<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>063</td>
</tr>
<tr>
<td>7.2</td>
<td>Method of etching</td>
<td>064</td>
</tr>
<tr>
<td>7.3</td>
<td>Etch patterns on (001) habit faces</td>
<td>065</td>
</tr>
<tr>
<td>7.4</td>
<td>Etching of (001) matched cleavages</td>
<td>067</td>
</tr>
<tr>
<td>7.4.1</td>
<td>Low angle grain boundaries</td>
<td>067</td>
</tr>
<tr>
<td>7.4.2</td>
<td>Twinning</td>
<td>070</td>
</tr>
<tr>
<td>7.4.2.1</td>
<td>Growth twins</td>
<td>071</td>
</tr>
<tr>
<td>7.4.2.2</td>
<td>Thermal or transformation twins</td>
<td>072</td>
</tr>
<tr>
<td>7.4.2.3</td>
<td>Mechanical twinning</td>
<td>073</td>
</tr>
<tr>
<td>7.4.2.4</td>
<td>Twinning in natural topas</td>
<td>074</td>
</tr>
<tr>
<td>7.5</td>
<td>Conclusions</td>
<td>075</td>
</tr>
</tbody>
</table>
7.1 Introduction

Etch figures are the solution cavities, having some definite shape and orientation, produced by momentary or prolonged action of some suitable etchant on the faces of the crystals. The shapes of the etch figures formed on crystal faces are strictly related to the nature of the etchant and the symmetry of the crystal face. In recent years, etching of crystal faces is taken up with a view to gain information regarding the history of growth of the crystals and the structural defects such as edge and screw dislocations, twinning, grain boundaries etc. The chief among the several investigators, who have used this technique on habit and cleavage faces of various crystals are Vogel et al. (1953), Amelinkx (1954), Gilman and Johnston (1956), Patel et al. (1962, 1965, 1970), Dec and Sharma (1964), Pandya and Pandya (1959), Pandya and Saraf (1968), Pande and Murty (1969), Joshi et al. (1967, 1968, 1969).

It was Gevers (1953) who, for the first time, obtained etch figures on natural topaz crystals. Etch pits associated with beaks were obtained by Patel et al. (1969) on (001) cleavages of topaz and formation of beaks was explained by them by assuming the existence
of fission tracks in the body of crystal near dislocation lines.

In the present investigation a detailed study of etch patterns on (001) habit as well as cleaved faces of topaz crystals was undertaken. In this chapter, etch patterns on (001) habit faces, low-angle grain boundaries and oppositely oriented etch patterns on matched cleavage faces are described.

For etching experiments, (001) cleavage faces and thin flakes were obtained by parting topaz crystals along (001) cleavage planes by giving a gentle blow to the flat head of a chisel with a small hammer, the sharp edge of the chisel being held in a surf almost parallel to the basal plane.

7.2 Method of etching

It is essential to obtain suitable conditions of etching to produce well defined etch pits on crystal faces. To begin with, therefore, etching experiments were carried out on crystal faces by etching them in KOH at different temperatures. For such experiments the crystal to be etched was held by a nickel hook and with the help of a fork the hook with the crystal was dropped into the etchant in a nickel crucible placed in
the furnace maintained at a constant desired temperature. At the end of etching time the crystal was removed from the etchant and subsequently cleaned in nitric acid, hydrogen peroxide and distilled water and was then examined. It was found that as the temperature of KOH is increased, etch rate also increases. At or above 660°C, the reactivity of the reagent is so great that within a very short time a large portion of the crystal is simply eaten away and thus the chemical action between KOH and topaz becomes uncontrollable. Suitable conditions of etching were, however, adjusted by etching the crystals in KOH at 440°C. The temperature was maintained constant within an accuracy of ± 10°C. For obtaining well defined etch pits the minimum time required was found to be 10 seconds.

7.3 Etch patterns on (001) habit faces

Some of (001) habit faces were etched in KOH, as described, for about 10 seconds. Examination of etched faces revealed the presence of both point-bottomed and flat-bottomed etch pits. One such case is shown in an electronmicrograph in figure 60. All these rhombus-shaped etch pits have their longer diagonals parallel to y-axis, whereas their shorter diagonals parallel to x-axis. Etch pits of the same shape and orientation produced by
natural etching on (001) habit faces have been reported by Buckley (loc. cit.). It is, therefore, suggested that such etch pits should grow and develop in nature on (001) habit faces only in presence of KOH in the neighbourhood of 440°C temperature.

Etch patterns identical in shape and orientation to those shown in figure 60 are also observed to grow on (001) cleavage faces when such faces are etched in KOH. All the etch pits on (001) habit faces or cleavage faces grow bigger in size and become deeper on successive etching, which means that these pits nucleate at the sites of dislocations. As will be seen from the observations described in the following section and in the subsequent chapters, enough evidence has been obtained to prove that all the etch pits are formed at the dislocation sites.

In regions marked A and B of figure 60 two pits should have grown initially at each of these regions which, with the progress of etching, have merged together forming what apparently looks like a single pit in each of these regions. Development of etch pits in this way can take place if the dislocations associated with these pits are present in the form of half-loops. In fact, enough evidence has been obtained
to prove that the dislocation in the form of half-loops are common in natural topaz crystals, details of which are given in chapter 9.

7.4 Etching of (001) matched cleavages

Study of etch patterns on the matched cleavages may be useful in the understanding of the mechanism of etching, the dislocation contents and their nature and the growth history of crystals. Such studies were carried out in the present investigation. During the course of study, rows of etch pits resembling those formed at low angle grain boundaries were observed in quite a few cases. In some cases twinning was also detected. All these observations are described in what follows.

7.4.1 Low angle grain boundaries

A boundary separating two crystals (or grains) that differ either in crystallographic orientation, composition or dimensions of the crystal lattice is defined as a grain boundary. Grain boundaries are known as planar lattice faults. Ever since the beginning of the studies on crystals, various theories have been put forward for the formation of grain boundaries by different workers (Amorphous cement theory by Sears, 1906; Bengough, 1912; Rosenhain and Humphery, 1913; the
transition lattice theory by Jeffries et al., 1954; Hargreaves and Hills, 1929; dislocation theory by Burgers and Bragg, 1940; island theory by Mott, 1948). Various other mechanisms for the formation of grain boundaries have also been conceived by Koh (1949), Smoluchowski (1953) and Friedel, Cullity and Crussard (1953).

Out of all the theories mentioned above the most successful theory is that of Burgers and Bragg (loc. cit.). They showed that when the adjoining grains have a small difference in orientation, an array of edge dislocations forming a tilt boundary emerges naturally from the crystal geometry. The difference in orientation is given by the relation

$$\theta = \tan^{-1} \frac{b}{D}$$

for small angles and

$$\frac{b}{D} = 2 \sin \frac{\theta}{2}$$

for large angles, where 'b' is the Burgers vector of each dislocation and 'D' the spacing between two dislocations.

Using Read's (1953) general mathematical formula for the model of grain boundaries, Amelinksx (1957, 1959) investigated the geometry of
dislocation nets and fold boundaries for different crystallographic structures. The first direct verification of dislocation model for a grain boundary is due to Vogel and his co-workers (1953). The relation \( \theta = b/D \) for small angle tilt boundaries in germanium was experimentally verified by them.

Frank (1950) proposed a relation for three grain boundaries meeting at a point, in terms of the number 'n' of dislocations per unit length and Burgers vector 'b'. According to Frank (loc. cit.), the following condition should be satisfied for the intersection of three tilt boundaries A, B and C (or T-type intersection of grain boundaries)

\[
A = B + C
\]

i.e. the linear pit density in one boundary equals the sum of pit densities in the other two. For two intersecting tilt boundaries (or L-type intersection), the relation \( A = C \), should be satisfied. This is because, here, \( B = 0 \). The relations for the T and L type junctions in the case of low angle grain boundaries have been verified by many investigators (Amelink in NaCl, 1954; Pfann and Vogel in germanium, 1957; Wernick et. al., in antimony, 1958;
In order to investigate the existence of grain boundaries in natural topaz, a few pairs of matched cleavage faces were etched in KOH as stated for 20 seconds. In some cases, exactly similar rows of etch pits having perfect one-to-one correspondence were produced on matched faces. Figures 61(a) and 61(b) illustrate one such case. The mirror image of the row of equally spaced etch pits on the matched halves indicates that the row of etch pits represents a grid of dislocations caused by a small angle tilt boundary. On etching this matched pair for 40 seconds more, the pits along the row were found to grow larger in size and become deeper (see figures 62(a) and 62(b)). The average distance between the consecutive pits comes out to be the same in both the matched faces. These observations confirm that these etch pits in a row correspond to an array of dislocations, the terminal ends of which are to be found on both the matched surfaces.

7.4.2 Twinning

Twinning is an abnormality of growth and is commonly observed in minerals and artificial...
chemical compounds. Different mechanisms of formation of twinned crystals have been discussed by Cahn (1954), Phillips (1963) and Ford (1963). There are three main types of twins viz. growth twins, thermal or transformation twins and mechanical twins. A brief summary of these three types of twinning is as follows.

7.4.2.1 **Growth twins**

Growth twins are formed during the growth of crystals. The growth twins, in which two (or more) identical crystals grow from the same nucleus with a specific crystallographic relationship to each other, are frequently found in monomer and polymer crystals. The twin crystals are governed by different laws of twinning. Growth twins are of two types viz. contact twins and penetration twins. In the former type, the two individuals are in contact along a twin symmetry plane. However, if the individuals related in this way occur alternately, we speak of lamellar twinning. Such twinning is mostly caused by the generation of stacking faults during the growth of crystals. In many minerals very fine lamellae occur in large numbers which give rise to what is known as polyhedral twinning.

Penetration twins are those in which
two or more complete crystals interpenetrate, as if they are crossing through each other. Normally, the crystals have a common centre, which is the centre of axial system for both. Practically, however, as in contact twins great irregularities occur.

7.4.2.2 Thermal or transformation twins

Phase transformation in the solid state are often accompanied by the formation of twins. These arise in two ways. When a crystal of phase stable at low temperatures is heated, mechanical stresses arise which cause the generation of twins. Such twins are called thermal twins. When a crystal of high temperature phase is cooled through the transformation temperature, twins may again form in the low temperature phase. This is due to the fact that the transformation, on cooling from a phase of high symmetry to one of low symmetry, may involve co-operative atom movements in a nuclear region. The crystals generated by such a process may be in the twin relationship to each other. The twin-related crystals may or may not be lamellar. A good example of twins formed in this way are the Dauphine (penetration) twins in quartz which changes from hexagonal to trigonal symmetry during cooling.

7.4.2.3 Mechanical twinning

Twinning produced in an untwinned
crystal by mechanical deformation of the crystal is called mechanical twinning. According to Cahn (loc. cit.), dislocations play an essential role in the formation and development of this type of twinning. It has been suggested by Buckley (loc. cit.) that substances which do not by themselves readily form twins can sometimes be made to do so by adding specific impurities.

From the study of surface structures of hematite crystals Sunagawa (1959) has proposed an explanation of contact twins. According to him, a twin boundary is often curved having irregular bands. There is always a level difference at the twin boundary. Such a boundary is formed during the growth of crystal by a fault and the amount of fault is such that some portion of the step remains always unfilled. In his papers (1960, a, b, c) Sunagawa has discussed that in case of twin crystals growth features have opposite orientation on different portions of the crystal faces.

Any type of twinning is usually difficult to detect in natural crystals from their exterior form. The best method of detecting twinning is by etching the surface with a suitable etchant. Using this method, twinning has been detected by Startsev in calcite, 1960; Konstantinova in triglycine sulphate, 1963; Raju in
selenite, 1968; Kotru in quartz, 1968. The author in
the present work made a similar approach to look for
twinning in topaz crystals.

7.4.2.4 Twinning in natural topaz

With a view to investigate the nature of
twinning in topaz crystals, some of the matched faces
cleaved along (001) planes were etched in KOH for
30 seconds. On some matched cleavages, matching of
oppositely oriented pits was observed. One such case
is shown in figures 63(a) and 63(b). The following
points are noteworthy in these figures:

1. The orientation of the etch pits on one side
   of the boundary is exactly opposite to that
   on the other side (i.e., the pits are
   oppositely oriented by 180°).

2. All the pits are of the same shape and have
   perfect matching on the match halves, i.e., all
   the pits are formed at the sites of dislocations.

These points strongly suggest the existence of twinning in natural topaz. It is suggested
that due to the fluctuations in the conditions of
growth, some twinned regions may develop during the
growth of topaz which may then act as twinned growth
nuclei and give rise to twinning in such crystals.
Since etch pits are nucleated at the sites of dislocations and according to Cahn (loc. cit.) dislocations play an important role in the development of mechanical twinning, it is reasonable to believe that twinning detected here may be of the mechanical type.

7.5 Conclusions

1. Etch patterns obtained on (001) habit as well as cleaved faces reveal the presence of linear defects in topas crystals.

2. Existence of grain boundaries and twinning in topas is revealed by etching technique.