Revisiting the phase transition in $SrTiO_3$: type of transition and precursor effects

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$SrTiO_3$ is one of the best investigated perovskite oxides and still under intense current research. It is well known that at T_S=105K a structural phase transition from cubic to tetragonal takes place associated with the softening of a transverse acoustic mode. Simultaneously a long wave length transverse optic mode softens reminiscent of a ferroelectric instability. The complete softening is, however, inhibited by quantum fluctuations which lead to the introduction of quantum paraelectricity. Accompanied with the soft optic mode is an enormous increase in the dielectric constant which could be useful for cryogenic applications.

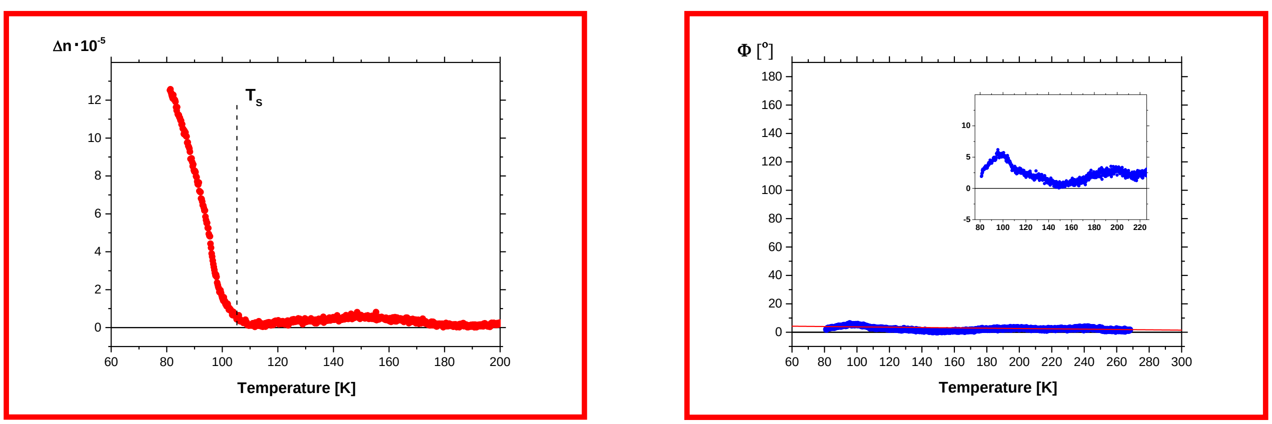
For a long time the structural instability at T_S has been considered to be purely displacive since the transverse acoustic mode softening continues smoothly up to T_S. A certain doubt about this “displacive only” behavior has been raised from EPR measurements where order-disorder dynamics were observed. Thus it clearly appeared that it is impossible to separate different dynamics from each other in an unambiguous way but that coexistence of both dynamics needs to be taken into account where length and time scales differ substantially. In addition, it was shown that the phase transition is preceded by precursor effects which persist up to a certain critical temperature from where on they become manifest and are well detectable. Here we focus on this latter point and provide experimental as well as theoretical evidence for their existence and their implications on the phase transition mechanism.

Experimentally birefringence and elastic constant measurements have been carried through which exhibit pronounced deviations from what would be expected from a Landau free energy expansion (Fig. 1a). Obviously a clear sign of birefringence is seen far above T_S which gets more and more pronounced when approaching T_S. Simultaneously a softening of the elastic constants takes place which is beyond any mean-field approach.

Theoretically, the polarizability model has been employed with focus on the long wave length dynamics. Here pronounced mode-mode coupling takes place which leads to an anomalous acoustic mode dispersion and local mode softening. The length scale of these dynamical clusters increases steadily with decreasing temperature and diverges upon approaching T_S. These additional features are a consequence of strong anharmonicity and anomalous mode-mode coupling which is absent in purely rigid ion models but caused by transition metal d and oxygen ion p dynamical covalency.

Early measurements by Courtens [1] suggested that the birefringence in the ferroelastic phase varied with temperature with a critical exponent for the order parameter of 0.36(2). More recent measurements [2], in which birefringence imaging was used to make sure that a domain-free region of the crystal was measured gave a mean-field exponent close to 0.5. It was suggested that Courten's measurement, which was carried out by averaging over a field of view of the crystal, might have been affected by the presence of domains appearing within the low-temperature phase. More importantly for the purposes of this report, Courtens observed a curious cusp appearing just above the phase transition that he explained in terms of critical fluctuations. Such behavior was not seen in the work [2]. In this report we will show that this cusp can be avoided if only the phase transition is observed at no change in the indicatrix orientation during the structural transformation (Fig 1b). At the same time the temperature behavior of birefringence below T_S is not pointing to a purely displacive transition type. Above Ts the precursor dynamics are present [3] independent on crystal technology and its temperature range is in good agreement with temperature range reported also for micro- and nanoceramics of $SrTiO_3$ by Hehlen et al [4].

1. E. Courtens, Phys. Rev. Letters, 29, No. 20, 1972
2. M. A. Geday and A. M. Glazer, J. Phys.: Condens. Matter 16, 3303–3310, 2004
3. K. Roleder, A. Bussmann-Holder, M. Górny K. Szot and A. M. Glazer, Phase Transitions, 85, No. 11, 939–948, 2012
4. B. Hehlen, A. Al-Zein, C. Bogicevic, P. Gemeiner, and J-M. Kiat, Phys. Rev. B87, 014303 (2013)



a) b)

Figure 1

Temperature dependence of birefringence for SrTiO3 single crystal (a) at almost constant orientation of optical indicatrix (b). Up to ca. 170K non-zero birefringence is present (a).