Development of new heavy and efficient scintillators for medical imaging and radiation detection

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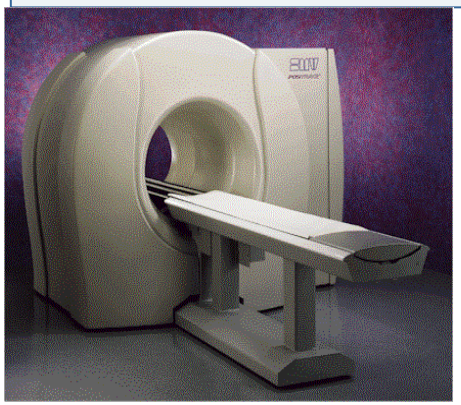
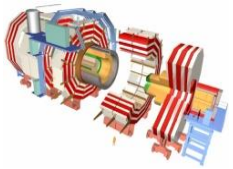
3rd Jagiellonian Symposium on Fundamental and Applie
Subatomic Physics, Krakow, Poland, June 24-28, 2019

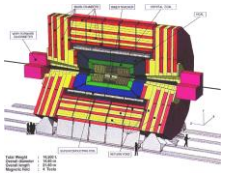
Application of Scintillators

Medical application



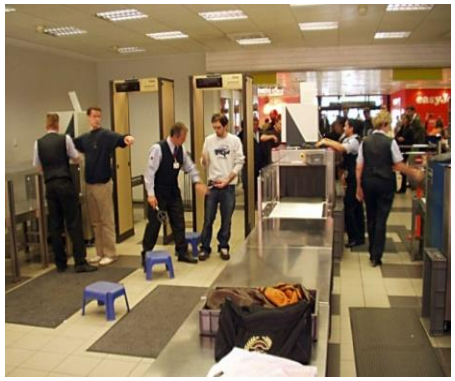
High energy physics





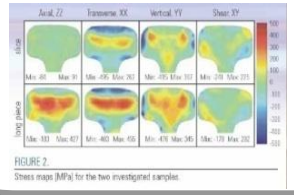
Astro-particle physics, ...

Security check

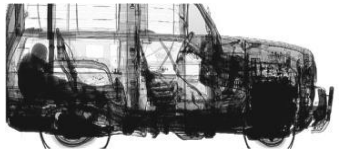


X-ray scanning

Nondestructive analysis



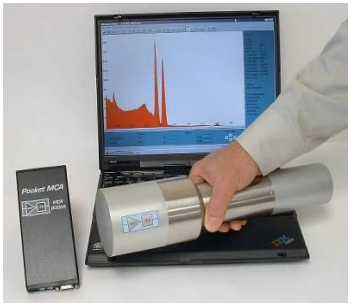
Board inspection



Radiation monitoring

Scintillation Detectors

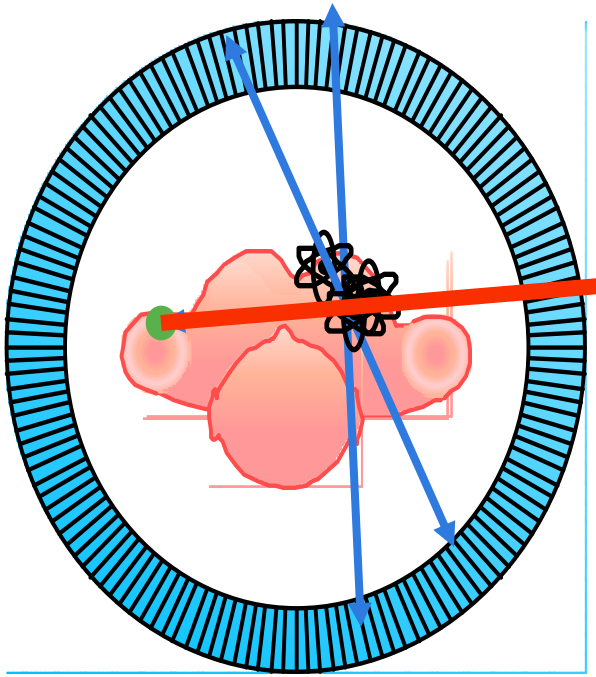
NaI(Tl) Spectrometer

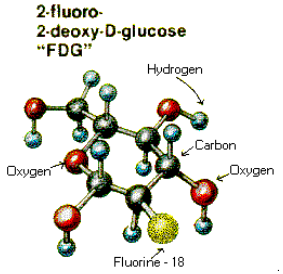


Scintillation Surveymeter

Positron Emission Tomography (PET)

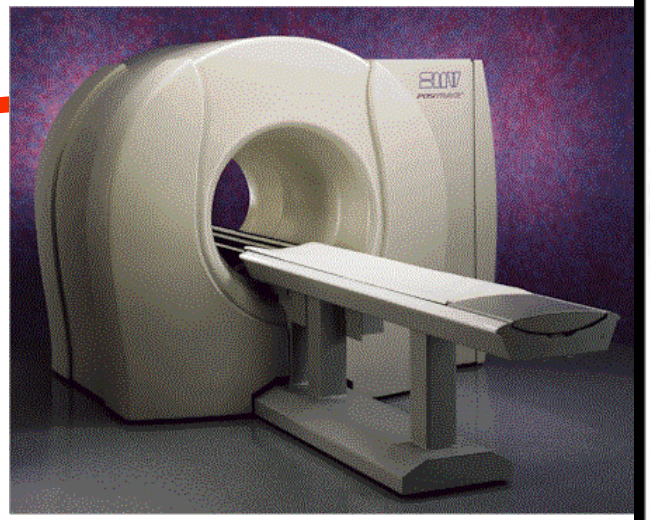
Ring of Photon Detectors

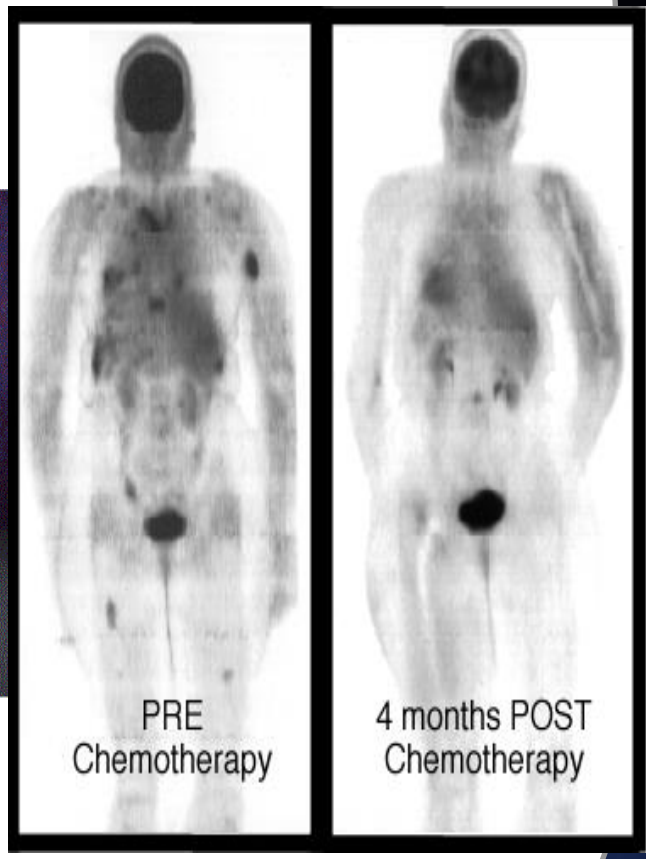




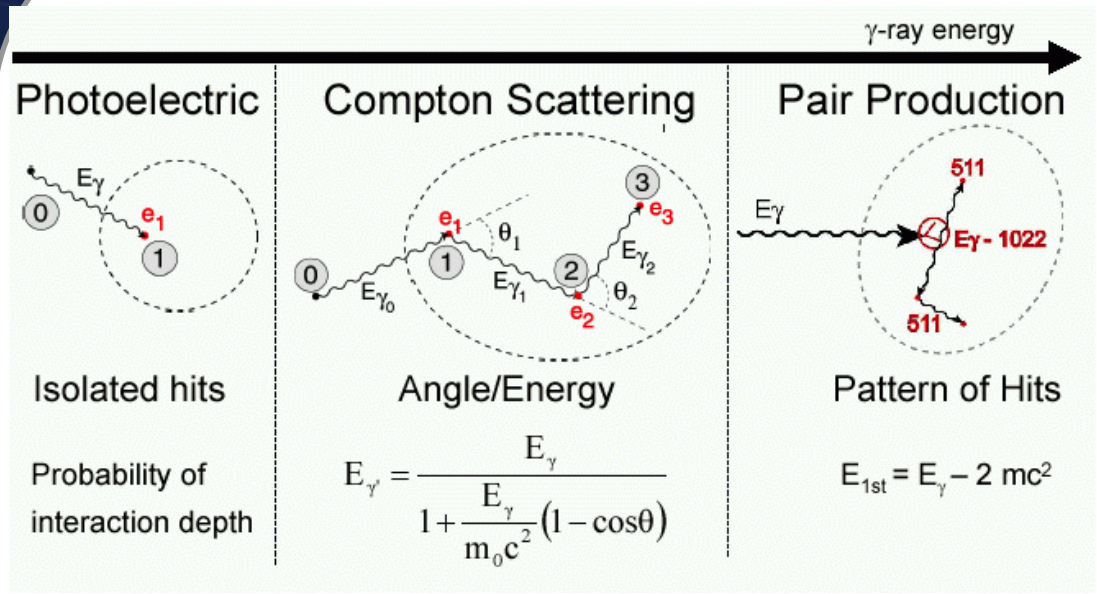
POSiTRACE

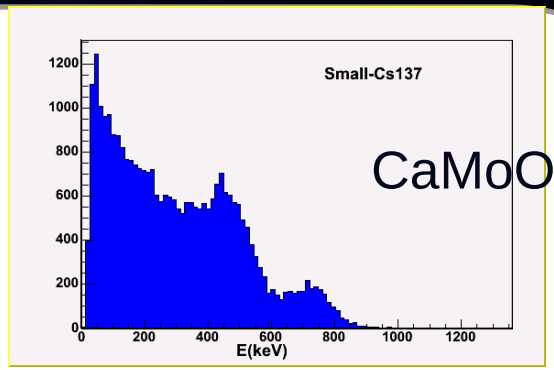
Dual Mode PET/CT
Oncology System

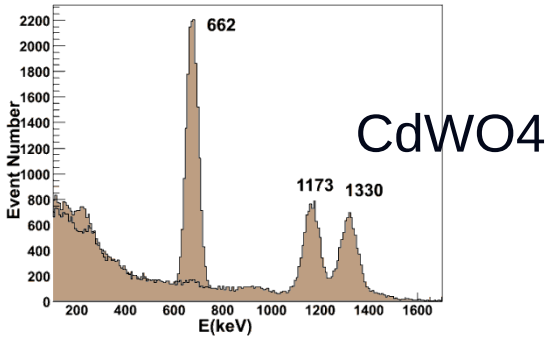




Detection Efficiency of X-ray and γ







Photoelectric effect : ρZ_{eff}^{3-4}

Compton scattering : ρ

Pair production : ρZ

High ρ & Z_{eff}!

Motivation

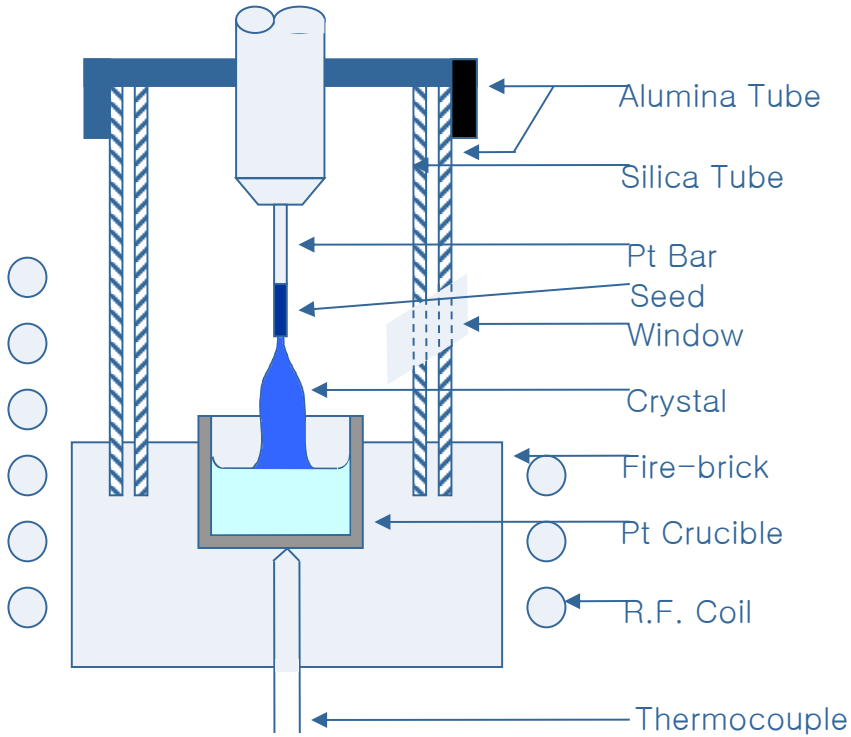
- Our research work is to explore and develop new Tl-based inorganic halide scintillators for different application such as high energy and nuclear physics, radiation monitoring, homeland security as well as medical imaging.

- Alteration of the energy band gap, enhancement of Z_{eff} and density using Tl ion with high density (ρ=11.8 g/cm^3) and high Z-number (Z=81). Disadvantage of Tl is highly toxic that extreme care should be taken. (ex: TlBr, KRS-5, KRS-6 CsI:Tl, NaI:Tl)

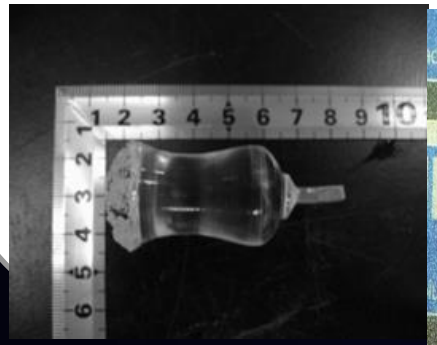
- Not only with intrinsic luminescence of Tl, with Ce^{3+} and Eu^{2+} doping for the improvement of scintillation properties.

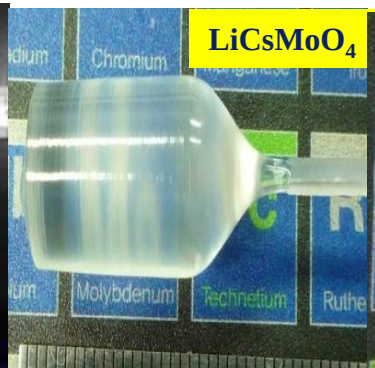
- They could be applied PET, SPECT, Gamma Camera & CT

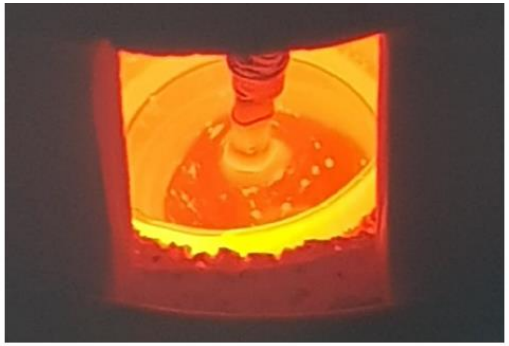
Crystal growing system with Czochalski method



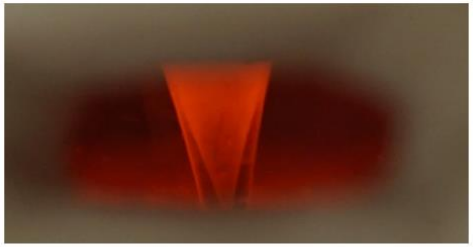
At KNU



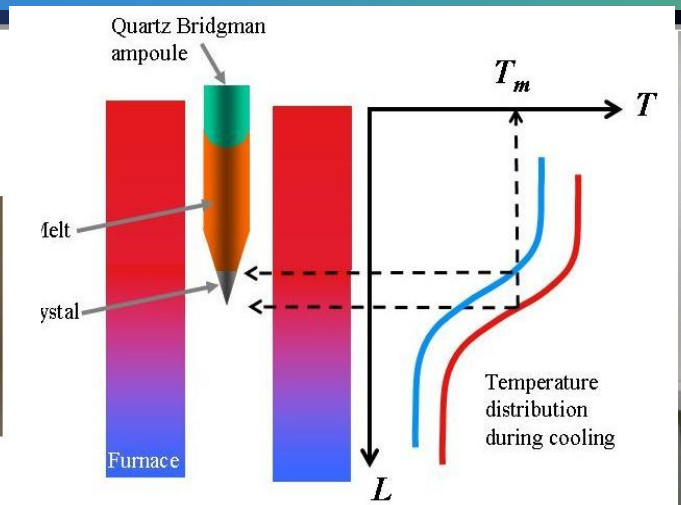




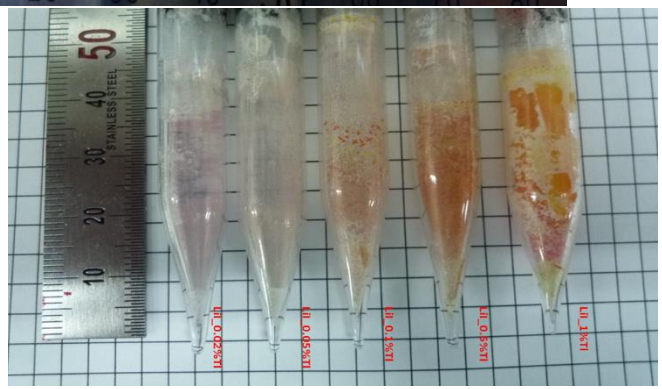
Bridgman Crystal Growing Methods



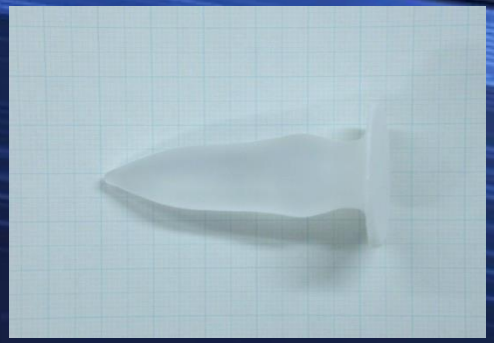
Crystal is growing in Bridgman furnace



At KNU



Crystals growing at KNU for 20 years

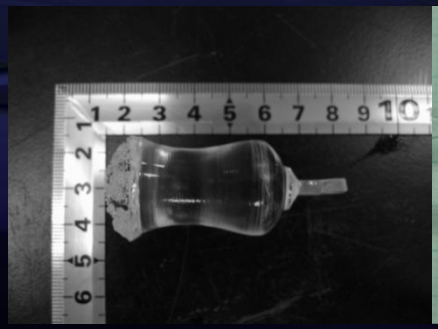


$SrCl_2(Eu)$

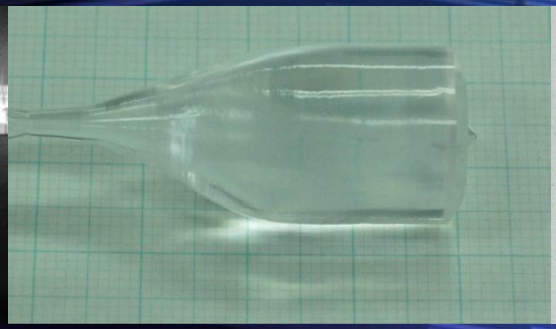
$CeCl_3$

$LaCl_3(Ce)$

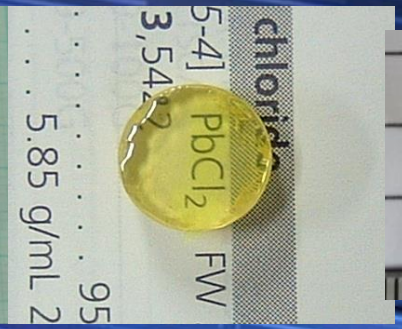
$CeBr_3$



CsI



$Ba_{0.2}Sr_{0.8}Cl_2$

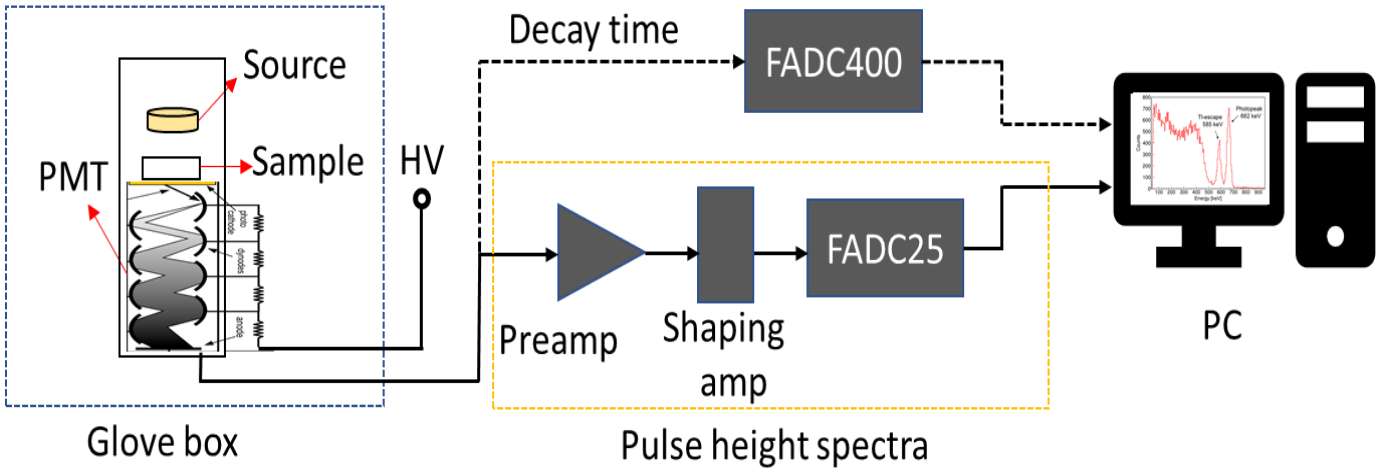


$PbCl_2:Eu^{2+}$

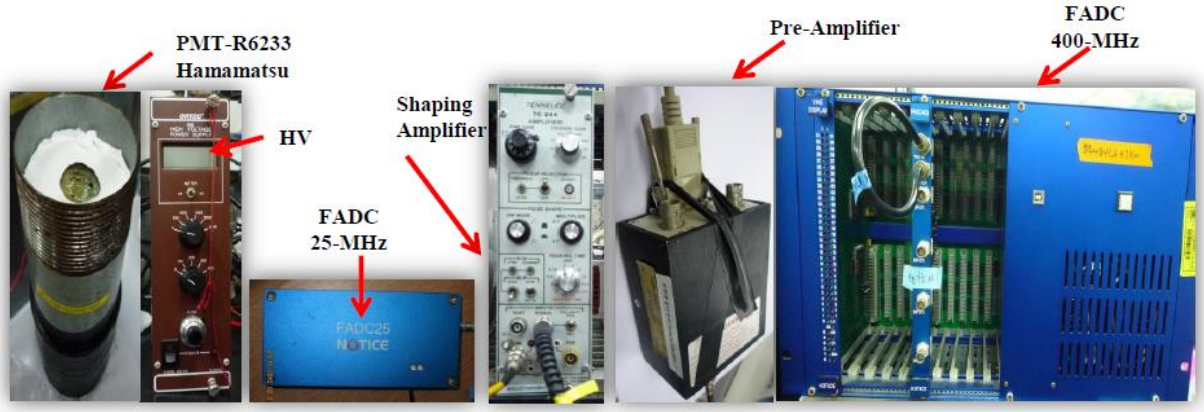
BGSO

- NaI:Tl, CsI(Tl, Co3, Na), BGO, BSO, BGSO, SrWO4, CaMoO4, SrMoO4 et al.
- New material : BaSrCl2, CsCe2Cl7, Cs(Rb)2Li(Na)CeCl6, Cs2LiGd(Lu)Cl(Br)6:Ce, Li6Lu(Gd,Y)(Bo3)3, NaGd(Wo4)3 , Tl-based scintillators et al.

Experimental Setup



- **For the γ-ray spectroscopy**



Development of Elpasolite scintillators

Elpasolite scintillators : X_2YReZ_6 w/wo Ce^{3+} doping
(X=Cs, Rb; Y=Li, Na; Re= Rare Earth, and Z=Cl,Br,I)

Most studied examples: Cs_2LiYCl_6:Ce(CLYC), $Cs_2LiLaCl_6$:Ce, $Cs_2LiLaBr_6$:Ce, $Cs_2LiLuCl_6$:Ce, Rb_2LiYBr_6:Ce (neutron detection
Studied by our group:
$Cs_2LiCeCl_6$, $Cs_2LiCeBr_6$, $Cs_2NaCeCl_6$, $Cs_2NaCeBr_6$
$Cs_2LiGdCl_6$:Ce, $Cs_2LiGdBr_6$:Ce, $Cs_2NaGdCl_6$:Ce, $Cs_2NaGdBr_6$:Ce
$Rb_2LiGdCl_6$:Ce , $Rb_2LiGdBr_6$:Ce, $Rb_2LiCeCl_6$, $Rb_2LiCeBr_6$
$Cs_2LiLuBr_6$:Ce => More than 13 publications and 4 patents

New High Z-number elpasolite scintillator?
X-> Tl ($Tl_2LiGdCl_6$:Ce,Tl_2LiYCl_6:Ce, $Tl_2LiGdBr_6$ & so on)

Discovery of Tl based scintillators

We started a pioneer work in 2009 on the development of Tl-based compounds and published $Tl_2LiGdCl_6:Ce^{3+}$ paper as a first Tl-based scintillator in 2015 and presented $Tl_2LiYCl_6:Ce^{3+}$ SCINT2015.

$Tl_2LiLnX_6:Ce$

- $Tl_2LiGdCl_6:Ce^{3+}$ [1]
- $Tl_2LiGdBr_6:Ce^{3+}$ [2]
- $Tl_2LiYCl_6:Ce^{3+}$ [3,4]
- $Tl_2LiLuCl_6:Ce^{3+}$ [5]
- $Tl_2LiScCl_6$:Pure

$Tl_xLnX_y:Ce$

- $Tl_2LaCl_5:Ce^{3+}$ [7]
- $Tl_2LaBr_5:Ce^{3+}$ [8]
- $Tl_2GdCl_5:Ce^{3+}$ [9]
- $TlGd_2Cl_7:Ce^{3+}$ [10]

$Tl_xAEX_y:Eu$

- $TlSr_2Br_5$: Pure [11]
- $TlCaCl_3$: Pure [12]
- $TlSr_2I_5:Eu^{2+}$ [13]

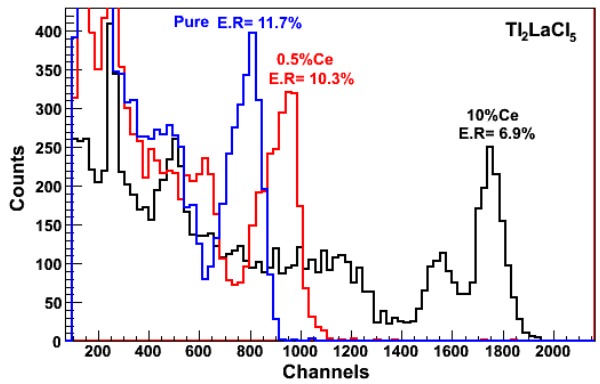
[1] H.J. Kim et al., J. Lumin., 164 (2015) 86–89.
[2] H. J. Kim et al., Rad. Measurem., 90 (2016) 279-281.
[3] H. J. Kim et al., IEEE Trans. Nucl. Sci., 63 (2) (2016) 439.
[4] G. Rooh et al., J. Cryst. Growth, 459 (2017) 163–166.
[5] G. Rooh et al., J. Lumin.,187 (2017) 347–351.

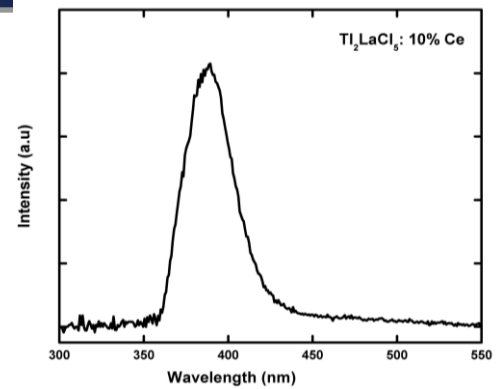
[7] H.J. Kim et al., J. Lumin., 186 (2017) 219–222.
[8] H.J. Kim et al., NIMA., 849 (2017) 72–75.
[9] G. Rooh et al., IEEE TNS., 65 (8) (2018) 2157
[10] A. Khan et al., IEEE TNS., 65 (8) (2018) 2152

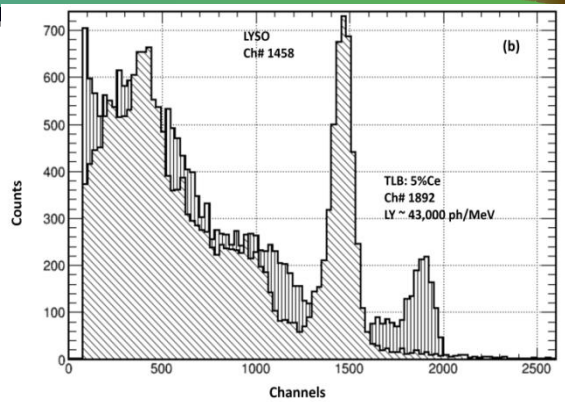
[11] G. Rooh et al., Opt. Mater., 73 (2017) 523.
[12] A. Khan et al., Rad. Measurem., 107 (2017) 115.
[13] H.J. Kim et al., Opt. Mater., 82 (2018) 8

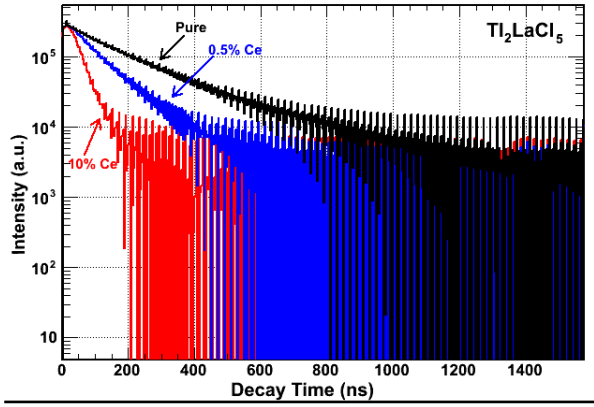
2 US and 1 EU patents, 1 is under review

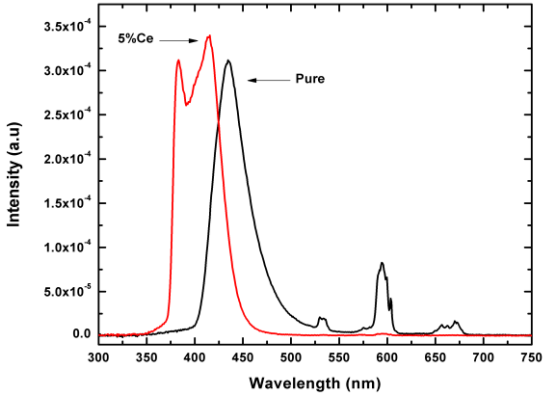
Ce-doped Tl_2LaCl_5 and Tl_2LaBr_5 Scintillators

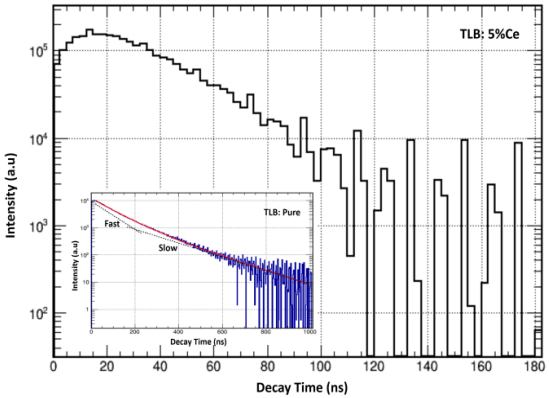






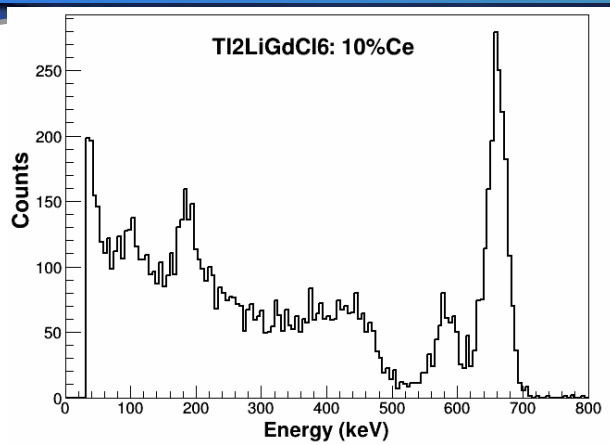


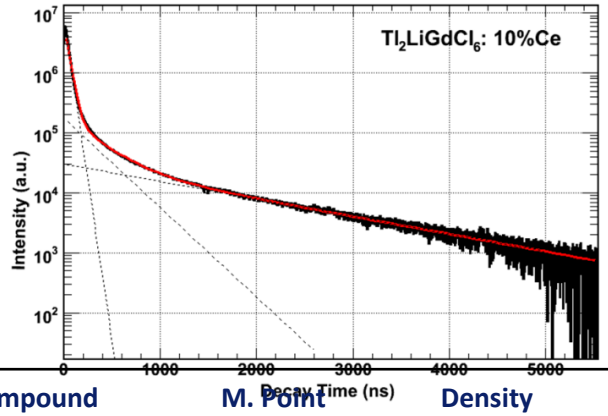


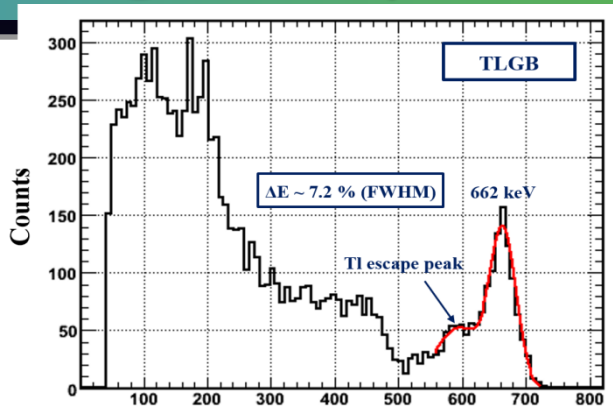


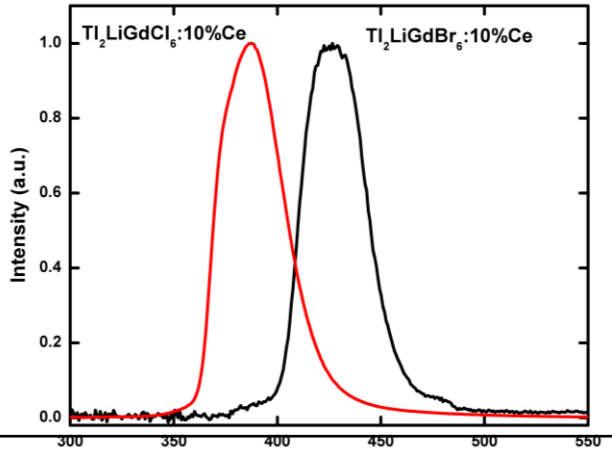
Compound	M.P (°C)	Density g/cm³	Z_{eff}	E.R	L.Y (ph/MeV)	Decay time (ns)	Ref.
Tl_2LaCl_5: 10% Ce	510	5.20	71	6.9%	51,000	31(87%) +111	[6]
Tl_2LaBr_5: 5% Ce	548	5.90	67	6.3%	43,000	25	[7]
$LaBr_3$: Ce^{3+}	783	5.08	46.9	3.0%	61,000	32	[10]

Ce-doped $Tl_2LiGdCl_6$ single crystal





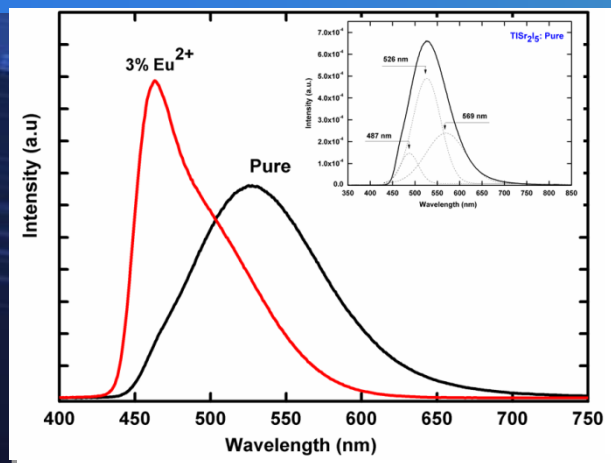


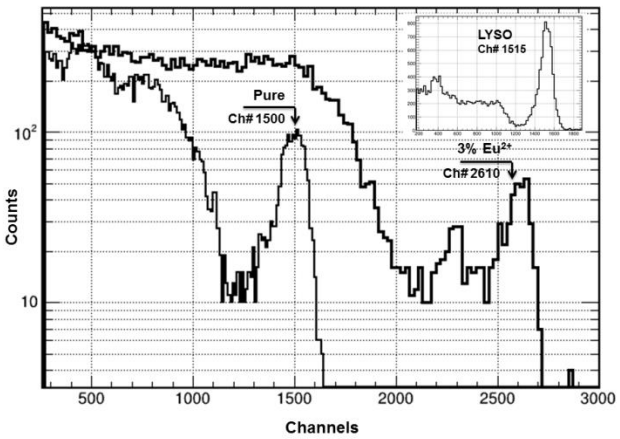


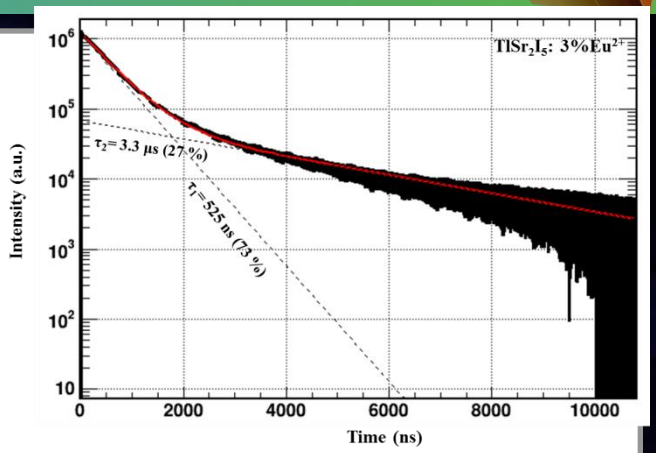
Compound	M. Point (°C)	Density g/cm³	Z_{eff}	E.R @662 keV	L.Y (ph/MeV)	Decay time (ns)	Ref.
$Tl_2LiGdCl_6$	540	4.75	70	4.6%	58,000	34 (81%)	[1]
$Tl_2LiGdBr_6$: Pure	450	5.30	66	7.2%	27,000	56+slow	
$LaBr_3$: Ce^{3+}	783	5.08	46.9	3.0%	61,000	32	[11]

[11] P. Dorenbos et al., IEEE Trans. Nucl. Sci., NS-51 (2004) 1289.

Eu^{2+} doped $TlSr_2I_5$





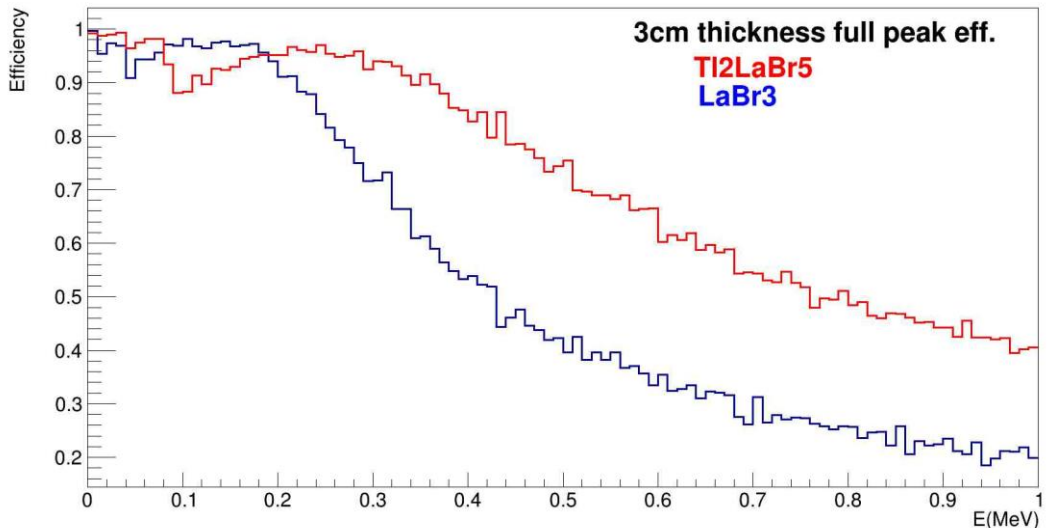


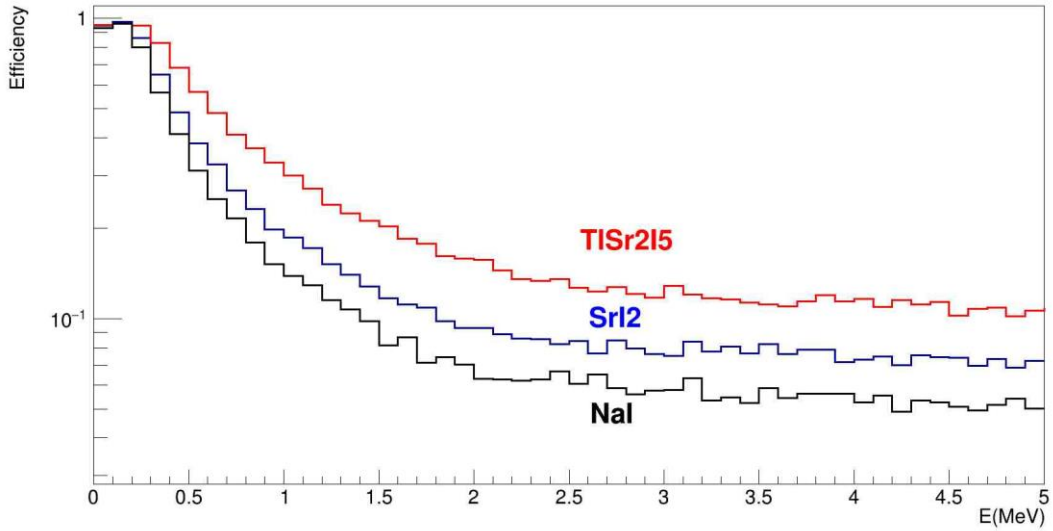
Compound	M.P (°C)	Density g/cm³	Z_{eff}	E.R (FWHM)	L.Y (ph/MeV)	Decay time (ns)
$TlSr_2I_5$: 3%Eu^{2+}	480	5.30	61	4.2%	70,000	525 + slow
SrI: Eu^{2+}	538	4.6	49	3%	120,000	1200+slow [14]
KSr_2I_5: Eu^{2+}	471	4.39	50	2.4%	94,000	990 + slow [15]

[14] Y. T. Wuet al., Cryst. Growth Des., 15 (2015) 3929.
[15] L. Stand et al., Nucl. Instrum. Methods Phys. Res. A 780 (2015) 40.

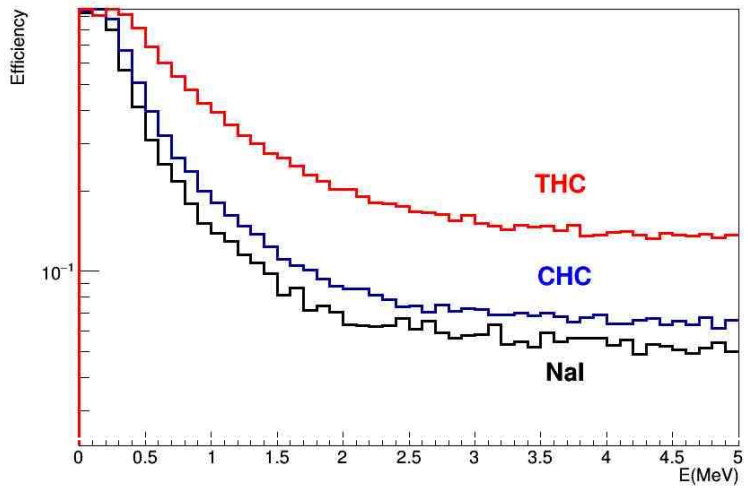
- Improvement is expected with material purification, optimized with Eu^{2+}-doping concentration and with co-doping.

Full peak efficiency comparison



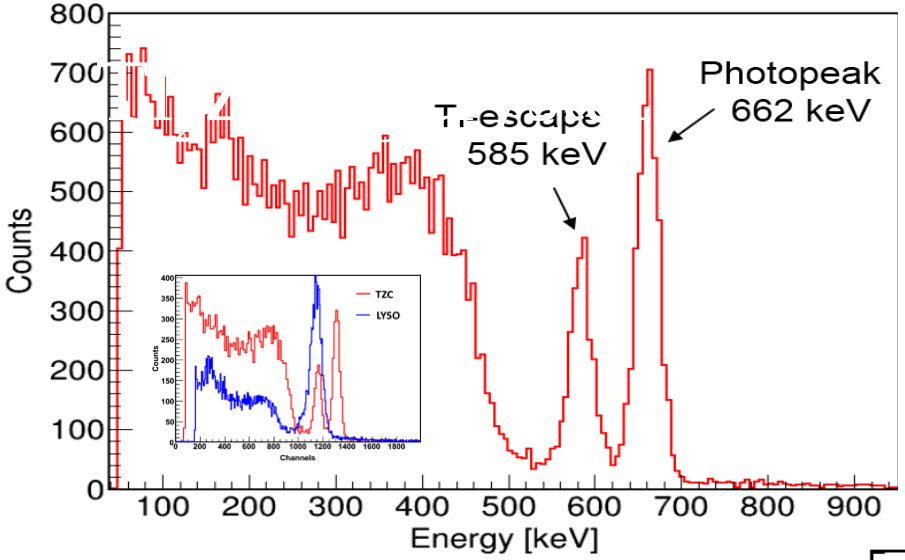


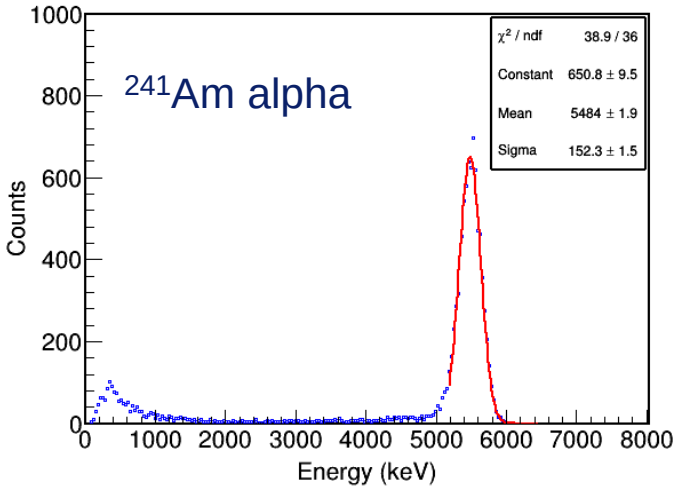
New crystal scintillators 2018



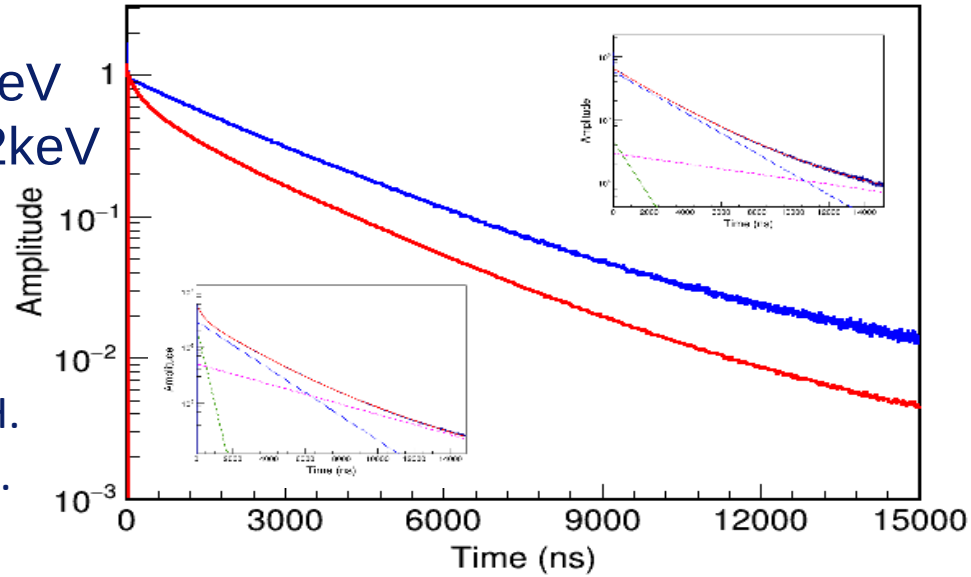
Scintillation material	Effective atomic number	Density (g/cm3)	Light yield (ph/MeV)	Major decay time (ns)
NaI(Tl)	50.8	3.67	38000	250
CsI(Tl)	54	4.51	52000	1000
BGO	75.2	7.13	9000	300
LYSO	65	7.1	33000	40
Cs_2HfCl_6(1)	58	3.86	54000	4100
Tl_2ZrCl_6(2)	**69**	**4.65**	**47000**	**2700**
Tl_2HfCl_6	**71**	**5.25**	**32000**	**1000**

Tl_2ZrCl_6 crystal



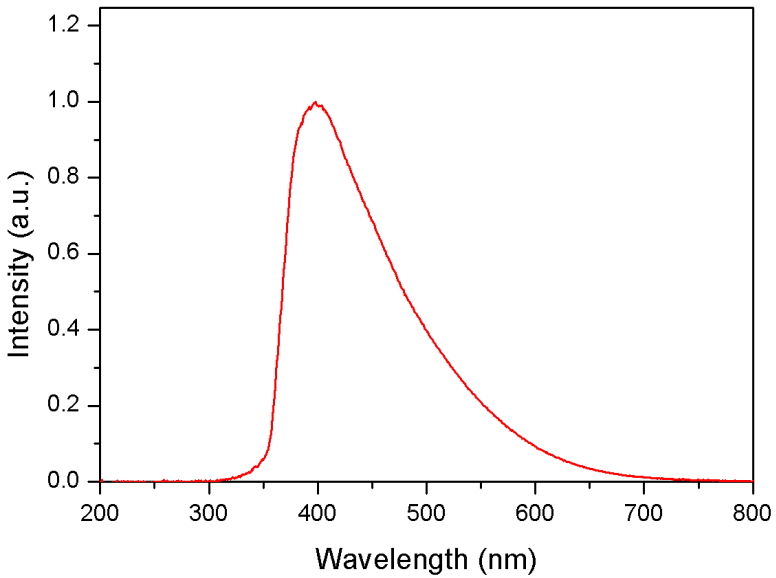


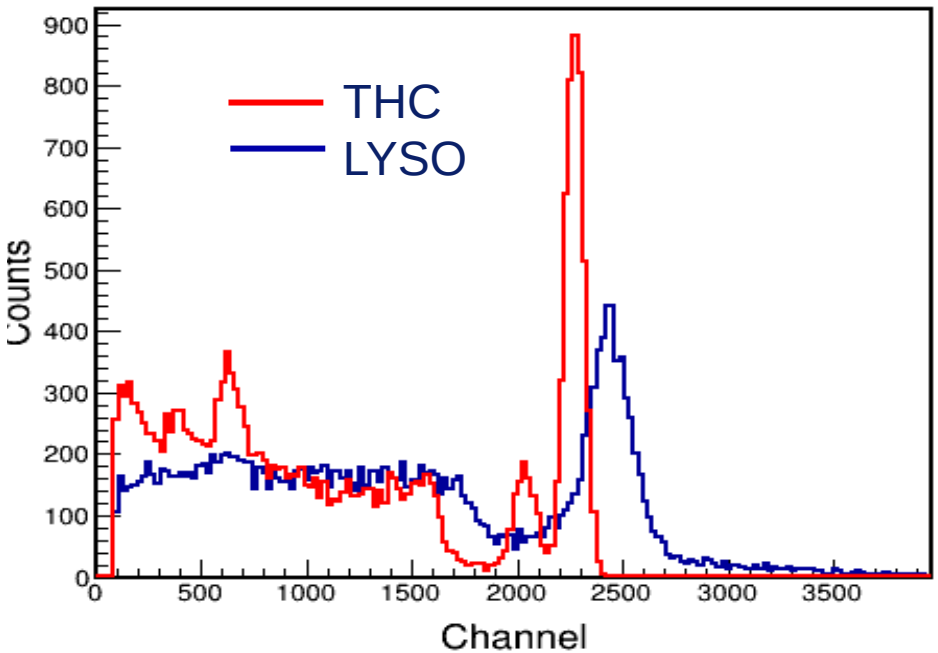
Light yield : 47.000 photons/MeV
Energy resolution :4.3% @ 662keV
Main decay time :



[2] Q.V. Phan, H.J. Kim, G. Rooh, and S.H. Kim, J. Alloys Compd. **766**, 326 (2018).

Tl_2HfCl_6 pulse height spectra





- Emission peak at 400 nm
- Light yield : 32.000 photons/MeV
- Energy resolution :4.0% @ 662keV
- Better than Cs_2HfCl_6

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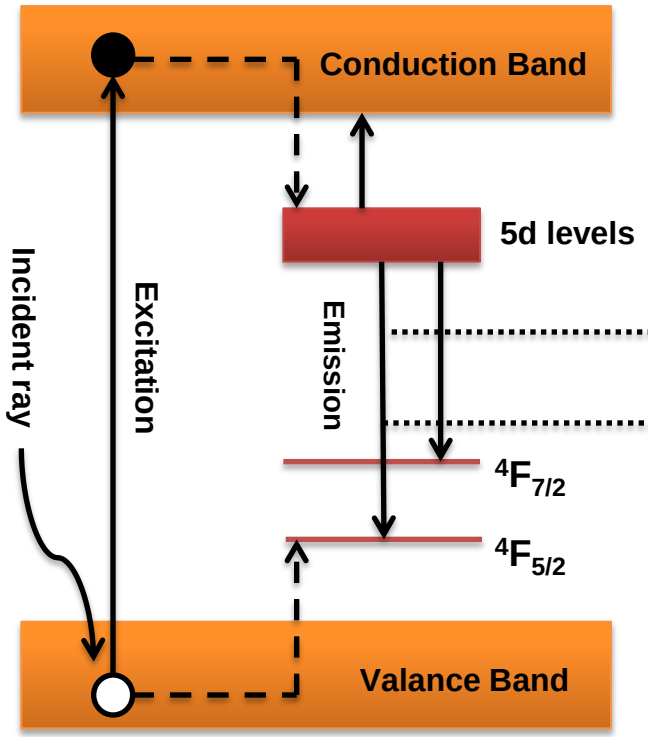
Summary and future perspect

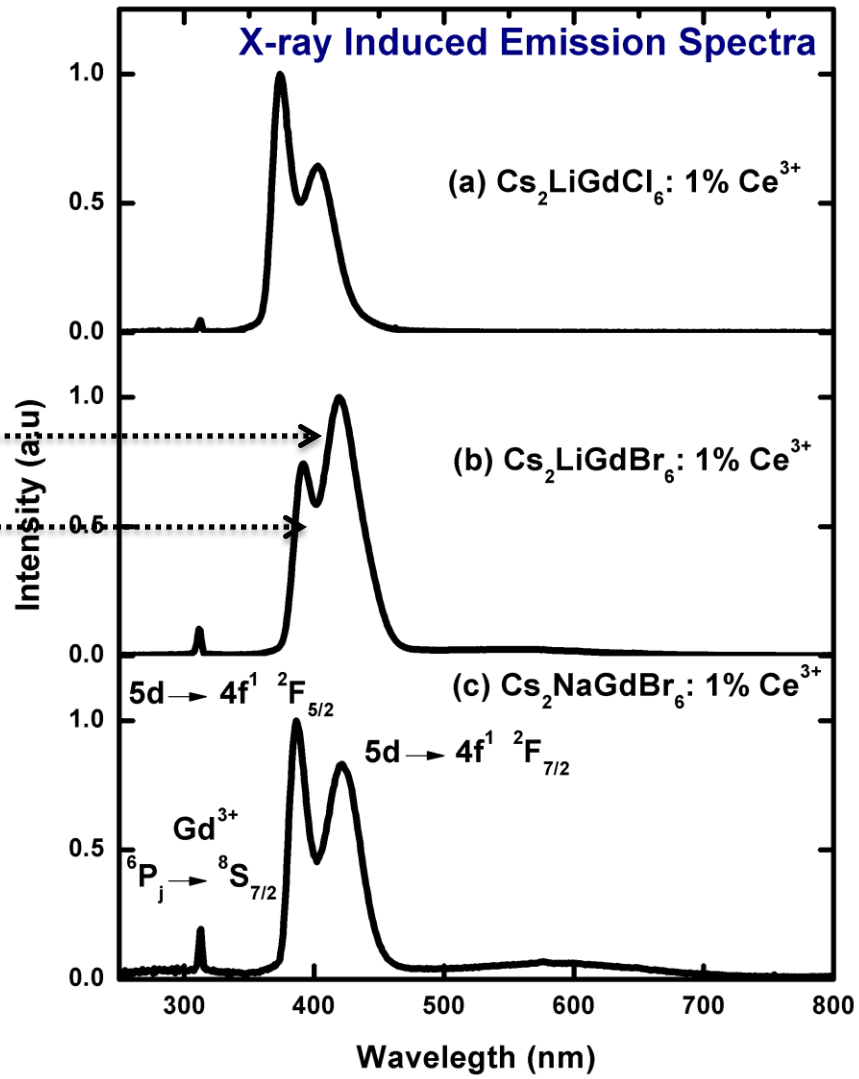
- New Tl-based scintillators are discovered and reported.
- Preliminary results showed promising performance with high light yield, high effective Z-number, fast decay time, good energy resolution and moderate density.
- Excellent detection efficiency of X- and gamma rays due to the high effective Z-number can be used for the radiation detection (ex: $TlSr_2I_5$:Eu) and medical imaging (ex: $Tl_2LaCl_5(Br_5)$:Ce) while Li-based scintillator can be used for neutron detection (ex: Tl_2LiYCl_6:Ce).
- Since, optimization of the growth condition, dopant concentration, co-doping and purification are under way, therefore, further improvement of the scintillation performance is expected.

Thank you for your attention!

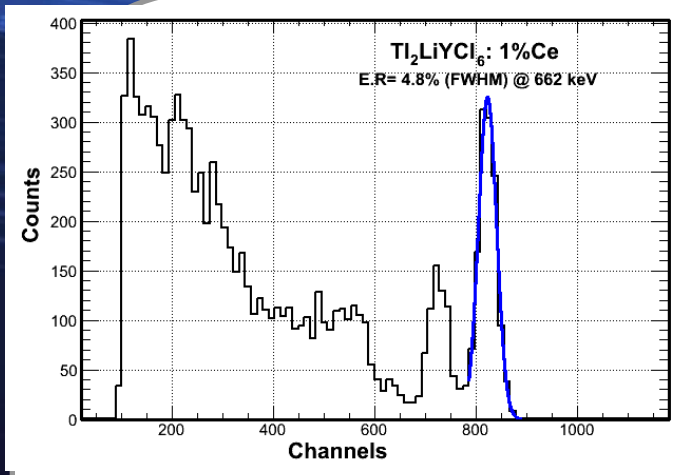
X-ray Induced Emission Spectra

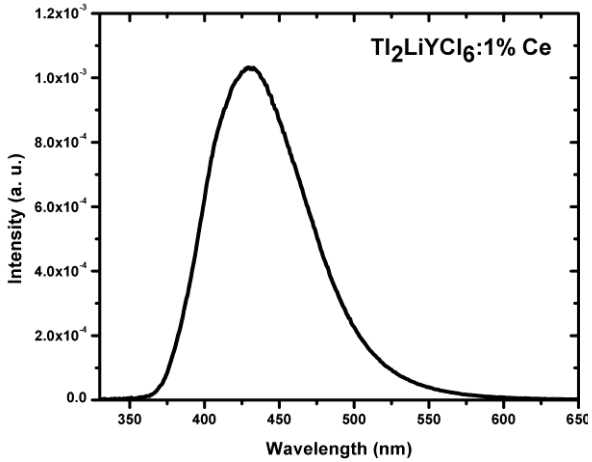
Ce^{3+} Emission

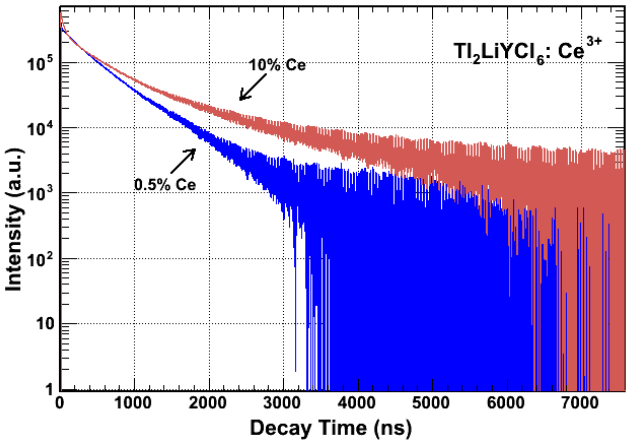




Ce-doped Tl_2LiYCl_6 (TLYC)





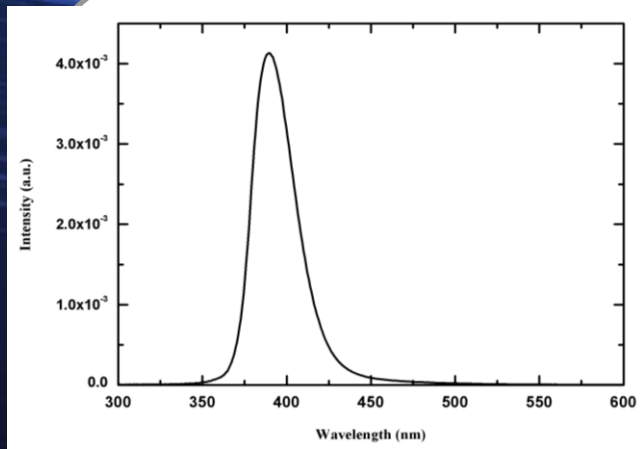


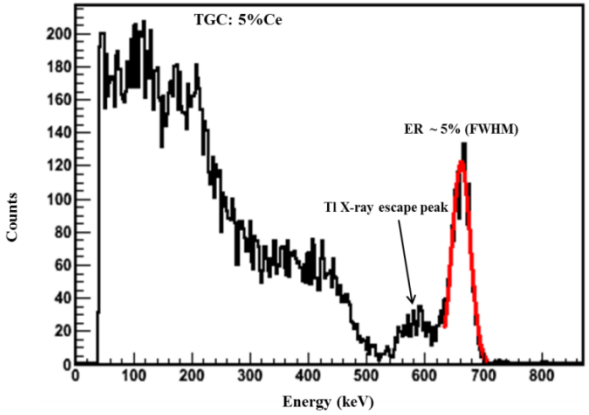
[12] J. Glodo et al., IEEE Trans. Nucl. Sci., 55(3) (2008) 1206.
[13] R. Hawrami et al., IEEE Trans. Nucl. Sci., 63(6) (2016) 2838.

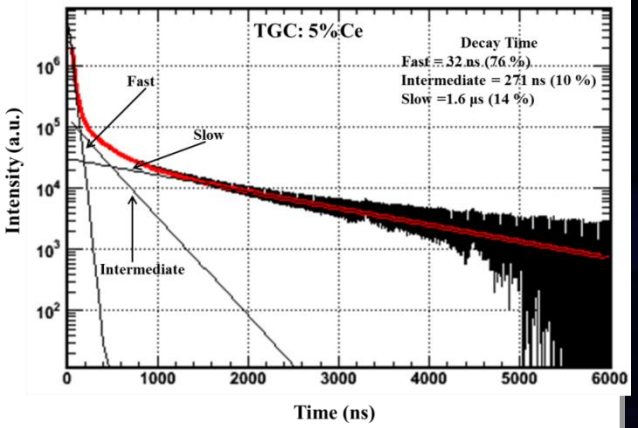
Compound	M. Point (°C)	Density g/cm³	Z_{eff}	E.R @662 keV	L.Y (ph/MeV)	Decay time (ns)	Ref.
Cs_2LiYCl_6	640	3.31	45	5.1%	20,000	129 + Slow	[12]
Tl_2LiYCl_6	490	4.58	69	4.8%	30,500	57(9%) + Slow	[3,4]

- TLYC of both gamma and thermal neutron detection efficiency is better than the Cs_2LiYCl_6 reported by RMD group [13].

Ce-doped Tl_2GdCl_5

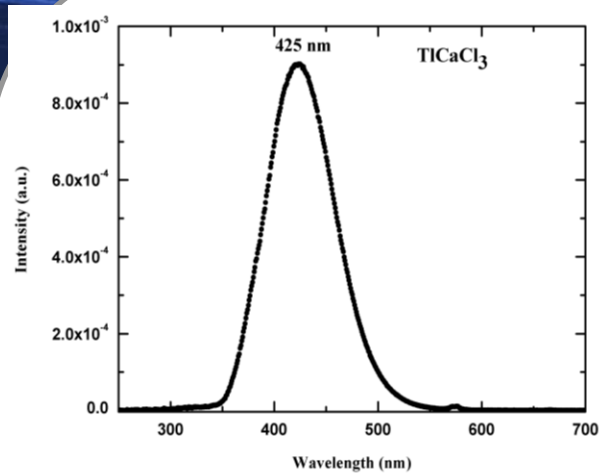


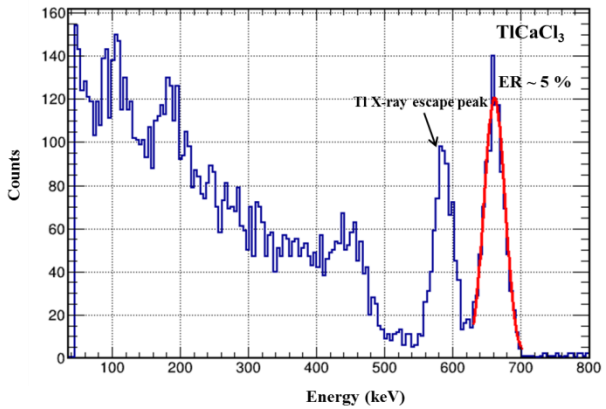


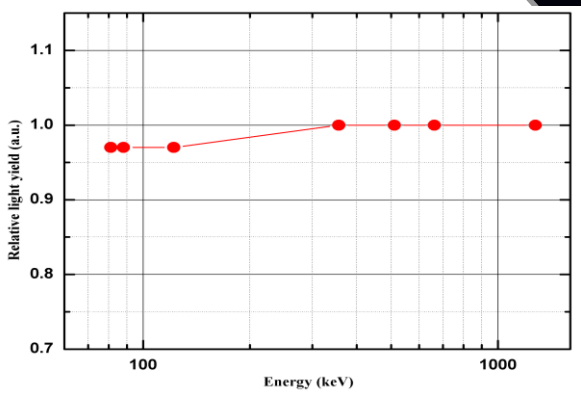


Compound	M.P (°C)	Density g/cm³	Z_{eff}	E.R @662 keV	L.Y (ph/MeV)	Decay time (ns)
Tl_2GdCl_5	490	5.10	71	5.0%	53,600	32 (76%)

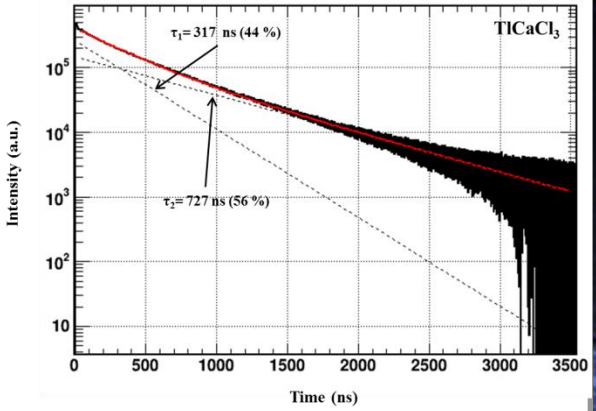
Perovskite type ; $TlCaCl_3$: Pure



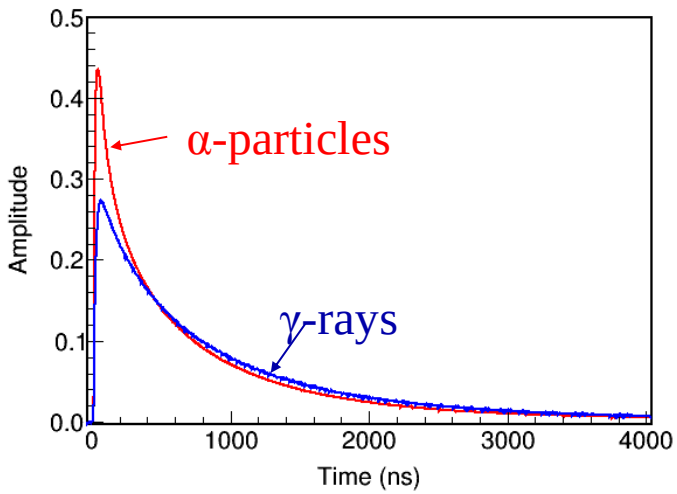




Compound	M.P (°C)	Density g/cm³	Z_{eff}	E.R (FWHM)	L.Y (ph/MeV)	Decay time (ns)
$TlCaCl_3$	680	3.80	65.5	5%	31,000	317 + 727
NaI: Tl	661	3.67	50.8	~ 7%	38,000	250

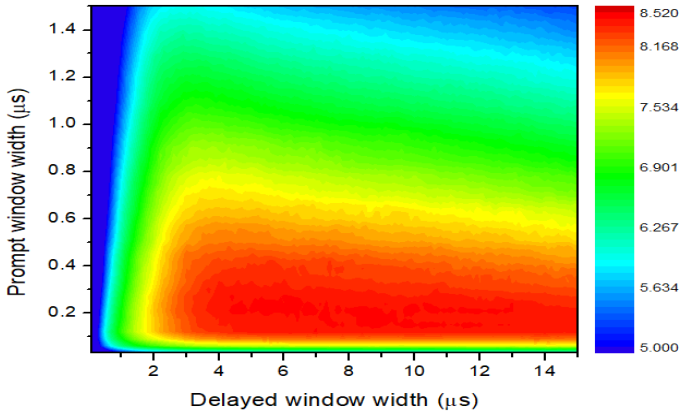


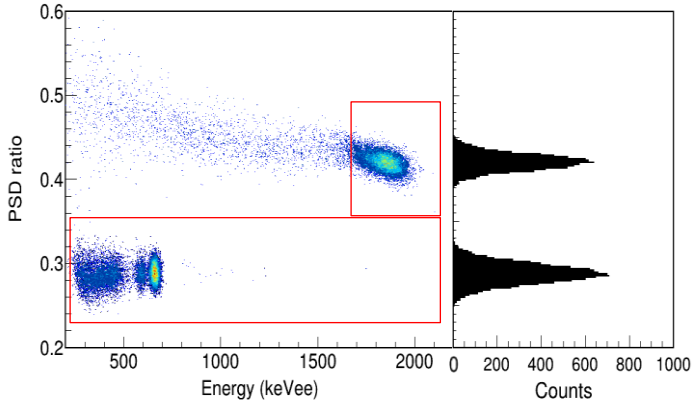
Tl_2HfCl_6 crystal



Type of irra diation	Decay constants (s) and their relative intensities (% of total)			
	τ_1 (I_1)	τ_2(I_2)	τ_3 (I_3)	τ_4 (I_4)
γ	0.36(17.5)	1.04(61.2)	14.9(19.8)	
α	0.09(8.5)	0.46(28.6)	1.04(44.8)	11.2(17.9)

FOM=8.5 with Charge comparison method





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