A time resolved microfocus XEOL facility at the Diamond Light Source

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Abstract. We have constructed a Time-Resolved X-ray Excited Optical Luminescence (TR-XEOL) detection system at the Microfocus Spectroscopy beamline I18 at the Diamond Light Source. Using the synchrotron in "hybrid bunch mode", the data collection is triggered by the RF clock, and we are able to record XEOL photons with a time resolution of 6.1 ps during the 230 ns gap between the hybrid bunch and the main train of electron bunches. We can detect photons over the range 180-850 nm using a bespoke optical fibre, with X-ray excitation energies between 2 and 20 keV. We have used the system to study a range of feldspars. The detector is portable and has also been used on beamline B18 to collect Optically Determined X-ray Absorption Spectroscopy (OD-XAS) in QEXAFS mode.

1. Introduction

I18 is the microfocus spectroscopy beamline on the Diamond Light Source [1]. The beamline has cryogenically cooled Si(111) monochromator producing an X-ray energy range of 2.1 - 20.8 keV and since 2010 uses mechanically-bent Kirkpatrick-Baez mirrors (Instrument Design Technology) to produce a beam, whose size at the focus point can be varied from below 2 x 2 microns to ca. 50 x 50.

Most XEOL reported in the literature involves the use of soft X-rays often in imaging heterogeneous samples e.g. [2],[3]. XEOL on a synchrotron probes the whole photo-luminescence energy range and also can give element specificity by using incident beam energies near the absorption edge energy of one of the elements in the sample. Hard X-ray XEOL has been used to study some system by OD-XAS e.g. [4] but the prevalent view as expressed by Soderholm [5] is that OD-XAS is only visible from major elements in a sample and also is susceptible to energy transfer between luminescent centres and thus not widely applicable.

We hypothesized that by looking at the short lifetime XEOL emissions, we might see OD-XAS from minor elements in a sample. Using time resolution to isolate the optical emission of the absorber element, and removing the effect of longer-lived delocalized emissions, the spectra would be localized...
on the element and thus might give an XAS-related signal from trace elements. We were particularly interested in studying the environment of Fe in feldspars, where conventional microXAFS is difficult to interpret, as there are often nanosized iron oxide intergrowths in the mineral host. Thus a TR-XEOL system was designed and installed on the I18 beamline to test the hypothesis.

The XEOL detector system was built as a flexible system, so that it could be used for a range of microbeam XEOL experiments and also on a standard XAS beamline at Diamond to collect OD-XAS.

2. Experimental Set-Up

The I18 XEOL set-up uses a Triax 190 spectrometer (Horiba JY) fitted with a Synapse CCD (Horiba JY). We have fitted a R8309U-50 photo multiplier tube (PMT) (Hamamatsu) fitted to the Triax auxiliary port. The XEOL is delivered from the sample into the spectrometer via a custom-made optical fibre that is positioned around 2 mm from the sample (Figure 1). The whole experimental setup is covered in a thick black cloth, which also covers the surface of the granite experimental table as that can give off optical light from scattered X-rays.

The fibre is made from strands of two different materials, one optimized for 200 - 500 nm light and the other for 450 - 900 nm strands. Hence we can observe XEOL photons from the UV through to the far infra-red. The spectrometer has three gratings, two for high resolution at low and high wavelength respectively and a coarse grating that enables a spectrum from 180 - 850 nm to be collected on the synapse in a single shot. A switch mirror in the spectrometer enables the light to be directed either at the CCD or the PMT. The PMT output is processed through an Ortec 9327 combined amplifier and timing discriminator. For conventional XEOL this signal is then output into the beamline data collection chain while for time resolved measurements it is passed into an Ortec 566 time-to-amplitude converter. The signal from this goes through an AIM 566 multi-channel analyzer (Canberra) enabling the time structure of the photons to be collected in 8196 bins. The path from X-ray to data acquisition system is shown in a schematic in Figure 1.

The spectrometer and the CCD can be used using the Horiba JY proprietary software or an EPICS based interface and the CCD read out directly via an application programming interface into the Diamond Generic Data Acquisition software or into proprietary software.

![Schematic of the XEOL system](image)

Figure 1. A photo of the XEOL set-up on I18, showing the fibre end, small I0 ion chamber and video microscope (left). A schematic of the XEOL system (right).
2.1. Time resolved mode.

Time-resolved XEOL is collected using the hybrid bunch mode of Diamond. In this mode there is a lone bunch with ca 240 ns gap before and after it. There are 686 bunches at normal (ca. 2ns) gaps in the remainder of the ring. The RF clock signal is fed into a Diamond-designed timer card, which allows synchronization of the data collection by the Time-to-Amplitude converter (TAC) with the arrival of the hybrid X-ray pulse at the sample. The TAC facilitates the length of the data collection window. The TAC has a recording range of 50, 100 or 200 ns and thus is a good match for the time gap after the hybrid bunch; to achieve better time resolution a shorter time range can be used.

The emission data obtained was fitted to obtain decay lifetimes for the excited states in the program Igor Pro 6.22 (Wavemetrics).

3. Examples of TR-XEOL results.

A typical time-resolved XEOL lifetime dataset collected using the system in ten minutes is shown in Figure 2a, which is the signal collected at 340 nm from an albite sample using a 5 µm beam.

No time-resolved OD-XAS signal at the Fe K-edge was observed in a range of feldspars that were studied, thus to prove the principle and compare TR-OD-XAS and conventional OD-XAS, a sample of powdered Eu₂O₃ was studied at the Eu L3-edge using a 5 µm beam. In Figure 2b the TR-OD-XAS data from a short lifetime emission at 360 nm is compared with that from conventional OD-XAS at 610 nm. The white line heights are noticeably different showing the short lifetime XEOL does not probe exactly the same set of energy transitions as the conventional XEOL. It gives a slightly higher resolution spectrum similar to X-ray emission spectroscopy. We have also observed OD-XAS and TR-OD-XAS from a at the Eu L3 edge 3% Eu-doped apatite; this concentration is approximately an order of magnitude higher percentage content than the standard Fe content in feldspars.

![Figure 2a](image1.png)

![Figure 2b](image2.png)

Figure 2a. A typical decay profile recorded at 410 nm with a 5µm beam and an excitation energy of 4050 eV from a microcline microperthite from Prins Christians Sund, South Greenland. The data is fitted with two exponential decays with lifetimes of 0.7 and 7.5 ns. The data was collected in ten minutes.

Figure 2b. Normalised Eu L3 edge OD-XANES spectra from Eu₂O₃ powder sample with a 5 µm beam collected using the only short lifetime emission at 362 nm (TR-XEOL) and total XEOL signal at 608 nm.
4. Conventional OD-XAS on beamline B18

The system has recently been used to collect OD-XAS on some zinc oxide and germanium oxide nanostructures that were supported on Silicon and on B18 at Diamond [6]. The zinc oxide samples were nanorods, which have a strong photoluminescence signal in the green. For this strong XEOL signal the PMT was replaced with a femtowatt silicon photoreceiver (Newport Spectra-Physique) and data could be collected in minutes using QEXAFS mode (Figure 3a); the sensitivity of the system is shown by the EXAFS recorded in two hours of QEXAFS scanning from the weakly emitting Ge quantum dot sample, where the CCD recorded less than 100 c/s emission peak height. An example of the OD-XAS collected from both systems is shown in Figure 3b.

Figure 3a. \( k^2 \)-weighted Zn K-edge OD-EXAFS recorded in 9 minutes of data collection at 500 nm from zinc oxide nanorods collected using the silicon photoreceiver.

Figure 3b. \( k^2 \)-weighted Ge K-edge OD-EXAFS recorded in 120 minutes of data collection at 600 nm from germanium oxide nanoparticles collected on the PMT.

5. Summary

Hence a versatile XEOL spectrometer system for the X-ray absorption beamlines at Diamond has been constructed which can be used for time-resolved or conventional XEOL data collection. The data chain interfaces with the Diamond data acquisition system and can be set up rapidly on any hard X-ray beamline and with an auxiliary lens and vacuum window could also be used on soft X-ray beamlines.

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