

# Fast timing with nanocrystalline lead halide perovskite thin films on scintillating wafers

K. Děcká<sup>1,2</sup>, J. Král<sup>2</sup>, F. Hájek<sup>1,2</sup> P. Průša<sup>2</sup>,  
V. Babin<sup>1</sup>, E. Mihóková<sup>1,2</sup> and V. Čuba<sup>2</sup>



<sup>1</sup>*Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic*

<sup>2</sup>*FNSPE, Czech Technical University in Prague, Prague, Czech Republic*

# Fast timing

nanoparticles

quantum confinement

enhanced optical properties  
vs bulk counterparts

High quantum efficiency

Ultrafast decay

Promising candidates

**Cesium lead halide perovskites**  
 **$\text{CsPbX}_3$  (X=Cl, Br, I)**

**fast Mott-Wannier exciton emission**

$\text{CsPbX}_3$  (X=Cl, Br, I) nanocrystals



L. Protesescu et al., Nanolett. **15**, 3692 (2015)

**application potential for solar cells,  
LEDs, displays ...**

**High quantum yields**

**Decay times 1-29 ns**

**Tunable emission over all VIS range**  
depending on nanoparticle size and  
composition (X)

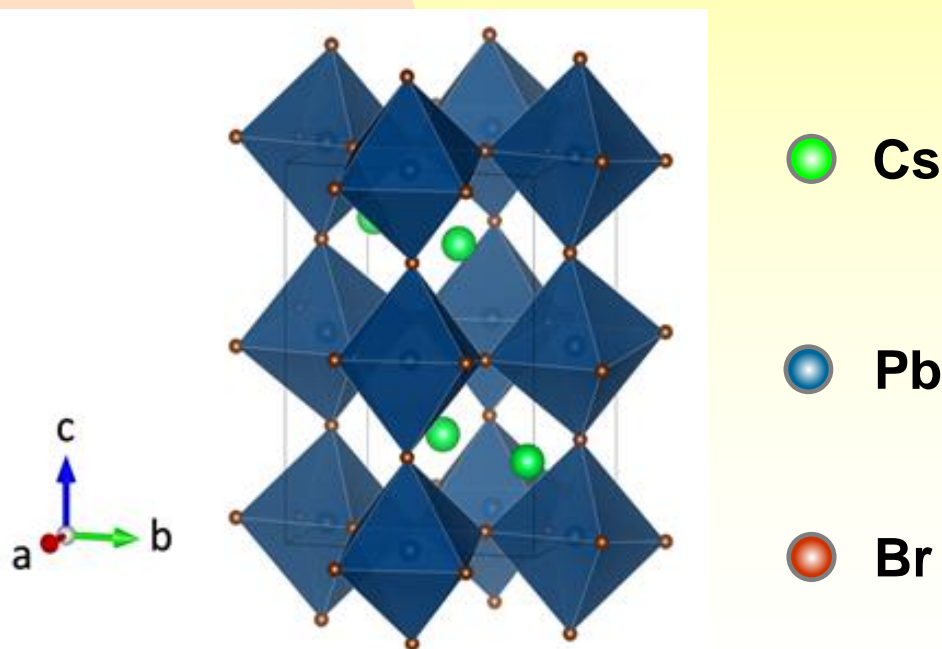
# CsPbBr<sub>3</sub> nanocrystals

poor chemical stability in air

solution : encapsulation in inert matrices or organic polymers

Presentation K. Děcká

CsPbBr<sub>3</sub>  
3D perovskite

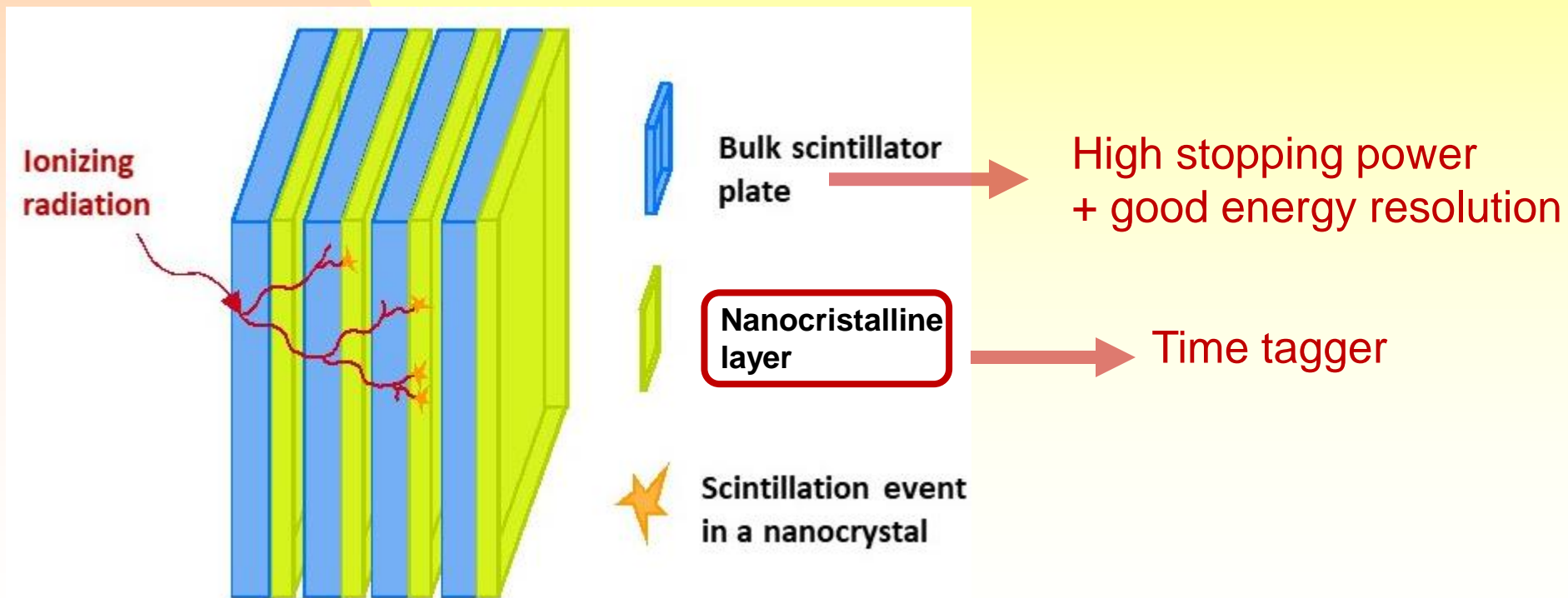


corner sharing PbBr<sub>6</sub><sup>4-</sup> octahedra

# CsPbBr<sub>3</sub> nanocrystals for scintillator applications

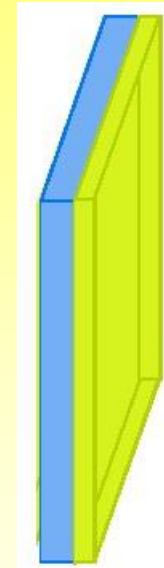
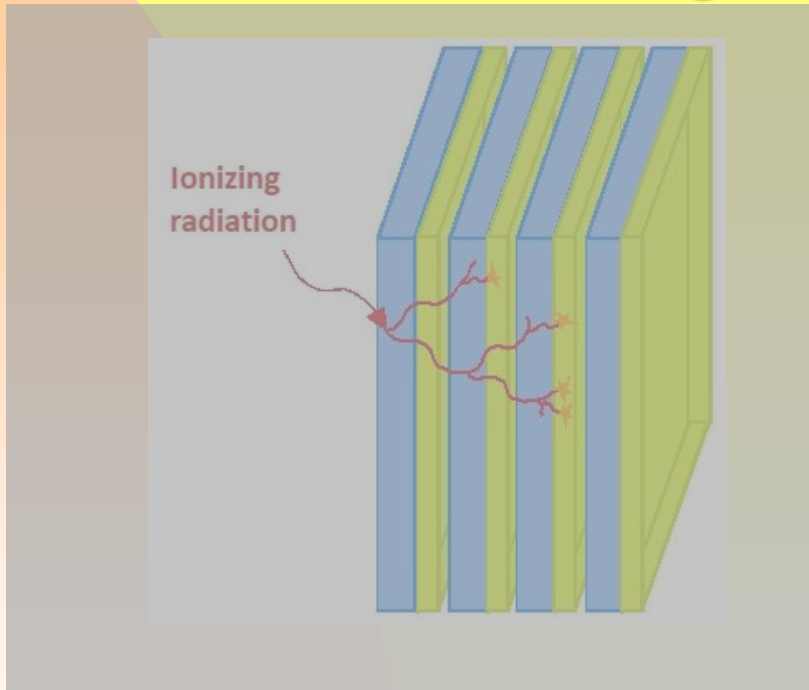
The most serious issue: poor stopping power

Solution: heterostructure



# Goal

To fabricate **CsPbBr<sub>3</sub>** thin films on scintillating wafers



To test whether such nanocomposite can be a candidate for fast timing detector

# Hot injection (HI) synthesis of CsPbBr<sub>3</sub>

L. Protesescu et al., Nanolett. **15**, 3692 (2015)

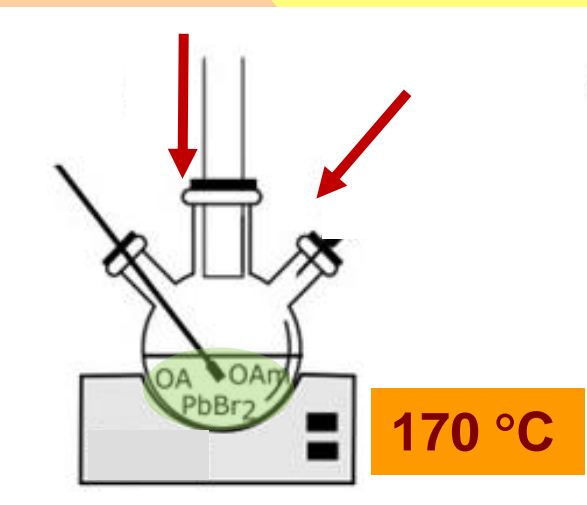


Schlenk line installed at the FNSPE CTU

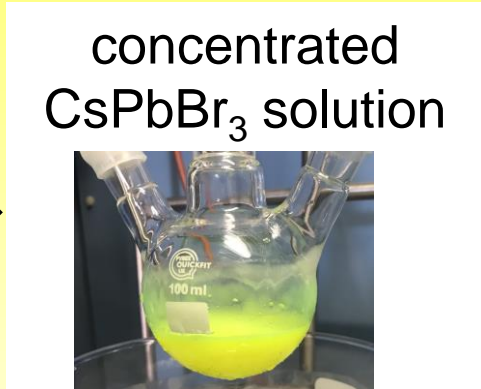


# Hot injection (HI) synthesis of CsPbBr<sub>3</sub>

L. Protesescu et al., Nanolett. 15, 3692 (2015)

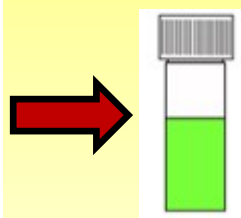


OA – oleic acid  
OAm – oleylamine



concentrated CsPbBr<sub>3</sub> solution

CsPbBr<sub>3</sub> capped with OA, OAm



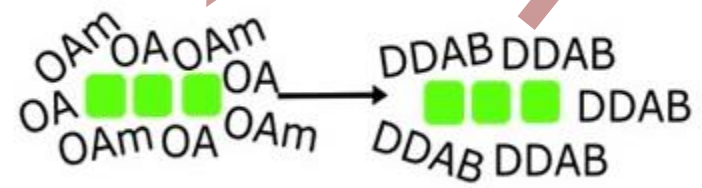
CsPbBr<sub>3</sub> capped with DDAB

characterization

## Ligand exchange procedure

M. Imran et al., ACS Energy Lett. 4, 819 (2019)

at RT in air



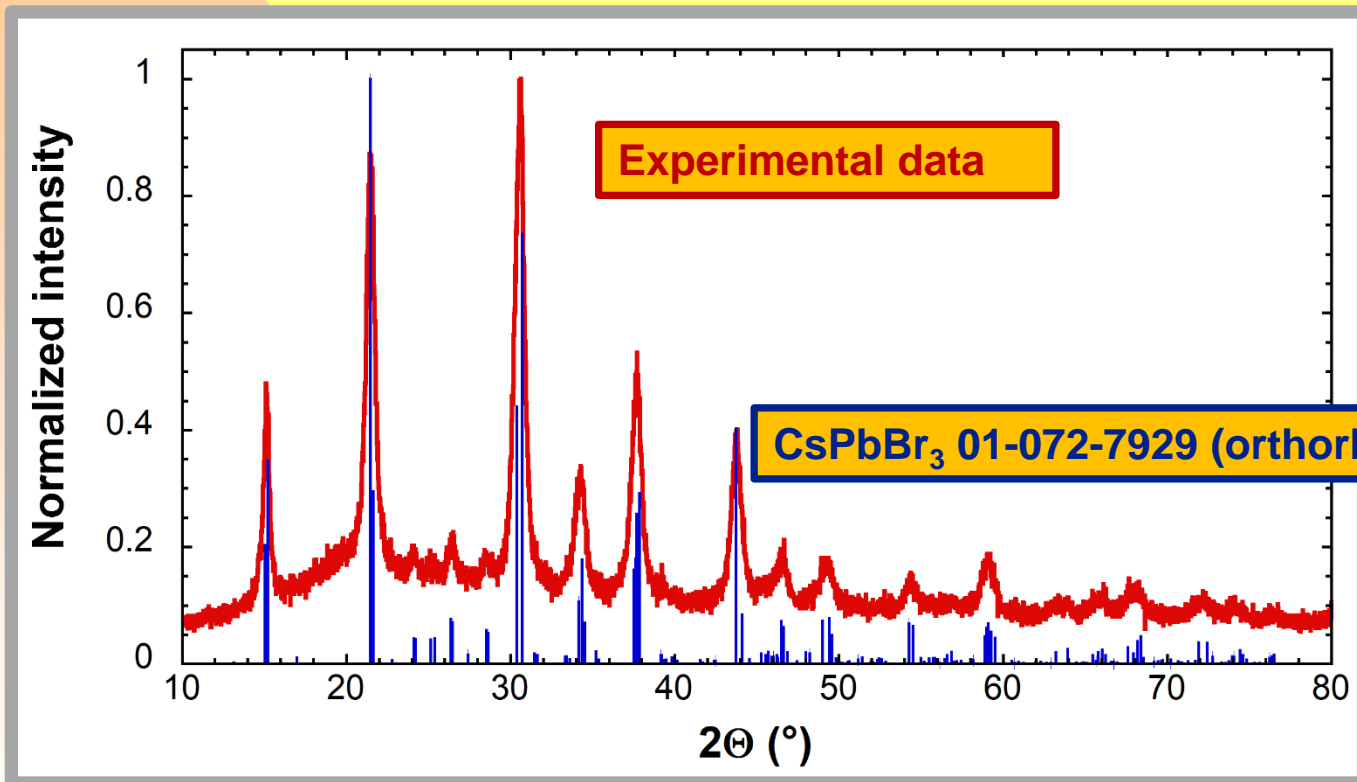
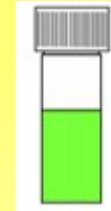
Thicker films  
More intense RL

DDAB – didodecyldimethylammonium bromide



# X-ray powder diffraction

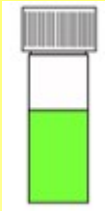
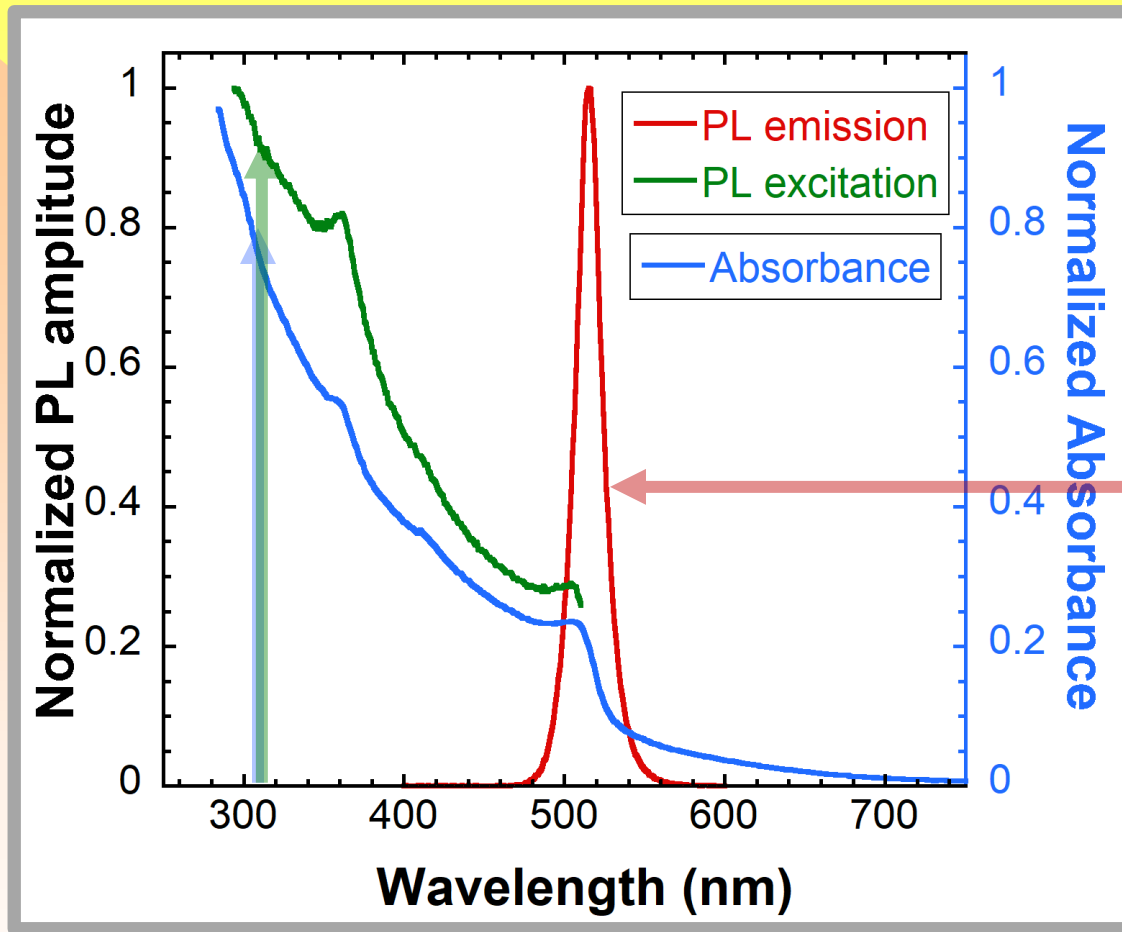
XRPD pattern of the synthesized material used for the spin coating



mean crystallite size  
 $13.8 \pm 0.6$  nm



# Absorption and photoluminescence



Single excitonic peak at **515 nm**

Lack of the **peak (dip)** at 310 nm in **absorbance** and **PLE spectra** (characteristic of  $\text{Cs}_4\text{PbBr}_6$  impurity) confirms the purity of  $\text{CsPbBr}_3$  phase

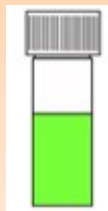
Small Stokes shift – problem of reabsorption

# CsPbBr<sub>3</sub> thin film fabrication

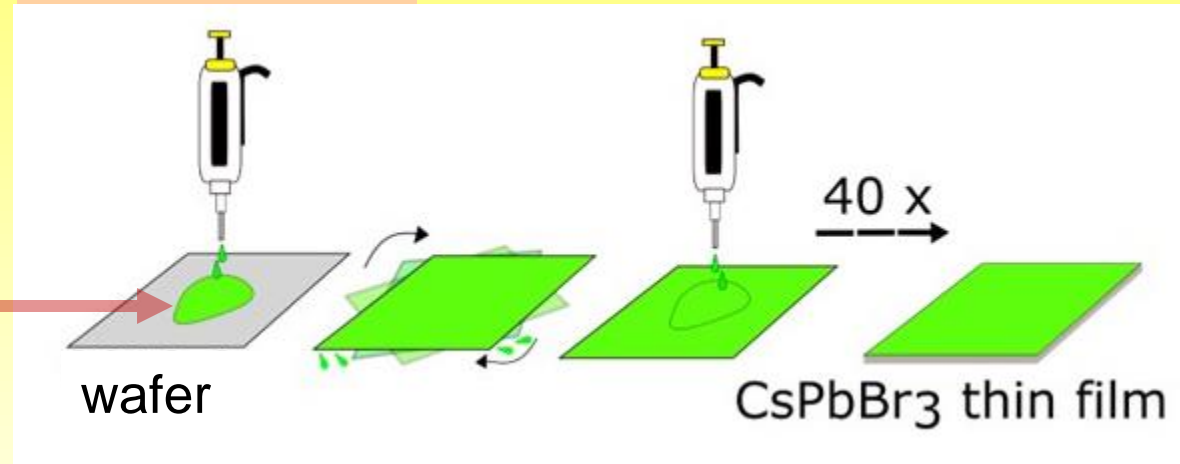
Spin coating on wafer: glass, GGAG:Ce



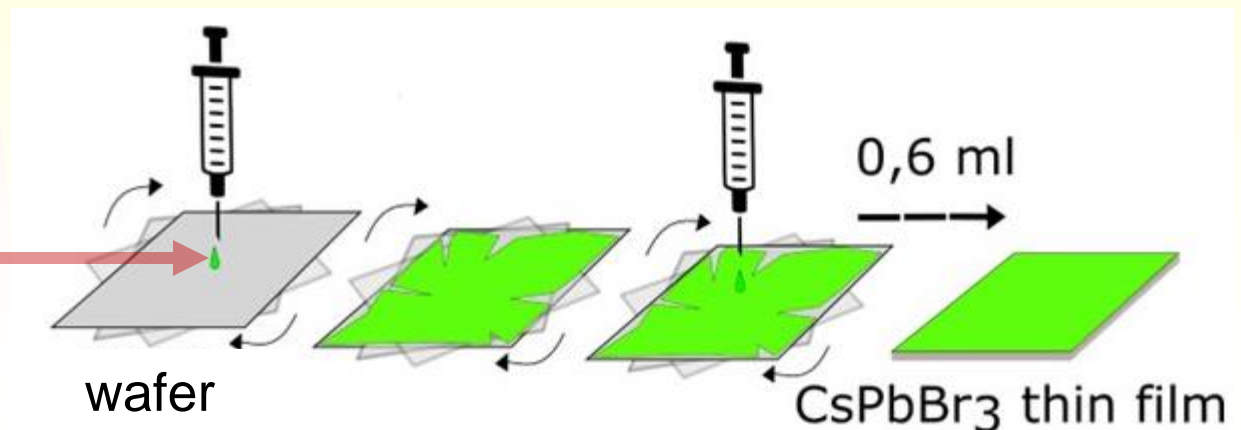
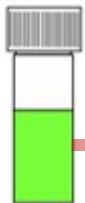
Static method



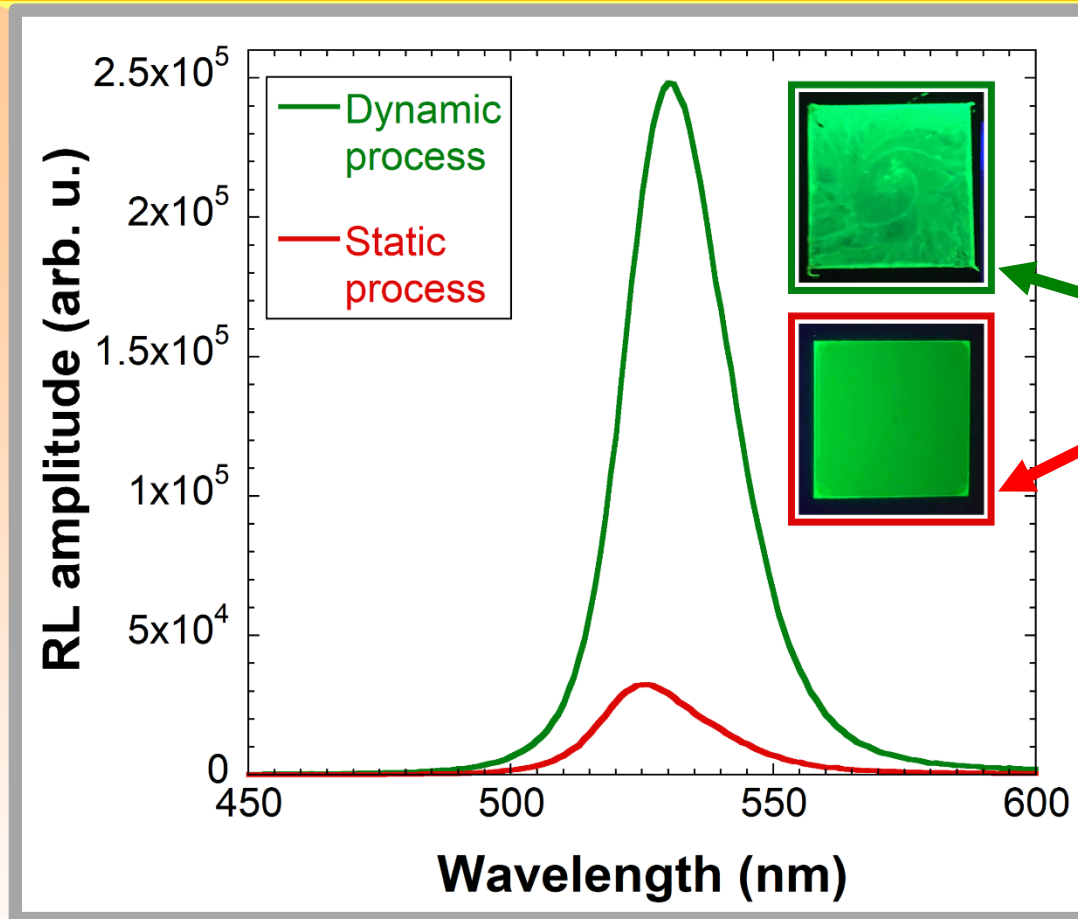
Concentrated solution of CsPbBr<sub>3</sub> capped with DDAB



Dynamic method



# Radioluminescence of thin films on glass



Photographs under UV illumination

**Dynamic process** – more intense RL

– less material used (0.6 mL vs 1.6 mL for 40 layers of the static process)

**Static process** – much higher homogeneity

Is homogeneity important for intended application ?

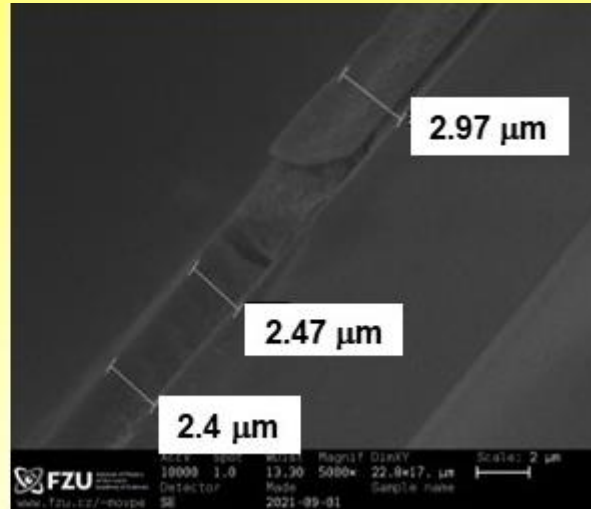
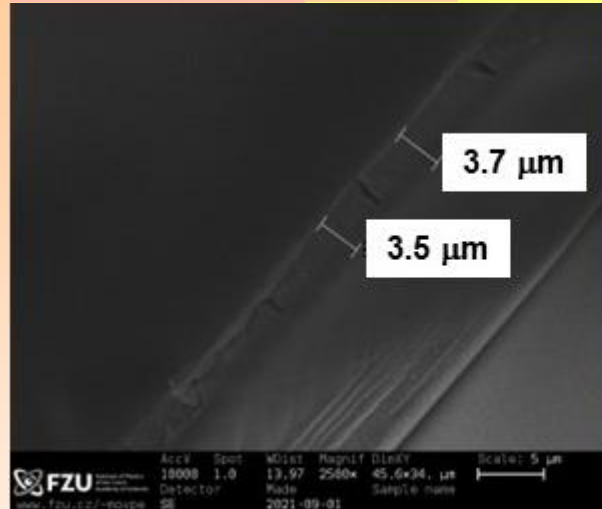
# Thin films on GGAG:Ce - mean thickness

SEM images of the thin film edge

**Static process**

**50 layers**

Mean thickness:  $\sim 3 \mu\text{m}$

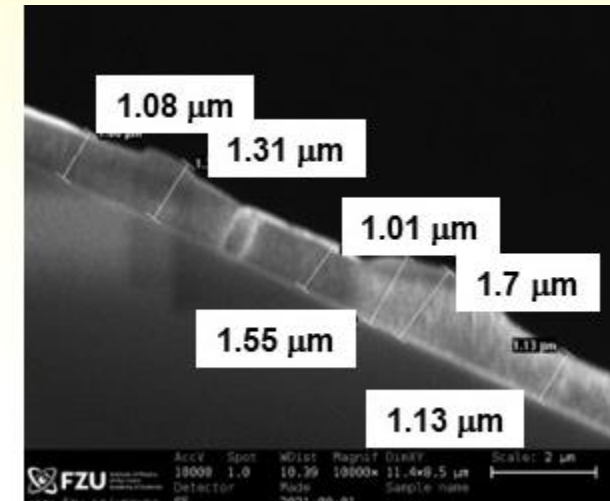
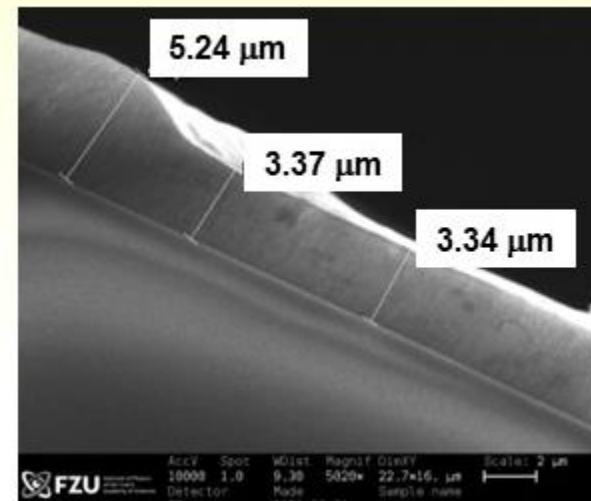
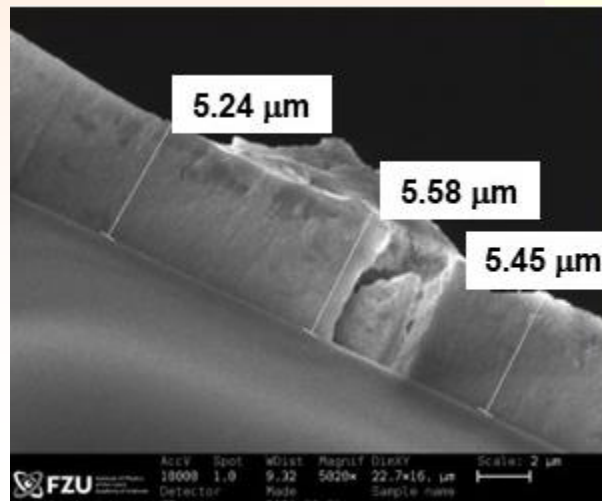


← Much better homogeneity

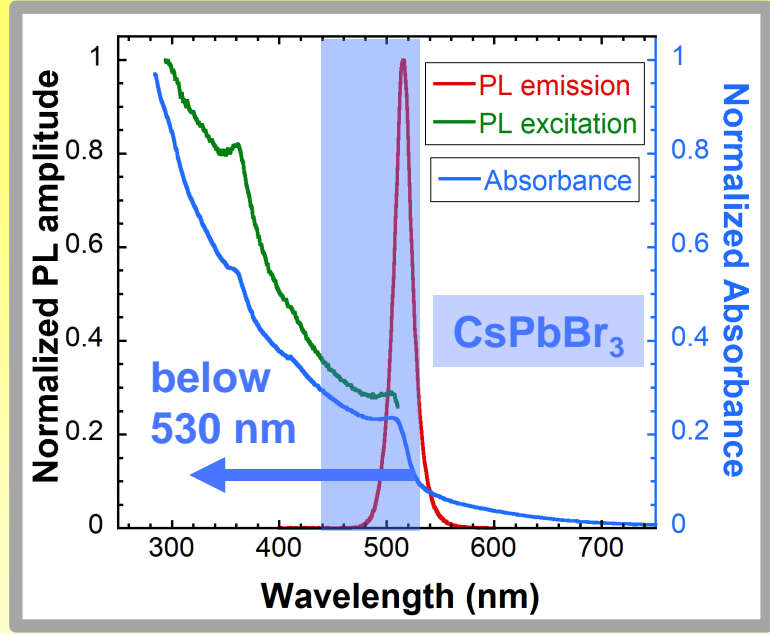
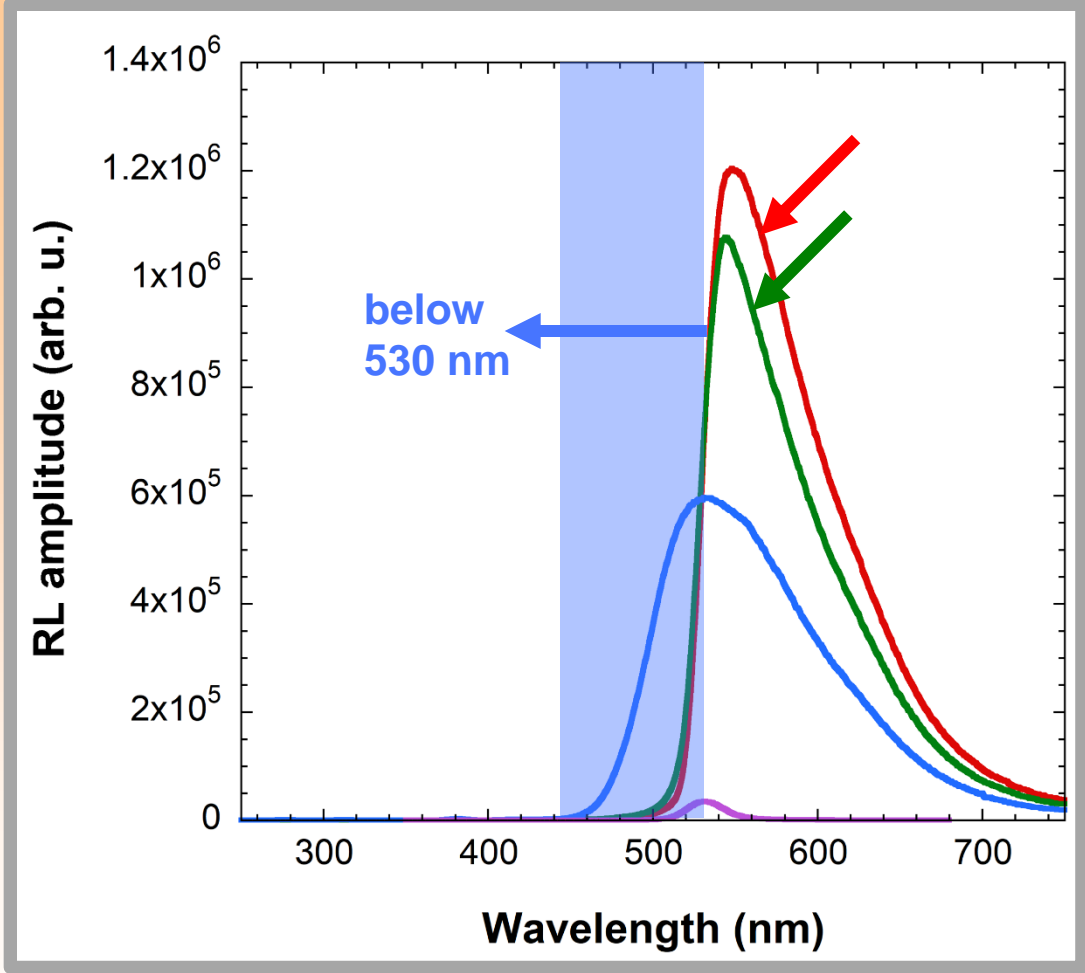
**Dynamic process**

**0.6 mL**

Mean thickness:  $\sim 3 \mu\text{m}$



# Radioluminescence of CsPbBr<sub>3</sub> thin films



CsPbBr<sub>3</sub> on glass  
Static process

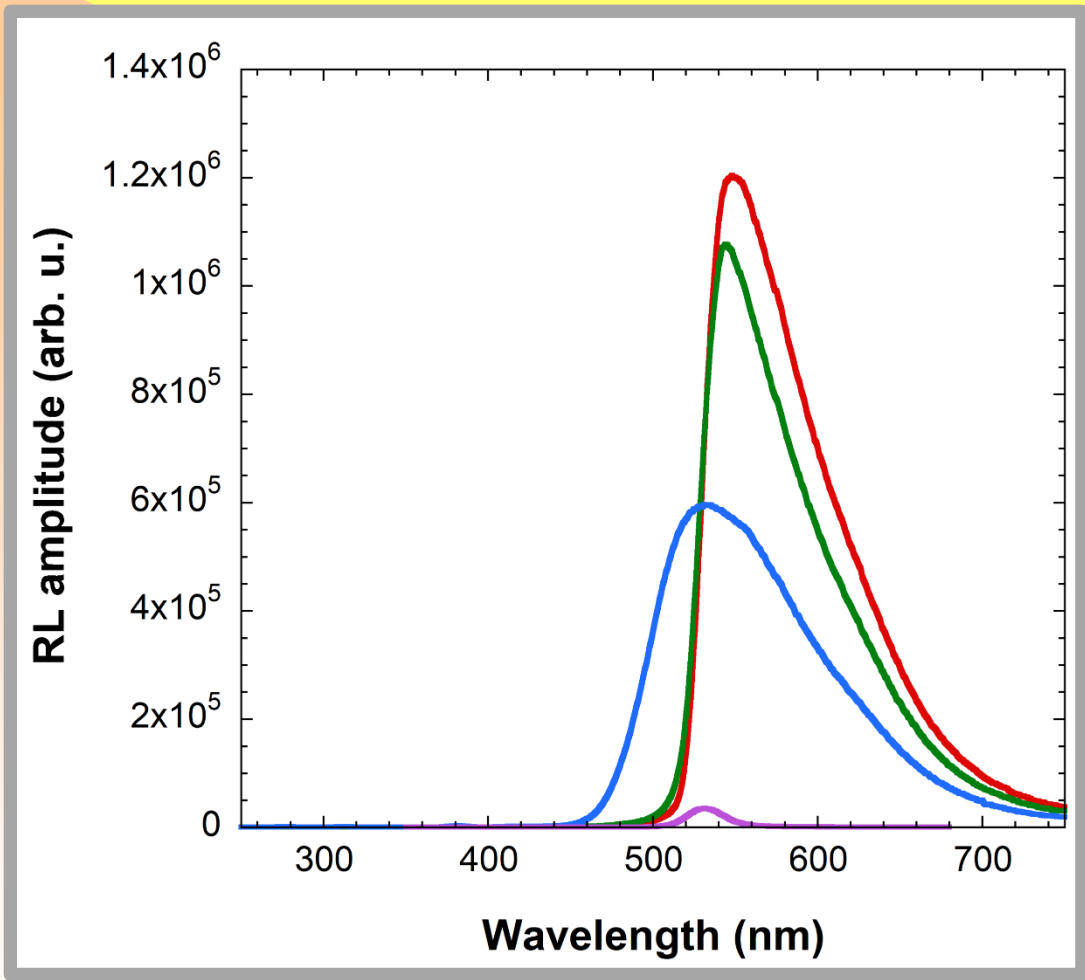
Quantitative comparison  
of RL not appropriate  
glass wafer is larger

GGAG:Ce wafer

CsPbBr<sub>3</sub> on GGAG:Ce  
Dynamic process

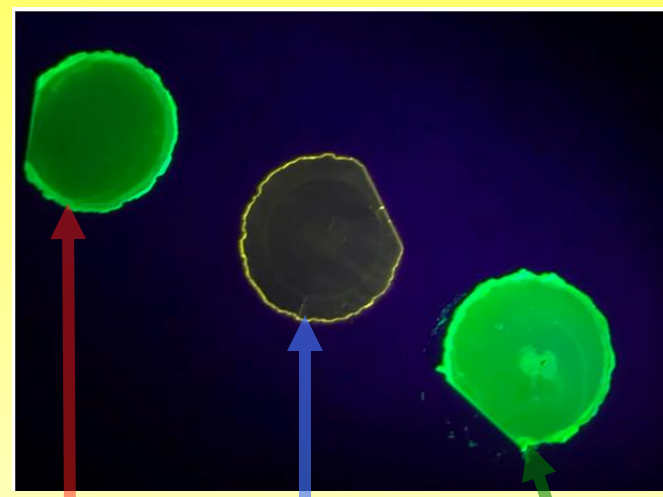
CsPbBr<sub>3</sub> on GGAG:Ce  
Static process

# Radioluminescence of CsPbBr<sub>3</sub> thin films



CsPbBr<sub>3</sub> on glass  
Static process

Quantitative comparison  
of RL not appropriate



GGAG:Ce wafer

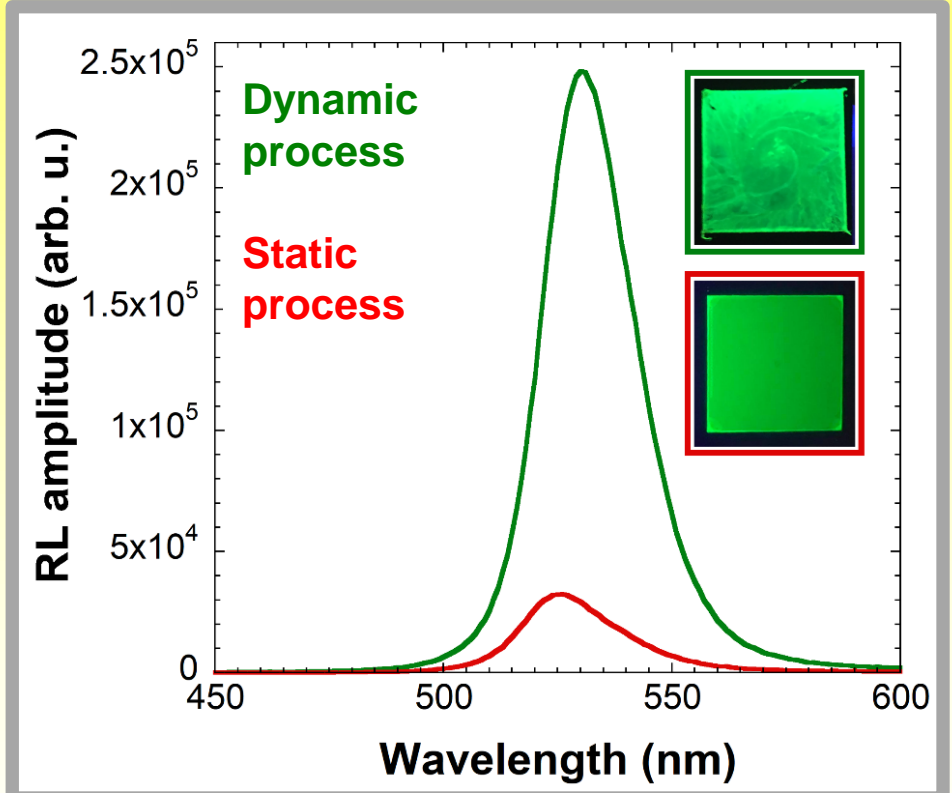
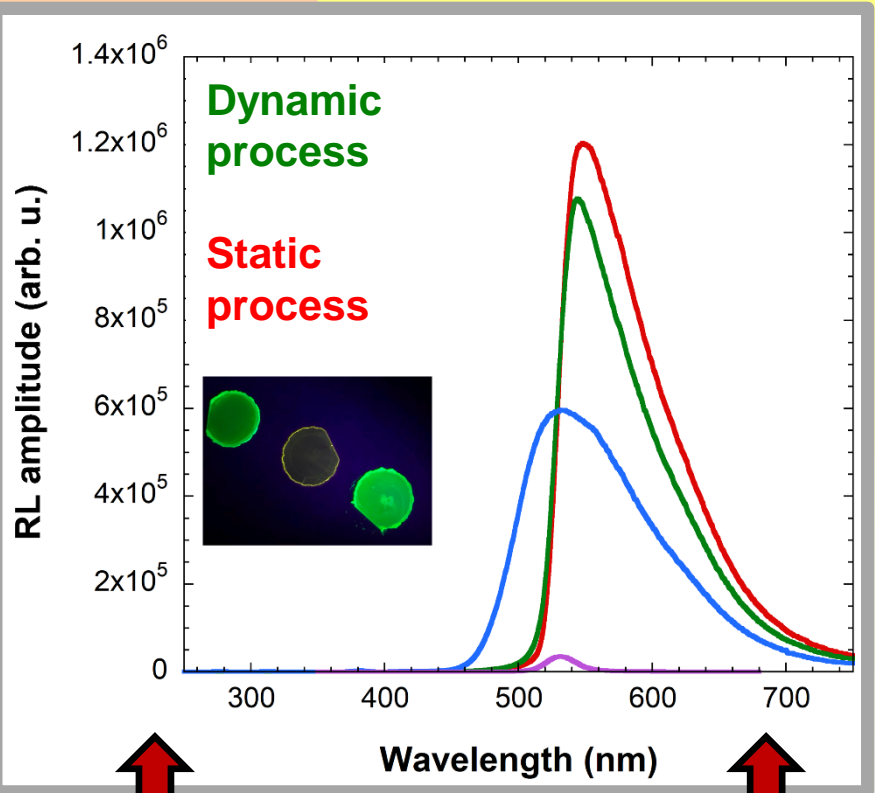
CsPbBr<sub>3</sub> on GGAG:Ce  
Dynamic process

CsPbBr<sub>3</sub> on GGAG:Ce  
Static process

# Radioluminescence of CsPbBr<sub>3</sub> thin films

GGAG:Ce wafer

glass wafer

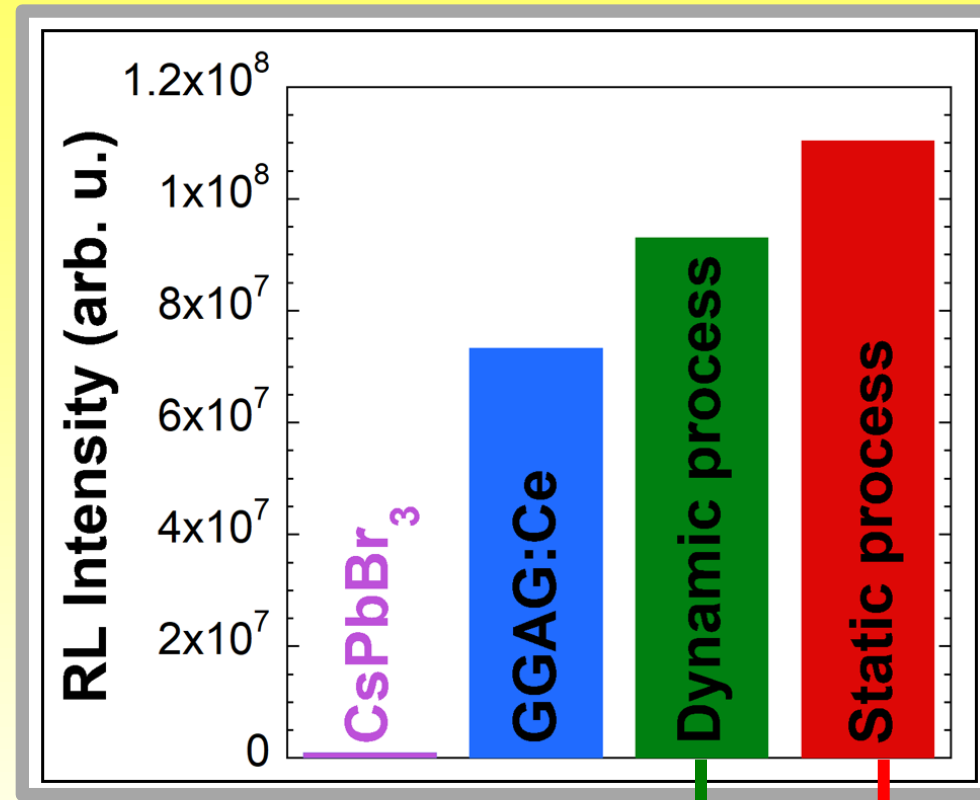
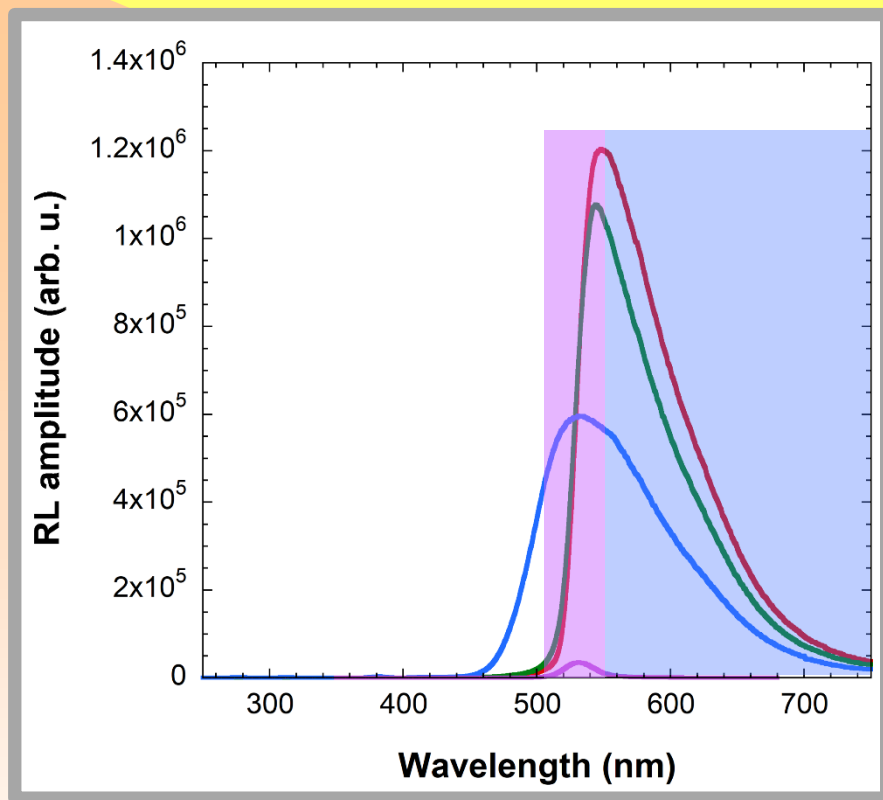


Not too different RL intensity of thin films prepared by different methods  
**static process** results in **higher RL**

Homogeneity of the film not too significant in the RL intensity of nanocomposite ?



# Radioluminescence of CsPbBr<sub>3</sub> thin films



Overall RL intensity of nanocomposite CsPbBr<sub>3</sub> on GGAG:Ce is higher than a simple sum of two emissions

Both emissions are enhanced

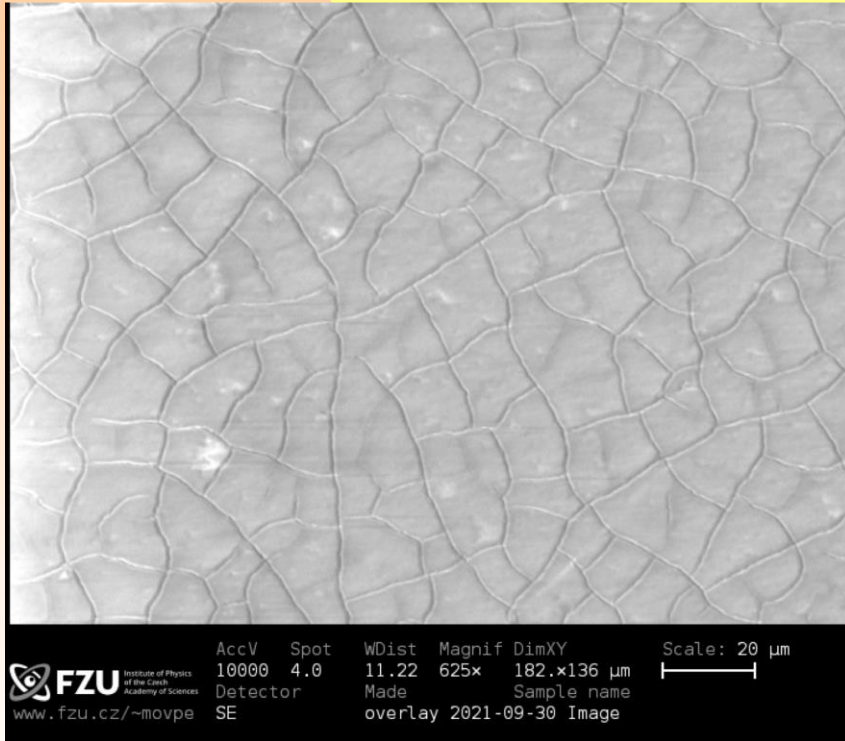
CsPbBr<sub>3</sub> probably enhanced by absorption and subsequent reemission of GGAG:Ce light

Enhancement of GGAG:Ce cannot be easily explained

# CsPbBr<sub>3</sub> thin film on GGAG:Ce

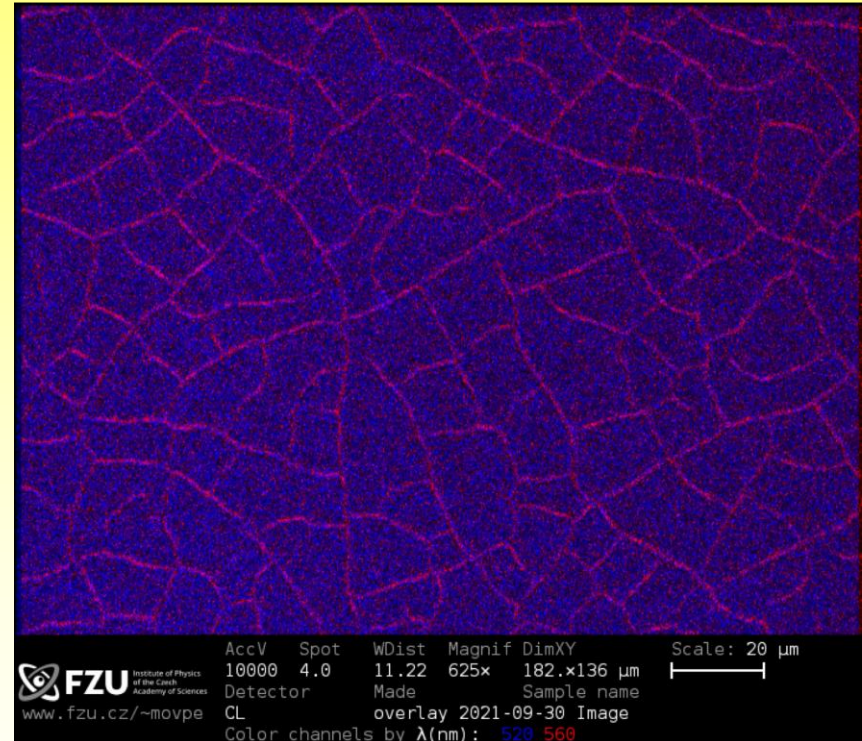
## Enhancement of GGAG:Ce emission

SEM image, static method



Thin film has cracks

CL image, static method



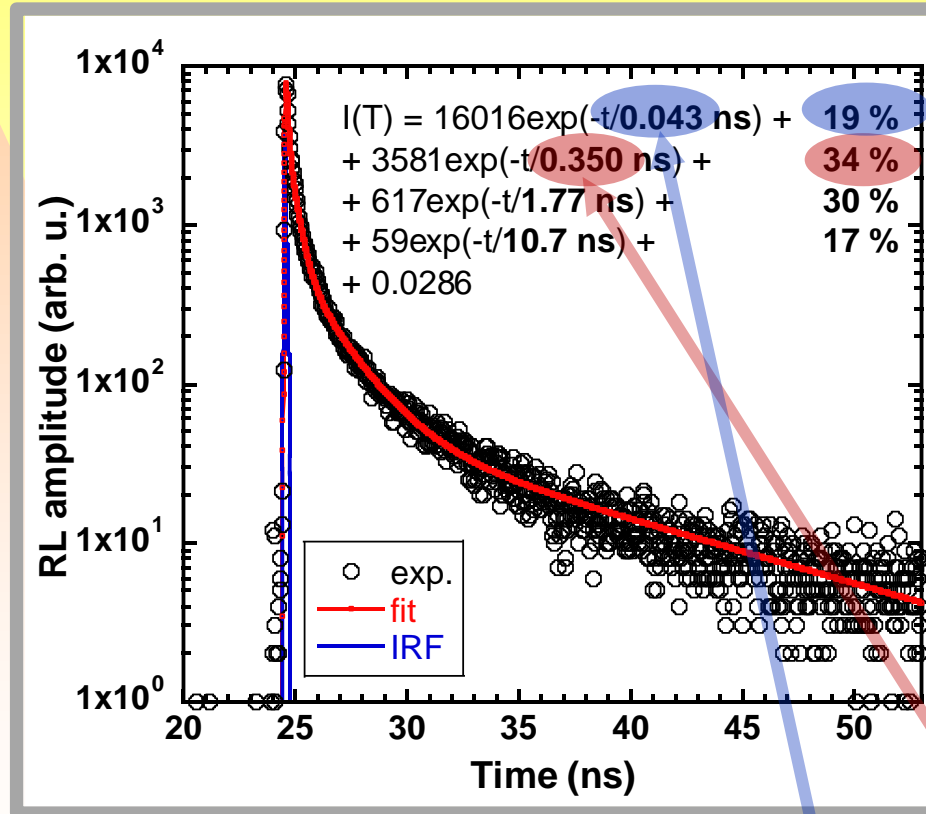
**520 nm light** emitted by CsPbBr<sub>3</sub>  
**560 nm light** emitted by GGAG:Ce

Cracks probably serve as light guide for GGAG:Ce emission

# Scintillation decay

## CsPbBr<sub>3</sub> on glass: static process (50 layers)

### Short time window



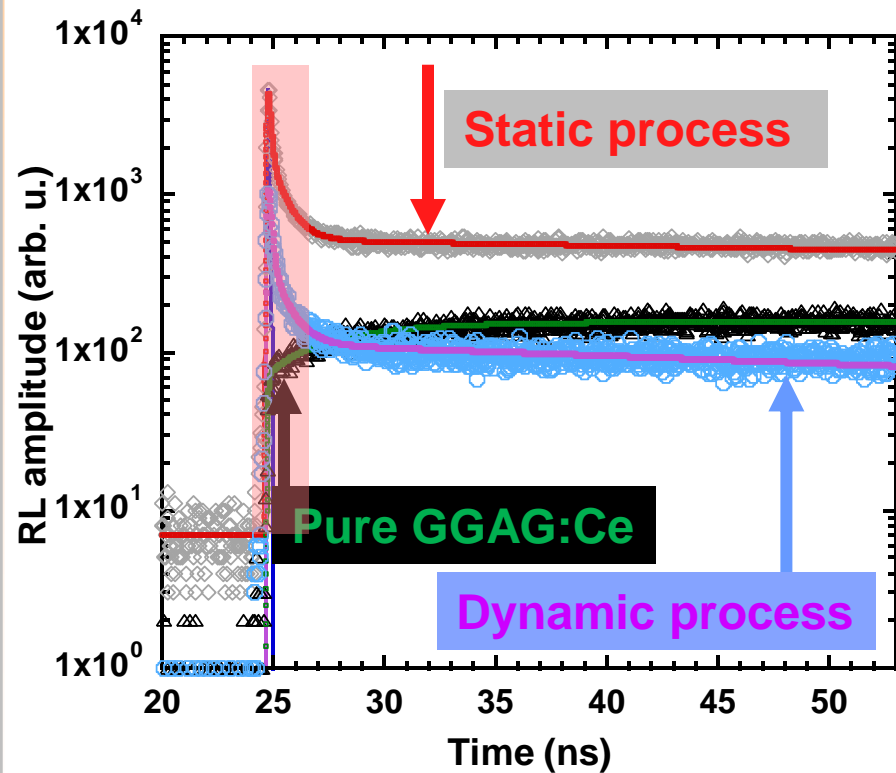
Two subnanosecond components 40 ps, 350 ps

More than **50% of light** emitted within subnanosecond time gate

# Scintillation decay

## CsPbBr<sub>3</sub> on GGAG:Ce

### Short time window

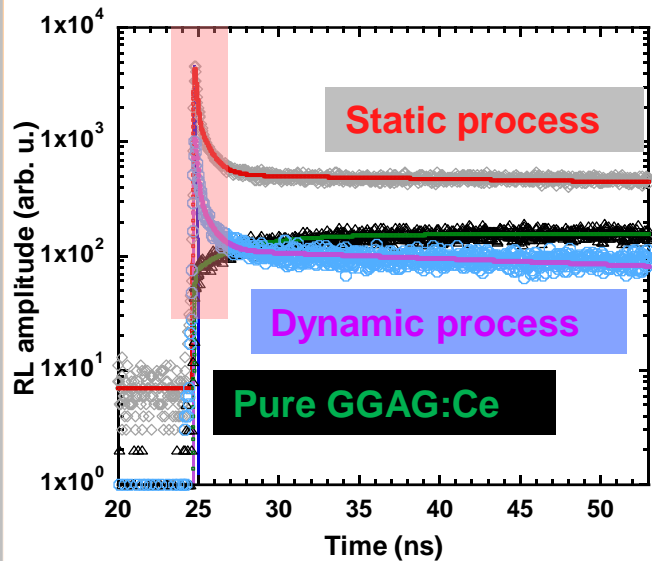


Ultrafast CsPbBr<sub>3</sub> emission preserved

# Scintillation decay

## CsPbBr<sub>3</sub> on GGAG:Ce

### Short time window



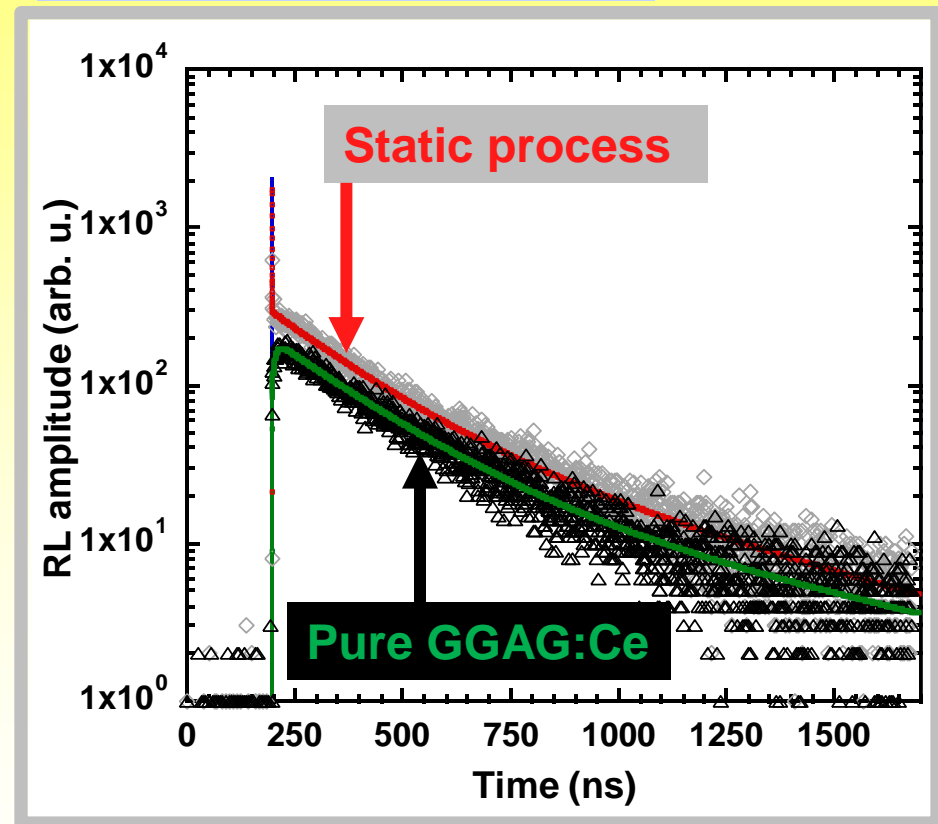
Sample	Rise time	Decay time	Light sum
GGAG:Ce	8 ns	200 ns	63 %
		660 ns	37 %
Static process	50 ps	80 ps	1 %
		700 ps	1 %
		long	98 %
Dynamic process	30 ps	120 ps	3 %
		770 ps	2 %
		long	95 %

Ultrafast CsPbBr<sub>3</sub> emission preserved

# Scintillation decay

**CsPbBr<sub>3</sub> on GGAG:Ce**

Long time window

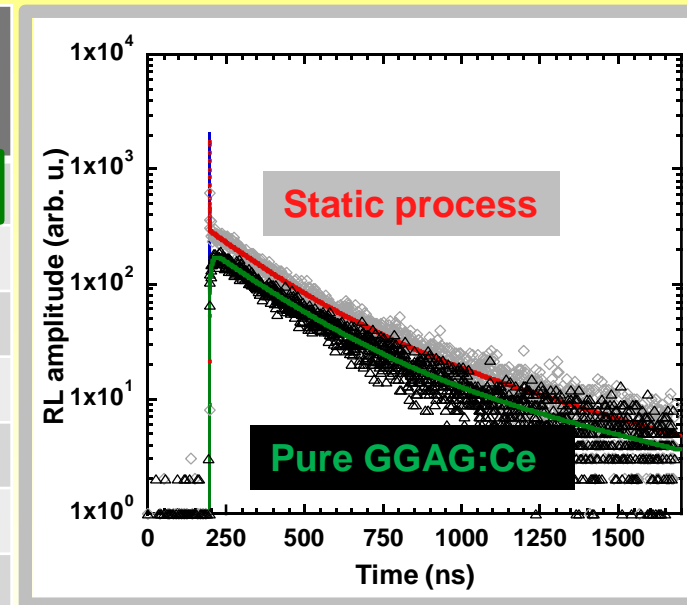


# Scintillation decay

## CsPbBr<sub>3</sub> on GGAG:Ce

### Long time window

Sample	Rise time	Decay time	Light sum
GGAG:Ce	8 ns	200 ns	63 %
		660 ns	37 %
Static process	50 ps	80 ps	1 %
		700 ps	1 %
		long	98 %
Dynamic process	30 ps	120 ps	3 %
		770 ps	2 %
		long	95 %



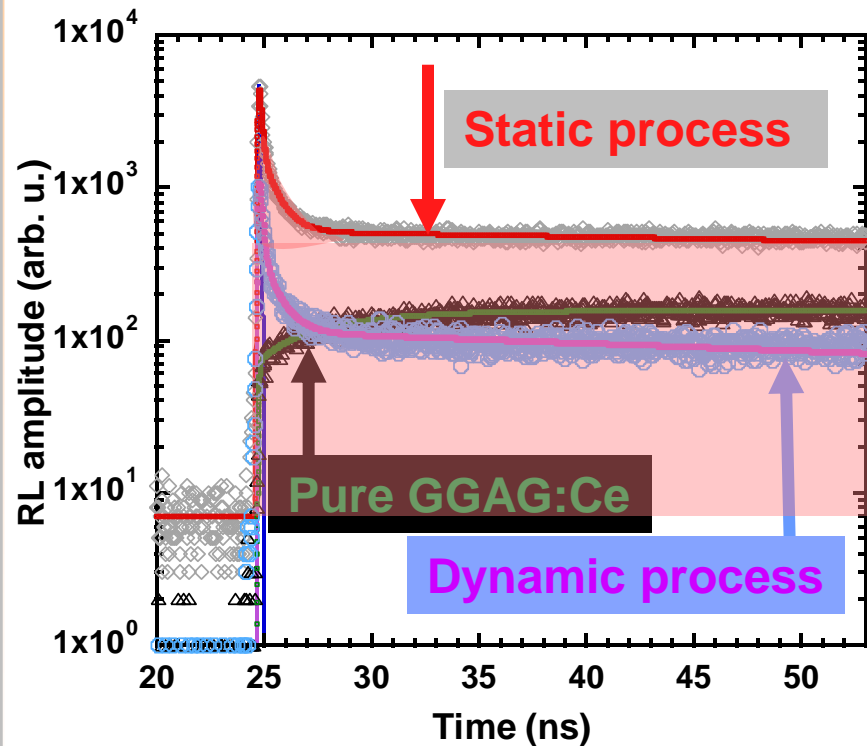
Slow emission of GGAG:Ce preserved



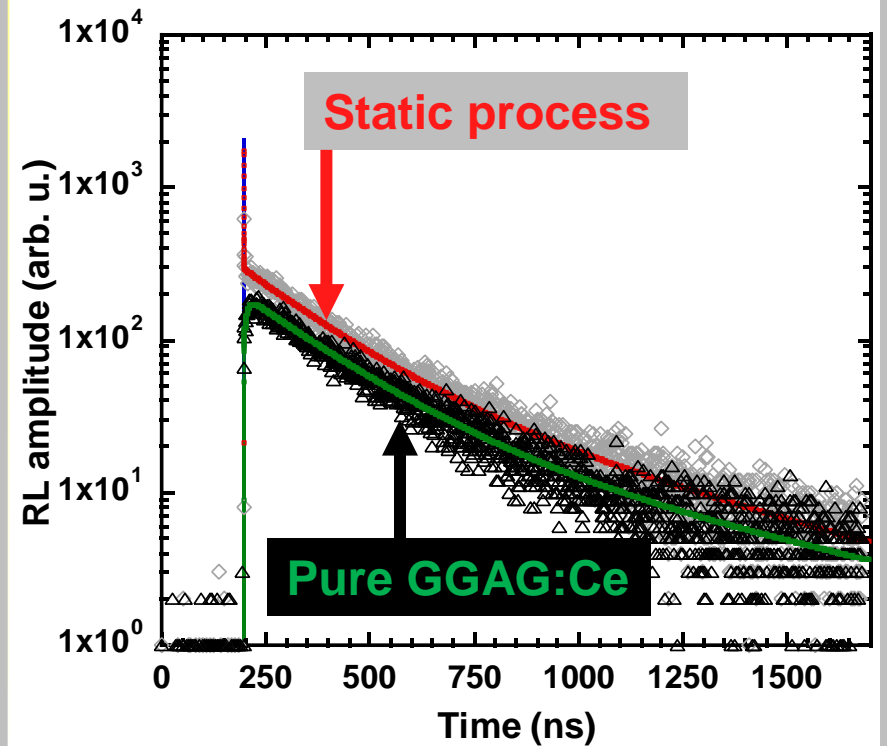
# Scintillation decay

## CsPbBr<sub>3</sub> on GGAG:Ce

### Short time window



### Long time window



Ultrafast CsPbBr<sub>3</sub> emission preserved

Slow emission of GGAG:Ce preserved

**Static process results in higher overall RL intensity**

Some level of the film homogeneity needed for light guiding effect

# Summary

- We prepared CsPbBr<sub>3</sub> thin films on glass and GGAG:Ce scintillating wafer
- We compare two methods for the film preparation: Dynamic process is more effective in terms of material consumption, the static process yields much more homogeneous films
- Homogeneity of the film is important since the static films exhibited higher intensity in both the RL spectra and decays
- Synergic effect by combining CsPbBr<sub>3</sub> nanoscintillator with the bulk GGAG:Ce scintillator – resulting nanocomposite exhibited enhanced RL intensity while preserving ultrafast CsPbBr<sub>3</sub> decay
- Thin nanocomposite layer is able to perform as efficient time tagger in a sampling detector geometry

**Thanks are expressed to all collaborators**

**and to**

**the audience for kind attention**



# Acknowledgements

- ❑ Czech Science Foundation, Grant No. GA20-06374S
- ❑ Ministry of Education Youth and Sports, project “Center for advanced applied science,” No. CZ.02.1.01/0.0/0.0/16\_019/0000778
- ❑ Grant Agency of the Czech Technical University in Prague, Grant No. SGS20/185/OHK4/3T/14