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A novel nitridogallate fluoride $LiBa_5GaN_3F_5$ — Synthesis, crystal structure, and band gap determination

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ABSTRACT

$LiBa_5GaN_3F_5$ was obtained as red crystals by reaction of Ba, Ga, NaN_3 and EuF_3 in a Na/Li flux at 760 °C in weld-shut tantalum crucibles. The crystal structure (*Pnma* (no. 62), $a = 15.456(3)$, $b = 5.707(1)$, $c = 12.259(3)$ Å, $Z = 4$) was solved on the basis of single-crystal X-ray diffraction data. In the solid there are trigonal planar $[GaN_3]^{6-}$ ions and zigzag chains of vertex sharing LiF_6 octahedrons surrounded by Ba^{2+} ions. Optical measurements and calculations of the electronic structure revealed a band gap of ≤1.9 eV. According to the calculations, the observed transition occurs from a nitrogen state into a hybrid Ba/N state.

1. Introduction

Ternary nitrides of Ga in combination with alkaline earth metals (e.g., Sr, Ba) are known since a couple of years [1–4], but only a small number of quaternary examples have been reported recently [5–7]. Most of these compounds have been synthesized in sodium melts which due to addition of alkaline earth metals exhibit an increased solubility of nitrogen [8]. Syntheses were performed in closed niobium crucibles, utilizing additional azides as nitrogen source. Sr_3GaN_3, Sr_6GaN_5 [2], Sr_4GaN_3O and $Sr_4GaN_3(CN_2)$ [5] contain non condensed ("isolated") $[GaN_3]^{6-}$ while $Ba_3Ga_2N_4$ and $Sr_3Ga_2N_4$ are made up of trans edge sharing GaN_4 tetrahedrons building infinite chains [1,4]. Two- or three-dimensional networks of vertex sharing GaN_4 tetrahedrons have been found in $Ca_3Ga_2N_4$, $Sr_3Ga_3N_5$ [4] and $LiSrGaN_2$ [6], respectively. Thus, structural motifs similar to nitridosilicates (e.g., $BaSi_7N_{10}$; Eu_2SiN_3) [9,10] occur in the nitridogallates mentioned above. Recently, we have reported about synthetic approaches to control the dimensionality of nitridosilicates employing lithium melts [11]. In comparison with nitridosilicates, the field of nitridogallates is more unexplored but utilization of the lithium flux technique may lead to a larger structural variety analogously to our experience with nitridosilicates.

2. Experimental

The synthesis of $LiBa_5GaN_3F_5$ was carried out in Ta crucibles (30 mm length, 9.5 mm diameter, 0.5 mm wall thickness). Under argon atmosphere (glove box Unilab, MBraun), 0.35 mmol (22.8 mg) NaN_3 (Acros, 99%), 0.138 mmol (9.6 mg) Ga (AluSuisse, 99.999%), 0.549 mmol (75.4 mg) Ba (Sigma Aldrich, 99.99%) and 0.027 mmol (5.7 mg) EuF_3 (Sigma Aldrich, 99.99%) were mixed and filled into the Ta crucible. For the flux 2.174 mmol (50.0 mg) Na (Sigma Aldrich, 99.95%) and 0.145 mmol (1.0 mg) Li (Sigma Aldrich, 99.9%) were added. The Ta crucible was sealed under argon by arc welding. To protect the Ta crucible from oxidation, it was placed into a silica tube under argon atmosphere. In a tube furnace the crucible was heated to 760 °C with a rate of 50 °C h^{-1}. The temperature was maintained for 48 h and then lowered with 3.7 °C h^{-1} to 200 °C. Once the temperature reached 200 °C, the furnace was turned off and cooled down to room temperature. The Ta crucible was opened and Na was separated from the reaction products by evaporation at 320 °C under vacuum (0.1 Pa) for 18 h. From the inhomogeneous gray product, red needle-shaped single crystals (200–600 μm) were isolated (cf. Fig. 1), enclosed in glass capillaries and sealed under argon atmosphere. X-ray diffraction data were collected at room temperature with a STOE IPDS I

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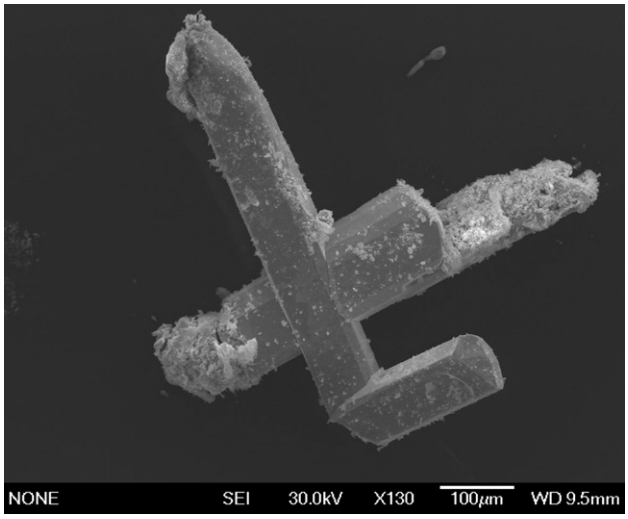

Fig. 1. SEM micrograph of $LiBa_5GaN_3F_5$ crystals.

Table 1
Crystallographic data of $LiBa_5GaN_3F_5$.

Formula	$LiBa_5GaN_3F_5$
Crystal system	orthorhombic
Space group	*Pnma* (no. 62)
Lattice parameters (Å)	$a = 15.456(3)$, $b = 5.707(1)$, $c = 12.259(3)$
Cell volume (Å^3)	1081.3(4)
Formula units per unit cell	4
Density (g cm^{-3})	5.531
μ (mm^{-1})	20.41
T (K)	293(2)
F(000)	1520
Profile range	$5.8 \le 2\theta \le 63.2$
Index ranges	$-20 \le h \le 18$ $-6 \le k \le 6$ $-15 \le l \le 15$
Independent reflections	1286 [R(int) = 0.072]
Refined parameters	89
Goodness of fit	1.057
R_1 (all data); R_1 ($F^2 > 2\sigma(F^2)$)	0.0230, 0.0212
wR_2 (all data); wR_2 ($F^2 > 2\sigma(F^2)$)	0.0512, 0.0505
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.56, −2.13

diffractometer. A numerical absorption correction using the programs XRED [12] and XSHAPE [13] was applied. The crystal structure was solved by using direct methods with SHELXS [14]. The refinement of the structure was carried out by the method of least-squares using SHELXL [14]. The chemical composition was confirmed by energy dispersive X-ray spectroscopy (EDX) using a JSM-6500F scanning microscope (Jeol) provided with a Si/Li EDX detector (Oxford Instruments, model 7418). Optical spectra of $LiBa_5GaN_3F_5$ were measured with a modified microcrystal spectrophotometer CARY 17 (Spectra Services, ANU Canberra, Australia) [15–17]. Calculations of the band gap were carried out with the program package WIEN2K [18] utilizing the structural data from the single-crystal structure refinement.

Further details of the crystal structure investigations can be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein–Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-421592.

3. Results and discussion

3.1. Crystal structure

The crystal structure was solved and refined in orthorhombic space group *Pnma* (no. 62) with $a = 15.456(3)$, $b = 5.707(1)$ and $c = 12.259(3)$ Å. The crystallographic data of $LiBa_5GaN_3F_5$ is summarized in Table 1, the atomic coordinates and the isotropic displacement parameters are listed in Table 2.

In the crystal $LiBa_5GaN_3F_5$ zigzag chains of vertex sharing LiF_6 octahedrons running along [010] (cf. Fig. 2). Perpendicular to these chains, Ba atoms are arranged in layers. Likewise perpendicular to [010] "isolated" trigonal planar $[GaN_3]^{6-}$ ions are found. The Ga–N bond-lengths range from 1.90 to 1.95 Å (Fig. 3) and agree well with the sum of the ionic radii [19–21] as well as with typical Ga–N distances (e.g., Sr_4GaN_3O, Ga–N:1.88–1.92 Å) [5]. Similar $[GaN_3]^{6-}$ ions have been found in Sr_3GaN_3, Sr_6GaN_5 [2], Sr_4GaN_3O and $Sr_4GaN_3(CN_2)$ [5]. The coordination sphere of the trigonal planar $[GaN_3]^{6-}$ ions can be described as three-capped trigonal prisms of Ba^{2+} atoms. In Sr_3GaN_3 [2] similar trigonal prism of Sr^{2+} atoms have been observed. The N^{3-} atoms are likewise surrounded in distorted octahedrons of five Ba^{2+} and one Ga^{3+} atom.

Li^+ does not directly coordinate to the $[GaN_3]^{6-}$ ions but is surrounded by six F^- in a distorted octahedron. The Li–F distances are ranging between 1.97 and 1.98 Å for the equatorial F2 and F1 and 2.33–2.39 Å for the axial F3 and F4 (cf. Fig. 3). The latter ones exceed significantly the sum of the ionic radii (2.06 Å) [19] while the equatorial Li–F distances are slightly shorter than reported distances in other LiF_6 octahedrons (K_2LiAlF_6, Li–F: 2.109 Å) [22,23]. In the second coordination sphere, the octahedron LiF_6 is coordinated by eight Ba^{2+} in a cubic way, comparable with the cubic Ca^{2+}-coordination of Ti^{4+} in $CaTiO_3$. The coordination of F^- occurs in distorted octahedrons of five Ba^{2+} and one Li^+. Only F2 is coordinated by two Li^+ and four Ba^{2+}. The atomic distances Ba–F and Li–F are mentioned above. The thermal displacement parameter $U_{iso}{}^*/U_{eq}$ of F4 is considerably higher (cf. Table 3) in comparison with the other values for fluorine atoms. One reason for this observation may be the fact, that – considering the octahedron LiF_6 – the F4 atom is a "free" one and does not connect to the next octahedrons. Additionally, the U_{11} value for F4 is almost three times higher than the values for the other F^-. The short distance between Ba4–F4 (2.83 Å) may be responsible for this observation. The F3 atom has an even shorter distance to Ba4 (2.76 Å) and is also a non-bridging one. Here we can also observe a little higher $U_{iso}{}^*/U_{eq}$ value.

Table 2
Atomic coordinates and isotropic displacement parameters (Å^2) of $LiBa_5GaN_3F_5$, standard deviations in parentheses.

Atom	Wyckoff position	x	y	z	$U_{iso}{}^*/U_{eq}$
Ba1	4*c*	0.43534 (2)	¼	0.68180 (2)	0.0092 (1)
Ba2	4*c*	0.51012 (2)	−¼	0.87769 (3)	0.0090 (1)
Ba3	4*c*	0.34365 (2)	−¼	0.47028 (3)	0.0089 (1)
Ba4	4*c*	0.24513 (2)	−¼	0.77891 (3)	0.0100 (1)
Ba5	4*c*	0.16417 (2)	¼	0.63252 (2)	0.0109 (1)
Ga1	4*c*	0.35910 (4)	¼	0.92467 (4)	0.0076 (2)
F1	8*d*	0.4111 (2)	0.0121 (5)	0.3013 (2)	0.0151 (6)
F2	4*a*	½	0	½	0.0131 (7)
F3	4*c*	0.4075 (3)	−¼	0.6854 (3)	0.0171 (8)
F4	4*c*	0.1779 (4)	−¼	0.9936 (3)	0.027 (1)
N1	4*c*	0.4799 (4)	¼	0.8980 (4)	0.014 (2)
N2	4*c*	0.2813 (4)	¼	0.8020 (4)	0.013 (2)
N3	4*c*	0.3152 (4)	¼	1.0734 (5)	0.012 (2)
Li1	4*c*	0.459 (2)	¼	0.4020 (8)	0.026 (3)