## Data collection

| | |
|---|---|
| Nonius CAD-4 diffractom-eter | $R_{int} = 0.052$ |
| $\omega/2\theta$ scans | $\theta_{max} = 35°$ |
| Absorption correction: | $h = -16 \rightarrow 16$ |
| $\psi$ scan (North *et al.*, 1968) | $k = 0 \rightarrow 14$ |
| | $l = -11 \rightarrow 11$ |
| $T_{min} = 0.494$, $T_{max} = 0.667$ | 3 standard reflections frequency: 120 min |
| 2928 measured reflections | intensity decay: 2.0% |
| 1469 independent reflections | |

## Refinement

| | |
|---|---|
| Refinement on $F^2$ | $\Delta\rho_{max} = 2.168$ e Å$^{-3}$ |
| $R[F^2 > 2\sigma(F^2)] = 0.037$ | (at 0.62 Å from Mo2) |
| $wR(F^2) = 0.095$ | $\Delta\rho_{min} = -1.759$ e Å$^{-3}$ |
| $S = 1.135$ | (at 0.66 Å from Mo1) |
| 1469 reflections | Extinction correction: |
| 65 parameters | SHELXL93 (Sheldrick, |
| $w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 2.6794P]$ | 1993) |
| where $P = (F_o^2 + 2F_c^2)/3$ | Extinction coefficient: 0.0006 (3) |
| $(\Delta/\sigma)_{max} < 0.001$ | Scattering factors from *International Tables for Crystallography* (Vol. C) |

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a^i a^j \mathbf{a}_i . \mathbf{a}_j .$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Mo1 | 0.27128 (5) | 0 | 0.40442 (8) | 0.00776 (13) |
| Mo2 | 1/2 | 0.24850 (6) | 0 | 0.00722 (13) |
| Co1† | 1/2 | 0.32151 (10) | 1/2 | 0.0080 (2) |
| Fe1‡ | 1/2 | 0.32151 (10) | 1/2 | 0.0080 (2) |
| Co2§ | 0.19949 (9) | 0 | −0.14440 (13) | 0.0077 (2) |
| Fe2¶ | 0.19949 (9) | 0 | −0.14440 (13) | 0.0077 (2) |
| O1 | 0.3662 (4) | 0.1562 (5) | 0.4720 (7) | 0.0234 (8) |
| O2 | 0.1415 (5) | 0 | 0.5393 (7) | 0.0090 (8) |
| O3 | 0.4576 (3) | 0.3472 (4) | 0.1959 (5) | 0.0109 (6) |
| O4 | 0.3577 (4) | 0.1440 (4) | −0.1093 (6) | 0.0187 (7) |
| O5 | 0.2016 (6) | 0 | 0.1458 (8) | 0.0230 (13) |

† Site occupancy = 0.57 (9).    ‡ Site occupancy = 0.43 (9).    § Site occupancy = 0.82 (9).    ¶ Site occupancy = 0.18 (9).

Table 2. *Selected bond lengths (Å)*

| | | | |
|---|---|---|---|
| Mo1—O1 | 1.731 (4) | Co1—O3$^{iii}$ | 2.066 (3) |
| Mo1—O1$^i$ | 1.731 (4) | Co1—O3 | 2.066 (3) |
| Mo1—O5 | 1.748 (6) | Co1—O2$^{iv}$ | 2.163 (3) |
| Mo1—O2 | 1.841 (5) | Co1—O2$^v$ | 2.163 (3) |
| Mo2—O4 | 1.731 (4) | Co2—O5 | 2.032 (6) |
| Mo2—O4$^{ii}$ | 1.731 (4) | Co2—O4 | 2.057 (4) |
| Mo2—O3 | 1.807 (3) | Co2—O4$^i$ | 2.057 (4) |
| Mo2—O3$^{ii}$ | 1.807 (3) | Co2—O3$^{vi}$ | 2.093 (4) |
| Co1—O1 | 2.026 (4) | Co2—O3$^{vii}$ | 2.093 (4) |
| Co1—O1$^{iii}$ | 2.026 (4) | Co2—O2$^{viii}$ | 2.126 (5) |

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

The occupancy factors for Co and Fe were refined as least-squares parameters with the sum for each site constrained to be 1, but without constraints for the overall Co:Fe ratio.

Data collection: *CAD-4 Diffractometer Control Software* (Nonius, 1993). Cell refinement: *CAD-4 Diffractometer Control Software*. Data reduction: *X-RED* (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990).

Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

## References

Abrahams, S. C. & Reddy, J. M. (1965). *J. Chem. Phys.* **43**, 2533–2543.
Ehrenberg, H., Wltschek, G., Trouw, F., Kroener, T., Weitzel, H. & Fuess, H. (1994). *J. Magn. Magn. Mater.* **135**, 355–360.
Nonius (1993). *CAD-4 Diffractometer Control Software.* Nonius GmbH, Solingen, Germany.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A46, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Sleight, A. W. & Chamberland, B. L. (1968). *Inorg. Chem.* **7**, 1672–1675.
Stoe & Cie (1996). *X-RED. Data Reduction Program.* Stoe & Cie, Darmstadt, Germany.

# Potassium $\beta''$-aluminogallate

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## Abstract

The single-crystal structure of a non-stoichiometric potassium $\beta''$-aluminogallate, $K_{1.67}Mg_{0.67}Al_{8.58}Ga_{1.75}O_{17}$, has been determined by X-ray diffraction. The Ga atoms were found to occupy predominantly a tetrahedral 6c site (space group $R\bar{3}m$) in the middle of a spinel block of aluminium oxide with a site occupation of 51.6%. All the charge-stabilizing $Mg^{2+}$ ions are found in the same site. Ga atoms are also found with a site occupation of 12.7% in the other tetrahedral 6c site, a site occupation of 7.6% in an octahedral 18h site and a site occupation of 0.9% in the second octahedral 3a site. The $K^+$ ions lie distributed along edge-linked hexagonal pathways with

two maxima, one at a 6c site and one at an 18h site with an occupation ratio of 69:31.

## Comment

Potassium $\beta''$-alumina is well known for its high K$^+$ ion conductivity (Brown et al., 1981) and can as such be used in many technical applications as a solid electrolyte or sensor. The K$^+$ ions can easily be exchanged for other positive mono-, di- or trivalent ions by simply immersing a single crystal or a powder of K$^+$ $\beta''$-alumina in a salt melt at elevated temperatures containing the ion to be exchanged (Kummer, 1972). Thus, good silver, lithium and sodium ionic conductors can be obtained. The present study was performed in order to monitor the effect that changing the spinel framework of a $\beta''$-alumina has on the mobile ion properties and to facilitate ion-exchange possibilities. By exchanging some of the Al atoms in $\beta''$-alumina for Ga atoms and thus creating a $\beta''$-aluminogallate structure, new insight into subtle structural details of charge compensation and transport mechanisms in these non-stoichiometric materials can be obtained (Aka et al., 1990).

The title structure can be described as trigonal with spinel blocks of aluminium oxide interleaved by conduction planes containing the K$^+$ ions (Fig. 1). There are four crys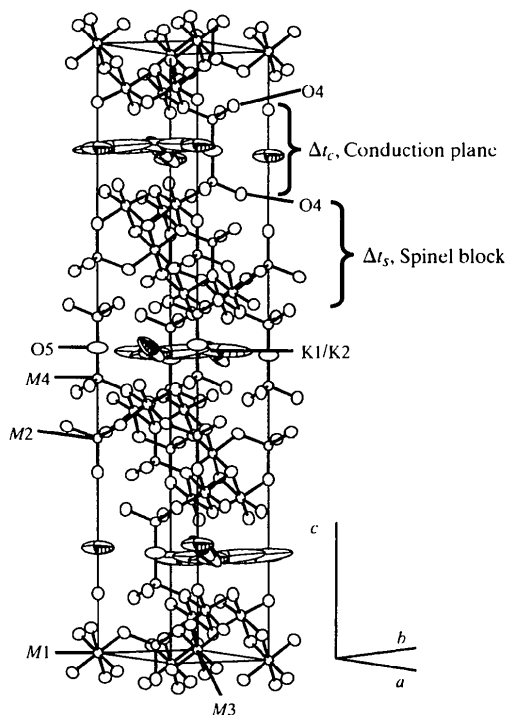tallographically independent Al sites in the spinel block that can be exchanged for Ga atoms, i.e. two octahedral sites and two tetrahedral sites. The structure is charge-stabilized by Mg$^{2+}$ ions at tetrahedral 6c positions in the middle of the spinel block. The K$^+$ ion mobility occurs in two-dimensional honeycomb pathways around the column O5 atom in the conduction plane.

The results of this study show that the Ga atoms preferentially occupy the same tetrahedral 6c site (M2) in the middle of the spinel block as the charge-stabilizing Mg$^{2+}$ ions (Fig. 1 and Table 1). The other three sites are also partially substituted by Ga atoms, but the exchange pattern is quite complex. It is not as simple as just assuming that the Ga atoms prefer the tetrahedral sites to the octahedral sites compared with Al atoms, as suggested earlier (Aka et al., 1990). By comparing the results obtained here with those from an earlier study on a series of Na$^+$ $\beta''$-aluminogallate crystals with different gallium substitutions (Edström et al., 1998), a clearer picture of the substitution pattern emerges (Fig. 2). As can be seen in Fig. 2, the first site in the spinel block to exchange for Ga atoms is the M2 site (a tetrahedral 6c site). The second most substituted aluminium site is the tetrahedral M4 site (also crystallographically a 6c site). The third M3 site to be substituted is the octahedral 18h site. The most difficult site to substitute is M1, the second octahedral 3a site. The substitution pattern, however, is similar in all these three exchanged sites in all the aluminogallates examined (Fig. 2). After the M2 site has been completely filled with 67% gallium (the remainder, 33%, is magnesium, see Fig. 2) at 30% total gallium substitution, all the other three sites are substituted at an equal rate. The electronic structure of gallium offers an explanation of the nature
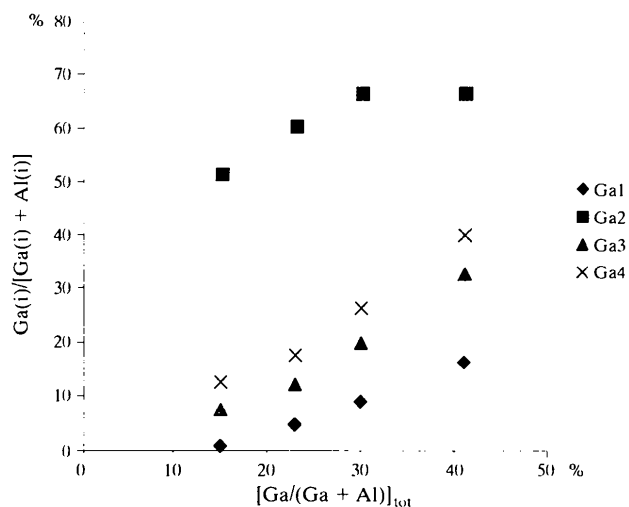


Fig. 1. The structure of K$^+$ $\beta''$-aluminogallate. Atoms are drawn to include 99% probability.



Fig. 2. The gallium content of each metal atom site-type (y axis) for each composition (x axis) of 15% Ga in K$^+$ $\beta''$-aluminogallate, and 23, 30 and 41% Ga in Na$^+$ $\beta''$-aluminogallate (Edström et al., 1998).

of site occupation in $\beta''$-aluminogallates. Aluminium and gallium have similar chemical reactivities, one difference being that gallium has a filled $d$ shell, giving it a tendency to form covalent bonds using $sp^3$ hybrid orbitals. This can explain the tendency for gallium to prefer a tetrahedral coordination compared with aluminium and hence replace the tetrahedral aluminium more readily than the aluminium at the octahedral sites, though the replacement pattern as demonstrated in this study seems to be more subtle then earlier believed (Taulelle *et al.*, 1993).

Earlier studies performed on the substitution of aluminium by gallium in polycrystalline $\beta$-alumina (Brinkhoff, 1974) show that the unit-cell parameters increase linearly with gallium content, but this increase did not change the $Na^+$ ion conductivity. $K^+$ ion conductivity, on the other hand, decreased with increasing gallium content. The first report regarding the existence of a $\beta''$-aluminogallate phase was presented by Aka *et al.* (1990). Here also an increase in unit-cell parameters with increasing gallium substitution was reported. One of the considerations here was to determine whether the increase in the $c$-axis parameter influences transport properties and gives an increase in width of the conduction plane. From a knowledge of the thickness of the spinel block, $\Delta t_s$ (Fig. 1), defined as the distance between the planes that are parallel to the conduction plane and which contain the O4 atoms, and the thickness of the conduction slab, $\Delta t_c = \frac{1}{3}(c - 3\Delta t_s)$, a determination of the increase in conduction plane width can be assessed with increasing gallium substitution (Michiue *et al.*, 1989; Iyi *et al.*, 1986). In the study of $Na^+$ $\beta''$-aluminogallate, it could be shown how the increase in the $c$-axis parameter had a relatively small effect on the thickness of the conduction slab (Edström *et al.*, 1998). From this result, it was not surprising that conductivity values for 30 and 41% total gallium substitution are virtually identical to those of $Na^+$ $\beta''$-alumina (Faltens & Dunn, 1993). In comparison, the calculated thickness of the spinel block and conduction slabs are 6.70 and 4.66 Å for $K^+$ $\beta''$-alumina [calculation based on data from Brown *et al.* (1981)], and 6.679 (1) and 4.728 (1) Å for the $K^+$ $\beta''$-aluminogallate reported here. These values can be compared with values of 6.80 and 4.70 Å in $K^+$ $\beta''$-gallate (Michiue *et al.*, 1989). The small increase in the $c$-axis parameter has relatively little effect on the thickness of the conduction slab.

The $K^+$ ion distribution is so spatially extended that the refined models are to some extent inadequate. Large correlations exist between the positional, occupational and displacement parameters of the $K^+$ ions. The best model found to describe the distribution is one in which all the $K^+$ ions are found in two sites, namely a 6$c$ site with the distribution best described by $\beta_{ij}$- and $\gamma_{ijk}$ tensors, and an 18$h$ site described by $\beta_{ij}$ tensors (Figs. 3 and 4). Generally, however, the refined $K^+$ ion distribution is similar to that reported for $K^+$ $\beta''$-alumina

(Bettman & Peters, 1969; Iyi *et al.*, 1986; Brown *et al.*, 1981) and $K^+$ $\beta''$-gallate (Michiue *et al.*, 1989). Partial occupation of gallium in the spinel block seems to influence the $K^+$ ion distribution in the conduction plane, resulting in the broader ion distribution reported for $K^+$ $\beta''$-alumina (Brown *et al.*, 1981). The displacement parameter for O5 is unusually high (Table 1), which has also been seen to be the case at temperatures as low as 30 K (Edström *et al.*, 1997). Molecular dynamics simulations (Thomas & Zendejas, 1989) have shown an influence of the mobile ion on the O5 atoms in $Na^+$ $\beta''$-alumina. The high displacement parameter would thus be a sign of a positional disorder. The extended electron density for the $K^+$ ions combined with the unusually high displacement parameter of the O5 atom in the conduction plane is consistent with the ionic conductivity reported for $K^+$ $\beta''$-aluminogallate and the good ion-exchange property observed for this compound (Faltens & Dunn, 1993).
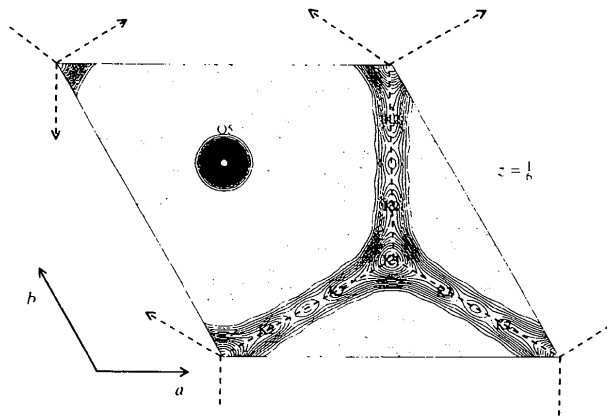


Fig. 3. Final $F_{obs}$ synthesis for $K^+$ $\beta''$-aluminogallate at $z = \frac{1}{6}$. Contour intervals are 1.0 e Å$^{-3}$.
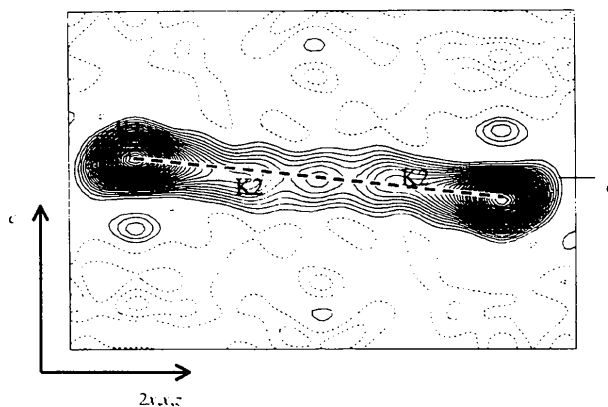


Fig. 4. Observed Fourier synthesis perpendicular to the conduction path. Contour intervals are 1.0 e Å$^{-3}$.

## Experimental

Single crystals of $Na^+$ $\beta''$-aluminogallate were grown by the flux-evaporation technique using $Na_2CO_3$ fluxes (Aka *et al.*, 1990). The starting compounds were $Al_2O_3$, $Ga_2O_3$, $Na_2CO_3$, NaF and MgO. The crystal was grown in air at 1798 K over a period of 10 d. The resulting crystals were of good size ($5 \times 5 \times 1$ mm) and quality. The composition of $Na^+$ $\beta''$-aluminogallate was then determined by atomic absorption analysis with the element content (in moles): Na 1.66 (1), Mg 0.66 (1), Al 8.53 (1) and Ga 1.87 (1) (Aka *et al.*, 1990). The $Na^+$ ions were then ion-exchanged for $K^+$ ions in a stepwise manner in a series of mixed $KNO_3/NaNO_3$ salts containing 10, 50 and 100% $KNO_3$ at 623 K. The crystal was soaked for several hours during each step, and also washed and weighed between steps to monitor the exchange. To have an estimate of the crystal content after the ionic exchange, the experimental linear absorption coefficient was measured as 5.1 (1) $mm^{-1}$ (which is in agreement with the calculated value of 5.023 $mm^{-1}$). From the fully exchanged crystal, which was found to be hygroscopic, was cut a piece suitable for X-ray diffraction. Prior to the X-ray investigation, the crystal was heat treated at 575 K to get rid of any water present. The crystal was then mounted in a glass capillary to prevent water uptake.

### Crystal data

$K_{1.67}Mg_{0.67}Al_{8.58}Ga_{1.75}O_{17}$
$M_r = 699.39$
Trigonal
$R\bar{3}m$
$a = 5.6665\,(2)$ Å
$c = 34.2196\,(17)$ Å
$V = 951.56\,(7)$ Å$^3$
$Z = 3$
$D_x = 3.6972$ Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 25$–$30°$
$\mu = 4.661$ mm$^{-1}$
$T = 293$ K
Triangular
$0.13 \times 0.11 \times 0.05$ mm
Colourless

### Data collection

Stoe diffractometer
$\theta/2\theta$ scans
Absorption correction:
  by integration (explicit crystal size and shape)
$T_{min} = 0.670$, $T_{max} = 0.769$
3571 measured reflections
3571 independent reflections (1267 reflections after merging)

3375 reflections with $I_{net} > 2\sigma(I_{net})$
$R_{int} = 0.025$
$\theta_{max} = 50°$
$h = -5 \rightarrow 10$
$k = -5 \rightarrow 10$
$l = -73 \rightarrow 73$
5 standard reflections
  frequency: 180 min
  intensity decay: 1.2%

### Refinement

Refinement on $F^2$
$R(F) = 0.018$
$wR(F^2) = 0.062$
$S = 1.81$
3375 reflections
54 parameters
$w = 1/[\sigma^2(F) + 0.02F^2]$
$(\Delta/\sigma)_{max} = 0.100$
$\Delta\rho_{max} = 0.73$ e Å$^{-3}$
$\Delta\rho_{min} = -1.19$ e Å$^{-3}$

Extinction correction: Becker & Coppens (1974), isotropic (type 1)
Extinction coefficient: $1.613 \times 10^5$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* $(\text{Å}^2)$

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

| | Occupancy | | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|---|
| K1 | 0.36 (1) | 6c | 0 | 0 | 0.17131 (7) | 0.0390 (3) |
| K2 | 0.16 (1) | 18h | 0.173 (2) | 0.0863 (11) | 0.16808 (5) | 0.113 (8) |
| Mg | 0.1111 | 6c | 0 | 0 | 0.34985 (1) | 0.00380 (5) |
| Ga1 | 0.00895 (6) | 3a | 0 | 0 | 0 | 0.00409 (14) |
| Al1 | 0.99105 (6) | 3a | 0 | 0 | 0 | 0.00409 (14) |
| Ga2 | 0.5162 (1) | 6c | 0 | 0 | 0.349850 (4) | 0.00380 (5) |
| Al2 | 0.1505 (1) | 6c | 0 | 0 | 0.349850 (4) | 0.00380 (5) |
| Ga3 | 0.0763 (2) | 18h | 0.33381 (2) | 0.16690 (1) | 0.070602 (4) | 0.00471 (6) |
| Al3 | 0.9237 (2) | 18h | 0.33381 (2) | 0.16690 (1) | 0.070602 (4) | 0.00471 (6) |
| Ga4 | 0.1266 (1) | 6cc | 0 | 0 | 0.44921 (1) | 0.00470 (6) |
| Al4 | 0.8734 (1) | 6c | 0 | 0 | 0.44921 (1) | 0.00470 (6) |
| O1 | 1 | 18h | 0.15171 (3) | 0.30343 (6) | 0.03426 (1) | 0.00704 (12) |
| O2 | 1 | 6c | 0 | 0 | 0.29440 (2) | 0.00673 (10) |
| O3 | 1 | 6c | 0 | 0 | 0.09591 (2) | 0.00655 (15) |
| O4 | 1 | 18h | 0.16374 (3) | 0.32748 (5) | 0.23574 (1) | 0.00692 (12) |
| O5 | 1 | 3b | 1/3 | 2/3 | 1/6 | 0.0150 (3) |

Table 2. *Selected distances* (Å)

| | | | |
|---|---|---|---|
| K1—O3 | 2.580 (3) | Mg—O1 | 1.8831 (3) |
| K1—O4 | 2.728 (2) | Mg—O2 | 1.8975 (6) |
| K1—O4 | 2.728 (2) | Al3—O1 | 2.0020 (3) |
| K1—O4 | 2.728 (2) | Al3—O1 | 2.0020 (3) |
| Ga1—O1 | 1.8951 (3) | Al3—O2 | 1.9602 (3) |
| Ga1—O1 | 1.8951 (3) | Al3—O3 | 1.8530 (3) |
| Ga1—O1 | 1.8951 (3) | Al3—O4 | 1.8651 (2) |
| Ga1—O1 | 1.8951 (3) | Al3—O4 | 1.8651 (2) |
| Ga1—O1 | 1.8951 (3) | Al4—O4 | 1.7782 (3) |
| Ga1—O1 | 1.8951 (3) | Al4—O4 | 1.7782 (3) |
| Ga2—O1 | 1.8831 (3) | Al4—O4 | 1.7782 (3) |
| Ga2—O1 | 1.8831 (3) | Al4—O5 | 1.7380 (2) |
| Ga2—O1 | 1.8831 (3) | Al1—O1 | 1.8951 (3) |
| Ga2—O2 | 1.8975 (6) | Al1—O1 | 1.8951 (3) |
| Ga3—O1 | 2.0020 (3) | Al1—O1 | 1.8951 (3) |
| Ga3—O1 | 2.0020 (3) | Al1—O1 | 1.8951 (3) |
| Ga3—O2 | 1.9602 (3) | Al1—O1 | 1.8951 (3) |
| Ga3—O3 | 1.8530 (3) | Al1—O1 | 1.8951 (3) |
| Ga3—O4 | 1.8651 (2) | Al2—O1 | 1.8831 (3) |
| Ga3—O4 | 1.8651 (2) | Al2—O1 | 1.8831 (3) |
| Ga4—O4 | 1.7782 (3) | Al2—O1 | 1.8831 (3) |
| Ga4—O4 | 1.7782 (3) | Al2—O2 | 1.8975 (6) |
| Ga4—O4 | 1.7782 (3) | K2—K1 | 2.43 (1) |
| Ga4—O5 | 1.7380 (3) | K2—O3 | 2.611 (4) |
| Mg—O1 | 1.8831 (3) | K2—O4 | 2.702 (2) |
| Mg—O1 | 1.8831 (3) | K2—O4 | 2.702 (2) |

The intensity measurements were corrected for background (Lehman & Larsen, 1974), and the standard reflections were used to scale intensities and s.u.'s (McCandlish *et al.*, 1975). Refinements were carried out using a PC version of the full-matrix least-squares program *DUPALS* (Lundgren, 1982). All refinements were based on an unmerged data set. The reason for this is mainly to avoid merging reflections which are uncorrected for extinction. Anomalous dispersion terms and coherent scattering amplitudes used for $Al^{3+}$, $O^{2-}$, $Mg^{2+}$, $Ga^{3+}$ and $K^+$ were those taken from *International Tables for X-ray Crystallography* (Vol. IV, 1974). The structure was refined in the $R\bar{3}m$ space group. A scale factor was first refined using the structural parameters taken from $Na^+$ $\beta''$-alumina (Bettman & Peters, 1969). The occupation of the Mg atoms at site Mg2 (Table 1) was kept constant during the refinement. This assumption was based on chemical analysis by atomic absorption spectroscopy (Aka *et al.*, 1990) and neutron diffraction studies of $Na^+$ $\beta''$-alumina (Frase *et al.*, 1983), where it has been shown that magnesium only occupies one site in the structure, a tetrahedral $6c$ site. The Ga atoms in the spinel block could then be located in a difference

Fourier synthesis. A negative peak was found at the $M2$ site, indicating that too much electron density was present in this site to model the structure. This peak suggests either more Mg atoms in this site or some Al atoms still remaining. The chosen model assumed the latter (Table 1). The $K^+$ ion distribution was then determined. The K1 ion was refined in a $6c$ site described with $\beta_{ij}$ displacement parameters: $\beta_{11} = \beta_{22} = 2\beta_{12} = 0.0402\,(5)$ and $\beta_{33} = 0.000126\,(5)$, and third-order cumulant displacement parameters, $\gamma_{ijk}$: $\gamma_{111} = -\gamma_{222} = 2\gamma_{112} = -2\gamma_{122} = 0.018\,(1)$, $\gamma_{333} = -0.00003\,(1)$ and $\gamma_{133} = -\gamma_{233} = 2\gamma_{123} = 0.00054\,(6)$. An extra $K^+$ ion had to be included at an $18h$ site with isotropic displacement parameters. The total number of $K^+$ ions was constrained to be 1.67 per formula unit. This constraint was also based on the starting amount of sodium ions as determined by chemical analysis with atomic absorption spectroscopy and the weight-exchange measurements. Refinement tests were carried out on the reliability of the constraints of the occupations for the Mg atoms and the $K^+$ ions. The occupations were refined freely but no significant difference from the constrained occupations was noticed. The constraints were then kept in the final refinements to reduce the number of refined parameters.

Data reduction: STOEDATR (Lundgren, 1982). Program(s) used to refine structure: DUPALS (Lundgren, 1982). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: DISTAN (Lundgren, 1982).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1232). Services for accessing these data are described at the back of the journal.

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### References

Aka, G., Dunn B., Foreman, J. & Farrington, G. C. (1990). Solid State Ionics, 40/41, 83–86.
Becker, P. J. & Coppens, P. (1974). Acta Cryst. A30, 129–147.
Bettman, M. & Peters, C. R. (1969). J. Phys. Chem. 73, 1774–1780.
Brinkhoff, H. C. (1974). J. Phys. Chem. Solids, 35, 1225–1229.
Brown, G. M., Schwinn, D. A., Bates, J. B. & Brundage, W. E. (1981). Solid State Ionics, 5, 147–150.
Edström, K., Faltens, T. A. & Dunn, B. (1998). Solid State Ionics, 110, 137–144.
Edström, K., Thomas, J. O. & Farrington, G. (1997). Acta Cryst. B53, 631–638.
Faltens, T. A. & Dunn, B. (1993). Solid State Ionics, 66, 321–329.
Frase, K. G., Thomas, J. O. & Farrington, G. C. (1983). Solid State Ionics, 9/10, 307–310.
Iyi, N., Inoue, Z. & Kimura, S. (1986). J. Solid State Chem. 61, 81–89.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kummer, J. T. (1972). Progress in Solid State Chemistry, Vol. 1, edited by H. Reiss & J. O. McCaldin, pp. 141–175. Oxford: Pergamon.
Lehman, M. S. & Larsen, F. K. (1974). Acta Cryst. A30, 580–584.
Lundgren, J.-O. (1982). Crystallographic Computer Programs. Report UUIC-B13-04-05. Institute of Chemistry, University of Uppsala, Sweden.

McCandlish, L. E., Stout, G. H. & Andrews, L. C. (1975). Acta Cryst. A31, 245–249.
Michiue, Y., Watanabe, M. & Fujiki, Y. (1989). Solid State Ionics, 35, 223–227.
Taulelle, F., Maquet, J., Lucas, V., Thery, J., Kahn-Harari, A., Faltens, T. A. & Dunn, B. (1993). Appl. Magn. Reson. 4, 101–106.
Thomas, J. O. & Zendejas, M. A. (1989). J. Comput.-Aided Mol. Des. 3, 311–325.

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# (NH4)2[Mg4(H2O)18(H2W12O42)]·10H2O, a new compound containing chains formed by magnesium and paradodecahedral tungstate ions

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## Abstract

A new ammonium magnesium paradodecatungstate decahydrate, namely diammonium octadecaaquahydrogentetramagnesiododecatungstate decahydrate, $(NH_4)_2[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]\cdot 10H_2O$, was prepared by the reaction of $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ with $MgCl_2$ in aqueous solution. The skeleton of the paradodecatungstate ion, $[H_2W_{12}O_{42}]^{10-}$, is basically the same as those in the known paradodecatungstates. It consists of 12 interconnected $WO_6$ octahedra and its centre is located at a crystallographic inversion centre. Both independent Mg atoms are octahedrally coordinated by six O atoms. One magnesium octahedron shares an O atom with a paradodecatungstate group and the other magnesium octahedron shares two O atoms, each with different paradodecatungstate groups, to form a one-dimensional $[Mg_4(H_2O)_{18}(H_2W_{12}O_{42})]_n^{2n-}$ chain along the $b$ direction.

## Comment

Many paradodecatungstates have been investigated by X-ray diffraction methods; examples include $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ (D'Amore & Allman, 1972), $Na_{10}[H_2W_{12}O_{42}]\cdot 20H_2O$ (Chrissafidou et al., 1995), $K_{10}[H_2W_{12}O_{42}]\cdot 7.5H_2O$ (Evans et al., 1993) and $Mg_5$-$[H_2W_{12}O_{42}]\cdot 38H_2O$ (Tsay & Silverton, 1973). The po-