

with other known transition and noble metal nitrides.

Keywords: high pressure, synthesis, novel materials

## MS.47.3

*Acta Cryst.* (2008). A64, C85

### High pressure synthesis of nanocrystalline superhard materials

Leonid S. Dubrovinsky

Bayerisches Geoinstitut, University of Bayreuth, Universitaetstr. 30, Bayreuth, D, 95440, Germany, E-mail : Leonid.Dubrovinsky@uni-bayreuth.de

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

## MS.47.4

*Acta Cryst.* (2008). A64, C85

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

Simona Quartieri<sup>1</sup>, Silvia Ori<sup>2</sup>, Giovanna Vezzolini<sup>2</sup>

<sup>1</sup>University of Messina, Dipartimento di Scienze della Terra, Salita Sperone 31, Messina S. Agata, Italy, 98166, Italy, <sup>2</sup>University of Modena and Reggio Emilia, Dipartimento di Scienze della Terra, Via S. Eufemia 19, 41100 Modena, Italy, E-mail: simona.quartieri@unimore.it

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

## MS.47.5

*Acta Cryst.* (2008). A64, C85

### Pressure induced transition in nano-TiO<sub>2</sub>: An X-ray absorption spectroscopy study

Jean-Paul Itie<sup>1</sup>, Anne-Marie Flank<sup>1</sup>, Pierre Lagarde<sup>1</sup>, Alain Polian<sup>2</sup>, Giovanni R Hearne<sup>3</sup>

<sup>1</sup>Synchrotron SOLEIL, L'Orme des merisiers, St Aubin, BP48, Gif-sur-Yvette cedex, idf, 91192, France, <sup>2</sup>Physique des Milieux Denses, IMPMC, CNRS, Universite P.et M. Curie-Paris 6, 140 rue de Lourmel 75015 Paris France, <sup>3</sup>School of Physics & DST-NRF CoE in Strong Materials, WITS University, Johannesburg, South Africa, E-mail : jean-paul.itie@synchrotron-soleil.fr

The novel phenomenon of grain-size dependent pressure induced amorphisation (PIA) in TiO<sub>2</sub> 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-TiO<sub>2</sub> 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

## MS.48.1

*Acta Cryst.* (2008). A64, C85-86

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

Yimei Zhu

Brookhaven National Laboratory, Condensed Matter Physics and Materials Science, Building 480, Upton, NY, 11973, USA, E-mail : zhu@bnl.gov

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