High Pressure Research At GSECARS 13-BM-C After The APS Upgrade

Dongzhou Zhang[1], Vitali Prakapenka[1], Stella Chariton[1], Young-Jay Ryu[1], Peter Eng[1], Joanne Stubbs[1], Mark Rivers[1]

[1]GeoSoilEnviroCARS, University of Chicago, Argonne, IL 60439, USA

Abstract

The GSECARS 13-BM-C beamline at the Advanced Photon Source has been providing crystallographic research capabilities to the high pressure community since 2015. This beamline utilizes focused X-rays at two fixed energies: 15 and 29 keV, and a unique 6-circle heavy duty diffractometer. The instrument is optimized for a variety of advanced crystallography experiments including interface studies, powder and single crystal structure determination, equation of state studies and atomic dynamics research. Currently we support high-pressure and variable-temperature experiments using diamond anvil cells, resistive-/laser-heating and cryostats. We have achieved P-T conditions of 100 GPa and 150-3000 K. Results of multiple recent experiments, including powder and single crystal diffraction over a range of P-T conditions, equations of state and atomic dynamics will be presented to demonstrate the experimental capabilities. These new capabilities are available to all researchers interested in studying deep earth materials through the APS General User Proposal system.

Science case 1: High pressure crystal structure of $CsPbBr_3$ (Zhang et al., 2024, 10.1038/s42004-024-01265-5)

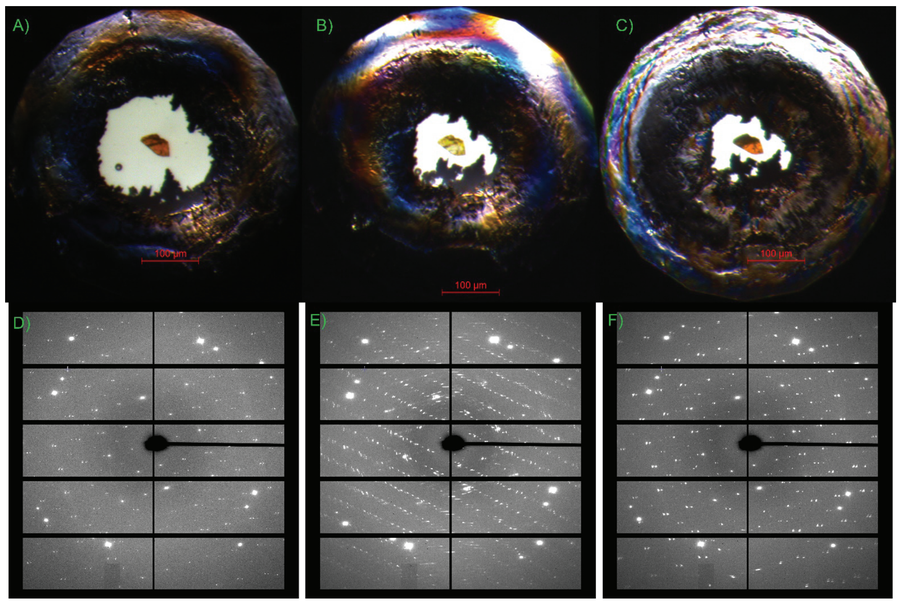


Figure 1. Optical images (top) and corresponding merged diffraction images (bottom) of $CsPbBr_3$ at various pressures. Sample is located at the center of the Re-gasket hole and a small piece of ruby sphere is located close to the sample as pressure marker. A&D): 0.27 GPa (right after gas loading). B&E): 2.08 GPa (right after the structural transition). C&F): 1 bar after decompression.

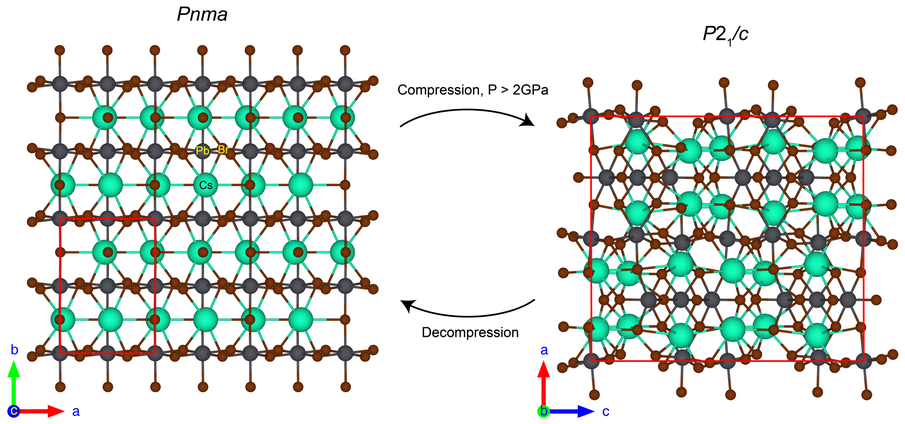


Figure 2. Crystal structure of the low pressure (left) and high pressure (right) crystal structures of $CsPbBr_3$ determined from single crystal X-ray diffraction. The red boundaries indicate the unit-cell of each phase.

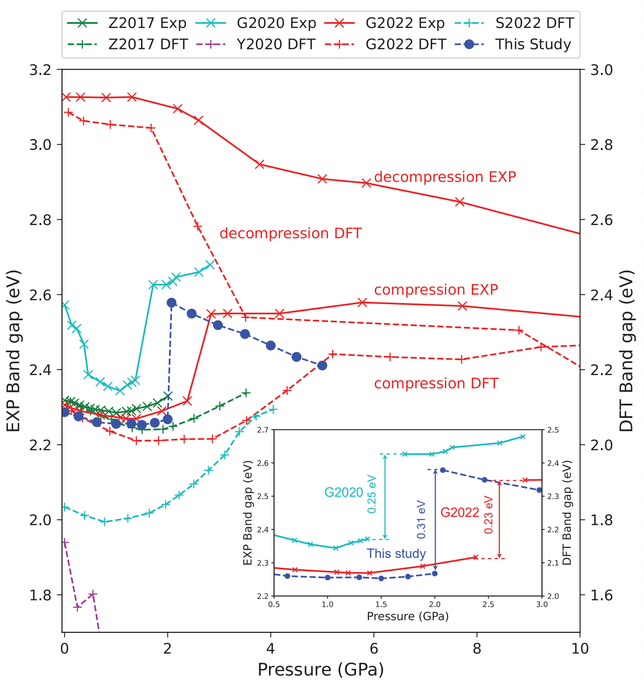
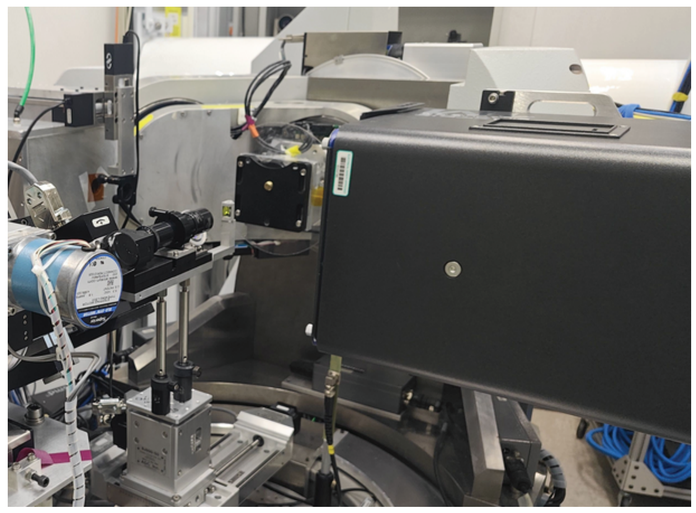
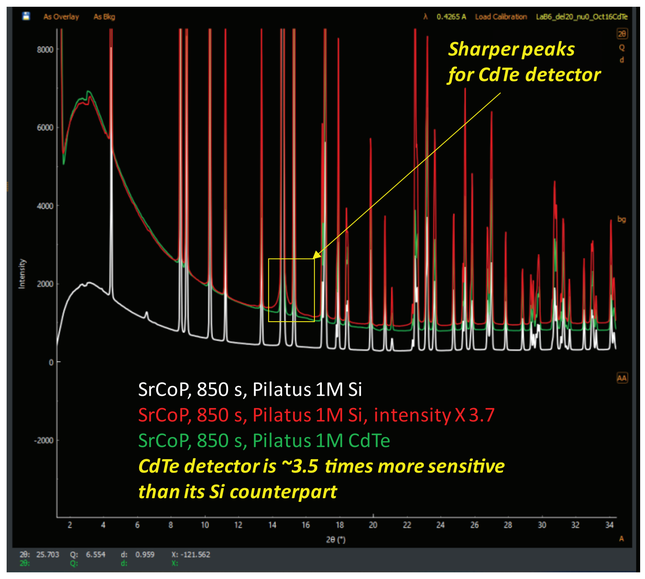


Figure 3. Experimentally determined and DFT computed electronic band gap of $CsPbBr_3$ as functions of pressure. Plus-signs and dashed curves: results from DFT calculations. Multiply-signs and solid curves: results from experimental measurements. Blue circles: band gap determined from this study using experimentally determined crystal structure as the initial structure for DFT calculations. Note the band gap from DFT (right axis) is shifted by 0.2 eV up relative to the band gap measured by experiments (left axis) to highlight the consistency between different studies. Inset: Comparison between the band gap jump across the transition boundary in this study (blue) and two experimental measurements.

New instrument: Pilatus3X 1M Cd-Te detector





Science case 2: Si isotope fractionation in mantle silicates (Zhang et al., 2025, 10.1029/2023GL107954)

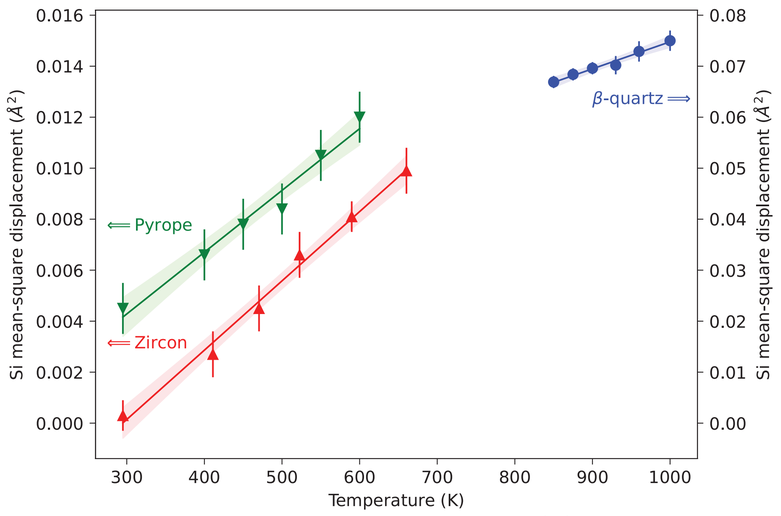


Figure 4: The Si atomic mean square displacement $\langle u^2 \rangle$ as a function of temperature determined by the high-T XRD experiments from this study. Best linear fits and fitting error ranges are shown as the straight lines and shaded regions.

Atomic force constant is the physical quantity that describes the restoring force that exerts on an atom when the atom is displaced from its equilibrium position. There are two different kinds of force constants, namely the resilience and the stiffness.
Resilience (Nr) is defined as:

$$N_r = \frac{k_B}{d\langle u^2 \rangle / dT}$$

where k_B is the Boltzmann constant, $\langle u^2 \rangle$ is the atomic mean square diplacement, which is measureable from single crsytal X-ray diffraction.

Stiffness (Ns) is defined as:

$$N_s = \int M \left(\frac{E}{\hbar}\right)^2 D(E) dE$$

where M is the atomic mass the isotope, ħ is the reduced Planck constant and D(E) is the partial phonon density of states.

Ns is used to calculate the isotope fractionation β-factor [Dauphas et al., 2018]:

$$ln\beta_{l/l^*} = \left(\frac{\hbar^2}{8k_B^2}\frac{N_s}{T^2} - \frac{5\hbar^4}{2016k_B^4 M}\frac{N_s^2}{T^4} + \frac{25\hbar^6}{326592k_B^6 M^2}\frac{N_s^3}{T^6}\right)\left(\frac{1}{M^*} - \frac{1}{M}\right)$$

In our earlier work [Zhang et al., 2021], we have established an empirical relationship between Ns and Nr for tetracoordinated Si in crust and mantle silicates:

$$\frac{N_r}{N_s} = 1.63 \times 10^{-3} N_r - 5.20 \times 10^{-3}$$

After calculating Ns from Nr using the calibration above, Ns will be further corrected by:

$$N_{sC} = N_s \times \frac{\mathrm{ECoN}}{4}$$

where ECoN is the effective coordiation number. Using these equations, we can compute the isotope fractionation β-factor of Si from single crystal X-ray diffraction data collected from crust and mantle silicates at various temperatures.

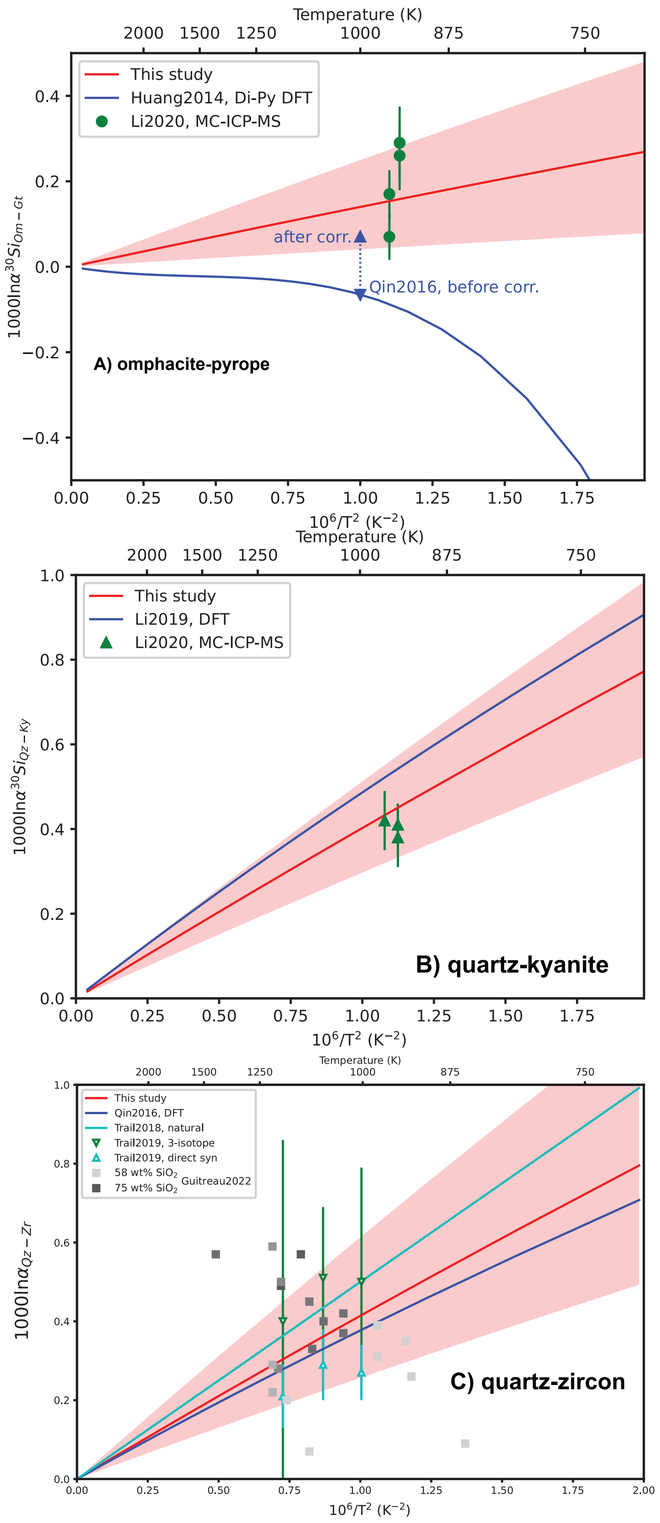


Figure 5: Equilibrium Si isotope fractionation between A) omphacite and pyrope, B) quartz and kyanite and C) quartz and zircon. Red curve: force constants approach. Red shaded region: uncertainty range of the force constants approach, determined from the distribution of the resiliences of the two minerals. Blue curve: DFT calculations. Green/cyan triangles: mass spectroscopy measurements. C) Cyan curve: estimation from mass spectroscopy measurements on natural sample [Trail et al., 2018]. Grey squares: Si isotope fractionation between natural zircon and host granite, [Guitreau et al., 2022]. The shades of grey indicate the SiO_2 content in the whole granite (58-75 wt%).

Acknowledgements

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