m36.o05

High pressure response of nanophase materials

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Keywords: high pressure phase transformations, nanophase materials, synchrotron X-ray diffraction

We consider the behaviour of nanophase materials under high pressure thermodynamic conditions along the room temperature isotherm. Concurrent high temperatures exceeding a few hundred degrees at high pressure are avoided to ensure that no grain-coarsening occurs, in which case there may be a reversion back to investigating bulk behavior. The effect of pressure in the bulk is normally to induce a structural transition to a high pressure phase which has the lowest Gibbs free energy in *P-T* phase space. What are the implications for such phase transitions in ultrafine nanophase materials with grain sizes approaching critical dimensions, *d*~10 nm in some systems? More than one quarter of the total atoms in such a nano-grain are constituted in the surface, and the surface energy cost involved in the formation of a new phase is significant. The pressure response of ultrafine nano-materials will be exemplified by the anatase polymorph of TiO_2 - a highly topical wide band-gap material. Anatase is particularly useful in this respect because the pressure response is not sensitively dependent on the quality (e.g., stoichiometry) of the sample, nor on whether a pressure transmitting medium for quasi-hydrostaticity is used or not. The implications of nanometer size grains on the known pressure-induced phase transitions of anatase have been investigated up to 30-40 GPa, using synchrotron XRD complemented by laser Raman measurements.
At room temperature the bulk material undergoes a crystallographic transition from the tetragonal structure to the orthorhombic _-PbO_2-type structure at 2-5 GPa, and then to the monoclinic baddeleyite phase at 12-15 GPa. The pressure response of ultrafine nano-anatase of *d* (10 nm grain size, is shown to be radically different to that of its macro-crystalline analog [1,2]. The anatase polymorph is stable to appreciably higher pressure than in bulk. In these ultrafine nano-anatase samples long range order eventually collapses at $P > 20$ GPa, although signatures of short-range ''crystallinity'' of the anatase polymorph are apparent up to the highest pressure of this study. The ''ultra-stability'' of nano-anatase is specific to grain sizes of *d*~10 nm and below. This may be rationalised in terms of the thermodynamics involved in a mechanism of nucleation and growth of a new phase, and partly by using MD simulations for the ultrafine samples where computational work is tractable. The effect of grain-size on mechanical properties (e.g., compressibility-ductility) is also deduced from the pressure response (*P-V* EOS data). The inverse Hall-Petch relationship explains the maximum or plateau in stiffness-hardness at a critical value of small grain size.
There will be brief mention of the pressure response of other nanophase systems.

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m37.o01

Structural Analysis of Multi-enzymatic Complexes by Small Angle X-ray Scattering

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Keywords: small angle X-ray scattering, conformational analysis of macromolecules, cellulose degradation

Cellulose, the main structural component of plant cell walls, is the most abundant carbohydrate polymer in nature. To break down plant cell walls, anaerobic microorganisms have evolved a large extracellular enzyme complex termed cellulosome. This megadalton catalytic machinery organizes an enzymatic assembly, tenaciously bound to a scaffolding protein via specialized intermodular ''cohesin-dockerin'' interactions that serve to enhance synergistic activity among the different catalytic sub-units. All these different domains are separated by linker peptides. Because of the putative intrinsic flexibility of these complexes, the atomic structure of only the isolated domains (enzymes, cohesin, dockerin) could be solved. However the recent advances of small angle scattering enable now to study the structure of such complexes.We analyzed the solution structure properties of cellulosome-like assemblies using small angle X-ray scattering and molecular dynamics. We investigated the conformational events occurring upon complexation of the enzymes onto the scaffolding protein [1]. With this strategy, we could also generate atomic models of mini-cellulosomes of increasing size, made of one, two, and three enzymes, which reveal the existence of various conformational states existing in solutions [2]. These results provide the first clues on the mechanisms by which these protein assemblies attain their remarkable synergy.

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