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$Na_{13}K_4Ga_{47.45}$: a New Sodium Potassium Gallide Phase Containing Trimeric Icosahedral Gallium Clusters

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Abstract

$Na_{13}K_4Ga_{47.45}$ was isolated from a melt prepared from the elements taken in the atomic proportion 3:1:12. It crystallizes in the trigonal $R\bar{3}m$ space group [a = 16.325 (3), c = 35.135 (5) Å]. The structure results from the packing of icosahedral Ga_{12} units and trimeric Ga_{28} units. The latter are formed by the condensation of three Ga_{12} units by triangular-face sharing. The interpolyhedral space is filled with K^+ and Na^+ cations.

Comment

The structure of $Na_{13}K_4Ga_{47.45}$ contains three different clusters: icosahedron *A* with $\bar{3}m$ symmetry located at the 3*a* special position (0,0,0), icosahedron *B* centered around the 9*d* position (1/2,0,1/2) with 2/*m* symmetry and icosahedral trimer *C* centered around the 6*c* position

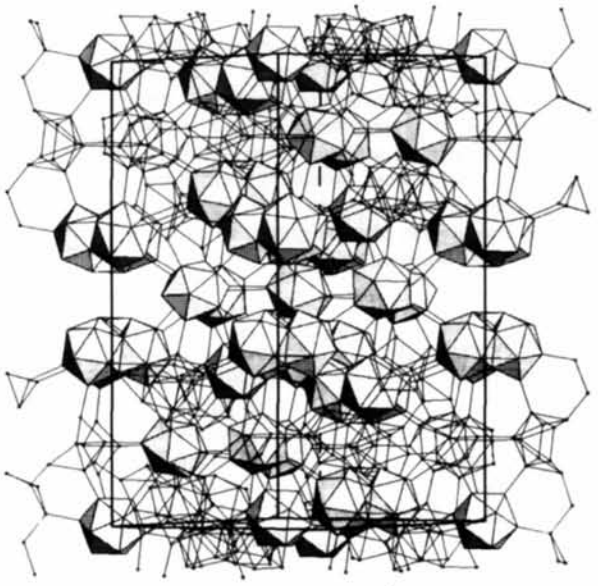

Fig. 1. Representation of the structural packing in $Na_{13}K_4Ga_{47.45}$. The unit cell contains 12 monomeric and 3 trimeric icosahedral gallium units.

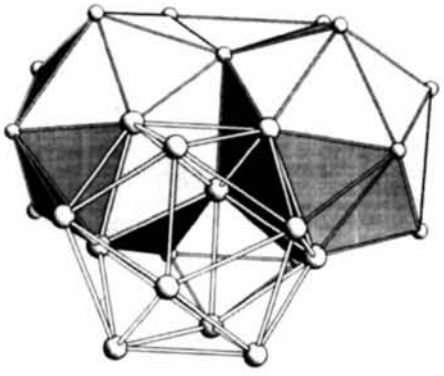

Fig. 2. The trimeric icosahedral unit resulting from the condensation of three icosahedra by face sharing. Each icosahedron shares two faces (five vertices) with its neighbours.

with $3m$ symmetry. While the icosahedral monomers are considered as *closo* polyhedra according to Wade's terminology (Wade, 1976), the trimeric unit is *nido* as a result of the partial occupancy of sites Ga4, Ga12 and Ga13, leading to the formulation $Ga_{23.5}$ in place of Ga_{28}. This compound is a new example among ternary and quaternary gallium rhombohedral intermetallic phases containing various oligomeric icosahedral units (Belin & Tillard-Charbonnel, 1993; Chahine *et al.*, 1994), and provides new insight into the ability of these intermetallic phases to adapt structure according to the electronic content (size and electron tuning).

Experimental

This new ternary Na–K–Ga intermetallic compound was prepared from the elements taken in the atomic proportion 3:1:12 and fused together in a weld-sealed niobium reactor. The mixture was first homogenized and left at 773 K for 24 h, then allowed to cool slowly at the rate of 3 K h^{-1} for crystal growing. The product of the reaction looked reasonably homogeneous. Crystals were checked for crystallinity and characterized by X-ray methods.

Crystal data

$Na_{13}K_4Ga_{47.45}$	Mo $K\alpha$ radiation
M_r = 3763.48	λ = 0.71070 Å
Trigonal	Cell parameters from 25 reflections
$R\bar{3}m$	θ = 13.08–24.79°
a = 16.325 (3) Å	μ = 23.593 mm^{-1}
c = 35.135 (5) Å	T = 293 (2) K
V = 8110 (3) $Å^3$	Wedge
Z = 6	0.40 × 0.35 × 0.25 mm
D_x = 4.624 Mg m^{-3}	Metallic lustre
D_m not measured	

Data collection

Nonius CAD-4 diffractometer	1026 reflections with $I > 2\sigma(I)$
ω–$2/3\theta$ scans	R_{int} = 0.065
Absorption correction: numerical (*SHELX*76; Sheldrick, 1976)	θ_{max} = 24.95°
	$h = -16 \rightarrow 0$
T_{min} = 0.083, T_{max} = 0.210	$k = 0 \rightarrow 19$
3335 measured reflections	$l = 0 \rightarrow 41$
1328 independent reflections	3 standard reflections
	frequency: 60 min
	intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 3.04 e $Å^{-3}$
$R[F^2 > 2\sigma(F^2)]$ = 0.054	$\Delta\rho_{min}$ = −2.59 e $Å^{-3}$
$wR(F^2)$ = 0.138	Extinction correction: *SHELXL*93 (Sheldrick, 1993)
S = 1.071	
1110 reflections	Extinction coefficient: 0.000015 (12)
131 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0760P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	Scattering factors from *International Tables for Crystallography* (Vol. C)
$(\Delta/\sigma)_{max} < 0.001$	

Table 1. *Selected geometric parameters (Å)*

Ga1—Ga7^{i}	2.639 (4)	Ga5—Ga6	2.605 (5)
Ga1—Ga6^{i}	2.661 (4)	Ga5—Ga8^{xv}	2.680 (3)
Ga1—Ga2	2.712 (4)	Ga5—Ga5^{xvi}	2.684 (6)
Ga1—Ga1^{ii}	2.807 (6)	Ga5—Ga8^{xvii}	2.694 (4)
Ga1—Ga2^{iii}	2.811 (4)	Ga6—Ga7^{xviii}	2.745 (5)
Ga1—Ga1^{iv}	2.848 (6)	Ga7—Ga9	2.614 (4)
Ga2—Ga2^{iii}	2.599 (4)	Ga7—Ga2^{xv}	2.780 (3)
Ga2—Ga3^{v}	2.621 (3)	Ga8—Ga10^{viii}	2.557 (5)
Ga2—Ga6^{vi}	2.686 (3)	Ga8—Ga5^{i}	2.680 (3)
Ga2—Ga7^{i}	2.780 (3)	Ga8—Ga8^{xix}	2.684 (4)
Ga3—Ga11^{vii}	2.528 (3)	Ga8—Ga5^{xx}	2.694 (4)
Ga3—Ga13	2.67 (2)	Ga9—Ga12^{xxi}	2.575 (3)
Ga3—Ga10^{viii}	2.705 (3)	Ga9—Ga10	2.652 (5)
Ga3—Ga3^{ix}	2.723 (5)	Ga11—Ga14^{xxii}	2.486 (4)
Ga3—Ga4^{x}	2.854 (4)	Ga11—Ga13^{xxiii}	2.647 (10)
Ga4—Ga12^{xi}	2.531 (6)	Ga11—Ga12^{xxii}	2.771 (5)
Ga4—Ga4^{xii}	2.676 (7)	Ga12—Ga14	2.586 (7)
Ga4—Ga10^{vi}	2.694 (4)	Ga12—Ga12^{xxiv}	2.633 (9)
Ga4—Ga11^{xiii}	2.724 (4)	Ga13—Ga13^{xxiv}	2.52 (4)
Ga4—Ga9^{vi}	2.765 (4)	Ga13—Ga14	2.57 (2)
Ga4—Ga4^{xiv}	2.995 (7)		

Symmetry codes: (i) $1+y, 1-x+y, 1-z$; (ii) $1-x+y, y, z$; (iii) $x-y, -y, 1-z$; (iv) $x, x-y-1, z$; (v) $1-x, -y, 1-z$; (vi) $-y, x-y-1, z$; (vii) $x-y, x, 1-z$; (viii) $\frac{2}{3}-x, -\frac{2}{3}-y, \frac{4}{3}-z$; (ix) $-y, -x, z$; (x) $x-y-\frac{1}{3}, x-\frac{2}{3}, \frac{4}{3}-z$; (xi) $\frac{2}{3}-x, \frac{1}{3}-y, \frac{4}{3}-z$; (xii) $\frac{2}{3}+y, x-\frac{2}{3}, \frac{4}{3}-z$; (xiii) $\frac{2}{3}+x, \frac{1}{3}+y, \frac{1}{3}+z$; (xiv) $1-y, 1-x, z$; (xv) $x-y, x-1, 1-z$; (xvi) $2-x+y, -x, z$; (xvii) $\frac{1}{3}+x, y-\frac{1}{3}, z-\frac{1}{3}$; (xviii) $1-x, -1-y, 1-z$; (xix) $\frac{2}{3}+y, \frac{1}{3}-x+y, \frac{4}{3}-z$; (xx) $x-\frac{1}{3}, \frac{1}{3}+y, \frac{1}{3}+z$; (xxi) $\frac{2}{3}+y, -\frac{2}{3}-x+y, \frac{4}{3}-z$; (xxii) $-x, -y, 1-z$; (xxiii) $y, -x+y, 1-z$; (xxiv) $-x+y, -x, z$.

Refinement of the occupancy of the Ga sites while holding the alkali metals fixed showed that the Ga sites are fully occupied except for three sites within the trimeric icosahedral unit. A similar refinement for the alkali-metal site occupancies (holding the Ga sites fixed) confirmed that, within the 3σ limits, these sites are also fully occupied.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1992).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OH1104). Services for accessing these data are described at the back of the journal.

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