Tracking ultrafast and irreversible creation of light-induced structural orders

Ultrafast light-matter interactions have emerged as a powerful approach for creating and manipulating new states of matter, offering unprecedented control over novel material properties that are challenging or impossible to achieve through conventional equilibrium approaches. For example, in an oxide thin film heterostructure of $PbTiO_3/SrTiO_3$, our team shows that three-dimensionally ordered superstructures, which we dubbed "supercrystals", can emerge after exposing the sample to femtosecond laser pulses [1]. Although the ultrafast light-matter interaction only occurs within 100 femtoseconds of the laser pulse width, this supercrystal can remain stable in ambient conditions for years until thermal cycling to 450 K and back to room temperature restores the initial phases. Despite the knowledge of the initial and final state of the transformation, a fundamental question regarding to the transition pathway remains to be answered, namely, how these new states emerge and evolve into a nonvolatile form. Answering this question can provide precise mechanistic insights into the creation of these exotic functional states of matter.

However, due to the irreversible and ultrafast nature of the process, tracking the creation of supercrystals is challenging because the typical stroboscopic pump-probe technique cannot be applied. In this work [2], we utilize the unique properties of X-ray pulses from free electron lasers, namely the single-bunch brightness and its ultrafast pulse duration, to allow us to access the transient state of irreversible processes. At one pristine site, only one pump-probe event at a specific time delay can be performed. To capture the sequence of the transformation, the sample needs to be replenished by moving to a fresh spot for each pump-probe event at various time delays. By repeating this "move-and-measure" procedure, we were able to record and assemble a time-lapse movie to reveal the structural details on how the supercrystal forms. The initial measurements were performed at SACLA **BL3** beamline and additional data were collected at the X-ray pump-probe beamline at the LCLS.

By tracking the diffraction pattern changes, we found that the creation of supercrystal started with the collapse of the as-grown vortex (V) and ferroelectric (FE) order within 300 fs femtoseconds as the diffraction peaks intensities are significantly reduced (Fig. 1(a)). The FE phase is erased and turns into a weakly disordered metastable nanopolar phase (D-FE) stabilized by the photoinduced charge injection. At the same time, the V phase transforms into a metastable FE-like (c^+/c^-) phase, up-and-down polarized nanoregions; in this phase, the vorticity is suppressed as the vortices unwind. Within a few picoseconds, the collapse of preexisting orders enters the 'soup' state, providing an empty canvas before the vortex supercrystal (VSC) emerges. After a significant incubation time, over a timespan of 10 ps to a few nanoseconds, a labyrinthine stripe phase (L) starts to appear and the c^+/c^- phase strengthens, and its periodic satellite pattern persists throughout the transformation (Fig. 1(b)). This mixing of phases evolves under a long-lasting interplay between the charge carrier screening of depolarizing fields and reduced mesoscopic ferroelastic strains at the phase boundaries. As the sample cools down on tens of nanoseconds due to thermal transport from the film to the substrate, the

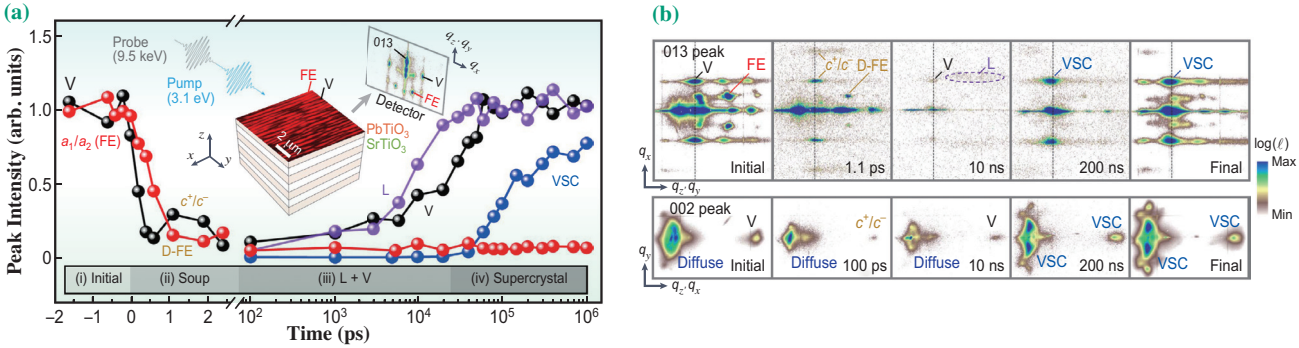

Fig. 1. Capturing the pathway of phase transformation. **(a)**Twin a_1/a_2 FE- and V-phase coexistence in the initial state as superdomains with ~400 nm periodicity along the y axis (inset: dark-field X-ray microscopy). After the initial collapse of the V and FE orders on the ~1 ps timescale, a 'soup' of D-FE and metastable V forms in the intermediate stages, followed by the correlated emergence of an L phase with the recovery of the V phase on a timescale of a few nanoseconds. The L and V phases undergo simultaneous conversion to the VSC supercrystal phase after 20 ns. **(b)** Representative detector images show diffuse diffraction patterns recorded near the 002 and 013 Bragg geometries tracking the evolution of the phases in (a). In the 013 geometry, the black vertical dashed line tracks the q_z value (proportional to ε_{33} normal strain) of the initial V phase, whereas the VSC satellites (marked in the inset at 200 ns and the final state) are shifted to larger q_z, corresponding to its ε_{33} normal strain value. The larger q_z corresponds to the left side of detector images. [2]

original V and FE phases do not recover. Instead, the VSC phase starts to nucleate and grow, as evidenced by the satellite peaks of VSC phases in the diffraction pattern. On microsecond time scales, the phase conversion process completes.

With the direct structural characterization that spans from femtosecond to microseconds, an unprecedented seven orders of magnitude time scale, insights into the formation of new order parameters can be gained by comparing the experimental results with the theoretical simulation. A dynamical phase-field model has been developed to simulate this entire process including important parameters such as time-dependent carrier concentration, inhomogeneous strain, and gradient energy. The microscopic insights obtained by the spatial dependence of the shear strain as well as carrier concentration are shown by Fig. 2(a). The shear strain (ε_{23}) correlated well with the evolution of the carrier concentration: the shear strain arises at the boundary between the nanodomains with varying polar textures due to the mismatch of lattice deformations associated with polarization reorientations across these boundaries. This correlation illustrates the critical role of the optically excited carriers in the formation of VSC. The dynamical trajectory of successive phase transformations is summarized in Fig. 2(b) as a function of charge and ε_{23}, illustrating the reorganization of the starting phases along the pathway of phase conversions. A larger shear strain promotes the FE polarization to continuously 'curl' in an intermediate direction. The VSC structure starts to appear when the combination of carrier concentration, strain, and temperature reaches the optimal condition on nanosecond time scales.

Our work highlights that controlling phase competition is an essential ingredient for creating new ordered states. Most of the nanoscopic information in this work was derived from the characterization of the reciprocal space. Looking forward, direct real-space visualization of these phases would be critical to disentangle the nanoscale interactions among them. Our recent work has demonstrated the capability of imaging mesoscopic domain network creation using *in situ* X-ray diffraction microscopy at synchrotron [3]. We show that a richer phase diagram containing more complex nanostructures can be accessed by controlling the optical dosage. The interplay of emergent phases in real space can be visualized by scanning X-ray diffraction imaging. We envision that the development of spatiotemporal imaging at the FELs can offer unprecedented insights into real-space phase competitions, thus achieving a microscopic understanding of light-induced phase transformation at the level of phonons.

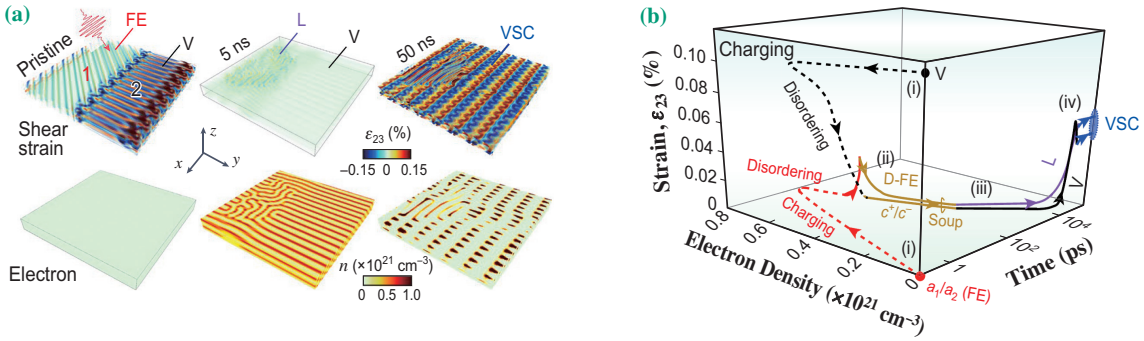

Fig. 2. Understanding the pathway of phase transformation. **(a)** Dynamical phase-field simulation (DPFM) of the spatiotemporal evolution of shear strain ε_{23} and electron concentration within two PTO plus two STO layers after excitation with single optical pulses. L fluctuations form inside the original FE region (region 1) and coexist with V (region 2) at 5 ns after single-shot optical excitation. At 50 ns, the VSC is formed. **(b)** DPFM evolution prediction of ε_{23} and electron density in the spatial regions (marked in (a)) where the initial phases (V and FE) reside. Sub-picosecond non-equilibrium disordering of the V and FE phases observed in experiments is indicated by the dashed lines. After the subsequent thermalization of the system, on the timescale of a few picoseconds, the V phase converts to c^+/c^-, whereas the FE converts to D-FE, forming the 'soup' stage. Until the VSC nucleates after 10 ns, L fluctuations gradually replace D-FE, whereas the V phase re-emerges. At the longest time delays (>20 ns), L and V merge into the VSC phase when a sudden increase in ε_{23} occurs in both 1 and 2 regions. [2]

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