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TITLE: A NOVEL INSTRUMENT FOR HIGH-PRESSURE RESEARCH AT
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**A NOVEL INSTRUMENT FOR HIGH-PRESSURE RESEARCH AT
ULTRA-HIGH TEMPERATURES***

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Abstract

A resistively heated diamond-anvil cell has been used to achieve pressures of 110 kbar at temperatures exceeding 1200 C for periods long enough to collect x-ray powder diffraction data with energy-dispersive techniques using "white" x-radiation produced at the Stanford Synchrotron Radiation Laboratory.

Keywords: high-temperature/high-pressure

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In this note, we report the successful operation of a resistively heated diamond-anvil high-pressure cell to temperatures in excess of 1200 C, while simultaneously maintaining pressures in excess of 100 kbar. "White" x-radiation produced at the Stanford Synchrotron Radiation Laboratory (SSRL) was used to obtain energy-dispersive x-ray diffraction data from samples in the cell under these conditions. The practical limit in temperature for these devices was previously accepted to be about 800 C.[1] Laser heating of samples in diamond-anvil cells (DAC) is a very promising technique, which has been used to study physical and chemical transformations at high pressures with temperatures in the range from 2000 to 4000 C.[2,3] However, laser heating allows only a small portion of the sample volume to be heated and necessarily involves an extremely large thermal gradient across it. We are unaware of any in situ physical measurements which have been made on samples while heating with this method. The techniques being reported here do allow both x-ray and optical studies for extended periods.

Normally, problems with materials make high pressure experiments with DAC's very difficult at temperatures above 800 C. Diamonds will oxidize in air and the transformation of diamond to graphite, the thermodynamically stable form of carbon under normal conditions, is accelerated at temperatures above 800 C. The graphitization takes place even in a vacuum, but it is hastened by the presence of small amounts of oxygen.[4] Many of the alloys normally used as gaskets or load-bearing components in a DAC melt below 1200 C or are subject to rapid creep deformation. Many transition metals form solid solutions or eutectics with carbon below 1200 C. These problems impose severe constraints on the design of a DAC for operation at such temperatures. A final complication is that no DAC can be constructed to maintain these conditions indefinitely, and the data must be taken quickly. Thus, x-ray diffraction requires energy-dispersive techniques and an intense synchrotron x-ray source. [5]

The design of the new DAC is described fully elsewhere;[6] however, a brief description is presented here. Each diamond is mounted on a stack of boron carbide plates which has a total length of 20 mm and which is mounted in one of the triangular plates of a Merrill-Bassett cell. [7] The design is unique in that it sacrifices long-term durability to achieve the highest temperatures and pressures permitted by the diamonds for brief periods of time. This DAC makes use of the following facts:

1. Diamonds can survive temperatures of 1200 C in high vacuum for several hours.
2. Several useful refractory metals, such as tungsten, molybdenum and rhenium, form carbon eutectics or compounds only above 1500 C.
3. X-ray diffraction measurements can be made in minutes using energy-dispersive techniques with "white" synchrotron-produced radiation.

The new DAC is constructed of the strongest and most temperature-resistant materials available. The cell is operated in a high-vacuum oven and all the materials are suitable for high-vacuum systems, even at the highest temperatures. The materials are also chosen so that they will not react with each other. Because the components have limited lifetimes, the

design is modular and any components can be replaced within a relatively short time. The design also allows good x-ray and optical access to the sample and pressures can be controlled and varied at any sample temperature.

Heating is accomplished with two sets of resistance heaters. A small heater heats the cavity around the diamonds from the outside. Alumina heat shields prevent the sample, thermocouples and diamonds from direct exposure to the thermal radiation of the heater coil. The temperatures around the sample are thus well characterized and uniform. Because the small heater cannot provide enough power to overcome all the thermal losses, the DAC is placed in a container which is heated to 700 C in order to achieve sample temperatures of 1200 C. As with the smaller inner heater, the components of the cell are shielded from direct exposure to thermal radiation from this heater coil. Additional heat shields between the heated sections and the water-cooled outer jacket minimize power losses. Both heaters are made of tantalum wire, which also serves as a getter to keep the diamond environment absolutely free of oxygen. Because this gettering action tends to destroy the heaters after a few days, they are designed to allow simple replacement without the necessity of releasing the pressure.

Temperatures are measured with W-5% Re--W-26% Re thermocouples. The calibrations of the thermocouples were checked by mounting them in the cell exactly as they were to be in the actual high-temperature/high-pressure experiments and then observing the melting of Pb, Al and Au at zero pressure.

For each run, diamonds with 600 μ m culet tip diameters were used. The gaskets were made from Mo-13% Re sheet of thickness 250 μ m, prepressed to 50 μ m, with a hole diameter of 180 μ m. Samples of Au + NaCl were loaded with the intent of comparing the Au and NaCl high-temperature pressure scales. Difficulties with the gaskets, however, prevented accurate comparison of the pressures obtained from the two scales. Above approximately 400 C, the NaCl tended to extrude, leaving the Au trapped between the gasket and the diamond. Therefore, pressures had to be determined from essentially ungasketed Au samples. To do this, the Au isotherms[8] were compared with the lattice constants obtained with energy-dispersive x-ray diffraction using "white" x-radiation produced at SSRL. Only 2 to 15 minutes were required to collect each diffraction pattern.

A series of three diffraction patterns taken during one high-temperature/high-pressure run is shown in Fig. 1. The history of the sample is traced from the starting conditions at T=24 C and P=0 (Fig. 1a), to T=1045 C and P=110 kbar (Fig. 1b), and finally cooling to T=30 C at P=55 kbar (Fig. 1c). The NaCl peak was too weak to be observed at 1045 C. The boron carbide peaks appeared after the NaCl extruded.

The DAC has withstood pressures over 110 kbar at temperatures over 1200 C. To date only one pair of diamonds has failed. Before failure, they had been subjected to thermal cycling between T=24 and T>1000 C. The cumulative time at temperatures above 1000 C, and pressures in the range 20-110 kbar, was several days. Problems with the vacuum system resulted in slight discoloration of the exposed diamond surfaces, but the areas in contact with metal or boron carbide were completely undamaged. The run during which the diamonds finally failed was not markedly different from previous runs that they had endured.

These experiments show that it is possible to take useful x-ray diffraction data up to at least T=1200 C and P=110 kbar, using a resistively heated DAC to achieve uniform and well-characterized temperatures. Because the DAC can maintain such conditions for only a limited time, an intense synchrotron x-ray source and energy-dispersive x-ray diffraction techniques are vital in order to make the measurements quickly enough. The main limitation to the pressures and temperatures that we can obtain is due to the gasket material. The best material which we have been able to fabricate gaskets from is the Mo-13% Re alloy. This alloy is not strong enough for gasketed samples, although it is quite satisfactory if no hole is required in the gasket.

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Figure Caption

FIG. 1. Energy spectra for Au + NaCl at simultaneous high temperatures and high pressure. Initial spectrum at $T = 24$ C and $P = 0$ (Fig. 1a); spectrum at $T = 1045$ C and $P = 110$ kbar (Fig. 1b); spectrum after cooling to $T = 50$ C at $P = 55$ kbar (Fig. 1c).