Halide Crystal Growth

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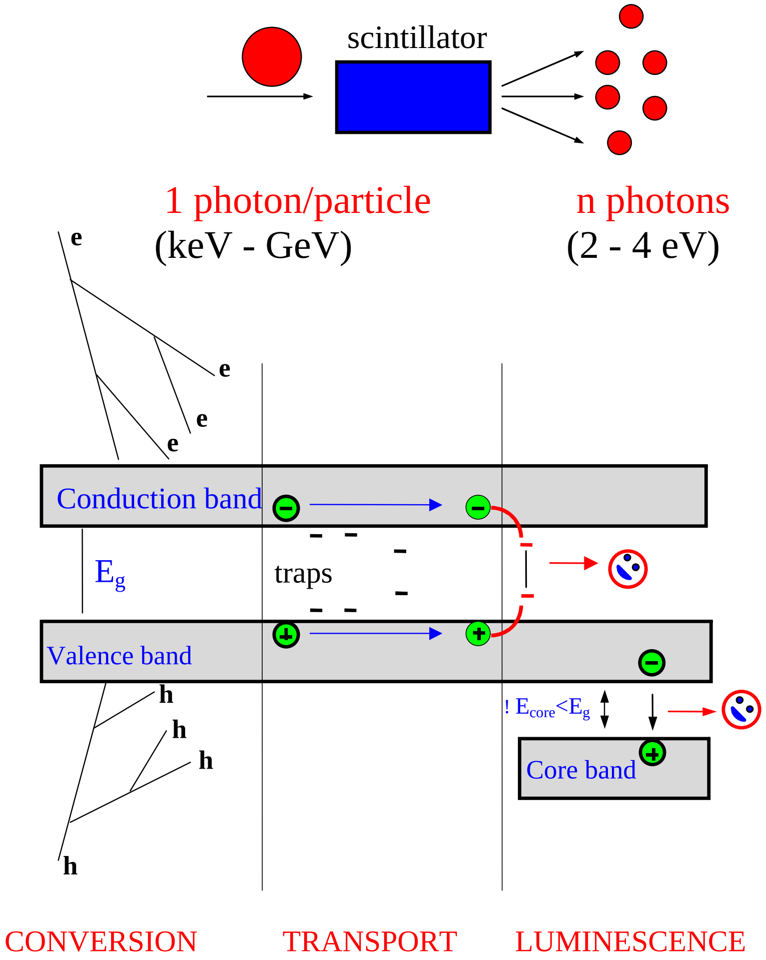
Principle of scintillators



Scintillators

- detectors of radiation
- convertors the energy of ionizing radiation into VUV/UV/visible light

Application

- medical imaging, homeland security, high energy physics, etc.

Transport

- shallow traps/defects influence transport of charge carriers to luminescence centers

- slow components in the scintillation decay

Ternary alkali metal halides

general formula

$$A_2MX_6 = 2\,AX + MX_4$$

A = Li, Na, K, Rb, Cs

M^{4+} = Ti, **Zr, Hf,** Pt, Sn, Se, Te

X = F, Cl, Br, I

	Cs_2HfCl_6
m.p. [°C]	826
Melting	congruent
Phase transition [°C]	no
Density [g/cm^3]	3.8
Crystal. structure	cubic
Space group	Fm-3m

doping

$(UO_2)^{2+}$, Te^{4+}, Sn^{4+}, Re^{4+} Os^{4+}, Mo^{3+}, Ir^{4+}, Na^{+}, Ce^{3+}, Eu^{2+}

Application of Cs_2HfCl_6

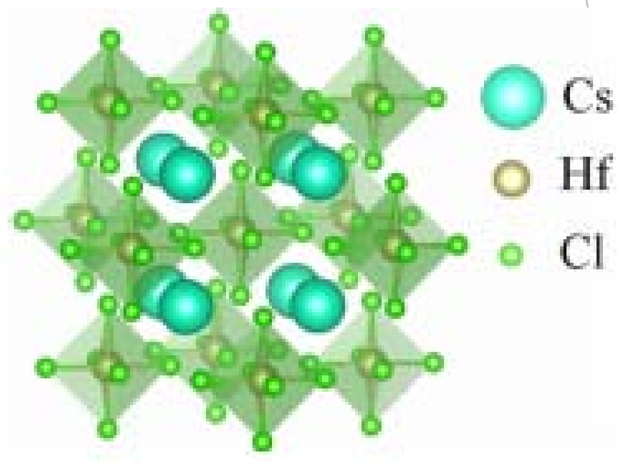
- ✓ as cost-effective radiation detector (scintillators)
- ✓ highly proportional light yield
- ✓ even without doping with any intentional activator

Properties

	Cs_2HfCl_6	Tl:NaI	Tl:CsI	Eu:SrI_2	Ce:$LaBr_3$
Density [g/cm^3]	3.8	3.4	4.5	4.6	5.3
m.p. [°C]	826	661	621	538	783
Cryst. structure	Cubic	Cubic	Cubic	Orthorhom.	Hex.
Eg [eV]	6.3	5.8	6.1	5.5	5.9
Zeff	58	50	51	49	47
Emission max. [nm]	380	410	540	430	360
Decay time [ns]	300 (5%); 4400 (95%)	230	1100	600-2400	35
Light yield [ph/MeV]	54,000	38,000	66,000	80,000-120,000	61,000
Resolution [%] @662 eV	3-4	7	6	3-4	3
Hygroscopicity	low	yes	yes	yes	yes

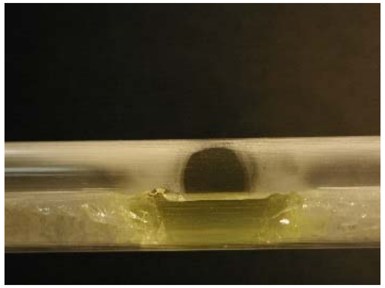
Cs_2HfCl_6 growth

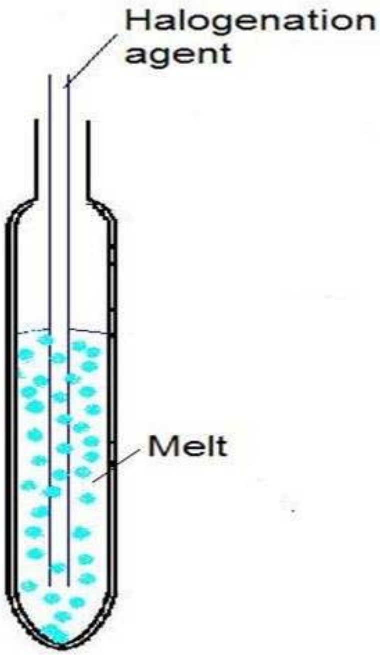
- Hygroscopic starting materials (CsCl, $HfCl_4$)
- Purification of starting materials
- $HfCl_4$ low sublimation point (320 °C) vs. Cs_2HfCl_6 congruent melting point (826 °C)
- High vapor pleasure in ampoules



Material refinement

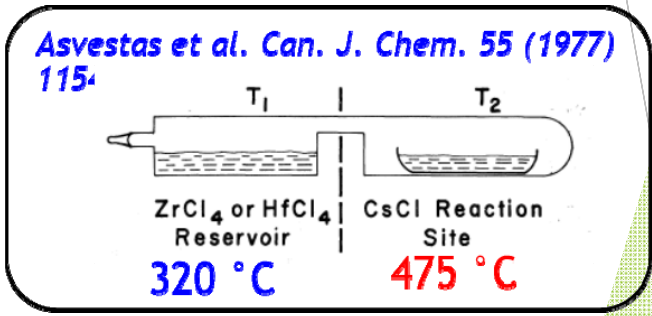
- CsCl
  - Zone refining





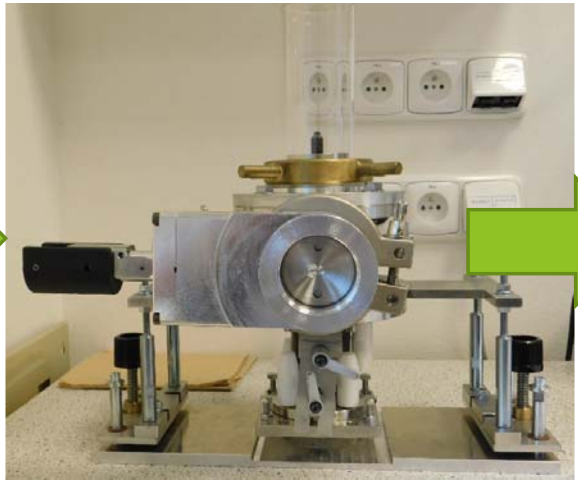
  - Halogenating agents

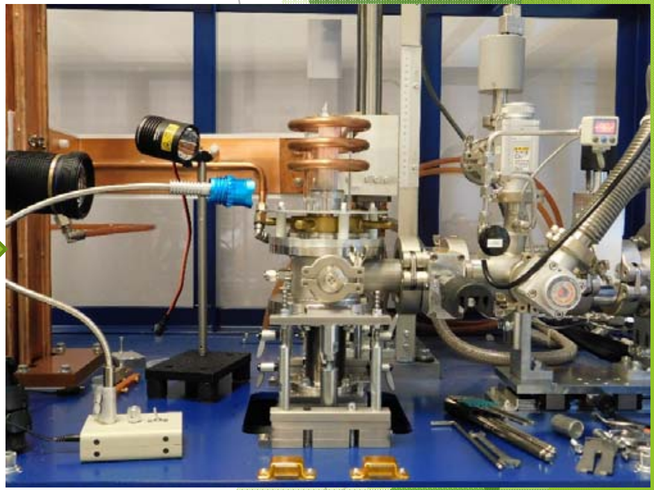
- $HfCl_4$
  - Resublimation



  - Halogenating agents

Smaple preparation and transport



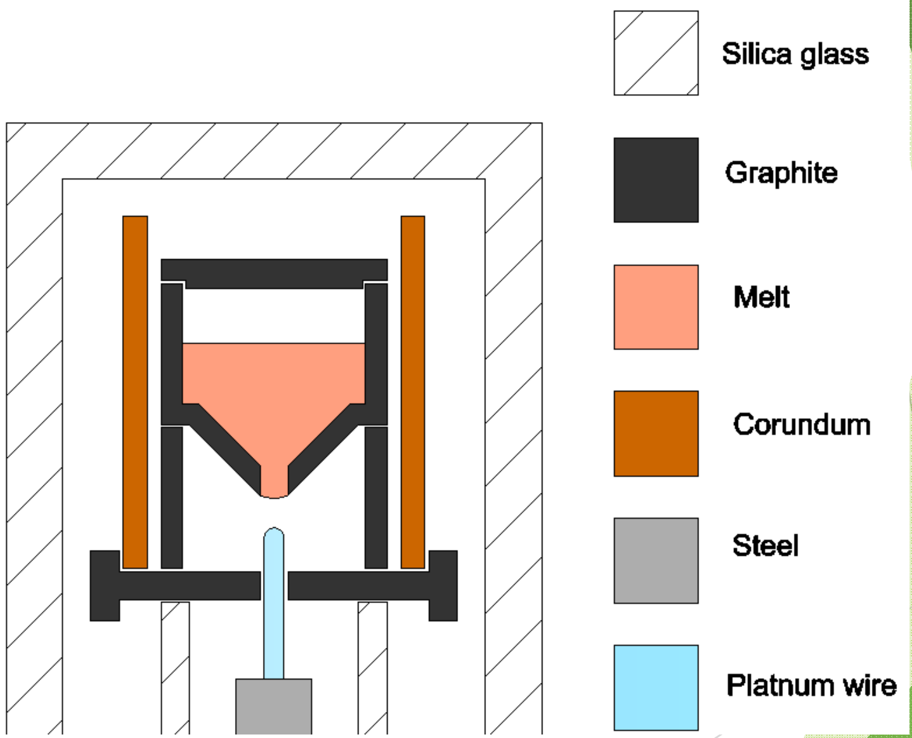


Halide μ-pulling-down apparatus

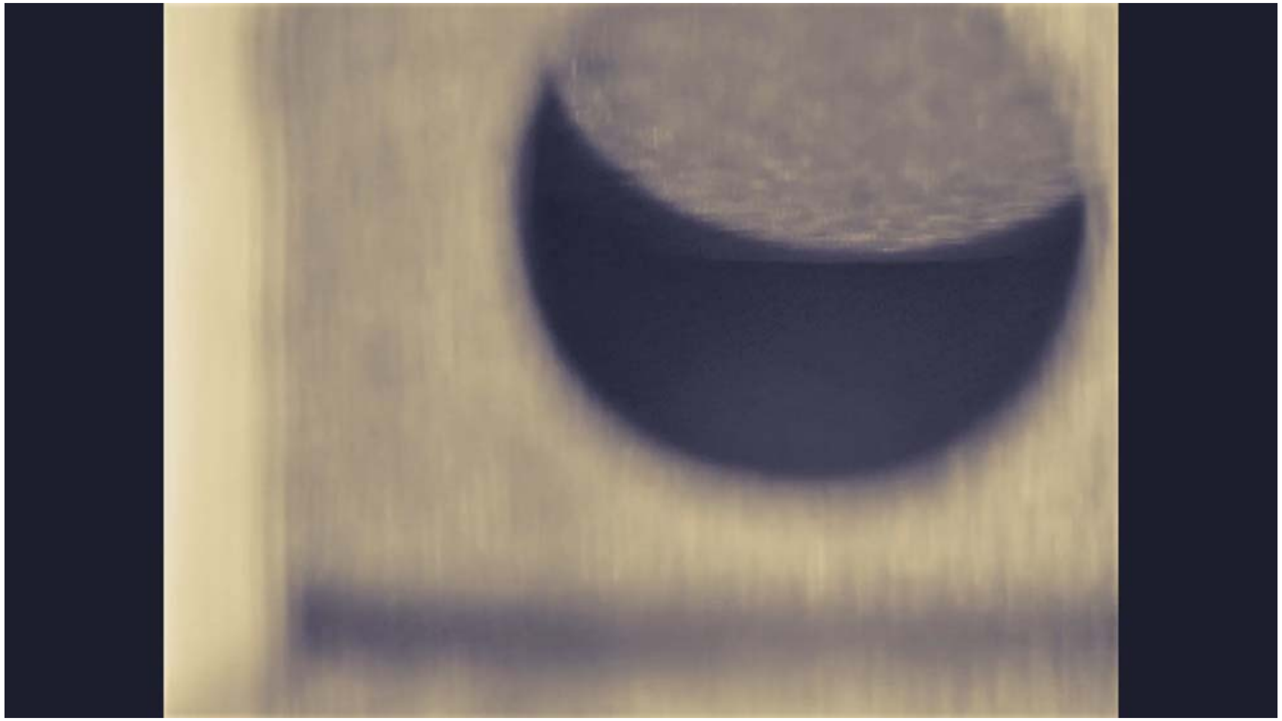
- Enclosed growth ampule
- Growth atmosphere control
- RF heating
- Remote control
- Capable of VB growth

Micro-pulling-down (mPD)

- Seeded growth
- RF heating with graphite crucible
- Crystal shape control
- Pulling rates 0.6 – 6 mm/h
- Diameter: 2-3 mm
- Length: 20 – 40 mm

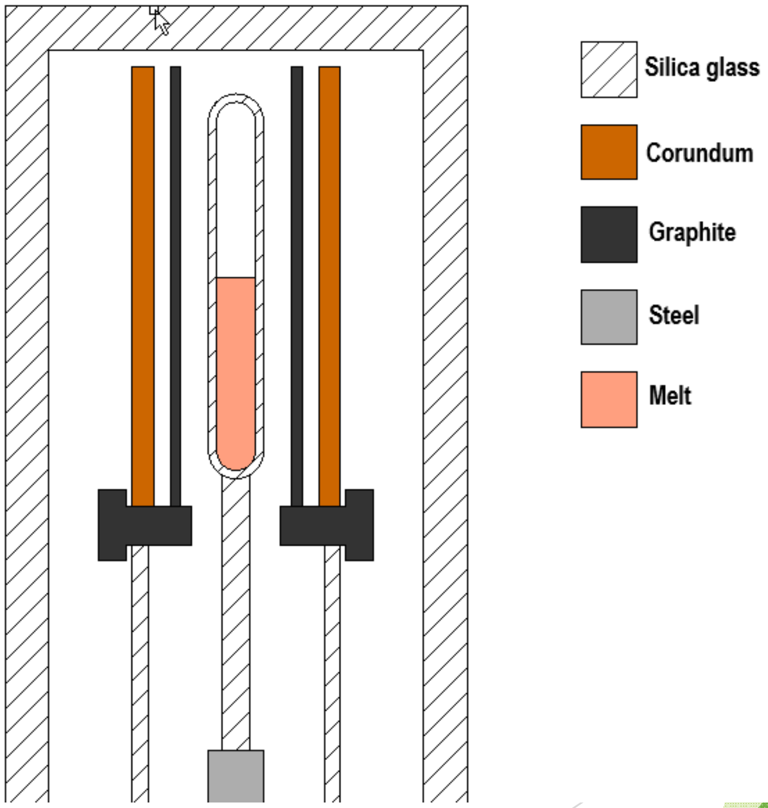


mPD growth



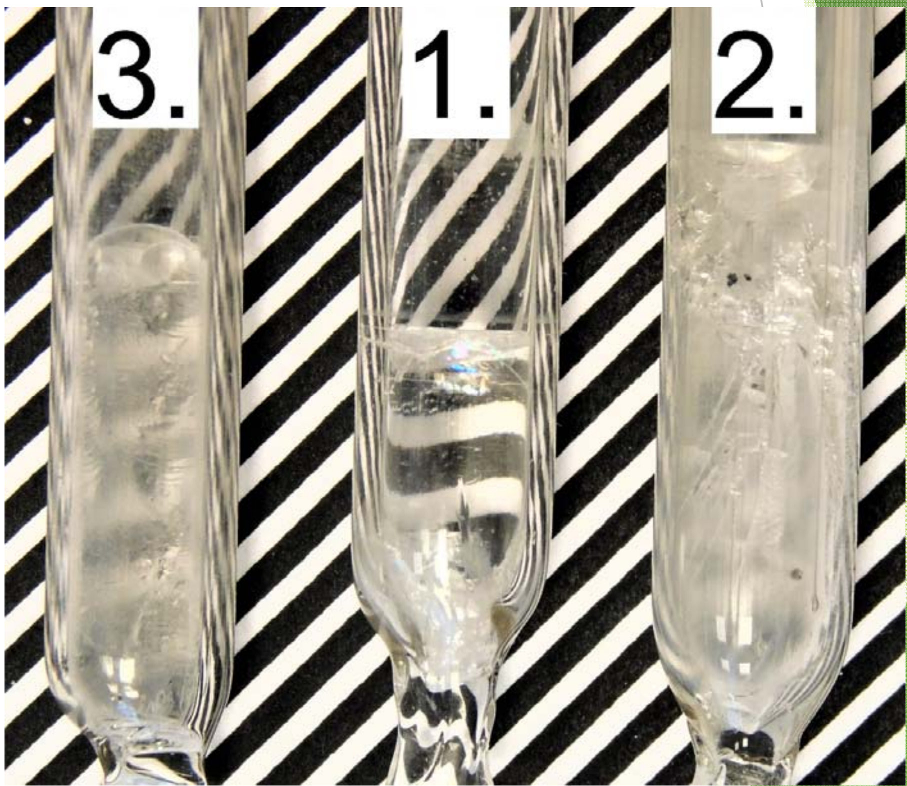
Vertical Bridgman (VB) method

- Unseeded growth
- RF heating with graphite heater
- Silica glass ampules
- Pulling rates 0.6 – 1.2 mm/h
- Diameter: 7 mm
- Length: 20 – 40 mm



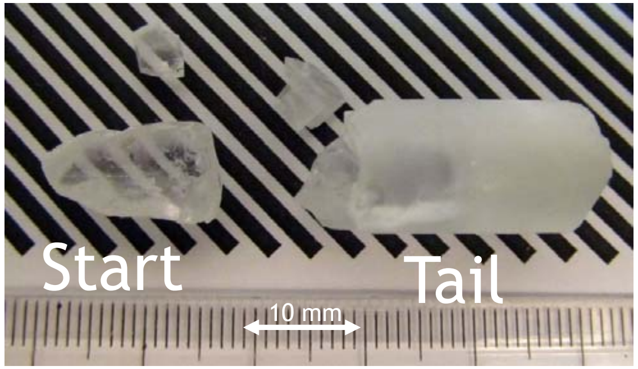
NaCl VB growth

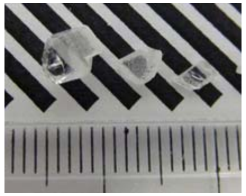
- Cubic crystal structure
- Melting point 801 °C
- 3 samples
- 0.6 and 1.2 mm/h pulling rate
- 1. Nitrogen atmosphere
- 2. Perforated ampule
- 3. Growth under vacuum



As-grown Cs_2HfCl_6 crystal

- vertical Bridgman growth
- charges of Cs_2HfCl_6 from opened system: 2, 3, and 4
- 12 x 40 mm (D x L), colorless
- polycrystalline, homogeneous grains
- tip and bulk – transparent
- tail – nontransparent





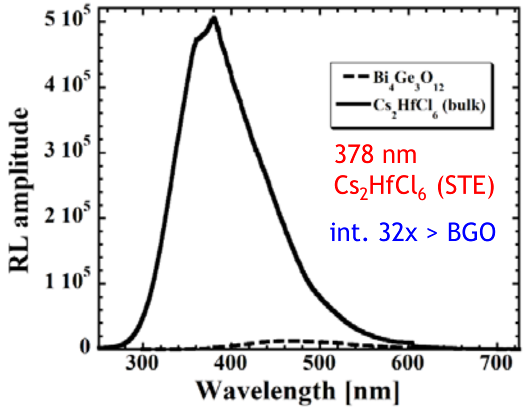
- Cleaved samples
- direction <111>

XRD

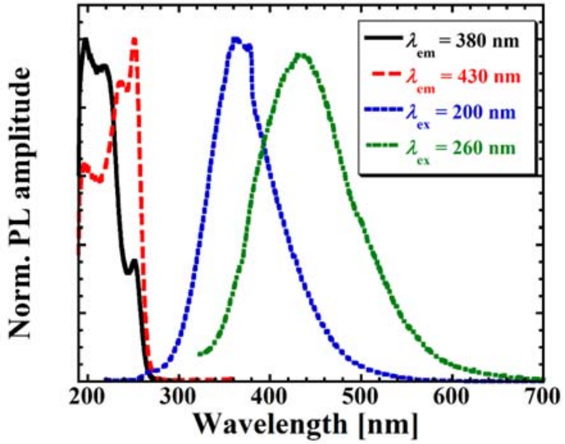
Comp.	Start [mol%]	Tail [mol%]
Cs_2HfCl_6	97	22
CsCl	3	78

Cs_2HfCl_6, single crystal, START

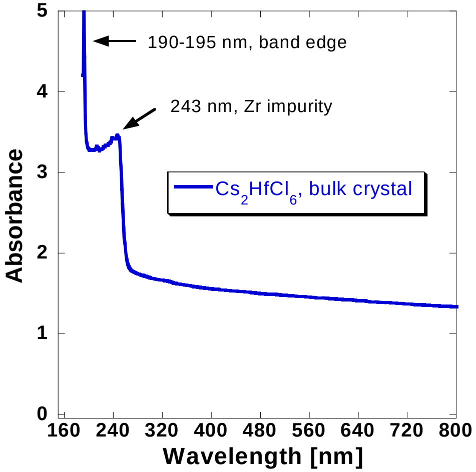
Radioluminescence, RT



PL, PLE spectra, RT

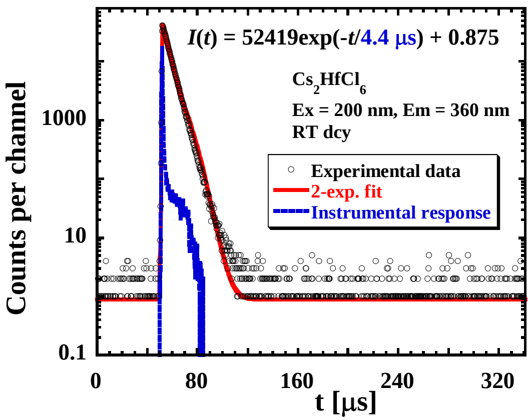


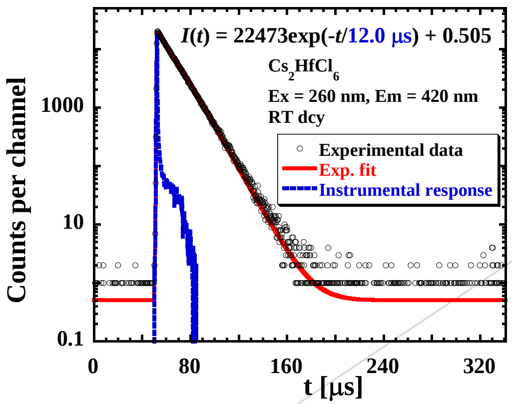
Absorption, RT



- ✓ band edge 195 nm -> band gap 6.3 eV
- ✓ Zr absorption 243 nm

- ✓ **360 nm** - em. of STE in Cs_2HfCl_6, PL decay **4.4 μs**
- ✓ **440 nm** - em. of STE of Zr impurity, PL decay **12.0 μs**





Future plans

- Development of CHC growth by VB method
- Growth of undoped CHC single crystals
- Monovalent ns^2 cations doping (Tl^+, In^+)
- Tetravalent cations doping (Ti^{4+}, Zr^{4+}, Sn^{4+}, Mo^{4+}, W^{4+})
- Anion admixture ($Cs_2HfCl_{6-x}Br_x$ etc.)
- Optical measurements (RL, PL, PLE, LY, DT, RT)
- Stability measurements (hygroscopicity)

Thank you for your attention!