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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.

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Keywords: polyethylene, high pressure phase transition, phase diagram

P.20.01.2

Vibrational Dynamics and Phase Diagram of KNbO3 up to 30 GPa and from 10 to 500 K

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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.

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Compressibility and Evidence of Amorphisation of 6 nm TiO2 Nano-anatase

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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 ~30nm.

TiO_2 nano-anatase with an average grain size of ~ 6 nm has been studied at room temperature and high pressure up to ~30 GPa using synchrotron X-ray diffraction. The nano-anatase phase remains stable up to ~18 GPa, after which the degree of disorder increases progressively and the material becomes completely amorphous at pressures beyond ~24 GPa. The effect of external pressure on ultrafine nano-anatase (d<10nm) 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~6 GPa where there is a monotonic decrease of the volume, a Birch-Murnaghan fit to the data yielded a bulk modulus $K = 237 \pm 3$ 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.

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A Novel Facility for Diamond Anvil Cell Diffraction at the SRS, Daresbury, UK

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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 100μm 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 ($CaSO_4.H_2O$) 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

P20