

***In situ* EXAFS, X-ray diffraction and photoluminescence for high-pressure studies**

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A new facility for simultaneous extended X-ray absorption of fine structure (EXAFS), X-ray diffraction and photoluminescence measurements under high pressures has been developed for use on station 9.3 at the Daresbury Laboratory Synchrotron Radiation Source. This high-pressure facility can be used at any suitable beamline at a synchrotron source. Full remote operation of the rig allows simultaneous collection of optical and structural data while varying the pressure. The set-up is very flexible and can be tailored for a particular experiment, such as time- or temperature-dependent measurements. A new approach to the collection of high-pressure EXAFS data is also presented. The approach significantly shortens the experimental times and allows a dramatic increase in the quality of EXAFS data collected. It also opens up the possibility for EXAFS data collection at any pressure which can be generated using a diamond cell. The high quality of data collected is demonstrated with a GaN case study. Particular attention will be paid to the use of energy-dispersive EXAFS and quick-scanning EXAFS techniques under pressure.

Keywords: EXAFS; high pressures; X-ray diffraction; photoluminescence.

1. Introduction

The need for combined structural studies of materials has been well understood for some time now. Combined techniques are widely used by scientists today and show significant advantages for providing structural information on materials (Sankar *et al.*, 1995; Claunsen, 1998; Epple *et al.*, 1997; Colyer *et al.*, 1997; Shannonn *et al.*, 1997; Aletru *et al.*, 1999; Perlin *et al.*, 1992). Combined extended X-ray absorption of fine structure (EXAFS) and X-ray diffraction (XRD) studies can provide the most comprehensive information on materials' structure due to their intrinsic sensitivity to short- and long-range order structure, respectively. The wide use of *in situ* combined structural studies has been significantly hampered by the lack of appropriate facilities at synchrotron sources. Recently there have been developments of such facilities taking place at several synchrotron radiation sources (*e.g.* DW11A at LURE and ID24 at ESRF, France). However, there are some disadvantages specific to each of these facilities. For example, at LURE, experimental EXAFS and XRD data are actually collected at different stations which involves moving the high-pressure cell physically from one station to another. At the ESRF, although there are significant advances in the quality of the focusing optics, the EXAFS range is still quite limited [sometimes to XANES only (Pascarelli *et al.*, 1999)].

The techniques which are currently used for combined high-pressure structural experiments are energy-dispersive EXAFS (EDE) and powder diffraction. There are some advantages in this approach, *e.g.* fast spectra-collection times. At the same time there are significant disadvantages intrinsic to the EDE technique which make the use of it in combination with XRD rather inconvenient. These include the strict requirements on stability and size of focus: both are crucial if high-quality EXAFS data are to be collected. The use of focusing also degrades the experimental resolution. However, the most significant disadvantage is restriction on choice of wavelength for diffraction, if XRD and EXAFS experiments are to be performed *in situ*. One is normally restricted in the choice of energy for XRD by the range used for EDE, since the EDE set-up is a time-consuming procedure and a change of region is quite impossible within the time scale of standard experiments. Moreover, one is generally restricted to the EXAFS pre-edge energies, since resonance effects can affect an XRD spectrum in the absorption-edge region of an EXAFS spectrum. Thus, one of the main advantages of synchrotron radiation for such studies – flexibility in choice of wavelength for XRD – is lost.

Several years of experiments at different synchrotron radiation sources (Lyapin *et al.*, 1996; Sapelkin *et al.*, 1996) have led us to the conclusion that QEXAFS (Frahm, 1989) (except when data-collection times of microseconds are required) can also be the technique of choice for combined

EXAFS/XRD experiments, since it has the advantage of being a standard transmission technique and requires relatively short (of the order of minutes) spectra-collection times. These advantages would not only allow the collection of high-quality EXAFS data under high pressures without the loss of resolution associated with the EDE detection, but would also minimize the distortions in the EXAFS spectrum due to Bragg reflections from diamonds in a reasonable amount of time. The culmination of our work is an EPSRC-funded facility (code-named HI-PREXX) to be commissioned on station 9.3 at Daresbury Laboratory for high-pressure EXAFS, XRD and ruby fluorescence measurements. This is now being upgraded for the possibility of general photoluminescence (PL) studies. Such studies can provide important information on band-gap states in semiconductors and their pressure dependencies (Perlin *et al.*, 1996a). We shall present in this paper the design of the facility and the first data collected, and shall discuss the directions for further development.

2. Experimental facility

A schematic drawing of the experimental facility is presented in Fig. 1. All parts of the system are arranged on a $900 \times 1200 \times 50$ mm breadboard. X-ray diffraction data are collected using an imaging-plate detector and monochromatic X-ray beam. EXAFS data can be collected either in energy-dispersive or standard transmission mode. Optical parts of the system are diverted from the path of the X-rays by using a mirror, with a hole for X-ray access. The mirror is positioned at 45° to the direction of the X-rays. The X-ray and optical alignment procedures are decoupled using fibre optics. In this way, alignment of the diamond anvil cell (DAC) for X-rays does not interfere with the optical alignment for the laser radiation and PL. PL spectroscopy is carried out using a He–Cd (325 nm and 442 nm) laser by Kimmon, TRIAX 320 spectrometer by ISA Inc., and a PC for data acquisition and motor control. Pressure calibration is carried out with the above optical system using the fluorescence from ruby chips mounted with the sample inside the DAC. Successful collection of PL data involves scanning over a wide wavelength range (sometimes from the UV to IR region). The dispersion of the refractive index in such a wide range becomes important and therefore UV achromats have to be used. The confocal geometry of the optical arrangement makes optical alignment straightforward.

A breadboard with optics is mounted on translational and rotational stages for positioning the diamond anvil cell with the sample mounted inside. Translations are necessary to align the sample in the X-ray beam and rotations are required to minimize the influence of diamond glitches in the EXAFS spectrum. The issue of glitches will be discussed later in this paper. We used a DXR-GM diamond anvil cell by Diacell Products Ltd with low-fluorescence 0.3 mm culet diamonds. A GaN powdered sample was loaded into a pre-indented gasket with a 0.1 mm hole for

the sample, ruby chip and pressure-transmitting medium. An imaging plate was used as X-ray detector for XRD studies. All functions of the facility including pressure variation can be remotely controlled from the outside of an experimental hutch.

Experiments were carried out at beamline 1-BM-A at the Advanced Photon Source, Chicago, USA, and on station 9.3 at Daresbury Laboratory Synchrotron Radiation Source, UK. Transmission EXAFS data in QEXAFS mode (Frahm, 1989) have been collected on station 9.3 (5 T wiggler 1) using the double-crystal Si(220) monochromator. In the QEXAFS method the monochromator scanned at constant speed and data were collected by recording the signal at regular time intervals. The collection time for each spectrum was 10 min. The EXAFS experimental resolution was estimated to be ~ 1 eV. The X-ray beam was collimated down to a diameter of 0.150 mm by a set of horizontal and vertical slits.

3. Case study: GaN powder

GaN is a relatively new optoelectronic material which is used in the manufacturing of blue-light-emitting devices (Fasol & Nakamura, 1997). The structural pressure dependencies as well as the nature of PL in the material have been extensively studied. However, most of these studies have been performed on either GaN films grown on a range of substrates (see, for example, Wetzel *et al.*, 1996) or on GaN monocrystals (see, for example, Perlin *et al.*,

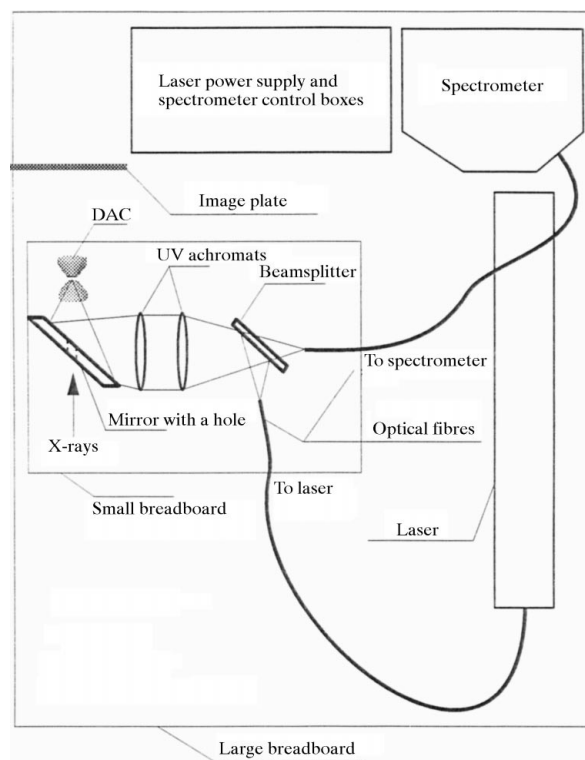


Figure 1
HI-PREXX optics.

1992, 1996a). Several methods of preparation of GaN in the form of powder have been reported (Balkas & Davis, 1996; Grzegory & Krukowski, 1991; Gonsalves *et al.*, 1997; Argoitia *et al.*, 1997). The preparation of GaN powder in terms of quantity is much more efficient than in other methods. However, to our knowledge, there have been no investigations of the structural and PL properties of GaN powder under high pressures in order to compare its properties with those of monocrystals and thin films.

GaN crystalline powder was prepared by the method described by Balkas & Davis (1996). The structure of the GaN powder was checked using a laboratory X-ray source and was found to be hexagonal (space group $P6_3/mmc$).

The collection of ruby fluorescence was straightforward – we observed a well resolved double peak up to the maximum achieved pressure of 41 GPa.

One of the main problems in high-pressure EXAFS is diamond glitches. X-rays passing through the diamonds undergo Bragg scattering and therefore some energy points

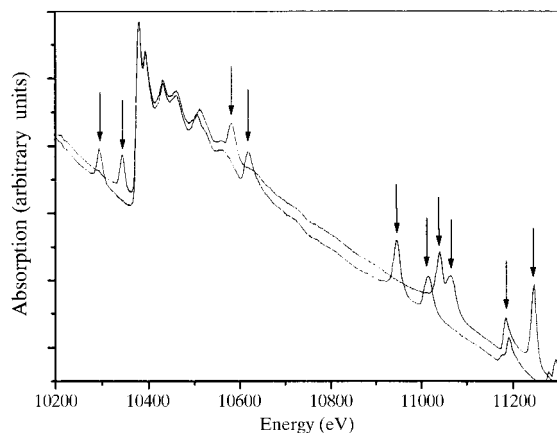


Figure 2
Glitches (marked by arrows) in Ga K -edge EXAFS from GaN.

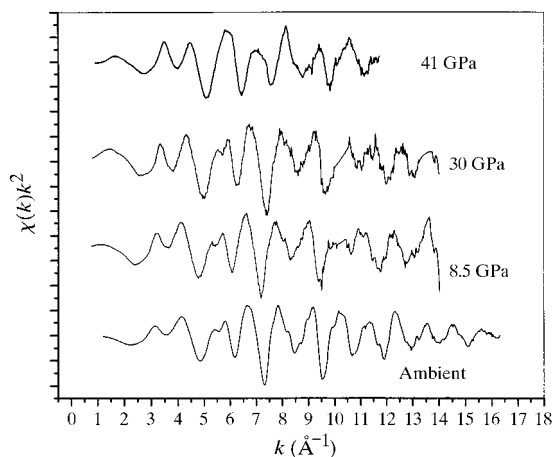


Figure 3
EXAFS from GaN collected under high pressures. The lower spectrum is collected at ambient conditions on station 9.3 at Daresbury Laboratory in standard transmission mode.

are missing from the absorption spectrum (see Fig. 2). This problem can be dealt with by rotating the DAC around up to three axes and thus shifting glitches out of the region of interest. However, at some energies (~ 10 keV) this becomes extremely difficult due to the large number of peaks. We overcame this problem in the following way. First, glitches were moved out of the region of interest as much as possible by DAC rotation. A data set was collected. The DAC was then rotated by an arbitrary angle. This moved the glitches to new positions. Another data set was then collected. During the data-analysis procedure the glitches were manually removed from the spectra and those spectra were then summed. The result of such a procedure is presented in Fig. 2. This method allowed the useful EXAFS range to be increased to $k = 12\text{--}14 \text{ \AA}^{-1}$. In fact, high-pressure EXAFS data were collected up to 41 GPa comparable in quality with those collected at ambient conditions using the standard transmission technique. Typical EXAFS spectra collected at different pressures are presented in Fig. 3. The pressure dependence of nearest-neighbour distances (Ga–N and Ga–N–Ga) are presented in Fig. 4. The Ga–N–Ga distance extracted from EXAFS spectra corresponds to the a lattice parameter. The observed dependence is similar to that found by Ueno *et al.* (1994) where GaN powder was studied by X-ray diffraction.

The high-pressure dependence of GaN powder PL is displayed in Fig. 5. The dip in the spectra at around 475 nm is due to a harmonic from a notch filter used to cut the 325 nm laser line. One can observe that the luminescence peaks (A and B) shift towards shorter wavelength with an increase in pressure. This effect is typical of different types (thin films, single crystals) of GaN (see, for example, Perlin *et al.*, 1996b). We found that the pressure dependence of GaN ‘yellow’ luminescence (peak B) was found to be $\sim 37 \text{ meV GPa}^{-1}$ and close to that reported by Perlin *et al.*

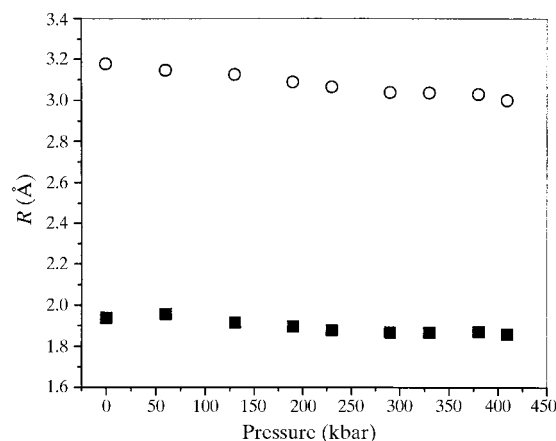


Figure 4
Pressure dependence of nearest-neighbours distances of GaN powder extracted from EXAFS data. Open circles correspond to Ga–N–Ga distances and solid squares correspond to Ga–N distances.

(1996a) for a monocrystal. The pressure dependence of the position of peak *A* was found to be $\sim 30 \text{ meV GPa}^{-1}$.

Collection of image-plate diffraction data was straightforward and similar to the procedure described by Nelmes *et al.* (1992). The pressure dependence of powder diffraction was also found to be similar to that reported by Ueno *et al.* (1994). An example of an X-ray diffraction pattern is presented in Fig. 6. One can observe a triplet typical of the hexagonal phase of GaN. The arrow marks a reflection due to the gasket.

4. Discussion

EXAFS under high pressures is not new to researchers (Lyapin *et al.*, 1996; Sapelkin *et al.*, 1996; Gauthier *et al.*, 1996). However, it is not a widespread technique of choice for high-pressure studies. There are only a few scientific centres that would routinely perform this kind of experiment. There are several reasons for such a situation to be the case. The technique used for this kind of experiment for some time now has been energy-dispersive EXAFS (EDE). In this approach a range of X-ray energies is selected from a white beam (usually about 1 keV wide) and then focused into a gasket hole using a bent mirror. The main advantage of this technique is fast spectra-collection times (usually of the order of seconds) and, therefore, the ability to minimize the influence of diamond glitches (see Fig. 2) in an EXAFS spectrum in real time. The glitches occur in an EXAFS spectrum because X-rays undergo diffraction by diamonds. This leads to the corresponding energies being absent from an EXAFS spectrum. These glitches complicate the EXAFS analysis significantly and even make it impossible to extract any, but qualitative, information from an EXAFS spectrum. The usual way of dealing with this problem is to rotate the diamond cell on a goniometer and thus, hope-

fully, move glitches out of the region of interest. Unfortunately, it is quite a time-consuming task and at some X-ray energies (above $\sim 11\text{--}12 \text{ keV}$) is impossible.

The combined experiments described in this paper have demonstrated the similarity in high-pressure behaviour of powdered and monocrystalline GaN.

Because of all the above, we used the QEXAFS technique for high-pressure experiments. Although QEXAFS data-collection times are longer than in EDE, they are still significantly faster than standard EXAFS, and QEXAFS lacks all disadvantages of the EDE set-up.

5. Conclusion

We have shown that, despite significant difficulties encountered in the area of high-pressure EXAFS research, it is possible to collect XRD, EXAFS and PL spectra in an *in situ* experiment. The EXAFS data collected under high pressures in a DAC are comparable in quality with EXAFS data collected at ambient conditions. We have also proposed a new procedure to deal with the diamond glitches in an EXAFS spectrum. The procedure allows one to use experimental time more effectively, and one can now collect high-quality EXAFS data at any pressure which DACs can achieve. In fact, for the first time we have been

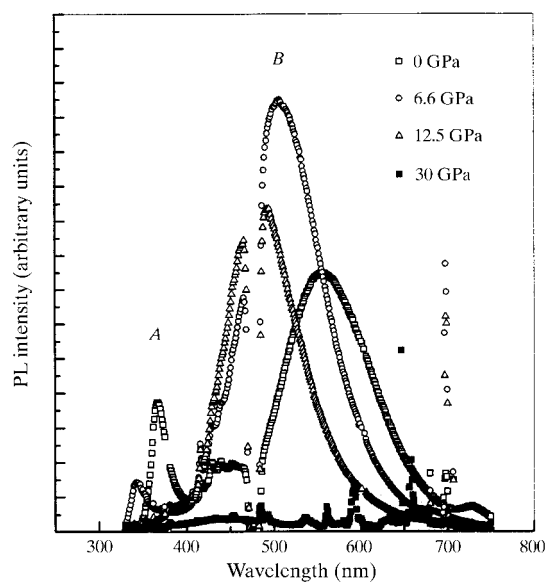


Figure 5
Photoluminescence signal from GaN.

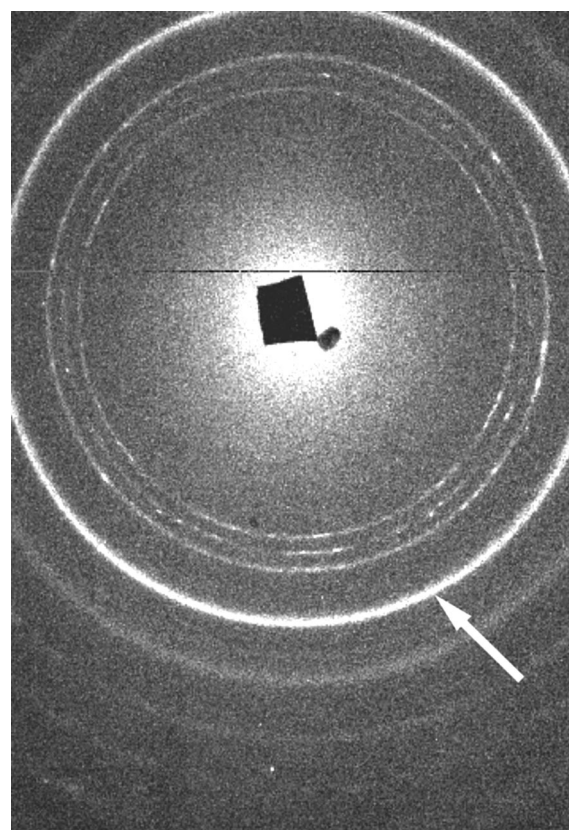


Figure 6
X-ray diffraction pattern of GaN at 30 GPa. The arrow marks a reflection due to the gasket.

able to collect high-quality EXAFS spectra of GaN (EXAFS range $\simeq 800$ eV) at pressures as high as 41 GPa. Our experimental method also allows one to use in full the flexibility of synchrotron sources in the choice of wavelength for EXAFS/XRD experiments. The new facility does not require the use of special focusing optics on an X-ray beamline and, therefore, its use can be extended to all types of experimental EXAFS stations which can provide an X-ray beam of sufficient intensity.

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References

- Aletru, C., Greaves, G. N. & Sankar, G. (1999). *J. Phys. Chem.* **103**(20), 4147–4152.
- Argoitia, A., Hayman, C. C., Angus, J. C., Wang, L., Dyck, J. S. & Kash, K. (1997). *Appl. Phys. Lett.* **70**(2), 179–181.
- Balkas, C. B. & Davis, R. F. (1996). *J. Am. Ceram. Soc.* **79**, 2309–2312.
- Claunsen, B. S. (1998). *Catal. Today*, **39**(4), 293–300.
- Colyer, L. M., Greaves, G. N., Carr, S. W. & Fox, K. K. (1997). *J. Phys. Chem.* **101**(48), 10105–10114.
- Epple, M., Sankar, G. & Tomas, J. M. (1997). *Chem. Mater.* **9**(12), 3127–3131.
- Fasol, G. & Nakamura, S. (1997). *The Blue Laser Diode*. Berlin: Springer.
- Frahm, R. (1989). *Physica B*, **158**(1–3), 342–343.
- Gauthier, M., Chervin, P. P. J. C. & Polian, A. (1996). *Phys. Status Solidi B*, **198**(1), 223–233.
- Gonsalves, K. E., Rangarajan, S. P., Carlson, G., Kumar, J., Yang, K., Benaissa, M. & Jose-Yacaman, M. (1997). *Appl. Phys. Lett.* **71**(15), 2175–2177.
- Grzegory, I. & Krukowski, S. (1991). *Phys. Scr.* **T39**, 242–249.
- Lyapin, A. G., Brazhkin, V. V., Bayliss, S. C., Sapelkin, A. V., Itie, J. P., Polian, A. & Clark, S. M. (1996). *Phys. Rev. B*, **54**(20), 14242–14245.
- Nelmes, R. J., Hutton, P. D., McMahon, M. I., Piltz, R. O., Crain, J., Cernik, R. J. & BushnellWye, G. (1992). *Rev. Sci. Instrum.* **63**(1), 1039.
- Pascarelli, S., Neisius, T., DePanfilis, S., Bonfim, M., Pizzini, S., Mackay, K., David, S., Fontaine, A., San Miguel, Itié, J. P., Gauthier, M. & Polian, A. (1999). *J. Synchrotron Rad.* **6**, 146–148.
- Perlin, P., Jauberthie-Carillon, C., Itie, J. P., Miguel, A. S., Grzegory, I. & Polian, A. (1992). *Phys. Rev. B*, **45**(1), 83–89.
- Perlin, P., Knap, W., Camassel, J., Polian, A., Chervin, J. C., Suski, T., Grzegory, I. & Porowski, S. (1996a). *Phys. Status Solidi B*, **198**(243), 223–233.
- Perlin, P., Knap, W., Camassel, J., Polian, A., Chervin, J. C., Suski, T., Grzegory, I. & Porowski, S. (1996b). *Phys. Status Solidi B*, **198**(1), 223–233.
- Sankar, G., Thomas, J. M., Rey, F. & Greaves, G. N. (1995). *J. Chem. Soc. Chem. Commun.* pp. 2549–2550.
- Sapelkin, A. V., Bayliss, S. C., Lyapin, A. G., Brazhkin, V. V., Itie, J. P., Polian, A., Clark, S. M. & Dent, A. J. (1996). *Phys. Status Solidi B*, **198**(1), 503–508.
- Shannon, I. J., Maschmayer, T., Sankar, G., Tomas, J. M., Oldroyd, R. D., Sheehy, M., Madill, D., Waller, A. M. & Townsend, R. P. (1997). *Catal. Lett.* **44**(1–2), 23–27.
- Ueno, M., Yoshida, M., Onodera, A., Shimomura, O. & Takemura, K. (1994). *Phys. Rev. B*, **49**(1), 14–21.
- Wetzel, C., Chen, A. L., Suski, T., Ager, J. W. III & Walukiewicz, W. (1996). *Phys. Status Solidi B*, **198**(243), 243–249.