

P(2)	O(3)	O(3 ^{iv})	O(6)	O(6 ^v)
O(3)	1.529 (8)	2.49 (1)	2.53 (2)	2.52 (2)
O(3 ⁱⁱⁱ)	109.1 (7)	1.529 (8)	2.52 (2)	2.53 (2)
O(6)	109.9 (4)	110.3 (4)	1.548 (8)	2.49 (2)
O(6 ⁱⁱ)	110.3 (4)	109.9 (4)	107.3 (6)	1.548 (8)
Rb(1)—O(6) × 8	3.005 (8)		Rb(2)—O(3 ⁱ)	3.148 (9)
Rb(2)—O(1 ⁱⁱ)	2.92 (2)		Rb(2)—O(3 ⁱⁱ)	3.148 (9)
Rb(2)—O(2 ⁱⁱⁱ)	3.107 (8)		Rb(2)—O(3 ⁱⁱⁱ)	3.148 (9)
Rb(2)—O(2 ^{iv})	3.107 (8)		Rb(2)—O(3 ^{iv})	3.148 (9)
Rb(2)—O(2 ^v)	3.107 (8)			
Rb(2)—O(2 ^{vi})	3.107 (8)		Ba—O(4) × 4	2.61 (2)

Symmetry code: (i) 1 - x, y, z; (ii) y, x, -z; (iii) 1 - x, 1 - y, z; (iv) 1 - y, x, -z; (v) y, x, 1 - z; (vi) -y, x, 1 - z; (vii) y, 1 - x, -z; (viii) -y, 1 - x, -z; (ix) y, 1 - x, 1 - z; (x) -y, 1 - x, 1 - z.

Experimental

Crystal data

Ba_{0.84}Rb₃Nb₈P₅O₃₄

M_r = 1814

Tetragonal

*P*4*m*2

a = 10.6604 (8) Å

c = 6.4434 (4) Å

V = 732.2 (1) Å³

Z = 1

D_x = 4.11 Mg m⁻³

Mo Kα radiation

Data collection

Enraf-Nonius CAD-4

diffractometer, graphite monochromator

Bisecting geometry,

ω-4/3θ scans

Absorption correction:

none

3414 measured reflections

3414 independent reflections

Refinement

Refinement on *F*

Final *R* = 0.039

wR = 0.046

S = 1.009

975 reflections

70 parameters

w = *F*sin(θ/λ)

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 18–25°

μ = 9.2 mm⁻¹

T = 294 K

Rod

0.103 × 0.032 × 0.026 mm

Black

975 observed reflections

[*I* > 3σ(*I*)]

θ_{max} = 45°

h = 0 → 21

k = 0 → 21

l = 0 → 12

3 standard reflections

frequency: 50 min

intensity variation: <0.1%

(Δ/σ)_{max} = 0.004

Δρ_{max} = 2.7 e Å⁻³

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Lists of structure factors and anisotropic thermal parameters, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55242 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1000]

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Ba₁₅Al_{13.4}Ga_{14.5}, a Disordered Structure Derived from Sr₅Al₉

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Abstract

The structure of the title compound may be derived from the ordered Sr₅Al₉ structure by redistribution of the Ga and Al atoms. In Ba₁₅Al_{13.4}Ga_{14.5}, the Al1 site is occupied by a mixture of 63% Al and 37% Ga and the Al2 site is totally filled by Ga. Only 69% of the Al3 site is occupied by Al, the remaining 31% being replaced by pairs of Ga atoms in a new partially filled position. The structure has features, characteristic of the Sr₅Al₉ and the ternary Rb₄Au₇Sn₂ types, which are related to the Laves phases, and can be described as an intergrowth of MgZn₂ and Ba₃Al₅ slabs (69%) as found in Sr₅Al₉, and Rb₂Au₃Sn₂ and Ba₃Al₅ slabs (31%).

Comment

By substituting one partner element for another in the binary phases formed by alkaline-earth and rare-earth metals, it is possible to make a more detailed study of the effect of a smooth variation of certain atomic properties such as atom size, electronegativity or electron concentration. Iandelli (1987) applied such an approach to MA_{12-x}Ga_x systems where *M* is a bivalent element (Ca, Sr, Eu or Yb) and *x* is in the range 0–2. The structure of the equi-atomic phase CaAlGa, a disordered variant of the CeCu₂-type, has also been refined (Fornasini & Pani, 1991). As no data were available for the analogous barium system, an alloy with nominal composition BaAlGa was prepared and the crystal structure determined. Weighed amounts of the three elements (Ba 99.5%, Al and Ga 99.999% pure) were placed in a tantalum crucible, arc welded under an argon atmosphere and melted in an induction furnace. As there is a close similarity between the crystal data, Sr₅Al₉ (Manyako, Zarechnyuk & Yanson, 1987) was used as starting model in the refinement.

There are, however, some recognizable differences (Table 1). The 18(*h*) position, filled with Al atoms in Sr₅Al₉, is now labelled X and occupied by a mixture of 63% Al and 37% Ga. Its *x* coordinate has changed from 0.171 to 0.196 and the 6(*c*) position is filled by Ga1 instead of Al. The simultaneous presence of the atoms Ga2 and Al should cause interatomic distances that are too short but the 3(*a*) position, fully occupied by Al in Sr₅Al₉, is now partially filled with Al atoms (69%) with the missing atoms being replaced by pairs of Ga2 atoms in a new position with 31% occupation.

The precise composition of the examined phase (hereafter BaAlGa) is Ba₁₅Al_{13.4(2)}Ga_{14.5(2)}. The structure of BaAlGa shows features characteristic of both Sr₅Al₉ (Manyako, Zarechnyuk & Yanson, 1987) and Rb₄Au₇Sn₂ (Sinnen & Schuster, 1981). These phases, which crystallize in the same space group *R* $\bar{3}m$, all have similar lattice constants (*a* = 5.9–6.8 and *c* = 29.1–36.6 Å). They can be described as an intergrowth of two types of slabs which alternate along the *c* axis with sideways displacements as required by the rhombohedral symmetry (six slabs per unit cell). As shown in the upper part of Fig. 1, Sr₅Al₉ consists of slabs taken from the Laves phase MgZn₂ and from Ba₃Al₅ (Fornasini, 1988), while in Rb₄Au₇Sn₂ an MgZn₂-type slab alternates with another with the composition Rb₂Au₃Sn₂ typical of this structure. Indeed, Rb₄Au₇Sn₂ may be derived from a hypothetical RbAu₂ (MgCu₂-type) compound by substituting one-eighth of the Au atoms with Sn—Sn pairs. Consequently, while one slab of the structure remains part of

the MgCu₂ or MgZn₂ Laves phases with the same composition, the other slab (Rb₂Au₃Sn₂) which contains the Sn—Sn pairs is modified substantially. The situation is more complicated for BaAlGa which can be described as having a sequence of MgZn₂ and Ba₃Al₅ slabs (69%) as found in Sr₅Al₉, and Rb₂Au₃Sn₂ and Ba₃Al₅ slabs (31%). These slabs are drawn in the lower part of Fig. 1.

The interface between the slabs always consists of Kagomé nets of smaller atoms filling the 18(*h*) position. In Sr₅Al₉, nearly regular nets form the common basis of two double Al tetrahedra which are joined by a vertex to give a four-tetrahedra unit. In both Rb₄Au₇Sn₂ and BaAlGa, the nets formed by Au and X atoms deviate from ideality. As reported in Table 2, the coordination polyhedra surrounding Ga1 and Ga2 are nearly identical, except for the different occupation (Ba instead of Ga) at one of the vertices. An icosahedron and a defective icosahedron surround the Al and X atoms respectively. An alternative location in the same polyhedron had to be considered for Ga2 and Al because of the partial occupation of their sites. Apart from Ba₃Al₅ and Sr₅Al₉, similar coordinations are found in Ba₇Al₁₃ (Fornasini & Bruzzone, 1975), Ba₄Al₅ (Fornasini, 1975) and Ba₁₆Ag₇Al₂₇ (Cordier & Roehr, 1991) which contain Ba₃Al₅ fragments and are related to the Laves phases. Another feature of these structures is the short distance between the alkaline-earth atoms, which in BaAlGa is 17% shorter than the sum of the metallic radii. As in the pure element, a close contact is found for the Ga2—Ga2 pairs.

Experimental

Crystal data

Ba₁₅Al_{13.4}Ga_{14.5}
M_r = 3432.4
 Rhombohedral
R $\bar{3}m$
a = 6.077 (1) Å
c = 36.659(6) Å
V = 1172.4 (3) Å³
Z = 1
D_x = 4.86 Mg m⁻³
 Mo *K*α radiation

λ = 0.7107 Å
 Cell parameters from 25 reflections
 θ = 25–28°
 μ = 21.6 mm⁻¹
T = 293 K
 Prism
 0.14 × 0.10 × 0.07 mm
 Metallic

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: empirical and spherical
T_{min} = 0.47, *T_{max}* = 1.0
 2491 measured reflections
 490 independent reflections
 449 observed reflections
 [*F* > 3σ(*F*)]

R_{int} = 0.040
 θ_{max} = 30°
h = -8 → 8
k = 0 → 8
l = -51 → 51
 1 standard reflection
 frequency: 60 min
 intensity variation: none

Refinement

Refinement on *F*
 Final *R* = 0.053

Δρ_{max} = 3.4 e Å⁻³
 Δρ_{min} = -4.0 e Å⁻³

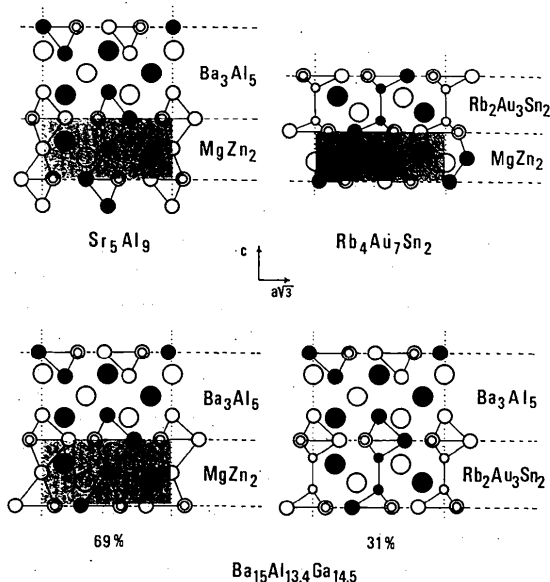


Fig. 1. Structural slabs, projected in the (110) plane, which can be used to construct the rhombohedral structures of Sr₅Al₉, Rb₄Au₇Sn₂ and Ba₁₅Al_{13.4}Ga_{14.5}. Large circles: Sr, Rb, Ba; medium circles: Al, Au, Al—Ga; small circles: pairs Sn—Sn and Ga—Ga. Open, filled and double circles correspond to heights of 0, 1/2 and 1/4 + 3/4 respectively.

$wR = 0.081$
 $S = 5.8$
 449 reflections
 25 parameters
 $w = 1/[\sigma^2(F) + 0.00063F^2]$
 $(\Delta/\sigma)_{\max} = 0.003$

Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV, Table 2.2)

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Structure of Phase III of $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$

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Data collection: Enraf-Nonius CAD-4 software. Cell refinement: Enraf-Nonius CAD-4 software. Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ba1	0.0000	0.0000	0.2148 (1)	0.0131 (4)
Ba2	0.0000	0.0000	0.3165 (1)	0.0134 (4)
Ba3	0.0000	0.0000	0.5000	0.0220 (5)
Ga1	0.0000	0.0000	0.1218 (1)	0.0205 (6)
Ga2	0.0000	0.0000	0.0338 (3)	0.023 (3)
Al	0.0000	0.0000	0.0000	0.037 (5)
X	0.1960 (4)	0.8040 (4)	0.0721 (1)	0.045 (1)

Site occupancies: Ga2 = 0.31 (1); Al = 0.69 (1); X = 0.63 (1)Al + 0.37 (1)Ga.

Table 2. Interatomic distances (Å) in the coordination polyhedra of the Ga and Al atoms up to $d/\Sigma r = 1.18$

Ga1—X	2.75 (1)	×3	Al—X	3.35 (1)	×6
Ga1—Ga2	3.23 (1)		Al—Ba2	3.56 (1)	×6
Ga1—Ba1	3.41 (1)		X—Ga2	2.49 (1)	
Ga1—Ba1	3.51 (1)	×3	X—X	2.50 (1)	×2
Ga1—Ba3	3.87 (1)	×3	X—Ga1	2.75 (1)	
Ga2—Ga2	2.48 (2)		X—Al	3.35 (1)	
Ga2—X	2.49 (1)	×3	X—Ba1	3.50 (1)	×2
Ga2—Ga1	3.23 (1)		X—Ba2	3.57 (1)	
Ga2—Ba2	3.56 (1)	×3	X—Ba2	3.66 (1)	×2
Ga2—Ba2	3.97 (1)	×3	X—Ba3	3.76 (1)	

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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 55341 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1010]

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Abstract

Contrary to previous results, phase III of triammonium hydrogen selenate $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ (which is stable in the temperature range 279–302 K) is found to be triclinic with a small deviation from the monoclinic *C*-centered lattice cell. The triclinic deformation and presence of two non-equivalent $\text{H}(\text{SeO}_4)_2$ groups is in good agreement with ESR measurements.

Comment

Triammonium hydrogen selenate (TAHSe) belongs to the family of compounds $M_3\text{H}(\text{XO}_4)_2$ (where $M = \text{NH}_4^+$, K^+ , Rb^+ or Cs^+ , and $X = \text{S}$ or Se) which undergo numerous phase transitions. The room-temperature crystal structures of $(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$ (Leclaire, Ledésert, Monier, Daoud & Damak, 1985), $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$ (Tanaka & Shiozaki, 1981), $\text{K}_3\text{H}(\text{SO}_4)_2$ (Noda, Uchiyama, Kafuku, Kasatani & Terauchi, 1990), $\text{K}_3\text{D}(\text{SO}_4)_2$ (Noda, Kasatani, Watanbe, Terauchi & Gesi, 1990) and $\text{Rb}_3\text{H}(\text{SO}_4)_2$ (Makarova, Verin & Shchagina, 1986) have been determined as monoclinic, although Davis & Johnson (1984) have found a triclinic deformation of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$. The lattice parameters of $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ with a monoclinic cell were measured by Kamoun, Halouani & Daoud (1987) and Furukava, Akahoshi, Fukami & Hukuda (1990). The triclinic deformation has probably been overlooked as a result of the insufficiently accurate photographic methods used by both research groups. The triclinic deformation follows both from the lattice-parameter measurements and from the comparison of R_{int} values (0.0265 and 0.0560 for space groups $C\bar{1}$ and $C2/c$ respectively).

The non-conventional setting $C\bar{1}$ and the pseudo-monoclinic *C*-centered lattice cell have been adopted