A Rietveld Refinement of the Structure of K_2ZnGeO_4 and Its Relationship to a Revised Model of the $KGaO_2$ Structure Type

J. GRINS[1]

Department of Inorganic Chemistry, Arrhenius Laboratory,
University of Stockholm, S-10691 Stockholm, Sweden

AND D. LOUËR

Laboratoire de Cristallochimie, UA CNRS 254, Université de Rennes I,
avenue du Général Leclerc, F-35042 Rennes Cédex, France

The K_2ZnGeO_4 structure has been refined, from X-ray powder diffractometer data, in space group $Pca2_1$ and with the unit cell $a = 11.0769(10)$ Å, $b = 5.5216(5)$ Å, $c = 15.8465(13)$ Å, $V = 969.2$ Å³, to residual factors $R_F = 4.9\%$ and $R_{wp} = 16.2\%$. Constraints on the positional parameters (pair-wise linking) were used in order to obtain a convergent refinement. The structure is a stuffed cristobalite-type structure with the K atoms within voids in a framework of corner-sharing ZnO_4 and GeO_4 tetrahedra. Guinier–Hägg photograph data indicate that K_2ZnSiO_4 and Rb_2ZnGeO_4 are isostructural compounds. The K_2ZnGeO_4 structure is found to be isotypic with the $KGaO_2$ structure. A reevaluation of the published single crystal X-ray data for $KGaO_2$ suggests that one reported oxygen position is erroneous. © 1990 Academic Press, Inc.

Introduction

Studies of some alkali-ion conducting silicates and germanates (*1*) have shown that compounds isotypic with the high-temperature modification of Na_2ZnSiO_4 exhibit considerable ionic conductivities. These phases are denoted below as *C*-type phases.

The basic structure type of the *C*-type phases was established by the structure determination of Na_2BeSiO_4 by the Rietveld technique (*2*) and subsequently and independently by studies of twinned crystals

(*3*). The structures of other *C*-type phases have recently been refined; the sodium-deficient phases $Na_{1.8}(Ga_{0.1}Zn_{0.9})MO_4$ with $M =$ Si or Ge (*4*) and the mixed-alkali phase $(Na_{1.4}K_{0.6})ZnGeO_4$ (*5*).

The basic $A_2M'M''O_4$ *C*-type structure is related to the cristobalite structure, with an orthorhombic unit cell related to the ideal cubic cristobalite axis $a_c \approx 7$ Å by $a_{ort} \approx 10$ Å $= \sqrt{2}a_c$, $b_{ort} \approx 5$ Å $= \sqrt{2}/2\,a_c$, and $c_{ort} \approx 14$ Å $= 2\,a_c$. The $M'O_4$ and $M''O_4$ tetrahedra share corners and form a cristobalite-type framework. The alkali ions are located on a diamond type lattice within the framework.

The ionic conductivity properties of K_2ZnGeO_4 and the solid solutions $K_{2x}Zn_xGe_{2-x}O_4$ and $K_{2x}Ga_{2x}Ge_{x-2x}O_4$,

[1] To whom correspondence should be addressed.

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$1.8 \leq x \leq 2.0$, have been studied by Maazas and Delmas (6).

The structure of K_2ZnGeO_4 has been refined to establish the structural relation to the C-type structures and to other stuffed cristobalite-type structures.

The compounds K_2ZnGeO_4 and $KGaO_2$ exhibit nearly identical orthorhombic unit cells (see below) and powder patterns and are therefore believed to be isotypic (6) and to possess a C-type structure.

A closer comparison between the $KGaO_2$ structure and the C-type structures hitherto studied (2–5) shows, however, that one of the reported oxygen atom positions in $KGaO_2$ is different from the corresponding position in the C-type structures. The published single crystal X-ray data of $KGaO_2$ are therefore also reevaluated below in order to compare the $KGaO_2$ and K_2ZnGeO_4 structures.

In addition, the compounds K_2ZnSiO_4 and Rb_2ZnGeO_4 have been synthesized and characterized by their Guinier–Hägg powder photographs.

Experimental

The K_2ZnGeO_4 compound was synthesized by solid state reaction in air, using dried K_2CO_3, ZnO, and GeO_2 as starting materials. A ground mixture of appropriate amounts of the starting materials was fired at 1125 K for 1 day. The material was then twice reground and tempered at 1125 K for 1 day.

K_2ZnSiO_4 and Rb_2ZnGeO_4 were synthesized in the same manner at the temperatures 1225 and 1275 K, respectively. The Rb_2ZnGeO_4 compound was found to be hygroscopic and had to be handled in a dry atmosphere.

X-ray powder photographs were recorded with a Guinier–Hägg focusing camera using $CuK\alpha_1$ radiation and Si as internal standard and were evaluated with a film scanning system (7).

The powder diffractometer data for the profile refinements were recorded with a CGR (Compagnie Generale de Radiologie) powder diffractometer operating at 45 kV and 30 mA. Monochromatic incident $CuK\alpha_1$ radiation was used, obtained with a curved crystal quartz monochromator. There was no Soller slit in the diffracted beam. Consequently, peak asymmetry is present at low angles. The powder pattern was scanned in steps of $2\theta = 0.02°$ and the data were collected employing a fixed time counting strategy (48 sec). The sample was mixed with an equal amount of amorphous silica and side-loaded in order to minimize preferred-orientation effects. Due to the previously observed slight hygroscopicity of K_2ZnGeO_4, the data were collected with the sample chamber flushed with dry N_2 gas.

Indexing of Powder Pattern and Rietveld Refinement

The X-ray Guinier–Hägg powder pattern of K_2ZnGeO_4 was indexed on the basis of an orthorhombic unit cell, given in Table I. The unit cell dimensions and systematically absent reflections, $h0l$ $h \neq 2n$ and $0kl$ $l \neq 2n$, indicate that the structure is of the basic C-type (2, 3). The first 20 observed reflec-

TABLE 1

CRYSTAL DATA FOR K₂ZnGeO₄

Stoichiometry	K₂ZnGeO₄
Space group	$Pca2_1$
Z	8
F.W.	280.16
a (Å)	11.0769(10)
b (Å)	5.5216(5)
c (Å)	15.8465(13)
V (Å³)	969.2(2) Å³
d_{calcd} (g/cm³)	3.84
Cell figures-of-merit:	
M_{20}	20
F_{20}	28 (0.0104,70)

tions of the indexed powder pattern are listed in Table II.

Besides peaks assignable to K_2ZnGeO_4 the X-ray diffractometer data showed additional weak Bragg peaks attributable to K_2GeO_3, which was included in the refinement as a second phase. The amount of K_2GeO_3 in the sample was calculated from the scale factors and was found to be very small, 2.8 wt %.

The powder patterns of K_2ZnSiO_4 and Rb_2ZnGeO_4 could also be indexed on the basis of orthorhombic unit cells with cell parameters $a = 10.917(2)$ Å, $b = 5.433(1)$ Å, $c = 15.553(2)$ Å, and $V = 922.5$ Å³ for K_2ZnSiO_4, and $a = 11.395(2)$ Å, $b = 5.636(1)$ Å, $c = 16.324(4)$ Å, and $V = 1048.3$ Å³ for Rb_2ZnGeO_4. The powder patterns are pseudo-cubic, but the orthorhombic symmetry is shown by the splitting of the reflections 214/400/020. On the basis of Guinier–Hägg data we thus conclude that K_2ZnSiO_4 and Rb_2ZnGeO_4 are isostructural with K_2ZnGeO_4.

The number of positional parameters to refine for K_2ZnGeO_4 with all atoms in $4(a)$ positions of the space group $Pca2_1$ is 47 (one z coordinate fixed). In order to have a satisfactory over-determination it was necessary to decrease this number of parameters by introducing additional constraints. The number of positional parameters may be reduced from 47 to 24 by linking coordinates of pairs of atoms according to x, y, z and $x, y + \frac{1}{2}, -z + \frac{1}{2}$. The constraints correspond to adding a third symmetry plane perpendicular to the c-axis with a glide component along the b-axis, or alternatively to geometrically adding a center of symmetry. The structural consequences of the added constraints are discussed below.

The K_2ZnGeO_4 structure was thus refined with $Pca2_1$ symmetry and with the added constraints detailed above and a total of 41 parameters: (i) for K_2ZnGeO_4, 24 positional, 3 temperature, and 3 cell parameters and 1 scale factor; (ii) for K_2GeO_3, 3

TABLE II

OBSERVED AND CALCULATED 2θ VALUES FOR THE GUINIER–HÄGG POWDER DIFFRACTION PATTERN OF K_2ZnGeO_4 UP TO THE 20TH OBSERVED LINE

$h\,k\,l$	$2\theta_{obsd}$	$\Delta\,(2\theta)$	d_{obsd} (Å)	I_{obsd}	I_{calcd}
2 0 2	19.569	0.029	4.533	272	263
0 1 2		−0.011		175	178
2 0 3	23.246	−0.007	3.8234	10	9
1 1 4	28.874	0.013	3.0896	20	20
2 1 4	32.137	0.000	2.7830	1000	1000
4 0 0	32.298	−0.003	2.7695	276	266
0 2 0	32.403	0.001	2.7608	259	252
1 2 0	33.436	0.014	2.6778	21	21
1 1 5	33.598	0.033	2.6653	9	9
3 1 3	33.755	0.008	2.6532	21	21
1 2 1	33.920	0.009	2.6407	25	25
0 0 6		0.005		0	0
2 1 5	36.471	0.008	2.4616	39	31
3 1 4	37.026	0.005	2.4260	28	27
4 1 2	38.083	0.028	2.3611	4	4
4 0 4	39.705	0.026	2.2682	2	3
3 2 0	40.782	0.005	2.2108	18	18
3 2 1	41.180	−0.010	2.1903	3	2
2 2 4	43.139	0.026	2.0953	2	2
2 0 7		0.004		0	0
4 0 5	43.349	−0.007	2.0856	6	6
3 2 3	44.360	−0.019	2.0404	3	4
0 0 8	45.772	0.002	1.9807	72	74

Note. The observed intensities are from the diffractometer data and the calculated intensities are as calculated by the DBW3.2 program. $\Delta(2\theta) = 2\theta_{obsd} - 2\theta_{calcd}$. $\lambda = 1.5406$ Å.

cell and 1 overall temperature parameter and 1 scale factor; and (iii) 3 half-width (U, V, W), 1 asymmetry, and 1 zero-point parameter.

The starting coordinates for K_2ZnGeO_4 were taken from the Na_2BeSiO_4 structure determination (2) and the atomic coordinates for K_2GeO_3 from Ref. (8). The refinements were considered converged when the shifts were less than 1/10 of the e.s.d.'s. The program used was a local version of DBW 3.2 (9). Step intensities in the range $10° \leq 2\theta \leq 77.5°$ were included in the refinements comprising 291 theoretical Bragg reflections. The calculations show that the

TABLE III

POSITIONAL PARAMETERS AND TEMPERATURE
FACTORS FOR K_2ZnGeO_4

Atom	x/a	y/b	z/c	B (Å²)
Zn 1	0.2370(6)	0.0340(12)	0.4358(6)	0.47(6)
Zn 2	0.0093(8)	0.5127(14)	0.6914(6)	0.47(6)
Ge 1	0.0093(8)	0.0127(14)	0.8086(6)	0.47(6)
Ge 2	0.2370(6)	0.5340(12)	0.0642(6)	0.47(6)
K 1	0.0160(12)	0.4971(34)	0.9349(10)	0.8(1)
K 2	0.0160(12)	0.9971(34)	0.5651(10)	0.8(1)
K 3	0.2338(14)	0.5524(20)	0.3197(10)	0.8(1)
K 4	0.2338(14)	0.0524(20)	0.1803(10)	0.8(1)
O 1	0.1617(32)	0.0850(58)	0.8466(22)	1.1(2)
O 2	0.1617(32)	0.5850(58)	0.6534(22)	1.1(2)
O 3	0.1942(32)	0.3322(62)	0.4836(20)	1.1(2)
O 4	0.1942(32)	0.8322(62)	0.0164(20)	1.1(2)
O 5	0.0946(34)	0.8987(64)	0.4008(24)	1.1(2)
O 6	0.0946(34)	0.3987(64)	0.0992(24)	1.1(2)
O 7	0.0197(30)	0.8272(66)	0.2078(26)	1.1(2)
O 8	0.0197(30)	0.3272(66)	0.2922(26)	1.1(2)

Note. Standard deviations in parentheses.

fraction of weak reflections is large, with only 33 reflections exceeding a relative intensity of 1%.

The obtained final coordinates and temperature factors are listed in Table III. The e.s.d.'s for the coordinates in Table III are multiplied by 2 in order to compensate for serial correlation in the diffractometer data (*10*). The corresponding R factors are $R_F = 4.9\%$ and $R_{wp} = 16.2\%$.

A corresponding refinement using the full number of positional parameters, 47, did not converge, with the positional parameters oscillating up to 3 e.s.d.'s in subsequent refinement cycles. The R factors were $R_F = 4.7\%$ and $R_{wp} = 16.0\%$. The e.s.d.'s for the atomic coordinates increased by a factor of ~3 compared with the 24 parameter refinement. The differences in atomic coordinates between the two refinements were found to be less than 4 e.s.d.'s. The refinement with the reduced number of parameters is considered to be preferable because (i) the refinement con-

verged, (ii) the R factors did not increase significantly by the introduction of the constraints, (iii) no significant differences in atomic coordinates was observed between the 24-parameter refinement and the 47-parameter refinement, and (iv) the e.s.d.'s were markedly lower for the refinement with the reduced number of parameters.

The pair-wise linked atomic positions in the 24-parameter refinement are consistent with 8(*c*) positions in the space group *Pcab*. Furthermore, alternative distributions of Zn and Ge atoms on their available sites cannot be distinguished due to the very similar X-ray scattering power of Zn and Ge. The K_2ZnGeO_4 structure may therefore equally well be refined in the truly centrosymmetric space group *Pcab* as in *Pca2₁* with the added constraints. The space group *Pcab* is however not compatible with an ordering of the ZnO_4 and GeO_4 tetrahedra analogous with that found for the other *C*-type phases (*cf.* Discussion).

Description of the K₂ZnGeO₄ Structure

The structure is a stuffed cristobalite-type structure with a $ZnGeO_4^{2-}$ framework formed by corner-sharing and alternating ZnO_4 and GeO_4 tetrahedra. The K atoms are found within the cavities of the framework. The structure is illustrated in Fig. 1 and intratomic distances are given in Table IV.

The constraints on atomic coordinates causes nonequivalent atoms in space group *Pca2₁* to have identical surroundings *geometrically*. The Zn1,Ge2, Zn2,Ge1, K1,K2, and K3,K4 pairs of atoms, respectively, exhibit thus identical oxygen surroundings (*cf.* Table III and IV).

Each K atom is tetrahedrally surrounded by four nearest neighbor K atoms. The K atom sites are interconnected via bottlenecks formed by the edges of six interconnected (Zn, Ge)O₄ tetrahedra.
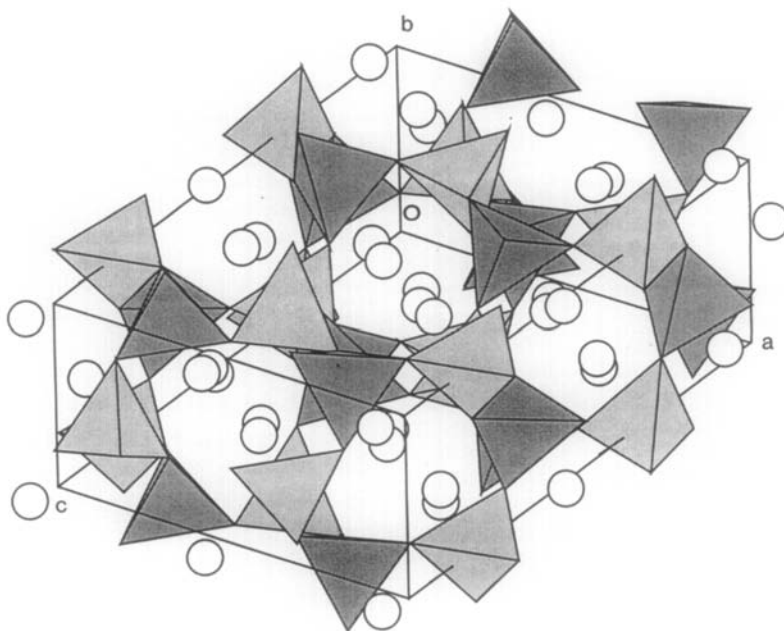
FIG. 1. A perspective drawing of the K_2ZnGeO_4 structure viewed from [210]. Dark-shaded tetrahedra contain Zn and light-shaded tetrahedra contain Ge.

The cavity around a K atom in an ideal high-cristobalite filled structure is shown in Fig. 2a. The K atoms are coordinated by 12 equivalent oxygens at a distance of ~3.5 Å. The K atom sites are connected by regular hexagonal bottlenecks.

The cavities formed around the K1 and K4 atoms in K_2ZnGeO_4 are shown in Figs. 2b and 2c, respectively. The $ZnGeO_4^{2-}$ framework is distorted and collapsed relative to the framework of an ideal cristobalite structure. The collapse may be calculated as being ~20% by volume.

As a consequence of the collapse of the framework some of the 12 oxygen atoms around K become more closely coordinated to K than the others. The K1 and K2 atoms are coordinated by 6 oxygens at distances 2.6–3.1 Å and K3 and K4, by 8 oxygens at distances 2.8–3.2 Å.

Reevaluation of the $KGaO_2$ Structure

von Vielhaber and Hoppe determined the structure of $KGaO_2$ by X-ray single crystal diffraction technique using Weissenberg film data obtained with $MoK\alpha$ radiation (*11*). The final atomic coordinates were obtained from a three-dimensional difference electron density map using 360 observed reflections.

The structure is orthorhombic with space group symmetry *Pcab* (given in an alternative orientation as *Pbca* in Ref. (*11*)) with all atoms in general eight-fold positions. The unit cell $a = 11.07$ Å, $b = 5.51$ Å, $c = 15.81$ Å, and $V = 964$ Å^3 contains 16 $KGaO_2$ formula units. The structure is a stuffed cristobalite type structure. The given atomic coordinates are listed in Table V. For comparison the obtained atomic coor-

TABLE IV

SELECTED INTERATOMIC DISTANCES, Å,
IN K$_2$ZnGeO$_4$

ZnO$_4$ and GeO$_4$ tetrahedra

Zn1–O1	Ge2–O2	1.83(4)	O1–O3	O2–O4	3.02(5)
O3	O4	1.87(4)	O1–O4	O2–O3	3.05(5)
O4	O3	1.86(3)	O1–O5	O2–O6	3.02(5)
O5	O6	1.83(4)	O3–O4	O4–O3	3.07(5)
	m	1.85	O3–O5	O4–O6	2.94(5)
			O4–O5	O3–O6	2.99(5)
				m	3.02
Zn2–O2	Ge1–O1	1.84(4)	O2–O6	O1–O5	2.97(5)
O6	O5	1.92(4)	O2–O7	O1–O8	3.16(5)
O7	O8	1.92(4)	O2–O8	O1–O7	3.02(5)
O8	O7	1.85(4)	O6–O7	O5–O8	3.04(5)
	m	1.88	O6–O8	O5–O7	3.19(6)
			O7–O8	O8–O7	3.07(5)
				m	3.08

K–O polyhedra

K1–O8	K2–O7	2.49(4)	K3–O8	K4–O7	2.72(4)
O5	O6	2.56(4)	O5	O6	2.78(4)
O3	O4	2.63(4)	O1	O2	2.86(4)
O6	O5	2.80(4)	O2	O1	2.89(4)
O4	O3	3.00(4)	O3	O4	2.90(4)
O1	O2	3.12(4)	O1	O2	3.19(4)
O3	O4	3.43(4)	O8	O7	3.27(4)
			O7	O8	3.33(4)
O4	O3	3.57(4)			

K–K distances

K1–K2	K1	3.44(3)	K3–2K4	K4–2K3	3.54(2)
K2	K1	3.49(3)	K1	K2	3.33(2)
K3	K4	3.33(2)	K1	K2	3.33(2)
K3	K4	3.33(2)			

Note. Standard deviations in parentheses.

dinates for K$_2$ZnGeO$_4$ are also listed in Table V, transcribed from $Pca2_1$ to $Pcab$ by x, $y - \frac{1}{4}, -z$.

The coordinates of corresponding atoms in the two structures are very similar except for O4 which is located at $x/a \approx 0.98$ for K$_2$ZnGeO$_4$ and $x/a \approx 0.49$ for KGaO$_2$. The difference in oxygen atom positions is due to corresponding MO_4 tetrahedra ($M =$ (Zn, Ge) or Ga) pointing their apices in opposite directions along the b-axis in the two models.

The single crystal X-ray data for KGaO$_2$ were reassessed by using the published structure factors as input in a series of refinements with the SHELX program.

The 24 positional parameters and 8 individual isotropic temperature factors were refined using the given 360 observed structure factors, $|F_o|$. The statistics of the weighted differences of $\Delta F = |F_o| - |F_c|$ improved significantly by using the Hughes weighting scheme ($w = 1/(h^2|F_{o,min}|^2)$ for $|F_o| \leq h |F_{o,min}|$ and $w = 1/|F_o|^2$ for $|F_o| \geq h |F_{o,min}|$ with $h = 4$ and an estimated value of $|F_{o,min}| = 100$) to establish individual weights in the final refinements.

The initial coordinates were taken from Ref. (*11*). Comparative refinements were made with the x coordinate of the O4 position given as $x/a \approx 0.49$ (named $R1$ below) and with $x/a \approx 0.99$ ($R2$), respectively. The
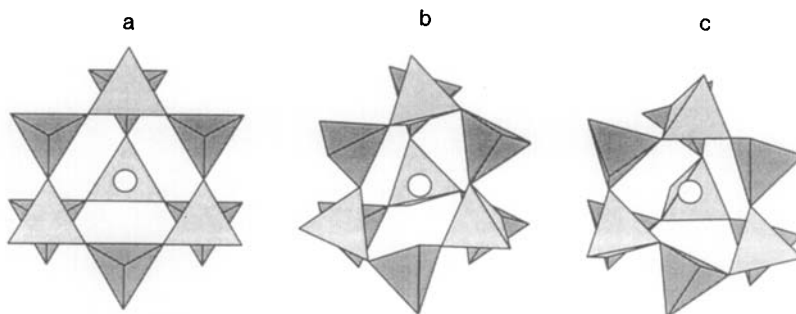

FIG. 2. Illustrations of the cavities containing K$^+$ ions in (a) an ideal filled high-cristobalite structure, (b) K$_2$ZnGeO$_4$, K1 and K2 sites, and (c) K$_2$ZnGeO$_4$, K3 and K4 sites.

TABLE V

ATOMIC COORDINATES FOR KGaO$_2$ AND
K$_2$ZnGeO$_4$ IN *Pcab*

		I[a]	II[b]	III[c]	U
Ga1	x/a	0.008	0.0093(8)	0.0089(2)	0.0129(9)
	y/b	0.260	0.2627(14)	0.2596(7)	
	z/c	0.811	0.8086(6)	0.8111(1)	
Ga2	x/a	0.264	0.2630(6)	0.2634(2)	0.0139(9)
	y/b	0.280	0.2840(12)	0.2803(8)	
	z/c	0.935	0.9358(6)	0.9352(1)	
K1	x/a	0.015	0.0160(12)	0.0142(4)	0.0211(14)
	y/b	0.751	0.7471(34)	0.7580(15)	
	z/c	0.938	0.9349(10)	0.9376(3)	
K2	x/a	0.265	0.2662(14)	0.2643(5)	0.0221(15)
	y/b	0.799	0.8024(20)	0.7983(18)	
	z/c	0.814	0.8197(10)	0.8153(3)	
O1	x/a	0.296	0.3058(32)	0.2985(16)	0.0310(47)
	y/b	0.574	0.5822(62)	0.5723(46)	
	z/c	0.987	0.9836(20)	0.9859(11)	
O2	x/a	0.402	0.4054(34)	0.4083(15)	0.0258(43)
	y/b	0.153	0.1487(64)	0.1553(41)	
	z/c	0.894	0.9008(24)	0.8934(11)	
O3	x/a	0.174	0.1617(32)	0.1671(15)	0.0293(49)
	y/b	0.306	0.3350(58)	0.3145(44)	
	z/c	0.845	0.8466(22)	0.8444(11)	
O4	x/a	0.486	0.9803(30)	0.9818(17)	0.0398(57)
	y/b	0.925	0.9228(66)	0.9431(50)	
	z/c	0.775	0.7922(26)	0.7803(12)	

[a] Coordinates given in Ref. (*11*) for KGaO$_2$.

[b] The corresponding atomic coordinates of K$_2$ZnGeO$_4$ in Table III transcribed to *Pcab* for comparison.

[c] Atomic coordinates obtained from refinement R2 of the KGaO$_2$ structure (see text).

$R2$ refinement yielded the linear $R = 10.5\%$ and the weighted $wR = 12.6\%$ residual factors and the $R1$ refinement, $R = 11.8\%$ and $wR = 14.9\%$.

The resulting distribution of weighted $(\Delta F)^2$ differences, $w(\Delta F)^2$, was considerably better in the $R2$ than in the $R1$ refinements. Thus the average $w(\Delta F)^2$ for the odd k reflections, which were unreasonably high in the $R1$ case, were lowered toward normal values in the $R2$ case. The $R2$ case

is therefore clearly preferable from a statistical point of view.

The atomic coordinates and temperature factors obtained in refinement $R2$ are given in Table V. A selection of interatomic distances in the $R2$ model are given in Table VI together with the distances from the initial structure determination (*11*), as well as corresponding distances found in K$_2$ZnGeO$_4$.

Thus the refinement with $x/a \approx 0.98$ for the O4 position also yielded expected interatomic distances and better discrepancy R factors than the corresponding refinement using $x/a \approx 0.48$.

We conclude that the x coordinate should be $x/a \approx 0.98$ and not $x/a \approx 0.48$ and that the structures of KGaO$_2$ and K$_2$ZnGeO$_4$ are isotypic.

Discussion

Several compounds with the general formula AMO_2 where A = Na, K, Rb, Cs and M is a trivalent metal atom have been reported to have stuffed cristobalite structures.

Compounds which are allegedly isostructural with KGaO$_2$ include γ-NaGaO$_2$ (*11*), RbGaO$_2$ (*11*), CsGaO$_2$ (*11*), RbFeO$_2$ (*12*), KAlO$_2$ (*13*), and KFeO$_2$ (*13, 14*). Of these only the KFeO$_2$ structure has been refined from neutron powder diffraction data (*14*). The atomic coordinate x/a for O4 was given as $x/a \approx 0.48$, but in analogy with our present results (cf. above) for KGaO$_2$ it is more likely to be $x/a \approx 0.98$.

The compound KCoO$_2$ does not fit into the same group. It is known in two modifications (*15*), both believed to be stuffed cristobalite-type structures. The α form exhibits a tetragonal cell with $a = 5.37$ Å and $c = 7.87$ Å. The β form is also tetragonal with $a = 5.71$ Å and $c = 7.29$ Å and is related to the $I\bar{4}2d$ type high-cristobalite structure (*16*).

TABLE VI

SELECTED INTERATOMIC DISTANCES IN KGaO₂ AND CORRESPONDING DISTANCES
IN K₂ZnGeO₄

	I[a]	II[b]	III[c]		I[a]	II[b]	III[c]
			Ga–O tetrahedra				
Ga1–O4	1.72	1.79(2)	1.85(4)	O2–O3	3.12	2.99(3)	2.97(5)
O2	1.83	1.84(2)	1.92(4)	O2–O4	3.20	2.99(3)	3.19(6)
O4	1.84	1.84(3)	1.92(4)	O2–O4	2.45	3.01(3)	3.04(5)
O3	1.93	1.86(2)	1.84(2)	O3–O4	2.79	3.07(2)	3.16(5)
m		1.83	1.88	O3–O4	3.09	2.93(3)	3.02(5)
				O4–O4	2.92	2.92(1)	3.07(4)
				m		2.99	3.08
Ga2–O1	1.80	1.83(2)	1.86(3)	O1–O1	2.97	2.99(1)	3.07(4)
O1	1.85	1.84(2)	1.87(4)	O2–O1	2.99	2.95(3)	2.94(5)
O2	1.80	1.84(2)	1.83(4)	O2–O1	2.92	2.97(3)	2.99(5)
O3	1.74	1.80(2)	1.83(4)	O3–O1	3.01	3.03(3)	3.02(5)
m		1.83	1.85	O3–O1	2.97	3.02(3)	3.05(5)
				O2–O3	2.77	2.94(2)	3.01(5)
				m		2.98	3.01
			K–O polyhedra				
K1–O2	2.65	2.64(2)	2.56(4)	K2–O3	2.71	2.75(2)	2.86(4)
O1	2.72	2.68(2)	2.63(4)	O4	2.62	2.81(2)	2.71(4)
O4	2.77	2.71(2)	2.49(4)	O2	2.85	2.85(2)	2.77(4)
O2	2.86	2.79(2)	2.80(4)	O3	2.94	2.91(3)	2.88(4)
O1	2.99	2.96(2)	2.99(4)	O1	2.85	3.00(2)	2.90(4)
O3	3.36	3.32(2)	3.12(4)	O3	3.01	3.08(3)	3.20(4)
O1	3.35	3.40(2)	3.43(4)	O4	3.50	3.18(2)	3.33(4)
O2	3.59	3.50(2)	3.60(4)	O4	3.39	3.28(2)	3.27(4)
				O1	3.56	3.56(2)	3.57(4)
			K–K distances				
K1–K1	3.39	3.34(2)	3.49(4)	K2–K1	3.40	3.39(1)	3.33(2)
K1	3.41	3.48(2)	3.44(4)	K1	3.40	3.39(1)	3.33(2)
K2	3.40	3.39(1)	3.33(2)	2K2	3.42	3.45(1)	3.54(2)
K2	3.40	3.39(1)	3.33(2)				

[a] As obtained from the initial structure determination (11).

[b] From refinement R2 (see text).

[c] Corresponding distances in K₂ZnGeO₄.

Several compounds with a general formula $A_2M'M''O_4$, where A is an alkali atom, M' a divalent metal atom, and M'' a tetravalent metal atom exhibit structures isotypic with the KGaO₂ structure; Na₂BeSiO₄ (2, 3), the high-temperature modifications of Na₂ZnSiO₄ and Na₂ZnGeO₄ (1), Na₁.₈(Ga₀.₂Zn₀.₈)SiO₄ and Na₁.₈(Ga₀.₂Zn₀.₈)GeO₄ (4), (Na₁.₄K₀.₆)ZnGeO₄ (5), K₂ZnGeO₄, K₂ZnSiO₄, and Rb₂ZnGeO₄ (this study).

In general, the space group for the C-type structures of the $A_2M'M''O_4$ compounds will be determined by the distribution of the $M'O_4$ and $M''O_4$ tetrahedra in the structure. A statistical distribution implies that the space group is Pcab while an ordered and alternating arrangement implies that the space group is Pca2₁.

The space group Pca2₁ is in principle distinguishable from the space group Pcab by the presence of observed reflections hk0

with $k \neq 2n$, which are allowed in $Pca2_1$ but systematically absent in $Pcab$. For Na_2BeSiO_4 and $Na_{1.8}(Ga_{0.2}Zn_{0.8})SiO_4$ it is clear that the space group is $Pca2_1$ and that the $M'O_4$ and $M''O_4$ tetrahedra alternate. The observed relative intensity of the 210 reflection, the strongest $hk0$ reflection with $k \neq 2n$, is 27 and 15%, respectively. Alternative distributions of $M'O_4$ and $M''O_4$ tetrahedra markedly increase the R factors compared with the alternating arrangement.

For the above listed C-type $A_2M'M''O_4$ compounds with $M' = Zn$ and $M'' = Ge$, the distributions of ZnO_4 and GeO_4 tetrahedra could not be determined from the X-ray diffractometer data, due to the very similar X-ray scattering power of Zn and Ge. The observed relative intensity of the 210 reflection is consequently much lower for these compounds; $\approx 1\%$ for $(Na_{1.4}K_{0.6})ZnGeO_4$, $\approx 0.3\%$ for $Na_{1.8}(Ga_{0.2}Zn_{0.8})GeO_4$, and $\approx 0.1\%$ for K_2ZnGeO_4. For $(Na_{1.4}K_{0.6})ZnGeO_4$ the 210 peak is clearly visible, implying that the correct space group is $Pca2_1$. For $Na_{1.8}(Ga_{0.2}Zn_{0.8})GeO_4$, the data are insufficient to establish the presence of the 210 peak and thus the correct space group.

In the case of K_2ZnGeO_4, the 210 peak clearly appears to have a nonzero intensity. Unfortunately the peak is partly overlapped by a K_2GeO_3 impurity peak and its presence cannot be affirmed with full certainty. For the analogous compound K_2ZnSiO_4 the 210 peak is clearly visible in overexposed Guinier–Hägg films and has an estimated intensity of $\approx 1\%$.

We conclude that the X-ray data used in the refinement of the K_2ZnGeO_4 structure are not sufficient to determine the correct space group or distribution of ZnO_4 and GeO_4 tetrahedra. The alternating arrangement of $M'O_4$ and $M''O_4$ tetrahedra is, however, found for all the $A_2M'M''O_4$ compounds for which one is able to distinguish alternative distributions. The alternating arrangement furthermore offers a better local

electroneutrality than a statistical distribution, which suggests that the correct space group for the K_2ZnGeO_4 structure is $Pca2_1$ and that ZnO_4 and GeO_4 tetrahedra alternate.

The compounds $K_2M'M''O_4$ with $M'M'' =$ BeSi, MgGe, CdSi, CdGe, and ZnSi have been reported as cubic-filled cristobalites (17).

Finally it may be noted that the C-type structure is a high-temperature modification in the case of $NaGaO_2$, Na_2ZnSiO_4, and Na_2ZnGeO_4, while the similar compounds γ-$NaFeO_2$ and γ-$NaAlO_2$ apparently do not adopt this structure (18), but are isostructural with γ-$LiAlO_2$ (19).

Acknowledgments

Note added in proof. Recently Prof. R. Hoppe and coworkers have reinvestigated the $KGaO_2$ structure using MoKα radiation and single crystal diffractometer data. The atomic coordinates in their study agree well with the corresponding coordinates for K_2ZnGeO_4 given in this study. (Private communication).

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