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Portable laser-heating system for diamond anvil cells

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The diamond anvil cell (DAC) technique coupled with laser heating has become the most successful method for studying materials in the multimegabar pressure range at high temperatures. However, so far all DAC laser-heating systems have been stationary: they are linked either to certain equipment or to a beamline. Here, a portable laser-heating system for DACs has been developed which can be moved between various analytical facilities, including transfer from in-house to a synchrotron or between synchrotron beamlines. Application of the system is demonstrated in an example of nuclear inelastic scattering measurements of ferropericlase $(Mg_{0.88}Fe_{0.12})O$ and h.c.p.-$Fe_{0.9}Ni_{0.1}$ alloy, and X-ray absorption near-edge spectroscopy of $(Mg_{0.85}Fe_{0.15})SiO_3$ majorite at high pressures and temperatures. Our results indicate that sound velocities of h.c.p.-$Fe_{0.9}Ni_{0.1}$ at pressures up to 50 GPa and high temperatures do not follow a linear relation with density.

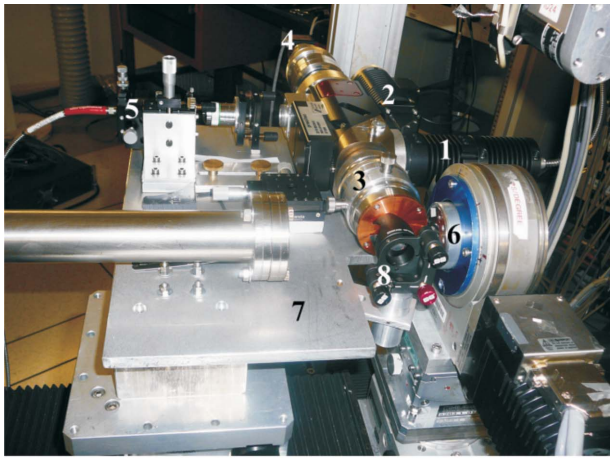
Keywords: laser heating; diamond anvil cells; portable system; NIS; XANES.

1. Introduction

The diamond anvil cell (DAC) technique initiated in the late 1950s provides opportunities for high-pressure researchers with Mössbauer, infrared and Raman spectroscopy, resistivity measurements, X-ray diffraction and inelastic scattering (Eremets, 1996). During the last few decades the DAC technique has become the most successful method of pressure generation capable of working in the multimegabar pressure range (Duffy, 2005; Dubrovinsky *et al.*, 2007; Dewaele *et al.*, 2007). However, there are still a number of problems related to high-temperature experiments in DACs. There are two major methods of heating in DACs: laser and electrical (Eremets, 1996; Dubrovinskaia & Dubrovinsky, 2005). Electrical heating is very efficient at temperatures below ~1000 K at pressures over 250 GPa, but laser-heating experiments become very demanding if higher temperatures are required (Dubrovinskaia & Dubrovinsky, 2005). Laser-heating techniques cover a wide P–T field: $P > 200$ GPa, $T = 1300$–5000 K (Hirose, 2006; Dewaele *et al.*, 2007; Dubrovinsky *et al.*, 2007). The sample preparation for laser-heating experiments is relatively easy and there is practically no risk to the diamonds owing to heating. There are numerous DAC laser-heating facilities in geo-, material-, physics- and chemistry-oriented laboratories (including the Bavarian Geoinstitute), and there are a number of examples of successful coupling of an *in situ* laser-heating system with synchrotron radiation facilities, including specialized beamlines at the third-generation synchrotrons: European Synchrotron Radiation Facility (ESRF), Advanced Photon Source (APS) and SPring-8 (Shen *et al.*, 2001; Hirose, 2006; Schultz *et al.*, 2005; Prakapenka *et al.*, 2008). However, so far all existing DAC laser-heating systems are stationary: they are linked either to certain equipment (an optical or Raman spectrometer, for example) or to a beamline. Studies of various physical properties and chemical reactions at high pressures and temperatures in DACs require mobility of the laser-heating system; for example, the ability to move laser-heating equipment (preferably together with the same DAC, at the same pressure) between different analytical facilities, including transfer from in-house to a synchrotron or between synchrotron beamlines. Here we report on the design, mode of operation and some examples of application of a portable laser-heating system for DACs.

2. Design of a portable laser-heating system for DACs

The system consists of two major components: the source of laser light and the universal laser-heating head (UniHead) (Figs. 1 and 2). As a laser source we tested two SPI Lasers UK models, a G3 (30 W fibre-coupled pulse laser, weight 9 kg, excitation wavelength 1064 nm) and a SPI100 modulated high-power fibre laser (100 W, weight 40 kg, excitation wavelength



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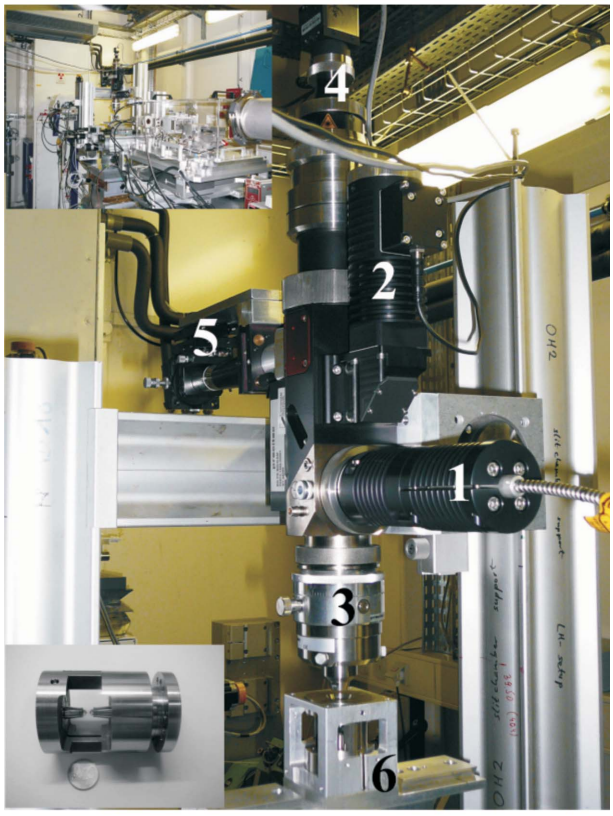

(*b*)

Figure 1
The universal laser-heating head (UniHead) mounted at beamline ID24 (*a*) for X-ray absorption near-edge spectroscopy measurements and at beamline ID18 (*b*) at ESRF (Grenoble, France) (inset in upper left corner) for nuclear inelastic scattering experiments in a large side-opening DAC (inset in bottom left corner). 1, connector for the SPI100 fibre laser; 2, illumination unit; 3, lenses unit for focusing of the incoming laser light; 4, digital video camera; 5, module for spectroscopic measurements; 6, DAC mounted inside the holder; 7, mounting plate; 8, holder for a carbon laser mirror.

1064 nm). The 30 W pulse laser was used only to verify (successfully) that all optical components (see below) could sustain high-peak power up to 300 W at 50 kHz repetition rate; all results presented in this paper were obtained using the SPI100 laser.

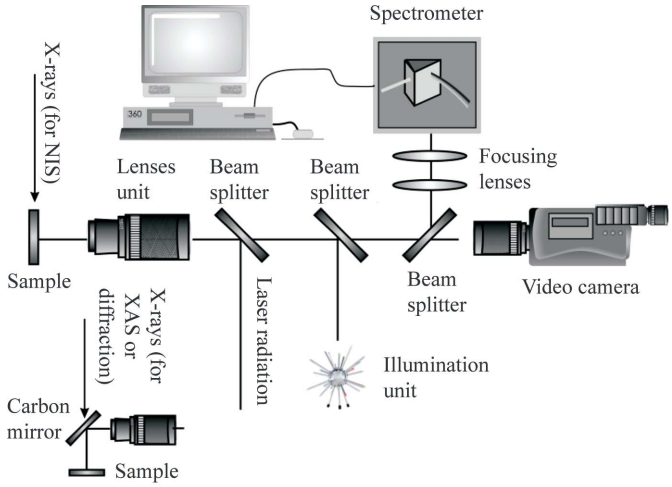

Figure 2
Schematic diagram of the optical components of the UniHead. The insert in the bottom left corner shows the arrangement for laser heating in perpendicular geometry.

The UniHead is based on the finite cutting laser head produced by Precitec KG (Germany) (weight ∼4.5 kg). Originally the FCS (fine cutting system) was developed for three-dimensional cutting, cutting of filigree contours for the medicine industry, and applications in the fine mechanics and watch industry. It could work with a maximum laser power of 500 W for wavelengths of 1030–1090 nm (Nd:YAG, disc and fibre optical lasers).

The functions of the UniHead in the portable laser-heating system are to focus incoming laser light onto the sample within the DAC, to provide illumination by white light for observation of the sample in the DAC, and to give access for optical spectroscopic measurements (multiwavelength spectro-radiometry, ruby fluorescence measurements, Raman spectroscopy *etc.*).

For focusing of the 1064 nm laser radiation, the UniHead employs a bending mirror (which also acts as a beam splitter transparent for light within the 400–900 nm wavelength range) and a set of lenses with a 80 mm working distance. The position of the mirror and the lenses can be adjusted in order to achieve an optimum (circular) beam shape and its centring with respect to the optical axis of the instrument. With a beam diameter of ∼3 mm produced by the SPI100 laser, the distribution of intensity has a Gaussian shape with a half width at half-maximum of ∼30 µm and a focus depth of ∼10 µm at the focal position, whereas if the ×2 beam expander is used the beam size increases to ∼60 µm and the focus depth is ∼3–4 µm. Note that, although we did not conduct actual tests with laser-beam shapers as proposed by Prakapenka *et al.* (2008), it appears to be a straightforward strategy if one would like to modify the laser-beam intensity profile delivered by the UniHead.

Illumination of the sample is achieved owing to a built-in halogen 50 W lamp. Through the lens, the diffuser and the beam splitter it delivers a homogeneous light stream to the sample.

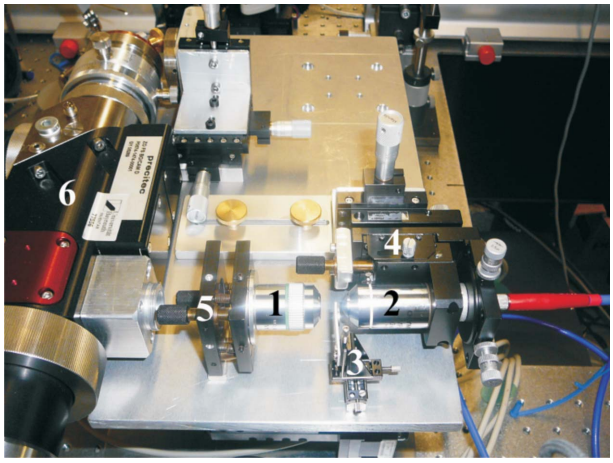

Figure 3
Module for spectroscopic measurements attached to the UniHead (6). 1 and 2 are ×50 objectives mounted on three-dimensional (4) and two-dimensional (5) tilt stages. A pinhole is mounted on a miniature three-dimensional stage (3).

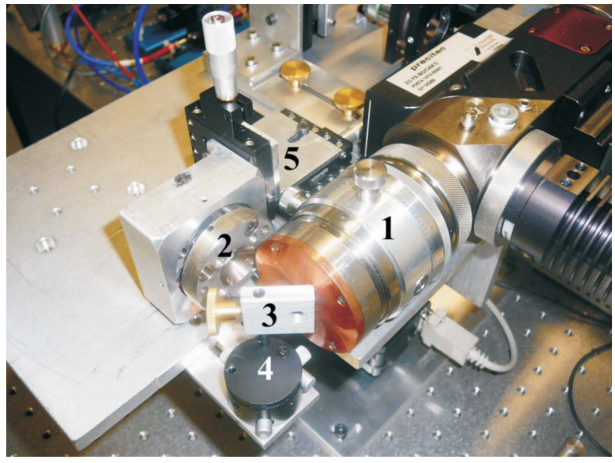

Figure 4
The UniHead (1) and DAC (2) in perpendicular (90° between optical axes of the DAC and UniHead) geometry mounted on an aluminium plate. 3, holder for a diamond laser mirror; 4, rotary stage; 5, three-dimensional mechanical stage for DAC positioning.

For observation of the sample in the DAC and for the process of laser-heating we use a high-resolution GigE uEye (SUXGA, 2048 × 1536) digital camera. The software of the digital camera makes it possible to enlarge a part of the observed area, and to mark and to trace a certain position in the image, which is very useful for alignment of the system.

The module for spectroscopic measurements exploits the optical access window used in the original (industrially produced FCS by Precitec KG) system for control of cutting processes (Figs. 1 and 2). The module includes two ×50 objectives separated by a pinhole in confocal configuration (Fig. 3). With a pinhole of 50 µm in diameter the observation area reduces to about 5 µm, which is several times smaller than the size of a laser beam spot. One of the objectives is mounted on a small three-dimensional stage and coupled with an optical fibre. The second objective is mounted on a small two-dimensional tilt-stage for alignment purposes. One end of the laboratory-grade splitter optical fibre assembly (Ocean Optics) is connected to a small solid-state 100 mW 532 nm laser (used for exciting ruby fluorescence), and the other is attached to the Ocean Optics QE65000 spectrometer (which is primarily used for measurements of the thermal radiation emitted by a laser-heated sample, but also could be used either for ruby fluorescence measurements, or for Raman spectroscopy in a laser-heated cell).

3. Mode of operation

Owing to the modular construction, the portable laser-heating system can be used in different modifications for heating a sample in an alone-standing DAC or in a cell coupled directly to the UniHead with 'normal' (optical axes of the DAC and the UniHead coincide) or 'perpendicular' (90° between optical axes of the DAC and the UniHead; Figs. 2 and 4) geometries, with or without a spectroscopic or radio-spectrometric module. However, the first step in the work with any modifications of the system is the alignment of the laser position in the DAC. The SPI100 laser is equipped with a low-power (1 mW) red (735 nm) guide laser. It greatly simplifies the primary location of the heated area, but owing to construction peculiarities of optical fibres and optics the beam size of the guide laser at the focal point is ∼500 µm in diameter. For precise location of the heated spot we use a metal foil (mostly Pt) or a polished block of pyrophyllite ('pipestone'). A laser power as low as 1–2 W is usually sufficient to form a bright glowing spot. A focusing lens incorporated into the UniHead in front of the digital camera (Fig. 2) should be adjusted until a clear and sharp image of a heated spot appears on the computer screen and then the centre of the spot is marked using a special software option.

In order to align the spectrometer, one of the ends of the splitter optical fibre assemblage is attached to the visible (in our experiments 532 nm) diode laser and its spot is focused and placed exactly at the position of the centre of the heated area using the adjustment screws of objectives of the module for spectroscopic measurements (Fig. 3).

For the case of the normal configuration no further alignment is necessary. For the perpendicular geometry (Figs. 2 and 4) a glassy carbon or diamond mirror (Diamond Material, 10 mm diameter, 0.3 mm thick, Pt coated) should be adjusted by a miniature three-dimensional rotary stage (Edmund Scientific) until the shape of the heated spot becomes ideally circular.

It is important to underline that the assembly from components and the full alignment of the portable laser-heating system is rather simple and can be done even by an inexperienced user within one hour.

4. Examples of application of the portable laser-heating system

The portable laser-heating system has been successfully used at the Bavarian Geoinstitute in-house for routine experiments with DACs for samples annealing, melting experiments,

Raman spectroscopy in laser-heated DACs, measurements of electrical resistance in DACs at high pressures and temperatures *etc.*

The clearest test of portability of our system was an experiment performed at beamline ID18 (Rüffer & Chumakov, 1996) at the ESRF. The whole system was transferred from Germany to France in a car, and then mounted and aligned in a hutch of beamline ID18 during about 2 h.

The experiments were performed during the hybrid and the 16-bunch modes of the storage-ring operation. The beam was focused to about 4 μm × 20 μm using a Kirkpatrick–Baez mirror, and a MAR CCD detector was installed on the beamline to enable collection of X-ray diffraction data at the same pressure–temperature conditions as the nuclear inelastic scattering (NIS) and nuclear forward scattering (NFS) spectra. For NIS data collection the DAC was oriented with the gasket horizontal to the beam (*i.e.* both the beam and the incoherent signal passed through the gasket; Fig. 1*b*), while NFS data were collected in either horizontal or vertical geometry of the DAC (or both). The procedure of data collection and analysis has been described in previous publications (Chumakov *et al.*, 1996; Chumakov & Sturhahn, 1999; McCammon *et al.*, 2008).

The NIS of geophysically and geochemically important materials, *i.e.* the iron–nickel alloy $Fe_{0.9}Ni_{0.1}$, ferropericlase $(Mg_{0.875}Mg_{0.125})O$ and silicate perovskite $(Mg_{0.88}Fe_{0.12})SiO_3$, were studied at pressures over 100 GPa and temperatures up to 2000 K. A detailed description of observations and analysis of the results will be published elsewhere, while here our goal is to illustrate the performance of the new portable laser-heating system.

Fig. 5 shows an example of the energy dependence of NIS spectra of $Mg_{0.88}Fe_{0.12}O$ ferropericlase at 37 (2) GPa and different temperatures. The material was compressed in a specially designed cell (Fig. 1, inset) in a Be gasket, and the pressure was determined by ruby fluorescence and/or the ferropericlase thermal equation of state (Fei *et al.*, 2007). The UniHead has a 50 mm distance between the end of optical components and the focal plane of the laser allowing a DAC with a large (37 mm) opening in the gasket plane (the distance between the end of the DAC and the sample is 47 mm) to be used. There is a remarkable increase in relative intensities of the Stokes and anti-Stokes parts of the NIS spectra (Fig. 5) at high temperature. Note that NIS measurements are time-consuming and the portable laser-heating system allowed temperatures of the order of 2000 K to be maintained for two hours continuously.

Measurements of the energy dependency of NIS spectra of $Fe_{0.9}Ni_{0.1}$ alloy (Glazyrin *et al.*, 2009) allowed us to extract information on changes of the sound velocities at high pressures and elevated temperatures. Combined with X-ray diffraction studies of the thermal equation of state (Dubrovinsky *et al.*, 2007; Glazyrin *et al.*, 2009), this information is essential to model the dependence of the sound velocity as a function of density (Lin *et al.*, 2005). According to Birch's law, the sound velocities of materials are linearly scaled with density, and this approximation is widely applied by the geophysical community for extrapolation of the results of experiments at ambient temperature and middle (a few dozens of GPa) pressure range to conditions of deep Earth interiors. However, Lin *et al.* (2005) demonstrated that the behaviour of h.c.p.-Fe at high temperatures significantly deviates from Birch's law. Fig. 6 shows that sound velocities of h.c.p.-$Fe_{0.9}Ni_{0.1}$ alloy decrease substantially with increasing temperature under moderately high pressures and, as in the case of h.c.p.-Fe, do not follow a linear relation with the density, thus confirming Lin *et al.*'s (2005) results.

At the energy-dispersive X-ray absorption spectroscopy beamline ID24 at the ESRF the portable laser-heating system was used for Fe *K*-edge XANES of $(Mg_{0.85}Fe_{0.15})SiO_3$ majorite at high pressure and temperature. For *in situ* high-pressure micro-XANES measurements in the DAC we used diamonds with 250 μm culet size and ∼1.5 mm thickness. For

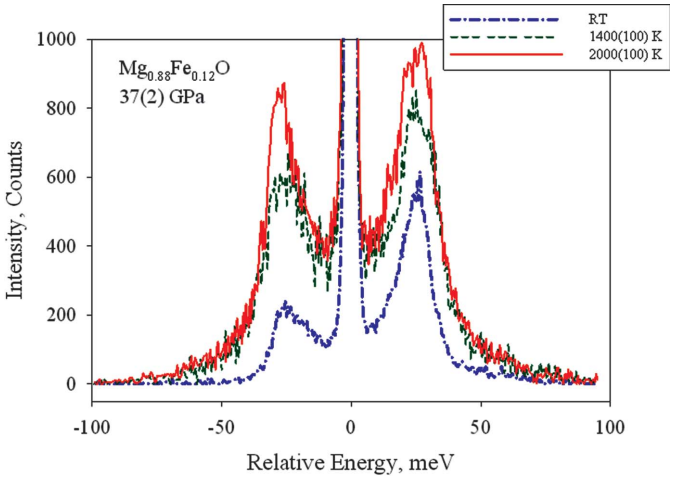

Figure 5
Energy dependencies of NIS for ferropericlase $(Mg_{0.88}Fe_{0.12})O$ at 37 (2) GPa and different temperatures at beamline ID18 at the ESRF in a laser-heated DAC. Temperatures are derived from analysis of the intensities of the Stokes and anti-Stokes parts of the spectra.

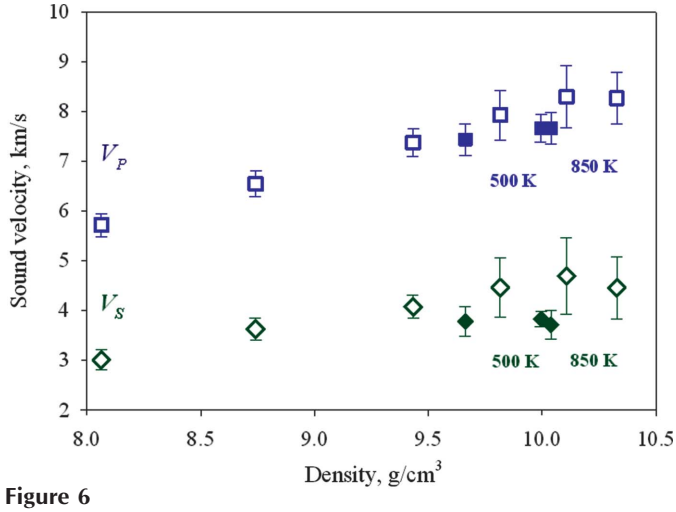

Figure 6
Experimental results of aggregate compressional V_P and shear V_S sound velocities of h.c.p.-$Fe_{0.9}Ni_{0.1}$ alloy at high pressures and ambient (empty symbols) and high (solid symbols) temperatures. Temperatures are given next to the solid symbols.

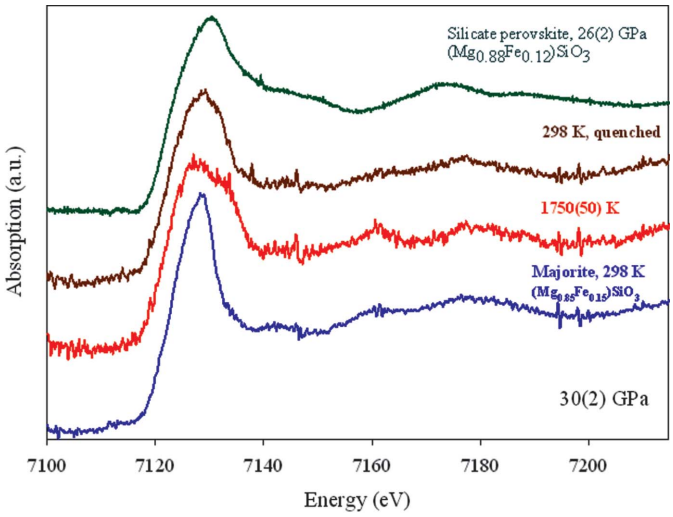

Figure 7
XANES spectra of $(Mg_{0.85}Fe_{0.15})SiO_3$ majorite at 30 (2) GPa before, during and after laser-heating. Upper spectra are from $(Mg_{0.88}Fe_{0.12})SiO_3$ silicate perovskite collected at ambient temperature at 26 (2) GPa (Narygina *et al.*, 2009).

pressure calibration and evaluation of the pressure gradient we used small ruby chips that were loaded into the cell along with the sample. We noted that strong ~7 keV X-ray radiation is sufficient to excite ruby fluorescence and we were able to measure the pressure using the spectroscopic module of UniHead. Temperatures were measured spectro-radiometrically during data collection.

The beam was focused horizontally using a curved polychromator Si(111) crystal in Bragg geometry and vertically with a bent Si mirror placed at 2.8 mrad with respect to the direct beam (Narygina *et al.*, 2009). The Bragg diffraction peaks arising from the diamond anvils were removed from the energy range of interest by changing the orientation of the DAC and following in real time the intensity of the transmitted beam on a two-dimensional detector. The measured XANES spectra were analyzed using the *VIPER* program. The flat part of the pre-edge region of the spectrum was fitted to the Victoreen function ($F = a + bE^{-3}$, where E is the absorption energy, and a and b are fit parameters) and this baseline was extended over the entire energy region. The post-edge jump in X-ray absorption was then normalized to unity.

In experiments at beamline ID24 we employed UniHead in the perpendicular geometry (Figs. 1*a* and 2) with a carbon mirror. Glassy carbon used as a substrate for silver coating does not introduce any structure into XANES spectra, but the thickness of the mirror appears to be critical for success of the experiment; with a 2 mm-thick mirror we were not able to collect any spectra, while with a mirror of thickness 0.9 mm the quality of the spectra are acceptable (Fig. 7) and we could clearly observe a transition from $(Mg_{0.85}Fe_{0.15})SiO_3$ majorite to silicate perovskite at 30 (2) GPa and 1750 (50) K.

5. Conclusions

We have developed a portable laser-heating system which consists of two major components: the fibre laser and the universal laser-heating head (UniHead). The main components of the system are industrially produced, which makes its duplication to be a rather straightforward task. The modular construction of the portable laser-heating system allows its application in different modifications: for heating a sample in an alone-standing DAC or in a cell attached and moved together with the UniHead with normal (optical axes of the DAC and UniHead coincide) or perpendicular (90° between optical axes of the DAC and UniHead) geometries, with or without a spectroscopic module. The system has been tested for in-house routine experiments with laser-heated DACs (samples annealing, melting experiments, Raman spectroscopy in laser-heated DACs *etc.*) as well as for *in situ* high-pressure high-temperature NIS and NFS studies at ESRF.

References

Chumakov, A. I., Rüffer, R., Baron, A. Q. R. & Gruensteudel, H. (1996). *Phys. Rev. B*, **54**, R9596–R9599.
Chumakov, A. I. & Sturhahn, W. (1999). *Hyperfine Interact.* **123/124**, 781–808.
Dewaele, A., Mezouar, M., Guignot, N. & Loubeyre, P. (2007). *Phys. Rev. B*, **76**, 144106.
Dubrovinskaia, N. & Dubrovinsky, L. (2005). *Advances in High-Pressure Techniques for Geophysical Applications*, pp. 487–501. New York: Elsevier.
Dubrovinsky, L., Dubrovinskaia, N., Narygina, O., Kantor, I., Kuznetzov, A., Prakapenka, V. B., Vitos, L., Johansson, B., Mikhaylushkin, A. S., Simak, S. I. & Abrikosov, I. A. (2007). *Science*, **316**, 1880–1883.
Duffy, T. S. (2005). *Rep. Prog. Phys.* **68**, 1811–1859.
Eremets, M. E. (1996). *High Pressure Experimental Methods*, p. 408. Oxford: Oxford Science.
Fei, Y., Zhang, L., Corgne, A., Watson, H., Ricolleau, A., Meng, Y. & Prakapenka, V. (2007). *Geophys. Res. Lett.* **34**, L17307.
Glazyrin, K., McCammon, C., Narygina, O., Dubrovinsky, L. & Chumakov, A. I. (2009). *Phys Rev. Lett.* To be submitted.
Hirose, K. (2006). *Rev. Geophys.* **44**, 1–44.
Lin, J.-F., Sturhahn, W., Zhao, J., Shen, G., Mao, H. K. & Hemley, R. J. (2005). *Science*, **308**, 1892–1894.
McCammon, C., Kantor, I., Narygina, O., Rouquette, J., Ponkratz, U., Sergeev, I., Mezouar, M., Prakapenka, V. & Dubrovinsky, L. (2008). *Nat. Geosci.* **1**, 684–687.
Narygina, O., Mattesini, M., Kantor, I., Pascarelli, S., Wu, X., Aquilanti, G., McCammon, C. & Dubrovinsky, L. (2009). *Phys. Rev. B*, **79**, 174115.
Prakapenka, V. B., Kubo, A., Kuznetsov, A., Laskin, A., Shkurikhin, O., Dera, P., Rivers, M. L. & Sutton, S. R. (2008). *High Press. Res.* **28**, 225–235.
Rüffer, R. & Chumakov, A. I. (1996). *Hyperfine Interact.* **97/98**, 589–604.
Schultz, E., Mezouar, M., Crichton, W., Bauchau, S., Blattmann, G., Andrault, D., Fiquet, G., Boehler, R., Rambert, N., Sitaud, B. & Loubeyre, P. (2005). *High Press. Res.* **25**, 71–83.
Shen, G., Rivers, M. & Wang, Y. (2001). *Rev. Sci. Instrum.* **72**, 1273–1280.