http://dx.doi.org/10.5012/bkcs.2012.33.5.1759

Notes

Synthesis and Crystal Structure of a New Quaternary Nitride, $Li_4Ca_{13}Ge_6N_{18}$

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Received January 4, 2012, Accepted February 9, 2012

Key Words : Quaternary nitride, Nitridometallate, Single crystal structure

Many alkaline-earth containing nitride compounds have been synthesized by the Na-flux method in molten Na.[1-16] It was suggested that the alkaline earth elements enhanced solubility of nitrogen, a major reactant, into the flux. Single crystals of many different Ge- or Ga- containing ternary and quaternary nitride compounds could be obtained when Li was added to reaction mixtures of their constituent elements. A small amount of Li in the mixtures of reactants apparently facilitated the growth of single crystals. Examples of nitride single crystals synthesized in the Li-containing reaction mixtures are Sr_3GaN_3,[16] Sr_6GaN_5,[16] $Sr_6Ge_5N_2$,[11] $Ba_6Ge_5N_2$,[11] β-Sr_2GeN_2,[10] $Ba_9Ge_3N_{10}$,[13] Sr_3GeMgN_4,[9] Ba_3GeMgN_4,[17] $Sr(Mg_3Ge)N_4$,[12] $Sr(Mg_2Ga_2)N_4$,[12] and Sr_2GeGaN.[14]

In several occasions, Li was also incorporated into the products, generating Li-containing quaternary nitrides, such as $LiSrGaN_2$,[15] and $Li_4Sr_3Ge_2N_6$.[8] One usually chooses cations that are as different as possible in size, number of valence electrons, and electronegativity, in order to prepare quaternary nitrides. Among a handful of known quaternary nitrides reported by others,[18,19] many compounds also contain Li. A few examples of Li-containing quaternary nitrides produced by others are $LiBa_2[ReN_4]$,[20] $LiSr_2[ReN_4]$,[20] $Li_3Ba_2NbN_4$,[21] $Li_3Sr_2NbN_4$,[22] $Li_3Ba_2TaN_4$,[23] $Li_3Sr_2TaN_4$,[22] $Ba_2Li[Fe_2N_3]$,[24] $Sr_2Li[Fe_2N_3]$,[24] $LiSr_2[CoN_2]$,[25] and $Li_3Sr_3Ni_4N_4$.[26] It is interesting to note that large and heavy alkaline earth metals (Sr and Ba) are prevalent, and Ca containing quaternary nitride is rare. Furthermore, those Sr- or Ba-containing quaternary nitrides are usually obtained as isostructural pairs. Such isostructural feature has also been observed among nitrides obtained by us, such as $Sr_6Ge_5N_2$,[11] $Ba_6Ge_5N_2$,[11] Sr_3GeMgN_4,[9] and Ba_3GeMgN_4.[17] Isostructural pair was also obtained as subnitrides, such as Sr_2GeGaN,[14] and Ba_2GeGaN.[5] For these examples, our effort to synthesize a Ca analogue was not as productive as one might hope.

Here we report synthesis of single crystals of $Li_4Ca_{13}Ge_6N_{18}$, a rare example of both Li- and Ca-containing quaternary nitride. Crystallographic data on $Li_4Ca_{13}Ge_6N_{18}$ are provided in Table 1 and 2. Basic structural units of the crystal structure of $Li_4Ca_{13}Ge_6N_{18}$ are the metal-centered tetrahedra. Ge is coordinated to four N, generating pseudo-tetrahedron of $[GeN_4]$. These Ge-centered tetrahedra combine through corner-sharing into the infinite chain of $^1{}_\infty[GeN_3]^{-5}$, as shown in Figure 1(a). These one-dimensional chains of $^1{}_\infty[GeN_3]^{-5}$ stretch along [101] direction, as shown in Figure 2(a). Bond lengths of Ge-N are within the range, from 1.84 to 2.01 Å, observed for those in previously reported quaternary nitride, $Li_4Sr_3GeN_6$.[8] Compared to the edge-shared tetrahedral $[GeN_4]$ in the 'bow tie' unit of $[Ge_2N_6]^{-10}$ in $Li_4Sr_3GeN_6$, corner-shared tetrahedral $[GeN_4]$ in $Li_4Ca_{13}Ge_6N_{18}$ are less distorted. Ge-N bond lengths and angles are more evenly distributed in corner-shared tetrahedral $[GeN_4]$ in $Li_4Ca_{13}Ge_6N_{18}$. This corner-linked one-dimensional chain is similar to the ones found in pyroxene silica compounds ($MgSiO_3$).[27,28]

Li is also in a tetrahedral N-coordination. Li is coordinated

Table 1. Crystallographic data for $Li_4Ca_{13}Ge_6N_{18}$

Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 12.328(1) Å
	b = 12.662(1) Å
	c = 14.711(1) Å
	β = 108.688(5)°
Volume (Å^3)	2175.2(3)
Z	4
Density (calcd/mg m^{-3})	3.776
Absorption coefficient (mm^{-1})	11.293
Temperature (K)	173(2)
F(000)	2360
Crystal size (mm^3)	0.22 × 0.10 × 0.05
θ range for data collection (°)	2.37 to 30.51
Index ranges	-17≤h≤17, -17≤k≤18, -20≤l≤20
Reflections collected	16797
Independent reflections	3319 [R(int) = 0.0383]
Data / restraints / parameters	3319 / 0 / 177
Goodness-of-fit on F^2	1.074
Final R indices [I > 2sigma(I)]^a	R1 = 0.0227, wR2 = 0.0568
R indices (all data)^a	R1 = 0.0295, wR2 = 0.0583
Largest diff. peak and hole (e.Å^{-3})	0.940 and -1.108

^{a}R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. wR2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$, where w = $1/\sigma(F_o^2)^2 + (gP)^2 + jP$], P = $[\max(F_o^2,0) + 2F_c^2]/3$. g = 0.0273, j = 1.3116.

Table 2. Atomic parameters ($\times 10^{-4}$) for $Li_4Ca_{13}Ge_6N_{18}$

atom	site	x	y	z	U_{eq}[a]
Ge(1)	8f	795(1)	3165(1)	1181(1)	2(1)
Ge(2)	8f	851(1)	1546(1)	5481(1)	2(1)
Ge(3)	8f	2578(1)	1730(1)	2870(1)	2(1)
Ca(1)	8f	1458(1)	4775(1)	2822(1)	6(1)
Ca(2)	8f	1474(1)	5203(1)	428(1)	5(1)
Ca(3)	8f	1652(1)	3028(1)	4150(1)	8(1)
Ca(4)	8f	1894(1)	1467(1)	379(1)	4(1)
Ca(5)	8f	3517(1)	3598(1)	2033(1)	4(1)
Ca(6)	8f	4807(1)	1712(1)	1281(1)	4(1)
Ca(7)	4e	0	1536(1)	2500	5(1)
N(1)	8f	22(2)	1790(2)	4148(1)	4(1)
N(2)	8f	64(2)	4408(2)	3813(1)	5(1)
N(3)	8f	1578(2)	2901(2)	2495(1)	5(1)
N(4)	8f	1729(2)	3357(2)	429(2)	4(1)
N(5)	8f	1849(2)	456(2)	2943(1)	5(1)
N(6)	8f	1965(2)	496(2)	5566(1)	4(1)
N(7)	8f	3425(2)	2093(2)	4183(1)	4(1)
N(8)	8f	3549(2)	1646(2)	2148(1)	4(1)
N(9)	8f	4894(2)	3760(2)	1199(1)	5(1)
Li(1)	8f	1010(3)	118(4)	1469(3)	8(1)
Li(2)	8f	1066(3)	320(3)	4127(3)	2(1)

[a]The equivalent isotropic displacement parameters, U_{eq} in $Å^2 \times 10^{-3}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

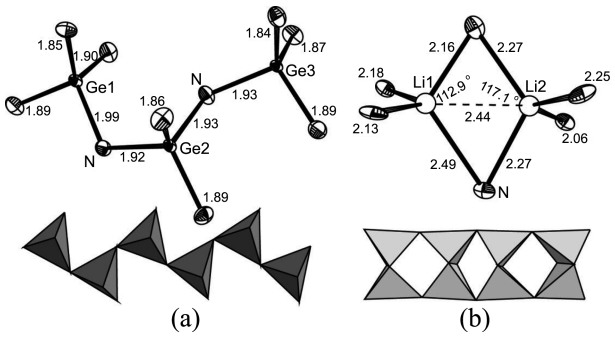

Figure 1. (a) Coordination sphere around Ge, and a segment of the one-dimensional chain of $^1_\infty[GeN_3]^{-5}$ which is generated by corner shared tetrahedral $[GeN_4]$. (b) A 'bow tie' unit of $[Li_2N_6]$ which is generated by edge shared tetrahedral $[LiN_4]$, and a segment of the one dimensional chain of $^1_\infty[Li_2N_4]^{-10}$ which is generated from the 'bow tie' units *via* corner sharing.

to N at the normal bond lengths of Li-N, ranging from 2.13 to 2.27 Å. But one exceptionally long Li1-N bond has much longer distance of 2.49 Å, introducing substantial distortion to the pseudo-tetrahedral unit around Li1. As in the $Li_4Sr_3GeN_6$, these Li-centered tetrahedra in $Li_4Ca_{13}Ge_6N_{18}$ also generate 'bow tie' units of $[Li_2N_6]$ by sharing a common edge, as shown in Figure 1(b). These 'bow tie' units are connected *via* corner-sharing and generate the one dimensional infinite chain of $^1_\infty[Li_2N_4]^{-10}$, which runs along c-axis, as shown in Figure 2(b).

Those one-dimensional infinite chains of $^1_\infty[GeN_3]^{-5}$ and $^1_\infty[Li_2N_4]^{-10}$ mutually crisscross, interwoven into the three-dimensional framework of anionic nitridometallate, shown

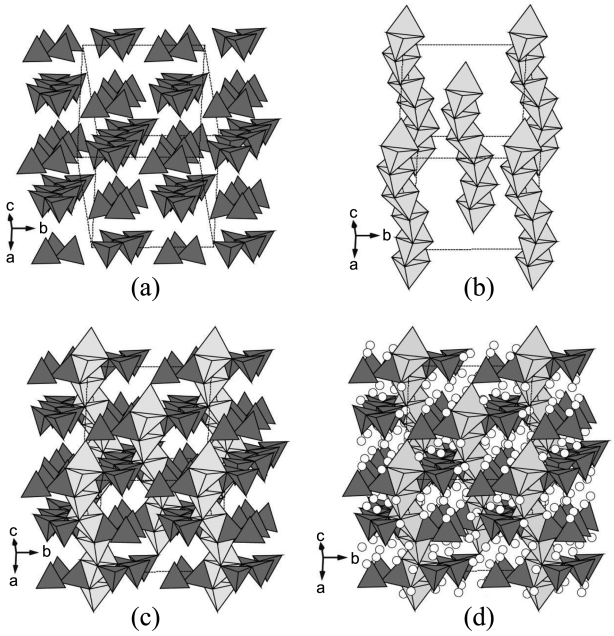

Figure 2. (a) One dimensional chains of $^1_\infty[GeN_3]^{-5}$ extending along [101] direction. (b) One dimensional chains of $^1_\infty[Li_2N_4]^{-10}$ running along the c-axis. (c) By crisscrossing these one-dimensional chains of $^1_\infty[GeN_3]^{-5}$ and $^1_\infty[Li_2N_4]^{-10}$ each other, three dimensional framework of nitridometallate anion is generated. (d) Crystal structure of $Li_4Ca_{13}Ge_6N_{18}$. Charge balance is attained by filling Ca^{+2} cations (open circles) in the vacant spaces of the anionic nitridometallate.

in Figure 2(c). Anionic charge of the nitridometallate is balanced by Ca^{+2} cations located in the vacant spaces of the three-dimensional framework, which complete the crystal structure of the $Li_4Ca_{13}Ge_6N_{18}$, shown in Figure 2(d). All Ca are located in octahedral coordination sphere, surrounded by six adjacent N. These octahedral $[CaN_6]$ connect to adjacent $[CaN_6]$ *via* face-sharing, and to adjacent tetrahedral $[GeN_4]$ and $[LiN_4]$ *via* edge-sharing.

When the structure of $Li_4Ca_{13}Ge_6N_{18}$ is compared to that of the $Li_4Sr_3GeN_6$,[8] an interesting feature of the structural development emerges. In $Li_4Sr_3GeN_6$, the 'bow tie' units of $[Li_2N_6]$ had been connected to each other side by side *via* sharing not only their corners but also the edges, thereby, generating two-dimensional double sheet of $_\infty[Li_4N_6]^{-14}$.[8] In $Li_4Ca_{13}Ge_6N_{18}$, these 'bow tie' units generated the one-dimensional chain of $^1_\infty[Li_2N_4]^{-10}$ by sharing only their corners. We can see the structural motif has been shifted from the two-dimensional slab into the one-dimensional chain, as the relative ratio of Li to Ge is decreased from Li:Ge=4:1 (in $Li_4Sr_3GeN_6$) to Li:Ge=4:6 (in $Li_4Ca_{13}Ge_6N_{18}$). The structural motif observed for the Ge-centered teterahedra also exhibits the same trend, conforming to this observation. As Ge:Li ratio decreased from 6:4 (in $Li_4Ca_{13}Ge_6N_{18}$) down to 1:4 (in $Li_4Sr_3GeN_6$), the one-dimensional chains of $^1_\infty[GeN_3]^{-5}$ in $Li_4Ca_{13}Ge_6N_{18}$ disintegrated into the isolated islands of $[Ge_2N_6]^{-10}$ embedded in between the stacked layers of $_\infty[Li_4N_6]^{-14}$ in $Li_4Sr_3GeN_6$. This structural comparison provides an interesting example which shows that

the structural motif observed for the anionic nitridometallate in quaternary nitrides is strongly influenced by the relative stoichiometry between constituent metals.

Experimental

$Li_4Ca_{13}Ge_6N_{18}$ was synthesized as single crystals from constituent elements in molten Na, as described in previous reports on other nitrides.[8-17] Reactants used for the synthesis were NaN_3 (90.5 mg, Aldrich, 99%), Na (200 mg, Aldrich, 99%), Ca (22.4 mg, Aldrich, +99%), Ge (80.1 mg, Cerac, 99.999%), and Li (2.2 mg, Aldrich,99.9%). The molar ratio of Na:Ge:Ca:Li was 10:1:0.5:0.25.

Product was obtained as shiny powder which readily decomposed when it was exposed in air. Under microscope, it was a mixture of silvery shining multifaceted granules (analyzed to be known nitride, Ca_2GeN_2)[6] and clear transparent rectangular prisms with prominent facets. WDX (wavelength dispersive X-ray) and Semi-quantitative EDX (energy dispersive X-ray) analyses were carried out on several clear crystals by using a JEOL JXA-8900R WD/ED combined microanalyzer. Nitrogen in the crystals was qualitatively identified by observing nitrogen peak by WDX analysis. The atomic ratio of Ca to Ge was measured to be 2.1 ± 0.1 by EDX analysis.

X-ray diffraction data were collected with a Bruker X8 APEX II diffractometer equipped with 4K CCD detector. Poly(butene) oil was used to prevent decomposition of the crystals in air during X-ray diffraction data collection. Initial orientation matrix was obtained by using APEX2 program.[29] Indexing on the single crystal diffraction peaks obtained from the clear rectangular crystal indicated it is a new compound, which belongs to monoclinic system, with unit-cell parameters of a = 12.328(1), b = 12.662(1), c = 14.711(1) Å, and β = 108.688(5)°. The integration of the diffraction data was carried out by the program SAINT.[30] An empirical absorption correction was applied using SADABS.[31] Systematic extinctions in the diffraction data suggested the space group of *C*2/*c*.The initial input file for solving the crystal structure was prepared by XPREP.[32] Initial structure solution was obtained by the direct method, using SHELXS.[33] Ten crystallographic sites with substantial electron densities were immediately allocated for Ge and Ca. Refinement of the structure was carried out by the full-matrix least square method (on F^2), using SHELXL.[33] By including nine N and two Li into the solution, structural refinement reached the level of R1=2.27%. The atomic ratio between Ca and Ge was 13:6, which conforms to the value obtained by EDX analysis. The empirical formula came out to be $Li_4Ca_{13}Ge_6N_{18}$. The atomic parameters were standardized by using STRUCTURE TIDY.[34] The space group was verified by using ADDSYM.[35]

Supplementary Material. Supplementary material has been sent to Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html), as **CSD No. 424022**, and can be obtained by contacting the FIZ and quoting the article details and the corresponding CSD number.

Ackowledgments. DGP appreciates support by Sookmyung Women's University for his sabbatical leave.

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