

MS.74.5

Acta Cryst. (2011) A67, C167**Powder X-ray diffraction combined with solid state and ^{129}Xe NMR to study supramolecular crystalline materials**

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The study of crystalline architectures showing permanent porosity that can absorb molecules from the gas phase or include selectively target polymer segments in the nanochannels will be addressed [1]. The porous crystalline matrices span from dipeptide crystals and molecular zeolites to metal-organic frameworks and crystalline hybrid organosilicas [2], [3]. The open pore structure of the nanochannels and the diffusion rates of the gases was established by hyperpolarized Xenon NMR whilst gases such as carbon dioxide and methane were observed directly by ^1H and ^{13}C NMR spectroscopy after gas diffusion into the cavities. We recognized, for the first time, the presence of parallel and aligned molecular rotors in the crystalline pore walls of nanoporous hybrid materials, yielding an unusual anisotropic arrangement of surface-exposed molecular rotors in a 3D framework [4]. The entrapment of molecules inside the channels could successfully regulate the fast molecular rotor dynamics.

The spontaneous formation of the supramolecular architectures were realized by a solvent-free mechanochemical approach or by thermal treatment of a host molecule and block copolymers, as demonstrated by *in situ* synchrotron X-ray diffraction. The driving force for the fabrication of crystalline inclusion compounds with target segments of copolymers was based on the establishment of cooperative noncovalent intermolecular interactions, while steric effects prevented the formation of the inclusion-crystals with the remaining blocks. The 2D ^1H - ^{13}C solid state and fast- ^1H MAS NMR provided direct evidence of the intimate interactions between the host and selected block. The large magnetic susceptibility generated by the aromatic host groups surrounding the included segments could be described by *ab initio* calculations that enabled the evaluation of short intermolecular distances between the host and the target block, demonstrating the existence of a diffuse network of multiple $\text{CH}\cdots\pi$ host-guest interactions. The partitioning of the copolymer blocks in inclusion crystals regularly alternated by amorphous nanophases could fabricate architectures on molecular and nanometric hierarchical scales, as demonstrated by high resolution SEM images.

By a similar strategy, a flexible homopolymer was transformed into a semicrystalline polymer through the partial inclusion of chain segments within the cavities of a crystalline host [5]. The self-assembly process was realized by simple co-grinding of minor amounts of host molecules and the polymer bulk. This assembly led to the formation of innovative nanocrystalline adducts which behaved as cross-linking nanodomains. A multitechnique approach comprising powder XRD and fast- ^1H solid state NMR enabled the identification of the unusual phase architecture in the material.

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[2] A. Comotti, S. Bracco, P. Sozzani, S. Horike, S. Kitagawa *J. Am. Chem. Soc.* **2008**, *130*, 13664-13672. [3] A. Comotti, S. Bracco, G. Distefano, P. Sozzani *Chem. Commun.* **2009**, 284-286. [4] A. Comotti, S. Bracco, M. Beretta, P. Valsesia, P. Sozzani *Angew. Chemie Int. Ed.* **2010**, *49*, 1760-1764. [5] S. Bracco, A. Comotti, P. Valsesia, M. Beretta, P. Sozzani *Cryst. Eng. Commun.* **2010**, *12*, 2318-2321.

Keywords: NMR, inclusion, dynamics

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Acta Cryst. (2011) A67, C167**Structure of silicate liquids in the deep Earth**

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The structure of silicate liquids undergoes major change over the pressure regime of Earth's mantle. This structural evolution affects thermodynamic and transport properties in ways that have profound significance for the origin and long term thermal evolution of Earth's interior. Conclusions are drawn from our first principles molecular dynamics simulations based on density functional theory. The simulations are predictive (parameter-free and independent of experiment) and accurate (results agree well with extant experimental data) and have been used to explore a wide range of compositions in the SiO_2 -MgO-CaO-FeO- H_2O system.

A unifying theme is the change in the Si-O coordination number on compression (mean number of O bonded to Si). The Si-O coordination number increases smoothly and nearly linearly on compression from 4-fold near zero pressure to 6-fold on two-fold compression where the pressure is similar to that at the base of the mantle. Among the important implications of the large change in structure are: 1) the density of the liquid surpasses that of coexisting crystals deep in the mantle, permitting the survival of deep melt layers and 2) the Grüneisen parameter in the liquid increases on compression, making deep magma oceans much hotter than previously thought.

Liquid structure differs fundamentally from crystalline structure and does not represent a disordered form of any crystal. For example, at intermediate compressions, we find that 5-fold Si-O coordination is the most abundant in contrast to crystalline silicates in which 5-fold coordination is rare. The abundance of five-fold coordination explains minimum values of the viscosity on compression.

Fe and H behave differently from other cations. Fe undergoes a gradual transition from a high-spin state to a low-spin state on compression. The decrease in spin tends to increase the density by shrinking coordination environments. H occurs primarily as molecules in silicate liquids at low pressure (OH and H_2O), but this picture rapidly changes on compression. More extended structures ($-\text{O}-\text{H}-\text{O}-\text{H}-$) rapidly form on compression, integrating the H_2O component with the silicate network. The change in H-speciation explains the approach towards ideal behavior on compression: the partial molar volume of water in silicate liquids, small at low pressure, converges to the volume of pure water at mid-mantle pressures, implying unlimited solubility of water in silicate liquids over most of the mantle regime. H remains highly mobile in silicate liquids on compression even under conditions where the silicate network is essentially static, a state resembling a superionic conductor, and allowing connections to deep electromagnetic sounding of the mantle.

Keywords: liquid, silicate, pressure

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Acta Cryst. (2011) A67, C167-C168**Structure of water under high temperature and pressure**

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Liquid water at ambient pressure shows unique properties and