

P.20.01.1*Acta Cryst.* (2005). A61, C461**Study of the High P-T Phase Diagram of Crystalline Polyethylene**
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Polyethylene is of paramount importance both from the fundamental and technological points of view, since it is the most common polymeric material and a model low-dimensional bead springs system. It is also a crystalline polymer, and the amount of crystallinity is related to the density. High pressure studies of polyethylene have been performed in the last four decades, in a limited P-T range. The room temperature solid phase of polyethylene is assessed to be orthorhombic *Pnam* (two chains per cell) [1]. A monoclinic structure has also been revealed at room pressure in stressed samples, having metastable character [2], while an high P-T reversible modification has been found to an hexagonal phase above 0.35 GPa and 500 K [3-5]. Knowledge of the extreme P-T conditions phase diagram of crystalline polyethylene, beyond 3.2 GPa and 770 K, was still lacking up today.

We investigated the pressure evolution of the infrared spectra of polyethylene in the 0-20 GPa and 300-620 K P-T range, in order to discover new possible high pressure modifications of this material, to characterize its extended phase diagram and investigate its overall chemical and mechanical stability. An extra peak appears above 4 GPa centred at about 1450 cm^{-1} , e.g. close to the bending mode doublet of the orthorhombic phase lying at 1463-1482 cm^{-1} , whose intensity steeply increases with pressure. This modification is reversible, in the sense that the new peak disappears on releasing pressure below 3-4 GPa and the spectrum of the orthorhombic phase is recovered. We suggest that a proper first order thermodynamic phase transition does occur in crystalline polyethylene, at about 4 GPa, between the orthorhombic crystal and a new phase, having lower symmetry. Also, the phase transition boundary has been determined up to 620 K, and it appears to be nearly temperature independent, at least below 470 K, indicating that the two phases are isentropic. Measurements by XRD and Raman spectroscopy are in progress.

[1] Bunn C.W., *Structure of long-chain normal paraffin hydrocarbons. "Shape" of CH_2 groups*, Trans. Faraday Soc., 1939, 75, 6113-6118. [2] Kobayashi M., *J. Chem. Phys.*, 1979, 70, 505. [3] Bassett D.C., Block S., Piermarini G.J., *J. Appl. Phys.*, 1974, 45, 4146. [4] Yasuniwa M., Enoshita R., Takemura T., *Jap. J. Appl. Phys.*, 1976, 15, 1421. [5] Yamamoto T., Miyaji H., Asai K., *Jap. J. Appl. Phys.*, 1977, 16, 1891.

Keywords: polyethylene, high pressure phase transition, phase diagram**P.20.01.2***Acta Cryst.* (2005). A61, C461**Vibrational Dynamics and Phase Diagram of KNbO_3 up to 30 GPa and from 10 to 500 K**Philippe Pruzan^a, D. Gourdain^a, J.C. Chervin^a, B. Canny^a, M. Hanfland^b, *"Physique des Milieux Denses, IMPMC UMR 7590, Université P. et M. Curie, case 77, F-75252 Paris Cedex 05, France*. ^b*ESRF, BP 220 Grenoble, F-38043 France*. E-mail: php@pmc.jussieu.fr

The phase diagram of KNbO_3 was investigated with Raman scattering up to 30 GPa and in the 10 to 500 K temperature range. Macroscopic ferroelectricity vanishes on compression and the various ferroelectric solids, rhombohedral, orthorhombic and tetragonal (R-O-T), were found to exist in close domains of the pressure-temperature plane. Specifically the T solid vanishes below 200 K and the R and O solids exits very likely down to 0 K. The transition to the cubic paraelectric phase is of the displacive type at low temperature whereas it is of the order-disorder type at high temperature. In the cubic solid, first-order Raman scattering, assigned to structural distortion due to dynamical disorder, was observed. The distortion is orthorhombic below 200 K and tetragonal above, which may stems from the rapid decrease with temperature of the Nb ion dwelling time in its site. The phase diagram from Raman will be compared with results obtained from conventional x-ray diffraction.

[1] Pruzan Ph., Gourdain D., Chervin J.C., *High Pressure Research*, 2002, 22, 243, and references therein. [2] Pruzan Ph., Gourdain D., *High Pressure Research*, 2004, 24, 129, and references therein.

Keywords: high pressure, phase transition, ferroelectrics**P.20.02.1***Acta Cryst.* (2005). A61, C461**Compressibility and Evidence of Amorphisation of 6 nm TiO_2 Nano-anatase**Vittoria Pischedda, Anna Marie Dawe, John Edward Lowther, Giovanni R. Hearne, *School of Physics, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg-Gauteng, South Africa*. E-mail: pischeddav@physics.wits.ac.za

TiO_2 in the macrocrystalline and nanocrystalline forms is an important material with a variety of industrial applications. Recent high pressure experimental studies have demonstrated that the behavior of nano-anatase may be quite different to that of the macrocrystalline form [1],[2],[3]. Although, to date there has been no XRD structural characterization of nano-anatase at high pressures for grain sizes less than $\sim 30\text{nm}$.

TiO_2 nano-anatase with an average grain size of $\sim 6\text{ nm}$ has been studied at room temperature and high pressure up to $\sim 30\text{ GPa}$ using synchrotron X-ray diffraction. The nano-anatase phase remains stable up to $\sim 18\text{ GPa}$, after which the degree of disorder increases progressively and the material becomes completely amorphous at pressures beyond $\sim 24\text{ GPa}$. The effect of external pressure on ultrafine nano-anatase ($d < 10\text{nm}$) has been investigated in conjunction with molecular dynamics (MD) simulations, in an attempt to elucidate the mechanism of pressure-induced amorphisation.

Ultrafine nanocrystals are constituted of a core/surface shell structure that may have distinct elastic properties. Above $P \sim 6\text{ GPa}$ where there is a monotonic decrease of the volume, a Birch-Murnaghan fit to the data yielded a bulk modulus $K = 237 \pm 3\text{ GPa}$ (with $K' = 4$, fixed). Thus the 6 nm nano-anatase shows an enhanced bulk modulus in comparison with the macrocrystalline counterpart and is equal to that reported for 30 nm nano-anatase[3]. The MD simulations suggest that the disorder is initiated in the shell and propagates to the core of the nano-structure.

[1] Wang Z., Saxena S.K., *Solid State Commun.*, 2001, 118, 75-78. [2] Hearne G.R., Zhao J., Dawe A.M., Pischedda V., Maaza M., Niewoudt M.K., Kibasomba P., Nemraoui O., Comins J.D., Witcomb M.J., *Phys. Rev.*, 2004, B70, 134102. [3] Swamy V., Dubrovinsky L.S., Dubrovinskaia N.A., Simionovici A.S., Drakopoulos M., Dmitriev V., Weber H.P., *Solid State Commun.*, 2003, 125, 111.

Keywords: nanoanatase, synchrotron, bulk modulus**P.20.02.2***Acta Cryst.* (2005). A61, C461-462**A Novel Facility for Diamond Anvil Cell Diffraction at the SRS, Daresbury, UK**Alistair Lennie, David Laundry, Mark Roberts, Graham Bushnell-Wye, *CCLRC Daresbury Laboratory, Warrington, Cheshire, UK*. E-mail: a.lennie@dl.ac.uk

A new focusing monochromator has been installed for diffraction experiments from samples at high pressures in diamond anvil cells. The X-ray source is a 5 Tesla superconducting wiggler magnet. The monochromator, a sagittally bent silicon crystal, produces a monochromatic beam at 27.94 keV deflected horizontally from the incident beam, and focuses 4mm of the available vertical radiation fan from the wiggler down to a line focus approximately 100 μm high. The band width of the beam is 3×10^{-3} with a divergence in the vertical direction, caused by the focusing, of 1 milli-radian. This is well matched to experimental requirements and gives a flux gain of approximately 100, compared to the station with a simple Si 111 channel-cut monochromator previously used for these experiments.

The new station has been used to record image plate exposures from gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) at elevated P in a diamond anvil cell [0.7, 2.2 GPa]. Measurements taken with exposures of 120s show well defined powder patterns. Unit cell parameters and atomic positions for

Ca, S and O have been refined from these data, following calibration of the sample to image plate distance with silicon powder.

Keywords: synchrotron X-ray diffraction, high-pressure X-ray diffraction, monochromator

P.20.02.3

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High Pressure Synthesis of $\text{EuGa}_{2-x}\text{Si}_{4+x}$ [$x = 1.3(1)$]

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The title compound was prepared using a pressure of 8 GPa and a temperature of 1000 °C followed by slow cooling under pressure. After releasing pressure the sample was examined by x-ray powder diffraction, metallographical and EDX analysis. In the sample after the preparation, the compound $\text{EuGa}_{2-x}\text{Si}_{4+x}$ is found to coexist with $\text{EuGa}_{4-x}\text{Si}_x$ (EuGa_4 type) and Si.

$\text{EuGa}_{2-x}\text{Si}_{4+x}$ is the second representative of the EuGa_2Ge_4 structure type [1] and crystallizes in space group *Cmcm* with $a = 4.348(1)$ Å, $b = 10.457(1)$ Å and $c = 11.938(2)$ Å ($V = 542.8$ Å³). Gallium and germanium build up a three-dimensional network of four-bonded atoms with europium located in large voids. By replacing germanium with silicon the volume decreases by about 12 %. This change in volume is pronouncedly anisotropic; the length of the a axis increases by 4.6 % whereas the b and c axis shorten by 7.2 % and 9.3 %, respectively.

Due to a partial replacement of gallium by silicon, the electron balance can be written as $\text{Eu}^{2+}[\text{Ga}(3b)]^{1-0.7}[\text{Si}(4b)]^{0.5,3} \cdot 1.3e^-$. Thus, we expect metal-type conductivity. Magnetic susceptibility, electrical resistance and thermoelectric properties of the silicon compound are currently under investigation.

[1] Carrilo-Cabrera W., Paschen S., Grin Yu., *J. Alloys Comp.*, 2002, 333, 4.

Keywords: high-pressure synthesis, high-pressure crystal structure, physical properties

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The Phase Transition of Hydrogen-bonded Ferroelectric PbHPO_4 under High Pressure

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PbHPO_4 (LHP), undergoes a phase transition from Phase I to Phase II at $T_c = 310$ K under ambient pressure. The lower-temperature ferroelectric phase (Phase II) with pseudo-one dimensional hydrogen bonded structure has a space group of *Pc*. The paraelectric phase (Phase I) has been assumed to have *P2/c*. The T_c is gradually lowered with increasing pressure and then T_c goes down to room temperature. The transition pressure has been determined to be 0.15 GPa [1]. But the phase transition was no more found over 3 GPa. In this present work, x-ray powder diffraction study of LHP was carried out using synchrotron radiation with diamond anvil pressure cell under hydrostatic conditions at room temperature on BL-18C (KEK), Tsukuba. We could not detect any differences in the diffraction patterns of Phase II and Phase I with increasing pressure up to 5 GPa. By further compression a new pressure-induced phase (Phase III) appears at about 6.5 GPa. We have determined that the structure of Phase III has a possible space group of *Pmmm*, which is stable up to 17 GPa. During decompression cycle, phase III is covered back to the original phase I at 0.7 GPa.

[1] Mylov V. P., et al., *Sov. Phys. - Crystallogr.*, 1979, 24, 738.

Keywords: ferroelectrics, high pressure, phase transition

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High Pressure Structures and Compressibilities of YF_3 and LaF_3

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Many studies have been devoted to the study of laser-hosting *Ln* ($Ln = \text{REE}, \text{Y}, \text{Sc}$) fluorides; particularly ALnF_4 phases crystallizing in the scheelite structure. Yet, for many *Ln* chemistries the scheelite form is unknown and, in the case of those known compositions, e.g. LiGdF_4 , decomposition, to $\text{LiF} + \text{LnF}_3$, occurs at high- p [1]. We have investigated how the LnF_3 structure controls both the synthesis and the decomposition of the binary fluoride phase at high p conditions.

YF_3 crystallizes in the $\beta\text{-YF}_3$ -type structure at ambient p . It has been proposed [2], though not observed, that the high- p , RT structure is the same as that of LaF_3 , tysonite-type. This conjecture we can confirm, in addition to obtaining compressibilities of high- and low- p forms. These data allow calculation of molar volumes at high- p , e.g. LiYF_4 cf. $\text{LiF} + \text{YF}_3$ and judge the effect of increase in REE-coordination at phase transitions on phase stability.

LaF_3 has no known binary fluoride scheelite forms and undergoes a phase transition at $p > 12$ GPa to a structure previously described in *Cmma* and *I4/mmm* symmetries (subgroups of CaF_2 structure) [3,4]. We will present our determination of the high- p structure of this phase that extends the currently known transition sequence for LnF_3 , thus:

$\delta\text{-UO}_3$ (ReO_3) to dist-ReO_3 to $\alpha\text{-UO}_3$ to $\beta\text{-YF}_3$ to LaF_3 to *Pmmm*.

[1] Grzechnik, et al., *J. Phys.: Cond. Matt.*, 2004, 16, 7779. [2] Atavaeva E.Y., Bendeliani N.A., *Inorganic Materials*, 1979, 15, 1487. [3] Dyuzheva, et al., *J. Alloys Comps.*, 2002, 335, 59. [4] Winkler, et al., *J. Alloys Comps.*, 2003, 349, 111.

Keywords: high-pressure structures, transformation, fluorides

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Isosymmetric Reversible Phase Transition in Sodium Oxalate

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Oxalate ions are widely used in the design of supramolecular structures. Anhydrous metal oxalates (like sodium oxalate) are interesting because they have not H-bonds and their structures are determined by the interactions in the system "oxalate-anions - metal cations" only.

At 3.8 GPa an isosymmetric phase transition was observed, preserving the *P21/c* space group despite a jumpwise change in cell parameters and volume. The orientation of oxalate-ions and the coordination of sodium-cations by oxygen atoms change jumpwise at the transition point. The packing of the centroids of oxalate-anions remains preserved to a large extent. It distorts anisotropically with increasing pressure.

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Keywords: phase transitions, pressure, powder method

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Isostructural Transformation and Polymorphism of Thiourea Dioxide at High Pressure

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