Cooperative ordering of impurity dipoles in KNbO₃ single crystals

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Abstract. The impurity atoms forming dipoles in the structure of KNbO₃ are arranged regularly in the structure. The locations of the dipole sites were observed by etching technique, when dilute HNO₃ 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 Giogar 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 KNbO₃ 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 KNbO₃ 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 HNO₃ (prepared by taking 1 part by volume of concentrated HNO₃ 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°, in which case, the domain line was parallel to the [001] direction, or 60° where the domain line was at 45° 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° with the [100] direction.

![Figure 1. (× 390) Photomicrograph of a, pseudocubic (001) crystal surface and b, after etching the crystal surface.](image-url)