

## Time Resolved Phonons as a Microscopic Probe for Solid State Reactions

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Solid state reactions are usually monitored by the time-evolution of the crystalline structure or of macroscopic dielectric, optic, thermal, mechanical or magnetic quantities. Frequently, the elementary steps of the underlying microscopic mechanism are, however, not directly accessible. In those cases, the study of phonons and their variation during transformations provide new and unique information about the changes in chemical bonding and microscopic trajectories. The experimental determination of phonons in a wide range of wave vectors and frequencies is a domain of inelastic neutron scattering and requires usually rather long counting times. Real-time investigations therefore need sophisticated techniques in order to access the time regime down to microseconds [1]. In this contribution, the potential of time-resolved phonon spectroscopy is illustrated by two different examples, namely the kinetics of demixing processes in model systems after a temperature quench and the kinetics of field induced ferroelectric phase transitions.

Using silver-alkali halides as model systems we were able to show that the demixing process is dominated by nucleation and growth at sufficiently high temperatures and by spinodal decomposition based on concentration fluctuations at low temperatures [2]. The formation of the product phases is associated not only with a splitting of Bragg reflections due to the different lattice parameters but also with a splitting of phonons due to the difference in interatomic interactions and atomic masses. While the time-evolutions of Bragg- and phonon profiles go hand in hand within the nucleation regime, they become dramatically different in the spinodal range. Here, phonon spectra vary on a time-scale of seconds while the average structure as reflected by Bragg-peaks remains almost unchanged. Only on a much longer time-scale of hours or months (depending on the invariant halide sublattice) the equilibrium structures are formed [3-5]. Hence, phonons directly prove that chemical demixing, in fact, takes place within seconds and the relaxation of the lattice is another aspect of the decomposition process. More detailed information can be obtained from the time-dependent phonon line widths. As long as the size of the precipitates is small, the phonons are heavily damped and the spectra are broadened. Only if the precipitates reach a critical size of about 8-10 nm due to coarsening effects, the phonon line widths start to decrease, demonstrating that the correlation length is of the same order of magnitude.

The knowledge of the microscopic mechanism enables one to control the demixing process and to produce well defined self-assembled nanostructures that can be characterized by atomic force microscopy [6].

As an example of much faster processes on a microsecond time-scale, the electric field induced ferroelectric transition of SrTiO<sub>3</sub> at temperatures below 40 K was studied. At zero field, SrTiO<sub>3</sub> remains in a quantum paraelectric phase down to the lowest temperatures [7]. Only by applying a sufficiently strong electric field, the quantum fluctuations are suppressed and the ordered ferroelectric phase is entered [8]. This transition is driven by a soft phonon mode at the Brillouin zone-center. Using stroboscopic methods, the time-evolution of this soft-mode was observed at 30 K under the influence of strong pulsed electric fields. It could be shown, that without any delay the soft-mode spectrum changes hand in hand with the electric field. The switching into the ferroelectric phase and the variation of the soft-mode spectrum could be detected on a microsecond time-scale. This finding demonstrates that neither defects nor domains walls that are formed on cooling across the ferrodistortive transition at 105 K, have a significant influence on the ferroelectric phase. This is in contrast to modulated ferroelectrics of the A<sub>2</sub>BX<sub>4</sub>-family that have been studied previously and exhibit diffuse field induced phases [9-11].

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