

## Ferroelectric phase transitions in stressed SrTiO<sub>3</sub> thin films

A. I. Lebedev

Physics Department, Moscow State University, Moscow, 119991, Russia

The strain engineering is a widely used technique in modern electronics. When searching for new applications of ferroelectrics, the first-principles studies of the strain effects are usually performed using the fixed-strain boundary conditions. At the same time, for studying the strain effects in substrate-free thin films or thick films, the using of *fixed-stress* boundary conditions seems more preferable. In this work, we use the first-principles density functional theory to study the ferroelectric instability in stressed strontium titanate thin films, calculate the phase diagram of this system, and discuss possible application of the bistability revealed in the ferroelectric properties of this system.

The calculations of the equilibrium lattice parameters and atomic coordinates of thin films of SrTiO<sub>3</sub> subjected to biaxial tensile or compressive stress were performed within the first-principles density functional theory using the ABINIT program. The film was relaxed in the direction normal to its surface. The exchange-correlation interaction was described in the local density approximation. The pseudopotentials of atoms were constructed following the RKKJ scheme. The cut-off energy was 30 Ha. The integration over the Brillouin zone was performed on the 8×8×8 Monkhorst–Pack meshes for the cubic cell or meshes with equivalent density of *k*-points for lower-symmetry phases. To obtain the ground-state structure for each in-plane stress, the phonon spectrum and elastic tensor were calculated for all possible phases and it was checked whether the frequencies of all optical phonons at all points of the Brillouin zone are positive and if the determinant and all principal minors constructed of the elastic tensor components are positive (the stability criterion).

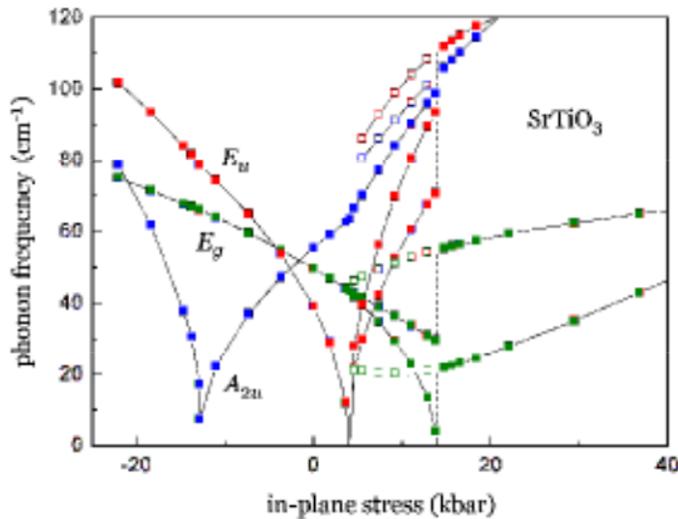


Fig. 1. The frequencies of the phonon spectrum in the ground-state structures of stressed SrTiO<sub>3</sub> thin film at different in-plane stresses.

Under the biaxial stress, the structure of high-temperature cubic phase of SrTiO<sub>3</sub> is reduced to tetragonal (*P4/mmm* space group), and the *I4/mcm* phase is the ground state in the pressure range from  $p = -13$  kbar to  $p = +4.1$  kbar (Fig. 1). The existence region of this phase is limited by the softening of the ferroelectric *A<sub>2u</sub>* mode (under the compressive conditions) and of the *E<sub>u</sub>* one (under tensile conditions). When crossing these limits, the structure of the ground state changes to *I4cm* or *Ima2*, respectively. An analysis of the behavior of the *A<sub>2u</sub>* soft mode at the *I4/mcm*–*I4cm* phase transition shows that the magnitudes of the mechanical stresses at which the frequency

of this mode vanishes on both sides of the boundary differ by 0.74 kbar. This means that the *I4/mcm*–*I4cm* phase transition is actually a first-order one.

Since the  $E_u$  mode is doubly degenerate, to find the ground-state structure at  $p > 4.1$  kbar we considered two structures described by the two-component order parameters of  $(P_x, 0)$  and  $(P_x, P_x)$ , and chose among them the one that has a lower enthalpy. Under the biaxial stress, the enthalpy is calculated using the formula  $H = E_{\text{tot}} + pV(u_{11} + u_{22})$ , where  $E_{\text{tot}}$  is the total energy,  $p$  is the stress,  $V$  is the unit cell volume, and  $u_{11}$  and  $u_{22}$  are the in-plane components of the strain tensor. Among two possible solutions with space groups  $Fmm2$  and  $Ima2$ , the latter phase had the lower enthalpy.

Much more interesting phenomena are observed in the case of tensile stress. In the  $I4/mcm$  phase not only the  $E_u$  mode is softened with increasing tensile stress, but also the  $E_g$  mode, which splits into two components upon the transition to the  $Ima2$  phase, and the frequency of one of its components becomes zero at a pressure of +13.8 kbar (Fig. 1). This triggers another phase transition into a phase with the same space group (denoted below as  $Ima2(\text{II})$ ), which has a different picture of octahedra rotations. Because the  $E_g$  mode is genetically derived from the  $R_{25}$  mode of cubic  $\text{SrTiO}_3$ , the cause of this phase transition is the structural instability. At this phase transition the direction of the rotation axis abruptly changes from the direction normal to the film plane to the direction along the polar axis.

An interesting feature of the  $Ima2(\text{II})$  phase is the behavior of the soft mode as a function of stress. At the isostructural  $Ima2$ – $Ima2(\text{II})$  phase transition, the frequency of many modes changes abruptly (dashed lines in Fig. 1) and the frequency of the soft mode in the  $Ima2(\text{II})$  phase does not vanish when approaching the phase boundary. This means that this phase transition is of the first order. This is also clearly evidenced by the possibility to preserve the stability of the  $Ima2(\text{II})$  phase when gradually decreasing tensile stress (open circles in Fig. 1)—up to a pressure of about 4 kbar, when the enthalpies of the  $I4/mcm$  and  $Ima2(\text{II})$  phases become equal and the  $Ima2(\text{II})$  phase transforms to the  $I4/mcm$  one. Thus, a large hysteresis loop occurs on the phase diagram at the stresses between +4.1 and +13.8 kbar. The comparison of the enthalpies of two phases shows that in the hysteresis region the ground state (which corresponds to the minimum enthalpy) is the  $Ima2(\text{II})$  phase, whereas the  $Ima2$  phase is metastable (for both phases the above criterion of stability is fulfilled).

The specific feature of the considered system is that the ferroelectric phase transition around 4 kbar goes from the non-polar to *metastable polar* phase, which transforms into the stable polar phase only at higher pressure. The properties of two polar phases coexisting in the hysteresis region are significantly different. For example, the values of spontaneous polarization in these phases at +11 kbar are  $0.128 \text{ C/m}^2$  in the  $Ima2$  phase and  $0.182 \text{ C/m}^2$  in the  $Ima2(\text{II})$  phase. The difference of the band gaps in the two phases is 61 meV.

The phase sequence revealed in stressed  $\text{SrTiO}_3$  films suggests another possible application of ferroelectrics—in phase change memory devices. Indeed, after the transition to the ferroelectric  $Ima2$  phase induced by an applied stress at low temperatures, the film is in a uniform metastable state in which regions of stable  $Ima2(\text{II})$  phase can be created by the local optical heating. Because the system is bistable, both states can coexist at low temperatures, and the contrast in the optical properties of the two phases can be used for nondestructive read-out of the stored information. Erasing of information can be achieved simply by reducing the applied stress. Such a device can work only at low temperatures because at high temperatures the system will transform from the  $I4/mcm$  phase to the thermodynamically stable  $Ima2(\text{II})$  phase with increasing stress.

One should add that the described bistability is not specific to  $\text{SrTiO}_3$  but is possible in other systems with competing instabilities.

**Acknowledgments.** This work was supported by the Russian Foundation for Basic Research, projects 11-02-01317 and 13-02-00724.

