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Optical, etching, and interferometric studies on ferroelectric $PbNb_2O_6$

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Abstract. Optical, interferometric and etching studies of (001) surfaces of ferroelectric $PbNb_2O_6$ are presented. It is found that crystal growth takes place mainly by layer formation. The layer boundaries can be distinguished from the domain lines by interferometric studies. Thermal etch pits are found near 90° domain walls and the layer boundaries. The etching studies show that these pits are at the sites of dislocations, and it is deduced that no extensive motion of dislocation takes place at the Curie-temperature in the process of domain formation.

Keywords. Domain; dislocation; thermal etch pits.

1. Introduction

The ferroelectric properties of lead (meta) niobate, $PbNb_2O_6$ were first discovered by Goodman (1953). The crystal exists in the orthorhombic phase at the room temperature and the Curie temperature is 570°C. The crystal structure and some ferroelectric properties have been studied among others by Roth (1957), Francombe and Lewis (1958), Subbarao (1960), Labbe *et al* (1973). Recently the present authors (Ingle and Bangre 1978a, b) studied the domain structure and the grain structure in these crystals. In the present paper some optical, etching and interferometric studies are presented on (001) naturally grown faces of the crystal. The method of crystal growth adopted has already reported (Ingle and Bangre, 1978a). The crystals were not subjected to any thermal, mechanical or electrical treatment before use.

2. Optical studies

Optical studies were carried out under reflected unpolarized light using a metallurgical microscope. The polarized light under transmission is useful to study the domain pattern (Ingle and Bangre 1978a). The crystal surfaces under reflection were studied in order to obtain information on the microstructure observable on the crystal surfaces which are useful to understand the mechanism of crystal growth, domain structure, behaviour of impurities, etc. These studies were supplemented wherever necessary by etching and interferometric studies.

Observations on numerous crystals show that the surface can be categorised as unfinished, nearly finished or well-finished indicating the successive stages of development of these crystals. The unfinished surfaces of the crystals show stray nucleations, autonucleation (Jackson 1967) and layer boundaries. Figure 1a shows stray nucleations with prismatic growth structure at the central region of the surface showing a somewhat covalent character of the crystal (Bunn 1949). Figure 1b illustrates autonucleations and their interaction with growth fronts. The autonucleation is the nucleation of material on a crystal of same material (Jackson 1967) but distinct from dendrites. The linear fronts moving from the bottom (smoother surface) to the top (rougher surface) are curved as a result of interaction with the autonucleations at AB, CD, EF, GH, etc. The nearly finished surfaces show predominantly the layer growth boundaries (figure 2). On well-finished surfaces these layer boundaries appear much straighter and look like domain lines (figure 3a). A series of parallel lines are observed in this photomicrograph. It has been shown in case of $KNbO_3$ that interferometric studies are necessary to distinguish a domain line from the layer boundary (Ingle *et al* 1977). If a crystal is thin, a polarizing microscope can be used, since in the interferometric test the crystal surface is spoiled by silver deposition. The interferogram over the same crystal surface (figure 3b) however shows that some lines are domain lines, while the others represent layer boundaries. In the case of layer boundaries, there is a discontinuous jump of the fringe at the boundary and the fringes are seen moving continuously in the same direction as in the lower part of the figure 3b. One finds in figure 3b that in the top left region the interference fringes continue to move in straight lines undisturbed at the domain lines unlike the lower region. This is because the lines in the region are domain lines. In the case of this crystal no fringe bending across the domain wall is expected as in the case of 60° and 90° domains in $KNbO_3$ (Deshmukh and Ingle 1971a, b) and 90° domains in $BaTiO_3$ (Bhide and Bapat 1963). It is interesting to see that the patterns AB and CD look like wedges formed by 90° domains (figure 3a). The interferograph (figure 3b) shows, however, that there is a shift as the interference fringes cross the lines forming the wedge-shaped patterns implying the formation of patterns by layer boundaries and not by domain lines. The lines of impurity segregations as observed in $KNbO_3$ (Mishra and Ingle 1974) are not observed in $PbNb_2O_6$. We had suggested in the case of $KNbO_3$ that the impurities segregate at the arrays of dislocations lying along the central regions of 60° domains forming such lines. In $PbNb_2O_6$, no such arrays of dislocations are obtained (Ingle and Bangre 1978b), and consequently there is no expectation of the lines of the impurity segregations, as is observed in practice in the interferogram.

Occasionally dendritic patterns occur as shown in figure 4. However, in general, ferroelectric $PbNb_2O_6$ is found to grow through layer growth mechanism. Where the growth fronts move faster, they become curved and irregular producing different types of patterns. The impurities also play a significant role in changing the directions of the growth fronts and forming fresh growth fronts.

Another interesting observation was the presence of small pits by the side of layer growth boundaries as well as 90° domain lines (figure 5). Here one can see a series of pits (white dots) by the side of layer boundaries whether the boundaries are straight as in lower region or curved as in upper region. These pits are almost clearly visible on unfinished and nearly finished surfaces. On the well-finished surfaces the pits are not visible, perhaps due to subsequent deposition of the materials. Since these pits are observed on the naturally grown faces when the crystals are not subjected to any further chemical, thermal or mechanical treatment, it is obvious that they are produced on the faces during growth at the high temperature of crystal growth and hence are of the nature of thermal etch pits.

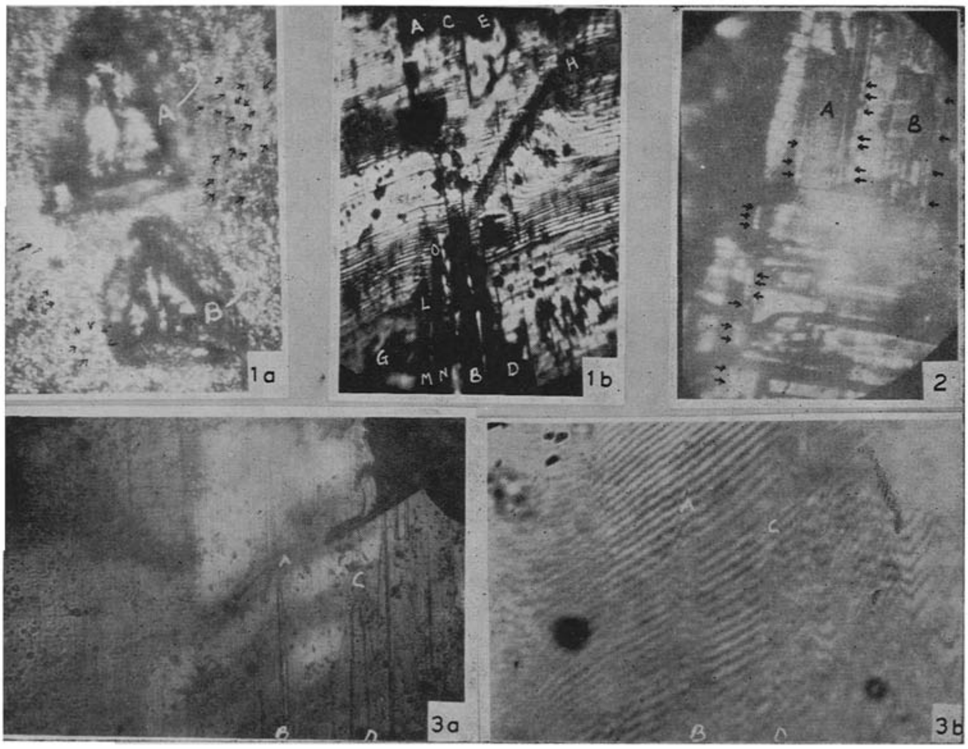
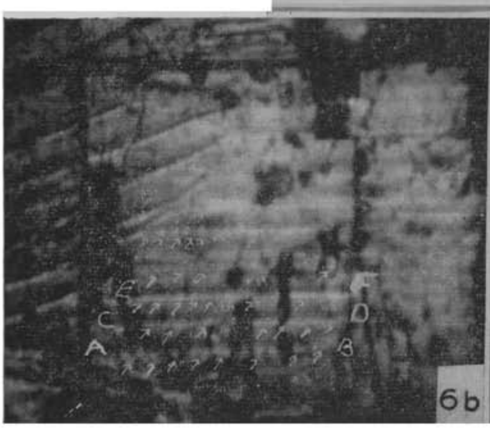


Figure 1a. Unfinished surface showing stray nucleations with prismatic growth structures (*A* and *B*) and thermal etch pits (white dots shown by arrows) **b.** interaction of growth fronts and autonucleations at *AB*, *CD*, *EF*, *GH*, etc. (×405)

Figure 2. Nearly developed natural surface. Plates *A* and *B* bounded by rectangular layer growth boundaries are seen with thermal etch pits on the plates shown by arrows (×360)

Figure 3a. A well-developed surface showing series of parallel lines at the top left region (layer growth boundaries and domain lines) and wedge shaped patterns *AB*, *CD*, etc. **b.** Interferograph over the surface shown in **3a** (×405)



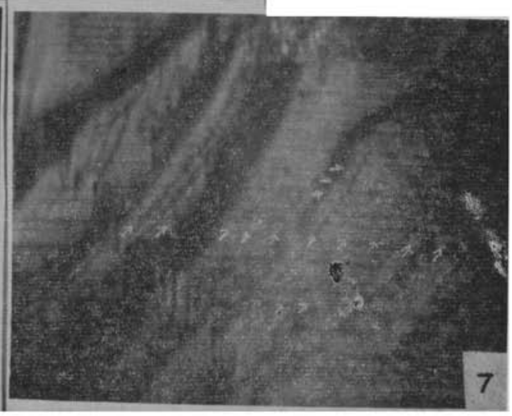


Figure 4. Dendritic growth in $PbNb_2O_6$ ($\times 270$)
Figure 5. Layer growth boundaries associated with thermal etch pits (white dots shown by arrows) ($\times 360$)
Figure 6. **a.** Naturally grown surface showing 90° domain lines *AB*, *CD*, *EF*, *GH*, etc. associated with thermal etch pits (shown by arrows) **b.** Crystal surface etched in an etchant known to reveal the site of dislocations. The attack exactly at the sites of thermal etch pits can be noted ($\times 360$).
Figure 7. Naturally grown crystal surface of $KNbO_3$ showing thermal etch pits in the central region of 60° domain lines ($\times 360$).

2. Thermal etch pits and etching studies

As such pits are at the sites of defects, the nature of the defect involved in the case of thermal etch pits was assessed by the etching technique. It was interesting to note that the etchant attacking the sites of dislocations on (001) plane (Ingle and Bangre 1978b) attack the crystal surface exactly at the sites of thermal etch pits. Figure 6a shows a photomicrograph of naturally grown crystal surface. The black lines AB, CD, EF, GH, etc. are domain lines and near these lines numerous small sized etch pits (shown by arrows) can be observed. This crystal was etched in an etchant containing 0·5 g of NH_4NO_3 in 6 ml of 20% dil. HNO_3 for 30 min. It has already been shown by the authors that this etchant attacks the sites of dislocations (Ingle and Bangre 1978b). The existing etch pits are found to grow in size (figure 6b), which means that the thermal etch pits are at the sites of dislocations and if they are not, separate dislocation pits would have been produced and shown along with the thermal etch pits shown in figure 6b. The location of the thermal pits observed in various photomicrographs also agrees with the theoretically anticipated positions. For example, in $PbNb_2O_6$ the tendency of the dislocation is to be drawn towards 90° domain walls through a domain dislocation interaction. Correspondingly, the thermal etch pits are expected to be found near 90° domain walls as is nearly found in practice. The domain dislocation interaction is more pronounced in $KNbO_3$ than in this crystal. There the dislocations lie along central regions of 60° domains through domain dislocation interaction. One indeed finds arrays of thermal etch pits along the central region of 60° domains (figure 7). The dislocations are also known to form at the layer boundaries during the growth period as suggested by Seitz (1950) and Frank (1952), and correspondingly the thermal etch pits are found along the layer boundaries (figure 5). In the case of $KNbO_3$ also such thermal etch pits near the layer boundaries are found.

The observation on thermal etch pits settles one important question regarding domain dislocation interaction in $PbNb_2O_6$ and $KNbO_3$. One finds that at room temperature the domains have regular correlation with the dislocation substructure. The question that arises now is whether there is an extensive motion of dislocation at the Curie temperature to produce appropriate domain structure with minimum possible free energy, or whether the dislocations are already so arranged during growth. The observations on thermal etch pits make it clear that the dislocations that exist in the form of loops already exist in their proper positions, and no extensive motion of dislocation is called for at the Curie temperature.

4. Conclusion

Thus the above optical interferometric and etching studies show that the main mechanism of crystal growth is by layer formation. There is no distortion at the surface at 90° domain wall as in the case of 60° and 90° domains in $KNbO_3$ (Deshmukh and Ingle 1971a, b) and 90° domain in $BaTiO_3$ (Bhide and Bapat 1963), and the dislocation substructure is already present in a suitable way to influence the domain formation at the Curie temperature.

References

Bhide V G and Bapat N J 1963 *J. Appl. Phys.* **34** 181
Bunn C W 1949 *Disc. Faraday Soc.* **5** 132
Deshmukh K G and Ingle S G 1971a *J. Phys.* **D4** 124
Deshmukh K G and Ingle S G 1971b *J. Phys.* **D4** 1633
Francombe M H and Lewis B 1958 *Acta Crystallogr.* **11** 696
Frank F C 1952 *Adv. Phys.* (*Philos. Mag. Suppl.*) **1** 91
Goodman G 1953 *J. Am. Ceram. Soc.* **36** 368
Ingle S G, Choudhari R M and Mishra M B 1977 *Indian J. Pure Appl. Phys.* **15** 323
Ingle S G and Bangre B M 1978a *Pramana* **10** 163
Ingle S G and Bangre B M 1978b *Pramana* **10** 505
Jackson K A 1967 *Progress in Solid State Chemistry* ed. H Reiss (London: Pergamon Press) **4** 53
Labbe Ph, Frey M and Allais G 1973 *Acta Crystallogr.* **B29** 2204
Mishra M B and Ingle S G 1974 *J. Appl. Phys.* **45** 5153
Roth R S 1957 *Acta Crystallogr.* **10** 437
Seitz F 1950 *Phys. Rev.* **79** 723
Subbarao E C 1960 *J. Am. Ceram. Soc.* **13** 439