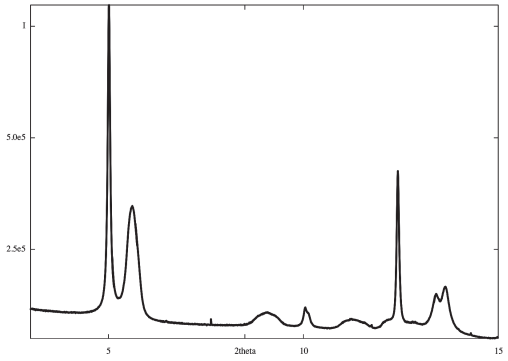
A phenomenological model, based on strongly anisotropic strain, fits well the pattern but provides no structural insight. In fact, the resulting nonconvex strain isosurfaces are unphysical and must be attributed to some other displacive disorder phenomenon. Turning the tables, we chose the Debye Function Analysis (DFA) method [3] – a bottom-up method for modeling powder diffraction patterns based on the set of interatomic distances – to study different disorder phenomena as possible causes. Within DFA the interatomic distances distribution can be modified so as to include *whole canonical ensembles* of atomic configurations, that is a great advantage when considering stochastic models of disorder. Moreover, the interplay of displacive disorder with size/shape and chemical disorder is intrinsically considered. Reverse Monte Carlo methods can also be combined effectively within this method.

We have considered different phenomena to arrive to a comprehensive understanding of this peculiar disorder model in detail, including size/shape, coherent twinning, antiphase domains and Markov-chain anisotropic paracrystallinity based on nearest-neighbor displacement correlations [4]. A detailed analysis of the structural ordering phenomena in $[Ru(CO)_4]_n$ is presented. This work was supported by Fondazione CARIPLO (2009-2446).



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Keywords: total scattering, paracrystal, metal-organic framework

MS.19.1

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High-pressure synthesis, structure and properties of novel superhard phases

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The growing demand for advanced superhard materials simulated the search for novel high-pressure phases that are more thermally and chemically stable than diamond and harder than cubic boron nitride (cBN). Following the discovery of diamond-like BC_2N [1] and BCN [2], very recently a number of new superhard phases has been synthesized.

New high-pressure form of elemental boron, orthorhombic γ-B_{28} theoretically predicted by Oganov [3] has been synthesized from high-purity β-B_{106} in the 12-20 GPa range at temperatures above 1800 K. The cell parameters resulting from the Le Bail refinement are a = 5.056(1) Å, b = 5.641(1) Å, c = 6.995(1) Å and R_{wp} = 2.46 %. γ-B_{28} is the least compressible form of elemental boron (B_0 = 237 GPa [4]) and has Vickers hardness of 50 GPa [5], which is higher than the hardness of other boron polymorphs.

A new metastable high-pressure phase, diamond-like BC_5 (d-BC_5), has been synthesized by phase transformation of graphite-like B–C solid solutions at pressures above 20 GPa and temperatures of about 2200 K [6]. Lattice parameter of d-BC_5 at ambient conditions is a = 3.635(8) Å which is slightly larger than that diamond. According to TEM-SAED data, boron and carbon atoms are homogeneously distributed over the diamond-like crystal lattice not forming superstructures. At high temperatures d-BC_5 demonstrates a clear tendency to segregate into carbon and boron carbide, however, at ambient pressure it has been found to be much more thermally stable (to 1900 K) than nanocrystalline diamond of the same grain size. Among superhard phases, the bulk modulus of d-BC_5 (B_0 = 335 GPa) is exceeded only by the bulk moduli of diamond and cBN. Well-sintered millimeter-sized bulks synthesized in a multianvil press are semi-conductive and exhibit extreme hardness (H_V = 71 GPa) comparable with that of single-crystal diamond and very high fracture toughness (K_{1C} = 9.5 MPa $m^{0.5}$).

New boron subnitride, rhombohedral $B_{13}N_2$ has been synthesized by crystallization from the B–BN melt at 5 GPa [7,8]. The structure of $B_{13}N_2$ belongs to the R-3m space group (a = 5.4585(8) Å, c = 12.253(2) Å) and represents a new structural type produced by the distorted B_{12} icosahedra linked together by N–B–N chains and inter-icosahedral B–B bonds [9]. $B_{13}N_2$ has bulk modulus of 200 GPa [10] and is expected to be superhard with Vickers hardness of 40 GPa [11].

Ultrahard nanocrystalline cubic boron nitride with hardness of H_V = 85 GPa (enhancement up to 100% in comparison with polycrystalline cBN) has been synthesized from graphite-like BN with "ideal random layer" structure at pressures above 20 GPa and moderate (~1770 K) temperatures [12]. The material has extremely high fracture toughness (K_{1c} = 10.5 MPa $m^{0.5}$), wear resistance ($W_H \sim 5.9$) and thermal oxidation stability (to 1450 K).

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Keywords: pressure, temperature, material

MS.19.2

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Amorphization, insertion and reactions in microporous materials at high pressure

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Microporous materials, such as zeolites and aluminum phosphates, exhibit low-density structures built up of corner-sharing tetrahedra (SiO_4, AlO_4, PO_4) and are used extensively as molecular sieves

and catalysts. Pressure-induced amorphization (PIA) is commonly observed in such open framework structures. Incorporation of guest species and PIA may confer useful properties in these materials for new potential applications, related to their high porosity, in the field of the absorption of mechanical shocks. PIA**,** guest insertion and chemical reactions at high pressure were investigated in two prototype systems, the pure SiO_2 siliceous zeolite, silicalite (MFI type) and the aluminum phosphate $AlPO_4$-54 (VFI type) by a combination of x-ray scattering techniques and Monte Carlo modelling.

In the case of silicalite, which exhibits a 3-D pore structure with a relatively small diameter of about 5 Å, reverse Monte Carlo refinements of total x-ray scattering data indicate that PIA corresponds to the collapse of the structure of the crystalline phase around the empty pores keeping the same structural topology, but with strong geometrical distortions [1]. This material is a novel topologically ordered, amorphous form of SiO_2. Whereas amorphization begins in silicalite with empty pores below 2 GPa, the incorporation of CO_2 or argon stabilizes the structure of silicalite up to at least 25 GPa [2]. This is well beyond the stability range of tetrahedrally-coordinated SiO_2. Both x-ray diffraction and Monte Carlo simulations show that the bulk modulus of silicalite strongly increases due to the incorporation of CO_2 or Ar. The insertion of these species deactivates the normal compression and PIA mechanisms in this material. However, when heated at high-pressure, silicalite is found to react with CO_2 forming a disordered SiO_2-CO_2 compound [3]. This indicates that a new oxide chemistry exists at high pressure.

$AlPO_4$-54 exhibits among the largest pores known for zeolites and aluminum phosphates, with a diameter of 12 Å. The material was found to begin to amorphize near 2 GPa using either a non-penetrating pressure transmitting medium (PTM) or no PTM. When H_2O is used as a PTM, superhydration effects are observed and no decrease in the unit cell volume is observed up to the beginning of PIA below 1 GPa, due to insertion of the H_2O molecules in the pores. The opposite effect of guest insertion on PIA in this present case may be due to interactions between the water molecules and the Al^{3+} cations providing a possible mechanism for PIA. The present results show that the incorporation and/or reaction with guest species can be used to strongly modify the stability of microporous materials with respect to PIA, the pressure range over which they can be retained and can give rise to new materials.

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Keywords: pressure, microporous, amorphization

MS.19.3

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High-Pressure synthesis of transition metal-hydrides

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The application of extreme conditions, namely high pressures and temperatures, provide an ideal testing ground to study the behaviour of hydrogen and its effect on other materials [1]. The chemical potential of hydrogen rises steeply with pressure and the formation of novel hydrides can be observed in elements that were previously not known to form hydride phases. The process of hydrogenation can induce drastic changes in the material ranging from structural phase transitions to the emergence of superconductivity.

Here, we present our most recent results from studies on the properties of novel metal-hydride phases at high pressures. Metal samples were loaded into a diamond anvil cell under a hydrogen atmosphere of ~2 kbar. Synchrotron based *in-situ* X-ray diffraction studies enabled the observation of the synthesis and subsequent characterization of a hydride up to pressures of ~ 50 GPa. In this talk, emphasis will be on the unusual properties of binary platinum hydride (PtH), the synthesis of which was first reported in 2008 at pressures above 26 GPa and room temperature [2]. Platinum is often used in science and industry and is valued for its chemical inertness. Although the observation of a bulk PtH phase came as a surprise and should have encouraged further studies, its structural, electronic and mechanical properties remained unknown.

We confirmed the formation of platinum hydride and observed a coexistence of two PtH-phases (PtH-I and PtH-II) at pressures between 26 and 42 GPa [3]. At higher pressures only the PtH-II phase is visible and can be identified as a NiAs type structure, where hydrogen atoms occupy every octahedral interstitial site of the metal lattice. A detailed analysis of the equation of state of PtH-II revealed an increase of the bulk modulus in comparison to pure Pt. Both, the decreased compressibility and the fcc-to-hcp transition are highly unusual findings for a transition metal hydride. Most interestingly however, ab-initio calculations indicate that PtH is superconducting at pressures above 85 GPa with pressure dependent critical temperatures up to 12K, an enhancement by 4 orders of magnitude compared to pure Pt and an effect otherwise only observed in palladium.

The same technique as described above has been applied to study further d-metal systems. Our latest results of studies on hydrides in the tungsten and rhenium systems will be presented as well.

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Xe-H_2O compound synthesized at extreme conditions

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Water is an important component of terrestrial and giant planets so that any reactivity with Xe at depth would have strong consequences on our knowledge of planetary dynamics as it heavily relies on Xe isotopes geochemistry. The chemistry of 'noble gas' has seen fascinating experimental and theoretical advances during the last twenty years as highlighted by review papers [1], [2]. Noble gas chemistry proceeds essentially by photosynthesis of precursors in a low-temperature noble-gas matrix. The pressure variable has seldom been investigated as a mean to enforce Xe to bond other elements [3]. Xe is among the gases that stabilize clathrate hydrates through van der Waals interactions. Xe hydrates are stable up to 2.5 GPa, before dissociating into Xe plus ice VII [4]. However, the chemistry of water with solid Xe has been successfully explored by UV photolysis [5], [6]. Those findings plus our own results on the stability of Xe oxides in the terrestrial crust