$SeB_{11}H_{10}$ 1·715 (12)–1·934 (13), mean 1·762 (12) Å (Ni Dhubhghaill *et al.*, 1989). The B—I distances in $As_2B_{10}H_8I_2$ [2·161 (7) and 2·170 (7) Å] span the B—I distance found in 12-I-1-$SeB_{11}H_{10}$ of 2·167 (7) Å and are also comparable with the value found in 1-I-$B_{10}H_{13}$ [2·17 (1) Å] (Sequeira & Hamilton, 1967).

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# Structure of Sodium $\beta''$-Gallate

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**Abstract.** $Na_{1+x}Ga_{11-x/3}O_{17}$ ($x = 0·98$), $M_r = 1061·72$, rhombohedral, $R\bar{3}m$, with hexagonal cell; $a = 5·855$ (1), $c = 34·570$ (10) Å, $V = 1026·3$ (5) Å$^3$, $Z = 3$, $D_x = 5·15$ g cm$^{-3}$, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 219$ cm$^{-1}$, $F(000) = 1466$, $T = 296$ K, final $R = 0·033$ for 707 independent reflections. Sodium $\beta''$-gallate is isostructural with sodium $\beta''$-alumina. Sodium substitutes for 16·3% of Ga atoms at tetrahedral sites in the spinel block. The size of the tetrahedron is enlarged compared with that of the usual $GaO_4$ moiety because of this substitution. In the conduction plane, an $Na^+$ ion is located at the 6(c) and 18(h) sites with occupancies 35 and 16%, respectively, and an O atom is randomly distributed at the 18(h) sites, or at six positions around each 3(b) site. This is the first case where a random distribution of O atoms in the conduction plane is observed for a $\beta''$-gallate, although it has been known in some $\beta''$-aluminas. The deviation of the O atom from the 3(b) site is 0·54 Å.

**Introduction.** $\beta$- and $\beta''$-gallates, which are gallium analogs of $\beta$- and $\beta''$-aluminas, which are well known as solid electrolytes, also exhibit high ionic conductivities. The synthesis, structure and conductivities of these gallates have been widely studied. Sodium $\beta''$-gallate was first synthesized by Boilot, Thery & Collongues (1973), and its single crystals were grown by the evaporation method (Foster & Scardefield, 1977). The ionic conductivities of sodium $\beta''$-gallate were examined by Chandrashekhar & Foster (1977), who discussed charge compensation mechanisms of sodium $\beta''$-gallate on the basis of the results of structure analysis (Anderson, Foster & La Placa, 1981). However, no atomic coordinates were given in their paper and structural details of sodium $\beta''$-gallate have never been discussed. The reason is that the material is unstable due to its hygroscopic properties (Foster & Arbach, 1977), which gives rise to difficulty in the precise refinement of structural parameters. The present study has been undertaken in order to obtain stable single crystals of sodium $\beta''$-gallate and to determine the structural parameters with an accuracy comparble to the results for potassium and ammonium $\beta''$-gallate (Tsurumi, Ikawa, Nishimura, Urabe & Udagawa, 1987). Although they are isostructural with each other, these compounds show some inter-

esting differences which may have critical effects on stability and/or conductivity.

**Experimental.** A mixture of $Na_2CO_3$, $TiO_2$ and $Ga_2O_3$ in the molar ratio 1·5:0·6:4·7 was heated at 1573 K in a furnace for 15 h. The products were then cooled to 1273 K at 4 K h$^{-1}$, and removed from the furnace. Hexagonal plates of sodium $\beta''$-gallate were obtained as a by-product of the main reaction which forms $Na_{1-x}Ti_xGa_{5-x}O_8$. EPMA analysis showed a negligible amount of Ti in the sodium $\beta''$-gallate crystals.

A single crystal, ca $0·15 \times 0·15 \times 0·035$ mm, was mounted on an automated four-circle diffractometer (Rigaku AFC-5), Mo $K\alpha$ radiation, graphite monochromator; 24 independent reflections in the $2\theta$ range 35–45° were used for refinement of the cell dimensions, $\omega$–$2\theta$ scan mode; scan speed 2° min$^{-1}$ ($\theta$), $2\theta \le 90°$; $0 \le h \le 9$; $0 \le k \le 9$; $0 \le l \le 40$; equivalent reflections $(-h,h+k,l)$ related by a mirror plane were also measured and averaged after absorption corrections (min. and max. transmission factors 0·075 and 0·452); three standard reflections measured every 50 reflections, drop in intensities within 5·6%; 1742 reflections collected, 707 independent reflections with $F_o > 3\sigma(F_o)$ used for the refinement; initial values for the positional parameters were taken from potassium $\beta''$-gallate (Tsurumi, Ikawa, Nishimura, Urabe & Udagawa, 1987). Fourier synthesis, difference Fourier synthesis, and full-matrix least-squares calculations based on $F$. Anisotropic thermal parameters used for all atoms; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), including $f'$ and $f''$. Final $R = 0·033$, $wR = 0·023$, $\Delta\rho_{min} = -1·6$, $\Delta\rho_{max} = 2·2$ e Å$^{-3}$, $(\Delta/\sigma)_{max} = 0·21$, $w = 1/\sigma(F_o)^2$. Programs used were ACACA (Wuensch & Prewitt, 1965), RSSFR-5 (Sakurai, 1967), RADY (Sasaki, 1982) and BADTEA (Finger & Prince, 1975).

**Discussion.** Final atomic parameters, equivalent isotropic thermal parameters and site occupancies are listed in Table 1* and interatomic distances in Table 2.

The structure is the typical $\beta''$-alumina type, where the unit cell consists of a stacking of three pairs of the spinel block and a conduction plane along [001]. In spinel blocks, O atoms construct a close-packed arrangement and Ga atoms are accommodated in tetrahedral [Ga(2)] or octahedral [Ga(1),

**Table 1.** *Occupancies and positional and equivalent isotropic thermal parameters*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

$$y = -x.$$

| | Position | N* | x | z | $B_{eq}$ (Å²) |
|---|---|---|---|---|---|
| Ga(1) | 18(h) | 1 | 0·16702 (6) | −0·07202 (2) | 0·58 (1) |
| Ga(2) | 6(c) | 0·837 | 0 | 0·35010 (4) | 0·40 (3) |
| Ga(3) | 6(c) | 1 | 0 | 0·45035 (3) | 0·50 (2) |
| Ga(4) | 3(a) | 1 | 0 | 0 | 0·43 (3) |
| O(1) | 18(h) | 1 | 0·1553 (3) | 0·0348 (1) | 0·80 (4) |
| O(2) | 18(h) | 1 | 0·1611 (4) | 0·2339 (1) | 0·95 (5) |
| O(3) | 6(c) | 1 | 0 | 0·2948 (2) | 1·02 (19) |
| O(4) | 6(c) | 1 | 0 | 0·0983 (3) | 1·05 (18) |
| O(5) | 18(h) | $\frac{1}{6}$ | 0·0535 (45) | 0·5004 (40) | 2·48 (25) |
| Na(1) | 6(c) | 0·353 | 0 | 0·1735 (11) | 6·84 (197) |
| Na(2) | 18(h) | 0·158 | −0·0659 (68) | 0·1725 (12) | 6·68 (14) |
| Na(3) | 6(c) | 0·163 | 0 | 0·35010 (4) | 0·40 (3) |

* Occupancy.

**Table 2.** *Interatomic distances* (Å)

| Ga(1)—O(1)$^i$ | 2·083 (3) × 2 | Na(1)—O(2) | 2·65 (4) × 3 |
|---|---|---|---|
| O(2)$^{ii}$ | 1·912 (3) × 2 | O(4) | 2·60 (4) |
| O(3)$^{iii}$ | 2·046 (4) | O(5)$^{viii}$ | 2·85 (5) × 3 |
| O(4)$^{iv}$ | 1·922 (5) | | |
| Ga(2)—O(1)$^v$ | 1·910 (2) × 3 | Na(2)—O(2) | 3·13 (3) |
| O(3) | 1·912 (7) | O(2)$^{ix}$ | 2·56 (3) × 2 |
| | | O(4) | 2·65 (4) |
| Ga(3)—O(2)$^{vi}$ | 1·849 (3) × 3 | O(5)$^{viii}$ | 2·58 (3) × 2 |
| O(5) | 1·81 (13) × 3 | | |
| O(5)$^{vii}$ | 1·79 (13) × 3 | | |
| Ga(4)—O(1) | 1·982 (3) × 6 | | |

Symmetry codes: (i) $-x$, $-x+y$, $-z$; (ii) $x+\frac{1}{3}$, $x-y-\frac{1}{3}$, $z-\frac{1}{3}$; (iii) $x+\frac{1}{3}$, $y-\frac{1}{3}$, $z-\frac{1}{3}$; (iv) $-x$, $-y$, $-z$; (v) $x-\frac{1}{3}$, $y+\frac{1}{3}$, $z+\frac{1}{3}$; (vi) $-x+\frac{1}{3}$, $-y-\frac{1}{3}$, $-z+\frac{1}{3}$; (vii) $-x$, $-y$, $-z+1$; (viii) $-x+\frac{1}{3}$, $-x+y+\frac{2}{3}$, $-z+\frac{2}{3}$; (ix) $x$, $x-y$, $z$.

Ga(4)] sites. Ga(3) resides in a tetrahedral coordination formed by three O atoms in the spinel block and one O atom in the conduction plane.

The atomic arrangement in the conduction plane exhibits one of the most striking differences between sodium and potassium $\beta''$-gallate. The oxygen atom O(5) in sodium $\beta''$-gallate is not positioned at the 3(b) site $(0,0,\frac{1}{2})$, but at one of six 18(h) sites (0·0535, −0·0535, 0·5004) around the 3(b) site. These sites are 0·54 Å apart from the center sites. The conduction plane in sodium $\beta''$-gallate is about 0·3 Å thinner than that in potassium $\beta''$-gallate, and this is due to the smaller size of Na$^+$ compared with K$^+$ (Michiue, Watanabe & Fujiki, 1989). In sodium $\beta''$-gallate, therefore, the interatomic distance of two Ga(3) atoms bridged by O(5) is shortened. This results in the deviation of O(5) from the ideal 3(b) site in order to reduce the steric hindrance between Ga(3) and O(5); if O(5) remains at the 3(b) site, the interatomic distance Ga(3)—O(5) is only 1·72 Å. Actually it is elongated to about 1·80 Å which is a normal distance in GaO$_4$ tetrahedra.

Fig. 1 shows a schematic view of the conduction plane, where two kinds of Na sites, Na(1) and Na(2), exist. It is unlikely that three Na(2) sites around an Na(1) site are filled at the same time because of the

short distances among them. The coordination state of the Na atom is modified from that of the K atom in potassium $\beta''$-gallate due to the shifts of O(5) and Na itself. Na(1) is primarily coordinated by three O(2) atoms and an O(4) atom in two spinel blocks interleaving the plane. In addition, Na(1) can interact with the nearest O(5) atom at a distance of 2·85 (5) Å. The coordination state of Na(2) is rather different from that of Na(1). Na(2) is 3·13 (3) Å from one of three O(2) atoms and very close to one of the O(5) atoms [2·58 (3) Å].

The substitution of Na$^+$ for K$^+$ also has significant influence on the spinel block. It is worthwhile,

Table 3. *Selected oxygen–oxygen distances* (Å) *in the coordination polyhedra*

|  |  | Sodium $\beta''$-gallate | Potassium $\beta''$-gallate* |
|---|---|---|---|
| Ga(1)O$_6$: | O(1)—O(4) | 2·702 (9) | 2·669 (7) |
|  | O(2)—O(2)$^i$ | 2·830 (2) | 2·864 (3) |
|  | O(2)—O(3) | 2·665 (6) | 2·694 (7) |
| Ga(2)O$_4$: | O(1)—O(1)$^{ii}$ | 3·127 (3) | 3·121 (4) |
|  | O(1)—O(3)$^{iii}$ | 3·112 (6) | 3·090 (7) |
| Ga(3)O$_4$: | O(2)—O(2)$^{iv}$ | 3·025 (5) | 2·992 (5) |

\* Calculated from the positional parameters of Tsurumi *et al.* (1987). Symmetry codes: (i) $x, x - y, z$; (ii) $x, x - y - 1, z$; (iii) $x + \frac{1}{3}, y - \frac{1}{3}, z - \frac{1}{3}$; (iv) $-x + y + 1, y, z$.

therefore, to compare in detail the configuration of the spinel blocks of the two salts in order to understand how the strain of the framework structure (which is due to the size variation of the substituted cations) is relieved.

When the structure is seen as a linkage of coordination polyhedra, the spinel block consists of three kinds of layers, $T$, $O$ and $TO$ as shown in Fig. 2. $T$ layers are constructed by Ga(3)O$_4$ tetrahedra and $O$ layers by Ga(1)O$_6$ octahedra. $TO$ layers contain both Ga(2)O$_4$ tetrahedra and Ga(4)O$_6$ octahedra. Selected O—O edge distances of these polyhedra are compared with those in potassium $\beta''$ gallate in Table 3.

The Ga(3)O$_4$ tetrahedron nearest to the conduction plane is the most distorted of all the coordination polyhedra. As a result of the shift of the O(5) atom, the O(2)—Ga(3)—O(5) angle varies from 92 (2) to 127 (2)°. In addition, the tetrahedron is expanded in the $ab$ plane. As indicated in Table 3, the O(2)—O(2) distance in sodium $\beta''$-gallate is 0·033 Å longer than that in potassium $\beta''$-gallate, that is, the triangle consisting of three O(2) atoms is expanded (Fig. 2c, No. 1). As O(2) atoms also coordinate to alkali cations in the conduction plane, this shift of O(2) atoms results in the shortening of the distance between O(2) and the alkali cations. Therefore, this expansion can be considered to occur because Na$^+$ is smaller than K$^+$. Consequently, the Ga(3) atom shifts towards the expanded triangle, which brings about the contraction of the tetrahedron along the $c$ axis and the expansion of the O(2)—Ga(3)—O(2) angles in sodium $\beta''$-gallate [Na-$\beta''$:109·75 (11), K-$\beta''$:107·65 (12)°].

The next $O$ layer (Fig. 2c, No. 2) is slightly deformed as a result of cation substitution in the conduction planes. O(2)—O(2) and O(2)—O(3) in sodium $\beta''$-gallate are shorter than in potassium $\beta''$-gallate, again due to the shift of O(2) atoms. The decrease of O(1)—O(4) in potassium $\beta''$-gallate is due to the shift of O(4) along the $c$ axis, which also explains the fact that Ga(1)—O(4) is shorter in potassium $\beta''$-gallate [1·908 (3) Å] than in sodium $\beta''$-gallate. In this structure, the thickness of the
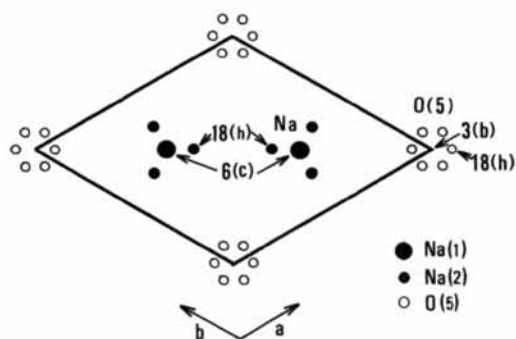


Fig. 1. Schematic representation of Na and O distributions in the conduction plane ($z = \frac{1}{2}$) of sodium $\beta''$-gallate. 3($b$), 6($c$) and 18($h$) are site symbols of the space group.
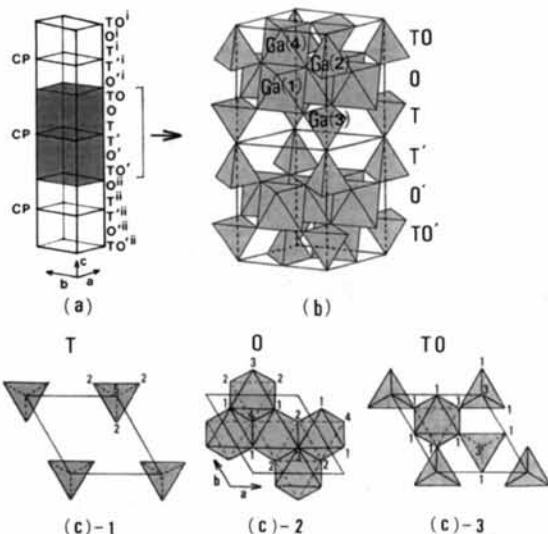


Fig. 2. Typical structure of $\beta''$-gallates. (*a*) Stacking of layers in a unit cell. *CP*: the conduction plane. A prime indicates the symmetry operation of inversion at ($\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$). Superscripts (i), (ii) express translations; (i) $x + \frac{2}{3}, y + \frac{1}{3}, z + \frac{1}{3}$; (ii) $x + \frac{1}{3}, y + \frac{2}{3}, z - \frac{1}{3}$. (*b*) Partial structure expressed by the coordination polyhedra. (*c*) View of the $T$, $O$ and $TO$ layers along [001]. Numbers 1–5 at the edge of each polyhedron indicate the oxygen atoms O(1)–O(5).

conduction plane is unable to expand infinitely because the spinel blocks interleaving the plane are joined with the Ga(3)—O(5)—Ga(3) bond. In order to relax the steric repulsion between $K^+$ and O(4), the Ga(3)—O(5)—Ga(3) bond, which is kinked in sodium $\beta''$-gallate, becomes straight and the O(4) atom recedes from the $K^+$ ion. On the other hand, in sodium $\beta''$-gallate, the conduction plane is thick enough for $Na^+$ and hence the O(4) atom is allowed to keep moderate distances from Ga(1) and O(1).

The TO layer (Fig. 2c, No. 3) is placed in the midst of the spinel block and furthest from the conduction planes. Ga(4) is coordinated with six O(1) atoms. This octahedron exhibits hardly any deformation owing to different cations in the conduction plane. The mismatches observed between sodium and potassium $\beta''$-gallate are within 0·001 Å in the Ga(4)—O(1) distance, and within 0·3° in the O(1)—Ga(4)—O(1) bonding angle. However, the Ga(2)O$_4$ tetrahedron exhibits distinct changes between the two salts, although it would be little influenced by the conduction planes. Na atoms are introduced into the Ga(2) site in sodium $\beta''$-gallate. Potassium $\beta''$-gallate, obtained by cation exchange from sodium $\beta''$-gallate, also contains Na atoms at the Ga(2) site in the spinel blocks. The occupancies of Na at the Ga(2) site in sodium and potassium $\beta''$-gallate, 16·3 and 8·7%, reflect the mean Ga(2)—O distances in the gallates, 1·911 and 1·902 Å, respectively. The expansion of Ga(2)O$_4$ tetrahedra in sodium $\beta''$-gallate is mainly caused by the shift of O(3) atoms. Ga(2)—O(1) is only 0·006 Å longer in sodium $\beta''$-gallate than in potassium $\beta''$-gallate, while Ga(2)—O(3) is 0·018 Å longer. O(1)—O(1) distances in both sodium and potassium $\beta''$-gallate are almost the same, while the former has O(1)—O(3) distances clearly larger than the latter.

Therefore, the Ga(2)O$_4$ tetrahedron in sodium $\beta''$-gallate is mainly expanded in the direction of the $c$ axis.

The effect of cation substitution in $\beta''$-gallates appears most prominently in the dimension of the $c$ axis, which has been roughly explained by the variation in the thickness of the conduction planes. Furthermore, Tsurumi et al. (1987) noted that some differences in coordination polyhedra are observed between the spinel blocks of potassium and ammonium $\beta''$-gallate. The present study has shown that the deformation of coordination polyhedra in the spinel block is caused by the substitution of Na for K, differing from the situation observed between potassium and ammonium $\beta''$-gallate.

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# Orientational Disorder of the Nitrite Anion in the Sodalite Na8[AlSiO4]6(NO2)2

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**Abstract.** $M_r = 990\cdot30$, cubic, $P\bar{4}3n$, $a = 8\cdot923$ (1) Å, $V = 710\cdot45$ Å$^3$, $Z = 1$, $D_m = 2\cdot35$, $D_x = 2\cdot31$ Mg m$^{-3}$, $\lambda$(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 0\cdot70$ mm$^{-1}$, $F(000) =$ 488, room temperature, $R = 0\cdot021$ for 304 unique observed reflections. The sodalite framework is an ordered and alternating array of corner-sharing AlO$_4$