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in Barium Titanate Ceramics**

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STUDY OF THE STRUCTURE OF FERROELECTRIC DOMAIN WALLS IN BARIUM TITANATE CERAMICS

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Abstract

The structure of 90° ferroelectric domain boundaries in barium titanate ceramics has been studied by means of Transmission Electron Microscopy and High Resolution TEM. Tilts of specific fringes across domain walls are measured on HREM images and Selected Area Diffraction Patterns. They are in a good agreement with the twin model admitted for these domain boundaries. A computerized method has been developed to give access to quantitative information about atomic displacements across these ferroelectric domain walls. The so calculated displacement field is then compared with Landau-Ginzburg based theoretical predictions.

Introduction

At room temperature barium titanate ceramic is a stable ferroelectric perovskite material mainly used as a type II dielectric. This phase is a result of a cubic/tetragonal phase transformation at the Curie temperature. The considerable internal elastic strain created during this transformation can be partially accommodated by the nucleation of 90° domains. Owing to the symmetry reduction (Pm3m to P4mm), type and main features of domain walls can be deduced easily [1,2]: 90° domain walls lay on {101} type planes, spontaneous polarizations lay along [001] directions and the tilt angle between the c axis of the two domains is $(90-2\text{Arctg}(a/c))^{\circ}$. However, the intimate structure of domain walls can not be anticipated from symmetry considerations and one has to introduce a thermodynamic model of the transformation to access the atomic structure of domain walls. The Landau-Ginzburg energy which take into account the strain/polarization coupling, the nonlinearity of the polarization and the nonlocal coupling of the polarization (polarization gradient term) can provide a dislocation-free explanation of the twin boundary structure [3,4,5]. Analytic quasi-one-dimension soliton solutions for the order parameter variation allow one to calculate probable atomic displacements and the associated energy across domain walls.

Many attempts to characterise the structure of different kinds of twin boundaries have been carried out but most of them could not access quantitative information precise enough for a direct comparison with models. The width of domain walls have been investigated in several ferroelectrics by means of conventional TEM [6-10] as well as high resolution TEM [11-15] but none of these works could give quantitative information about the structure of domain walls. Using Electron Holography a detailed investigation of domain walls in BaTiO₃ [16] has shown a good agreement between the measured polarization variations and the kink solution proposed by Zhimov. However this method does not consider any strain field variation in the vicinity of the wall and only the magnitude of the projected polarization is considered. S. Stermmer et al. did a very careful study of the atomic structure of 90° domain walls in PbTiO₃ by means of HRTEM and image processing. Using a Quasi-1-Dimension method for lattice parameter variation measurements, a good agreement with models [5] was found. However it has to be noticed that variations are assumed to be dependent only on distance to the wall and average method parallel to the wall does not allow any detection of "steps" or other "defects" with regard to models.

In this paper, we report some 2-dimension results of a Transmission Electron Microscopy study of ferroelectric domain walls in barium titanate ceramics. We will first give general SADP and HRTEM results concerning domain wall symmetry and imaging. We will then be concerned with quantitative measurements of specific feature displacement field on HRTEM images. We will finish by giving a comparison with theoretical predictions.

Experimental procedures

Observation of TEM specimen prepared under standard conditions were either made at 800kV on the Jeol Atomic Resolution Microscope "ARM 1000" or at 200kV on a Jeol 200cx and a TopCon OO2B. To prevent from charging, samples observed at 800kV were carbon coated.

For all the processing, large images (1024x1024 or 2048x2048 pixels) were digitized using a 6000 element CCD Leafscan 45 scanner connected to a Macintosh computer. In order to avoid any kind of additional distortions digitization was carried out directly on the original negatives. Image processings were performed on a Macintosh computer by means of commercial softwares and "custom functions" written by the authors.

Results

Measurements on SADP of 90° a-a domain walls confirm the general configuration and symmetry of domain walls in tetragonal barium titanate: domains are twin-related, the twin plane being {011} and the tilt angle 0.4° [15,19].

HRTEM images of both Ti and Ba lattices have been obtained away from any distorted areas but only a 4Å lattice was observed close to domain boundaries. This lower resolution can be explained by two main considerations. Firstly, a minimum thickness seems to be required to obtain ferroelectric domain walls: because of the mechanical relaxation in very thin areas domains can shift easily under the electron beam. More, the surface relaxation in thin edges can be dominant and domains as well as ferroelectricity can disappear [18]. Secondly, degradation of the atomic as well as polarization periodicity across the wall can alter significantly the resolution of a phase contrast image.

In spite of the difficulty to locate domain walls at high magnification on pure phase contrast images, a careful study of micrographs confirms measurements made on SADP and diffractograms that indicates the presence of distortions in the vicinity of the wall.

A computerized method has been developed to quantify this distortion. This method uses the following logic: noise reduction in the Fourier space, local peak finding including sub-pixel refinement and calculation of center of mass of plateaus, creation of a 2-D perfect lattice from a non distorted area of the image and comparison of node positions of this lattice to the peak positions of the entire image. It has to be noticed that image scanning must be carried out without any kind of interpolation somehow on a area centered in the negative plate or small enough to avoid additional nonlinear distortions coming from "S-aberration" of projector lenses. On account of the computer memory, calculation time and needed accuracy, the required resolution appears to be 8 to 10 pixels for describing one atomic column diameter. This allows to reach a precision order of about 0,1 Å.

This method has been applied to a number of HTREM images in which we could check that experimental conditions (say defocus, thickness, "macroscopic" tilt of the specimen...) do not significantly change from one area of the image to another. The displacements so obtained with this method are thus measurements of the effect on the image formation of both real atomic displacements and polarization variations.

Figure 1 shows a displacement vector plot associated to a <100> type zone axis HRTEM domain wall image. In this example the atomic displacement field is regular and its overall direction lies on a {110} type plane. The average domain wall thickness is of the order of 10 unit cells. The displacement vector plot in figure 2 shows a more distorted domain wall structure which is definitely not visible on the HREM image. The overall direction of the domain wall lies on a {110} type plane although there is local {100} faceting. The average domain boundary width, more difficult to determine in this case, seems to be of the order of 6 unit cells. This small thickness as well as the 2-dimension "non regular" structure of the wall increases the energy of the boundary, therefore decreasing its mobility. This structure may be compared to theoretical calculations estimating that a domain wall description has to be 3-dimensional or must include external constraints or continuous distribution of dislocations [20]. This comparison is now under progress.

Simulations of domain walls have been performed on the basis of first-order square-rectangular transition predictions[4]. A soliton displacement solution given in [4] was corrected so that the reference used for the comparison was not the high symmetry phase but a lattice created from a "non-distorted" part of the tetragonal phase. Solution is then directly comparable to displacements field measured on images. It has to be noticed that the model considers a pure ferroelastic transformation (order parameter being strain) with no consideration for the polarization. This model was chosen because our measurements were not able to separate the effect of polarization variations from atomic displacements. At first these measurements were assumed to be a measurement of atomic displacements only. Values of the coefficients in the free energy expansion were chosen to satisfy the following criterion: tetragonal spontaneous strain in the bulk is $e_{20}=(a-c)/a_0(2)^{1/2}=0.007759$ (in accordance with x-ray measurements), the temperature-dependent term in the free energy expansion is $A=-0.006283$ at room temperature and relations between coefficients given in [4] are respected. One can easily see that the theoretical simulation does not fit experimental displacement-vector results given here. Strains in the vicinity of domain walls are higher than predicted. Displacement vectors are not as parallel with the interface as they should be according to the theory meaning that each unit cell deformation is not isotropic across the wall. More, defects present in the wall or close to the wall induce a 2D-strain field which is actually not described by Q1D soliton solutions. 3D solution (including defects) of phase transition remains a challenging problem [20].

Conclusions and perspectives

HRTEM has proven to be a very useful technique to provide information on the atomic structure of ferroelectric domain walls in barium titanate ceramics. A numerical method has been developed to measure the position of specific features on images and to compare them with a perfect lattice created from the image. Then one can see easily the presence of a domain wall, its width, structure, etc. 90° domain walls have a thickness of about 30 to 40 Å. Different kinds of structures have been observed, some of them presenting steps on $\{100\}$ type plane. The Q1D soliton model is then no more valid for such a structure. The energy of such domain walls is probably higher than wide, planar boundaries, decreasing their mobility under an applied electric field or an external constraint. The elastic energy estimation of these domain walls is now under progress.

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Fig. 1 Atomic displacement vector plot of an edge-on ferroelectric domain of $\langle 100 \rangle$ zone axis HRTEM image of BaTiO₃. Model used for the displacement calculation was created from a non-distorted part of the upper part of the image. A defect (visible on the origin image) pins the domain wall in the upper left corner

Fig. 2 Atomic displacement vector plot of a domain wall HREM image. Displacements are measured in relation to a model which origin has been chosen above the domain wall in the "upper right" corner.

Fig. 3 Calculated displacement vector plot of a theoretical 90° ferroelastic domain wall described by the soliton solution of [4]. Origin of the "model" has been chosen in the "lower left" corner.