



**Experiment title:**  
Time resolved X-ray excited optical luminescence  
(XEOL) with subnanosecond time resolution

**Experiment  
number:**  
HC-160

**Beamline:**  
ID12/BL6

**Date of experiment**  
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**Shifts:**  
9

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*Received at ESRF:*

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**Report:**

We have exploited the subnanosecond time structure of ESRF in multibunch operation mode to carry out time resolved XEOL expedients. Luminescence decay kinetics and XEOL-XAFS spectra of a zinc metalloporphyrin (TPP:Zn) at Zn K-edge and of CsPbCl<sub>3</sub> single crystal at Cl K-edge have been measured.

The detection system was based on a dissector operating in stroboscopic mode [1]. This detector is used to measure fast optical processes ( a few of picosecond ) with a high repetition rate ( up to 100 Mhz ) and is the most suitable for time resolved experiments with synchrotrons radiation (SR). To synchronize the data acquisition with SR pulses RF signal corresponding to 64\* harmonic of the bunch repetition was used as a sweeping voltage. Measured time resolution of dissector at this sweeping frequency ( 22 Mhz ) was 12 ps. Due to the high intensity and stable temporal structure of SR on one side and all advantages of the dissector in stroboscopic mode we have been enable to record. (i) steady-state luminescence or XEOL-XANES spectra; (ii) luminescence decay curves; (iii) XEOL-XANES spectra simultaneously in 8 time windows ( 50 ps wide ) separated by 22 ns with variable delay relative to excitation pulses.

The XEOL spectrum of a CsPbCl<sub>3</sub> single crystal consists of narrow line at 420 nm. This emission could be assigned to the radiative decay of biexcitons localised at the point

defects in the crystal and is characterised by ultrafast decay time ( $\tau \approx 60$  ps) (see fig. 1 a.). The XEOL-XANES spectrum recorded by monitoring the intensity of this emission exhibits a positive edge jump at the Cl K-edge (fig. 1 b.).

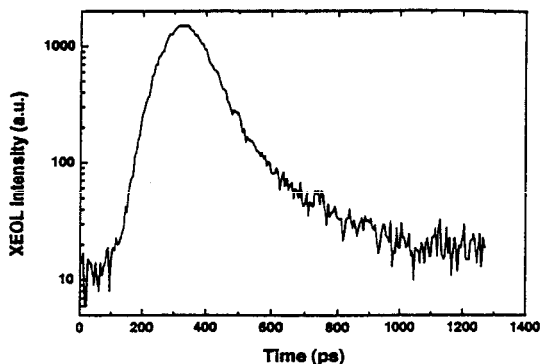


Fig. 1a. XEOL decay curve of CsPbCl<sub>3</sub> crystal.  
Excitation photon energy is 2.835 keV.

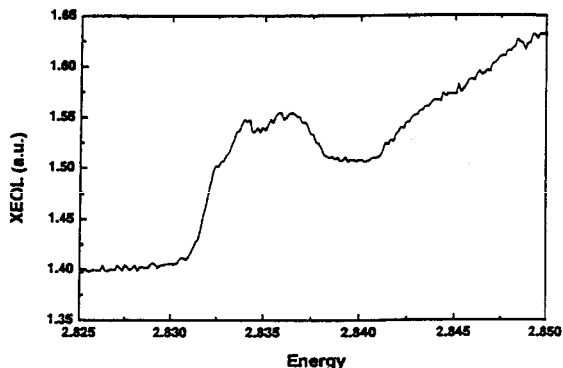


Fig. 1b. XEOL-XANES spectra of CsPbCl<sub>3</sub> crystal  
measured at Cl K-edge.

The emission of TPP:Zn is due to intramolecular transitions which are also characterised by very fast decay times. The luminescence decay curve measured at 100 K and 9.65 keV excitation energy is shown in fig.2.a. Decay is strongly non-exponential and could be decomposed in two exponential with decay times  $\tau_1 < 15$  ps and  $\tau_2 = 650$  ps. It means that emission is quenched by self-absorption or non-radiative energy transfer. The Zn K-edge XANES spectrum (see fig.2.b.) recorded at 100 K by monitoring only the fast luminescence component has a positive edge as observed earlier [2].

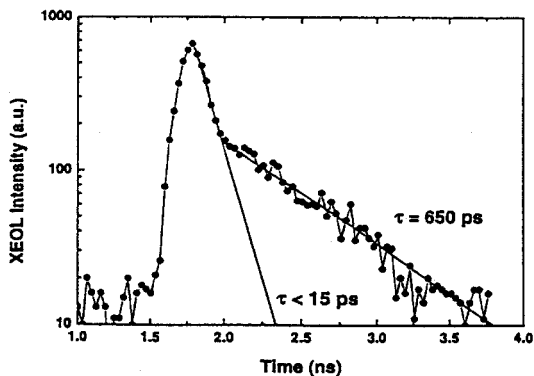


Fig. 2a. XEOL decay curve of TPP:Zn at 100K.

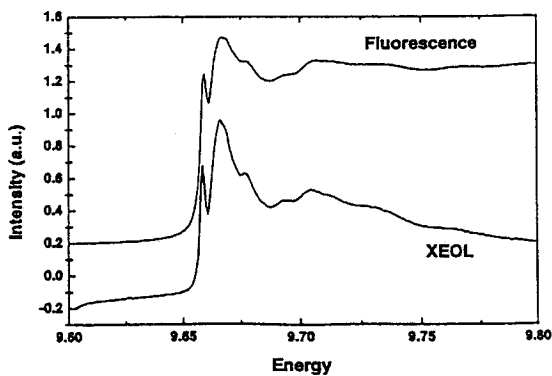


Fig. 2.b. Zn K-XANES spectra of TPPZn recorded  
by XEOL and X-ray fluorescence

#### References:

- [1] E.I.Zinin NIM, v.A308 (1978), pp. 386-391
- [2] J. Goulon et al. in: EXAFS and Near Edge Structure III ed. by K. C). Hodgson, B. Heddman and J.E. Penner-Hahn, Springer-Verlag, 1984, p.490-495