

Optically induced transient enhancement of a structural order parameter

M. Porer^{1,*}, M. Fechner^{2,3}, E. M. Bothschafter¹, L. Rettig¹, A. Narayan², M. Radovic¹, M. Savoini^{1,4}, V. Esposito¹, J. Rittmann^{1,5}, M. Kubli⁴, T. Kubacka⁴, T. Huber⁴, M. Neugebauer⁴, E. Abreu⁴, S. Gröbel¹, P. Beaud^{1,5}, G. Ingold^{1,5}, G. Lantz⁴, S. Parchenko¹, S. Song⁶, T. Sato⁶, U. Aschauer⁷, N. Spaldin², S. L. Johnson⁴, and U. Staub^{1,**}

¹Swiss Light Source, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland

²Materials Theory, ETH Zürich, 8093 Zürich, Switzerland

³Max Planck Institute for the Structure and Dynamics of Matter, CFEL, 22761 Hamburg, Germany

⁴Institute for Quantum Electronics, ETH Zürich, 8093 Zürich, Switzerland

⁵SwissFEL, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland

⁶LCLS, SLAC National Accelerator Laboratory, Menlo Park, California 94025, USA

⁷Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland

Abstract. We photoexcite SrTiO₃ and EuTiO₃ in their purely soft-mode-driven structurally distorted phase and trace the structural order parameter via ultra-short x-rays. We observe a rapid decay for SrTiO₃ and an intriguing transient enhancement for EuTiO₃.

1 Introduction

We study the ultrafast photoinduced dynamics of the structural order parameter in a class of perovskites where phonon-phonon interactions are believed to be the primary mechanism of the thermodynamic transition. EuTiO₃ (ETO) and SrTiO₃ (STO) undergo a soft-mode-driven [1,2] structural phase transition from cubic to tetragonal symmetry given by an antiferrodistortive (AFD) rotation of the oxygen octahedra around the Ti ions (Fig. 1a). This structural transition does not involve electronic ordering (i.e. no charge/orbital order, superconductivity) and the soft-mode double-well potential is purely given by phonon occupations [3].

While the structural dynamics associated with melting an electronically driven transition has been studied intensely for a wide range of electronic ordering phenomena (such as charge/orbital order [4,5]), little is known about the optically induced relaxation dynamics of purely structural order. Here we employ above-bandgap femtosecond pulses to excite two perovskites with similar structural distortion out of the low-temperature equilibrium phase and monitor the subsequent dynamics of the order parameter via the intensity of distortion-induced superlattice (SL) reflections using ultrashort hard x-ray pulses (Fig. 1b). The fundamental question is whether melting of the structural order is delayed by lattice heating (i.e. transfer of the electronic excess energy to the phonon bath). As the valence band of ETO and STO is formed by Eu 4f and O 2p states, respectively (Fig. 1c), we furthermore can assess the influence of different charge-transfer excitation pathways.

*e-mail: michael.porer@psi.ch

**e-mail: urs.staub@psi.ch

We studied STO at the FEMTO slicing facility at SLS using bulk $\text{Ca}_{0.03}\text{Sr}_{0.97}\text{TiO}_3$. 3% Ca doping elevates the transition temperature to 285 K but leaves the nature of the transition unchanged [6]. This enables cooling with a IN_2 jet. The study on ETO was conducted on a PLD grown 40 nm ETO film on STO (100) substrate at LCLS/SLAC.

2 SrTiO_3 : Fast melting of structural order

Above bandgap photoexcitation of Ca:STO results in a rapid drop of the SL reflection intensity with a timescale of ~ 0.2 ps (Fig. 2a). This is much faster than expected from melting of the AFD order via lattice heating [7]. To understand the origin of the fast decay component, we calculate the AFD double well potential as a function of O 2p hole doping via DFT. Combining this with a time dependent doping given by the laser pulse yields an equation of motion for the AFD coordinate. Its solution explains the fast drop as a consequence of optically injected O 2p holes [8]. A similar calculation for electron doping shows that population of the conduction states has a much smaller effect on the AFD distortion [9].

3 EuTiO_3 : Transient increase of antiferrodistortive order

After photoexcitation, the intensity of the AFD superlattice reflection of ETO first increases and remains above the equilibrium state for up to 0.3 ps (Fig. 2b). The subsequent decay can be described with a biexponential decay with time constants decreasing with the excitation fluence (down to $\tau_1 \approx 0.2$ ps and $\tau_2 \approx 1.0$ ps at $\lambda_{\text{pump}}=266$ nm).

Most notably, the transient intensity increase represents an optically induced ultrafast increase of the structural order parameter, which stands in contrast to the reduction of the distortion for an increased internal energy in equilibrium. Furthermore, we observe that the ratio of the intensity drop at later times to the amplitude of the initial increase rises with the electronic excess energy set by the excitation wavelength (Fig. 2b).

Preliminary DFT calculations performed analogously to the study of STO show that the equilibrium position of the antiferrodistortive soft-mode of ETO is indeed expected to increase for simultaneous Ti 3d electron and Eu 4f hole doping. Further theoretical and experimental work is ongoing to assess the roles of hot carrier populations, carrier lifetimes

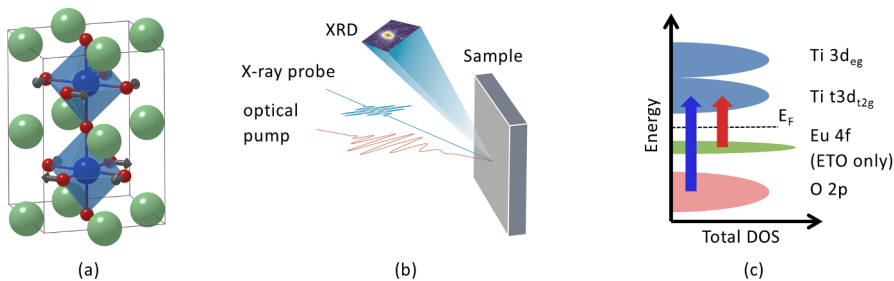


Figure 1. (a) Distorted unit cell of ETO/STO (Eu/Sr: green; Ti: blue; O: red). Arrows highlight the atomic motions towards the antiferrodistortive phase. (b) Schematic of the optical-pump/x-ray-probe experiments. (c) Optical excitation pathways and schematic location of the bands for ETO and STO (after [3]).

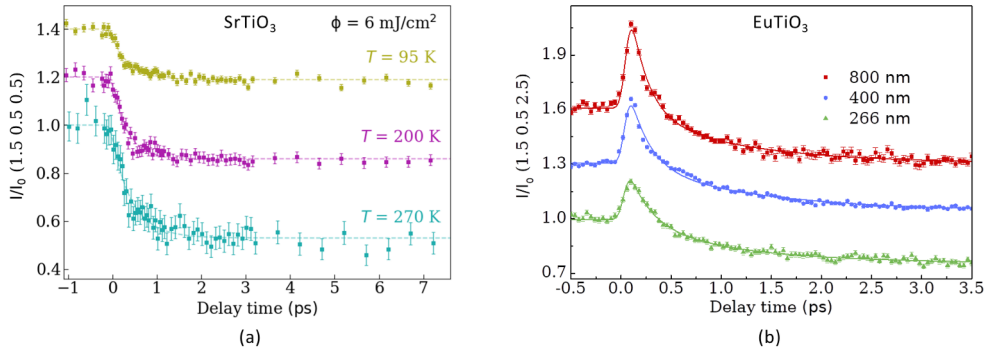


Figure 2. Ultrafast dynamics of AFD induced x-ray superlattice reflections after photoexcitation of STO and ETO. (a) Reflection intensity of STO probed with 140 fs x-ray pulses on excitation with 100 fs pulses centered at 266 nm for a series of base temperatures. (b) Transient intensity of a similar reflection of ETO probed with 40 fs x-ray pulses for a series of excitation wavelengths at $T = 110 \text{ K}$ and excitation fluencies yielding a similar drop below the initial baseline. Curves are separated by a constant vertical offset for clarity.

and the electronic excess energy. We currently address this from the theory side with time-dependent DFT with the aim to answer whether a transient occupation of antibonding conduction states before carrier cooling can result in transient interatomic forces that lead to a short lived enhancement of the AFD order. This approach may also clarify why the ratio of the suppression/enhancement amplitudes scales with the electronic excess energy.

4 Conclusion

Our results indicate that in systems with phonon-mediated equilibrium phase transitions electronic interactions with the soft mode play an important role in the nonequilibrium case. The coupling of excited charge carriers with the distorted crystal lattice can lead to structural dynamics on a timescale comparable to the melting of the structural component of an electronically induced phase transition [4]. A universal theoretical description of this kind of experiments calls for calculations beyond equilibrium DFT to fully capture the transient enhancement of the order parameter in the case of ETO. Our results point out a route for ultrafast manipulation of structural order instead of purely suppressing it.

5 References

- [1] G. Shirane and Y. Yamada, *Physical Review*, **177**, 858 (1969).
- [2] A. Bussmann-Holder, *et al.*, *Phys. Rev. B* **83** 212102 (2011).
- [3] R. Cowley, *Advances in Physics*, **29** 1–110, (1980).
- [4] P. Beaud, *et al.*, *Nature Materials* **13**, 923 (2014).
- [5] A. Cavalleri, *et al.*, *Phys. Rev. Lett.*, **87** 237401, (2001).
- [6] S. Mishra, *et al.*, *J. of Sol. St. Chem* **178**, 2846 (2005).
- [7] J. Shah, *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures*, Springer, 1999.
- [8] M. Porer, M. Fechner, *et al.*, arXiv:1805.00580, *Phys. Rev. Lett.* (2018) (in press)
- [9] C. Cancellieri, *et al.*, *Nature Communications*, **7** 10386, (2016).