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morphological analysis is ambiguous, the crystallization of a small amount of the compound on a seed crystal, ground to a sphere, is useful. By this procedure, faces of additional forms (and often of the characteristic general form) appear as small facets on the sphere and their interfacial angles can be measured.

In favourable cases, even the space group can be derived from the morphology of a crystal: this is based on the so-called *Bravais–Donnay–Harker principle*. A textbook description is given by Phillips (1971, ch. 13).

Furthermore, measurements of the interfacial angles by means of the optical goniometer permit the determination of the relative dimensions of a 'morphological unit cell' with good accuracy. Thus, for instance, the interaxial angles α, β, γ and the axial ratio a:b:c of a triclinic crystal may be derived. The ratio a:b:c, however, may contain an uncertainty by an integral factor with respect to the actual cell edges of the crystal. This means that any one unit length may have to be multiplied by an integer in order to obtain correspondence to the 'structural' unit cell.

3.2.2.3. Etch figures

Additional information on the point group of a crystal can be gained from the face symmetry, which is usually determined by observation of etch figures, striations and other face markings. Etch pits are produced by heating the crystal in vacuum (evaporation from the surface) or by attacking it with an appropriate reagent, which should not be optically active. The etch pits generally appear at the end points of dislocation lines on the face. They exhibit the symmetry of one of the ten two-dimensional point groups which, in general,[22] corresponds to the symmetry of the crystal face under investigation.

The observation of etch figures is important when the morphological analysis is ambiguous (*cf.* Section 3.2.2.2). For instance, a tetragonal pyramid, which is compatible with point groups 4 and 4mm, can be uniquely attributed to point group 4 if its face symmetry is found to be 1. For face symmetry m, group 4mm would result. The (oriented) face symmetries of the 47 crystal forms in the various point groups are listed in column 6 of Table 3.2.1.3 and in column 3 of Table 3.2.3.2.

In noncentrosymmetric crystals, the etch pits on parallel but opposite faces, even though they have the same symmetry, may be of different size or shape, thus proving the absence of a symmetry centre. Note that the orientation of etch pits with respect to the edges of the face is significant (*cf.* Buerger, 1956), as well as the mutual arrangement of etch pits on opposite faces. Thus, for a pinacoid with face symmetry 1, the possible point groups $\bar{1}$, 2 and m of the crystal can be distinguished by the mutual orientation of etch pits on the two faces. Moreover, twinning by merohedry and the true symmetry of the two (or more) twin partners ('twin domains') may be detected.

The method of etching can be applied not only to growth faces but also to cleavage faces or arbitrarily cut faces.

3.2.2.4. Optical properties

Optical studies provide good facilities with which to determine the symmetry of transparent crystals. The following optical properties may be used.

[22] It should be noted, however, that asymmetric etch figures may occur that are due, for example, to an inclination of dislocation lines against the surface.

Table 3.2.2.3
Categories of crystal systems distinguished according to the different forms of the indicatrix

Crystal system	Shape of indicatrix	Optical character
Cubic	Sphere	Isotropic (not doubly refracting)
Tetragonal, Trigonal, Hexagonal	Rotation ellipsoid	Uniaxial — Anisotropic (doubly refracting)
Orthorhombic, Monoclinic, Triclinic	General ellipsoid	Biaxial — Anisotropic (doubly refracting)

3.2.2.4.1. Refraction

The dependence of the *refractive index* on the vibration direction of a plane-polarized light wave travelling through the crystal can be obtained from the optical indicatrix. This surface is an ellipsoid, which can degenerate into a rotation ellipsoid or even into a sphere. Thus, the lowest symmetry of the property 'refraction' is $2/m\ 2/m\ 2/m$, the point group of the general ellipsoid. According to the three different forms of the indicatrix, three categories of crystal systems have to be distinguished (Table 3.2.2.3).

The orientation of the indicatrix is related to the symmetry directions of the crystal. In tetragonal, trigonal and hexagonal crystals, the rotation axis of the indicatrix (which is the unique optic axis) is parallel to the main symmetry axis. For orthorhombic crystals, the three principal axes of the indicatrix are oriented parallel to the three symmetry directions of the crystal. In the monoclinic system, one of the axes of the indicatrix coincides with the monoclinic symmetry direction, whereas in the triclinic case, the indicatrix can, in principle, have any orientation relative to a chosen reference system. Thus, in triclinic and, with restrictions, in monoclinic crystals, the *orientation* of the indicatrix can change with wavelength λ and temperature T (orientation dispersion). In any system, the *size* of the indicatrix and, in all but the cubic system, its *shape* can also vary with λ and T.

When studying the symmetry of a crystal by optical means, note that strain can lower the apparent symmetry owing to the high sensitivity of optical properties to strain.

3.2.2.4.2. Optical activity

The symmetry information obtained from *optical activity* is quite different from that given by optical refraction. Optical activity is in principle confined to the 21 noncentrosymmetric classes but it can occur in only 15 of them (Table 3.2.2.1). In the 11 enantiomorphism classes, a single crystal is either right- or left-handed. In the four non-enantiomorphous classes m, $mm2$, $\bar{4}$ and $\bar{4}2m$, optical activity may also occur; here directions of both right- and left-handed rotations of the plane of polarization exist in the same crystal. In the other six noncentrosymmetric classes, $3m$, $4mm$, $\bar{6}$, $6mm$, $\bar{6}2m$, $\bar{4}3m$, optical activity is not possible.

In the two cubic enantiomorphous classes 23 and 432, the optical activity is isotropic and can be observed along any direction.[23] For the other optically active crystals, the rotation of the plane of polarization can, in practice, be detected only in directions parallel (or approximately parallel) to the optic axes. This is because of the dominating effect of double refraction. No optical activity, however, is present along an inversion axis or along a direction parallel or perpendicular to a

[23] This property can be represented by enantiomorphic spheres of point group 2∞, *cf.* Table 3.2.1.6.

mirror plane. Thus, no activity occurs along the optic axis in crystal classes $\bar{4}$ and $\bar{4}2m$. In classes m and $mm2$, no activity can be present along the two optic axes if these axes lie in m. If they are not parallel to m, they show optical rotation(s) of opposite sense.

3.2.2.4.3. Second-harmonic generation (SHG)

Light waves passing through a noncentrosymmetric crystal induce new waves of twice the incident frequency. This second-harmonic generation is due to the nonlinear optical susceptibility. The *second-harmonic coefficients* form a third-rank tensor, which is subject to the same symmetry constraints as the piezoelectric tensor (see Section 3.2.2.6). Thus, only 20 noncentrosymmetric crystals, except those of class 432, can show the second-harmonic effect; *cf.* Table 3.2.2.1.

Second-harmonic generation is a powerful method of testing crystalline materials for the absence of a symmetry centre. With an appropriate experimental device, very small amounts (less than 10 mg) of powder are sufficient to detect the second-harmonic signals, even for crystals with small deviations from centrosymmetry (Dougherty & Kurtz, 1976).

3.2.2.5. Pyroelectricity and ferroelectricity

In principle, *pyroelectricity* can only exist in crystals with a permanent electric dipole moment. This moment is changed by heating and cooling, thus giving rise to electric charges on certain crystal faces, which can be detected by simple experimental procedures.

An electric dipole moment can be present only along a polar direction that has no symmetry-equivalent directions.[24] Such polar directions occur in the following ten classes: $6mm$, $4mm$, and their subgroups 6, 4, $3m$, 3, $mm2$, 2, m, 1 (*cf.* Table 3.2.2.1). In point groups with a rotation axis, the electric moment is along this axis. In class m, the electric moment is parallel to any direction in the mirror plane (direction $[u0w]$). In class 1, any direction $[uvw]$ is possible. In point groups 1 and m, besides a change in magnitude, a directional variation of the electric moment can also occur during heating or cooling.

In practice, it is difficult to prevent strains from developing throughout the crystal as a result of temperature gradients in the sample. This gives rise to piezoelectrically induced charges superposed on the true pyroelectric effect. Consequently, when the development of electric charges by a change in temperature is observed, the only safe deduction is that the specimen must lack a centre of symmetry. Failure to detect pyroelectricity may be due to extreme weakness of the effect, although modern methods are very sensitive.

A crystal is *ferroelectric* if the direction of the permanent electric dipole moment can be changed by an electric field. Thus, ferroelectricity can only occur in the ten pyroelectric crystal classes, mentioned above.

3.2.2.6. Piezoelectricity

In piezoelectric crystals, an electric dipole moment can be induced by compressional and torsional stress. For a uniaxial compression, the induced moment may be parallel, normal or inclined to the compression axis. These cases are called longitudinal, transverse or mixed compressional piezoeffect, respectively. Correspondingly, for torsional stress, the electric moment may be parallel, normal or inclined to the torsion axis.

The *piezoelectricity* is described by a third-rank tensor, the moduli of which vanish for all centrosymmetric point groups. Additionally, in class 432, all piezoelectric moduli are zero owing to the high symmetry. Thus, piezoelectricity can only occur in 20 noncentrosymmetric crystal classes (Table 3.2.2.1).

The piezoelectric point groups 422 and 622 show the following peculiarity: there is no direction for which a longitudinal component of the electric moment is induced under uniaxial compression. Thus, no longitudinal or mixed compressional effects occur. The moment is always normal to the compression axis (pure transverse compressional effect). This means that, with the compression pistons as electrodes, no electric charges can be found, since only transverse compressional or torsional piezoeffects occur. In all other piezoelectric classes, there exist directions in which both longitudinal and transverse components of the electric dipole moment are induced under uniaxial compression.

An electric moment can also develop under hydrostatic pressure. This kind of piezoelectricity, like pyroelectricity, can be represented by a first-rank tensor (vector), whereby the hydrostatic pressure is regarded as a scalar. Thus, piezoelectricity under hydrostatic pressure is subject to the same symmetry constraints as pyroelectricity.

Like 'second-harmonic generation' (Section 3.2.2.4.3), the piezoelectric effect is very useful for testing crystals for the absence of a symmetry centre. There exist powerful methods for testing powder samples or even small single crystals. In the old technique of Giebe & Scheibe (*cf.* Wooster & Brenton, 1970), the absorption and emission of radio-frequency energy by electromechanical oscillations of piezoelectric particles are detected. In the more modern method of observing 'polarization echoes', radio-frequency pulses are applied to powder samples. By this procedure, electromechanical vibration pulses are induced in piezoelectric particles, the echoes of which can be detected (*cf.* Melcher & Shiren, 1976).

[24] In the literature, the requirement for pyroelectricity is frequently expressed as 'a unique (or singular) polar axis'. This term, however, is misleading for point groups 1 and m.

references