



Soviet-era science, translated into English

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1965

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Abstract

Full Text

CRYSTALLOGRAPHY

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GROWTH FORMS OF CRYSTALS

AND THE CRYSTAL STRUCTURE OF $YCl(OH)_2$

(Presented by Academician N. V. Belov, 19 XII 1964)

Crystalline yttrium hydroxychloride $YCl(OH)_2$ was obtained, along with other solid phases, during the hydrothermal synthesis of yttrium-iron garnet crystals (¹). Its single crystals have the form of plates elongated in one of the directions and sometimes acquiring a needle-like form.

The relatively isometric platy crystals are the best developed; these were used for a photogoniometric study on a two-circle optical goniometer GD-1.

The results of the measurements, after their treatment on a stereographic projection, are given in Table 1. The z axis was taken as the most developed direction in the crystal, and the y axis as the direction perpendicular to the plane of the crystal plate.

Table 1

Face number in the positive octant	Angle with axis $+x$	Angle with axis $+y$	Angle with axis $+z$	Face symbol	Number of faces	Simple growth form
1	60°	90°	30°	(101)	4	Rhombic prism
2	45	45	90	(120)	4	» »
3	26	64	90	(110)	4	» »
4	14	76	90	(210)	4	» »
5	61	76	33	(111)	8	Rhombic dipyramid
6	90	0	90	(010)	2	Pinacoid

From the stereographic projection it follows that the $YCl(OH)_2$ crystals belong to the class

Figure 1

Figure 1: Figure 1

$$\frac{2}{m} \frac{2}{m} \frac{2}{m} = mmm$$

(the rhombic-dipyramidal class). The faces of the pinacoid (010) are the most developed. Along the direction [010] the unit-cell parameter should be the largest, in agreement with the parameter ratio $a : b : c = 0.499 : 1 : 0.288$, obtained from the unit face on the stereographic projection. Along the faces of the pinacoid (100), $\text{YCl}(\text{OH})_2$ single crystals possess cleavage.

For X-ray structural studies, $\text{YCl}(\text{OH})_2$ single crystals of size $0.2 \times 0.4 \times 0.8 \text{ mm}^3$ were selected. The unit-cell parameters, obtained from rotation X-ray photographs of the crystal about the principal crystallographic directions, from zero-layer line development photographs, and also from a Debyeogram taken in an RKU-114 camera, are:

$$a = 6.21, \quad b = 12.56, \quad c = 3.62 \text{ \AA}$$

(hence $a : b : c = 0.494 : 1 : 0.288$). With $D_{\text{meas.}} = 3.71 \text{ g/cm}^3$, the unit cell contains 4 formula units.

On an X-ray goniometer, the zero, 1st, 2nd, and 3rd layer-line developments of rotation about the c axis and the zero-layer development about the a axis were recorded. Since the absorption edge of the Y K_α -series is very close to the wavelength

waves of Mo K_α (usually used in X-ray structural studies), the photographs were taken with Ag K_α -Cu K_α radiation. Because of the nonspherical shape of the specimens, absorption introduced a considerable error into the estimation of intensities, especially when Cu K_α radiation was used. Therefore the Cu-radiation photographs were used chiefly to determine the dimensions of the crystal unit cell, while the subsequent X-ray structural study was based on X-ray patterns taken with Ag K_α radiation.

Fig. 1. Y-polyhedron formed by Cl and O(OH) atoms $\sqrt[4]{2}$

Analysis of the reflection intensities showed that the structure of $\text{YCl}(\text{OH})_2$ has a pseudoperiod $b' = b/2$.

Systematic extinctions of reflections with $k = 2n + 1$ were observed only in the $0kl$ zone, and reflections with $h + l = 2n + 1$ in the $h0l$ zone; thus the possible space groups are $D_{2h}^{16} = Pbnm$ and $C_{2v}^9 = Pbn2_1$. Since optical-goniometric studies indicate the presence of a center of symmetry in the crystals in the absence of piezoelectricity, we adopted for this compound the Fedorov group

Figure 2

Figure 2: Figure 2

$D_{2h}^{16} = Pbnm$. The intensities of the observed reflections were estimated visually by a blackening scale with a step of $\sqrt[4]{2}$, after which the usual method was used to obtain the arrays F_{hkl}^2 and F_{hkl} .

Table 2

Atoms	x	y	z
Y	0.250	0.055	0.250
Cl	0.108	0.215	0.750
(OH) _I	0.125	-0.050	0.750
(OH) _{II}	0.508	0.083	0.750

The x and y coordinates of the yttrium atoms were determined from the Patterson projection $P(uw)$. The first projections of the electron density $\rho(xy)$ were constructed from the amplitudes F_{hk0} , with signs taking into account first only the yttrium atoms, then yttrium and chlorine, and finally all atoms. The discrepancy factor calculated from the coordinates of all atoms for the F_{hk0} array at this stage was 16.9% for 87 nonzero amplitudes. To determine the z coordinate of the atoms, the Patterson projection $P(uw)$ was used; from it it followed that all atoms are located in mirror planes m . Refinement of the atomic coordinates was carried out on a large computer by the least-squares method ⁽²⁾. A total of 260 nonzero amplitudes F_{hkl} were used.

Fig. 2. Character of the formation of a layer from Y-polyhedra

The finally accepted atomic coordinates are given in Table 2.

The discrepancy factor of the structure over all nonzero amplitudes F_{hkl} , calculated from the refined coordinates, is 16.5% ($\sin \vartheta/\lambda \leq 0.915$). Taking into account 102 reflections for which $F_{\text{exp}} = 0$ ($\sin \vartheta/\lambda \leq 0.60$), the factor is 21.7% (the intensity of these reflections was taken to be equal to half the minimum observed value). The significant increase in R is explained by the large number of introduced experimental “zeros” (about 50%), arising because of the presence of a pseudoperiod in the structure.

Interatomic distances. The nearest neighbors to yttrium proved to be 8 neighbors: two Cl atoms and 6 O atoms (hydroxyl groups), which form around yttrium an octahedron—a trigonal prism with semioctahedra on two faces (Fig. 1).

The distances Y–OH in this polyhedron are: 2.30; 2.33; 2.37(2); 2.44(2) Å; Y–Cl = 2.85(2) Å.

Fig. 3. Projection of the structure of $\text{YCl}(\text{OH})_2$ in coordination polyhedra onto the (001) plane

Figure 3: Fig. 3. Projection of the structure of $\text{YCl}(\text{OH})_2$ in coordination polyhedra onto the (001) plane

Fig. 4. Positions of atoms in the structure of $\text{YCl}(\text{OH})_2$ (xy projection)

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Fig. 3. Projection of the structure of $\text{YCl}(\text{OH})_2$ in coordination polyhedra onto the (001) plane

The edges of the polyhedron are OH–Cl: 3.34(2); 3.11(2); 2.99(2) Å; Cl–Cl: 3.62 Å; OH–OH: 3.62(2); 2.94(2); 2.91(2); 2.77(2); 2.70(2) Å.

The principal motif in the structure should be regarded as continuous walls of octahedra extending parallel to the (010) plane.

Fig. 4. Positions of atoms in the structure of $\text{YCl}(\text{OH})_2$ (xy projection)

Within the walls the polyhedra are joined to one another in the [001] direction along the faces of the base of the prism into columns, which, in turn, in the “lateral” direction [100] are joined along the edges of the semioctahedra (Figs. 2 and 3). The entire structure as a whole consists of such layers; moreover, the first, third, fifth, etc., layers are translationally identical. The intermediate layers are displaced relative to the principal ones, being connected with them by glide planes n , passing through $1/4b$ and $3/4b$.

The arrangement of atoms in the structure corresponds to the noted pseudoperiod $b/2$. Indeed, from Fig. 4 it is clearly seen that for yttrium atoms there is a half-translation along the b axis, whereas the remaining, lighter atoms Cl and O are connected by the full translation $-b$.

From consideration of the structure one should expect the presence in $\text{YCl}(\text{OH})_2$ crystals of a glide plane parallel to the layers (010); the direction

the slip direction [001], and, accordingly, the greatest growth rate of the crystals in the [001] direction, leading to the formation of needle-like crystals, can be explained by the preferential emergence in this direction of screw dislocations, which are growth centers and arise when the lattice is disturbed as a result of the incorporation of impurities, the capture of inclusions, and abrupt changes in temperature. On the growing face of the pinacoid (010), a screw dislocation can apparently form only by the attachment of a three-dimensional nucleus to the stepped surface according to the mechanism proposed in ⁽³⁾.

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Received
20 XI 1964

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