Synthesis, Characterization, and X-Ray Powder Structure of K₂ZrGe₂O₇

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A potassium zirconium pyrogermanate, $K_2ZrGe_2O_7$, was synthesized hydrothermally at 180°C from a mixture of zirconium propionate, GeO_2, and KOH. The crystal structure was solved from in-house X-ray powder data by direct methods and Fourier analysis. Refinement of the structure was effected by the Rietveld full-pattern technique. The compound is monoclinic, space group $C2/c$, $a = 9.9619(2)$ Å, $b = 5.5578(1)$ Å, $c = 12.9555(3)$ Å, $\beta = 105.169(1)°$, $Z = 4$. The structure is remarkably like that of α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, except that the layers are crosslinked by the pyrogermanate group to form a three-dimensional lattice. Exchange of the K^+ ions is minimal as they are strongly held within the confines of narrow tunnels. The relationship of this newly synthesized pyrogermanate to a sodium zirconium pyrogermanate prepared hydrothermally at 500°C and $Na_3H(GeO_4)_2$ is discussed. © 1999 Academic Press

INTRODUCTION

Recent efforts in our groups have been directed toward the synthesis and structure of inorganic ion-exchange materials that may be useful for nuclear waste remediation (1–3). Synthesis of a number of silicates and germanates under mild hydrothermal conditions has yielded framework compounds with tunnel and cavity structures that exhibit high selectivities to ions of specific size and charge. Among these we cite $Na_2Ti_2O_3(SiO_4) \cdot 2H_2O$ (4, 5), $K_2ZrSi_3O_9 \cdot H_2O$ (6), and $K_3HTi_4O_4(SiO_4)_3 \cdot 4H_2O$ (7) and its germanium analogues (8–13). Because of the interesting ion-exchange properties of these germanates we were encouraged to further explore the preparation of similar compounds.

Ilyushin has summarized results on the hydrothermal crystallization of compounds in the $Na_2O–ZrO_2–GeO_2–H_2O$ system (14). At 300°C two compounds, $Na_4Zr_2Ge_5O_{16} \cdot H_2O$ (15) and $Na_3HZr(GeO_4)_2$, were obtained. Raising the temperature to 500°C yielded three additional compounds: Na_2ZrGeO_5, $Na_2ZrGe_2O_7$, $Na_4Zr_2(GeO_4)_3$. The structures of the pyrogermanate and $Na_3HZr(GeO_4)_2$ have been described (14, 16). These compounds are discussed in relationship to the present compound, $K_2Zr(Ge_2O_7)$, which was prepared hydrothermally at 180°C.

Nosyrev *et al.*, examined the system $ZrO_2–GeO_2–KF–H_2O$ under hydrothermal conditions (500–550°C, 1500–2500 atm) (17). Only one potassium zirconium germanate was obtained. However, it was found to exist over such a broad composition range that it was designated by the general formula $K_xZr_yGe_pO_q$. The crystals are hexagonal with $a = 14.3$ Å and $c = 10.8$ Å. Most likely this compound exists as a solid solution with a broad composition range.

EXPERIMENTAL

Reagents. All reagents were of analytical grade (Aldrich) and were used without further purification.

Synthesis. The potassium zirconium germanate, $K_2ZrGe_2O_7$, was prepared as follows: 4.16 g of GeO_2 (39.7 mmol), dissolved in 15 ml of a 6.6 M KOH solution, was added to 4.45 ml (9.94 mmol) of 70% $Zr[OCH_2CH_2CH_3]_4$ solution in 1-propanol. The reaction mixture was thoroughly mixed, transferred into a 30-ml Teflon-lined high-pressure vessel, and treated hydrothermally (180°C) for 10 days. The product obtained was filtered, washed with distilled water, and dried at 70–80°C in air. Lower ratios of Ge to Zr produced mixtures of products.

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Analytical procedures. The diffractometer used was a Seifert–Scintag PAD-V with CuKα radiation. Zirconium, germanium, and potassium contents in the solid were determined by using a SpectraSpec Spectrometer DCP-AEC after dissolving a weighed amount of sample in HF (aq). IR spectra were obtained on a Perkin–Elmer 1720-X FT spectrophotometer by the KBr pellet technique. Thermal analysis was performed with a DuPont Instruments TA 4000 unit (under nitrogen, at a heating rate of 10°C/min). Electron micrographs were recorded with a JEOL JSM 6100 electron microscope operating at 20 kV.

X-ray data collection, structure solution, and refinement. The X-ray pattern was collected with a conventional powder diffractometer, Philips 1050, using graphite monochromatized CuKα radiation operating in Bragg–Brentano $(\theta/2\theta)$ geometry. The sample of $K_2ZrGe_2O_7$ was gently ground in an agate mortar, side-loaded into a holder to minimize the effects of preferred orientation, and the data were collected at room temperature over the angular range $11°–110°$ 2θ with a step size of $0.02°$ and a count time of 10 s/step.

The pattern was indexed using the program TREOR (18) from the angular positions of 20 low-angle accurately measured, unambiguously indexed reflections. A monoclinic cell was obtained: $a = 14.112(2)$ Å, $b = 5.556(1)$ Å, $c = 9.961(2)$ Å, $\beta = 117.74(1)°$ [figures of merit $M_{20} = 17$ and $F_{20} = 24(0.0089, 95)$]. Systematic absences indicated the space group $C2/c$. Reflection intensities were extracted from the diffraction pattern using the LeBail method (19). Eight hundred fifty-one F^2 values extracted from the data were used as input for the direct methods program SIRPOW (20). The solution with the best figure of merit was selected, and after 20 cycles of Fourier recycling plausible values of the coordinates of all atoms were revealed. The starting structural model was refined in RIET94, a local version of Wiles and Young's program (21). The peak shape was described using the split pseudo-Voigt function (22). Before refinement was commenced the unit cell was transformed to the values shown in Table 1. The parameters refined included terms for the background function, unit-cell parameters, zero point error, and profile coefficients. Final refinement yielded good agreement factors and minimal profile differences.

RESULTS

Figure 1 shows two electron micrographs of the pyrogermanate. At low magnification the particles appear mainly as spherical aggregates. At higher magnification the aggregates are seen to be composed of approximately 1- to 2-μm platelike particles of ∼6:1 aspect ratio. As might be expected, the IR spectrum contains few absorption bands. The major band is at 776 cm^{-1} with shoulders at 726 and 880 cm^{-1}. The band at 880 cm^{-1} is most likely the asym-

metric Ge–O–Ge stretching vibrations while the symmetric stretch is at 539 cm^{-1}. The bands at 776 and 726 cm^{-1} are due to GeO$_3$ vibrations (23). Although the compound was found not to contain water the bands for water are present at 3436 and 1623 cm^{-1}. This anomaly may result from the presence of surface water. To determine whether this is so, a thermogravimetric weight loss analysis was carried out. The curve is characteristic of surface water as the total weight loss was only 1.0% in the temperature range 25–150°C. However, an additional 0.6% water was lost to 415°C. This latter weight loss may indicate that the surface is terminated by OH groups.

Crystal Structure

Crystal data and details of the refinement are collected in Table 1. Final atomic positional and thermal parameters for $K_2ZrGe_2O_7$ are reported in Table 2 and the selected interatomic distances and angles are presented in Table 3. The final difference plot of the X-ray Rietveld refinement is shown in Fig. 2.

The crystal structure of $K_2ZrGe_2O_7$ is built up from ZrO$_6$ octahedra and GeO$_4$ tetrahedra. The Zr atoms are located on centers of symmetry and bonded to oxygen atoms O1, O2, and O3 and their centrosymmetric equivalents that in turn bond to six different germanium atoms as shown in Fig. 3. This connectivity constrains the germanate groups to lie alternately above and below the plane of the zirconium atoms, with each germanate group bonding to three different Zr atoms, resulting in formation of two-dimensional
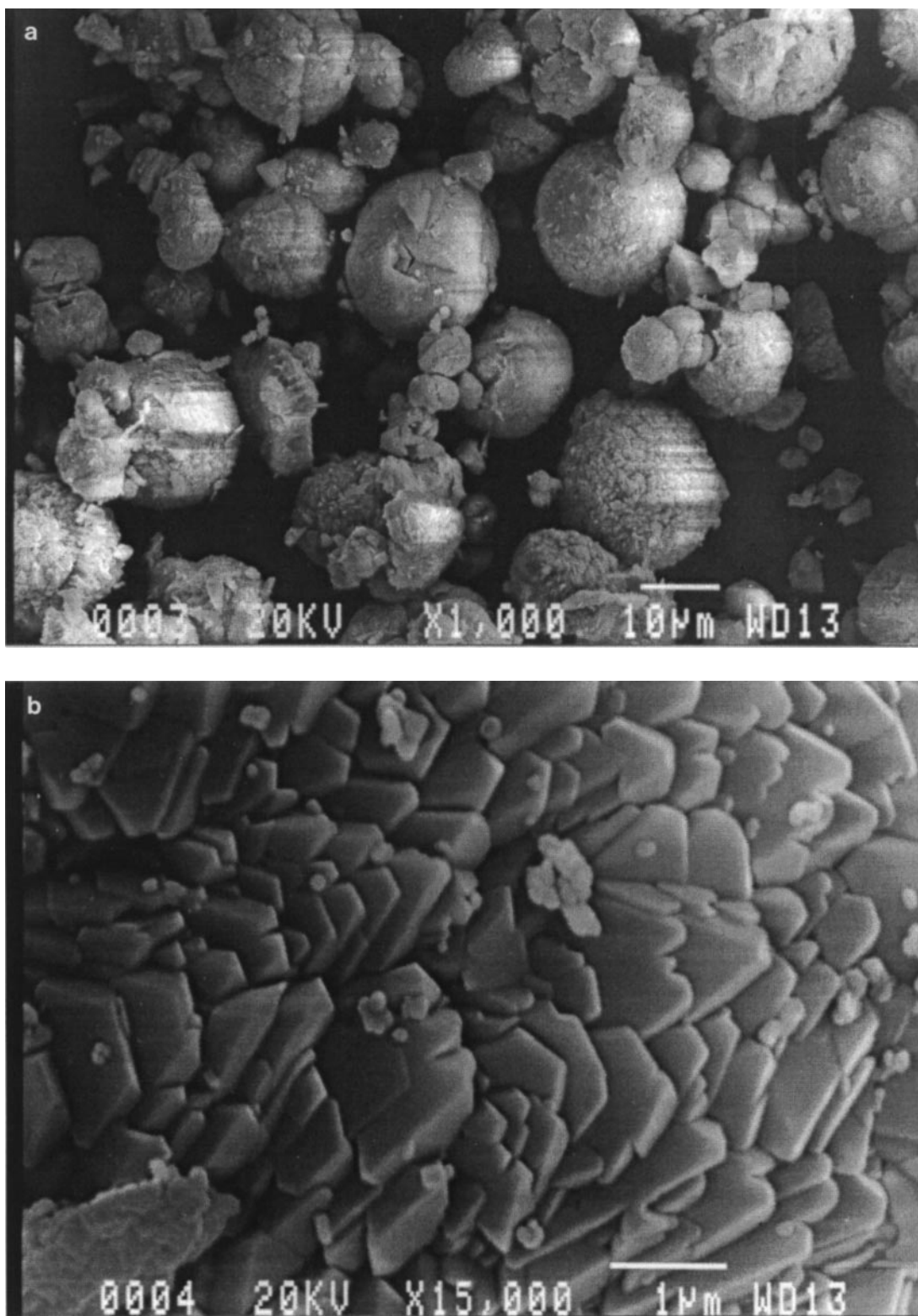
TABLE 1
Crystal Data on $K_2ZrGe_2O_7$

Empirical formula	$K_2ZrGe_2O_7$
Formula weight	426.60
Crystal system	Monoclinic
Space group	$C2/c$
a	9.9619(2) Å
b	5.5578(1) Å
c	12.9555(3) Å
β	105.169(1)°
V	692.31(2) Å^3
Z	4
λ (CuKα)	1.54180
ρ_{calc}	4.093 g/cm^3
μ	33.28 mm^{-1}
Parameters	40
R_{wp} (%)	8.84
R_{exp} (%)	4.52
R_B (%)	3.66
χ^2	3.82

$$R_B = \sum|F_o^2 - F_c^2|/\sum F_o^2|, \quad R_{wp} = [\sum\omega(I_o - I_c)^2/\sum(\omega I_o^2)]^{1/2}$$

$$R_{exp} = [N - P/\sum\omega[I_{obs}]^2]^{1/2}$$

FIG. 1. Electron micrographs of $K_2ZrGe_2O_7$ at magnifications of (a) $1000 \times$ and (b) $15,000 \times$.

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\mathrm{\mathring{A}}^2 \times 10^3$) for $K_2ZrGe_2O_7$

	x	y	z	U(eq)[a]
Zr	2500	7500	0	21(1)
Ge	−360(2)	7193(3)	1218(1)	22(1)
O(1)	1275(8)	6640(10)	1028(5)	19(3)
O(2)	−1291(9)	9500(10)	436(6)	29(3)
O(3)	−1191(8)	4470(10)	1264(5)	23(3)
O(4)	0	8580(20)	2500	32(3)
K	1502(4)	2110(5)	1802(2)	37(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

layers as shown in Fig. 4. The layers are centered at exactly 0 and $\frac{1}{2}c$ by the positioning of the Zr atoms. These layers are connected to each other through O4 atoms creating $Ge_2O_7^{6-}$ pyrogermanate groups. The structure is thus three-dimensional and possesses channels parallel to the b-axis direction circumscribed by a 12-membered ring consisting of two Zr atoms, four Ge atoms, and six oxygen atoms (Fig. 5). The potassium ions reside within these channels. We note that the Ge–O–Ge bonding is bent with an angle of 128.7(7)°.

The Zr–O bond distances are regular, being well within the range of those obtained in similar octahedral–tetrahedral structures from single-crystal data (14, 24). The bond angles deviate only slightly from 90°. The Ge–O bond distances (1.737(7)–1.776(3) Å) are also regular (13, 14), and both average Zr–O and Ge–O bond lengths are equal (within experimental error) to the sum of their ionic radii for their respective coordination numbers (Zr–O, 2.12 Å; Ge–O 1.78 Å) (25).

TABLE 3
Selected Bond Distances (Å) and Angles (°) for $K_2ZrGe_2O_7$

Zr–O1	2.084(2) × 2	Ge–O1	1.737(7)
Zr–O2	2.048(6) × 2	Ge–O2	1.743(6)
Zr–O3	2.113(5) × 2	Ge–O3	1.734(6)
Ge–Ge	3.209	Ge–O4	1.780(3)
K–O1	2.698(5)	K–O2[b]	2.989(8)
K–O3	2.903(6)	K–O3[a]	2.916(7)
K–O3[g]	2.959(7)	K–O4[d]	2.759(6)
K[a]–O4[d]	2.759(6)		
O1–Zr–O2[c]	87.9(4) × 2	O1–Zr–O2[g]	92.2(4) × 2
O1–Zr–O3[h]	88.2(3) × 2	O1–Zr–O3[b]	91.8(3) × 2
O2[g]–Zr–O3[b]	89.5(4) × 2	O2[c]–Zr–O3[b]	90.5(4) × 2
O1–Ge–O2	115.1(4)	O1–Ge–O3	108.9(6)
O1–Ge–O4	104.0(4)	O2–Ge–O3	118.4(4)
O2–Ge–O4	99.8(4)	O3–Ge–O4	109.1(5)
Ge–O4–Ge[a]	128.7(7)	Zr–O1–Ge	141.09(4)
Ge–O2–Zr[c]	160.8(5)	Ge–O3–Zr[b]	129.0(3)

[a] $-x, y, \frac{1}{2} - z$; [b] $-x, 1 - y, -z$; [c] $-x, 2 - y, -z$; [d] $x + x, 1 - y, -\frac{1}{2} + z$; [g] $\frac{1}{2} + x, y - \frac{1}{2}, z$; [h] $\frac{1}{2} + x, \frac{1}{2} + y, z$.
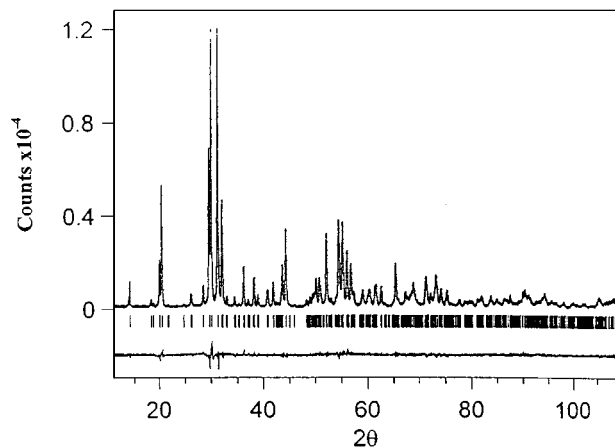
FIG. 2. X-ray diffraction pattern of $K_2ZrGe_2O_7$. Crosses correspond to observed data; the solid line represents the calculated profile. Ticks mark the positions of allowed reflections, and a difference curve, at the same scale, is plotted at the bottom of the pattern.

The potassium ions reside inside the channels and bond to the framework oxygens through six oxygens that are in the layer above or below the K^+ along the c-axis direction. The K–O bond distances range from 2.698(5) to 2.989(8) Å. The sum of the ion radii is 2.78 Å (24). The K^+–K^+ distance is 3.881(5) Å. This close approach arises from adjacent potassium ions that have the same y parameter but $\pm x$ values. They are bonded to the same O4 whose x parameter falls exactly between the two potassium x values. For example, the potassium ions at 0.1502, 0.2110, 0.1802 and −0.1502, 0.2110, 0.3198 are bonded to the O4 at 0, −0.142, 0.25 at a distance of 2.759(6) Å (Fig. 3, Table 3). A second set of tunnels is formed by the bridging of the layers through the pyrogermanate O4 atoms running parallel to the b axis (Fig. 5). The two K^+-bonded to O4 are now seen to be in adjacent tunnels in this direction. For example, the O4 at $\frac{1}{2}$, 0.642, $\frac{3}{4}$ bonds to K^+ ions at 0.3498, 0.289, 0.818 and 0.6502, 0.289, 0.682. However, within these tunnels the adjacent potassium ions ($xyz; \frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$) have an even closer approach of 3.613(4) Å. There are no oxygen atoms between them as they are each bonded to five oxygen atoms of the nearest layer plus an O4 atom.

Exhaustive treatment of the potassium zirconium pyrogermanate with 0.1 M HNO_3 removed only small quantities of the K^+. Thus, the potassium ion appears to be firmly held within the framework even though four of the six K–O bonds are long.

DISCUSSION

Potassium zirconium pyrogermanate has a structure that is related to that of layered α-zirconium phosphate (α-ZrP), $Zr(HPO_4)_2 \cdot H_2O$ (24). The latter compound is monoclinic, $P2_1/n$, with $a = 9.060(2)$ Å, $b = 5.297(1)$ Å, $c = 15.414(3)$ Å,
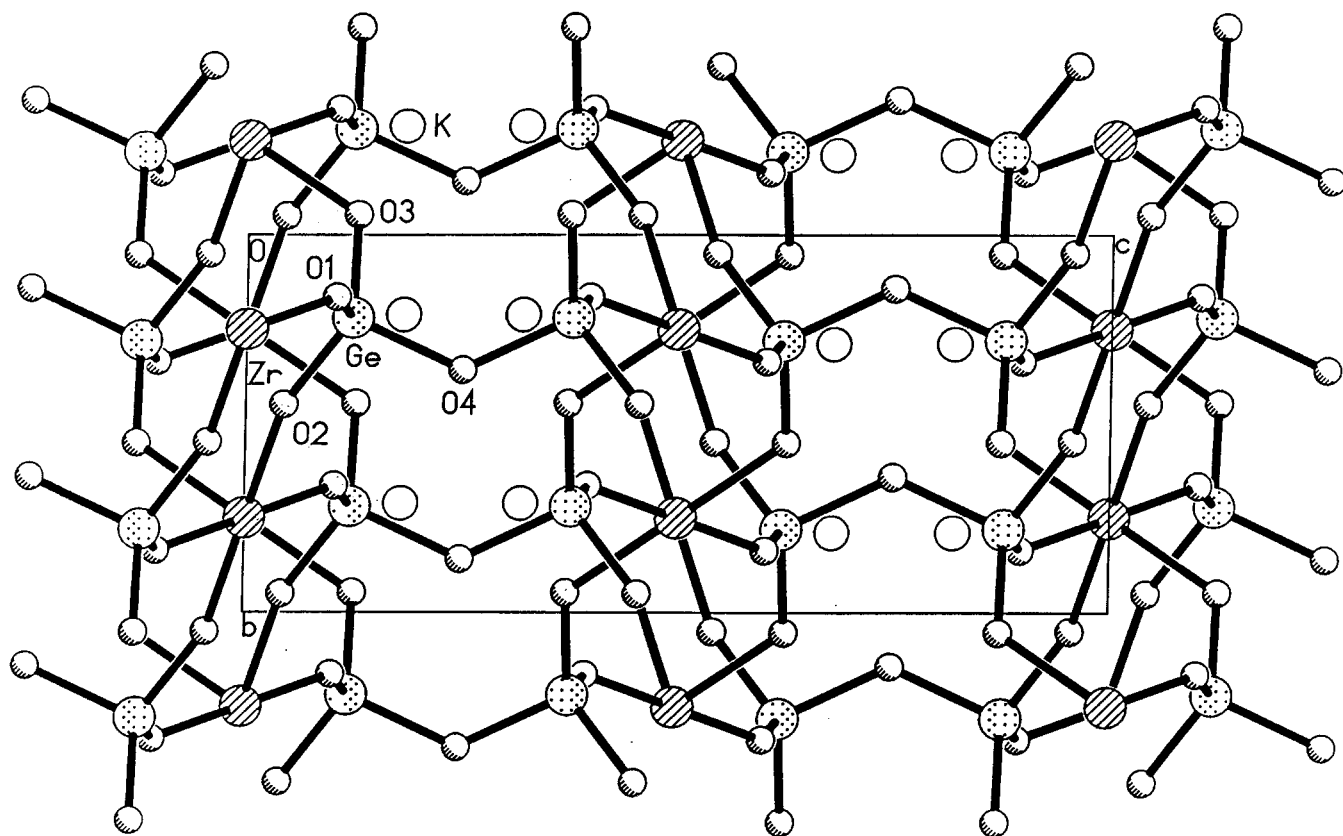
FIG. 3. Ball-and-stick representation of the $K_2ZrGe_2O_7$ structure as viewed down the a axis. The potassium ions are above and below the adjacent O4 atoms.

$\beta = 101.71(2)°$. Comparison with the germanate cell dimensions shows that the a and b axes, which are the in-plane dimensions of α-ZrP, are quite similar. The c axis of the pyrogermanate is smaller than the corresponding one for α-ZrP by 2.6 Å because of the condensed nature of the pyrogermanate group. In α-ZrP the P–OH groups point into the interlayer space and leave a van der Waals gap between the layers within which the water molecule resides.

The lower symmetry of α-ZrP arises from the fact that the Zr atoms are slightly above and below the layer mean planes at $c = 0$, $\frac{1}{2}$. In zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, the zirconium atoms lie precisely in the mean planes at $c = 0$ and $\frac{1}{2}$ and the space group is $C2/c$ (26). The unit-cell dimensions of the phenylphosphonate are $a = 9.0985(5)$ Å, $b = 5.4154(3)$ Å, $c = 30.235(2)$ Å, $\beta = 101.333(5)°$. In this compound, the phenyl groups replace the monohydrogen phosphate OH groups, resulting in the very large c axis.

Given the crystallographic relationships described above one might suspect that hydrolysis of the potassium zirconium germanate should lead to a layered compound, $K_2H_2Zr(GeO_4)_2$, that is, the germanate analogue of α-ZrP. In fact the compound $Na_3HZr(GeO_4)_2$ fits that role. The

structure was solved in space group $I2/m$, with $a = 9.298$ Å, $b = 14.064$ Å, $c = 5.664$ Å, $\gamma = 91°$ (15). The Zr atoms are at $b = 0$ and $\frac{1}{2}$. Rearrangement of the axes into the more conventional space group (i.e., $b = c$, $c = b$, $\gamma = \beta$) immediately shows the relationship of this compound to the pyrogermanate. In fact the layered phase should be an excellent ion exchanger, with high capacity judging from the behavior of α-ZrP (27).

It should be noted that $Na_3HZr(GeO_4)_2$ was prepared hydrothermally at 300°C whereas the pyrogermanate was obtained at 180°C. It might be expected that the condensed phase would form at the higher temperature rather than the other way round. For example, it has been suggested (28) that α-ZrP forms a pyrophosphate on heating at $\sim$500°C that also has the layers joined as for the pyrogermanate. α-ZrP undergoes a series of phase transformations on heating and loses a mole of water by condensation above 400°C (29) but the resultant phase is essentially amorphous. Long annealing at 500°C produced a poorly developed X-ray pattern of insufficient quality to characterize this high-temperature phase. However, a silicon phosphate analogue of α-ZrP is known (30). Heating this phase to the state of condensation or pyrophosphate formation also produced
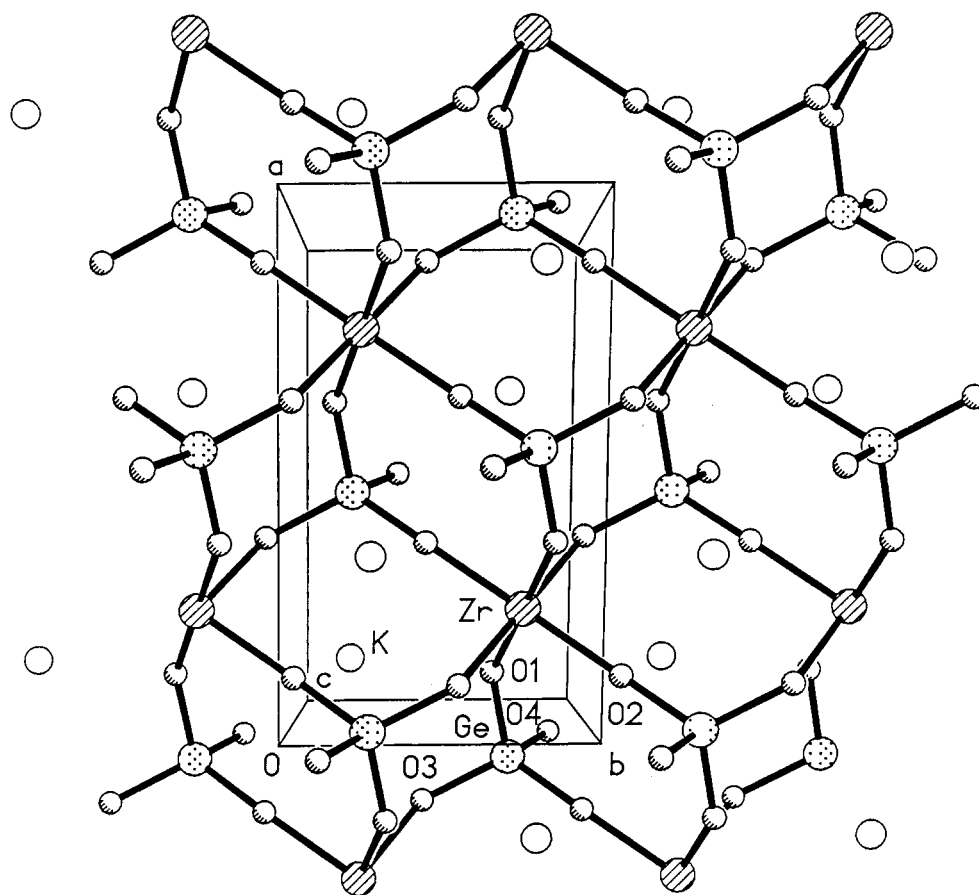
FIG. 4. Ball-and-stick representation of a single layer in the *ab* plane that connects through Ge–O–Ge linkages to similar layers in the *c*-axis direction. Atom representations are as given in Fig. 3.

a poorly crystalline solid. However, the crystalline pyrophosphate, SiP_2O_7, Form I, was prepared by heating SiO_2 in enriched phosphoric acid at 250°C. The structure was solved (31) from X-ray powder data and found to have a framework similar to that of the pyrogermanate but without any exchangeable alkali metal cations.

A sodium zirconium pyrogermanate of composition $Na_2ZrGe_2O_7$ has been prepared hydrothermally at 500°C (14). It is triclinic with $a = 5.630$ Å, $b = 6.677$ Å, $c = 9.108$ Å, $\alpha = 70.60°$, $\beta = 88.85°$, $\gamma = 87.04°$, space group P-1, $Z = 2$. This compound has structural similarities to the subject compound. It also consists of layers formed from ZrO_6 octahedra and GeO_4 tetrahedra. However, in the sodium compound the center of symmetry is halfway between adjacent sodium ions, whereas in the potassium pyrogermanate the Zr atoms sit on the centers of symmetry. As a result the octahedra are closer to ideal in the potassium phase. As seen in Fig. 3 the bent bonds by which the germanium atoms bridge across layers through oxygen in the potassium compound all bend in the same direction in one interlayer region and in the opposite direction in the adjac-

ent layers. However in the sodium pyrogermanate alternate Ge–O–Ge groups bend in opposite directions (Fig. 6) with a Ge–O–Ge angle of 121.2(6)°. Thus, each unit cell contains two half-layers bridged by the bent Ge–O–Ge connectivity, producing a cell with a single such layer. In the potassium compound the alternate layer Ge–O–Ge connections bend in opposite directions as required by the centers of symmetry at the Zr atoms. Thus, the unit cell extends over two complete layers. As a result the *c* axis in the potassium compound is 12.9555(3) Å as compared with the *b* axis of the triclinic sodium pyrogermanate, 6.677 Å. The other two unit-cell dimensions in both compounds are very close in value to each other.

Because of the lower symmetry there are two symmetry-independent sodium ions in the unit cell. Na1 is located at opposite corners of the unit cell as shown in Figs. 6 and 7. The one at a *b* value of ∼0.9 is approximately at $a \cong \frac{3}{4}(0.731)$ and the centrosymmetrically related Na1 is at $a \cong \frac{1}{4}$. There are two distances of close approach of these sodium ions. This is best visualized by reference to Fig. 8 where four unit cells are shown as viewed down the *a*-axis direction. At the
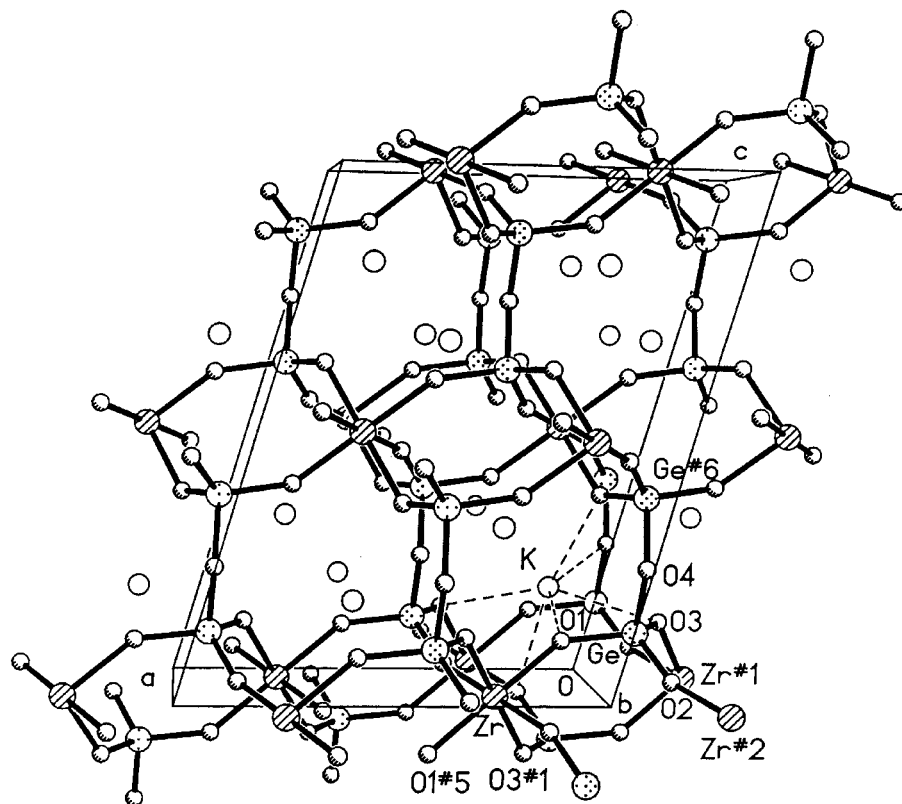
FIG. 5. Ball-and-stick representation of $K_2ZrGe_2O_7$ as viewed down the b axis, showing the bonding of K^+ to the lattice oxygens (dashed lines).
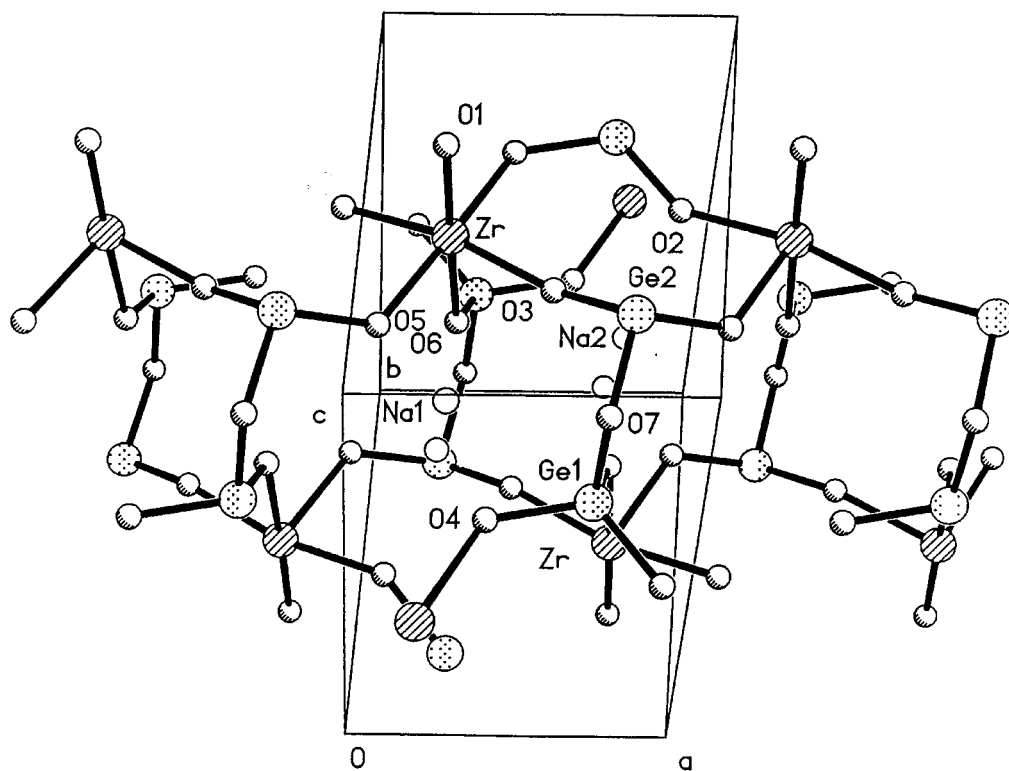

FIG. 6. Ball-and-stick representation of two half-layers of $Na_2ZrGe_2O_7$ as viewed down the c axis, showing the alternating in and out bend of the Ge–O–Ge bonds.
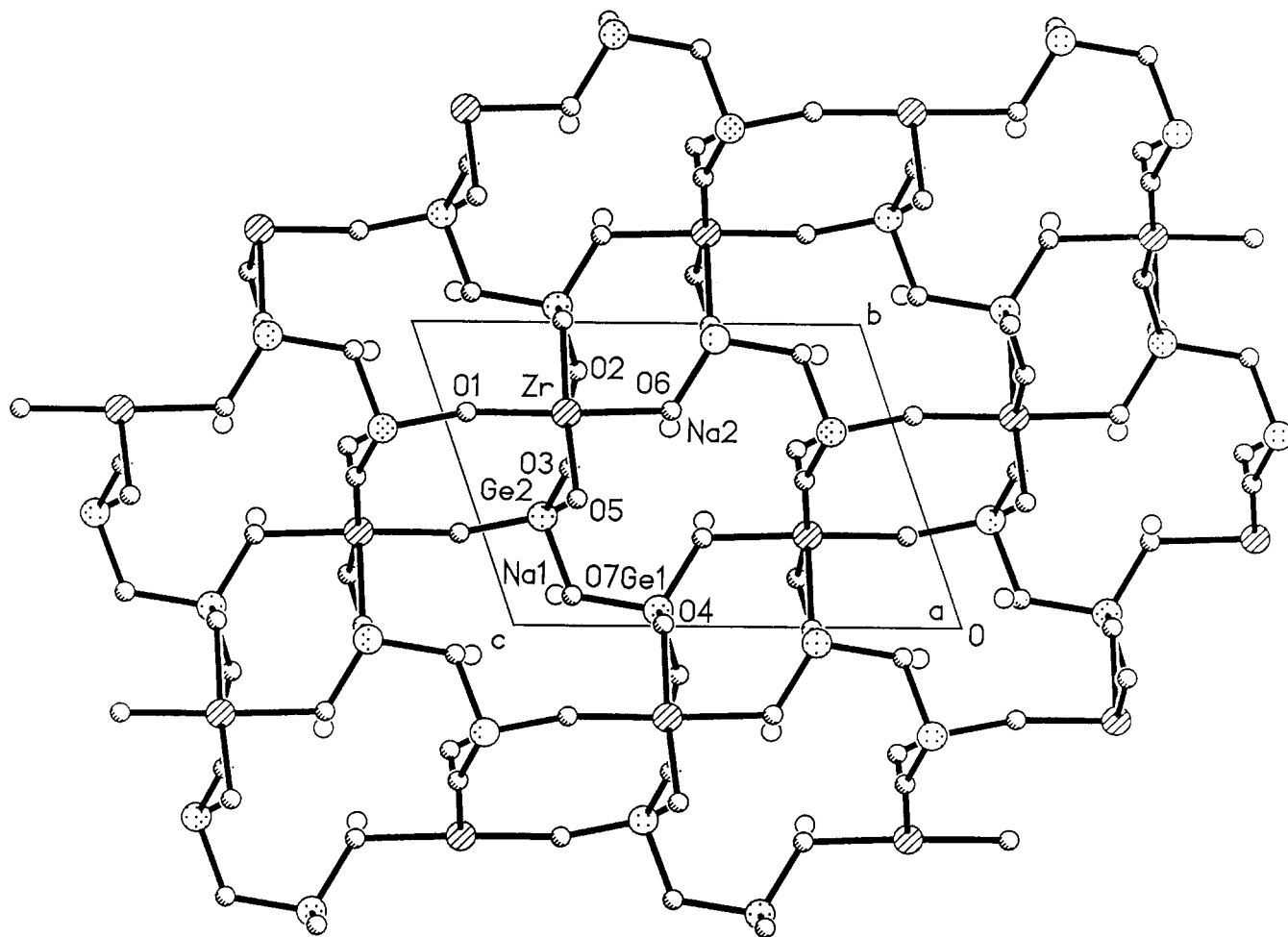
FIG. 7. Ball-and-stick projection of $Na_2ZrGe_2O_7$ structure down the a axis. Note the different positions of Na1 and Na2 and their closeness of approach as described in the test.

intersection of the four unit cells, the Na$^+$ at $b \cong 0.9$, $a \cong \frac{3}{4}$ is at a distance of 3.318 Å from one diagonally across the intersection of the four unit cells at a value of $\sim\frac{1}{4}$. There is also another distance of close approach of 3.705 Å with the same sodium ion one unit cell up in the a direction.

The Na2 sodium ions are near the center of the cell along the c axis, 0.497 and 0.503, respectively, but at $a = \pm 0.233$ and $b = \pm 0.344$. This Na2–Na2 distance is only slightly greater at 3.357 Å. These sodiums are bonded to framework oxygens in a fashion similar to that of the K$^+$ in the potassium zirconium pyrogermanate. Na1 has almost the same b and c positional parameters as O7, the oxygen bridging the Ge atoms. Thus, it forms two bonds to O7: the one where the oxygen is below the Na1 ion is 2.541 Å, and the second bond is with the O7 diagonally across the intersection of the four unit cells , 2.364 Å. Na1 is also bonded to O1, O4, and O5 at bond distances of 2.567, 2.377, and 2.329 Å, respectively. Na2 is very near O6 as seen in Figs.

7 and 8. This bond distance is 2.430 Å but there are two other O6 atoms adjacent to Na2 at about half a unit cell away in the $\pm$ a-axis direction with distances of 2.812 and 2.863 Å. Na2 also forms bonds with O2 (2.396 Å) and O3 (2.544 Å). The details of this sodium zirconium pyrogermanate presented here were not apparent from the original paper and were recalculated by us. Furthermore, no estimated standard deviations were given in the original paper so they are not included in the above discussion.

ACKNOWLEDGMENTS

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