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Solid-state amorphization transitions, induced via heating or the application of pressure, significantly increase the range of materials that might yield amorphous phases. The debate about the materials that result from such transitions is whether they are ‘typical’ (i.e. similar to those produced via melt-quenching), whether they form a new amorphous class or indeed whether they should be classed as amorphous at all.

Determination of their structure is the key to resolving this debate. Here we use atomistic modelling, based on the reverse Monte Carlo method, of x-ray and neutron diffraction to investigate the structures that result from pressure-induced amorphization (PIA) and temperature-induced amorphization (TIA) of ZrW_2O_8 and the zeolitic imidazolate framework material ZIF-4, respectively. In both cases the amorphous phase forms from a low-density crystal phase with a connected framework structure. We show that whereas amorphous ZrW_2O_8 has a structure that can be reconciled with a displacive-like phase transition from the crystal structure [1], [2], the structure of amorphous ZIF is more akin to a continuous random network that would only come from ZIF-4 via a reconstructive phase transition [3], [4]. As well as describing the phase transitions and structures of these two materials, we will discuss the implications of this work on PIA and TIA in general.

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Diffraction and nanoscale molecular electronic

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The Organic semiconductors are key components of photovoltaic cells, light-emitting diodes, and organic thin-film transistors. In these systems, knowledge of the molecular organization in the bulk, in the film, and in the interface region is crucial for any technological development. X-Ray Diffraction techniques have provided a host of information that guided the development of these devices [1].

Often it is impossible to grow crystalline samples of size and quality suitable for complete structural analysis. Less conventional structural powder diffraction methods, from which one can also retrieve otherwise inaccessible structural information, can come to the rescue. Grazing Incidence X-ray Diffraction (GIXD) gives information at nano-scale on the structure of films during the first stages of formation, as well as on their evolution during growth. X-Ray Reflectivity (XRR) measurements contribute to describe growth mechanisms (layer by layer or 3D) and monitor surface morphology.

Perylenes di-imide (PDI), and its derivatives, are considered most promising candidates for high performances organic electronics [2]. In order to establish the relationship between a PDI derivative film structure and its device performance, an assessment of the molecular arrangement was carried out by combining powder and thin film diffraction techniques. Moreover XRR performed *in situ* and in real time, during the high vacuum deposition, allowed us to identify the

structural and orientational transitions, which determine the charge mobility of the device. The role of temperature and the deposition flux on the growth mechanism were elucidated.

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Debye-Waller factor and thermal expansion in gold nanoparticles

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High q-space x-ray diffraction measurements are used to determine the Debye-Waller factor and the thermal expansion coefficient of Gold Nanoparticles of 2, 4 and 9 nm sizes. Bulk Gold was also measured for comparison purposes. Given the broad peaks present in nanoparticles, the solution to extract more information from the diffraction experiment lies in using the high q region of the diffraction pattern. In this work we measured the diffraction patterns up to 20 \AA^{-1} at 50, 150, 200, 250 and 300 K for each nanoparticle size. The diffraction patterns were then fit using the 15 K data as a ‘model’, so that only the Debye-Waller factor, the thermal expansion coefficient and a scale factor were optimized in a fitting code developed by the authors. The results show that the thermal expansion coefficient and the Debye-Waller factor depend on the nanoparticle size. The smaller the nanoparticle the smaller are both, the Debye-Waller factor and the thermal expansion coefficient. This surprising result could be explained by the strong surface effects present in the nanoparticles.

Keywords: gold nanoparticles, thermal expansion, Debye-Waller factor

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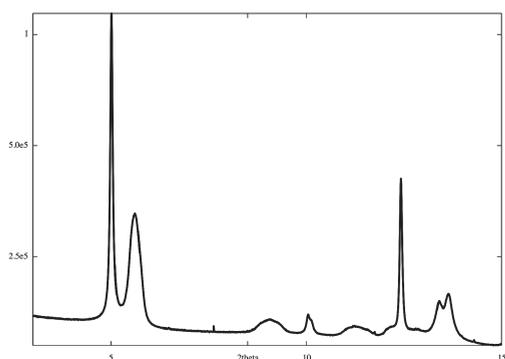
Debye function analysis on disordered metal-organic compounds: the pathfinder $[\text{Ru}(\text{CO})_4]_n$

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Several metal-organic compounds (such as, for instance, polymeric $[\text{Ru}(\text{CO})_4]_n$ [1]) show a peculiar form of anisotropic paracrystalline disorder where all Bragg peaks are dramatically broadened, except those along some axis – in this case the $h00$, $0k0$ and $00l$ peaks – which instead are sharp, as shown in figure. This kind of disorder is of high interest currently as it often occurs in Metal-Organic Framework materials (MOFs), a recent member of the smart materials family, and it relates to the actual display of the properties that make them attractive [2].

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 $[\text{Ru}(\text{CO})_4]_n$ is presented. This work was supported by Fondazione CARIPO (2009-2446).



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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 $R_{\text{wp}} = 2.46$ %.

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 ($d\text{-BC}_5$), 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 $d\text{-BC}_5$ at ambient conditions is $a = 3.635(8)$ Å which is slightly larger than that of 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 $d\text{-BC}_5$ 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 $d\text{-BC}_5$ ($B_0 = 335$ 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 ($K_{\text{IC}} = 9.5$ MPa $\text{m}^{0.5}$).

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 $R\text{-}3m$ 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 intericosahedral 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].

Ultra-hard 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 ($K_{\text{IC}} = 10.5$ MPa $\text{m}^{0.5}$), wear resistance ($W_H \sim 5.9$) and thermal oxidation stability (to 1450 K).

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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