The Crystal Structure of β-Potassium Dizirconate β-$K_2Zr_2O_5$

By B. M. GATEHOUSE and D. J. LLOYD*

(*Department of Chemistry, Monash University, Clayton, Victoria,* 3168 *Australia*)

Summary The crystal structure of β-potassium dizirconate comprises face-, edge-, and corner-shared ZrO_6 octahedra.

As part of a structural study of the K_2O–ZrO_2 system, the crystal structure of β-potassium dizirconate has been determined using single-crystal *X*-ray diffraction techniques.

The compound was first prepared[1] by fusing ZrO_2 with KOH at 800°. A more extensive characterization appeared later.[2] In the present study, single crystals were obtained by dissolving ZrO_2 in K_2O at 1050° under a dry nitrogen atmosphere and evaporating off the excess of solvent.

β-$K_2Zr_2O_5$ crystallises in the orthorhombic system, space group *Pnna*, with unit cell $a = 5{\cdot}85$, $b = 10{\cdot}79$, $c = 8{\cdot}76$ Å; $Z = 4$, $D_c = 4{\cdot}09$. A total of 267 independent reflections

were collected using the Weissenberg technique and Cu-K_α radiation. The structure was solved using three-dimensional Patterson and Fourier syntheses and refined using the full-matrix least-squares technique. With anisotropic temperature factors for the metal atoms, the structure has been refined to a conventional agreement factor of $R = 0{\cdot}10$.

β-$K_2Zr_2O_5$ has a very condensed structure containing infinite chains of two types, each having alternating face- and edge-shared ZrO_6 octahedra running in the x-direction. Each chain is surrounded by and joined laterally to four chains of the other type by corner sharing of octadedra (see Figure). The potassium ions occupy interchain positions in irregular six-fold co-ordination with oxygen; they effectively spiral through the structure in the z-direction. The K–O distances are in the range 2·57—3·28 Å with an average value of 2·88 Å (±0·03 Å) which is in agreement with the values found in other structures as recorded in International Tables.[3] The ZrO_6 octahedra are distorted slightly from ideality with Zr–O distances in the range 2·01—2·22 Å (standard deviation 0·03—0·04 Å). Zr–Zr distances for face-shared octahedra are 3·052 and 3·066 ± 0·008 Å; for edge-shared octahedra 3·272 ± 0·008 Å; and 4·054 and 4·066 ± 0·006 Å for corner-shared octahedra. This demonstrates the condensed nature of the ZrO_6 octahedral chains in this structure.

This work forms part of a project supported by a grant from the Australian Research Grants Committee.

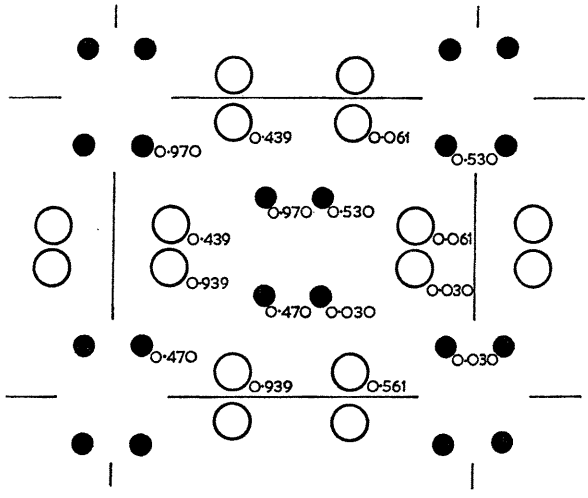

FIGURE. *A* (100) *projection of the* β*-potassium dizirconate structure, with the oxygen atoms omitted for clarity, showing an end-on view of the chains of zirconium atoms. The solid circles represent zirconium atoms while the unfilled ones represent potassium atoms. The* x*-co-ordinates of the atoms are shown (to the lower right of the atom concerned).*

(*Received, March 28th,* 1969; *Com.* 436.)

[1] H. A. Lehmann and O. Erzberger, *Z. anorg. Chem.*, 1959, **301**, 233.
[2] M. Tournoux, *Ann. Chim.* (*France*), 1964, **9**, 579.
[3] "International Tables for X-ray Crystallography," vol. III, Kynoch Press, Birmingham, 1962.