

with other known transition and noble metal nitrides.

Keywords: high pressure, synthesis, novel materials

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High pressure synthesis of nanocrystalline superhard materials

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The exceptional physical properties of diamond, cBN, and other superhard materials make them not only valuable gems but also important materials in a wide variety of industries where their extreme hardness, toughness, high refractive index, transparency over a broad spectral range, and high thermal conductivity are exploited. Diamond-like carbon (DLC) nanocrystalline films, polycrystalline cubic diamond and cBN have been attracting rapidly increasing interest that focuses on the design of optimum materials by reducing grain dimensions and on how new useful properties could be achieved. We will discuss fundamental issues of high-pressure, high-temperature synthesis and characterization of advanced superhard nano-materials. The new fields of their application will be also considered. Special emphasis will be given to the novel phases, such as nanodiamond, nano-cBN, diamond-like phases in the B – C – N system, spinel nitrides, oxides, and carbides.

Keywords: high-pressure synthesis, nanophase systems, novel structures

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Pressure-induced over-hydration of zeolites: New insights from the elastic behavior of gismondine

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High-pressure (HP) structural studies on zeolites compressed in aqueous media have recently attracted great interest on the pressure-induced hydration (PIH) phenomenon - characterized by the penetration of additional water molecules into the zeolite channels - which can in principle modify the zeolite properties, opening possible new scenarios for their industrial applications. This paper reports the results of an in-situ HP synchrotron powder diffraction study performed on the natural zeolite gismondine from Pamb to 7.9 GPa, using methanol:ethanol: water (16:3:1) mixture (m.e.w.) as penetrating P-transmitting medium. The P-induced deformation mode consists in a slight distortion of the double crankshaft chains forming gismondine framework, and in the deformation of the 8-membered rings delimiting the channel apertures, which become more elliptic. From 0.6 GPa, the water content is slightly higher than the initial one, as a result of a moderate over-hydration. Moreover, at about 2 GPa, a significant water molecule system re-arrangement occurs, characterized by an ordering of part of the water molecules from four partially occupied sites to only two fully occupied ones. PIH, but not the water ordering, is substantially irreversible upon

pressure release. At about 3 GPa a phase transition to triclinic symmetry is observed. The comparison of the cell volume reductions and of the bulk moduli of gismondine compressed in m.e.w. and in silicone oil reveals that this is the unique zeolite with a higher compressibility in penetrating vs. non-penetrating P-transmitting media. This is ascribed to the re-organization of the water molecule system upon compression in m.e.w., which leaves a larger free volume inside the pores with respect to the phase compressed in silicone oil.

Keywords: high-pressure-induced over-hydration, high-pressure phase transition, zeolites-microporous materials

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Pressure induced transition in nano-TiO₂: An X-ray absorption spectroscopy study

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The novel phenomenon of grain-size dependent pressure induced amorphisation (PIA) in TiO₂ nano-materials has been evidenced by several experiments in recent years. Until now, there is no experimental evidence of the length scale of disorder of the amorphous structures nor is there a clear picture, specifically in the case of pressure amorphised anatase-TiO₂ starting material. The open questions of the structural details of the high density amorphous (HDA) phase have been addressed in an x-ray absorption spectroscopy (XAS) pressure study at the Ti K-edge. The local environment of the cation, to within a few nearest neighbour shells, has been monitored up to ~30 GPa where the HDA phase is stabilised. The XAS investigations of this study suggest that a precursor ordered structural phase is observed before amorphisation, the nature of which depends on the experimental conditions. A new structure is stabilized in all cases of samples decompressed from the HDA phase to ambient conditions, characterised by five-fold coordinated Ti. These conceptual pictures are derived from both the EXAFS and the pre-edge parts of the absorption spectra.

Keywords: absorption spectroscopy, nanocrystals, high pressure phases

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Quantitative electron and X-ray diffraction study of charge density in complex oxides

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We report our studies on electronic structure and charge density distribution of complex oxides using quantitative electron diffraction, x-ray diffraction and density functional theory (DFT) calculations. The electron diffraction was based on the unique diffraction-imaging

coupled technique, PARallel Recording Of Dark-field Images (PARODI). It is a new breed of convergent beam electron diffraction developed at Brookhaven to accurately determine structure factors of low-order reflections that are sensitive to valence electron distribution. The synchrotron based single-crystal x-ray diffraction was used to determine the structure factors of high-order reflections that are sensitive to atomic positions and Debye-Waller factors. The two sets of experimental data were combined and refined, and then compared with DFT calculations. Examples on charge density studies including $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ oxide that exhibits extremely high dielectric constant (~ 104) over a wide range of frequencies and temperatures will be given [1,2]. Our recent work on electron scattering amplitudes involving non-spherical orbitals (p and d orbitals) of transition-metal elements will also be reported. We demonstrate that it is possible to accurately measure valence electron distribution, electron orbitals and bonding characteristics of complex functional materials using quantitative electron and x-ray diffraction. Collaborations with J.C. Zheng, L. Wu, J. Hanson, P. Northrup and W. Ku are acknowledged. This work is supported by U.S. DOE under Contract No. DE-AC02-76CH00016.

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Keywords: charge density, convergent-beam electron diffraction, perovskite oxides

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Bonding electrons visualization in photo-excited state using synchrotron X-ray powder diffractometry

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The synchrotron X-ray powder diffractometry has been recognized as one of powerful methods for materials science research. By using Maximum Entropy Method (MEM) as an analytical method for the powder diffraction data, bonding electrons can be visualized to reveal the structure-property relationship. The reliability of the MEM charge density depends on 'accuracy' and 'precision' of experimental data. In present studies, we have succeeded in visualizing bonding electrons in the photo-excited state [1]. So far the accuracy of structural analysis under photo irradiation has not reached bonding electrons level. That can be attributed to inhomogeneous excitation caused by large difference between probe light (X-ray) and excitation light (visible laser) energy. In order to overcome the difficulties, we designed sample packing method into a capillary and photo irradiation system for homogeneous excitation. As a result charge density analysis under photo irradiation was successfully achieved in one of spin crossover complexes, $\text{Fe}(\text{phen})_2(\text{NCS})_2$, which shows a dynamical photo-induced phase transition (PIPT). The bonding nature between Fe and N under photo irradiation is clearly suppressed compared with both ground low-spin phase and temperature induced high-spin phase. The bonding nature created by visible laser may characterize the faster relaxation process of the dynamical PIPT. In my talk, charge density study of persistent PIPT materials (transition metal cyanides [2, 3]) and transient PIPT materials (charge transfer organic materials) will be presented with the dynamical PIPT material.

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Keywords: synchrotron powder diffraction, maximum-entropy method, charge density distribution

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Structure based design of new thermoelectric materials

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There is an urgent need to develop new environmentally friendly energy sources and improving energy efficiency in many technologies and processes. One interesting possibility is thermoelectric energy conversion. Thermoelectric materials are functional materials, which are attracting huge attention due to their dual ability of electrical-thermal energy conversion. Thus, thermoelectric materials are used either for cooling or for energy production. In spacecrafts the preferred method of energy generation is conversion of heat from a radioactive plutonium source to electricity using multi-step thermoelectric converters. There are a vast number of waste heat sources in modern societies that could be harvested in similar ways. In the talk the interplay between structure and thermoelectric properties will be discussed for a range of new complex thermoelectric materials. The materials design has particular focus on lowering the lattice contribution to the thermal conductivity e.g. by introduction of rattling guest atoms or interstitial atoms. The talk will cover materials with applications in high temperature (inorganic clathrates [1-3]) and intermediate temperature (zinc antimonides [4-6]) energy conversion as well as low temperature cooling (iron antimonides [7]).

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Experimental measurements of bond density at the Si(111)-7x7 surface

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Measurement of valance charge density, the distribution of electrons important to bonding, in bulk materials is a rather well established technique in the diffraction community. In principle, the ability to directly measure the charge density at a surface is at least as interesting as in the bulk, if not more so. The exact structure of these surfaces dictates their usefulness and, in particular, the charge density determines the physical, chemical, and electronic properties important to building a device, or designing a catalytic reaction. We have used a combination of electron and x-ray diffraction