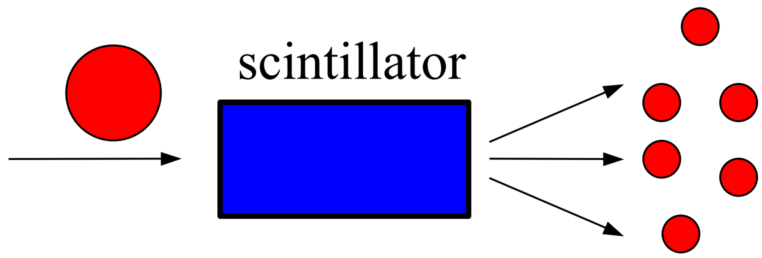
Next-Generation Scintillation Materials: Low-Dimensional Perovskite-like Cu(I) halides

Yuntao Wu (吴云涛)

SICCAS Since 1928

Principle of a scintillator

Spectral transformer

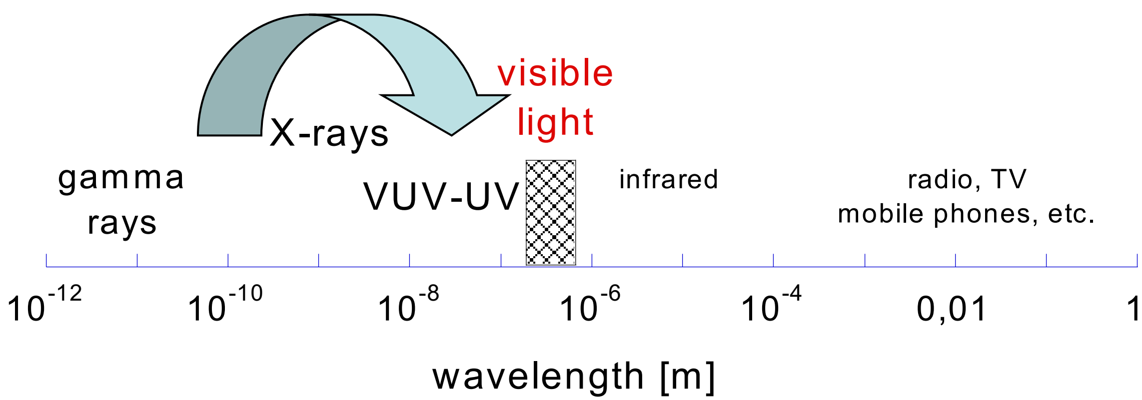


1 photon
(keV - GeV)

n photons
(2 - 4 eV)

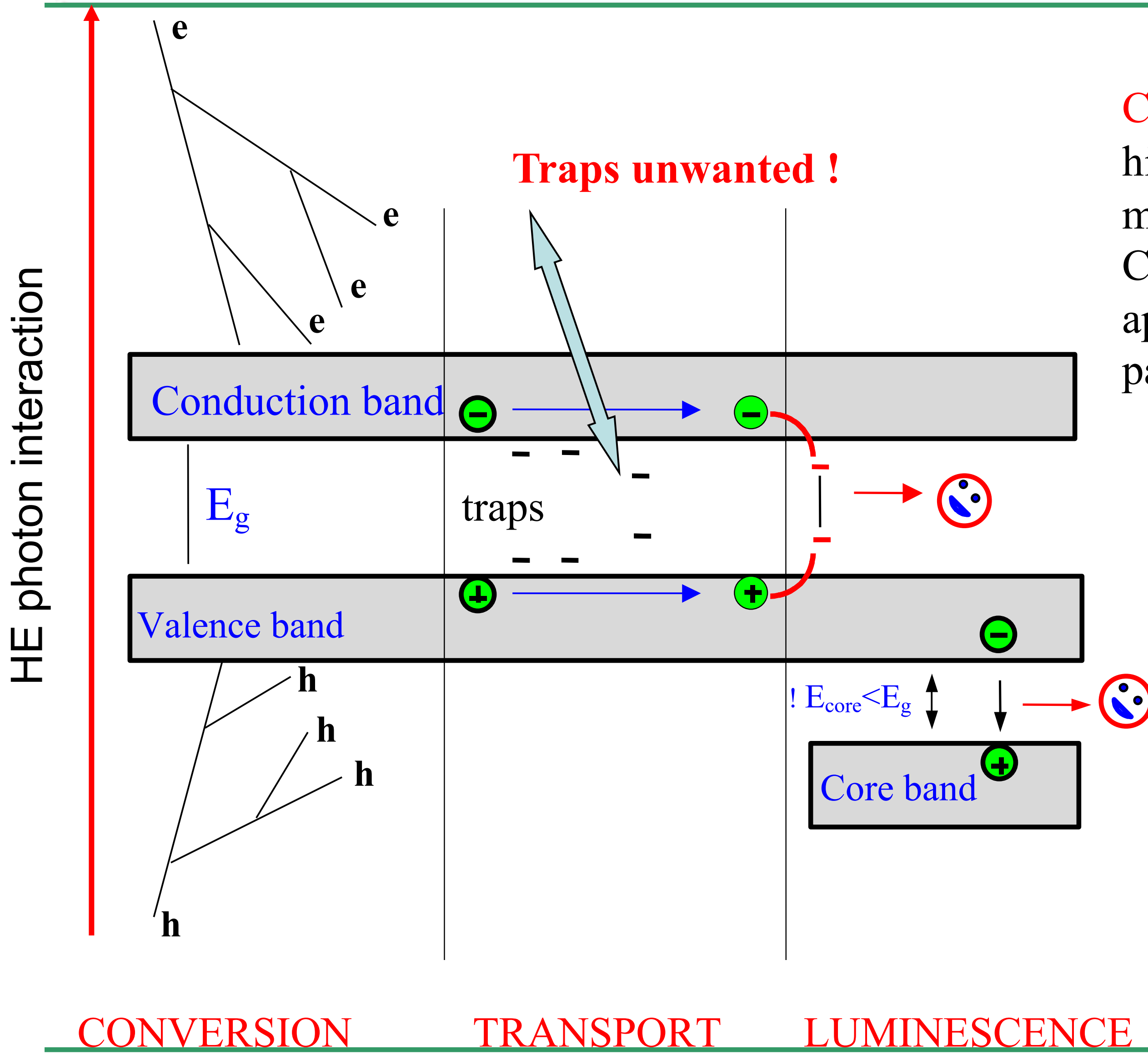
Counting of HE photons!

Fast response needed !



Why we need them – there are no direct sensitive detectors for photons with energy above a few keV

Principle of a scintillator



CONVERSION -interaction of a high-energy photon with a material through photoeffect, Compton effect, pair production, appearance of electron-hole pairs and their ther-malization

TRANSPORT - diffusion of electron-hole pairs (excitons) through the material, possible (repeated) trapping at defects, nonradiative recombination

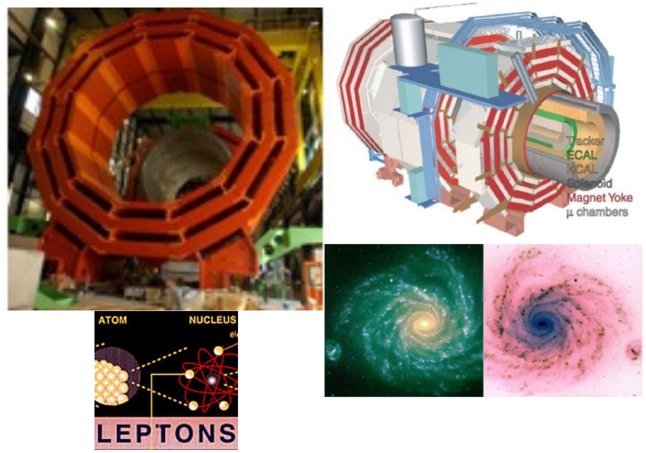
LUMINESCENCE -trapping of charge carriers at the luminescence centre and their radiative recombination

Applications of scintillators

Medical application

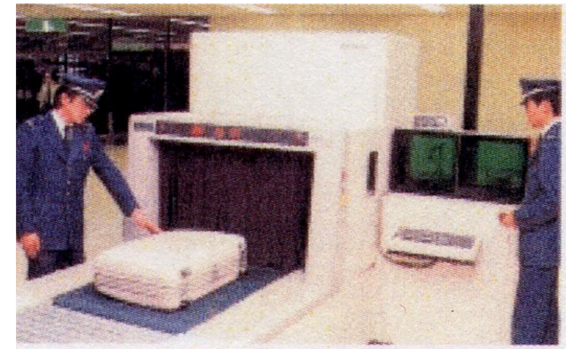
PET, SPECT, CT

High energy physics



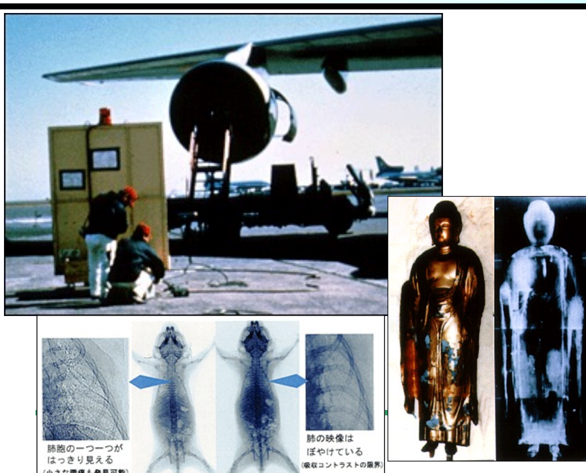
Particle physics, …

Security check



X-ray scanning

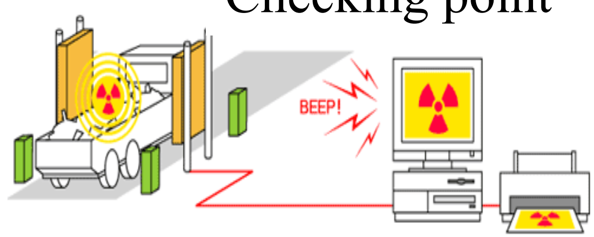
Nondestructive analysis



Computed tomography

X&Neutron-based

Checking point



Remote detection

Other applications

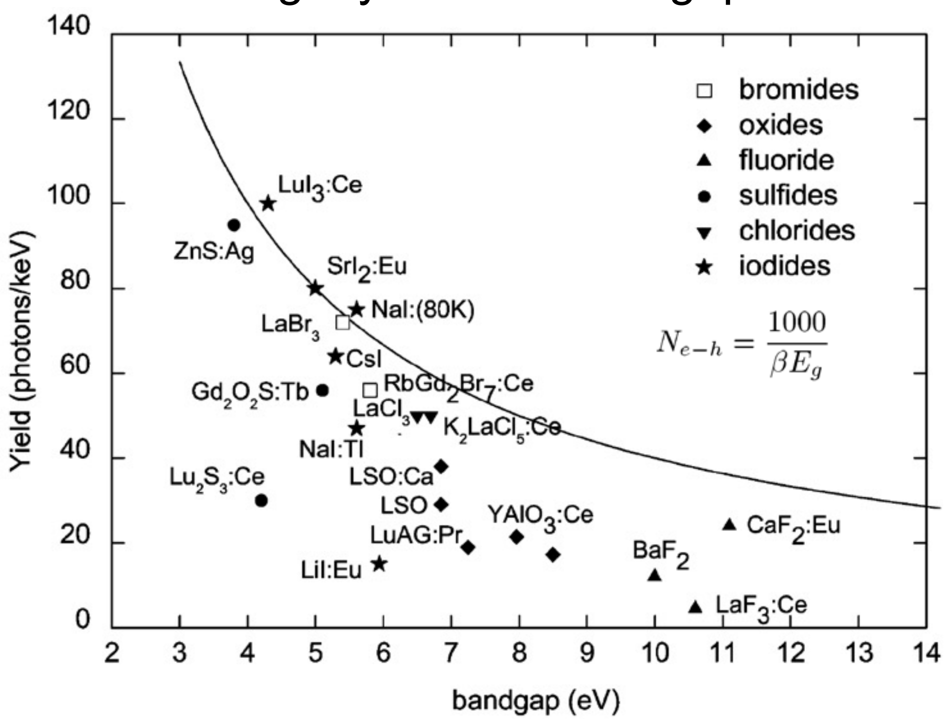
Hazards,disasters, geology

Application requirements

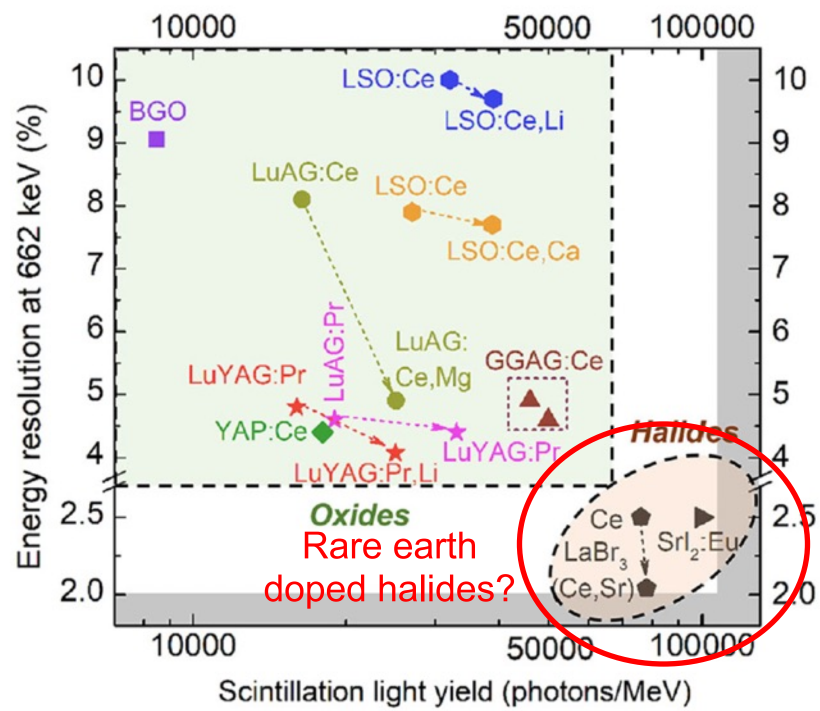
Application	High light yield	High energy resolution	Fast decay time	High density	High Z	Low afterglow
High energy Physics			✓	✓		
Nuclear physics	✓	✓	✓	✓	✓	
Homeland security	✓	✓				
Molecular Imaging (PET)	✓	✓	✓	✓	✓	
Molecular Imaging (CT)	✓					✓
Space Physics	✓			✓		

High yield and high resolution: Metal halides

Light yield VS band-gap



P. Dorenbos*, IEEE TNS, 57, 1162 (2010)



Y. Wu*, et al. PHYS. REV. APPLIED 13, 064060 (2020)

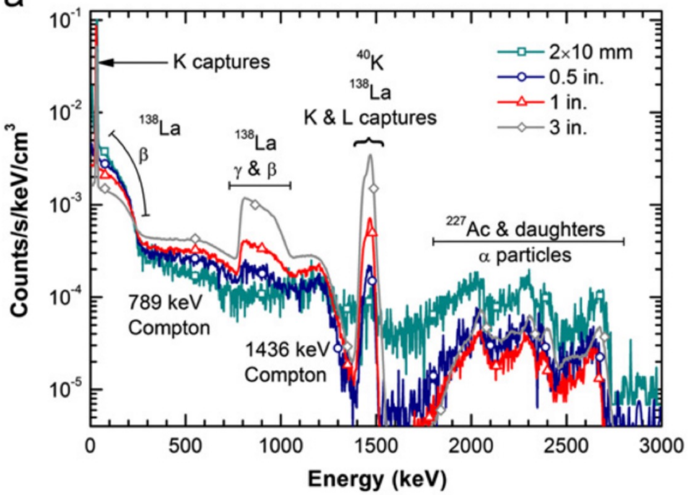
Main issues of existed high-performance metal halide scintillators:

➢ **Radioactive background**
($LaBr_3$:Ce)

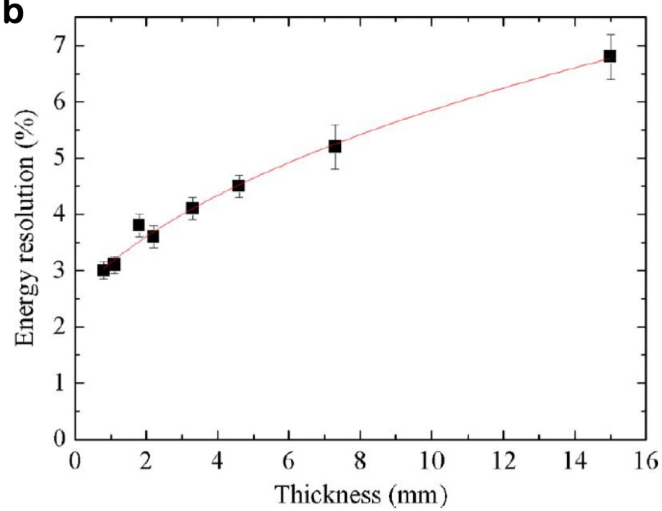
➢ **Self-absorption**
(SrI_2:Eu)

➢ **Hygroscopic**

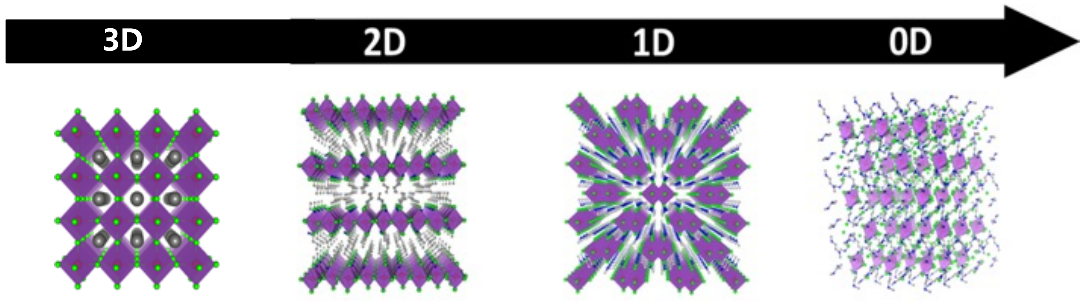
a



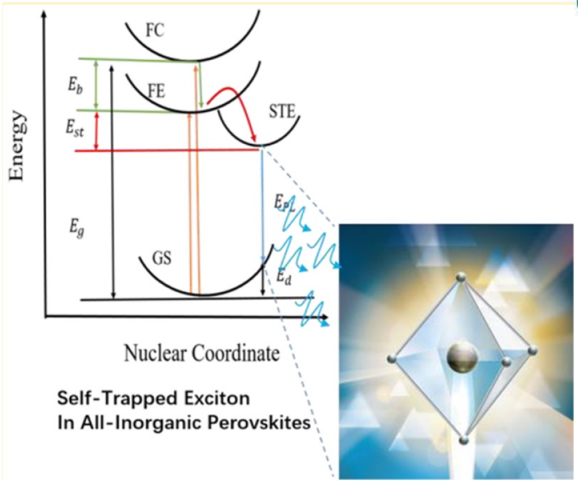
b



Low-dimensional perovskites with self-trapped exciton emission

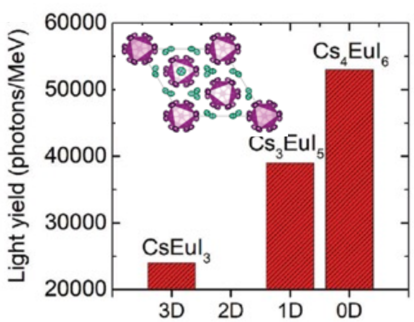


Molecular Level Low Dimensional Organometal Halide Hybrids



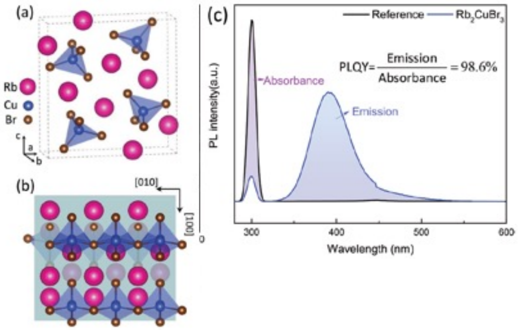
Self-Trapped Exciton
In All-Inorganic Perovskites

0D perovskite: Cs_4EuBr_6
(78,000 ph/MeV)



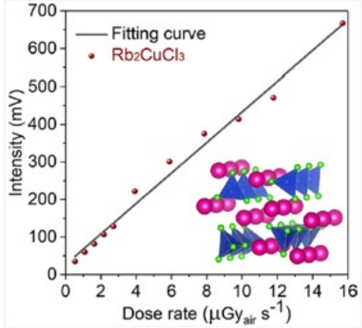
Y. Wu* et al. J. Mater. Chem. C, 2018, 6, 6647.

1D perovskite Rb_2CuBr_3
(PLQY≈1; 90,000 ph/MeV)



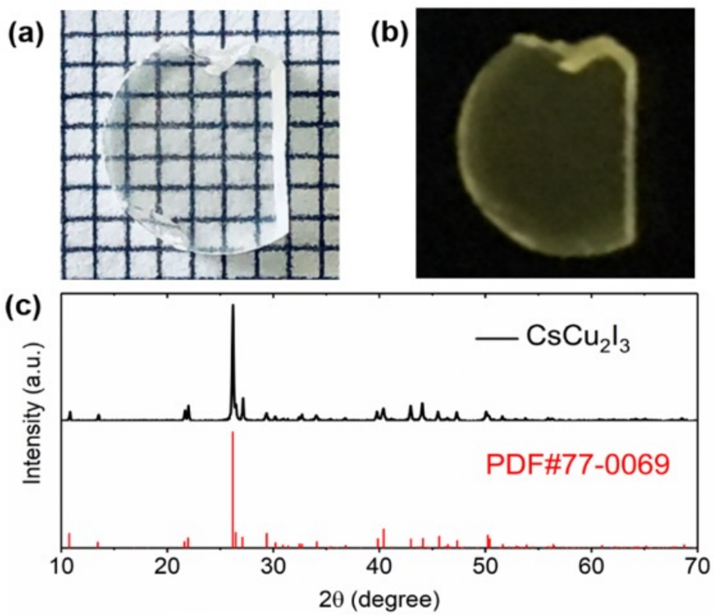
J. Tang*, et al. Adv. Mater. 2019, 1904711.

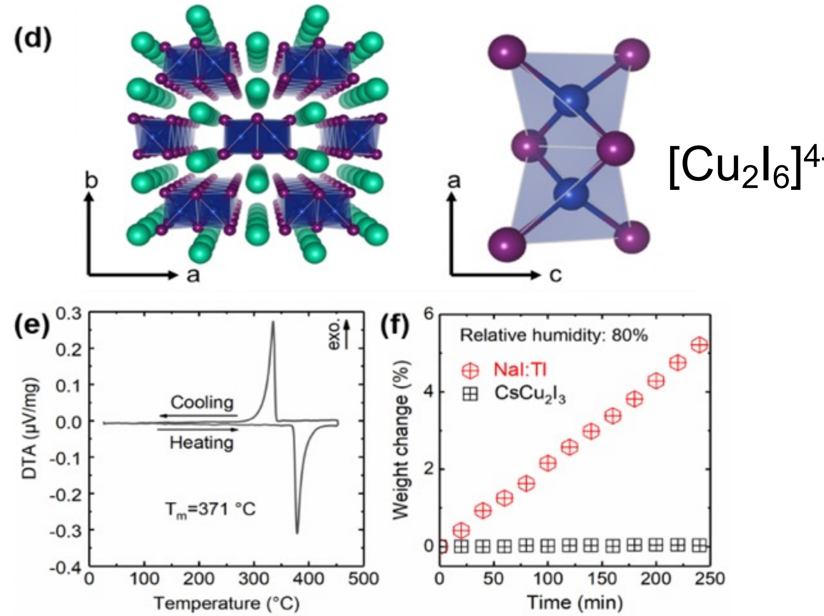
1D perovskite: Rb_2CuCl_3
(PLQY≈1; 16,600 ph/MeV)



J. Tang*, et al. J. Phys. Chem. Lett. 2020, 11, 1873.

➤ 1D perovskite $CsCu_2I_3$





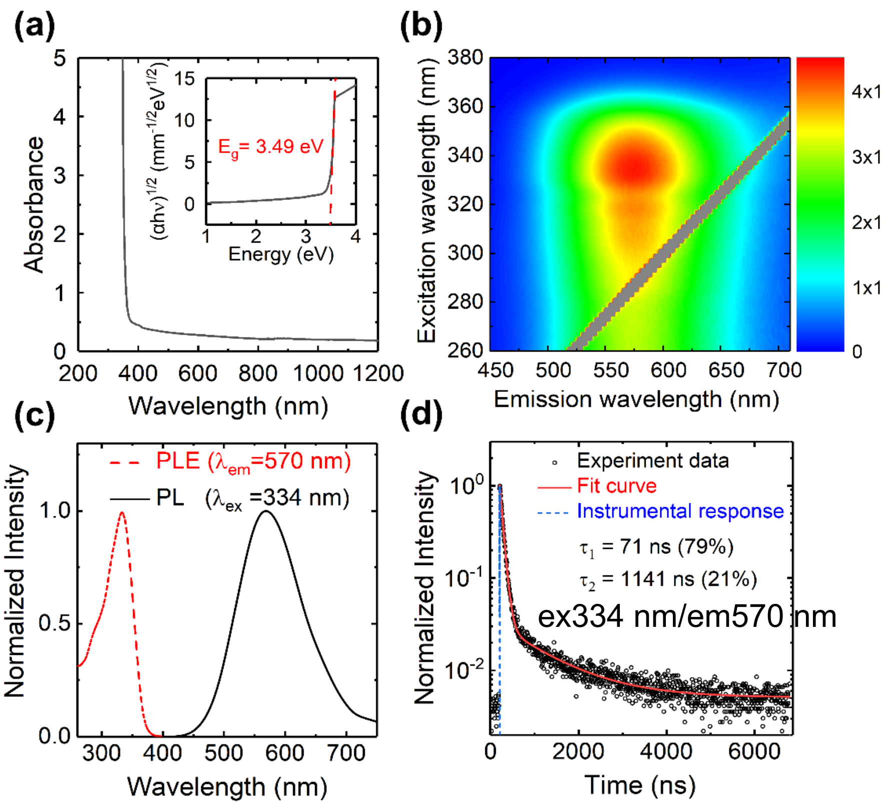
- **Orthorhombic**

- **Low melting point：371 ℃**
- **Non-hygroscopic**

Wu,* et al. *ACS Applied Materials and Interfaces* 13 (2021) 12198-12202.

➤ Luminescence properties of $CsCu_2I_3$

Absorption (a), PL&PLE spectra (b,c), PL decay (d)



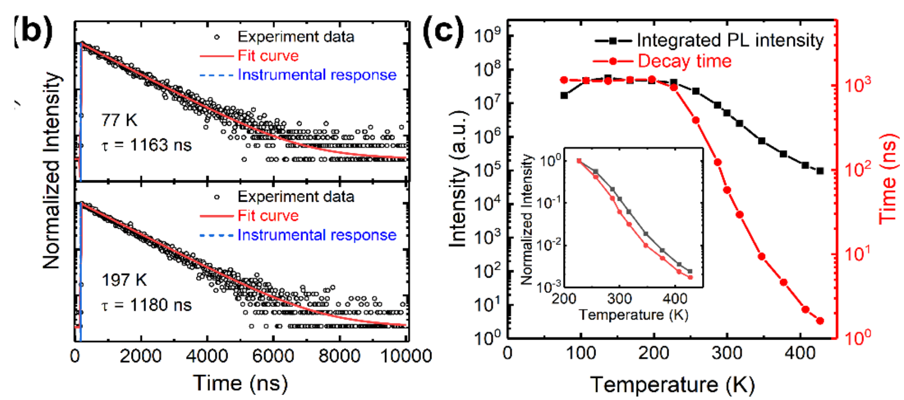
The activation energy of thermal quenching (E_a) :

$$1/\tau_{mea} = 1/\tau_{rad} + w\exp[-E_a/k_B T]$$

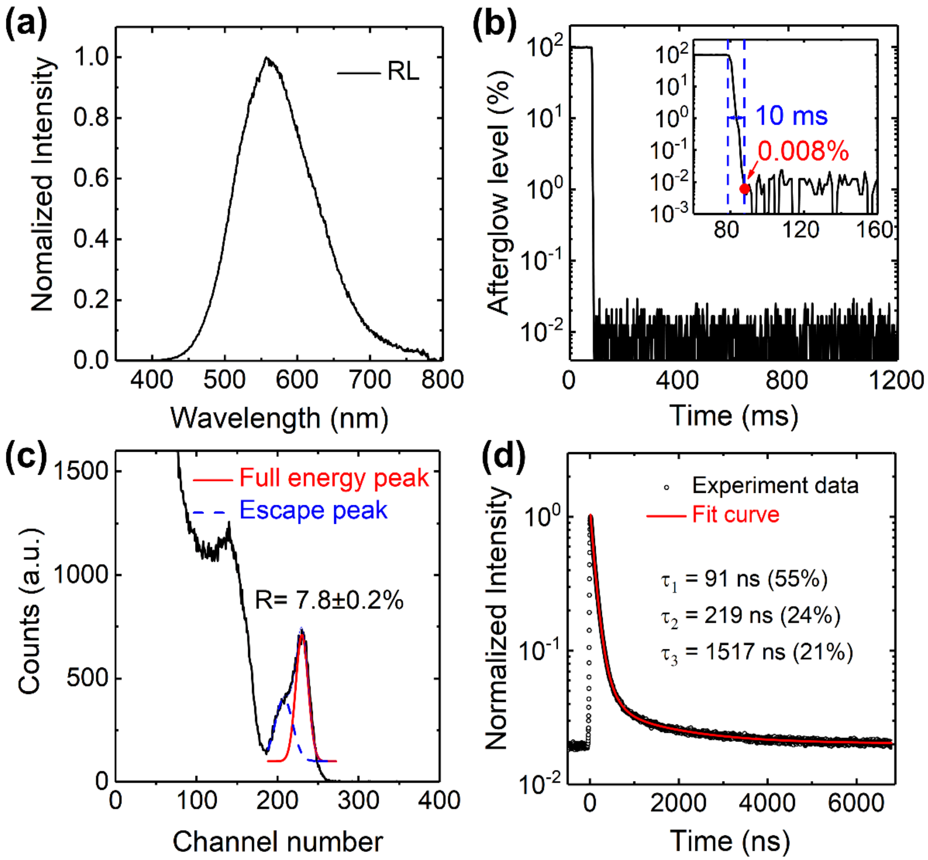
τ_{mea} is the decay time at temperature (T), τ_{rad} is the decay time at 77 K, w is the frequency factor, and k_B is the Boltzmann constant. The derived parameters are $w = 7.6 \times 10^{12}$ s^{-1} and **E_a = 340 ± 12 meV.**

Quenching is due to classical thermal quenching to ground state & exciton ionization (disintegration). **The latter explains slower tails in PL decays at high T.**

PL decays at low temperatures (b) Temperature dependence of PL spectra integrals and dominant decay time (c)



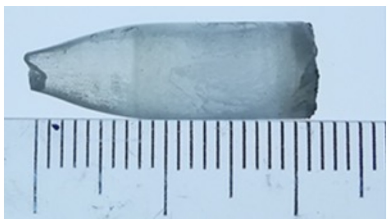
➢ Scintillation properties of $CsCu_2I_3$



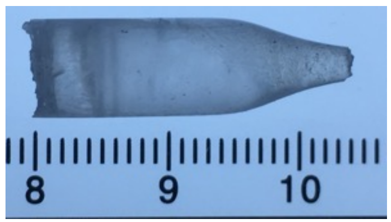
- High density of 5.01 g/cm^3, Z_{eff} of 50.6
- Large Stokes shift of 236 nm (1.54 eV).
- Scintillation yield 16,000 phot/MeV with a principal decay time of 97 ns.
- ***Scintillation yield is lowered by low QE of exciton emission** due to thermal quenching and/or disintegration (exciton engineering possible?).
- An increase of its thermal stability could increase its scintillation yield up to one order of magnitude, i.e. well beyond 100,000 photons/MeV.
- Extremely low afterglow level of 0.008% at 10 ms - **three orders of magnitude lower than in CsI:Tl scintillator.**

➢ 0D perovskite $Cs_3Cu_2I_5$、$Cs_3Cu_2I_5$:Tl

$Cs_3Cu_2I_5$

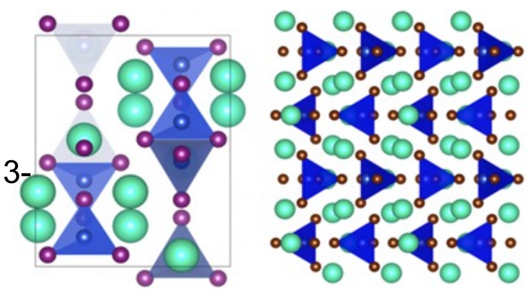


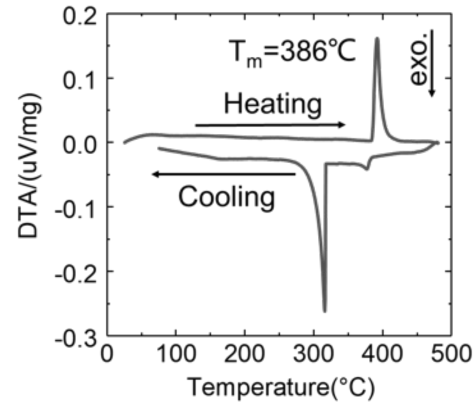
$Cs_3Cu_2I_5$:Tl

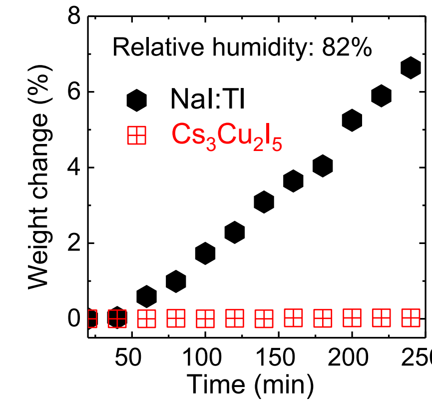


- **Orthorhombic**

$[Cu_2I_5]^{3-}$



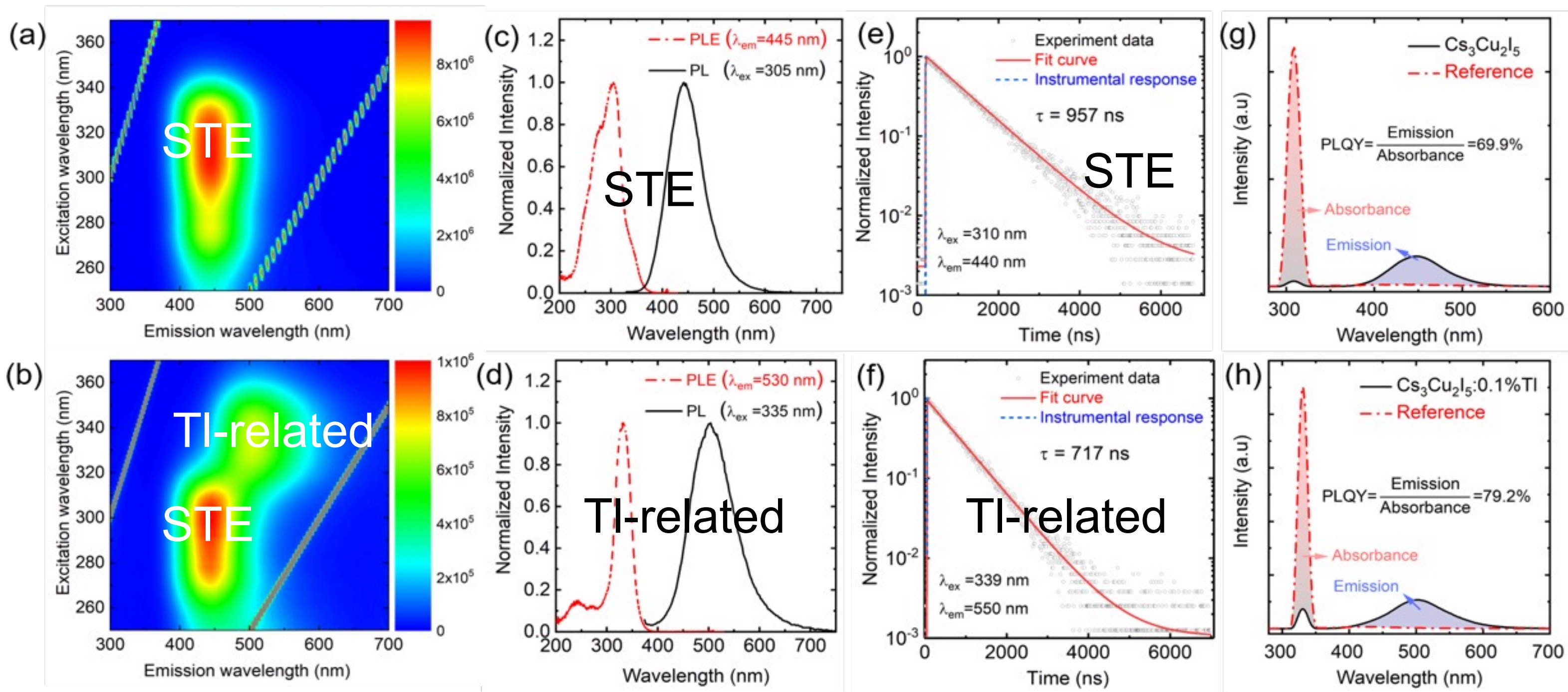




	T_{melt} (℃)	Hygroscopicity	Density (g/cm^3)
$Cs_3Cu_2I_5$	386	No	4.51

Wu,* *Advanced Optical Materials* 10 (2022) 2200304 1-8.
Wu,* *Advanced Optical Materials* 9 (2021) 2100460 1-7.
Wu,* *Physica Status Solidi (RRL)* 15 (2021) 2100422 1-4.
Wu,* *Physica Status Solidi (RRL)* 14 (2020) 2000374 1-4.

➢ Luminescence properties of $Cs_3Cu_2I_5$ and $Cs_3Cu_2I_5$:Tl

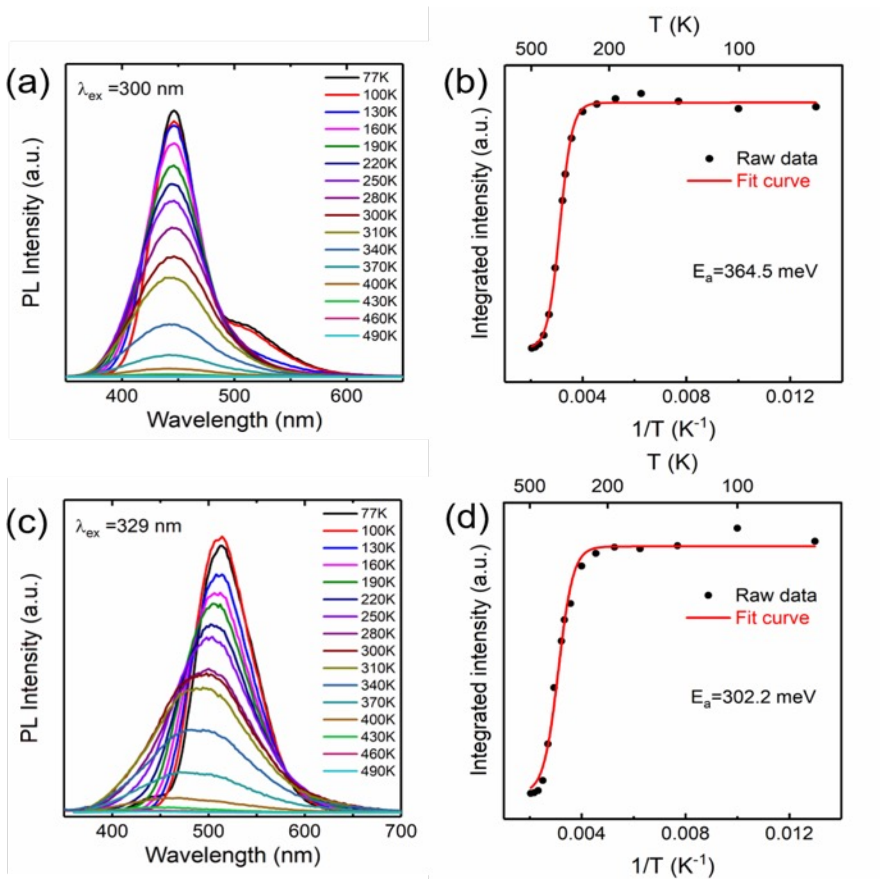


➢ PLQY increases from 70% to 79.2%

➢ Temperature dependent luminescence of undoped and Tl-doped $Cs_3Cu_2I_5$

STE emission

Tl-related emission

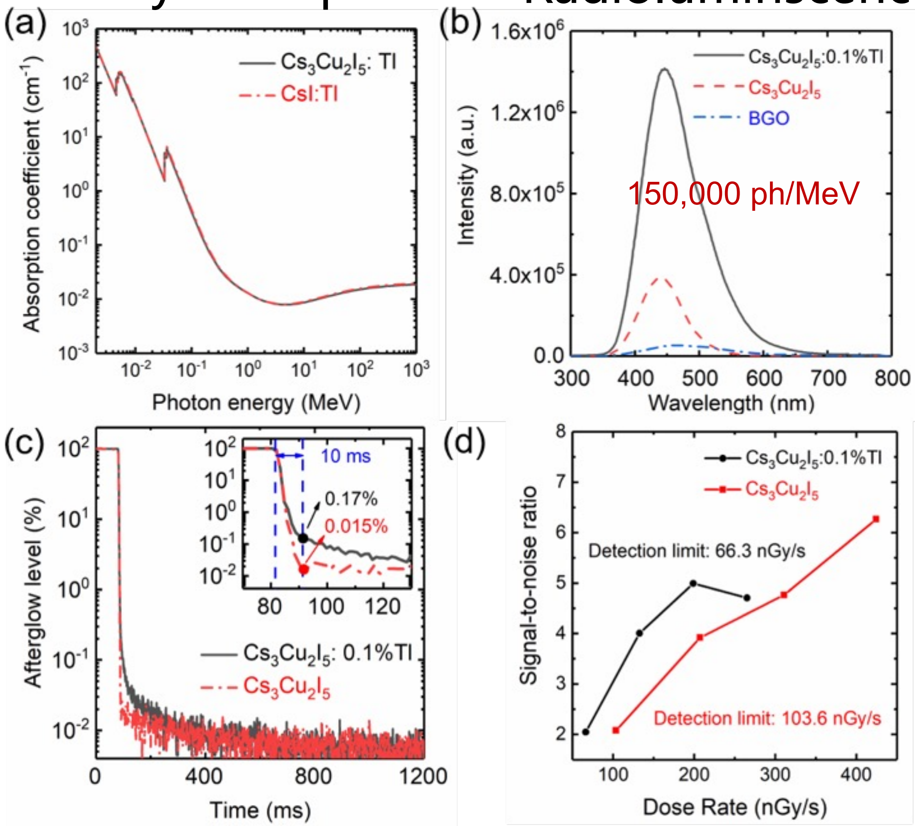


- STE bonding energy：364.5 meV
- Onset of thermal quenching around RT

- Thermal activation energy of Tl-related emission：302.2 meV
- Onset of thermal quenching around RT

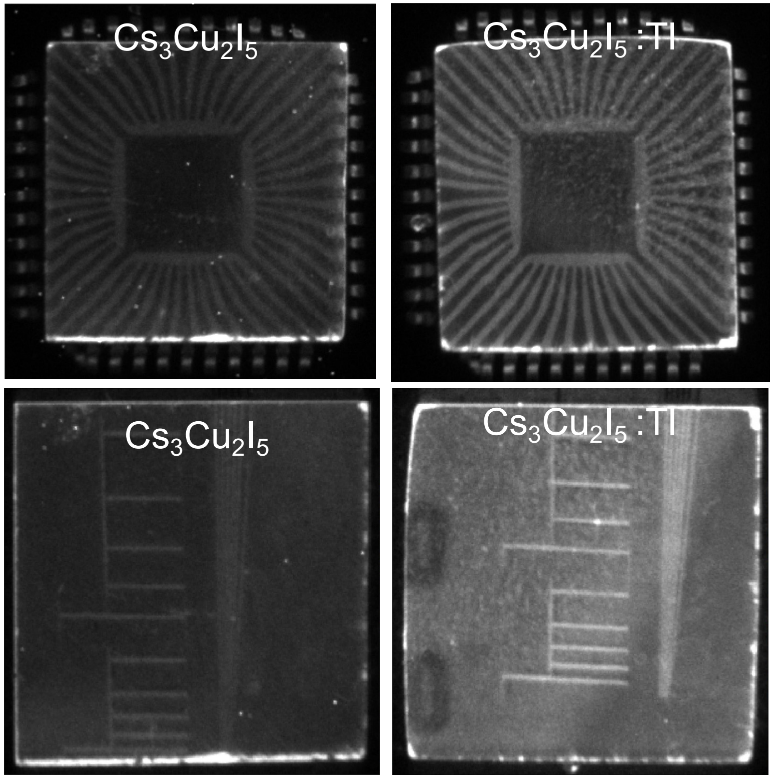
➢ Excellent X-ray detection performance of undoped and Tl doped $Cs_3Cu_2I_5$

X-ray absorption Radioluminscence

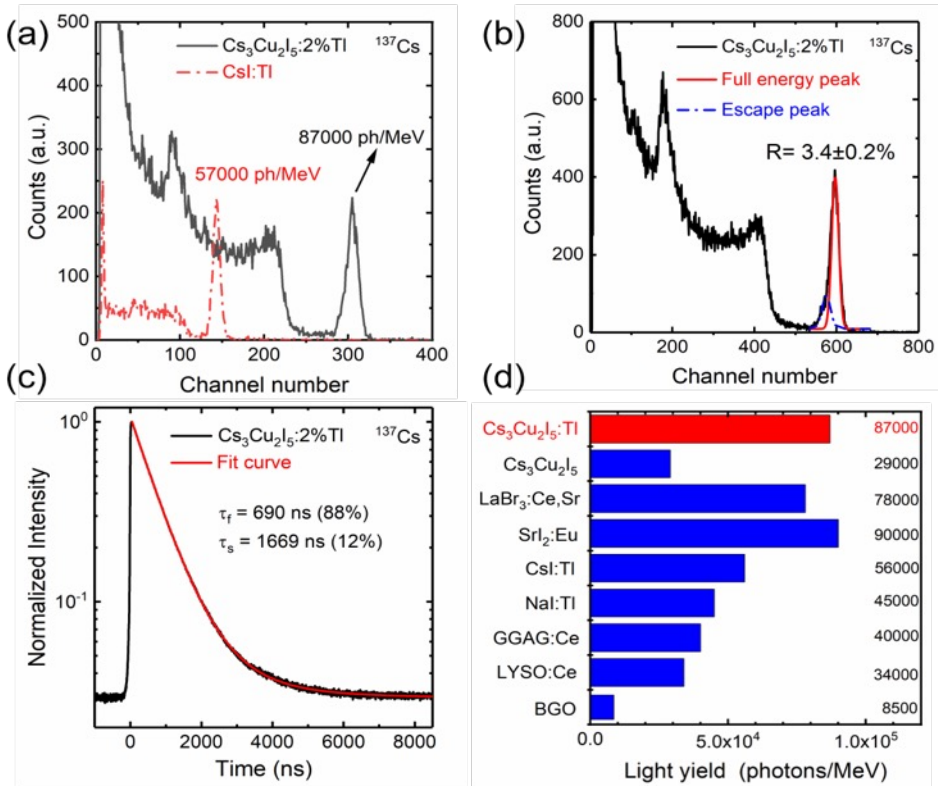


Afterglow X-ray detection limit

X-ray imaging resolution: 12 lp/mm



➢ Excellent gamma-ray detection performance of undoped and Tl doped $Cs_3Cu_2I_5$

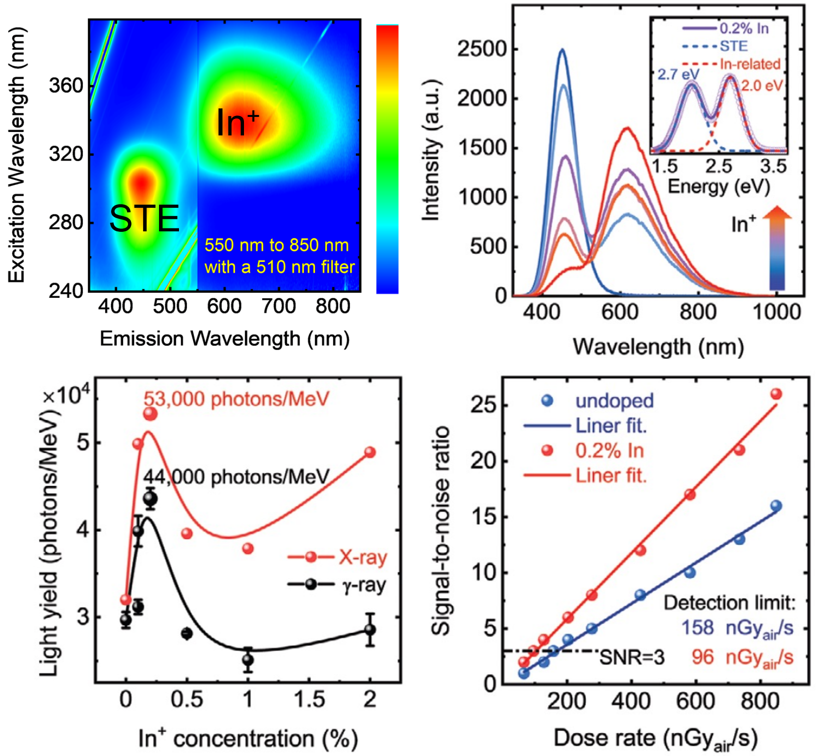


Scintillation decay   Light yield comparison

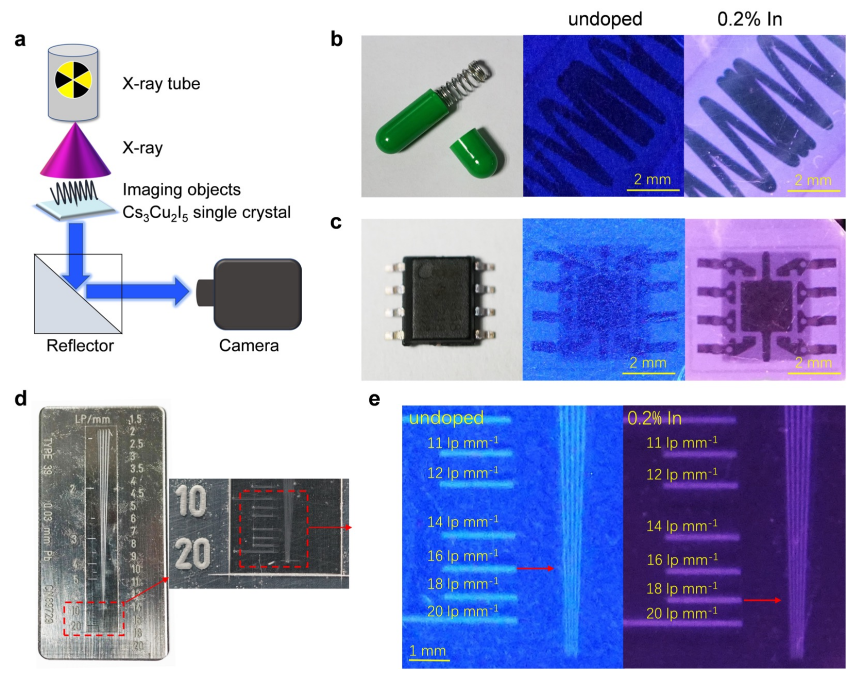
- **Light yield：87,000 ph/MeV (comparable with $LaBr_3$:Ce)**
- **Energy resolution：3.4% @ 662 keV (comparable with $CeBr_3$)**
- **Scintillation decay:** 690 ns (88%), 1669 ns (12%)

➢ 0D perovskite $Cs_3Cu_2I_5$:In

High RL efficiency (53,000 ph/MeV)
Excellent detection limit (96 nGy$_{air}$/s)

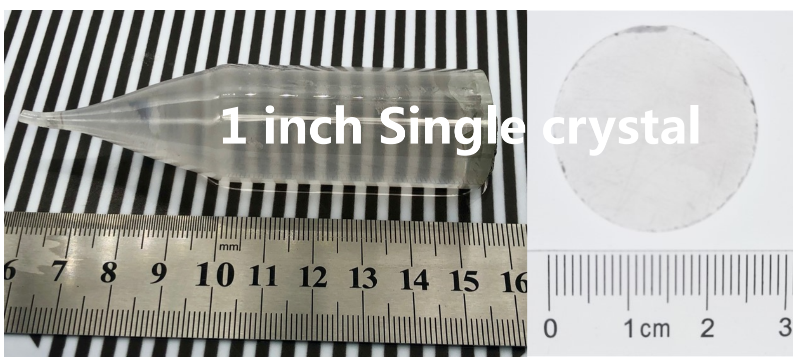


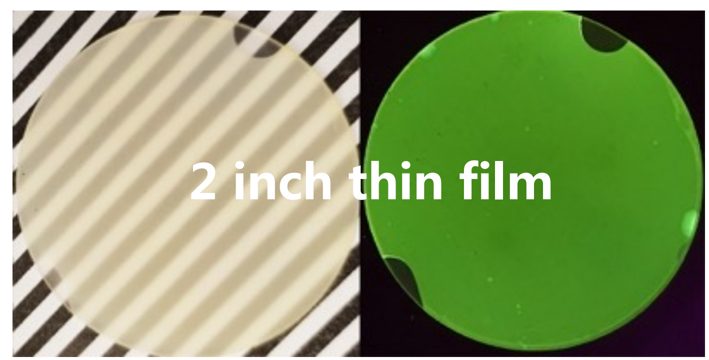
High Spatial resolution (18 lp/mm)



➢ Summary

Composition	Hygroscopicity	Density (g/cm^3)	Light yield (ph/MeV)	Energy resolution 662 keV(%)	Scintillation decay (ns)	Afterglow 10 ms (%)	X-ray detection limit (nGy/s)
$Cs_3Cu_2I_5$	No	4.51	29,000	3.4	51 (4%) 967 (96%)	0.015	103.6
$Cs_3Cu_2I_5$:In	No	4.51	53,000	6-7	556 3746	1	96.2
$Cs_3Cu_2I_5$:Tl	**No**	**4.51**	**87,000**	**3.4**	**690 (88%) 1669 (12%)**	**0.17**	**66.3**
$CeBr_3$	Strong	5.22	68,000	3.7-4.3	17	-	-
NaI:Tl	Strong	3.67	45,000	7.1	230	-	-



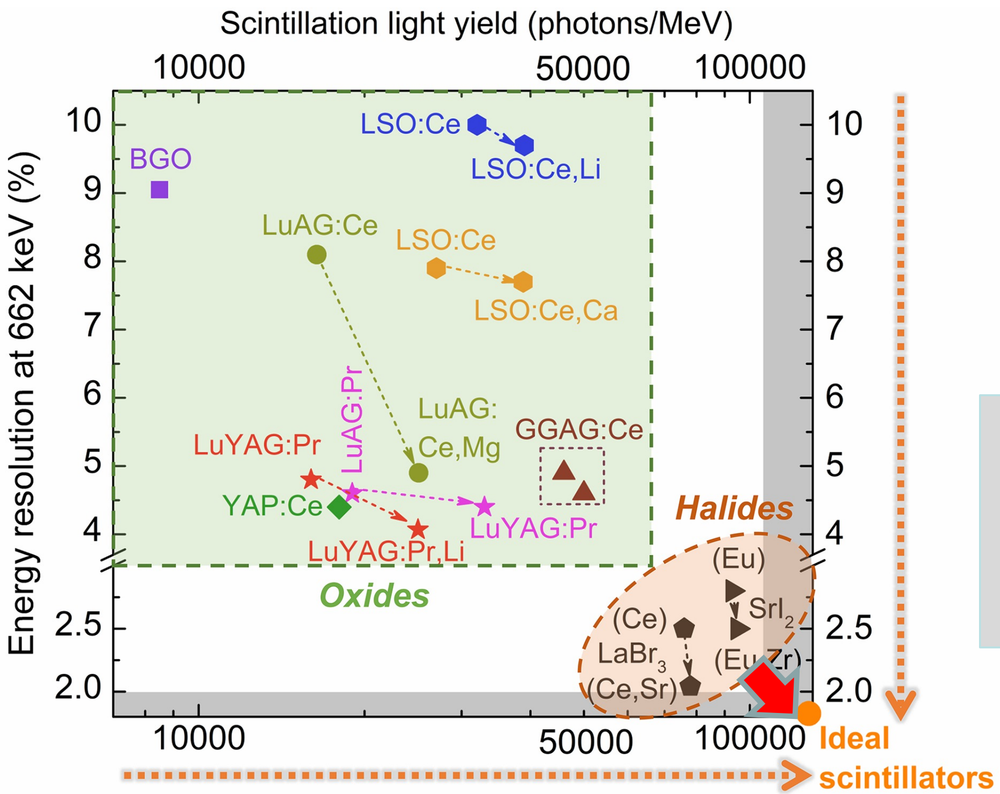


专利：PCT/CN2021/099440、202210177453.6 、202210079484.8 、202110446361.9、202010573954.7

Can Cs-Cu-I materials compete with classical NaI:Tl and CsI:Tl scintillators?

- Comparable price of raw materials and preparation process. Comparable density and Z_{eff}. Growth of large crystals is in question, not studied yet
- Not hygroscopic
- Much lower afterglow enabling the use in CT and fast framing applications
- Lower band gap (due to Cu energy levels which decrease CB bottom edge) lowers the energy to create an electron-hole pair
- Tl-doping feasible, in $Cs_3Cu_2I_5$ host reported light yield above 80 000 phot/MeV with afterglow still at least one order lower compared to CsI:Tl
- Ternary compound provides broader space for electronic band structure engineering, i.e. manipulation with the intrinsic defect/trap states

Grand Challenges for X-ray and gamma-ray detection



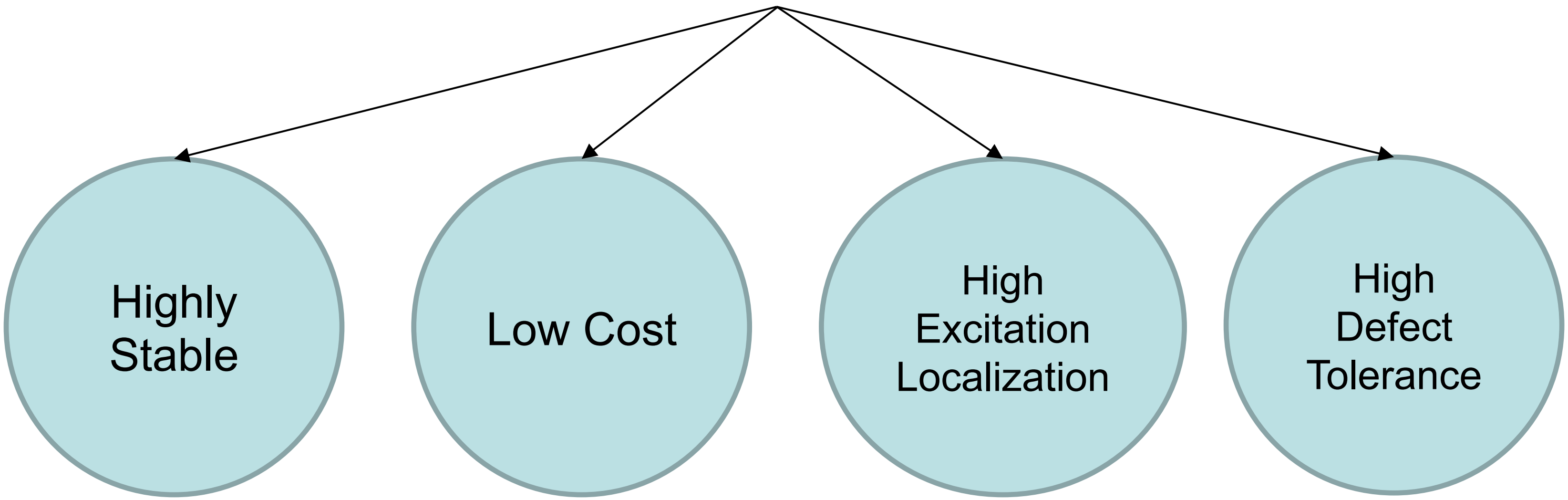
Metal halides

Light yield >100,000 ph/MeV

Energy resolution @662keV ∽ 1%?

Novel low-dimensional perovskite halides could be promising candidates toward ultra high LY and ER.

Low-dimensional Cu(I) halides



Significant potential in detecting and imaging of X-ray, γ-ray, neutron, proton…

Acknowledgment

NSFC

THE CHINESE ACADEMY OF SCIENCES

上海市科学技术委员会
（上海市外国专家局）

THANK YOU

ANY QUESTIONS?