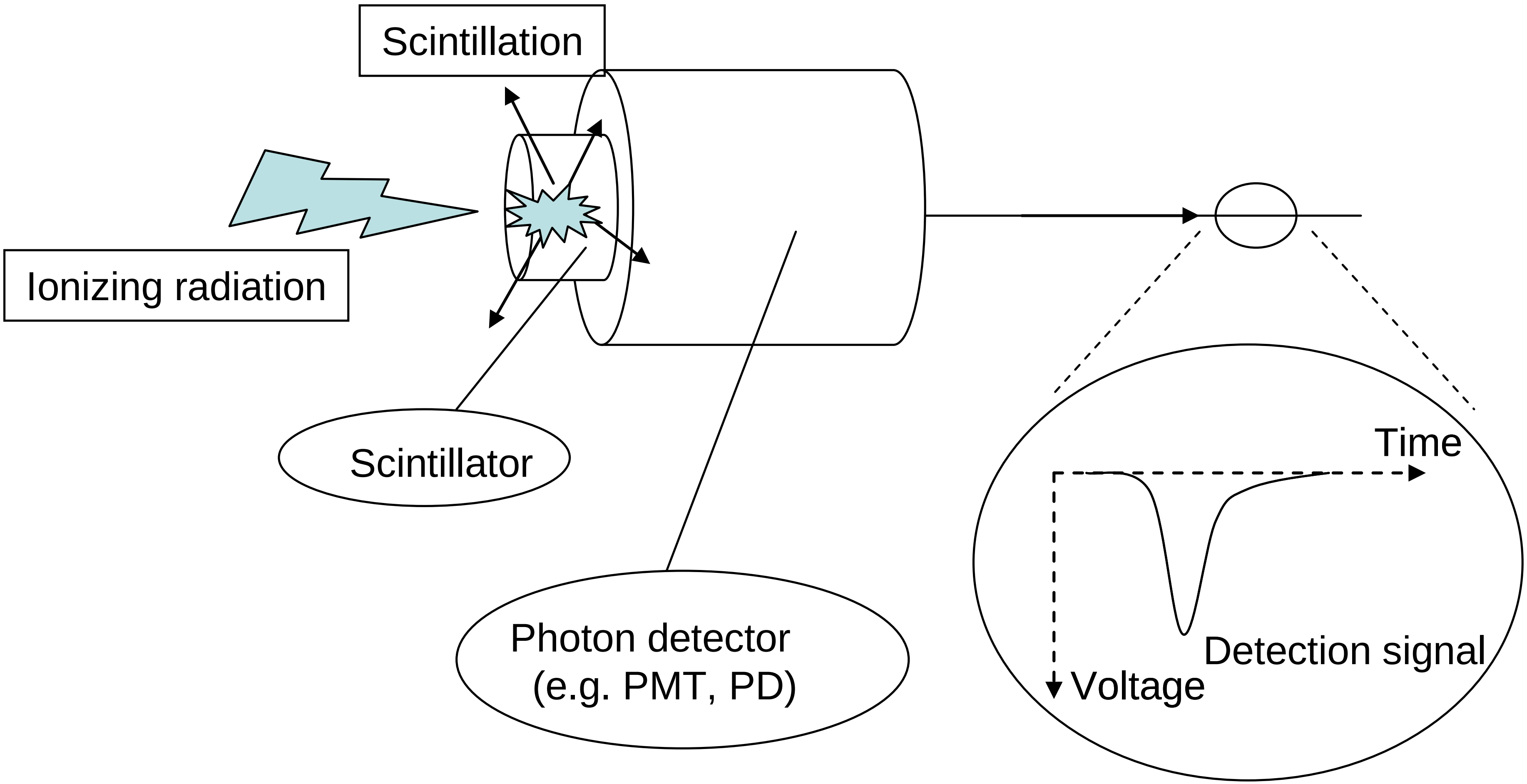
ナノ材料を用いた高速シンチレータ開発

東北大学大学院工学研究科　応用化学専攻
越水　正典

Scintillators and scintillation detectors

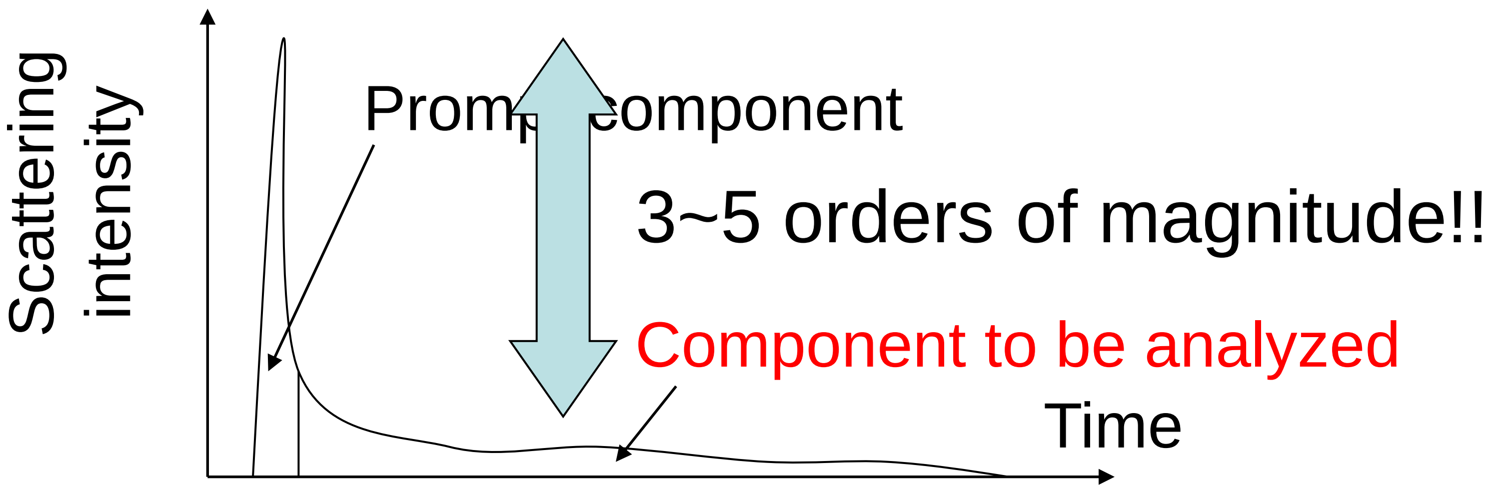


High-energy X-ray detection applications

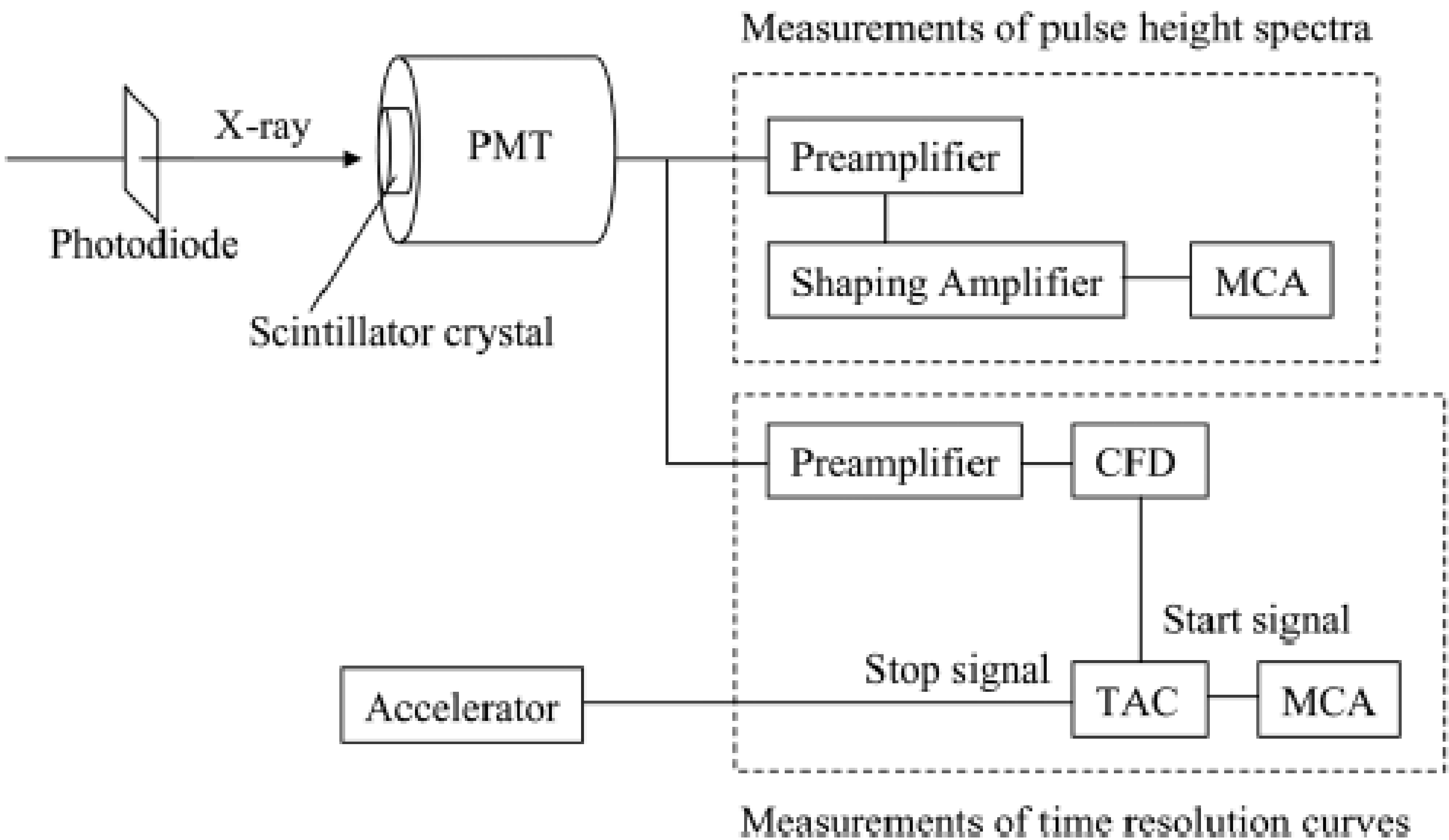
> 20 keV: APD is not suitable because fast response and high detection efficiency cannot simultaneously be achieved.

- High counting rate measurements
  (e.g. diffraction measurements using intense beam)

- Nuclear resonant scattering measurements



Characterization @ PF



Today's contents

1. Fast scintillation mechanism.

2. Fast scintillators using Auger-free luminescence or self-trapped exciton luminescence.

3. Fast scintillators having nanostructures.

Possible fast scintillation mechanism

・Auger-free luminescence (e.g. BaF_2)

・Self-trapped exciton luminescence (e.g. CsI)

（・Charge transfer luminescence in Yb-doped crystals (e.g. Lu_2O_3:Yb)）

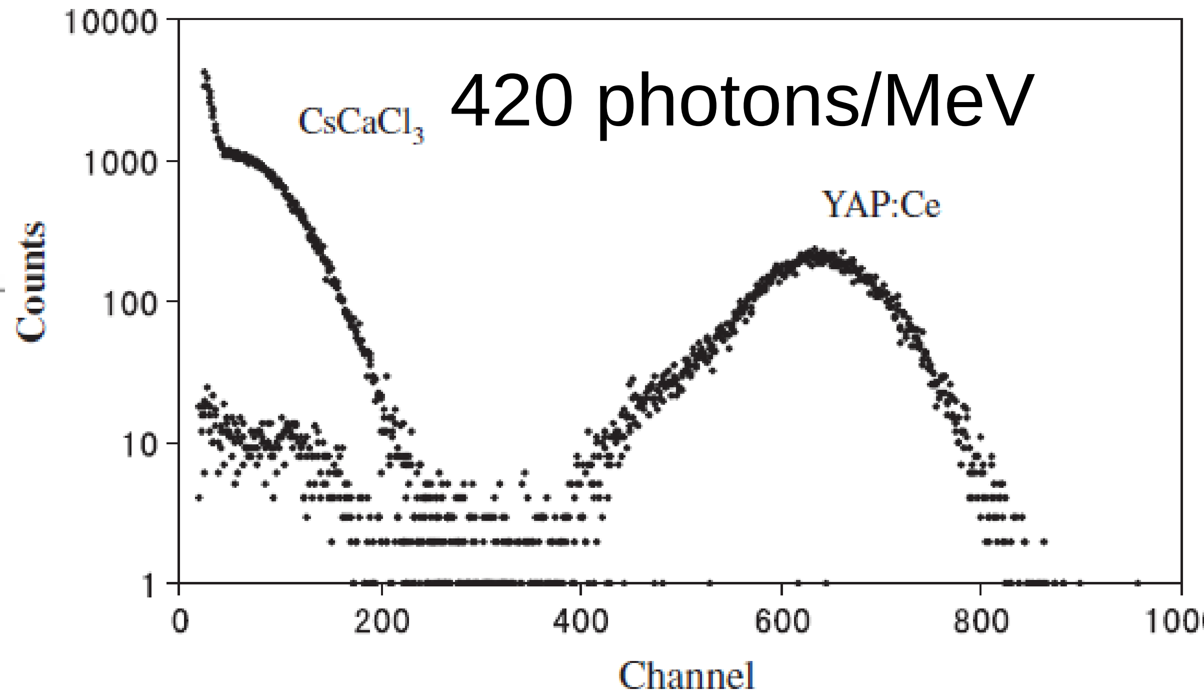
・Luminescence from organic fluorophores (e.g. plastic scintillators)

・Wannier excitons luminescence

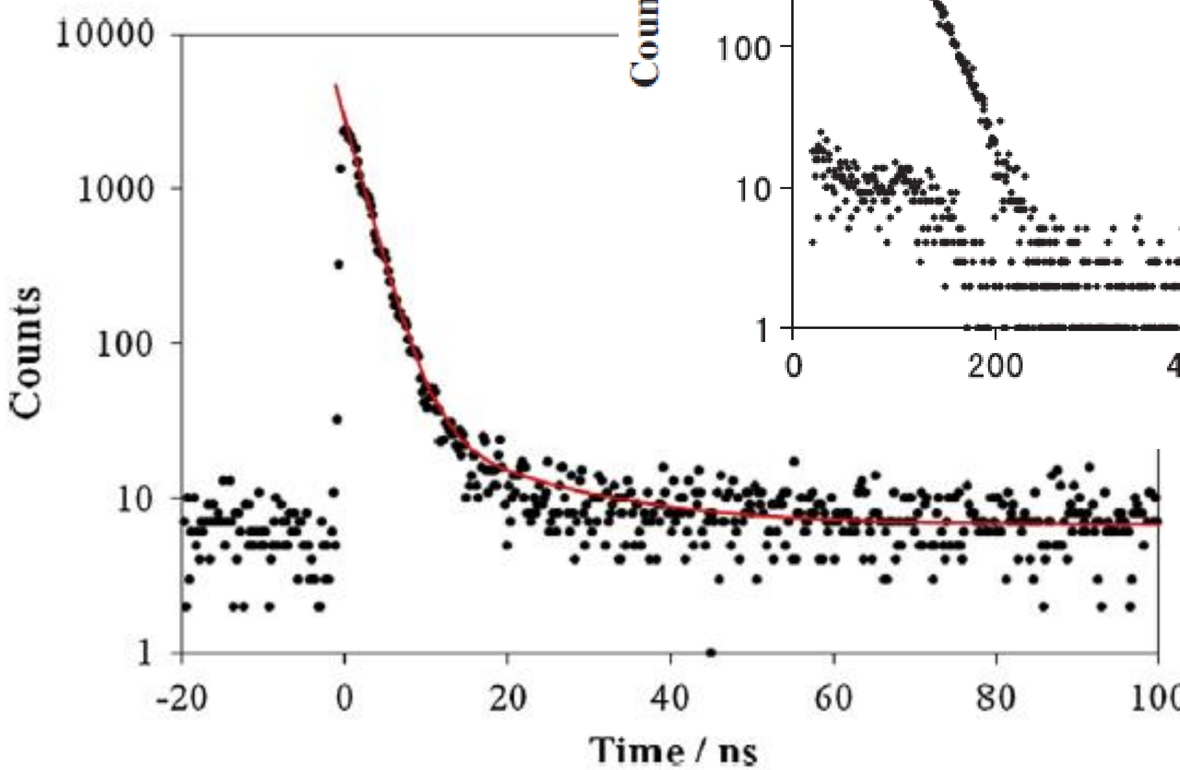
Fast scintillators developed by us (without nanostructures)

Auger-free luminescence ($CsCaCl_3$)

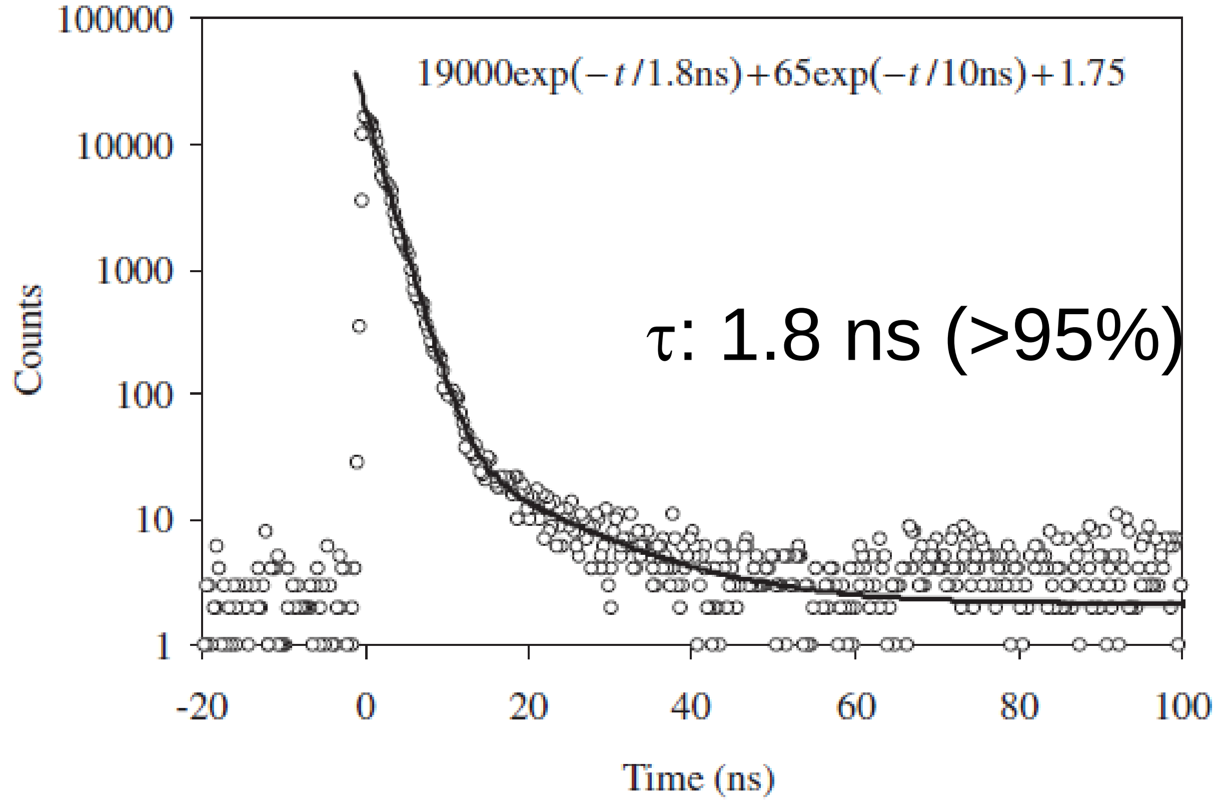
420 photons/MeV



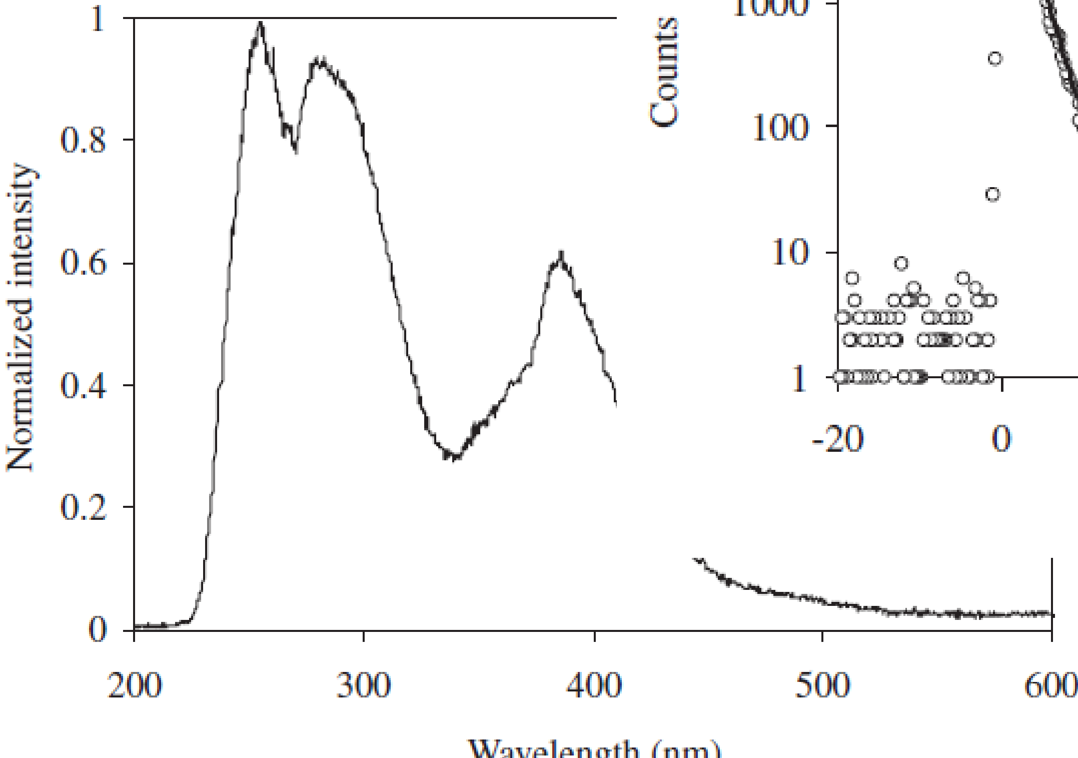
τ: 2.3 ns (58%)



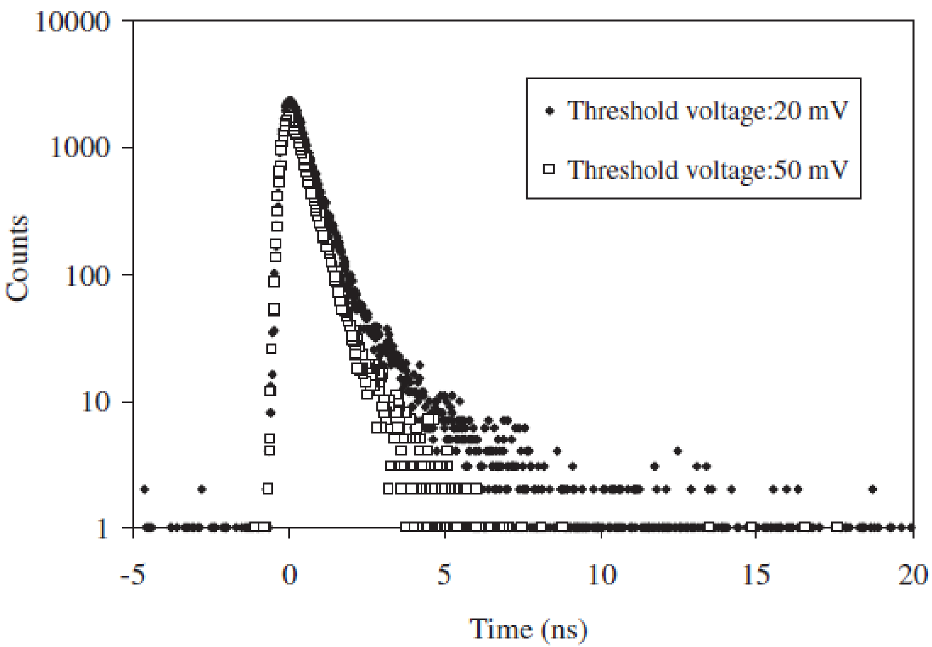
Auger-free luminescence (Cs_2ZnCl_4) - 1

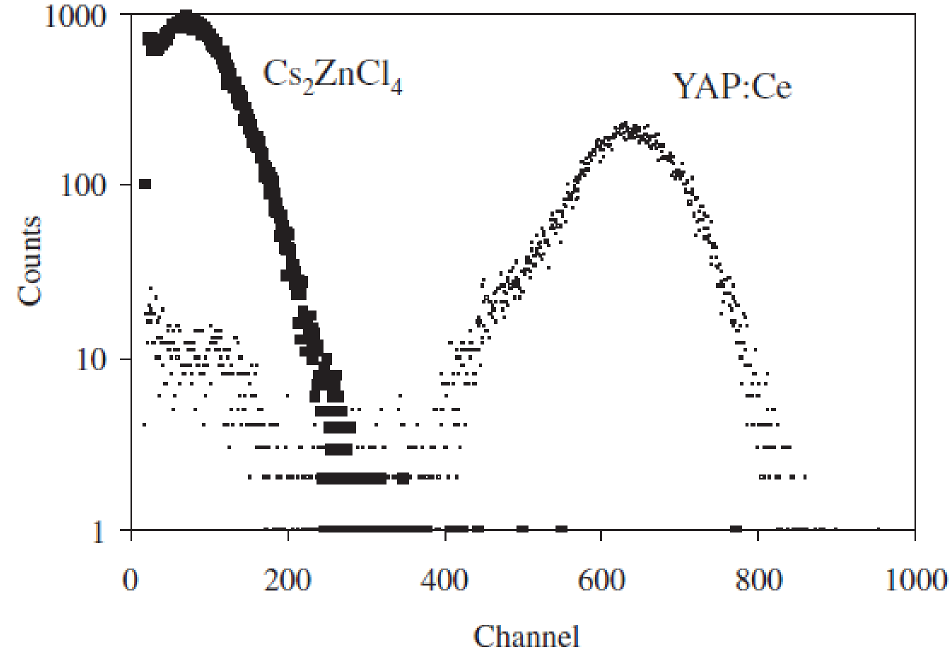


τ: 1.8 ns (>95%)



Auger-free luminescence (Cs_2ZnCl_4) - 2



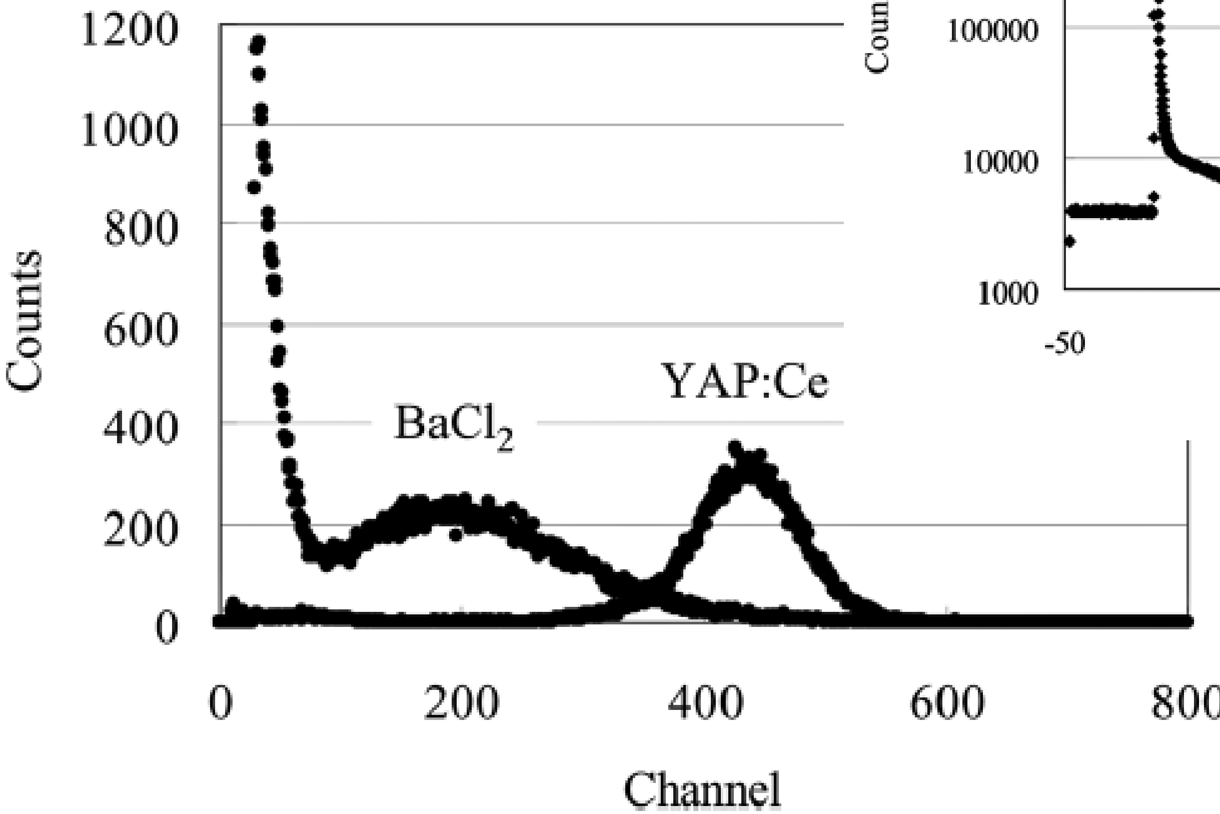


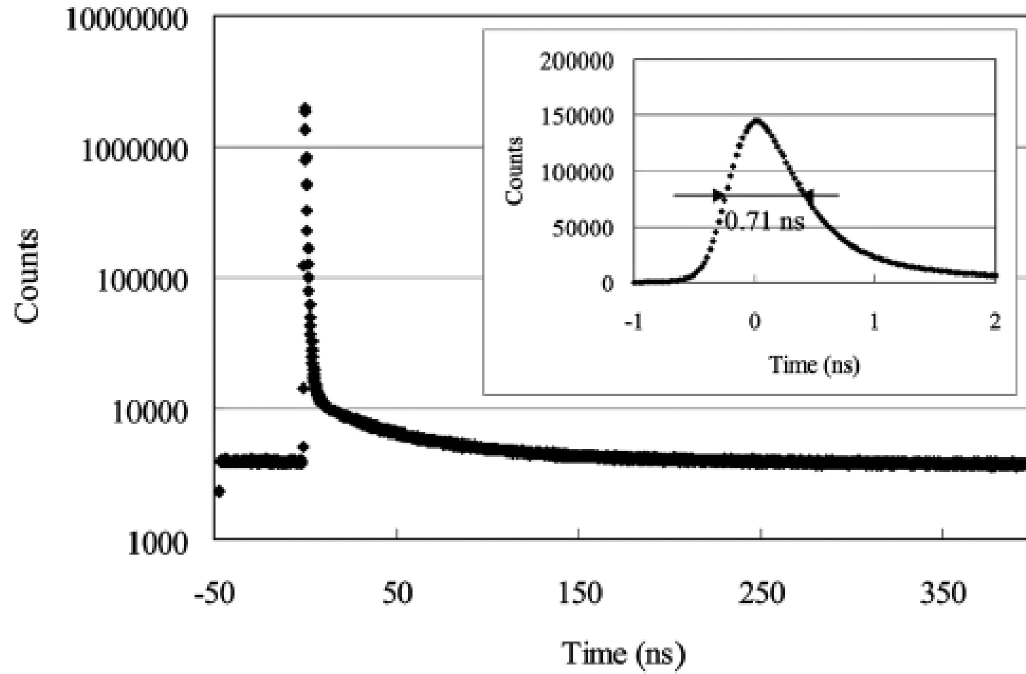
Time resolution: ~0.7 ns

630 photons/MeV @67.4 keV
~1000 photons/MeV @662 keV

Self-trapped exciton luminescence ($BaCl_2$)

950 photons/MeV





τ: 1.5 ns (34%)

Development of fast scintillators having nanostructures

Advantages of Nanostructured for fast scintillation materials

1. Use of quantum confinement effects

Fabrication of low-dimensional quantum confinement structure in self-organized manner.

Wannier exciton luminescence can be utilized at RT.

Fast and efficient scintillation is expected.

2. Incorporation of inorganic nanoparticles into plastic scintillators

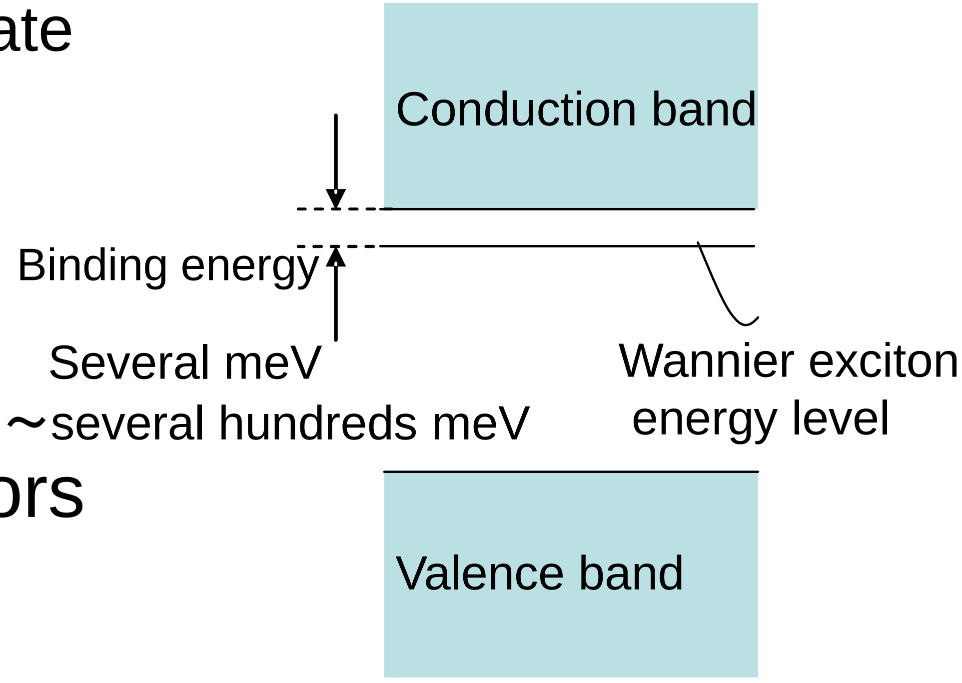
Novel approach to synthesize loaded organic scintillators.

Detection efficiency can be effectively enhanced.

1. Use of quantum confinement effects

Use of Wannier exciton luminescence

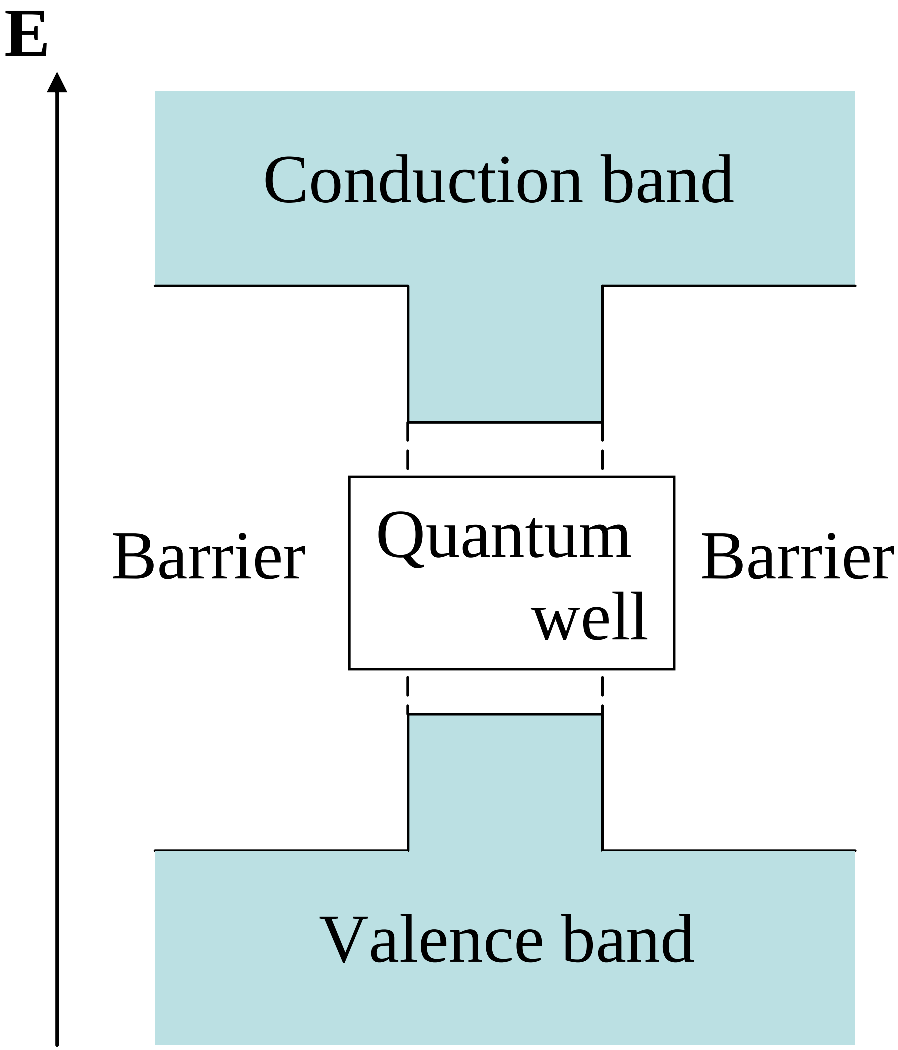
Wannier exciton:
Hydrogen-atom-like bound state
of an electron-hole pair



Emission lifetime < 10 ns
in direct-gap semiconductors

Binding energy > *kT*
-Thermally stable exciton

2D quantum confinement
- quantum well structure



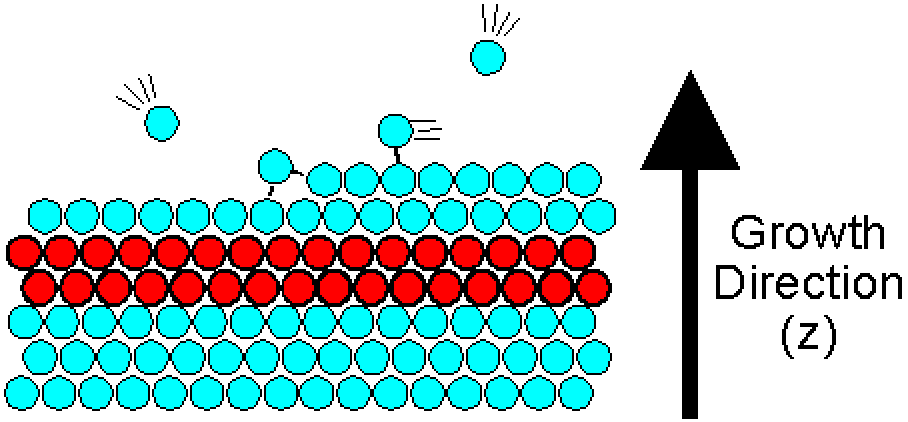
Wannier excitons in 2D structure

Large binding energy
- Exciton is stable at RT

Enhanced oscillator strength
- Fast radiative decay

Requirements and difficulties in scintillator applications

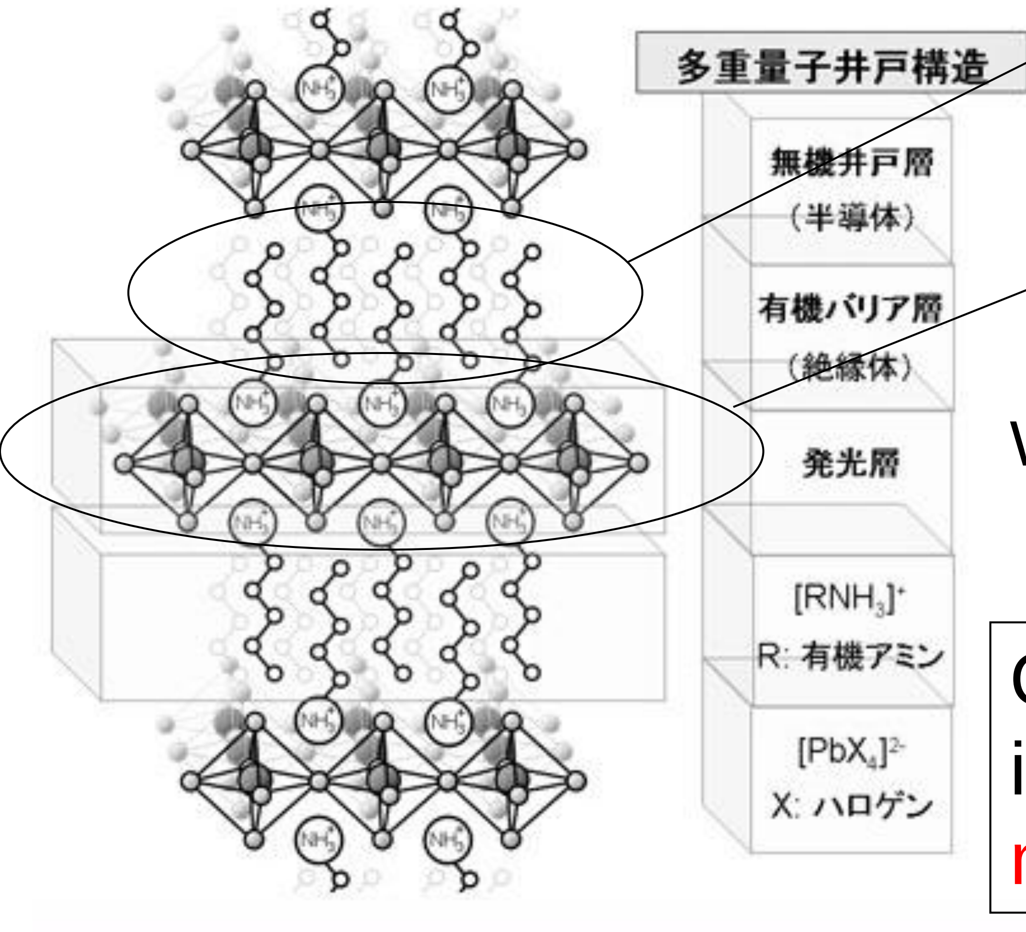
Typical synthesis methods of quantum well structure
- Thin film deposition techniques



Thickness: ~ several microns
- too thin to detect X-ray or γ-ray.

Thin film deposition technique is not suitable.

Organic-inorganic perovskite-type compounds



Organic amine layer
(Barrier layer)

Inorganic PbX_4^{2-} layer
(Well layer)

Wannier excitons are confined.

Quantum well structure
is formed in self-organized
manner.

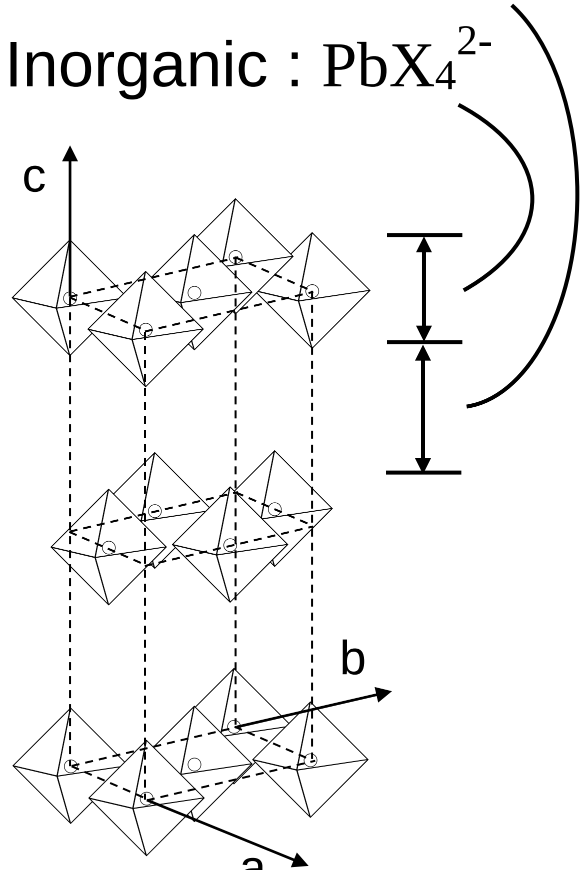
Composition and structure

Chemical formula:

$$(RNH_3)_2(CH_3NH_3)_{m-1}Pb_mX_{3m+1}$$

Organic : RNH_3^+

Inorganic : PbX_4^{2-}



m: Thickness of the inorganic layer
- Influence on exciton confinement.

X: Halogen
- Influence on band-gap energy in inorganic layer.

RNH_2: alkylamine
- Influence on crystal structure. energy transfer process?

General trend of scintillation properties

Thickness of the inorganic layer

Light yield was the highest for m=1.
(Well layer was monomolecular thickness.)

Halogen

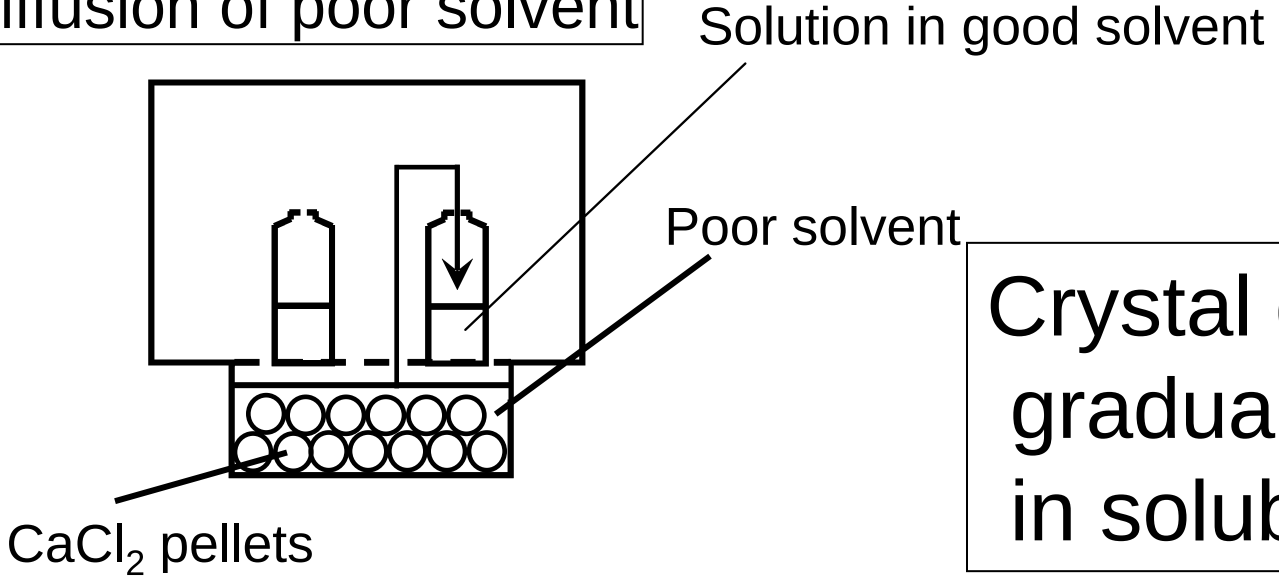
Bromide was best. Iodide was second best.

RNH_2: alkylamine

Much different for different amine molecules.
(Amine molecules: Phe, Ben, C4)

Single crystal growth

Diffusion of poor solvent

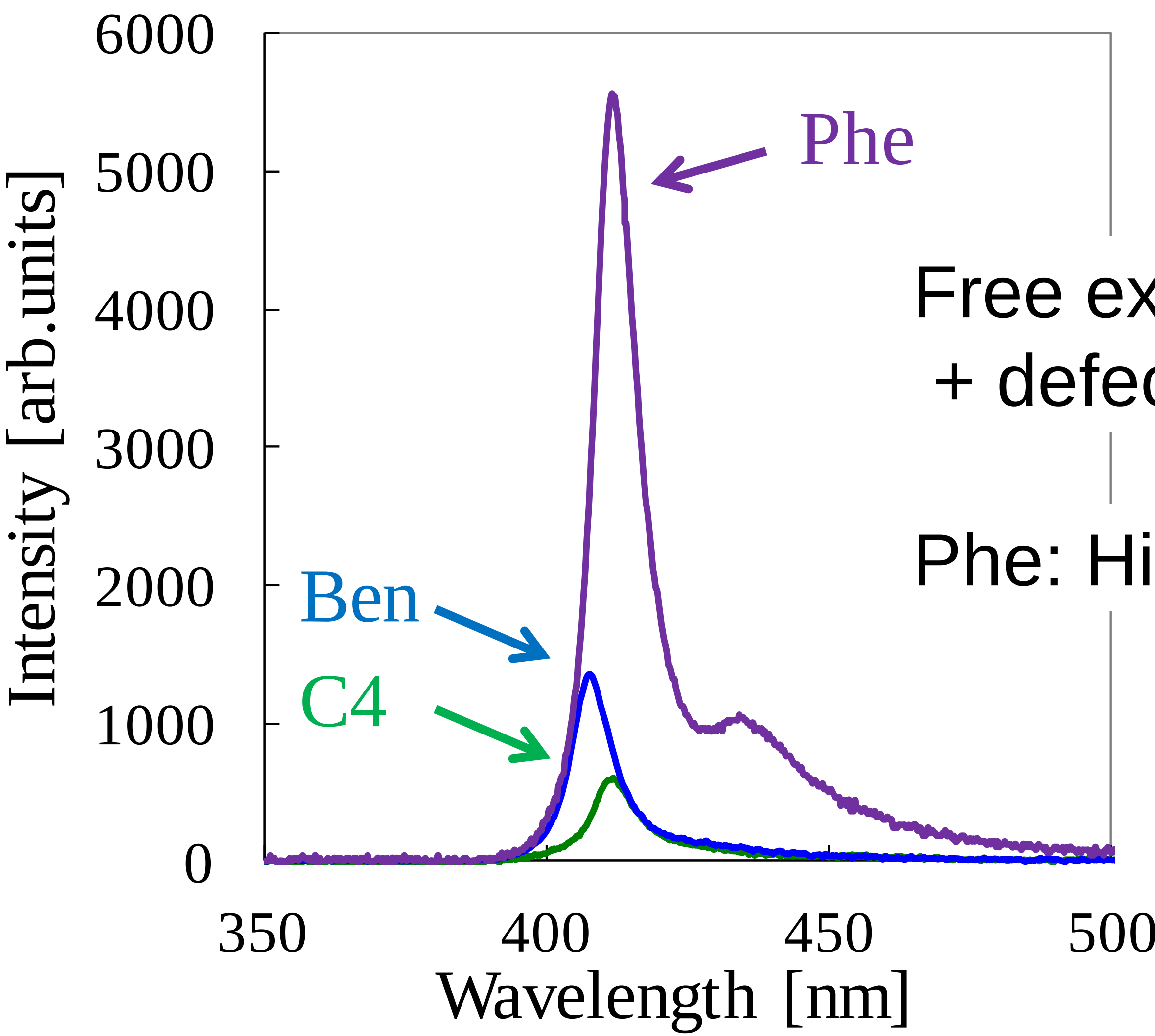


Crystal growth by gradual decrease in solubility.

Max. size: 20×20 mm^2 ×4mmt

(Phe was used in organic layers.)

Luminescence spectra



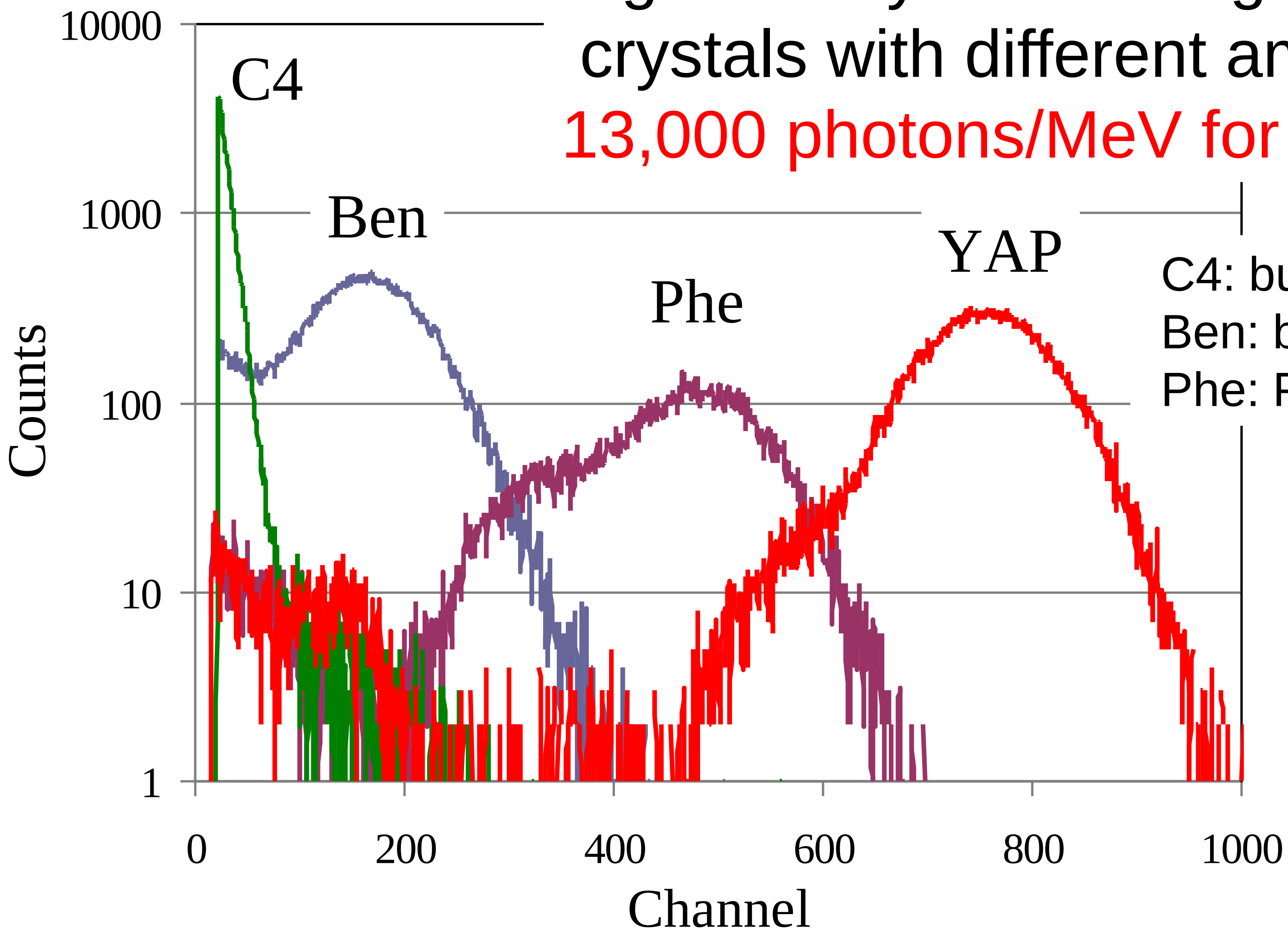
Free exciton line
+ defect band

Phe: Highest intensity

Pulse height spectra for 67.4 keV X-ray

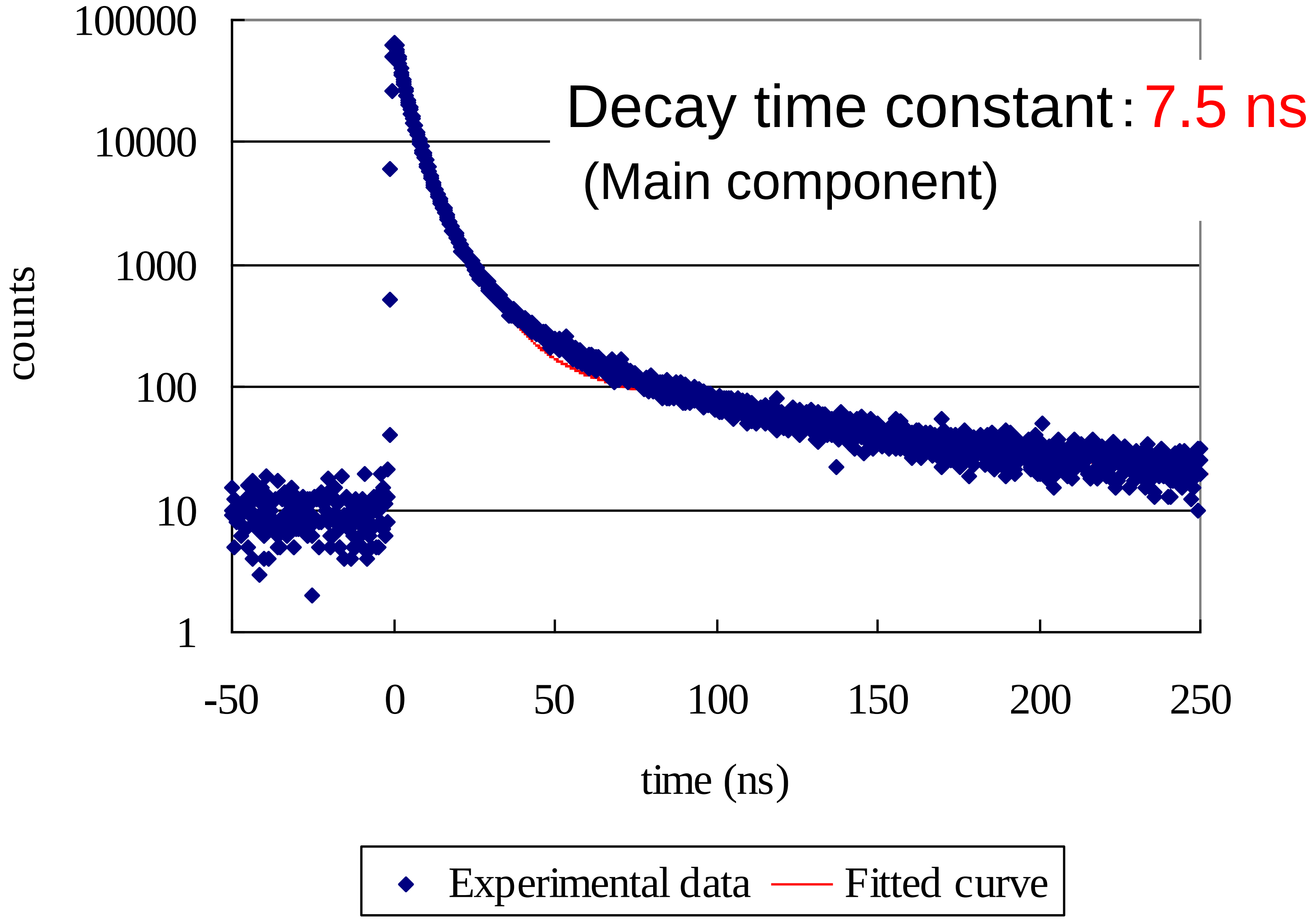
Significantly different light yield for crystals with different amine.

13,000 photons/MeV for Phe crystal.

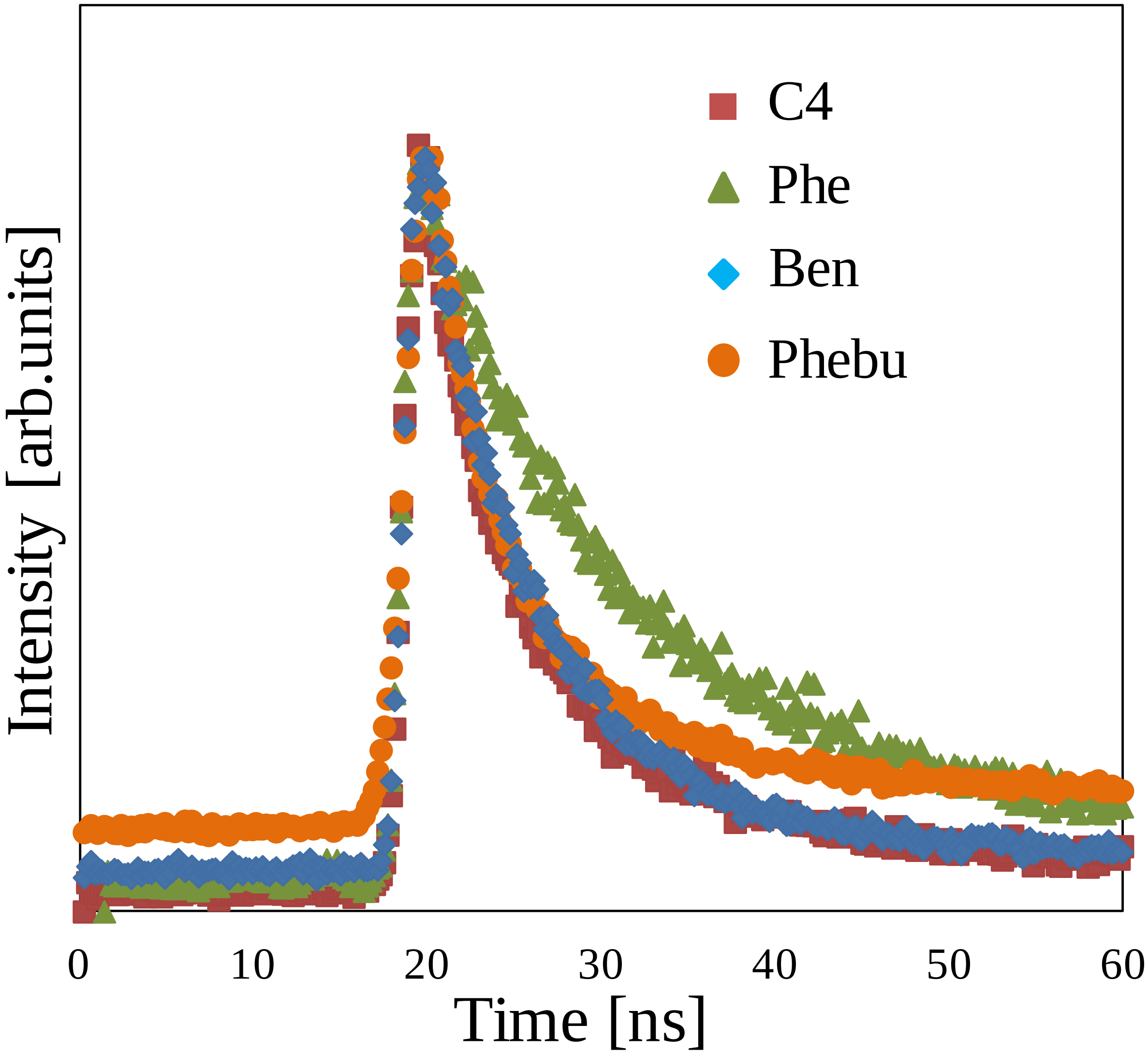


C4: butylamine,
Ben: benzylamine,
Phe: Phenetylamine

Scintillation decay (Phe)

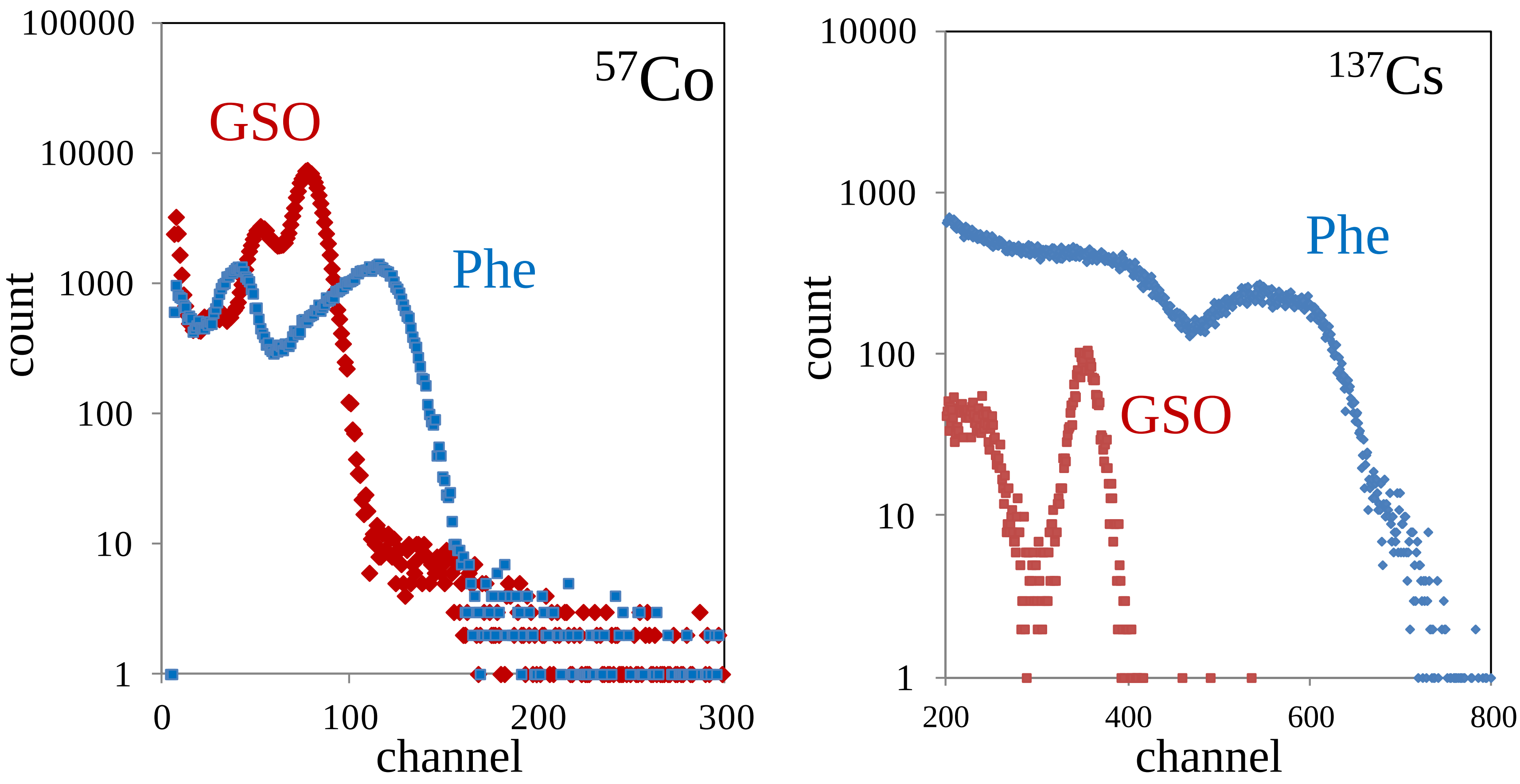


Scintillation decay



τ < 10 ns

Gamma-ray detection



Light yield of Phe was 1.5 times of GSO.
→ 15,000 photons/MeV

Scintillation properties of Phe

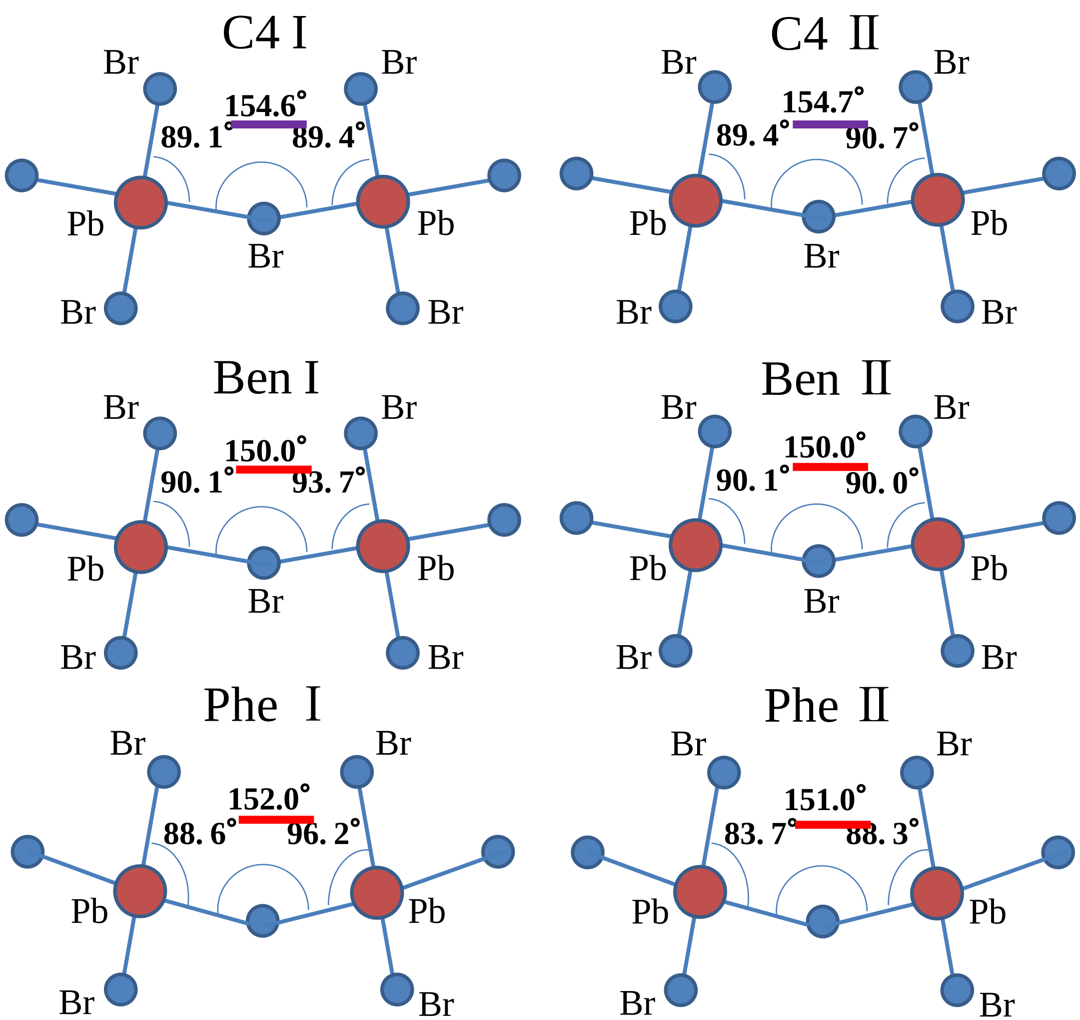
Light yield: 12,000 photons/MeV (67.4 keV)
15,000 photons/MeV (>100 keV)

Comparable to rare-earth-doped crystals

Scintillation decay time constant: 10 ns

Much faster than rare-earth-doped crystals

Crystal structure



Pb–Br–Pb angle

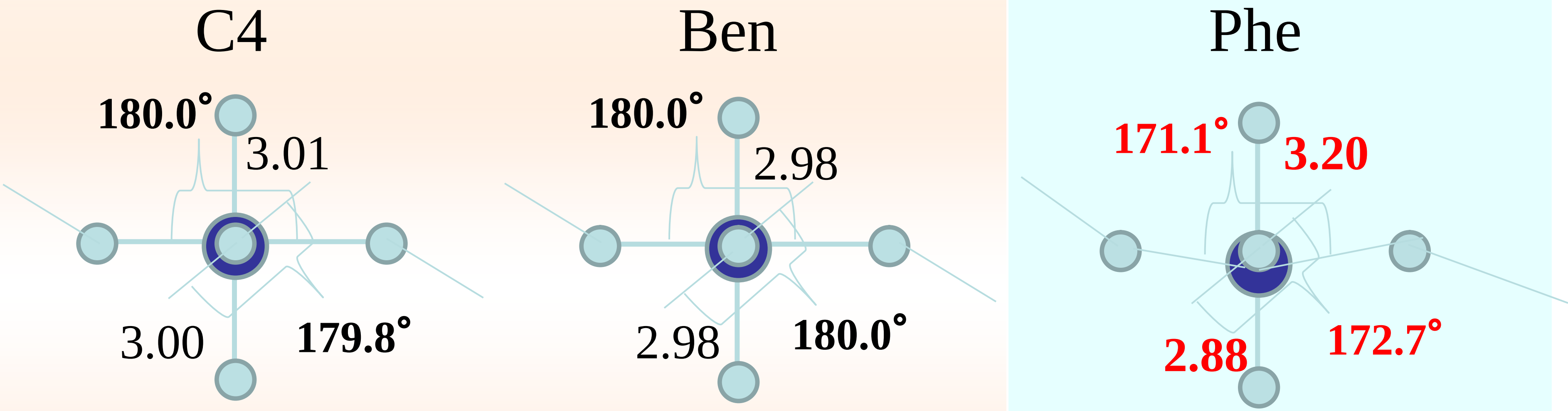
C4 : 155°

Ben : 150°

Phe : 151, 152°

Larger distortion between Octahedra in Phe and Ben.

Crystal structure



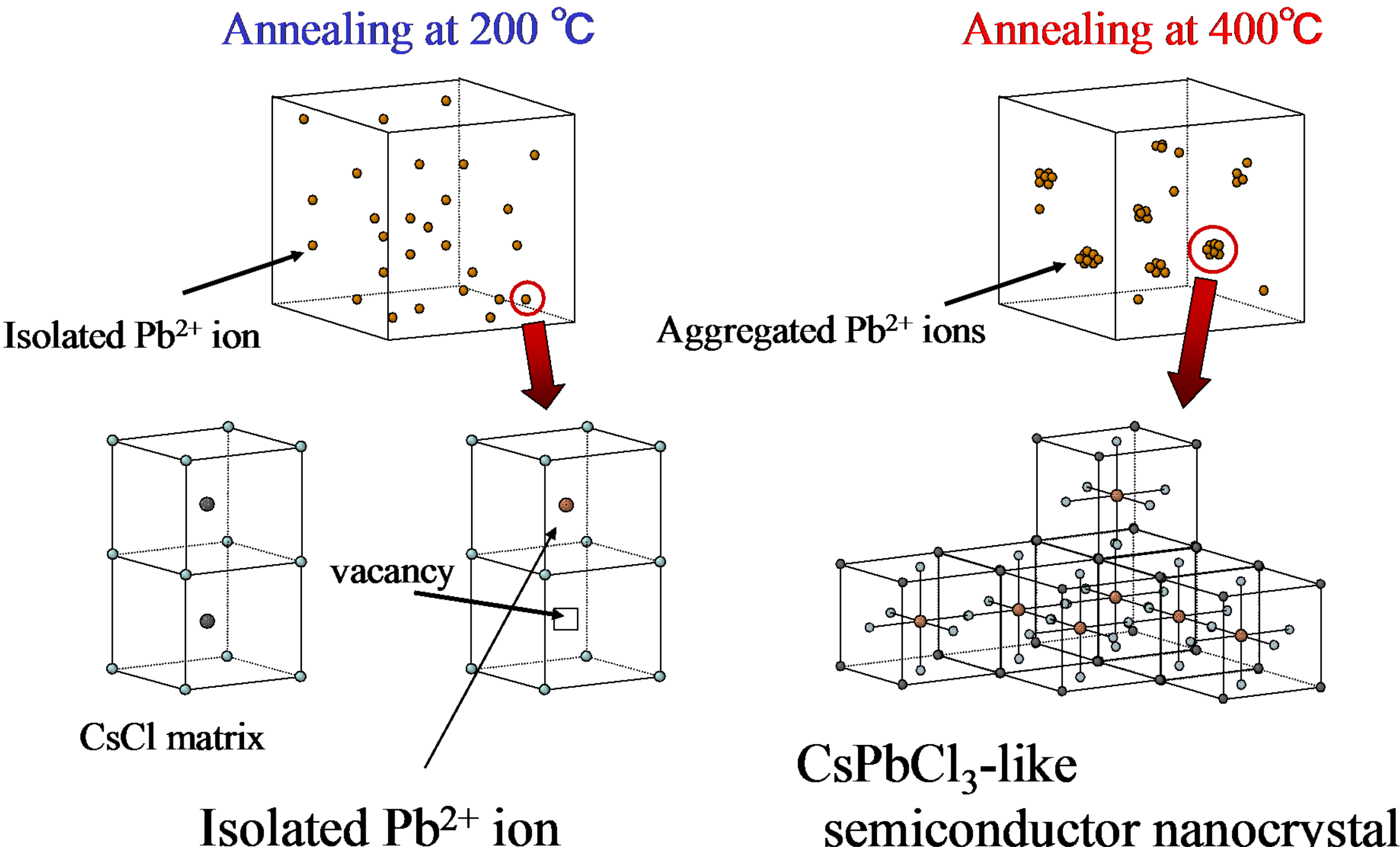
Almost no distortion in octahedra.

Pb ion is located off the octahedra center.

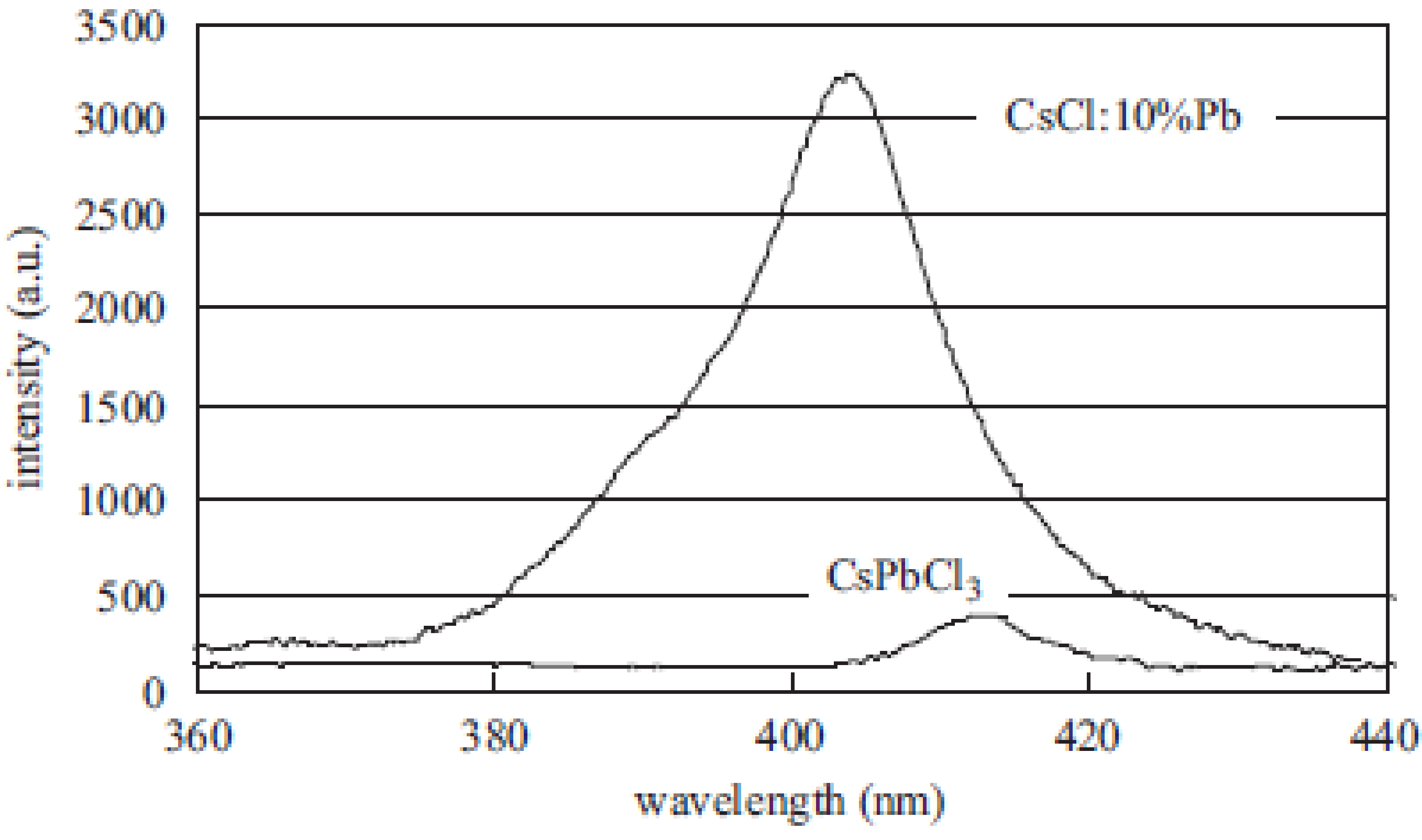
Significant distortion inside octahedra in Phe.

Use of luminescence from semiconductor nanocrystals

$CsPbCl_3$ nanocrystals in CsCl:Pb single crystals



Luminescence spectra



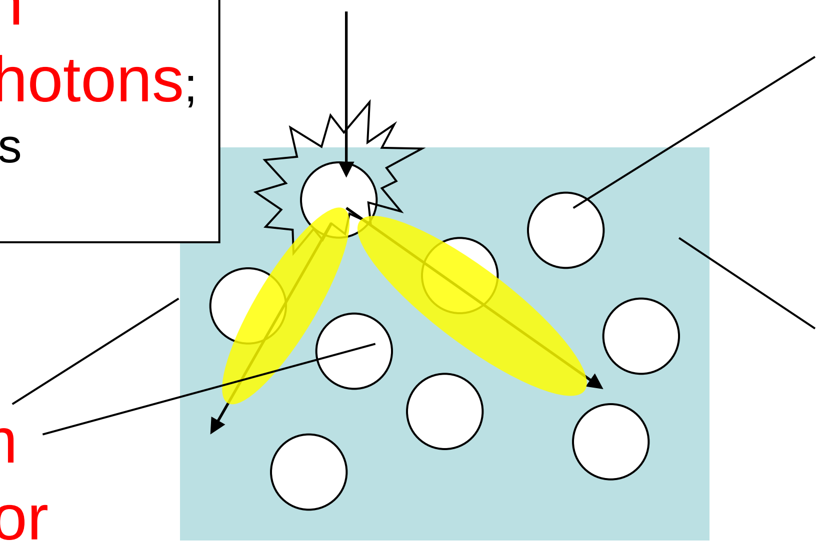
Scintillation properties in CsCl:Pb single crystals

CsCl:10%Pb (Pb aggregated)	CsCl:10%Pb (Pb isolated)
0.42 ns (27%)	
2.0 ns (62%)	1.7 ns (86%)
18.3 ns (11%)	17.0 ns (14%)

Scintillation yield: < 500 photons/MeV

2. Incorporation of inorganic nanoparticles into plastic scintillators

Expected scintillation mechanism



High-Z inorganic nanoparticles are incorporated in order to obtain high interaction efficiency with high-energy photons.

Why nanoparticles?

Mie scattering
- Scattering of light at the scatterer larger than the wavelength.

The wavelength of scintillation: several hundreds nm

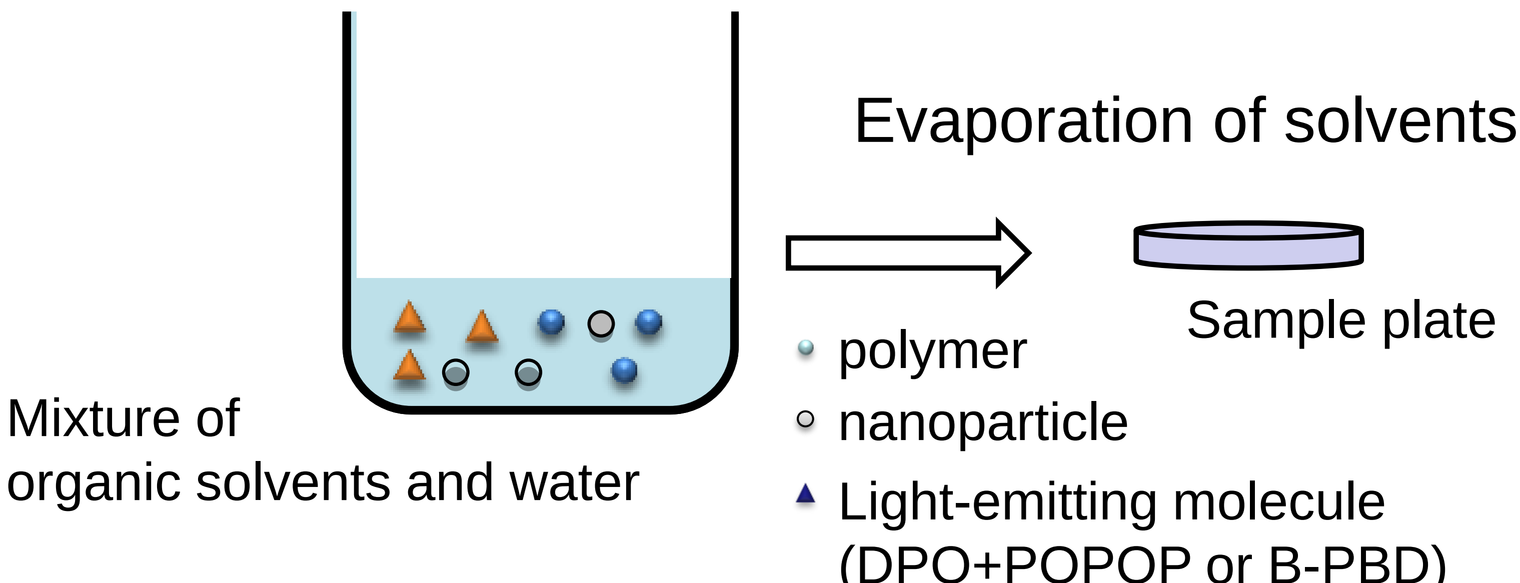
The nanoparticle size should be less than several hundreds nm in order to achieve transparency for scintillation light.

Preparation method 1
- two step synthesis

Preparation of nanoparticles

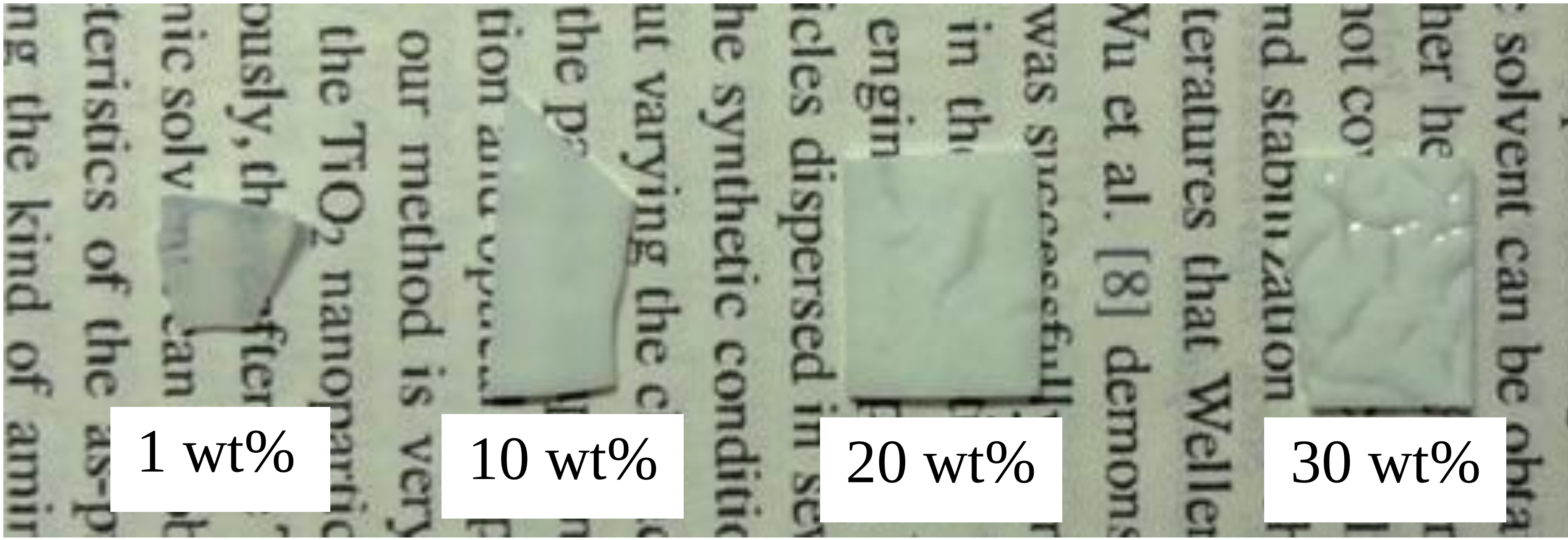
- Preparation by solution methods.
- Commercially available nanoparticles can also be used.

Preparation of organic-inorganic hybrid materials

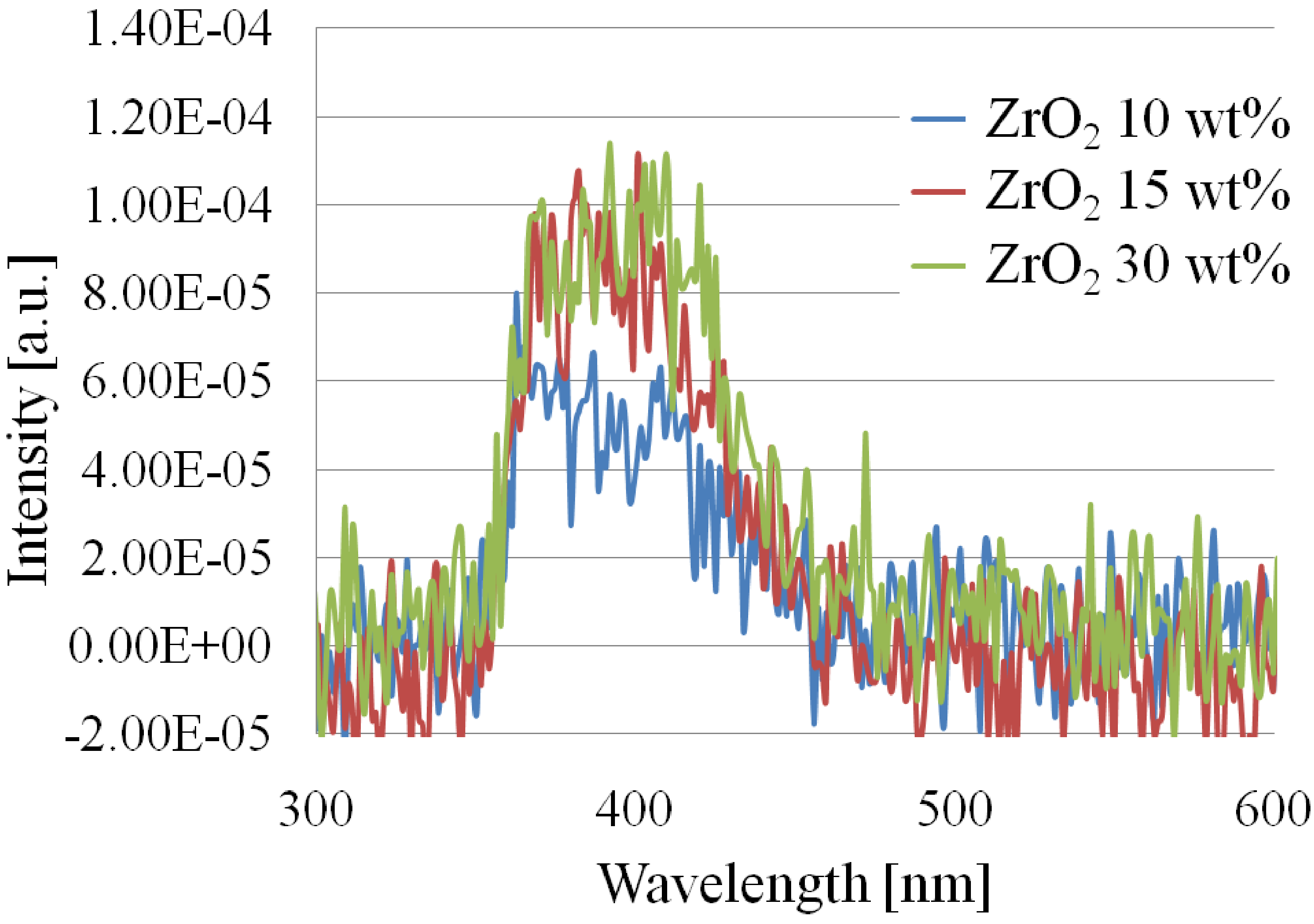


Plastic scintillators loaded with commercial ZrO_2 nanoparticles

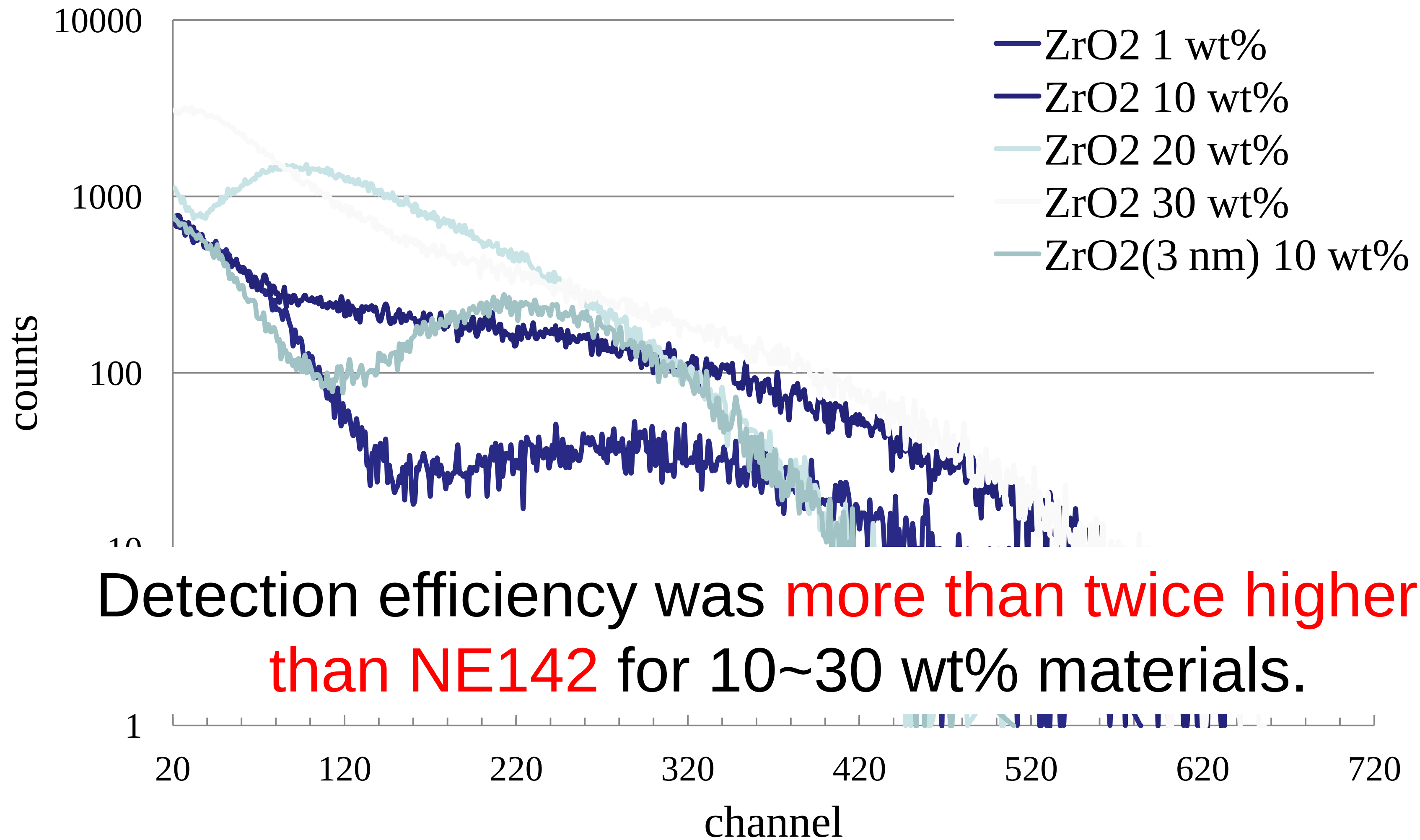
Photographs



Scintillation spectra



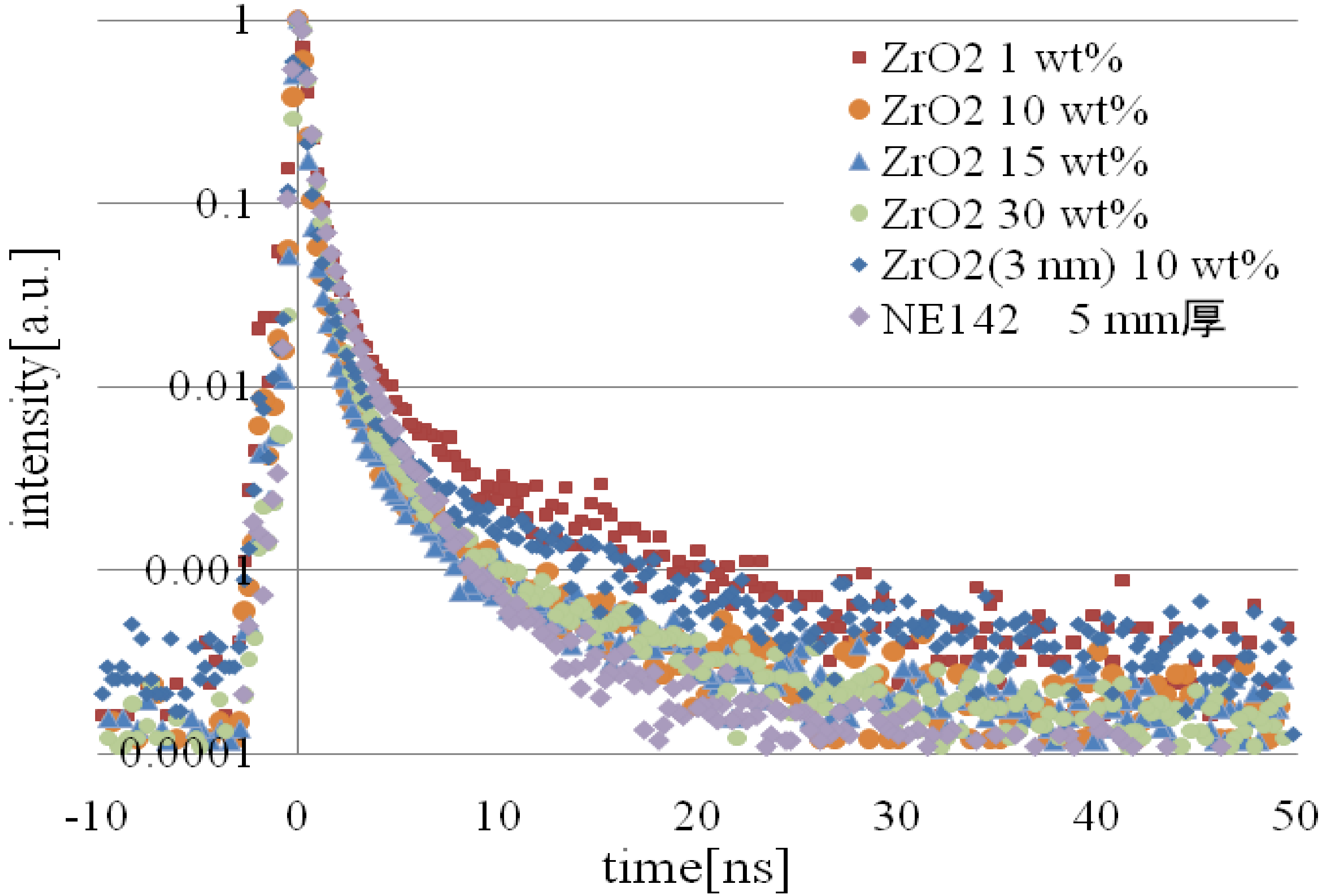
Pulse height spectra of 67.4 keV X-ray



Detection efficiency was more than twice higher than NE142 for 10~30 wt% materials.

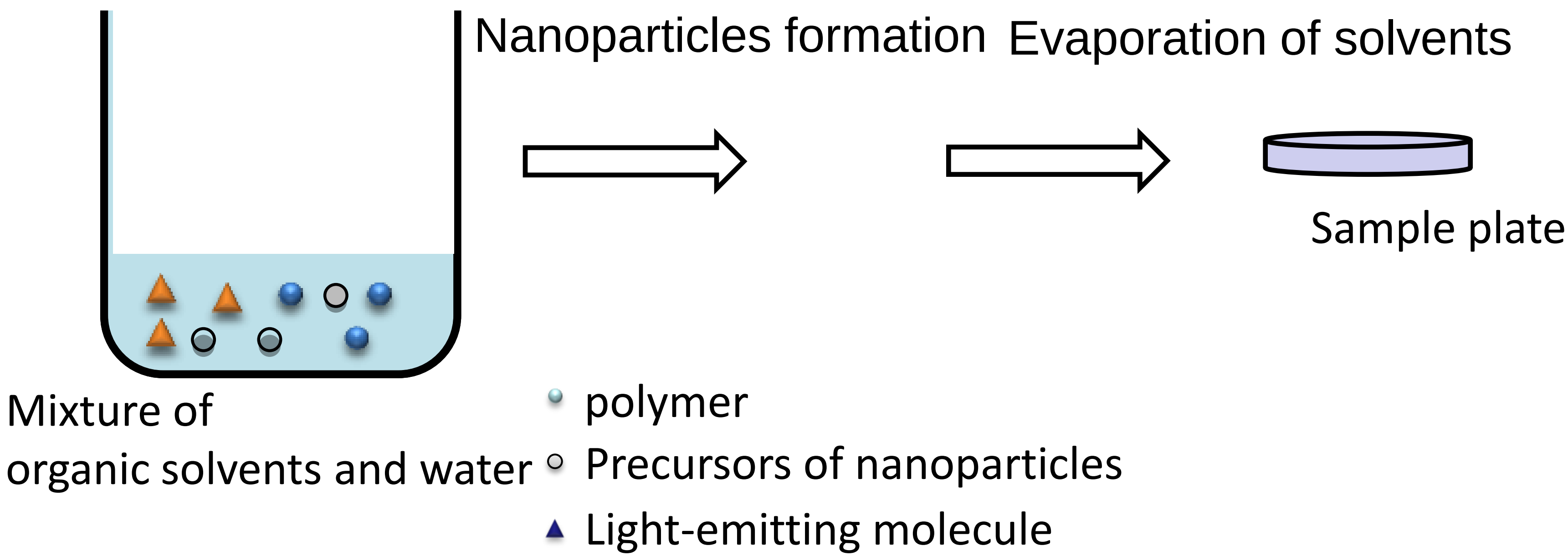
Clear peak was observed for plastic scintillator incorporated with nanoparticles of 3 nm size.

Time resolution curve



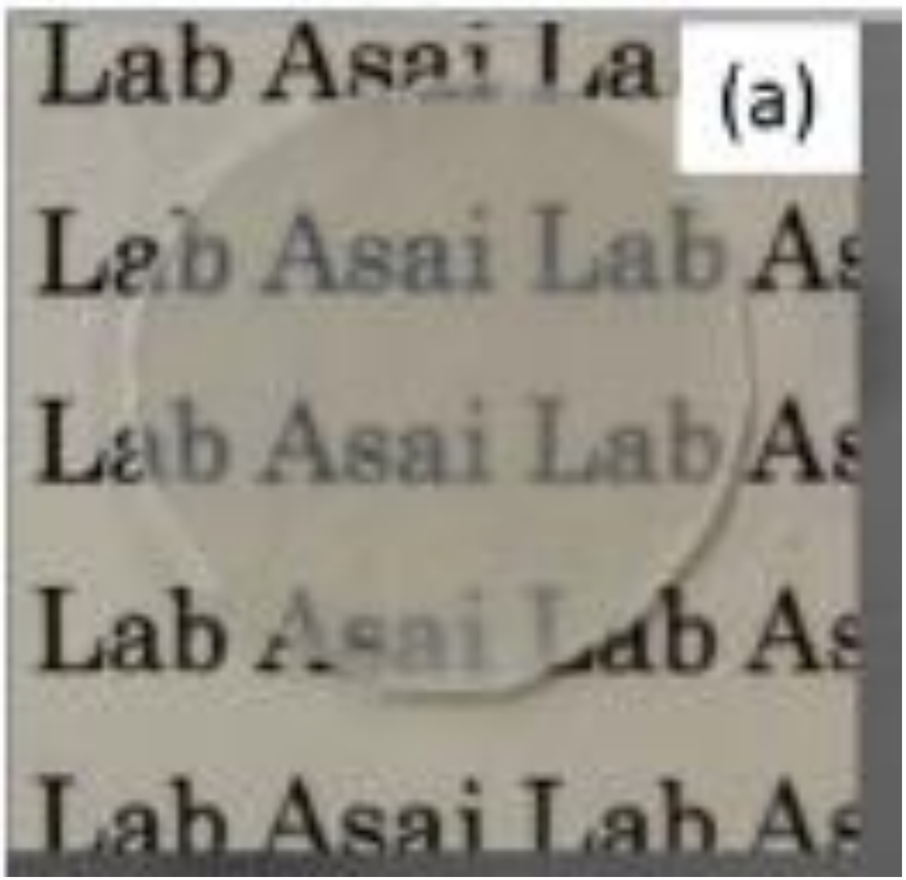
Plastic scintillators loaded with $HfSiO_2$ nanoparticles by one-pot method

Preparation method 2
- one step synthesis

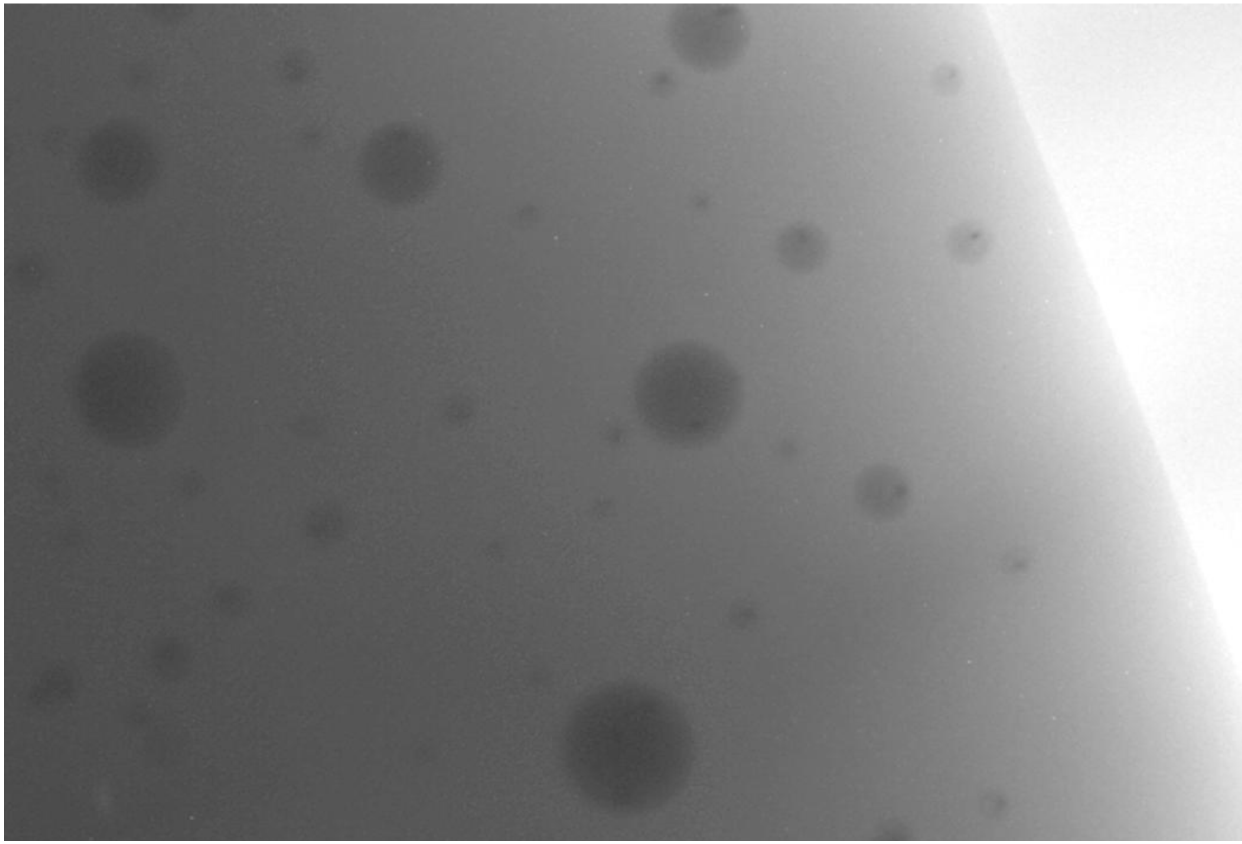


Hf-Si oxide nanoparticles were synthesized
in polymers by one step synthesis.

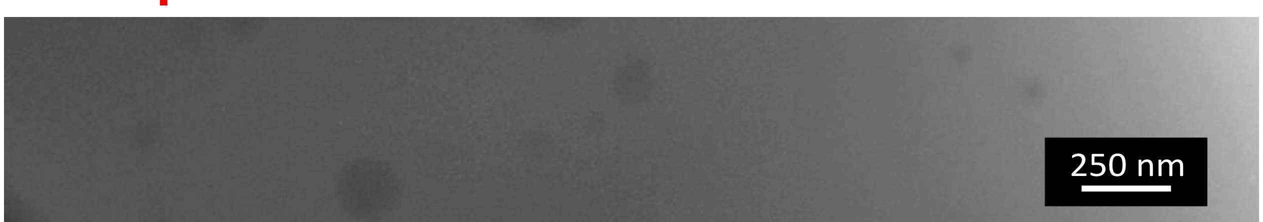
Photograph


(a)
Lab Asai La
Lab Asai Lab As
Lab Asai Lab As
Lab Asai Lab As
Lab Asai Lab As

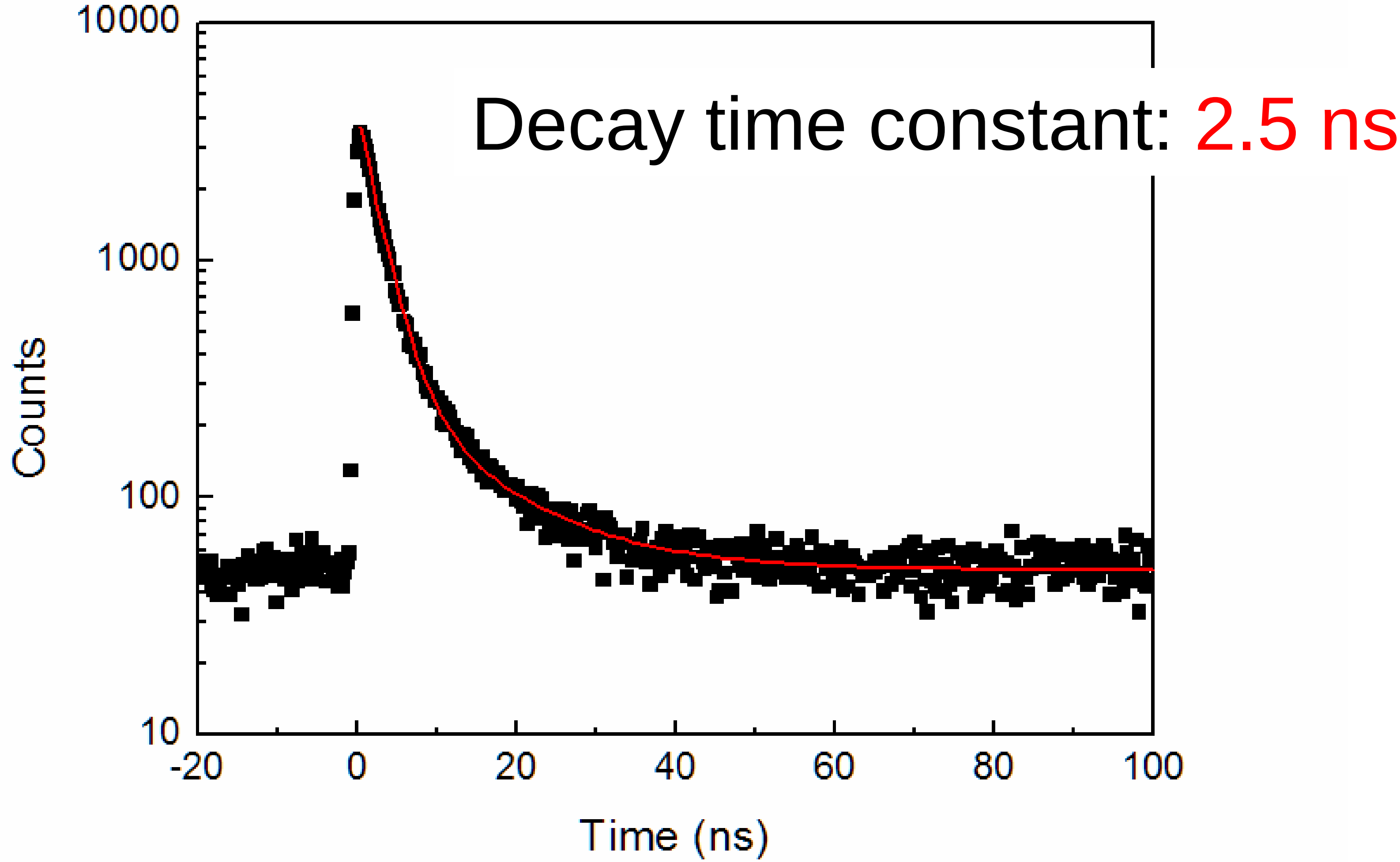
TEM image



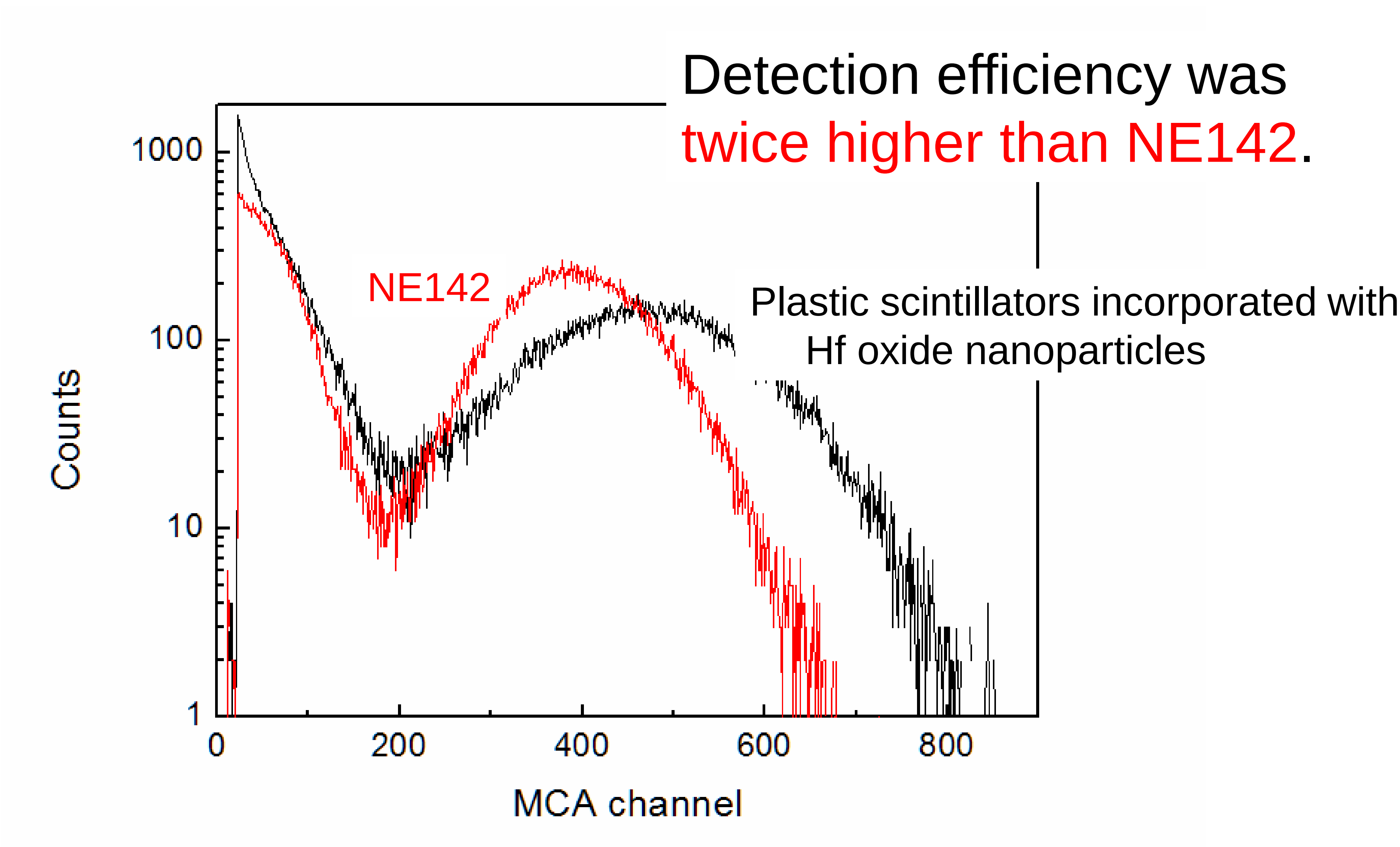
Nanoparticle size: less than 300 nm



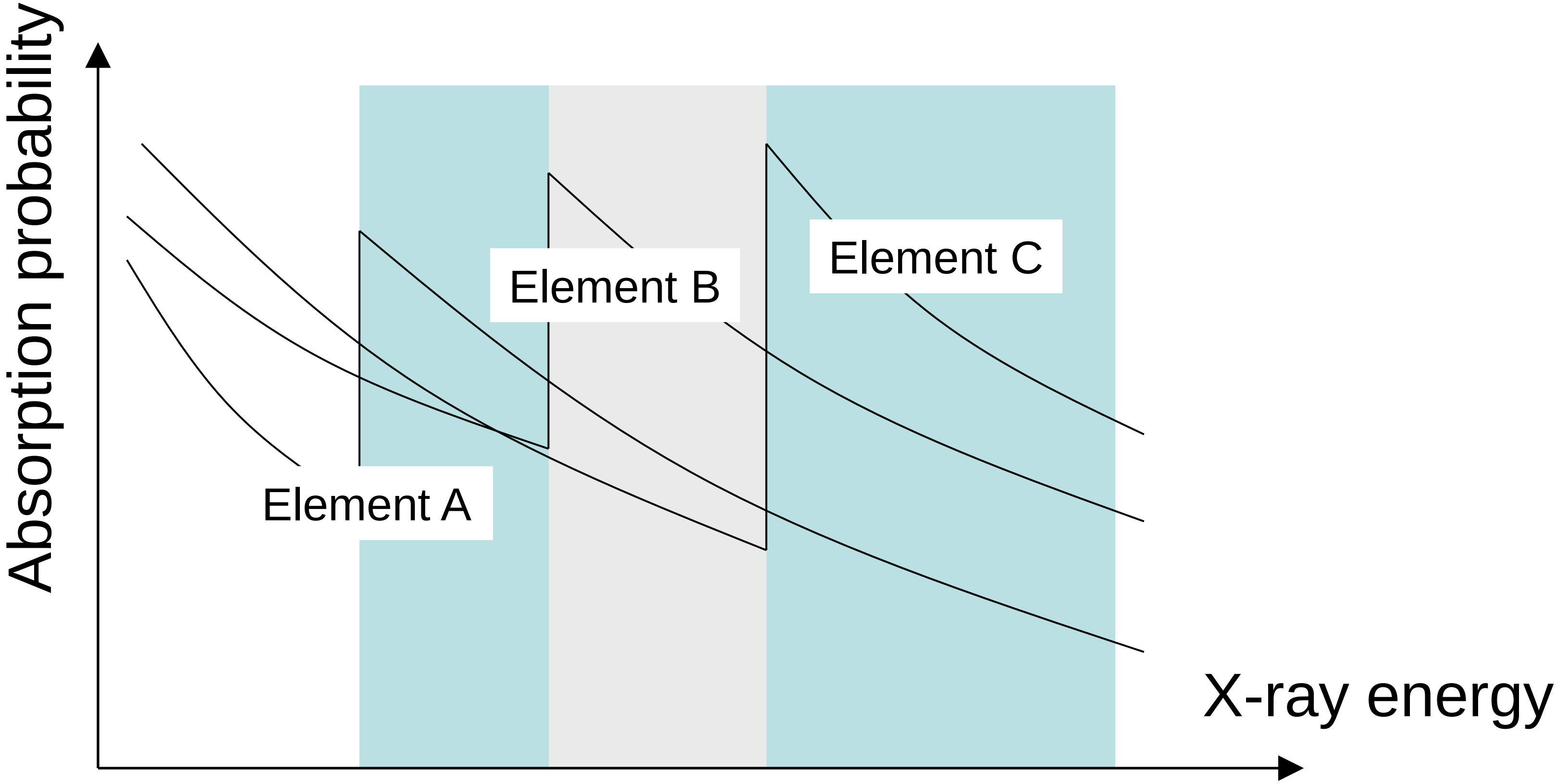
Decay kinetics



Pulse height spectra of 67.4 keV X-ray

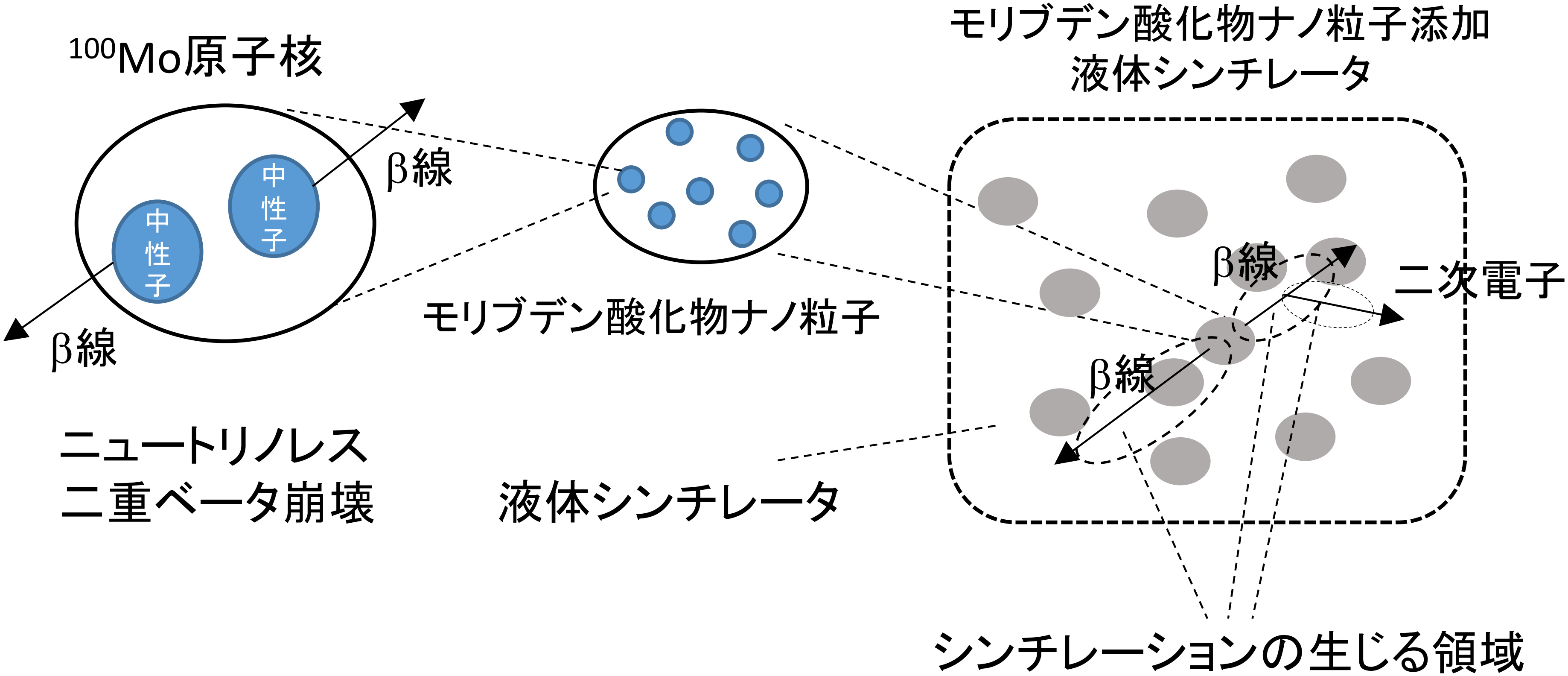


Plastic scintillators incorporated with nanoparticles – Future prospect



Incorporated element can be chosen according to the X-ray energy to be detected.

Further prospects for organic scintillators loaded with nanoparticles



Summary

1. Use of quantum confinement effects

Efficient scintillation due to
quantum confined Wannier exciton was achieved.
Scintillation process should be revealed.

2. Incorporation of inorganic nanoparticles
into plastic scintillators

Enhancement in detection efficiency
has successfully been demonstrated.

Nanoparticle size and distribution is the key
to improve scintillation properties.

Future prospects

1. Use of quantum confinement effects

・Control over crystal structure → Higher light yield
・Growth of larger crystals.
・Search for crystals having semiconductor precipitates.

2. Incorporation of inorganic nanoparticles into plastic scintillators

・Synthesis of smaller nanocrystals with good dispersion in plastic scintillators.
・Synthesis of nanocrystals exhibiting fast scintillation.

Thank you for your kind attention.