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Icosahedral Li clusters in the structures of $Li_{33.3}Ba_{13.1}Ca_3$ and $Li_{18.9}Na_{8.3}Ba_{15.3}$

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Abstract

The intermetallic phases $Li_{33.3}Ba_{13.1}Ca_3$ and $Li_{18.9}Na_{8.3}Ba_{15.3}$ have been prepared and their crystal structures have been determined. According to single-crystal X-ray diffraction data, both compounds crystallize in new structure types with trigonal unit cells ($Li_{33.3}Ba_{13.1}Ca_3$: $R\bar{3}c$, $a = 19.9127(4)$ Å, $c = 90.213(3)$ Å, $Z = 18$, $V = 30{,}978(1)$ Å^3 and $Li_{18.9}Na_{8.3}Ba_{15.3}$: $P\bar{3}$, $a = 20.420(3)$ Å, $c = 92.914(19)$, $Z = 18$, $V = 33{,}550(10)$ Å^3). The first compound can be described as a complicated variant of the arsenic structure. The second has similar packing of the Ba atoms but differs from the Ca-containing phase in the packing of the light elements. Both compounds contain icosahedron-based polytetrahedral clusters, typical for Li-rich phases, e.g. $Ba_{19}Li_{44}$.

Keywords: Subnitride; Barium; Sodium; Lithium clusters; Intermetallic compounds

1. Introduction

A number of binary compounds between alkali and alkaline-earth elements have been reported. Two compounds are known for Ba and Li ($BaLi_4$ [1,2] and $Ba_{19}Li_{44}$ [3]), two for Sr and Li (Sr_6Li_{23} [4] and Sr_3Li_2 [5]) and one for Ca and Li ($CaLi_2$ [6,7]). Two binary compounds were found for Na and Ba (Na_2Ba [8] and NaBa [9]), but none with the heavier homologues of Na, neither barium–calcium nor sodium–lithium phases. The chemistry of ternary alkali–alkaline-earth metal compounds was opened by the discovery of $Li_{13}Na_{29}Ba_{19}$ [10] during efforts to prepare subnitrides. Our exploration into quaternary Li–Na–Ba and Li–Ba–Ca subnitrides again led to new ternary intermetallic phases which turned out to be $Li_{33.3}Ba_{13.1}Ca_3$ and $Li_{18.9}Na_{8.3}Ba_{15.3}$, respectively. Here, we report these compounds and compare them with Ba–Li intermetallics and metal-rich nitride phases.

2. Experimental

2.1. Reagents

Ba metal and Ca metal (Merck, 99%, distilled twice with intermediate heating in a closed tantalum container at 1200 K in vacuum to remove hydrogen), Li metal (Merck, 99%) and $Ba(N_3)_2$ (Schuchardt, 98.5%, recrystallized and dried under vacuum) were used for syntheses.

2.2. Syntheses

Due to the extreme sensitivity of the reagents and products to air, all handling was performed under purified argon using Schlenk technique or a glove box (Ar 99.996%, $H_2O < 0.1$ ppm; $O_2 < 0.05$ ppm). Reactions were run in closed tantalum containers which were arc-welded and sealed inside Pyrex glass ampoules.

$Li_{33.3}Ba_{13.1}Ca_3$: Three samples were prepared with the overall stoichiometries $Li_8Ba_2Ca_2N$ (sample A: 366.7 mg Ba, 116.5 mg Ca, 81.5 mg Li and 53.7 mg $Ba(N_3)_2$), $Li_{33}Ba_{13}Ca_3$ (sample B: 500.0 mg Ba, 33.6 mg Ca and 64.7 mg Li) and $Li_{50}Ba_{13}Ca_3$ (sample C: 500.0 mg Ba, 33.6 mg Ca and 98.0 mg Li).

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$Li_{18.9}Na_{8.3}Ba_{15.3}$: Two samples were prepared with the overall stoichiometries $Li_8Na_8Ba_6N$ (sample D: 486.1 mg Ba, 111.6 mg Na, 34.0 mg Li and 22.4 mg $Ba(N_3)_2$) and $Li_{30}Na_{8.4}Ba_{15.3}$ (sample E: 500.0 mg Ba, 46.0 mg Na and 50.0 mg Li). All these were heated to 350 °C and annealed at this temperature for 30 h, followed by cooling to 120 °C at a rate of 1 °C h^{-1}, further annealing for 1 month, and cooling to room temperature by switching off the furnace.

Single crystals of $Li_{33.3}Ba_{13.1}Ca_3$ (**I**) and $Li_{18.9}Na_{8.3}Ba_{15.3}$ (**II**) for X-ray analysis were selected from samples A and D, respectively. Single crystals of **II** were also found in other samples where this phase observed together with $Li_{13}Na_{29}Ba_{19}$, NaBa, $BaLi_4$ and some subnitride phases in two- or three-phase samples. In attempts to prepare bulk powder samples from a mixture of the elements, **I** was observed with maximal yield about 60% in sample C and **II** prepared as pure product (sample E) according to powder X-ray diffraction analysis. In sample B aimed at the stoichiometric composition of **I**, this compound was observed together with $BaLi_4$, $CaLi_2$ and metallic Ba. **II** was obtained together with approximately 25% of NaBa (according to powder X-ray diffraction analysis) and presumably Li that could be explained by inhomogeneity of the samples.

2.3. X-ray diffraction and structure refinement

Single crystals of **I** and **II** were sealed under argon atmosphere in glass capillaries for X-ray investigation. Single-crystal diffraction data were collected at room temperature using a STOE IPDS II diffractometer with monochromatized Mo$K\alpha$ radiation by oscillation of the crystal around the ω-axis. The starting atomic parameters derived via direct methods using the program SIR 97 [11] were subsequently refined with the program SHELX-97 [12] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms for **I** and for Ba for in the case of **II** within the WinGX program package [13] in the space groups $R\bar{3}c$ and $P\bar{3}$, respectively. The positions of the Li atoms were found in difference Fourier maps according to reasonable interatomic distances. Large remaining electron density 5.30 and $-4.78\ e^-\ Å^{-3}$ in direct vicinity (0.5–0.9 Å) to heavy atom positions cannot be assigned to any new atom. Details of the crystal structure investigation are summarized in Tables 1–3.

X-ray powder diffraction patterns were collected on a powder diffractometer STOE STADI P with monochromated Mo$K\alpha_1$ radiation ($3° \leqslant 2\theta \leqslant 33°$, step size 0.1°, measurement time per step 120 s). The calculated X-ray powder pattern from the obtained crystal structure is in the best agreement with the experimental pattern of sample E (Fig. 1).

2.4. Thermal analysis

All thermal analyses were performed with sample amounts of 20–40 mg in an argon atmosphere. The

Table 1
Details of the crystal structure investigation and refinement for $Li_{33.3}Ba_{13.1}Ca_3$ and $Li_{18.9}Na_{8.3}Ba_{15.3}$

Empirical formula	$Li_{33.305(3)}Ba_{13.076(7)}Ca_{2.95(1)}$	$Li_{18.9(7)}Na_{8.3(7)}Ba_{15.3(1)}$
Formula weight	2145.5	2422.8
Temperature (K)	293(2)	
Wavelength (Å)	0.71073	
Crystal system	Trigonal	
Space group	$R\bar{3}c$	$P\bar{3}$
a (Å)	19.9127(4)	20.420(3)
c (Å)	90.213(3)	92.914(19)
Volume (Å^3)	30,978(1)	33,550(1)
Z	18	18
Density (calculated) (g cm^{-3})	2.070	2.159
μ (mm^{-1})	7.559	8.683
Crystal size (mm)	$0.14 \times 0.12 \times 0.12$	$0.22 \times 0.22 \times 0.18$
$F(0\,0\,0)$	12,600	19,500
Index ranges	$-24 \leqslant h \leqslant 24$ $-24 \leqslant k \leqslant 24$ $-112 \leqslant l \leqslant 112$	$-20 \leqslant h \leqslant 18$ $-20 \leqslant k \leqslant 20$ $-77 \leqslant l \leqslant 79$
Reflections collected	65,919	51,202
Independent reflections	6588	17,813
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	6588/0/226	17813/0/863
Data averaging	$R_{int} = 0.122$, $R_\sigma = 0.053$	$R_{int} = 0.046$, $R_\sigma = 0.069$
Goodness-of-fit on F^2	1.32	1.09
Final R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.102$, $wR_2 = 0.1586$	$R_1 = 0.111$, $wR_2 = 0.310$
R indices (all data)	$R_1 = 0.121$, $wR_2 = 0.164$	$R_1 = 0.178$, $wR_2 = 0.337$
Largest diffraction peak and hole (e$^-$ Å^{-3})	1.32 and −1.40	5.30 and –4.78

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = [\sum[w(F_o^2 - F_o^2)]/[\sum(w|F_o|^2)^2]]^{1/2}$.

Table 2
Atomic coordinates and equivalent/isotropic thermal displacement parameters for $Li_{33.3}Ba_{13.1}Ca_3$

Atom	Position	*x*	*y*	*z*	$U_{eq/iso}$ (Å^2)	*G*
Ba1	12*c*	0	0	0.10696(3)	0.031(1)	0.68(2)
Ca1	12*c*	0	0	0.10696(3)	0.031(1)	0.32(2)
Ba2	12*c*	0	0	0.06148(3)	0.031(1)	0.49(2)
Ca2	12*c*	0	0	0.06148(3)	0.031(1)	0.51(2)
Ba3	18*e*	0.86971(8)	0	0.25	0.0327(7)	0.90(2)
Ca3	18*e*	0.86971(8)	0	0.25	0.0327(7)	0.10(2)
Ba4	18*e*	0.65184(7)	0	0.25	0.0335(5)	1
Ba5	36*f*	0.21206(6)	0.33229(6)	0.02215(1)	0.0340(4)	1
Ba6	36*f*	0.32391(6)	0.19655(6)	0.14529(1)	0.0350(5)	0.96(1)
Ca6	36*f*	0.32391(6)	0.19655(6)	0.14529(1)	0.0350(5)	0.04(1)
Ba7	36*f*	0.32403(6)	0.19304(6)	0.02163(1)	0.0342(5)	0.95(2)
Ca7	36*f*	0.32403(6)	0.19304(6)	0.02163(1)	0.0342(5)	0.05(2)
Ba8	36*f*	0.12647(6)	0.00005(6)	0.20963(1)	0.0344(5)	0.96(1)
Ca8	36*f*	0.12647(6)	0.00005(6)	0.20963(1)	0.0344(5)	0.04(1)
Ba9	36*f*	0.00681(8)	0.19931(8)	0.12100(2)	0.0328(6)	0.71(1)
Ca9	36*f*	0.00681(8)	0.19931(8)	0.12100(2)	0.0328(6)	0.29(1)
Ba10	36*f*	0.00708(8)	0.19881(8)	0.04672(2)	0.0315(7)	0.61(1)
Ca10	36*f*	0.00708(8)	0.19881(8)	0.04672(2)	0.0315(7)	0.39(1)
Li1	6*b*	0	0	0	0.02(1)	1
Li2	12*c*	0	0	0.1740(5)	0.04(1)	1
Li3	18*e*	0.2103(3)	0	0.25	0.058(13)	1
Li4	36*f*	0.101(2)	0.099(2)	0.0261(3)	0.037(6)	1
Li5	36*f*	0.190(2)	0.181(2)	0.0538(4)	0.039(7)	1
Li6	36*f*	0.269(2)	0.249(2)	0.0837(3)	0.040(7)	1
Li7	36*f*	0.099(2)	0.100(3)	0.1434(5)	0.056(9)	1
Li8	36*f*	0.001(2)	0.316(2)	0.2205(4)	0.036(6)	1
Li9	36*f*	0.095(2)	0.180(2)	0.0841(4)	0.054(9)	1
Li10	36*f*	0.007(2)	0.163(2)	0.0057(4)	0.049(8)	1
Li11	36*f*	0.186(1)	0.081(1)	0.0838(3)	0.023(5)	1
Li12	36*f*	0.161(2)	0.160(2)	0.1772(3)	0.024(5)	1
Li13	36*f*	0.004(2)	0.157(2)	0.1642(3)	0.030(6)	1
Li14	36*f*	0.195(2)	0.333(2)	0.0652(4)	0.035(6)	1
Li15	36*f*	0.349(2)	0.176(2)	0.0651(3)	0.039(6)	1
Li16	36*f*	0.347(2)	0.174(2)	0.1017(3)	0.043(7)	1
Li17	36*f*	0.188(2)	0.180(2)	0.1133(4)	0.044(7)	1
Ca18	36*f*	0.0066(6)	0.3352(6)	0.0134(1)	0.035(4)	0.29(3)
Li18	36*f*	0.0066(6)	0.3352(6)	0.0134(1)	0.035(4)	0.71(3)
Ca19	36*f*	0.240(1)	0.240(1)	0.2112(3)	0.03(1)	0.06(3)
Li19	36*f*	0.240(1)	0.240(1)	0.2112(3)	0.03(1)	0.94(3)

Table 3
Atomic coordinates and equivalent/isotropic thermal displacement parameters for $Li_{18.9}Na_{8.3}Ba_{15.3}$

Atom	Position	*x*	*y*	*z*	U_{eq} (Å^2)	*G*
Ba1	2*c*	0	0	0.06145(7)	0.046(2)	1
Ba2	2*c*	0	0	0.43861(7)	0.051(2)	1
Ba3	2*c*	0	0	0.39417(7)	0.046(2)	1
Ba4	2*c*	0	0	0.10585(7)	0.045(2)	1
Ba5	2*d*	0.3333	0.6667	0.77233(8)	0.044(3)	0.86(2)
Ba6	2*d*	0.3333	0.6667	0.27229(6)	0.026(1)	1
Ba7	2*d*	0.3333	0.6667	0.72758(8)	0.047(3)	0.85(2)
Ba8	2*d*	0.3333	0.6667	0.22748(6)	0.025(1)	1
Ba9	2*d*	0.3333	0.6667	0.3954(2)	0.090(9)	0.48(2)
Ba10	2*d*	0.3333	0.6667	0.89500(9)	0.041(3)	0.73(2)
Ba11	2*d*	0.3333	0.6667	0.93931(9)	0.042(3)	0.76(2)
Ba12	2*d*	0.3333	0.6667	0.4397(2)	0.09(1)	0.45(2)
Ba13	2*d*	0.3333	0.6667	0.6052(1)	0.047(5)	0.53(2)
Ba14	2*d*	0.3333	0.6667	0.5606(1)	0.051(5)	0.58(2)
Ba15	2*d*	0.3333	0.6667	0.0605(5)	0.09(2)	0.20(2)
Ba16	2*d*	0.3333	0.6667	0.1037(4)	0.09(2)	0.23(2)
Ba17	6*g*	0.0021(1)	0.3506(2)	0.25011(4)	0.045(1)	1
Ba18	6*g*	0.0010(2)	0.5468(2)	0.18942(4)	0.049(1)	1
Ba19	6*g*	0.3444(2)	0.2051(2)	0.18904(4)	0.050(1)	1
Ba20	6*g*	0.2102(2)	0.3449(2)	0.18912(4)	0.045(1)	1
Ba21	6*g*	0.3434(2)	0.2054(2)	0.31110(4)	0.050(1)	1
Ba22	6*g*	0.1352(1)	0.4733(1)	0.21363(3)	0.0275(8)	1
Ba23	6*g*	0.2097(2)	0.3459(2)	0.31096(4)	0.044(1)	1
Ba24	6*g*	0.3245(2)	0.1212(2)	0.47751(5)	0.058(1)	1
Ba25	6*g*	0.0034(2)	0.5479(2)	0.31067(4)	0.048(1)	1
Ba26	6*g*	0.4765(2)	0.1329(2)	0.28639(4)	0.035(2)	0.83(1)
Ba27	6*g*	0.1225(2)	0.3228(2)	0.47747(4)	0.056(1)	1
Ba28	6*g*	0.1245(2)	0.3209(2)	0.02241(4)	0.053(1)	1
Ba29	6*g*	0.4769(2)	0.1333(2)	0.21377(4)	0.059(1)	1
Ba30	6*g*	0.1990(2)	0.1940(2)	0.11991(4)	0.045(1)	1
Ba31	6*g*	0.3346(2)	0.1223(2)	0.14406(4)	0.054(1)	1
Ba32	6*g*	0.1949(2)	0.1934(2)	0.45274(4)	0.051(1)	1
Ba33	6*g*	0.1270(1)	0.1272(1)	0.28841(4)	0.0417(9)	1
Ba34	6*g*	0.1247(2)	0.3311(2)	0.35594(5)	0.062(1)	1
Ba35	6*g*	0.3265(2)	0.1196(2)	0.02260(4)	0.056(1)	1
Ba36	6*g*	0.1978(2)	0.1956(2)	0.38019(4)	0.047(1)	1
Ba37	6*g*	0.1360(1)	0.4741(1)	0.28631(3)	0.0254(8)	1
Ba38	6*g*	0.4632(2)	0.0013(2)	0.47765(4)	0.057(2)	1
Ba39	6*g*	0.3314(2)	0.1224(2)	0.35600(4)	0.055(1)	1
Ba40	6*g*	0.1276(1)	0.0001(2)	0.25004(4)	0.0444(9)	1
Ba41	6*g*	0.4652(2)	0.0053(2)	0.02233(4)	0.057(1)	1
Ba42	6*g*	0.1250(2)	0.3273(2)	0.14423(5)	0.060(1)	1
Ba43	6*g*	0.4711(2)	0.0078(2)	0.14431(5)	0.064(2)	1
Ba44	6*g*	0.1965(2)	0.1921(2)	0.04725(4)	0.052(1)	1
Ba45	6*g*	0.1272(1)	0.1269(1)	0.21159(4)	0.0409(9)	1
Ba46	6*g*	0.4676(2)	0.0007(2)	0.35583(5)	0.070(1)	1
Ba47	6*g*	0.3267(2)	0.3231(2)	0.41670(6)	0.073(2)	1
Ba48	6*g*	0.3307(2)	0.3191(1)	0.08338(6)	0.056(2)	1
Ba49	6*g*	0.4688(2)	0.3262(2)	0.11954(5)	0.038(2)	0.72(1)
Ba50	6*g*	0.3256(5)	0.4614(4)	0.4534(1)	0.093(5)	0.51(1)
Ba51	6*g*	0.4654(2)	0.3253(2)	0.04675(5)	0.047(2)	0.74(1)
Ba52	6*g*	0.3237(4)	0.4672(4)	0.3808(1)	0.079(4)	0.48(1)
Ba53	6*g*	0.2068(2)	0.5390(2)	0.04490(5)	0.049(2)	0.78(1)
Ba54	6*g*	0.3332(2)	0.5388(2)	0.08338(5)	0.0516(19)	0.80(1)
Ba55	6*g*	0.5402(4)	0.2046(4)	0.3783(1)	0.079(4)	0.47(1)
Ba56	6*g*	0.5384(4)	0.3326(4)	0.4169(1)	0.072(4)	0.46(1)
Ba57	6*g*	0.2057(2)	0.5401(2)	0.12183(5)	0.052(2)	0.79(1)
Ba58	6*g*	0.5379(4)	0.2063(4)	0.4550(1)	0.075(4)	0.47(1)
Ba59	6*g*	0.4649(3)	0.3256(3)	0.45318(7)	0.052(3)	0.57(1)
Ba60	6*g*	0.4684(3)	0.3269(3)	0.38048(7)	0.048(3)	0.56(1)
Ba61	6*g*	0.3334(3)	0.5397(3)	0.41671(7)	0.048(3)	0.56(1)
Ba62	6*g*	0.2073(3)	0.5394(3)	0.45515(7)	0.047(3)	0.56(1)
Ba63	6*g*	0.2065(3)	0.5405(3)	0.37832(7)	0.050(3)	0.57(1)
Ba64	6*g*	0.5400(8)	0.3333(8)	0.2120(2)	0.035(4)	0.16(1)
Ba65	6*g*	0.5397(9)	0.2063(9)	0.2502(2)	0.024(7)	0.14(1)
Ba66	6*g*	0.5403(9)	0.3337(9)	0.2882(2)	0.039(4)	0.16(1)
Ba67	6*g*	0.5393(8)	0.2040(9)	0.1217(2)	0.081(8)	0.24(1)
Ba68	6*g*	0.5375(9)	0.3317(8)	0.0832(2)	0.088(8)	0.26(1)
Ba69	6*g*	0.5366(8)	0.2057(8)	0.0450(2)	0.084(8)	0.25(1)
Na1	2*c*	0	0	0.3228(5)	0.09(1)	1
Na2	6*g*	0.0010(9)	0.343(1)	0.1802(3)	0.074(8)	1
Na3	6*g*	0.0019(9)	0.343(1)	0.3200(3)	0.064(7)	1
Na4	6*g*	0.002(1)	0.326(1)	0.5130(4)	0.087(9)	1
Na5	6*g*	0.0016(9)	0.244(1)	0.2875(2)	0.062(5)	1
Na6	6*g*	0.0020(9)	0.2432(9)	0.2127(2)	0.058(5)	1
Na7	6*g*	0.171(1)	0.001(1)	0.1777(3)	0.070(6)	1
Na8	6*g*	0.330(1)	0.324(1)	0.0128(4)	0.078(8)	1
Na9	6*g*	0.3335(9)	0.3287(9)	0.1533(3)	0.067(8)	1

Table 3 (*continued*)

Atom	Position	*x*	*y*	*z*	U_{eq} (Å^2)	*G*
Na10	6*g*	0.331(1)	0.330(1)	0.3466(4)	0.09(1)	1
Na11	6*g*	0.328(1)	0.449(1)	0.0458(3)	0.064(6)	1
Na12	6*g*	0.3215(8)	0.4669(8)	0.1194(2)	0.039(4)	1
Na13	6*g*	0.168(2)	0.500(2)	0.5058(5)	0.12(1)	1
Na14	2*c*	0	0	0.1774(6)	0.07(2)	0.7(1)
Li14	2*c*	0	0	0.1774(6)	0.07(2)	0.3(1)
Na15	2*d*	0.3333	0.6667	0.3442(7)	0.10(3)	0.75(2)
Li15	2*d*	0.3333	0.6667	0.3442(7)	0.10(3)	0.25(2)
Na16	2*d*	0.3333	0.6667	0.1567(6)	0.07(2)	0.7(1)
Li16	2*d*	0.3333	0.6667	0.1567(6)	0.07(2)	0.3(1)
Na17	2*d*	0.3333	0.6667	0.0097(7)	0.07(2)	0.6(1)
Li17	2*d*	0.3333	0.6667	0.0097(7)	0.07(2)	0.4(1)
Na18	2*d*	0.3333	0.6667	0.6559(9)	0.05(3)	0.3(1)
Li18	2*d*	0.3333	0.6667	0.6559(9)	0.05(3)	0.7(1)
Na19	6*g*	0.171(1)	0.001(1)	0.3222(3)	0.058(9)	0.88(8)
Li19	6*g*	0.171(1)	0.001(1)	0.3222(3)	0.058(9)	0.12(8)
Na20	6*g*	0.164(1)	0.163(1)	0.3357(3)	0.06(1)	0.74(8)
Li20	6*g*	0.164(1)	0.163(1)	0.3357(3)	0.06(1)	0.26(8)
Na21	6*g*	0.166(1)	0.163(1)	0.1647(3)	0.08(1)	0.89(9)
Li21	6*g*	0.166(1)	0.163(1)	0.1647(3)	0.08(1)	0.11(9)
Na22	6*g*	0.334(1)	0.499(1)	0.1553(4)	0.08(1)	0.79(9)
Li22	6*g*	0.334(1)	0.499(1)	0.1553(4)	0.08(1)	0.21(9)
Na23	6*g*	0.001(1)	0.102(1)	0.1431(4)	0.07(1)	0.58(8)
Li23	6*g*	0.001(1)	0.102(1)	0.1431(4)	0.07(1)	0.42(8)
Na24	6*g*	0.001(2)	0.100(2)	0.3568(4)	0.06(1)	0.47(7)
Li24	6*g*	0.001(2)	0.100(2)	0.3568(4)	0.06(1)	0.53(7)
Na25	6*g*	0.333(1)	0.497(1)	0.0102(3)	0.09(1)	0.86(9)
Li25	6*g*	0.333(1)	0.497(1)	0.0102(3)	0.09(1)	0.14(9)
Na26	6*g*	0.500(2)	0.330(2)	0.0038(4)	0.10(1)	0.86(9)
Li26	6*g*	0.500(2)	0.330(2)	0.0038(4)	0.10(1)	0.14(9)
Na27	6*g*	0.167(1)	0.502(1)	0.1692(4)	0.06(1)	0.61(7)
Li27	6*g*	0.167(1)	0.502(1)	0.1692(4)	0.06(1)	0.39(7)
Na28	6*g*	0.332(2)	0.570(2)	0.1905(4)	0.07(2)	0.53(8)
Li28	6*g*	0.332(2)	0.570(2)	0.1905(4)	0.07(2)	0.47(8)
Na29	6*g*	0.506(2)	0.329(2)	0.1606(6)	0.11(2)	0.5(1)
Li29	6*g*	0.506(2)	0.329(2)	0.1606(6)	0.11(2)	0.5(1)
Na30	6*g*	0.499(2)	0.168(2)	0.5077(4)	0.08(2)	0.64(8)
Li30	6*g*	0.499(2)	0.168(2)	0.5077(4)	0.08(2)	0.36(8)
Na31	6*g*	0.333(2)	0.570(2)	0.3087(5)	0.06(2)	0.31(8)
Li31	6*g*	0.333(2)	0.570(2)	0.3087(5)	0.06(2)	0.69(8)
Na32	6*g*	0.003(3)	0.151(3)	0.5060(7)	0.04(2)	0.10(7)
Li32	6*g*	0.003(3)	0.151(3)	0.5060(7)	0.04(2)	0.90(7)
Na33	6*g*	0.333(2)	0.5005(2)	0.3441(4)	0.10(2)	0.67(9)
Li33	6*g*	0.333(2)	0.5005(2)	0.3441(4)	0.10(2)	0.33(9)
Na34	6*g*	0.504(2)	0.330(2)	0.3416(5)	0.09(2)	0.52(9)
Li34	6*g*	0.504(2)	0.330(2)	0.3416(5)	0.09(2)	0.48(9)
Na35	6*g*	0.160(3)	0.316(3)	0.2662(7)	0.07(2)	0.22(8)
Li35	6*g*	0.160(3)	0.316(3)	0.2662(7)	0.07(2)	0.78(8)
Na36	6*g*	0.164(2)	0.499(2)	0.3306(4)	0.06(2)	0.43(8)
Li36	6*g*	0.164(2)	0.499(2)	0.3306(4)	0.06(2)	0.57(8)
Na37	6*g*	0.507(2)	0.167(2)	0.1724(6)	0.09(2)	0.39(9)
Li37	6*g*	0.507(2)	0.167(2)	0.1724(6)	0.09(2)	0.61(9)
Na38	6*g*	0.499(2)	0.164(2)	0.3290(5)	0.09(2)	0.55(9)
Li38	6*g*	0.499(2)	0.164(2)	0.3290(5)	0.09(2)	0.45(9)
Na39	6*g*	0.320(2)	0.401(2)	0.2501(6)	0.06(2)	0.25(7)
Li39	6*g*	0.320(2)	0.401(2)	0.2501(6)	0.06(2)	0.75(7)
Na40	6*g*	0.191(3)	0.002(3)	0.4456(7)	0.06(2)	0.15(7)
Li40	6*g*	0.191(3)	0.002(3)	0.4456(7)	0.06(2)	0.85(7)
Na41	6*g*	0.213(3)	0.203(3)	0.2502(8)	0.05(3)	0.09(7)
Li41	6*g*	0.213(3)	0.203(3)	0.2502(8)	0.05(3)	0.91(7)
Li42	1*a*	0	0	0	0.06(4)	1
Li43	1*b*	0	0	0.5	0.06(3)	1
Li44	2*d*	0.3333	0.6667	0.843(1)	0.02(2)	1
Li45	2*d*	0.3333	0.6667	0.511(2)	0.04(3)	1

Table 3 (*continued*)

Atom	Position	*x*	*y*	*z*	U_{eq} (Å^2)	*G*
Li46	6*g*	0.001(3)	0.533(3)	0.2674(8)	0.03(2)	1
Li47	6*g*	0.162(3)	0.575(4)	0.2495(8)	0.06(2)	1
Li48	6*g*	0.001(4)	0.091(4)	0.473(1)	0.06(2)	1
Li49	6*g*	0.159(3)	0.342(3)	0.0994(8)	0.03(2)	1
Li50	6*g*	0.162(3)	0.316(3)	0.2333(8)	0.02(1)	1
Li51	6*g*	0.314(3)	0.159(3)	0.2668(7)	0.02(1)	1
Li52	6*g*	0.009(4)	0.498(4)	0.066(1)	0.05(2)	1
Li53	6*g*	0.006(4)	0.491(4)	0.0999(9)	0.04(2)	1
Li54	6*g*	0.004(3)	0.533(3)	0.2315(9)	0.03(2)	1
Li55	6*g*	0.112(4)	0.448(4)	0.084(1)	0.06(2)	1
Li56	6*g*	0.330(3)	0.134(3)	0.0997(8)	0.03(2)	1
Li57	6*g*	0.318(3)	0.309(3)	0.2803(9)	0.04(2)	1
Li58	6*g*	0.329(3)	0.483(3)	0.2792(8)	0.03(2)	1
Li59	6*g*	0.324(3)	0.309(3)	0.2136(8)	0.03(2)	1
Li60	6*g*	0.191(3)	0.003(3)	0.1130(8)	0.03(2)	1
Li61	6*g*	0.315(4)	0.160(4)	0.234(1)	0.05(2)	1
Li62	6*g*	0.149(3)	0.147(3)	0.0068(7)	0.01(1)	1
Li63	6*g*	0.329(3)	0.477(3)	0.2221(8)	0.03(2)	1
Li64	6*g*	0.095(5)	0.002(5)	0.026(1)	0.07(3)	1
Li65	6*g*	0.169(3)	0.351(4)	0.0653(9)	0.04(2)	1
Li66	6*g*	0.239(4)	0.484(4)	0.2498(8)	0.03(1)	1
Li67	6*g*	0.002(3)	0.495(3)	0.3988(9)	0.03(2)	1
Li68	6*g*	0.191(3)	0.008(3)	0.3864(9)	0.04(2)	1
Li69	6*g*	0.001(3)	0.188(3)	0.0542(9)	0.04(2)	1
Li70	6*g*	0.115(4)	0.452(4)	0.416(1)	0.05(2)	1
Li71	6*g*	0.162(4)	0.341(4)	0.399(1)	0.04(2)	1
Li72	6*g*	0.338(4)	0.143(4)	0.066(1)	0.05(2)	1
Li73	6*g*	0.330(5)	0.154(5)	0.394(1)	0.07(3)	1
Li74	6*g*	0.165(5)	0.348(5)	0.433(1)	0.07(3)	1
Li75	6*g*	0.016(5)	0.358(4)	0.115(1)	0.06(2)	1
Li76	6*g*	0.011(4)	0.346(4)	0.446(1)	0.05(2)	1
Li77	6*g*	0.341(4)	0.158(4)	0.4345(9)	0.04(2)	1
Li78	6*g*	0.102(5)	0.186(5)	0.415(1)	0.09(3)	1
Li79	6*g*	0.106(4)	0.187(4)	0.083(1)	0.06(2)	1
Li80	6*g*	0.189(4)	0.091(4)	0.086(1)	0.05(2)	1
Li81	6*g*	0.005(3)	0.500(4)	0.4352(9)	0.04(2)	1
Li82	6*g*	0.441(4)	0.096(4)	0.086(3)	0.05(2)	1
Li83	6*g*	0.460(4)	0.117(4)	0.417(1)	0.05(2)	1
Li84	6*g*	0.001(4)	0.265(4)	0.416(2)	0.09(3)	1
Li85	6*g*	0.192(5)	0.099(5)	0.416(1)	0.08(3)	1
Li86	6*g*	0.006(4)	0.342(5)	0.386(1)	0.05(3)	1
Li87	6*g*	0.016(5)	0.348(5)	0.057(1)	0.07(3)	1
Li88	6*g*	0.007(4)	0.270(6)	0.085(2)	0.05(3)	1
Li89	6*g*	0.404(5)	0.311(5)	0.250(2)	0.05(3)	1

temperature was recorded with a sensitive micro-voltmeter Hewlett Packard 3457A. Laser-welded tantalum ampoules (diameter 2 mm, length approximately 15 mm) and Pt–PtRh thermocouple thermocoax were used in a home-made device throughout this investigation. The temperature calibration was performed and frequently checked by measuring the extrapolated onset temperatures of the last phase transition (125 °C) and melting (170 °C) peaks of NH_4NO_3. The sample was heated up to 300 °C with a rate of 3 °C min^{-1} and cooled with 1 °C min^{-1}.

I decomposes at 123(3) °C. This temperature is somewhat lower than that of a subnitride of high Na content—Na_5Ba_3N (133 °C) [14] and the structurally related intermetallic phase $Ba_{19}Li_{44}$ (126 °C) [3]. **II** melts at 151(2) °C and solidifies at 149(2) °C, indicating congruent melting,

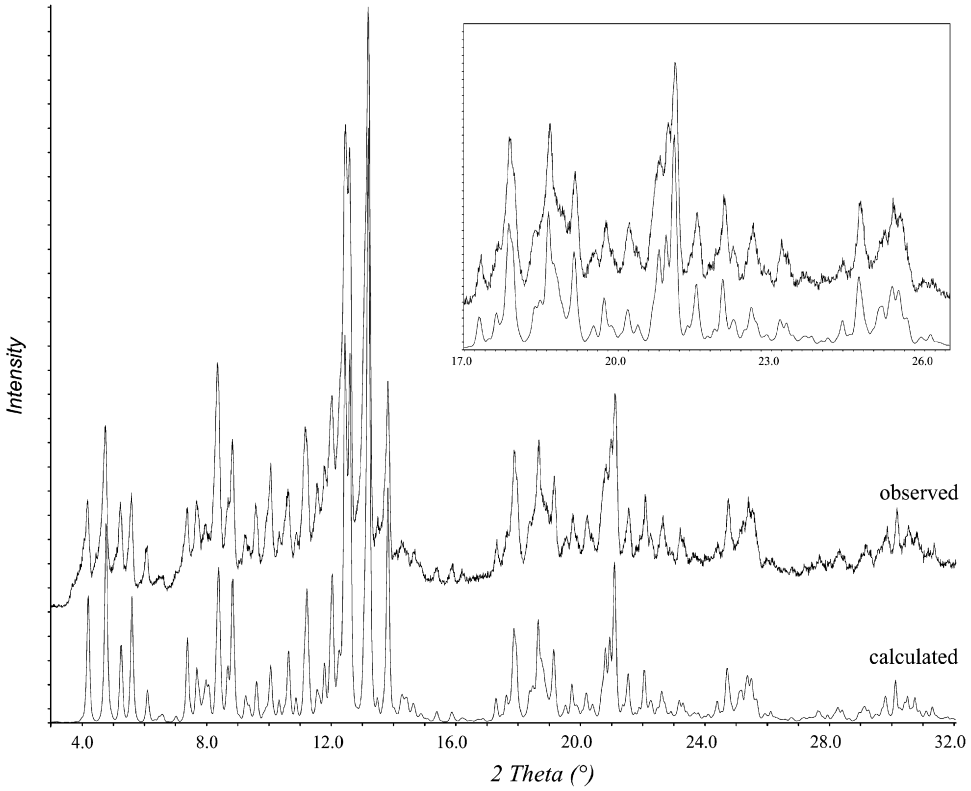

Fig. 1. Observed and calculated powder patterns of $Li_{18.9}Na_{8.3}Ba_{15.3}$ (Mo$K\alpha_1$ radiation).

very similar to $Li_{13}Na_{29}Ba_{19}$ [10] (149(2) °C). This temperature is comparable with those for the binary-phase $BaLi_4$ [2] (156 °C), and some subnitrides: $Na_{22}Ba_{14}CaN_6$ [14] (152 °C), $Li_{80}Ba_{39}N_9$ [15] (165 °C) and $Na_{14}Ba_{14}CaN_6$ (168 °C) [14].

2.5. Elemental analysis

The chemical compositions of the products in the samples C and E were determined by energy-dispersive X-ray analysis (EDX) performed on a Tescan 5130MM scanning electron microscope (SEM) equipped with an Oxford EDX detector. Selected crystals of **I** and **II** were fixed on the SEM sample holder using carbon tape. Data were collected by applying a 20 kV accelerating voltage with an accumulation time of 60–90 s. Chemical analysis of the second compound (sample E) was performed in the Mikroanalytisches Labor Pascher in Remagen-Bandorf, Germany.

According to EDX investigations, the atomic ratio of both Ba and Ca in **I** from sample A (Ba:Ca from 4.04:1 to 4.13:1), and of Ba/Na (from 2.0:1 to 1.9:1) in **II** from sample D are in good agreement with the results of the X-ray diffraction analyses. Chemical analysis of the sample E showed 29.95 at% Ba, 16.65 at% Na and 53.4 at% Li. The atomic ratio Ba/Na = 1.80 is almost the same as found from the X-ray structure investigation (1.82) and a little lower than that of the EDX analysis.

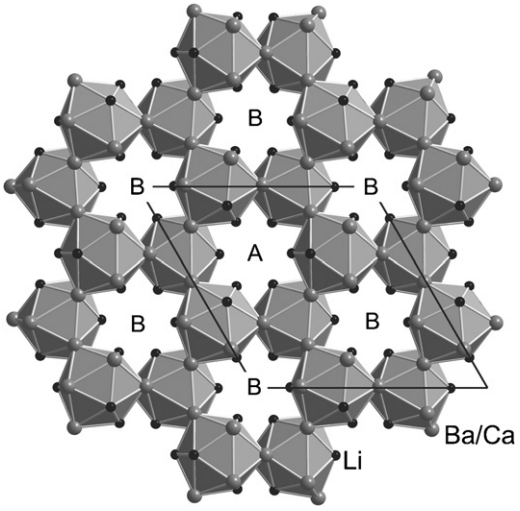

Fig. 2. Icosahedrally coordinated Ca/Li positions forming the basic substructure of **I** with Li_{12} (A) and Li_9Ba_3 (B) centered icosahedra between them.

3. Results and discussion

$Li_{33.3}Ba_{13.1}Ca_3$ **(I)** crystallizes in a new structure type of trigonal symmetry. Its crystal structure can be described as a complicated hierarchical variant of the arsenic structure [16]. Ca18/Li18 positions in an icosahedral coordination present the backbone of the structure (Fig. 2). The space between these polyhedra is occupied by centered Li_{12} (A)

and Li_9Ba_3 (B) icosahedra. The Ba atoms from these icosahedra form interlayer bridges from two face-condensed octahedra. Typical for Li-rich phases, polytetrahedral Li clusters (Fig. 3) fill the space between different layers. Each of these clusters is surrounded by cages with five-fold symmetry, Li_{13} by a $(BaCa)_{20}$ pentagondodecahedron and Li_{19} by a $(BaCa)_{25}$ polyhedron, respectively (Fig. 4). Calcium atoms in this structure have no position of their own, but occupy partially either Ba or Li positions.

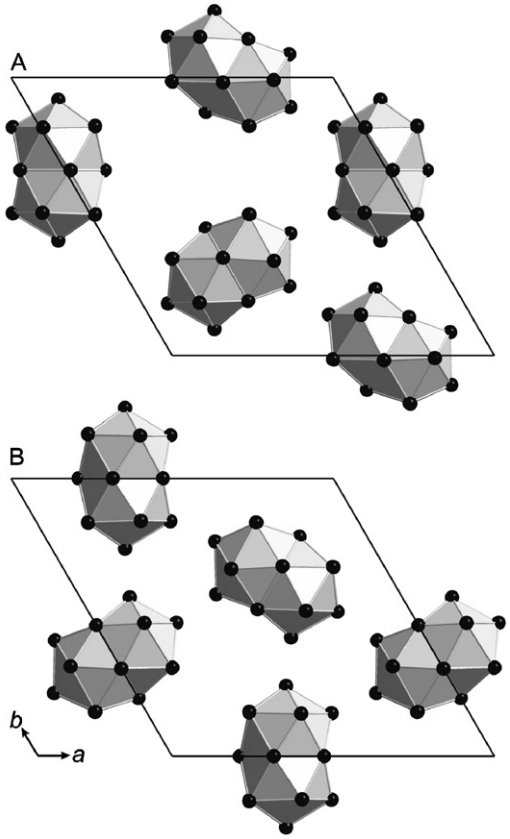

Fig. 3. Li_{19} clusters in the structure of **I**.

Typically as for other intermetallic compounds [2,3], all Li atoms in the structure have coordination number 12 and icosahedral coordination. The Li_{19} cluster in **I** is formed by two centered, interpenetrating icosahedra and contains 35 close-packed tetrahedra. Endohedral Li–Li distances in these clusters are in the range 2.89(3)–3.30(3) Å. This cluster was predicted to be stable in the gas phase [17] and is one of the six most stable Li anti-Mackay clusters [18,19]. In the solid state, the same cluster was found in $Ba_{19}Li_{44}$ [3]. This 19-atom double icosahedron is also known from the structure of Al_5Co_2 [20] and $Al_{10}Mn_3$ [21], however, there it is formed of different atom types. M_{19} clusters are known as structural subunits in many decagonal phases [22, 23].

Barium together with calcium forms Frank–Kasper polyhedra the majority of which contain 15, some of them 16 and 17 atoms and 4–6 neighboring Ba atoms. The interatomic distances in this compound range from 4.12(2) to 4.450(1) Å for Ba–Ba/Ca and Ba/Ca–Ba/Ca, 3.89(3)–4.11(4) Å for Ba–Li, 4.14(2) Å for Ba–Ca/Li, 3.934(9)–4.12(3) Å for Ba/Ca–Ca/Li, 3.65(4)–4.09(4) Å for Ba/Ca–/Li, 3.33–3.42(2) Å for Ca/Li–Li, and 2.88–3.27 Å for Li–Li.

It should be emphasized that compounds with mixed (Ba/Ca and Ca/Li) occupation of positions are known [24–27], but **I** is the first example where both cases occur at the same time. In $Ca_{8-x}Li_xAl_3$ [24], doping of the third element stabilizes the structure and transforms it in the case of $Ca_{1.65}Li_{1.85}Si_4$ [26]. In our case, adding small amounts of calcium complicates the structure of $Ba_{19}Li_{44}$ [3] with a significant increase of the lattice constants, but retaining of the Li_{19} clusters and similar M^I/M^{II} ratios (2.1 in $Li_{33.3}Ba_{13.1}Ca_3$ and 2.3 in $Ba_{19}Li_{44}$).

$Li_{18.9}Na_{8.3}Ba_{15.3}$ (**II**) crystallizes in trigonal symmetry with an own structure type. Its crystal structure is somewhat related to that of **I**. It has practically the same Ba atom packing, however, with defect Ba positions instead at a mixed Ba/Ca occupation, and it contains icosahedron-based polytetrahedral clusters $(Li_{15})_6Li_{13}$

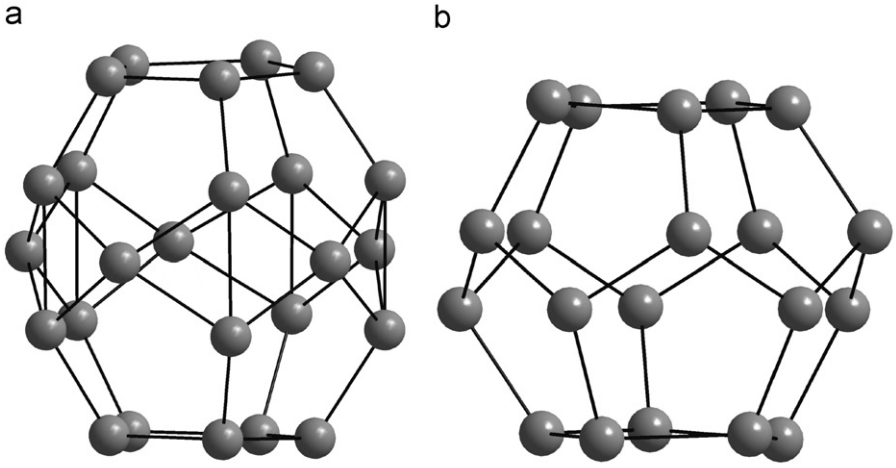

Fig. 4. Ba_{25} and Ba_{20} cages for Li_{19} and Li_{13} clusters in the structures of **I** and **II**.

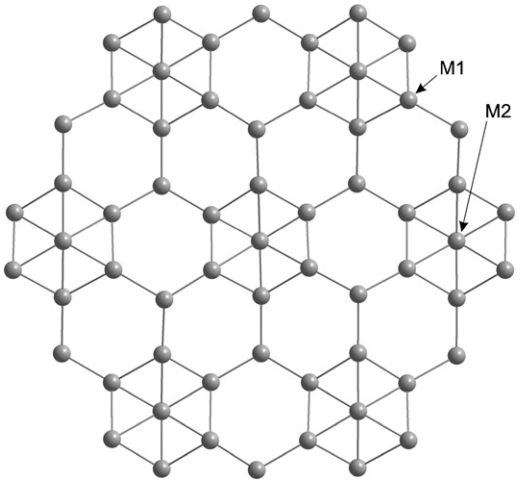

Fig. 5. Na/Li layers in the crystal structure of **II** viewed along the *c*-axis.

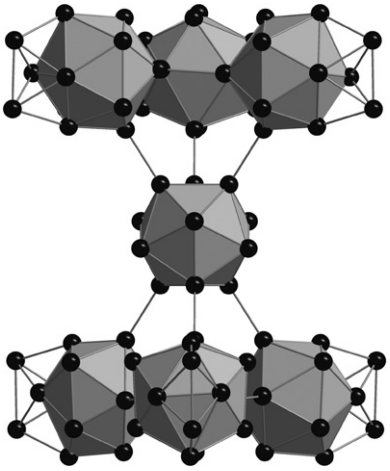

Fig. 6. $(Li_{15})_6Li_{13}$ icosahedron-based polytetrahedral clusters in the structure of **II**.

instead of $(Li_{19})_6Li_{13}$ in **I**. The crystal structure of **II** could also be described on the basis of a complicated arsenic type structure, but now with somewhat different structural elements. Layers built either from centered (chair conformation: M_1–M_1–M_1 and M_1–M_2–M_1 angles in the ranges 106.74(5)–109.92(4)°, and 61.25(5)–61.48°, respectively, with M_1 and M_2 being peripheral and central positions of Na, Li and Li/Na, respectively) or not centered (nearly planar: $\angle M_1$–M_1–$M_1 = 117.55(5)$–$122.61(6)°$) Li/Na hexagons (Fig. 5)) lie in the basis of the structure, very similar as in the structure of $Na_{15}Li_8Ba_{12}N_6$ [28]. By analogy with the **I**, the space between these layers is filled with polytetrahedral $(Li_{15})_3$ and $(Li_{15})_6Li_{13}$ units, and in the second case hexagon layers are formed also with Li_{13} icosahedra at $z = 0$ and 0.5 (Fig. 6) as well as different Ba atom polyhedra of mostly Frank–Kasper-type with CN = 12–16. All defect Ba atoms in the structure of **II** form polyhedra (Fig. 7c) with very short interatomic distances (approximately 2.97(1) to 3.31(1) Å). These polyhedra could be described as superimposed two face-

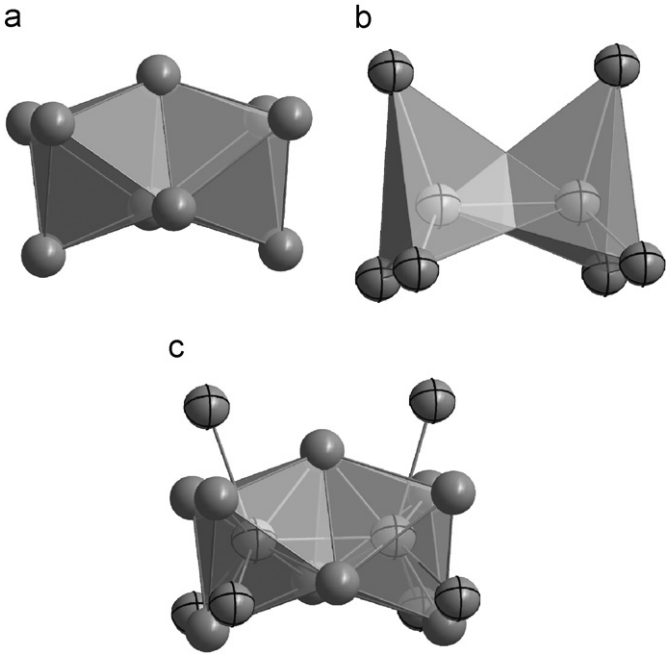

Fig. 7. Ba_6 face-sharing bioctahedra (a) and interpenetrating Ba_4 tetrahedra (b) resulting in a polytetrahedral Ba cluster (c) formed of defect Ba atoms in the structure of **II**.

sharing Ba_6 octahedra (Ba_9) and two interpenetrating Ba_4 tetrahedra (Ba_8) (Fig. 7a and b). All Ba atoms in the Ba_9 bioctahedra have nearly the same occupations, as it is also found for the Ba_7 polyhedra, both together amounting to 100%. This means a mutually exclusive occupation by both types of polyhedra. Ba–Ba interatomic distances within both polyhedra are in the ranges 4.20(5)–4.49(2) Å. As in the structure of **I** Ba cages around the Li clusters are present, a Ba_{20} pentagondodecahedron and a distorted variant of the Ba_{25} polyhedron. Interatomic distances between fully occupied sodium and barium positions are also in the ranges for known intermetallic compounds.

No compound in the Na–Li system and only one ternary s-bonded intermetallic compound [10] with Li–Na contacts is known. **II** is the first example with a very great number of Li–Na contacts and also mixed occupancy of Na/Li positions. These contacts are always surrounded by Ba pentagons, as in $Li_{13}Na_{29}Ba_{19}$. Each of the mixed Na/Li positions could also be refined as defect Na atoms, but the Ba/Na ratio found from EDX and chemical analysis corresponds to the first variant. All Li atoms in the structure of **II** have icosahedral coordination, similar to **I** and other binary and ternary Li/Ba compounds and also like Na in NaBa [9], Na_2Ba [8] and $Li_{13}Na_{29}Ba_{19}$ [10]. Polytetrahedral Li_n clusters as found in these compounds are often observed in other Li-rich intermetallic or subnitride compounds as well, infinite rows of face-sharing Li_{13} icosahedra in $BaLi_4$ [2], Li_{17} unit in the Li/Ba subnitride $Li_{80}Ba_{39}N_9$ [15], Li_{19} unit in $Ba_{19}Li_{44}$ [3], and Li_{26} in $Li_{13}Na_{29}Ba_{19}$ [10].

4. Summary

Two new intermetallic compounds were detected and structurally characterized by single-crystal X-ray diffraction. Both these compounds could be synthesized from the metals. The structures of $Li_{33.3}Ba_{13.1}Ca_3$ and $Li_{18.9}Na_{8.3}Ba_{15.3}$ contain very similar Ba atom nets, however because of the light atom positions their symmetries differ. The structures of both can be described on the basis of the arsenic structure type, containing polytetrahedral Li clusters, face-sharing Ba octahedra and mixed occupied positions (Ba/Ca and Ca/Li in the first and Na/Li in the second). The thermal stability of $Li_{33.3}Ba_{13.1}Ca_3$ is comparable to the related binary phase $Ba_{19}Li_{44}$ as is the stability of $Li_{18.9}Na_{8.3}Ba_{15.3}$ compared to another Li/Na/Ba compound, $Li_{13}Na_{29}Ba_{19}$.

5. Supporting information

The crystallographic files in CIF format for $Li_{33.3}Ba_{13.1}Ca_3$ and $Li_{18.9}Na_{8.3}Ba_{15.3}$ have been deposited with FIZ Karlsruhe as CSD numbers 418125 and 418126. These data may be obtained by contacting FIZ Karlsruhe at: +49 724 780 8666 (fax) or per e-mail (crysdata@fiz-karlsruhe.de).

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