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Journal of Solid State Chemistry 172 (2003) 166–170

JOURNAL OF  
SOLID STATE  
CHEMISTRY

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# Synthesis and structure of $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ : a new quaternary nitride containing $\text{Ge}_2\text{N}_6^{10-}$ anions

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Received 30 July 2002; received in revised form 28 October 2002; accepted 19 November 2002

## Abstract

A new Li-containing quaternary nitride,  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ , was obtained as single crystals from constituent elements in molten Na. It crystallizes in space group  $C2/m$  (No. 12) with  $a = 6.1398(7)$  Å,  $b = 10.021(1)$  Å,  $c = 6.3130(7)$  Å,  $\beta = 91.279(2)^\circ$ , and  $Z = 2$ . It contains the first example of isolated nitridogermanate anions of  $\text{Ge}_2\text{N}_6^{10-}$ , which is also the first example of edge-sharing tetrahedral  $[\text{GeN}_4]$ .

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## 1. Introduction

Though understanding of metal-nitride compounds has greatly expanded in recent years [1–10], synthesis and characterization of new nitride compounds is still challenging, in part due to their propensity for hydrolysis or oxidation in air. During last two decades, many new nitrides have been obtained via just a few different synthetic routes. In particular, the molten Na method has been a very productive way to obtain single crystals of many new ternary nitrides [11–20].

Still, only a handful of quaternary nitrides have been reported [21,22]. Among those quaternary nitrides, many contain lithium as a constituent, such as  $\text{LiSr}_2[\text{ReN}_4]$  [23],  $\text{LiBa}_2[\text{ReN}_4]$  [23],  $\text{Li}_3\text{Ba}_2\text{NbN}_4$  [24],  $\text{Li}_3\text{Ba}_2\text{Ta}_2\text{N}_4$  [25],  $\text{Sr}_2\text{Li}[\text{Fe}_2\text{N}_3]$  [26],  $\text{Ba}_2\text{Li}[\text{Fe}_2\text{N}_3]$  [26],  $\text{LiSr}_2[\text{CoN}_2]$  [27],  $\text{Li}_3\text{Sr}_2\text{NbN}_4$  [28],  $\text{Li}_3\text{Sr}_2\text{Ta}_2\text{N}_4$  [28],  $\text{Li}_3\text{Sr}_3\text{Ni}_4\text{N}_4$  [29], and several phases in  $\text{Li}/(\text{Ca},\text{Sr})/\text{Cu}/\text{N}$  [30]. Li is rather polarizing toward anions, since it has a high charge density (or equivalently, small ionic radius). In order to produce quaternary nitride phases, one usually chooses three cations that are as different as possible in size, electronegativity and valence electron count. All of the above mentioned quaternary nitrides would seem to fit the requirements—especially in size and oxidation state. Based on such logic, we introduced

Li to Sr–Ge–Na–N system, and obtained a new quaternary nitride compound,  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ .

Tetrahedral  $[\text{SiO}_4]$  in oxides almost exclusively connect to other metal polyhedra through corner-sharing. On the contrary, edge-sharing of metal-centered tetrahedral units of  $[\text{MN}_4]$  is commonly found in many ternary nitride compounds, especially in ternary gallium and silicon nitrides [16,18,19,31]. The edge-sharing tetrahedra are also found in silicon chalcogenides [32] or gallium phosphides [33]. However, edge-sharing has not been reported in any previously known ternary or quaternary nitrides of Ge. Most of the known ternary germanium nitrides, such as  $\text{Ca}_2\text{GeN}_2$ ,  $\text{Sr}_3\text{Ge}_2\text{N}_2$ ,  $\text{Sr}_2\text{GeN}_2$ ,  $\text{Ba}_3\text{Ge}_2\text{N}_2$ , or  $\text{Ba}_2\text{GeGa}_2\text{N}_4$ , contain ‘dumb-bell-shaped’ bent  $\text{GeN}_2^{4-}$  anions [13,15,17,20].  $\text{Ca}_4\text{GeN}_4$  contains isolated tetrahedral anions of  $\text{GeN}_4^{8-}$  [13], and  $\text{Ca}_5\text{Ge}_2\text{N}_6$  has infinite chains of corner-shared  $[\text{GeN}_4]$  [13].  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  contains the first example of edge-sharing  $[\text{GeN}_4]$ , in isolated nitridogallate anions of  $\text{Ge}_2\text{N}_6^{10-}$ .

## 2. Experimental

Under argon in a VAC dry-box,  $\text{NaN}_3$  (98.6 mg, Aldrich, 99%), Na (194.3 mg, Aldrich, 99%), Ge (78.0 mg, Cerac, 99.999%), Sr (88.7 mg, Aldrich, 99+%), and Li (13.6 mg, Aldrich, 99.9%) were loaded in a Nb container, which was made by welding one end

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of Nb tubing (110 mm long, 3/8" o.d. and 1 mm thickness) in an argon atmosphere, using a Centorr Associates arc furnace. The molar ratio of Na:Ge:Sr:Li was 10:1:1:2. After the remaining end was welded closed, the container was put into quartz tubing and sealed under vacuum to protect it from oxidation during heat treatment. The reaction container was then heated in a muffle furnace at a rate of 50°C/h to 760°C. The temperature was maintained at 760°C for 48 h, and lowered linearly to 200°C over 200 h. Thereafter, the furnace was turned off. After top end of the Nb container was cut open in the dry-box by using a tube cutter, the open end was hooked up to a homemade vacuum sublimation device. This device has a liquid-N cooled U-trap (1/4 in. o.d. copper tubing) with one end connected to dynamic vacuum, and the other end to a union which accepts the Nb container. By heating one end of the container, Na was separated from the product by being sublimed to the cooler end. Once separated, the products could be retrieved from the Nb container in the dry box.

X-ray diffraction data were collected with a Bruker SMART system with a CCD detector from a single crystal of  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  mounted in a drop of poly (butene) oil sustained in a plastic loop. A cold nitrogen gas flow over the sample solidified the oil, thereby protecting the sample from contact with air. The SAINT software package was used for integration of the diffraction data [34]. An empirical absorption correction was applied using SADABS [35]. The structure was solved by the direct method, using SHELXS [36]. Refinement of the structure was carried out by the full-matrix least-squares method, using SHELXL [36]. The atomic parameters were standardized by using STRUCTURE TIDY [37]. The space group was verified by using ADDSYM [38]. Semi-quantitative (without standards) EDX (energy dispersive X-ray) analysis was carried out on several clear crystals of rectangular shape. Nitrogen in the crystals was qualitatively identified by WDX (wavelength dispersive X-ray) analysis. Both EDX and WDX analyses were performed using a JEOL 8900 Electron Microprobe.

### 3. Results and discussion

The product was obtained as a mixture of two different crystals; clear transparent rectangular columns, and black shiny rectangular needles. EDX analyses on several crystals in columnal shape indicated Sr:Ge ratio to be near 3:2 ( $56.7:43.3 \pm 1.3\%$ ), which conforms to the empirical formula of  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ . Chemical and structural analyses on the black needles suggested that they are a new intermetallic compound;  $\text{LiSrGe}_2$ . The structural details on  $\text{LiSrGe}_2$  will be reported elsewhere.

Table 1  
Crystallographic data for  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$

Crystal system	Monoclinic
Space group	$C2/m$
$a$ (Å)	6.1398(7)
$b$ (Å)	10.0208(12)
$c$ (Å)	6.3130(7)
$\beta$ (deg)	91.279(2)
$V$ (Å <sup>3</sup> )	388.32(8)
$Z$	2
$D$ (calcd) (m <sup>3</sup> )	4.446
$T/K$	173(2)
Abs. coeff (mm <sup>-1</sup> )	28.063
$F(000)$	464
Crystal size (mm <sup>3</sup> )	$0.1 \times 0.02 \times 0.02$
$\theta$ (deg)	$3.23\text{--}31.77^\circ$
Index ranges	$-8 \leq h \leq 9, -14 \leq k \leq 12, -9 \leq l \leq 8$
Refln. collected	1952
Independent refln.	662
Data/restraints/parameters	662/0/36
Goodness-of-fit on $F^2$	1.168
Final $R$ indices [ $I > 2\sigma(I)$ ] <sup>a</sup>	$R_1 = 0.0317, wR_2 = 0.0611$
$R$ indices (all data)	$R_1 = 0.0376, wR_2 = 0.0626$
Extinction coefficient	0.0082(8)
Largest diffraction peak and hole	1.051 and $-1.668 \text{ e.Å}^{-3}$

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^2)^2]^{1/2}$ , where  $w = 1/[\sigma(F_o^2)^2 + (gP)^2 + jP]$ ,  $P = [\max(F_o^2, 0) + 2F_c^2]/3$ ,  $g = 0.0285$ ,  $j = 0.8574$ .

Table 2  
Atomic parameters ( $\times 10^{-4}$ ) for  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$

Atom	Site	$x$	$y$	$z$	$U_{\text{eq}}^a$
Sr(1)		0	1898(1)	5000	5(1)
Sr(2)		0	0	0	7(1)
Ge		6122(1)	0	3213(1)	3(1)
N(1)		2054(5)	3445(4)	1993(5)	5(1)
N(2)		3009(7)	0	3697(7)	6(1)
Li		3625(11)	1795(8)	1147(12)	9(1)

<sup>a</sup> The equivalent isotropic thermal displacement parameter,  $U_{\text{eq}}$  in  $\text{Å} \times 10^{-3}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Systematic extinctions suggested the space groups  $C2$ ,  $Cm$ , or  $C2/m$ . N positions were obvious in the early stages of the refinement on the starting model, which was obtained in  $C2/m$ . Residual electron density in the difference Fourier map suggested the existence of Li. By adding the Li into the model, the refinement reached the lowest  $R_1$  of 3.1%. Crystallographic data for  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  are provided in Tables 1–4.

A major component of the crystal structure of  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  is the 'bow tie' unit of  $[\text{M}_2\text{X}_6]$ . Ge is coordinated to four N, generating a pseudo-tetrahedron of  $[\text{GeN}_4]$ . Two of the  $[\text{GeN}_4]$  combine through edge-sharing into nitridogermanate anions of  $\text{Ge}_2\text{N}_6^{10-}$ , shown in Fig. 1a. These anions are isolated from each other, and are surrounded by Sr and Li, as shown in Fig. 1b. Such edge-sharing of tetrahedral  $[\text{GeN}_4]$  has not

Table 3  
Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Sr(1)	5(1)	5(1)	4(1)	0	-1(1)	0
Sr(2)	7(1)	6(1)	7(1)	0	4(1)	0
Ge	3(1)	2(1)	3(1)	0	1(1)	0
N(1)	4(1)	5(2)	7(1)	-1(1)	0(1)	2(1)
N(2)	7(2)	5(2)	5(2)	0	2(2)	0

The anisotropic displacement factor exponent takes the form:  
 $-2\pi^2[h^2a^2U_{11} + 2hka^*b^*U_{12} + \dots]$ .

Table 4  
Selected atomic separation ( $\text{\AA}$ ) and bond angles (deg) in  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$

(Ge-centered distorted tetrahedron)			
Ge–N1	1.835(4)	N1–Ge–N1	116.2(2)
Ge–N2	1.942(5)	N1–Ge–N2	112.5(1)
	2.011(5)	N1–Ge–N2'	109.2(1)
Ge–Ge	2.669(1)	N2–Ge–N2'	95.1(2)
(Li-centered distorted tetrahedron)			
Li–N1	1.994(8)	N1–Li–N1'	105.7(4)
Li–N1'	2.031(8)	N1–Li–N1''	119.8(4)
Li–N1''	2.174(8)	N1–Li–N2	110.5(3)
Li–N2	2.449(8)	N1'–Li–N1''	113.8(4)
Li–Li	2.25(2)		
(Sr1-centered distorted octahedron)			
Sr1–N1	2.615(3)	Sr1–N1'	2.776(3)
Sr1–N2	2.788(3)		
(Sr2-centered distorted octahedron)			
Sr2–N1	2.717(3)	Sr2–N2	2.944(5)

been observed in any previously known ternary [13,17,20,39] or quaternary germanium nitride [15].

Bond lengths of Ge–N2 bridging bonds are 1.942 and 2.011 Å, which are longer than known Ge–N bonds. Reported Ge–N bond lengths range from 1.851 to 1.950 Å in ternary germanium nitride compounds [13,17,20]. Those Ge–N2 bonds are also considerably longer than Ge–N1 bonds (1.835 Å), which are shorter than reported Ge–N bonds. The bond angle between those Ge–N2 bridging bonds ( $\angle \text{N2–Ge–N2} = 95.05^\circ$ ) is substantially smaller than the ideal angle for a tetrahedron ( $109^\circ$ ). On the contrary, the opposing angle ( $\angle \text{N1–Ge–N1} = 116.2^\circ$ ) is substantially larger than  $109^\circ$ . This seemingly concerted distortion of the tetrahedron indicates more *p* character was drawn into the Ge–N2 bridging bonds, whereas more *s* character was drawn into the other bonds. The repulsive interaction between two Ge in the centers of the tetrahedra may result in such a distortion by 'pushing' them further apart. The distance between those two Ge, 2.669(1) Å, is shorter than that between two Ge in elemental Ge (2.74 Å) [40]. This concerted distortion is seen in many previous examples of edge-sharing tetrahedral nitrido-

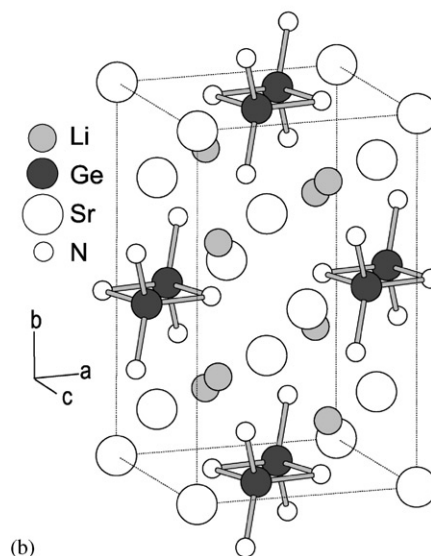
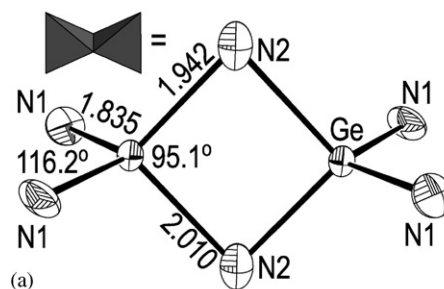


Fig. 1. (a) The 'bow tie' unit of  $[\text{Ge}_2\text{N}_6]$  is generated by edge-sharing between two tetrahedral  $[\text{GeN}_4]$ . The thermal ellipsoids are shown at 99% level, (b) the crystal structure of  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ , which shows isolated 'bow tie' anions of  $\text{Ge}_2\text{N}_6^{10-}$ .

gallates: Ga–N bridging bonds are considerably longer than other remaining bonds, and bond angle between those Ga–N bridging bonds is substantially smaller than ideal angle for tetrahedron [14,16,18]. Such a distortion was also observed in corner-connected  $[\text{Al}_2\text{N}_6]$  of  $\text{Ca}_3[\text{Al}_2\text{N}_4]$ , [41] or in  $[\text{Si}_2\text{N}_6]$  of  $\text{Ba}_5\text{Si}_2\text{N}_6$  and  $\text{BaSi}_7\text{N}_{10}$  [19,31].

The Li in  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  also form 'bow tie' units of  $[\text{M}_2\text{N}_6]$ . Li is coordinated to three N at the normal bond length of Li–N, 1.994–2.174 Å, and is bonded another N at a substantially longer distance of 2.449 Å. The Li is also facing a second Li at a relatively short distance of 2.25 Å. Counting only near neighbor N, Li is seen to be in a heavily distorted tetrahedral N-coordination. By sharing an edge, two of these  $[\text{LiN}_4]$  combine into 'bow tie'  $[\text{Li}_2\text{N}_6]$ , shown in Fig. 2a. The concerted distortion commonly observed for edge-sharing  $[\text{GaN}_4]$  [14,16,18] or in  $\text{Ge}_2\text{N}_6^{10-}$  (see above) does not occur for the  $[\text{Li}_2\text{N}_6]$ . These 'bow tie' units of  $[\text{Li}_2\text{N}_6]$  connect to each other side by side in the *ab*-plane via sharing their corners and edges (edge-sharing along [100] direction and corner-sharing along [010] direction), thereby, generating a two-dimensional double-sheet of

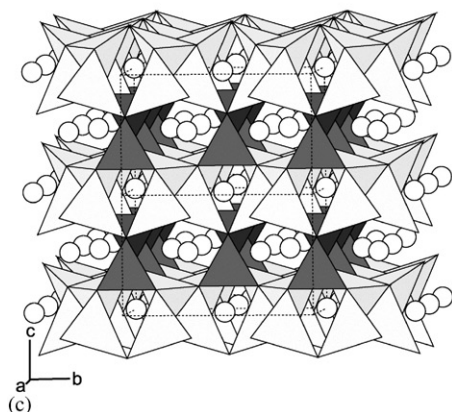
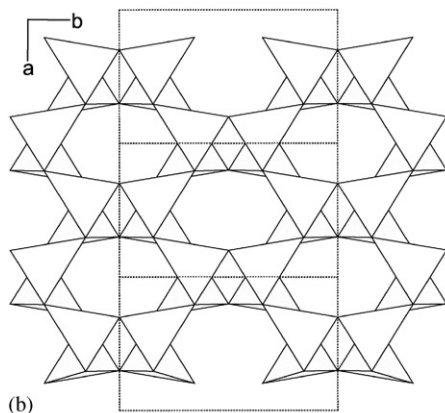
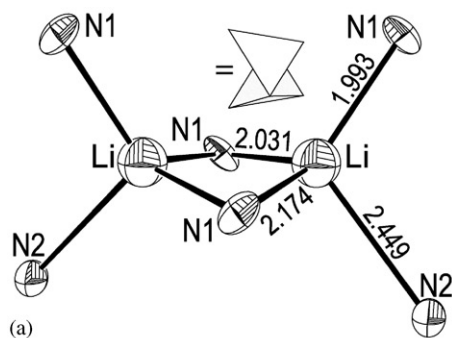


Fig. 2. (a) The 'bow tie' unit of  $[\text{Li}_2\text{N}_6]$ . The thermal ellipsoids are shown at 99% level, (b) two dimensional double sheet of composition  $\infty[\text{Li}_4\text{N}_6^{14-}]$ , which is generated from 'bow tie' units of  $[\text{Li}_2\text{N}_6]$ , (c) the crystal structure of  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  shows stacked layers of  $\infty[\text{Li}_4\text{N}_6^{14-}]$ , which are interleaved by isolated 'bow tie' anions of  $\text{Ge}_2\text{N}_6^{10-}$ .

composition  $\infty[\text{Li}_4\text{N}_6^{14-}]$ , which is shown in Fig. 2b. The layers of  $\infty[\text{Li}_4\text{N}_6^{14-}]$  repeat along the  $c$ -axis, and they are separated by isolated nitridogermanate anions of  $\text{Ge}_2\text{N}_6^{10-}$  as in Fig. 2c. This combination generates a nitridometallate network of Ge and Li, with resulting empty spaces occupied by Sr. Each Sr is coordinated to six N in a distorted octahedral environment of  $[\text{SrN}_6]$ , which is shown in Fig. 3.

In  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ , N is seven-coordinate to surrounding metals, generating a decahedron (which corresponds to a highly distorted mono-capped octahedron). N2 is

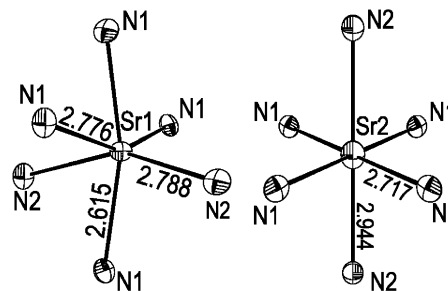


Fig. 3. Coordination around Sr1 and Sr2 generates distorted octahedra of  $[\text{SrN}_6]$ .

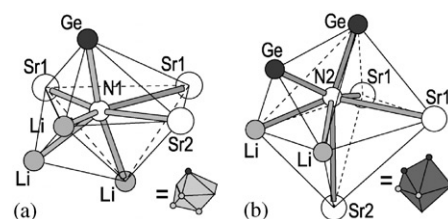


Fig. 4. (a) N1 coordinates to one Ge, three Li, and three Sr, generating a distorted decahedron, (b) N2 coordinates to two Ge, two Li, and three Sr, also generating a distorted decahedron, which has a larger size than the N1-centered decahedron.

coordinate to three Sr, two Ge, and two Li, whereas, N1 is coordinate to three Sr, one Ge, and three Li. Those two different decahedrons are shown in Figs. 4a and b. In the N1-decahedron, bond lengths range from 1.835, 1.994–2.174, and 2.615–2.776 Å, for Ga–N, Li–N, and Sr–N, respectively. In the N2-decahedron, they are 1.942–2.011, 2.449, and 2.788–2.944 Å for Ga–N, Li–N, and Sr–N, respectively. It is apparent that the overall bond lengths are considerably longer in N2-decahedron than in N1-decahedron, which suggests replacing a Ge by a Li (in N1-decahedron) may have alleviated the repulsive interaction between surrounding metals.

The two different N-centered decahedrons of  $[\text{Li}_3\text{GeSr}_3\text{N}]$  (Fig. 4a) and  $[\text{Li}_2\text{Ge}_2\text{Sr}_3\text{N}]$  (Fig. 4b) combine into a building block, which is repeated to build the crystal structure of  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  (Fig. 5). Two  $[\text{Li}_2\text{Ge}_2\text{Sr}_3\text{N}]$  and four  $[\text{Li}_3\text{GeSr}_3\text{N}]$  join by edge-sharing into the basic building block, which is shown in Fig. 5a. The building block repeats itself by connecting to others via edge-sharing, generating the N-centered polyhedral representation of  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$ , in Fig. 5b.

#### 4. Summary

$\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  contains isolated 'bow tie' anions of  $\text{Ge}_2\text{N}_6^{10-}$ , which is generated by edge-sharing of two tetrahedral  $[\text{GeN}_4]$ . It also contains 'bow tie' units of  $[\text{Li}_2\text{N}_6]$ , which generate layers of composition  $\infty[\text{Li}_4\text{N}_6^{14-}]$ . Those layers are separated by the  $\text{Ge}_2\text{N}_6^{10-}$

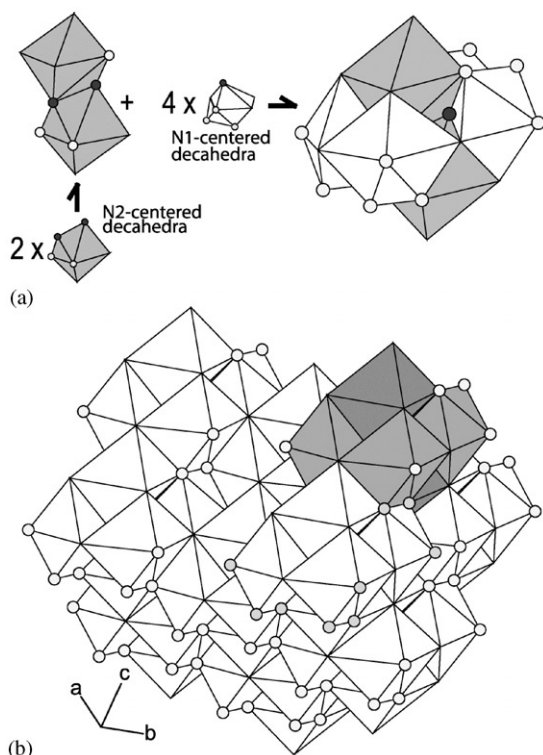


Fig. 5. (a) Via edge-sharing, two N2-centered decahedra and four N1-centered decahedra are combined together into a hypothetical building block of composition  $[\text{Li}_{12}\text{Sr}_{10}\text{Ge}_2\text{N}_6]$ , (b) by repeating this building block via edge-sharing, a N-centered polyhedral representation of the crystal structure of  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  is obtained. A representative unit of the building block is shaded dark.

anions.  $\text{Li}_4\text{Sr}_3\text{Ge}_2\text{N}_6$  is the first example of a compound containing edge-sharing tetrahedra of  $[\text{GeN}_4]$ .

### Acknowledgments

This work was supported by the National Science Foundation through Grant DMR-9805719. We thank Dr. E. Lobkovsky (single-crystal diffraction) and Mr. J. Hunt (SEM microprobe) for the use of their facilities at Cornell University. The SEM microprobe is one of the Cornell Center for Materials Research Shared Experimental Facilities, supported through the National Science Foundation Materials Research Science and Engineering Centers program (DMR-0079992). D.G. Park's research activity during his sabbatic stay at Cornell was partly funded by Seoam Foundation in Korea, and by KOSEF (Korea) through R06-2002-007-01005-02002.

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