ACTA CHEMICA SCANDINAVICA 15 (1961) 663–669

The Crystal Structure of $K_2Ti_2O_5$

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The crystal structure of $K_2Ti_2O_5$ has been determined by Fourier projections and refined by a least squares analysis. The structure consists of layers of composition $(Ti_2O_5)^{2-}$, in which the titanium atoms have five coordination, separated by the potassium ions. The probable formation of a hydroperovskite $KHTiO_3$ as a hydration product is also discussed.

The alkali metals and earths form many ternary oxides with the metals of Groups IV, V, and VI of the periodic table, and much effort is at present directed towards certain structural types, notably the perovskite ABO_3, the pyrochlor $A_2B_2O_7$, and the tetragonal tungsten bronze AB_2O_6. We have noticed that the alkali metals form a composition series of compounds with titanium dioxide $A_2O \cdot nTiO_2$, where n has been given values from one to seven [1–3]. Of these, only the structure of Li_2TiO_3, which can exist in two forms, has been reported [4]. Several of the other phases with differing values of n are being examined by us, and the crystal structure determination of $K_2Ti_2O_5$, a brief account of which appeared elsewhere [5], is now reported in some detail.

EXPERIMENTAL

$K_2Ti_2O_5$ was readily prepared as colorless needles by melting K_2CO_3 and TiO_2 (anatase) in the molar ratio 1:2 at 1 300°C in a platinum crucible. Whilst the crystals could be kept for long periods in a desiccator, they decomposed on exposure to moist air and required protection during X-ray exposures. Despite a thick coating of cellulose acetate, an additional diffuse single crystal diffraction pattern appeared on the films which were well exposed for the intensity estimations, and the significance of this will be discussed at the end of this paper.

The crystallographic data are summarised in Table 1, the lattice dimensions having been determined from a Guinier film internally calibrated with KCl. These data agree with Schmitz-Dumont and Reckhard's brief description [1] but with two reservations. Firstly these authors gave the space group symbol *Cm* which was unsubstantiated by

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Table 1. Crystallographic data for $K_2Ti_2O_5$.

United cell dimensions:	$a = 11.37$ Å
	$b = 3.80$ Å
	$c = 6.62$ Å
	$\beta = 100.1°$
Systematic absent reflexions:	*hkl* with $h + k \neq 2n$
Possible space groups	*Cm* (No. 8)
	C2 (No. 5)
	C2/m (No. 12)
D_{obs}	2.95 g.cm^{-3} (Ref.[1])
D_{calc}	2.99 g.cm^{-3}
z	2

additional evidence, whereas the absent reflexions lead to the alternatives *C*2 and *C*2/*m* as well. The intensity distributions for *h*0*l* and *h*2*l* were observed by us to be virtually identical, and this was strong presumptive evidence for the centrosymmetrical space group *C*2/*m* in which a satisfactory structure was subsequently found. Secondly their value for the length for the *z* axis was twice that in Table 1; whilst the diffuse reflexions caused by the decomposition of the phase could doubtless be misinterpreted, we do not dismiss the possibility that a second form of $K_2Ti_2O_5$, closely related in structure to the present one, can also exist.

The *h*0*l* and *h*1*l* intensities were recorded by multiple film Weissenberg photographs exposed with filtered copper radiation. The measurements, made by comparison with a standard intensity scale, were reduced to $|F|$ values by the usual methods. No corrections for absorption were made, although they would have been desirable in the latter part of the refinement. The scattering curve for titanium which was used had been derived by the self consistent field method[6] for Ti^{3+}. This was rounded off from the point $\sin \Theta = 0.3$ to a value of 18.0 at $\sin \Theta = 0$. Curves derived by Freeman[7] for K^+ and for O^{2-} by Suzuki[8] were also used. Fourier summations were made on SILLIAC, a high speed computer at the University of Sydney, and the structure factors and least squares calculations by hand.

STRUCTURE DETERMINATION

The derivation of the structure was a relatively simple matter. It was supposed that the space group was *C*2/*m* for reasons given earlier, and because the *y* axis was short a minimum of overlap would occur. One oxygen could be placed in the special position 2(a), and the other atoms, one titanium, one potassium and two oxygens would then be in general positions 4(i). The Patterson function $P(u,w)$ was computed, and a model selected from it which refined by successive F_o and $F_o - F_c$ Fourier summations until the reliability factor was 18.9 %. Beyond this point this method proved troublesome and a least squares treatment was adopted. In this, the function

$$R = \Sigma\ w(h0l)\ [|F_o(h0l)| - |F_c(h0l)|]^2$$

was minimised, the observed and non-observed reflexions being weighted simply by $w = 1$ and 0, respectively. The positions of the atoms K and O_2 which, in the electron density projections were free of overlying atoms, were refined by neglecting the off-diagonal coefficients. The complete matrix expression was used for Ti and O_3 for which overlap occurs in projection down the *y* axis. Two cycles reduced the reliability to 13.4 %, and at this stage the estimated standard deviations for the atoms were in all cases greater than the

Table 2. Fractional atomic parameters and estimated standard deviations. Space group $C2/m$ ($\frac{1}{2}$ $\frac{1}{2}$ 0 +) .

Atom	Point position	x	y	z
Ti	4(i)	0.1495 ±.0008	0	0.9072 ±.0017
K	4(i)	0.4022 ±.0010	0	0.6439 ±.0021
O_1	2(a)	0	0	0
O_2	4(i)	0.128 ±.003	0	0.664 ±.006
O_3	4(i)	0.325 ±.003	0	0.008 ±.007

corresponding changes to the positional parameters. The final values of these are given in Table 2 together with the deviations reduced to fractions of the cell edges.

There was some evidence from the $F_o - F_c$ Fourier projections for anisotropic thermal motion, the maximum vibration being directed approximately normal to the (100) plane. However, no additional treatment of the data was considered. The crystal absorption and the overall temperature factor effectually cancel one another and the calculated structure factors, compared in Table 3 with the observations, contain no corrections of either kind. Despite considerable absorption, the *h*0*l* terms gave a reliability of 17.9 % on comparison with the model for the space group $C2/m$ and this is considered to be adequate proof of the structure which is shown in Fig. 1.

DESCRIPTION

The principle feature of interest is the coordination of the titanium atom. It is bonded to five oxygens which are grouped in the form of a trigonal bipyramid, somewhat distorted. The metal-oxygen bond distances vary from 1.57 Å to 2.00 Å, and this is considered to be due to the repulsion between the nearest neighbour metal atoms. There is also a wide diversity of oxygen to oxygen distances, the shortest of 2.54 Å being an edge which is common to two of the bipyramids (Fig. 2(a)). The double unit formed in this way is an endless string extending in the y direction. Strings of a similar kind are joined

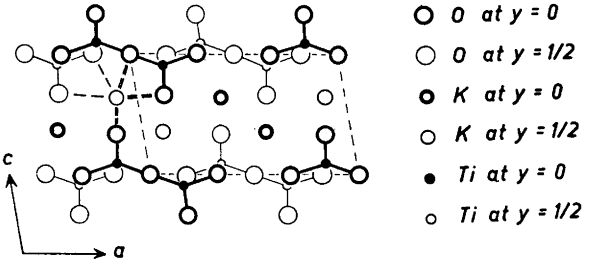

Fig. 1. Structure of $K_2Ti_2O_5$ projected on to (010). The $(Ti_2O_5)^{2-}$ sheets are parallel to the x direction. The bonds from one potassium atom to its eight oxygen neighbours are drawn as heavy broken lines. The unit cell is indicated by weaker broken lines.

Table 3. Comparison between observed and calculated structure factors.

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	10.0	12.8	605	7.8	$\overline{9.2}$	$120\bar{1}$	12.0	14.8	$51\bar{2}$	7.5	8.8
2	9.1	10.1	4	< 7.4	$\overline{0.5}$	$\bar{2}$	6.4	5.6	$\bar{3}$	16.7	19.4
3	21.6	22.2	3	11.8	$\overline{9.8}$	$\bar{3}$	14.7	15.5	$\bar{4}$	< 6.6	2.5
4	17.9	$\overline{15.9}$	2	< 6.1	2.7	$\bar{4}$	6.4	8.5	$\bar{5}$	< 6.8	2.9
5	8.6	$\overline{7.2}$	1	17.4	17.6	$\bar{5}$	4.9	$\overline{3.3}$	$\bar{6}$	< 7.5	4.3
6	< 7.4	2.9	0	10.8	8.8	1400	< 4.0	1.3	$\bar{7}$	9.9	$\overline{13.4}$
7	13.7	$\overline{11.4}$	$\bar{1}$	28.4	26.5	$\bar{1}$	6.4	10.8	716	10.8	$\overline{10.4}$
8	< 4.6	5.6	$\bar{2}$	23.3	22.7	116	9.3	$\overline{8.3}$	5	< 4.1	$\overline{0.5}$
208	< 3.7	$\overline{1.7}$	$\bar{3}$	< 6.1	1.1	5	13.5	$\overline{14.1}$	4	15.0	$\overline{12.7}$
7	9.6	$\overline{6.1}$	$\bar{4}$	8.8	10.1	4	11.3	11.9	3	7.2	3.4
6	< 7.4	$\overline{3.8}$	$\bar{5}$	7.3	$\overline{2.3}$	3	6.6	7.1	2	17.0	16.5
5	11.8	12.9	$\bar{6}$	13.7	$\overline{14.0}$	2	5.7	5.2	1	< 6.4	0.9
4	7.4	8.1	$\bar{7}$	< 6.1	2.4	1	25.6	32.1	0	25.7	21.2
3	17.2	14.4	806	< 4.2	2.7	0	5.3	2.3	$\bar{1}$	3.6	$\overline{4.5}$
2	25.0	26.9	5	6.9	$\overline{9.3}$	$\bar{1}$	3.6	$\overline{4.5}$	$\bar{2}$	8.2	9.3
1	6.9	$\overline{4.3}$	4	< 7.1	4.6	$\bar{2}$	3.2	4.5	$\bar{3}$	6.7	5.3
0	< 2.5	$\overline{0.6}$	3	11.8	16.3	$\bar{3}$	14.0	$\overline{21.5}$	$\bar{4}$	< 7.1	$\overline{7.3}$
$\bar{1}$	15.2	$\overline{12.7}$	2	< 7.1	$\overline{1.2}$	$\bar{4}$	8.5	$\overline{11.3}$	$\bar{5}$	14.6	$\overline{17.8}$
$\bar{2}$	25.0	$\overline{26.9}$	1	15.7	14.1	$\bar{5}$	< 6.9	$\overline{3.5}$	915	10.9	11.1
$\bar{3}$	8.8	$\overline{6.7}$	0	9.8	8.7	$\bar{6}$	8.4	$\overline{8.5}$	4	14.0	15.7
$\bar{4}$	8.8	$\overline{9.5}$	$\bar{1}$	14.5	$\overline{15.2}$	$\bar{7}$	< 6.4	7.6	3	9.1	6.6
$\bar{5}$	8.6	$\overline{5.0}$	$\bar{2}$	< 6.7	$\overline{1.9}$	316	18.0	16.6	2	16.8	13.6
$\bar{6}$	11.0	13.5	$\bar{3}$	12.7	$\overline{12.4}$	5	7.2	6.7	1	< 7.2	3.8
$\bar{7}$	7.8	4.6	$\bar{4}$	15.4	$\overline{18.6}$	4	22.7	20.8	0	8.2	$\overline{7.6}$
$\bar{8}$	< 4.9	4.6	$\bar{5}$	< 7.2	1.3	3	17.1	16.6	$\bar{1}$	< 7.0	$\overline{1.2}$
407	12.5	14.6	$\bar{6}$	< 6.6	$\overline{3.3}$	2	9.0	$\overline{7.6}$	$\bar{2}$	11.7	$\overline{10.9}$
6	< 7.0	$\overline{1.6}$	$\bar{7}$	< 5.1	0.4	1	15.1	11.9	$\bar{3}$	7.3	$\overline{6.6}$
5	11.5	12.6	1005	< 3.9	6.7	0	9.5	$\overline{7.0}$	$\bar{4}$	< 7.2	6.0
4	7.8	7.2	4	< 5.8	2.3	$\bar{1}$	22.7	$\overline{21.0}$	$\bar{5}$	< 6.8	1.2
3	17.9	$\overline{20.0}$	3	8.6	9.7	$\bar{2}$	10.9	13.2	1113	10.9	$\overline{12.8}$
2	< 5.1	0.9	2	< 7.2	$\overline{6.9}$	$\bar{3}$	< 5.3	$\overline{1.0}$	2	13.5	$\overline{11.9}$
1	12.5	$\overline{13.0}$	1	9.8	$\overline{9.5}$	$\bar{4}$	< 6.2	3.2	1	< 6.8	$\overline{1.2}$
0	30.9	$\overline{30.0}$	0	< 7.4	$\overline{0.4}$	$\bar{5}$	20.8	25.5	0	18.2	$\overline{16.1}$
$\bar{1}$	15.9	13.3	$\bar{1}$	15.7	$\overline{16.2}$	$\bar{6}$	< 7.3	6.9	$\bar{1}$	< 7.1	$\overline{0.5}$
$\bar{2}$	< 4.0	1.3	$\bar{2}$	< 7.4	$\overline{0.6}$	$\bar{7}$	< 6.4	$\overline{8.3}$	$\bar{2}$	7.0	10.9
$\bar{3}$	< 5.4	1.4	$\bar{3}$	7.4	9.6	516	8.1	7.2	$\bar{3}$	< 7.4	$\overline{4.9}$
$\bar{4}$	25.0	27.1	$\bar{4}$	< 7.1	$\overline{1.4}$	5	< 7.2	1.0	$\bar{4}$	10.3	12.9
$\bar{5}$	7.3	6.7	$\bar{5}$	11.3	14.4	4	13.7	$\overline{16.5}$	1311	8.1	10.2
$\bar{6}$	< 7.4	2.6	$\bar{6}$	14.0	13.3	3	9.2	6.0	0	9.7	9.6
$\bar{7}$	12.5	8.6	1203	6.1	7.5	2	16.6	13.0	$\bar{1}$	7.6	6.1
$\bar{8}$	10.0	$\overline{9.8}$	2	< 5.8	3.2	1	22.6	$\overline{16.9}$	$\bar{2}$	11.2	13.3
607	< 3.6	0.9	1	7.4	$\overline{6.7}$	0	9.8	7.8			
6	6.2	$\overline{2.9}$	0	6.4	6.9	$\bar{1}$	< 4.9	3.4			

together by having the oxygen atoms O_1 in common, leading to an infinite two dimensional sheet of composition $(Ti_2O_5)^{2-}$, the median of which is the plane (001) *.

Sheets are then separated from one another by the potassium ions, each having eight oxygens as near neighbours. Six are approximately at six of the eight corners of a cube, and the other two are on the same level as the potas-

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* If each alternate string of bipyramids in a sheet is rotated through 180° in the plane normal to (001), the structure of it is identical with a single layer of the V_2O_5 structure [9].

sium, in a plane parallel to (010) which bisects the figure (Fig. 2(b)). It appears simply as if potassium occupies the best positions which can be created by the $(Ti_2O_5)^{2-}$ sheets when they are packed together (Fig. 1) and no other significance is attached to its coordination.

The trigonal bipyramid is rare in oxide structures but has been shown to occur in vanadium compounds; in V_2O_5 [9], for certain of the atoms in the alkali metal vanadium bronzes [10,11] as well as for the hydrated metavanadates $KVO_3 \cdot H_2O$ [12] and $Ca(VO_3)_2 \cdot 2H_2O$ [13] (the mineral metarossite). It has never before, to our knowledge, been demonstrated for titanium.

THE DECOMPOSITION PRODUCTS OF $K_2Ti_2O_5$

$K_2Ti_2O_5$ reacts readily with water. The diffuse single crystal diffraction pattern, which was recorded together with the reflexions of $K_2Ti_2O_5$, had pronounced pseudo cubic symmetry which could not be related to anatase, identified by Schmitz-Dumont and Reckhard [1] as one of the end products of the decomposition.

The unit cell was monoclinic, space group $P2_1$ or $P2_1/m$ with the dimensions

$$a = 9.6, \quad b = 3.8, \quad c = 10.8 \text{ Å}, \quad \beta = 112°.$$

The relationship between this and the sub cell is expressed by the axial transformation

$$\text{cubic} \rightarrow \text{monoclinic} = \bar{1}02/010/300$$

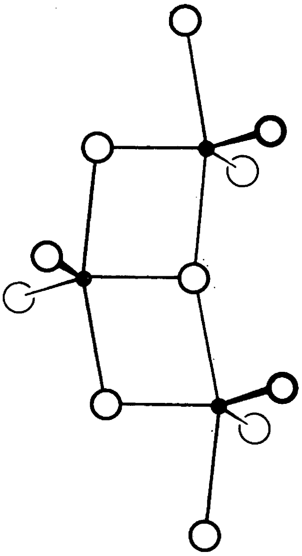

Fig. 2(a). Perspective drawing of the strings of double bipyramids formed by titanium (small black circles) and oxygen (larger open circles).

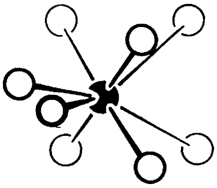

Fig. 2(b). The oxygen atom environment of a potassium atom (black circle) in a perspective drawing.

Table 4. Interatomic distances in Å.

	$Ti-O_1$	1.67 ± .02
	$Ti-O_2$	1.57 ± .04
	$Ti-O_3^1$	2.00 ± .04
(2)	$Ti-O_3$	2.00 ± .04
	O_1-O_2	2.86 ± .04
	$O_2-O_3^1$	2.90 ± .05
	$O_3^1-O_1$	3.69 ± .04
(2)	$O_3-O_3^1$	2.54 ± .08
(2)	O_3-O_1	2.76 ± .04
(2)	O_3-O_2	2.86 ± .05
	$Ti-Ti^1$	3.09 ± .02
	$K-O_2^{11}$	3.14 ± .04
	$K-O_3$	2.71 ± .04
(2)	$K-O_1$	3.08 ± .03
(2)	$K-O_2^1$	3.18 ± .04
(2)	$K-O_2$	2.76 ± .04
	$K-K^1$	3.17 ± .02

and this is shown in Fig. 3 which is also a possible interpretation of the crystal structure.

The sub cell reflexions were characteristic of the perovskite structure, and the true unit cell contains several of these units. Whilst it was obviously impossible to gain evidence of the chemical composition of this phase, it seemed not improbable that it was formed simply by the reaction

$$K_2Ti_2O_5 + H_2O \rightarrow 2KHTiO_3$$

to become a "hydroperovskite" containing hydrogen ions. On hydration, $K_2Ti_2O_5$ would be expected to undergo extensive rearrangement. The water molecules entering the lattice will undoubtedly change the titanium coordina-

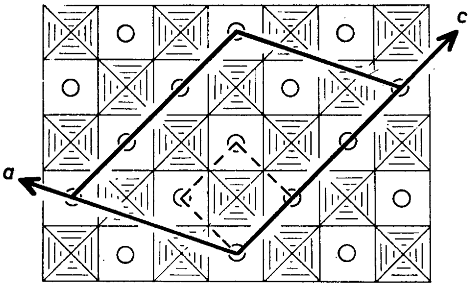

Fig. 3. The possible structure of the hydration product of $K_2Ti_2O_5$, seen in projection down the y axis. The titanium-oxygen octahedra are drawn as shaded squares, the potassium as open circles. The perovskite sub-cell is outlined by broken lines, the superstructure unit cell by the heavy lines, with the axial directions shown as arrows. Contraction, presumably the result of hydrogen bonding, occurs principally in the x direction.

tion from five to six, and can achieve this only at the expense of the original structure.

The superstructure could arise from the displacements of atoms from ideal cubic positions under the combined influence of polarisation effects and of hydrogen bonding. We had intended to attempt to solve the detailed structure of this phase, but were prevented from doing so by the too few reflexions which were recorded. In an attempt to increase the data, the original crystal, still with its heavy coating of cellulose acetate, was kept in moist air for several months, and again exposed in an X-ray camera. There was no trace of the structure of $K_2Ti_2O_5$, and the perovskite-like decomposition product also was no longer present. The crystal, still preserving its original form, was virtually amorphous. Attempts to prepare $KHTiO_3$ by heating together equimolar proportions of KOH and TiO_2, met with no success, the only product being $K_2Ti_2O_5$ identical with the former specimens. Whether or not this is the correct interpretation of the chemistry and structure of the decomposition product, the phase evidently has only a transitory existence.

The authors desire to thank Dr. B. Dawson and Mr. R. Grenfell Thomas for helpful comments.

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Received October 18, 1960.