An explanation of anomalous optical properties of topaz

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SUMMARY. A study has been made of topaz crystals showing a sectoral texture related to the growth of the crystal, and showing anomalous optical properties within the sectors. The growth surfaces responsible for the development of most of the sectors have been identified. The fluorine/hydroxyl sites in topaz are symmetrically equivalent in the solid crystal, but at a growth surface this equivalence may be lost, resulting in a reduction in the crystal symmetry and the ordering of fluorine and hydroxyl, the ordering scheme being retained once the crystal has formed. The reduction in symmetry expected to be produced by this ordering is in general agreement with the actual reduction in symmetry indicated by the optical properties. Heating of the topaz to about 950 °C results in the almost complete disappearance of the optical anomalies due to disordering, which may be related to the loss of hydroxyl from the crystal. Anomalous pyro- and piezoelectric phenomena may also be the result of ordering. Published optical and X-ray determinative curves for fluorine in topaz may give erroneous results for ordered topaz.

THE crystal structure of topaz, $Al_2SiO_4(F,OH)_2$ was determined independently by Pauling (1928) and by Alston and West (1928). The crystal structure was described as belonging to the orthorhombic centrosymmetric space group *Pbnm* and the structure has been successfully refined in that space group (Ribbe and Gibbs, 1971). However, topaz has some physical properties that must be considered anomalous if the crystal structure as described is correct and complete, as these properties indicate lower symmetry for topaz than that determined.

Topaz normally has the optic orientation $\alpha = a$, $\beta = b$, $\gamma = c$, OAP(010) and $Bx_a = [001]$. However, optical anomalies in topaz have long been known to occur (see Dana, 1892). A study of topaz showing sectoral texture in thin section was made by Rinne (1926) who found that not only did the orientation of the optic axial plane vary in different sectors, but

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also that the optic axial angle and the direction of the acute bisectrix could vary. In an X-ray study by Rinne, in spite of the wide variation in the orientation of the optical indicatrix in different sectors, no variation of the orientation of the crystallographic axes was detected. Rinne also reported that the anomalous optical effects disappeared after heating the sections to 950 °C for three to five hours.

Observations. Sectoral texture has been observed in a group of five orange-coloured uniterminal prismatic topaz crystals from Ouro Preto, Brazil (Department of Geology, University of Manchester, specimen number M900, distinguished as A, B, C, D, and E). The crystals were each about 8 mm across and 30–40 mm long. The prism faces of all the crystals show striations parallel to the prism axis about $\frac{1}{2}$ mm apart. Thin sections were cut as nearly as possible perpendicular to the prism axis, aided by the prominent edges of the [001] zone and by the very good (001) cleavage. When observed between crossed polars these sections show sectors that extinguish at different angles. The number and distribution of the sectors vary between the different crystals. Study of the sectors conoscopically shows interference figures that are not all centred, the small degree of off-centring varying from one sector to another, as also does the optic axial angle. Photographs of (001) thin sections of M900A, B, and C, observed between crossed polars, are shown in fig. 1. Detailed studies have been made of the crystals M900B and M900C using a universal stage and a tungsten lamp. Fig. 2 is a schematic diagram showing the sectoral texture observed in M900C on which the values of the optic axial angle $(2V_\gamma)$ and the extinction angle $(\beta:b)$ are indicated. A three-dimensional study of the crystal M900C shows that the sectors are related to the crystal faces and this indicates that they are produced during the growth of the crystal. The thin sections of the crystals observed show an outer rim of sectors corresponding to the prism growth planes and an inner core corresponding to the pyramidal growth planes.
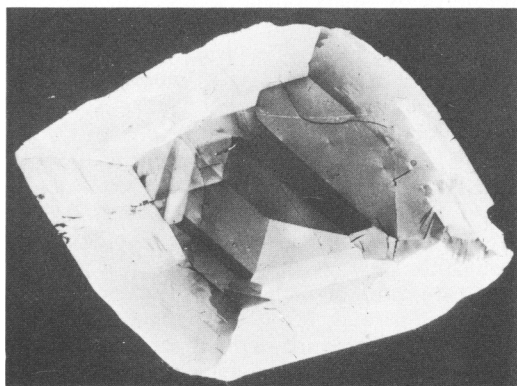
a

2mm
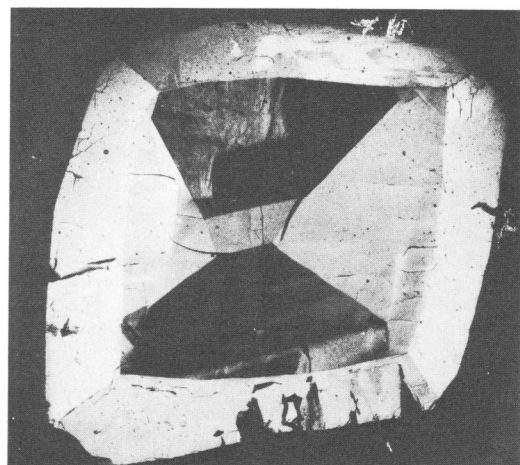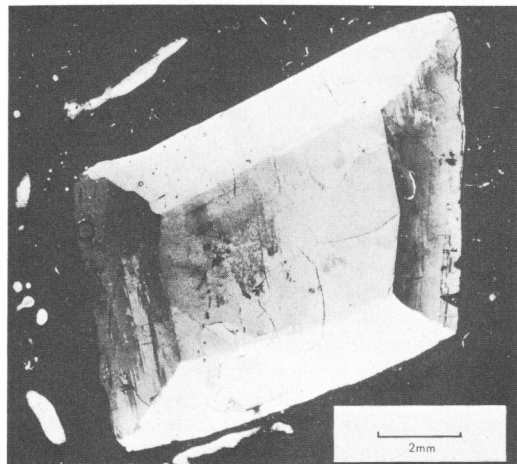
b

c

FIG. 1. Optical micrographs of (001) thin sections of topaz seen between crossed polars. (a) M900A; (b) M900B; (c) M900C. All × 11.

In the rim the indices of the growth planes giving rise to the sectors have been determined from growth bands and are found to be {110}, {120}, and {010}. The optic axial plane in each of these sectors is parallel to the c-axis and the indicatrix rotates about the acute bisectrix, which is normal to (001). The prism faces are believed to be alternations of {110} and {120} faces, which results in the observed surface striations. The sectors corresponding to the prism faces arise mainly from intergrowths on the two types of plane. The optic axial angle varies from 45° for {110} growth sectors to 58° for {120} sectors with intermediate values corresponding to the intergrowths. The extinction angles (β:b) vary from 9° for {110} sectors to 20° for {120} sectors. Although {010} faces are not seen on the surface of the crystal, {010} growth sectors are observed inside the crystal for which the value of $2V_\gamma$ is 50° and the extinction angle is zero. In some sectors near to the {010} sectors the growth bands are not sufficiently distinct to enable the growth planes giving rise to the sectors to be indexed with certainty but, by analogy with forms common in other topaz crystals, they are possibly {130} or {250}. The value of $2V_\gamma$ of 58° for these sectors is greater than for the {120} sectors, and the extinction angle is 22°.

The only pyramidal faces seen on the surface of the crystal M900C are {111}, although other pyramidal faces must have existed during crystal growth to produce the observed sectors. The sectors marked M in fig. 2 have sharp boundary traces parallel to (110) or (1$\bar{1}$0) and their growth planes can be represented by {11l}. From a thin
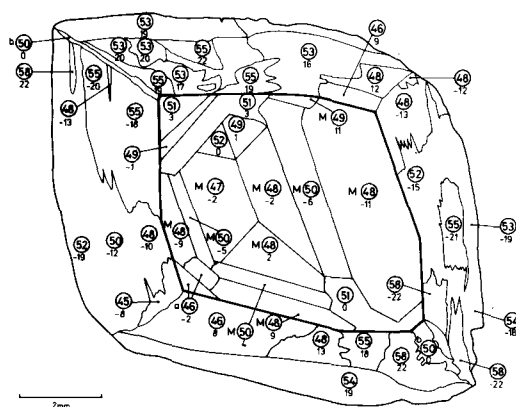

2mm

FIG. 2. Schematic diagram showing the sectoral texture and optical properties of M900C. The core and rim are separated by a heavy line. The letters M and a in the core indicate {11l} and {ho$l$} sectors respectively. The letter b in the rim indicates {010} sectors. Values of $2V_\gamma$ are circled, values of the extinction angles are shown below the values of $2V_\gamma$ for the corresponding sectors.

section cut parallel to the c-axis and normal to the {11l}-planes it was determined that the outermost sectors in the core are {111} sectors and the next and the innermost sectors are {112} and {114} sectors respectively. The sectors marked a in fig. 2, with sharp boundaries parallel to the b-axis, probably arise from growth on {h0l} planes, possibly {101} because {101} is dominant in {h0l} (Seki, 1963), although the indices could not be determined. The positive acute bisectrix is inclined at about 3° and 1° to c for the M{11l} and a{h0l} sectors respectively.

The variation of $2V_\gamma$ and extinction angle for the various zones of M900C has been plotted in fig. 3a. The points relating to the intergrowths of {110} and {120} sectors can be seen to be close to a straight line between the points for the {110} and {120} sectors themselves (as also do the points relating to the {111} sectors). A plot of $2V_\gamma$ against extinction angle for M900B is shown in fig. 3b. In this case the linear trend of the points for the rim zones, which are again believed to be intergrowths of {110} and {120} sectors, is clearly visible. The values for $2V_\gamma$ are systematically lower for M900B than for M900C and this is believed to be due to a small difference in average composition.

Discussion. Topaz occurs with a range of compositions varying from $Al_2SiO_4F_2$ to about Al_2SiO_4-$[F_{0.7}(OH)_{0.3}]_2$, and the variations in composition have been correlated with variations in optical constants including $2V_\gamma$ (Ribbe and Rosenberg, 1971). If the variation in $2V_\gamma$ observed in the crystals studied results from composition variations across the crystal the fluorine content would be expected to vary by about 3 wt %. An electron-microprobe study of the crystal showed that fluorine content is constant to within ±0.5 wt % over the whole section, indicating that the variation in $2V_\gamma$ is not the result of compositional variation.

Although the sector boundaries are distinct when the thin section is viewed between crossed polars, in unpolarized light there is no sign of grain boundaries within the crystal and this fact, combined with the over-all shape of the crystal, indicates that it is not an intergrowth of topaz crystals in appreciably different orientations. This has been confirmed for crystal M900A. Single-crystal X-ray photographs of small flakes of the topaz that included a sector boundary show that the crystal is apparently single. A 2.3 mm disc of M900A showing a sector boundary between crossed polars was thinned with an ion-beam etching machine and observed in an electron microscope. No trace of the boundary was evident either as misorientation in the electron diffraction pattern or as strain features in electron micrographs. Sector boundaries were, however, evident in studies of topaz by the X-ray topographic technique (Isogami and Sunagawa, 1975; Phakey and Horney, 1976). It is clear that any misorientation of crystal structure across sector boundaries can only be small and is not therefore in itself responsible for the large optical anomalies.

The variation in the orientation of the optical indicatrix in each of the various sectors requires a reduction of the symmetry of the topaz from the orthorhombic space group to which it is normally assigned. The {010} growth sectors in the crystal rim behave as if they had retained their orthorhombic symmetry, the {hk0} sectors in the rim behave as if they had monoclinic symmetry with the diad parallel to the c-axis and the {hkl} sectors in the core of the crystal behave as if their symmetry were triclinic. These reductions in symmetry are believed to arise as a result of ordering of the hydroxyl and fluorine ions during the growth of the crystal.

In the space group *Pbnm* to which topaz is normally assigned the eight fluorine (or hydroxyl) sites in the unit cell are all equivalent, and the fluorine and hydroxyl are generally assumed to be
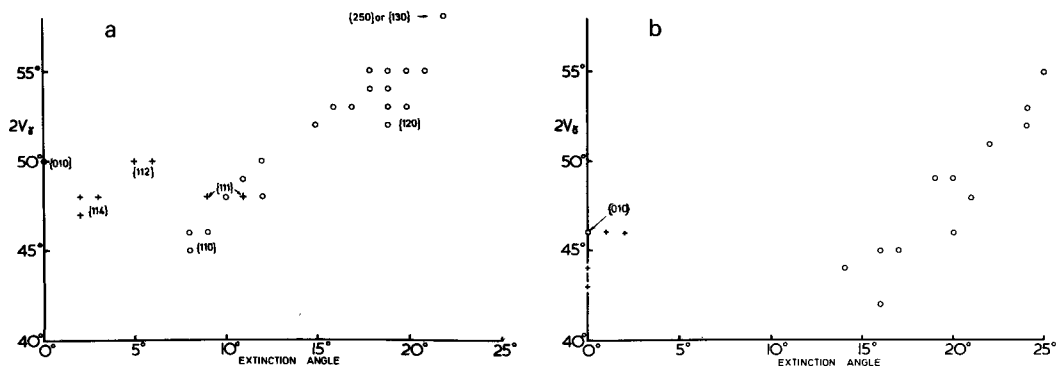

FIG. 3. Relationship of $2V_\gamma$ and extinction angles for (a) M900C and (b) M900B. Points relating to core sectors are indicated by a cross and rim sectors by a small circle.

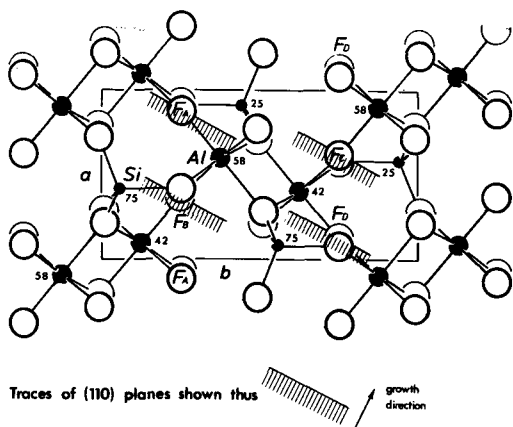Traces of (110) planes shown thus ///// / growth direction

FIG. 4. The crystal structure of topaz projected on to (001), with (110) growth planes indicated.

disordered in hydroxyl-bearing topaz. At a growth surface of the crystal, however, the sites may not be equivalent. Fig. 4 shows the crystal structure of topaz projected on (001). Only the contents of half of the unit cell are shown, the remaining contents of the cell being related by mirror planes perpendicular to the c-axis. The position and direction of growth of the (110) planes are indicated. It can be seen that the immediate surroundings of the fluorine/hydroxyl sites are different with respect to the growth plane for each of the sites and therefore, at the growth surface, the four sites are not equivalent. If this non-equivalence results in different relative preferences for fluorine and hydroxyl on the sites then ordering will occur and the symmetry of the crystal will be reduced. By considering the symmetry of the crystal relative to different growth planes it is possible to predict the symmetry that would be expected to occur by ordering for each type of plane. For a general $\{hkl\}$ growth plane the symmetry would be triclinic, for $\{okl\}$, $\{hol\}$, and $\{hko\}$ growth planes the symmetry would be monoclinic (with the mirror plane perpendicular to the a-, b-, and c-axes respectively) and for $\{100\}$, $\{010\}$, and $\{001\}$ growth planes the symmetry would remain orthorhombic. The symmetries predicted in this way for the various sectors in the topaz are consistent with the optical effects observed. The degree of ordering, and hence the actual values of $2V_\gamma$ and the extinction angle would be expected to vary for different growth planes producing the same crystal symmetry, as the environment of a particular fluorine/hydroxyl site will not be the same in relation to the different planes.

Basal (001) cleavage plates of M900B and M900C were heated in air at 950 °C for 4 h (a weight loss of about 0.1 % being detected in each case).

When thin sections cut from the plates were observed in a polarizing microscope the variation in extinction angles had almost disappeared and the value of the optical axial angle was found to be 44° in the crystal rim and 46° in the core for M900B and 49° in the rim and 51° in the core for M900C. The differences in $2V_\gamma$ between the rim and the core could reflect a small compositional variation, as it is possible that the non-equivalence of fluorine/hydroxyl sites on different growth planes would result in an over-all higher preference of one of the anions for particular faces. The difference in fluorine content required to produce a difference of 2° in $2V_\gamma$ would be no more than 0.2 wt %, rather less than the precision of ±0.5 wt % fluorine determined by electron microprobe. The disappearance of the variation in extinction angle can be attributed to disordering of the hydroxyl and fluorine ions on heating. A study of the thermal breakdown of topaz M900A (Hampar, 1973) has shown that at about 950 °C the topaz begins to break down by losing water and the crystal structure becomes strained. The removal of some of the hydroxyl ions at this stage could possibly result in vacancies occurring in the structure, which would allow the diffusion of the large fluorine and hydroxyl ions required for disordering.

The ordering of hydroxyl and fluorine on the various sites need not be complete in order to produce detectable optical effects because of the large difference in polarizability of the fluorine ion and the asymmetrical hydroxyl ion. Thus the degree of ordering and hence the actual values of extinction angles and $2V_\gamma$ for corresponding growth sectors are likely to vary between two crystals that have grown under slightly different conditions, particularly with regard to rate of growth.

Because of the very similar size and X-ray scattering power of hydroxyl and fluorine ions the additional X-ray reflections that might be expected to be produced by the ordered topaz would be very weak, and because of the partial degree of ordering that may be present they might also be expected to be diffuse. Accordingly, it is not surprising that no such additional reflections have been reported. The non-observation of such additional reflections does not in the authors' view invalidate the ordering theory proposed.

Piezo- and pyroelectricity. Piezoelectricity has been detected in topaz (Adams and Graham, 1926) although some topaz specimens give a negative result (Greenwood, 1935). The ordering that occurs during growth can result in the loss of the centre of symmetry present in disordered topaz, and therefore the detection of a piezoelectric effect in some but not all topaz can readily be explained.

Friedel and Curie (1885) reviewed apparently contradictory results of studies of pyroelectricity in topaz, and in particular referred to the facts that topaz can exhibit the same charge at opposite ends of an axis on heating, and that more than one pyroelectric axis may be detected. Mack (1886) described the results of pyroelectric tests made on an (001) topaz section that showed optical anomalies. His results indicate that within the prism sectors there was a horizontal pyroelectric axis roughly at right angles to the crystal faces, and that in the pyramidal sectors the pyroelectric axes were at an angle to the section. Thus the pyroelectric properties appear to mirror the anomalous optical properties.

General conclusions. A single crystal can be considered as being made up of pyramid-shaped sectors each with its apex at the centre of the crystal and its base at a face. It is known that the chemical compositions of these sectors can differ in some minerals, and the origin and possible growth mechanisms of compositional sector zoning in staurolite and clinopyroxene has been discussed in detail by Hollister (1970) and by Hollister and Gancarz (1971) respectively. Hollister (1970) suggested that rate of growth combined with a favourable surface configuration of cation sites can be a factor in producing disorder in a crystal and speculated as to whether sectoral differences in symmetry could exist without a chemical difference. We believe that topaz is just such a case, where the sectoral texture results from the ordering of fluorine and hydroxyl ions on different schemes and to different degrees in the several sectors. Compositional variations between the sectors are small or non-existent. Another such case has been studied by Akizuki *et al.* (1978) who have proposed that the sectoral texture observed in adularia is correlated with ordering of aluminium and silicon ions produced during growth.

Ribbe and Rosenberg (1971) derived determinative curves for fluorine in topaz based on unit cell and optical measurements. From the present work it is clear that the optical properties of topaz depend also on the degree of ordering in the crystal, and great care must be taken when using optical properties to estimate the composition of topaz. The cell parameters of topaz might also depend on the degree of ordering, although the effect would be small. Whether it is large enough to affect the precision of Ribbe and Rosenberg's determinative curves is not known.

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