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CRYSTAL STRUCTURE OF Y-OXYSILICATE $Y_2[SiO_4]O$

The initial data on synthetic oxysilicate Y_2SiO_5 are given in ([1–4]). In ([4]), from the mappings of three layers $hk0$, $hk1$, and $hk2$ (CuK_α radiation–

Table 1

Y_2SiO_5. Coordinates of the basis atoms and isotropic thermal corrections

Atom	x/a	y/b	z/c	U_j
Y_I	0.056 ± 0.003 (0.058)	0.378 ± 0.002 (0.330)	0.141 ± 0.003 (0.143)	0.340 (1.3)
Y_{II}	0.179 ± 0.003 (0.182)	−0.257 ± 0.002 (−0.250)	−0.037 ± 0.003 (−0.037)	0.350 (0.9)
Si	0.123 ± 0.006 (0.130)	−0.093 ± 0.006 (−0.096)	0.181 ± 0.006 (0.184)	0.020 (1.5)
O_I	0.050 ± 0.009 (0.042)	−0.287 ± 0.009 (−0.287)	0.118 ± 0.009 (0.126)	0.410 (2.2)
O_{II}	0.196 ± 0.009 (0.184)	−0.002 ± 0.009 (−0.008)	0.089 ± 0.009 (0.090)	0.610 (5.2)
O_{III}	0.218 ± 0.009 (0.221)	−0.157 ± 0.009 (−0.128)	0.298 ± 0.009 (0.296)	0.650 (4.5)
O_{IV}	0.013 ± 0.009 (0.034)	0.071 ± 0.009 (0.094)	0.203 ± 0.009 (0.188)	0.380 (4.8)
O_V	0.132 ± 0.009 (0.125)	0.398 ± 0.009 (0.415)	−0.015 ± 0.009 (−0.019)	0.720 (4.0)

* The results of the authors of ([4]) are given in parentheses.

Table 2

Interatomic distances in the structure of $Y_2[SiO_4]O$

Y_I-octahedron

Y_I—O_I = 2.28 (2.27)	O_I—O_V = 2.98	O_{IV}—O_{IV} = 2.73
O_{IV} = 2.29 (2.06)	O_I—O_{III} = 3.45	O_{IV}—O_V = 3.33
O_V = 2.33 (2.39)	O_I—O_{IV} = 3.18	O_V—O_V = 2.80
O_{III} = 2.30 (2.26)	O_I—O_V = 2.93	O_V—O_{III} = 2.87
O_{IV} = 2.31 (2.62)	O_{IV}—O_V = 3.98	O_V—O_{III} = 3.52
O_V = 2.21 (2.19)	O_{IV}—O_{III} = 3.34	O_{III}—O_{IV} = 3.61

Y_{II}-octahedron

Y_{II}—O_{II} = 2.33 (2.35)	O_V—O_{III} = 3.26	O_V—O_V = 2.75
O_V = 2.39 (2.38)	O_V—O_{II} = 4.24	O_I—O_{II} = 4.09
O_V = 2.35 (2.36)	O_V—O_I = 2.93	O_{III}—O_{II} = 2.76
O_{II} = 2.37 (2.46)	O_{III}—O_{III} = 2.79	O_{III}—O_V = 2.86
O_{III} = 2.32 (2.45)	O_{III}—O_I = 3.73	O_I—O_{III} = 3.25
O_V = 2.15 (2.27)	O_{III}—O_V = 3.46	O_{II}—O_V = 3.01

Si-tetrahedron

Si—O_I = 1.60 (1.66)	O_I—O_{II} = 2.52 (2.53)
O_{II} = 1.66 (1.57)	O_I—O_{III} = 2.67 (2.75)
O_{III} = 1.63 (1.55)	O_I—O_{IV} = 2.69 (2.72)
O_{IV} = 1.66 (1.64)	O_{II}—O_{III} = 2.76 (2.70)
	O_{II}—O_{IV} = 2.71 (2.36)
	O_{III}—O_{IV} = 2.66 (2.60)

···200 nonzero structural amplitudes), a preliminary determination of the crystal structure of Y_2SiO_5 was given. The coordinates of 8 independent atoms found in ([4]) and the interatomic distances calculated from them are presented in Tables 1 and 2. Among several unsatisfactory ones, one Y—O distance, equal to 2.064 Å, stands out, and in the Si tetrahedron O—O = 2.36 Å.

In our refinement of the atomic coordinates of the crystal structure of Y_2SiO_5, 800 nonzero structural amplitudes from 7 layers, $hk0$—$hk5$ and $h0l$, were used. The intensities (Mo K_α radiation,

$$\max \sin \vartheta/\lambda = 0.9 \text{ Å}^{-1}$$

) were estimated visually using a $\sqrt[4]{2}$ blackening scale.

Fig. 1. Structure of Y_2SiO_5, projection xz. Along the long axis (c) extend serrated ribbons of deformed Y-octahedra. The light and dark ribbons are located in two successive layers at different levels. SiO_4 tetrahedra connect

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The entire set of intensities was obtained from a crystal elongated along the c axis, with dimensions $0.08 \times 0.1 \times 0.3$ mm^3. Single-crystal samples of the compound Y_2SiO_5 were obtained by hydrothermal crystallization in the system K_2O—Y_2O_3—SiO_2—H_2O at 450° and $\sim$ 1500 atm. According to X-ray spectral analysis (V. V. Lider, Institute of Crystallography), the crystals studied contain no impurities. The quantitative composition, confirmed by the results of chemical analysis (Y_2O_3 79.21%; SiO_2 20.43%; K_2O 0.006%; H_2O 0.2%; $\Sigma = 99.9\%$, analyst V. S. Bykova), also raises no doubts.

The parameters of the monoclinic cell, refined on a DRON-I diffractometer (Cu K_α radiation), are:

$$a = 10.410 \pm 0.003 \text{ Å}, \qquad b = 6.721 \pm 0.002 \text{ Å}, \qquad c = 12.490 \pm 0.005 \text{ Å};$$

$$\beta = 102°39' \pm 2'$$

and coincide with the results of ([3]). $Z = 8$ ($d = 4.6$). The space group is $C_{2h}^6 = I2/c(a)$.

From the entire three-dimensional array, a three-dimensional function was calculated···

Patterson, the analysis of which agrees well with the results of ([4]). The refinement of the structure of Y_2SiO_5 was carried out by the least-squares method.

Since the absorption edge for yttrium coincides with the K_α series of Mo radiation, for the Y atom a correction for anomalous scattering was used, $f_{\text{corr}} = f_0 + \Delta f'$. The initial R factor, equal to 17.3% ($B = 0.32$, absorption was not

Figure 2

Figure 2: Figure 2

taken into account; $\mu R = 0.9$), upon refinement of the positional parameters of the Y atoms decreased to 14.7%. Refinement of the lighter Si and O atoms led to a further decrease of the discrepancy coefficient to 10.1%. The final coordinates of the 8 independent atoms and the interatomic distances calculated from them are presented in Tables 1 and 2, together with the data of ([4]).

Fig. 2. Vertical (parallel to the elongation) chains of Y octahedra (toothed)

The crystal structure of yttrium oxysilicate Y_2SiO_5 may be regarded as built of orthotetrahedra SiO_4 and octahedra YO_6. In the Si tetrahedron the mean Si–O distance is 1.63 Å and O–O = 2.70 Å, with an insignificant spread: the limiting Si–O values are 1.60-1.66 and O–O = 2.52-2.76 Å. The yttrium atoms occupy two general crystallographic positions in distorted YO_6 octahedra. The mean Y–O distance is 2.3 Å, with limiting values of 2.21-2.33 Å in the Y octahedron and 2.15-2.39 Å in the Y octahedron. The next distances in magnitude are 3.06 and 2.66 Å in the Y and Y octahedra, respectively. The lengths of the oxygen edges of the Y octahedra vary over wide limits, 2.76-4.24 Å.

In Fig. 1 the principal architectural features of Y oxyorthosilicate Y Y $[SiO_4]O$ are evident. Along the long axis c = 12.49 Å extend toothed ribbons of Y polyhedra connected by common edges. The core of the ribbon is a chain in which the Y octahedra alternate in pairs at two levels with a small difference in height. The teeth are Y octahedra, connected to the core Y octahedra of their level by a common edge. Translationally identical ribbons along a are connected into a layer, parallel to the xz plane, by orthotetrahedra SiO_4. The next underlying layer is identical to the one just described, but is displaced by the oblique translation of the body-centered cell $(a+b+c)/2$. In Fig. 1 its dark ribbons appear between the light ribbons of the layer above. The flat layers in which the ribbons of octahedra lie are not isolated, but are connected with the ribbons of the layers above and below by toothed octahedra. These octahedra, connected by common edges, form columns along the b = 6.721 Å axis (Fig. 2), and it is they that determine the elongation of the crystals. The previously described, less effective chains parallel to the long c axis make the elongated crystals platy, with indistinct cleavage on (100).

The inclusion in the coordination sphere of the Y octahedron also of a 7th O with an elongated Y–O bond of 2.64 Å leads to the appearance of a common edge between the toothed octahedra of two neighboring translationally identical chains and to a less desirable common edge at the Si tetrahedron and Y octahedron. Both circumstances substantially worsen the valence balance. Transformation of the Y semipolyhedron into a distorted octahedron (we amputate one normal bond Y_2–O = 2.33 Å, but retain the elongated Y_2–O = 2.66 Å!) and the subsequent idealization of the octahedra leads to the "manifestation" in the

structure of an ideal closest cubic packing of O atoms, in which for every four Y octahedra there are six vacant ones (Fig. 3). The same ratio $^2/_3$ is obtained from the formula Y_2SiO_5, since in the case of close-

Fig. 3. Idealized motif of YO_6-octahedra. Occupied and empty octahedra alternate in the ratio 4 : 6

With the densest packing of 5 O anions in the compound Y_2SiO_5, there must be 5 octahedral voids, 2 of which are filled by the two types of Y represented in the formula.

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Note: Figure translations are in progress. See original paper for figures.