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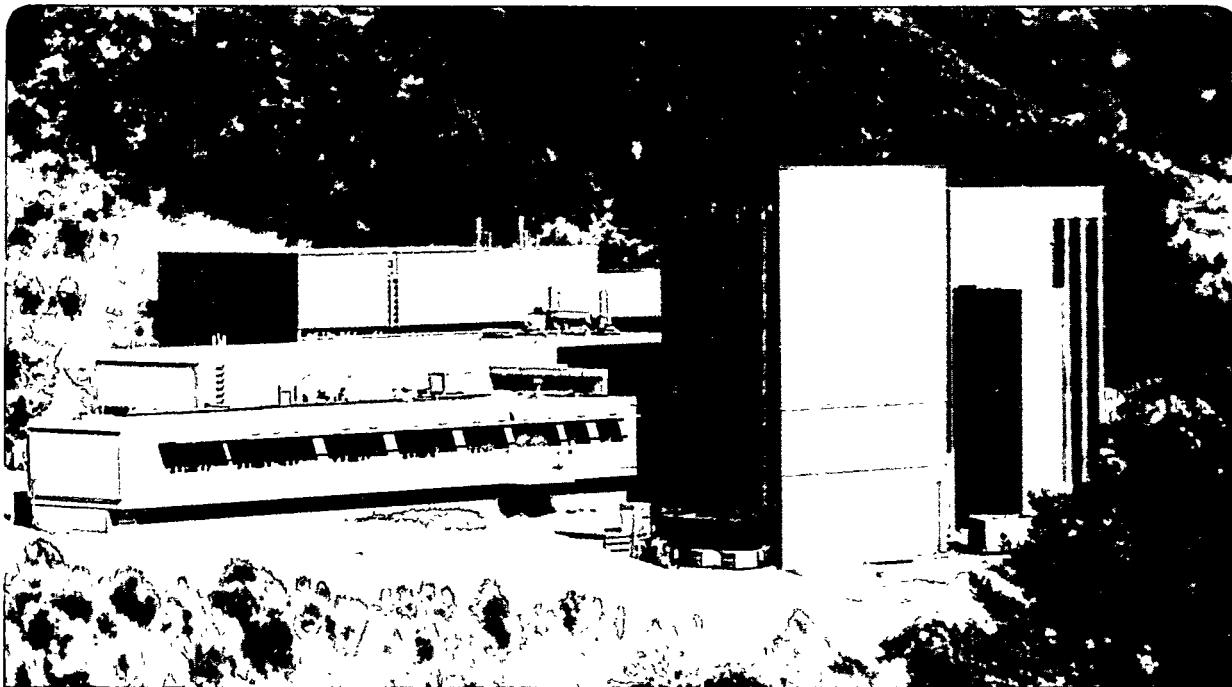
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STRUCTURE OF 90° DOMAIN WALLS IN FERROELECTRIC BARIUM TITANATE CERAMICS

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ABSTRACT

Ferroelectric domain walls in tetragonal ferroelectric barium titanate ceramics are studied by means of electron microscopy. SEM and TEM observations are consistent with domain configuration already proposed. Conventional TEM measurements on SADP agree very well with twin-related model currently admitted for ferroelectric domains. In spite of the very small lattice parameter variation during cooling (involving a small spontaneous strain) of BaTiO₃ ceramics, displacements of specific features associated with atomic column positions are measured across domain walls on high resolution images. Using a dedicated image analysis software, these displacements are calculated with a high precision. 2D vector-maps of the atomic displacements show different kinds of atomistic structure for different domain walls

INTRODUCTION

For the past thirty years the general influence of the domain configuration on the dielectric and the ferroelectric properties has been studied by many scientists (1 for a general overview). They pointed out how characteristics such as permittivity, piezoelectric coupling, dielectric fatigue or switching time were strongly wall structure dependant.

For instance, it has recently been shown (2) that thin ferroelectric layers which could be used in Ferroelectric Memory Field-Effect Transistors undergo a very strong dielectric fatigue when increasing the switching domain cycles. This fatigue is due to an increase of the necessary energy required to switch domains and is probably the direct consequence of a stronger interaction with specific defects in the material and a change of the domain wall structure; understanding of the depolarization mechanisms first requires a good knowledge of the chemical and crystallographical structure of domain walls and of the polarization instabilities across them.

Several authors have modeled domain walls in ferroelectric and ferroelastic materials with a continuum Landau-Ginzburg theory (3 for an overview). However there is still a lack of fine experimental results whereby one could quantitatively confirm theoretical predictions of elastic distortions across domain walls. Many studies have been carried out by means of High Resolution Transmission Electron Microscopy (HRTEM): domain walls in

$\text{YBa}_2\text{Cu}_3\text{O}_7$ have been investigated by Zhu et al. (4-5), Bursill et al. reported on BaTiO_3 , LiTaO_3 and other ferroelectric materials (6), detailed studies of domain walls in BaTiO_3 have also been investigated by Tsai et al. (7) and Normand et al. (8). But none of these works has shown quantitative measurements of atomic displacements at the immediate vicinity of the walls.

However the quantification of dimensional variations across a domain wall is difficult since the tetragonality introduced by the paraelastic/ferroelastic phase transition is very small. Then the validation of theoretical models thanks to HRTEM images of domain walls has not been successfully made so far.

In this project we have been using HRTEM to study the atomic structure of 90° domain walls in a tetragonal ferroelectric pure barium titanate ceramic. The first part of this paper will show results obtained from conventional TEM observations; the second part will give quantitative measurements of the strain field across domain walls from calculations on digitized HRTEM images.

MATERIALS AND EXPERIMENTAL PROCEDURES

Industrial ceramic materials sintered in a conventional way from well defined starting powders were used in this work. Observations were made at room temperature where the ferroelectric tetragonal phase is stable. This phase, which stability domain ranges between 0°C and 130°C , appears during cooling when the high temperature cubic structure undergoes the paraelectric/ferroelectric transition at the Curie temperature.

The symmetry reduction ($\text{m}3\text{m}$ to 4mm) occurring with this phase transition causes a domain structure to appear in which the c axis and the spontaneous polarization (resulting from a different motion of ions) lay along one of the six $[001]$ pseudo-cubic directions. Two types of domains can be formed : 90° and 180° domains. In 90° domains the direction of the polarization is at 90° from that of the next domain (exactly $2\text{xArctan}[a/c]$ if a and c are the tetragonal lattice parameters) (cf. fig.1). For those domains the walls are $\{110\}$ type planes ; in 180° domains the polarization is at 180° from the next domain. 180° domain walls are $\{100\}$ type planes and are assumed to be purely ferroelectric.

Electron transparent foils were prepared from bulk material by mechanical dimpling followed by Ar ion-milling. Specimen were either observed at 800kV on the Jeol Atomic Resolution Microscope "ARM 1000" or at 200kV on a Jeol 200cx and a TopCon 002B. 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 distortion digitization were 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

Scanning Electron Microscope (SEM) observations:

A backscattered electron SEM image is given in fig.2. The crystallographic contrast attached to this SEM imaging technique reveals a set of ferroelectric domains intersecting at about 60° or 90° . Explanation for such a pattern can be found in a spatial configuration for ferroelectric domains previously proposed by Arlt et al. (fig.3)(9).

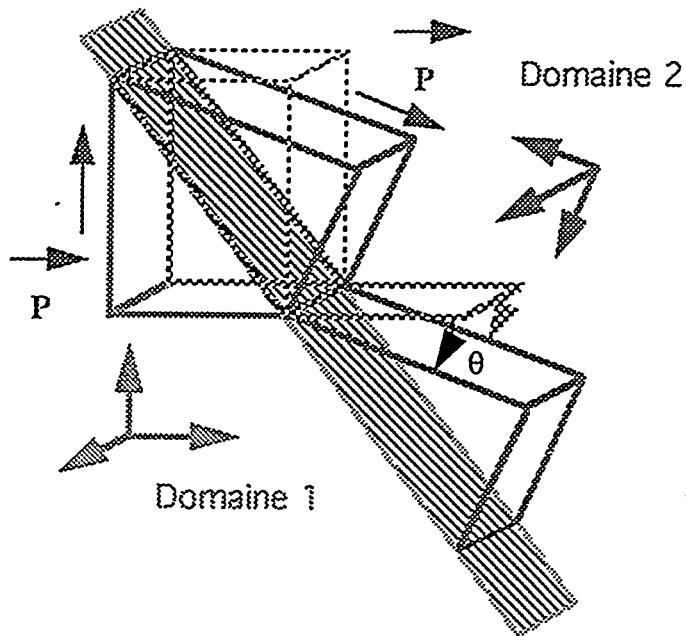


Fig. 1 Schematic sketch of a 90° domain boundary; Tetragonality has been exaggerated to emphasize the lattice plane rotation across the wall.

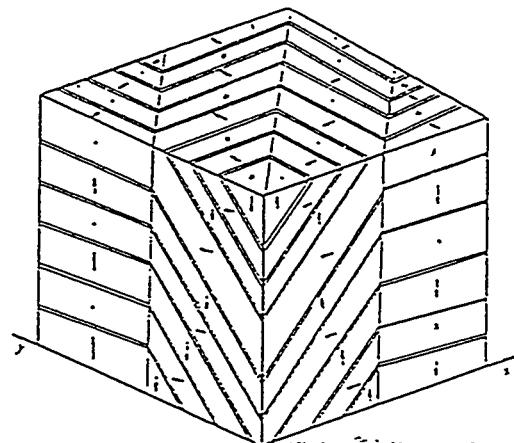


Fig.3 Domain configuration as seen in a cubic part of a grain (axes of the cube corresponding to principal crystallographic axes) (from (9)).

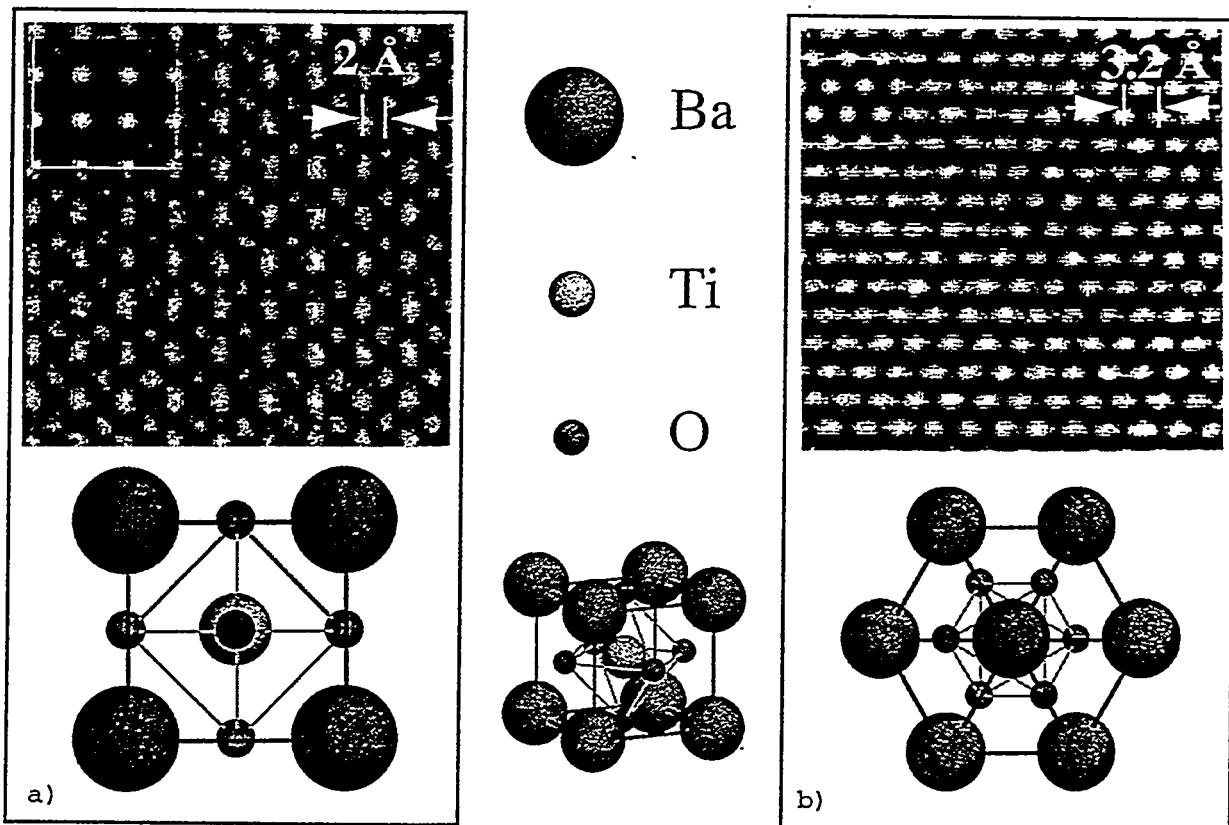


Fig.4 High resolution images of BaTiO₃ and associated oriented crystallographic model; (a) $<100>$ zone axis; (b) $<111>$ zone axis

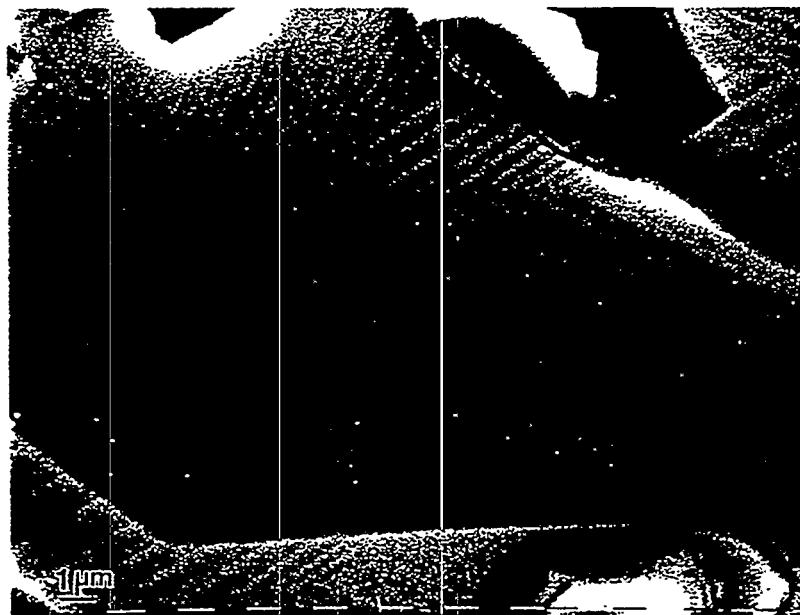


Fig. 2 Backscattered electron SEM of pure baryum titanate.

TEM observations:

Figure 5a shows a typical 90° domain configuration within a BaTiO_3 grain observed at a low magnification. For a $\langle 100 \rangle$ type orientation, two different kinds of Selected Area Diffraction Patterns (SADP) can occur depending on the domain wall type:

- For a a-a domain boundary (so call because the viewing direction is parallel to the a direction of the two domains), the twin plane is edge-on and the rotation axis is parallel to the viewing direction. In this orientation the SADP is the result of the superimposition of the two SADP of individual domains rotated around the zone axis so that $(0kk)_1$ reflections of domain 1 overlay the $(0kk)_2$ reflections of domain 2. Maximum spot splitting occurs then for $(0\bar{k}k)_1$ reflections for which the direction of the splitting is almost parallel to the domain wall. From the splitting of these spots it is then possible to know directly the rotation angle of the lattice planes due to the tetragonality of the structure as well as the domain boundary plane. Figure 5b shows the SADP of a-a domains corresponding to figure 5a. It can be then inferred to that the domains are twin-related, the twin plane being $\{011\}$ and the tilt angle 0.4° .

- For a a-c domain boundary (so call because the viewing direction is parallel to the a direction of one domain and to the c direction relative the other domain), the twin plane is inclined at about 45° to the viewing direction (fringes contrast is present on images). Information on the tilt angle accros the boundary and on the twin plane itself is then more difficult to obtain.

Measurements made from conventional TEM micrographs and SADP are consistent with the crystallographic model currently admitted to explain domain orientation relationships and domain walls type. Gathering further relevant informations requires a higher level of spatial resolution such as HRTEM.

In this study we have been able to observe HREM images of both barium and titanium lattices away from any domain wall (fig.4); close to the domain walls only a two-dimensional 4\AA lattice which periodicity fits that of Ba or Ti could be seen. The degradation of the resolution is probably due to an atomic as well as polarization periodicity loss across the domain wall.

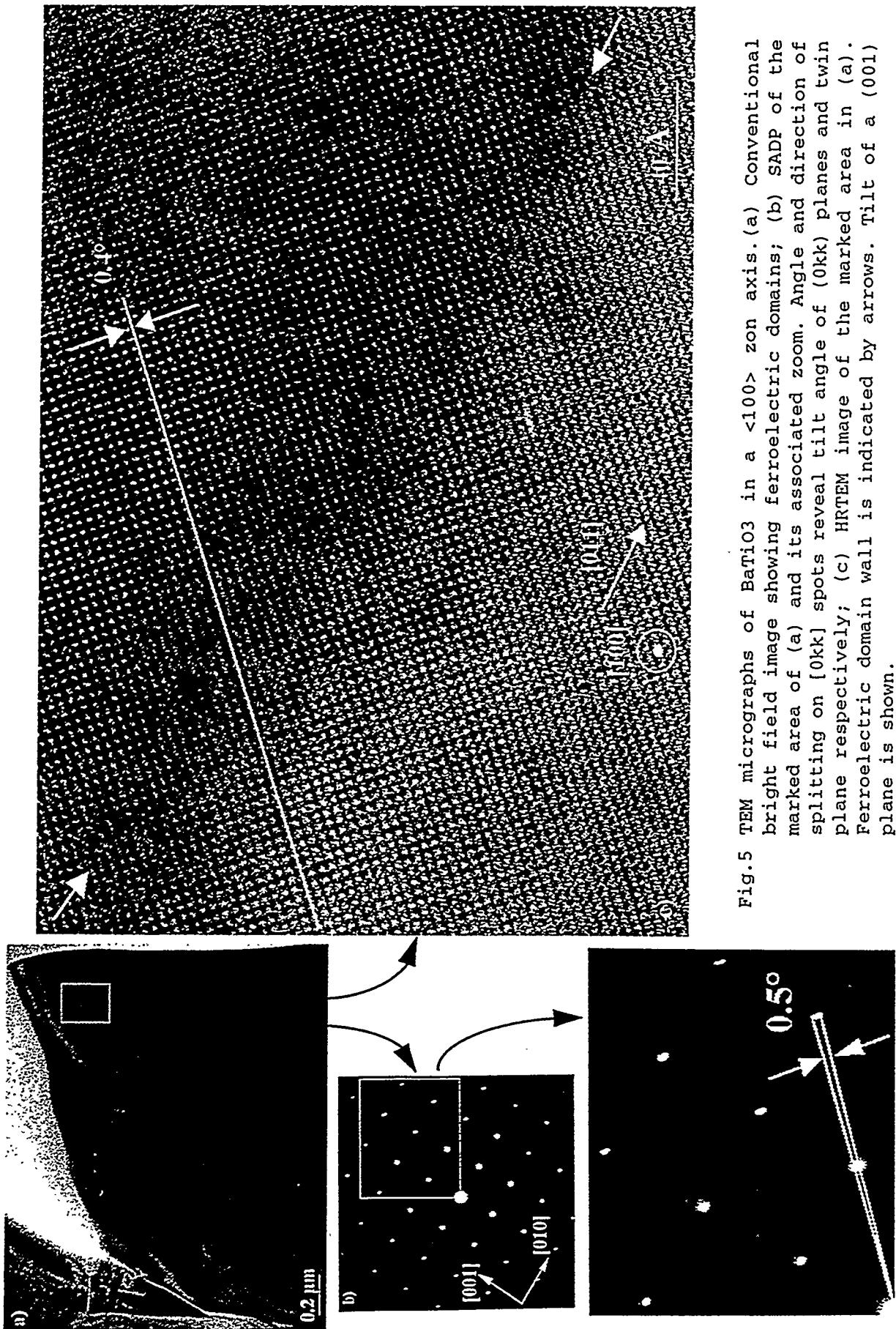


Fig.5 TEM micrographs of BaTiO₃ in a <100> zone axis. (a) Conventional bright field image showing ferroelectric domains; (b) SADP of the marked area of (a) and its associated zoom. Angle and direction of splitting on [0kk] spots reveal tilt angle of (0kk) planes and twin plane respectively; (c) HRTEM image of the marked area in (a). Ferroelectric domain wall is indicated by arrows. Tilt of a (001) plane is shown.

This should be confirmed by image simulations now in progress. More, if images of ferroelectric domain walls are clearly seen at low magnification through pure crystallographic contrast conditions, they are much less visible and more difficult to locate at high magnification on phase contrast images.

$<100>$ and $<111>$ type zone axis images (fig.5c and 6) are presented here: it is still possible to see clearly ferroelectric domain boundaries. A 0.5° tilt angle can be measured across domain walls on HREM images providing additional confirmation for the general crystallographic configuration already proposed. Two glancing angle views of a $<111>$ zone axis HRTEM image are given on figure 6. They show a 0.5° tilt of the $[112]$ direction (corresponding to a $<111>$ projection of the $[010]$ and $[101]$ directions) across the domain wall but also a distortion along the $[211]$ direction (corresponding to a $<111>$ projection of the $[100]$ and $[001]$ directions).

On all HRTEM micrographs, a 40\AA wide non regular diffuse dark contrast along the domain walls could be observed. Calculated diffractogram patterns from a 256×256 pixels region (about 24×24 unit cells) on a HREM image including a domain wall show that diffraction spots are more diffuse than those for a region away from any domain wall. In addition to the tilting across the boundary, the diffuse contrast associated with the domain walls is to be related to a lattice distortion in the immediate vicinity of the domain wall (6 and 7) as well as to a possible phase modification of the incoming electronic wave due to the local polarization. Respective influences of elastic and electric contribution to the observed diffuse contrast are indeed not very well known so far.

Image processing:

A computerized method has been developed for measuring quantitatively the atomic displacement field associated with a domain wall from high-resolution images. The "template matching method" appeared to be inadequate because of a too limited resolution. The required precision has been successfully attained with the "peak finding method" which has been used to quantify the 2D lattice displacements. The general flow diagram can be seen on figure 7. It is of the utmost importance to notice that the digitization must be carried out without any kind of interpolation at a scanning resolution carefully chosen on account of the computer memory, calculation time and needed accuracy. In our work, it appears that the required scanning resolution is 8 to 10 pixels for describing one atomic column.

This method is based on the comparison between a "perfect lattice" created from a non distorted region of the HREM image and the image in its whole. Calculation of the "perfect lattice" from a relatively large area of the experimental image takes into consideration little lattice parameter modifications due to variations in the imaging conditions and pixellation effect; the average modelled lattice so obtained will then help to reduce effects of small "displacements" present in the entire scanned image. Peak positions are calculated with a sub-pixel accuracy, allowing to reach a precision order of about 0.1\AA .

Since only the spatial evolution of differences between peak positions and model nodes are measured here, we checked by contrast simulation that experimental conditions (say defocus, thickness, "macroscopic" tilt of the specimen...) do not significantly change from one area of the image to the other. Furthermore the method has been applied to $1000\text{\AA} \times 1000\text{\AA}$ areas of HREM images free of domain walls: no observable strain field were calculated. It was then concluded that all variation in the displacement partition obtained with this method was a real measurement of the atomic position variations associated with the presence of a domain wall.

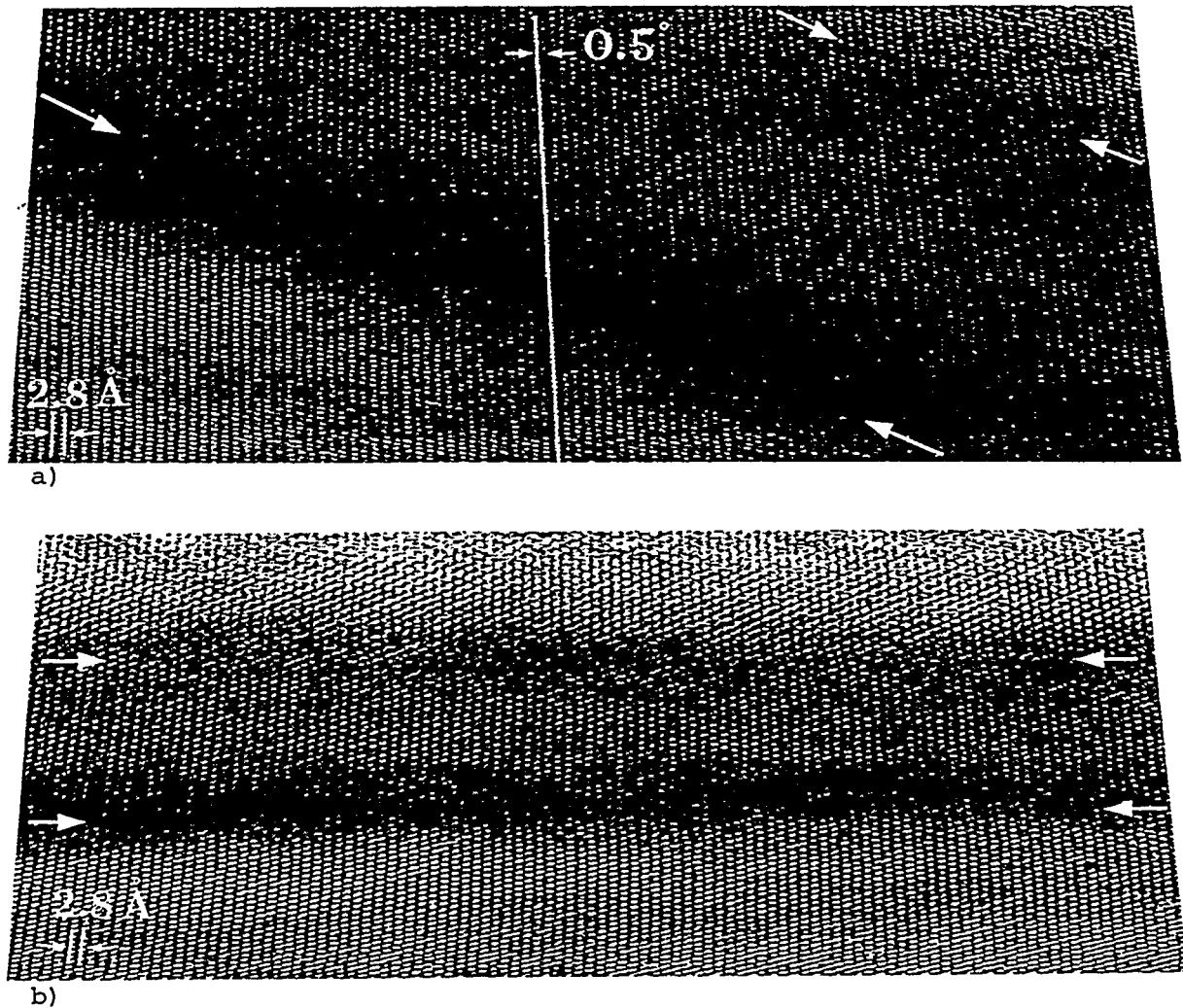


Fig.6 Glancing angle view of two <111> zone axis HRTEM images of BaTiO₃.
 (a) Tilt of [-1-12] direction (<111> projection of [010] and [101] directions); (b) Distortions along [-211] direction (<111> projection of [100] and [001] directions)

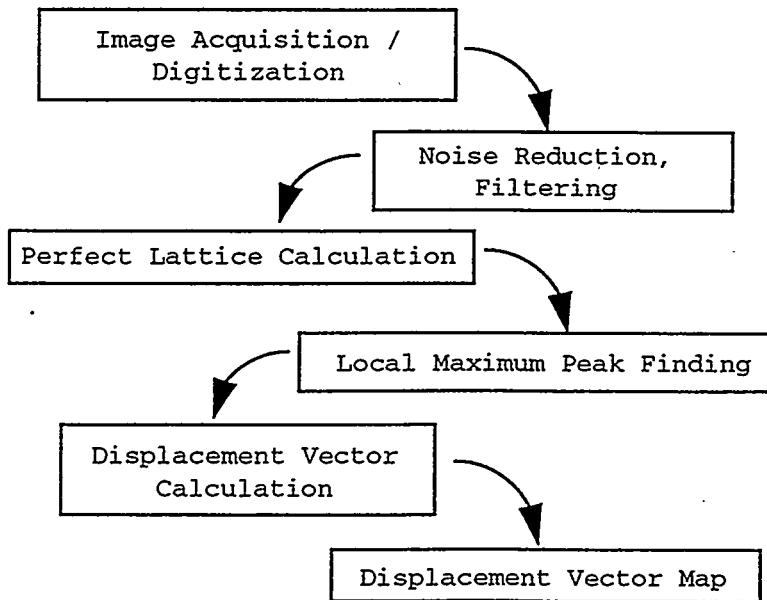


Fig.7 Flow diagramm of image processing used to map atomic displacements of HRTEM images.

Figures 8 and 9 show $<100>$ type zone axis high resolution images of domain walls with their associated displacement vector plots. One can clearly see that the domain walls are extremely difficult to locate on the HREM images whilst their position and structure are definitely observable on vector plots. Average domain walls thickness is of the order of 10 unit cells. Different atomic displacement fields can be observed: on figure 8b one can see that the overall direction of the domain wall lies on a $\{110\}$ type plane with a local $\{100\}$ faceting which is absolutely not visible on the HREM image. In this case the energy and the dynamic of the domain wall will significantly differ from theoretical predictions which does not take into account the kinks revealed on this vector plot. Motions of such ferroelectric domain walls, which have been previously studied in-situ in a microscope by the authors (10, 11), will then be more favorable by lateral displacements or by a growth of the tips of the domain, increasing or decreasing consequently the energy barrier required to switch domains with a specific electric field. Figure 9 shows a more regular atomic strain field. It also illustrates the interaction and the associated pinning effect due to the presence of a small crystallographic defect: the distorted region is increased and the local modifications of the direction of the boundary are smoothed.

Quantitative mapping of the atomic column displacements across the image has to be considered with caution especially when sudden and steep discrepancies arises between two neighbouring points. These quantitative displacement measurements are indeed made by comparison between "experimental peak position" and the nearest node of the model. This method will twist the real displacement vector in the case of a position variation greater than the lattice parameter. In most cases, a carefull checking of the data has proved the calculations to be correct. However it appeared important to develop an "a posteriori" criterium to check this calculation; this work is now under developement.

Conclusions and perspectives

Transmission electron microscopy study of domain walls in barium titanate has given not only confirmation of theoretical predictions but also important informations on the atomic structure of these walls.

(1) Tilt of crystallographic directions across the domain walls in pure BaTiO_3 was found to be in the range of 0.4° to 0.5° from SADP, HRTEM micrographs and Fourier analysis, which is in a good agreement with previous observations and ferroelectric twin model.

(2) High resolution images of both barium and titanium lattices were obtained in thin areas away from any domain boundary but only a 4 \AA lattice could be seen at the vicinity of the ferroelectric domain walls.

(3) A numerical method has been developed to obtain quantitative informations from high resolution images with a accuracy good enough to detect and map lattice distortions as small as 0.1 \AA . (4) 90° domain walls have a thickness of about 40 \AA .

(5) Different kinds of domain wall structures, sometime presenting nanometer scale kinks, were observed; the influence of such microstructural features on the wall energy and mobility is pointed out.

Comparison with predictions based on the Landau-Ginzburg theory and domain wall energy estimation are in progress.

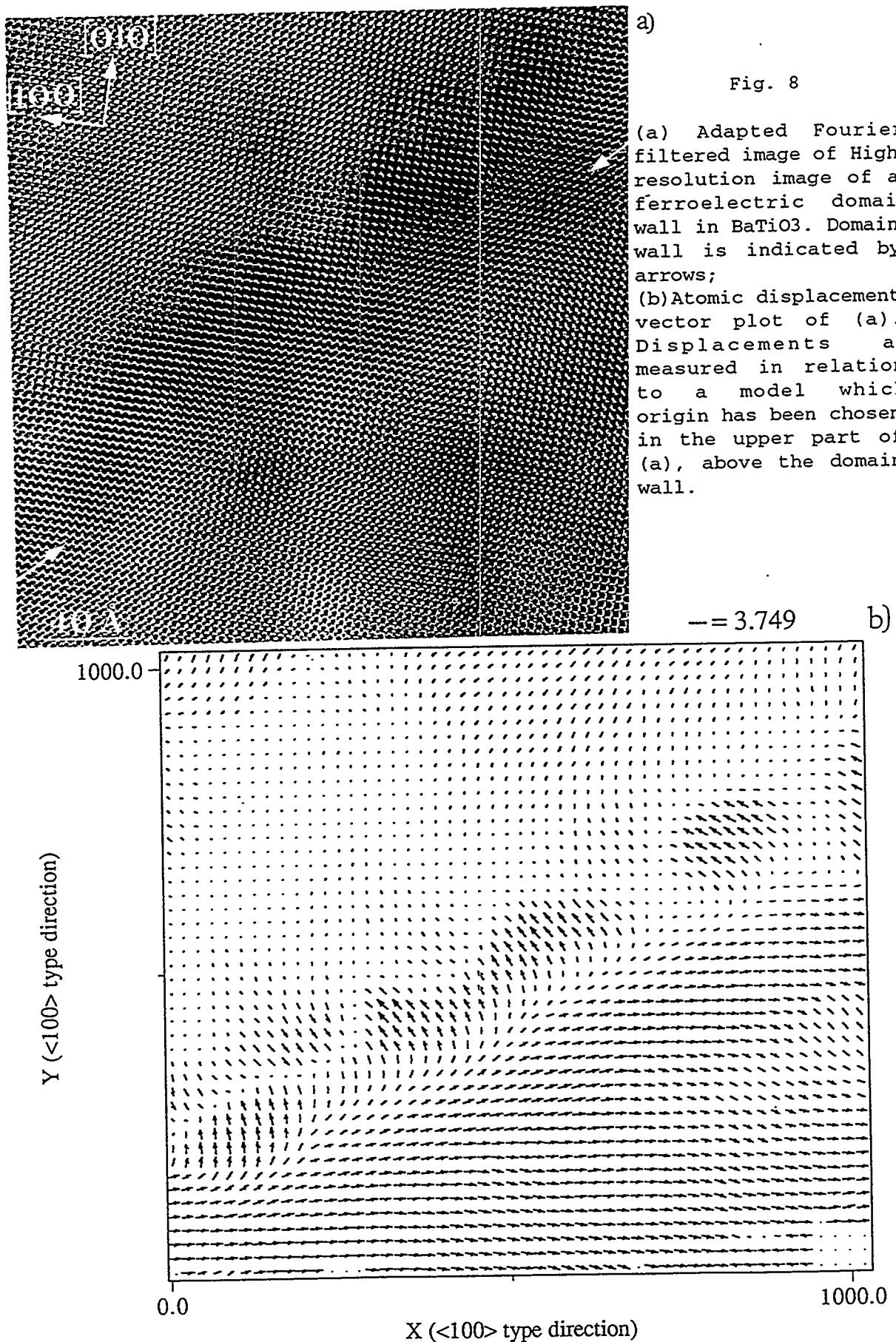
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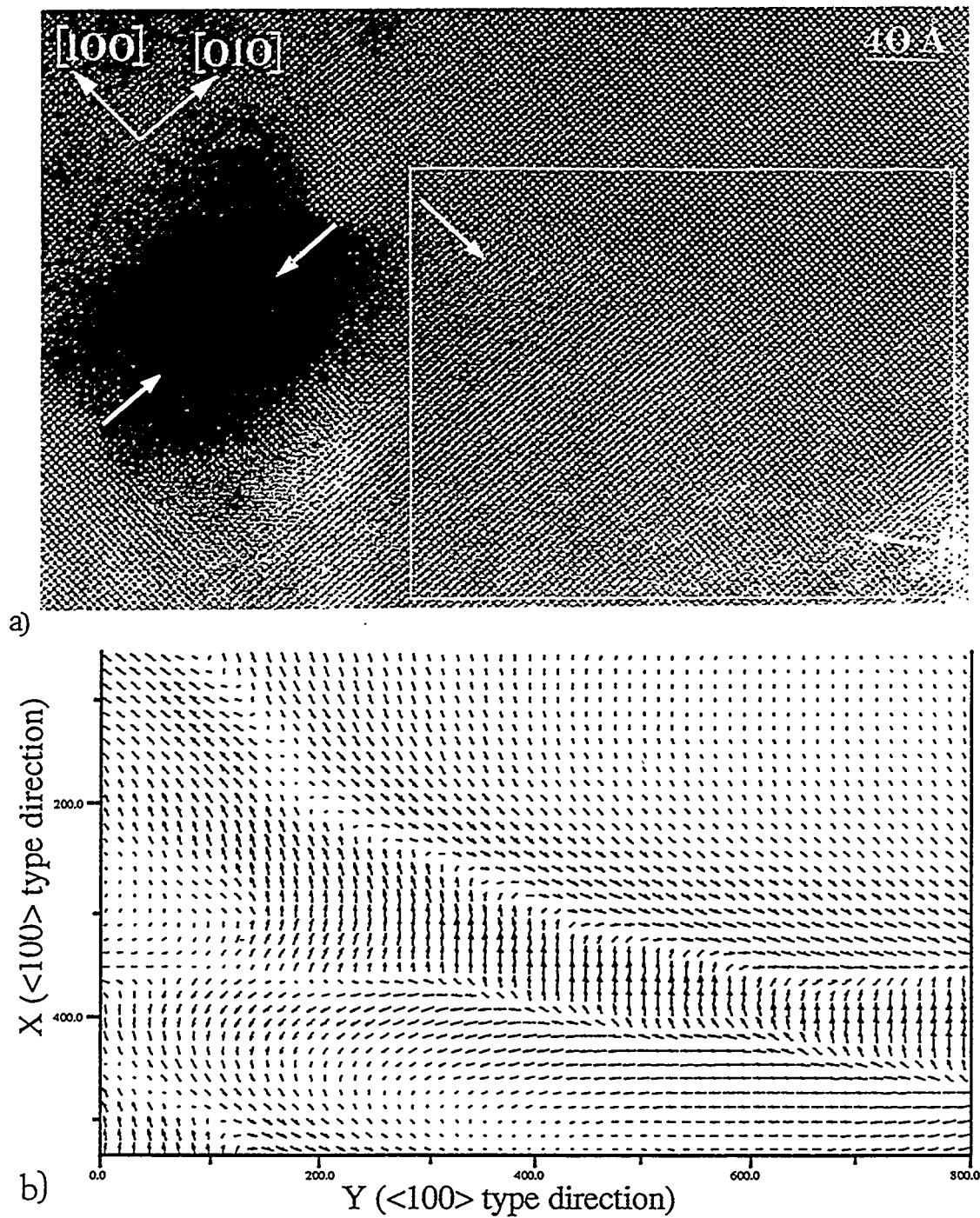


Fig. 9 (a) $<100>$ zone axis HRTEM image of BaTiO₃. An edge on ferroelectric domain wall (not visible at this magnification by a contrast variation) is indicated by arrows. A defect pins the domain wall; (b) Atomic displacement vector plot of the selected area of (a). Model used for the displacement calculation was created from a non-distorted part of the upper part of the image. Origin of this so created "perfect lattice" was placed at the upper right corner of the marked area.