

**Experiment title:**

Real-time study of polarization dynamics in ferroelectric phase transitions by ultrafast x-ray diffraction

Experiment number:

HS 1564

Beamline:

ID09B

Date of experiment:

from: 29-11-01 to: 3-12-01

Date of report:

15-12-03

Shifts:

12

Local contact(s):

Dr. M. Wulff

*Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):****Dr. A. Plech *****Dr. M. Aspelmeyer *****Prof. Dr. U. Klemradt *****Report:**

The aim of the present experiment was to study the reaction of ferroelectric crystals on the impulsive excitation by a femtosecond laser pulse. Barium titanate served as model system, as it exhibits a ferroelectric phase transition at 120 °C, which is directly monitored by the cubic to tetragonal lattice distortion, when lowering the temperature below the ferroelectric point. This implies a spontaneous polarization of the unit cell, leading to a macroscopically polar crystal.

We used pulses of 800nm light to excite powder samples of BaTiO₃ having grain sizes in the micrometer range. Although there is no resonant interaction of the crystals with the laser field, it is possible to deposit energy in the lattice such that the lattice temperature increases above the phase transition temperature (see fig. 1). The temperature was stabilized by a cryogenic cooler (Cryostream) while the laser energy was augmented to approach the transition.

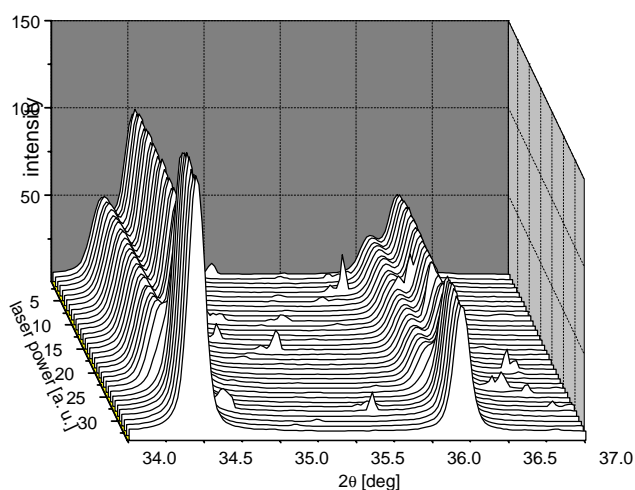


Fig. 1: Laser-induced phase transition $m3m-4mm$ in BaTiO₃. From back to front the laser intensity was increased, which leads to a reduction of the tetragonal peak splitting and finally a degenerated reflection of the cubic symmetry.

Working at laser energies around the occurrence of the transition allows to resolve the lattice dynamics within the 100ps resolution of the beamline. We found, that the BaTiO₃ powder filled in a narrow capillary does not allow sufficient control of the temperature. The thermal gradient in time was too small to achieve considerable cooling rates to cross the transition point within the time frame of 1ms (as determined by the repetition frequency of the experiment). Instead a very constant temperature in time was conserved, which cancels out transient structure changes of thermal origin.

We still observed a very distinct transient temperature change within the first nanoseconds, which in contrast is related to the impulsive nature of the light-phonon interaction. Fig. 2 displays difference scattering profiles for the fundamental (111) reflection as well as the order parameter carrying (200) reflection.

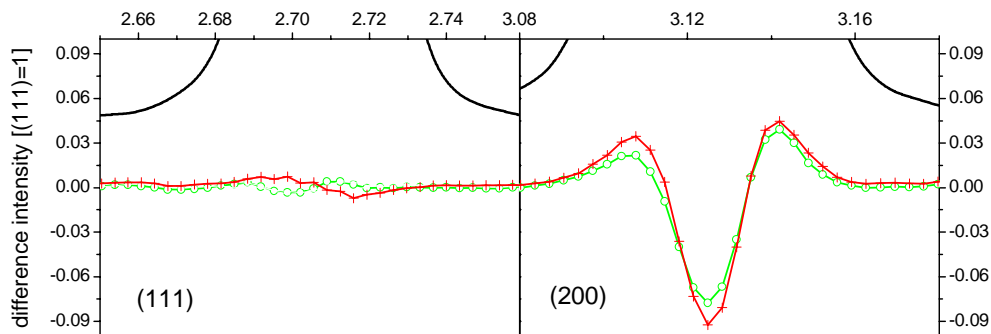


Fig. 2: Peak profiles of two reflections in the cubic symmetry. While the (111) reflection is degenerate in the cubic as well as in the tetragonal symmetry, no splitting occurs for short time delays after the laser excitation. In contrast, there is an increase in intensity on the wings of the (200) reflection, which indicates an increase in peak splitting along the two tetragonal axes. The black lines are the base of the full reflection profile, whereas the line with open circles and the line with crosses stand for different time delays in the sub-nanosecond range.

We find an increase of tetragonal distortion upon laser excitation of the crystal lattice, corresponding to inducing the low temperature phase after the laser pulse impact. A similar effect is known from another ferroelectric transition, which is induced by a charge transfer reaction within the compound TTF-CA [1, 2].

For further studies a better control of temperature and excitation volume is planned to separate thermal from athermal effects.

[1] E. Collet, M.-H. Lemeé-Cailleau, M. Buron-Le Cointe, H. Cailleau, M. Wulff, T. Luty, S.-Y. Koshihara, M. Meyer, L. Toupet, P. Rabiller, S. Techert: Light-Induced Ferroelectric Structural Order in an Organic Charge-Transfer Crystal, *Science*, 25. April 2003

[2] L. Guérin, E. Collet, M.-H. Lemée-Cailleau, M. Buron-Le Cointe, H. Cailleau, A. Plech, M. Wulff, S.-Y. Koshihara and T. Luty: Probing photoinduced phase transition in a charge-transfer molecular crystal by 100 picosecond x-ray diffraction, *Chemical Physics*, forthcoming.