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The Crystal Structure of $NaGa_{11}O_{16}(OH)_2$

A. NØRLUND CHRISTENSEN

Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

The compound $NaGa_{11}O_{16}(OH)_2$ was prepared using hydrothermal techniques. X-Ray diffraction shows the compound to be monoclinic, the space group is $P2_1/m$ with $a=8.602(5)$ Å, $b=8.906(5)$ Å, $c=9.571(4)$ Å, $\beta=117.1(2)°$; there are 2 formula units per cell.

Least squares refinement with 801 reflections gave a final R-value of 7.5 % for 73 parameters. The intensity data were collected on an automatic diffractometer using monochromatized Cu$K\alpha$-radiation.

The structure contains GaO_6 octahedra and GaO_4 tetrahedra. The mean gallium-ogygen distance within the octahedra is 2.00 Å, $\sigma=0.01$ Å, while the mean gallium-oxygen distance within the tetrahedra is 1.85 Å, $\sigma=0.01$ Å.

A high pressure high temperature hydrothermal investigation of metal oxides has resulted in preparation of dense metal oxide hydroxides with crystal structures of the indium oxide hydroxide type or of the tetragonal type of the ytterbium oxide hydroxide structure.[1-4]

The hydrothermal investigation of the Ga_2O_3-H_2O-Na_2O system yielded a monoclinic compound of unknown composition.[1] A three-dimensional X-ray analysis has shown that this compound, which in Ref. 1 was called a gallium hydroxide phase, [Ga(I)], has the formula $NaGa_{11}O_{16}(OH)_2$.

EXPERIMENTAL

The preparation of $NaGa_{11}O_{16}(OH)_2$, together with its X-ray powder pattern, is given in Ref. 1. The crystal used was 0.012 cm in length and 0.004 by 0.004 cm in cross section. It was mounted with its [010] axis as rotation axis, and was investigated using Weissenberg and precession methods. Only the reflections $0k0$ with $k=2n+1$ were absent, indicating the space group $P2_1$ or $P2_1/m$. A total of 801 independent hkl reflections with $I>2\sigma(I)$ were measured with a Picker diffractometer, using Cu$K\alpha$ radiation monochromatised by reflection from a graphite crystal and a scintillation counter in conjunction with a pulse height analyzer. Lorentz-polarization corrections were applied and a correction was made for absorption using Well's method.[5]

STRUCTURE DETERMINATION

The space group $P2_1/m$ (No. 11) has been used in the structure determination. The structure was solved using direct methods. The program SYMBAD [6] was used to normalize the structure factors and the program MULTAN [7] to determine four sets of phases for 152 reflections. Using the program JIMDAP,[8] three-dimensional Fourier maps were calculated, and those showing positions of heavy atoms at (0.35, 0.60, 0.05), (0.35, 0.25, 0.05), (0.35, 0.10, 0.35), (0.35, 0.75, 0.35), (0.95, 0.60, 0.25), and (0.70, 0.10, 0.35) were used. After a series of refinement cycles and Fourier calculations all the atoms required by the formula $NaGa_{11}O_{16}(OH)_2$, except the hydrogen atoms, were located. Refinement was carried out with the Fortran crystallographic least squares program LINUS,[9] using isotropic temperature coefficients and the refinement converged at a conventional R-value of 7.5 %. Parameters refined were atomic coordinates, thermal parameters, and two scale factors.

CRYSTAL DATA

The formula of the compound is $NaGa_{11}O_{16}(OH)_2$, and the unit cell contains two formula units. The crystal system is monoclinic, and the space group is $P2_1/m$ (No. 11). The unit

Table 1. Atomic coordinates and temperature factors for $NaGa_{11}O_{16}(OH)_2$, with their standard deviations.

Atom	x/a	y/b	z/c	B (Å²)
Na_1	0.041(1)	0.25	0.057(1)	1.7(2)
Ga_1	0.3679(3)	0.5771(3)	0.0490(2)	0.77(6)
Ga_2	0.3727(4)	0.25	0.0465(3)	0.74(7)
Ga_3	0.3471(3)	0.0848(3)	0.3597(2)	0.76(6)
Ga_4	0.3600(4)	0.75	0.3615(4)	0.86(7)
Ga_5	0.9698(3)	0.5786(3)	0.2579(2)	0.79(6)
Ga_6	0.7133(3)	0.0760(3)	0.3469(2)	0.77(6)
Ga_7	0.8877(4)	0.75	0.5404(4)	0.74(7)
O_1	0.612(1)	0.083(1)	0.478(1)	0.2(2)
O_2	0.368(2)	0.25	0.509(2)	0.7(3)
O_3	0.341(2)	0.582(1)	0.231(1)	0.4(2)
O_4	0.338(2)	0.25	0.230(2)	0.5(3)
O_5	0.554(1)	0.081(1)	0.130(1)	0.0(2)
O_6	0.546(2)	0.75	0.120(2)	0.1(3)
O_7	0.098(1)	0.091(1)	0.305(1)	0.0(2)
O_8	0.847(2)	0.25	0.368(2)	0.6(3)
O_9	0.794(1)	0.584(1)	0.050(1)	0.1(3)
O_{10}	0.849(1)	0.593(1)	0.376(1)	0.2(2)
O_{11}	0.097(2)	0.75	0.282(2)	0.4(3)
O_{12}	0.784(2)	0.25	0.052(2)	0.8(4)

Table 2. Interatomic distances (Å) and bond angles (degrees). Standard deviations in parentheses.

Na_1-O_{12}''	2.19(3)	$O_7'-Na_1-O_7$	65.6(5)
Na_1-O_7	2.61(2)	$O_7-Na_1-O_9'''$	140.0(5)
Na_1-O_7'	2.61(2)	$O_9'''-Na_1-O_9''$	70.3(6)
Na_1-O_4	2.33(2)	$O_9''-Na_1-O_7$	140.0(5)
Na_1-O_9''	2.57(2)	$O_{12}''-Na_1-O_4$	141.9(9)
Na_1-O_9'''	2.57(2)		
Ga_1-O_3	1.86(2)	$O_3-Ga_1-O_5'$	93.2(5)
Ga_1-O_5'	2.01(1)	$O_5'-Ga_1-O_9''$	86.5(5)
Ga_1-O_6	2.06(1)	$O_9''-Ga_1-O_{12}'$	99.2(5)
Ga_1-O_5''	2.10(2)	$O_{12}'-Ga_1-O_6$	78.6(5)
Ga_1-O_9''	1.92(1)	$O_3-Ga_1-O_5''$	169.7(5)
Ga_1-O_{12}'	1.96(1)		
Ga_2-O_4	1.91(2)	$O_5'-Ga_2-O_5$	94.3(5)
Ga_2-O_5	2.05(1)	$O_5-Ga_2-O_9'''$	84.1(5)
Ga_2-O_5'	2.05(1)	$O_9'''-Ga_2-O_9''$	97.0(5)
Ga_2-O_6'	2.01(2)	$O_9''-Ga_2-O_5'$	84.1(5)
Ga_2-O_9'''	1.97(1)	$O_4-Ga_2-O_6'$	169.9(6)
Ga_2-O_9''	1.97(1)		
Ga_3-O_7	1.96(1)	$O_2-Ga_3-O_1''''$	93.8(5)
Ga_3-O_1''''	2.06(1)	$O_1''''-Ga_3-O_3''$	82.3(5)
Ga_3-O_2	2.00(1)	$O_3''-Ga_3-O_4$	101.5(6)
Ga_3-O_1	2.03(1)	$O_4-Ga_3-O_2$	82.1(6)
Ga_3-O_3''	1.91(1)	$O_7-Ga_3-O_1$	163.7(5)
Ga_3-O_4	1.90(1)		
Ga_4-O_{11}	2.03(2)	$O_1'''-Ga_4-O_1''$	92.1(5)
Ga_4-O_1''	2.07(1)	$O_1''-Ga_4-O_3$	82.2(5)
Ga_4-O_1'''	2.07(1)	$O_3-Ga_4-O_3'$	103.4(6)
Ga_4-O_2'	2.09(2)	$O_3'-Ga_4-O_1'''$	82.2(5)
Ga_4-O_3	1.91(1)	$O_{11}-Ga_4-O_2'$	167.6(8)
Ga_4-O_3'	1.91(1)		
Ga_5-O_{10}	1.86(2)	$O_9-Ga_5-O_{10}$	103.9(6)
Ga_5-O_7''	1.80(1)	$O_9-Ga_5-O_7''$	113.2(5)
Ga_5-O_{11}'	1.83(1)	$O_9-Ga_5-O_{11}'$	105.0(5)
Ga_5-O_9	1.87(1)	$O_{10}-Ga_5-O_7''$	110.7(6)
		$O_{10}-Ga_5-O_{11}'$	109.5(7)
		$O_7''-Ga_5-O_{11}'$	114.0(6)
Ga_6-O_1	1.83(2)	$O_5-Ga_6-O_1$	114.9(5)
Ga_6-O_{10}''	1.84(1)	$O_5-Ga_6-O_{10}''$	106.1(5)
Ga_6-O_8	1.89(1)	$O_5-Ga_6-O_8$	101.4(6)
Ga_6-O_5	1.90(1)	$O_1-Ga_6-O_{10}''$	112.7(6)
		$O_1-Ga_6-O_8$	110.9(7)
		$O_{10}''-Ga_6-O_8$	110.0(6)
Ga_7-O_2'	2.03(2)	$O_7''''-Ga_7-O_7'''$	89.5(5)
Ga_7-O_7'''	2.01(1)	$O_7'''-Ga_7-O_{10}$	91.0(5)
Ga_7-O_7''''	2.01(1)	$O_{10}-Ga_7-O_{10}'$	88.0(5)
Ga_7-O_8'	2.04(2)	$O_{10}'-Ga_7-O_7''''$	91.0(5)
Ga_7-O_{10}	2.01(1)	$O_2'-Ga_7-O_8'$	169.5(8)
Ga_7-O_{10}'	2.01(1)		

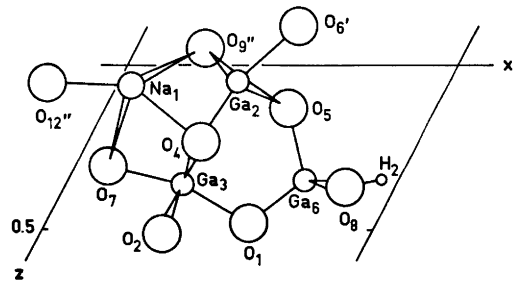


Fig. 1. Projection of metal-oxygen coordination polyhedra on (010). The y coordinates of the metal atoms are: Na_1 (0.25), Ga_2 (0.25), Ga_3 (0.0848), and Ga_6 (0.0760). O_3' is covered by O_4, O_1'''' by O_2, and O_{10}'' by O_8. O_5' is over O_5, and O_9''' is over O_9''. (The atoms with primes after the suffix numbers are symmetry related to the atoms with the same suffix number of which atom the coordinates are listed in Table 1).

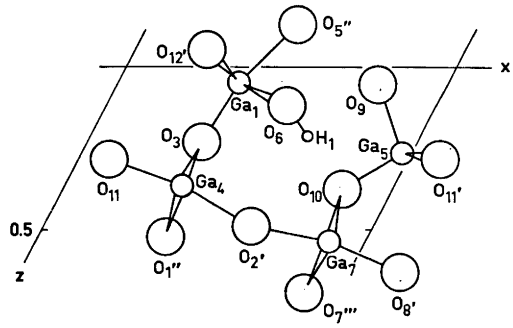
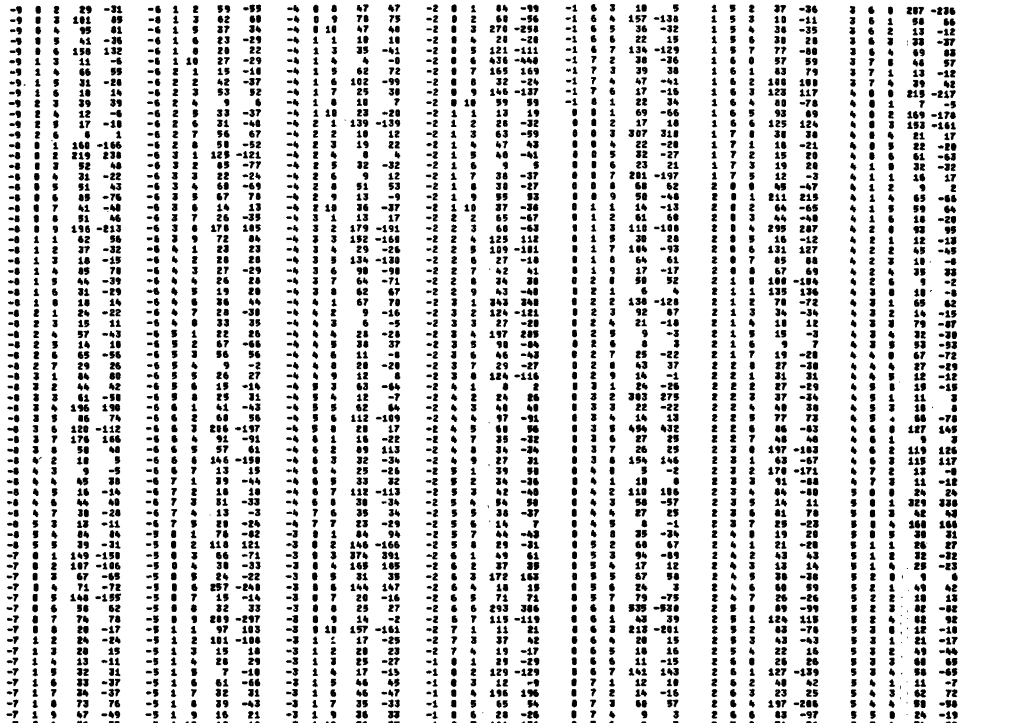


Fig. 2. Projection of metal oxygen coordination polyhedra on (010). The y coordinates of the metal atoms are: Ga_4 (0.75), Ga_7 (0.75), Ga_1 (0.5771), and Ga_5 (0.5786). O_9'' is covered by O_{12}', O_5' by O_6, and O_7'' by O_{11}'. O_3' is over O_3, O_1'' is over O_1''', O_{10}' is over O_{10}, and O_7'''' is over O_7'''.

Table 3. Observed and calculated structure factors. Reading from left to right, the columns are h, k, l, F_{obs}, F_{calc}.



cell parameters are $a = 8.602(5)$ Å, $b = 8.906(5)$ Å, $c = 9.571(4)$ Å, and $\beta = 117.1(2)°$. The calculated density is 5.52 g/cm³, and the absorption coefficient for *Cu*-radiation is 287 cm⁻¹. The structure factors for the atoms were calculated from atomic scattering factors reported by Cromer and Mann.[10] Atomic coordinates and temperature factors are listed in Table 1, interatomic distances and bond angles in Table 2, and observed and calculated

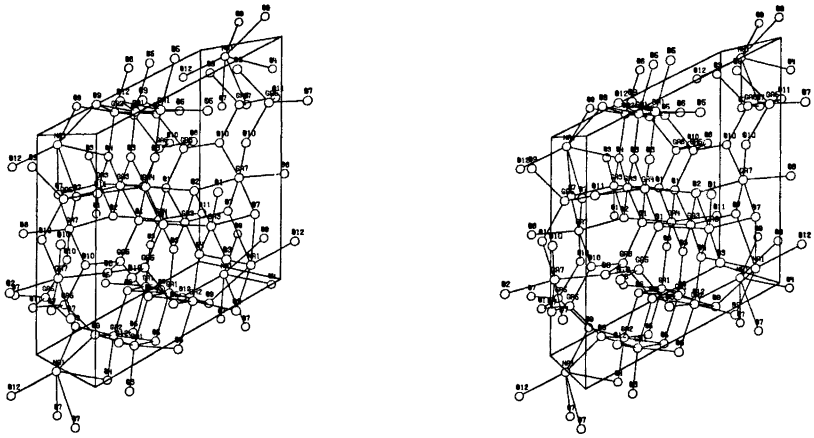


Fig. 3. Three-dimensional model of the crystal structure of $NaGa_{11}O_{16}(OH)_2$.

structure factors in Table 3. Fig. 1 is a projection on (010) showing the metal-oxygen coodination polyhedra for the metal atoms Na_1, Ga_2, Ga_3, and Ga_6, and Fig. 2 is a projection on (010) showing the coordination polyhedra for the metal atoms Ga_1, Ga_4, Ga_5, and Ga_7. Fig. 3 shows a three-dimensional model of the structure.

DISCUSSION

The crystal structure of $NaGa_{11}O_{16}(OH)_2$ contains GaO_6 octahedra and GaO_4 tetrahedra The Ga_1, Ga_2, Ga_3, Ga_4, and Ga_7 atoms are coordinated by six oxygen atoms, while the Ga_5 and Ga_6 atoms are coordinated by four oxygen atoms. The GaO_6 octahedra are distorted and resemble the octahedra found in the diaspore modification of GaOOH [11] and of AlOOH.[12] The distances from gallium to oxygen within the octahedra have a mean of 2.00 Å, $\sigma = 0.01$ Å, in good agreement with the Ga – O distances of 2.00 Å found in the GaO_6 octahedra of the β-Ga_2O_3 structure.[13] The GaO_4 tetrahedra are fairly regular and the gallium oxygen distances have a mean of 1.85 Å, $\sigma = 0.01$ Å, also in good agreement with the Ga – O distance of 1.834 Å found in the GaO_4 tetrahedra of the β-Ga_2O_3 structure.[13] The sodium atom is coordinated by six oxygen atoms in a rather distorted octahedron, the Na – O distances having a mean of 2.48 Å, $\sigma = 0.02$ Å.

The oxygen atoms O_1, O_2, O_4, O_5, O_7, and O_9 are tetrahedrally coordinated by metal atoms, and the oxygen atoms O_3, O_6, O_8, O_{10}, O_{11}, and O_{12} are each coordinated by three metal atoms giving coordination polyhedra with geometries close to that of an ammonia molecule. It was not possible to determine the positions of the two hydrogen atoms from the last difference Fourier. It is, however, likely that the hydrogen atoms are bonded to two of the four oxygen atoms: O_6, O_8, O_{11}, and O_{12} which are all situated on mirror planes. From packing considerations it is suggested that one hydrogen atom at (0.66, 0.75, 0.21) is bonded to O_6, and the other hydrogen atom at (0.94, 0.25, 0.34) is bonded to O_8.

The temperature factor coefficients for the oxygen atoms are within three standard deviations similar to the temperature factor coefficients of the gallium atoms. It is normally found in oxide structures where the metal oxygen coordination polyhedra have a dense packing, that the temperature factor coefficients of the metal atoms and of the oxygen atoms are of the same order of magnitude.[14,15]

The compound was not a pure gallium hydroxide phase as assumed in Ref. 1, but was a sodium gallium oxide hydroxide. It has a rather dense packing of atoms in the structure and the density of the compound is comparable with that of β-Ga_2O_3. The stacking of the GaO_6 coordination octahedra found in this structure is similar to the stacking of the octahedra in the β-Ga_2O_3 structure.[13] Although the formula of the compound $NaGa_{11}O_{16}(OH)_2$ resembles that of β-alumina,

$NaAl_{11}O_{17}$, and that of the isomorphous gallium compound, $NaGa_{11}O_{17}$, the crystal structures of these two compounds [16,17] are different from that of $NaGa_{11}O_{16}(OH)_2$.

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