ESRF	**Experiment title:** Lattice dynamics of laser excited ferroelectrics – a high duty cycle experiment	**Experiment number**: MA706
Beamline:	**Date of experiment**: from: 28-04-10 to: 03-05-10	**Date of report**: 10-09-10
Shifts:	**Local contact(s)**: Dr. M. Wulff, Dr. L. Guerin	*Received at ESRF:*

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Report:

Typically a setup at ID09b uses a high frequency chopper that synchronizes a single transmitted x-ray pulse and laser pulses from a femtosecond amplifier to collect x-ray scattering data with a 2D detector, which was no intrinsic time resolution. Thus weakly scattering signals can be recorded and a maximum time resolution of 100 ps can be obtained at chosen time delays. In an experiment, where a continuous delay needs to be recorded this approach is rather time consuming. In addition this approach is only possible with a special timing mode of the synchrotron.

For the lattice dynamics of ferroelectric crystals we wanted to record long time spans from early steps of excitation as change of the structure factor up to long lasting relaxation of strain in the crystal. Therefore we examined a new approach, where the timing property of the chopper is not used, but rather fast detectors together with a time resolving histogramming unit can allow for going to fast events.

The principle of the experiment is that the scattered photons from the sample (ferroelectric BaTiO3) are collected by an avalanche photodiode (ESRF/Cyberstar/FMB), which can resolve some nanoseconds and record the events in a histogramming card with a 4 ns binning interval (Picoquant Nanoharp). As such the experiment is rather conventional, but allows for a rapid sampling of a large delay span.

The sample was heated by a thermoelectric heated close to the phase transition while intense near infrared pulses (790 nm) excite the surface. The chosen crystal was a poled single crystal with a (110) surface, where one of the two domains with polarization component perpendicular to the surface was probed. The (440) and the (430) reflections served as signatures of the lattice and structure state.

Fig. 1 shows clear signals of the scattering change due to the laser excitation. In fact the change of the structure factor should be opposite for a pure thermal excitation [1] and a displacive phase transition model [2], where the titanium atom would return to the centrosymmetric position within the unit cell when approaching the phase transition. Both the diffusive model [3] and a Raman like excitation [4] would help to explain this feature. Indeed the excitation at near infrared wavelength is far from an excitation across the band gap plus the bandwidth of the laser allowing for a stimulated Raman process. Similar effects have been seen in a BaTiO3 powder, however less clear [1].

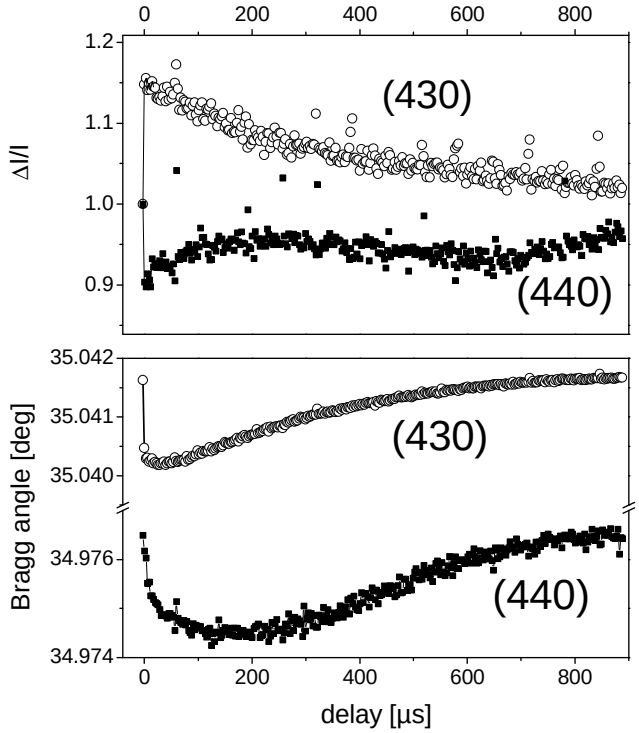

Fig. 1

Top: change of the Bragg intensity of the (430), resp. (440) reflections as function of time delay after laser excitation. While the structure factor of the (430) increases immediately after excitation, that of the (440) reflection decreases slightly.

Bottom: Change of the angular position of the same reflections as above. Both rotation of the domains and lattice expansion contribute to the signal.

The positional change of the Bragg angle consists both of a rotational component due to the slight tilt of the domains relative to the surface and a lattice expansion part, both add to a reduction of the incidence angle in the present configuration. This is consistent in both reflections. While the structure factor change is very rapid, the angle change contains an additional slower component due to strain propagation within the crystal.

It was also possible to analyse the shorter time scales down to the nanosecond range, where the data suffered, however, from the strongly structured fill pattern (24/8+1) and the resulting fluctuations in the count rate of the individual channels. As the laser timing was additionally instable a considerably higher noise is found in the fitted Bragg parameters, as seen in figure 2. This should be strongly improving for homogenous filling modes or alternatively a decoupling of the laser frequency from the synchrotron time structure. The proposed method can therefore deliver valuable data for multiple time scale kinetics as well as without the chopper synchronization scheme.

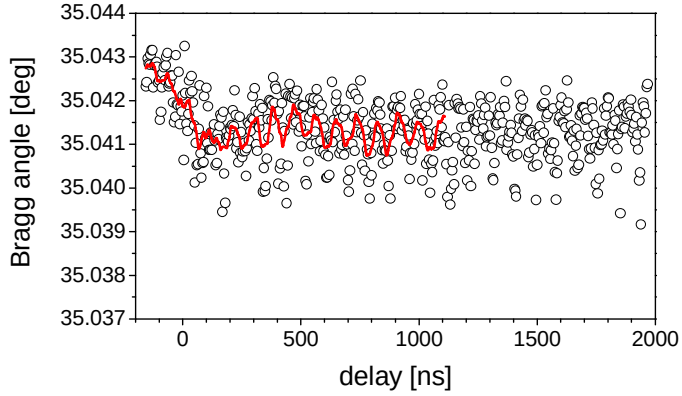

Fig. 2: Short delay scale of the angular change of the (430) reflection. The added line is a smoothed curve of the primary data set, showing an oscillatory component due to the 24 superbunches present in the ring.

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[3] B. Ravel, E. A. Stern, R. I. Vedrinskii, and V. Kraizman: Local structure and the phase transitions of $BaTiO_3$, Ferroelectrics **206–207**, 407 (1998).

[4] T. P. Dougherty, et al: *Femtosecond time-resolved spectroscopy of soft modes in structural phase transitions of perovskites*, Phys. Rev. B **50**, 8996 (1994)