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Comparison of the Crystal Structures of Sodium Orthosilicate, Na_4SiO_4, and Sodium Orthogermanate, Na_4GeO_4

Short Communication

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The crystal structures of Na_4SiO_4 and Na_4GeO_4 are isotypic, despite a difference in coordination numbers: in Na_4SiO_4 only one of the four symmetrically independent sodium atoms is four coordinated, in Na_4GeO_4 two of them are.

(Keywords Sodium orthosilicate; Sodium orthogermanate; Coordination numbers; Reduced cells)

Vergleich der Kristallstrukturen von Natriumorthosilikat, Na_4SiO_4, *und Natriumorthogermanat,* Na_4GeO_4 *(Kurze Mitteilung)*

Die Kristallstrukturen von Na_4SiO_4 und Na_4GeO_4 sind isotyp, trotz eines Unterschiedes in den Koordinationszahlen: im Na_4SiO_4 ist nur eines der symmetrisch unabhängigen Natriumatome vierfach koordiniert, während es im Na_4GeO_4 derer zwei sind.

The crystal structure of Na_4GeO_4 has been determined recently [1] and found to be isotypic with the known crystal structures of Na_4CoO_4, K_4GeO_4, K_4SnO_4 and K_4PbO_4. *Halwax* and *Völlenkle* [1] assumed on the basis of a cell constant determination of Na_4SiO_4 [2] that it is isostructural with Na_4GeO_4. Actually the crystal structure of Na_4SiO_4 has been determined with high precision five years ago [3].

The proposed transformation [1] of the cell constants as determined by *Kautz* et al. [2] does not conform to the setting used for Na_4GeO_4, nor does it result in a reduced cell [4] (Tab. 1). *Barker* and *Gadd* [3] used the

Table 1. *Cell constants of* Na_4SiO_4 *and* Na_4GeO_4, *as originally reported and as transformed.* The cell constants are given in the sequences a, b, c and α, β, γ

Compound	Cell constants		Transformation matrix		
	[Å]	[°]			
Na_4SiO_4 [2]	5.58	102.95		—	
(original)	6.20	95.9		—	
	8.51	123.6		—	
Na_4SiO_4 [2]	5.58	71.9	1	0	0
(transformed to	5.59	81.3	1	1	0
reduced cell)	8.38	67.4	1	1	1
Na_4SiO_4 [3]	5.576	103.13		—	
(original)	6.191	95.50		—	
	8.507	123.72		—	
Na_4SiO_4 [3]	5.576	80.92	−1	−1	0
(transformed to	5.576	71.84	−1	0	0
reduced cell)	8.393	67.44	−1	−1	−1
Na_4GeO_4 [1]	5.688	81.32		—	
(original)	5.701	71.50		—	
	8.583	67.95		—	

previously established setting [2] for their structure determination of Na_4SiO_4. However, the reduced cell for their determination of the unit cell is not identical in its orientation to the reduced cell based on the older work (compare the exchange of α and β, and of the rows in their transformation matrices, in the two reduced cells in Tab. 1). The reason for this is that the two shortest lattice vectors in Na_4SiO_4 are essentially equal in length. The orientation of the reduced cell is consequently different depending on which of the vectors is accidentally found to be shorter in a given experiment. The near equality of a and b does not mean that the actual symmetry of Na_4SiO_4 is higher than originally assumed [5]. The *Niggli* matrix obtained from the reduced cell corresponds to lattice character case 31 [4] and does not show any specializations indicating higher symmetry. Therefore the lattice on which the structure is based is definitely triclinic.

Barker and *Gadd* [3] determined the crystal structure of Na_4SiO_4 from 1267 symmetrically independent intensities and refined it to $R = 0.054$ and $R_w = 0.063$. For the cell constants see Table 1, the space group is $P\bar{1}$ and the cell contains two formula units: $Z = 2$. The calculated density is $D_x = 2.672\,\mathrm{g\,cm^{-3}}$, and not $1.336\,\mathrm{g\,cm^{-3}}$ as stated in the original publication.

Table 2. *Positional coordinates of* Na_4SiO_4 *(first row of each atom entry) and* Na_4GeO_4 *(second row) with estimated standard deviations of the least significant digit in parentheses. The values for* Na_4SiO_4 *are transformed to correspond with the coordinates of* Na_4GeO_4. The numbering used by *Barker* and *Gadd* [3] is included for purposes of identification. The Δ are the deviations [Å] between corresponding atoms in Na_4SiO_4 and Na_4GeO_4 when referred to a unit cell with its cell dimensions taken as an average of both compounds

Atom	No. [3]	x	y	z	Δ
Na(1)	3	0.4545 (2)	0.7319 (2)	0.1113 (1)	0.07
Na(1)		0.449 (1)	0.738 (1)	0.1053 (6)	
Na(2)	1	0.7351 (2)	0.2565 (2)	0.4803 (1)	0.06
Na(2)		0.740 (1)	0.258 (1)	0.4845 (6)	
Na(3)	4	0.9038 (2)	0.7640 (2)	0.3318 (1)	0.10
Na(3)		0.895 (1)	0.770 (1)	0.3226 (6)	
Na(4)	2	0.9828 (2)	0.2323 (2)	0.0617 (2)	0.03
Na(4)		0.981 (1)	0.236 (1)	0.0635 (6)	
Si		0.3438 (1)	0.2252 (1)	0.2521 (1)	0.03
Ge		0.3436 (2)	0.2217 (2)	0.2550 (1)	
O(1)	1	0.1564 (3)	0.0428 (3)	0.3074 (2)	0.12
O(1)		0.140 (2)	0.036 (2)	0.306 (1)	
O(2)	4	0.2093 (3)	0.4625 (3)	0.1259 (2)	0.05
O(2)		0.204 (2)	0.472 (2)	0.124 (1)	
O(3)	3	0.3473 (3)	0.3558 (4)	0.4116 (2)	0.12
O(3)		0.355 (2)	0.352 (2)	0.424 (1)	
O(4)	2	0.6498 (3)	0.0443 (3)	0.1486 (2)	0.10
O(4)		0.664 (2)	0.033 (2)	0.139 (1)	

The positional coordinates found for Na_4SiO_4 and Na_4GeO_4 agree very well with eath other (Tab. 2). Judging from these parameters there seems to be no doubt about the isotypism of the two structures. Also the individual and mean bond lengths around sodium atoms Na(1), Na(2) and Na(4) agree nicely with each other in both structures (Tab. 3). However, atom Na(3) is clearly four coordinated in Na_4GeO_4, but is in a distorted five coordination in Na_4SiO_4. The Na(3)—O(3) distance measures 3.07 Å in Na_4GeO_4, but only 2.824 Å in Na_4SiO_4. *Brunner* [6] has proposed to use gaps in the distance spectrum as delimiters in the count of coordinating contacts around a cation. According to his criterion O(3), at a distance of 2.824 Å from Na(3), is coordinated to this sodium atom. The fact that the mean distance Na(3)—O is then longer than for the other five coordinated sodium atoms in Na_4SiO_4 and Na_4GeO_4 is not a counter argument. The mean distances to oxygen atoms surrounding sodium atoms show usually

Table 3. *Sodium-oxygen distances [Å] in* Na_4SiO_4 [3] *and* Na_4GeO_4 [1]. The distances listed below the mean are in each case for the next neighbors outside the coordination polyhedron. Estimated standard deviations in units of the least significant digit in parentheses. All bond lengths are recalculated from positional coordinates and unit cell parameters given in the original papers

	Na_4SiO_4	Na_4GeO_4		Na_4SiO_4	Na_4GeO_4
Na(1)—O(2)	2.334 (2)	2.382 (12)	Na(2)—O(3)	2.252 (4)	2.260 (20)
Na(1)—O(1)	2.337 (2)	2.380 (12)	Na(2)—O(1)	2.299 (2)	2.310 (15)
Na(1)—O(2)	2.357 (3)	2.375 (18)	Na(2)—O(3)	2.303 (2)	2.282 (13)
Na(1)—O(4)	2.455 (2)	2.432 (12)	Na(2)—O(1)	2.306 (3)	2.349 (12)
Na(1)—O(4)	2.482 (3)	2.515 (18)			
mean	2.393	2.417	mean	2.290	2.300
Na(1)—O(3)	3.076 (2)	3.279 (11)	Na(2)—O(4)	3.417 (2)	—
			Na(2)—O(3)	—	3.601 (20)
Na(3)—O(3)	2.330 (2)	2.358 (12)	Na(4)—O(2)	2.309 (2)	2.328 (13)
Na(3)—O(2)	2.366 (2)	2.369 (12)	Na(4)—O(2)	2.328 (3)	2.366 (18)
Na(3)—O(4)	2.390 (2)	2.362 (14)	Na(4)—O(4)	2.342 (3)	2.368 (19)
Na(3)—O(1)	2.417 (3)	2.379 (18)	Na(4)—O(4)	2.423 (2)	2.388 (13)
Na(3)—O(3)	2.824 (3)		Na(4)—O(1)	2.465 (2)	2.481 (13)
mean	2.465	2.367	mean	2.373	2.386
Na(3)—O(1)	3.250 (2)	—	Na(4)—O(4)	3.731 (3)	—
Na(3)—O(3)	—	3.069 (16)	Na(4)—O(3)	—	3.814 (15)

much variability, as can be seen in Na_2MgSiO_4 [7], where the mean Na—O distances (in tetrahedral four coordination) range from 2.30 to 2.38 Å. Thus in Na_4SiO_4 one sodium atom is four coordinated, while the remaining three are five coordinated. In Na_4GeO_4 on the other hand, two sodium atoms are four coordinated and two are five coordinated. Despite this difference in coordination numbers, the overall similarity between Na_4SiO_4 and Na_4GeO_4 is so pronounced that they should be held to be isotypic. The distance from an atom in Na_4SiO_4 to its corresponding atom in Na_4GeO_4 does not exceed 0.12 Å and is on average 0.08 Å (when calculated in a unit cell with the cell dimensions taken as the arithmetic mean of the cell constants of Na_4SiO_4 and Na_4GeO_4, see Table 2). Both, Na(3) and O(3), are atoms with large relative displacements, thus causing the change in the coordination number of Na(3).

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