CRYSTALLOGRAPHY

UNIT I

SYLLABUS

Dfinotion of cryastal .Morphology character of crystal :faces_-form-edge-solide angles-interfical angles.contact goinometer and its uses .Symmetry elements in crystal .crystallographic axis and axial ratio-parameters -indices and symbols: millers system of notation .laws of crystallography:law of constancy of interfacial angles.law of rational indices .classification of crystal system.study of :holohedral,hemihedral hemimorphic and and enantiomorphous of crystal.

Definition of crystal

Crystal, any solid material in which the component atoms are arranged in a definite pattern and whose surface regularity reflects its internal symmetry.

Morphological characters of crystals

Faces

The crystal are bounded by flat surfaces which are known as faces. A crystal may have only two faces of the same geometrical shape or it may have up to forty-eight faces of a combination of geometrical shapes.(or)

crystal face One of the relatively flat surfaces by which a crystal is bounded. Faces are produced naturally during the process of crystal growth. Cut and polished gemstones are bounded by plane faces which are often produced artificially and which, therefore, are not crystal faces.

Forms

A crystal form is a set of crystal faces that are related to each other by symmetry. To designate a crystal form (which could imply many faces) we use the Miller Index, or Miller-Bravais Index notation enclosing the indices in curly

Edges

The line of intersection formed by any two adjacent faces in a crystal is call an edge.

Solid angle

The points of intersection formed by three or more adjacent faces in a crystal are called solid angle.

Interficial angle

In a crystal, the angle between normal of two adjacent faces is called ‘interfacial angle’ . Interfacial angles are measured either with a contact goniometer or a reflecting goniometer.

Contact goniometer and its uses

A contact goniometer consists of two metal rules pivoted together at the centre of a graduated semicircle. The instrument is placed with its plane perpendicular to an edge between two faces of the crystal to be measured, and the rules are brought into contact with the faces. The angle between the rules, as read on the graduated semicircle, then gives the angle between the two faces. The rules are slotted, so that they may be shortened and their tips applied to a crystal partly embedded in its matrix. The instrument illustrated is employed for the approximate measurement of large crystals.

n crystallography, goniometers are used for measuring angles between crystal faces. They are also used in X-ray diffraction to rotate the samples. The groundbreaking investigations of physicist Max von Laue and colleagues into the atomic structure of crystals in 1912 involved a goniometer.

Symmetry elements in crystals

crystal symmetry In well-formed crystals, the symmetrically arranged faces reflect the internal arrangement of atoms. The symmetry of individual crystals is determined by reference to three elements.

Plane of symmetry

The plane of symmetry (also called the 'mirror plane' or 'symmetry plane') is a plane by which the crystal may be divided into two halves which are mirror images of each other.

Axis of symmetry

The axis of symmetry is a line about which a crystal may be rotated through 360°/n until it assumes a congruent position; n may equal 2, 3, 4, or 6 (but not 1), depending on the number of times the congruent position is repeated. These correspond respectively to 2-fold (diad), 3-fold (triad), 4-fold (tetrad), and 6-fold (hexad) axes.

if an object can be rotated about an axis and repeats itself every 90o of rotation then it is said to have an axis of 4-fold rotational symmetry. The axis along which the rotation is performed is an element of symmetry referred to as a rotation axis. The following types of rotational symmetry axes are possible in crystals.

1-Fold Rotation Axis - An object that requires rotation of a full 360o in order to restore it to its original appearance has no rotational symmetry. Since it repeats itself 1 time every 360o it is said to have a 1-fold axis of rotational symmetry.

2-fold Rotation Axis - If an object appears identical after a rotation of 180o, that is twice in a 360o rotation, then it is said to have a 2-fold rotation axis (360/180 = 2). Note that in these examples the axes we are referring to are imaginary lines that extend toward you perpendicular to the page or blackboard. A filled oval shape represents the point where the 2-fold rotation axis intersects the page.

3-Fold Rotation Axis- Objects that repeat themselves upon rotation of 120o are said to have a 3-fold axis of rotational symmetry (360/120 =3), and they will repeat 3 times in a 360o rotation. A filled triangle is used to symbolize the location of 3-fold rotation axis.

4-Fold Rotation Axis - If an object repeats itself after 90o of rotation, it will repeat 4 times in a 360o rotation, as illustrated previously. A filled square is used to symbolize the location of 4-fold axis of rotational symmetry.

6-Fold Rotation Axis - If rotation of 60o about an axis causes the object to repeat

itself, then it has 6-fold axis of rotational symmetry (360/60=6). A filled hexagon is used as the symbol for a 6-fold rotation axis.

Centre of symmetry

The centre of symmetry is a central point which is present when all faces or edges occur in parallel pairs on opposite sides of the crystal. Using these elements of symmetry, crystallographers have recognized 32 crystal classes and seven crystal systems. Symmetry is highest (high symmetry) in the cubic system, where many elements are repeated, and lowest (low symmetry) in the triclinic system, where only a centre of symmetry may be present (i.e. there may be no plane or axis of symmetry).

Crystallography axes and axial ratio

The crystallographic axes are imaginary lines that we can draw within the crystal lattice. These will define a coordinate system within the crystal. For 3-dimensional space lattices we need 3 or in some cases 4 crystallographic axes that define directions within the crystal lattices. Depending on the symmetry of the lattice, the directions may or may not be perpendicular to one another, and the divisions along the coordinate axes may or may not be equal along the axes. As we will see later, the lengths of the axes are in some way proportional to the lattice spacing along an axis and this is defined by the smallest group of points necessary to allow for translational symmetry to reproduce the lattice.

We here discuss the basic concepts of the crystallographic axes. As we will see, the axes are defined based on the symmetry of the lattice and the crystal. Each crystal system has different conventions that define the orientation of the axes, and the relative lengths of the axes.

Axial ratios are defined as the relative lengths of the crystallographic axes. They are normally taken as relative to the length of the b crystallographic axis. Thus, an axial ratio is defined as follows: Axial Ratio = a/b : b/b : c/b.

where a is the actual length of the a crystallographic axis, b, is the actual length of the b crystallographic axis, and c is the actual length of the c crystallographic axis.

For Triclinic, Monoclinic, and Orthorhombic crystals, where the lengths of the three axes are different, this reduces to

a/b : 1 : c/b (this is usually shortened to a : 1 : c)

For Tetragonal crystals where the length of the a and b axes are equal, this reduces to

1 : 1 : c/b (this is usually shorted to 1 : c)

For Isometric crystals where the length of the a, b, and c axes are equal this becomes

1 : 1 : 1 (this is usually shorted to 1)

For Hexagonal crystals where there are three equal length axes (a1, a2, and a3) perpendicular to the c axis this becomes:

1 : 1 : 1: c/a (usually shortened to 1 : c)

Parameters

The relative intercepts made by a crystal face on the three (or four) crystallographic axes are known as its parameters. For instance in Fig. 10.9, the three crystallographic axes are represented by XOX', YOY' and ZOZ', with their relative lengths as Ox = a, OY = b and OZ = c.

Their indices (Miller's System) are:

100, 010, $\bar{1}$00, 0$\bar{1}$0, 001, 00$\bar{1}$.

Obviously, the six faces together make a form in which each face has an identical mathematical relationship with the three axes. This may be read as “each axis being parallel to two axes and intercepting the third at a unit length.”

This statement can also be mathematically written as 100, which is a generalization for all the six faces of this particular form.

Hence 100 (one zero zero) is the symbol for the form in question and is written as (100), i.e. in brackets. This also happens to be the indices of one of the faces of the form. Hence a symbol may also be defined as the simplest of all the indices of a form.

Indices and symbols

Miller Indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.

Miller Index notation to designate crystal forms. A crystal form is a set of crystal faces that are related to each other by symmetry. To designate a crystal form (which could imply many faces) we use the Miller Index, or Miller-Bravais Index notation enclosing the indices in curly braces, i.e.{hkl} or {hkil}

Such notation is called a form symbol.

The method by which indices are determined is best shown by example. Recall, that there are three axes in crystallographic systems (*except sometimes in the hexagonal system adopts a convention where there are four axes). Miller indices are represented by a set of 3 integer numbers.

Example of the (111) plane:

If you want to describe the orientation of a crystal face or a plane of atoms within a crystal lattice, then there are series of steps that will lead you to its notation using

Miller indices.

1. The first thing that must be acertained are the fractional intercepts that the plane/face makes with the crystallographic axes. In other words, how far along the unit cell lengths does the plane intersect the axis. In the figure above, the plane intercepts each axis at exact one unit length.

2. Step two involves taking the reciprocal of the fractional intercept of each unit length for each axis. In the figure above, the values are all 1/1.

3. Finally the fractions are cleared (i.e., make 1 as the common denominator).

4. These integer numbers are then parenthetically enclosed and designate that specific crystallographic plane within the lattice. Since the unit cell repeats in space, the notation actually represents a family of planes, all with the same orientation. In the figure above, the Miller indice for the plane is (111).

Example of the (101) plane:

Example of the (102) plane:

Example of the (-102) plane:

Examples of the (102) and (201) planes:

Symbols

It is the simplest and most representative of the indices for a set of similar faces that constitute a crystallographic form. For instance, in Fig. 10.10, there are six exactly identical crystal faces, which have same mathematical relationship with all the three crystallographic axes.

Their indices (Miller's System) are:

100, 010, $\bar{1}$00, 0$\bar{1}$0, 001, 00$\bar{1}$.

Obviously, the six faces together make a form in which each face has an identical mathematical relationship with the three axes. This may be read as "each axis being parallel to two axes and intercepting the third at a unit length."

This statement can also be mathematically written as 100, which is a generalization for all the six faces of this particular form.

Hence 100 (one zero zero) is the symbol for the form in question and is written as (100), i.e. in brackets. This also happens to be the indices of one of the faces of the form. Hence a symbol may also be defined as the simplest of all the indices of a form.

Miller system of notation

The Miller indices can be used to specify directions and planes in a crystal [Ashcroft76,Kittel96]. The Miller indices of a plane are defined in the following way: First, three lattice vectors have to be defined. For cubic crystal systems, the lattice vectors are chosen along the edges of the crystallographic unit cell (unit cube). Any crystal plane intercepts the axes in certain points. The Miller indices are the ratios of these points and are given as a triplet of integer values (hkl). A Miller index 0 means that the plane is parallel to the respective axis. Negative indices are indicated with a bar written over the number.

In the notation of [Ashcroft76], (hkl) with square brackets instead of round brackets,

denotes a direction in the basis of the lattice vectors. The notation (hkl) denotes all planes that are equivalent to (hkl) by the symmetry of the crystal. Similarly, the notation (hkl)denotes all directions that are equivalent to(hkl) by symmetry.

In cubic crystal systems the Miller indices of a plane are the same as those of the direction perpendicular to the plane.

Law of crystallography

Crystallography is based on three fundamental laws.

(i) Law of constancy of interfacial angles: This law states that angle between adjacent corresponding faces is inter facial angles of the crystal of a particular substance is always constant inspite of different shapes and sizes and mode of growth of crystal. The size and shape of crystal depend upon the conditions of crystallisation. This law is also known as Steno's Law.

(ii) Law of rational indices: This law states that the ratio of intercepts of different faces of a crystal with the three axes are constant and can be expressed by rational numbers that the intercepts of any face of a crystal along the crystallographic axes are either equal to unit intercepts (i.e., intercepts made by unit cell) a, b, c or some simple whole number multiples of them e.g., na, n' b, n''c, where n, n' and n'' are simple whole numbers. The whole numbers n, n' and n'' are called Weiss indices. This law was given by Hauy.

(iii) Law of constancy of symmetry: According to this law, all crystals of a substance have the same elements of symmetry is plane of symmetry, axis of symmetry and centre of symmetry.

Classification of crystal system

In a crystal system, a set of point groups and their corresponding space groups are assigned to a lattice system. Of the 32 point groups that exist in three dimensions, most are assigned to only one lattice system, in which case both the crystal and lattice systems have the same name. However, five point groups are assigned to two lattice systems, rhombohedral and hexagonal, because both exhibit threefold rotational symmetry. These point groups are assigned to the trigonal crystal system. In total there are seven crystal systems: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal, and cubic.

Holohedral

It is that form in a crystal system, which shows development of all the possible faces in its domain. For instance, octahedron is a holohedral form because it shows all the eight faces developed on the crystal. Generally, holohedral forms develop in the crystals of highest symmetry in a crystal system. Such class of highest symmetry in a system is called its normal class

Hemihedral

It shows, as the name indicates, only half the number of possible faces of a corresponding holohedral form of the normal class of the same system. As such, all hemihedral forms may be assumed to have been derived from holohedral forms.

Obviously, two complimentary hemihedral forms (termed positive and negative or right and left) will necessarily embrace all the faces and characters of the parent holohedral form.

A hemihedral form develops due to decrease in the symmetry of a crystal. (Fig. 10.12)

Example:

Octahedron is the holohedral form and Tetrahedron (only four faces) is a hemihedral form developed from it. It has only four faces and occurs in crystals of Tetrahedrite class of isometric system, which has a lower symmetry than normal class.

Hemimorphic

It is also derived from a holohedral form and has only half the number of faces as in hemihedral form. In this case, however, all the faces of the form are developed only on one extremity of the crystal, being absent from the other extremity. In other words, such a crystal will not be symmetrical with reference to a center of symmetry. (Fig. 10.13

Enantiomorphous

An enantiomorphous form is composed of faces placed on two crystals of the same

mineral in such a way that faces on one crystal become the mirror image of the form of faces on the other crystal. Despite that, each form is independent, that is, though having an identical mathematical relationship, and one form cannot be interchanged with its counterpart on the other crystal. As right hand and left hand having similar relation to the body axis are not interchangeable, so is the case with enantiomorphous forms.

The forms and the corresponding crystals showing these forms are referred as left and right handed.

Crystals of quartz show best-developed enantiomorphous forms.

By

M.P.Kowsalya