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Growth and Characterization of $Cs_2AgBiBr_6$ Double Perovskite Single Crystals for Ionizing Radiation Detection

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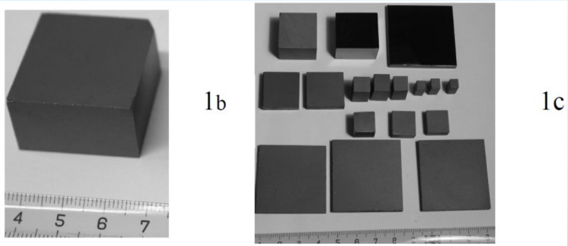
Introduction & Motivation

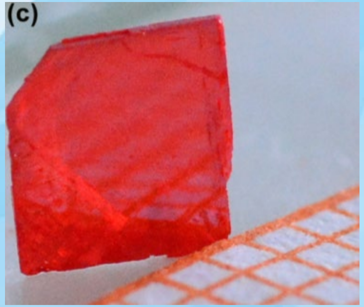
- High-Purity Germanium (HPGe) (energy resolution: ~ 0.3% at 662 keV, high cost ~ 100 K, needs cryogenic cooling)
- Cadmium Zinc Telluride (CdZnTe or CZT) (expensive, material non-uniformity, Te inclusions/precipitates)
- Thallium Bromide (TlBr) (electromigration issue of halide ions, may be solved using Tl contact)
- Mercury Iodide (HgI_2) (low carrier mobility, charge trapping, limited by crystallographic perfection)

HPGe detector (ORTEC)



CdZnTe single crystals, Li et al., 2004

TlBr semiconductor CapeSym, Inc.



α-HgI_2, Zhang et al., 2015

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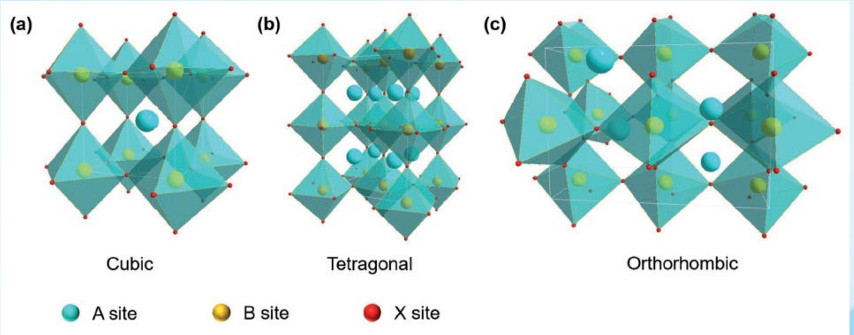
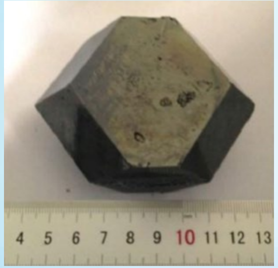
Perovskite Materials

- Common molecular formula ABX_3

Example: A=$CH_3NH_3^+$ (MA) or $CH(NH_2)_2^+$ (FA), Cs^+, B=Pb^{2+}, X=Halogen elements (e.g., Br^-, I^-, Cl^-)

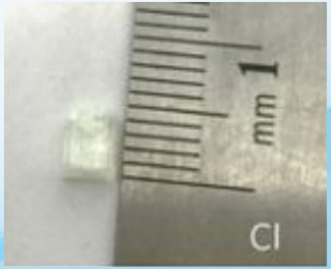


Perovskite crystal structure
Liu et al., 2018

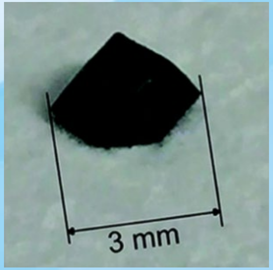


MAPbI_3
Zhang et al.

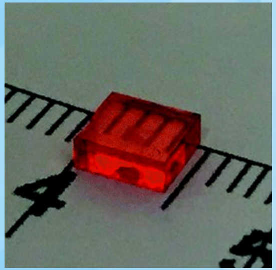
MAPbBr_3
Said et al.



MAPbCl_3
Fang et al.



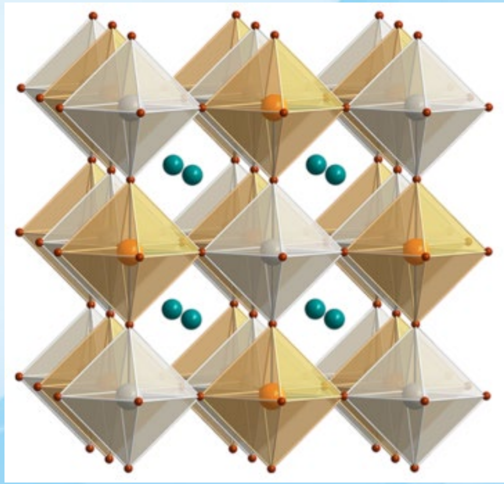
FAPbI_3
Said et al.



FAPbBr_3
Said et al.

Benefits of Perovskite Single Crystals

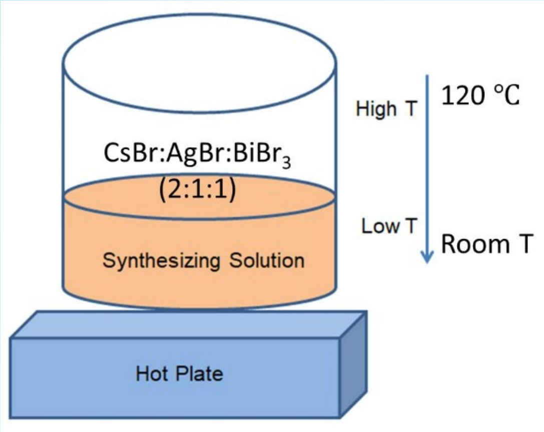
- Benefits of hybrid (organic-inorganic, MA or FA-based) perovskites:
  - Large mobility (μ)- lifetime (τ) product (~ 10^{-2} cm^2/V)
  - Low material cost (\$0.5-\$1.0 per cm^3)
  - Low density of charge traps (10^9-10^{11} cm^{-3})
  - Low dark carrier density (10^9-10^{11} cm^{-3})
  - High resistivity (10^7-10^{10} Ω·cm)
  - High density (e.g., $MAPbI_3$: 4.16 g/cm^3)
  - High average atomic number Z (e.g., $MAPbI_3$ & $FAPbI_3$: Pb=82, I=53)
  - Suitable bandgap (e.g., $MAPbI_3$: 1.51 eV, $FAPbI_3$: 1.4 eV)

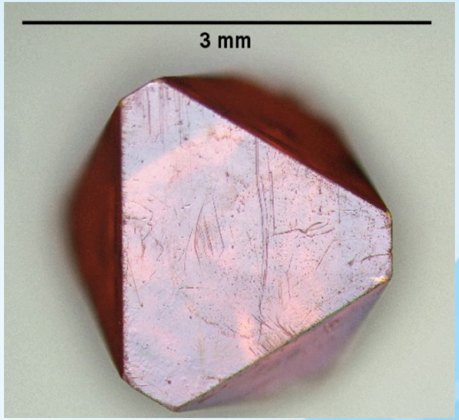


$Cs_2AgBiBr_6$ crystal structure
Slavney et al., 2016
Orange: Bi, Gray: Ag
Turquoise: Cs, Brown: Br

- Double Perovskite $Cs_2AgBiBr_6$
  - Lead-free and no organic atoms
  - No facile phase transition at room temperature

Growth of $Cs_2AgBiBr_6$ Double Perovskite

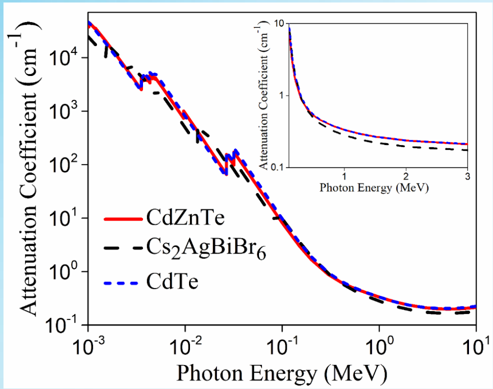


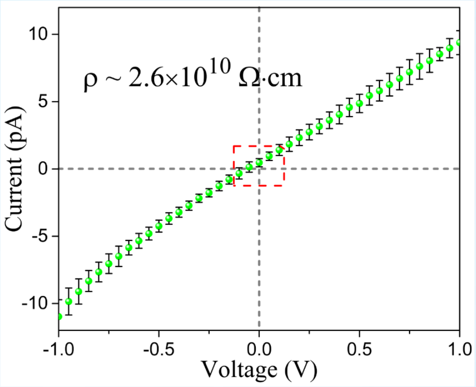


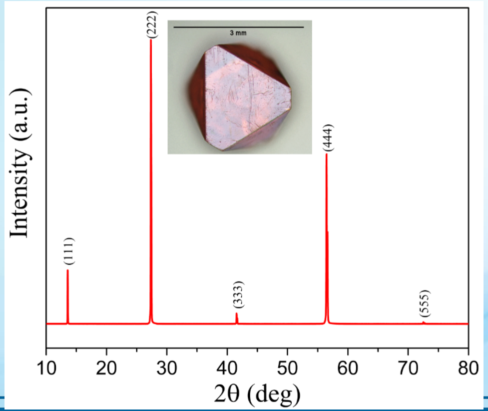
- Single crystals were harvested by filtering the solution using PTFE filters
- Crystal surfaces were rinsed with ethanol/isopropanol
- Red-brown color, 10mm×8mm×7mm (x, y, z) (the largest), octahedral shape

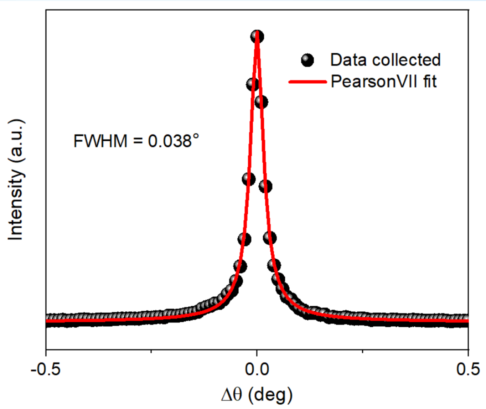
Materials Characterization

(Photon Attenuation, XRD Pattern, I-V Measurement)





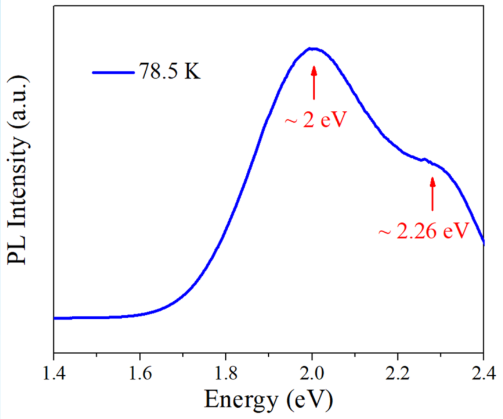


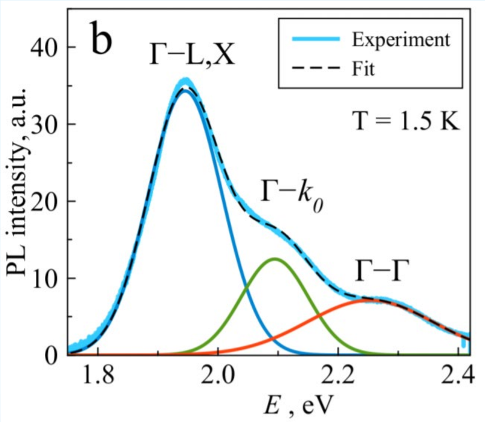


- XRD pattern matches well with the reference pattern (ICSD collection #252164)
- FWHM of 0.038° indicates the obtained $Cs_2AgBiBr_6$ single crystal has excellent crystalline quality
- Bulk crystal resistivity is estimated to be 2.6×10^{10} Ω·cm, comparable to CdZnTe

Materials Characterization

(Bandgap Energy of $Cs_2AgBiBr_6$)





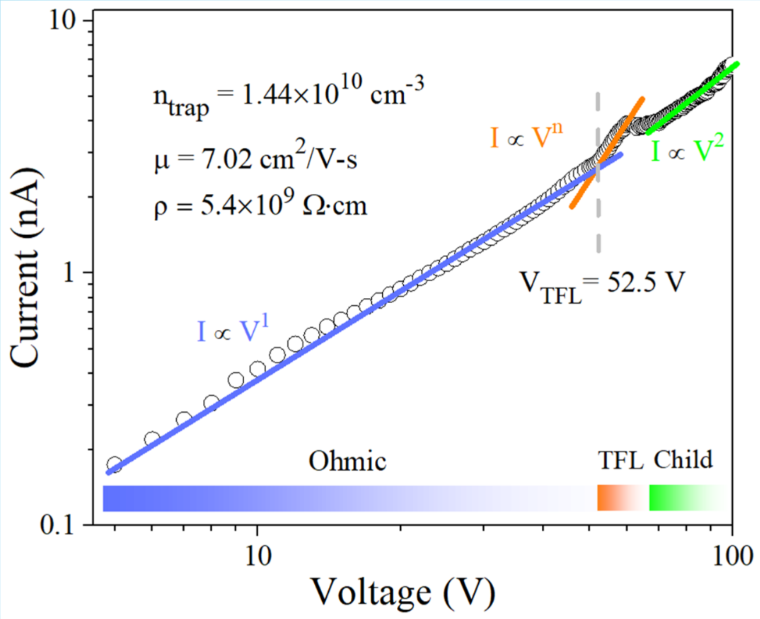
Lozhkina et al., 2017

- 2.00 eV (indirect) and 2.26 eV (direct) bandgap energies reflected by photoluminescence (PL) spectrum

	DFT modelling		PL spectra	
	E, eV	ΔE, eV	E, eV	ΔE, eV
Γ-L and Γ-X	1.782	0	1.946	0
Γ-k0	1.820	0.038	2.095	0.149
Γ-Γ	1.899	0.117	2.254	0.308

Materials Characterization

(Space Charge Limited Current (SCLC) Study)



Device Structure: Au/$Cs_2AgBiBr_6$/Au
measured at 23 ℃

Density of trap states: (1.44×10^{10} cm^{-3})

$$n_t = \frac{2\varepsilon\varepsilon_0}{eL^2}V_{TFL}$$

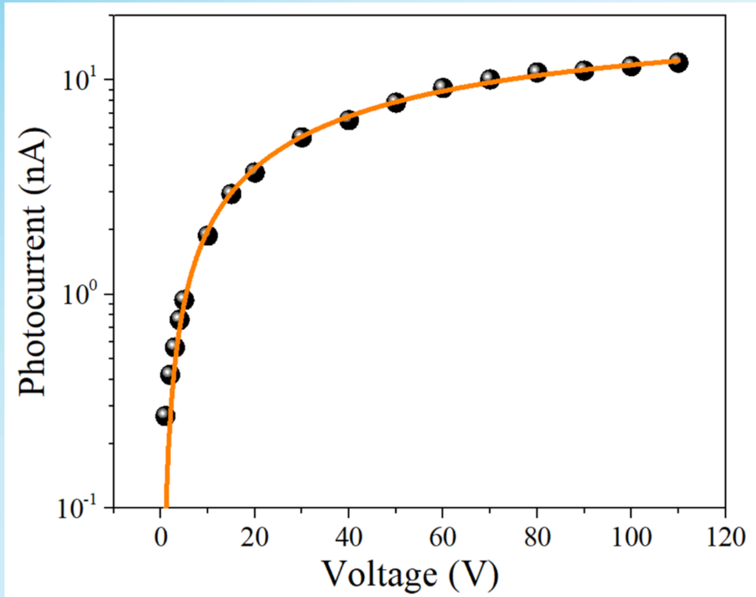
Charge carrier mobility: (7.02 cm^2/V-s)

$$\mu = \frac{8J_DL^3}{9\varepsilon\varepsilon_0V^2}$$

Very low mobility, but it is the μ-τ product that determines the charge carrier drift distance.

Materials Characterization

(Mu-Tau (μ-τ) Product)



Many's Eqn.: (or modified Hecht model)

$$I = \frac{I_0 \mu\tau V}{L^2} \frac{1 - \exp(-\frac{L^2}{\mu\tau V})}{1 + \frac{L}{V}\frac{s}{\mu}}$$

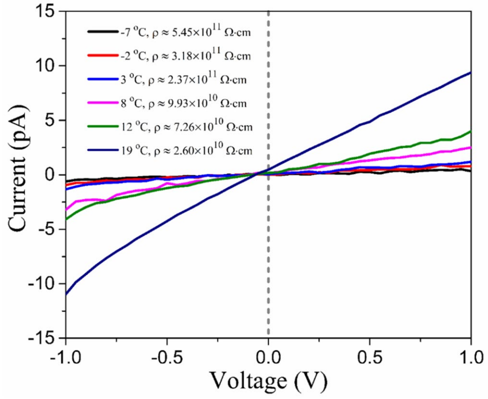
Estimated μ-τ ~ 2.48×10^{-3} cm^2/V

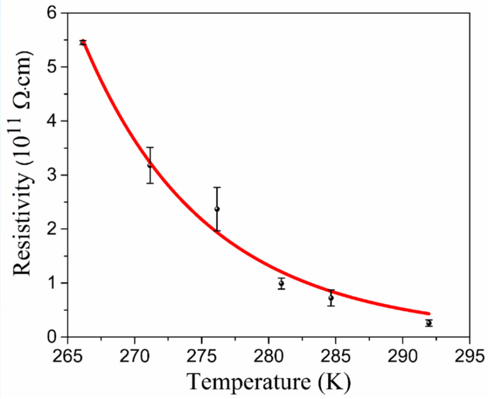
Surface recombination velocity
s ~ 2367.6 cm/s

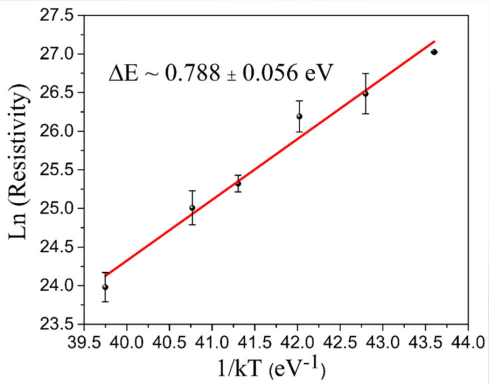
Material	μ-τ product (cm^2/V)
$Cs_2AgBiBr_6$	2.48×10^{-3}
$MAPbI_3$ (He et al.)	0.8×10^{-3}
$CsPbBr_3$ (He et al.)	~ 10^{-4}
CdZnTe (Prokesch et al.)	~ 10^{-2}

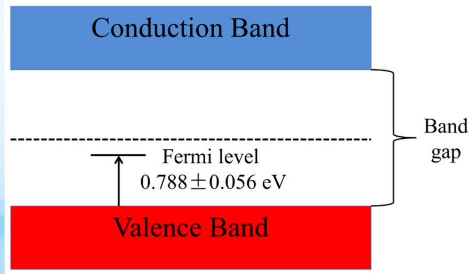
Materials Characterization

(Fermi Level)









$$\rho = \frac{1}{q(\mu_e n + \mu_h p)}$$

$$n = N_c \exp(-\frac{E_c - E_F}{kT})$$

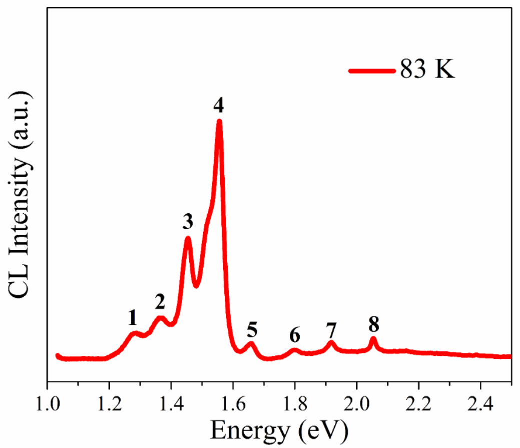
$$p = N_v \exp(-\frac{E_F - E_v}{kT})$$

$$\downarrow$$

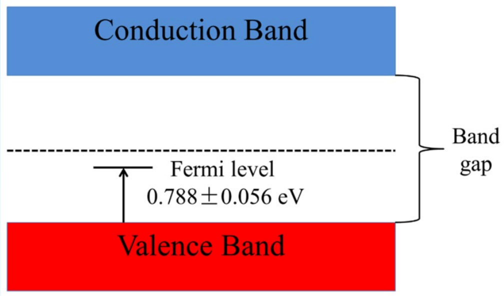
$$\ln(\rho) = \frac{\Delta E}{kT} + constants$$

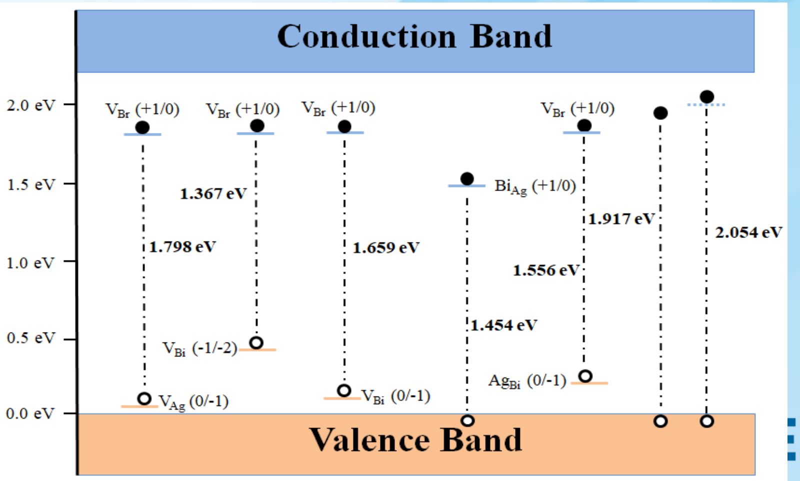
Materials Characterization

(Fermi Level Pinning)



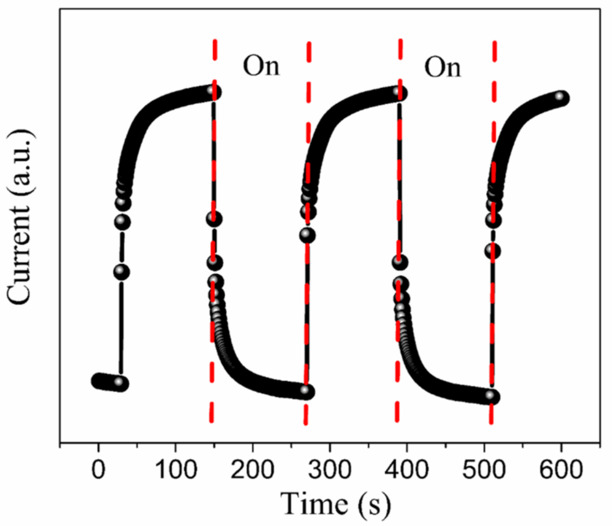
Peak Number	Energy (eV)
1	1.288
2	1.367
3	1.454
4	1.556
5	1.659
6	1.798
7	1.917
8	2.054



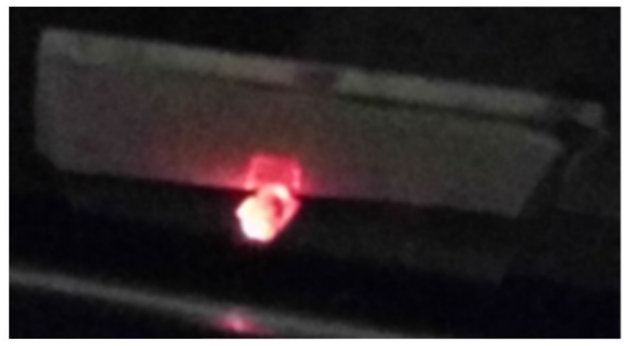


- Fermi level may have been pinned at 1.288 eV; however, this needs more studies to confirm (e.g., adopt thermal annealing technique).

Response to LED and Visible Light



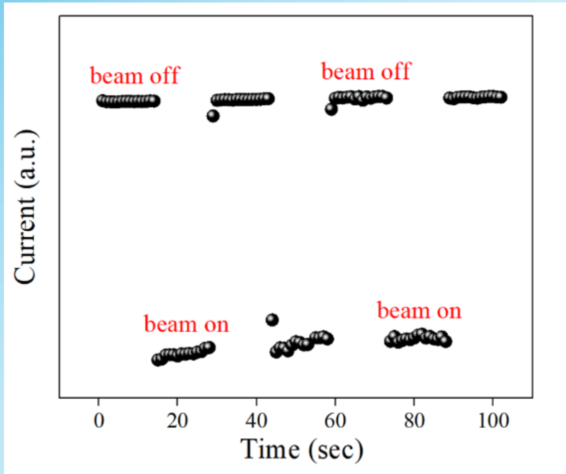
LED light at 472 nm, bias voltage -5 V

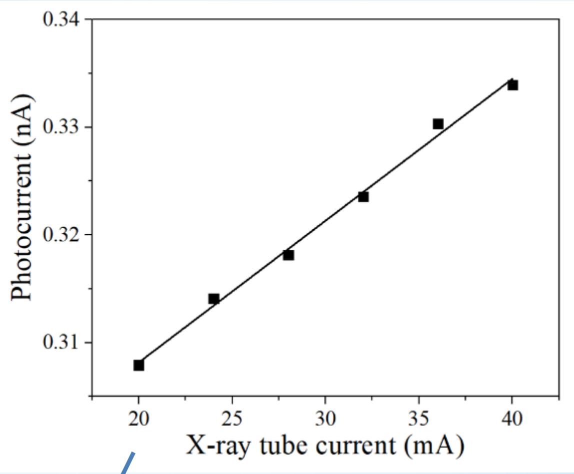


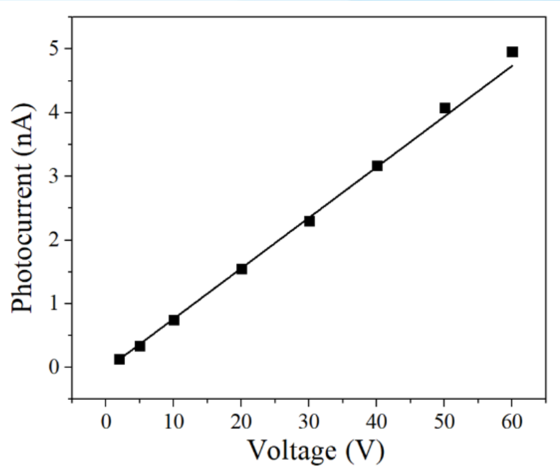
Luminescence under 400-nm visible light

- $Cs_2AgBiBr_6$ is very popular in solar cell research.
- Here, $Cs_2AgBiBr_6$ showed strong response to LED and visible light.

Response to X-Rays







Bias voltage: -5 V

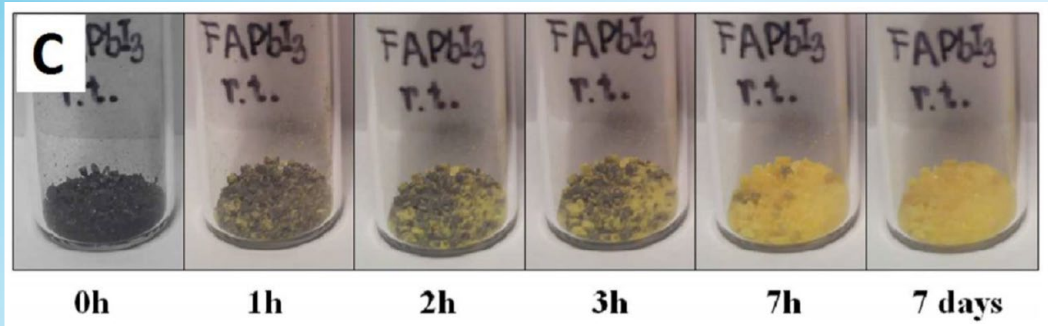
Bias voltage: +5 V

$$\text{Detector Sensitivity} = \frac{\text{Current Density}}{\text{Dose Rate}}$$

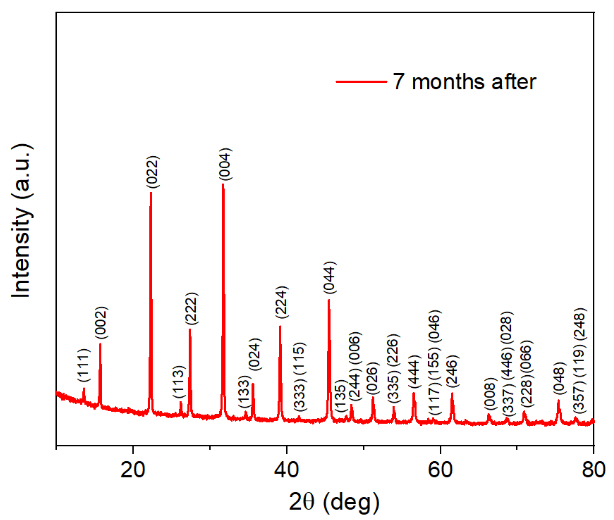
X-ray induced current in $Cs_2AgBiBr_6$ shows linear response to the variation of copper X-ray tube current (a representative of relative dose rate).

X-ray tube current is fixed at 30 mA. The detector sensitivity has increased more than 15 times from 5 V to 60 V.

Stability of the material against ambient air

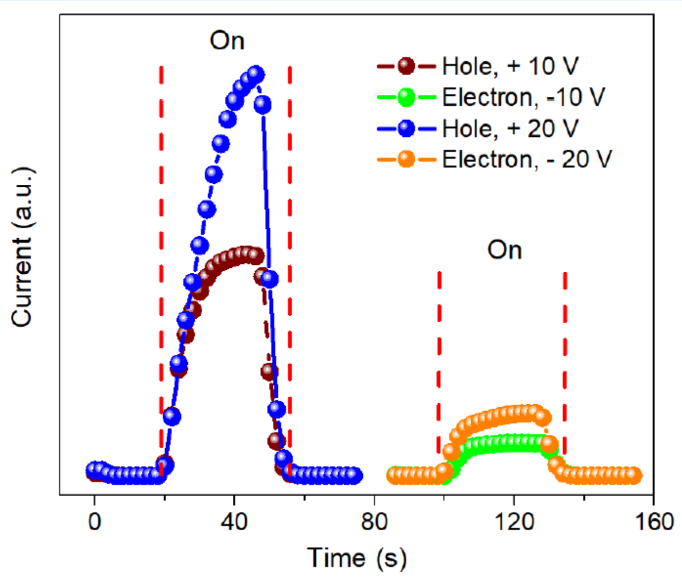


Han et al. 2016



- Excellent stability even after exposure under ambient air conditions for over six months.
(PXRD peaks were labeled according to previous report, Pan et al. 2017)

Relatively poor electron transport



- In $Cs_2AgBiBr_6$ thin films, the electron diffusion length is only 30 nm compared to >150 nm for holes (Longo et al., 2020)

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Summary and Conclusions

- $Cs_2AgBiBr_6$ showed high resistivity (10^9-10^{11} Ω·cm), comparable to CdZnTe, for room-temperature detection applications.

- Bandgap energy of $Cs_2AgBiBr_6$ may be further reduced by using cation doping and halide element substitutions.

- Excellent absorption ability to X-ray and gamma photons, low material cost (~$6/cm^3), and high response to low-energy soft X-rays render $Cs_2AgBiBr_6$ as a promising candidate as next generation semiconductor-based X-ray detector material.

- Larger $Cs_2AgBiBr_6$ single crystals is desired using the flux growth method or by adding additive to suppress the formation of multiple nucleation sites.

- The response of $Cs_2AgBiBr_6$ double perovskite single crystals to gamma-ray and alpha particles will be further explored.

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Thanks for your attention!