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TITLE: HIGH-TEMPERATURE/HIGH-PRESSURE X-RAY DIFFRACTION: RECENT DEVELOPMENTS

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HIGH-TEMPERATURE/HIGH-PRESSURE X-RAY DIFFRACTION: RECENT DEVELOPMENTS*

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ABSTRACT

We have developed two Merrill-Bassett diamond-anvil cells for specialized high-temperature uses. The first is constructed largely of rhenium to provide uniform, constant P and T on the order of 20 GPa at 1200 K for extended periods. The second is for single-crystal x-ray diffraction, but can be heated to 630 K at 20 GPa to grow single-crystal samples which cannot be produced at room temperature. With this cell, the crystal structure of ϵ-O_2 was shown to be monoclinic with $a = 3.649$ A, $b = 5.493$ A, $c = 7.701$ A, and $\beta = 116.11°$ at 19.7 GPa.

KEY WORDS

Diamond-anvil cell, high-temperature, high-pressure, rhenium, x-ray, ϵ-O_2.

INTRODUCTION

For several years, we have used resistively-heated diamond-anvil cells (DACs) for x-ray diffraction and Raman spectroscopy (Schiferl et al., 1986, 1987; Zinn et al., 1986). While we have reached temperatures as high as 1800 K, most of our most recent developments have involved improvements for lower temperature work. In this paper we describe two of these developments: the construction of a Merrill-Bassett (1974) DAC made mostly of pure rhenium; and the use of high-temperature technology to solve the ϵ-O_2 structure.

RHENIUM DIAMOND-ANVIL CELL

We have recently built a Merrill-Bassett (1974) DAC largely of rhenium in order to maintain constant P,T conditions on the order of 20 GPa at 1200 K for many hours at a time. Because the entire cell is heated to a uniform temperature in a vacuum oven, thermocouples can be used to determine temperatures to better than ± 10 K. Once the thermocouple calibration has been checked, the sample temperatures can actually be trusted to this accuracy.

The basic design of these DACs is described by Zinn et al. (1986), and the only substantial change is in the materials used for the various parts. The diamond-anvils rest on seats which are made of tungsten carbide or boron carbide. The rest of the load-bearing parts are rhenium. The device is quite expensive, primarily because the machining is so difficult.

Once constructed, the rhenium DAC proved to be simple and reliable to use. A particularly convenient feature is the fact that the rhenium bolts turn well in the mating internally-threaded rhenium pieces, even after cooling from the highest temperatures. (We have found that rhenium bolts turn more freely than any others for cells made from Inconel 718, Udimet 700, and MoRe, as well.)

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ϵ-O_2 STRUCTURE

Ever since its discovery (Nicol et al., 1979) a decade ago, ϵ-O_2 has proved to be an especially intriguing phase. The most apparent feature is that the color of the crystals changes dramatically with orientation, appearing clear and colorless, amber or dark rust red. Optical absorption spectra (Syassen and Nicol, 1981; Nicol and Syassen, 1983), as well as infrared and Raman spectra (Agnew et al., 1987), suggest the presence of strong intermolecular forces between parallel O_2 molecules in the ϵ-phase.

Calculation of the electronic structure and bonding properties requires knowledge of the crystal structure of ϵ-O_2. Olinger et al. (1984) did extensive powder diffraction studies on oxygen from 6 to 13 GPa, but were unable to solve the ϵ-O_2 structure from their patterns, which contained up to seven lines. Desgreniers et al. (1988) obtained nine diffraction lines using energy-dispersive powder diffraction with synchrotron radiation, but were unable to solve the structure. They did show that the diffraction pattern remained unchanged between 10 and 61 GPa, indicating no further structural transitions.

Single-crystal diffraction studies on ϵ-O_2 are required to solve its structure. Unfortunately, no single-crystal samples of ϵ-O_2 suitable for x-ray diffraction have ever been grown by pressurizing at room temperature. The intermediate β-δ and δ-ϵ transitions are both destructive, the latter particularly so because it is accomplished by a large volume change. Yen and Nicol (1987) showed that a crystal of ϵ-O_2 can be grown directly from the melt above the β-ϵ-fluid triple point at 645 K and 16.3 GPa, or produced by strain annealing close to the melting curve.

We constructed a Merrill-Bassett (1974) DAC which achieved 20 GPa at 630 K and which is suitable for single-crystal x-ray diffraction at room temperature. A temperature-compensated design (Schiferl, 1987) was used so that cooling would not cause pressure changes and thus destroy the single-crystal sample. The triangular pressurizing plates and bolts were both made from heat-treated Inconel 718. The backing plates were Kawecki-Berylco HIP-50 beryllium with the preferred orientation carefully controlled to provide maximum strength under the diamond anvils (Schiferl, 1979). The diamond anvils were each about 1/4 carat with a culet-tip diameter of 0.4 mm. The gasket was Inconel 718, prepressed to 60-μm thickness with a hole diameter of 100 μm.

The diamond-anvil cell was then placed in a vacuum oven (Zinn et al., 1986). The pressure was raised to 19.5 GPa and the sample was strain annealed by heating to 630 K, followed by slow cooling to room temperature. During the entire heating and cooling cycle, the pressure remained between 19.2 and 19.9 GPa.

After cooling, examination of the sample under crossed-polarizers revealed nine crystals with four showing no detectable strain. The colors of the different crystals indicated that they had a wide range of orientations. Thus, a complete composite data set could be collected.

Graphite monochromatized Mo K-alpha radiation was produced with a Rigaku rotating anode generator, and a Picker four-circle diffractometer was used to collect the data. Reflections were then sorted according to the crystal from which each originated. A complete reciprocal lattice was constructed. At 19.7 GPa the structure of ϵ-O_2 proved to be monoclinic with lattice constants a = 3.649 A, b = 5.493 A, c = 7.701 A, β = 116.11° and eight molecules per unit cell (Johnson et al., 1989). Single-crystal samples of several other substances, such as the new N_2-O_2 alloys (Baer and Nicol, 1989), as well as Sb(II), Bi(II), and Bi(III), can be grown at temperatures well within the capability of this DAC.

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