Since *Aa* is a polar space group we expect evidence for ferroelectricity in this case. However, the shape of the dielectric-constant curve (Gesi, 1981) is reminiscent of that of an antiferroelectric, being incompatible with the polar space group *Aa*. At present, neither a ferrorelectric nor an antiferroelectric hysteresis loop has been observed (Gesi, 1980). Thus it is still uncertain which is more plausible. Furthermore, an anomalously large *B* value for the D atom is noted at 110 and 25 K, although hardly significant. Thus we cannot exclude that the *A*-base centering is broken if we take the H atom into consideration, although X-ray data cannot detect the difference. Some additional work will be needed to clear up this point. Powder neutron analysis, which is now in progress, is expected to give more decisive information.

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Structure of $NaGaTi_5O_{12}$

BY YUICHI MICHIUE, MAMORU WATANABE, YOSHIZO KITAMI AND YOSHINORI FUJIKI

National Institute for Research in Inorganic Materials, Namiki 1-1, *Tsukuba, Ibaraki,* 305 *Japan*

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Abstract. $NaGaTi_5O_{12}$, $M_r = 524.11$, monoclinic, $C2/m$, $a = 15.221$ (2), $b = 3.7310$ (5), $c = 9.3273$ (9) Å, $\beta = 122.042$ (6)°, $V = 449.01$ (9) Å^3, $Z = 2$, $D_x = 3.88$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 72.7$ cm^{-1}, $F(000) = 496$, $T = 295$ K, final $R = 0.024$ for 1947 independent reflections. The structure consists basically of MO_6 (M = Ti, Ga) octahedra, which form a novel tunnel accommodating Na ions. Mean M—O distances in three nonequivalent octahedra are quite similar to each other (1.978–1.985 Å). Ga atoms are distributed at these three octahedral sites with occupancies of 10.6, 25.3 and 14.1%, respectively. Na atoms are located at the center of the tunnel and in a square-planar coordination of four O atoms. This compound is closely related to the sodium titanates, $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$.

Introduction. In the pseudo-ternary system A_2O–Ga_2O_3–TiO_2 (A: alkali metal), several compounds such as $Na_{1-x}Ti_xGa_{5-x}O_8$ ($x \simeq 0.3$) (Chandrashekhar, Bednowitz & La Placa, 1979), $K_xGa_{2+x}Ti_{2-x}O_7$ ($x \simeq 0.14$) (Watanabe, Sasaki, Kitami & Fujiki, 1987) and $K_{1-x}Ti_{2+x}Ga_{5-x}O_{12}$ ($x \simeq 0.2$) (Watanabe, Fujiki, Yoshikado & Ohachi, 1989) have been reported. These compounds, whose structures have one-dimensional tunnels containing alkali cations, are promising ionic conductors. From the crystallographic point of view, it is also interesting that

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various types of frameworks can be found in this system. We have examined the system Na_2O–Ga_2O_3–TiO_2 and obtained a novel compound with a mixing ratio of Na_2O:Ga_2O_3:TiO_2 = 1:1:10. The structure has proved to have a framework similar to that of the hypothetical bronze-like compound '$B_2Ti_6O_{12}$' which Anderson & Wadsley (1962*a*) predicted but did not succeed in preparing.

Experimental. Single crystals of $NaGaTi_5O_{12}$ were obtained by a flux method (Fujiki, Michiue & Watanabe, 1991). The flux melt of Na_2CO_3–MoO_3 containing TiO_2 and Ga_2O_3 was kept at 1623 K for 10 h, then cooled to 1273 K at a rate of 4 K h^{-1}. The crystals grown were taken out of the crucible by dissolving the flux in hot water. Needle-shaped crystals of $NaGaTi_5O_{12}$ were obtained along with $Na_{1-x}Ti_xGa_{5-x}O_8$. Diffraction intensity was measured with a Rigaku AFC-5 automated four-circle diffractometer and cell parameters were refined from 24 reflections with $50 < 2\theta < 60°$; crystal dimensions $0.1 \times 0.2 \times 0.4$ mm, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan mode, scan speed 2° $\min^{-1}(\theta)$, $2\theta \leq 90°$ ($-30 \leq h \leq 30$, $0 \leq k \leq 7$, $0 \leq l \leq 18$). Three standard reflections measured every 100 reflections, intensity variation within 1.6%. 2129 reflections collected, 1947 independent reflections with $|F_o| > 3\sigma(|F_o|)$ used for the structure determination. Absorption correction applied, min. and max. transmission factors 0.258 and 0.579, respectively. Metal positions were determined from Patterson maps and the high-resolution structure image along [010] taken by the transmission electron microscope JEM-2000 EX (JEOL) (Fig. 1). Na and O atoms found by Fourier syntheses and difference Fourier syntheses. Full-matrix least-squares calculation based on $|F|$, anisotropic thermal parameters for all atoms, an isotropic extinction parameter $g = 2.92\,(4) \times 10^{-5}$. Na was located at the 2(*a*) site (0,0,0) only, and its occupancy was fixed at unity because the chemical composition obtained by EPMA (electron probe microanalysis) was in good agreement with the stoichiometric composition of $NaGaTi_5O_{12}$ and the *R* factor did not show any significant reduction with Na occupancy less than unity. Although Na located at the 2(*a*) site has an equivalent isotropic temperature factor larger than those of other atoms, the positional disordering model for Na was not adopted for the following reasons. (i) The difference Fourier map with no occupancy for Na showed a peak at the 2(*a*) site which was rather broadened but not split. (ii) The least-squares calculation by the disordering models for Na [*i.e.* Na is located at the 4(*i*) site (*x*,0,*z*) or at both of the 2(*a*) and the 4(*i*) sites with appropriate occupation ratios] showed no improvement for the thermal parameters of Na and the reliability factor. (iii) The B_{eq} [4.77 (9) Å^2] of Na at the 2(*a*) site is acceptable for the value of the alkali cations accommodated in the tunnel. The occupation ratios of Ti to Ga at three metal positions were refined under the constraint of keeping charge neutrality of the formula and full occupation at each site. That is, Ti occupancies at *M*(1) and *M*(2) sites were refined independently, and Ga occupancies at *M*(1), *M*(2) and *M*(3) and Ti occupancy at *M*(3) were dependent upon the values above. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol, IV), including f' and f'' for all atoms. Final $R = 0.024$, $wR = 0.027$. $(\Delta/\sigma)_{max} = 0.0031$, $w^{-1} = \sigma(|F_o|)^2$, $\rho_{min} = -1.2$, $\rho_{max} = 1.6$ e Å^{-3}. Programs used were *ACACA* (Wuensch & Prewitt, 1965), *RSSFR*-5 (Sakurai, 1967), *RADY* (Sasaki, 1982) and *BADTEA* (Finger & Prince, 1975).

Discussion. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* The structure projected along [010] is shown in Fig. 2(*a*).

There are three nonequivalent octahedra, $M(1)O_6$, $M(2)O_6$ and $M(3)O_6$, which constitute the framework enclosing the Na ions. The framework is described as a linkage of the triple zigzag ribbons of octahedra extending along [010] shown in Fig. 2(*b*). This triple octahedral ribbon is the structural unit common to $Na_2Ti_3O_7$ (Andersson & Wadsley, 1961), $Na_2Ti_6O_{13}$ (Andersson & Wadsley, 1962*a*) and the present compound. In tri- and hexatitanate, ribbons are connected mutually by corner-sharing, while in the present compound ribbons forming a framework

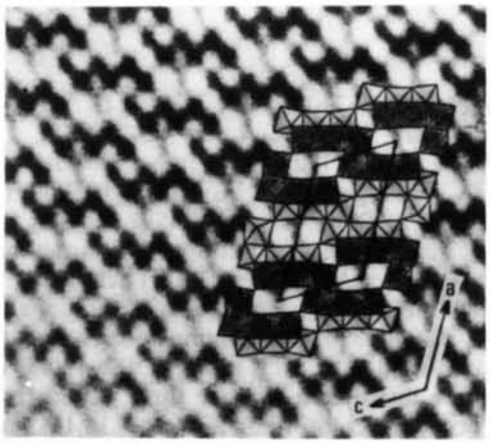

Fig. 1. The high-resolution structure image and the schematic projection drawn with coordination octahedra along [010].

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54717 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^5$) *and equivalent isotropic thermal parameters* ($\times 10^3$ Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

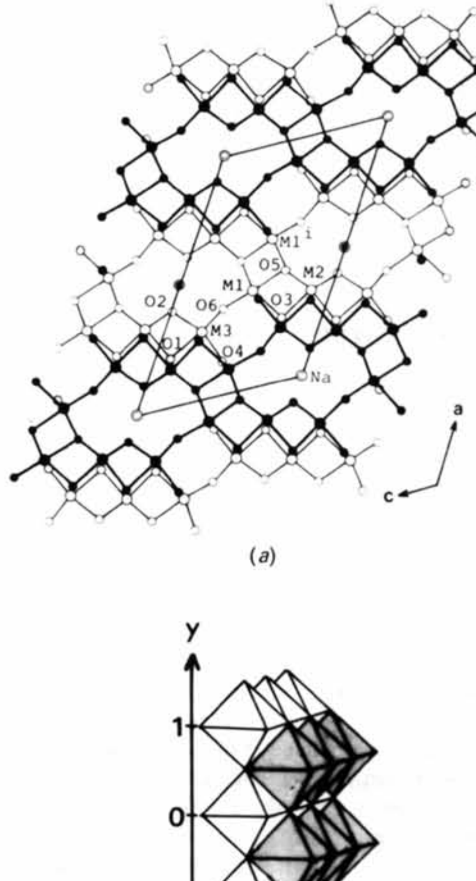
	x	y	z	B_{eq}
Na	0	0	0	4766 (92)
$M(1)$	39941 (2)	0	50918 (3)	459 (7)
$M(2)$	34252 (2)	0	12173 (3)	379 (6)
$M(3)$	27837 (2)	0	75087 (3)	423 (7)
O(1)	19699 (9)	0	89370 (14)	460 (29)
O(2)	39302 (9)	0	98421 (15)	603 (31)
O(3)	25930 (10)	0	26114 (15)	516 (29)
O(4)	13415 (10)	0	54100 (15)	552 (29)
O(5)	45799 (9)	0	34194 (15)	586 (31)
O(6)	35873 (11)	0	66449 (17)	825 (36)

Occupancies of Ti and Ga at metal sites; $M(1)$ 0.894 (1) and 0.106; $M(2)$ 0.747 (2) and 0.253; $M(3)$ 0.859 and 0.141.

Table 2. *Interatomic distances* (Å)

$M(1)$—$M(1^{i})$	3.1563 (8)		$M(2)$—O(1^{iv})	2.105 (1)	
—$M(2)$	3.2387 (6)		—O(1^{ii})	1.9418 (5)	×2
—$M(2^{i})$	3.5962 (6)		—O(2^{iv})	1.812 (2)	
—$M(3)$	3.5894 (6)		—O(3)	2.246 (2)	
—$M(3^{ii})$	3.1179 (4)	×2	—O(5)	1.865 (1)	
$M(2)$—$M(2^{iii})$	3.1278 (5)	×2	Mean	1.985	
—$M(3^{ii})$	3.2554 (5)	×2	$M(3)$—O(1)	2.249 (2)	
—$M(3^{iv})$	3.0553 (5)		—O(2)	1.937 (1)	
			—O(3^{ii})	1.9373 (5)	×2
$M(1)$—O(3)	2.160 (1)		—O(4)	2.023 (1)	
—O(4^{ii})	1.9252 (4)	×2	—O(6)	1.786 (2)	
—O(5)	2.169 (2)		Mean	1.978	
—O(5^{i})	1.855 (1)		Na—O(2^{ii})	2.429 (1)	×4
—O(6)	1.853 (2)				
Mean	1.982				

Symmetry codes: (i) $-x+1, y, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+1$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z$; (iv) $x, y, z-1$.



(*a*)

(*b*)

Fig. 2. (*a*) The structure of $\mathrm{NaGaTi_5O_{12}}$ projected along [010]. Open and filled circles are at $y = 0$ and $-\frac{1}{2}$, respectively. (*b*) The unit of a triple zigzag ribbon extending along [010].

structure are connected not only by corner-sharing but by edge-sharing: $M(1)\mathrm{O}_6$ is linked to $M(3)\mathrm{O}_6$ of a neighboring ribbon by sharing corners and to $M(1^{i})\mathrm{O}_6$ of another ribbon by edge-sharing [Fig. 2(*a*)]. Thus the difference in linkage mode of the ribbons gives rise to variation of the structure type. Tunnels along [010] are found in the framework of $\mathrm{NaGaTi_5O_{12}}$. The tunnel formed consists of a doubled row of polyhedra similar to cubes described by Andersson & Wadsley (1962*a*). The Na atom is not at the center of each cube but on the interface of the two cubes in a doubled row. Consequently Na is located at the center of the tunnel and surrounded by four O(2) atoms forming a pseudo-square.

Interatomic distances are listed in Table 2. Metal–metal distances between edge-sharing octahedra range from 3.0553 (5) to 3.2554 (5) Å. $M(1)$—$M(2^{i})$ and $M(1)$—$M(3)$ distances are smaller than the usual values between corner-sharing octahedra. The angle $M(2)$—$M(1)$—$M(1^{i})$, which would be 90° for the same linkage of normal octahedra, is only 68.42 (1)°.

Mean M—O distances in three nonequivalent octahedra are quite similar to each other. In $M(1)\mathrm{O}_6$ and $M(2)\mathrm{O}_6$ octahedra, six M—O bonds can be classified into three groups; that is, short, medium and long bonds. Each group has two M—O bonds, which is roughly explained by the off-centering of metal atoms in coordination octahedra. In $M(1)\mathrm{O}_6$, for example, the metal atom shifts toward the O(5^{i})—O(6) edge, which brings about two short M—O bonds [$M(1)$—O(5^{i}) and $M(1)$—O(6)] and two long ones [$M(1)$—O(3) and $M(1)$—O(5)]. The $M(1)$—O(4^{ii}) bond belongs to the medium bond group. Since the direction of $M(1)$—O(4^{ii}) is approximately normal to the *ac* plane, displacement of $M(1)$ along the *ac* plane has less influence on the $M(1)$—O(4^{ii}) distance than on the other $M(1)$—O distances. In $M(3)\mathrm{O}_6$, the metal atom shifts toward O(6), which results in $M(3)$—O(6) having the shortest bond length of all the M—O bonds in the structure. O(1) is, on the contrary, at a long distance from $M(3)$.

The Na position is of interest in such a tunnel structure. It is probable that the Na ion is, as seen in the sodium titanium bronze Na_xTiO_2 (Andersson & Wadsley, 1962*b*), located at the 'cubic position': the center of the oxygen pseudo-cube. (The Na occupancy, then, may be reduced to one half in order to relieve electrostatic repulsion between Na ions at the neighboring cubic positions at the same level of *y*.) In practice, however, Na is at the 2(*a*) site which is the center of a pseudo-square consisting of four O(2) atoms. One of the reasons why Na is actually found at the 2(*a*) site only may be that the 2(*a*) site is preferable to the 'cubic position' for Na to be accommodated in view of the electrostatic stability. If Na is located at the 'cubic position', Na again forms a square-planar coordination with two O(2) and two O(6) atoms at a distance of 2.540 (1) Å due to the striking distortion of the cube. Although the value of 2.540 Å would also be probable for the distance between Na and O atoms, Na is more stabilized at the 2(*a*) site, surrounded by four O(2) atoms, at a distance of 2.429 (1) Å.

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Structure of Lithium Niobium Nitride

By Deborah A. Vennos and F. J. DiSalvo

Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853-1301, *USA*

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Abstract. Lithium niobium(V) nitride, Li_7NbN_4, $M_r = 197.49$, cubic, $Pa3$, $a = 9.829$ (1) Å, $V = 949.6$ (4) Å^3, $Z = 8$, $D_x = 2.77$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 22.8$ cm^{-1}, $F(000) = 720$, $T = 298$ K, final $R = 0.031$ for 369 unique reflections. Li_7NbN_4 crystallizes as a superstructure of the *anti*-fluorite structure. Each octant of the cubic structure contains a distorted Li_7Nb cube, which is oriented so that the eight Nb atoms in the unit cell occupy successively each of the distorted cube vertices. The Li_7Nb cube is further surrounded by a larger cube with N atoms at the vertices and face center positions. The Nb ordering produces rows along [100] containing three Li atoms and one Nb atom per unit cell, and an equal number of rows containing only Li atoms. The structure obtained differs from those previously proposed for cubic Li_7VN_4 and for distorted Li_7NbN_4 and Li_7TaN_4 [Juza, Giernn & Haug (1959). *Z. Anorg. Allg. Chem.* **300**, 61–71].

Introduction. Recently we have reported structures and properties of ternary transition-metal nitrides containing electropositive metals. These compounds are relatively simple to prepare as polycrystalline powders; however, in only a few instances have we been able to prepare single crystals (Vennos, Badding & DiSalvo, 1990). In an attempt to grow crystals of Ca_2ZnN_2 (Chern & DiSalvo, 1990) in an Nb tube using Li_3N as a flux, Ca was excluded and crystals of Li_7NbN_4 grew. Many of the known Li–transition-metal nitrides adopt superstructures of the *anti*-fluorite type; these include Li_3FeN_2 (Gudat, Kneip, Rabenau, Bronger & Ruschewitz, 1990), Li_6MoN_4 and $Li_{15}Cr_2N_9$ (Gudat, Haag, Kneip & Rabenau,

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