ESRF	**Experiment title:** Investigation of the crystal structure of TiOCl and TiOBr at the pressure-induced insulator-to-metal transition	**Experiment number:** HS-3108
Beamline: ID09A	**Date of experiment:** from: 9 Dec 2006 to: 12 Dec 2006	**Date of report:** 17 Jan 2011
Shifts: 9	**Local contact(s):** Dr. Michael HANFLAND (e-mail: hanfland@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants :
Prof. Dr. Christine KUNTSCHER
Experimentalphysik II, Institut für Physik
Universität Augsburg
Universitätsstrasse 1, 86159 Augsburg
Germany

Report:

Published paper #1:
C. A. Kuntscher, S. Frank, A. Pashkin, H. Hoffmann, A. Schönleber, S. van Smaalen, M. Hanfland, S. Glawion, M. Klemm, M. Sing, S. Horn and R. Claessen,
Phys. Rev. B **76**, 241101(R) (2007):

Abstract:
We investigated the pressure-dependent optical response of the low-dimensional Mott-Hubbard insulator TiOBr by transmittance and reflectance measurements in the infrared and visible frequency range. A suppression of the transmittance above a critical pressure and a concomitant increase of the reflectance are observed, suggesting a pressure-induced metallization of TiOBr. The metallic phase of TiOBr at high pressure is confirmed by the presence of additional excitations extending down to the far-infrared range. The pressure-induced metallization coincides with a structural phase transition, according to the results of x-ray powder diffraction experiments under pressure.

Published paper #2:
C. A. Kuntscher, A. Pashkin, H. Hoffmann, S. Frank, M. Klemm, S. Horn, A. Schönleber, S. van Smaalen, M. Hanfland, S. Glawion, M. Sing, and R. Claessen,
Phys. Rev. B **78**, 035106 (2008).

Abstract:
Pressure-dependent transmittance and reflectance spectra of TiOBr and TiOCl single crystals at room temperature suggest the closure of the Mott-Hubbard gap, i.e., the gap is filled with additional electronic states extending down to the far-infrared range. According to pressure-dependent x-ray powder diffraction data the gap closure coincides with a structural phase transition. The transition in TiOBr occurs at slightly lower pressure (p=14 GPa) compared to TiOCl (p=16 GPa) under hydrostatic conditions, which is discussed in terms of the chemical pressure effect. The results of pressure-dependent transmittance measurements on TiOBr at low temperatures reveal similar effects at 23 K, where the compound is in the spin-Peierls phase at ambient pressure.

Published paper #3:
C. A. Kuntscher, J. Ebad-Allah, A. Pashkin, S. Frank, M. Klemm, S. Horn, A. Schönleber, S. van Smaalen, M. Hanfland, S. Glawion, M. Sing, and R. Claessen,
High Pressure Research **29**, 509 (2009).

Abstract:
By pressure-dependent infrared microspectroscopy we observe the filling of the Mott-Hubbard gap in TiOCl and TiOBr above a critical pressure P_c. Concomitant with the gap filling a structural phase transition occurs at P_c. According to our pressure-dependent powder x-ray diffraction data a mixture of the ambient-pressure orthorhombic $Pmmn$ phase and a dimerized, monoclinic $P2_1/m$ phase exists above P_c.

Published paper #4:
J. Ebad-Allah, A. Schönleber, S. van Smaalen, M. Hanfland, M. Klemm, S. Horn, S. Glawion, M. Sing, R. Claessen, and C. A. Kuntscher,
Phys. Rev. B **82**, 134117 (2010).
Abstract:
We studied the crystal structure of TiOCl up to pressures of p=25 GPa at room temperature by x-ray powder diffraction measurements. Two pressure-induced structural phase transitions are observed: At $p_{c1}\approx$15 GPa emerges an $2a\times2b\times c$ superstructure with b-axis unique monoclinic symmetry (space group $P2_1/m$). At $p_{c2}\approx$22 GPa all lattice parameters of the monoclinic phase show a pronounced anomaly. A fraction of the sample persists in the ambient orthorhombic phase (space group $Pmmn$) over the whole pressure range.