ESRF	**Experiment title:** Crystal chemistry and properties of $CaTiOSiO_4$ (titanite) at high pressure and temperature	**Experiment number:** HS-349
Beamline: ID 30	**Date of experiment:** from: 2. 12. 97 to: 7. 12. 97	**Date of report:** 12. Aug. 98
Shifts: 14	**Local contact(s):** Tristan LeBihan	*Received at ESRF:* 02 SEP. 1998

1

Names and affiliations of applicants (* indicates experimentalists):

Martin Kunz*, Laboratory of Crystallography, ETH Zurich, CH-8092 Zurich
Dimitrios Xirouchakis, University of Minnesota, Minneapolis MN 55455, USA.
John B. Parise, ChiPR and ESS, SUNY Stony Brook, NY-l 1794 USA.
Ross J. Angel, Bayrisches Geoinstitut, Universitat Bayreuth, D-95440 Bavreuth.

Report:

The experiment HS349 was remarkably successful in that a large number (45) of high-quality powder diffraction data of $CaTiOSiO_4$ could be recorded at various combinations of pressure and temperature in the range between 0 to 5 GPa and 300 to 700 K.

The data were of good quality and allowed (i) an unambiguous location of the $P2_1/a$ <-> A2/a phase transition in P-T space, (ii) the extraction of a P-V-T equation of state of titanite in the range of interest, and (iii) full scale Rietveld refinements of the structural parameters at various pressures and temperatures.

(i) Phase transition at high-temperature and high-pressure: By following the evolution of the only two non-overlapping *k+l=odd* reflections we were able to monitor the $P2_1/a$ <-> A2/a phase transition in P-T space. We found the phase transition to have a negative slope of - -175 K/GPa (Fig. 1). This suggests that the high-pressure phase transition located at 3.5 GPa (Kunz et al. 1996) seems to be related to the high-temperature phase transition around 825 K (e.g. Zhang et al., 1997), rather than to the

one at 495 K (e.g. Kek et al., 1997).

(ii) P-V-T-equation of state: a preliminary analysis based on an inversion of the 3rd-order Birch-Murnaghan equation of state (Fiquet et al., 1998) yields the following results (K' = fixed at 4, a, = fixed at 0)

$P2_1/a$ phase: $K_{298.0}$ = 104(3), $(\partial K_{T.0}/\partial T)_P$ = -0.02(3) $GPaK^{-1}$, $V_{298.0}$ = 369.4(8) $Å^3$, $\alpha_0 = 2.7(4)\ 10^{-5}$

A2/a-phase: $K_{298.0}$ = 123(5), $(\partial K_{T.0}/\partial T)_P$ = -0.05(2) $GPaK^{-1}$, $V_{298.0}$ = 367.8(6) $Å^3$, $\alpha_0 = 1.4(5)\ 10^{-5}$.

For both sets of results the isothermal bulk-modulus is lower than the one reported from a room-temperature study of Angel et al (1998). Remarkably, however, the $V_{298.0}$ extracted from our data coincides exactly with the experimental value measured for an ideal end-member titanite (Xirouchakis et al., 1997).

(iii) Rietveld refinement: Simultaneous refinement of titanite and quartz, which was added as an internal standard, was possible for all data-sets. Weighted profile R-values ranged between 1.5 % and 3.0 %. $R(F^2)$ for titanite varied between 5.5% and 8.5 % . Further work on these results will focus on the evolution of the structure as a function of temperature and pressure.

Angel, R.J., Kunz, M., Miletich, R., Woodland, A.B., Koch, M., and Knoche R.L. (1998): submitted to American Mineralogist (Prewitt Volume).

Fiquet, G., Andrault, D., Dewaele, A., Charpin, T., Kunz, M., Hausermann D. (1998): Physics of the Earth and Planetary Interiors. 105,21- 31.

Kek, S., Aroyo, M., Bismayer, U., Schmidt, C., Eichhorn, K. and Krane H.G. (1997): Zeitschrift für Kristallographie., 212. 9 – 19.

Kunz, M., Xirouchakis, D., Lindsley, D.H., Hausermann, D. (1996): American Mineralogist, 81, 1527 - 1530.

Xirouchakis, D., Kunz, M., Parise, J.B., Lindsley, D.H. (1997): American Mineralogist, 82, 748 - 754.

Zhang, M., Salje, E.K.H., Bismayer, U. (1997): American Mineralogist, 82, 30 – 35.

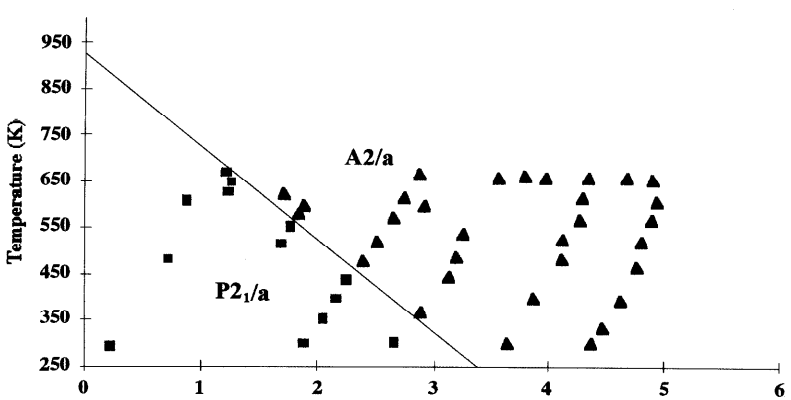

Fig. 1: Phase boundary in P-T space between $P2_1/a$ and A2/a phase of $CaTiOSiO_4$