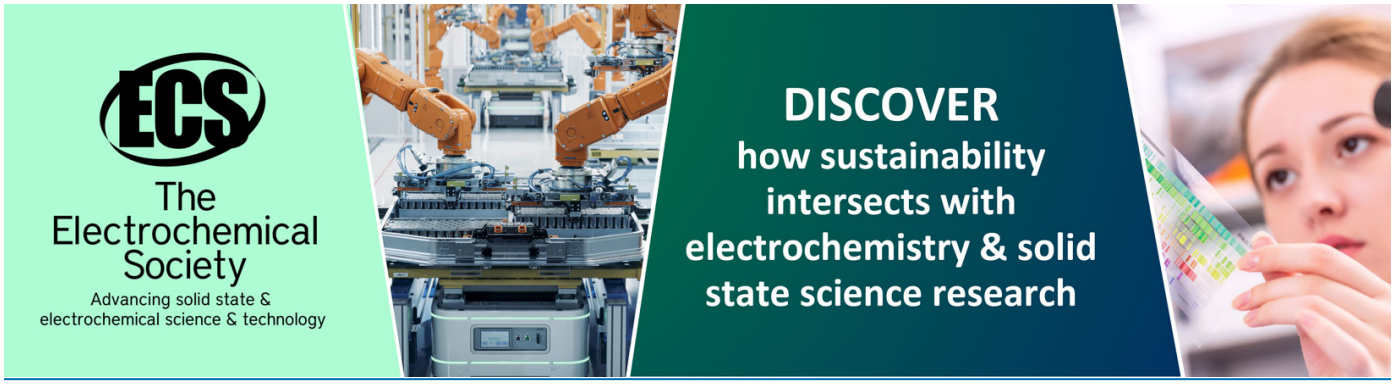
Pressure calibration of diamond anvil Raman gauge to 410 GPa



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Pressure calibration of diamond anvil Raman gauge to 410 GPa

Yuichi Akahama and Haruki Kawamura

Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigohri, 678-1297, Japan

E-mail: akahama@sci.u-hyogo.ac.jp

Abstract. The first-order Raman band of diamond anvils has been investigated at pressure up to 410 GPa in order to develop an optical pressure determination method. The high-frequency edge of the band was calibrated by the pressure scale of the equation of state of Pt. A unique relationship between the edge-frequency and the sample pressure was confirmed up to the highest pressure, while the edge frequency reaches to 1907 cm^{-1} at 410 GPa. Usefulness of the diamond anvil Raman gauge as a laboratory-based pressure determination method in the multimegabar pressure range has been discussed.

1. Introduction

The recent development of the diamond anvil cell (DAC) technique has extended the scope for materials research under high pressure to the multimegabar pressure range. At present, the predicted value of metallization pressure of hydrogen [1, 2] is coming within the range of attainable pressure by the DAC. In such extremely high-pressure conditions, the widespread ruby fluorescence method is often inapplicable and we have to use equations of state (EOS) of standard materials for determination of the sample pressure. Consequently, x-ray diffraction experiments using a synchrotron radiation source are required for estimating the volume of them. Therefore, a convenient method for the laboratory-based pressure determination has strongly been desired in order to advance material science under such extreme conditions.

Recently, the pressure shift of the first-order Raman band of diamond anvils has attracted many attentions as an optical pressure determination method in this pressure range. This optical method was firstly proposed by Hanfland and Syassen [3] and availability of the pressure determination method have recently been reported [4-12]. Though the pressure shift of the high-frequency edge of the band is calibrated and applied for a pressure scale, the edge is often different in shape depending on the pressure condition and/or the configuration of the optical system. Despite of this, the investigation of the Raman scattering in the multimegabar range has been limited to a few reports. For the reliable pressure determination by this method, further experiments to confirm the universality of the calibration curve are needed.

In this study, the pressure shift of the first-order Raman band of diamond anvils has been calibrated at pressure up to 410 GPa on the basis of the Pt EOS as the primary scale and proposed as a pressure gauge in the multimegabar pressure range.

2. Experimental details

The high-pressure generation of multimegabar pressures was performed using double-bevel diamond anvils. The diameter of the flat face of diamond anvils, which had a loading axis along the [001]

crystal direction, was from 15 to 30 μm. Typical dimensions of the first bevel diameter and angle, and the second bevel diameter and angle were 250 μm and 8.0º, and 450 μm and 15º, respectively. The diamond crystals were Ia-typed ones with low fluorescence in the visible range, so-called, "the low fluorescence diamonds" and a pair of opposite anvils was cut from a single stone.

Raman scattering experiments were carried out using a micro-spectrometer system with the backscatter geometry. Raman spectra from the center of the anvil culet were collected with a He-Ne laser (632.8 nm, 35 mW) as an excitation source. For reliable pressure determination, the definition of the edge frequency without any arbitrariness is needed. In this work, it was defined as a minimum of the differential spectrum. The accuracy by this manner was within 3 cm^{-1}.

Pressure was determined on the basis of the Pt EOS scale by Holmes *et al*. [13]. The volume of the Pt pressure marker in the sample chamber was estimated by powder x-ray diffraction experiments on the BL10XU beamline at SPring-8. The experimental details were described elsewhere [14, 15]. A typical diffraction pattern of the Pt marker at 408 GPa is shown in figure 1. The uncertainty in the pressure measurement in the multimegabar range was estimated to be typically within 9 GPa from the pressure distribution in the sample and the error of the lattice parameter of the marker. The pressure inhomogeneity was estimated to be about 6 GPa from the line-broadening of the diffraction line. The error in the average pressure, which was estimated from the standard deviation (*std*) of the lattice parameter, was within 3 GPa. This error is due to the deviatoric stress effect [14].

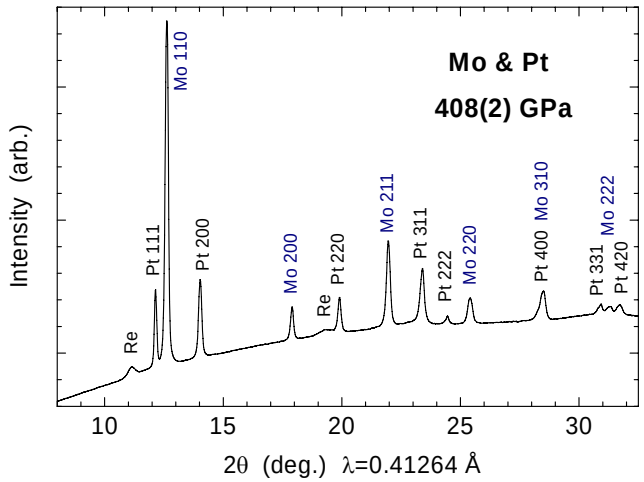

Figure 1. Typical diffraction pattern of the Pt pressure marker and Mo sample collected at pressure in the multimegabar range using diamond anvils with a culet diameter of 20 μm. The estimated pressure was 408(2) GPa. The diffraction lines of Pt and Mo are indexed as *fcc* and *bcc* lattices with lattice constants of a=3.3777(14) Å and 2.6530(12) Å, respectively.

Table 1. The relation between sample pressure and the edge frequency of the first-Raman band for the loaded diamond anvils, together with loading conditions.

P (GPa)	error (GPa)	ω (cm^{-1})	error (cm^{-1})	P scale	sample	culet dia.(μm)
265	6	1768	2	Pt	Mo	15
305	9	1830	3	Pt	Mo	15
372	9	1872	2	Pt	Ni	30
375	9	1877	2	Pt	Ni	30
408	9	1907	3	Pt	Mo	20

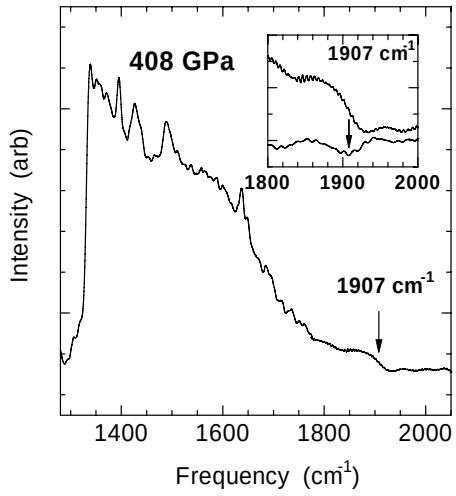

Figure 2. Typical Raman spectra from the center of the diamond anvil culet at 408 GPa. Inset shows magnified drawing around the high-frequency edge and its differential spectrum, dI/dω. The high-frequency edge of the Raman band was defined as a minimum of the dI/dω.

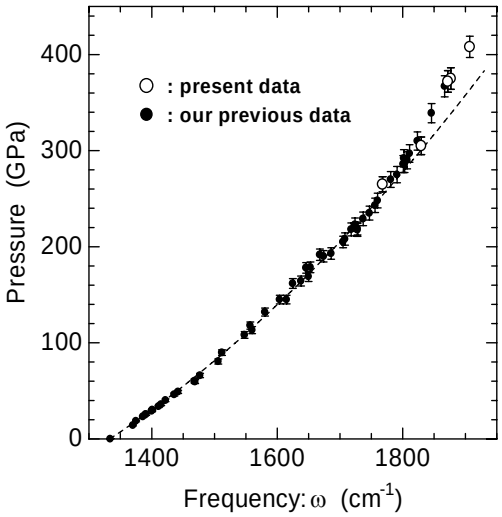

Figure 3. Pressure dependence of the edge frequency together with previous data [6, 8]. The errors in the pressure measurement and the edge-frequency of the present data are typically within 9 GPa and 3 cm^{-1}, respectively. The broken line corresponds to the curve of equation (1) in the text.

3. Results and Discussion

Typical Raman spectrum at highest pressure of 408(2) GPa in the study is shown in figure 2. This is characterized by the steep edges at the high- and low-frequency sides, which come from the spectra of the culet and the table faces of the anvil, respectively. The high-frequency edge, which corresponds to the singlet mode of the split band of the triply degenerated F_{2g} optical phonon mode in the case of [001] anvils [11], was defined as a minimum of the differential spectrum. The edge frequency reached to 1907(3) cm^{-1}.

The obtained value of the edge frequency in this work are summarized in table 1, together with loading conditions; the sample pressure, pressure marker, the contents in the sample chamber and the culet size. Figure 3 shows the obtained pressure dependence together with our previous data [11]. These data show a clear correlation to the sample pressure. The correlation is unique and almost independent of the loading conditions though the variety of the conditions and the experimental frequency are still limited at present.

The broken line in the figure corresponds to the following function proposed by us previously [11].

$$P(GPa) \cong A\frac{\Delta\omega}{\omega_0}\left[1+\frac{1}{2}(B-1)\frac{\Delta\omega}{\omega_0}\right], \quad (1)$$

where $\Delta\omega$, ω_0, $\Delta\omega/\omega_0$ correspond to the frequency shift, frequency at ambient pressure and the relative Raman frequency change, and A and B are fitting parameters. The function was reformulated from the pressure-density relation of diamond proposed by Aleksandrov *et al*. [16]. Using the analytical form of equation (1) with the edge frequency ω_0 = 1334 cm^{-1} at ambient pressure, our present and previous experimental data of pressure versus the edge frequency were fitted by a least-squares method. If an uncertainty of 3% is assigned to pressure values, a satisfactory fit was obtained at pressure up to 300

GPa. This pressure uncertainty is reasonable considering the experimental error of pressure. The obtained values for the parameters *A* and *B* in equation (1) were 547(11) GPa and 3.75(20), respectively.

However, observed data above 300 GPa remarkably deviate to higher pressure side from the fitting curve (see figure 4) and it was difficult to fit the whole data using a quadratic function. The reason for the deviation may come from certain change in stress-state on the culet face of diamond anvils or the accuracy of the pressure scale. In order to get the calibration curve for the optical pressure gauge in the multimegabar pressure range, setting the limit to the pressure range above 200 GPa, the observed data were fitted by the following quadratic expression.

$$P(GPa) = 3141_{3} - 4.157_{20}\,\omega + 1.429_{12} \times 10^{-3}\,\omega^{2}. \qquad (2)$$

The quadratic curve, which is shown in figure 4, fitted the data within the 2% error of the pressure value. By using above formula (2), we can easily estimate the pressure in the sample chamber within the 2% error of the pressure value. In addition, the optical method does not require any pressure standard materials in the sample chamber. Commonly, under such high-pressure condition, the volume of the sample chamber is considerably limited itself and these materials often contaminate the x-ray diffraction data and spectroscopic data. Therefore, the method is useful and available so much from the viewpoint of measuring the intrinsic and pure signal of samples.

In addition, the possibility of the pressure generation beyond 400 GPa has recently been pointed out from the direct observation of the stress-state of the loaded diamond anvil using a Raman scattering method [9, 11]. This was confirmed in this study.

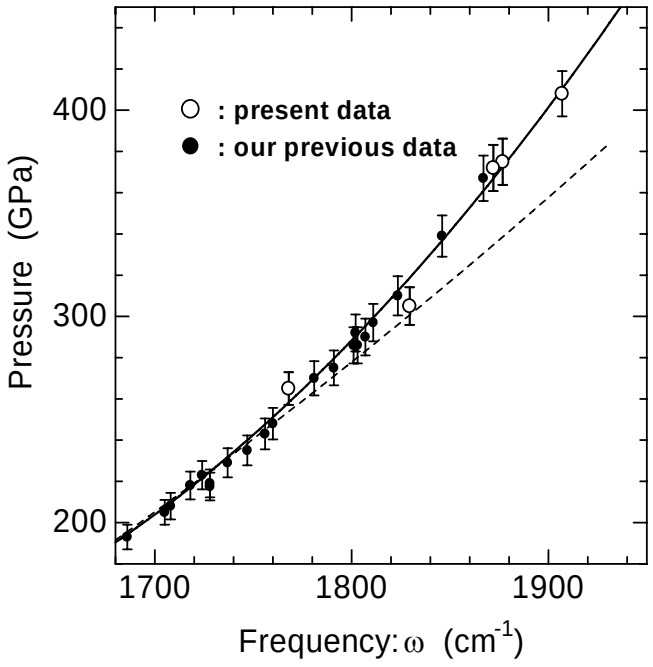

Figure 4. Pressure dependence of the edge frequency in the multimegabar pressure range. The solid line represents the calibration curve proposed in this study.

4. Conclusion

In this study, Raman scattering experiments were extended to 410 GPa. Uniqueness of the relationship between the sample pressure and the edge-frequency was confirmed up to 410 GPa and the calibration curves were proposed, while the usefulness of the diamond anvil Raman gauge was demonstrated.

Acknowledgments

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