Supporting information

Structural Dynamics of a Novel Pseudohalide Perovskite $Cs_2Pb(SeCN)_2Br_2$ Investigated with Nonlinear Infrared Spectroscopy

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Crystal structure determination

Single crystals of $Cs_2Pb(SeCN)_2Br_2$ were kept in a N_2 atmosphere before the measurements, coated with Paratone-N® oil, and then mounted on a Kapton® loop. The data were collected using a Bruker D8 diffractometer equipped with a Photon II CMOS detector at the Stanford Nano Shared Facilities (17.445 keV Mo-Kα radiation, λ = 0.71073 Å). During the course of measurements, a flow of N_2 enveloped the crystal and the crystal didn't show signs of degradation. The unit-cell parameters were refined against all data. Frames were collected using ω and φ scans, integrated and corrected for Lorentz and polarization effects using SAINT 8.34a, and then corrected for absorption effects using SADABS V2014.[1] Space-group assignments were based on systematic absences, E-statistics, agreement factors for equivalent reflections, and successful refinement of the structures. The structures were solved by direct methods and refined against all data using the SHELXL-2014[2] software package as implemented in Olex2.[3]

Powder X-ray diffraction

The PXRD measurements were performed under ambient conditions on a Bruker D8 Advance diffractometer equipped with a Cu anode ($K\alpha_1$ = 1.54060 Å, $K\alpha_2$ = 1.54443 Å, $K\alpha_2/K\alpha_1$ = 0.5), fixed divergence slits with a nickel filter, and an LYNXEYE detector. The instrument was operated in a Bragg-Brentano geometry with a step size of 0.02°. Fine power samples were dispersed in toluene and transferred to a clean glass slide. The thin films for PXRD measurements were fabricated using the methods described in the manuscript. The measurements were conducted under ambient atmosphere and the samples were brought from the glovebox immediately prior to the measurements. The simulated powder patterns were calculated using the crystallographic files (CIFs) from single-crystal X-ray experiments or downloaded from a database.

Absorption measurements

Absorption measurements of thin films were taken using a Shimadzu UV-2600 spectrometer in transmission mode. Quartz substrates were used for thin film fabrications. Thin films of

$Cs_2Pb(SeCN)_2Br_2$ were kept sealed under N_2 until immediately before the measurement but the collection was conducted in air.

Supplementary figures and tables

Table S1. Crystallographic data for $Cs_2Pb(SeCN)_2Br_2$

Compound	$Cs_2Pb(SeCN)_2Br_2$	$Cs_2Pb(SeCN)_2Br_2$
Empirical formula	C2Br2Cs2N2PbSe2	C2Br2Cs2N2PbSe2
Formula weight (g/mol)	842.79	842.79
Temperature (K)	100	300
Crystal system	orthorhombic	orthorhombic
Space group	*Pmmn*	*Pmmn*
a (Å)	17.6784(9)	17.965(4)
b (Å)	5.9903(3)	6.0210(13)
c (Å)	6.0735(3)	6.0989(16)
Volume (Å^3)	643.18(6)	659.7(3)
Z	2	2
Density, calc. (g/cm^3)	4.352	4.243
Absorption coefficient (mm^{-1})	30.518	29.753
F(000)	712	712
Crystal size (mm^3)	0.02 × 0.02 × 0.01	0.02 × 0.02 × 0.01
Radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
2θ range (°)	6.708 to 59.142	6.680 to 61.108
Index ranges	$-23 \le h \le 24$, $-6 \le k \le 8$, $-8 \le l \le 8$	$-25 \le h \le 20$, $-8 \le k \le 8$, $-8 \le l \le 8$
Reflections collected/unique	8603/1010	9201/1136
Completeness to θ_{max}	0.997	0.998
Max. and min. transmission	0.4322, 0.2914	0.4330, 0.2788
Data/restraints/parameters	1010/0/37	1136/0/37
Goodness-of-fit on F^2	1.050	1.099
Final *R* indices [$I > 2\sigma(I)$][a]	R_1 = 0.0195 wR_2 = 0.0340	R_1 = 0.0201 wR_2 = 0.0407
R indices (all data)[a]	R_1 = 0.0258 wR_2 = 0.0363	R_1 = 0.0231 wR_2 = 0.0420
Largest diff. peak/hole (e/Å^3)	1.06, –0.94	1.274, –1.071

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$

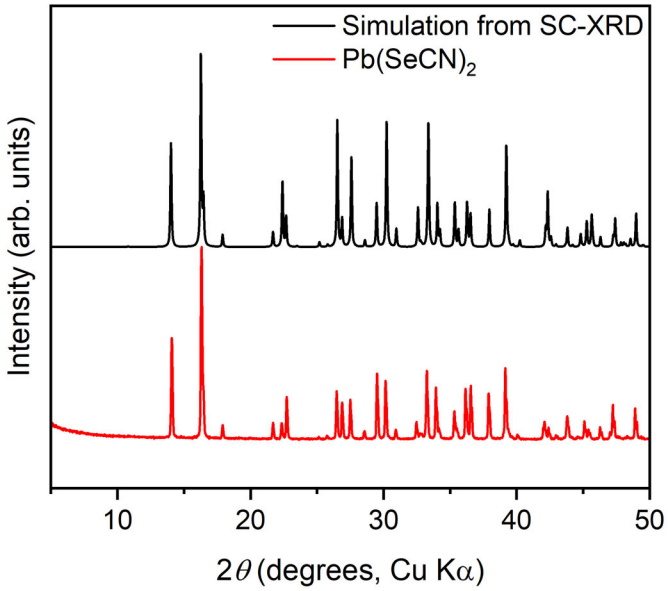

Figure S1. Experimental PXRD pattern of $Pb(SeCN)_2$, compared with the simulated pattern from SC-XRD.

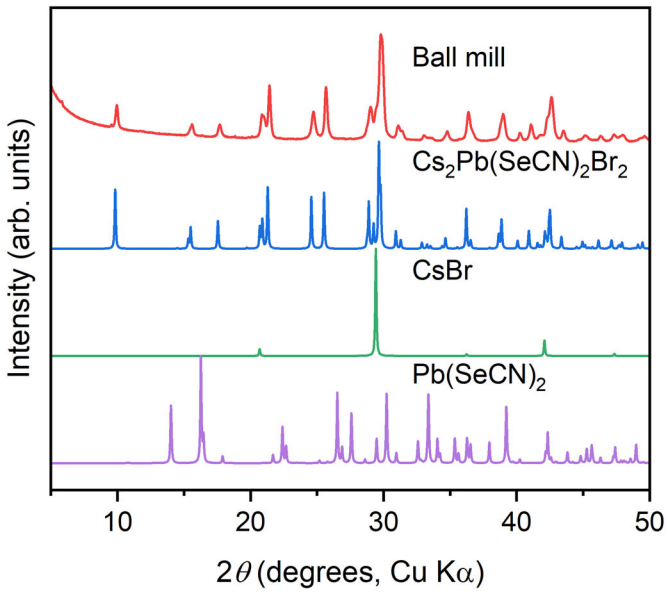

Figure S2. Experimental PXRD pattern of $Cs_2Pb(SeCN)_2Br_2$ powder synthesized by ball milling (red line), compared with the simulated patterns of the product and precursor phases.

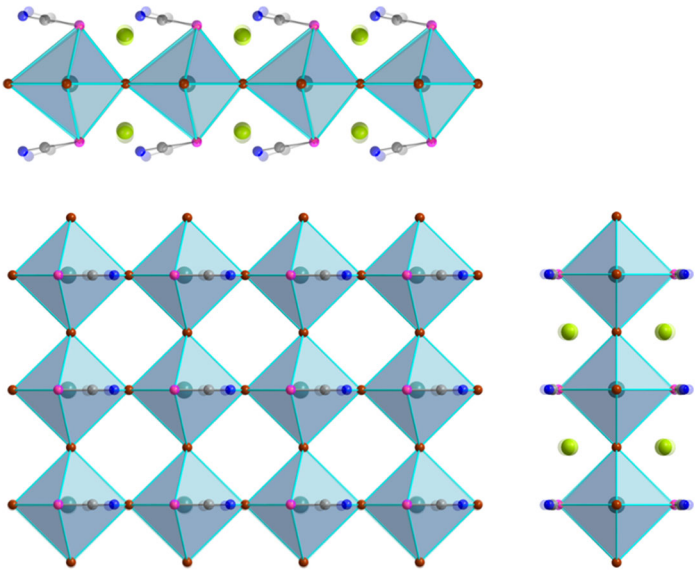

Figure S3. The overlay comparison of $Cs_2Pb(SeCN)_2Br_2$ and $Cs_2Pb(SCN)_2Br_2$ crystal structures along *a*, *b*, and *c* directions. The $Cs_2Pb(SeCN)_2Br_2$ structure is shown on the top. Green, turquoise, brown, yellow, pink, gray, and blue spheres correspond to Cs, Pb, Br, S, Se, C, and N atoms, respectively.

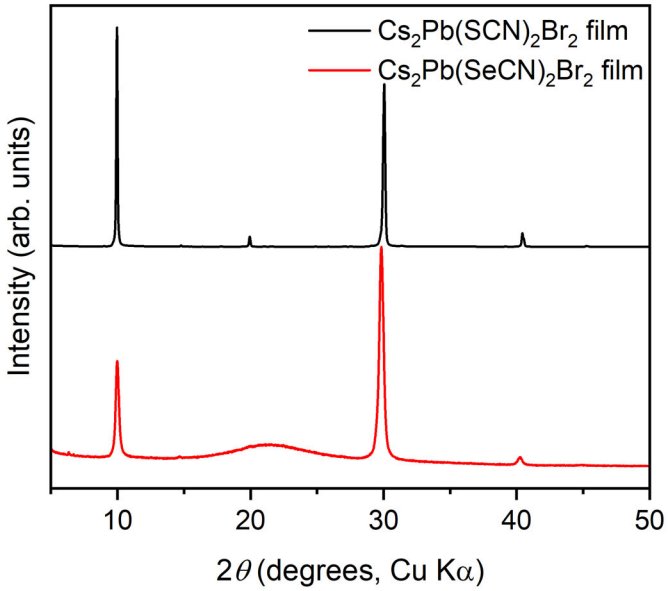

Figure S4. Experimental PXRD patterns of $Cs_2Pb(SCN)_2Br_2$ and $Cs_2Pb(SeCN)_2Br_2$ thin films.

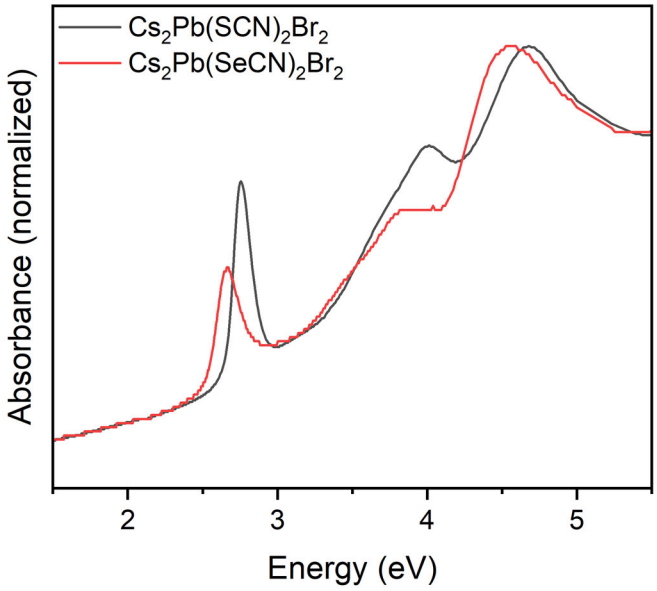

Figure S5. Absorption spectra of $Cs_2Pb(SCN)_2Br_2$ and $Cs_2Pb(SeCN)_2Br_2$ thin films.

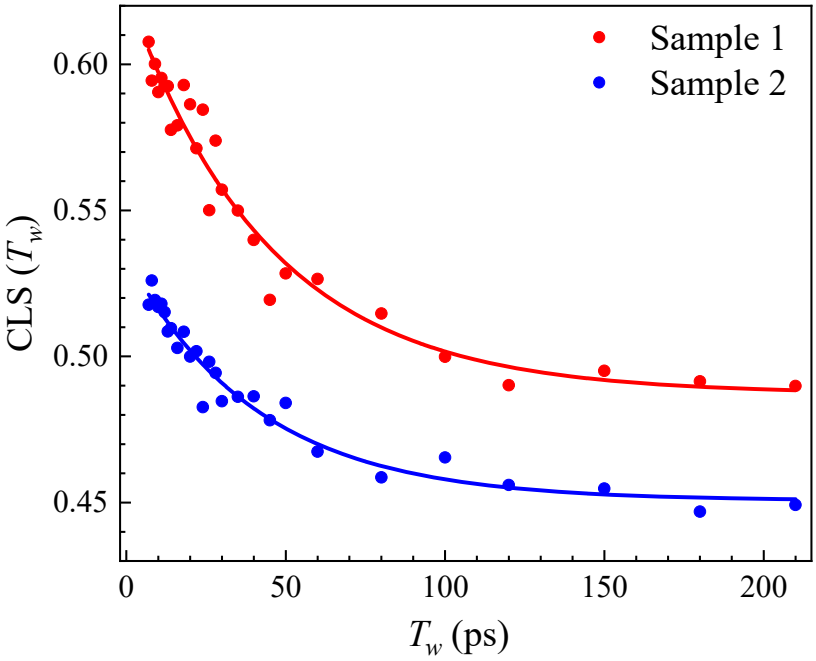

Figure S6. CLS decay curves of two individual samples. Static offsets of the CLS decay curves vary from sample to sample as shown here.

References:

(1) Bruker, APEX. SAINT and SADABS Bruker AXS Inc. *Madison, Wisconsin, USA* 2007.

(2) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* 2015, *71* (1), 3–8.

(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. a. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* 2009, *42* (2), 339–341.