Selective etching of habit faces of ferroelectric $\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{CO}_2)_6$ crystals

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Abstract. Crystallographically oriented etch traces produced by selective etchant on {111} and (110) habit faces of dicalcium strontium propionate $[\text{Ca}_2\text{Sr}(\text{C}_2\text{H}_5\text{CO}_2)_6]$ crystals are attributed to the growth traces nucleated during the superficial growth of crystal. This view is supported by the absence of such etch traces on seized habit faces and from the observations of layer structure on the bottom faces. Mother liquid acting as an etchant produces circular terraced depressions on habit faces. These depressions originate at the sites of isolated impurity centres. Identical features such as circular etch structures bounded by cylindrical outer periphery produced on cooled faces are attributed to isolated domains.

Keywords. Dislocation etch pits; etch traces; impurity sites; isolated domains; dentrite.

1. Introduction

Studies on interaction between domains and dislocations are of interest to understand the formation and behaviour of domains in ferroelectric crystals. Unfortunately sophisticated experimental techniques for detecting dislocations are not useful for low transition organic ferroelectrics. Etching techniques has been successfully used to identify the sites of dislocations and types of domains in Rochelle salt (Nakamura 1956), KH_2PO_4 (Toshev 1963) and triglycine sulphate (Konstantinova 1962; Meleshina 1964; Sawada and Abe 1967) crystals. Dicalcium strontium propionate is ferroelectric (Matthias and Remeika 1957) with transition temperature of 8.5°C . The dislocation etchant established for this crystal does not provide any information with respect to the domain structures. Hence several etchants were tried and the results of selective etching characteristics are presented in this paper.

2. Experimental

Crystals of dicalcium strontium propionate were grown from solution. Calcium carbonate (mol. wt. 100.09, NH_4 0.05%, Na 0.02%, Mg 0.01%, Ba 0.01%, silicate 0.01%, NO_3 0.01%) and strontium carbonate (mol. wt. 147.63, assay 99%, chloride 0.001%, sulphate 0.01%, iron 0.001%) (both AR grades) in 2:1 mole ratio, were separately dissolved in propionic acid (AR grade) ($\text{C}_3\text{H}_6\text{O}_2$) (mol. wt. 74.08 density ($d_{20^\circ/4^\circ}$) 0.993-0.994, water 0.1%) and then mixed together. To this mixture an excess of propionic acid was added. The residue of the powder was dissolved in distilled water warmed and kept for evaporation. Crystals of various sizes were collected at appropriate stages. By trial and error method, it was established that methyl alcohol (CH_3OH) (referred to as the dislocation etchant) produces etch pits at the sites of dislocations on habit and cleavage faces of dicalcium strontium propionate crystals (Chaudhari and Krishnakumar 1987). Several organic solvents

were used for studying the topology of the surface etched with the etchant having normal rate of dissolution and less than that of methyl alcohol. 2-methyl-propan-2-ol (tert-butylalcohol) ($(\text{CH}_3)_3\text{COH} = 74.12$) was found suitable as a selective etchant. The crystal faces were observed under a metallurgical microscope.

3. Observations and results

The visibility of dislocation etch pits produced by methyl alcohol on (111) habit face is quite contrastive of normal dissolution (figure 1). The general criteria for studying the domains in organic solids require the normal dissolution rate V_n to compete with the surface dissolution rate V_s , whereas in the case of dislocation etch pits V_n/V_s is approximately 0.1. However, simultaneous etching of domains and dislocations with this rate reported by Meleshina (1964) in TGS crystal was found unsuitable for studying dicalcium strontium propionate crystals. 2-methyl propan-2-ol (tert-butylalcohol) was found to have the normal dissolution rate less than that of methyl alcohol. Figure 2 represents the net pattern of etch traces produced by the selective etchant on a habit (111) face. Similar pattern is observed on a habit (110) face as shown in figure 3. Most of the etch traces exist along definite crystallographic directions. On (111) face, the net pattern is formed due to etch traces along the $[110]$ $[11\bar{2}]$ directions and on (110) face along the $[110]$ direction. Shallow triangular and boat-shaped etch pits are also observed on (111) and (110) faces as seen in figures 2 and 3 respectively. Such traces disappear on prolonged etching. In addition, few peculiar etch patterns have also been observed on habit (111) face as shown in figure 4(a). The geometry of etch pits differs from those observed on habit (111) faces. This clearly indicates that these faces are not true (111) faces. Etching characteristics of such inclined or deviated faces have been reported by Konstantinova and Neklyudova (1960) in TGS crystals revealing the domains. Along with the etch pits and few circular structures, the sharp lines are observed whose thickness is different from that of the network formed by the etch traces. It is interesting to note that, except etch pits, the periphery of etch structures changes on further etching (figure 4(b)). However, these structures finally get washed out on prolonged etching.

Figure 1. Dislocation etch pits on (111) habit face of DSP crystal. ($\times 100$)

Figure 2. Network produced by selective etch on the top (111) habit face. ($\times 50$).

Figure 3. Network of etch traces along with the dislocation pits observed on the bottom (110) habit face. ($\times 100$)

Figure 4. **a.** Etch pattern consisting of etch pits, sharp lines and circular etch structures on (111) face and **b.** region of (**a**) observed at successive stage of etching. Note the change in shape of outer boundary of circular etch features. ($\times 100$)

Such structures have not been produced by the dislocation etchant on (111) faces. The mother liquid acts as a dissolving agent (figure 5(a)) which is an untreated

Figure 5. a. Circular features of assorted sizes and depths on a habit face before etching and b. etch pattern of the region of a. ($\times 100$)

crystal face. Terraced circular features without distinct centres and triangular features resembling etch figures are observed. The topography of these circular figures differs from those produced by chemical etching [figure 3(a)] with respect to the shape of outer periphery and the nature of terracing. The same face was re-etched and the etch pattern on the corresponding region is shown in figure 5(b). It is noted that all circular etch features get dissolved except one and new circular etch features develop. Such structures in TGS have been reported by Sawada and Abe (1967). Figure 6 shows a rare case of dissolved layer structure on a prismatic (111) face. To find the cause of formation of etch structures as seen in figure 4(a), crystal faces were heated or cooled and then etched. Results in respect of dislocation density and domain walls have been obtained. However, such structures have been observed on cooled faces (-4°C , 36 h) before etching. Thus an elliptical structure enclosing two circular features with distinct centres is observed in figure 7.

4. Discussion

Chaudhari and Krishnakumar (1987) reported that dicalcium strontium propionate crystals obtained by the method described in § 2 grow by layer deposition mechanism. The general form of growth layers is shown in figure 8. The geometry of layers interesting the habit faces is similar to the etch traces produced by the selective etchant. But perfect crystallographically oriented etch traces on (111) and (110) habit faces get washed out on prolonged etching. This suggests that their origin does not run through the body of the crystal. Hence the possibility that these etch traces reveal the inter-section of layers on habit faces can be ruled out. The other alternative is that these traces might have been formed during the superficial growth representing the final stage of crystal growth (Buckley 1951). This indicates that during superficial growth, layer deposition is favoured rather than the dendrites as observed in $\text{K}_2\text{Cr}_2\text{O}_7$ crystals (Buckley 1951). Thus the superficial growth traces revealed by these etch traces are supported by the fact that no such etch traces are observed on the habit faces of the crystal whose growth is seized abruptly i.e. unfinished crystals were removed from the mother liquid, dried and then etched.

Figure 6. Topography of an etched prismatic (111) face. ($\times 150$)

Figure 7. Features observed on a cooled habit face. ($\times 200$)

Figure 8. Layer structure observed on the bottom face of a tiny crystal. ($\times 100$)

Granular terraced growth features (depressions) getting washed out on etching and identical etch features produced by the etchant on habit faces may be attributed to the isolated impurity sites attacked by the mother liquid acting as an etchant. The

mother liquid acting as an etchant is confirmed from the relative etch features seen in figure 5(a). Other confirmation with respect to the etching characteristics of the impurity sites on matched faces is out of question because the observations are made on the habit faces. The thickness of the sharp lines shows that they are neither attacked at the intersection of layers on habit faces nor the growth traces nucleated during the superficial growth. The geometry of the outer boundary of isolated circular etch features changes with respect to time and get washed out on prolonged etching. Such structures observed on cooled (unetched) faces suggest that they may reveal isolated domains on habit faces. This is due to the fact that the selective etching characteristics of domains differ with respect to their coupling (Meleshina 1964).

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