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Defect characterization of KTP single crystals

G DHANARAJ, T SHRIPATHI* and H L BHAT
Department of Physics, Indian Institute of Science, Bangalore 560 012, India
*Permanent address: Inter-University Consortium for DAE Facilities, University Campus, Khandwa Road, Indore 452 001, India

Abstract. Potassium titanyl phosphate (KTP) is a relatively new nonlinear optical material with excellent combination of physical properties. This paper presents the combined etching and X-ray topographic studies carried out on KTP crystals with a view to characterizing their defects. KTP crystals employed in this investigation were grown from flux. Optical microscopic study of habit faces revealed growth layers and growth hillocks on {100} and {011} faces respectively. Etching of {011} habit faces proved that growth hillocks corresponded to the emergence point of dislocation out crops on these faces. The suitability of the new etchant to reveal dislocation was confirmed by etching the matched pairs obtained by cleaving. The defects present in the crystal were also studied by X-ray topography. The defect configuration in these crystals is characteristic of crystals grown from solution. The dislocations are predominantly linear with their origin either at the nucleation centre or inclusions. In general, grown crystals were found to have low dislocation density and often large volumes of crystals free from dislocation could be obtained.

Keywords. Flux growth; growth hillocks; etching; X-ray topography; dislocations.

1. Introduction

Potassium titanyl phosphate, $KTiOPO_4$, commonly known as KTP, is one of the technologically important ferroelectric crystals with Curie temperature 934°C (Bierlein and Vanherzeele 1989; Yanovskii and Voronkova 1986). Its crystal structure belongs to orthorhombic space group $Pna2_1$ (Tordjman *et al* 1974). It has excellent combination of properties such as high nonlinear optical coefficients, high damage threshold, thermally insensitive phase matching and good chemical and mechanical properties that makes it useful for second harmonic generation of the 1·06 μm Nd:YAG laser (Zumsteg *et al* 1976). Its large electro-optic coefficients and low dielectric constant make it more attractive for various electro-optic applications especially in wave guides. Even though its physical properties have been extensively studied and applied in various device fabrication for the past several years, there does not seem to be much systematic work carried out on defect characterization of KTP crystals. Cai and Yang (1986) reported the etch pit micrographs without giving any details. Bolt *et al* (1991a, b) carried out X-ray topographic studies as well as etching studies. However, the latter were restricted to only habit faces and not on cleaved plates. In this paper we present our results on the assessment of the quality of the grown crystals employing both chemical etching and X-ray topographic techniques. In particular, etching was carried out both on habit and cleaved faces. Our optical microscopic study has also given some insight to the growth mechanism of these crystals.

2. Experimental procedure

The crystals employed in this investigation were grown from potassium phosphate flux ($K_6P_4O_{13}$) by slow cooling method. The appropriate amounts of ingredients i.e. KH_2PO_4, K_2HPO_4 and TiO_2 were taken in a platinum crucible and heated to 1050°C for homogenization. After two days, the temperature was brought down to 975°C after which the charge was cooled down to 650°C at controlled cooling rates. The cooling rate ranged from 2°C/h to 7°C/day. Figure 1 shows typical KTP crystals grown in our laboratory.

Optical microscopy of the grown crystals was carried out employing a polarizing microscope (Leitz Orthoplan). Whenever necessary the reflectivity of the faces under examination was enhanced by depositing a thin layer of silver on the surface by vacuum evaporation. The etching experiment was carried out in a well-protected constant temperature bath. The etchant, a mixture of HCl and HF in the ratio 2:1 was taken in polyethylene container. Etching was done at 100°C for 45–120 min. Crystals with habit faces as well as cleaved plates were used in this study. The etched faces were cleaned in distilled water and dried carefully without any damage to the surface and were then studied under optical microscope.

For X-ray topographic work, (100) plates were prepared by cutting the grown KTP crystals using a diamond saw. The crystal plates were thinned down to 0·75 mm by lapping using 0·5 μ alumina abrasive powder. Mechanical strain present on the surface due to lapping of the crystal was removed by dissolving the surface in HF. X-ray topographs were recorded on Agfa Dentus M2 film with MoKα radiation using Lang method. A Rigaku micro focus X-ray generator was used ($\mu = 3{\cdot}2\ mm^{-1}$ for 0·709 Å). (040) reflection was selected because of its high intensity.

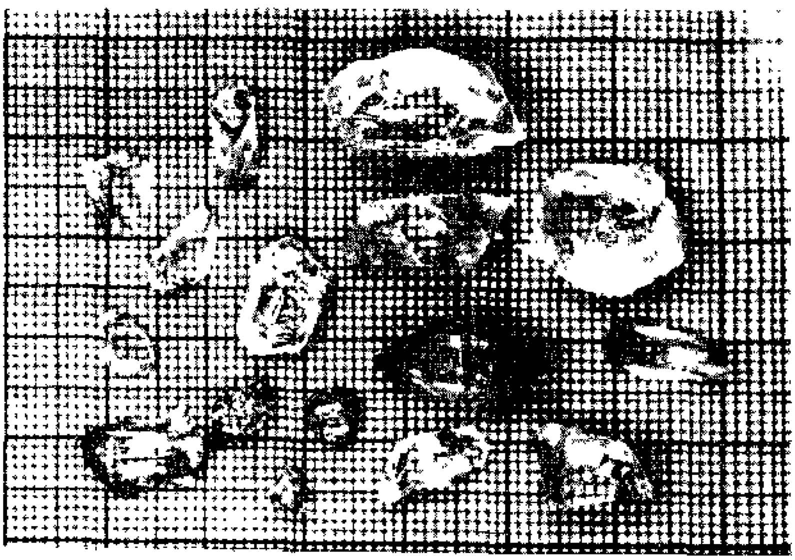


Figure 1. Typical KTP crystals grown from flux (mm scale).

3. Results and discussions

3.1 *Surface structure*

Although the phosphate flux has its own advantage like the ability to give high purity crystal, the viscosity of this flux is high when compared to tungstate flux (Ballman *et al* 1986; Iliev *et al* 1990). Therefore, depending upon the temperature range and cooling rate, the surface structure of the KTP crystal and the extent of flux inclusion vary. When the cooling rate is 1°C/h the resulting crystal surfaces exhibit coarse dendritic structure. Such dendritic structures are seen on both {100} and {201} habit faces. Figure 2 shows a typical dendritic pattern on (201) face of a crystal grown under the above mentioned cooling rate. As the cooling rate decreases the surface dendritic patterns change from coarse to finer structure. The detailed study correlating the surface structure to cooling rate was reported earlier (Dhanaraj *et al* 1990). Further, it is important to note that at high cooling rates flux inclusion in the bulk of the crystal is rather high. This flux inclusion deteriorates the optical quality of the crystal. As we decrease the cooling rate, the flux inclusion decreases and hence it is possible to grow crystals free from visible inclusions and dendritic structure on the habit faces.

When the crystal surfaces are free from dendritic structure the underlying growth features become visible which reflect the true mechanisms operating in the growth of these crystals. The most prominent habit face (100) contains step pattern spreading smoothly over the entire face suggesting layer growth. On the other hand {011} habit faces exhibit growth hillocks of various shapes and steepness. Figure 3a shows an asymmetric hillock on {011} habit face whereas figure 3b shows a pyramid-like hillock on the same face. As we shall see later these growth hillocks are an external

Figure 2. Dendritic pattern on (201) habit face (× 100).

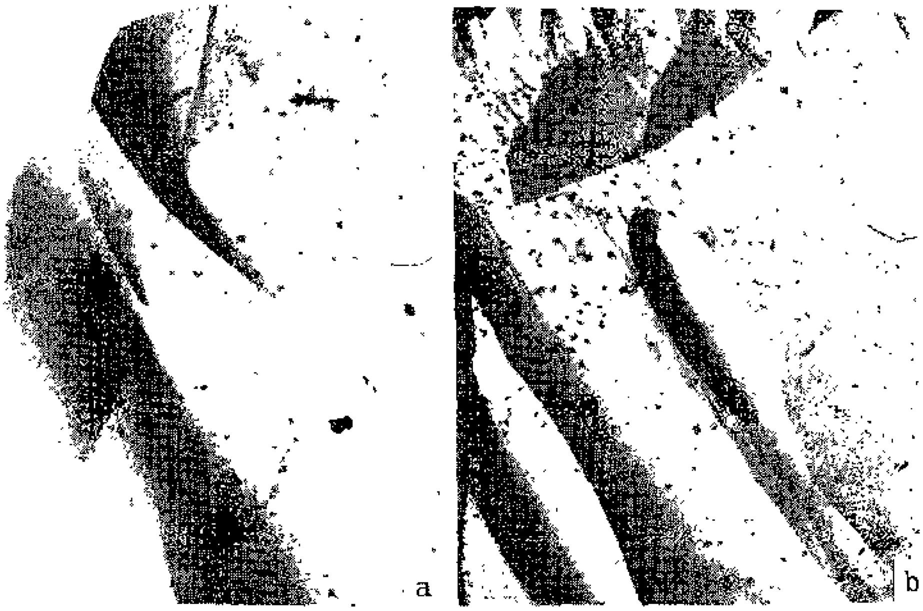


Figure 3. Hillocks on {011} habit faces (× 150). a. Symmetric and b. asymmetric.

manifestation of the internal defect structure of the crystal. The probable reasons for different shapes of these hillocks will be discussed later.

3.2 *Etching studies*

In order to study the dislocations present in the grown crystal, etching studies were carried out. The crystals were etched in a 2:1 ratio HCl and HF mixture at 100°C for 45–120 min. This etchant revealed dislocations on both the cleavage and habit faces. Figure 4 shows a typical etch pattern produced on (011) habit face. Etch pits could be produced on other habit faces as well. The shape of the pits produced on the habit faces reflected the symmetry of these faces. The fact that this etchant was capable of revealing dislocations was first confirmed by etching the complimentary crystal surfaces obtained by cleaving. Figures 5a and b show etch patterns on one such cleaved {100} matched pair. Here one can clearly see a one-to-one correspondence between the number and the position of the etch pits proving that the pit was due to dislocation emerging out of (100) plane. A magnified image of the dislocation pit is shown in figure 5c. The tail-like nature of the dislocation etch pit is likely to be due to the fact that dislocation line is seen inclined to [100] direction. Further, it should be noted here that the entire face contained only one dislocation etch pit which in turn reflected high degree of perfection of the grown crystal. A few other shallow pits which do not show a one-to-one correspondence may be due to clusters of point defects. As a matter of fact, on many occasions, one could not see any pits in the entire cleaved plates when etched. Figure 6 shows a large area of cleaved (100) plate etched with the above etchant. It shows smooth dissolution pattern without any etch pit revealing that there is no growth or process-induced dislocation emerging

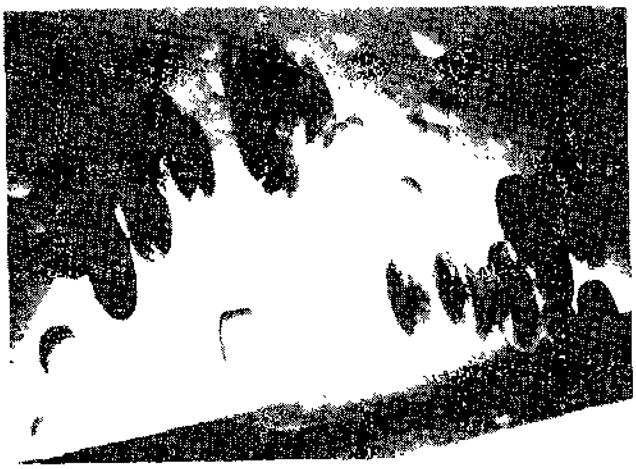


Figure 4. Typical etch pattern on (011) habit face ($\times 150$).

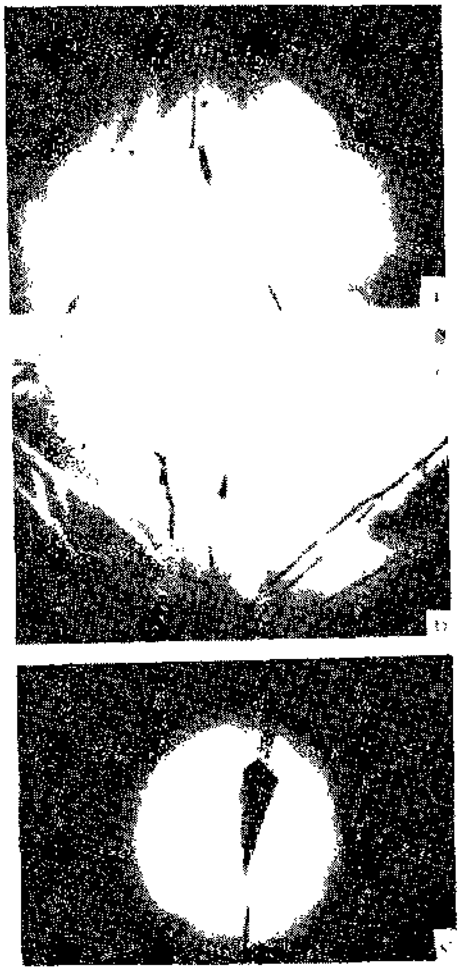


Figure 5. **a–b.** Etch patterns on cleaved {100} matched pair $\left(\times 100 \times \frac{5\cdot5}{7\cdot5}\right)$. **c.** Magnified image of dislocation etch pit shown in figure 5a $\left(\times 300 \times \frac{5\cdot5}{7\cdot5}\right)$.

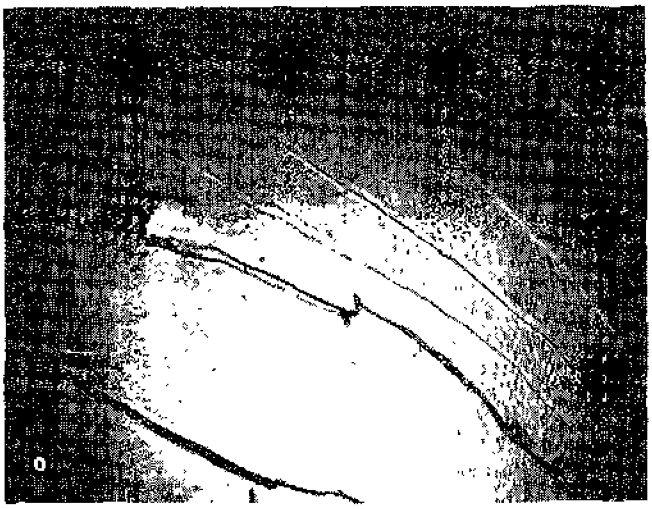


Figure 6. Etch pattern on cleaved (100) plate showing smooth dissolution of the surface without etch pits (× 150).

Figure 7. Etch pattern on cleaved (100) plate showing piling of dislocations (× 150).

out in (100) plane. In this etching study the dislocation densities were measured by counting the number of etch pits. The dislocation density ranged from a few dislocations per cm^2 to $10^3/cm^2$ depending upon the growth conditions.

Since KTP crystal is mechanically quite stable (its hardness being 5·7 in Mohs scale), one cannot introduce mechanical dislocations easily into the crystal. Consequently normal handling procedures do not adversely affect the quality of the crystal. However, sometimes it is possible to see process-induced dislocations in cleaved crystals when cleaving is not perfect. Figure 7 shows one such cleaved plate in which dislocation pits are piled up in rows, to attain minimum energy configuration. An identical etch pit pattern was observed on the counter-part of the cleaved crystal. These are certainly dislocations introduced during cleavage process.

In order to understand the origin of the hillocks on {011} faces of these crystals

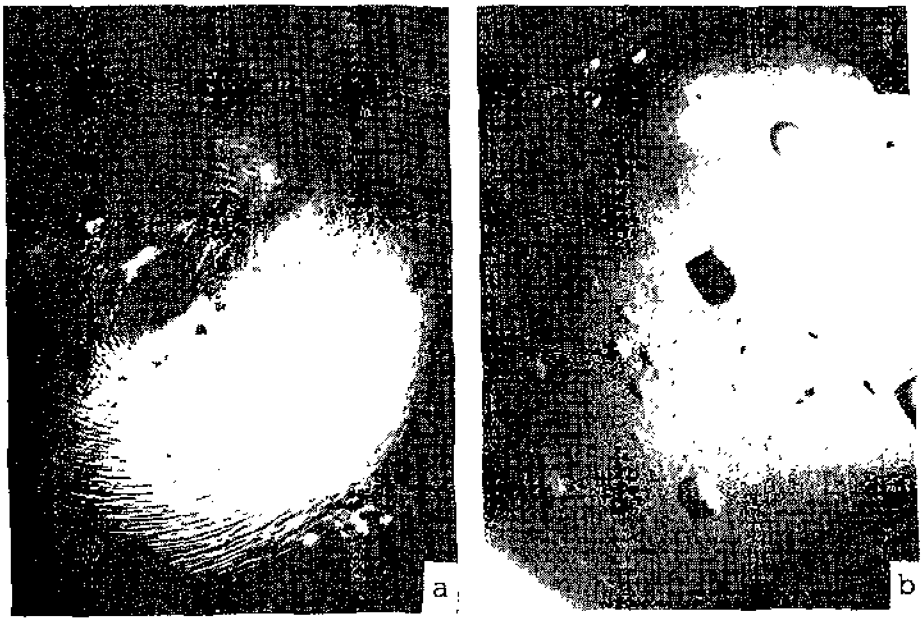
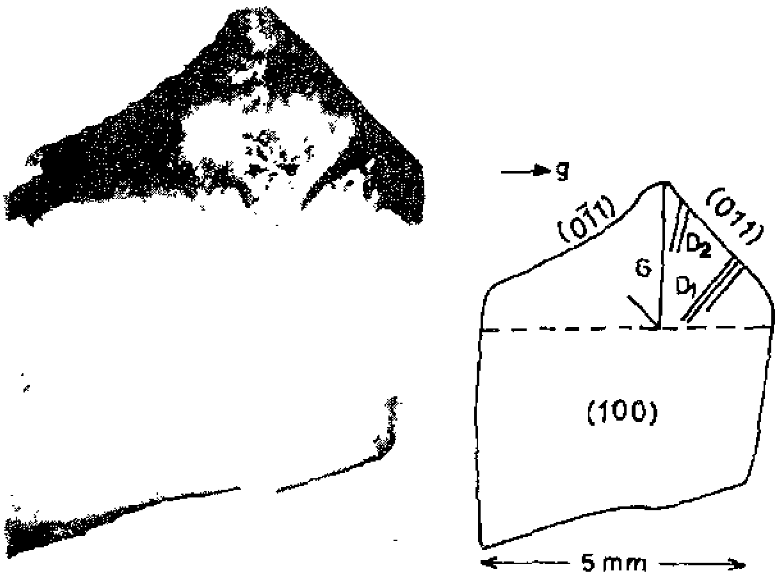


Figure 8. a. Growth hillock on (011) habit face (× 150). b. The etch pit produced at the centre of this growth hillock (× 200).

we have carried out etching studies on the hillock faces. Etching of these faces resulted in the formation of well-defined etch pits on the top of the hillocks. Figures 8a and b show the hillock and the dislocation pit produced at the centre of the same hillock by etching. This clearly suggests that the growth hillocks are formed at the emergence point of dislocations on these habit faces.

3.3 *X-ray topographic study*

It was mentioned earlier that on {011} faces the hillocks of both symmetric and asymmetric shapes could be seen. In order to check if this has anything to do with the inclination of the dislocation line with respect to the observation plane, we imaged the dislocations by Lang topography. A transparent crystal free from all visible defects was chosen. In our investigation (100) KTP plate containing (011) sectors was imaged using (040) reflection so that the distribution and inclination of dislocations emerging on the {011} faces could be seen. The topograph is shown in figure 9a and the schematic diagram of the topograph in figure 9b. In the topograph, the lower portion of the crystal was not imaged properly because of the increase in thickness of the crystal. As can be seen from figure 9b the dislocation configuration is characteristic of solution grown crystals. The dislocations are straight and mainly originate from the central nucleus though some dislocations also originate from inclusions. The topograph also reveals that a large volume of KTP crystals which are relatively defect-free can be obtained by employing the flux technique. Referring to figure 9b, two types of dislocations are seen to emerge from (011) face. Those marked D_1 emerge more or less normally to the growing face whereas those marked D_2 emerge at oblique angles. Also, because of their oblique nature, D_2 type usually emerge at the peripheral regions



(a) (b)

Figure 9. a. Topograph of KTP crystal, (040) reflection. b. Schematic diagram of the topograph. D_1, D_2, dislocations; G, growth sector boundary.

of the (011) faces. It is likely that the D_2 dislocations give rise to asymmetric hillocks while those of D_1 give symmetric hillocks. This is further confirmed by the fact that the asymmetric hillocks are always formed at the peripheral regions of {011} habit faces as is evident from figure 3b.

4. Conclusions

The KTP crystals grown using potassium phosphate flux are, in general, of high perfection. The flux inclusions and dendritic features could be minimized by optimizing the growth condition. Layer growth mechanism was observed on {100} habit faces. Growth hillocks were observed on {011} habit faces at the emergence points of dislocations and their shapes seem to have a correlation with the inclination of the emerging dislocation. Etching and preliminary X-ray topographic studies carried out on these crystals confirm that crystals with very low dislocation density can be grown employing the flux method.

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