A Structural Comparison between a New Quaternary Nitride, Ba₃GeMgN₄, and Its Isostructural Sr analogue

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Many ternary and quaternary nitrides containing Ge or Ga have been synthesized by flux method in molten Na.[1-16] Those nitrides usually contain alkaline earth element, which was added to enhance solubility of nitrogen into the melt. As volume of structural information on those nitrides increases, a few common structural features start to become apparent. It is suggested that not all alkaline earth elements behave in a same manner. Distinction in structural characteristics is most prominent in Mg when it is compared to heavier family members, especially Sr and Ba. A few interesting aspects of structural features in alkaline earth containing nitrides are described in relation with the crystal structure of a new quaternary nitride, Ba₃GeMgN₄, which was synthesized by flux method in molten Na.

Crystallographic data on Ba₃GeMgN₄ are provided in Table 1-4. Ba₃GeMgN₄ is isostructural with Ba₃Ga₂N₄,[13] Sr₃Ga₂N₄,[14] and Sr₃GeMgN₄.[6] It contains one-dimensional chains of nitridometallate anions extending along the b-axis, shown in Figure 1a. Ba cations are distributed among those chains, balancing the charges. The one-dimensional chain is generated by edge-sharing of Ge or Mg centered tetrahedra connected in alternating

Table 1. Crystallographic data for Ba₃GeMgN₄

Crystal system	Orthorhombic
Space group	Pnna
Unit cell dimensions (Å)	a = 6.159(1)
	b = 10.558(2)
	c = 10.048(2)
Volume (Å³)	653.4(2)
Z	4
Density (calcd/mg·m⁻³)	5.743
Absorption coefficient (mm⁻¹)	22.390
Temperature (K)	173(2)
F (000)	960
Crystal size (mm³)	0.09 × 0.06 × 0.06
Theta range for data collection (°)	2.80 to 30.50
Index ranges	−8 ≤ h ≤ 6, −10 ≤ k ≤ 15, −14 ≤ l ≤ 10
Reflections collected	4581
Independent reflections	982 [R(int) = 0.0397]
Data/restraints/parameters	982/0/44
Goodness-of-fit on F^2	1.105
Final R indices [I > 2sigma (I)]ᵃ	R_1 = 0.0304, wR_2 = 0.0578
R indices (all data)	R_1 = 0.0399, wR_2 = 0.0604
Largest diff. peak and hole (e.Å⁻³)	1.548 and −2.102

ᵃ$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$, where w = $1/\sigma(F_o^2)^2 + (gP)^2 + jP]$, P = [max(F_o²,0) + 2F_c²]/3. g = 0.0178, j = 5.6203.

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for Ba₃GeMgN₄

	Wyckoff	x	y	z	U(eq)
Ba(1)	8e	6156(1)	1564(1)	893(1)	6(1)
Ba(2)	4c	2500	0	5923(1)	9(1)
Ge(1)	4c	2500	0	2681(1)	5(1)
Mg(1)	4d	1612(5)	2500	2500	4(1)
N(1)	8e	254(9)	836(5)	1664(6)	9(1)
N(2)	8e	3704(9)	3631(5)	1324(6)	9(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

**Table 3.** Anisotropic displacement parameters (Å² × 10³) for Ba₃GeMgN₄

	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
Ba(1)	5(1)	6(1)	6(1)	−1(1)	0(1)	1(1)
Ba(2)	8(1)	12(1)	9(1)	0	0	2(1)
Ge(1)	5(1)	5(1)	5(1)	0	0	−1(1)
Mg(1)	4(2)	3(2)	4(2)	0(1)	0	0
N(1)	8(3)	10(3)	10(3)	2(2)	0(2)	−3(2)
N(2)	9(3)	5(3)	12(3)	0(2)	2(2)	2(2)

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

Table 4. Selected bond lengths [Å] and bond angles [°] in Ba₃GeMgN₄ and Sr₃GeMgN₄

		Ba₃GeMgN₄	Sr₃GeMgN₄
Bond lengths			
	Ge-N1	1.933(6)	1.920(8)
	Ge-N2	1.908(5)	1.892(8)
	average Ge-N	1.921*	1.906*
	Mg-N1	2.119(6)	2.081(8)
	Mg-N2	2.118(6)	2.126(8)
	average Mg-N	2.119*	2.104*
Bond angles			
	N1ᵃ-Ge-N2ᵃ	102.1(2)	103.8(3)
	N1ᵃ-Mg-N2ᵃ	89.7(2)	91.0(3)
	average Nᵇ-Ge-Nᵇ	113.5**	112.5**
	average Nᵇ-Mg-Nᵇ	119.2**	118.3**
	Ge-N1ᵃ-Mg	83.5(2)	82.6(3)
	Ge-N2ᵃ-Mg	84.2(2)	82.1(3)

ᵃbridging N on a shared edge. ᵇN on two opposing shared edges. *average taken from 4 lengths. **average taken from 4 angles.
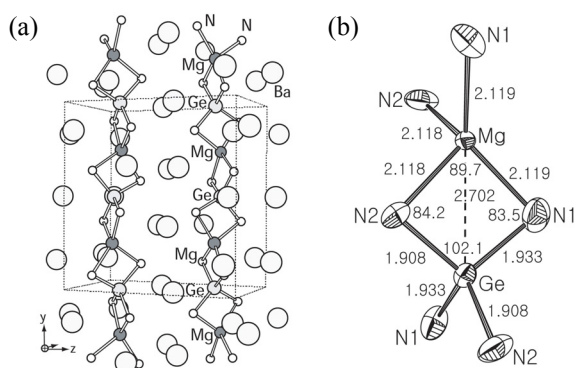
Figure 1. (a) Crystal structure of Ba_3GeMgN_4. (b) Detailed coordination of a part of the one dimensional chain. GeN_4 and MgN_4 tetrahedra are connected by edge-sharing along the b-axis.

manner. In isostructural $Ba_3Ga_2N_4$, those tetrahedra are all centered by Ga. Ba_3GeMgN_4 was obtained by replacing two Ga^{3+} in $Ba_3Ga_2N_4$ by one Ge^{4+} and one Mg^{2+} in alternating manner. Substitution of $2 \times Ga^{3+}$ by Ge^{4+} and Mg^{2+} has also been observed before in $Sr(Mg_3Ge)N_4$ [isostructural with $Sr(Mg_2Ga_2)N_4$][10] and Sr_3GeMgN_4 (isostructural with $Sr_3Ga_2N_4$).[6] Such charge balanced aleovalent substitution has frequently been observed in oxides, but not in nitrides other than these rare examples.

The basic unit of the edge-shared tetrahedra in the one-dimensional nitridometallate chain for Ba_3GeMgN_4 is shown in Figure 1b, and selected bond lengths and angles are provided in Table 4. The Ge-N bond lengths are 1.908(5) and 1.933(6) Å, and the Mg-N bond lengths are 2.118(6) and 2.119(6) Å. The bond angles between two bridging N on a shared edge, $\angle$ N1-Ge-N2 and $\angle$ N1-Mg-N2, are 102.1(2)° and 89.7(2)°, respectively. These bond angles are substantially smaller than remaining ones, which implies those tetrahedra are stretched along the chain. Those bond lengths and angles in its Sr analogue, Sr_3GeMgN_4, are also provided in Table 4 for comparison.[6] It is apparent that those tetrahedra are more stretched along the chain in Ba_3GeMgN_4 than in Sr_3GeMgN_4. The Ge-N and Mg-N bonds were elongated in average. The bond angles between two bridging N on a shared edge became smaller, and the angles between N on two opposing edges became bigger, as Sr are replaced by Ba. Distance between Ge and opposing Mg also increased from 2.644 in Sr_3GeMgN_4 to 2.702 Å in Ba_3GeMgN_4. It is interesting to note that the distortions of those tetrahedra which extended along the chain occurred in concerted manner when Sr was replaced by Ba.

The crystal structures of alkaline earth containing nitrides have conventionally been illustrated by introducing nitridometallate anions whose negative charge has been balanced by alkaline earth cations. In doing so, two different bonding schemes have been presumed. One is bonding within nitridometallate unit, which is expected to be predominantly covalent. The other is bonding between the nitridometallate anions and alkaline earth cations, which is considered to be mostly ionic. Based on this structural perspective, it is anticipated that the change in bond lengths and angles within the nitridometallate unit will be in concerted manner when electron density on it changes with the replacement of Sr by Ba. The observed outcome above conforms to this anticipation, which provides a supportive evidence

Table 5. Ionic radii and charge density for Ge and alkaline earth cations

Ion	Ionic radii[CN^a][20] (Å)	Charge density[CN] (C·mm^{-3})
Ga^{+3}	0.47[4]	1100[4]
Ge^{+4}	0.39[4]	2580[4]
Mg^{+2}	0.59[4], 0.76[6]	372[4], 204.7[6]
Ca^{+2}	1.00[6]	76.4[6]
Sr^{+2}	1.18[6]	46.5[6]
Ba^{+2}	1.35[6]	31.0[6]

^{a}CN = Coordination number.

for the conventional interpretation of the crystal structure of nitrides.

Ba_3GeMgN_4, together with other known Mg-containing quaternary nitrides [$Sr(Mg_3Ge)N_4$, $Sr(Mg_2Ga_2)N_4$, and Sr_3GeMgN_4],[6,10] exemplifies a peculiar property of Mg which behaves quite differently from its family members, Ca, Sr, and Ba. In all known alkaline earth containing Ge or Ga nitrides, six-coordination is prevalent for Ca, Sr, and Ba,[1-16] and not one example has been observed with those elements in four-coordination. On the contrary, Mg has been obtained only in four-coordination.[6,10,17-19] It may be explained by small ionic radius of Mg^{2+}. But, not only for the coordination number, has an interesting aspect emerged in regard to the bonding characteristics. The aleovalent substitution of $2 \times$ Ga with Ge and Mg in those Mg-containing quaternary nitrides verifies the fact that Mg goes into the anionic nitridometallate unit. Not only for those quaternary nitrides, in all other known Ge- or Ga-containing nitrides, Mg has been observed as being a member of the nitridometallate anions rather than just a counter cation.[6,10,18,19] It is quite comparable to the fact that Ca, Sr, and Ba almost invariable behave as counter cations against nitridometallate anions. These observations suggest a strong involvement of covalency in the bonding between Mg and N. This covalent characteristic of Mg-N bonding is quite different from those by other three alkaline earth elements which behave as counter cations in those nitrides.

Underlying cause for this characteristic difference may be explained by relatively large charge density of Mg^{2+}. The theoretical values of the charge density were calculated from ionic radii reported by Shannon,[20] and provided in Table 5 for Ge^{4+}, Ga^{3+}, and those alkaline earth cations. The values show sudden, almost 5-fold increase in going from Ca^{2+} to Mg^{2+}. A cation in such large charge density would polarize electron density of N^{3-} and nitridometallate anions, thereby introducing covalency to the bonding between them. The ionic radii for O^{2-} and N^{3-} are 1.38 and 1.46 Å, respectively.[20] Polarizing effect of Mg^{2+} is demonstrated in covalent bonding between Mg and relatively large and sometimes anionic organic ligands, which provides Grignard reagents. Considering N^{3-} and nitridometallate anion is more polarizable than O^{2-}, it is suggested that Mg-N bond contains more covalency than Mg-O, thereby causing it to behave quite differently from its family members in nitride compounds.

It is also interesting to note that isostructural relationship is commonly observed in pairs for Sr or Ba containing nitrides, such as in pairs of $Sr_3Ge_2N_2/Ba_3Ge_2N_2$,[1,2] $Sr_6Ge_5N_2/Ba_6Ge_5N_2$,[9] Sr_2GeGaN/Ba_2GeGaN,[3,12] $Sr_3Ga_2N_4/Ba_3Ga_2N_4$,[13,14] and Sr_3Ge-

MgN$_4$/Ba$_3$GeMgN$_4$.[6] This structural feature indicates Sr-N and Ba-N bondings share a common nature, whereas they are very different from that of the Mg-N bonding, which appears to be covalent.

The structural characteristics observed in a series of nitride compounds suggest that the bonding between alkaline earth element and N goes from covalent to ionic as going down through the family. It is interesting to note that Ca has to be placed in a dividing line between Mg and other family members. Considering Ca was observed as the counter cations in all those nitrides, the nature of Ca-N bonding is expected to be more inclined toward Sr-N and Ba-N ones, thereby alluding to the peculiarity of Mg-N bonding.

Experimentals

Ba$_3$GeMgN$_4$ was synthesized as single crystals from constituent elements in molten Na, as described in previous report on synthesis of isostructural Sr analogue, Sr$_3$GeMgN$_4$.[6] Reactants used for the synthesis were NaN$_3$ (65 mg, Aldrich, 99%), Na (93 mg, Aldrich, 99%), Ba (206.1 mg, Aldrich, 99+%), Ge (36.3 mg, Cerac, 99.999%), Mg (12.2 mg, Aldrich, 99.98%). The molar ratio of Na:Ge:Mg:Ba was 10:1:1:3. Product was obtained as silvery powder, which readily decomposed when it was exposed in air. Observation under microscope revealed that the silvery color came from remnant Na, not from the title crystals. X-ray diffraction data were collected with a Bruker X8 APEX II diffractometer equipped with 4 K CCD detector. Initial orientation matrix was obtained by using APEX2 program.[21] The integration of the diffraction data was carried out by the program SAINT.[22] An empirical absorption correction was applied using SADABS.[23] The initial input file for solving the crystal structure was prepared by XPREP.[24] The structure was solved by the direct method, using SHELXS.[25] Refinement of the structure was carried out by the full-matrix least square method (on F^2), using SHELXL.[25] The atomic parameters were standardized by using STRUCTURE TIDY.[26] The space group was verified by using ADDSYM.[27] Bond valences and Madelung potentials were calculated by EUTAX.[28] WDX (wavelength dispersive X-ray) and semi-quantitative (without standard) EDX (energy dispersive X-ray) analyses were carried out by using a JEOL JXA-8900R WD/ED combined microanalyzer.

Under microscope, the product was observed to be a mixture of yellow transparent crystals with well-defined facets, and black crystals of Ba$_9$Ge$_3$N$_{10}$.[11] Both crystals readily decomposed in air. The yellow crystal was mounted in a drop of poly(butene) oil sustained in a plastic loop, and the oil was solidified by flowing cold nitrogen gas over it to protect the crystal from contact with air. Indexing on the single crystal diffraction peaks obtained from the yellow crystal indicated the crystal is a new compound, which belongs to orthorhombic system, with unit-cell parameters of a = 6.159(1), b = 10.558(2), c = 10.048(2) Å. EDS semi-quantitative analyses indicated the yellow crystal contained both Ge and Mg together with Ba. Na was not detected by the analysis, and N was qualitatively identified by WDX analysis. The Ba/Ge/Mg molar ratio of the crystal was determined to be 3(±0.4):1(±0.2):1(±0.2).

Systematic extinctions in the diffraction data suggested the pace group of Pnna. Initial structural model was obtained for heavy atoms by the direct method in Pnna, and N1 and N2 were located in early stages of the refinement on the starting model. The final refinement was obtained with R$_1$ = 3.0%. The atomic ratio between Ba, Ge, and Mg was 3:1:1, which conforms to the value obtained by EDS analyses. The empirical formula came out to be Ba$_3$GeMgN$_4$.

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. **422186**, and can be obtained by contacting the FIZ and quoting the article details and the corresponding CSD number.

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