

The Crystal Structure of Hydrated Sodium Aluminate, $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$, and Its Dehydration Product

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The crystal structure of hydrated sodium aluminate, $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$, has been determined *ab initio* from synchrotron powder diffraction data. The compound crystallizes in the acentric primitive tetragonal space group $P4_2m$, with $a = 10.53396(4)$ Å and $c = 5.33635(3)$ Å at 27°C, and $Z = 8$. The structure consists of single layers parallel to (001) made of corner-sharing AlO_4 tetrahedra, joined into 4- and 8-rings. The topology of the layers is that of framework 18 of Smith and Rinaldi (14). The layers are held together by two types of Na: one 6-coordinate, with nearly ideal octahedral geometry, and the second 7-coordinate, with a capped octahedral coordination. Two independent water molecules also occupy the interlayer regions, forming hydrogen bonds to framework O atoms. One oxygen of each AlO_4 coordination sphere is a hydroxyl group, which points into the interlayer region. Dehydration of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ causes a structural transformation to NaAlO_2 , surprisingly involving no intermediate phases. The crystal structure of dehydrated NaAlO_2 was refined by the Rietveld method using laboratory powder X-ray data. This compound crystallizes in $Pna2_1$, with $a = 5.3871(2)$ Å, $b = 7.0320(2)$ Å, and $c = 5.2180(2)$ Å at 25°C, $Z = 4$. The structure is based on a three-dimensional framework of corner-linked AlO_4 tetrahedra and is isostructural to $\beta\text{-NaFeO}_2$. NaAlO_2 can be rehydrated to form $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$; the dehydration process, which is accompanied by large changes in framework topology, is reversible. © 1995 Academic Press, Inc.

INTRODUCTION

Sodium aluminate is an important industrial inorganic chemical. It is used in water treatment and also as a convenient source of aluminum in synthetic applications. Sodium aluminate is often used as the aluminum source in the preparation of zeolites and other catalytic materials.

The most commonly encountered form of sodium aluminate is the solid obtained by crystallization from concentrated aqueous solutions (1). At low temperatures

(5–45°C), $\text{NaAlO}_2 \cdot 3/2\text{H}_2\text{O}$ crystallizes, while at higher temperatures (60–140°C), $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ is produced. A phase diagram for the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ at 30° has been reported (1).

Although powder patterns have been reported for $\text{NaAlO}_2 \cdot 3/2\text{H}_2\text{O}$ (Powder Diffraction File Entry 2-1025), $\text{NaAlO}_2 \cdot 3\text{H}_2\text{O}$ (29-1165 (2)), and $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ (41-638 (3)), the crystal structures have never been reported. The unit cell of the sesquihydrate has been reported as tetragonal, with $a = 10.53$ Å and $c = 11.40$ Å (2). For $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$, ²⁷Al and ¹H NMR and infrared spectroscopic studies (3) indicate the presence of highly polymerized anions with tetrahedrally coordinated Al. The unit cell of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ has been reported (4) as tetragonal, with $a = 10.530(5)$ Å and $c = 5.300(5)$ Å.

The crystal structure of $\text{KAlO}_2 \cdot 3/2\text{H}_2\text{O}$ has been determined (5). The structure contains discrete $(\text{OH})_3\text{AlOAl}(\text{OH})_3^-$ ions, composed of two corner-sharing tetrahedral Al. Other hydrated alkali metal aluminates for which some powder diffraction information has been reported are $\text{RbAlO}_2 \cdot 3/2\text{H}_2\text{O}$ (PDF 33-1099), $\text{CsAlO}_2 \cdot 3/2\text{H}_2\text{O}$ (36-465), $\text{LiAlO}_2 \cdot 1/4\text{H}_2\text{O}$ (21-487), $\text{LiH}(\text{AlO}_2)_2 \cdot 5\text{H}_2\text{O}$ (24-617), $\text{LiAl}_2(\text{OH})_7 \cdot x\text{H}_2\text{O}$ (31-704), $\text{LiAlO}_2 \cdot 8\text{H}_2\text{O}$ (34-810), $\text{LiAl}_2(\text{OH})_7 \cdot 2\text{H}_2\text{O}$ (40-710), and $\text{Li}_{0.04}\text{Al}_{0.96}\text{AlO}_2$ (42-222).

Commercial reagent sodium aluminate, $\text{NaAlO}_2 \cdot x\text{H}_2\text{O}$, is surprisingly crystalline. The laboratory pattern can be indexed (6) on a primitive tetragonal unit cell, having $a = 10.5349(4)$ Å and $c = 5.3358(3)$ Å. We have attempted unsuccessfully to solve the crystal structure using laboratory powder data.

Since hydrated sodium aluminates of differing stoichiometry have been reported, we sought to determine if new phases could be synthesized by partial dehydration of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$. It is known that the completely dehydrated material, NaAlO_2 , is isostructural to $\beta\text{-NaFeO}_2$ (7–9). We suspected that the dehydration of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ might take place in several steps, each involving a distinct intermediate phase.

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EXPERIMENTAL

 $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$

The material used in this study was E. Merck $\text{NaAlO}_2 \cdot x\text{H}_2\text{O}$ reagent, Lot 8352. Thermogravimetric analysis indicated that this material contained 21.55 wt% water. Since powder diffraction indicated that the dehydrated material is NaAlO_2 , the stoichiometry of the hydrated material is $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$. From the observed density and the unit cell dimensions, the cell contents are $\text{Na}_8\text{Al}_8\text{H}_{20}\text{O}_{26}$.

^{27}Al MASNMR (magic angle spinning NMR) studies indicated the presence of two types of tetrahedral Al. Variable relaxation time studies indicated that the vast majority of the Al is represented by one of the peaks, and that the other represents Al in impurity phases.

The sample used for the data collection was mixed with NIST 640b silicon internal standard at a concentration of 4.14 wt%. The sample was milled in a McCrone Micronising Mill using *n*-hexane as the milling liquid.

Data collection was carried out at beamline X3B1 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The pattern was measured from 7.000° to $64.695^\circ 2\theta$ in 0.005° steps, counting 4 sec/step. The sample was rocked 1° in ω at each data point. The wavelength used was $0.699341(5) \text{ \AA}$ (determined using the SRM 1976 alumina plate and the Si internal standard), and the diffractometer zero was $-0.002(1)^\circ 2\theta$.

A powder pattern measured on a Scintag PAD V diffractometer in our laboratory could be indexed (6) on a primitive tetragonal cell having $a = 10.5358(3) \text{ \AA}$ and $c = 5.3366(2) \text{ \AA}$; the figure of merit was 149.2. (The powder pattern contained a few weak lines which were not indexable on the tetragonal cell. The quality of the cell was high enough that the most likely explanation for these lines is the presence of impurity phases.) These lattice parameters were used as the initial values for the refinement of the synchrotron pattern. The systematic absences were consistent with the acentric space groups $P\bar{4}2_1m$ (No. 113) and $P42_12$ (No. 90). $P\bar{4}2_1m$ was selected and confirmed by successful solution and refinement.

Initial data processing was carried out using GSAS (10). A three-term cosine Fourier series background function, a scale factor, the lattice parameters, and the cauchy profile terms X and Y were refined. The structure model used was an Al atom at the largest peak in an E-map derived during our unsuccessful attempts to solve the structure using laboratory data. The Le Bail extraction procedure incorporated into GSAS was used to extract 357 individual observed structure factors for $2\theta < 50^\circ$ ($d > 0.83 \text{ \AA}$).

These structure factors were used to create a SHELXTL Plus (11) data file. The structure was solved

in $P\bar{4}2_1m$ using direct methods. (Attempts to solve the structure in $P42_12$ yielded much poorer combined figures of merit.) The strongest peak in the E-map corresponded to a reasonable Al position. Successive cycles of least-squares refinement and difference Fourier synthesis revealed the positions of the remaining heavy atoms. The final SHELX refinement of 27 variables using 322 observations yielded the residuals $R = 0.3379$ and $R_w = 0.4241$.

Final refinement of the structure was carried out using GSAS. The nonhydrogen atoms were refined independently, subject to a soft constraint of $1.74(1) \text{ \AA}$ on the Al–O–Al bridge bonds. The Al and two independent Na were refined anisotropically. The oxygen atoms were refined isotropically, with independent displacement coefficients.

The hydrogen atoms could not be located in difference Fourier maps and were included in the structure factor calculations in calculated positions, 0.85 \AA from the oxygens to which they are bonded covalently. The water molecule oxygen O4 was 2.63 \AA from two framework oxygens O2, and the hydrogen H4 was positioned on the O4–O2 vector. The water molecule oxygen O5 was located 2.74 \AA from two framework oxygens O3, and the hydrogen H5 was located on the O5–O3 vector. The shortest O1–O1 distances were 3.20 \AA . The hydroxyl hydrogen was placed in two half-occupied positions along the shortest O1–O1 vectors. Attempts to refine the hydrogen atom positions subject to a soft constraint were unsuccessful. The hydrogen isotropic displacement coefficients were fixed at 0.05 \AA^2 . Refinement of the water molecule occupancies yielded values insignificantly different from unity.

Included in the refinement were a scale factor and the lattice parameters. The peak profiles were described by a pseudo-Voigt function. The refined coefficients were the Gaussian U , cauchy X and Y , asymmetry, sample displacement, and anisotropic strain and size broadening terms (unique axis = $[001]$). The background was described by an eight-term real-space pair correlation function, which used three characteristic interatomic distances.

The isotropic displacement coefficient of the Si of the silicon internal standard was refined, as well as the X , Y , and asymmetry profile coefficients and a scale factor.

Two impurity phases were identified and included in the refinement: α -quartz (SiO_2) and thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$). At least one additional unidentified crystalline phase is present. For each of the impurity phases a scale factor and a cauchy X profile coefficient were refined.

The final refinement of 64 variables using 11,541 observations yielded the residuals $R_{wp} = 0.1085$ and $R_p = 0.0747$. The final reduced χ^2 was 7.488. The Bragg $R(F)$ was 0.0849. The agreement between F_o and F_c is poorest for the weak, high-angle reflections. The observed, calcu-

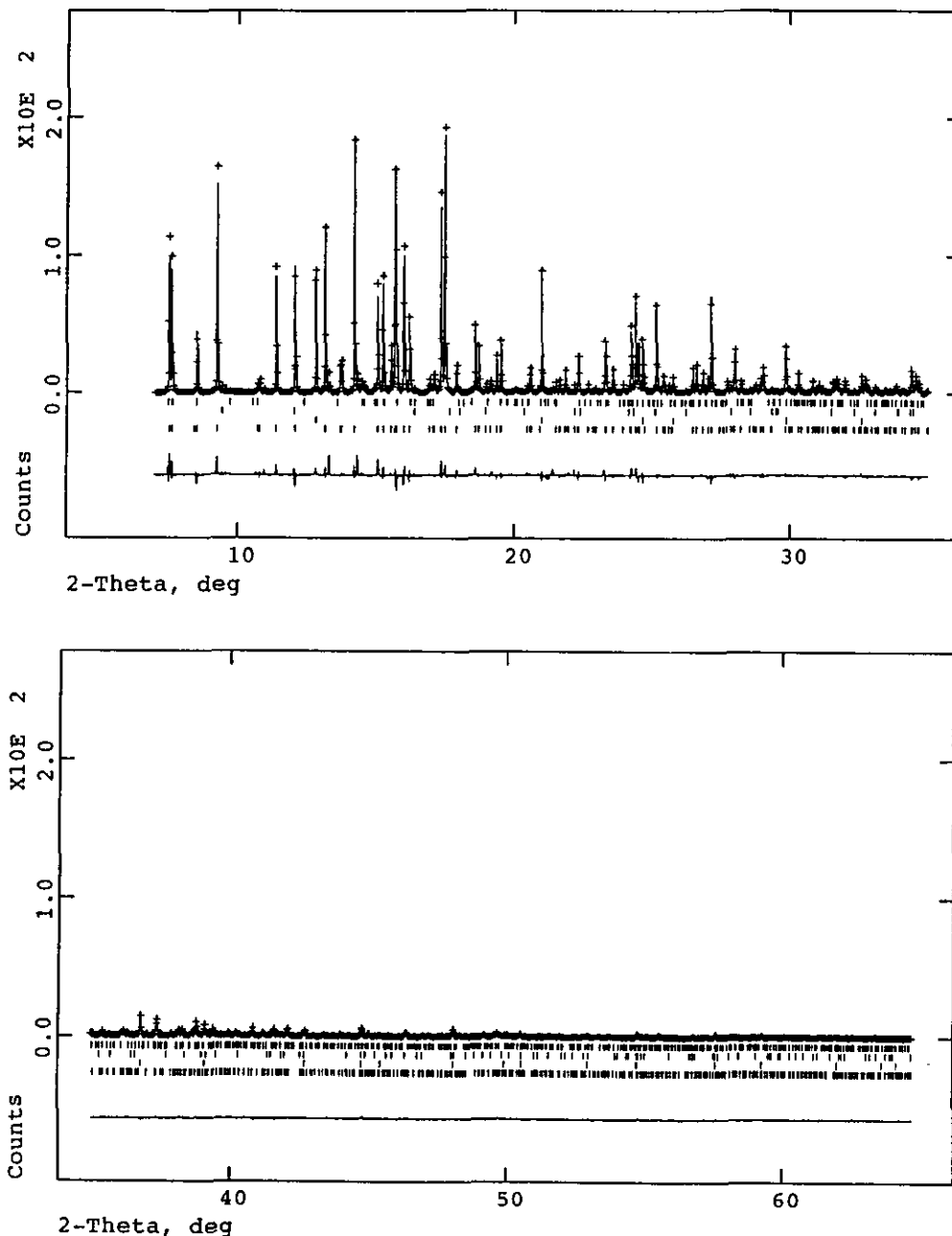


FIG. 1. Observed, calculated, and difference diffraction patterns of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$. The crosses represent the experimental points and the solid line the calculated pattern. The difference curve is plotted at the same scale as the other patterns. The bottom row of tick marks represents the positions of the $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ peaks. Successive rows upward represent the Si, SiO_2 , and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ peak positions.

lated, and difference profiles are illustrated in Fig. 1. The largest errors result from the peaks of the unidentified phases and the silicon internal standard. The slope of the final Wilson plot suggests that the ESDs are underestimated by a factor of 2.

The final structural parameters are reported in Table 1. The global parameters are included in Table 2. The bond distances and angles are reported in Tables 3 and

4. The observed and calculated structure factors are given in Table 5.

Dehydration of Sodium Aluminate

Aliquots of the starting material were dehydrated to produce several samples having different water contents. The starting material was loaded into a glass vial (outside

TABLE 1
Final Structural Parameters of NaAlO₂ · 5/4H₂O

Anisotropic thermal factors are defined by $T = \exp(h^2 a^{*2} U_{11} + \dots + 2h^* k^* a^* b^* U_{12} + \dots)$

Space group $P\bar{4}_2/m$

The lattice is acentric primitive tetragonal; Laue symmetry, $4/mmm$

Multiplicity of a general site is 8

The equivalent positions are

(1)	X	Y	Z	(2)	Y	$-X$	$-Z$
(3)	$-X$	$-Y$	Z	(4)	$-Y$	X	$-Z$
(5)	$1/2 - X$	$1/2 + Y$	$-Z$	(6)	$1/2 + Y$	$1/2 + X$	Z
(7)	$1/2 + X$	$1/2 - Y$	$-Z$	(8)	$1/2 - Y$	$1/2 - X$	Z

Lattice constants are

$a = 10.53396(5) \text{ \AA}$ $b = a$ $c = 5.336351(26) \text{ \AA}$ at 27°C
 $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$

Name	X	Y	Z	$U_i/U_c \cdot 100(\text{\AA}^2)$	Site symmetry	Mult	Type	Sequence	Fraction
Al	0.81175(13)	0.09450(13)	0.10055(23)	2.48*	1	8	Al	1	1.0000
Na1	0.60138(14)	0.10138(14)	0.59605(35)	2.84*	$m(+ - 0)$	4	Na	2	1.0000
Na2	0.80414(15)	0.30414(15)	0.67529(37)	4.18*	$m(+ - 0)$	4	Na	3	1.0000
O1	0.81046(23)	0.09109(22)	0.4388(4)	3.28(8)	1	8	O	4	1.0000
O2	0.93909(20)	0.18870(24)	0.0043(4)	2.05(6)	1	8	O	5	1.0000
O3	0.66923(20)	0.16923(20)	0.0129(6)	1.72(10)	$m(+ - 0)$	4	O	6	1.0000
O4	0.38579(20)	0.11421(20)	0.7128(6)	2.88(10)	$m(110)$	4	O	7	1.0000
O5	0.500000	0.000000	0.2176(9)	3.54(14)	$mm2d001$	2	O	8	1.0000
H1A	0.836240	0.017130	0.471510	5.00	1	8	H	9	0.5000
H1B	0.884900	0.117730	0.471510	5.00	1	8	H	10	0.5000
H4	0.322160	0.096780	0.805390	5.00	1	8	H	11	1.0000
H5	0.552400	0.052400	0.154660	5.00	$m(+ - 0)$	4	H	12	1.0000

Atomic displacement parameters (\AA^2) multiplied by 100.0

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	3.55(11)	2.61(9)	1.29(7)	-0.22(8)	0.34(8)	-0.26(7)
Na1	3.03(10)	3.03(10)	2.46(15)	0.05(14)	-0.55(9)	-0.55(9)
Na2	4.70(10)	4.70(10)	3.14(16)	-0.41(15)	0.54(11)	0.54(11)
O1	3.28(8)	3.28	3.28	0.00	0.00	0.00
O2	2.05(6)	2.05	2.05	0.00	0.00	0.00
O3	1.72(10)	1.72	1.72	0.00	0.00	0.00
O4	2.88(10)	2.88	2.88	0.00	0.00	0.00
O5	3.54(14)	3.54	3.54	0.00	0.00	0.00
H1A	5.00	5.00	5.00	0.00	0.00	0.00
H1B	5.00	5.00	5.00	0.00	0.00	0.00
H4	5.00	5.00	5.00	0.00	0.00	0.00
H5	5.00	5.00	5.00	0.00	0.00	0.00

diameter, 12 mm × length, 37 mm) and then heated at various temperatures in flowing air for 200 ± 20 min. The sample dehydrated at 500°C was obtained using a high-temperature tube furnace (Lindberg Model 59344), and those below 200°C were obtained using a drying oven (Blue M Model OV-490A-2). The samples dried at 100, 125, 150, and 500°C retained 92.7, 88.0, 76.0, and 72.5% of their initial weights, respectively. Complete dehydration of NaAlO₂ · 5/4H₂O corresponds only to

a 21.5% weight loss. The larger observed weight loss at 500°C reflects the presence of impurities (particularly Na₂CO₃ · H₂O), which lose water and CO₂ on heating to high temperature.

X-ray powder patterns were measured on a Scintag PAD V diffractometer (unfiltered CuK α radiation, intrinsic Ge detector, optics which yield instrumental full width at half-maximum of 0.07° at $2\theta = 30^\circ$). The samples were protected from the atmosphere by a 5- μ m-thick polycar-

TABLE 2
Global Parameters from the Rietveld Refinement of
 $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$

Parameter	$\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$	Si	SiO_2	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
Scale factor	0.3603(9)	0.0688(6)	0.0120(4)	0.0385(6)
Profile coefficients (centidegrees)				
<i>U</i>	5.22(35)	0	0	0
<i>X</i>	0.79(3)	0.80(5)	2.50(12)	8.51(22)
<i>Y</i>	8.72(22)	6.57(30)	0	0
<i>asym</i>	0.43(0)	0.37(1)	0	0
<i>trns</i>	0			
<i>shift</i>	-1.07(1)			
<i>stec</i>	-1.69(32)			
<i>ptec</i>	0.09(5)			
Background coefficients, real space pair correlation function				
BK1	2.09(1)			
BK2	-0.0098(3)			
BK3	1.79(7)			
BK4	3.249(12) Å			
BK5	1.63(5)			
BK6	2.587(9) Å			
BK7	1.98(7)			
BK8	3.833(12) Å			

bonate window, attached to the sample cell with silicone grease. *In situ* heating experiments were conducted on a Scintag PAD X vertical θ - θ diffractometer equipped with a Buehler high-temperature furnace.

NaAlO_2

The powder pattern of the completely dehydrated (500°C heating) sample matched well that of NaAlO_2 (PDF 33-1200). A trace of Na_2CO_3 (19-1130) was also detected.

TABLE 3
Bond Distances in $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$

Bond	Distance (Å)	Bond	Distance (Å)
Al-O1	1.806(2)	Al-O2	1.746(2)
Al-O2A	1.730(2)	Al-O3	1.758(2)
Na1-O1	2.359(3)	Na1-O1A	2.359(3)
Na1-O3	2.443(4)	Na1-O4	2.359(2)
Na1-O4A	2.359(2)	Na1-O5	2.522(4)
Na2-O1	2.576(3)	Na2-O1A	2.576(3)
Na2-O2	2.565(3)	Na2-O2A	2.565(3)
Na2-O3	2.699(4)	Na2-O4	2.402(4)
Na2-O5	2.973(2)		
O1-H1A	0.843(2)	O1-H1B	0.851(2)
O4-H4	0.852(2)	O5-H5	0.850(2)

At least one additional unidentified crystalline impurity is also present.

A Rietveld refinement of the crystal structure of NaAlO_2 was carried out using GSAS (10). The $2\theta < 2\theta < 120^\circ$ portion of the pattern of the material heated at 500°C was used. The initial structure model was taken from that of β - NaFeO_2 (12), with the Fe replaced by Al. The *z*-coordinate of the Al atom was fixed at zero to define the origin in space group $Pna2_1$. An isotropic displacement coefficient was refined for each atom. No soft constraints on bond distances were applied. The Na_2CO_3 impurity was included in the refinement using a fixed average structural model (13).

Included in the refinements were scale factors and lattice parameters of the two phases. The peak profiles were described by a pseudo-Voigt function. For NaAlO_2 , the *W* (constant Gaussian), *X* (cauchy size), and *Y* (cauchy strain) terms were refined. The profile fits were notably

TABLE 4
Interatomic Angles (°) in $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$

O1-Al-O2	108.14(13)	O1-Al-O2A	107.72(12)
O1-Al-O3	105.56(16)	O2-Al-O2A	116.41(19)
O2-Al-O3	108.87(14)	O2A-Al-O3	109.59(16)
O1-Na1-O1A	87.67(12)	O1-Na1-O3	93.68(9)
O1-Na1-O4	174.45(14)	O1-Na1-O4A	89.78(9)
O1-Na1-O5	95.22(10)	O1A-Na1-O3	93.68(9)
O1A-Na1-O4	89.78(9)	O1A-Na1-O4A	174.45(14)
O1A-Na1-O5	95.22(10)	O3-Na1-O4	91.40(12)
O3-Na1-O4A	91.40(12)	O3-Na1-O5	167.13(13)
O4-Na1-O4A	92.33(15)	O4-Na1-O5	80.10(10)
O4A-Na1-O5	80.10(10)		
O1-Na2-O1A	78.76(12)	O1-Na2-O2	84.72(8)
O1-Na2-O2A	146.14(12)	O1-Na2-O3	83.21(9)
O1-Na2-O4	83.13(9)	O1A-Na2-O2	146.14(12)
O1A-Na2-O2A	84.72(8)	O1A-Na2-O3	83.21(9)
O1A-Na2-O4	83.13(9)	O2-Na2-O2A	93.27(12)
O2-Na2-O3	65.51(8)	O2-Na2-O4	124.15(8)
O2A-Na2-O3	65.51(8)	O2A-Na2-O4	124.15(8)
O3-Na2-O4	162.30(13)		
Al-O1-Na1	111.20(14)	Al-O1-Na2	118.21(13)
Na1-O1-Na2	76.21(8)		
Al-O2-AlA	145.15(21)	Al-O2-Na2	98.58(10)
AlA-O2-Na2	107.72(13)		
Al-O3-AlA	133.92(20)	Al-O3-Na1	111.16(11)
Al-O3-Na2	87.92(11)	AlA-O3-Na1	111.15(11)
AlA-O3-Na2	87.92(11)	Na1-O3-Na2	72.56(11)
Na1-O4-Na1A	79.62(13)	Na1-O4-Na2	97.91(12)
Na1A-O4-Na2	97.91(12)	H4-O4-H4A	90.15(29)
Na1-O5-Na1A	73.58(15)	H5-O5-H5A	133.5(6)

TABLE 5
Observed and Calculated Factors of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$

H= 0 K= 0	H= 2 K= 2	H= 4 K= 0	H= 5 K= 0	H= 5 K= 5	H= 6 K= 4	H= 7 K= 2
1 32246 30644	0 13065 11913	0 46288 47104	2 42156 41732	3 5525 5827	4 1001 1019	7 2335 1970
2 52890 49530	1 31830 30217	1 5678 5512	3 31909 30785	4 13554 13397	5 6491 6085	
3 27578 26911	2 27274 26823	2 15673 13606	4 1281 1319	5 9223 8382	6 4049 3855	H= 7 K= 3
4 12350 10778	3 45632 45221	3 3132 2638	5 4300 4141	6 6101 9456	7 4334 3716	
5 8354 7741	4 4214 3294	4 8969 8373	6 11542 11673	7 2373 2101		0 11398 10247
6 11221 9439	5 2033 1784	5 3531 3532	7 5988 9507		H= 6 K= 5	1 20218 19446
7 0 7132	6 7719 6957	6 7944 7991		H= 6 K= 0		2 12919 13503
8 5620 4618	7 5555 9383	7 0 3821	H= 5 K= 1		0 4955 4386	3 24339 23896
	8 0 5902			0 2075 2010	1 6259 6325	4 851 795
H= 1 K= 0		H= 4 K= 1	0 25622 26000	1 14768 14799	2 8804 8994	5 1544 1646
	H= 3 K= 0		1 4633 4440	2 2297 1680	3 4603 4679	6 2651 3291
1 1998 1876		0 32063 33538	2 12697 13040	3 6354 5919	4 4232 4188	7 5829 5759
2 22169 21840	1 17068 16986	1 40654 39934	3 3980 3649	4 9880 10728	5 2454 2505	
3 1842 1812	2 10736 10874	2 13970 13324	4 5686 5323	5 1553 1541	6 721 2026	H= 7 K= 4
4 6172 5538	3 12897 13167	3 16002 15408	5 1526 1455	6 3829 7332	7 1985 2100	
5 296 324	4 11116 10649	4 26497 27558	6 4470 5171	7 556 473		0 14521 14970
6 2464 2337	5 5105 4726	5 18638 19276	7 0 3022		H= 6 K= 6	1 13065 13260
7 813 767	6 6239 5762	6 11733 12486		H= 6 K= 1		2 15961 17593
8 5004 4791	7 6925 8220	7 3859 5520	H= 5 K= 2		0 9618 9538	3 9679 9228
	8 0 2990			0 32242 31094	1 10318 9630	4 3886 3964
H= 1 K= 1		H= 4 K= 2	0 5498 5408	1 22534 23179	2 12609 12155	5 8528 8188
	H= 3 K= 1		1 3909 2559	2 9811 9707	3 8049 8001	6 542 578
1 23807 23501		0 15955 16073	2 10458 10883	3 17127 17130	4 7388 7465	7 1707 2882
2 41640 41219	0 23833 24725	1 16714 17041	3 10084 10100	4 9388 9465	5 8597 9546	
3 22397 21902	1 28729 27908	2 5487 5615	4 8552 8322	5 4583 4540	6 4928 5313	H= 7 K= 5
4 3029 2954	2 15673 16259	3 7844 6506	5 4827 4713	6 4567 4870		
5 12092 12253	3 14857 13854	4 7605 8432	6 3230 3433	7 5377 4960	H= 7 K= 0	0 4781 5012
6 5966 6141	4 11923 12646	5 3744 3769	7 4439 3998			1 9435 8507
7 5639 5710	5 5167 5270	6 7426 6656		H= 6 K= 2	1 4782 4666	2 6909 6676
8 3125 3514	6 9811 9119	7 1003 1026	H= 5 K= 3		2 3488 3221	3 4048 3068
	7 1166 1896			0 22003 21663	3 204 203	4 2198 2405
H= 2 K= 0	8 2549 3994	H= 4 K= 3	0 27433 27295	1 17951 17851	2 10232 9962	3 4261 4229
			1 17205 16593	2 10232 9962	3 8378 8635	4 4261 4229
0 21555 21811	H= 3 K= 2	0 14964 14925	2 14519 15244	3 8378 8635	4 10500 10177	5 2943 2985
1 7793 6998		1 14703 14588	3 9604 9992	4 10500 10177	5 4407 4206	6 1200 4219
2 8512 8286	0 13011 12735	2 10211 10108	4 4262 4219	5 4407 4206	6 6468 6419	7 450 355
3 13560 12919	1 28393 28992	3 19296 18617	5 6285 5536	6 6468 6419	7 751 882	H= 7 K= 1
4 3067 2541	2 6121 5423	4 11857 12207	6 3639 3706	7 1940 2007		0 104 103
5 7852 7552	3 19787 19197	5 2389 2300			H= 6 K= 3	1 5963 5706
6 3027 2882	4 7597 8077	6 10366 10483	H= 5 K= 4			2 7472 6998
7 35 297	5 18316 19900	7 2345 3723		0 1048 962	1 14812 14747	3 11283 10594
8 177 240	6 8696 8825			1 17503 16922	2 6663 7426	4 5216 4738
	7 1238 2373	H= 4 K= 4	0 354 369	2 7987 7726	3 4325 4562	5 2073 2625
H= 2 K= 1			1 1089 977	3 21071 21403	4 7838 7748	6 4905 5056
	H= 3 K= 3	0 25062 24802	2 15896 16096	4 11916 12176	5 2239 2035	H= 7 K= 7
0 12252 12934		1 10050 9845	3 3738 3565	5 2053 2166	6 3211 4976	
1 15743 15921	0 36487 37226	2 26831 26678	4 2956 2980	6 8981 9371	7 1379 1221	0 3215 3220
2 29558 29065	1 20409 19799	3 24672 24763	5 1595 1699	7 3654 3255		1 13114 11984
3 24985 24303	2 6080 4980	4 939 1000	6 1258 2387		H= 7 K= 2	2 7583 7440
4 9335 9549	3 35829 35971	5 8003 8319	7 1408 1187			3 18481 17417
5 5335 5200	4 12374 12898	6 6954 6265		H= 6 K= 4	0 22126 22088	4 1134 1018
6 9369 9333	5 8233 7983	7 4987 5927	H= 5 K= 5		1 23222 23153	5 0 499
7 2719 4039	6 8027 8719			0 1485 1386	2 6939 7197	6 4508 4199
8 0 3077	7 5196 6515	H= 5 K= 0	0 72206 73446	1 12196 12074	3 9642 8635	
			1 2327 2317	2 17641 17510	4 2959 2853	
		1 9246 9174	2 10892 12140	3 9717 9911	5 13291 12537	
					6 5280 5570	

improved by the inclusion of anisotropic size and strain broadening terms (unique axis [100]). For Na_2CO_3 , only the X profile coefficient was refined; the remaining terms were fixed at the instrumental values. Common sample transparency and sample displacement terms were refined. The background was described by a three-term cosine Fourier series.

The final refinement of 35 variables using 4887 observations yielded the residuals $R_{wp} = 0.1099$ and $R_p = 0.0805$. The final reduced χ^2 was 2.431. The Bragg $R(F)$ was 0.0354. The observed, calculated, and difference profiles are illustrated in Fig. 2. The largest errors result from background of the polycarbonate film and an unidentified crystalline impurity. The slope of the final

TABLE 5—Continued

H= 8 K= 0	H= 8 K= 5	H= 9 K= 2	H= 9 K= 8	H= 10 K= 4	H= 10 K= 10	H= 11 K= 6
0 29278 29258	3 10533 9487	1 3034 2903	0 8039 7857	0 9302 8517	3 3082 2895	0 7122 6461
1 19314 19276	4 5347 5061	2 2713 2541	1 4540 4126	1 3168 2974		1 9313 8363
2 17791 19016	5 1552 3967	3 6119 5745	2 3422 3053	2 3296 2966	H= 11 K= 0	2 6221 6064
3 8902 9798	6 4932 4872	4 3515 3193	3 4236 4256	3 869 826		3 9510 8885
4 389 379		5 491 622	4 2773 3937	4 3024 3916	1 2224 2109	4 673 908
5 881 798	H= 8 K= 6	6 3517 3625	5 2014 1718	5 531 1408	2 3828 4065	5 0 2044
6 2326 3956	0 4668 4437			6 2727 3484	3 1694 1554	
7 0 3009	1 6766 6212	H= 9 K= 3	H= 9 K= 9		4 3380 3398	H= 11 K= 7
	2 5271 4977	0 4540 4561	0 8890 8133	H= 10 K= 5	5 0 1120	
H= 8 K= 1	3 8197 7621	1 6999 7484	1 2654 2913	0 3985 3801		0 6385 6962
0 11709 12070	4 6688 6364	2 6108 5365	2 6793 6588	1 665 655	H= 11 K= 1	1 5457 5203
1 11148 11315	5 4222 4206	3 4113 3918	3 8097 7342	2 16238 13492	0 7541 6417	2 3684 3944
2 5870 6471	6 6395 5097	4 3784 3256	4 68 69	3 10824 9616	1 7662 6532	3 1542 1700
3 14539 13862		5 938 1421	5 1438 2265	4 1864 2805	2 7183 6860	4 3671 3162
4 10647 10863	H= 8 K= 7	6 2125 2610		5 2909 2860	3 2983 2768	H= 11 K= 8
5 4387 4212	0 2579 2440		H= 10 K= 0		4 2273 2742	
6 8287 8836	1 8480 7811	H= 9 K= 4	0 34650 32936	H= 10 K= 6	5 4087 4977	0 3838 3881
7 1457 2460	2 1154 1129	0 21215 19271	1 2669 2451	0 5683 6114		1 2576 3323
	3 7391 6737	1 7352 7363	2 3016 2847	1 1405 1296	H= 11 K= 2	2 2868 4080
H= 8 K= 2	4 916 2455	2 5599 5342	3 1397 1299	2 6994 6357	0 4758 4539	3 5785 5199
0 4953 4979	5 7725 7520	3 5619 5330	4 11314 10766	3 3747 4387	1 8948 8822	4 2128 1733
1 11076 10949	6 2829 3608	4 13540 12363	5 6858 6832	4 1375 1782	2 2883 2396	H= 11 K= 9
2 5548 5348		5 8912 9950	6 9922 7908	5 4482 3987	3 12488 11093	
3 17781 17610	H= 8 K= 8	6 7450 7000			4 4242 6384	0 0 1671
4 4058 3245	0 13763 14603		H= 10 K= 1	H= 10 K= 7	5 617 607	1 958 1559
5 2823 2929	1 5393 4992	H= 9 K= 5	0 2837 2823	0 7435 6710		2 0 2690
6 2744 3219	2 4916 5062	0 16490 14502	1 2105 1986	1 4282 3757	H= 11 K= 3	3 1609 1449
7 0 3035	3 9305 8701	1 1654 1688	2 4928 4534	2 6422 5909	0 3940 3332	H= 11 K= 10
	4 3795 6156	2 3554 3466	3 2566 2738	3 1636 2016	1 2764 3017	
H= 8 K= 3	5 3371 3503	3 1626 1386	4 2166 1925	4 2124 2511	2 1634 1657	0 2407 2305
0 72 77		4 5842 5707	5 667 909	5 1029 829	3 8345 8129	1 3194 3337
1 13821 13530	H= 9 K= 0	5 0 3805	6 1175 1132		4 7352 7119	2 4229 3506
2 2000 1838	0 16490 14502	6 5870 5007		H= 10 K= 8	5 6548 5971	3 2052 2950
3 3233 3088	1 790 728		H= 10 K= 2	0 4249 3882	H= 11 K= 4	H= 11 K= 11
4 5110 5103	2 13122 12942	H= 9 K= 6	0 470 421	1 3769 3609		
5 5091 6381	3 5624 5097	0 18143 16865	1 8729 8344	2 2110 2248	0 11406 10801	0 2252 2028
6 618 1191	4 1408 1566	1 4868 4856	2 5078 4550	3 1662 2764	1 7241 6098	1 994 856
	5 964 1309	2 4902 4874	3 5223 5044	4 4237 3917	2 5565 4894	2 0 1422
H= 8 K= 4	6 2978 2656	3 2799 2294	4 5398 6260		3 6600 6073	
0 5369 5409		4 3993 4110	5 0 6692	H= 10 K= 9	4 563 856	H= 12 K= 0
1 12303 11584	H= 9 K= 1	5 2524 2991	6 5634 4746		5 978 869	
2 10484 9983	0 11386 11976	6 538 2111		0 1733 2444		0 6788 6491
3 9650 9199	1 4613 5109		H= 10 K= 3	1 1221 1232	H= 11 K= 5	1 5218 4804
4 5713 5948	2 15353 14381	H= 9 K= 7	0 3705 2787	2 5109 4962		2 5474 4866
5 1997 2031	3 13637 12746	0 2427 2052	1 4922 4776	3 942 1890	0 1451 1711	3 1763 1822
6 5073 4654	4 599 577	1 2039 2225	2 6243 5798	4 1627 1320	1 4955 4670	4 583 1300
	5 3887 4033	2 4608 4673	3 9770 9308	H= 10 K= 10	2 235 212	5 1255 1248
H= 8 K= 5	6 4761 4381	3 3663 3568	4 5865 6051		3 1977 2933	
0 77 76		4 2288 2215	5 1633 4129	0 7592 9295	4 3889 4527	H= 12 K= 1
1 8158 7705	H= 9 K= 2	5 3094 2822	6 4794 4083	1 1095 2342	5 1017 836	
2 5804 5132	0 2217 2187			2 1111 1402		0 5063 4948
						1 5073 4611

Wilson plot suggests that the ESDs are underestimated by a factor of 1.4. No peaks or holes larger than 4% of an oxygen atom were present in the final difference Fourier map.

The refined structural parameters are reported in Table 6. The global parameters are included in Table 7. The bond distances and angles are reported in Tables 8 and

9. The observed and calculated structure factors are given in Table 10.

The patterns of the partially dehydrated materials were also refined using GSAS. Included in the refinements were scale factors for $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ and NaAlO_2 , the lattice parameters of both phases, the profile Y terms, and a three-term cosine Fourier series background function.

TABLE 5—Continued

H= 12 K= 1	H= 12 K= 5	H= 12 K= 10	H= 13 K= 4	H= 13 K= 9	H= 14 K= 4	H= 15 K= 2
2 8052 7183	1 2909 2805	0 655 554	0 6953 7031	0 1434 1230	0 5066 5238	0 3350 3077
3 3776 3795	2 876 950	1 2387 2061	1 2782 3589	1 948 1727	1 1061 1623	1 2111 1780
4 649 921	3 1665 2819	2 551 892	2 1634 2325		2 4277 3931	2 3557 3346
5 4484 3826	4 2799 2489		3 4258 3327	H= 14 K= 0	3 5834 4453	
		H= 13 K= 0	4 5223 4253			H= 15 K= 3
H= 12 K= 2	H= 12 K= 6			0 6574 9342	H= 14 K= 5	
0 3940 3617	0 5842 5911	1 5123 4941	H= 13 K= 5	1 1288 1538		0 730 767
1 8772 7290	1 3510 4273	2 1939 2102		2 2303 3359	0 4809 4603	1 3665 3340
2 4852 4367	2 1210 3052	3 2709 4585	0 3876 4213	3 1185 1293	1 3368 3520	2 2553 2056
3 11694 10886	3 1365 1355	4 1244 1106	1 1975 2481	4 0 1520	2 5865 4862	
4 391 388	4 3506 2989		2 2400 3275		3 2129 3059	H= 15 K= 4
5 1252 1232		H= 13 K= 1	3 1334 1248	H= 14 K= 1		
			4 1840 2331			
H= 12 K= 3	H= 12 K= 7	0 3504 3821		0 12656 11460	H= 14 K= 6	0 3178 2853
	0 8109 8248	1 6331 6036	H= 13 K= 6	1 2190 3471	0 4000 3340	1 2581 2763
0 4585 4100	1 9035 8172	2 5870 6284		2 3345 4275	1 1063 964	2 2184 2959
1 6595 5821	2 3823 4434	3 3934 4336	0 5546 6374	3 2291 1896	2 3381 2876	H= 15 K= 5
2 1338 1464	3 1148 1058	4 2780 2395	1 2428 3008	4 995 1487		
3 3707 5239	4 0 954	H= 13 K= 2	2 3226 3534		H= 14 K= 7	0 5695 4884
4 2111 2233			3 3167 2488	H= 14 K= 2	0 1829 2079	1 1157 2108
5 6147 5992	H= 12 K= 8	0 121 118	H= 13 K= 7	0 562 688	1 2831 2774	H= 16 K= 0
	0 2822 3810	1 3561 4426		1 477 1020		
H= 12 K= 4	1 3684 3884	2 450 713	0 0 1356	2 1162 1466	H= 15 K= 0	0 1230 1944
0 794 702	2 1974 2178	3 1161 1490	1 3820 3399	3 1167 1096		
1 1453 1338	3 6407 5351	4 592 745	2 2422 2143		1 173 155	H= 16 K= 1
2 842 2594		H= 13 K= 3	3 3505 4096	H= 14 K= 3	2 6155 5045	
3 0 2082	H= 12 K= 9			0 181 208	H= 15 K= 1	0 870 1858
4 2495 2364	0 2134 2191	0 4368 4421	H= 13 K= 8	1 2232 2765		
5 0 1677	1 2877 2577	1 0 1971	0 774 672	2 1351 1480	0 3053 3297	
H= 12 K= 5	2 3121 2557	2 1995 2348	1 3602 3062	3 2764 2172	1 618 710	
		3 1628 3062	2 1350 1236		2 3239 3157	
0 1087 1050		4 1201 965				

Note. The column headings are as follows: column 1, L ; column 2, $1000 \cdot (\text{sign}[\sqrt{\text{abs}(F_o^{**2})/\text{SCALE}}], F_o^{**2})$ (F_o^{**2} is the observed value corrected for absorption, etc.); and column 3, $1000 \cdot F_c$ computed to match F_o (the extinction correction, if used, is applied to F_c).

RESULTS AND DISCUSSION

NaAlO₂ · 5/4H₂O

The basic unit of the crystal structure of NaAlO₂ · 5/4H₂O is a single layer parallel to (001) made up of corner-sharing AlO₄ tetrahedra (Fig. 3). The tetrahedra are joined into sheets of 4-rings and 8-rings, in contrast to the double chains of 6-rings proposed by Gessner *et al.* (3).

Three of the four oxygens (two O2 and one O3) lie in the plane of the layers, while the fourth (O1, a hydroxyl group) points into the interlayer regions. The hydroxyls alternate UDUD around the 4-rings, and are UDDU-UD around the 8-rings.

The topology of the layer corresponds to number 18 of Smith and Rinaldi (14, 15). The general arrangement of the rings, though not the exact topology, is reminiscent of the apophyllite (15), scapolite (16, 17), and feldspar (18) structures.

The geometry of the AlO₄ tetrahedron is quite regular; the largest deviation from the ideal O-Al-O angle is 6.9°. Both O2 (general position) and O3 (site symmetry *m*) form

the Al-O-Al bridges. The Al-O2, Al-O2A, and Al-O3 distances of 1.746(2), 1.730(2), and 1.758(2) Å are close to the average value of 1.74 Å typically found in framework structures.

O2 forms the "UD" Al-O-Al bridge, and O3 forms the "UU" bridge. The twist angles, defined as the angles between the O1-Al-Al and O1A-Al-Al planes in the Al₂O₇ units centered on O2 and O3 (19), are 179.9° and 0.0°, respectively. The Al₂O₇ units are almost exactly eclipsed or staggered.

The Al-O1 bond (1.806(2) Å) is considerably longer than the Al-O-Al bridge bonds. Bond valence and charge balance considerations suggest that this oxygen represents a hydroxyl group.

The crystal structure is illustrated by a polyhedral rendering in Fig. 4. There are two crystallographically independent Na ions. The coordination of Na1 is octahedral (Fig. 5). The average deviation from the ideal angles is 4.6°; the largest deviations involve the water molecule O5. Coordinated to Na1 are two hydroxyl groups, one bridging oxygen, and three water molecules. Na2 is 7-

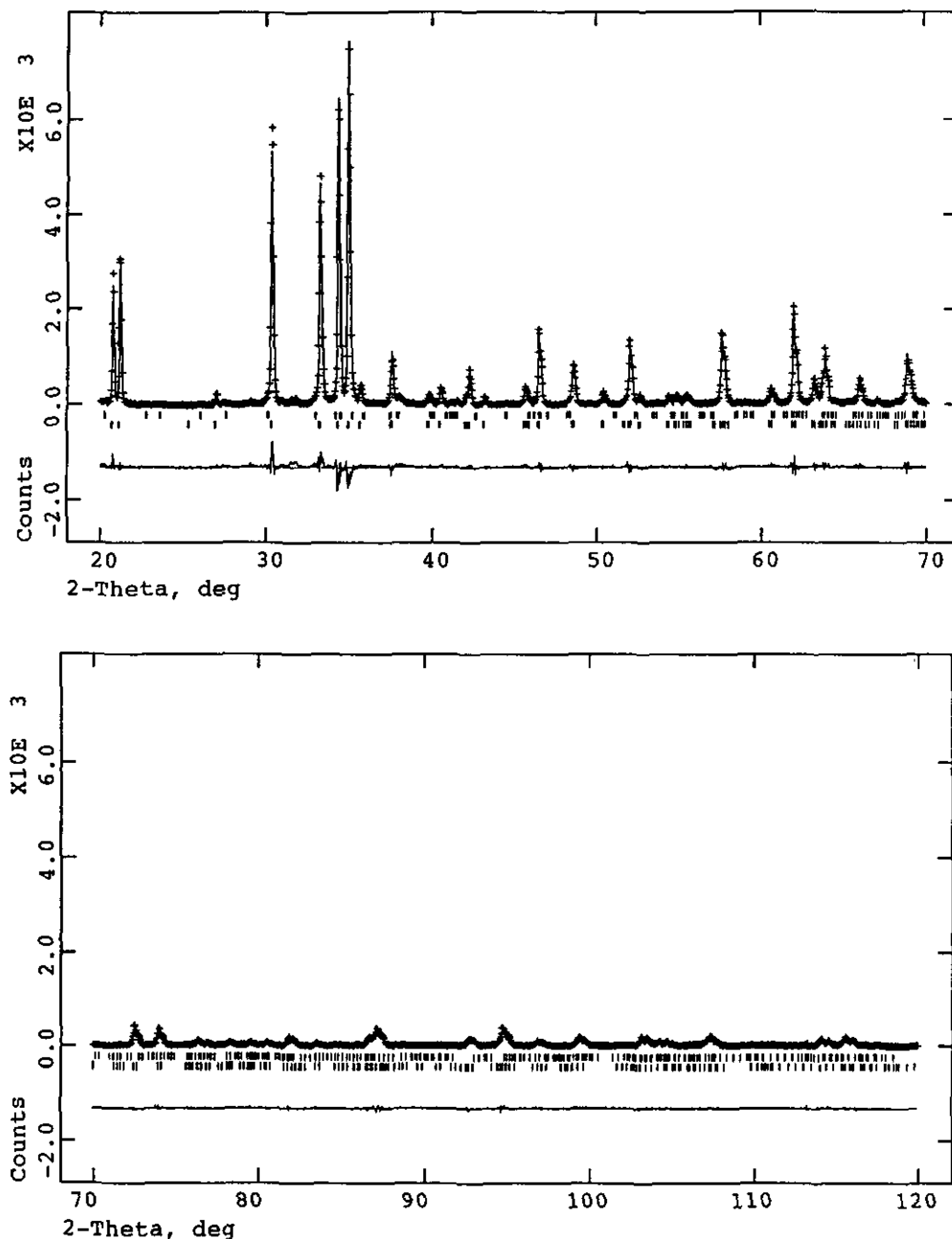


FIG. 2. Observed, calculated, and difference diffraction patterns of dehydrated NaAlO_2 . The crosses represent the experimental points and the solid line the calculated pattern. The difference curve is plotted at the same scale as the other patterns. The rows of tick marks represent the calculated line positions for NaAlO_2 and Na_2CO_3 .

coordinate (Fig. 5). Five of the Na–O distances are less than 2.60 Å, one distance to a framework oxygen is 2.70 Å, and a water molecule oxygen is 2.97 Å away. The Na2 coordination is best viewed as distorted octahedral, with an additional water molecule (O5) capping one of the octahedral faces. The average Na1–O distance is 2.40 Å, while the average Na2–O distance is 2.62 Å.

The aluminat layers are held together by coordination to the Na ions and by an extensive network of hydrogen

bonds involving the water molecules and the hydroxyl groups. Na1 is coordinated to two hydroxyl groups from one layer, one bridging oxygen from the adjacent layer, and three water molecules (Fig. 5). Na2 is coordinated to two hydroxyls from one layer, three bridging oxygens from the adjacent layer, and two water molecules (Fig. 5).

The water molecule O4 is coordinated to three sodium ions at normal distances, while the water molecule O5 is coordinated to four Na ions at relatively long distances.

TABLE 6
Refined Structural Parameters of NaAlO₂

Anisotropic thermal factors are defined by $T = \exp(h^2 a^{*2} U_{11} + \dots + 2h^* k^* a^* b^* U_{12} + \dots)$

Space group *Pna2*₁

The lattice is acentric primitive orthorhombic; Laue symmetry, *mmm*

Multiplicity of a general site is 4

The location of the origin is arbitrary in *z*

The equivalent positions are

(1) *X Y Z* (2) $1/2 - X \quad 1/2 + Y \quad 1/2 + Z$
(3) $1/2 + X \quad 1/2 - Y \quad Z$ (4) $-X \quad -Y \quad 1/2 + Z$

Lattice constants are

$a = 5.38712(18) \text{ \AA}$ $b = 7.03203(23) \text{ \AA}$ $c = 5.21798(17) \text{ \AA}$
 $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$

Name	<i>X</i>	<i>Y</i>	<i>Z</i>	$U_i/U_e^*100(\text{\AA}^2)$	Site symmetry	Mult	Type	Sequence	Fraction
Al	0.06101(28)	0.12513(29)	0.000000	0.75(5)	1	4	Al	1	1.0000
Na	0.43363(32)	0.12415(34)	0.4815(6)	1.32(6)	1	4	Na	2	1.0000
O1	0.0306(7)	0.0760(5)	0.3299(6)	0.87(10)	1	4	O	3	1.0000
O2	0.3763(5)	0.1747(4)	0.9330(7)	0.91(12)	1	4	O	4	1.0000

Atomic displacement parameters (\AA^2) multiplied by 100.0

Name	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	0.75(5)	0.75	0.75	0.00	0.00	0.00
Na	1.32(6)	1.32	1.32	0.00	0.00	0.00
O1	0.87(10)	0.87	0.87	0.00	0.00	0.00
O2	0.91(12)	0.91	0.91	0.00	0.00	0.00

TABLE 7
Global Parameters from the Refinement of NaAlO₂

Parameter	NaAlO ₂	Na ₂ CO ₃
Scale factor	247.7(10)	7.88(47)
Space group	<i>Pna2</i> ₁	<i>C2/m</i>
Lattice parameters		
<i>a</i> (\AA)	5.3871(2)	8.907(35)
<i>b</i> (\AA)	7.0320(2)	5.2398(22)
<i>c</i> (\AA)	5.2180(2)	6.0454(23)
β ($^\circ$)		101.28(3)
Profile parameters		
<i>W</i>	15.04(38)	7.194
<i>X</i>	0.05(21)	12.54(163)
<i>Y</i>	14.16(60)	4.939
<i>asym</i>	0	2.055
<i>stec</i>	6.58(115)	0
<i>ptec</i>	0.74(38)	0
<i>trns</i>	-4.73(34)	
<i>shift</i>	-0.29(10)	
Background coefficients, cosine Fourier series		
BK1	79.12(64)	
BK2	5.44(93)	
BK3	34.94(73)	

The water molecule oxygen O4 is 2.63 \AA from two bridging oxygens O2; the protons of this water molecule certainly lie close to the O4–O2 vectors. The water molecule oxygen O5 lies 2.74 \AA from two framework O3; the water protons certainly lie near the O5–O3 vectors. The nearest O1–O distances (for an “up” O1) are two O1 at 3.21 \AA ; these are two “down” O1 from the 4-ring in the adjacent layer. The “up” O1 is 3.26 \AA from the “up” O1 adjacent to it in the 8-ring. A water molecule oxygen O4 is 3.30 \AA from O1. All of these O–O distances are very long for hydrogen bonds. The most plausible geometry for the

TABLE 8
Bond Distances (\AA)
in NaAlO₂

Al–O1	1.763(3)
Al–O1A	1.741(4)
Al–O2	1.769(3)
Al–O2A	1.759(3)
Na–O1	2.335(4)
Na–O1A	2.312(4)
Na–O2	2.403(5)
Na–O2A	2.351(4)

TABLE 9
Bond Angles (°) in NaAlO₂

O1-Al-O1	108.19(15)	Al-O1-Al	133.08(19)
O1-Al-O2	108.71(22)	Al-O1-Na	102.47(20)
O1-Al-O2	107.35(19)	Al-O1-Na	100.16(19)
O1-Al-O2	109.36(20)	Al-O1-Na	102.04(16)
O1-Al-O2	112.86(16)	Al-O1-Na	120.16(18)
O2-Al-O2	110.26(13)	Na-O1-Na	87.83(13)
O1-Na-O1	103.09(14)	Al-O2-Al	131.43(20)
O1-Na-O2	103.53(15)	Al-O2-Na	106.75(17)
O1-Na-O2	103.83(14)	Al-O2-Na	102.76(17)
O1-Na-O2	103.28(14)	Al-O2-Na	103.91(16)
O1-Na-O2	132.84(13)	Al-O2-Na	116.58(16)
O2-Na-O2	107.08(16)	Na-O2-Na	85.25(13)

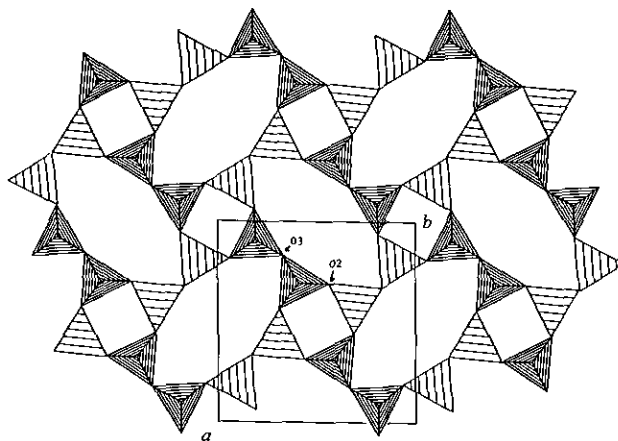


FIG. 3. A polyhedral rendering (STRUPLO (23)) of the aluminate layers in NaAlO₂ · 5/4H₂O. The view is down the *c*-axis.

hydroxyl group is to hydrogen bond to one of the hydroxyls from the adjacent layer. Since there are two possible positions, the hydroxyl is likely disordered and has been modeled with two half-occupied hydrogen positions.

TABLE 10
Observed and Calculated Structure Factors of NaAlO₂

H= 0 K= 0	H= 0 K= 7	H= 1 K= 5	H= 2 K= 2	H= 2 K= 7	H= 3 K= 5	H= 4 K= 4
2 13114 13282	1 1038 1040	0 2889 2923	0 1667 1657	0 1715 1625	2 442 400	0 233 206
4 6097 6160		1 1110 1050	1 1280 1279	1 487 534	3 1324 1352	1 5618 5499
	H= 1 K= 1	2 1309 1311	2 1330 1286			2 588 508
H= 0 K= 1		3 1059 908	3 1247 1334	H= 3 K= 1	H= 3 K= 6	3 4841 4839
	0 3195 3028	4 897 850	4 793 786			
1 3376 3332	1 957 956		5 955 920	0 3096 3203	0 4592 4386	H= 4 K= 5
3 2913 2823	2 1875 1856	H= 1 K= 6		1 1191 1171	1 1745 1804	
5 681 628	3 775 896		H= 2 K= 3	2 1568 1614	2 4358 4265	0 205 199
	4 2756 2793	0 2357 2058		3 1636 1672		1 341 329
H= 0 K= 2	5 191 182	1 6238 6195	0 1585 1552	4 716 721	H= 4 K= 0	2 1322 1315
		2 2084 2030	1 2326 2282			
0 0 22	H= 1 K= 2	3 4502 4362	2 489 478	H= 3 K= 2	0 653 684	H= 5 K= 1
2 1854 2095			3 2231 2268	1 6531 6612	1 1825 1807	0 5407 5243
4 1811 1848	0 7489 7248	H= 1 K= 7	4 886 869	2 1829 1844	2 503 506	1 1867 1795
	1 7247 7397			3 6830 6654	3 1080 1108	2 3769 3737
H= 0 K= 3	2 4928 4991	0 625 567	H= 2 K= 4	4 2013 1988	4 1083 1207	
	3 8708 8697	1 537 541				
1 3641 3592	4 2402 2536	2 1758 1814	0 6418 6310	H= 4 K= 1		H= 5 K= 2
3 2768 2819	5 4656 4459		1 5079 4873		0 1372 1253	0 770 743
5 370 351		H= 2 K= 0	2 4802 4751	H= 3 K= 3	1 1825 1807	1 410 390
	H= 1 K= 3		3 4351 4361	0 1798 1664	2 503 506	2 845 839
H= 0 K= 4		0 11646 11227	4 3425 3331	1 1980 1970	3 1080 1108	
	0 2042 2071	1 4627 4443		2 1549 1512	4 1083 1207	H= 5 K= 3
0 10772 10826	1 2331 2126	2 5716 5944	H= 2 K= 5	3 1203 1038		
2 8273 8206	2 2192 2159	3 5897 5824		4 910 866	H= 4 K= 2	0 1637 1608
4 5431 5313	3 1055 1115	4 3755 3777	0 1212 1213			1 1174 1294
	4 1960 1931	5 3869 3766	1 1405 1422	H= 3 K= 4	0 1902 1726	
H= 0 K= 5	5 387 367		2 1411 1415	1 624 633	1 624 633	
		H= 2 K= 1	3 426 399	2 1116 1203	2 1116 1203	H= 5 K= 4
1 2962 3012	H= 1 K= 4	0 2631 2334	4 1079 1206	1 2249 2270	3 605 548	
3 718 404		1 1498 1464		2 1016 1062	4 316 345	
	0 1206 1158	2 2318 2432	H= 2 K= 6	3 1207 1067		
H= 0 K= 6	1 1254 1319	3 1749 1648		4 1137 1244	H= 4 K= 3	
	2 1237 1258	4 2402 2321	0 1603 1266			
0 89 90	3 2207 2219	5 470 469	1 952 987	H= 3 K= 5	0 1873 1795	
2 1725 1545	4 1114 1068		2 1386 1103		1 976 833	
			3 1211 1287	0 712 646	2 526 495	
				1 1411 1037	3 1091 1162	

Note. The column headings are as follows: column 1, L ; column 2, $10^* (\text{sign}[\sqrt{\text{abs}(F_o^{**2})/\text{SCALE}}], F_o^{**2})$ (F_o^{**2} is the observed value corrected for absorption, etc.); column 3, $10^* F_c$ computed to match F_o (the extinction correction, if used, is applied to F_c).

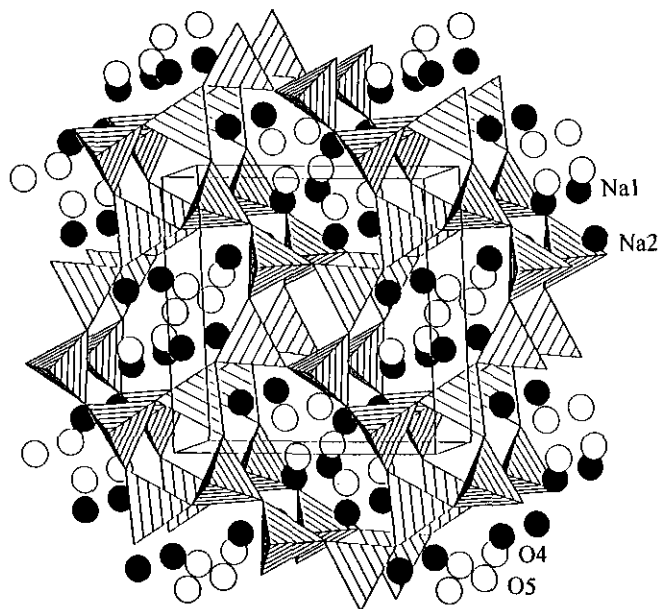


FIG. 4. A polyhedral rendering of the structure of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$, viewed approximately down the c -axis. The Na are represented by the solid circles and the water molecule oxygens by open circles. Na1 is near the long side of the 8-ring, and Na2 is near the "end" of the 8-ring. O5 lies on $mm2$ through the center of the 8-ring, and O4 lies on m displaced from the ring center. The view is down the c -axis, with a down and b to the right.

Bond valence sums for the heavy atoms (20) suggest that the Al is in a normal environment. Na1 appears to be crowded and Na2 to be loosely coordinated.

The bonding power of O1 is not satisfied, and it is clearly the location of the hydroxyl group. The valences of the framework oxygens O2 and O3 are not completely satisfied, which makes them plausible hydrogen bond acceptors.

The refined lattice parameters of the primitive tetragonal unit cell (space group $P4_2/m$) are $a = 10.53396(4)$ Å and $c = 5.33635(3)$ Å at 27°C. A search of the Crystal Data database (21) for sub- and supercells from 1/4 to 4 times the volume of the observed cell yielded no plausible isostructures. This structure type appears to be new.

The peak profiles exhibit significant line broadening compared to the narrowest peaks we have observed on this instrument. The profiles appear to be dominated by strain broadening, which is slightly anisotropic (unique axis [001]). The microstrain appears to be greater perpendicular to c (within the layers) than parallel to c (perpendicular to the layers).

There appears to be a diffuse background in the observed pattern. It is unclear whether this is a real feature or merely represents the overlap of peak tails. Significantly better refinements were obtained when a real-space pair correlation function was used to model the background. The three interatomic distances which arose out of the refinements were 2.59(1), 3.25(1), and 3.83(1) Å. The shortest distance corresponds roughly to the O–O distances in the AlO_4 tetrahedra. The 3.25 Å distance is approximately the average of the shortest Al–Al, Al–Na, and Na–Na distances in the structure. The 3.83 Å distance is close to second-nearest-neighbor Al–O and Na–O dis-

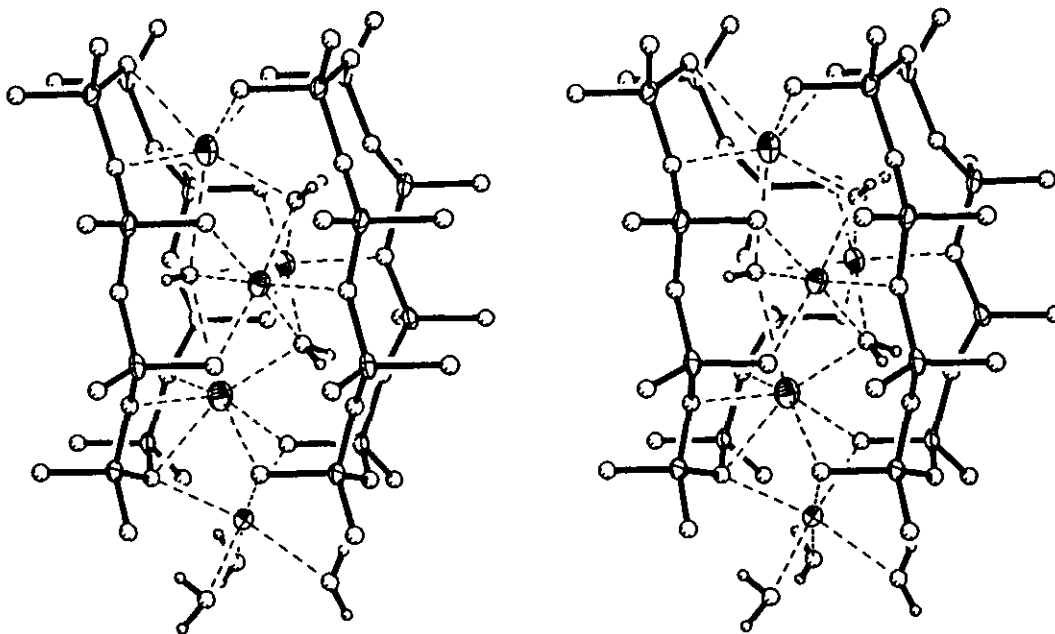


FIG. 5. A stereo view of the coordination polyhedra of the Na ions in $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$; 50% probability ellipsoids for the Na and Al atoms. Na–O bonds are indicated by dashed lines. The view is approximately down [110], with c to the right.

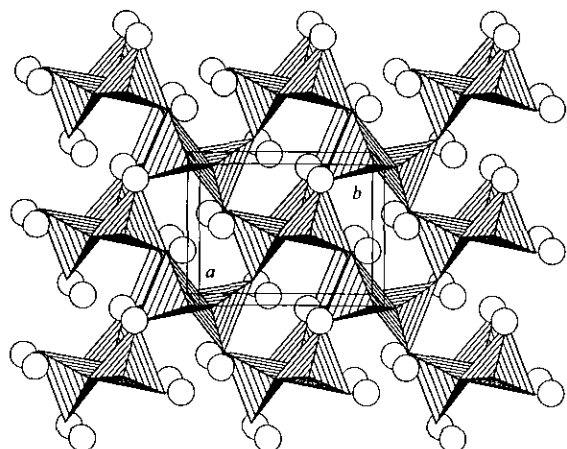


FIG. 6. A polyhedral rendering of the structure of NaAlO_2 , viewed approximately down the c -axis (001).

tances. These distances are physically plausible, but their significance is uncertain.

The quantitative phase analysis was calculated from the refined scale factors (22). The calculated 84.6(4) wt%

concentration of crystalline hydrated sodium aluminate is reasonable for a technical-grade reagent. We detect 5.4% thermonatrite and 0.6% quartz. The remaining crystalline and amorphous impurities account for 9.4% of the sample. These impurities appear to be water-soluble, since the unidentified peaks do not appear in the pattern of the residue obtained when the sample is dissolved in water and filtered on a Millipore filter.

The observed powder pattern corresponds well to the Powder Diffraction File pattern (41-638) reported for this phase (3). The observed pattern has been submitted to the International Centre for Diffraction Data for inclusion in the Powder Diffraction File.

Crystal Structure of NaAlO_2

NaAlO_2 is isostructural to $\beta\text{-NaFeO}_2$. This structure consists of a three-dimensional framework of corner-linked AlO_4 tetrahedra. The tetrahedra are joined into 6-rings and 4-rings. The 8-rings of the starting material do not persist. The structure is illustrated in Fig. 6.

The unconstrained refinement has led to reasonable values for bond distances and displacement coefficients.

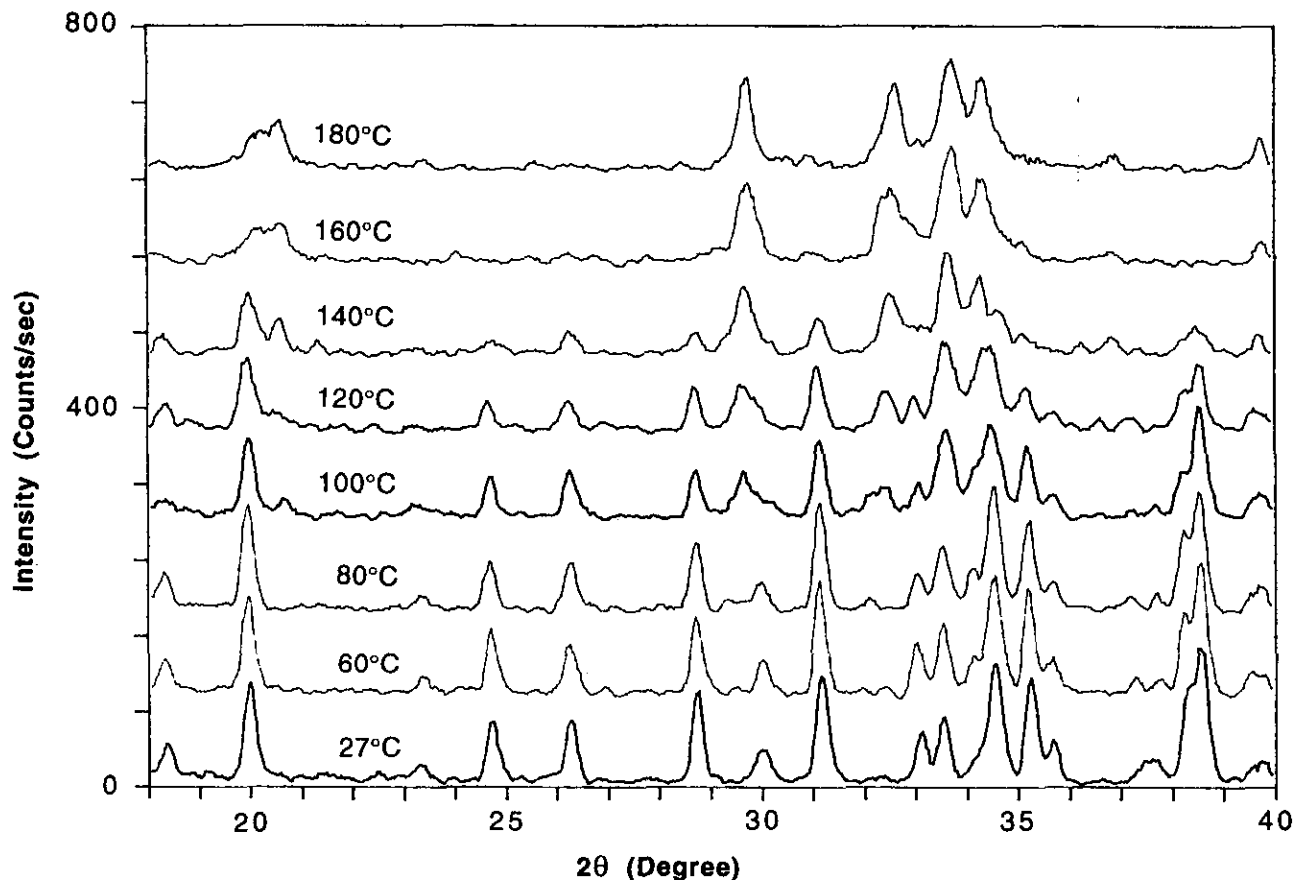


FIG. 7. XRD patterns of hydrated sodium aluminate on heating *in situ* in air. The time between two successive runs was about 25 min. The flow rate of air was $100 \text{ cm}^3/\text{min}$. The horizontal axis is 2θ in degrees.

The Al–O geometry is regular; the maximum deviation from the ideal tetrahedral angle is 3.4° .

The Na lies in a tetrahedral cavity, with Na–O distances of 2.312(4), 2.335(4), 2.351(4), and 2.403(5) Å. A fifth O is 2.900(5) Å from the Na. The tetrahedral coordination is distorted; one of the O1–Na–O2 angles is $132.8(1)^\circ$, while the others are close to the ideal values.

The sums of the bond valences (20) for Al and O1 agree with the anticipated values, but the valences of Na and O2 are slightly lower than expected. Inclusion of the long Na–O2 distance of 2.90 Å into these calculations raises the Na valence to 0.97 and that of O2 to 1.95. This may suggest that the long Na–O2 distance represents a real, though weak, interaction.

The structure is similar in all respects to that of $\beta\text{-NaFeO}_2$. Examination of the structures of the starting material and the dehydrated product indicates no simple transformation path. The network topologies are very different.

Dehydration of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$

Dehydration takes place at temperatures below 150°C . X-ray powder patterns of partially dehydrated samples demonstrate that these materials are two-phase mixtures of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ and NaAlO_2 ; no intermediate phases are detected (Fig. 7). Heating at temperatures as low as 100°C decomposes the $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ present in the starting material.

We have refined the patterns of the partially dehydrated samples using a two-phase model ($\text{NaAlO}_2 \cdot 5/4 \text{H}_2\text{O}$ and NaAlO_2). The values of x in $\text{NaAlO}_2 \cdot x\text{H}_2\text{O}$ calculated from the scale factors of $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ and NaAlO_2 agree well with those calculated from the experimental weight loss.

The lattice parameters of NaAlO_2 decreased slightly, but significantly, with increasing dehydration temperature. The profile Y (strain) term also decreased with increasing temperature. It appears that heating at higher temperatures reduces the strain in the NaAlO_2 formed during the dehydration. The strain in $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ increases with increasing temperature.

$\text{NaAlO}_2 \cdot 5/4 \text{H}_2\text{O}$ exists only in the region very close to $x = 1.25$. Dehydration of the material causes a phase transformation, and part of the material transforms to NaAlO_2 . For $x < 0.1$, the material is single-phase NaAlO_2 .

The dehydration process in sodium aluminate appears to be reversible. We have found that a slurry of NaAlO_2 and water transforms to $\text{NaAlO}_2 \cdot 5/4\text{H}_2\text{O}$ after heating at temperatures greater than 90°C overnight. The hydration process is preferably carried out at elevated temperature (close to 100°C) in an atmosphere free of CO_2 , to prevent the formation of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.

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