

CHEMICAL REACTIONS IN IRON-OXYGEN SYSTEM AT HIGH OXYGEN FUGACITY UNDER HIGH PRESSURE

Q. Shebanova, P. Lazor H. Annersten

Uppsala University Department of Earth Science, Mineralogy-Petrology Villavagen, 16 UPPSALA SE-752-36 SWEDEN

Oxygen fugacity belongs to parameters that control stability of phases in Fe-O system at high pressures and temperatures. Generally, it is neither fixed nor controlled in diamond anvil cell (DAC) experiments. For iron oxides, typical sample-loading procedures usually result in a reducing environment at sufficiently high temperatures for example during a laser heating. We report high-pressure DAC experiments on the Fe-O system in an oxidizing environment provided by the presence of platinum dioxide (PtO₂) in the mixture with magnetite sample. X-ray diffraction experiments were conducted at the European Synchrotron Radiation Facility in Grenoble employing an angle dispersive method with imaging plate detector.

Simple compression of the sample assemblage at room temperature without heating resulted in a nucleation of hematite first observed at 9-12 GPa, and progressing significantly at higher pressures up to 42 GPa, the maximum pressure of the study. This experimental observation is explained by the drastic increase of oxygen fugacity in the system at high pressure what served as a driving force for the hematite nucleation. Laser heating up to temperatures of about 2500 K resulted in a further dramatic increase of presence of hematite. The diffraction spectrum taken from the temperature-quenched sample contained also peaks of magnetite, platinum (product of breakdown of PtO₂), and yet unidentified new iron-oxide phase.

Keywords: HIGH PRESSURE, OXYGEN FUGACITY, IRON - OXYGEN SYSTEM

PROFILE FITTING FOR THE EXTRACTION OF ACCURATE INTENSITY DATA

R.J. Angel, J. Zhao N.L. Ross

Crystallography Laboratory Dept. Geological Sciences Virginia Tech BLACKSBURG VA 24060 USA

Changes in crystal structures with pressure and temperature are generally subtle, and therefore the most accurate intensity data is required to follow them. However, intensity data collected from single crystals held at non-ambient conditions, and particularly at high pressures, are of significantly lower quality than equivalent datasets collected in air. First, the diffracted intensities are affected by a number of processes including multiple diffraction and absorption by the cell components. Second, access to the sample is generally restricted, so the collection of equivalent reflections is limited, and the identification and rejection of aberrant intensities by averaging symmetry-equivalents is more difficult.

We have therefore further developed the use of profile-fitting methods to recover accurate intensities from step scan data, following from Pavese and Artioli [Acta Cryst. A52:890-897]. We first determine background parameters. Then the profile parameters of width, shape, and intensity ratio of the a_1/a_2 doublet are determined by fitting to the strong reflections. A first pass through the dataset is then made with these parameters fixed, while the position and intensity only are refined for each reflection. Subsidiary least-squares fits of the profile parameters are used to identify aberrant profiles for rejection. A second pass is then made of the weak reflections in which the reflection position is fixed to the value determined from a UB matrix and crystal offsets refined [following Dera & Katrusiak - J Appl. Cryst. 32:510-515] to the strong reflections.

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Keywords: HIGH PRESSURE INTENSITIES INTEGRATION

STRUCTURAL STUDY OF ICOSAHEDRAL Cd-Yb QUASICRYSTAL UNDER HIGH PRESSURE UP TO 40GPa

T. Watanuki¹ T. J. Sato² A. P. Tsai² O. Shimomura¹

¹Japan Atomic Energy Research Institute SPring-8 Kouto 1-1-1 MIKAZUKI HYOGO 679-5148 JAPAN ²National Institute for Materials Science

In order to understand the origin of the structural stability of quasicrystalline systems, it is important to investigate the pressure dependence of their structure. So, we have performed powder x-ray diffraction experiments for icosahedral Cd-Yb quasicrystal under pressure using a diamond anvil cell at room temperature (SPring-8 BL10XU). This icosahedral quasicrystalline phase is considered to be suitable for observing pressure effects, one of because this phase has an adjacent slightly dense crystalline phase with small difference of the atomic composition, and also because this quasicrystalline phase is expected to be very soft one among the icosahedral quasicrystals which have ever been discovered. As for the experimental technique, it is important to make a good hydrostatic condition, because applying not well defined stress fields often hinder the observation of the intrinsic structural change. So, we use He gas as a pressure medium, which can generate quasi-hydrostatic condition up to 50 GPa. The experimental results show no significant change of the x-ray diffraction profiles up to 40 GPa. With respect to the pressure dependence of the d-values, monotonic change was observed. However, gradual Bragg peak broadening was observed in the pressure region above 15 GPa. Summing up these results, we consider that icosahedral Cd-Yb quasicrystal is compressed isotropically under hydrostatic pressure up to 40 GPa, however, some imperfection such as local distortion is induced in the quasi-periodic lattice in the pressure region above 15 GPa. We also determine the bulk modulus, $B_0 = 49\text{GPa}$, which is very small value among the quasicrystals.

Keywords: QUASICRYSTAL, HIGH PRESSURE, DIFFRACTION

THE ELECTROLYTIC Nb(O) SOLID SOLUTION

A. Arakcheeva^{1,2} V. Grinevitch¹ V. Shamray¹ G. Chapuis²

¹Baikov Institute of Metallurgy Leninsky Pr. 49 MOSCOW 119991 RUSSIA

²Institute of Crystallography, University of Lausanne, Switzerland

Cubic single crystals of Nb metal (bcc) and solid solutions Nb(O_x), where $x < 0.2$, were obtained by electrolysis from the molten salt system ($T = 1023\text{ K}$, cathode current density = 0.2 A/cm^2). The x-parameter is known from other methods and $x < 0.007$ at 973 K and $x < 0.07$ at 1973 K for the cubic solid solution Nb(O_x). If the solid solution is obtained by oxidation at normal pressure, increasing x leads to a lower symmetry. The increase of the oxygen concentration in the electrolytic cubic Nb(O_x) phase has an effect similar to the high pressure of oxygen during the crystallisation process. Using x-ray single crystal diffraction study, the O atoms were localised in the electrolytic crystal NbO_{0.15} ($a = 3.3082(6)\text{ \AA}$; $R(F) = 0.0072$), and in the partially oxidised [with (HNO₃+3HCl)] electrolytic crystal NbO_{0.11} ($a = 3.3114(4)\text{ \AA}$; $R(F) = 0.0061$). No additional atomic position was observed in the pure Nb electrolytic crystal ($a = 3.2969(8)\text{ \AA}$; $R(F) = 0.0092$). In the bcc Nb structure, the occupation of the tetrahedral interstices with the 'electrolytic' O atoms ($d(\text{O-Nb}) = 1.85\text{ \AA} \times 4$) and the octahedral interstices with the chemisorbed ones ($d(\text{Nb-O}) = 1.66\text{ \AA} \times 2$ & $2.34\text{ \AA} \times 4$) has been determined. The location of O in the tetrahedral interstices results from capturing neutral O atoms by the negative charged crystal during cathode deposition. The small size ($r(\text{O}) = 0.6\text{ \AA}$) and isotropic bonds (Sp^3 hybridization) of O atom permits its high concentration without lowering the cubic symmetry of Nb(O_x).

Keywords: ELECTROLYTIC COMPOUNDS EFFECT SIMILAR TO HIGH PRESSURE