The Crystal Structure of the 2 : 5 phase in the K_2O–ZrO_2 System: $K_4Zr_5O_{12}$, a Compound with Octahedral and Trigonal Prismatic Zirconium(IV) Coordination

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$K_4Zr_5O_{12}$ crystallizes in the trigonal system with unit-cell dimensions $a = 5.821(2)$ Å, $c = 10.437(3)$ Å, and space group $P\bar{3}m1$. The structure was solved by Patterson and Fourier techniques. the 386 unique reflections measured by counter techniques were reduced to 334 with $I \geqslant 3\sigma(I)$; these were used in full-matrix least-squares refinement of the model to a conventional R of 0.0196 ($\omega R = 0.0228$). $K_4Zr_5O_{12}$ has a structure that may be described as consisting of perovskite-like layers (potassium ions are cube octahedrally coordinated) with sheets of hexagonal rings of edge-shared trigonal prismatically coordinated zirconium(IV) ions inserted between every third and fourth layer of the perovskite-like structure. The trigonal prisms are face shared to octahedra above and below alternately to form cavities that are occupied by pairs of potassium ions in ninefold coordination.

Introduction

During an investigation of the influence of potassium oxide on the cerium oxide–zirconium dioxide system (*1*) a compound was prepared and shown to be $K_4Zr_5O_{12}$. X-ray precession photographs showed that the single crystals were trigonal, and the powder diffraction data were indexed completely using a hexagonal unit cell with the dimensions $a = 5.812$ Å, $c = 10.428$ Å, space group probably $P\bar{3}m1$ (*1*).

An extensive study of the K_2O–ZrO_2 and K_2O–SnO_2 systems was reported by Tournoux (*2*), and evidence was given for the existence of the phases K_2ZrO_3, α- and β-$K_2Zr_2O_5$, and $K_2Zr_3O_7$. Earlier, the compound $K_2Zr_8O_{17}$ had been reported (*3*), but no mention was made of it in a subsequent review (*4*). The phase K_4ZrO_4 has also been reported and its relationship to the Ge, Ti, Sn, and Pb analogues discussed (*5*). A recent report (*6*) on X-ray diffraction data for the phase K_2O–2.5 ZrO_2 obtained by powder methods gives unit-cell dimensions very similar to those reported here and given previously (*1*). However, the composition proposed is clearly in error.

The structures of β-$K_2Zr_2O_5$ and K_2ZrO_3 have been reported from this laboratory (*7, 8*); we report here the structure of $K_4Zr_5O_{12}$.

Experimental

The crystals used in this study were kindly supplied by Dr. R. S. Roth, National Bureau of Standards, Washington, D. C., and were grown as described by Negas *et al.* (*1*).

A small, approximately hexagonal, crystal (primary faces 0.114 mm across, 0.016 mm deep) was mounted on a silica capillary using Araldite and the following data were then determined using a Philips computer-controlled four-circle diffractometer. The unit-cell dimensions were obtained by

centering on 15 reflections with θ values of about 10° and refining by least-square techniques.

Crystal Data

$K_4Zr_5O_{12}$, $M = 804.49$, $a = 5.821(2)$, $c = 10.437(3)$ Å trigonal, $Dc = 4.36$ g/cm^3 for $z = 2$. The amount of material was insufficient to measure an experimental density. $F(000) = 371.84$, $\mu = 50.59$ cm^{-1} for Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). There were no systematic absences. Possible space groups are $P321$, $P3m1$, or $P\bar{3}m1$; $P\bar{3}m1$ was shown by successful refinement.

Intensity Measurements

Intensity measurements were made with the crystal described above using the diffractometer and Mo$K\alpha$ radiation monochromated with a flat graphite crystal. A unique data set out to $2\theta = 60°$ was collected using the "ω" scan technique with a systematic scan range of ±0.65° from the calculated Bragg angle with an allowance for dispersion, at a scan rate of 0.03° sec^{-1}. No reflection was sufficiently intense to require the insertion of an attenuation filter. The 386 reflections were reduced to 334 with $I \geq 3\sigma(I)$. Three reflections, measured at 90-min intervals, showed no systematic variation in intensity.

The data were processed in a manner described previously (9) and an absorption correction, based on the indexed faces of the crystal, was made using the program "SHELX-76" (10). The atomic scattering factors used were for Zr(0), O(0), and K(0) from Ref. (11) and were corrected for anomalous dispersion using values from Ref. (12). All calculations were made on the Monash University B6700 computer, the major program used being that of Sheldrick (10).

Structure Solution and Refinement

The structure was solved for a zirconium atom position by conventional Patterson techniques and calculation of structure factors resulted in $R = \sum |F_o| - F_c| |/\sum|F_o| = 0.5931$. Difference Fourier syntheses enabled the remaining zirconium, potassium, and oxygen atoms to be located. Subsequent full-matrix least-squares refinement, the application of corrections for extinction and absorbtion, weighting of the data (individual weights of $[\sigma(F)^{-2}]$ were used), and use of isotropic thermal parameters gave $R = 0.036$. Final refinement, in which all atoms were assigned anisotropic thermal parameters, led to $R = 0.0196$:

$$\omega R = [\sum \omega (|F_o| - |F_c|)^2/\sum \omega F_o^2]^{1/2} = 0.0228.$$

TABLE I

FINAL ATOMIC PARAMETERS[a]

Atom	x/a	y/b	z/c	U_{11}[b]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr(1)	0	0	1/2	55(2)	55(2)	31(3)	0	0	27(1)
Zr(2)	1/3	2/3	240(1)	48(1)	48(1)	32(2)	0	0	24(1)
Zr(3)	1/3	2/3	7161(1)	56(1)	56(1)	24(2)	0	0	28(1)
K(1)	0	0	1780(1)	126(3)	126(3)	72(4)	0	0	63(2)
K(2)	1/3	2/3	3862(1)	125(3)	125(3)	126(5)	0	0	62(2)
O(1)	1651(1)	3302(3)	6212(2)	91(5)	91(5)	88(7)	−24(4)	24(4)	25(8)
O(2)	4905(2)	9810(3)	8772(2)	84(5)	84(5)	48(6)	−13(4)	13(4)	−30(7)

[a] Estimated standard deviations in parentheses ($\times 10^4$).

[b] The anisotropic temperature factor is of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$
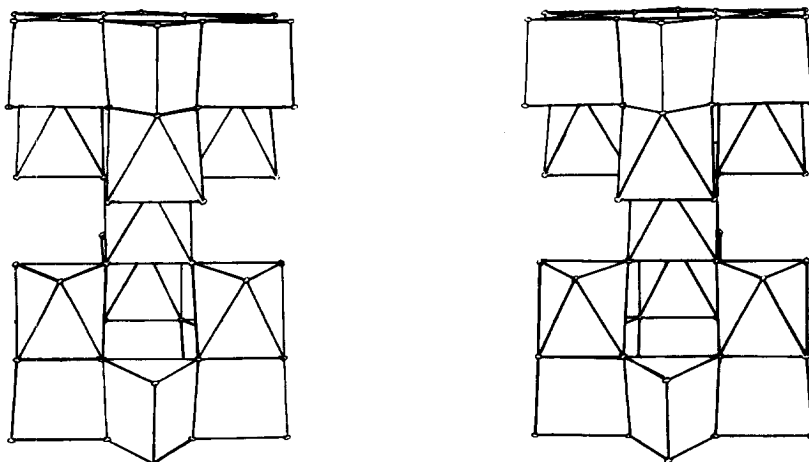
FIG. 1. Stereoscopic representation of the $K_4Zr_5O_{12}$ structure. The top and bottom layers are the rings of trigonal prisms between which are the three perovskite-like layers. The horizontal direction is parallel to (0 1 0) and the vertical parallel to (0 0 1).

The final parameters with their estimated standard deviations are presented in Table I.[1]

Description of the Structure

The structure of $K_4Zr_5O_{12}$ contains zirconium (IV) both octahedrally and tri-gonal prismatically coordinated by oxygen. It is best described in terms of layers of the perovskite structure (three octahedra deep) viewed down the octahedron threefold axis with a layer of trigonal prisms (one layer deep) between every third and fourth perov-skite layer (Fig. 1). The trigonal prisms are edge shared to one another, forming rings of six (Fig. 2). The prisms around the ring share their end faces with an octahedron above or below alternately.

[1] See NAPS document NO. 3450 for 4 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10017. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering, however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

Interatomic distances are set out in Table II. Zr(1) and Zr(3) are the corner-shared perovskite-type octahedra with Zr–Zr dis-tances of 4.047(1) Å whereas Zr(2) forms the
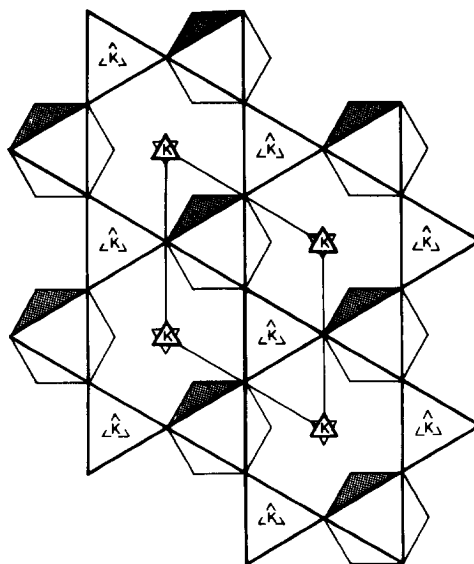

FIG. 2. The hexagonal rings of trigonal prisms are drawn as dark lines. The octahedra that are face shared to the top faces of the trigonal prisms are shown. Pairs of potassium ions (K(1)) occupy the centres of the rings of trigonal prisms, with the K(2) ions below alternate tri-gonal prisms as indicated.

TABLE II

Selected Interatomic Distances[a]

Zr(1)–O(1)	2.090(1)	[×6][b]	Oct.
Zr(2)–O(2)	2.204(2)	[×6]	Trig. prism
Zr(3)–O(1)	1.965(1)	[×3]	Oct. face
–O(2)	2.310(2)	[×3]	shared to trig. prism
K(1)–O(1)	2.677(1)	[×3]	
–O(2)	2.969(2)	[×6]	
K(2)–O(1)	2.911(2)	[×6]	
–O(1)	2.982(2)	[×3]	
–O(2)	3.273(2)	[×3]	
Zr(1)–Zr(3)	4.047(1)		Corner-shared oct.
Zr(2)–Zr(2)	3.399(1)		Trig. prism edge shared
–Zr(3)	3.213(1)		Oct.-trig. prism face shared
K(1)–K(1)	3.716(2)		Potassium ions facing each other
–K(2)	4.002(2)		
–Zr(1)	3.361(1)		
–Zr(2)	3.725(1)		
–Zr(2)	3.967(1)		
–Zr(3)	3.537(1)		
K(2)–K(2)	4.116(1)		
–Zr(1)	3.564(1)		
–Zr(2)	3.781(1)		
–Zr(3)	3.443(1)		

[a] Estimated standard deviations in parentheses (Å).
[b] Number of bonds of this type.

trigonal prisms which are all edge shared, with a Zr(2)–Zr(2) distance of 3.399(1) Å. Face sharing between the trigonal prisms, Zr(2), and the octahedra, Zr(3), results in a relatively short Zr–Zr distance (3.213(1) Å) and in the movement of Zr(3) away from the center of its octahedron, giving rise to three short and three long Zr(3)–O distances (Table II).

The potassium ions are in two different sites; the distorted cube-octahedral site (K(2)) with three different K–O distances, the longest, 3.267(3) Å, being to the trigonal prism oxygens (Fig. 3) and the K(1) sites enclosed by the rings of trigonal prisms (Fig. 2). The latter sites are nine coordinate, with six oxygens from around the ring of edge-shared prisms and three from the octahedron above or below the ring. This cavity may be
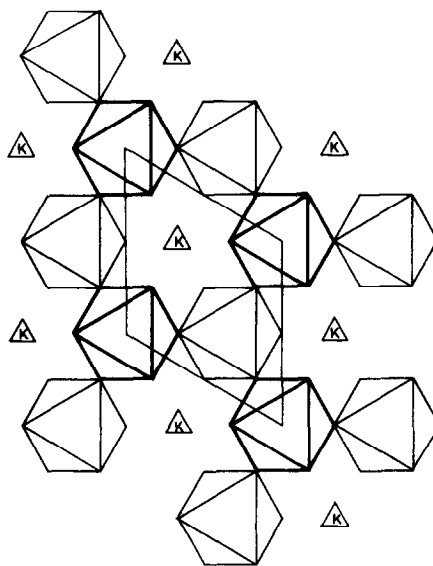

FIG. 3. Two of the three perovskite-like layers are illustrated showing the cube-octahedral sites occupied by the potassium ions K(2).

described as an elongated cube–octahedron, the elongation being due to the insertion of trigonal prisms into the perovskite structure. The potassium ions in this cavity face one another, resulting in sufficient repulsion for there to be a shift of 0.5763(1) Å out of the plane of the six oxygens toward the three of the octahedron above or below the ring.

Discussion

Phases in the K_2O–ZrO_2 system with metal to oxygen ratios given in Table III have now been structurally characterized. Both K_2ZrO_3 and β-$K_2Zr_2O_5$ are hygroscopic whereas $K_4Zr_5O_{12}$ is stable to moist air, implying that a decrease in oxygen to metal (o/m) results in an increase in the hygroscopic nature of the materials in this system. Based on this hypothesis the 2:1 phase, K_4ZrO_4, with o/m of 0.8 should be very hygroscopic. Crystalline material believed to be K_4ZrO_4 was prepared by Lloyd (13) using a method analogous to that for the preparation of K_2ZrO_3. The single crystals

TABLE III

SUMMARY OF DATA OF PHASES IN THE K_2O–ZrO_2 SYSTEM[a]

Phase	Oxygen to metal ratio (o/m)	Volume per oxygen (v/o $(\text{Å})^3$)
K_2ZrO_3	1:1.0	36.41
β-$K_2Zr_2O_5$	1:1.25	27.65
$K_4Zr_5O_{12}$	1:1.33	25.52
$K_2Zr_3O_7$	1:1.40	24.10 (if $Z=3$)

a Values decrease with increasing stability to water vapor.

produced were clear, extremely hygroscopic, and exhibited a pseudocubic triclinic cell or subcell with dimensions $a = 5.041$ Å, $b = 5.026$ Å, $c = 5.039$ Å, $\alpha = 88°35'$, $\beta = 88°26'$, $\gamma = 91°33'$. Data collection and structural solution could not be attempted due to severe sample decomposition.

K_2ZrO_3 consists of edge-shared ZrO_5 square pyramids (8), with a Zr–Zr distance of 3.212(3) Å, that form chains surrounded by potassium ions in irregular sixfold coordination. β-$K_2Zr_2O_5$ forms a structure that consists of pairs of face-shared octahedra edge and corner shared to one another forming chains that are encased in pseudohexagonal tunnels formed by the irregular eight-coordinate potassium ions (7). Both of these compounds are extremely hygroscopic, presumably as a result of the low coordination of zirconium in the former and the face sharing, in which every zirconium is involved, in the latter. This face sharing results in a Zr–Zr distance of 3.052(8) Å which is markedly shorter than that exhibited by the face-shared octahedron–trigonal prism unit of $K_4Zr_5O_{12}$.

Inspection of the volume per oxygen atom (v/o) for these phases (Table III) shows an analogous stability-related trend. The one-dimensional chain structure, K_2ZrO_3, has a v/o of 36.41 $(\text{Å})^3$. This value is very high and

possibly, in itself, explains the very hygroscopic nature of that phase. The three-dimensional array of $K_4Zr_5O_{12}$ has a v/o comparable to, though slightly higher than, known Zr(IV) perovskites; its value of 25.52 $(\text{Å})^3$ compared to that of $CaZrO_3$, 21.47 $(\text{Å})^3$ (14), is in the region expected for an air-stable perovskite-like compound.

If the 1:3 phase, $K_2Zr_3O_7$, that has been reported on several occasions, is to follow the trends observed for the structurally characterized phases in the K_2O–ZO_2 system it can be predicted to be stable in air and have zirconium in sixfold coordination or higher.

Despite the presence of the layer of trigonal prisms the structure of $K_4Zr_5O_{12}$ is very similar to a simple perovskite. It is not possible to form the perovskite structure with a combination of M^+ and M^{4+} ions. Three layers of the $K_4Zr_5O_{12}$ structure have the formula $[K_3Zr_3O_9]^{2-}$ and adopt the all corner-shared octahedral arrangement of perovskite. It is tempting to suggest that in order to achieve electrical neutrality a layer with a different composition forms next, namely $[KZr_2O_3]^{2+}$ followed by further perovskite-like layers.

The unusual characteristics of this structure, the layer of edge-shared trigonal prisms and the pairs of potassium ions occupying the sites formed within them, provide a very simple means for fusing together slabs of M^+M^{4+} perovskite into a three-dimensional structure while maintaining an overall charge balance.

Experiments are currently being conducted to ascertain which other elements in the four-plus oxidation state will form this structure.

Acknowledgments

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