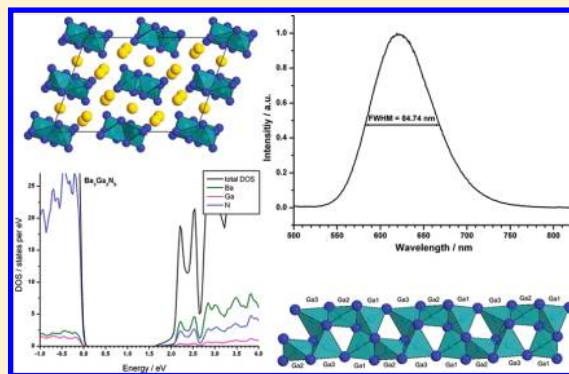


# Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub>—A Novel Host Lattice for Eu<sup>2+</sup>-Doped Luminescent Materials with Unexpected Nitridogallate Substructure

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**ABSTRACT:** The alkaline earth nitridogallate Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub> was synthesized from the elements in a sodium flux at 760 °C utilizing the weld shut tantalum ampules. The crystal structure was solved and refined on the basis of single-crystal X-ray diffraction data. Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub> (space group *C2/c* (No. 15), *a* = 16.801(3), *b* = 8.3301(2), *c* = 11.623(2) Å,  $\beta$  = 109.92(3)°, *Z* = 8) contains a hitherto unknown structural motif in nitridogallates, namely, infinite strands made up of GaN<sub>4</sub> tetrahedra, each sharing two edges and at least one corner with neighboring GaN<sub>4</sub> units. There are three Ba<sup>2+</sup> sites with coordination numbers six or eight, respectively, and one Ba<sup>2+</sup> position exhibiting a low coordination number 4 corresponding to a distorted tetrahedron. Eu<sup>2+</sup>-doped samples show red luminescence when excited by UV irradiation at room temperature. Luminescence investigations revealed a maximum emission intensity at 638 nm (FWHM = 2123 cm<sup>-1</sup>). Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub> is the first nitridogallate for which parity allowed broadband emission due to Eu<sup>2+</sup>-doping has been found. The electronic structure of both Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub> as well as isoelectronic but not isostructural Sr<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub> was investigated by DFT methods. The calculations revealed a band gap of 1.53 eV for Sr<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub> and 1.46 eV for Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub>.

**KEYWORDS:** nitridogallate, Eu<sup>2+</sup>-luminescence, DFT calculations, structure elucidation, band gap

**INTRODUCTION**

Gallium nitride GaN is a direct wide band gap semiconductor that has found increasing application in high performance light emitting diodes (LEDs).<sup>1–6</sup> While synthesis, crystal growth, and doping of GaN have been studied thoroughly,<sup>7–12</sup> the chemistry of ternary and higher nitridogallates deriving from binary GaN has been widely neglected as yet. In the literature, only a small number of ternary alkaline earth nitridogallates has been described, and thereof, only two compounds contain Ba.<sup>13–18</sup> Most nitridogallates are made up of GaN<sub>4</sub> tetrahedra which can be connected through both common corners and/or common edges.<sup>13,15,16</sup> Depending on the degree of condensation of the nitridogallate substructure, a broad range of structural motifs has been identified in nitridogallates, including one-dimensional chains of edge-sharing GaN<sub>4</sub> units (e.g., in Sr<sub>3</sub>Ga<sub>2</sub>N<sub>4</sub>), two-dimensional sheets made up of Ga<sub>2</sub>N<sub>6</sub> units which are further linked through corners (e.g., in Ca<sub>3</sub>Ga<sub>2</sub>N<sub>4</sub>), or three-dimensional networks built up from vertex- and corner-sharing tetrahedra (e.g., in Sr<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub>).<sup>16</sup> Synthesis of nitridogallates starts typically from the elements employing a sodium flux and increased nitrogen pressure. These synthesis conditions can be achieved easily by thermal decomposition of sodium azide in weld shut Ta or Nb ampules. The solubility of nitrogen in sodium can be further enhanced by addition of electropositive elements like alkaline earth metals.<sup>18,19</sup> Synthesis of highly condensed nitridogallates (i.e., atomic ratio

Ga:N > 1:2) has been pursued for a couple of years in order to reach a higher stability against hydrolysis. To accomplish this goal, either a higher nitrogen pressure or a lower metal amount is necessary.<sup>18</sup>

During the past decade, ternary and multinary alkaline earth nitrides emerged as important host lattices for doping with Eu<sup>2+</sup> exhibiting parity allowed intense broad band emission due to 4f<sup>6</sup>(<sup>7</sup>F)5d<sup>1</sup> → 4f<sup>7</sup>(<sup>8</sup>S<sub>7/2</sub>) transitions. Several of these nitrides turned out to be excellent optical materials for application in phosphor-converted (pc)-LEDs.<sup>20,21</sup> Nitridosilicates, nitridoaluminosilicates, and related SiAlONs have been intensively investigated in this respect.<sup>15,21–27</sup> However, these investigations have scarcely been extended to related alkaline earth containing tetrahedra based nitride materials, for example, nitridogallates or nitridophosphates.

**EXPERIMENTAL SECTION**

Synthesis of Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub> was carried out in a Ta ampule (30 mm length, 10 mm diameter, 0.5 mm wall thickness). All manipulations were done under argon atmosphere in recirculated glove boxes (Unilab, MBraun, Garching; O<sub>2</sub> < 1 ppm, H<sub>2</sub>O < 1 ppm). Single crystals of Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub> were obtained from a reaction of 0.312 mmol NaN<sub>3</sub> (20.3 mg, Acros,

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99%), 0.060 mmol Ba (8.2 mg, Sigma Aldrich, 99.99%), 0.005 mmol Sr (0.4 mg, Sigma Aldrich, 99.99%), 0.062 mmol Mg (1.5 mg, Alfa Aesar, 99.9%), and 0.252 mmol Ga (17.6 mg, AluSuisse, 99.999%) in 1.992 mmol Na-flux (45.8 mg, Sigma Aldrich, 99.95%). For doping purposes 2 mol % of  $\text{EuF}_3$  was added. Sr and Mg were introduced to the metallic melt in order to improve crystallinity of the product and for an initially targeted Ba–Mg–Ga–N compound. Reactions without these additional metals were unsuccessful. The filled Ta ampule was weld shut under argon atmosphere by arc melting and placed into a quartz tubing. The reaction mixture was then heated in a tube furnace ( $50^\circ/\text{h}$ ) to  $760^\circ\text{C}$ , maintained at that temperature for 48 h, and then cooled to  $200^\circ\text{C}$  with a rate of  $3.4^\circ/\text{h}$ . Subsequently, the furnace was turned off. The Ta ampule was opened in a glove box, and Na was separated from the product by sublimation at  $320^\circ\text{C}$  under vacuum (0.1 Pa) for 18 h.

Scanning electron microscopy was performed on a JEOL JSM 6500 F equipped with a field emission gun at an acceleration voltage of 30 kV. To confirm the chemical composition the samples were prepared on adhesive conductive pads and coated with a conductive carbon film. Each EDX spectrum (Oxford Instruments) was recorded with the analyzed area limited to one crystal face to avoid influence of possible contaminating phases.

Single-crystal X-ray diffraction data were collected on a STOE IPDS I diffractometer with graphite monochromated  $\text{Mo K}\alpha$  radiation (0.71073 Å). A numerical absorption correction was applied using X-RED.<sup>28</sup> The structure was solved using direct methods implemented in SHELXS-97.<sup>29</sup> Refinement of the structure was carried out with anisotropic displacement parameters for all atoms by full-matrix least-squares calculation on  $F^2$  in SHELXL-97.<sup>29</sup>

Density-functional theory (DFT) band structure calculations were carried out with the WIEN2k program package,<sup>30</sup> using full potential linearized augmented plane wave (LAPW)<sup>31</sup> method and the generalized gradient approximation by Perdew, Burke and Ernzerhof (PBE-GGA)<sup>32</sup> with a separation energy for core and valence states of  $-8$  Ry. The energy and charge convergence criteria were chosen to be  $10^{-5}$  Ry/cell and  $10^{-4}$  e/cell, respectively, and 92 to 105 irreducible  $k$ -points were used with a cutoff for plane waves  $R_{\text{mt}}K_{\text{max}} = 7.0$ .

Luminescence investigations were performed on single crystals placed in a capillary (diameter 0.2 mm, Hilgenberg) at room temperature. The capillaries were aligned with a Leitz Epivert microscope. The excitation source was a JobinYvon Traixl190 monochromator with 365 nm wavelength. As detector a CCD camera (LaVision DynaVision) was used. For recording the emission spectra a 500  $\mu\text{m}$  slit was chosen.

## RESULTS AND DISCUSSION

The heterogeneous reaction product was obtained as a light-orange powder with metallic impurities. Under the microscope, the title compound was observed in the form of orange crystals with a lathy shape. The crystals were sensitive to moisture and air. EDX analyses revealed an atomic ratio Ba:Ga:N = 1.0:1.0:1.6 that agrees well with the composition of  $\text{Ba}_3\text{Ga}_3\text{N}_5$ . No other elements were detected, although Sr and Mg were present in the starting material mixture and synthesis was performed in a sodium melt. For X-ray diffraction and luminescence investigations single crystals were placed in sealed capillaries to protect them from oxidation and hydrolysis.

**Crystal Structure of  $\text{Ba}_3\text{Ga}_3\text{N}_5$ .** The crystal structure of  $\text{Ba}_3\text{Ga}_3\text{N}_5$  was solved by using single-crystal X-ray diffraction data. The solution and refinement was performed in the monoclinic space group  $C2/c$  (No. 15) with  $a = 16.801(3)$ ,  $b = 8.3301(2)$ ,  $c = 11.623(2)$  Å, and  $\beta = 109.92(3)^\circ$ . The crystallographic data of  $\text{Ba}_3\text{Ga}_3\text{N}_5$  are summarized in Table 1. The atomic coordinates and anisotropic displacement parameters are listed in Tables 2 and 3. Selected bond lengths and angles are shown in Table 4. Further details of the structure investigations are available from the Fachinformationszentrum

**Table 1. Crystallographic Data for  $\text{Ba}_3\text{Ga}_3\text{N}_5$**

$\text{Ba}_3\text{Ga}_3\text{N}_5$	
formula mass, $\text{g}\cdot\text{mol}^{-1}$	691.21
temperature, K	293(2)
crystal system	monoclinic
space group	$C2/c$ (No. 15)
cell parameters, Å	$a = 16.801(3)$ $b = 8.330(2)$ $c = 11.623(2)$
$\beta$ , deg	109.92(3)
$V$ , Å <sup>3</sup>	1529.3(5)
formula units/cell	8
crystal size, mm <sup>3</sup>	$0.04 \times 0.04 \times 0.06$
X-ray density, $\text{g}\cdot\text{cm}^{-3}$	6.004
abs. coefficient, $\mu/\text{mm}^{-1}$	25.553
$F(000)$	2368
diffractometer, radiation	Stoe IPDS, I Mo $K\alpha$ ( $\lambda = 0.71073$ Å)
absorption correction	numerical <sup>28</sup>
$\theta$ range, deg	2.58–30.42
measured reflections	7973
independent reflections	2305
observed reflections	1616
refined parameters	102
GOF	1.008
R indices ( $F_o^2 \geq 2\sigma(F_o^2)$ )	$R1 = 0.0523$ , $wR2 = 0.1301$
R indices (all data)	$R1 = 0.0781$ , $wR2 = 0.1458$

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According to its formula,  $\text{Ba}_3\text{Ga}_3\text{N}_5$  exhibits a high degree of condensation  $\kappa = 3:5$  (i.e., the atomic ratio Ga:N). In accordance with most known nitridogallates,<sup>15,16,33</sup>  $\text{Ba}_3\text{Ga}_3\text{N}_5$  is built up from  $\text{GaN}_4$  tetrahedra (Figures 1 and Figure 2). The latter, centered either by Ga1 or by Ga3, exhibits cis-edge sharing while those around Ga2 show trans-edge sharing. The basic structural motif of the anionic substructure is thus formed by three edge-sharing tetrahedra (Ga1, Ga2, Ga3). By further cis-edge sharing, these units are connected to analogous units in opposite orientation (Ga3, Ga2, Ga1) forming infinite chains running along [010]. The strongly folded chains exhibit further corner-sharing of pairs of  $\text{GaN}_4$  tetrahedra around Ga1 and Ga3, respectively, resulting in three rings. Thus, the high degree of condensation ( $\kappa = 3:5$ ) is a result of the dominance of edge-sharing over corner-sharing, and there are no N-atoms which are terminally bound to Ga. The latter observation is rather atypical for strand-like arrangements of tetrahedra. Moreover, nitrogen atoms  $\text{N}^{[2]}$  and  $\text{N}^{[3]}$  occur in the atomic ratio 3:2 and are bound to two or three Ga atoms, respectively.

As mentioned above, there are only two other ternary Ba nitridogallates.  $\text{Ba}_3\text{Ga}_2\text{N}_4$ <sup>15</sup> contains edge-sharing single chains of  $\text{GaN}_4$  tetrahedra, which are not connected to each other, while  $\text{Ba}_6\text{Ga}_5\text{N}$  is a barium gallide nitride containing  $[\text{Ga}_5]^{7-}$  clusters.<sup>14</sup> In the field of alkaline earth nitridogallates, only  $\text{Sr}_3\text{Ga}_3\text{N}_5$ <sup>16</sup> and  $\beta\text{-Ca}_3\text{Ga}_2\text{N}_4$ <sup>13</sup> show a high degree of condensation of the anionic substructure, resulting in three-dimensional networks. Taking quaternary compounds into account, only in  $\text{Sr}(\text{Ga}_2\text{Mg}_2)\text{N}_4$  a higher degree of condensation of the  $(\text{Ga}/\text{Mg})\text{N}_4$  tetrahedra can be observed, building a three-dimensional network as well.<sup>34</sup> Some nitridogallates build either chains<sup>16</sup> or sheets<sup>16,33</sup> of  $\text{GaN}_4$

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (in Å<sup>2</sup>) of Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub><sup>a</sup>

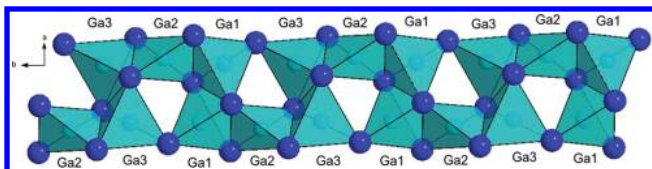
atom	site	x	y	z	U <sub>eq</sub>
Ba1	4e	1/2	0.15547(14)	1/4	0.02076(26)
Ba2	4e	1/2	0.66165(14)	1/4	0.02063(26)
Ba3	8f	0.31113(6)	0.41011(12)	0.11565(8)	0.02632(25)
Ba4	8f	0.29451(5)	0.87596(11)	0.16389(8)	0.02251(23)
Ga1	8f	0.57973(9)	0.43546(19)	0.05727(13)	0.01844(31)
Ga2	8f	0.40244(9)	0.24488(18)	0.95047(13)	0.01784(30)
Ga3	8f	0.57938(9)	0.06821(18)	0.99844(13)	0.01861(31)
N1	8f	0.4548(2)	0.0747(13)	0.8829(10)	0.0174(20)
N2	8f	0.4699(7)	0.3998(14)	0.0792(10)	0.0185(20)
N3	8f	0.3417(8)	0.4055(13)	0.8251(11)	0.0208(21)
N4	8f	0.3484(7)	0.1039(15)	0.0399(11)	0.0205(21)
N5	8f	0.06365(7)	0.2677(14)	0.0016(11)	0.0197(21)

<sup>a</sup>e.s.d.'s in parentheses.Table 3. Anisotropic Displacement Parameters (in Å<sup>2</sup>) for Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub><sup>a</sup>

atom	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Ba1	0.0225(5)	0.0195(5)	0.0187(5)	0	0.0053(4)	0
Ba2	0.0207(5)	0.0202(5)	0.0209(5)	0	0.0072(3)	0
Ba3	0.0207(4)	0.0345(5)	0.0235(4)	0	0.0072(3)	0
Ba4	0.0199(4)	0.0249(4)	0.0229(4)	0.0021(3)	0.0075(3)	0.0009(3)
Ga1	0.0182(6)	0.0178(7)	0.0189(6)	0.0011(5)	0.0057(5)	0.0008(5)
Ga2	0.0186(6)	0.0170(6)	0.0174(6)	0.0002(5)	0.0055(5)	0
Ga3	0.0177(7)	0.0181(7)	0.0192(7)	0	0.0052(5)	0
N1	0.022(5)	0.018(5)	0.017(5)	0	0.015(4)	0
N2	0.019(5)	0.019(5)	0.017(5)	0	0.005(4)	0
N3	0.028(6)	0.010(5)	0.0120(5)	0	0.003(4)	0
N4	0.014(5)	0.023(5)	0.024(5)	0	0.003(4)	0
N5	0.017(5)	0.022(5)	0.025(5)	0	0.013(4)	0

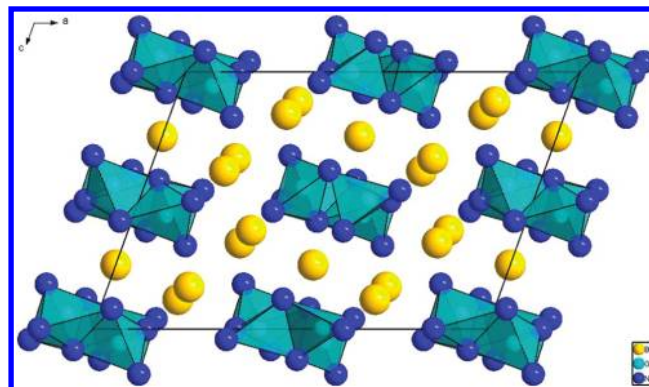
<sup>a</sup>e.s.d.'s in parentheses.Table 4. Selected Bond Lengths (Å) and Angles (deg) in Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub><sup>a</sup>

Ba1–	N1	2.727(10) × 2	Ba4–	N1	3.038(12)	N1–Ba1–N1	90.7(5)
	N2	2.767(11) × 2		N3	2.937(11)	N4–Ba1–N4	163.0(5)
	N4	2.898(11) × 2		N4	2.719(12)	N3–Ba3–N2	104.2(4)
Ba2–	N1	2.930(12) × 2	Ba3–	N4	2.677(11)	N4–Ba4–N3	146.1(4)
Ga1–	N2	1.970(12)	Ga3–	N1	2.047(11)		
	N2	2.048(11)		N1	2.067(12)		
	N3	2.034(12)		N4	2.024(12)		
	N5	1.923(11)		N5	1.913(12)		

<sup>a</sup>e.s.d.'s in parentheses.Figure 1. Highly condensed strands of GaN<sub>4</sub> tetrahedra running along [010].

tetrahedra. A number of alkaline earth nitridogallates contain no GaN<sub>4</sub> tetrahedra at all but show noncondensed trigonal planar GaN<sub>3</sub> units.<sup>17,18,35</sup>

In Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub>, there are four crystallographically different Ba<sup>2+</sup> sites whose coordination numbers vary from 4 to 8 (Figure 3). The fourfold coordination represents a distorted tetrahedron with rather short distances Ba3–N of 2.677 and 2.775 Å. Ba1 and Ba4 are coordinated by six nitrogen atoms in a distorted octahedron. A higher coordination number of eight is observed

Figure 2. Crystal structure of Ba<sub>3</sub>Ga<sub>3</sub>N<sub>5</sub>, viewing direction along [010]. Ba<sup>2+</sup> yellow, N<sup>3-</sup> dark blue, Ga<sup>3+</sup> inside the shown tetrahedra (light blue).



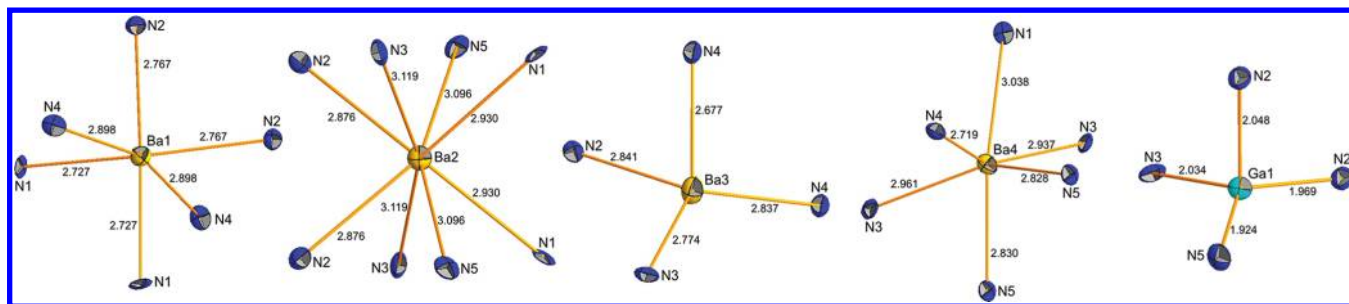


Figure 3. Coordination of metal ions in  $\text{Ba}_3\text{Ga}_3\text{N}_5$ . Atoms are shown in ellipsoids with 50% probability; bond lengths are given in Å.

around Ba2. The resulting irregular quadratic prism contains a particularly elongated Ba2–N3 distance (3.119 Å). This distance is slightly longer than expected from the sum of the ionic radii (2.88–3.0 Å) while the values for Ba3–N are smaller.<sup>36,37</sup> All other Ba–N bond lengths are in good agreement with the sum of the ionic radii. Typically, alkaline earth ions are coordinated by four or six nitrogen atoms in nitridogallates or nitridosilicates.<sup>15,16,38,39</sup> In contrast, the coordination number eight of an alkaline earth ion in nitridogallates or (oxo)nitridosilicates is only known for  $\text{LiSrGaN}_2$ ,<sup>33</sup>  $\text{Sr}(\text{Mg}_2\text{Ga}_2)\text{N}_4$ ,<sup>34</sup> and  $\text{BaSi}_2\text{O}_2\text{N}_2$ <sup>25</sup> so far.

An alternative description to the crystal structure may be achieved by introducing anion centered polyhedra. In  $\text{Ba}_3\text{Ga}_3\text{N}_5$ , most of the five nitrogen sites are coordinated by six metal atoms: N1 and N2 are each coordinated by three Ba and three Ga atoms, respectively. The sixfold coordination of N3 and N4 consists of two Ga and four Ba atoms. N2 and N4 are surrounded by quite regular octahedra, with typical distances Ga–N (2.006–1.974 Å) and Ba–N (2.726–2.886 Å).<sup>15,16</sup> The polyhedron around N1 is quite irregular, due to the short distance N1–Ba1 of 2.727 Å. The anisotropic displacement ellipsoid of N1 is elongated markedly pointing toward Ba1. The polyhedron around N3 is an octahedron which is distorted due to the long bond Ba2–N resulting in a squared pyramid.

Surprisingly, the crystal structure of the analogous Sr compound is completely different.  $\text{Sr}_3\text{Ga}_3\text{N}_5$ <sup>16</sup> was described recently by Clarke and DiSalvo. It was synthesized in a Na flux at 760 °C. The orange-yellow compound crystallizes in triclinic space group  $P\bar{1}$ . In this compound, a three-dimensional network of corner- and edge-sharing  $\text{GaN}_4$  tetrahedra typical for such a high  $\kappa$ -value was reported. In contrast, the anionic substructure of  $\text{Ba}_3\text{Ga}_3\text{N}_5$  contains a hitherto unknown structural motif as described above. In both compounds corner- and edge-sharing can be observed, but in the Ba compound edge-sharing is more dominant.

Calculations of the Madelung part of the lattice energy were carried out in order to confirm the crystal structure of  $\text{Ba}_3\text{Ga}_3\text{N}_5$ .<sup>40,41</sup> The results of these MAPLE<sup>42</sup> calculations are summarized in Table 5. The partial MAPLE values for all atoms are in good agreement with reference data reported before.<sup>43</sup> To verify the electrostatic consistency of the refined crystal structure, the calculated MAPLE sum of  $\text{Ba}_3\text{Ga}_3\text{N}_5$  was compared with total MAPLE values of constituting binary and ternary nitrides. One model contains a well-known nitridosilicate, and the other model contains the hypothetical binary nitride  $\text{Ba}_3\text{N}_2$ .<sup>44,45</sup> Both models differ only slightly from the calculated value for  $\text{Ba}_3\text{Ga}_3\text{N}_5$ . With these results the electrostatic consistency is proven and the refined crystal structure is confirmed.

Table 5. Partial MAPLE and Total MAPLE Values [in kJ/mol] of  $\text{Ba}_3\text{Ga}_3\text{N}_5$ <sup>a</sup>

		calculated MAPLE value	$\Delta$ , %
Ba		1628.06–1824.34	
Ga		4930.00–5090.14	
N		4379.99–4821.36	
$\text{Ba}_3\text{Ga}_3\text{N}_5$		41503.34	
+	3 GaN		
+	1.5 $\text{Ba}_2\text{Si}_5\text{N}_8$		
–	2.5 $\text{Si}_3\text{N}_4$	43830.36	0.75
	$\text{Ba}_3\text{N}_2$ <sup>44,45</sup>		
+	GaN	43683.77	0.41

<sup>a</sup>Typical partial MAPLE values [kJ/mol]:  $\text{Ba}^{2+}$ , 1500–2000;  $\text{Ga}^{3+}$ , 4500–6000;  $\text{N}^{3-}$ , 3000–6000.<sup>21,46–48</sup>

**Luminescence Investigations.**  $\text{Eu}^{2+}$ -doped samples of the title compound show red luminescence under UV irradiation. Luminescence investigations were performed on single crystals of  $\text{Ba}_3\text{Ga}_3\text{N}_5:\text{Eu}^{2+}$  ( $\text{Eu}^{2+}$  content ca. 2 mol %) sealed in glass capillaries. All measurements show comparable results, so an exemplary spectrum of one crystal is shown in Figure 4. The

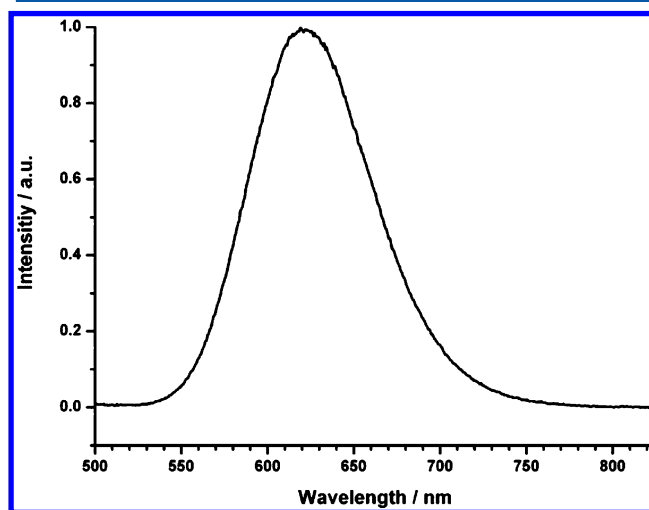
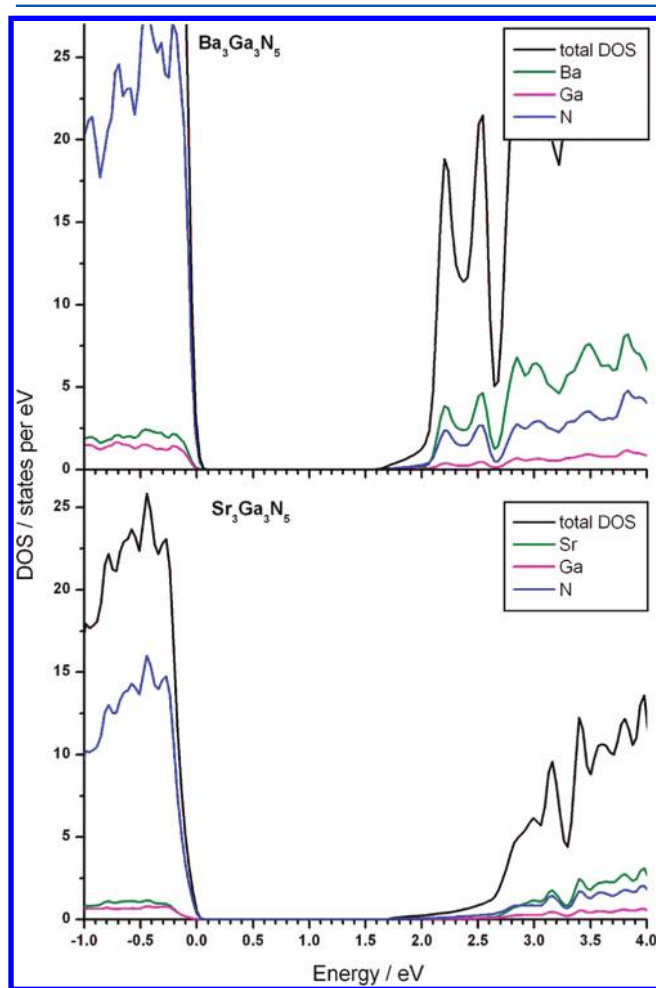


Figure 4. Emission spectrum of  $\text{Eu}^{2+}$ -doped  $\text{Ba}_3\text{Ga}_3\text{N}_5$ , excitation at 365 nm.

365 nm excitation yields an emission band peaking at 638 nm with a lumen equivalent of 173 lm/W and CIE color coordinates  $x = 0.644$ ,  $y = 0.347$ . The emission band is quite narrow with a full width at half-maximum (FWHM) of 2123  $\text{cm}^{-1}$  (84.7 nm). As a result of the strong red shift of the emission band, we expect the emission originating from  $\text{Eu}^{2+}$  in

octahedral coordination,<sup>49</sup> as found for the Ba1 and the Ba4 site. A comparison with other known red emitters is difficult, because to our knowledge this is the first time a luminescent Eu-doped nitridogallate is reported. Compared with other nitridic phosphor materials (e.g.,  $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ ),<sup>22,23,50–52</sup>  $\text{Ba}_3\text{Ga}_3\text{N}_5:\text{Eu}^{2+}$  shows emission in the same spectral region. For  $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$  (2 mol % Eu), an emission maximum around 620 nm is reported and also the color coordinates ( $x, y = 0.638, 0.359$ ) and emission width (FWHM  $\sim 1950 \text{ cm}^{-1}$ ) are comparable.<sup>53</sup> Other reported  $\text{Eu}^{2+}$ -doped Ba compounds (e.g.,  $\text{Ba}_{1.89}\text{Eu}_{0.11}\text{Si}_5\text{N}_8$ )<sup>54</sup> show an emission around 600 nm.

**DFT Calculations.** Calculation of the electronic structures for  $\text{Ba}_3\text{Ga}_3\text{N}_5$  and isoelectronic  $\text{Sr}_3\text{Ga}_3\text{N}_5$  were carried out. As WIEN2k allows only settings with a monoclinic angle  $\gamma$  the calculation of  $\text{Ba}_3\text{Ga}_3\text{N}_5$  was performed in monoclinic space group  $B2/b$ . Therefore, the crystal parameters were transformed accordingly. Figure 5 shows the resulting density of



**Figure 5.** Calculated density of states (DOS) of  $\text{Ba}_3\text{Ga}_3\text{N}_5$  (top) and  $\text{Sr}_3\text{Ga}_3\text{N}_5$  (bottom). Displayed are the respective overall DOS and the single contributions of the elements.

states (DOS) of  $\text{Ba}_3\text{Ga}_3\text{N}_5$  and  $\text{Sr}_3\text{Ga}_3\text{N}_5$ . The title compound shows an electronic band gap of 1.46 eV while the Sr-compound shows a slightly larger value of 1.53 eV. As a result of the insufficient description of the exchange correlation potential in DFT calculations, the calculated band gaps are usually smaller than the real ones. In both compounds the highest occupied states are mainly influenced by nitrogen

contributions (over 60%), whereas the lowest unoccupied states are dominated by nitrogen and Ba/Sr contributions. A similar result was reported earlier for  $\text{LiBa}_5\text{GaN}_3\text{F}_5$  where the transition also occurs from a nitrogen dominated state in a hybrid nitrogen metal state.<sup>43</sup>

## CONCLUSION

In this contribution, a new ternary Ba nitridogallate, the third known at all, was reported. This compound exhibits a novel structural feature of  $\text{GaN}_4$  tetrahedra that build up highly condensed strands along [010]. The coordination of the Ba atoms varies from a low coordination number of four to a higher coordination of eight nitrogen atoms. Employing anion centered polyhedra for structure description, four nitrogen sites are sixfold coordinated. The N5 site is surrounded by five cations, building a squared pyramid. Confirmation of the crystal structure was accomplished by MAPLE calculations. In contrast, the crystal structure of the isoelectronic compound  $\text{Sr}_3\text{Ga}_3\text{N}_5$ <sup>16</sup> shows a connection of  $\text{GaN}_4$  tetrahedra in all three directions, resulting in a three-dimensional anionic network. Luminescence investigations of  $\text{Eu}^{2+}$ -doped samples of the title compound show a strongly red-shifted peak emission at 638 nm with FWHM of  $2123 \text{ cm}^{-1}$ . The fact that as of yet  $\text{Ba}_3\text{Ga}_3\text{N}_5$  has only been obtained as a side phase limits the further development of  $\text{Ba}_3\text{Ga}_3\text{N}_5:\text{Eu}^{2+}$  as a LED phosphor. Nevertheless, the promising luminescence properties of this compound are a strong incentive to further optimize its synthesis. DFT calculations of  $\text{Ba}_3\text{Ga}_3\text{N}_5$  and the isoelectronic Sr compound were done to determine the band gap resulting in a value 1.46 eV for the Ba compound (1.53 eV for  $\text{Sr}_3\text{Ga}_3\text{N}_5$ ). The transition takes place from a nitrogen state to a hybrid metal (Sr or Ba) nitrogen state.

The results of this investigation illustrate the potential of nitridogallates as host lattices for  $\text{Eu}^{2+}$ -doped luminescent materials. Both from a structural point of view and also concerning their materials properties, there are similarities between nitridosilicates and nitridogallates.

## ASSOCIATED CONTENT

### Supporting Information

X-ray crystallographic information file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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