ESRF	**Experiment title:** Quasi in-situ investigations of the redox reaction of $Cs_2PdX_4 \cdot I_2$ (X=Cl,Br,I) to $Cs_2PdX_4I_2$	**Experiment number**: CH-1086
Beamline: ID30	**Date of experiment**: from: 30. May 2001 to: 2. June 2001	**Date of report**: 20.11.2006
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Report:

Parts of this work have been published in Zeitschrift für Anorganische und Allgemeine Chemie *Z. Anorg. Allg. Chem.* **(2003)** ***629,*** **545–550.**
A full paper has been accepted by the Journal of Inorganic Chemistry and publication is forseen for the end of 2006.

High–pressure X–ray diffraction experiments were performed in transmission geometry with a wavelength of λ = 0.37380 Å (ID30). Pressures for X–ray diffraction were generated by membrane driven diamond anvil cells[1] equipped with 300 µm diamond culets. Nitrogen was used as a pressure transmitting medium and preindented Inconel® gaskets (200 µm/60µm thickness) with centric holes of 120 µm in diameter were applied. Pressures were determined by the ruby luminescence method[2] using the calibration scale of Mao et al.[3] Images of the powder diffraction rings were collected using an image plate detector (mar345, diameter 345 mm, pixel size 100 µm x 100 µm) placed at a distance of approximately 420 mm to the sample. The aperture of the high–pressure cell was restricted to 25° in 2θ giving a resolution of ~1 Å. By movements of 10 µm to 15 µm in *x* and *y* direction perpendicular to the beam the so–called powder average was enhanced. The images were corrected for spatial distortion, non–linear background features, saturated pixels, Lorentz factor and polarization, before azimuthally integrating the diffraction rings using the software FIT2D.[4] Between ambient pressure and 218 kbar, twenty–two powder diffraction patterns of $Cs_2[PdBr_4] \cdot I_2$ were collected. Around 90 kbar (Figure 1) a new phase appears and shows new reflections and peak splitting. The lattice could be fully indexed and intensities were extracted by the Le Bail method. In the pressure range between 90 kbar and 104 kbar, both the initial phase and the new phase coexist. Above 104 kbar, only reflections of new phase were observed in the diffraction patterns. Up to the highest investigated pressure of 218 kbar the monoclinic phase remained stable. After pressure relese the initial structures is retained.

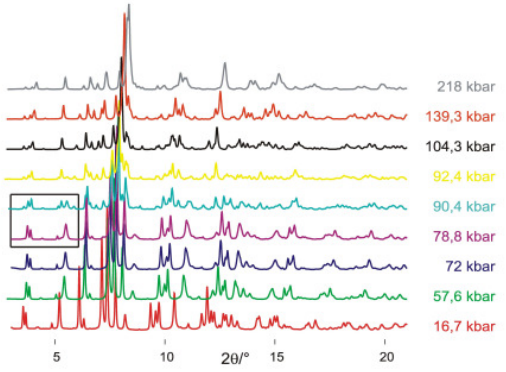

Figure 1: Selected Powder Patterns of $Cs_2PdBr_4 \cdot I_2$

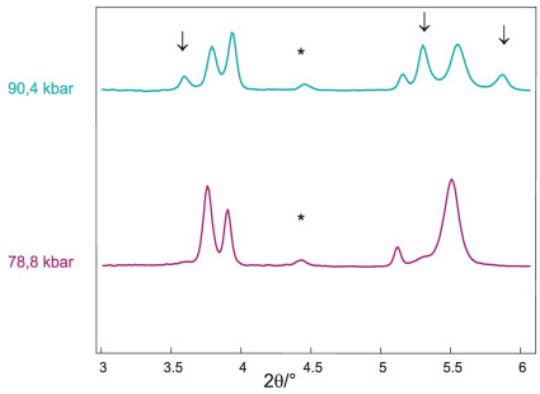

Figure 2: Zoom into ROI, arrows indicating new phase, * denoting solid nitrogen

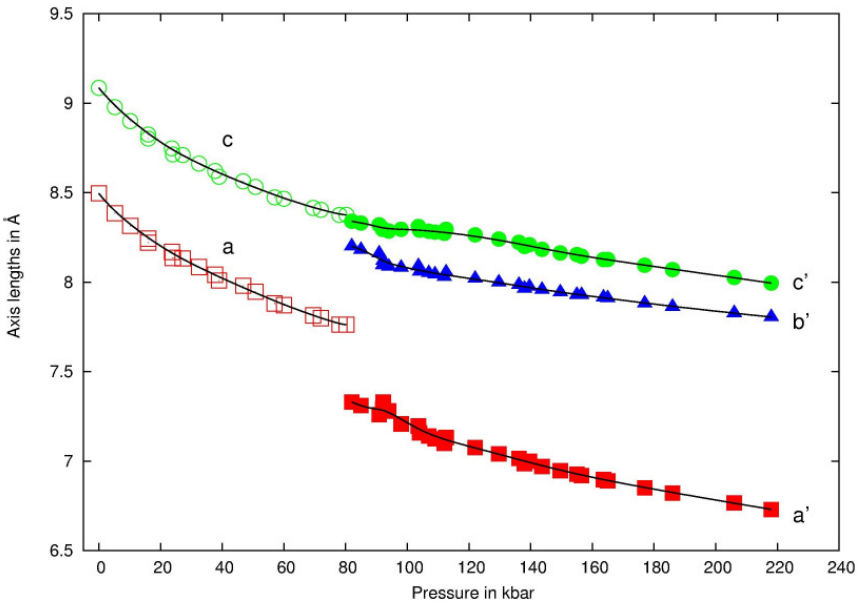

Figure 3: Unit cell axis vs pressue. Solid symbols represent new phase

References

[1] Le Toullec, R.; Princeaux, J. P.; Loubeyre, P.; *High. Press. Res*. 1988, *1*, 77–90.

[2] Piermarini, G. J.; Block, S.; Barnett, J. D.; Forman, R. A.; *J. Appl. Phys.* 1975, *46*, 2774–2780.

[3] Mao, H. K.; Xu, J.; Bell, P. M.; *J. Geophys. Res.* 1986, *B91*, 4673–4676.

[4] Hammersley, A; Svenson, S. O.; Hanfland, M.; Fitch, A. N.; Häuserman, D.; *High Press. Res.* 1996, *14*, 235–248.