THE CRYSTALLOGRAPHY OF SYNTHETIC $YTaO_4$ AND FUSED FERGUSONITE[1]

R. B. FERGUSON

University of Manitoba, Winnipeg, Canada

ABSTRACT

By fusing the appropriate oxides in the cratered graphite electrode of an arc lamp at roughly 2100° C, a minute fragment of $YTaO_4$ was obtained which yielded single-crystal *x*-ray photographs. These show that $YTaO_4$ is not tetragonal as previously thought but monoclinic with $a_0 = 5.34$, $b_0 = 10.94$, $c_0 = 5.07$ Å, $\beta = 95.3°$, probable space group $I2/a$, $Z = 4$, S.G. (calc.) = 7.47. The indexed powder data are given. The earlier tetragonal cell is unreal. The powder pattern of natural fergusonites fused in the arc lamp electrode show that this mineral is isostructural with $YTaO_4$. The suggestion is made that original fergusonite may not be tetragonal but only pseudo-tetragonal with the monoclinic cell of $YTaO_4$.

Introduction

Since the first morphological description of fergusonite by Haidinger (1826), this mineral has been considered to be tetragonal with symmetry $4/m$ and with an axial ratio of $a:c = 1:1.464$. Barth (1926) showed that natural fergusonite specimens are nearly always metamict, but that they crystallize on heating to 400°C or higher to a polycrystalline mass which gives an *x*-ray powder pattern similar to that of synthetic $YTaO_4$ and $YNbO_4$. Barth was able to index these patterns using a tetragonal *P* lattice and an axial ratio close to that of Haidinger (1826). This yielded cell dimensions for $YTaO_4$, for example, of $a_0 = 7.76$, $c_0 = 11.43$ Å. Apparently fergusonite is always metamict, for no report of single-crystal *x*-ray photographs of this mineral has ever been published. Furthermore it is well known that when a single morphological fragment of a metamict mineral is recrystallized by heating, the product is polycrystalline and not a single crystal. For these reasons it has been impossible to confirm by single-crystal methods the tetragonal cell deduced by Barth (1926) for fergusonite and related compounds from powder photographs. Recently Berman (1955) has pointed out that natural fergusonites heated to approximately 400°–800°C for some time give powder patterns which can be indexed on a tetragonal cell with the approximate cell dimensions $a_0 = 5.18$ Å, $c_0 = 5.48$ Å. Berman's

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[1] An abstract has already been published (Ferguson, 1955).

experiments showed that the fergusonite pattern indexed by Barth (1926) is obtained when the specimens are heated above 800°C.

Experimental Details

With the help of several graduate students the writer attempted a structure analysis of synthetic $YTaO_4$ using powder data indexed on the tetragonal cell of Barth (1926) for which the assumed cell content is $8(YTaO_4)$. In attempting to take new *x*-ray powder photographs of $YTaO_4$ we at first had difficulty in fusing the constituent Y_2O_3 and Ta_2O_5 powders. An oxy-acetylene flame and an induction furnace were both tried with little success, but presently satisfactory results were obtained by using a cratered graphite electrode of an arc lamp. A "run" could be made by this method in about five minutes. During several runs of the synthetic $YTaO_4$, temperature measurements were made on the sample with an optical pyrometer, and these gave measurements of the order of 2100°C. During the runs the samples appeared to be molten, so that the melting point of $YTaO_4$ is probably somewhat less than this temperature, likely the order of 2000°C.

From the carefully indexed powder photographs (the indexing was only slightly different from that of Barth (1926)) and from expected coordinations for the Y and Ta atoms, we tried to work out a reasonable structure. Our efforts were in vain, and so attempts were presently made to get single-crystal fragments of $YTaO_4$ to provide more definitive crystallographic data. This was done by crushing the bead after a run, and examining the fragments between crossed Nicols on a polarizing microscope. The anisotropic character of the material was easily seen, but the great majority of the fragments from all runs were either polycrystalline or seemingly twinned polysynthetically. An examination on the universal stage of some very small apparently single crystals suggested that the mineral is uniaxial. Later *x*-ray work showed that the crystals can be only pseudo-uniaxial, and the effect observed on the U-stage was presumably due either to this or to multiple growth of the fragments examined. The later cell dimensions suggest that the crystal might well be pseudo-uniaxial along *b*[010].

Many fragments that looked promising under the microscope were mounted and *x*-rayed in an attempt to find a rational axis of a single crystal. After much patient work one minute fragment about 0.05 mm. in size was found which finally permitted *x*-ray orientation about a rational axis, and an oscillation photograph and a series of Weissenberg photographs were taken around this axis. Although this particular fragment appeared single under the microscope, it gave a double set of spots, and the fragment apparently consists of two crystals with one common axis, that used for our photographs. The two sets of spots were, however, easy to distinguish as the plot of the 0–level Weissenberg (Fig. 1) shows. The single-crystal photographs show clearly that synthetic $YTaO_4$ is not tetragonal as previously assumed, but monoclinic with the following characteristics: $a_0 = 5.34 \pm 0.02$ Å, $b_0 = 10.94 \pm 0.04$ Å, $c_0 = 5.07 \pm 0.02$ Å, $\beta = 95.3 \pm 0.3°$, probable space group $I2/a$, $Z = 4$, S.G. (calc.) = 7.47. The powder data indexed on this cell are given in Table 1.

Fig. 1 shows that the rotation axis of our crystal is *b*[010], and that this is the axis common to the two crystals that make up the fragment. As the two crystals are related by a turn of $\beta°$ in one direction or of $\beta^{*°}$ in the opposite direction around *b* and not by any symmetry operation, we concluded that the fragment is a parallel growth and not a twin. We have not been able to determine whether the polysynthetic "twins" observed under the microscope are in reality twins or whether they are parallel growths of the type we have *x*-rayed.

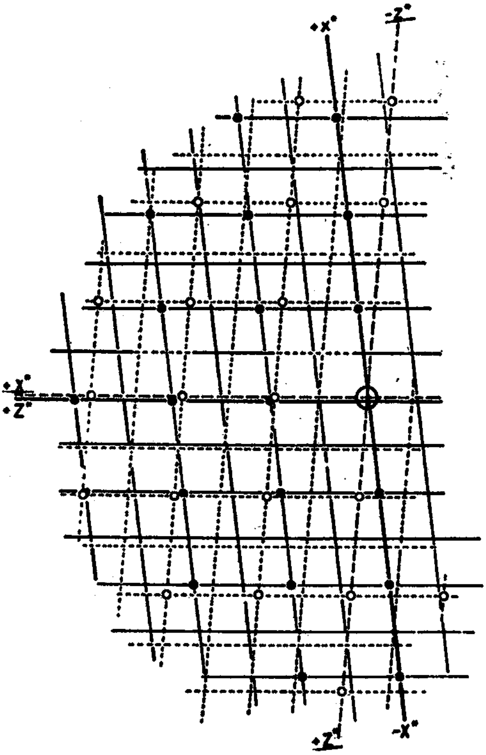

FIG. 1. Plot of 0-level Weissenberg photograph taken around *b*[010] showing the two reciprocal nets related by a turn of $\beta^{*°}$ around *b*.

TABLE 1. $YTaO_4$: *X*-RAY POWDER PATTERN

Monoclinic, $I2/a$; $a_0 = 5.34$, $b_0 = 10.94$, $c_0 = 5.07$ Å, $\beta = 95.3°$, $Z = 4$

I(obs.)	θ(Cu)	d (meas.)	(*hkl*)	d (calc.)
1	8.10°	5.47 Å	(020)	5.47 Å
4	9.25	4.79	(110)	4.78
10	14.20	3.14	$(\bar{1}21)$	3.14
½	14.80	3.02	(130)	3.01
10	15.20	2.94	(031) (121)	2.96 2.95
4	16.35	2.74	(040)	2.74
4	16.95	2.64	(200)	2.66
3	17.80	2.52	(002)	2.52
½	18.90	2.38	(220) $(\bar{2}11)$	2.39 2.39
½	19.60	2.30	$(\bar{1}12)$ (022)	2.31 2.29
3	21.0	2.15	(112) (141)	2.16 2.16
2	22.45	2.02	$(\bar{2}31)$ (150) (051)	2.03 2.02 2.01
3	23.63°	1.921 Å	(231) $(\bar{2}02)$	1.926 Å 1.921
5	23.90	1.901	(240)	1.906
6	24.65	1.846	(042)	1.855
3	26.25	1.741	(202) (310)	1.751 1.749
6	28.00	1.639	$(\bar{3}21)$ $(\bar{2}51)$	1.643 1.631
2	28.65	1.605	$(\bar{1}52)$	1.607
6	29.35	1.570	(251) $(\bar{2}42)$	1.574 1.572
3	29.80	1.549	(152)	1.552
5	31.00	1.494	(071)	1.493
2	31.65	1.467	$(\bar{2}13)$	1.472

Our monoclinic cell gives a calculated density of 7.47 which is appreciably greater than that given by Barth's tetragonal cell, 7.03. We have not been able to check the calculated density by a good measured specific gravity. We measured, on a Berman balance, the specific gravity of one $YTaO_4$ bead as 5.59, but when this bead was broken it was found to have large holes inside it which apparently resulted from the vigorous reaction in the electrode. A difficulty in calculating the density of a natural fergusonite using our monoclinic cell volume for $YTaO_4$ is that in the published chemical analyses Er has usually been determined with Y, and Nb with Ta, and both these pairs of elements have widely different atomic weights. However, three of the analyses quoted in Dana (1944) do list these elements separately. For one of these, that from Arendal, Norway the calculated value, 6.18, is again much higher than the measured, 5.27. This suggests that specimens of natural fergusonite, even after heating to about 800°C to restore the structure, are still fairly porous. Dr. Joseph Berman has agreed that this is probably so. It may be necessary to heat natural fergusonite specimens to 1800°C or so to make them fuse to a solid mass in order to get a good measured specific gravity.

Comparison of the Monoclinic and Tetragonal Cells

A comparison of the true monoclinic cell with the earlier tetragonal cell shows the latter to be unreal with $V_{\mathrm{tet.}} = 2\frac{1}{3}\, V_{\mathrm{mon.}}$, and with tetragonal [100], [010], and [001] quasi-equivalent to monoclinic $[\frac{1}{2}\frac{1}{2}1]$, $[\bar{\frac{1}{2}}\frac{1}{2}1]$, and $[20\bar{1}]$.

With metamict minerals such as fergusonite the question arises whether the material recrystallized by heating has the same structure as the original mineral. The fact that synthetic $YTaO_4$ is monoclinic whereas fergusonite is, from morphological measurements, tetragonal, suggests that in this case the two are different. On the other hand, $YTaO_4$ is at least dimensionally pseudo-tetragonal along *b*[010], and it has a tendency to still further simulate tetragonal symmetry along this axis by forming parallel growths or twins. Considering these facts along with the $4/m$ morphological symmetry and the probable poor quality of the faces originally measured, it is distinctly possible that original fergusonite is not tetragonal but, like $YTaO_4$, monoclinic and pseudo-tetragonal.

Note on the Crystal Structure

The crystal structure has not yet been determined although it is likely that both the 4Y and 4Ta atoms will be found to lie in 4-fold special positions and the 16 O atoms in 8-fold general positions. Because of the high atomic numbers of Y and Ta, 39 and 52, it will be difficult to deduce the positions of the light O atoms by intensity calculations; expected coordinations and spatial considerations will likely prove of most value in locating these atoms.

We have taken numerous powder photographs of natural fergusonite specimens after fusion in the arc lamp electrode, and of the synthetic compounds $YNbO_4$ and $YTa_{\frac{1}{2}}Nb_{\frac{1}{2}}O_4$, and all give essentially the same pattern. However, consideration of all of them will be left until the intensity changes they show can be explained in terms of substitution in their common crystal structure.

Acknowledgments

The graduate students who assisted at various times with this work were R. L. Butler, G. L. Fletcher, T. N. Irvine, L. C. Kilburn, H. R. McCabe, A. Michalkow, M. D. Moorhouse, and J. H. Shepherd. To Mr. Moorhouse goes special credit for producing the particular fragment which yielded the single-crystal photographs. The author is also indebted to the National Research Council for generous financial support.

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