MS40.P09

Acta Cryst. (2011) A**67,** C502

Pressure induced phase transitions in aperiodic composites

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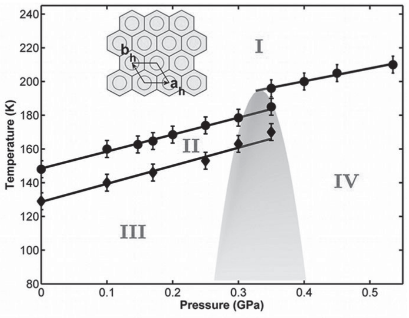
Aperiodicity in composite materials may appear rather naturally due to the possible misfit of host and guest parameters along their crystallographic directions. A huge simplification exists in one dimensional (1D) composite aperiodic crystals since the co-linearity of the incommensurate vectors is always maintained allowing a definite assignment of all the diffraction Bragg peaks [1,2]. Urea inclusion compounds (UIC) constitute such a family of molecular composite structures, where long-chain guest molecules are embedded in parallel channels of the host urea sublattice and among them, most of the n-alkane UIC are incommensurate. A large amount of work has been dedicated to the phase transitions in this prototype family but almost all experimental works were described considering conventional three-dimensional crystallography, ignoring their aperiodic feature [3]. Then, a unique phase transition was reported in almost all of these crystals, independently of the n-alkane guest. The same phase transition was assumed to occur under pressure and its evolution was established up to 0.2 GPa [4].

Aperiodicity actually offers many new degrees of freedom which create totally unexpected sequences of phases with long-range order well decribed within the crystallographic superspace approach [5]. This will be illustrated by the neutron diffraction determination of the (P,T) phase diagram of nonandecane-urea [6] and by the evidence of selective compressibility and pressure induced lock-in in heptane-urea [7,8]



(P,T) Phase diagram of nonadecane-urea : all phases are described within crystallographic superspaces.

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Keywords: aperiodic, pressure, host guest crystals

MS40.P10

Acta Cryst. (2011) A**67,** C502

Pair Distribution Function Studies of the Pressure-Induced Amorphisation of Zeolites

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Zeolites are framework materials with porosity at the molecular scale formed by the complete corner sharing of tetrahedral aluminosilicate groups. The aluminosilicate framework is negatively charged and there are charge-balancing cations inside the pores bonded to the oxygen atoms of the tetrahedra. Like many framework materials, the structures are very flexible and are known to undergo pressure-induced amorphisation at relatively low (< 10 GPa pressures). The amorphisation should not involve significant (Si,Al)–O bond breaking at these pressures but loss of long-range order due to severe and non-correlated distortions of the (Si,Al)–O–(Si,Al) bonds to form network glasses. We [1] and others [2,3] have recently started to use Pair Distribution Function analysis of total scattering data to study the quenched glasses. The goals of our work are both to understand the mechanism of amorphisation and nature of the glass, in particular to determine to what extent it might still have some of the secondary structural building units and porosity of the crystalline precursor.

All work published to date is based on *ex situ* studies of quenched glasses. We have now collected *in situ* high pressure total scattering data on several samples of zeolite A with different charge balancing cations as well as the pure silica polymorph ITQ-29. The analysis from this series allows us to determine the effects that the cations inside the pores have on the amorphisation mechanism and also, by comparing the glasses at pressure and then quenched back to room pressure, to study the reversibility of the process.

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Keywords: amorphization, zeolite, high pressure

MS40.P11

Acta Cryst. (2011) A**67,** C502-C503

Accurate thermodynamics in the quasiharmonic approximation

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Is it possible to calculate the thermodynamic properties of a solid with accuracy that rivals that of the experimental measurements for a wide range of pressures and temperatures? We discuss in this report the three main elements that can drive systematically to that result: (i) The density functional perturbation theory (DFPT) by Baroni et al [1] and its implementation in codes like Quantum Espresso [2] has made possible the ab initio calculation of thermodynamic properties of solids under the quasi harmonic approximation (QHA); (ii) The average of strain polynomials [3] is used to fit faithful and systematically the energy versus volume data, providing the best derivatives available and a statistically relevant estimation of the errors; (iii) The systematic error of the calculations due to the approximate nature of the exchange and correlation functional is repaired through an empirical energy correction scheme (EEC) based only in two experimental data (the equilibrium volume and bulk modulus). Several examples of the extraordinary success of this recipe are discussed.

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Keywords: thermodynamics, calculation, fitting

MS40.P12

Acta Cryst. (2011) A**67,** C503

Pressure-induced phase transitions in L-alanine and DL-alanine, revisited

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The effect of pressure on L-alanine and DL-alanine has been studied by X-ray powder diffraction, single-crystal X-ray diffraction, Raman spectroscopy and optical microscopy. No previously reported structural phase transitions in L-alanine and DL-alanine have been observed up to 12.3 and 8.3 GPa, respectively. In both compounds at about 1.5-2 GPa (close to the pressure of the previously reported phase transition in L-alanine into a tetragonal phase, 2.3 GPa [1], [2]), the cell parameters ***a*** and ***b*** become accidentally equal to each other, but without a change in the space group symmetry. Neither could be a polymorphic transformation in L-alanine from tetragonal into a monoclinic phase at about 9 GPa confirmed, the changes in the cell parameters till the highest measured pressures being continuous and the cell metrics remaining orthorhombic. Our Raman experiments confirmed the effects described previously for the spectra of L-alanine [1] and DL-alanine [3], but we have shown that the spectral changes are continuous and are not related to structural phase transitions. During a slow decompression of L-alanine single crystal (in a methanol-ethanol 4:1 mixture as a pressure-transmitting liquid) from about 6 GPa, new phases crystallized in the diamond anvil cell in the pressure range between 0.8-4.7 GPa, which recrystallized into L-alanine below 0.8 GPa. These previously unknown phases were characterized by powder X-ray diffraction and Raman spectroscopy and seem to be a solvate of L-alanine.

The study was supported by a grant from RFBR (09-03-00451), a BRHE grant RUX0-008-NO-06, a FASI Contract № 02.740.11.5102 and Integration Projects SB RAS (№13 & 109).

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Keywords: amino acids, high pressure, phase transitions

MS40.P13

Acta Cryst. (2011) A**67,** C503

Phase Changes of H_2 and He Hydrates under High pressure and Low Temperature

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Three phases of hydrogen hydrate have been known so for. One is a clathrate hydrate, sII [1], and others are filled ice II structure and filled ice Ic structure [2]. The ratio of water to hydrogen molecules for these phases are1:3, 1:6, 1:1, respectively. sII hydrogen hydrate is expected to be a hydrogen storage material, because it can contain relatively high hydrogen and its synthetic condition is mild comparable to industrial production. At room temperature, above about 1 GPa filled ice II and above 3 GPa filled ice Ic are formed. The latter one survives at least up to 90 GPa [3]. However, phase relations among them under high pressure and low temperature region have not yet been clarified. In this study, high pressure and low temperature experiments were performed by using diamond anvil cells and a helium-refrigeration cryostat in a region of 0.2 to 4.5 GPa and 130 to 300 K. X-ray diffractometry revealed a series of phase change from sII to filled ice Ic via filled ice II. For example, at 220K, sII transformed to filled ice II at approximately 0.6 GPa and further transformed to filled ice Ic structure at about 2.0 GPa. The present results experimentally confirmed the previous prediction.

Helium hydrate is known to form filled ice II structure [4], but the synthetic conditions reported have been limited. Similar experiments were carried in a region of 0.2 to 5.0 GPa and 200 to 300 K. The results showed that the filled ice II structure did not transformed to filled ice Ic structure, but decomposed into helium and ice VI or VIII.

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Keywords: hydrogen hydrate, helium hydrate, phase changes

MS40.P14

Acta Cryst. (2011) A**67,** C503-C504

Study of the behavior of alkali sulfides under pressure

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Pressure-induced phase transitions in antifluorite-type M_2S sulfides (M = Li, Na and K) into anticotunnite-type structures have recently been reported and, some of them, further transform into Ni_2In-type structures [1-3]. This high-pressure phase-transition path involves the increase of the cation coordination number from 8 in the antifluorite structure, through 9 in anticotunnite to 11 in Ni_2In-type structure.

Theoretical *ab initio* total-energy calculations have allowed to completely characterize the high-pressure phases observed experimentally in Li_2S, Na_2S and K_2S and to predict the most likely phases that are expected to be stable below 100 GPa for all alkali metal sulfides [4].

In the present work we have studied the behavior of both, Rb_2S and Cs_2S at high-pressure and room temperature using angle-dispersive X-ray powder diffraction in a diamond anvil cell (DAC). Our measurements have allowed us to identify the existing phase transitions and confirm the previously proposed antifluorite → anticotunnite → Ni_2In-type sequence of stable structures for M_2S sulfides with increasing pressure [5]. Strong luminescence is observed in Rb_2S above 2.6 GPa (band maximum at 703 nm) when the transition to the Ni_2In-type phase starts