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High pressure phase transformations in neodymium studied in a diamond anvil cell using diamond-coated rhenium gaskets

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Abstract. Diamond anvil cells are used to generate high static pressures up to several megabars (hundreds of GPa) in very small volumes of material. We have explored a technique which employs a microwave plasma chemical vapour deposited diamond layer on one side of the rhenium gasket. The high yield strength of the diamond layer prevents excessive thickness reduction of the sample in the gasket hole. As a test case, we show energy dispersive x-ray diffraction data on rare earth metal neodymium to high pressures of 153 GPa using a synchrotron source. The increased sample thickness results in an unambiguous crystal structure determination of a monoclinic phase in neodymium above 75 GPa.

Single crystal diamonds and metal gaskets are the two most important components in a modern diamond anvil cell (DAC) designed for research in the multi-megabar (100–1000 GPa) pressure range. Single crystal diamond anvils are carefully selected with low internal strains, low impurity level concentrations and high crystal perfection [1]. Static pressures of over 300 GPa can be reached in DAC devices, which employ the use of single crystal diamond anvils with bevelled tips. The sample of interest is placed within a small through-hole in a metal gasket, which is pressed between the two anvils. During pressurization, the gasket plastically flows around the tips of the opposing anvils and acts to maintain a uniform stress distribution within the sample, as well as to hold the sample in place. With increasing pressure, however, the sample thickness is reduced due to the large deformation of the gasket itself. For the case of a gasket compressed in a DAC in an axially symmetric manner between flat rigid anvils with a no-slip boundary condition between the gasket and anvils, the following relation holds between the gasket flow stress σ, the sample thickness h and the pressure distribution $\mathrm{d}P/\mathrm{d}r$.

$$\sigma = h(\mathrm{d}P/\mathrm{d}r). \tag{1}$$

If the sample thickness, h, within the gasket hole becomes too small, the reduced sample volume degrades the x-ray diffraction signals as well as optical signals generated using laser excitation.

Equation (1) has been employed to measure the flow stress of rhenium at high pressure [2] and more recently to measure the flow stress of uranium and tantalum at ultra-high pressure [3]. Recent finite-element modelling of diamond deformation at multi-megabar pressure [4] has under-scored the need for high yield strength gasket materials for optimizing sample thickness at high pressures. A diamond–metal composite gasket is one possible way to improve the sample thickness by utilizing the high yield strength of diamond and the plastic deformation of the metallic component.

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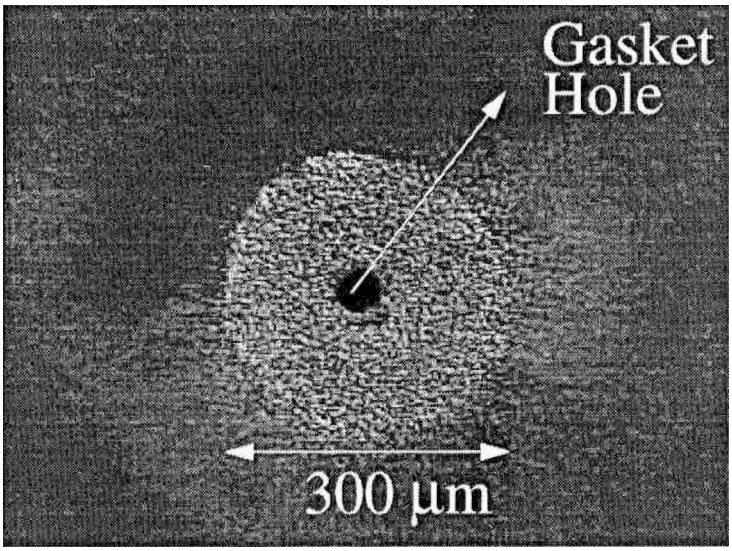

Figure 1. Optical micrograph of the diamond-coated rhenium gasket. The microcrystalline diamond film thickness is approximately 10 microns. The sample hole is 50 microns in diameter. This gasket was successfully tested to pressures of 153 GPa in a diamond anvil cell.

To address this problem, microwave plasma-enhanced chemical vapour deposition (CVD) was used to deposit a layer of polycrystalline diamond onto a rhenium gasket. The high yield strength of the diamond layer prevents excessive thickness reduction of the sample in the gasket hole. Rhenium is chosen for the gasket material because of its suitability for high pressure/high temperature measurements and earlier high pressure studies have shown that the ambient pressure hcp phase is stable to 216 GPa [5]. While CVD diamond deposition is routinely carried out on materials such as silicon (for electronic-based applications) as well as on several metals such as tungsten carbide and titanium alloys (for wear-resistant applications), diamond coating of rhenium has not, to the authors' knowledge, been published. One concern involving the vapour deposition of diamond on metals is the residual film stress caused by the significant thermal mismatch, which can lead to film delamination. For example, a residual stress of up to 7.1 GPa has been reported [6] for diamond-coated Ti–6Al–4V (a typical aerospace alloy). For rhenium, a residual thermal stress of about 5 GPa (compressive) is still expected, assuming a typical substrate deposition temperature of 1173 K. Despite the thermal stress expected in this coating, we have deposited a thick, well adhered diamond layer on the rhenium gasket and used it in high pressure experiments to 153 GPa on rare earth metal neodymium. The success in coating rhenium with diamond and in obtaining high pressures in the DAC may be related to the unusually high melting temperature (3459 K) of rhenium. The diamond deposition temperature (1173 K) is well below half of its melting temperature, at which point dislocations would normally begin to anneal out of the material and reduce the work-hardening effects induced during the gasket indentation process. Therefore, the CVD diamond coating process on rhenium would not degrade the work hardening of rhenium achieved during the pre-indentation process in a diamond anvil cell.

A standard diamond anvil cell using bevel diamonds of 70 micron central flat, 7° bevel, and 300 micron culet size was employed in the present experiments. Before depositing the diamond film onto the gasket, the gasket was indented in the DAC and a 50 micron diameter sample hole was drilled according to standard procedures. Figure 1 shows an optical micrograph of the

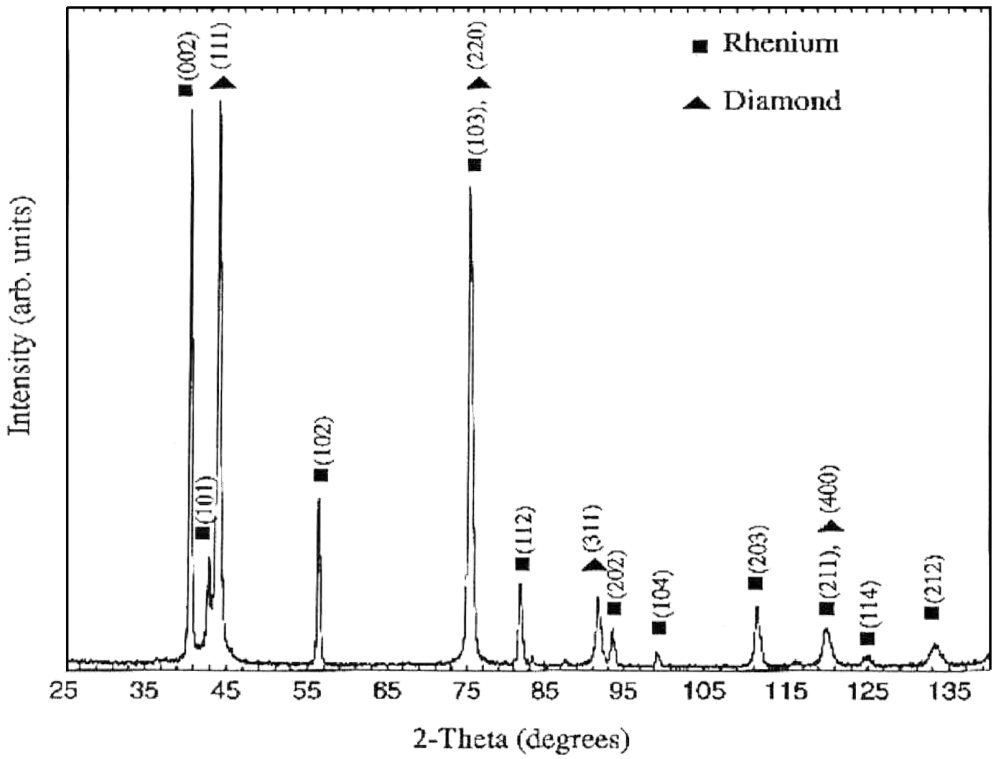

Figure 2. Glancing angle x-ray diffraction pattern (copper Kα radiation, $\lambda = 0.1542$ nm) from the diamond-coated hexagonal close-packed rhenium gasket at ambient pressure before placement in a diamond anvil cell. Diffraction peaks from both rhenium and diamond are labelled.

approximately 10 micron thick diamond layer on rhenium grown in a 6 kW microwave plasma CVD system. This coating was grown on one side of the gasket only at a processing pressure of 90 Torr, a methane fraction of 2% (in hydrogen), a microwave power of 1 kW and a substrate temperature of 1173 K. The deposition time was 6 hours. The side of the rhenium gasket exposed to plasma was covered with a homogenous and well adhered diamond layer. The film morphology shows well faceted, micron-size grains, which are of high diamond phase purity as determined by Raman spectroscopy. Figure 2 shows the glancing-angle x-ray diffraction spectrum of the diamond-coated rhenium gasket. The spectrum was indexed to a mixture of cubic diamond phase and a hexagonal close-packed phase of rhenium metal. The measured lattice parameters of rhenium are $a = 0.2772$ nm and $c = 0.4447$ nm, which are within 0.4% of the literature values. The measured lattice parameter of the cubic diamond structure is 0.3564 nm, which is within 0.1% of the literature value. Our attempts to deposit diamond layers on both sides of the gasket were not completely successful due to graphitization of the diamond layer not exposed to plasma. Therefore, all high pressure experiments were carried out using gasket coated with a diamond layer on one side only. Also, we expect some diamond coating of the inside walls of the gasket hole. However no cross-sectional studies on the gasket were performed to examine the details of diamond coating on the inside walls of the sample chamber.

We have chosen the rare-earth metal neodymium as a test case sample for the applicability of the diamond-coated rhenium gasket. Copper was employed as an internal pressure standard in our x-ray diffraction study. Phase transformations induced by ultra-high pressures in rare-earth metals are an active field of study at the present time [7, 8]. Complex crystal structures

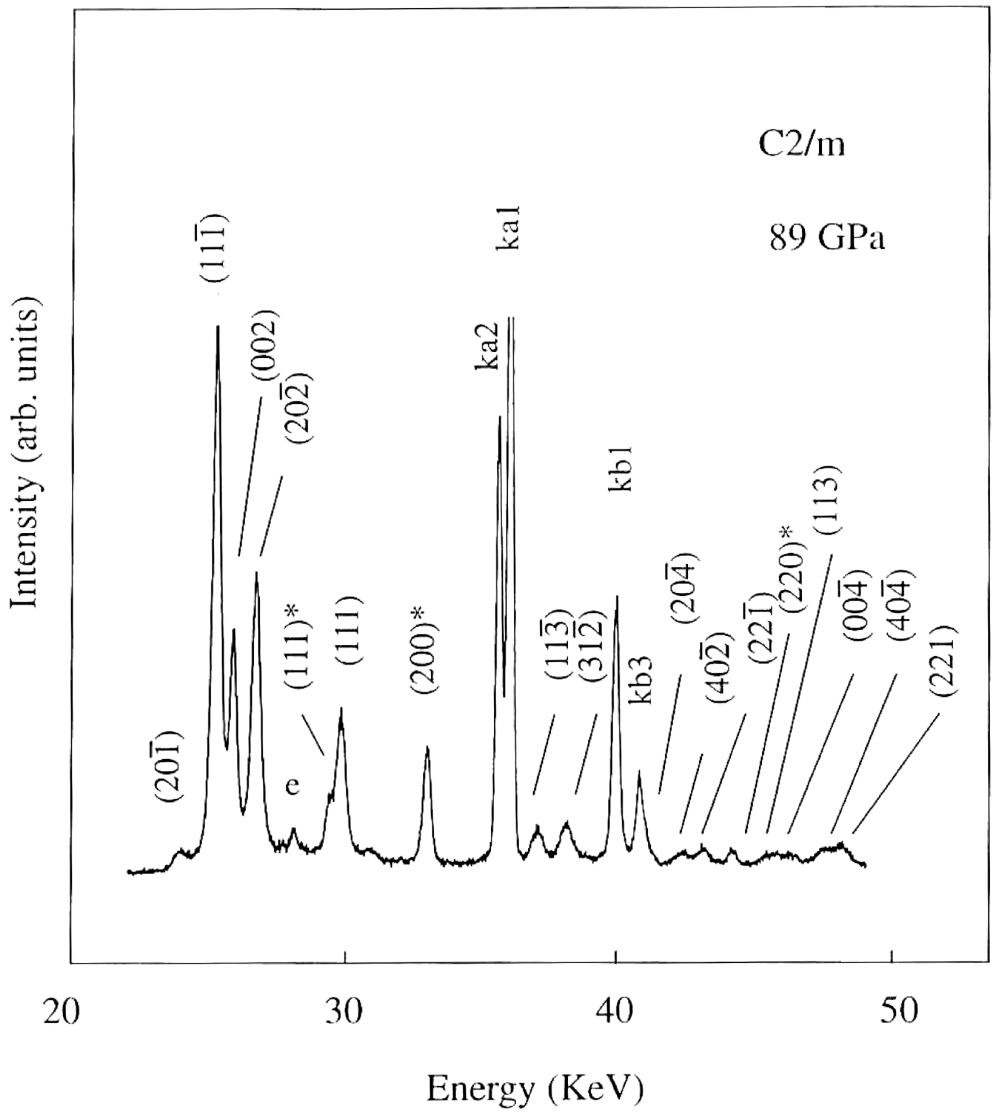

Figure 3. The energy dispersive x-ray diffraction spectrum from the neodymium (Nd) sample and a copper (Cu) pressure marker contained in a diamond-coated rhenium gasket at 89 GPa. The Cu diffraction peaks marked by * are labelled according to an fcc phase. The Nd diffraction peaks are indexed to space group $C2/m$ with $a = 0.4858 \pm 0.0004$ nm, $b = 0.2712 \pm 0.0002$ nm, $c = 0.5051 \pm 0.0004$ nm and $\beta = 118.6 \pm 0.2^{\circ}$. The fluorescence lines from Nd, Kα and Kβ are also labelled. e is an escape peak from the germanium detector.

are observed in rare-earth metals at high pressures and identification of these phases is limited by the quality of the x-ray diffraction patterns due to thin samples (few microns) at megabar pressures. Neodymium crystallizes in the double hexagonal close-packed (dhcp) phase at ambient pressures. The following sequence of transformations is known for neodymium [9, 10] to 60 GPa:

$$\text{dhcp} \overset{3.8\ \text{GPa}}{\longrightarrow} \text{fcc} \overset{18\ \text{GPa}}{\longrightarrow} \text{distorted fcc} \overset{40\ \text{GPa}}{\longrightarrow} \text{hp3}.$$

Table 1. Comparison of the observed and calculated interplanar spacings d_{hkl} and the observed and calculated intensities for the energy dispersive x-ray diffraction data for neodymium at 89 GPa. The calculated intensities are based on a monoclinic $C2/m$ phase described in the text.

hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	I_{calc}
$11\bar{1}$	2.287	2.287	100	100
002	2.218	2.218	32	47
$20\bar{2}$	2.128	2.128	51	41
111	1.850	1.851	31	55
$11\bar{3}$	1.418	1.417	8	20
$31\bar{2}$	1.371	1.369	10	3
$20\bar{4}$	1.262	1.262	12	5
$22\bar{1}$	1.185	1.186	4	1
113	1.116	1.114	4	5
$00\bar{4}$	1.107	1.105	1	2
$31\bar{4}$	1.093	1.092	6	1
$40\bar{4}$	1.062	1.059	4	2
221	0.937	0.936	2	1
$11\bar{5}$	0.909	0.908	2	1
$42\bar{1}$	0.886	0.886	7	1
131	0.852	0.853	2	1

The ultra-high pressure behaviour of neodymium above 60 GPa is of interest to investigate the f-shell delocalization phenomenon and related phase transformations. We have investigated high pressure transformations in neodymium to 153 GPa in a DAC using a diamond-coated rhenium gasket.

After the gasket was coated with diamond, a neodymium sample along with a copper pressure marker was placed in the gasket hole. Energy dispersive x-ray diffraction measurements were carried out at beam-line X-17C, NSLS, Brookhaven National Laboratory. A micro-collimated x-ray beam of 11 μm $\times$ 6 μm was employed in our x-ray diffraction measurements. In our experiments, the sequence of transformations observed below 60 GPa is similar to earlier results [9, 10] as documented above. We observed a new phase transformation in neodymium at a pressure of 75 ± 5 GPa from a hexagonal phase with three atoms/cell, hp3 phase [9], to a monoclinic $C2/m$ phase [11]. Figure 3 shows the energy dispersive x-ray diffraction spectrum from the neodymium sample and copper pressure marker contained in the diamond-coated rhenium gasket at 89 GPa. The pressures are calculated from the equation of state of copper based on the procedures described in [5] and [6]. The sample is indexed to the space group $C2/m$ (monoclinic phase with four atoms/cell) as described in [9] with $a = 0.4858 \pm 0.0004$ nm, $b = 0.2712 \pm 0.0002$ nm, $c = 0.5051 \pm 0.0004$ nm and $\beta = 118.6 \pm 0.2^{\circ}$. The four atoms occupy the 4(i) positions of $C2/m$ with coordinates $(0.280, 0, 0.252)$ similar to values determined for cerium [11]. Table 1 shows a comparison of the observed and calculated interplanar spacing d_{hkl} and the observed and calculated intensities for the x-ray diffraction data for neodymium at 89 GPa. It can be seen from table 1 that the $C2/m$ phase gives an excellent fit to the observed 17 diffraction peaks. The large numbers of observable diffraction peaks are due to a thicker sample afforded by the use of a diamond-coated rhenium gasket. The measured compression of neodymium at 89 GPa is $V/V_0 = 0.428$. The $C2/m$ phase is stable to the highest pressures of 153 GPa (volume compression $V/V_0 = 0.37$). The diamond layer on top of the rhenium metal did not crack to the highest pressure in these experiments.

We offer the following conclusions:

(1) Thick diamond films can be successfully deposited on rhenium metal using the standard CH_4/H_2 chemistry by a microwave plasma CVD process.
(2) High pressure x-ray diffraction studies on a neodymium sample were successfully carried out to 153 GPa in a diamond anvil cell with excellent diffraction pattern quality. We attribute the excellent diffraction pattern quality to a thicker sample afforded by the use of a diamond-coated rhenium gasket.
(3) The high quality x-ray diffraction patterns resulted in a positive identification of a $C2/m$ phase in compressed neodymium above 75 ± 5 GPa. This $C2/m$ phase is similar to the one observed in compressed cerium. This $C2/m$ phase of neodymium was found to be stable to pressures as high as 153 GPa.

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