

**Supporting Information: Kinetically Stable Single Crystals of Perovskite-
Phase CsPbI₃**

Daniel B. Straus, Shu Guo, and Robert J. Cava*

Department of Chemistry, Princeton University, Princeton, NJ 08544 USA

*Author to whom correspondence should be addressed. Email: rcava@princeton.edu

Methods

A stoichiometric ratio of PbI_2 and CsI are flame-sealed in a triple argon-flushed evacuated (~ 10 mTorr) quartz tube and heated at 550 °C for several hours, forming a dark purple melt. To form $\gamma\text{-CsPbI}_3$, the melt is slowly cooled at a rate of $2\text{-}9$ °C/hr to 370 °C and then quickly quenched in an ice-water bath, resulting in a shiny black solid. To directly synthesize $\delta\text{-CsPbI}_3$, the melt is cooled to room temperature at a rate of $2\text{-}4$ °C/hr. Kinetically stable $\gamma\text{-CsPbI}_3$ only forms when dry PbI_2 and CsI are used; we use ultra-dry PbI_2 (Alfa-Aesar, 99.999%) either without further purification or further purified by vapor transport, and either anhydrous CsI (Sigma-Aldrich, 99.999%) without further purification or CsI (Alfa Aesar, 99.999%) that is dried by placing the CsI in a quartz tube, flame melted under dynamic vacuum, sealed in an evacuated quartz ampoule with a piece of graphite to absorb residual moisture, heated to 650 °C overnight, and subsequently cooled to room temperature. The not-completely-anhydrous reagents used to synthesize the $\gamma\text{-CsPbI}_3$ shown in Figure 3A are CsI (Alfa Aesar, 99.999%) and PbI_2 (Alfa Aesar, 99.9985%) used without additional purification. All reagents are stored in an argon glove box with O_2 and H_2O levels ≤ 0.1 ppm

To acquire SCXRD data on $\gamma\text{-CsPbI}_3$, an evacuated quartz ampoule containing $\gamma\text{-CsPbI}_3$ synthesized using dry reagents is opened in an argon glove box. $\gamma\text{-CsPbI}_3$ is placed in degassed Parabar 10312 oil and removed from the glove box in a sealed vial. When selecting crystals for SCXRD, dry nitrogen flows over the crystals.

SCXRD data on are collected at 295 K on $\gamma\text{-CsPbI}_3$ with a Bruker Kappa Apex2 CCD diffractometer and on $\delta\text{-CsPbI}_3$ with a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector. An Oxford Cryostream 700 flows dry nitrogen at 295 K over the crystal during collection. Graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) is used. The raw

data are corrected for background, polarization, and the Lorentz factor and multi-scan absorption corrections are applied. The structures are analyzed by the Intrinsic Phasing method provided by the ShelXT structure solution program¹ (δ -CsPbI₃) or ShelXS structure solution program (γ -CsPbI₃)² and refined using the ShelXL least-squares refinement package with the Olex2 program.^{3,4} The ADDSYM algorithm in PLATON is used to double check for possible higher symmetry.⁵

UV-Visible diffuse-reflectance spectra are collected in an Agilent Cary 5000 spectrometer using an Agilent Internal DRA-2500 diffuse reflectance accessory on powders diluted with dry MgO to 10% w/w. Dry MgO is used as the reflectance standard. Data are taken every 1 nm with a 0.2 second integration time and a spectral bandwidth of 2 nm. For the data shown in Figure 2B, scans are taken every 2 minutes. Diffuse reflectance spectra are converted to absorption spectra using the Kubelka-Munk function. Band gaps are calculated using the algorithm in Ref. 6. Raman spectra are taken on a Thermo-Fisher DXR Smart Raman instrument with a 780 nm HP laser. Powder X-ray diffraction (PXRD) patterns are taken on a Bruker D8 Advance Eco with a Lynxeye 1D detector. A Bruker air-free sample holder is modified to flow gases over the powder in-situ (Figure S5). Rietveld refinements are performed using Topas 5⁷ using the SCXRD structures reported herein with lattice parameters fixed and instrumental corrections allowed to vary.

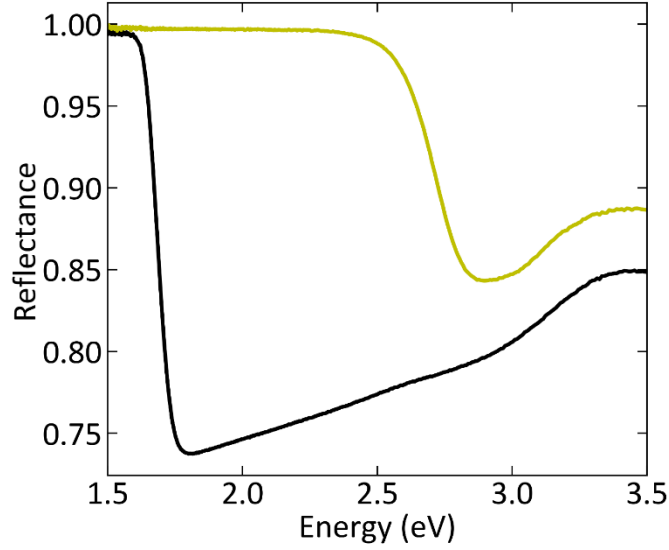


Figure S1: Reflectance spectra of (black) γ -CsPbI₃ and (yellow) δ -CsPbI₃.

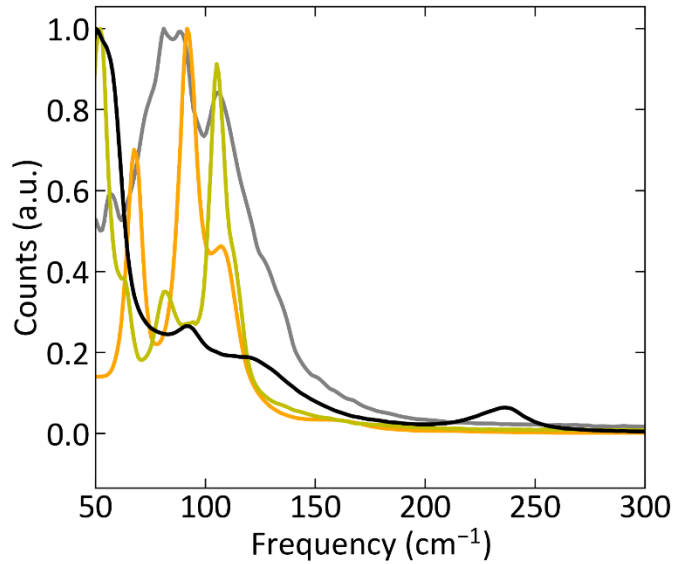


Figure S2: Raman scattering spectra for (black) γ -CsPbI₃, (yellow) δ -CsPbI₃, (grey) CsI, and (orange) PbI₂. γ -CsPbI₃ shows Raman scattering to about 150 cm⁻¹, with an additional peak at ~240 cm⁻¹ that is likely a second order replica caused by quasi-resonant 1.59 eV excitation.^{8,9}

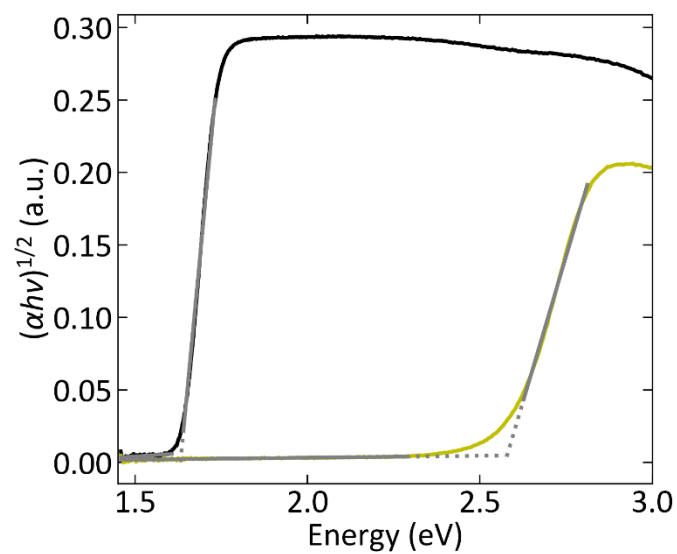


Figure S3: Direct band gap allowed transition Tauc plots of (black) γ -CsPbI₃ and (yellow) δ -CsPbI₃.

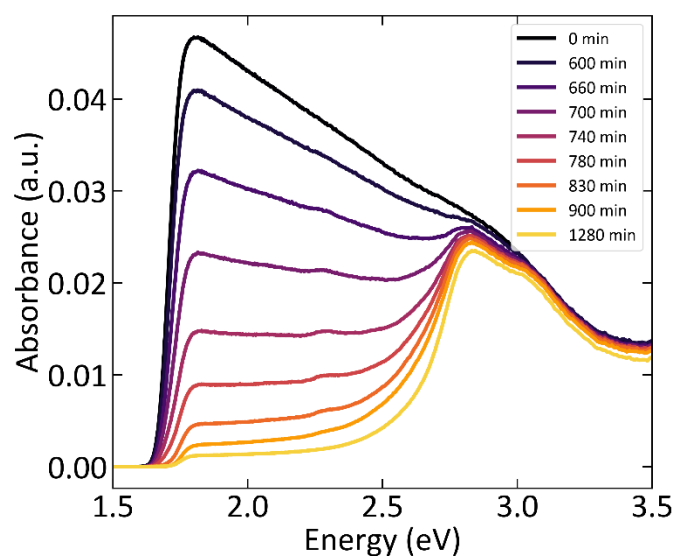


Figure S4: Select absorption spectra from Figure 2B.

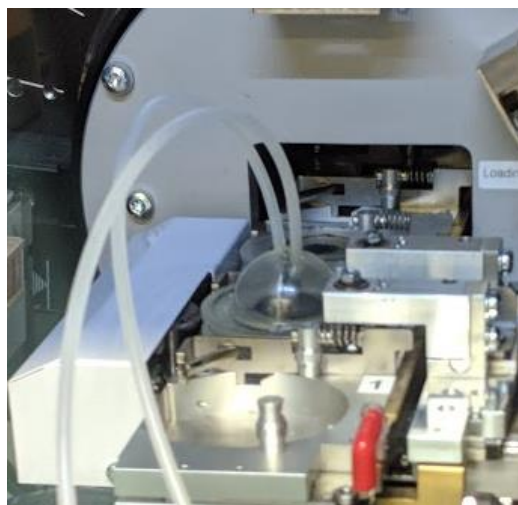


Figure S5: Sample holder for in-situ gas flow during PXRD experiments.

Table S1: Collection parameters for SCXRD structures

	γ -CsPbI ₃	δ -CsPbI ₃
F(000)	1184	1184
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/°	5.76 to 56.56	6.02 to 55.042
Index ranges	-11 \leq h \leq 11, -16 \leq k \leq 16, -9 \leq l \leq 11	-13 \leq h \leq 13, -6 \leq k \leq 6, -23 \leq l \leq 23
Reflections collected	7193	31390
Independent reflections	1231 [R _{int} = 0.0541, R _{sigma} = 0.0478]	1145 [R _{int} = 0.0591, R _{sigma} = 0.0173]
Data/restraints/parameters	1231/0/28	1145/0/31
Largest diff. peak/hole / e \AA^{-3}	1.61/-1.84	0.95/-0.65

Table S2: Fractional atomic coordinates (\AA) and equivalent isotropic displacement parameters (\AA^2)

Atom	γ -CsPbI ₃				Atom	δ -CsPbI ₃			
	x	y	z	U(eq)		X	y	z	U(eq)
Pb1	0	0	0	0.03112(13)	Pb1	0.66034(2)	0.75000	0.43800(2)	0.02803(8)
Cs1	0.43839(17)	0.25000	0.02006(17)	0.0786(4)	Cs1	0.58430(4)	0.25000	0.17092(2)	0.03520(11)
I1	0.50303(16)	0.25000	0.56458(16)	0.0700(4)	I1	0.46809(4)	0.25000	0.38549(2)	0.02938(11)
I2	0.19871(9)	0.03272(7)	0.30445(9)	0.0550(2)	I2	0.79913(4)	0.75000	0.28721(2)	0.03251(11)
					I3	0.83673(4)	0.25000	0.50160(2)	0.03143(11)

References

- (1) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8.
- (2) Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122.
- (3) Sheldrick, G. M. Crystal Structure Refinement with SHELXL . *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.
- (4) 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. Crystallogr.* **2009**, *42*, 339–341.
- (5) Spek, A. L. Single-Crystal Structure Validation with the Program PLATON . *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
- (6) Suram, S. K.; Newhouse, P. F.; Gregoire, J. M. High Throughput Light Absorber Discovery, Part 1: An Algorithm for Automated Tauc Analysis. *ACS Comb. Sci.* **2016**, *18*, 673–681.
- (7) Coelho, A. A. TOPAS and TOPAS-Academic : An Optimization Program Integrating Computer Algebra and Crystallographic Objects Written in C++. *J. Appl. Crystallogr.* **2018**, *51*, 210–218.
- (8) Nakashima, S. Raman Study of Polytypism in Vapor-Grown PbI₂. *Solid State Commun.* **1975**, *16*, 1059–1062.
- (9) Scott, J. F.; Leite, R. C. C.; Damen, T. C. Resonant Raman Effect in Semiconductors. *Phys. Rev.* **1969**, *188*, 1285–1290.