



Experiment title: The superstructure of ZrP₂O₇; a combined single crystal and high resolution powder diffraction experiment between 90 and 600 K

Experiment number:
CH-899

Beamline: BM01B	Date of experiment: 06.09.00 - 09.09.00 & 07.02.01 - 09.02.01	Date of report: 20.02.01
Shifts: 15	Local contact(s): Silvia Capelli (1st period) & Herman Emerich (2nd period)	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Poul Norby Department of Chemistry, University of Oslo, N-0315 Oslo, Norway

Henrik Birkedal* Institute of Crystallography, University of Lausanne, CH-1015 Lausanne, Switzerland

Philip Pattison* Institute of Crystallography, University of Lausanne, CH-1015 Lausanne, Switzerland

A. M. Krogh Andersen Department of Chemistry, University of Odense, DK-5230 Odense M, Denmark

Report:

The goal of the present experiment was to elucidate the crystal structure, thermal expansion and phase transition of ZrP₂O₇. This compound is part of a family which show unique thermal expansion properties. These materials include ZrV₂O₇ and TiP₂O₇ [1 and references therein].

Like all members of the family, ZrP₂O₇ undergoes a phase transition from a disordered cubic high temperature phase (space group Pa-3, a=8.29Å). This has been reported to occur at about 290°C [1,2]. The low temperature phase is a superstructure with a 3×3×3 supercell. For all previously investigated compounds, this phase was found to adopt the same space group as the high temperature phase, Pa-3. Based on neutron powder diffraction, the low-temperature phase of ZrP₂O₇ was described as cubic as well [2]. However, ³¹P MAS NMR indicates that the true symmetry is lower.

Recently, we managed to prepare single crystals of ZrP₂O₇ with dimensions in the 15-25 μm range. For the present experiment we performed both single crystal diffraction measurements on these microcrystals and very high resolution powder diffraction at ambient and high temperature.

Experimental

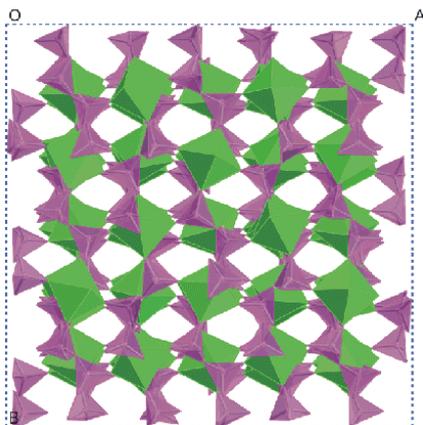
Single micro-crystal diffraction data were collected at the SNBL A station (BM01A) using the MAR345 area detector and focussing optics. Full data sets were collected at 295 and 120 K. Powder diffraction data were collected at the SNBL B station (BM01B) whose very high resolution powder diffractometer is equipped with Si (111) analyzer crystals before each of the four detectors. The temperature was controlled with a GSB 1300 Gas blower from the ESRF pool. The temperature was measured just above the sample position by an external thermocouple. The wavelength, calibrated with a NIST Si powder sample, was $\lambda = 0.79997(3)$ Å. The diffraction peaks were very narrow, FWHM ca. 0.01°. Therefore an effective step size of 0.002° was employed with a counting time of 1 s/step. We collected 14 patterns ($2\theta = 20$ -30°) at various temperatures slowly moving towards the phase transition. The standard uncertainty on the measured temperature was about 1.0°C.

The transition was observed already at T = 246°C, and heating was stopped at T = 272°C. We then lowered the temperature while measuring in the reduced range $2\theta = 24$ -27°. Finally, we went to T_{set} = 247°C where a full data set was collected ($2\theta = 9$ -50°).

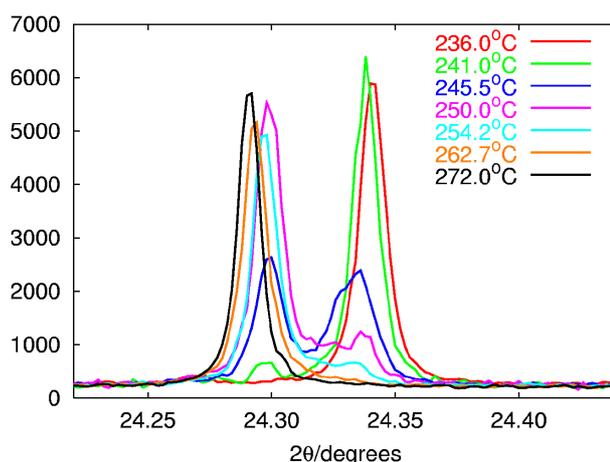
Results

The ambient temperature high resolution powder diffraction pattern showed the presence of superstructure peaks corresponding to the $3\times 3\times 3$ supercell. In addition, deviation from cubic symmetry was observed. Indeed, the pattern could only be interpreted using an orthorhombic unit cell. This observation was confirmed by the single crystal measurements. The space group was determined to be *Pbca* with room temperature lattice constants $a=24.752$, $b=24.734$ and $c=24.756\text{\AA}$ using DENZO/SCALEPACK. A preliminary data reduction of the room temperature data resulted in 12177 unique reflections. The structure was solved using this data set and could be successfully refined. The present model consists of no less than 136 atoms all refined with anisotropic displacement parameters; 1222 parameters, $R_1 = 3.83\%$ for 10512 reflections with $F_o > 4\sigma(F_o)$ and $R_1 = 4.66\%$ for all 12177 reflections. The structure is shown in the left hand figure. The 120 K can be also be interpreted with an orthorhombic unit cell and the space group *Pbca*. This shows that there are no phase transitions between room temperature and 120 K.

The high resolution powder measurements revealed several interesting points. First and foremost, the phase transition took place between $T_{\text{meas}} = 236.0$ and 245.5°C upon heating. This is almost 50 degrees below the value reported in the literature [1,2]. This discrepancy is currently under further investigation. The spectra obtained on cooling show that the observations are reversible and without hysteresis. This allows us to narrow the range containing the transition temperature to between $T_{\text{meas}} = 236.0$ and 241.0°C . The phase transition shows a large range of phase coexistence. This is shown in the right hand Figure. The observed phase coexistence range is larger than 26°C . This value is significantly larger than the horizontal temperature variation of the heating system (measured with a thermocouple). The high temperature phase is cubic with an $\sim 8\text{\AA}$ lattice constant. At the phase transition, the value of the small lattice constant (8\AA) is reduced by approximately 0.01\AA . There is no indication of an intermediate phase.



Crystal structure of ZrP_2O_7 viewed along the c -axis. The Zr-octahedra are in green while the P-tetrahedra are in purple.



Phase transition and phase coexistence as observed by high-resolution powder diffraction. The peak on the right (around 24.34°) corresponds to the low-temperature phase while the peak on the left (around 24.30°) is from the high temperature cubic phase.

In conclusion, we have found that the low temperature structure of ZrP_2O_7 is not cubic but orthorhombic, *Pbca*. The phase transition was found to occur well below the temperature reported in the literature [1,2]. Phase co-existence was observed over 26°C and the phase transition is connected with 0.01\AA jump in the small cubic lattice constant. This shows the first order character of this phase transition which can best be characterized as a non-ferroic lock-in transition: $\text{Pa-3} (V_{\text{cubic}}) \rightarrow \text{Pbca} (V=27V_{\text{cubic}})$. It is worth pointing out, that the distortions from cubic symmetry are so small that their detection was impossible with neutron powder diffraction [2]. Only with the use of high resolution synchrotron measurements has it been possible to shed light on this intriguing system.

References:

- [1] V. Korthuis, N. Khosrovani, A. W. Sleight, N. Roberts, R. Dupree & W. W. Warren Jr. (1995) *Chem Mater.* **7**, 412-417.
- [2] N. Koshrovani, V. Korthuis, A. W. Sleight & T. Vogt. (1996) *Inorg. Chem.* **35**, 485-489.