

**B4 - Structure of Nanocrystalline Materials****B4 - O1****ATOMIC PAIR DISTRIBUTION FUNCTION ANALYSIS AND POWDER DIFFRACTION OF NANOCRYSTALLINE MATERIALS****Simon J. L. Billinge***Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824 (USA)*

Nanostructured materials are currently of great interest worldwide with the hope that “nanotechnology” will revolutionize our lives. This remains to be seen, but the ability to study the atomic scale structure of nanostructured materials is clearly a prerequisite to this revolution. The problem is that nano-materials are not periodically long-range ordered and cannot be studied using conventional crystallography. One of the great challenges facing us is to characterize these nanostructures both quantitatively and

reliably. I will describe recent applications of the atomic pair distribution function (PDF) technique to the study of nanostructured materials. I will mention recent work in transition-metal oxides and chalcogenides, III-V and II-VI electronic materials, Cs ions intercalated in nanoporous hosts and aluminosilicate glasses.

B4 - O2**PM2K: A FLEXIBLE PROGRAM IMPLEMENTING WHOLE POWDER PATTERN MODELLING****M. Leoni, T. Confente, P. Scardi***University of Trento, Department of Materials Engineering and Industrial Technologies, 38050 via Mesiano 77, Trento Italy*

Whole Powder Pattern Modelling (WPPM) has been recently proposed as a self-consistent low-bias technique for the microstructural investigation of nanocrystalline materials. Through WPPM, a set of physical parameters actually describing the Fourier transform of a diffraction profile, can be easily extracted from the diffraction data.

In order to cope with the need for a higher flexibility (to test, compare and use new line broadening models) and with the request for additional features, the existing code implementing WPPM has been deeply redesigned and improved.

The result is a general tool for nonlinear least squares minimisation, problem-independent and user-customisable

through the use of macros or by a custom software development kit. A set of libraries have been written in the form of plug-ins, actually implementing WPPM and the microstructural models developed so far: size broadening due to an analytical or to a generic (unconstrained) distribution of crystallites, strain broadening due to the presence of dislocations, broadening due to stacking faults and anti-phase boundaries. The work shows software architecture and examples of application of the program to real cases of study.



B4 - O3

PECULIARITIES OF SIMULATION OF DIFFRACTION PATTERNS OF NANOSTRUCTURED MATERIALS

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Nanostructured materials are specific objects of structural analysis. Peculiarities of their diffraction patterns arise from presence of defects such as grain boundaries and planar defects (PDs), which are elements of nanostructure. High concentration of PDs gives rise to diffuse scattering both in vicinity of Bragg maxima (peak broadening or peak broadening with its shift) and/or in background region (appearance of diffuse peaks or halo). Software developed [1] makes it possible to calculate diffuse scattering in the terms of 1D disordered crystal model.

In the oxide systems PDs such as antiphase boundaries (APBs) shifting cation layers and keeping anion ones have different influence on diffraction lines arising from one plane system. We observed such diffraction effect on the diffraction patterns of γ - Fe_2O_3 and some low temperature oxides of aluminium. For example, 100 diffraction line is broader than 300 one on the X-ray diffraction pattern of γ - Fe_2O_3 received from hematite and 220 diffraction line is broader than 440 one on the X-ray diffraction patterns of γ -, β -, α - Al_2O_3 , received from boehmite, bayerite and gibbsite correspondingly. These diffraction phenomenon couldn't be explained by size or strain effects. Simulation of diffraction patterns shows, that presence of APBs along (001) planes in corundum type structures doesn't influence on diffraction lines for which $|h - k|$ is divisible by 3. At the same time other diffraction lines become broader with increasing density of APBs. For spinel type structures, simulation of diffraction patterns shows that APBs along (110) planes don't affect 440 diffraction line but 220 one becomes broader.

Another diffraction effect is *splitting of diffraction lines on broadened and non-broadened components*. Such effect can appear when PDs introduce additional anisotropy in crystal. For example, for cubic crystals, which have four equivalent directions, 111 peak consists of 8 components. Presence of PDs in one of these directions leads to broadening of six peak components whereas two components are kept without changes. Such splitting effect is given on the Fig.1, where diffraction pattern calculated for the model containing 20% PDs and experimental one for γ - Al_2O_3 are shown in the range of 111 peak.

High concentration of PDs randomly distributed in particle can cause appearance of asymmetric hk diffuse peaks in the positions of $hk0$ reflections. Such peaks appear as a result of loss of periodicity in one direction. Turbostratic carbon, which structure is characterised by random shift of graphite layers, can be considered as structure with high concentration (100%) of PDs. Simulation of X-ray scattering for turbostratic structures shows that only $00l$ and asymmetric hk reflections presents on the XRD patterns [1].

Another example is γ - Al_2O_3 , which also characterised by high concentration of PDs, which are well-defined translations because of dislocation splitting. High concentration (20%) of PDs in the (100) plane for spinel type structures also leads to appearance of diffuse peaks in the hk positions whereas reduced hkl reflections are still present on the simulated diffraction pattern. In some cases appearance of hk diffuse peaks near diffraction lines can cause *shift of gravity centre of these lines*. In particular, this is observed on the γ - Al_2O_3 diffraction patterns where 311 peak is shifted to smaller angles due to appearance of 31 diffuse peak.

PDs non-randomly distributed (or correlated) can lead to appearance of diffuse peaks in the positions characterising hypothetical or really existing polytypes. We use models with correlated PDs for fcc (3C-polytype) metals containing thin (less than 2 nm) twins or coherent hcp (2H-polytype) microdomains. In the first case diffuse peaks appear in the positions of 6H-polytype ABCACB. In the second case additional diffuse peaks appear in the positions of 2H-polytype. We observed the second effect on the diffraction pattern of metallic Co used as catalyst in the reaction of CO disproportionation [1].

To sum up: most of nanostructured materials have high concentration of PDs producing diffusion scattering, which can be analysed with use of simulation of XRD patterns for 1D disordered crystal models.

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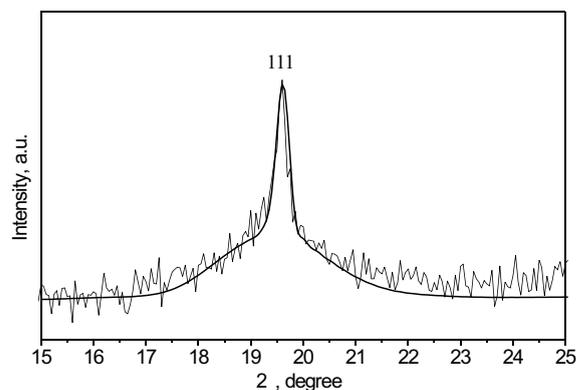


Figure1. Splitting of 111 peak.

B4 - O4

DIFFRACTION STUDIES OF THE ATOMIC VIBRATIONS OF BULK AND SURFACE ATOMS IN THE RECIPROCAL AND REAL SPACES OF NANOCRYSTALLINE SiC
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To describe and evaluate the vibrational properties of nanoparticles it is necessary to distinguish between the surface and the core of the particles. Theoretical calculations show that vibrational density of states of the inner atoms of nanograins is similar to bulk material but shifted to higher energies [1, 2] which can be explained by the fact that the grain core is stressed (hardened) due to the presence of internal pressure. Theoretical calculations also show that there is a difference between vibrational properties of a crystal lattice of the grain interior in isolated particles and in a dense (sintered) nanocrystalline material. This is probably due to a coupling of the modes inside the grains via the grain boundaries in dense nanocrystalline bodies [1].

We examined strains present in the surface shell based on examination of diamond [3] and SiC nanocrystals [4] in reciprocal (Bragg-type scattering) and real (PDF analysis) space analysis of neutron diffraction data. Recently we examined the atomic thermal motions in nanocrystalline SiC based on the assumption of a simple Einstein model for uncorrelated atomic motions [5]. According to this model, the Bragg intensity is attenuated as a function of scattering angle by the Debye-Waller factor. Based on this assumption overall temperature factors were determined from the Wilson plots [6].

Using the B_T values measured at different temperatures we estimated the Debye temperatures of loose powders and the same powders sintered under high-pressure high-temperature conditions [5]. We found that for a given SiC nano-powder the Debye temperature increased by a few hundred degrees after its sintering. From that we conclude that there is a "hardening" of the material accompanying the transformation of the free surface into the grain boundaries. The above results were obtained for one size (~11 nm) SiC nanocrystals where differences between the atomic motions are related to the surrounding of the crystallites [5].

The analysis of Bragg scattering data yields information on the overall lattice expansion and overall atomic motions without regard to whether they are correlated or not. To extract information on the correlated atomic motions alone the total scattered intensity has to be examined using the atomic Pair Distribution Function analysis [7] which, in principle, probes individual interatomic distances rather than the periodicity of the crystal lattice. Using the diffraction data measured at ESRF in the Q-range of 12-13 \AA^{-1} , we performed preliminary PDF analysis showing that there is a clear indication of a difference in elongation between the shortest (Si-Si, C-C) and Si-C interatomic distances, Fig. 1.

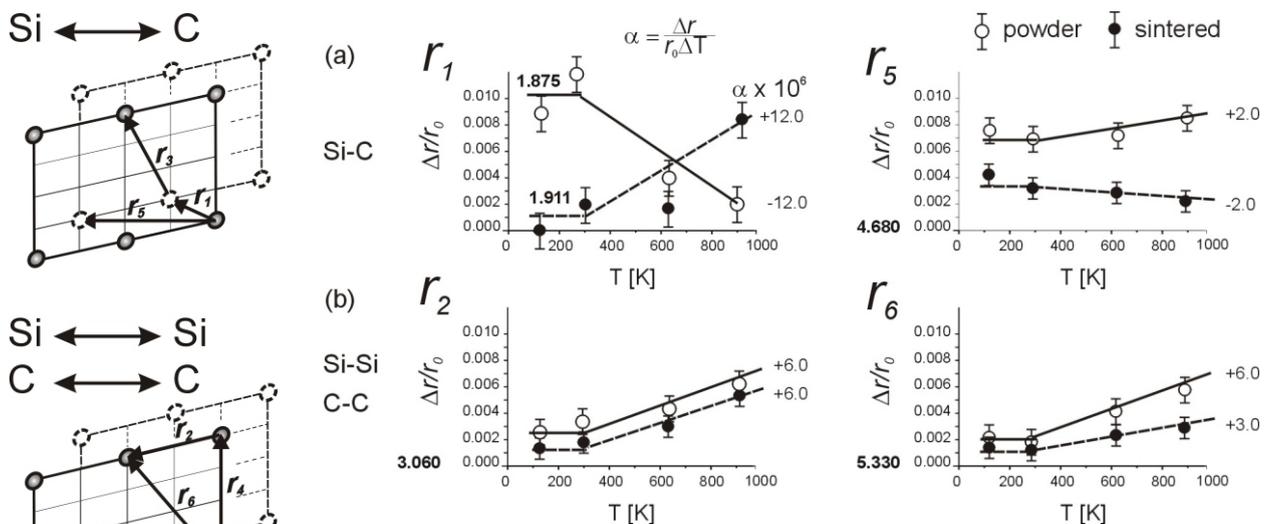


Fig.1. Change of inter-atomic distances Si-C and Si-Si (C-C) with temperature determined from the PDF analysis of X-ray diffractograms (BM06 line at ESRF, $Q_{\max} = 12 \text{ \AA}^{-1}$). Note: The thermal expansion coefficients determined from the positions of the Bragg reflections for powder and sintered SiC have the same value (about $4.5 \cdot 10^{-6} \text{ K}^{-1}$ [5]).



We showed that thermal expansion and thermal vibrations in nanocrystalline SiC are dependent on the processing conditions of the material. The observed differences between our samples can be understood and interpreted considering that the structure of the surface is strongly influenced by the environment of the crystallites. The thermal properties of the surface have a very strong effect on the overall thermal properties of the materials.

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B4 - O5

POWDER DIFFRACTION AND MOLECULAR MODELING IN NANO-MATERIALS DESIGN

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Investigation of structure-properties relationship in nanocomposites is very often obstructed with the structural disorder and low quality of powder diffraction data. In that case the molecular modeling using empirical force field represents very powerful tool of structure analysis, providing that the strategy of modeling is based on experiment (X-ray powder diffraction, IR/Raman spectroscopy, NMR....). Using combination modeling and experiment we analyzed structures of nanocomposite applicable in two fields:

Photofunction units

Polymer-clay nanocomposites

Technology in both cases is based on intercalation of layer silicates.

Intercalation of organic dyes into layered silicates is one method of producing ordered organic-inorganic hybrid materials with interesting photo-functions [1-3]. Especially the smectite group represents very convenient host structure for the intercalation of organic dyes for two reasons: (i) first of all smectites are transparent in the visible wavelength region and (ii) in addition smectites as host structures provide features attractive for intercalation (swelling behavior, ion-exchange properties). Various dye-clay systems offer an interesting area of material research targeted to the development of new photo-function units. The optical properties of these dyes are environmentally sensitive and depend on the arrangement and configuration of the dye molecules. Anchoring the dye molecule on the silicate layer or other host structure offers the tuning of the emit-

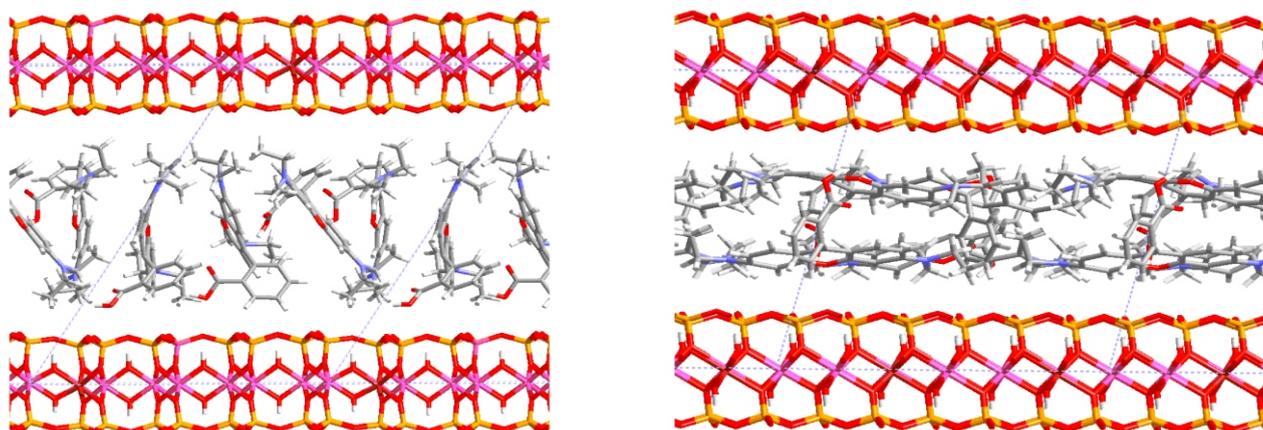


Figure 1

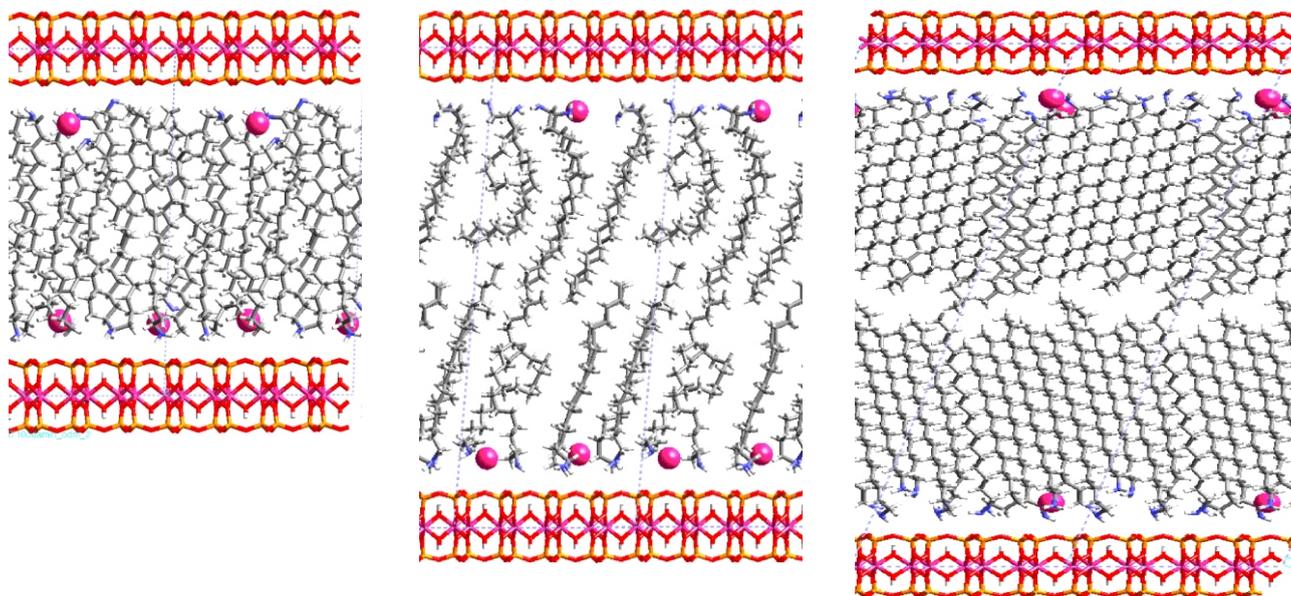


Figure 2

ted wavelength. Rhodamines, which have a high absorption coefficient and the fluorescence yield, are convenient dyes for collecting and utilizing photoenergy. Structure analysis of montmorillonite intercalated with Rhodamine B cations - $[\text{RhB}]^+$ was carried out using the combination of modeling, X-ray powder diffraction and IR spectroscopy. The results of structure analysis explained the fluorescence behavior (i.e. profile and position of bands in the emission spectrum) of RhB intercalated montmorillonite in dependence on Rhodamine B concentration and on the way of preparation [4, 5]. Figure 1 shows two examples of Rh-montmorillonite intercalated structures prepared under different conditions (different concentration of guest molecules in the intercalation solution).

Polymer-clay nano-composites exhibit thermal and mechanical properties which make this material attractive in construction business in building industry and machine building. The aim of intercalation is the separation (exfoliation) of the silicate layers by a convenient guest species (long alkyl chains). Two questions are interesting for the technology: (i) what is the optimum alkyl chain length and (ii) what is the optimum guest concentration for the preparation of precursor with the minimum exfoliation energy leading to the main goal: to obtain the polymer matrix with dispersed silicate layer plates. Silicate layer plates cause the hardening of polymeric material, which also become more thermally stable and more flame resistant. Combined structure analysis (modeling and powder diffraction) gave the answers for all the questions important for the technology. [6] Figure 2 shows the development of the structure of montmorillonite intercalated with octadecylamine in de-

pendence on the guest concentration. (Small balls are the Na-cations, present in the interlayer space of the original host structure and compensating the negative layer charge, as the guest species are neutral molecules.)

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