

PHASE DIAGRAM OF NITROGEN AT HIGH PRESSURES AND TEMPERATURES

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The phase diagram of nitrogen is very complex at moderate pressures and temperatures. It has been little studied over a wider range until recently, when a theoretically proposed dissociation of nitrogen molecules under pressure [1] was confirmed experimentally [2-4]. Here, we report in situ high-temperature (to 1100 K) Raman as well infrared absorption and x-ray diffraction data in a wide pressure (to 150 GPa) range. These data give a new information about vibrational properties, structure and stability range of nonmolecular phase η . We also discovered two new high-pressure molecular phases, τ and θ , with unusual vibrational properties, including strong infrared activity. The phases have exceptionally large regions of P-T stability (or metastability), including regions where ϵ and ζ are thought to be the only stable phases of nitrogen. The metastability of the ζ phase is also confirmed by low-temperature Raman and infrared measurements, which show that vibrational properties of solid nitrogen at low-T and moderate pressure depend on the transformation path.

References

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HIGH-PRESSURE CRYSTAL STRUCTURES OF HYDROGEN BONDED SMALL MOLECULES

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The application of moderate pressure (0-15 GPa) can cause significant changes in the structures of small molecules. Differences between low temperature and the corresponding high pressure phases have shown a great diversity in molecular packing arrangements, new structural motifs through variance in hydrogen bonding and even molecular conformational changes.

Previous structural analysis of small organic molecules has provided a range of new high pressure phases of hydrogen bonded systems: low molecular weight mono-alcohols (methanol and ethanol); acetone; and the small carboxylic acids (formic acid and acetic acid). The results provide an insight towards the differences between the low temperature and high-pressure phases arising from the range of hydrogen bonding, which can cause differences in molecular packing.

These studies have been extended to include the quaternary alcohols, cyclobutanol and tertiary butanol, and molecules with more than one functional group, for example the alpha-omega di-alcohols [HO(CH₂)_nOH] ethane-diol (n = 2) and propane-diol (n = 3). These small molecules have high-pressure phases that are different from their corresponding low-temperature phases. In the case of ethane-diol, not only do we observe major changes in the packing arrangement of the molecules, there is also a conformational change - this is the first example of such a difference between the phases under these conditions. For propane-diol, the high-pressure phase has two conformers in the asymmetric unit, one planar molecule and the other non-planar, compared to one conformer in the low-temperature analogue.

Keywords: HYDROGEN BONDING, HIGH PRESSURE, SMALL MOLECULES

PSEUDOMARTENSITIC TRANSFORMATION AT HIGH PRESSURES

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Phase transformations are generally classified into two groups: diffusional and diffusionless. Diffusionless transformation, known as martensitic transformation, has been well documented for metallic material. However, studies of this type of phase transformation in oxides are less extensive. Both transformation mechanisms have been proposed for the olivine-spinel phase transition, by theoretical modeling, transmission electron microscopy (TEM) and x-ray diffraction studies. Using time-resolved in situ x-ray diffraction, we have studied the olivine-spinel phase transition in fayalite at high pressure and temperature under controlled-stress conditions. Structure refinements show a pseudomartensitic transformation: diffusionless anion sublattice transition coupled with short-range diffusional cation reordering, in both stressed and unstressed samples. While it is generally believed that stresses give rise to a martensitic transformation, observation of pseudomartensitic transition in an unstressed sample is rare. On-site generated stresses due to the volume reduction accompanying the olivine-spinel phase transition is probably responsible for the cause of pseudomartensitic transition. A classical 'sphere-in-the-hole' elastic model can be used to illustrate the stress generation. This pseudomartensitic phase transition mechanism is operative in unstressed sample only at relative low temperature. High temperatures will weaken the materials, and therefore avoid generating the on-site stresses. The experiments are carried out at the high-pressure beamline X17B of the National Synchrotron Light Source (Upton, NY USA). A translating imaging plate system coupled with a cubic-anvil large-volume press is used for collecting the x-ray diffraction data.

Keywords: HIGH PRESSURE, PHASE TRANSITION, FAYALITE

NEUTRON DIFFRACTION STUDIES OF MINERALS AT HIGH PRESSURE AND TEMPERATURE

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The application of neutron powder diffraction to the study of mineral behavior at high temperature and high pressure is reviewed. The characteristics of neutrons that make them particularly amenable to such studies are outlined, and recent technological developments in the attainment of extreme sample environments are discussed. These developments include the design of new high-pressure cells, hydrothermal cells, and furnaces that allow in situ diffraction under extreme conditions. The application of this technology to problems of order-disorder and displacive phase transitions in minerals is illustrated in a series of recent examples.

Keywords: PHASE TRANSITION, PRESSURE, MINERAL