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The Crystal Structure of Beta-Potassium Dizirconate: β-$K_2Zr_2O_5$†

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A structural investigation of compounds existing in the K_2O–ZrO_2 phase system has started with the high temperature preparation of single crystals of the orthorhombic 1:2 compound, beta-potassium dizirconate which has unit cell dimensions of $a = 5.85$, $b = 10.79$, and $c = 8.76$ Å. The structure is of a new type containing a complicated three-dimensional network of distorted ZrO_6 octahedra which is best described as comprising very condensed chains of alternating face- and edge-sharing ZrO_6 octahedra which *double up* to allow corner sharing of octahedra removed in the chain by two units. This latter phenomena occurs in such a manner that, within the chains and running in the same direction, there exists a string of trigonal bipyramidal holes linked by a common pair of oxygen atoms. Each octahedral chain, encased in a pseudohexagonal tunnel of potassium ions, is surrounded by and joined laterally to four mirror images by corner-sharing of octahedra. Overall, an unusually wide variety of structural features exist in this compound.

Structural trends seen developing in the K_2O–ZrO_2 system from a consideration of the structure of the 1:1 and 1:2 compounds, are discussed and likely structures for the 2:1 and 1:3 compounds are presented.

Introduction

Compounds in the K_2O–ZrO_2 phase system are generally hygroscopic and structural studies are quite difficult to perform. Until now their characterization has been limited to sketchy and often conflicting chemical and physical properties, and unit cell data from powder X-ray diffractometry.

While the preparation of compounds in the system was reported long ago (*1*), rigorous systematic attempts to prepare and characterize member compounds have only more recently been reported (*2*), (*3*), (*4*), and (*5*).

One quite extensive study by Tournoux (*6*) uses the structural similarity of the analogous tin system to propose a structure for potassium metazirconate, K_2ZrO_3. However, recent work performed in this laboratory (*7*) on both potassium metazirconate and the tin analogue shows that the two compounds are isostructural but with a structure differing from that proposed by Tournoux.

Here the complete crystal structure of the orthorhombic beta-potassium dizirconate, β-$K_2Zr_2O_5$ is reported and discussed.

Experimental

Colourless single crystals of hygroscopic beta-potassium dizirconate were prepared by dissolving zirconium dioxide in potassium oxide formed from the thermal decomposition of potassium nitrate in Pythagoras furnace-ware at 1050°C under a dry nitrogen atmosphere and evaporating off the excess solvent.

A representative single crystal of dimensions 0.05 × 0.02 × 0.02 mm was optically examined for twinning and other defects, and found suitable for structural analysis. Subsequently, it was oriented in a pyrex capillary tube in dry oil about the needle axis (*a* axis); systematic absences and cell dimensions were taken from oscillation and Weissenberg photographs, and multiple film pack Weissenberg intensity series were collected for $h = 0$–5 using CuK_α radiation. A total of 267 independent reflections were indexed in the orthorhombic space group P_{nna} using the unit cell dimensions, $a = 5.85$, $b = 10.79$, and $c = 8.76$ Å and intensities of each were estimated by visual comparison with a calibrated film strip. After conversion of measured intensities to structure factors, and the application of absorption corrections (*8*), a three-dimensional

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Patterson synthesis[†] was produced and a solution sought using the Harker heavy atom method assuming four molecular weight units of $K_2Zr_2O_5$ in each cell. A position for an eightfold zirconium atom was found which, when used to phase reflections and generate a three-dimensional Fourier synthesis, indicated the position of all other atoms in the structure. Scattering curves for K^+, Zr^0 and O^0, corrected for dispersion effects in the case of the metals, were those of Cromer and Waber (*9*). At this stage, with an over-all scale factor and approximate individual isotropic temperature factors, the conventional agreement factor was $R = 0.17$. Full-matrix least-squares refinement of atomic positional parameters, scale factors and individual isotropic temperature factors reduced this to $R = 0.107$ and conversion to and refinement of anisotropic temperature factors for the metal atoms with a subsequent refinement of scale factors, reduced this to a limiting value of $R = 0.097$ where atomic coordinate changes were negligible compared with the associated errors. A three-dimensional difference Fourier synthesis revealed no maxima > 0.2 or minima < -0.2 of the mean electron density value of oxygen atoms in the structure. A data weighting scheme was considered but found unnecessary. Final fractional atomic coordinates and individual temperature factors are listed in Tables I and II, respectively, while Table III contains interatomic distances and angles with estimated standard deviations. The list of observed and calculated structure factors is given in Table IV.

Discussion

Beta-potassium dizirconate has a complicated structure consisting of a three-dimensional network of distorted ZrO_6 octahedra, and potassium ions, which is best described as comprising very condensed chains of alternating face- and edge-sharing ZrO_6 octahedra running in the x-direction, which double up to allow corner-sharing of octahedra removed by two in the chain (see Fig. 1). This doubling up concept is easily seen by consideration of Fig. 2 as follows: Zr(1) and Zr(2) have an octahedral face in common and Zr(2) is linked by edge-sharing to Zr(3) which in turn face-shares to Zr(4). Zr(1′), the beginning of the repeating unit, is edge-shared to Zr(4), but also corner-shares to Zr(2) [as well as face-sharing to Zr(2′)], thus producing a hole with trigonal bipyramidal geometry. A second hole is formed in an identical manner by zirconium atoms 4, 1′, 2′ and 3′, and is linked to the first by a common pair of oxygen atoms so forming the strings of holes through the structure in the direction of the main octahedral chains (see Figs. 1 and 2). The stereochemistry of the *chains* of holes is identical to that displayed in the strings of TiO_5 double pyramids in $K_2Ti_2O_5$ (*10*) and the sizes of the respective polyhedra are identical but for a slight axial elongation. Each octahedral chain, encased in a pseudohexagonal tunnel of potassium ions, is surrounded by and joined laterally to four mirror images by corner-sharing of octahedra (see Fig. 3).

TABLE I

β-$K_2Zr_2O_5$ FRACTIONAL ATOMIC PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	Point position	x	y	z
Zr	8(e)	0.9697(7)	0.0763(3)	0.1603(3)
K	8(e)	0.438(2)	0.3340(9)	0.077(1)
O	8(e)	0.136(5)	0.398(2)	0.554(2)
O	4(c)	0.25	0	0.255(5)
O	4(c)	0.25	0	0.677(4)
O	4(d)	0.040(8)	0.25	0.25

TABLE II

β-$K_2Zr_2O_5$ THERMAL PARAMETERS—E.S.D.'S IN PARENTHESES

Atom	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr	0.012(1)	0.0028(2)	0.0036(3)	0.0007(7)	0.0008(7)	0.00007(30)
K	0.014(5)	0.0060(9)	0.011(1)	0.001(2)	0.004(3)	−0.004(1)
O8(e)	0.6(5)					
O4(c)	1.7(8)					
O4(c)	1.2(7)					
O4(d)	1.5(7)					

[†] All calculations were made on the Monash University CDC 3200 computer.

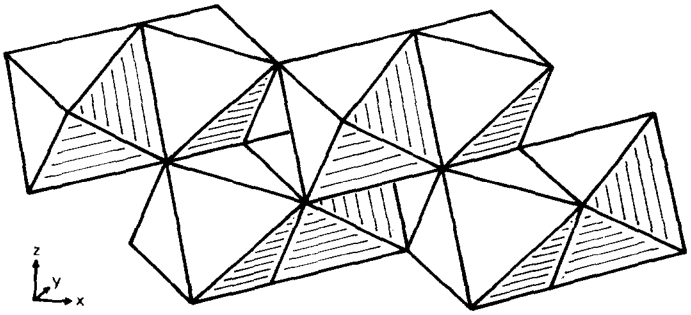

FIG. 1. Idealized representation of the ZrO_6 octahedral blocks comprising the main chains in β-$K_2Zr_2O_5$ showing face-, edge- and corner-sharing of octahedra and strings of trigonal bipyramidal holes.

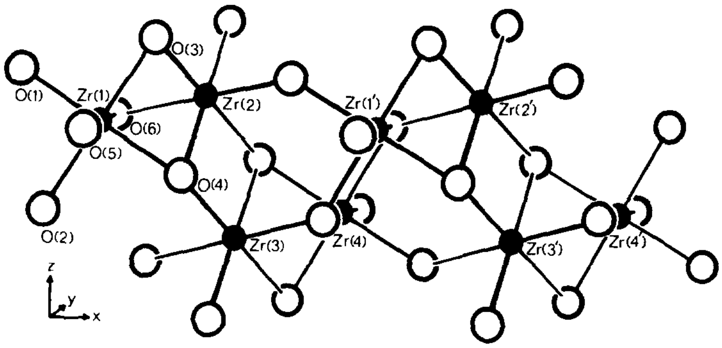

FIG. 2. A representation of the main ZrO_6 octahedral chains in β-$K_2Zr_2O_5$ used to explain the formation of the trigonal bipyramidal holes (see text). Relevant bond-lengths and angles are given in Table III.

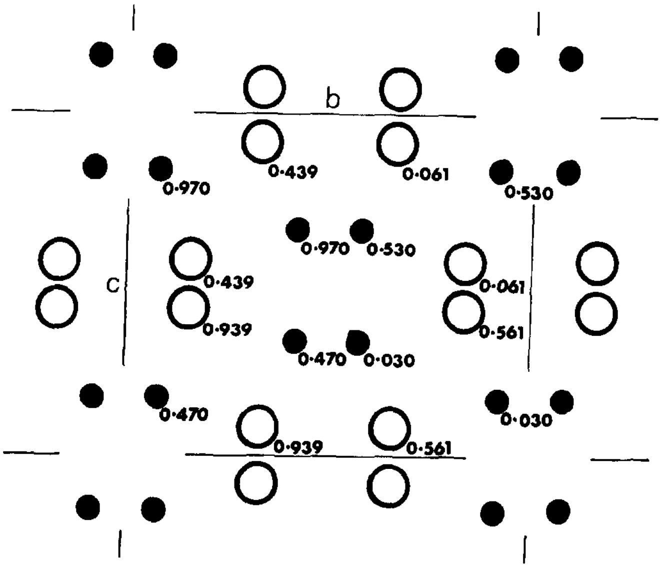

FIG. 3. A (100) projection of the β-$K_2Zr_2O_5$ metal atom structure showing an end-on view of one of the main chains of zirconium atoms (filled circles), and its relationship to the four surrounding mirror images which are linked by corner-sharing of ZrO_6 octahedra. The pseudohexagonal tunnel of potassium ions (open circles) is also shown in the projection.

TABLE III

β-$K_2Zr_2O_5$ INTERATOMIC DISTANCES AND ANGLES—E.S.D.'S IN PARENTHESES

Zr-Zr (see text)	3.052(8) Å	O–O (see Fig. 2)	
	3.273(8)	O(III)–O(VI)	2.69(5) Å
	3.669(7)	O(IV)–O(VI)	2.59(4)
	4.054(6)	O(III)–O(IV)	2.59(5)
	4.066(6)	O(II)–O(VI)	2.86(4)
Zr–O (see Fig. 2)		O(II)–O(V)	3.16(7)
Zr(1)–O(I)	2.09(3) Å	O(I)–O(V)	2.97(8)
O(II)	2.13(2)	O(I)–O(VI)	3.00(5)
O(III)	2.01(3)	O(IV)–O(V)	3.32(7)
O(IV)	2.19(2)		
O(V)	2.07(5)		
O(VI)	2.22(2)		
K–O (see Fig. 4)	3.28(3) Å	O–Zr–O	
	2.75(3)		77.8(4–20) degrees
	3.50(3)		
	2.57(3)		71.8
	3.06(4)		90.7
	2.70(4)		102.4
	2.94(6)		77.1
	3.06(6)		93.4
	Av. 2.98		102.3
K–K	2 × 3.220(9) Å		92.4
	3.53(1)		82.4
	3.90(1)		93.4
			92.9
			97.3

It is evident that five different Zr–Zr distances exist within the structure, each associated with a different type of sharing of octahedra. Corner sharing, by means of which the chains are linked, produces Zr–Zr distances of 4.066 Å while that between alternate chain members produced necessarily from the alternating face- and edge-sharing results in only slightly shorter intermetallic separations of 4.054 Å. The third type of corner-sharing, that produced when the chains are described as doubled up, creates distances significantly shorter at 3.669 Å. Other Zr–Zr distances are 3.052 and 3.273 Å for face- and edge-shared octahedra, respectively, within the chains. Overall then, a high degree of condensation appears within the main octahedral chains, and an unusual variety of sharing occurs throughout the structure.

The variation in Zr–O distances and O–Zr–O angles (see Table III) are indicative of the moderate distortions existing in the ZrO_6 octahedra. These distortions may be ascribed to the stringent stereochemical conditions existing within the octahedral chains in the structure.

The potassium ions in the structure form pseudohexagonal tunnels encasing the main chains of ZrO_6 octahedra, but breaching of these tunnels occurs to accommodate the interchain corner-sharing of octahedra. The irregular eightfold coordination of oxygen atoms to each potassium atom is illustrated in Fig. 4 and associated K–O distances are given in Table III.

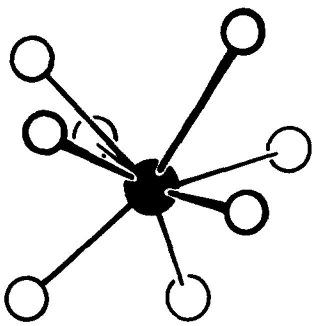

FIG. 4. A perspective representation of the irregular eightfold coordination of oxygen atoms (open circles) to potassium atoms (filled circle) in β-$K_2Zr_2O_5$.

It is thought that the interesting, condensed structure found to exist in beta-potassium dizirconate is a result of the relatively low oxygen atom to metal atom ratio (O/M = 1.25) coupled with the apparent favourability of zirconium atoms occupying high (6, 7, or 8) states of coordination. This view is supported by a study of the very hygroscopic 1:1 compound, potassium metazirconate K_2ZrO_3, where O/M is still lower at 1.0 and five-coordinate square-pyramidal stereochemistry of oxygen atoms about zirconium atoms exists (*7*). This structure is favoured over the model involving chains of all face-sharing ZrO_6 octahedra (*6*). Apparently, on proceeding down the series K_2O:nZrO_2 from $n = 2$ to $n = 1$, a limit to the condensation possible for an arrangement of ZrO_6 octahedra is reached and five-coordination is consequently forced by the decrease of O/M. One may predict then, that the structure of the 1:3 compound, potassium trizirconate $K_2Zr_3O_7$, in which O/M is higher at 1.4, could consist of a less condensed array of associated ZrO_6 octahedra and potassium ions, but an array whereby a higher coordination of oxygen atoms to zirconium atoms, and necessarily a greater degree of polyhedral sharing, is also possible. On the other hand, the lowest known member of the series, potassium orthozirconate K_4ZrO_4 (*11*), has O/M = 0.8, and is even more hygroscopic than the metazirconate. If the observed trend is followed, the structure of this compound is expected to contain either a highly shared network of zirconium atoms with fivefold coordination to oxygen atoms, or zirconium atoms

TABLE IV

β-$K_2Zr_2O_5$: OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
0	0	2	6.9	-5.9	1	1	2	5.3	4.5	2	1	3	16.6	-14.6	2	9	7	2.4	-2.8
0	0	4	9.8	-9.8	1	1	3	8.5	8.0	2	1	4	2.7	-3.4	2	10	3	2.0	2.9
0	0	6	6.0	7.0	1	1	5	8.3	8.8	2	1	5	5.5	5.5	2	10	7	2.1	-2.6
0	0	8	3.9	-4.6	1	1	7	2.2	-3.4	2	1	7	6.4	7.1	2	11	0	4.2	-4.4
0	0	10	9.3	-7.7	1	1	9	2.9	-3.4	2	1	9	6.2	-6.1	2	11	3	3.7	-3.8
0	1	1	8.2	8.5	1	2	1	3.5	3.4	2	2	0	2.0	1.6	2	11	5	1.9	2.1
0	1	3	13.3	-13.3	1	2	2	18.0	-17.9	2	2	1	3.7	-4.3	2	12	0	5.8	6.4
0	1	5	4.9	4.7	1	2	3	3.5	3.2	2	2	2	1.4	-1.4	2	12	4	3.0	-3.5
0	1	7	7.7	8.2	1	2	4	7.9	7.0	2	2	3	6.6	-6.6	2	13	1	2.1	2.6
0	1	9	7.9	-7.5	1	2	8	6.4	-6.4	2	2	4	5.5	-5.3	3	0	1	2.6	3.0
0	2	0	13.0	11.3	1	2	10	5.1	4.9	2	2	5	2.6	3.0	3	0	3	3.4	-2.2
0	2	2	7.5	-7.3	1	3	1	15.4	-13.1	2	2	6	7.0	7.7	3	0	5	5.4	-5.4
0	2	4	4.2	-4.6	1	3	2	4.0	-3.7	2	2	7	3.7	5.0	3	0	7	2.0	2.8
0	2	6	9.1	9.7	1	3	5	13.6	15.5	2	2	10	2.4	-2.7	3	0	9	2.6	2.7
0	2	10	3.8	-4.0	1	3	7	5.8	-7.0	2	3	0	4.5	3.8	3	1	1	3.0	-4.0
0	3	1	6.7	6.7	1	3	9	2.0	-2.4	2	3	1	6.7	6.1	3	1	2	8.7	7.8
0	3	5	3.5	-3.7	1	4	2	8.6	-8.8	2	3	2	5.1	-4.7	3	1	4	1.6	-1.9
0	4	0	8.6	-7.9	1	4	4	14.2	14.9	2	3	3	2.8	-2.6	3	1	5	3.1	2.7
0	4	2	5.9	-5.9	1	4	6	3.7	3.4	2	3	4	3.2	-2.8	3	1	8	3.2	3.2
0	4	4	5.0	4.9	1	4	8	10.9	-9.8	2	3	6	3.5	4.3	3	1	10	2.1	-2.2
0	4	6	1.5	-2.3	1	4	10	3.1	2.9	2	4	0	9.4	-8.4	3	1	10	2.0	-2.2
0	4	8	2.2	3.3	1	5	1	12.5	-12.7	2	4	1	5.7	4.9	3	2	1	4.3	4.9
0	4	10	2.1	2.4	1	5	2	2.8	-3.0	2	4	3	5.2	-5.0	3	2	2	8.3	-9.1
0	5	1	12.4	-12.4	1	5	3	4.4	-4.5	2	4	4	2.8	3.1	3	2	3	1.4	1.4
0	5	3	10.3	10.9	1	5	5	4.1	4.6	2	4	6	2.1	-2.8	3	2	4	3.5	3.0
0	5	7	1.6	-3.1	1	5	7	3.5	-3.9	2	4	9	1.7	-2.2	3	2	8	4.1	-4.1
0	5	9	7.0	6.4	1	5	8	2.1	-2.3	2	4	10	1.2	1.6	3	3	1	7.7	-7.6
0	6	0	10.0	-9.3	1	6	1	3.5	-3.4	2	5	1	6.5	-5.8	3	3	2	2.2	-1.9
0	6	2	6.4	6.8	1	6	2	3.8	-4.1	2	5	2	2.3	-2.8	3	3	3	2.4	-2.4
0	6	4	5.8	5.6	1	7	1	4.7	4.6	2	5	3	7.9	8.1	3	3	4	4.2	-4.2
0	6	6	10.6	-11.5	1	7	4	3.0	2.7	2	5	6	3.7	4.3	3	3	5	6.3	6.4
0	6	10	5.7	5.9	1	8	2	3.7	3.6	2	5	7	2.9	-4.0	3	3	7	5.2	-4.9
0	7	1	9.2	-10.0	1	8	4	8.1	-8.5	2	5	9	4.3	4.0	3	4	2	7.6	-6.4
0	7	3	10.6	11.6	1	8	6	3.0	-2.8	2	6	0	12.0	-10.7	3	4	4	6.0	5.7
0	7	7	4.7	-4.6	1	8	8	5.4	5.0	2	6	1	1.8	2.0	3	4	8	5.6	-5.4
0	7	9	8.0	7.7	1	9	1	6.8	7.3	2	6	2	7.9	8.7	3	5	1	5.7	-5.7
0	8	0	8.4	-8.1	1	9	5	7.8	-7.7	2	6	4	3.5	4.1	3	5	2	1.7	-1.9
0	8	4	7.3	7.4	1	9	7	6.0	5.7	2	6	6	10.3	-9.7	3	5	5	2.8	3.4
0	8	6	7.7	-5.9	1	10	2	10.4	10.3	2	7	0	3.8	3.8	3	5	8	3.0	-2.9
0	9	3	5.0	5.4	1	10	4	4.6	-4.9	2	7	1	6.3	-6.7	3	6	1	5.7	-5.0
0	9	5	3.0	-3.4	1	12	2	2.9	3.7	2	7	2	2.0	2.4	3	6	3	3.5	-4.3
0	9	7	5.2	-4.5	1	12	4	1.4	-1.7	2	7	3	7.4	8.5	3	6	7	2.7	-2.9
0	11	5	1.2	1.9	1	11	1	7.1	5.8	2	7	7	4.4	-4.2	3	6	5	2.8	2.7
0	12	0	10.4	9.7	1	11	5	6.9	-6.2	2	7	9	6.3	5.7	3	7	1	2.7	2.5
0	12	2	1.8	-2.5	2	0	2	4.2	-3.1	2	8	0	8.5	-9.5	3	7	2	1.9	-2.8
0	12	4	4.4	-3.7	2	0	4	11.7	-9.9	2	8	2	2.1	3.2	3	7	4	3.4	3.6
0	13	3	6.3	-6.6	2	0	6	6.4	7.4	2	8	4	5.2	5.1	3	7	8	2.7	-2.5
1	0	5	4.6	-4.5	2	0	10	4.7	-4.9	2	8	6	5.8	-5.1	3	8	1	2.0	-2.4
1	0	7	3.7	3.9	2	1	0	4.4	4.9	2	9	3	1.9	2.6	3	8	2	3.1	3.4
1	1	1	6.8	-6.1	2	1	1	4.8	5.6	2	9	6	1.7	-2.2	3	8	4	2.7	-2.9
3	8	5	4.1	3.4	4	1	7	2.8	2.8	4	5	2	2.5	-2.3	5	1	1	1.1	-1.4
3	8	7	2.7	-2.4	4	1	9	2.3	-2.1	4	5	3	3.6	4.4	5	1	2	3.1	3.1
3	9	1	5.0	4.4	4	1	4	2.3	-2.5	4	5	6	3.9	3.9	5	1	8	1.6	1.6
3	9	2	1.9	-2.4	4	2	0	3.4	3.7	4	5	7	2.2	-2.4	5	2	1	2.1	2.4
3	9	5	4.3	-3.9	4	2	3	4.7	-4.2	4	6	4	1.9	2.3	5	2	2	1.7	-1.7
3	9	7	2.8	3.3	4	2	4	1.7	-1.6	4	6	6	3.0	-3.5	5	2	4	1.5	1.8
3	10	2	4.7	5.0	4	2	5	2.6	2.2	4	7	3	4.5	4.4	5	2	8	1.4	-1.4
3	10	4	3.5	-3.4	4	2	6	2.3	2.6	4	7	7	2.2	-2.0	5	3	1	2.2	-2.1
3	11	1	3.1	3.1	4	2	7	3.5	3.3	4	8	1	2.6	-2.8	5	3	5	1.8	1.8
3	11	2	2.4	2.4	4	2	9	2.0	-1.9	4	8	4	2.3	1.9	5	5	4	3.0	2.6
3	12	2	1.1	1.5	4	3	2	2.3	-2.1	4	8	6	2.5	-2.3	5	6	5	2.2	2.0
4	0	2	4.4	-4.6	4	3	4	2.5	-2.3	4	9	0	2.7	-3.4	5	7	2	2.5	-2.2
4	0	4	2.8	-3.1	4	3	6	4.7	3.4	4	9	4	2.0	2.0	5	7	4	3.0	2.7
4	0	6	4.2	4.3	4	3	0	6.4	5.9	4	9	6	2.0	-2.0	5	8	1	1.4	-1.7
4	1	0	3.5	5.0	4	6	0	3.6	-3.2	4	10	3	3.2	2.9	5	8	5	1.2	1.2
4	1	1	1.1	1.5	4	4	1	5.0	4.7	4	11	0	2.9	-3.2	5	9	2	1.8	-2.0
4	1	3	4.8	-4.5	4	4	3	4.9	-4.1	5	0	7	2.2	2.3					

in four-coordinate sites with respect to oxygen atoms. Alternatively, the trend may be disrupted by the relative increase in alkali metal atoms, and the coordination requirements of potassium ions may be the structure controlling feature. In either case, the structure is of great interest with low coordination expected for either or both types of metal atom, and the possibility of further expansion of the chemistry of zirconium is imminent. Structural investigations on these and other members of the K_2O:ZrO_2 phase system are at present under way in this laboratory.

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