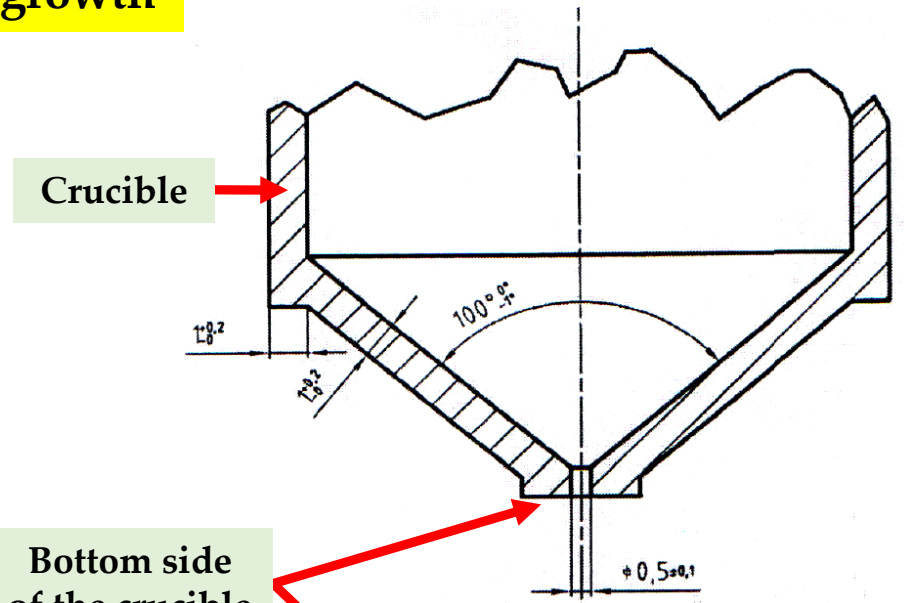
Micro-Pulling-Down method:

- High-temperature growth (even above 2000 °C for selected materials)
- Needs a dedicated crucible made of noble metal
- Fast and cheap method for crystal growth for the needs of laboratory research

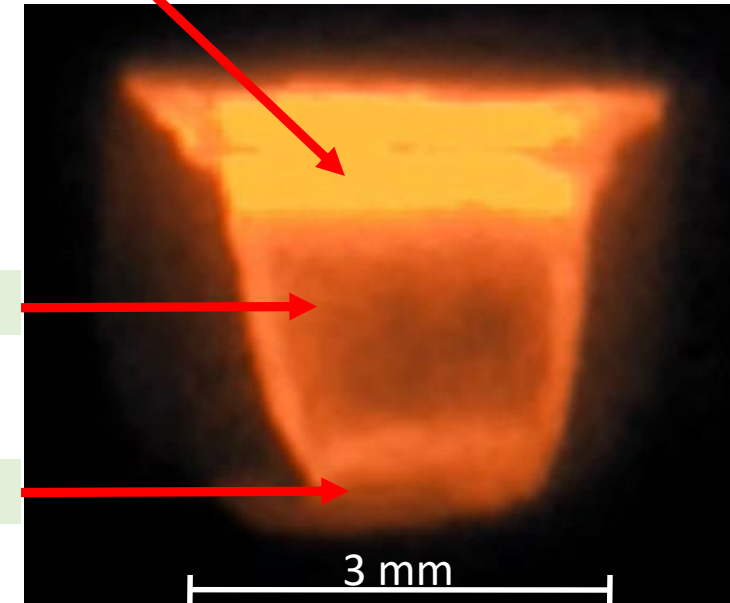




- Precise set of the relatively small thermal setup elements
- Lack of permanent fastening of thermal setup elements
- Not possible to run the process without a live view
- Melted material must flow through the micro channel in a controlled manner
- Stable contact of the seed with the melted material is needed
- Adequate temperature gradient needed for stable growth
- The crucible cleaning problems



Bottom side of the crucible



Growing crystal

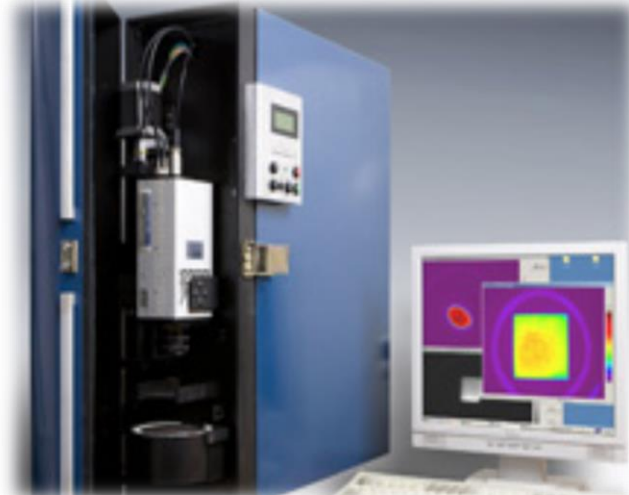
Seed

3 mm

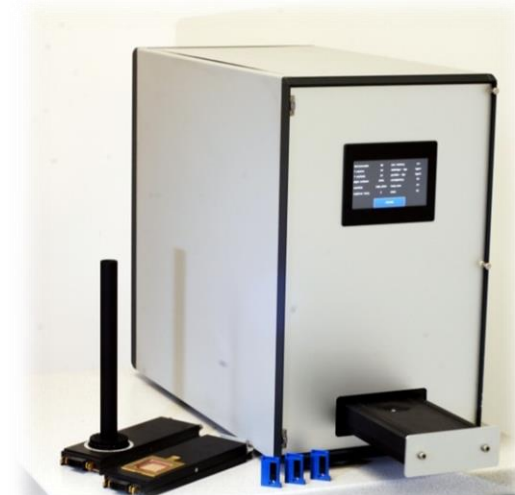
TL/OSL measurements



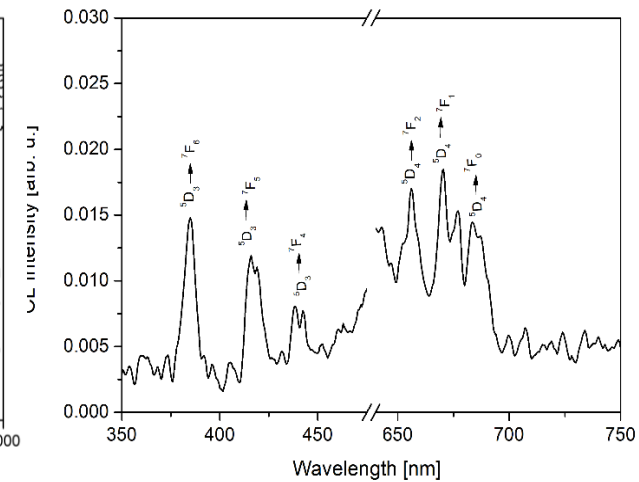
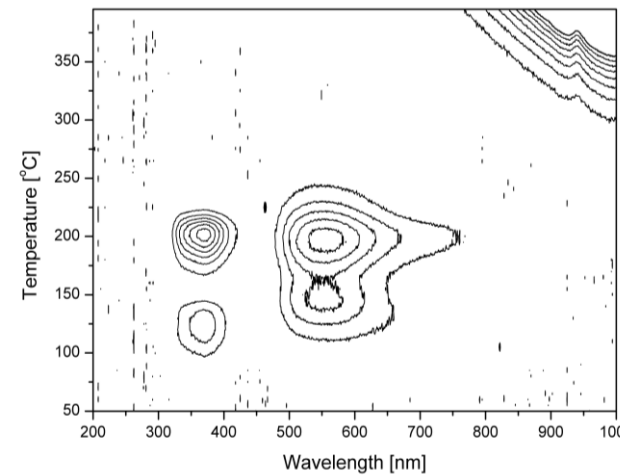
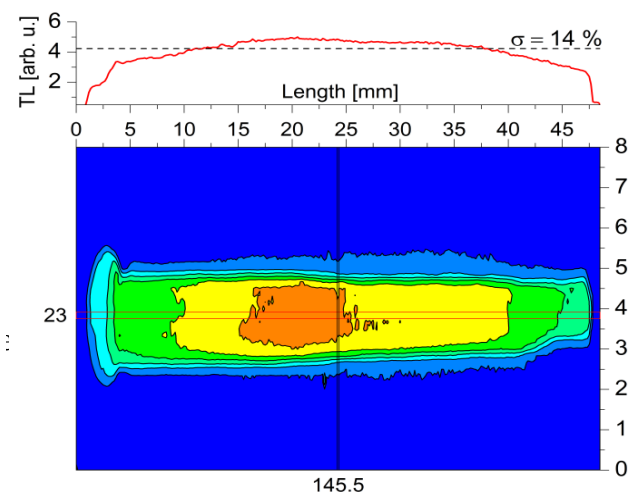
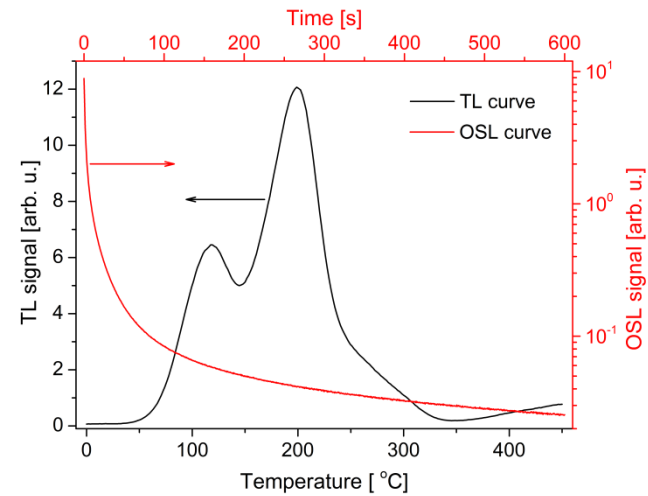
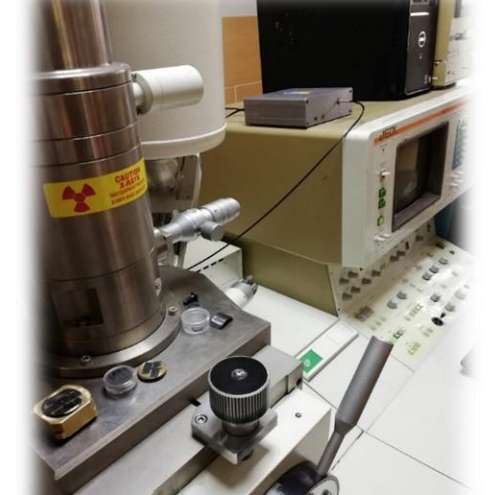
2D-TL measurements



Spectral measurements



CL measurements



Materials & Methods

Overview of crystal growth experiments

Matrix	Dopant	Doping strategy	Dopant concentration	Crucible material	Hot zone material	Protective atmosphere	Pulling rate
LiMgPO ₄	Tb	No doping or Single doping or Double doping or Triple doping	0.1 – 10 mol%	Ir Mo C	ZrO ₂ Al ₂ O ₃	Ar Ar/H ₂	0.03 – 5.0 mm/min
	B						
	Tm						
	Eu						
	Er						
	Y						
	Gd						
	Sm						
	Yb						

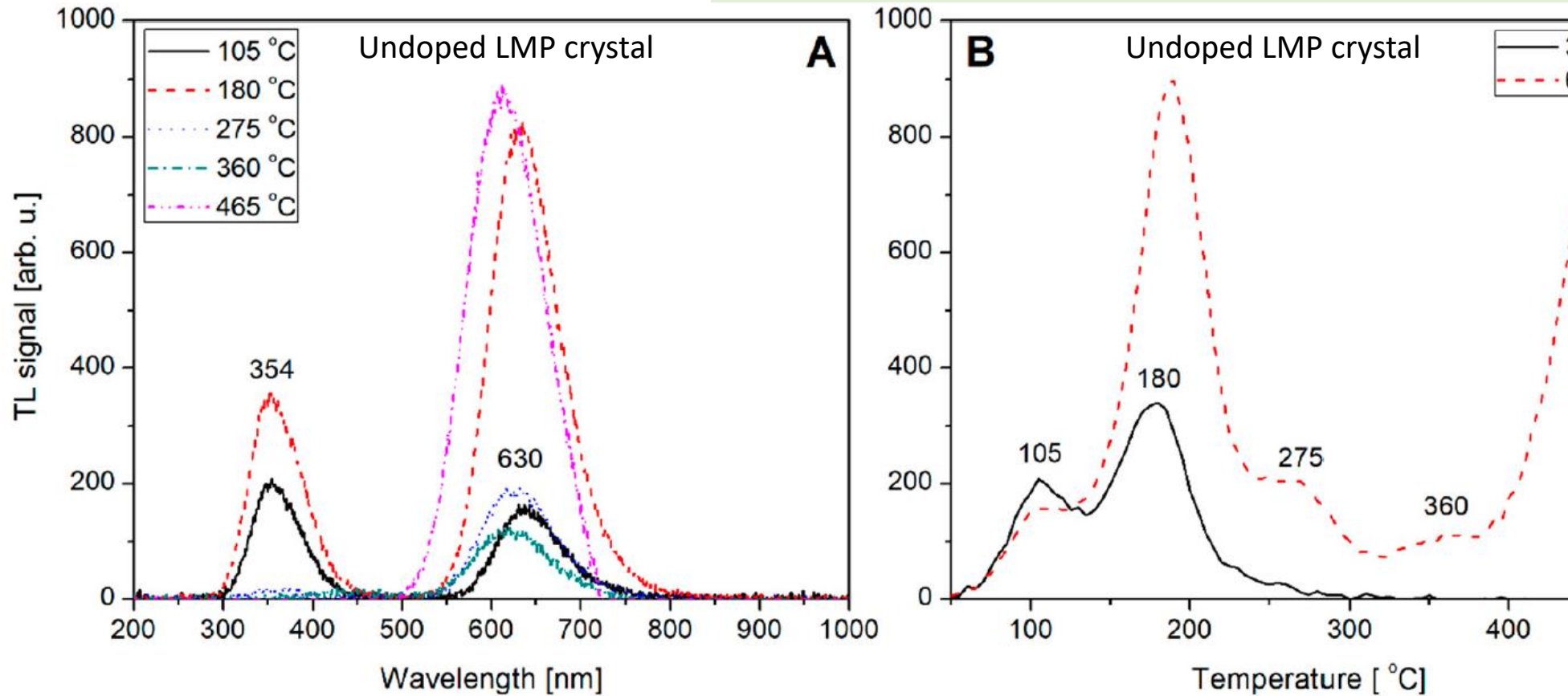
1 crystal/day with MPD

1 crystal/day with MPD method
1 crystal/week with Czochralski method



More than 100 different LMP crystals investigated within this work

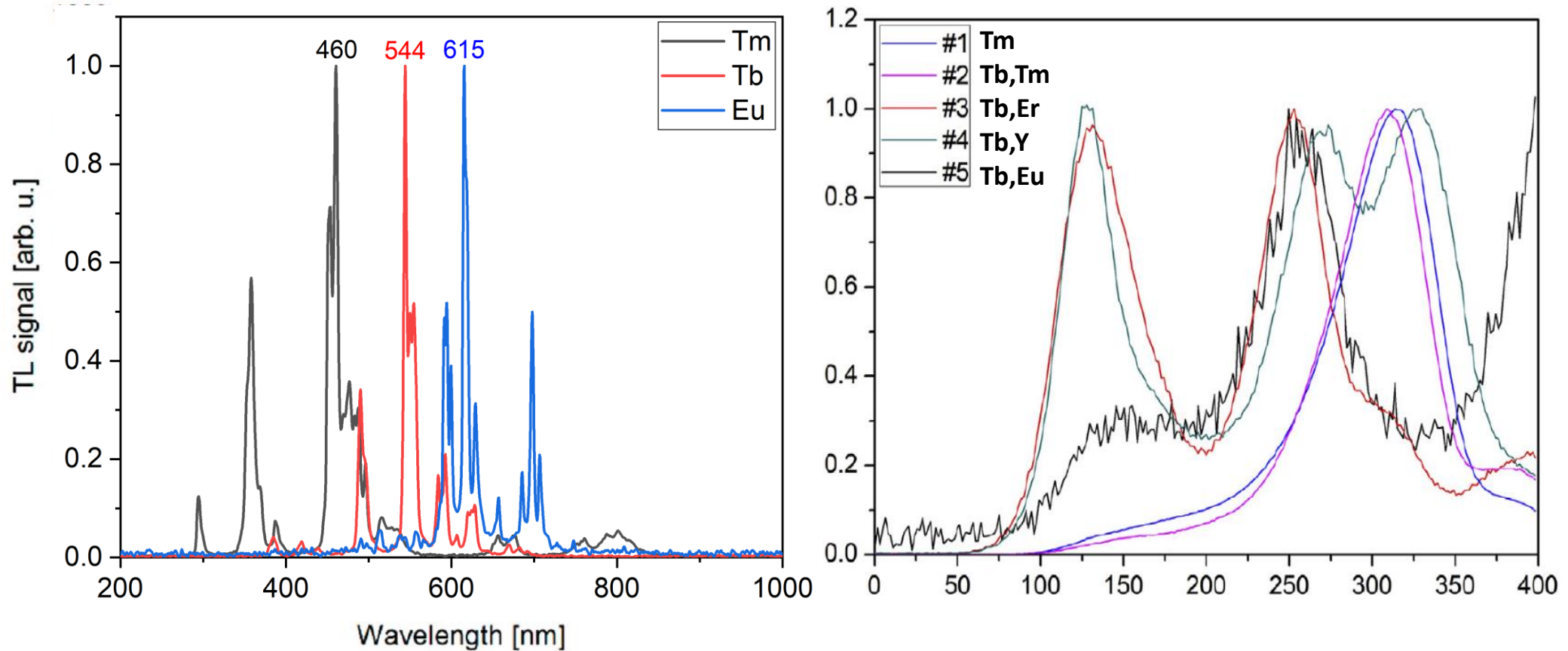
Short-wavelength emission is better for TL measurements



Undoped LMP crystal: Two broad emission bands: 354 and 630 nm – the emission of F^+ and F centers

In Tm-doped crystal all transitions characteristic for Tm ions visible and the emission is strongly shifted towards higher temperatures

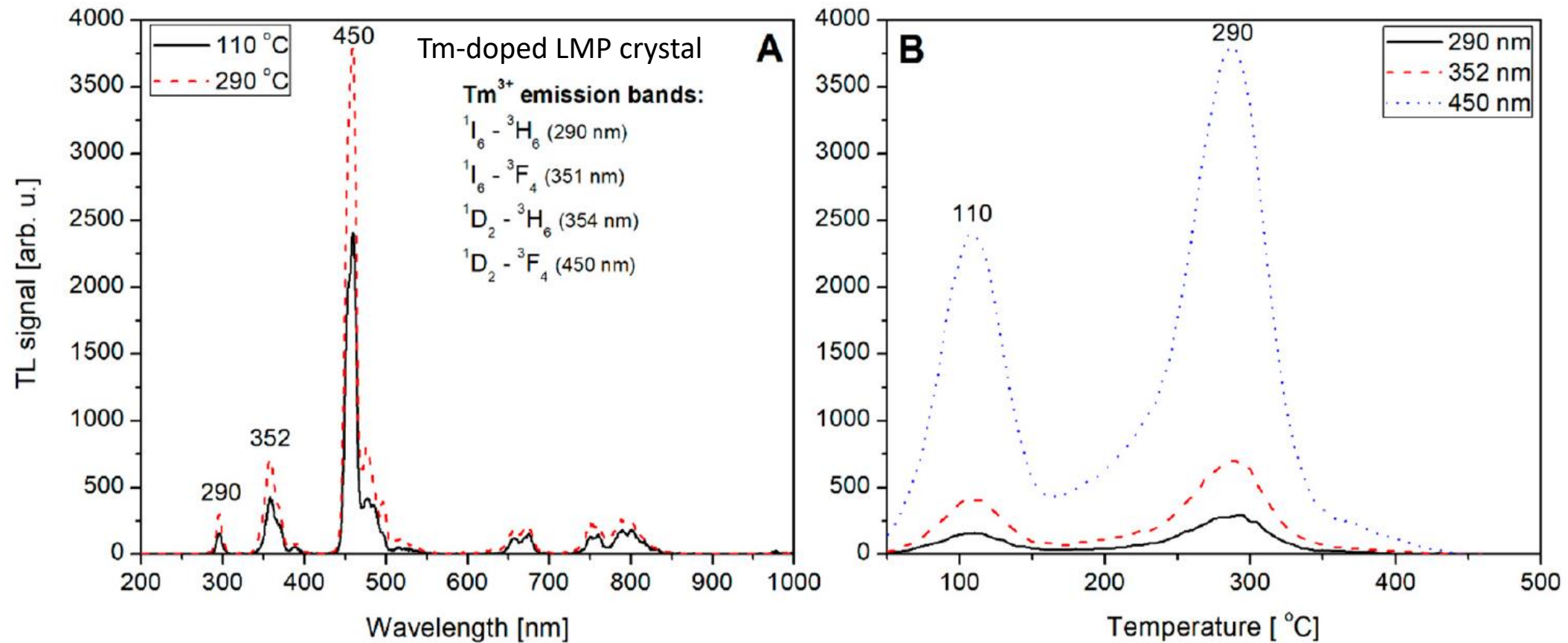
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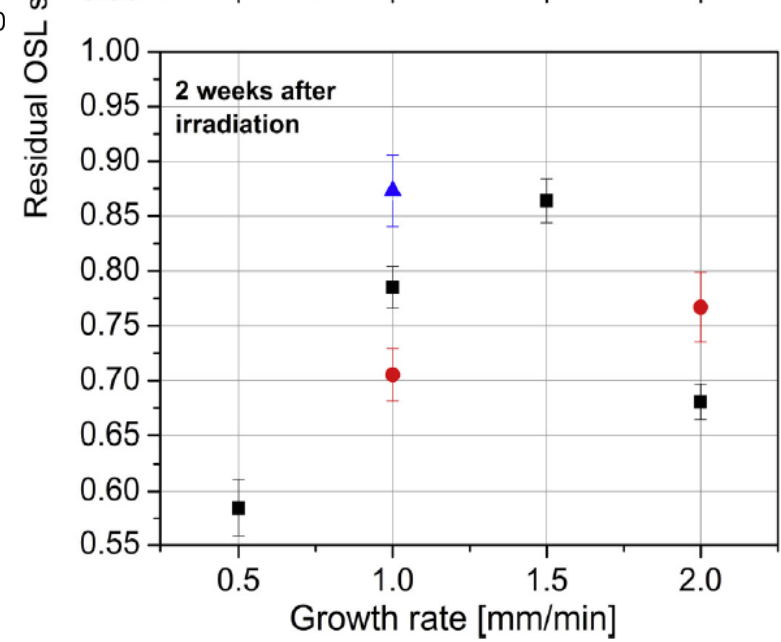
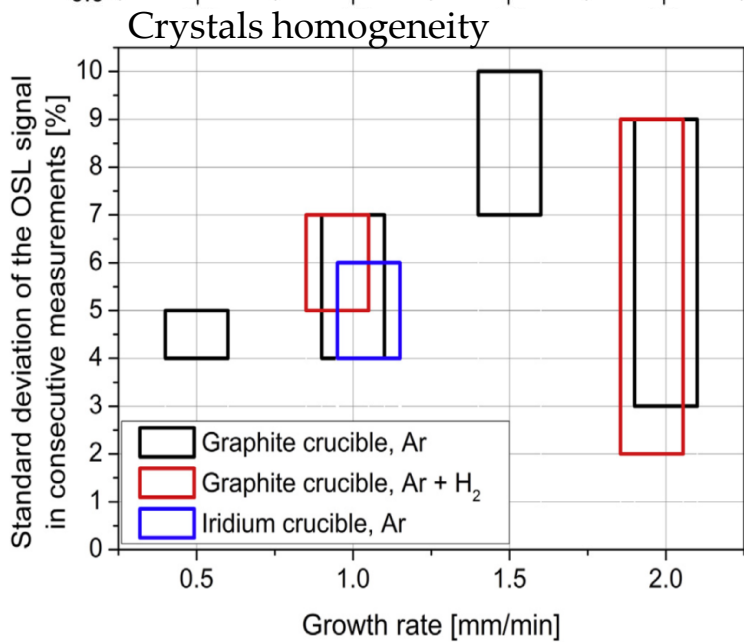
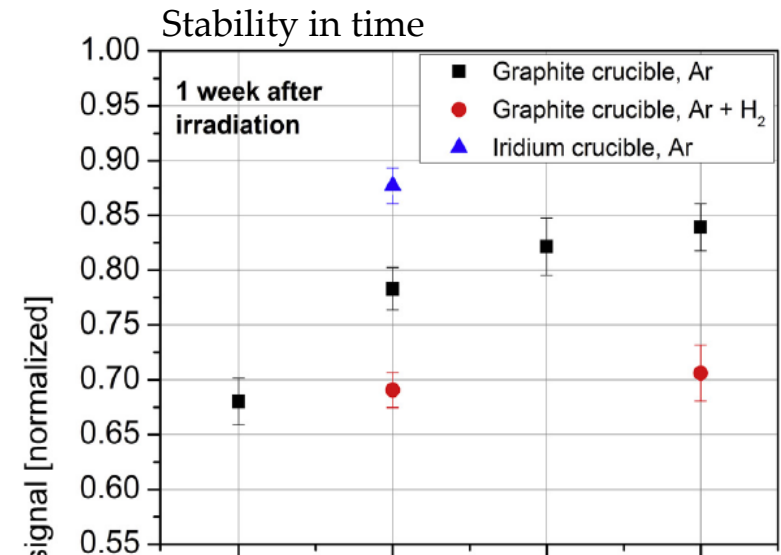
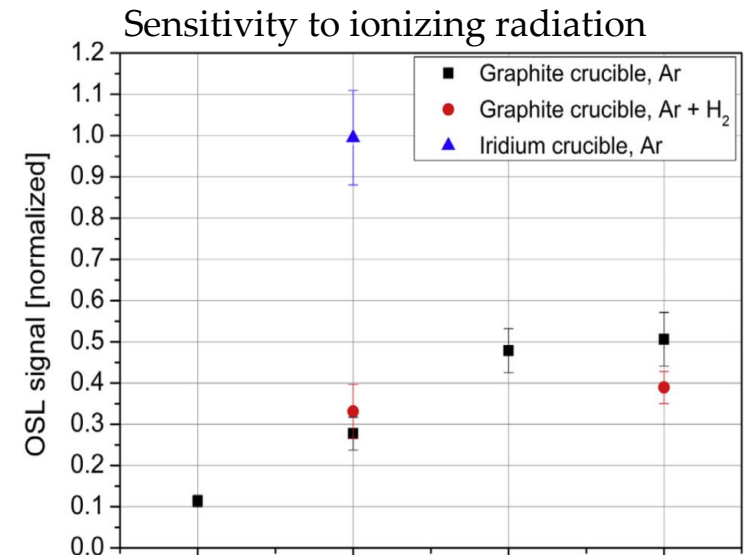
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Results

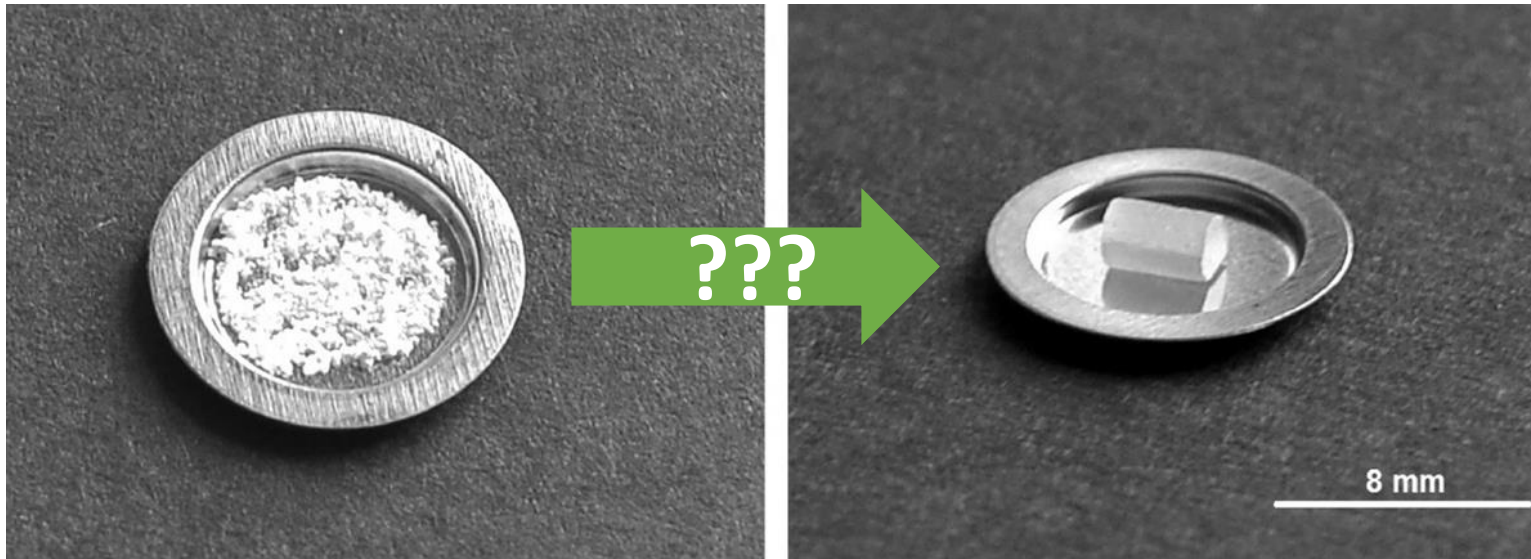
Luminescence emission vs. growth parameters

- LiMgPO₄ (LMP) compound
- Grown with MPD method
- Growth rates [mm/min]:
 - 0.5
 - 1.0
 - 1.5
 - 2.0
- Crucible material:
 - Graphite
 - Iridium
- Atmosphere:
 - Ar
 - Ar+H₂



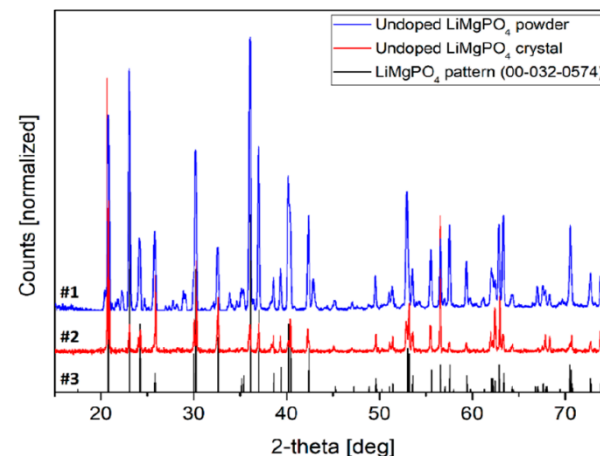
D. Kulig, W. Gieszczyk, P. Bilski, B. Marczewska, M. Kłosowski. Radiat. Meas. 90 (2016) 303 – 307

Do we really need crystals?



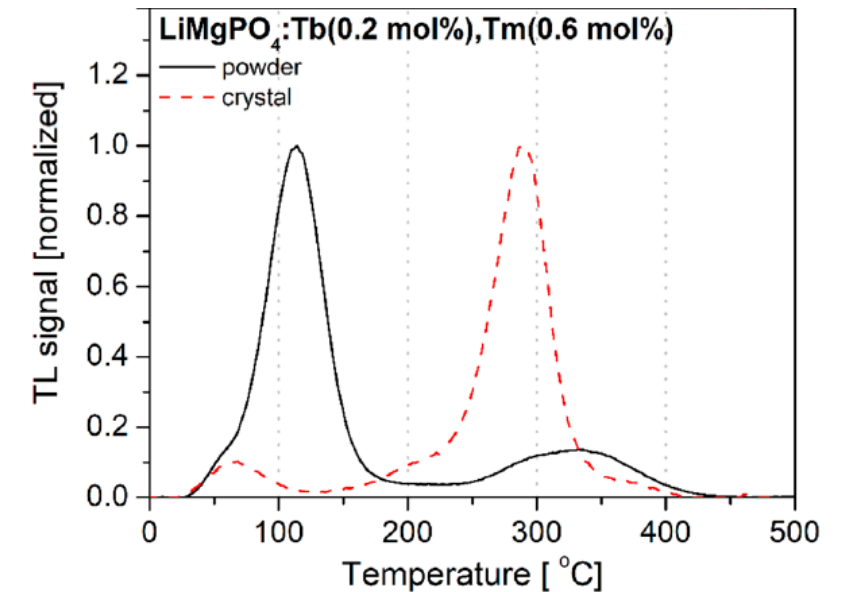
In general, we observed:

- Powders a little bit more sensitive to radiation
- Crystals exhibit lower fading
- Similar dose-response characteristics
- ...



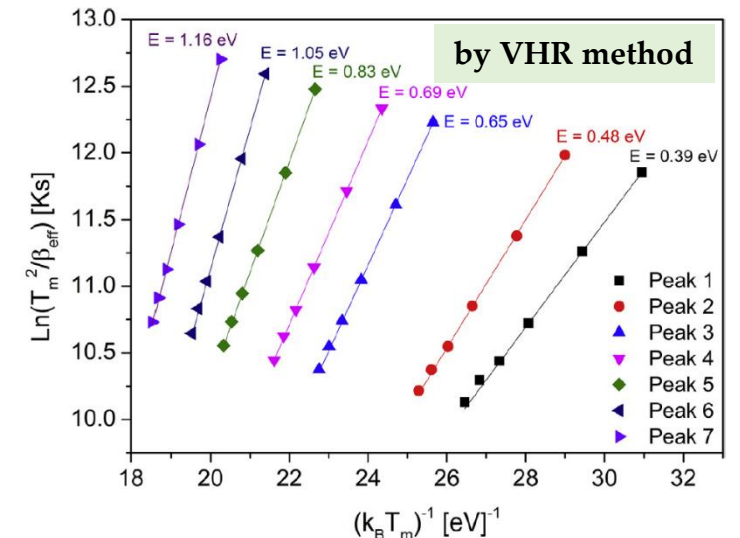
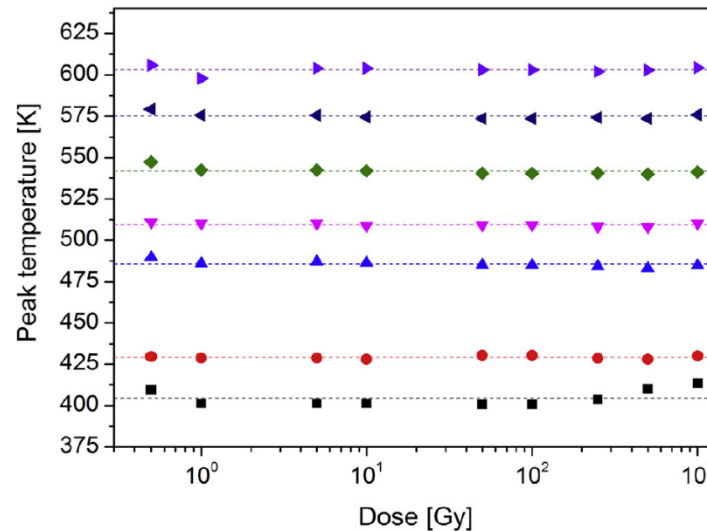
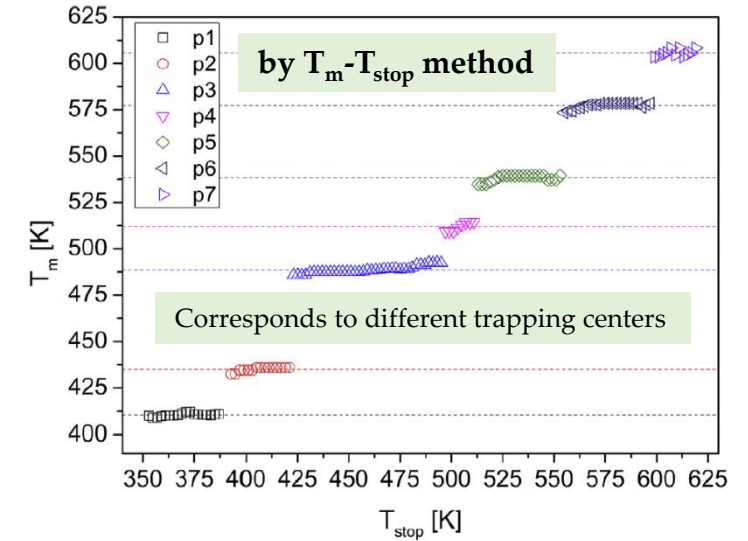
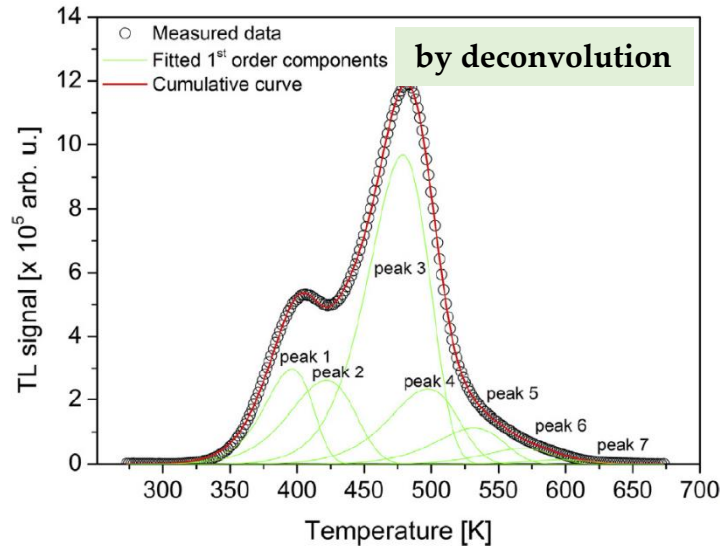
Advantages of using crystals:

- It is easier to operate with crystals ...



- High-temperature growth changes the distribution of TL-related structure defects what is manifested in the changes of the shape of the measured glow-curves
- The effect is repeatable
- May strongly influence the fading properties

- Free charge carriers can be trapped by trapping centers related to the defect sites
- Each trapping center is characterized by several different trapping parameters like e.g. I_m , T_m , E (in TL); τ , σ (in OSL)
- Knowing the values of trapping parameters we can expect a specific behavior regarding e.g. the response to increasing radiation dose or stability of luminescence in time
- Trapping parameters evaluated using different methods (deconvolution, T_m - T_{stop} , VHR)



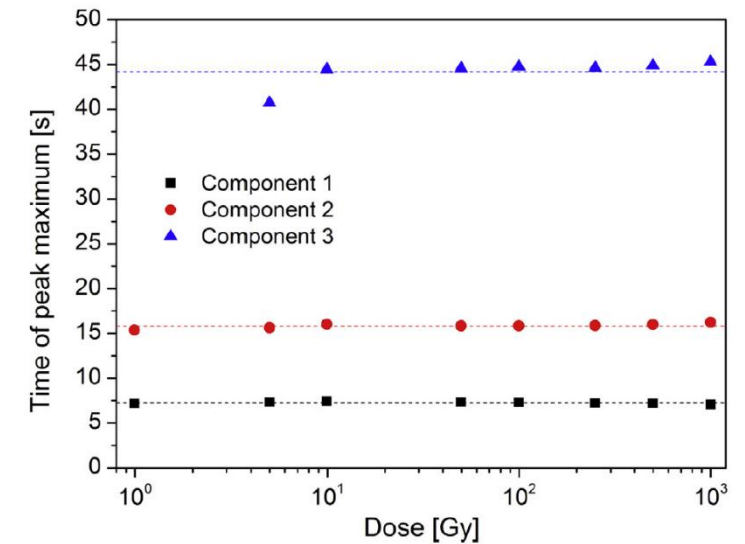
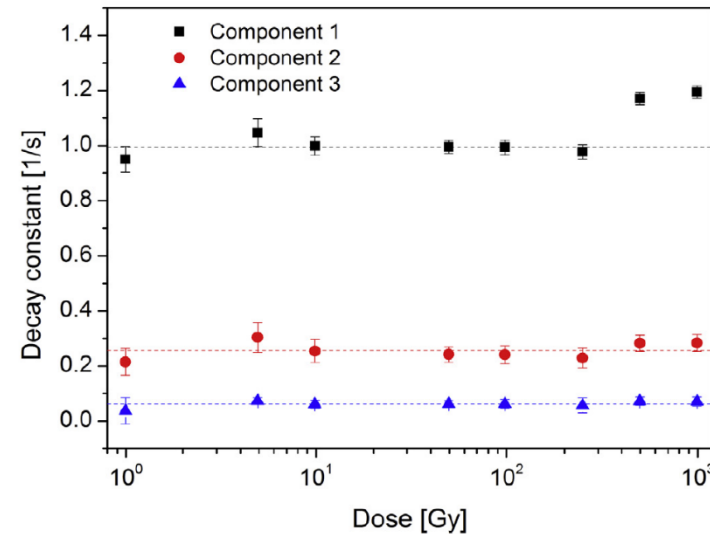
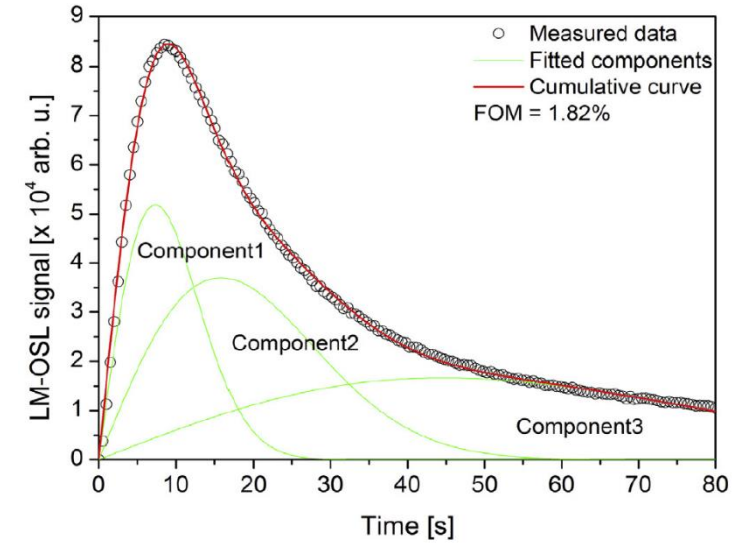
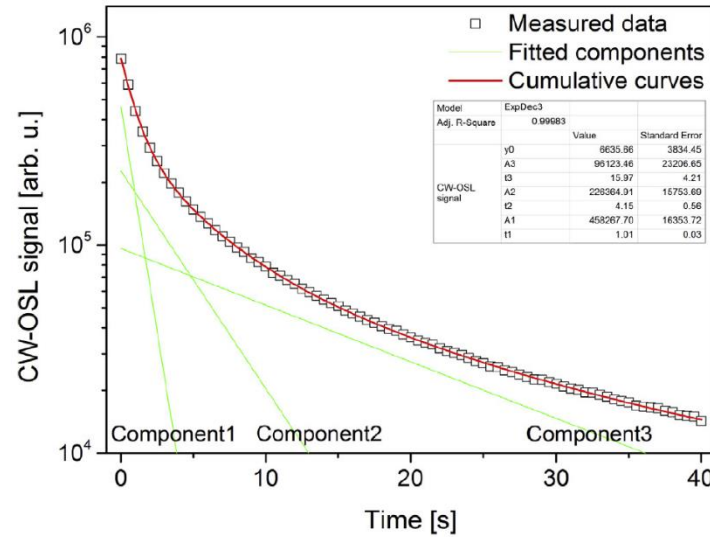
- Individual TL components separated from the measured glow-curves
- All the components were stable for increasing dose of radiation
- Dose-response was checked for each TL component
- Activation energy evaluated with VHR method

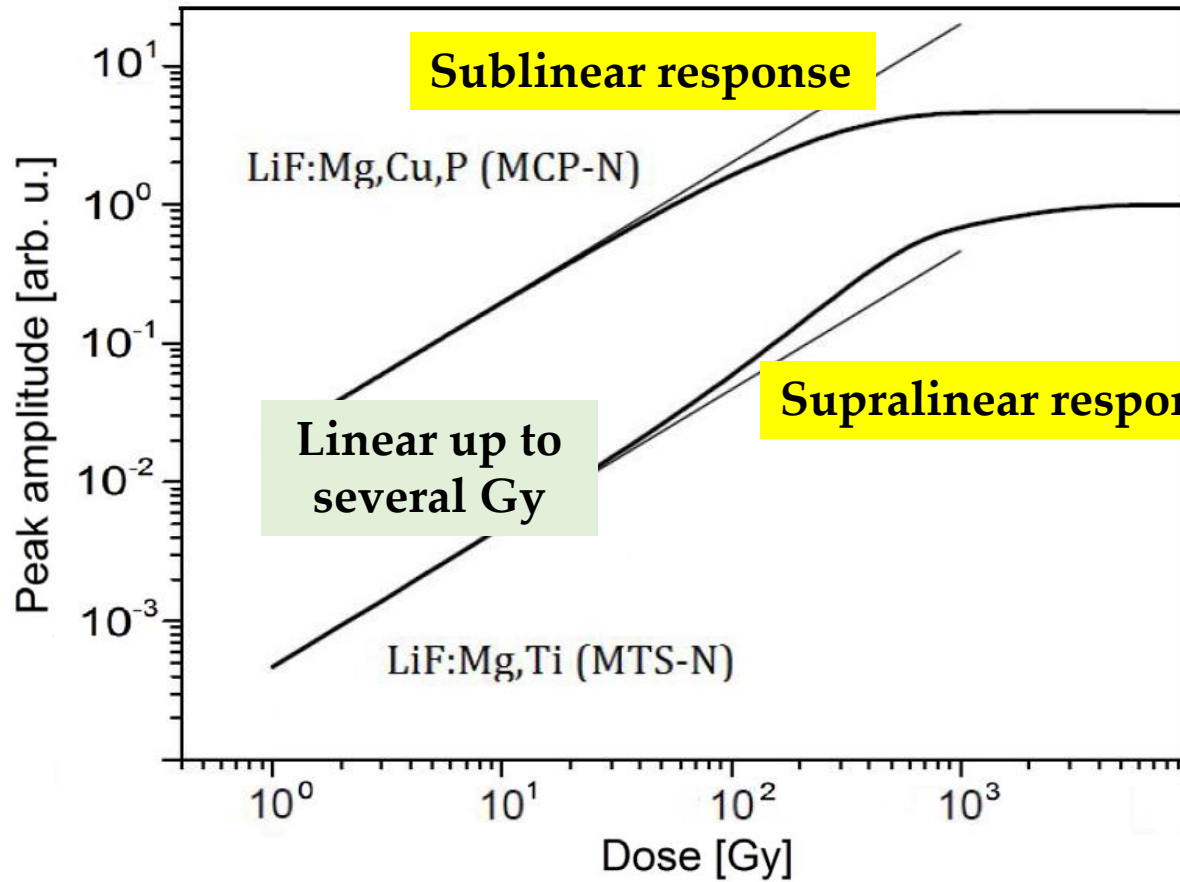
Exemplary results (OSL):

- The undoped LMP crystal
- CW- and LM-OSL curves analyzed

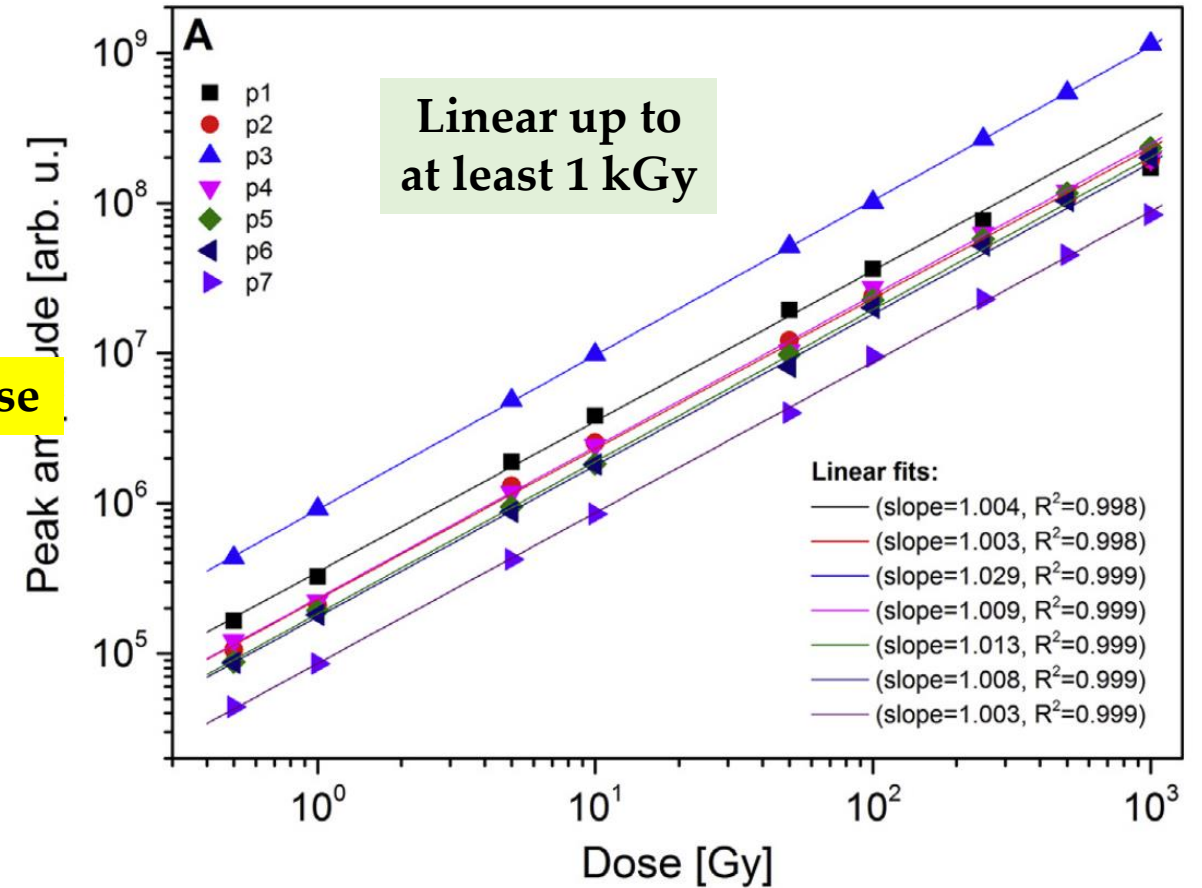
➤ Both TL and OSL emission does not follow the first order kinetics directly, but can be easily expressed as a linear combination of several first order components.

- We can expect:
 - Stability for increasing dose
 - No retrapping
 - High fading because of low E





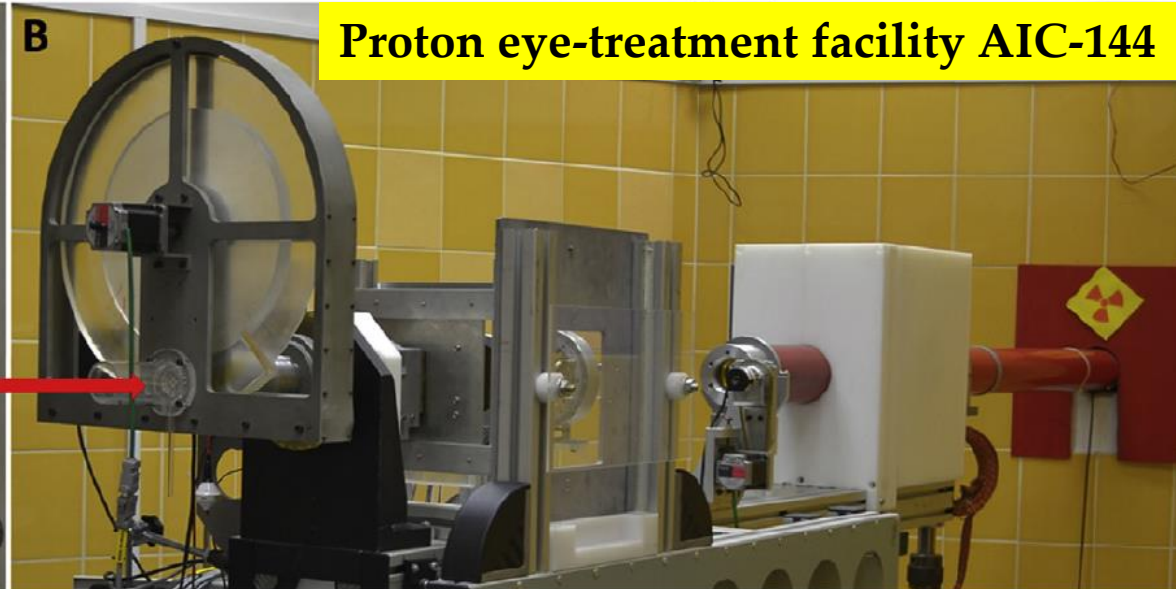
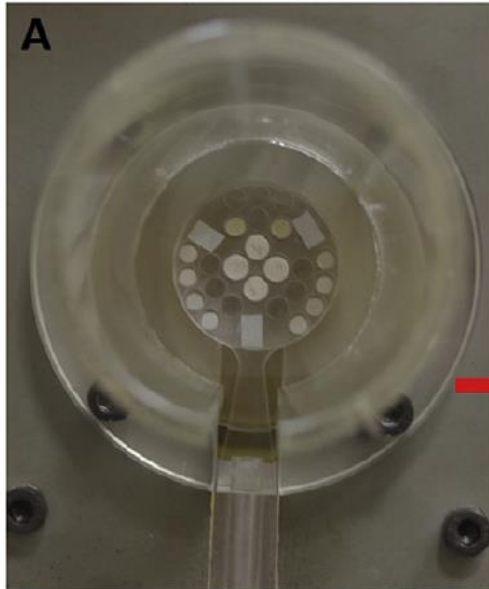
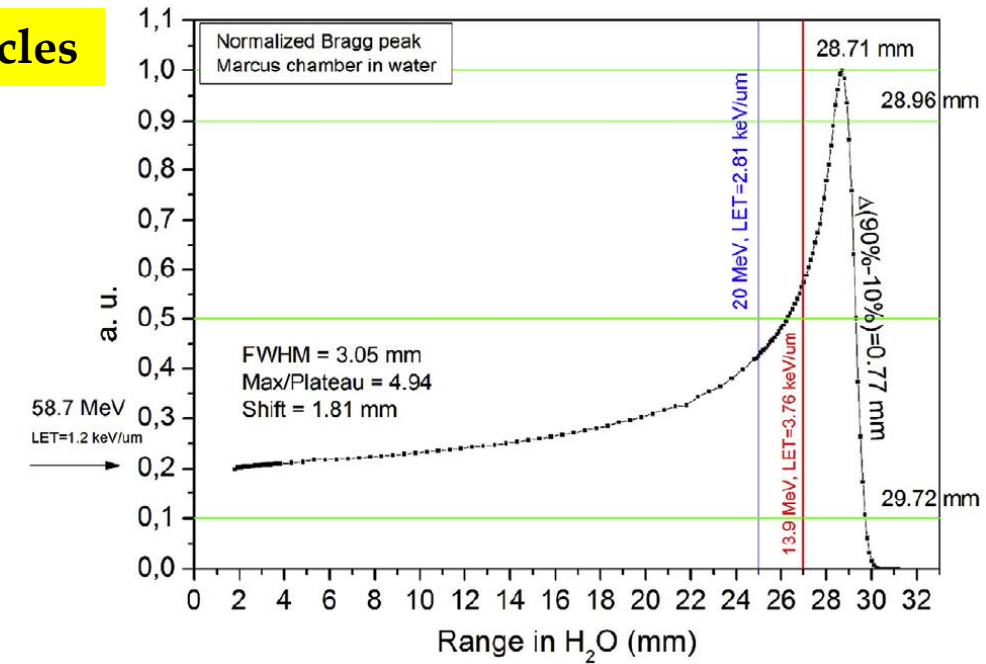
Perfect linear response



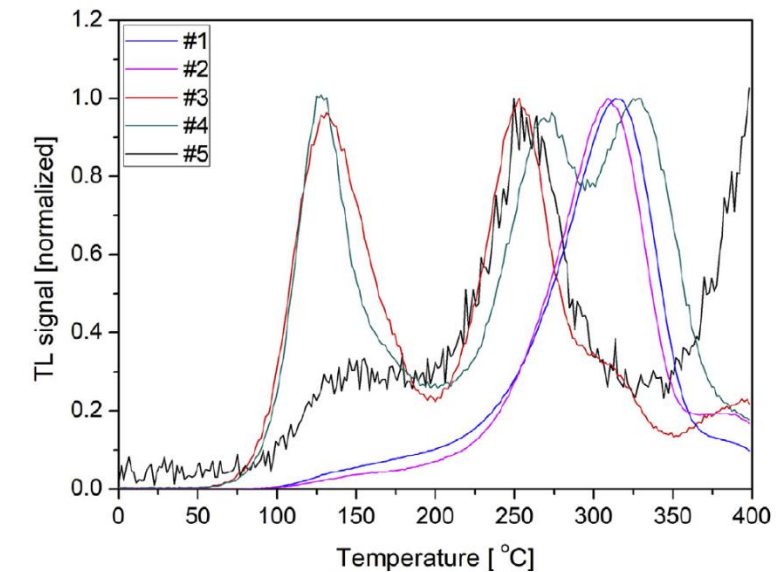
Important for high-dose measurements (e.g. hadron therapy)

Samples under study

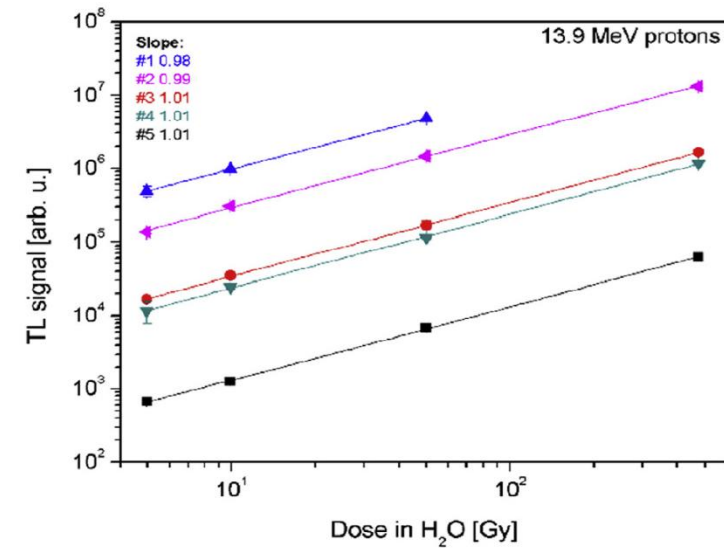
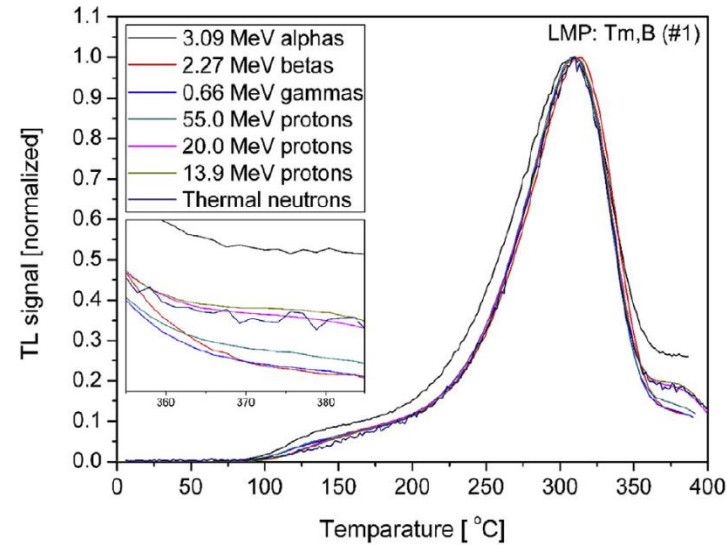
Sample ID	Raw material	Dopants concentration (%mol)						Sensitivity vs. LiF:Mg,Ti
		Tb	B	Eu	Er	Tm	Y	
#1	LiMgPO ₄	–	10	–	–	0.8	–	2.78
#2		0.2	10	–	–	0.6	–	0.56
#3		0.4	10	–	0.4	–	–	0.05
#4		0.2	10	–	–	–	0.6	0.05
#5		0.4	10	0.4	–	–	–	< 0.01
Reference	LiF:Mg,Ti, MTS-N	–	–	–	–	–	–	1.0



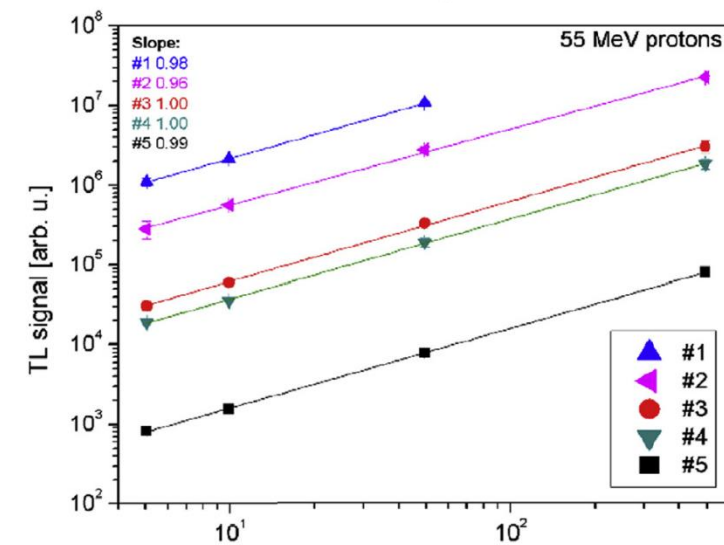
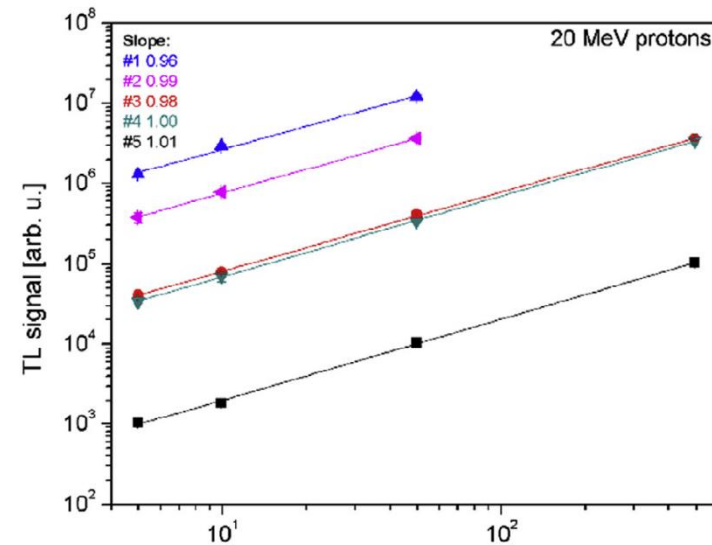
Proton eye-treatment facility AIC-144



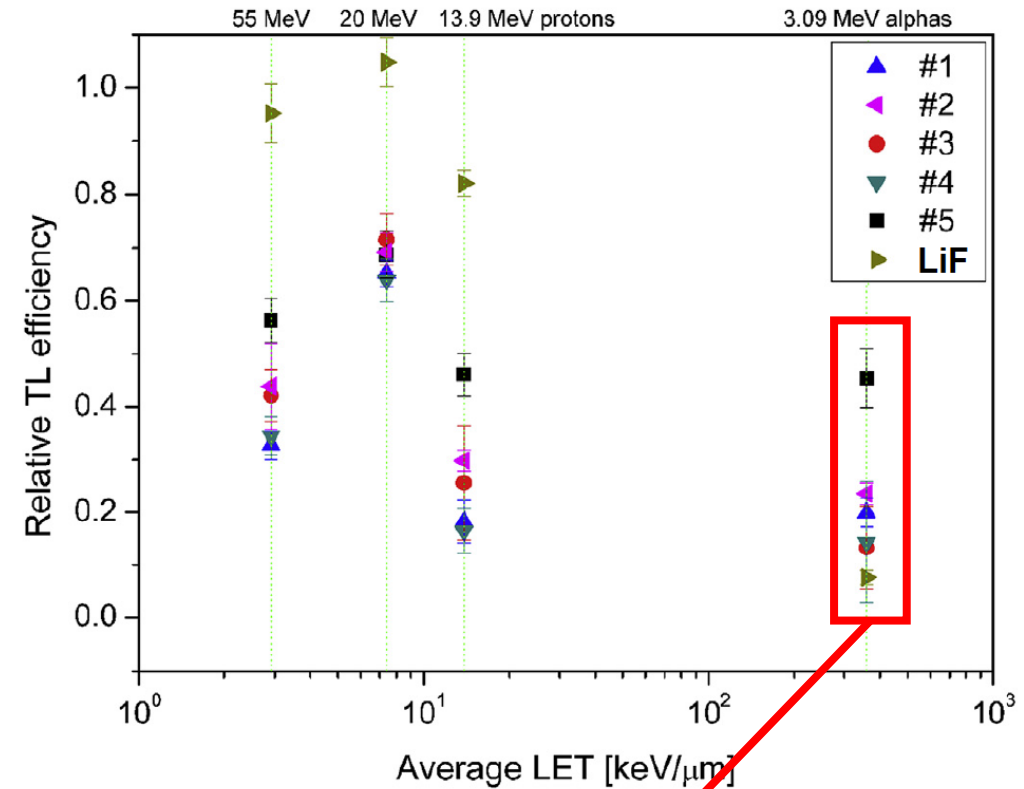
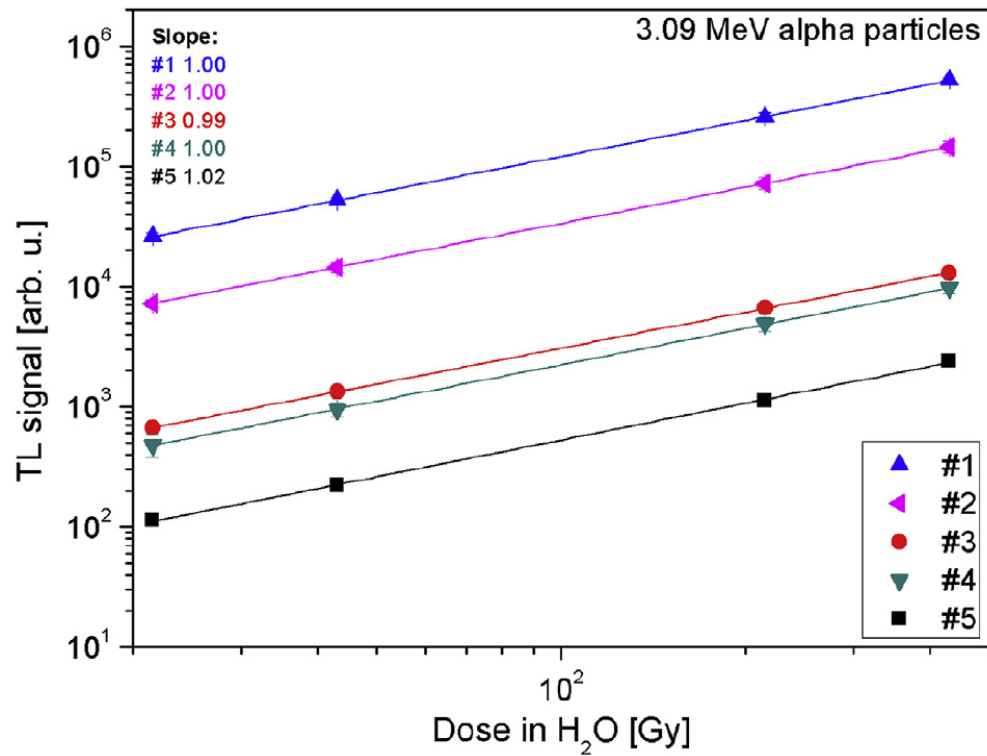
Practically the same shape of glow-curves regardless the radiation type



Perfect linear response regardless the proton beam energy



For α -particles the response is also perfectly linear

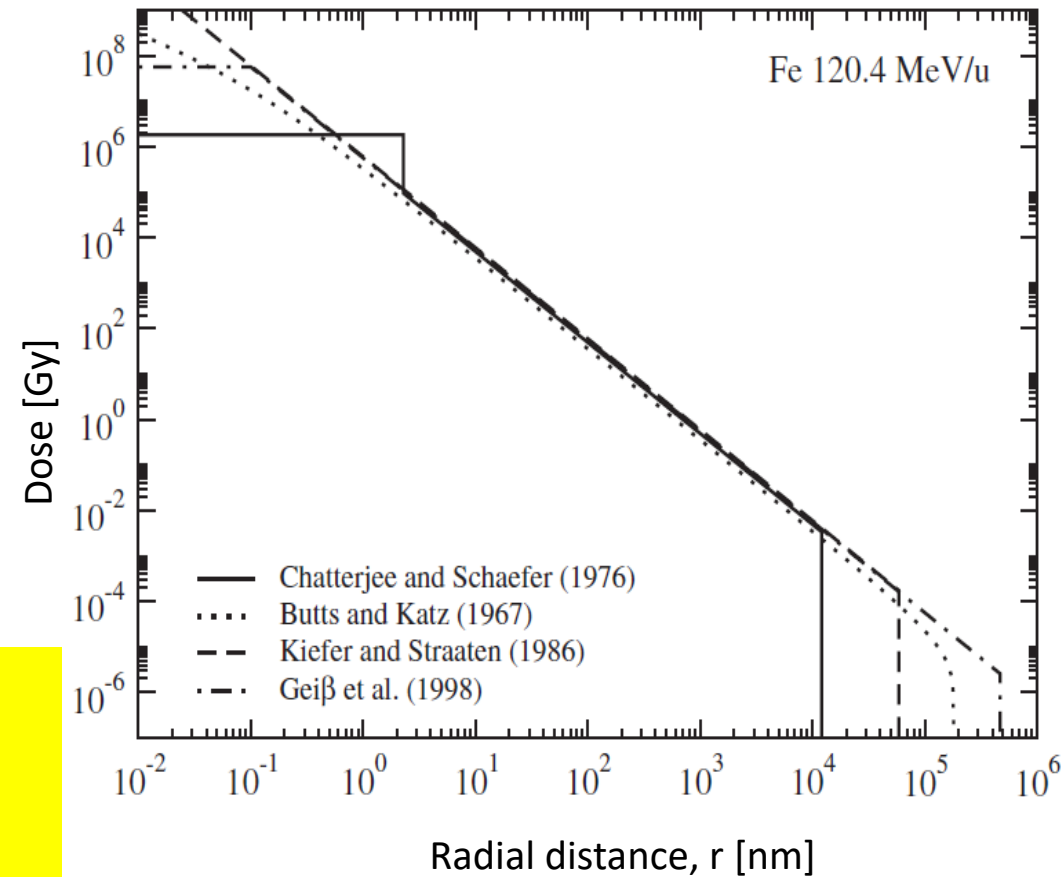
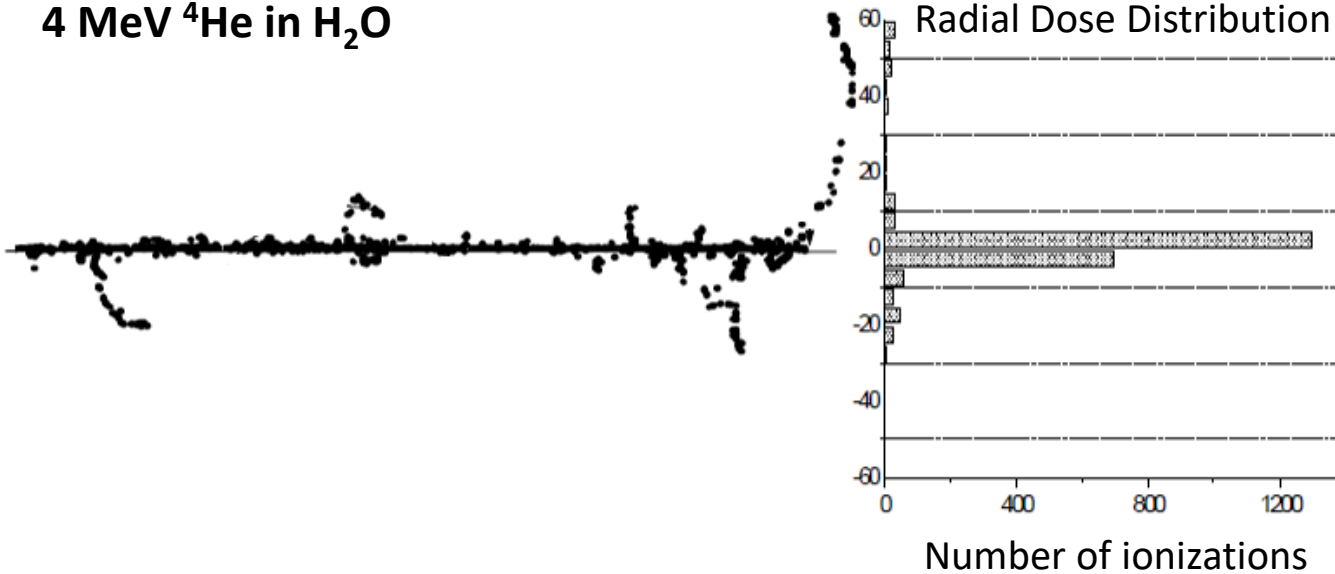


$$\eta_{\text{rel}} = \frac{\eta_i}{\eta_{\text{ref}}} = \frac{\text{TL}_i}{D_i \cdot m_i} \cdot \frac{D_{\text{ref}} \cdot m_{\text{ref}}}{\text{TL}_{\text{ref}}}$$

Even the LMP crystal of lowest efficiency shows a higher response to alpha particles than the reference LiF:Mg,Ti sample

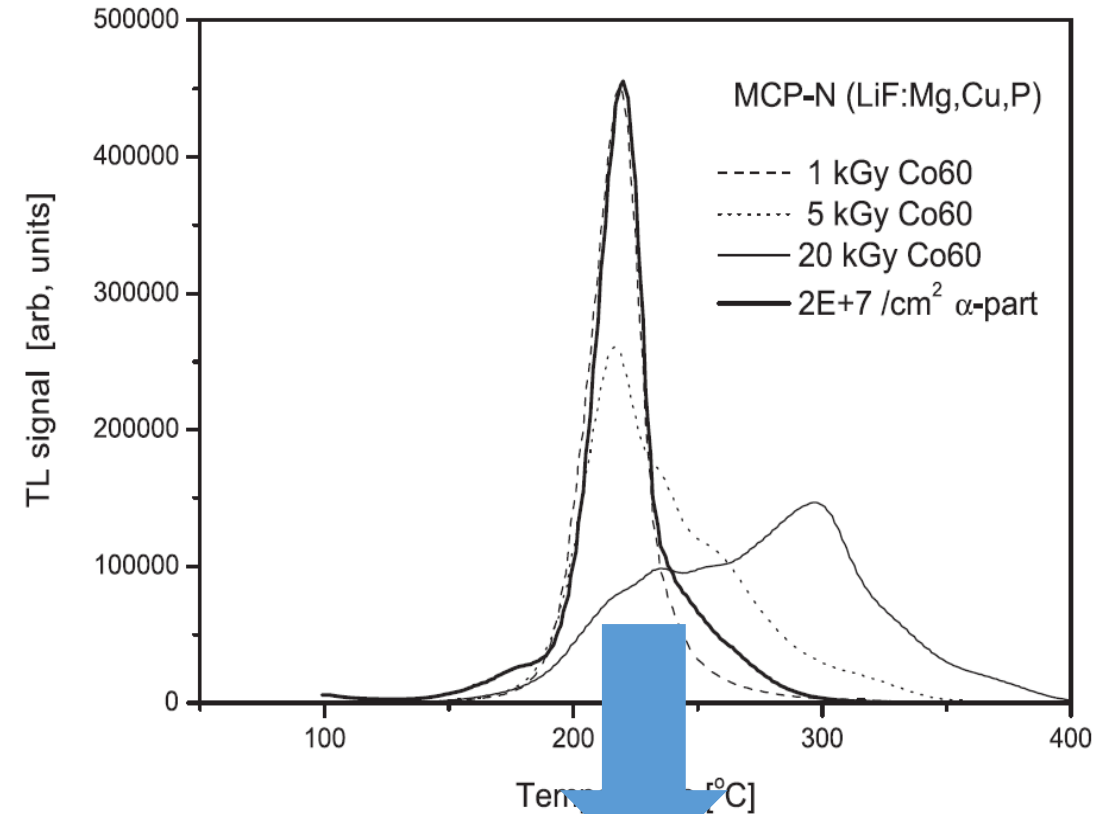
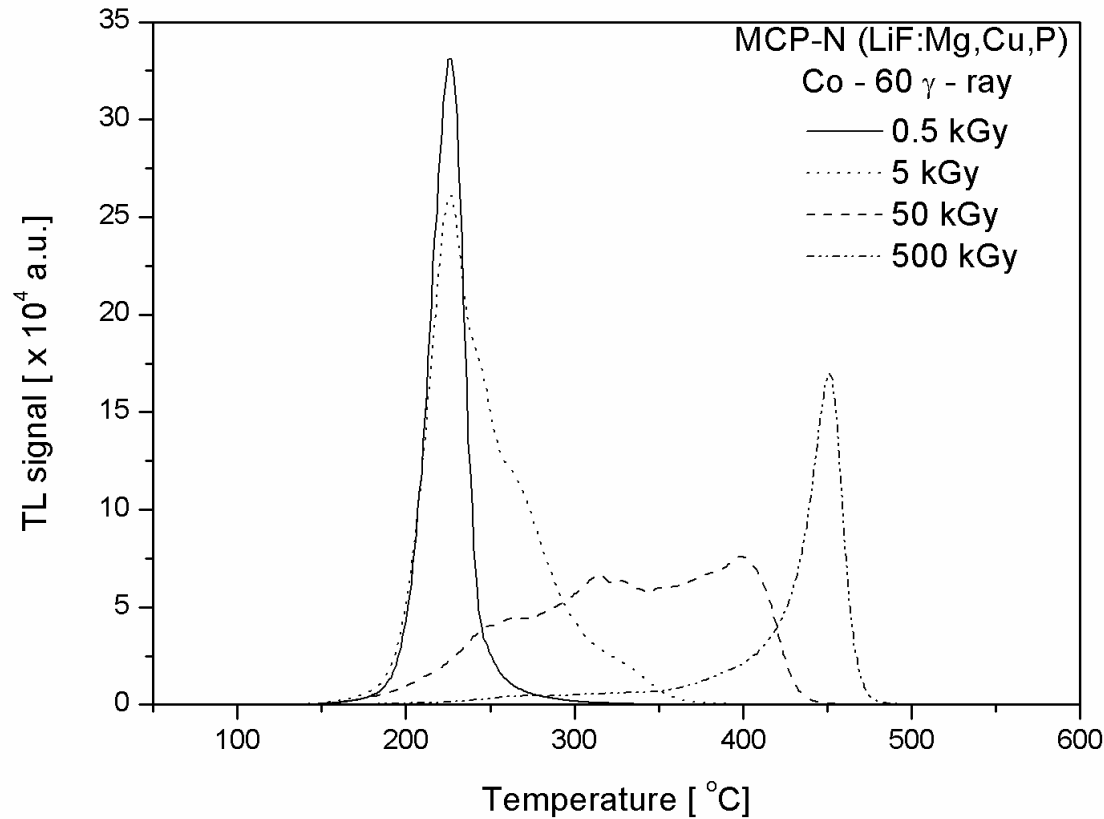
Probable explanation

4 MeV ^4He in H_2O



- Several models of RDD exist
- Predicted dose within track core $\sim 10^6$ Gy
- No experimental verification
- Lack of detectors of appropriate spatial resolution
- LiF detectors response saturates typically at around 10^3 Gy, but ...

... a high-temperature structure of LiF:Mg,Cu,P (MCP) glow-curve has been discovered

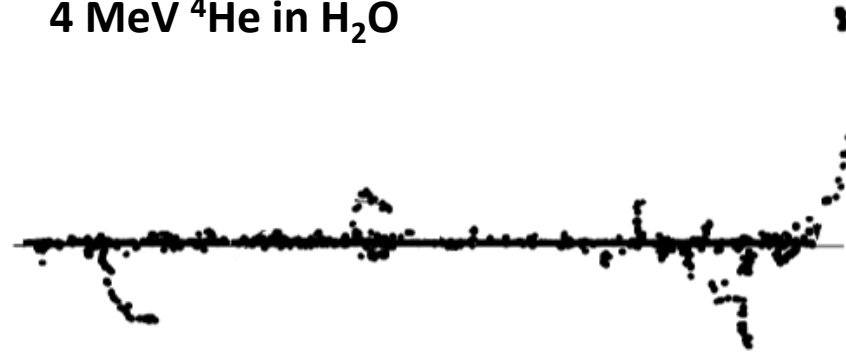


LiF main peak response is far saturated at this dose level while for the LMP no saturation observed at least to 10 kGy!!!

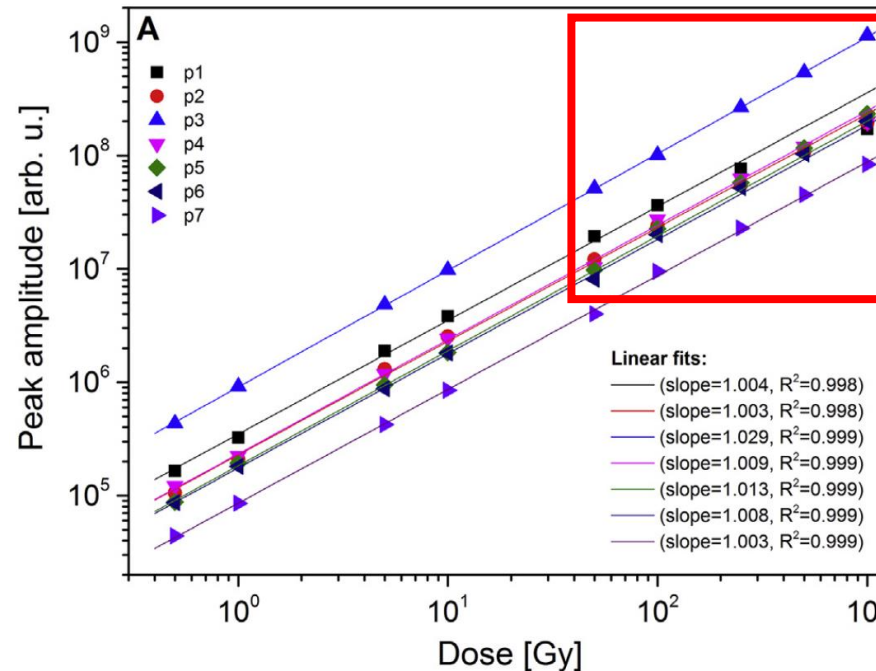
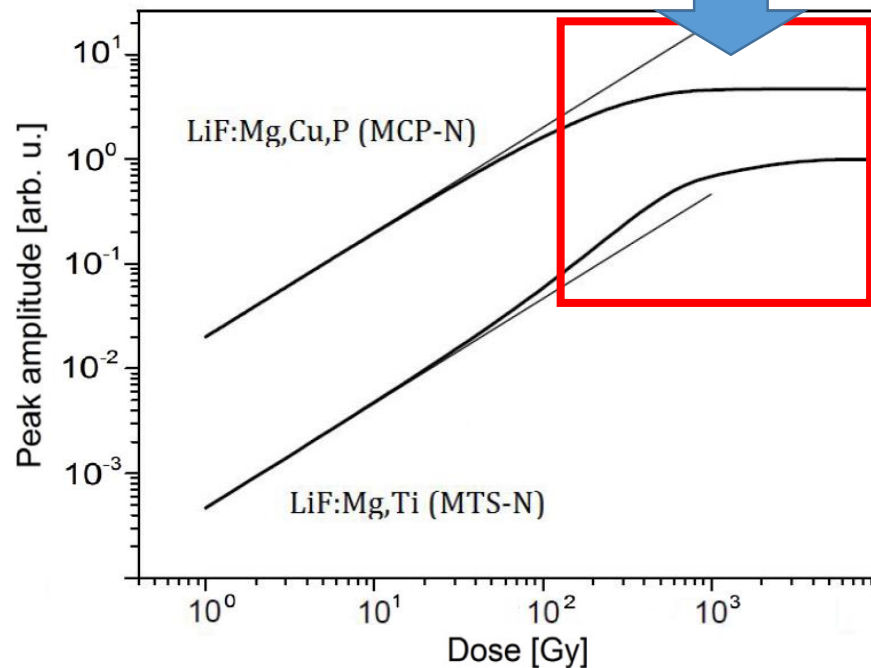
Around 20% of the entire energy of alpha particle is deposited with local doses $> 50\text{kGy}$

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4 MeV ^4He in H_2O

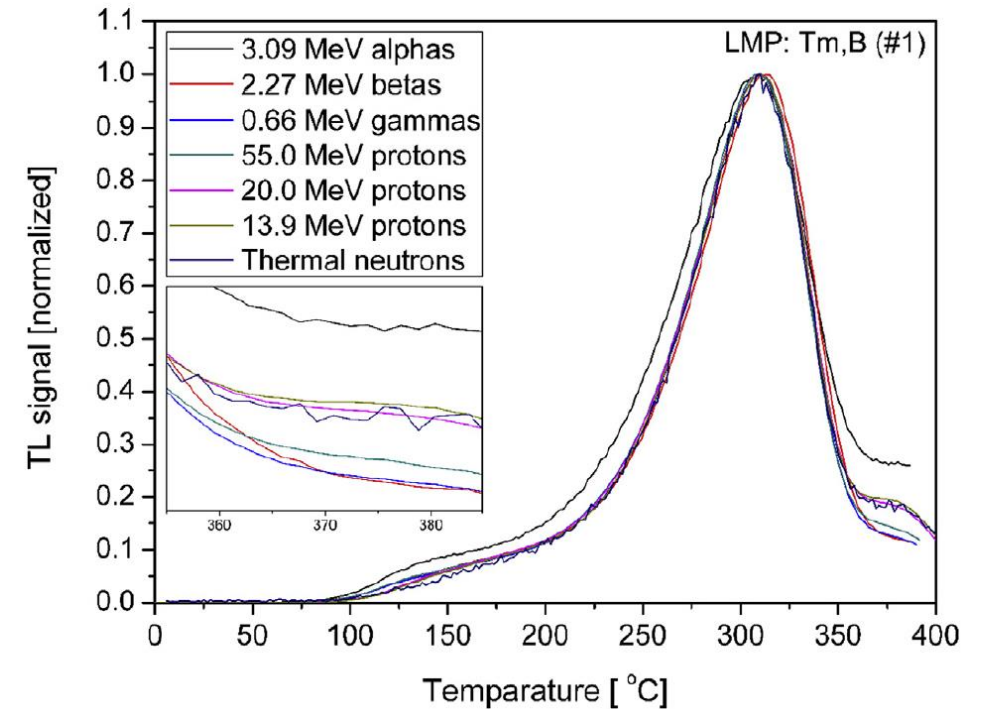


Response saturated = efficiency decreased



Results for differently doped LMP crystals

- $^{239}\text{Pu}/\text{Be}$ source moderated with 10 cm polyethylene;
- Neutron fluence rate: $1.42 \cdot 10^4 \text{ n/h}\cdot\text{cm}^2$ (evaluated with $^6\text{LiF:Mg,Ti}$ calibrated at PTB Geesthacht Neutron Facility);
- Gamma-ray background: $5.9 \mu\text{Gy/h}$ (measured with $^7\text{LiF:Mg,Cu,P}$);
- Gamma dose subtracted from the total response of LMP crystals;
- Irradiation time: 5d 18h 10 m (corresponds to the fluence of $1.96 \cdot 10^6 \text{ n/cm}^2$)
- Data corrected for the fading factor evaluated for the Co-60 gamma rays for the same irradiation time
- Samples were shielded from a daylight during the irradiation and transportation



Sample ID	Raw material	Dopants concentration (%mol)						Sensitivity ^a vs. LiF:Mg,Ti	Response to thermal neutrons [mGycm^2/n] ^b	Relative TL efficiency ^b			
		Tb	B	Eu	Er	Tm	Y			55 MeV p	20 MeV p	13.9 MeV p	3.09 MeV α
#1	LiMgPO ₄	-	10	-	-	0.8	-	2.78	$3.82 \cdot 10^{-6}$	0.33 ± 0.03	0.65 ± 0.02	0.18 ± 0.04	0.20 ± 0.03
#2		0.2	10	-	-	0.6	-	0.56	$3.52 \cdot 10^{-6}$	0.44 ± 0.08	0.69 ± 0.03	0.30 ± 0.02	0.23 ± 0.02
#3		0.4	10	-	0.4	-	-	0.05	$4.19 \cdot 10^{-6}$	0.42 ± 0.05	0.71 ± 0.05	0.26 ± 0.05	0.13 ± 0.03
#4		0.2	10	-	-	-	0.6	0.05	$5.11 \cdot 10^{-6}$	0.34 ± 0.03	0.64 ± 0.04	0.16 ± 0.03	0.14 ± 0.02
#5		0.4	10	0.4	-	-	-	< 0.01	-	0.56 ± 0.04	0.69 ± 0.04	0.46 ± 0.04	0.45 ± 0.05
Reference	LiF:Mg,Ti, MTS-N	-	-	-	-	-	-	1.0	$3.50 \cdot 10^{-6}$	0.95 ± 0.05	1.05 ± 0.05	0.82 ± 0.02	0.08 ± 0.01

The response of LMP to thermal neutrons is similar to the response of LiF

In both cases, the only element active to neutrons is Li

	LiF	LiMgPO ₄
Molar ratio	1:1	1:6

Response to thermal
neutrons [mGycm²/n]^b

3.82·10 ⁻⁶	LMP
3.52·10 ⁻⁶	
4.19·10 ⁻⁶	
5.11·10 ⁻⁶	
–	LiF
3.50·10 ⁻⁶	

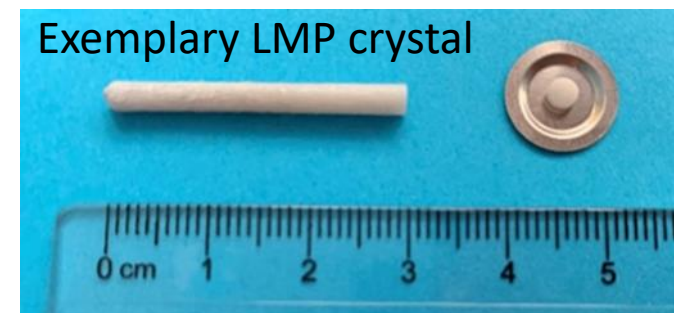
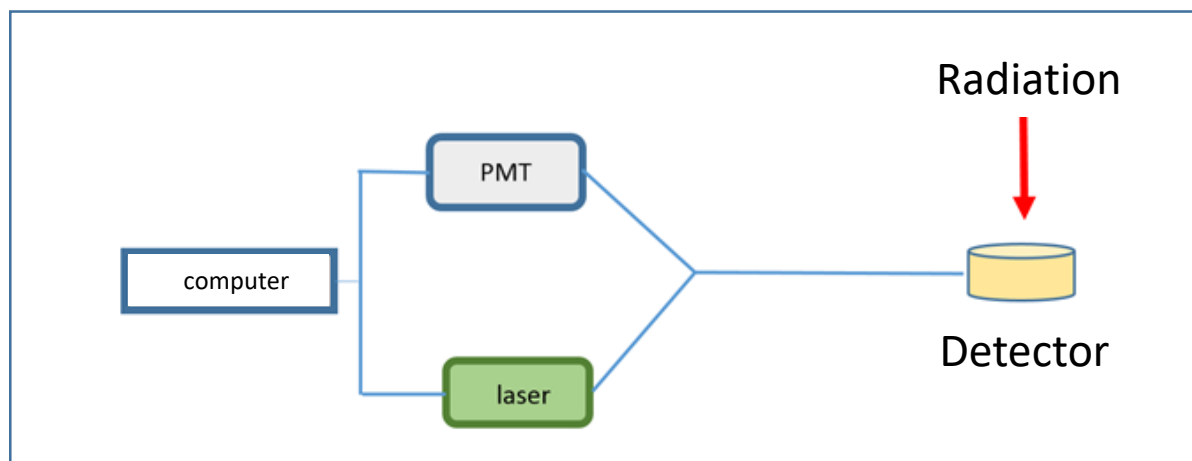
- The content of Li in LiF is much higher than in LiMgPO₄
- The main product of the interaction of neutrons with Li is alpha particle Li(n,α)³H
- Response of LMP to alpha particles is higher than the response of LiF
- These two effects compensate each other resulting in a similar efficiency to thermal neutrons

- High-dose dosimetry, kGy range (food preservation, sterilization)
 - Dosimetry of charged particles (hadron therapy)
 - Dosimetry of neutrons (monitoring of areas around particle accelerators)
- Real-time measurements of therapeutic proton beam (prof. B. Marczevska)
 - 2D/3D OSL dosimetric system based on LMP foils (dr. M. Sądel)



Concept:

- Small detector (crystal) placed at the end of optical fiber
- The optical fiber can be even several dozen meters long
- The optical fiber connects the crystal to the apparatus for stimulation and signal registration
- Different modes of measurements are possible
 - Simultaneous or sequential registration of RL and OSL signal
 - Constant or pulsed stimulation

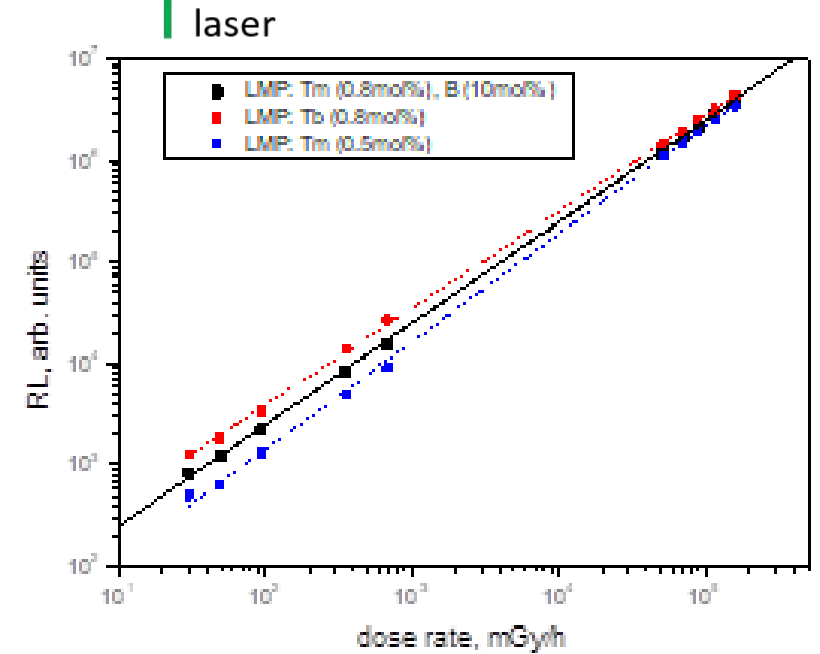
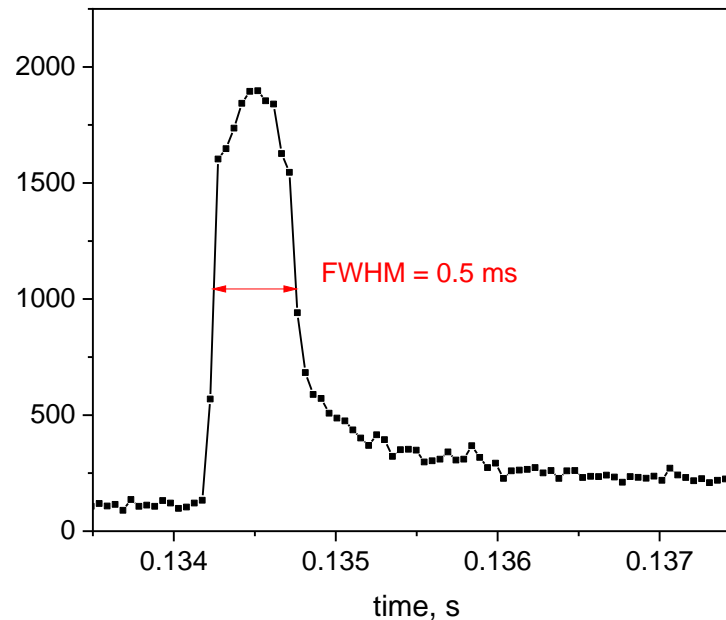
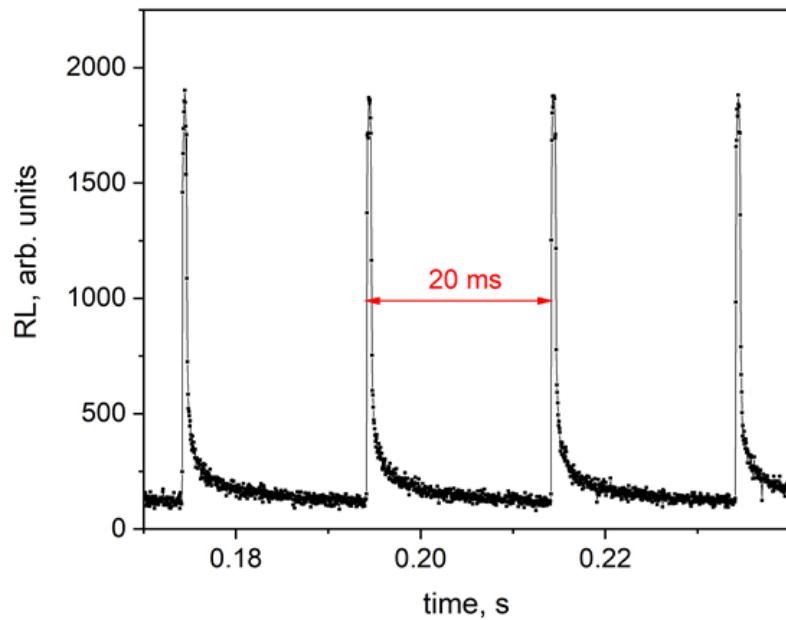
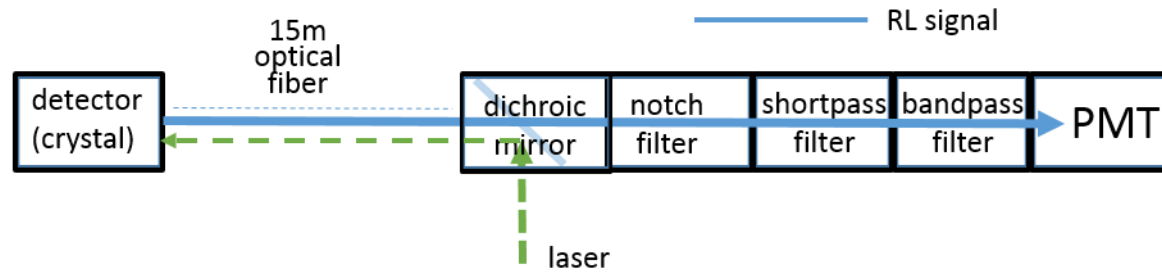


Detector:

- Sample of the volume of 1-3mm³ (spatial resolution)
- LiMgPO₄ crystals
- *in-vivo, in-situ, in real-time*

Novel applications

Real-time measurements of therapeutic proton beam (National Science Center, OPUS program – P.M. prof. Barbara Marczevska)

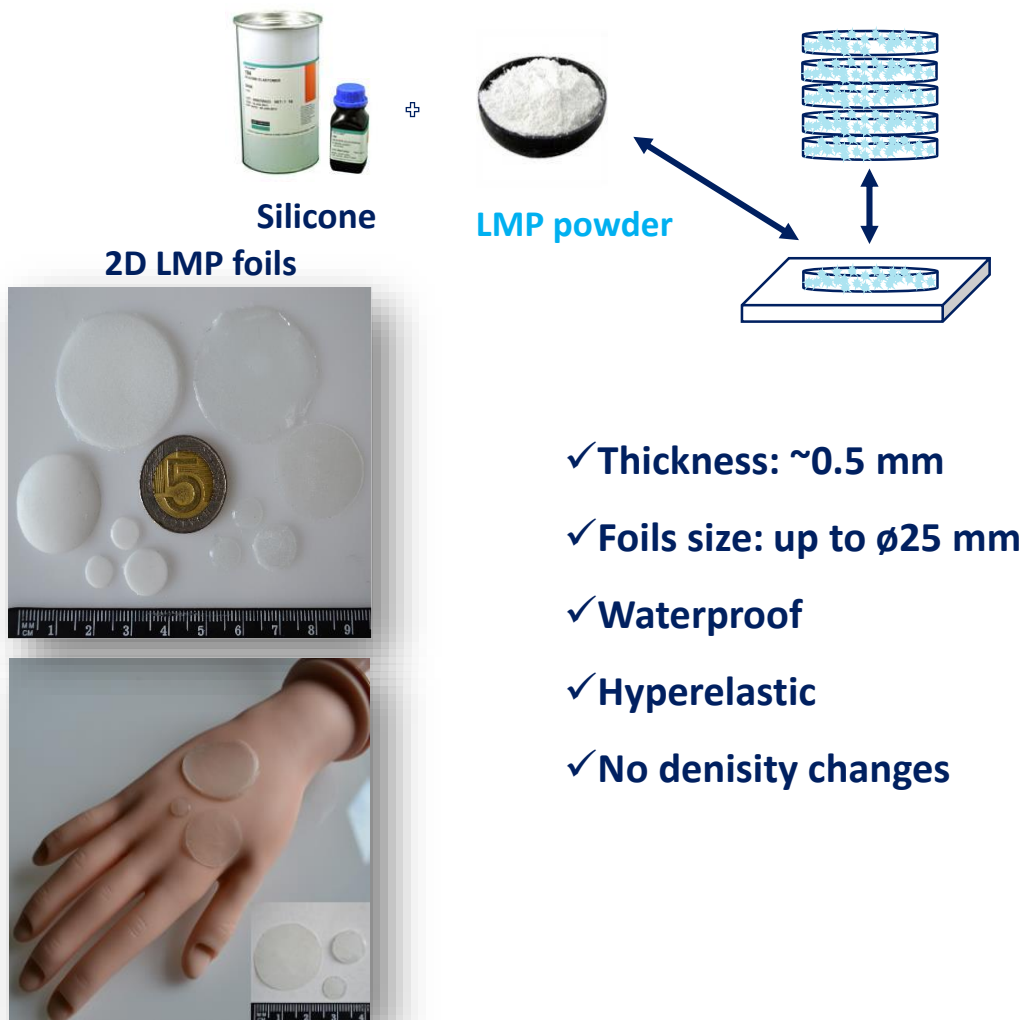


Measurements of time-structure of proton beam from AIC-144 cyclotron

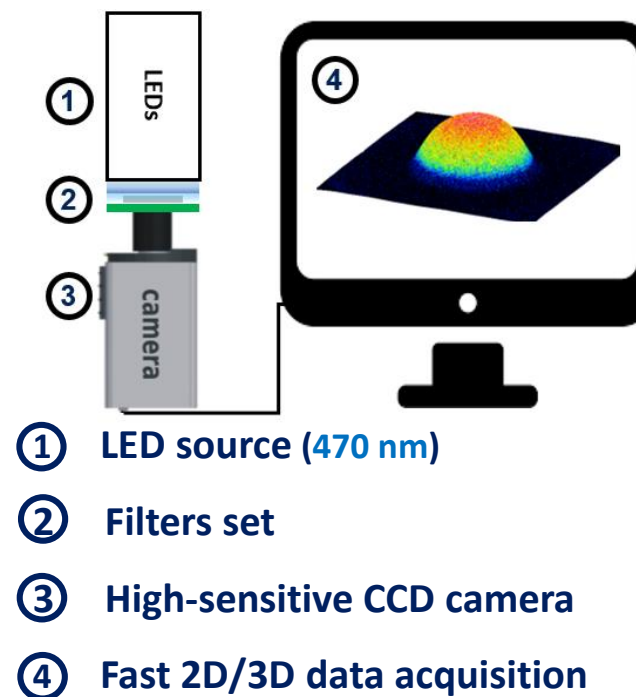
Dose-rate effect on the LMP RL emission measured over a broad range of dose-rates (performed with Cs-137 and Co-60 sources)

A. Sas-Bieniarz, B. Marczevska, P. Bilski, W. Gieszczyk, M. Kłosowski. Radiat. Meas. 136 (2020), 106408

Prototype foils preparation



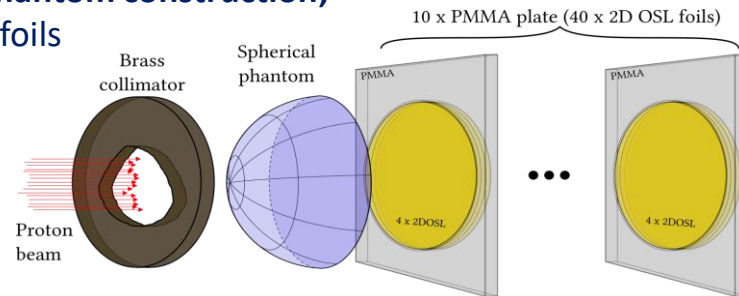
Optical imaging system



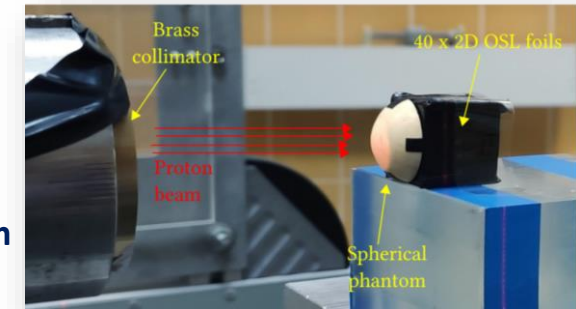
Verification of a real 3D eye-ball clinical treatment plan

Eyeball phantom construction;

- 40 LMP foils



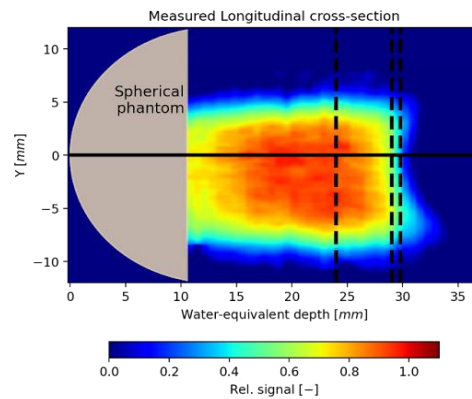
Experimental setup



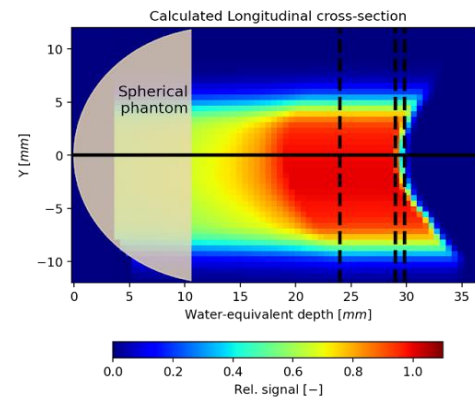
Proton beam;

- Protons: 60 MeV
- Range: 29 mm
- Modulation: 10 mm

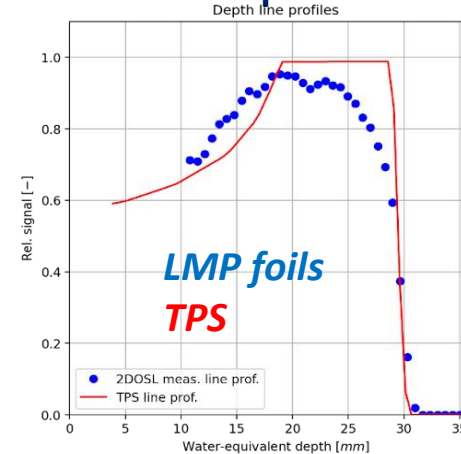
Measured (40 LMP)



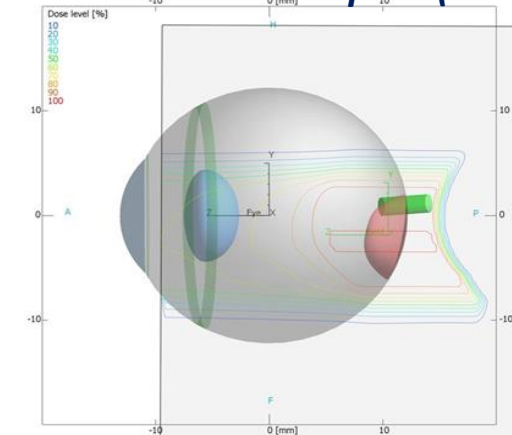
Calculated (TPS)



Proton depth-dose



Proton treatment plan (TPS)



Conclusions

New high-sensitive luminescent material has been developed and optimized

- Since 2014, more than 100 different compositions of LiMgPO_4 :RE compounds were investigated
- TL, OSL, RL, CL emissions have been studied for differently doped crystals
- Y, Sm, Eu, Gd, Tb, Er, Tm, Yb were investigated as possible dopants influencing efficiency of LMP crystals

LMP sensitivity comparable or higher than LiF (in TL) and Al_2O_3 (in OSL)

Investigations performed within this work

- Growth conditions have been optimized and their influence on crystal sensitivity has been checked
- Comparison between powders and crystals was performed showing a superiority of crystals
- Trapping parameters have been evaluated for selected LMP crystals
- Basic luminescence and dosimetric properties were studied:
 - Sensitivity to ionizing radiation against LiF detectors
 - Dose-response characteristics
 - Response to charged particles
 - Response to thermal neutrons

LMP crystal growth parameters optimized (crystals better than powders)

Tb dopant is best for OSL measurements
Tm dopant is best for TL and RL measurements

Eu-doped crystal showed highest relative efficiency for alpha-particles → best for HCP measurements

Novel applications presented

- Applications to real-time measurements and 2D dose distribution assessment

All investigated compositions showed linear response up to at least 1 kGy

General comment

- The obtained results clearly indicate that the LMP compound may be considered as promising material for dosimetric application

Published papers on LMP

D. Kulig (Wróbel), **W. Gieszczyk**[✉], P. Bilski, B. Marczevska, M. Kłosowski.

Thermoluminescence and optically stimulated luminescence studies on LiMgPO₄ crystallized by micro pulling down technique. **Radiation Measurements** 85 (2016), 88-92

D. Kulig (Wróbel), **W. Gieszczyk**[✉], P. Bilski, B. Marczevska, M. Kłosowski.

New OSL detectors based on LiMgPO₄ crystals grown by micro pulling down method. Dosimetric properties vs. growth parameters. **Radiation Measurements** 90 (2016), 303-307

D. Kulig (Wróbel), **W. Gieszczyk**[✉], B. Marczevska, P. Bilski, M. Kłosowski, A.L.M.C. Malthez.

Comparative studies on OSL properties of LiMgPO₄:Tb,B powders and crystals. **Radiation Measurements** 106 (2017), 94-99

W. Gieszczyk[✉], D. Kulig (Wróbel), P. Bilski, B. Marczevska, M. Kłosowski.

Analysis of TL and OSL kinetics in lithium magnesium phosphate crystals. **Radiation Measurements** 106 (2017), 100-106

W. Gieszczyk[✉], P. Bilski, M. Kłosowski, T. Nowak, L. Malinowski.

Thermoluminescent response of differently doped lithium magnesium phosphate (LiMgPO₄, LMP) crystals to protons, neutrons and alpha particles. **Radiation Measurements** 113 (2018), 14-19

A.L.M.C. Malthez, B. Marczevska, D. Kulig, P. Bilski, M. Kłosowski.

Optical and thermal pre-readout treatments to reduce the influence of fading on LiMgPO₄ OSL measurements. **Applied Radiation and Isotopes** 136 (2018), 118–120

W. Gieszczyk[✉], B. Marczevska, M. Kłosowski, A. Mroziak, P. Bilski, A. Sas-Bieniarz, P. Goj, P. Stoch.

Thermoluminescence enhancement of LiMgPO₄ crystal host by Tb³⁺ and Tm³⁺ trivalent rare-earth ions co-doping. **Materials** 12 (2019), 2861

B. Marczevska[✉], A. Sas-Bieniarz, P. Bilski, **W. Gieszczyk**, M. Kłosowski, M. Sądel.

OSL and RL of LiMgPO₄ crystals doped with rare earth elements. **Radiation Measurements** 129 (2019), 106205

A. Sas-Bieniarz, B. Marczevska[✉], P. Bilski, **W. Gieszczyk**, M. Kłosowski.

Study of radioluminescence in LiMgPO₄ doped with Tb, B and Tm. **Radiation Measurements** 136 (2020), 106408

A. Sas-Bieniarz, B. Marczevska, M. Kłosowski, P. Bilski, **W. Gieszczyk**[✉].

TL, OSL and RL emission spectra of RE-doped LiMgPO₄ crystals. **Journal of Luminescence** 218 (2020), 116839

W. Gieszczyk[✉], P. Bilski, A. Mroziak, M. Kłosowski, B. Marczevska, A. Sas-Bieniarz, M. Perzanowski, T. Zorenko and Yu. Zorenko.

Intrinsic and dopant-related luminescence of undoped and Tb plus Tm double-doped lithium magnesium phosphate (LiMgPO₄, LMP) crystals. **Materials** 13 (2020), 2032

Marczevska[✉], B., **Gieszczyk, W.**, Kłosowski, M., Książek, M., Bilski, P., Boroń, Ł.

Uniformity of thermoluminescence and optically stimulated Luminescence signals over the length of doped LiMgPO₄ crystal rods grown by micro-pulling-down method. **Materials** 14 (2021), 132

Acknowledgements:

To colleagues from the Institute of Nuclear Physics in Kraków:

- Paweł Bilski
- Mariusz Kłosowski
- Dagmara Kulig
- Leszek Malinowski
- Barbara Marczevska
- Anna Mroziak
- Tomasz Nowak
- Marcin Perzanowski
- Anna Sas-Bieniarz
- Michał Sądel

To colleagues from the Institute of Physics
Kazimierz Wielki University in Bydgoszcz:

- Yuriy Zorenko
- Tetiana Zorenko

To colleagues from the AGH University
of Science and Technology in Kraków

- Paweł Goj
- Paweł Stoch

To the polish institutions supporting our research



**Ministry of Science
and Higher Education**

Republic of Poland

**Thank you very much
for your attention!!! 😊**