

Introduction

Many of the nitrates show extensive polymorphism (BRIDGMAN, 1916) and two of these, KNO_3 and NaNO_3 , are of special interest because of their structural similarities to the carbonates. It was the prime concern in this study to check the previous results of JAMIESON (1956) on KNO_3 IV and to establish the cell type and structure, if possible. This effort seems warranted by the recent discovery of a high-pressure pattern of calcite (phase III) in this laboratory.

JAMIESON (1956) has previously obtained high-pressure x-ray data on KNO_3 IV by use of a single-crystal diamond bomb designed by LAWSON and TANG (1950). Jamieson did not undertake to index his lines by any general technique, evidently because his accuracy did not warrant it, but rather he sought out likely comparisons and found a reasonable fit of his data to the RbNO_3 -type structure (PAULING and SHERMAN, 1932). Our results have been obtained by way of a more general attack, making use of conventional indexing techniques.

Apparatus and procedure

A detailed description of the apparatus has been presented elsewhere (ADAMS and DAVIS, unpublished). Only a brief explanation and sketches are included here. Fig. 1A illustrates schematically a modified Bridgman anvil device, or "squeezer" (BRIDGMAN, 1935). Between upper and lower carboloy anvils is placed a beryllium pellet ranging from 1 to 4 mm in thickness (depending on the pressure to be applied and duration of the experiment). The sample, consisting of a thin pellet, or film, lies beneath the beryllium, the latter acting as the window as well as pressure medium. The field of the figure is but an enlarged part of the anvils which are supported in a six-inch press. The press is mounted on a spindle for insertion into a goniometer axis.

Figure 1B is a sketch of a simplified supported pressure vessel. In our most recent vessels the bottom is detachable to allow better sample removal. Slots through the steel supporting casing (see inset) allow the x-ray beam to pass through the beryllium cylinder and beryllium-powder pressure medium above the sample. The diffracted beam has a similar path to the scintillation counter. Several sizes of pistons and cylinder bores are currently in use in our most recent vessel; removable, steel-encased inserts are unscrewed from the main steel support and thus allow work with different sample sizes, pressure ranges, and piston types.

The entire pressure vessel stands less than two inches high and is about $1\frac{1}{2}$ inches in diameter. Like the "squeezer" apparatus it is mounted in a 6-inch press which fits into a goniometer.

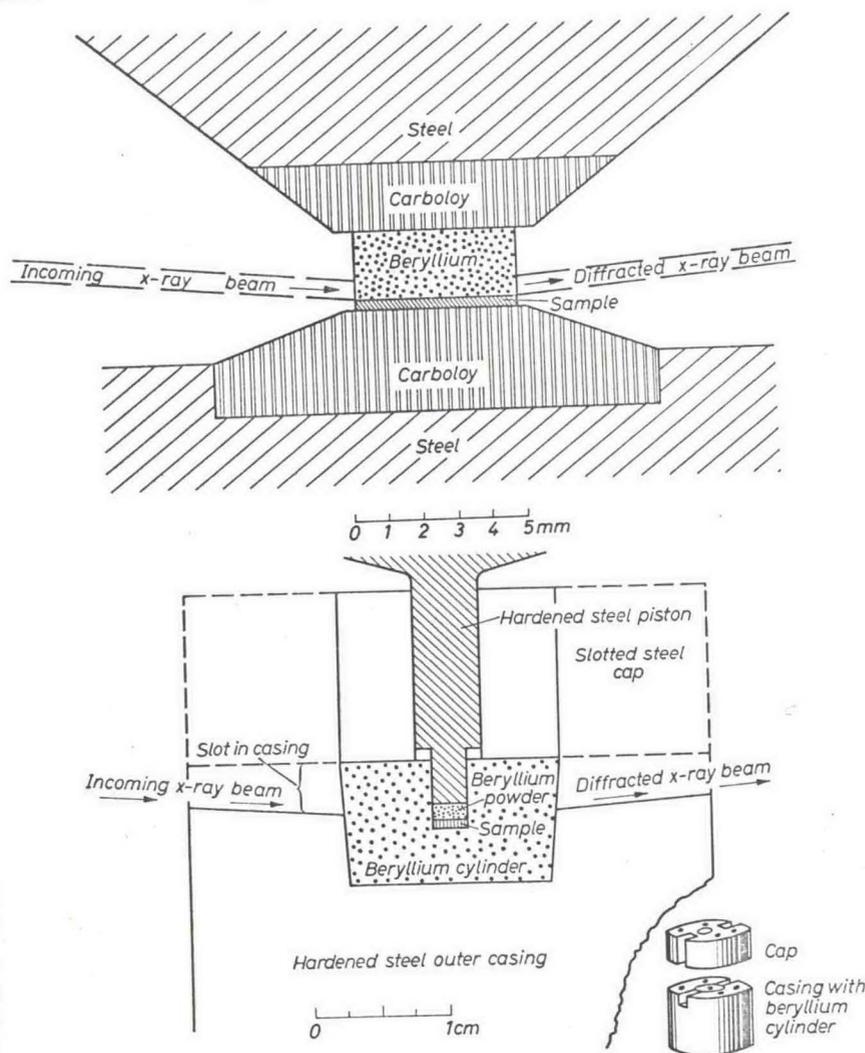


Fig. 1. A. Highly magnified sketch of modified Bridgman anvil device; B. Supported beryllium pressure vessel including cap and piston

Other essential equipment consists of a Philips x-ray diffraction unit, goniometer, counting panel and Brown recorder. The pressure is produced by a Blackhawk pump with a pressure hose leading to a

four-ton ram mounted on the base of the 6-inch press upon which is set either the "squeezer" or the supported beryllium cylinder.

Both $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiation were used in the study. The former was used only with the "squeezer" inasmuch as the thick walls of the cylinder reduced the beam strength considerably.

The sample was prepared by mixing 50 per cent KNO_3 and 50 per cent starch (by volume) and compressing the mixture into a 1-mm pellet by means of a pellet press. The pellet was pushed to the bottom of the cylinder bore and covered with a second pellet of compressed

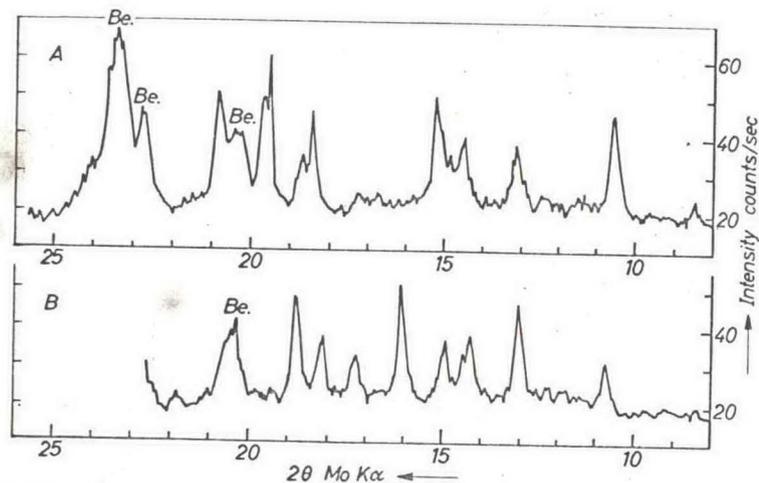


Fig. 2. A. KNO_3 II at room pressure, $\text{MoK}\alpha$ radiation. The large peak between ten and eleven degrees is actually a doublet, 111 and 021, not resolved. Supported beryllium cylinder; B. KNO_3 IV at 3.7 kb, $\text{MoK}\alpha$ radiation. Note the two peaks only slightly resolved at about 14.3 degrees. These are 030 and 400 of the high-pressure form. Supported beryllium cylinder. Attenuation 4-1-8. Pellet 4.6×1.0 mm diam.

beryllium powder, the latter serving to separate the sample reflecting surface from the steel or carboloy piston. Disks cut from beryllium rod may also be used, but because of creep, cause excessive friction at higher pressures. Not all KNO_3 pellets were half starch, but such a mixture tends to give more complete conversion in a shorter time than does the pure material alone. The pattern obtained with the pure material, however, shows somewhat sharper lines.

Figure 2 shows the low-pressure modification (KNO_3 II), and KNO_3 IV at 3.7 kbar (room temperature). These patterns were obtained in the supported vessel with piston and sample size of 4.6 mm, using

$\text{MoK}\alpha$ radiation and Zr filter. Scanning speed is $\frac{1}{4}^\circ/\text{min}$; scale factor of 4; 8-sec time constant; and chart speed of $\frac{1}{8}$ in./min. Earlier results with the diamond anvil showed some of these high-pressure peaks. Unfortunately three moderately strong beryllium lines are also present in the pattern and may even conceal some of the pattern. None of the lines observed by JAMESON are covered, however. It should be pointed out that this particular pattern was obtained after the sample had remained under this same pressure overnight. No low-pressure peaks are seen to remain.

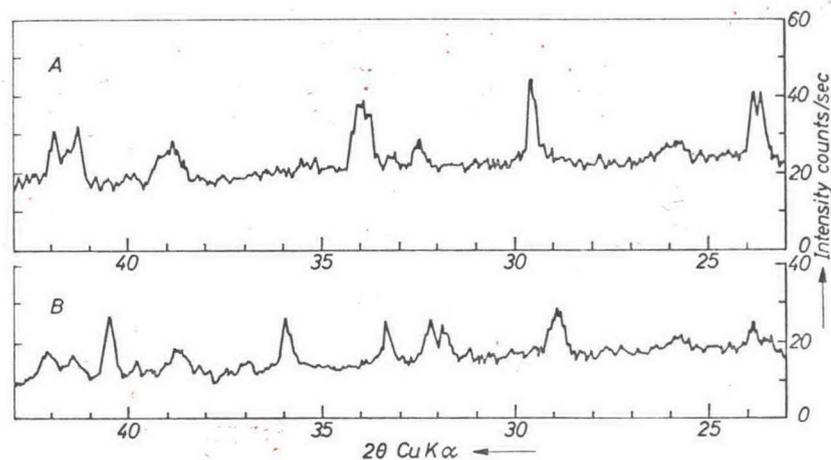


Fig. 3. A. KNO_3 II at room pressure. $\text{CuK}\alpha$ radiation. Note the partially resolved 111 and 021 peaks at 23° degrees, that were completely unresolved in Fig. 2A. Bridgman anvil device with beryllium pellets; B. KNO_3 IV at 6.6 kbar (nominal), $\text{CuK}\alpha$ radiation. Note the completely resolved 030 and 400 peaks at 32° degrees that were only partially resolved in Fig. 2B. Bridgman anvil device with beryllium pellet. Attenuation 4-1-8. Pellet 5.0 mm diam.

The data used for the indexing were obtained from a run using undiluted KNO_3 (Baker's Analyzer, ACS standard) and the sample was scanned at $\frac{1}{8}^\circ/\text{min}$, chart speed of $\frac{1}{8}$ in./min. Initially the lines were corrected for sample-height change by the position of a low-pressure line on the chart before conversion was complete. A compressibility of $5 \times 10^{-6}/\text{bar}$ was used to correct the shift of the low-pressure line due to compression up to the transition pressure. The assumption is made that when both low- and high-pressure phases are present the pressure on the remaining low-pressure phase is less than or equal to the equilibrium pressure. In the supported pressure vessel the pressure

should be more or less hydrostatic at high pressures, say 10 kb or above, but this may not be true at 3 or 5 kbar.

It was recently found that Cu radiation will penetrate beryllium sufficiently to give x-ray diffraction effects of samples under high pressures in the "squeezer" apparatus. Although the pattern of KNO_3 IV (see Fig. 3) obtained with Cu radiation was much weaker than one obtained with molybdenum radiation, it nevertheless sufficed for a refinement of the data obtained in the cylinder. Using several remanent low-pressure lines from a record obtained with copper radiation taken before completion of the transition, several high-pressure spacings were calculated and used to correct the other data. The final tabulation of corrected data is found in Table 1.

It was observed that initially there was considerable extrusion of sample in the "squeezer" due to shearing forces. With the sample under pressure for several hours to two or three days, the pattern improved in sharpness and intensity, and the low-pressure lines weakened considerably or even disappeared entirely. The latter effect is probably due to an increase of the pressure homogeneity with time as the beryllium anvil creeps and becomes dished. The pressure is calculated from the area of the carbony face (5 mm) since the initial beryllium pellet increases in diameter to this maximum. Using 1° slits and the correct beryllium pellet size, one can leave a sample at a pressure of 9 kbar for days without the sample height changing enough to reduce the pattern intensity noticeably.

Results

A. Indexing

Our first procedure was to compare with the Bell-Austin charts (Battelle Mem. Inst.) for possible hexagonal indexing, but no fit was found. Application of the Hesse-Lipson procedure with elimination of possible axial sets on density considerations yielded the final cell data. Indices and cell constants for the high-pressure modification were calculated and refined with the aid of an IBM 7090 computer. The final axial values determined are $a = 11.04_8 \text{ \AA}$, $b = 8.36_7 \text{ \AA}$, $c = 7.40_2 \text{ \AA}$ with $a : b : c = 1.320 : 1 : 0.885$ ($Z = 10$).

One line appeared to be a doublet on the molybdenum record and this was substantiated upon examination of the copper record. Only on the latter are the lines indexed as 030 and 400 clearly resolved. In spite of this discovery and also the discovery of a few weak lines not observed by JAMIESON, the pattern can still be indexed with axial

Table 1. X-ray diffraction data on KNO_3 IV; $a = 11.04_8 \text{ \AA}$, $b = 8.36_7 \text{ \AA}$, $c = 7.40_2 \text{ \AA}$, $Z = 10$

| <i>hkl</i> | d_{obs} | d_{calc} | $100 \frac{I^*}{I_0}$ |
|------------|------------------|-------------------|-----------------------|
| 020 | 4.18 Å | 4.18 Å | 6 |
| 002 | 3.70 | 3.70 | 29 |
| 310 | 3.37 | 3.37 | 3 |
| 112 | 3.25 | 3.24 | 5 |
| 202 | 3.08 | 3.08 | 100 |
| 030 | 2.80 | 2.79 | } |
| 022 | | 2.77 | |
| 400 | 2.76 | 2.76 | 95 |
| 320 | | 2.76 | } |
| 122 | 2.68 | 2.69 | |
| 230 | 2.49 | 2.49 | 53 |
| 222 | | 2.48 | 95 |
| 103 | 2.421 | 2.408 | 13 |
| 113 | 2.314 | 2.314 | 37 |
| 420 | | 2.305 | } |
| 402 | 2.213 | 2.213 | |
| 322 | | 2.214 | 69 |
| 412 | 2.141 | 2.140 | } |
| 510 | | 2.136 | |
| 232 | 2.071 | 2.066 | 83 |
| 140 | | 2.056 | } |
| 033 | 1.848 | 1.848 | |
| 512 | | 1.850 | 7 |
| 323 | | 1.841 | } |
| 600 | | 1.841 | |
| 333 | 1.652 | 1.652 | 12 |
| 304 | | 1.653 | } |
| 150 | | 1.654 | |
| 532 | 1.572 | 1.569 | 9 |
| 700 | | 1.578 | } |
| 251 | | 1.565 | |
| 334 | 1.421 | 1.422 | 20 |
| 632 | | 1.419 | } |
| 504 | | 1.419 | |
| 533 | | 1.418 | } |
| 524 | 1.343 | 1.343 | |
| 244 | | 1.344 | 7 |
| 811 | | 1.340 | } |
| 434 | | 1.346 | |
| 253 | | 1.338 | } |
| 812 | 1.281 | 1.279 | |
| 361 | | 1.284 | 4 |
| 732 | | 1.288 | |

* Integrated intensities.

elements comparable with those of RbNO_3 (orthorhombic, C -centered). They are $a = 16.07_8 \text{ \AA}$, $b = 9.94_1 \text{ \AA}$, $c = 7.67_8 \text{ \AA}$, $a : b : c = 1.617 : 1 : 0.687$ ($Z = 18$). JAMIESON (1956) gives for this cell the constants $a = 16.12 \pm 0.04 \text{ \AA}$, $b = 10.12 \pm 0.04 \text{ \AA}$, $c = 7.75 \pm 0.01 \text{ \AA}$.

The standard deviation of the spacings for the small cell ($Z = 10$) is 0.00623, and that for the large cell ($Z = 18$), 0.01307, indicating a somewhat better fit of the indexing for the former. A check of the $\sin^2\theta$ values for $h00$, $0k0$, and $00l$ of JAMIESON'S pattern against dense accumulations $\Delta \sin^2\theta$ on our bar graph (Hesse-Lipson procedure) showed a nearly complete lack of correspondence. Moreover, indexing of all lines of the pattern based on the large cell is not possible with $h + k = 2n$, a requirement for centering on C . In view of the above considerations it would seem preferable to adopt the smaller unit of structure.

From the indices listed in Table 1 it is possible to set up the following maximum restriction conditions:

$$\begin{array}{ll} h00 : h = 2n & hk0 : h + k = 2n \\ 0k0 : k = 2n & h0l : h + l = 2n \\ 00l : l = 2n & 0kl : k + l = 2n \end{array}$$

$$hkl : \text{no restriction.}$$

If these conditions are not fortuitous the space group is $P\frac{2_1}{n}\frac{2}{n}\frac{2_1}{n}$. With 10 molecules of KNO_3 per cell, however, space-group symmetry requires that triangular NO_3^- groups be placed on edges or corners of repeat units, which is not allowable. If one were to consider restrictions based on the best fit of data then h odd and $h + k$ odd must be allowed and the space groups should be either $P\frac{2}{m}\frac{2}{n}\frac{2}{m}$ or $Pmn2_1$. Again the former is rejected because of the triangular NO_3^- -group, but in $Pmn2_1$ several compact arrangements of 10 KNO_3 can be devised.

Although no one of four such arrangements based on $Pmn2_1$ gave agreement in intensity good enough to warrant its description here, certain features of one show promise for future study. If one were to place K^+ ions at 000 (two ions); $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ (four ions); and $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ (four ions), then the calculated intensities of 002 , 202 , 400 , $230 + 222$, and 402 would be medium to strong and would compare roughly with the observed values. The 020 (observed weak) line would also be strong, but by placing several O atoms in equipoints in the glide-plane between the sets of 4 K^+ ions this line would be weakened. Further work will

be required before a complete description of the structure can be given.

The cell constants determined yield a Δv of transition of $0.060_4 \text{ cm}^3/\text{g}$ at 3 kbar which may be compared with $0.04474 \text{ cm}^3/\text{g}$ by BRIDGMAN (1916).

B. Transition rate

Our experimental arrangement is especially suitable for studying transition rates. This is accomplished by fixing the goniometer at the 2θ value corresponding to a high-pressure line, and applying the pressure to the sample as suddenly as possible with the chart running.

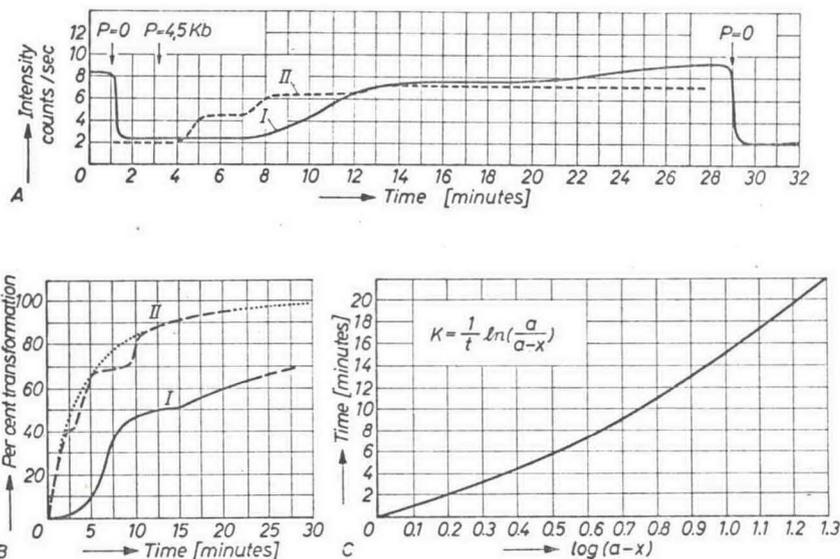


Fig. 4. A. Transformation rate of $\text{KNO}_3 \text{ II} \rightleftharpoons \text{KNO}_3 \text{ IV}$ as traced out by recording pen from growth of 230 peak. See text for explanation. Supported beryllium cylinder. Attenuation 2-1-4. Pellet $2.55 \times 0.4 \text{ mm}$.; B. Data of Fig. 4A plotted as per cent transformation vs time; C. Test of first-order kinetics for II-IV transition (see text). Plot is from data of Fig. 4B using dotted line

The final pattern is read in minutes horizontally and counts per second vertically. In this manner, as the high-pressure peak grows, the recording pen traces out directly the rate curve. Two such charts traced and reduced, are shown in Fig. 4A.

The rates have been investigated only in the supported beryllium pressure vessel since it is desirable to approach hydrostatic conditions in the sample as nearly as possible. In this instance a 2.55 mm sample was used. The attenuation used (scale factor = 2, multiplier = 1, time

constant = 4) allowed easily constructed curves (irregularities due to background scatter must be averaged out) and yet did not introduce a serious lag from the time constant.

An interesting feature of curve I is the levelling off of intensity part way along so that two stages of peak-height growth result. Furthermore, the reverse rate appears faster than the forward rate, thus producing an asymmetrical curve. A second experiment confirmed this phenomena even though the length of time to reach a final level was somewhat less. Such differences might be explained by sample preparation, or in variations in size of the beryllium disk between sample and piston, thereby creating differences in friction and of actual pressure on one sample as compared to the other. Also noted in the second experiment are three stages of growth instead of two.

When the curve has tapered off so that further growth is impractical to follow continuously, one can scan part of the pattern to ascertain the completion of the conversion. With curve I at the end of 20 minutes, 60 per cent of material was NK O_3 the IV; with curve II after 10 minutes, 80 per cent of the material had converted to the high-pressure form.

One rate carried out in an identical manner with NH_4I showed only slight asymmetry. Several other rate experiments with NH_4I , RbI , and cerium, however, showed neither asymmetry nor growth stages. It has been suggested that the asymmetrical shape of the KNO_3 II \rightleftharpoons KNO_3 IV curve is the result of friction release and adjustment of the pressure within the vessel. One would then have to explain why such adjustment does not take place with release of pressure, and why such phenomena have not been observed in rate studies with this apparatus on other materials. No reasonable explanation for the growth stages or asymmetry of the curve can be suggested that is compatible with the irreversible nature of the step-wise transformation. It has been observed with NH_4I that the slight asymmetry of the curve produced under conditions very near the phase boundary is eliminated and replaced by completely symmetrical curves when the transformation pressure is exceeded by 50, 100, or 200 per cent. Our work with rates on NH_4I and a few other materials has shown with certainty that the rate is dependent on the amount of excess pressure above the equilibrium value that is applied.

The pressure of Fig. 4 is $4\frac{1}{2}$ kbar, or 50 per cent above the transformation pressure. Perhaps with internal pressure of 6 or 8 kbar the asymmetry of the curve would disappear. A study of this rate at

lower pressures is more time consuming but further work in this direction is certainly desirable.

Figure 4B is a plot of the data from curves I and II, of Fig. 4A, in terms of per cent transformation vs time. It was desirable to see if the transition obeyed first-order kinetics, that is, if the amount being transformed at any given moment in time was proportional to the amount of unconverted material remaining in the vessel. The law is stated as

$$K = \frac{1}{C} \frac{dC}{dt},$$

where K is a constant, and the amount, C , at any instant can be replaced by $(a-x)$, a being the initial amount, and x the amount transformed at time t . Rearrangement and integration between the time limits 0 and t yields the "kinetic equation"

$$K = \frac{1}{t} \ln \frac{a}{(a-x)}.$$

A plot of $\log(a-x)$ against t should be a straight line if the data conform to first-order kinetics. As seen in Fig. 4C, the data for curve II plotted in 1-minute intervals yield a line with very slight curvature which is concave upwards. It should be noted that the growth stages, which in themselves show departure from first-order kinetics, were ignored in the above test. The data represent the general growth curve depicted by the dotted line fitted to curve II. The time lag before the growth and the subsequent shape of the curve in experiment I show obvious departure from first-order kinetics.

From the data obtained thus far it does not appear that the rate of transformation of KNO_3 II \rightleftharpoons KNO_3 IV is in accord with first-order kinetics even though an approach to such is indicated by the slight curvature of curve II. Since the differences between curve I and curve II is likely to be tied in with experimental factors it will be necessary to obtain curves under identical, more precisely controlled pressure conditions before reliable quantitative rate data may be presented.

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The crystal structure of potassium hexatitanate $\text{K}_2\text{Ti}_6\text{O}_{13}$

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With 11 figures

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Auszug

Die Struktur von Kaliumhexatitanat wurde neu bestimmt. Die Raumgruppe ist $C2/m$. Die Elementarzelle mit $a = 15,582 \pm 0,006 \text{ \AA}$, $b = 3,82 \pm 0,01 \text{ \AA}$, $c = 9,112 \pm 0,001 \text{ \AA}$, $\beta = 99,764^\circ \pm 0,008^\circ$ enthält $2(\text{K}_2\text{Ti}_6\text{O}_{13})$. Dreidimensionale Interferenzdaten wurden mit einem Zählrohr-Diffraktometer gewonnen und für Absorption und mit dem Lorentz-Polarisations-Faktor korrigiert. Im späteren Stadium der Untersuchung wurde auch eine Korrektur für anomale Streuung der Ti-Atome angebracht.

Eine dreidimensionale Patterson-Synthese deutet eine Struktur an, die sich aus Ti-Oktaedern aufbaut, deren eine Hauptachse der 2-zähligen Achse parallel ist. Ein Strukturmodell, das die richtige Zahl der O-Atome ergab, wurde mittels der Minimumfunktion bestätigt.

In dieser Struktur sind die Ti-Oktaeder durch Kanten und Ecken zu Ketten verknüpft, mit Zwischenräumen für die K-Ionen. Sie wurde zuerst durch dreidimensionale Fourier-Synthesen und schließlich nach der Ausgleichsmethode verfeinert, bis zum Endwert $R = 12,4\%$ für alle Interferenzen. Individuelle Temperaturfaktoren und Atomabstände stimmen mit Literaturdaten überein.

Abstract

The crystal structure of potassium hexatitanate has been determined. The space group is $C2/m$ and the cell dimensions are $a = 15.582 \pm 0.006 \text{ \AA}$, $b = 3.82 \pm 0.01 \text{ \AA}$, $c = 9.112 \pm 0.001 \text{ \AA}$, $\beta = 99.764 \pm 0.008^\circ$. This unit cell contains $2(\text{K}_2\text{Ti}_6\text{O}_{13})$.

Three-dimensional intensity data were collected by means of a single-crystal Geiger-counter diffractometer and the intensities were corrected for Lorentz-polarization factors and absorption. In later stages of the structure determination the three Ti were corrected for anomalous scattering.

A three-dimensional Patterson synthesis suggested a structure based on Ti octahedra with their axes parallel to the 2-fold axis. A model structure which gave the correct number of oxygens in this symmetry was confirmed by means