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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