

## Cooperative ordering of impurity dipoles in $\text{KNbO}_3$ single crystals

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**Abstract.** The impurity atoms forming dipoles in the structure of  $\text{KNbO}_3$  are arranged regularly in the structure. The locations of the dipole sites were observed by etching technique, when dilute  $\text{HNO}_3$  was used as an etchant. The dipoles along with the domain structure with which they are associated are stable with respect to temperature, and retain the same sites at Curie temperature. Thus the regular cooperative ordering observed at room temperature also exists at the Curie transition. The importance of this ordering is discussed in terms of domain formation and the basic problem of ferroelectricity in crystals.

**Keywords.** Cooperative ordering; impurity dipoles; phase transition.

### 1. Introduction

The role of impurities in ferroelectric crystals is increasingly being realized. They affect vital parameters like domain structure (Nakatani 1986) and phase transition temperature (Dvorak and Glogar 1966). Of particular importance is the observation that impurities can convert a nonferroelectric crystal into ferroelectric under suitable conditions (Vugmeister and Stefanovich 1985). It is thus obvious that these impurities develop a strong, large distance cooperative interaction in the structure, which is essential for ferroelectric behaviour. It is therefore important to know whether impurities develop such cooperative interactions in an already ferroelectric crystal. The present studies on  $\text{KNbO}_3$  single crystals were carried out from this point of view. This paper reports that impurities do develop cooperative interactions and are dipolar in nature.

### 2. Experimental

Single crystals of  $\text{KNbO}_3$  grown by the Deshmukh and Ingle's (1971) technique were used. The crystal had a smooth cleavage in pseudocubic  $\{001\}$  plane, and thin plates suitable for optical observation were easily obtained. It was earlier established (Deshmukh and Ingle 1972) that a careful cleavage does not disturb the domain structure in the crystal. Also, no new domain structure was created.

In the present investigation, the technique of etching was used to locate the sites of impurities on the  $\{001\}$  plane. It was established that a dilute solution of  $\text{HNO}_3$  (prepared by taking 1 part by volume of concentrated  $\text{HNO}_3$  and 12 parts by volume of distilled water) attacked preferentially at the site of the impurities. On some planes, the pits were deep while on others they were shallow, though in both cases the attack took place at the site of impurities. This can be understood in terms of the earlier work on impurities by Ingle and Kokate (1990) who found that impurities existed in the form of dipoles at the Curie temperature, and relaxed to the ionic state, as the temperature was lowered. Hence, at room temperature, one expects to find impurities either in relaxed ionic state or in the dipolar state. The dipolar impurities reacted

differentially with respect to the polar axis while etching took place. It was found that the polar axis was either in the plane of plate or perpendicular to it. Correspondingly, the etch pits were shallow or deep. It was considered useful to know if the polar axis lies in the plane of the plate or in the perpendicular plane.

The etching experiments carried out on various crystal plates showed that the pits were arranged in rows, and had regular correlation with respect to domain structure in the crystal. Two typical types of etch pit behaviour were observed. In the first case, the rows of etch pits parallel to each other were observed in neighbouring domains. These domains were  $90^\circ$ , in which case, the domain line was parallel to the  $[001]$  direction, or  $60^\circ$  where the domain line was at  $45^\circ$  with the  $[001]$  direction. The pits on either side of the line were always of the same type. Figure 1a is a photograph of the unetched crystal, while figure 1b shows the result of etching of the surface. In figure 1a the domain lines are parallel to the edge and the pits are shallow implying that the impurity dipoles lie in the plane of the plate on either side of the domain line. Figure 2 shows a similar situation as in figure 1b, but now the pits are deep. The dipoles are now in a plane perpendicular to the observed plane. Figures 3a and b show the situation of the third type, viz. that the domain line is at  $45^\circ$  with the  $[100]$

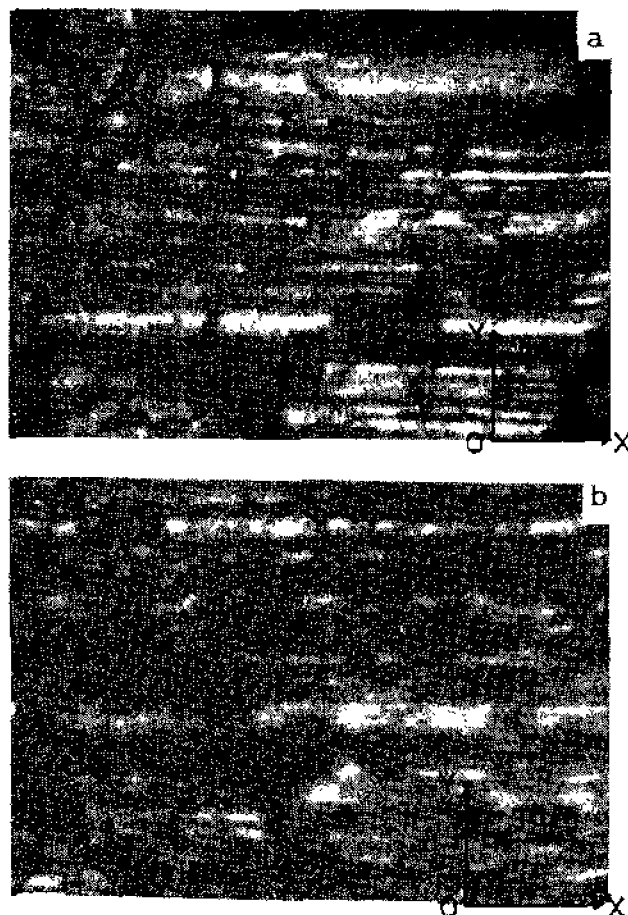


Figure 1. ( $\times 390$ ) Photomicrograph of a. pseudocubic (001) crystal surface and b. after etching the crystal surface.

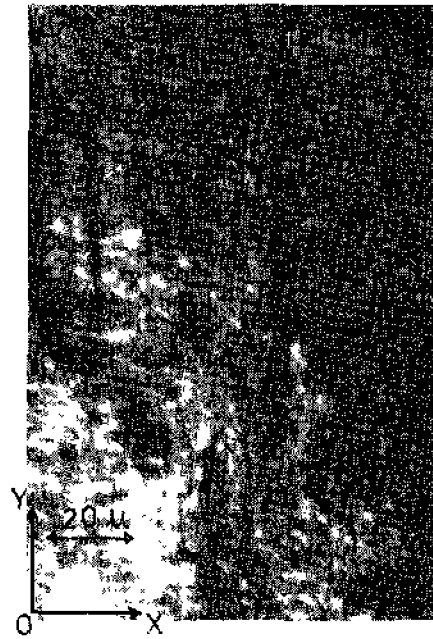


Figure 2. Photomicrograph obtained after etching the crystal surface ( $\times 818$ ).

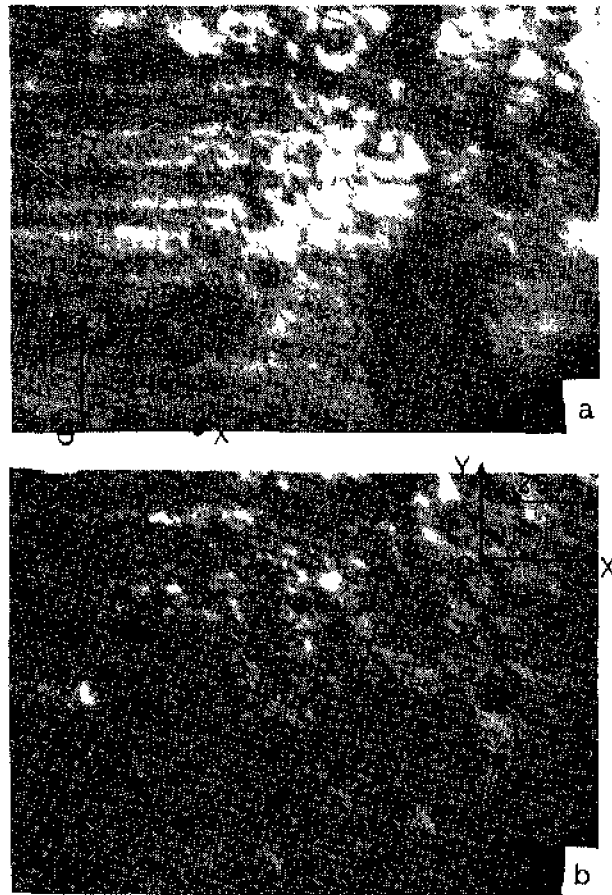


Figure 3. ( $\times 704$ ) Photomicrograph of **a.** pseudocubic (001) crystal surface and **b.** crystal surface after etching.

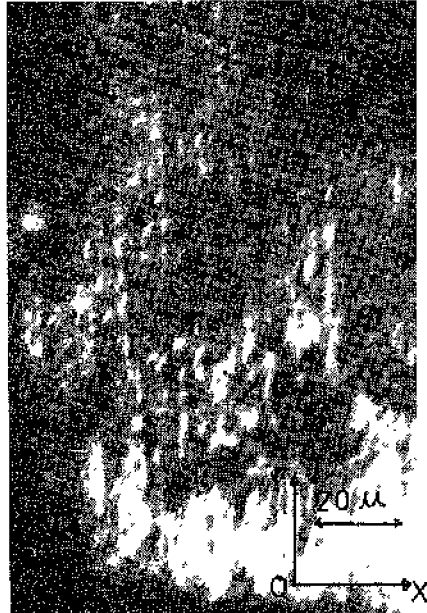


Figure 4. Photomicrograph of crystal surface after etching ( $\times 948$ ).

direction, and the pits are of deep variety on either side of the line (see marked region).

Yet another interesting type of etch pit structure was also observed. In figure 4 we find, that the domain line is parallel to  $[100]$  but the rows of etch pits are absent in one of the domains. These results are discussed in the next section.

### 3. Discussion of the results

The above results can be properly understood if one assumes that the direction of the impurity dipole is the same as the direction of polar axis in that domain. Such an assumption is justified in the light of the work of Ingle *et al* (1988) who showed that impurities caused nucleation of domains. During this process if the polar axis of the impurity was parallel to the polar axis in the domain, the electrostatic energy of the dipole was considerably reduced. Hence it was reasonable to conclude that the impurity dipole axis coincided with the polar axis. The type of etch pits indicated whether the dipole axis was in the plane of the plate or in the perpendicular plane, and also the domain structure associated with impurity dipoles. It is easy to check whether such domain structures were permissible. It is also possible to confirm the domain structure by other observations. The domain structures obtained in the case of figures 1 to 4 are shown respectively in figures 5(a-d). In each case it was found that the domain structure was a possible domain structure as allowed by the type of twinnings observed in this crystal (Forsbergh 1949). Also, it was confirmed that the domain structures derived on this basis (figure 5) agreed well with those derived by other observations.

It is thus clear that impurity dipoles participate in the process of domain formation, and before they do so, are ordered in the structure in the form of rows giving clear evidence of cooperative order binding them.

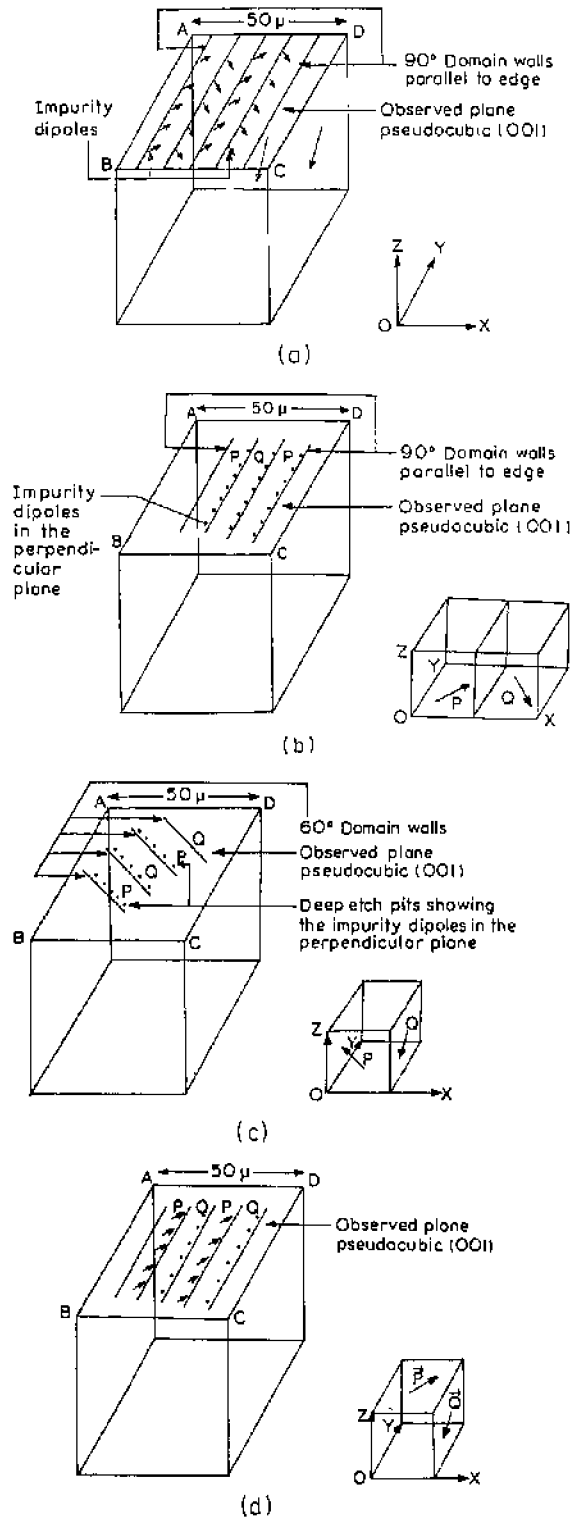


Figure 5. Domain structure in the crystal used for a. figure 1a, b. figure 2, c. figure 3a and d. figure 4.

#### 4. Conclusion

The present results indicate cooperative ordering of impurity dipoles at the Curie temperature in this ferroelectric crystal. It is of interest to know whether the cooperative ordering in ferroelectrics leads to cooperative ordering of impurity dipoles. However, since cooperative ordering is observed even in nonferroelectric systems, in which case, the material becomes ferroelectric, it is not proper to deduce that cooperative ordering is on account of the ferroelectric nature of the crystal. There exists a close relationship between the cooperatively acting dipoles and the phase transition temperature (Dvorak and Glogar 1966). Clearly, further studies into this aspect are vital to ferroelectricity.

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