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Forming Pressure Dependence of the Ferroelectric Domain Structure in Green Barium Titanate Pellets

P. Sarrazin,[a] B. Thierry[a] & J. C. Niepce[b]

[a]Laboratoire Matériaux Industriels, CRITT Céramiques Fines Techniques, Université de Valenciennes, 59600 Maubeuge, France
[b]Laboratoire Réactivité des Solides, URA CNRS no 23, Université de Bourgogne, BP 138, 21004 Dijon Cedex, France

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Abstract

Modifications of the X-ray diffraction line profiles by die pressing of fine grained powders of barium titanate have been studied. Two main parameters have been considered: the forming pressure and the mechanical characteristics of the binder. The higher the forming pressure, the greater the modifications of the line profiles. Furthermore, the phenomena seems to be related to pressing only; no significant effect related to the nature of the binder has been shown.

The modifications of the diffraction line profiles are interpreted by considering a reduction of the size of the ferroelectric domains during pressing. In order to confirm this interpretation, the behaviour of the domain structure of a $BaTiO_3$ single crystal under local compression has been studied. The average size of the domain is dramatically reduced by applying local pressure. Moreover, the domain structure modifications produced by the high stress state are largely preserved under a rather low residual pressure. There is a kind of hysteresis as a function of the pressure. This observation may explain the remanent modifications of the line profiles recorded after pressure relaxation.

Introduction

The X-ray diffraction line profiles of fine grained barium titanate powders are modified after the formation of green parts.[1] The effects of the different steps of the green part preparation on the line profile modifications have been determined within an experimental design approach.[2] The forming step is by far the parameter which has the largest influence. Indeed, the line profiles are closely dependent on the forming step and none of the other studied parameters seems to have any direct influence on the profile modifications. Forming was performed by slip casting or die pressing. Thus, the mechanical stress applied during the forming step is responsible for the studied phenomenon.

It is well-known that the line profiles of $BaTiO_3$ powders are quite dependent on the granulometric characteristics.[3–7] It has recently been shown that the diffraction diagram of a fine grained barium titanate is also dependent on the ferroelectric domain structure.[8,9] Thus, a full interpretation of the diffraction line profiles requires consideration of the ferroelectric domain structure with respect to the diffracted intensity.[1,10,11]

The influence of the die pressing pressure on the diffraction line profiles of a micronic barium titanate powder is studied in this paper. In order to fully evaluate the effect of residual stress, the mechanical characteristics of the binder are also considered.

Experimental

1 Sample preparation

A pure $BaTiO_3$ powder, with a narrow grain size distribution ($\varnothing_{10}$ = 1·0 μm, $\varnothing_{50}$ = 2·4 μm, $\varnothing_{90}$ = 4·9 μm), has been used in order to get well separated 002 and 200 diffraction lines (Fig. 1).

Two slips were prepared in organic media with two binders presenting quite different mechanical characteristics (Poly Vinyl Butyral PVB and paraffin 46–48°C). After slip drying and preparation of granules, two sets of discs were formed by die pressing. In both cases, the forming pressure range was 100–1000 MPa.

2 X-ray diffraction characterization

The samples were characterized after die forming by X-ray diffraction using a diffractometer fitted out with an INEL Curved Position Sensitive Detector (CPS120). Cu $K\alpha_1$ radiation has been selected with a focusing quartz monochromator. For each diagram, a 120° 2θ zone was recorded over 8196

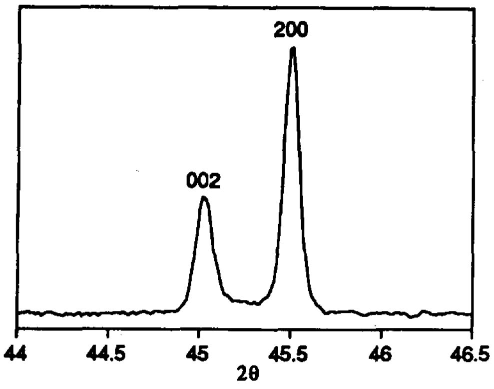


Fig. 1. 002 and 200 X-ray diffraction lines of the $BaTiO_3$ powder used for the sample preparation.

channels during one hour. All the lines of the diagram were fitted.

- The cell parameters' refinement has been carried out with the CELREF Software.
- The mean apparent crystallite size and the mean apparent amount of crystalline lattice distortion have been performed according to the Williamson and Hall[12] method. For this, the half widths (F.W.H.M.) of the 111 and 222 diffraction lines have been determined. They were corrected from the instrumental broadening by considering a Lorentzian approximation of the line profiles. The instrumental broadening approximation for the 111 and 222 lines were the half widths of the two corresponding lines of a well crystallized $BaTiO_3$ previously used as a broadening reference.[1]
- The diffracted intensity profile around the 002 and 200 lines was previously considered for the determination of both the distribution of the cell parameters[5] and the size of the 90° ferroelectric domains.[1,10,11] In the present study, only the two intensity maxima and the minimum of the diffracted intensity between the peaks have been carefully measured.

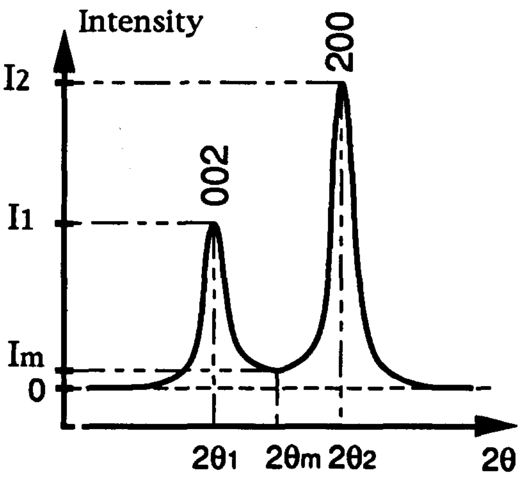


Fig. 2. Characterization by a relative number *R* of the diffracted intensity between the 002-200 lines.

From these intensities, the *R* ratios have been calculated in order to characterize the relative intensity between the two lines by a number.

$$R = \frac{(I_m)}{1/2(I_1 + I_2)_{\text{sample}}} \Bigg/ \left(\frac{(I_m)}{1/2(I_1 + I_2)}\right)_{\text{powder}}$$

These numbers were normalized by using the corresponding intensities of the initial powder diagram as a reference (Fig. 2).

Results

1 Evolution of the diffracted intensity profile around the 002-200 lines

The 002-200 line profiles obtained with the samples of each of the two sets display the same evolution. Some profiles of various samples prepared with PVB binder are presented in Fig. 3: the diffracted intensity between the two peaks increases with increasing forming pressure.

This first observation of the profiles evolution is numerically shown with the evolution of the *R* ratio. Figure 4 illustrates the evolution of *R* as a function of the forming pressure for the two sets of samples. The evolution of *R* is almost linear with the pressure and on the same straight line whatever the nature of the binder. The binder has no significant influence on the modifications of the line profiles.

Moreover, intensity appears on the two external sides of the line profiles. The two observed modifications are evident in Fig. 5 which presents the superposition of two 002-200 line profiles corresponding to the initial powder and a sample after pressing at 1000 MPa, respectively.

2 Evolution of the cell parameters

The results are presented in Fig. 6. The a parameter does not seem to present any variation whereas the c parameter is slightly decreasing with the forming pressure. The resulting c/a ratio shows a diminution of the cell tetragonality. This is the typical behaviour of a $BaTiO_3$ single crystal under hydrostatic pressure.[13] That means, from a macroscopic point of view, that the uniaxial pressing induces on the powder the same structural modifications as does hydrostatic pressing. This is due to the reaction forces of the die during the pressing and to the fact that the zones of contact between grains are not necessarily oriented perpendicularly to the pressing direction.

3 Evolution of the broadening of the 111 and 222 lines

The 111 line of $BaTiO_3$ and its harmonics are not affected by the tetragonal deformation of the

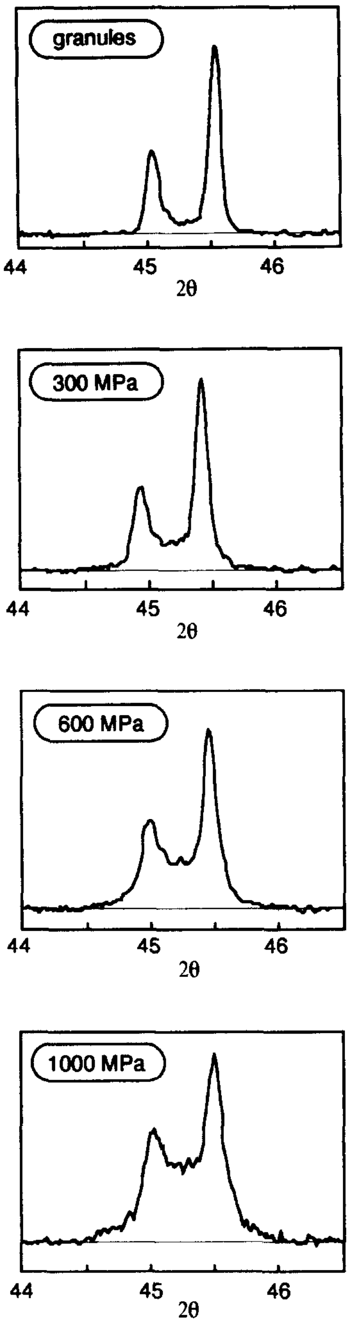


Fig. 3. 002-200 line profiles recorded on granules and discs formed at different pressures (samples prepared with PVB binder).

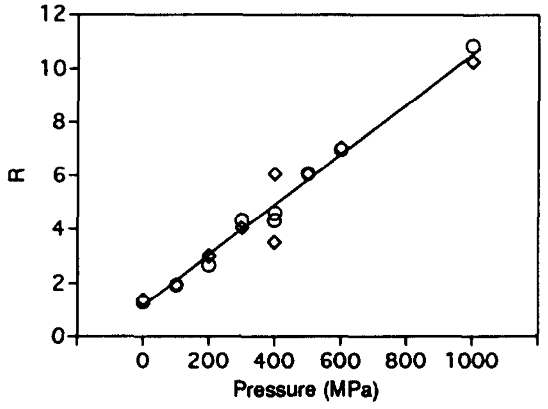


Fig. 4. Evolution of the R ratio with the forming pressure for the two sets of samples. ◇ samples prepared with PVB binder, ○ samples prepared with paraffin binder.

perovskite structure. Thus, 111 and 222 are the only true single lines of the $BaTiO_3$ diagram at room temperature. These lines were used to study the broadening involved by the pressing.

In Fig. 7, the widths of the 111 and 222 lines — corrected from the instrumental broadening — are reported as a function of the forming pressure. The higher the forming pressure, the broader the lines. Moreover, the broadening of the 222 line increases more rapidly than that of the 111 line. This is thought to be attributed to the formation of a kind of lattice distortions in the material.

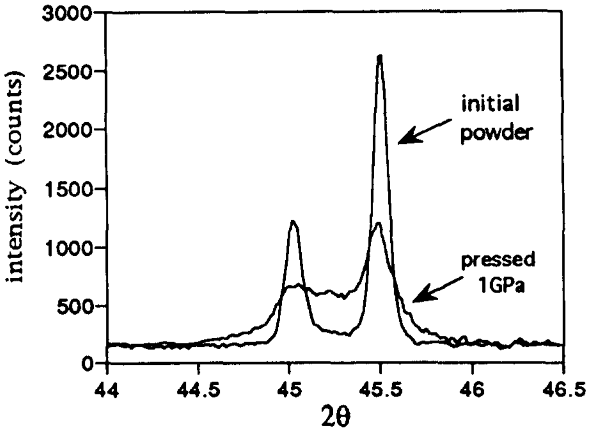


Fig. 5. 002-200 line profiles of the initial powder and of a sample pressed under 1 GPa.

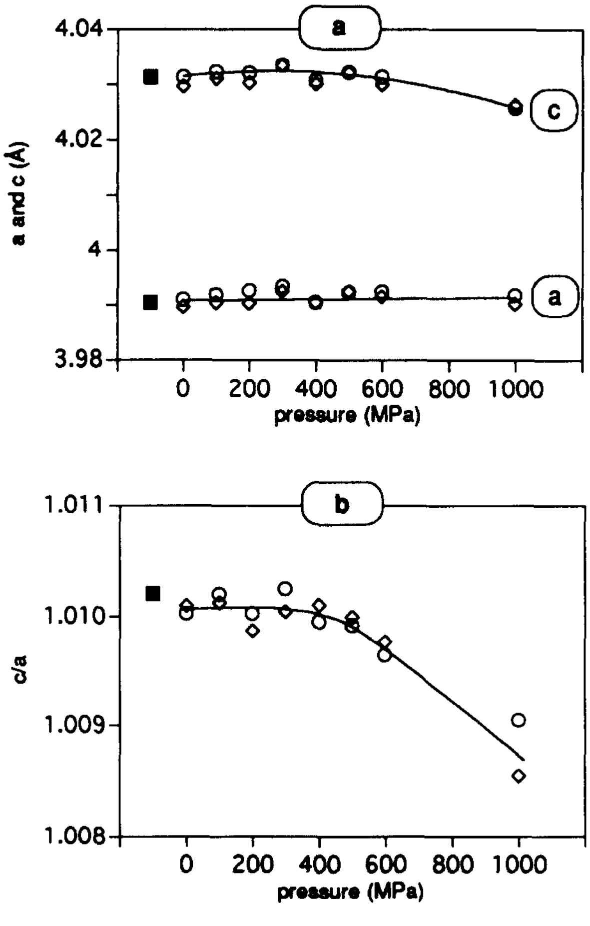


Fig. 6. Evolution of the cell parameters (a) and the c/a ratio (b) with the forming pressure: ■ initial powder; ◇ samples prepared with PVB binder; ○ samples prepared with paraffin binder.

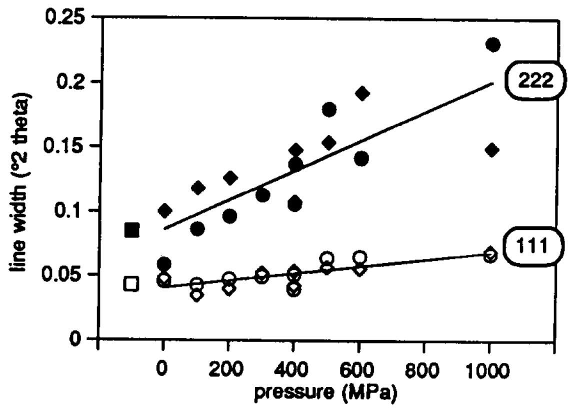


Fig. 7. Evolution of the 111 and 222 line widths with the forming pressure: □■ initial powder; ◇ ◆ samples prepared with PVB binder; ○● samples prepared with paraffin binder.

The Williamson and Hall method has been used to go further with this observation. In this representation, the harmonic lines describe a straight line which the origin ordinate corresponds to the size effect broadening and which the slope is due to the lattice distortion effect broadening. The origin ordinate and slope of each Williamson and Hall straight line are presented in Figs 8 (a) and (b) respectively. The origin ordinate does not exhibit any significant variation, whereas the slope increases with the forming pressure. Therefore, the modifications of the structure involved by the forming are seen as an increase in the lattice defects along the [111] axis without any variation of the size of the coherence domains.

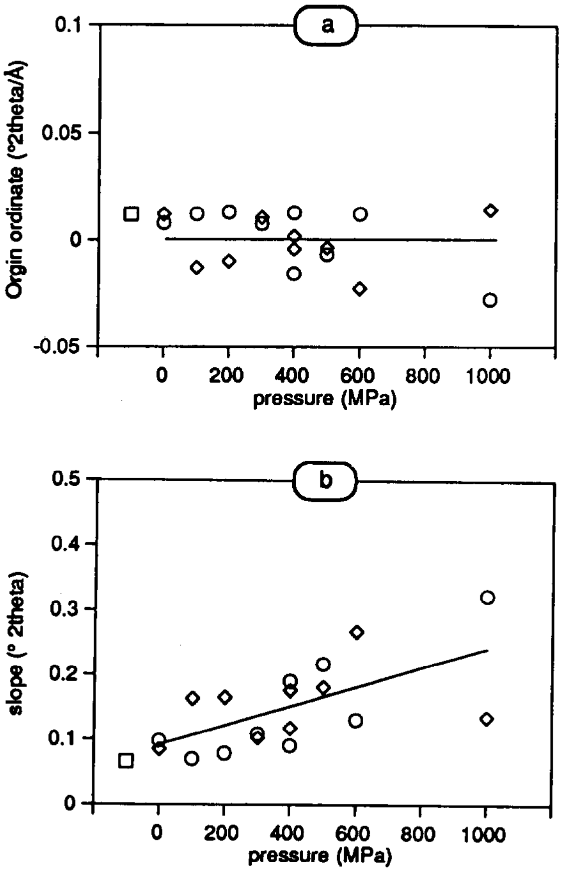


Fig. 8. Origin ordinates (a) and slopes (b) of the Williamson and Hall straight lines: □ initial powder; ◇ samples prepared with PVB binder; ○ samples prepared with paraffin binder.

Discussion and Further Results

1 Diffraction line profiles and organization of the material into ferroelectric domains

At room temperature, the $BaTiO_3$ grains are usually divided into ferroelectric domains which size is commonly correlated to the grain size.[14] This division allows a minimization of the overall deformation and polarisation induced during the paraelectric to ferroelectric transition.

The division into ferroelectric domains has an influence on the X-ray diffraction diagram of $BaTiO_3$ powders.[8,9] In particular, it has been shown that the size of the ferroelectric domains is partly responsible for the broadening of the line profiles:

— The subdivision of the $BaTiO_3$ crystallites into domains at 90° induces a broadening of the 002-200 lines related to the ferroelectric domain size. Moreover, decreasing the domain size increases a particular contribution to the diffracted intensity between these two lines. A model of the 002-200 line profile in relation to the ferroelectric domain size has been proposed.[1,10,11] Figure 9 shows the line profiles obtained with a rough model of a single crystalline grain containing two 90° domains for two different domain sizes.[11] From this figure, the reduction of the domain

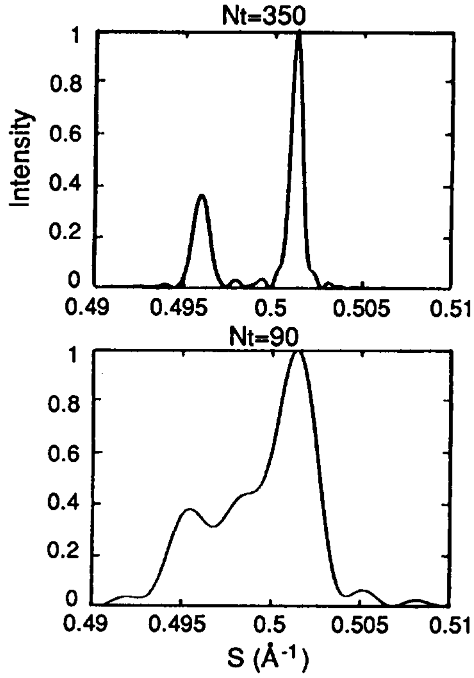
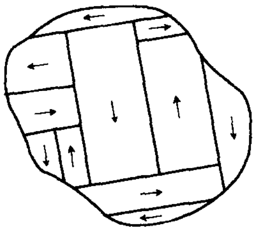


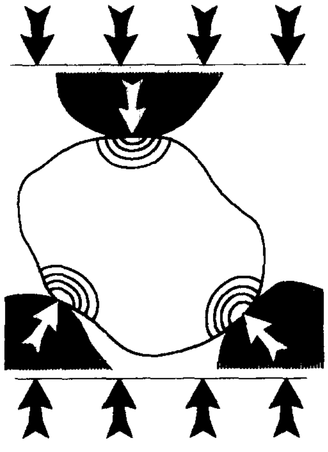
Fig. 9. 002-200 line profile performed with a two 90° domains model for the ferroelectric grain: Nt is the number of 002 and 200 planes in the considered direction.[11]

size involves an increase in the intensity of the middle zone and of the external sides of the line profiles.

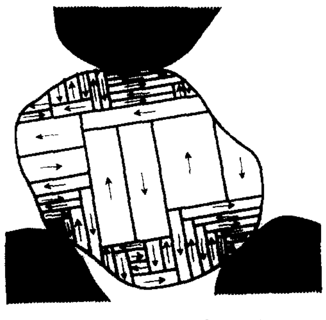
— On the contrary, the subdivision of the crystallites into ferroelectric domains does not involve any size effect broadening for lines such as 111 and 222. The division into domains also involves a broadening of these lines but now due to a lattice distortion effect. In fact, along the [111] axes, the lattice periodicity is almost completely preserved from one domain to another. Thus, the diminution of the domain size without any evolution of the grain size involves an increase in the lattice defects content along the [111] axis. Such a modification of the structure should induce a very particular evolution of the Williamson and Hall straight lines built with the 111 and 222 lines: the origin ordinate would be constant while the slope would increase.



Ferroelectric domain structure of grain of BaTiO3 powder before forming



Non uniform stress field developed in the grain during the pressing



Ferroelectric domain structure modification

Fig. 10. Proposition for a mechanism of ferroelectric domains fragmentation during the pressing.

2 Influence of the forming pressure on the ferroelectric domains organization of the grains of powder

The Williamson and Hall analysis of the present study has shown that the increase in the forming pressure involves an increase in the apparent lattice defects content while the apparent size of the coherence domains does not vary. This is the expected evolution of the 111 and 222 line profiles in the case of a reduction of ferroelectric domain size. Furthermore, the evolution of the 002-200 line profiles, as a function of the forming pressure, is very similar to that observed with the model of a two domains grain. This is evident by the comparison of Figs 5 and 9.

These observations allow us to interpret the line profile modifications as a reduction of the domain size induced by the pressing of the grains. Figure 10 proposes a diagrammatic mechanism of domain fragmentation. During forming, the grains of the powder develop small zones of contact through which the stress is transmitted. Therefore, the non-uniform stress field developed inside each grain involves local deformations. Since the material plasticity is low, the domain reorganization favours the deformation. These rearrangements are more efficient when increasing the number of domains, thus when the domain size is reduced. The fragmentation into ferroelectric domains allows the minimization of the mechanical energy of the material during forming. A similar mechanism has been proposed by Hennings[15] to explain the grain size dependency on the domain size in fine grained $BaTiO_3$ ceramics.

Nevertheless, this proposition of interpretation is not sufficient to account for the fact that the structural modifications are observed after the forming of the samples. Thus, this mechanism is only valid if the modifications of the domain structure involved during pressing are totally or partially kept after the pressure relaxation.

3 Macroscopic evidence of the pressing influence on the ferroelectric domains

In order to confirm this domain fragmentation, the behaviour of the domain structure of a $BaTiO_3$ single crystal under local compression has been studied. The domain walls of a polished crystal were observed with an optical microscope. Figure 11 shows the special device achieved for studying the local compression of the crystal. A metallic awl is kept in contact with the crystal and applies a compressing force adjusted with a

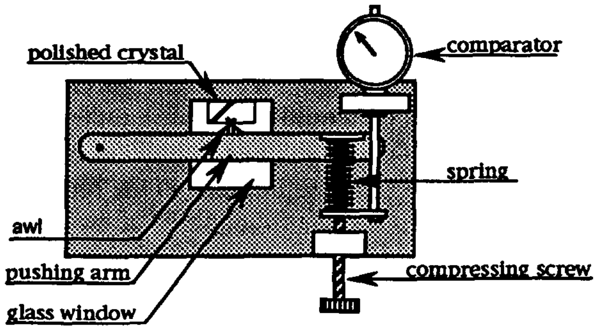


Fig. 11. Diagram of the special device realized for studying the influence of the local compression on the ferroelectric domains of $BaTiO_3$ single crystals.

spring. The compression of the spring is realized with a screw and controlled with a comparator. The calibration of the spring allows the calculation of the force applied on the crystal. This device was placed under an optical microscope to follow the evolution of the domain structure under local pressing.

Figure 12 displays the photographs taken with the microscope during a cycle of increase and decrease in the compressive force. It shows that the pressing of the crystal involves an increase in the density of domain walls around the awl; the higher the force, the broader the zone of high wall density.

Furthermore, the comparison of the pictures relative to the same stress states shows that the domain wall density is not identical depending on whether the pressure is increasing of decreasing. The structure involved under a 12 N force is almost entirely kept right down to a 4 N force. Thus, there is an hysteresis relation between the local pressure and the ferroelectric domain structure. This is in all likelihood due to the ferroelastic properties of $BaTiO_3$. This hysteresis is shown with the curve of Fig. 12 which presents a visual estimation of quantity of domain walls as a function of the force applied on the crystal.

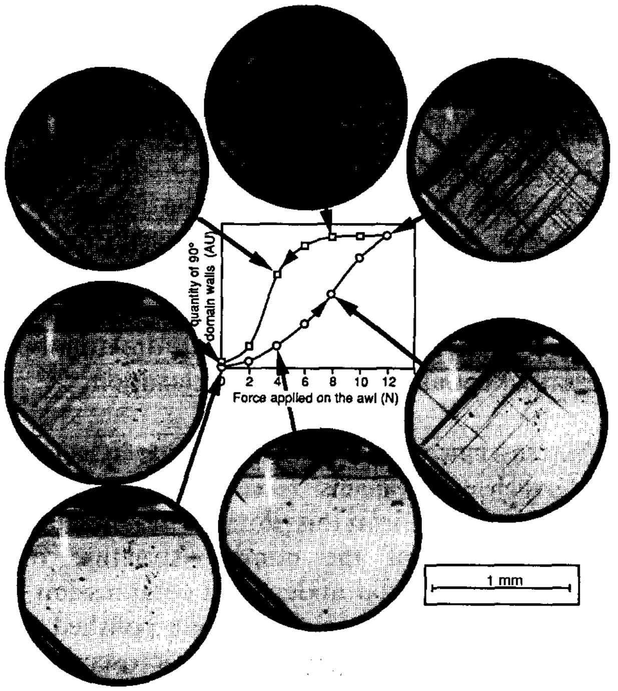


Fig. 12. Optical microscopy photographs of a $BaTiO_3$ single crystal during increase and decrease in the local applied pressure; visual estimation of the quantity of new domain walls as a function of the pressure.

So, a structure generated at high pressure is largely preserved with a rather low residual stress. This might explain the fact that the modifications appearing during the pressing of the $BaTiO_3$ powders are observed after the forming. These last experiments tend to confirm the hypothesis of a fragmentation of the ferroelectric domains during the pressing of the powder.

Conclusion

This study has shown that the modifications of the line profiles of barium titanate powders involved during the forming of pellets are essentially due to the pressure applied for the die forming. The nature of the binder, which was suspected to have some influence on this phenomenon, seems to have no noticeable effect. The different results obtained with the X-ray diffraction analysis let us think that a reduction of the ferroelectric domain size inside the material is responsible for these line profile modifications. The mechanism of domain fragmentation proposed is supported by the observation of the domain structure of a $BaTiO_3$ single crystal under local compression. Moreover, this last experiment shows that the modifications involved during the forming may be preserved after the pressure relaxation.

The present results are a new illustration of the influence of the domain structure of barium titanate powders on the X-ray diffraction line profiles. Moreover, this study points out the fact that the granulometric characteristics of the powder are not sufficient to define the domain structure of the grains, the mechanical history of the material has also to be considered.

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