

Synthesis and X-Ray Crystal Structure of the New Nonstoichiometric Phase $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$

M. CHARBONNEL AND C. BELIN

Laboratoire des Acides Minéraux, Université des Sciences et Techniques du Languedoc, 2, place Eugène Bataillon—34060 Montpellier Cédex, France

Received April 23, 1986; in revised form July 9, 1986

The structure of a crystal with the composition $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$ has been determined using single crystal diffractometry. The space group is $Fm\bar{3}m$ with lattice parameters $a = 25.086(5)$, $b = 46.036(17)$, and $c = 16.043(3)$ Å. Diffraction data with $4 \leq 2\theta \leq 50^\circ$ ($\text{MoK}\alpha$ radiation) were collected on a Nonius CAD4 diffractometer within the octant hkl . The structure was solved by trial methods and refined by full-matrix least-squares to a final $R(F) = 0.080$ for 1150 independent reflections with $I > 3\sigma(I)$. The structure of $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$ contains gallium icosahedra and "double-icosahedral" clusters (21 gallium atoms). Such polyhedra have already been encountered in $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$ structure. The three-dimensional anionic gallium network includes channels and cavities that are filled with the alkaline cations. © 1987 Academic Press, Inc.

Introduction

In 1980, the crystallographic structure of K_3Ga_{13} (1) was determined. It is the first compound of a new class of intermetallic Zintl phases. Succeeding works have now allowed to isolate numerous phases: $\text{Li}_3\text{Ga}_{14}$ (2, 3), $\text{Na}_{22}\text{Ga}_{39}$ (4), or $\text{Na}_7\text{Ga}_{13}$ (5, 6), KGa_3 and RbGa_3 (7, 8), RbGa_7 and CsGa_7 (9, 10). Excepting $\text{Li}_3\text{Ga}_{14}$, which has been found to be a lithium deficient phase derived from the not yet characterized Li_3Ga_7 , all these phases are stoichiometric. These intermetallic compounds are characterized by the existence of nonisolated structural gallium clusters forming a three-dimensional macroanionic lattice; these clusters are linked to each other directly or through isolated atoms on a relatively non-compact network leaving holes and cavities in which sit the ionized alkaline elements.

Some of these phases (particularly K_3Ga_{13}) have been found to be favorable to chemical or electrochemical insertion of large quantities of zero-valent lithium, so they can be used for the elaboration of very efficient negative electrodes in secondary lithium batteries (11). Recent investigation about the ternary systems alkali metal—gallium led us to the discovery of new compounds: $\text{LiGa}_{3.42}$ (12), $\text{K}_3\text{Li}_9\text{Ga}_{28.83}$ (13), $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$ (14), $\text{K}_4\text{Na}_{13}\text{Ga}_{49.57}$ (15), and $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$.

Owing to the partial occupancy of some of the gallium atoms, these phases are formed by basic clusters that are partially dismantled into opened polyhedra.

According to the extended concept developed by Schäfer and co-workers (16) a few years ago, these compounds can be classified into the family of Zintl's phases.

This work will describe the synthesis and

the crystal structure of the new phase $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$.

Experimental

The metals used were sodium from Merck laboratories and Alusuisse gallium. The rubidium was prepared by reduction of rubidium chloride (Merck) by calcium. The elements Rb, Na, Ga, in the ratio (1 : 2 : 9) were inserted in a tantalum tube which was then weld-sealed in an argon atmosphere.

The mixture was heated up to 650°C during an hour in an induction furnace to obtain a good homogenization. In a second step, the mixture was placed in a resistance furnace, heated again to 650°C, then allowed to cool slowly (0.3°C/min) to 230°C for crystal growing.

The resulting ingot appeared relatively homogeneous and brittle, so it could be broken into small pieces inside a glovebox filled with purified argon. Some fragments were qualitatively analyzed by flame spectrometry and they proved to contain the three elements; no presence of tetragonal crystals of NaGa_4 was detected. Some well crystallized pieces of the material were isolated, mounted in Lindemann-glass capillaries and checked by preliminary oscillation and Weissenberg photographs. All the crystals displayed the same orthorhombic symmetry with $a = 25.08$, $b = 46.04$, $c = 16.04$ Å; systematic absences were consistent with three possible space groups: $F222$, $Fmm2$ or $Fmmm$.

The crystal ($0.20 \times 0.13 \times 0.07$ mm) giving the best diffraction spots was mounted on an Enraf Nonius CAD4 automatic diffractometer. Accurate lattice parameters ($a = 25.086(5)$, $b = 46.036(17)$, and $c = 16.043(3)$ Å) were determined by least-squares refinement of the angular positions of 25 reflections automatically centered on the diffractometer. Integrated diffraction intensities were collected at room temperature in the range $4^\circ \leq 2\theta \leq 50^\circ$ within the

octant hkl , using graphite monochromated $\text{MoK}\alpha$ radiation with an ω - 2θ scan. Scan ranges were calculated from the formula $Sr = A + B \tan \theta$, where A depends on the mosaic spread of the crystal and B allows for increasing peak width due to $K\alpha_1$ and $K\alpha_2$ splitting; B was chosen as 0.35° and cautiously A was limited to 0.9° since the crystals were of medium quality. During data collection, the intensities of three standard reflections were checked after every 50 reflections, a slight loss in intensities (10%) was observed, so the data were scaled before treatment, corrected for background and Lorentz polarization effects.

Once the composition of the compound was exactly determined, the data were corrected for the effect of absorption using a psi-scan method (17, 18) ($\mu = 421.8 \text{ cm}^{-1}$ and transmission factors range from 0.043 to 0.186). The final data set consisted in 1167 independent reflections corresponding to the $I > 3\sigma(I)$ criterion.

The crystal used in the data collection was analyzed by flame spectrometry (Rb : Na : Ga ratio of 0.029(2) : 0.318(7) : 1).

Structure Solution and Refinement

Unfortunately, this structure could not be solved either by Patterson synthesis or by direct methods. This structure was solved by a trial method in the space group $Fmmm$ by analogy to the structure of $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$ (14) containing mainly icosahedra.

The icosahedron (A) with symmetry mmm was assumed to occupy the special position 4(b) ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), the icosahedron (B) with symmetry $2/m$, the 8(d) position ($\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$), and the third icosahedron (C), the 16(o) position on a mirror plane. The coordinates of 15 independent gallium atoms gave phases sufficiently close to correct for solving the structure in the space group $Fmmm$. After refining these positions, a subsequent Fourier synthesis revealed 15 other gallium

atoms. The positional and isotropic thermal parameters of the 30 gallium atoms were refined to $R = 0.21$; at this stage a Fourier synthesis revealed all the remaining atoms.

Five atoms initially considered as gallium displayed abnormally high-temperature factors in the order of 6 \AA^2 . However, the corresponding electron densities were too high to replace them by sodium atoms. Moreover, the interatomic distances between them and other gallium atoms were undoubtedly in the order of Ga–Ga bonds. Consequently, these positions were refined as nonstoichiometric gallium atoms with statistical site occupancy.

An other problem arose from the atom located at $x = 0.313$, $y = 0.431$, and $z = 0$ with an electron density intermediate between those of sodium and gallium. This atom displayed a highly negative temperature factor when refined as sodium and a large thermal motion when refined as gallium. On the other hand, distances to neighboring atoms, not less than 3.35 \AA , are close to distances Rb(2)–Ga observed in the structure (from 3.24 to 3.72 \AA). These considerations along with the chemical analysis suggested that this atom was a rubidium atom with a partial site occupancy of 54%.

Atoms Ga(23) on icosahedron (B) have very short distances (1.50 \AA) to the central rubidium atom Rb(3). This case of disorder was resolved by constraining the occupancies of both gallium and rubidium atoms to sum to unity during the refinement (Table I); convergence to correct thermal parameters was obtained. On the other hand nonstoichiometric Ga(13) was refined with a partial site occupancy.

The ratio Rb:Na:Ga of 0.030:0312:1, which was determined by crystallography, compares very well (in the limit of the 3σ) with that deduced by chemical analysis.

Finally all atomic positional parameters and isotropic temperature factors for all atoms as well as site occupancies for nonstoichiometric gallium and rubidium atoms were refined by full-matrix least-squares,

minimizing the function $w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma_c^2(F^2/4(F)^2 + (0.05F)^2)$ by using the data set corrected for absorption. Seventeen of the weakest and evidently mis-measured reflections were eliminated by the criterion $|F_c| - |F_o|/|F_c| \geq 1.1$, the final agreement factors were $R(F) = 0.080$ and $R_w(F) = 0.112$.¹

Attempts to refine the structure in the lower space groups *Fmm2* and *F222* while drastically raising the parameter-to-data ratio gave unsatisfactory results.

Results and Discussion

The final positional parameters with esd's are listed in Table I, interatomic distances in Tables II and III. The unit cell contains 32 formula units $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$.

Except for Ga(12, 13, 20, 30) all the gallium atoms are arranged on coordination polyhedral clusters. Among these 27 remaining independent gallium atoms, Ga(14, 21, 24) compose the icosahedron (A) centered on a $4(b)$ position with the symmetry *mmm*; Ga(1, 2, 22, 23) are arranged on icosahedron (B) with symmetry $2/m$ around the $8(d)$ position; Ga(3, 4, 5, 6, 15, 16, 17, 18) sit around the $16(o)$ position and form the icosahedron (C) with symmetry *m*; Ga(7, 8, 25, 26) compose the icosahedron (D) centered on the $8(c)$ position with $2/m$ symmetry.

The remaining gallium atoms Ga(9, 10, 11, 19, 27, 28, 29, 31) yield the 21-atom polyhedron (E) built from two icosahedra sharing a triangular face (Fig. 1), it sits on $8(h)$ position and displays the *mm* symmetry.

All these polyhedra are linked to each other either through direct interpolyhedral bonds or through bonds involving the isolated gallium atoms Ga(12, 13, 20, 30) (Fig. 2). A projection of the gallium lattice in the unit cell is given in Fig. 3.

¹ A complete list of calculated and observed structure factors is available upon request to the authors.

TABLE I
FINAL ATOMIC POSITIONS AND TEMPERATURE FACTORS FOR ATOMS IN
 $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$

	Position ^a	Site occupancy (%)	x	y	z	B_{iso} (\AA^2)
Ga (1)	32(p)	100	0.6727(2)	0.5301(1)	0.8163(5)	0.9(1)
Ga (2)	32(p)	100	0.7295(2)	0.5481(1)	0.6719(4)	0.8(1)
Ga (3)	32(p)	100	0.6978(2)	0.5943(1)	0.5855(5)	1.4(1)
Ga (4)	32(p)	100	0.6072(2)	0.6771(1)	0.5842(4)	0.6(1)
Ga (5)	32(p)	100	0.6062(3)	0.6216(1)	0.6360(4)	0.8(1)
Ga (6)	32(p)	100	0.6981(2)	0.6506(2)	0.6352(4)	1.0(1)
Ga (7)	32(p)	100	0.5937(3)	0.7308(1)	0.8177(5)	1.6(1)
Ga (8)	32(p)	100	0.5557(2)	0.7837(1)	0.8311(5)	0.8(1)
Ga (9)	32(p)	100	0.9118(3)	0.5607(1)	0.6431(4)	0.7(1)
Ga(10)	32(p)	100	0.5548(2)	0.6058(2)	0.7654(5)	0.9(1)
Ga(11)	32(p)	81(3)	0.5942(4)	0.6189(2)	0.9136(7)	2.9(4)
Ga(12)	32(p)	92(3)	0.6848(4)	0.7039(2)	0.8728(8)	4.8(4)
Ga(13)	32(p)	31(3)	0.1635(14)	0.1547(8)	0.0479(23)	4.2(12)
Ga(14)	16(o)	100	0.4482(4)	0.5453(2)	0.5	1.6(2)
Ga(15)	16(o)	100	0.5511(3)	0.6370(2)	0.5	0.7(2)
Ga(16)	16(o)	100	0.6982(4)	0.6839(2)	0.5	1.2(2)
Ga(17)	16(o)	100	0.6065(4)	0.5898(2)	0.5	1.4(2)
Ga(18)	16(o)	100	0.7476(5)	0.6334(2)	0.5	3.1(2)
Ga(19)	16(o)	100	0.9482(4)	0.5719(2)	0.5	1.1(2)
Ga(20)	16(o)	100	0.7662(4)	0.7242(2)	0.5	2.0(2)
Ga(21)	16(n)	100	0.4137(3)	0.5	0.5822(6)	0.9(2)
Ga(22)	16(n)	100	0.6726(3)	0.5	0.6688(6)	0.4(2)
Ga(23)	16(n)	67(2)	0.7337(6)	0.5	0.9157(12)	1.5(5)
Ga(24)	16(m)	100	0.5	0.5287(2)	0.6329(7)	0.7(2)
Ga(25)	16(m)	100	0.5	0.7419(2)	0.0866(6)	1.0(2)
Ga(26)	16(m)	100	0.5	0.6987(2)	0.8095(6)	0.9(2)
Ga(27)	16(m)	100	0.5	0.6444(2)	0.8533(7)	1.1(2)
Ga(28)	16(m)	100	0.5	0.5563(2)	0.7678(6)	0.9(2)
Ga(29)	16(m)	51(2)	0.5	0.5293(4)	0.9090(15)	3.5(9)
Ga(30)	16(k)	89(2)	0.75	0.6749(3)	0.75	4.7(7)
Ga(31)	8(h)	100	0.5	0.6224(3)	0.0	1.2(3)
Rb (1)	16(o)	54(2)	0.313(1)	0.431(1)	0.0	5.0(9)
Rb (2)	8(g)	100	0.396(1)	0.5	0.0	6.7(6)
Rb (3)	8(g)	33(2)	0.261(2)	0.0	0.0	4.5(13)
Na (1)	32(p)	100	0.193(1)	0.276(1)	0.167(1)	3.1(6)
Na (2)	32(p)	100	0.108(1)	0.441(1)	0.167(2)	3.7(7)
Na (3)	32(p)	100	0.189(1)	0.107(1)	0.194(2)	2.3(6)
Na (4)	32(p)	100	0.111(1)	0.166(1)	0.221(2)	3.6(7)
Na (5)	16(o)	100	0.069(2)	0.185(1)	0.0	3.4(10)
Na (6)	16(o)	100	0.119(1)	0.257(1)	0.0	2.7(9)
Na (7)	16(n)	100	0.067(1)	0.0	0.218(2)	4.4(11)
Na (8)	16(m)	100	0.5	0.155(1)	0.164(3)	4.9(12)
Na (9)	8(h)	100	0.0	0.302(1)	0.0	0.1(8)

^a Number of positions and Wyckoff notation.

TABLE II
 GALLIUM INTERATOMIC DISTANCES LESS THAN 3.5 Å

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
Ga(1)		Ga(2)		Ga(3)		Ga(4)	
Ga(2)	2.60(1)	Ga(1)	2.60(1)	Ga(18)	2.59(1)	Ga(8)	2.61(1)
Ga(23)	2.62(1)	Ga(22)	2.64(1)	Ga(17)	2.66(1)	Ga(15)	2.68(1)
Ga(9)	2.63(1)	Ga(3)	2.67(1)	Ga(2)	2.67(1)	Ga(16)	2.69(1)
Ga(22)	2.73(1)	Ga(2)	2.71(1)	Ga(6)	2.70(1)	Ga(5)	2.69(1)
Ga(1)	2.76(1)	Ga(23)	2.78(1)	Ga(5)	2.72(1)	Ga(4)	2.70(1)
Ga(2)	2.84(1)	Ga(1)	2.84(1)	Ga(3)	2.73(1)	Ga(6)	2.73(1)
Ga(5)		Ga(6)		Ga(7)		Ga(8)	
Ga(10)	2.56(1)	Ga(30)	2.51(1)	Ga(8)	2.63(1)	Ga(4)	2.61(1)
Ga(17)	2.62(1)	Ga(18)	2.62(1)	Ga(8)	2.64(1)	Ga(7)	2.63(1)
Ga(6)	2.66(1)	Ga(16)	2.66(1)	Ga(12)	2.74(1)	Ga(7)	2.64(1)
Ga(15)	2.67(1)	Ga(5)	2.66(1)	Ga(26)	2.77(1)	Ga(25)	2.72(1)
Ga(4)	2.69(1)	Ga(3)	2.70(1)	Ga(7)	2.80(2)	Ga(26)	2.77(1)
Ga(3)	2.72(1)	Ga(4)	2.73(1)	Ga(25)	2.86(1)	Ga(8)	2.79(1)
Ga(9)		Ga(10)		Ga(11)		Ga(12)	
Ga(19)	2.53(1)	Ga(5)	2.56(1)	Ga(13)	2.47(3)	Ga(20)	2.55(1)
Ga(1)	2.63(1)	Ga(11)	2.63(1)	Ga(10)	2.63(1)	Ga(13)	2.65(3)
Ga(28)	2.64(1)	Ga(27)	2.64(1)	Ga(31)	2.75(1)	Ga(7)	2.74(1)
Ga(10)	2.67(1)	Ga(28)	2.66(1)	Ga(19)	2.79(1)	Ga(30)	2.90(1)
Ga(29)	2.77(1)	Ga(9)	2.67(1)	Ga(27)	2.79(1)		
Ga(11)	2.83(1)	Ga(10)	2.73(1)	Ga(11)	2.81(2)		
				Ga(9)	2.83(1)	Ga(16)	
				Ga(13)	3.25(4)	Ga(20)	2.52(1)
Ga(13)		Ga(14)				Ga(18)	2.63(1)
Ga(13)	1.59(8)	Ga(17)	2.47(1)			2 Ga(6)	2.66(1)
Ga(11)	2.47(3)	2 Ga(21)	2.60(1)	Ga(15)		2 Ga(4)	2.69(1)
Ga(18)	2.56(2)	2 Ga(24)	2.61(1)	Ga(15)	2.57(2)		
Ga(12)	2.65(3)	Ga(14)	2.62(2)	Ga(17)	2.58(1)	Ga(19)	
Ga(11)	3.25(4)			2 Ga(5)	2.67(1)	2 Ga(9)	2.53(1)
				2 Ga(4)	2.68(1)	Ga(19)	2.61(2)
Ga(17)		Ga(18)				Ga(31)	2.66(1)
		2 Ga(13)	2.56(2)	Ga(20)		2 Ga(29)	2.74(2)
Ga(14)	2.47(1)	2 Ga(3)	2.59(1)	Ga(16)	2.52(1)	2 Ga(11)	2.79(1)
Ga(15)	2.58(1)	2 Ga(6)	2.62(1)	Ga(20)	2.53(1)		
2 Ga(5)	2.62(1)	Ga(16)	2.63(1)	2 Ga(12)	2.55(1)	Ga(24)	
2 Ga(3)	2.66(1)					Ga(28)	2.52(1)
		Ga(22)		Ga(23)		2 Ga(18)	2.61(1)
Ga(21)		Ga(21)	2.58(1)	2 Ga(1)	2.62(1)	Ga(24)	2.64(2)
Ga(22)	2.58(1)	2 Ga(2)	2.64(1)	Ga(23)	2.70(4)	2 Ga(21)	2.66(1)
2 Ga(14)	2.60(1)	Ga(23)	2.71(2)	Ga(22)	2.71(2)		
Ga(21)	2.64(1)	2 Ga(1)	2.73(1)	2 Ga(2)	2.78(1)	Ga(28)	
2 Ga(24)	2.66(1)					Ga(24)	2.52(1)
		Ga(26)		Ga(27)		Ga(29)	2.58(2)
Ga(25)		Ga(25)	2.59(1)	Ga(31)	2.56(1)	2 Ga(9)	2.64(1)
Ga(26)	2.59(1)	Ga(27)	2.61(1)	Ga(26)	2.61(1)	2 Ga(10)	2.66(1)
2 Ga(8)	2.72(1)	2 Ga(8)	2.77(1)	2 Ga(10)	2.64(1)		
Ga(25)	2.77(1)	2 Ga(7)	2.77(1)	2 Ga(11)	2.79(1)		
2 Ga(7)	2.86(1)						

TABLE II—Continued

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
		Ga(31)				Ga(29)	
		2 Ga(27)	2.56(1)			Ga(28)	2.58(2)
2 Ga(6)	2.51(1)	2 Ga(19)	2.66(1)			2 Ga(19)	2.74(2)
2 Ga(12)	2.90(1)	4 Ga(11)	2.75(1)			Ga(29)	2.75(4)
						2 Ga(9)	2.77(1)
						Ga(29)	2.90(5)

Icosahedron (A) is directly connected to $4\times(B)$, $4\times(C)$, and $4\times(E)$ polyhedra; icosahedron (B) to $2\times(A)$, $2\times(B)$, $4\times(C)$, and $4\times(E)$; icosahedron (C) to $1\times(A)$, $2\times(B)$, $1\times(C)$, $2\times(D)$, and $2\times(E)$; icosahedron (D) to $4\times(C)$, $2\times(D)$, $2\times(E)$; while polyhedron (E) is linked to $2\times(A)$, $4\times(B)$, $4\times(C)$, $2\times(D)$, and $1\times(E)$ through the double connection Ga(29)–Ga(29). On polyhedron (E), there are two Ga(29) atoms, each of them being linked to his homolog on the neighboring polyhedron (E).

Icosahedra (C) and (D) are coordinated to eight neighboring polyhedra through direct interpolyhedral bonds, the 12-coordination being achieved by bonds involving isolated gallium atoms.

For icosahedra (A) and (B), 12-coordination is attained through only direct interpo-

lyhedral bonds. For icosahedron (B), the coordination is actually less than 12 owing to the partial site occupancy of Ga(23). In fact, the rubidium atom Rb(3) counterbalances the missing gallium atoms creating a sandwich figure like in $\text{LiGa}_{3.42}$ (12) (two nido 11-vertex polyhedra sandwiching a lithium atom).

Actually, except for icosahedron (A), the coordination of the polyhedra are all lowered by the nonstoichiometry of some gal-

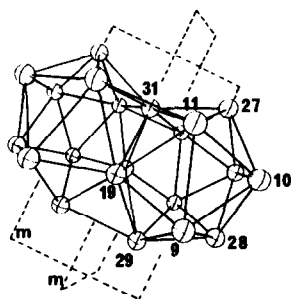


FIG. 1. The 21-atom polyhedron (E) (symmetry mm). Numbers (9 to 31) refer to gallium as labeled in Table I.

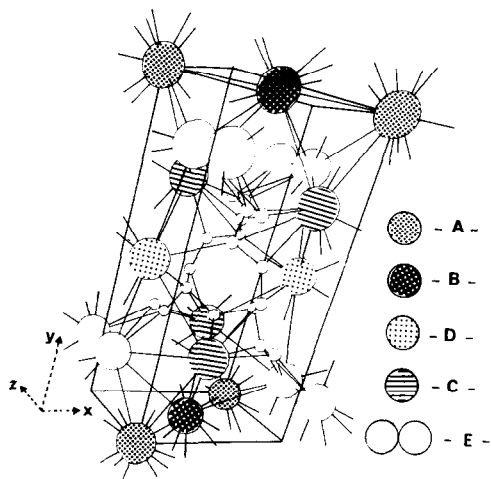


FIG. 2. Representation of the polyhedra packing within one-eighth of the unit cell centered at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ in $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$. A, B, C, D, and E refer to icosahedra (symmetry mmm , $2/m$, m , $2/m$) and double-condensed icosahedron (symmetry mm). Small circles represent isolated gallium atoms.

TABLE III
 DISTANCES AROUND ALKALI METAL ATOMS LESS THAN 4.2 Å

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
Rb(1)		Rb(2)		Rb(3)		Na(3)	
Ga(18)	3.35(3)	4 Ga(29)	3.24(3)	2 Ga(23)	1.50(3)	Ga(11)	2.95(3)
2 Ga(3)	3.38(2)	2 Ga(19)	3.54(1)	2 Ga(22)	3.19(3)	Ga(13)	3.22(5)
Ga(19)	3.41(3)	2 Ga(23)	3.59(3)	4 Ga(2)	3.54(1)	Na(4)	3.33(4)
2 Ga(9)	3.43(2)	2 Na(7)	3.60(4)	2 Rb(1)	3.69(3)	Ga(9)	3.39(3)
2 Ga(1)	3.50(1)	4 Ga(9)	3.64(1)	4 Ga(1)	3.94(3)	Ga(3)	3.40(2)
2 Na(3)	3.53(3)	4 Ga(1)	3.72(2)	Rb(2)	3.99(6)	Ga(6)	3.42(3)
2 Ga(11)	3.56(2)	2 Rb(1)	3.88(3)	2 Ga(21)	4.07(5)	Ga(10)	3.43(2)
2 Ga(2)	3.59(2)	Rb(3)	3.99(6)			Ga(2)	3.43(2)
2 Ga(23)	3.67(2)			Na(2)		Ga(5)	3.51(2)
Rb(3)	3.69(3)	Na(1)		Ga(5)	2.97(2)	Rb(1)	3.53(3)
Rb(2)	3.88(3)	Ga(30)	3.02(3)	Ga(10)	2.99(3)	Ga(1)	3.58(2)
2 Ga(13)	4.03(3)	Ga(20)	3.23(3)	Ga(9)	3.05(3)	Ga(6)	3.59(2)
Na(4)		Ga(16)	3.24(3)	Ga(21)	3.06(2)	Ga(30)	3.59(2)
Ga(12)	2.95(3)	Ga(7)	3.25(3)	Ga(24)	3.07(3)	Na(3)	3.61(5)
Ga(5)	3.07(3)	Ga(12)	3.27(3)	Ga(17)	3.07(3)	Ga(3)	3.63(3)
Ga(11)	3.07(3)	Ga(4)	3.32(3)	Ga(14)	3.10(3)	Ga(2)	3.64(3)
Ga(13)	3.08(4)	Na(6)	3.32(3)	Ga(2)	3.11(3)	Ga(18)	3.68(3)
Ga(7)	3.09(2)	Ga(12)	3.36(3)	Ga(3)	3.12(3)	Na(2)	3.78(4)
Ga(10)	3.12(2)	Ga(6)	3.44(3)	Ga(28)	3.12(3)	Na(5)	
Ga(4)	3.17(3)	Ga(8)	3.47(3)	Ga(22)	3.14(2)	2 Ga(13)	2.83(6)
Ga(27)	3.22(3)	Ga(12)	3.47(3)	Ga(1)	3.15(3)	Ga(31)	3.40(4)
Ga(6)	3.23(3)	Ga(7)	3.50(3)	Na(7)	3.40(4)	2 Ga(11)	3.41(4)
Ga(8)	3.24(3)	Na(1)	3.61(5)	Na(3)	3.77(4)	2 Ga(25)	3.46(4)
Ga(26)	3.24(3)	Ga(20)	3.70(3)	Na(7)		2 Ga(27)	3.50(3)
Na(3)	3.33(4)	Na(1)	3.72(5)	2 Ga(29)	2.97(4)	Na(6)	3.53(5)
Na(8)	3.42(4)	Na(4)	3.84(4)	2 Ga(1)	3.05(3)	Na(5)	3.55(10)
Ga(30)	3.51(3)	Na(1)	3.96(5)	2 Ga(9)	3.09(2)	2 Ga(26)	3.58(3)
Na(5)	3.81(4)	Na(6)		2 Ga(28)	3.09(2)	2 Ga(12)	3.61(4)
Na(1)	3.84(4)	Ga(20)	3.21(4)	2 Ga(24)	3.21(3)	2 Ga(7)	3.65(2)
Na(8)		2 Ga(7)	3.24(2)	Ga(22)	3.23(4)	2 Na(4)	3.81(4)
2 Ga(15)	3.01(5)	2 Na(1)	3.32(3)	Ga(21)	3.25(4)	Na(9)	
2 Ga(5)	3.11(2)	2 Ga(4)	3.34(3)	Na(7)	3.32(8)	2 Ga(25)	3.06(3)
2 Ga(10)	3.11(4)	Ga(16)	3.36(3)	2 Na(2)	3.40(4)	2 Ga(15)	3.12(3)
Ga(27)	3.11(5)	2 Ga(25)	3.39(3)	Rb(2)	3.60(4)	4 Ga(4)	3.16(1)
Ga(26)	3.12(5)	2 Ga(8)	3.41(2)			4 Ga(8)	3.17(1)
2 Ga(4)	3.13(2)	Na(5)	3.53(5)			2 Na(8)	3.29(5)
2 Ga(8)	3.16(4)	2 Ga(12)	3.56(3)			2 Na(6)	3.65(4)
Na(9)	3.29(5)	Na(9)	3.65(4)				
2 Na(4)	3.42(4)	Ga(20)	3.77(3)				

limum atoms in the clusters (Table I) and of the isolated gallium atoms Ga(12, 13, 30).

This structure appears quite similar to that of $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$; the only modification

resides in the fact that the compound contains one more gallium atom and that all the isolated gallium atoms are tetracoordinated. On the other hand, one can observe

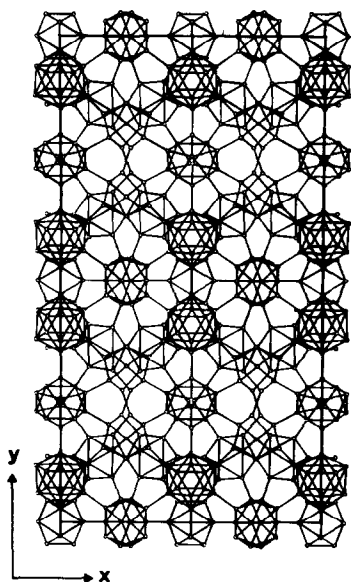


FIG. 3. Projection of the structure of the phase $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$ down the z axis. For clarity, rubidium and sodium atoms are not represented.

that the distribution of nonstoichiometric atoms on icosahedra is relatively different.

The presence of the fused double icosahedron (21 gallium atoms) is the major feature of both structures of $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$ and $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$. Such a condensed polyhedron has been already observed in the tetragonal structure of boron (19). A fused triple icosahedron has been already found in the intermetallic phase $\text{K}_4\text{Na}_{13}\text{Ga}_{49.57}$, with the same geometry as that observed in the β -rhombohedral structure of boron (20).

In $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$, $\text{K}_4\text{Na}_{13}\text{Ga}_{49.57}$, $\text{Li}_9\text{K}_3\text{Ga}_{28.83}$, and in the present compound, polyhedra are incomplete since some vertices are partially occupied by gallium.

In a recent article, we have presumed that, for such nonstoichiometric phases, the breaking of condensed polyhedra could be correlated to the M/Ga (M = alkali metals) ratio (15).

The breaking up rate B is defined as $B = (N - n)/N$, where N is the number of nuclei defining the full polyhedron and n the number of nuclei effectively present according to the nonstoichiometry.

$B = 8.3\%$ for polyhedron (E) in this work (M/Ga ratio: 0.34), this value is in good agreement with that observed for the fused triple icosahedron in $\text{K}_4\text{Na}_{13}\text{Ga}_{49.57}$ ($B = 8.7\%$ with $M/\text{Ga} = 0.34$) (15).

It would seem that B is not a function of the polyhedra type but would depend only on the M/Ga rate. In $\text{Li}_3\text{Na}_5\text{Ga}_{19.56}$ and in $\text{Rb}_{0.60}\text{Na}_{6.25}\text{Ga}_{20.02}$ with fused double icosahedra, B decreases respectively from 12.7 to 8.3%, with M/Ga ratio varying from 0.41 to 0.34.

There are not enough examples to give extended conclusions, so it will be necessary to discover some more new ternary phases to confirm the relationships between the alkali-metal/gallium ratio or the relative size of alkaline cations and the nonstoichiometry.

Acknowledgments

We thank the CNRS and the AFME for their financial support.

References

1. C. BELIN, *Acta Crystallogr. Sect. B* **36**, 1339 (1980).
2. C. BELIN AND R. G. LING, *J. Solid State Chem.* **45**, 290 (1982).
3. J. STHOR AND H. SCHAFER, *Rev. Chim. Min.* **19**, 122 (1982).
4. R. G. LING AND C. BELIN, *Acta Crystallogr. Sect. B* **38**, 1101 (1982).
5. U. FRANK-CORDIER, G. CORDIER, AND H. SCHAFER, *Z. Naturforsch. B* **37**, 127 (1982).
6. U. FRANK-CORDIER, G. CORDIER, AND H. SCHAFER, *Z. Naturforsch. B* **37**, 119 (1982).
7. R. G. LING AND C. BELIN, *C. R. Acad. Sci. Ser. B*, 1083 (1982).

8. R. G. LING AND C. BELIN, *Z. Anorg. Allg. Chem.* **480**, 181 (1981).
9. C. BELIN, *Acta Crystallogr. Sect. B* **37**, 2060 (1981).
10. J. H. N. VANVUCHT, *J. Less-Common Met.* **108**, 163 (1985).
11. A. LE MEHAUTE AND C. BELIN, "Electrode pour générateur électrochimique secondaire, son procédé de fabrication et générateur comportant une telle électrode." Brevet Français n° 8303245.
12. C. BELIN, *Rev. Chim. Min.* **21**, 263 (1984).
13. C. BELIN, *J. Solid State Chem.* **50**, 225 (1983).
14. M. CHARBONNEL AND C. BELIN, *Nouv. J. Chim.* **8**, 595 (1984).
15. C. BELIN AND M. CHARBONNEL, *J. Solid State Chem.* **64**, 57 (1986).
16. H. SCHAFER, B. EISENMANN, AND W. MULLER, *Angew. Chem. Int. Ed.* **12**, 694 (1973).
17. J. RIGOULT, A. THOMAS, AND C. GUIDO-MOROSINI, *Acta Crystallogr. Sect. A* **35**, 587 (1979).
18. J. DE MEULENAER AND H. TOMPA, *Acta Crystallogr.* **19**, 1014 (1965).
19. M. VLASSE, R. NASLAIN, J. S. KASPER, AND K. PLOOG, *J. Solid State Chem.* **28**, 289 (1979).
20. R. E. HUGHES, M. E. LEONOWICZ, J. T. LEMLEY, AND L.-T. TAI, *J. Am. Chem. Soc.* **99**, 5507 (1977).