

**MS18.03.08 A NEW SiO<sub>2</sub> PHASE AT PHYSICAL CONDITIONS OF EARTH'S LOWER MANTLE: THEORETICAL AND SYNCHROTRON X-RAY EVIDENCES.** L.S. Dubrovinsky, S.K. Saxena, A.B. Belonshko (Institute of Earth Sciences, Uppsala University, Sweden).

Numerous studies have suggested the existence of a post-stishovite phase. However, none of the experimental or theoretical studies discovered a phase which could be more stable than stishovite at high pressures, except for the possibility of transition into CaCl<sub>2</sub> structure (Kingma et al., 1995), which is likely to be a second order transition. Quasiharmonic lattice dynamic (QLD) and molecular dynamics (MD) study with recently developed interatomic potentials (Tsuneyuki et al, 1989; Belonoshko and Dubrovinsky, 1995) was used for simulation of phase diagram of silica up to 150 GPa. The possibility of a new silica phase with Pnc2 structure was found. This phase is more stable than stishovite at pressures above approximately 75-120 GPa at a wide range of temperature.

We used the Mao-Bell type diamond-anvil cell following the sample preparation method as described elsewhere. A 10 micron thick iron foil was surrounded by dried silica gel. Silica gel was taken as starting material to avoid the well-known kinetic problems in synthesizing of silica phases. An area of approximately 60 micron in diameter was heated to 2000±50 K with Nd:YAG laser for several minutes. The temperature was measured using spectroradiometric method. The quenched samples, still under pressure 080 GPa, were studied at Brookhaven National Laboratory synchrotron X-ray facility. Due to heating, the silica had recrystallized to a new dense form of SiO<sub>2</sub> over a large area. Based on the X-ray data taken at 080 GPa after heating at 2000 K, this phase may be assigned to a structure which is intermediate between aPbO<sub>2</sub> and ZrO<sub>2</sub> structure (space group Pnc2) with unit cell parameters a=4.300(1); b=3.899(2); c=4.689(4), V=11.84(2) cm<sup>3</sup>/mole. This phase is slightly denser than stishovite. It is likely to be more stable in the lower mantle than stishovite, if there is any free silica.

**MS18.03.09 PHASE TRANSITIONS WITHOUT SYMMETRY CHANGE, AND RELATED HIGH PRESSURE PHENOMENA.** R.J. Angel, Bayerisches Geoinstitut, Universitat Bayreuth, D-95440 Bayreuth, Germany.

Recent in-situ diffraction studies of a number of compounds at high pressures and temperatures have revealed the existence of phase transitions that occur without symmetry change. A variety of phase transition behaviour is displayed by such systems:

1: In materials such as KTiOPO<sub>4</sub> and its chemical derivatives the phase transitions are strongly first order in character. The transition is purely displacive in nature involving deformation of the structural framework of the material.

2: In (Mg,Fe)SiO<sub>3</sub> orthopyroxenes the transition at pressure is either very weakly first order or continuous, and results from a change in compression mechanism without major distortion of the structure.

3: In both anorthite-rich feldspars and (Mg,Fe)-clinopyroxenes there are two structurally distinct phases with the same symmetry, one stable at high temperatures and the other at high pressures. In-situ diffraction studies have revealed that in both systems the high-temperature and the high-pressure phases are structurally quite distinct. The stability fields in P-T space of the two phases are therefore expected to be separated by a transition line or crossover without symmetry change. In the case of anorthite the crossover has been observed directly by *in-situ* high-P,T single crystal diffraction.

A review of available high-pressure data suggests that the appearance of such transitions is restricted to structures that have significant degrees of internal structural freedom that allow them to take up different conformations between which transformations can occur that do not involve primary bond breaking.

**PS18.03.10 SYNCHROTRON X-RAY DIFFRACTION STUDY OF SOLID O<sub>2</sub>: THE CRYSTALLINE STRUCTURE OF THE e-PHASE** Serge Desgreniers<sup>a</sup> and Keith E. Brister<sup>b</sup>, <sup>a</sup>Institut de physique Ottawa-Carleton, Ottawa, Canada K1N 6N5, <sup>b</sup>CHESS, Cornell University, Ithaca NY, USA.

We present recent angle-dispersive X-ray diffraction results of dense solid oxygen samples obtained at high pressure in diamond anvil cells, using synchrotron radiation and image plate detection. At room temperature, solid oxygen is known to undergo a pressure-induced phase transition from  $\delta$ -O<sub>2</sub> to e-O<sub>2</sub> at around 10 GPa, the latter being stable to 96 GPa [1]. Although the structure of  $\delta$ -O<sub>2</sub> has been well characterized (Fmmm, Z=4), the proposal for the structure of e-O<sub>2</sub> had yet to be confirmed and refined. Angle-dispersive X-ray diffraction patterns of polycrystalline e-O<sub>2</sub> samples are well described by the A/2m monoclinic space group, as suggested earlier by Johnson et al. [2]. The following lattice parameters are measured for e-O<sub>2</sub> at 12.5±0.1 GPa and 297±3 K: a=3.68 Å, b=5.62 Å, c=7.94 Å and β=116.6°. Rietveld refinements, performed on diffraction patterns generated from data acquired on image plates, provide atomic positions in the lattice as well as insights on the crystal growth habit on the different phases occurring at high pressure. Furthermore, we comment on the existence of other solid oxygen phases at room temperature at around 10 GPa, intermediate to  $\delta$ -O<sub>2</sub> and e-O<sub>2</sub>. Finally, from angle-dispersive and energy-dispersive diffraction measurements, we calculate an equation of state for e-O<sub>2</sub> to high pressures.

[1] Akahama, Y, Kawamura, H., Häusermann, D., Hanfland, M., and Shimomura, O. *Phys. Rev. Lett.* **74**, 4690 (1995).

[2] Johnson, S., Nicol, M. and Schiferl, D., *J. Appl. Cryst.* **26**, 236 (1993).

**PS18.03.11 PRESSURE-INDUCED PHASE TRANSFORMATIONS IN ICE AT LOW TEMPERATURE.** J.L. Finney\* & C. Lobban, Dept of Physics & Astronomy, University College London, UK, and S. Klotz & J.M. Besson, Physique des Milieux Condensés (CNRS), Université Paris VI, France

Phase transformations on compressing D<sub>2</sub>O ice II and ice VI at 120K to pressures in excess of 4GPa have been observed, and neutron powder diffraction data taken on the various phases using the Paris-Edinburgh high-pressure anvil cell on the POLARIS instrument at the ISIS neutron source. For the compression of ice VI, at near 4.0GPa, a rapid transformation occurred to yield a good powder of a phase whose diffraction pattern resembled ice VII, the hydrogen DISordered structure that is the equilibrium phase ABOVE 280K at this pressure. Subsequent warming above 150K resulted in a transformation to the equilibrium hydrogen-ordered ice VIII; further warming to room temperature resulted in the expected transformation to the hydrogen-disordered ice VII phase. Compressing ice II at 120K again resulted in a rapid phase change close to 4GPa; although the diffraction pattern of this phase also resembled ice VII, there was extensive structural disorder, as evidenced by broadened powder peaks (particle size estimated between 50 and 100Å) and the presence of additional intensities. We tentatively identified this disordered phase with the ice VII' proposed on the basis of Raman results by Hemley et al (Nature 388 (1989) 638). On warming, this sample again transformed to ice VIII, but only at the higher temperature of about 200K, with further warming above 290K resulting in ice VII. During the initial pressure increases on both ices II and VI at 120K, there were strong indications of increased disordering, though on this instrument, we were unable to see clear evidence of the amorphous structure suggested by Hemley et al. Detailed results of the structural refinements of these phases will be presented.