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Functional interfaces are at the core of research in the emerging field of ‘domain boundary engineering’ where polar, conducting, chiral, and other interfaces and twin boundaries have been discovered. Ferroelectricity was found in twin walls of paraelectric CaTiO₃. We show that the effect of functional interfaces can be optimized if the number of twin boundaries is increased in densely twinned materials. Such materials can be produced by shear in the ferroelastic phase rather than by rapid quench from the paraelastic phase.

Keywords: twin boundaries; multiferroic; CaTiO₃; twinning

1. Introduction

Functional interfaces are not simple structural juxtapositions of adjacent bulk materials, but contain novel structural elements which do not exist in the bulk. Typical examples are superconducting domain boundaries in insulating materials [1,2], twin boundaries with high defect mobilities [3–6], two-dimensional electron gas at interfaces [7–10], unusual vortices near twin boundaries [11], or multiferroicity and chirality at domain boundaries [12–14]. If such properties are exclusively related to domain boundaries, such as twin walls, then they qualify as objects of the emerging field of ‘domain boundary engineering’ [15,16] which embodies the hope that functional domain boundaries can, one day, be reproduced in an engineering fashion for applications, say, in electronic industry. A typical example is the IBM racetrack memory based on the controlled movement of magnetic domain walls. Their movement is registered electromagnetically and their position is used as memory information. The desired breakthrough is now to find ferroelectric domain walls where the information can be written and read by simple application of electric fields. The memory is the location of the wall and the ferroelectric spontaneous polarization of that domain wall. The wider industrial consequence of such local structures as memory devices, conductors, holographic templates, or as membranes for batteries have motivated significant research efforts during recent years.

2. CaTiO₃ and high twin densities

One of the first materials, which was identified theoretically for domain boundary applications, was CaTiO₃. Experimentally, CaTiO₃ is the first ferroelastic material where the group at the Electron Microscopy for Materials Research (EMAT), University of Antwerp,

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succeeded in observing the predicted ferroelectric polarization inside a ferroelastic twin wall while the rest of the crystal remained centrosymmetric. Two lines of research came together in this material: first, it was shown that twin walls and antiphase boundaries represent sinks for oxygen vacancies. The stabilization energy for oxygen vacancies was predicted to be ~ 0.7 eV with a repulsive interaction between vacancies [5,17–19]. It was then expected that oxygen vacancies are rather uniformly distributed within twin walls and depleted in the bulk [20]. The second prediction was based on the inherent instability of regular TiO_6 octahedra where Ti positions tend to locate slightly off the geometrical midpoint of the octahedra [17]. Numerical calculations [17] had shown that twin walls in CaTiO_3 are ferrielectric with maximum dipole moments at the wall; a small ferroelectric dipole moment was found perpendicular to the wall with alternating (antiferroelectric) dipoles between neighboring walls. The same tendency for polar layers in CaTiO_3 , e.g. near surfaces, was also predicted for $\text{CaTiO}_3/\text{BaTiO}_3$ interfaces [21].

While computer simulations show polar twin walls rather clearly, the challenge for domain boundary studies is to observe the described singularities experimentally. Van Aert et al. [22] have shown that sufficient advances have been made using aberration-corrected transmission electron microscopy (TEM) imaging in combination with statistical parameter estimation theory [23–25] to investigate functional domain boundaries (see Figure 1). They confirmed that only the Ti positions take part in the polar deformation of the unit cell but that Ca remains, within experimental observations, inside the 12-fold

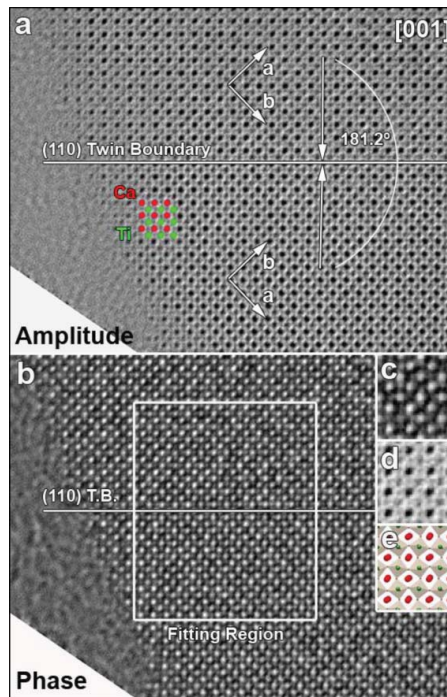


Figure 1. Exit-wave reconstructions of the (110) twin boundary (after [22]). (a) Amplitude of the reconstructed exit wave. The CaTiO_3 crystal is imaged along the [001] zone axis orientation; the (110) twin boundary is indicated by the horizontal white line. The Ca and Ti column positions are marked by red and green dots, respectively. The angle of 181.2° reveals the twin relation over the interface. (b) Phase of the reconstructed exit wave, the fitting region used for the statistical parameter estimation, is indicated by the white rectangle.

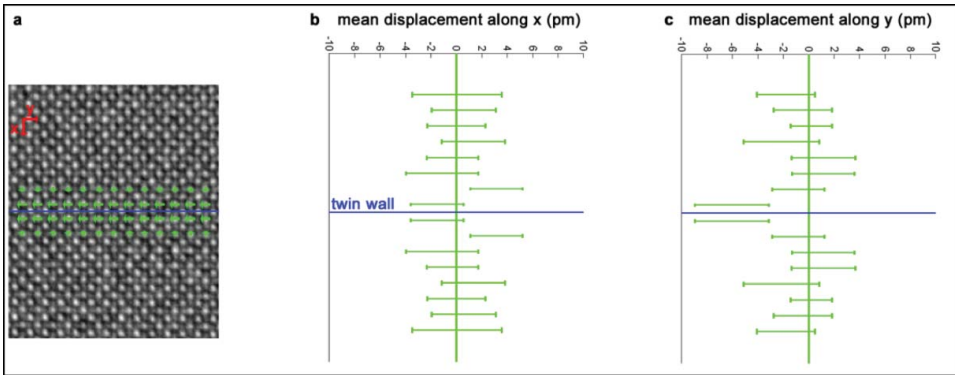


Figure 2. Map of the mean Ti atomic displacement vectors (after [22]). (a) Mean displacements of the Ti atomic columns from the center of the four neighboring Ca atomic columns and indicated by green arrows. Displacements of Ti atomic columns in the (b) x - and (c) y -directions averaged along and in mirror operation with respect to the twin wall together with their 90% confidence intervals.

coordinated cavity inside the perovskite structure. The functional character of the twin wall was hence proven (Figure 2a,b).

The question then arises: what other properties can be expected from such ‘exotic’ walls. Collective phenomena were discussed in [26,27] which leads directly to the practical proposition to make as many twin boundaries as possible in a sample. The dynamic behavior of twin walls under external forcing by applied strains to a sample depends sensitively on the inner structure of the wall. It can be expected that local pinning of chiral walls [12,28] will impede the speed of advancing walls. The wall movement is then a superposition of ballistic and jerky movements. Pinning centers for such movements are related to impurities, while intrinsic pinning occurs when walls intersect in so-called junctions. The twin density is closely related to the junction density. The key advance in this research is related to the way high twin densities are achieved [28,29], including the role played by the junction density and the internal properties of the ferroelastic material which allows such junctions to form [30]. Two options exist: first, one can quench a sample from a high temperature (the paraelastic phase) to temperatures well inside the stability field of the ferroelastic phase. This method has been used ever since ferroelastic crystals were discovered. It is the reverse of the slow cooling process, which was employed whenever twinning of a sample during a phase transition was considered unwanted (say in crystallographic investigations of single crystals) and researchers tried to avoid working with twinned materials. This situation has drastically changed: today we often wish to make as many twin boundaries as possible so that quenching rather than slow cooling becomes the method of choice. The second methodology to increase the twin density is to deform the crystal by external shear inside the stability field of the ferroelastic phase. This situation is encountered when thin films of one ferroelastic material are deposited onto another ferroelastic material at high temperatures. When the device is cooled to room temperature, the template will shear and impose this shear to the thin film. When this shear strain surpasses the yield strain, the thin film will spontaneously twin with a high twin boundary density. This pattern is then essentially stable under further shear. Driven systems [31] were used experimentally to generate high twin densities [32,33].

We can now discuss the difference between these two methods. When disorder is generated by structural rather than micro structural phenomena, one requires a source of disorder, which is commonly provided by local atomic disorder. Starting from uniform ground states, quench will freeze in some disorder of the para phase, which represents the initial state in the ferroelastic phase from where the microstructure evolves. Ref. [34] has derived the structure factor of the displacement – displacement correlation for $T > T_c$ in the simple case of Ornstein–Zernike fluctuations:

$$S_K \sim \left[\frac{1}{r_c^2} + a^2 \cos^2 \Theta + b^2 \sin^4 \Theta \sin^2 2\varphi + gk^2 \right]^{-1}.$$

This function is a four-armed starfish in three dimensions and represents the diffuse diffraction pattern in Figure 3(a). The equivalent microstructure is tweed [35] that evolves into stripe patterns that have a structure of dog's bones shown in Figure 3(b) [36–39]. The kinetic evolution is then for the quench experiment, the gradual change from the star to the dog's bone.

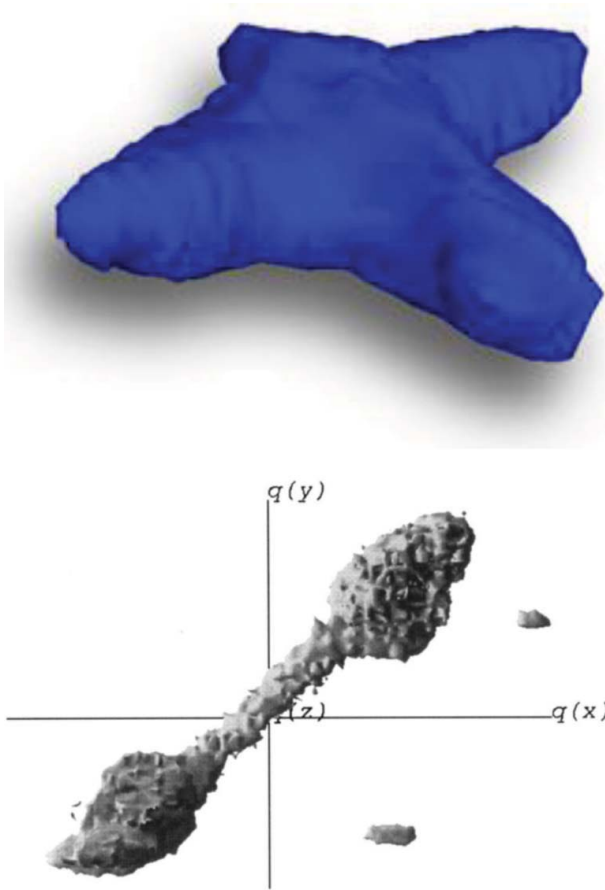


Figure 3. The kinetic effect of annealing tweed pattern with (a) a four-armed starfish-type structure factor $T > T_c$ to a stripe pattern with (b) a dog's bone structure.

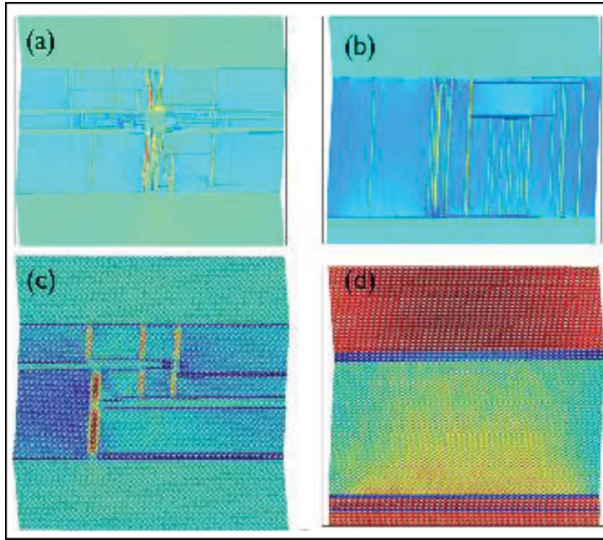


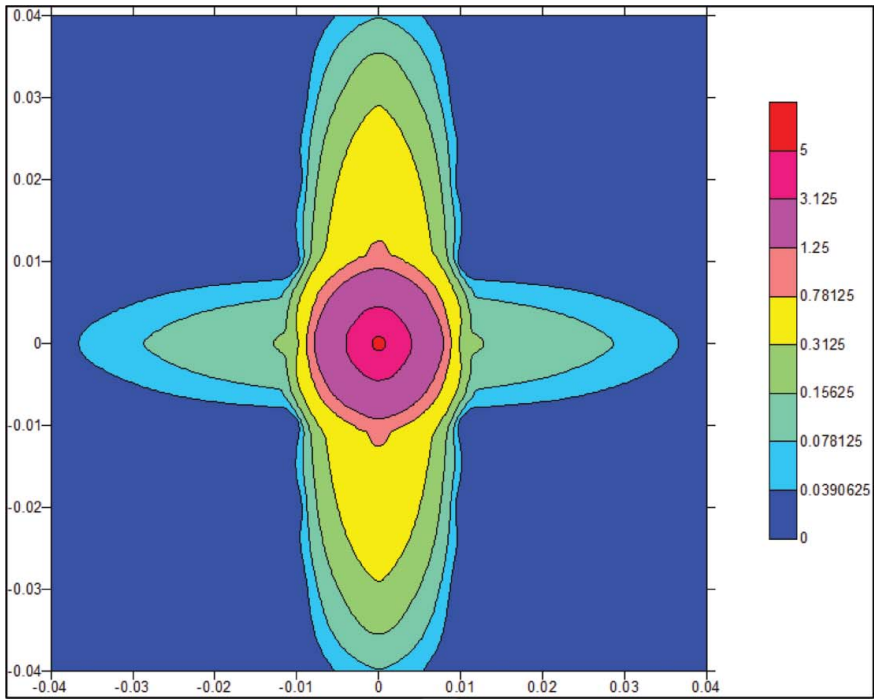
Figure 4. Domain pattern formed after the collapse at the yield stress for a large system with 10^6 atoms in (a) and (b) and for a small system (10200 atoms) in (c) and (d). (Length scales are 1000 atoms along one corner of the images in [a] and [b], and 101 atoms per corner in [c] and [d]). The images in (a) and (c) represent elastically soft systems, while images in (b) and (d) show elastically hard systems (the colors refer to the local shear angles, after [27]).

The statistical fluctuations in a system with order parameters with a local double well potential that are coupled with elastic interactions will show fluctuations, which aligned preferentially along the two elastically ‘soft’ directions. These are the four arms of the starfish with large fluctuations and suppressed fluctuations between the arms.

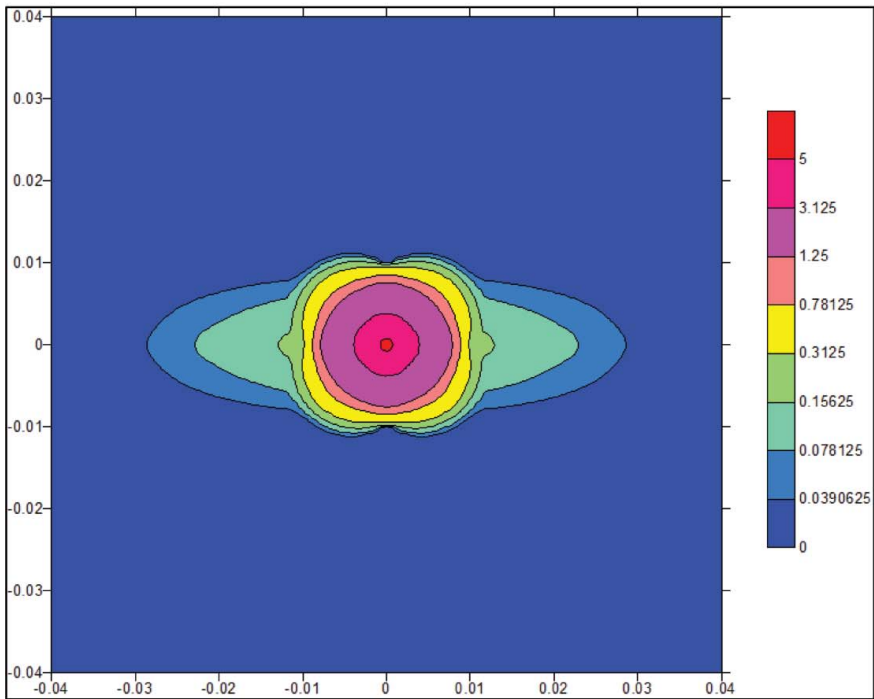
Below the transition point, the twin boundaries form along the first elastically soft direction and disallow fluctuations in the second elastically soft direction. The four arms of the starfish are then reduced to heterogeneities along only one direction and their shape reflects the more confined nature of the twin boundaries. Each twin boundary will then show a ‘dog’s bone’ structure. The superposition of all such structures is observed experimentally (see [27,38,39]) (Figures 4 and 5).

The range in k -space in Figure 5 is from $k = -0.04$ to 0.04 reciprocal units. These images would be observed in X-ray or neutron diffusion near the Bragg reflections, taken into account of the atomic scattering functions, and are equivalent to those in Figure 3 for simple elastic systems. The elastically soft system is shown in (a) and the hard system in (b). Note the slimmer arms of the starfish, as compared with the quenched sample in Figure 3. The stronger concentration of the diffuse scattering originates from the stricter confinement of the twin domains along the elastically soft directions and the smaller number of junctions compared with tweed pattern. The same conditions for a sample with ‘hard’ elastic interactions (Figure 5b) show the predominance of one domain orientation and fewer twin walls [27].

Comparison between the results in Figures 4 and 5 clearly shows that the microstructure of the quenched sample is different from that of the sheared sample. Quenching leads to quasi-harmonic fluctuations which can then sharpen up under low-temperature anneal. They will lead after long anneal to stripe patterns. Sheared samples are initially better organized and show twin boundaries which are largely parallel to each other right from



(a)



(b)

Figure 5. (a) and (b) Diffuse scattering (scattering factor) of strain-induced microstructures for a sample with 10^6 atoms and soft nearest neighbor interactions.

the point of their nucleation. Intersections of twin boundaries lead to the formation of junctions which are the main characteristics of the microstructure (rather than the twin density in a quenched stripe pattern). Computer simulation indicates that denser microstructures can be obtained by shear rather than by quench [27].

In conclusion, we find that the effect of functional interfaces, such as those in CaTiO_3 , can be optimized if the number of twin boundaries is increased. The optimal way to obtain highly twinned materials is not necessarily by rapid quench but rather by slow shear of the material in the ferroelastic phase.

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