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Report:

The aim of the present experiment was to resolve structural dynamics of laser-induced structural changes in ferroelectric $BaTiO_3$ crystals by picosecond pulsed x-ray scattering. As has been seen in earlier experiments (HS1564 and HS2648) one main effect is the thermal heating of $BaTiO_3$ single crystals or $BaTiO_3$ powders, which drives the crystal towards the high symmetry paraelectric phase. In particular, it was difficult to discern the steady state temperature increase from the transient temperature jump followed by each laser pulse. Powder samples showed a rather slow heat dissipation, when enclosed in a x-ray capillary.

We have reduced this problem by embedding a $BaTiO_3$ powder finely dispersed in a sodium silicate glass layer, in order to use the glass as heat sink. The accordingly prepared sample showed a strong opaqueness due to multiple scattering in the sample, while being optically thin enough to allow the excitation of the complete layer. The samples were excited by synchronous laser x-ray pulse pairs and the x-ray scattering has been recorded on a CCD camera (MarCCD). The laser wavelength was the fundamental of the femtosecond amplifier at 800nm, while the x-rays were monochromatized with a Si(111) channel cut crystal at an energy of 15 keV. We collected the powder pattern up to $Q=5.6\ A^{-1}$. The powder pattern could be analysed by a line profile analysis (Rietveld refinement with GSAS) to deduce the lattice structure and the atomic positions within the unit cell as function of delay between laser excitation and x-ray probe.

When increasing the laser fluence at 1 kHz, it could be seen that the two lengths of the long and short tetragonal axis approached each other gradually, until finally a cubic structure is obtained. This is explained by the cw heating of the laser, whose dissipation time on a macroscopic scale is still much larger than 1 ms. At a laser fluence of 250 mJ/cm^2 the transition from the tetragonal to the cubic phase is seen in fig. 1.

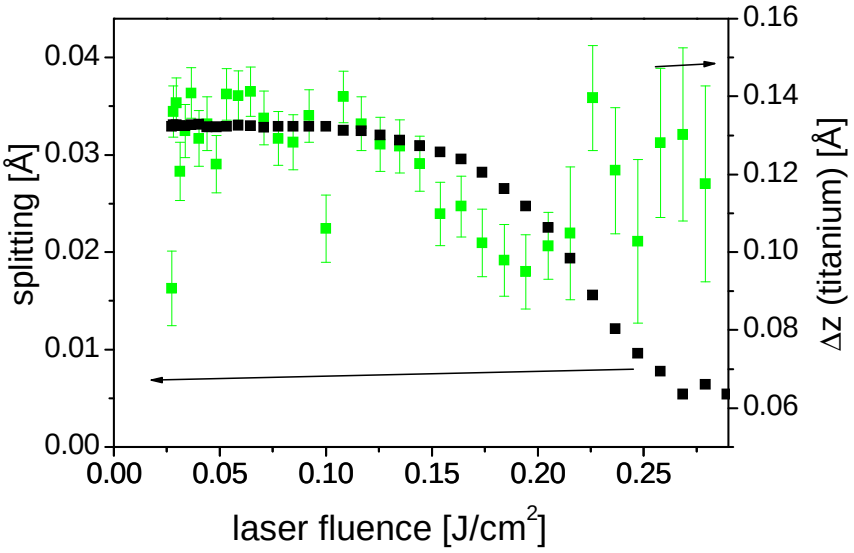

Fig. 1: *Parameters of the tetragonal splitting c-a and the position of the titanium relative from the high symmetry site in the cube center of the laser excited powder as function of laser fluence.*

At the same time the titanium atom relaxes towards the center of the unit cell, but does not reach the symmetric position. This is connected to the partial order-disorder character of the transition.

When resolving the transient change of the crystal structure as function of delay below the tetragonal-to-cubic transition one observes an instant decrease of the tetragonal splitting in accordance with the picture, that the excitation acts in general as an ultrafast heat pulse, which drives the system towards the symmetric phase. There is however one observation, which is not in line with this assignement. The titanium atom does not relax towards the symmetry position on the picosecond time scale, but rather appears to have larger excursions, as seen in fig. 2.

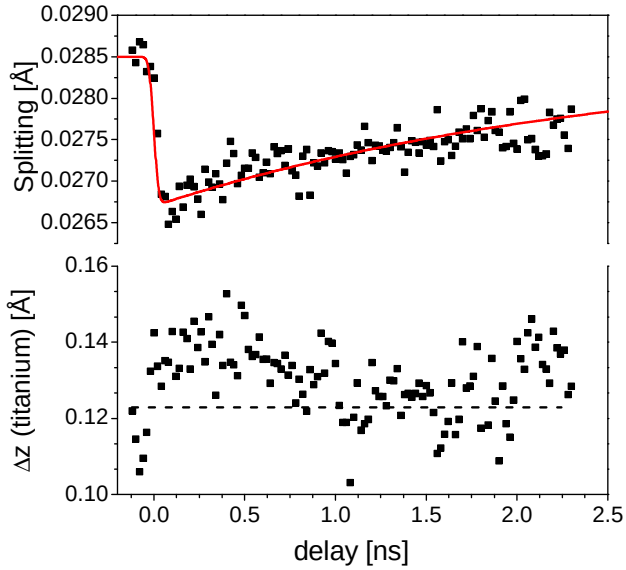

Fig. 2: Transient structure change induced by the laser excitation. The splitting reacts within the time resolution of the experiment by a reduction, which relaxes on the ns time scale. The titanium displacement shows a larger excursion within the first 500ps.

The titanium position is a direct measure for the electric polarization of the unit cell, where the position of the oxygen octaeder represents the charge counterpart. The oxygen positions have been fixed during the refinement, due to the low scattering power and the reduction of the confidence level.
It shows, that besides the thermal reaction, there exists a fast polarization response in $BaTiO_3$ crystals upon laser excitation. The results have been published recently [1].

[1] K. Istomin, V. Kotaidis, A. Plech, Q. Kong:*Dynamics of the laser-induced ferroelectric excitation in $BaTiO_3$ studied by x-ray diffraction;* Appl. Phys. Lett., 90 (2007) 022905.