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Double-Icosahedral Li Clusters in a New Binary Compound $Ba_{19}Li_{44}$: A Reinvestigation of the Ba–Li Phase Diagram[†]

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The binary Ba–Li system was reinvestigated for compositions with less than 80 at. % Li. A new compound, $Ba_{19}Li_{44}$, stable up to 126 °C, was found and structurally characterized. According to single-crystal X-ray diffraction data, the compound crystallizes in a new structure type with a tetragonal unit cell, space group $I\bar{4}2d$, $a = 16.3911(5)$ Å, $c = 32.712(1)$ Å, $Z = 4$, and $V = 8788.7(5)$ Å^3. It can be described as a complicated variant of the chalcopyrite structure. Typical for Li-rich phases, $Ba_{19}Li_{44}$ contains icosahedron-based polytetrahedral clusters.

Introduction

Numerous metal-rich nitrides of alkaline-earth metals, particularly of Ba in combination with Na, have been discovered.[1] No similar compounds with the heavier homologues of Na could be prepared so far; however, Li was found to be a good candidate for further development of subnitride chemistry. Parallel to the full investigation of the ternary Li−Ba−N system, the binary Ba−Li system was reexamined for the existence of unknown compounds as well.

A number of binary compounds between alkali and alkaline-earth elements have been reported, but not all were well established. One compound is known for Ca and Li ($CaLi_2$[2]), two for Sr and Li (Sr_6Li_{23}[3] and Sr_3Li_2[4]), and two for Na and Ba (Na_2Ba[5] and $NaBa$[6]). In the work of Wang,[7] the Ba−Li system was investigated and only one compound ($BaLi_4$) was identified. The published Ba−Li phase diagram is based primarily on one investigation.[8] In a previous study, we confirmed the existence and the reported crystal structure of $BaLi_4$.[9] Further investigations indicated that another compound with lower Li content also exists.

The current study was carried out to establish the composition, crystal structure, and thermal behavior of the new binary compound $Ba_{19}Li_{44}$. Structural relationships between Ba−Li intermetallic and metal-rich nitride phases are also discussed.

Experimental Section

Reagents. Ba metal (Merck, 99%, distilled twice with intermediate heating in a closed tantalum container at 1200 K in vacuum to remove hydrogen) and Li metal (Merck, 99%) were used for synthesis.

Synthesis. 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. Two samples were prepared with the overall stoichiometries $BaLi_2$ (Sample A: 500 mg Ba, 51.0 mg Li) and Ba_2Li_3 (Sample B: 500 mg Ba, 38.2 mg Li). These were heated to 250 °C and annealed at this temperature for 40 h, followed by cooling to 120 °C at a rate of 0.8 °C•h^{-1}, further annealing for 1 month, and cooling to room temperature by switching off the furnace. Single crystals of $Ba_{19}Li_{44}$ were obtained in the first sample, which was found to contain ~80 wt. % of the desired product contaminated by $BaLi_4$ and Ba according to powder X-ray diffraction. The second sample consisted of polycrystalline $Ba_{19}Li_{44}$ together with elemental barium.

[†] Dedicated to Prof. Dieter Fenske on the occasion of his 65th birthday.

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Table 1. Details of the Crystal Structure Investigation for $Ba_{19}Li_{44}$

empirical formula	$Ba_{19}Li_{44}$
formula weight	2914.82
temperature, °C	20
wavelength, Å	0.71073
crystal system	tetragonal
Z	4
crystal size, mm^3	0.16 × 0.16 × 0.15
space group	$I\bar{4}2d$
a, Å	16.3911(5)
c, Å	32.712(1)
volume, Å^3	8788.7(5)
density (calculated), g/cm^3	2.203
μ, mm^{-1}	8.349
F(000)	4784
2θ range, °	4.3−64.1
index ranges	$24 \leq h \leq 24$
	$24 \leq k \leq 24$
	$48 \leq l \leq 40$
reflections collected	51 584
independent reflections	7569
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	7569/0/89
GOF on F^2	0.952
final R indices [$I > 2\sigma(I)$]	R1 = 0.049, wR2 = 0.0439
R indices (all data)	R1 = 0.096, wR2 = 0.0484
largest diff. peak and hole, e$^-$/Å^3	1.429 and −1.417

Table 2. Atomic Coordinates and Equivalent/Isotropic Thermal Displacement Parameters for $Ba_{19}Li_{44}$

atom	position	x	y	z	$U_{eq/iso}$, Å^2
Ba1	4b	1/2	0	1/4	0.0330(2)
Ba2	8c	0	0	0.09525(2)	0.0337(1)
Ba3	16e	0.11195(3)	0.09593(3)	0.20204(2)	0.0317(1)
Ba4	16e	0.41522(3)	0.10003(3)	0.05021 (2)	0.0318(1)
Ba5	16e	0.00431(4)	0.30881(3)	0.25100(2)	0.0332 (1)
Ba6	16e	0.35705(3)	0.34933(3)	0.07488 (2)	0.0326(1)
Li1	8d	0.0097(13)	1/4	1/8	0.037(5)
Li2	8d	0.5393(18)	1/4	1/8	0.066(8)
Li3	16e	0.1723(11)	0.1708(11)	0.0844(5)	0.048(4)
Li4	16e	0.2815(8)	0.5619(8)	0.0321(4)	0.026(3)
Li5	16e	0.2340(9)	0.5191(9)	0.1307(5)	0.036(4)
Li6	16e	0.1346(9)	0.1622(8)	0.3152(5)	0.040(3)
Li7	16e	0.5727(8)	0.0626(8)	0.1434(4)	0.031(3)
Li8	16e	0.2435(9)	0.2705(9)	0.2586(4)	0.043(3)
Li9	16e	0.1158(9)	0.6376(9)	0.0683(5)	0.047(4)
Li10	16e	0.1511(9)	0.6765(8)	0.1609(5)	0.046(4)
Li11	16e	0.2874(9)	0.0752(9)	0.2830(5)	0.037(3)
Li12	16e	0.2850(10)	0.6873(10)	0.0945(6)	0.056(4)

Thermal Analysis. All thermal analyses were performed with sample amounts of 20−40 mg in an argon atmosphere. Temperature was recorded with a sensitive micro-voltmeter Hewlett-Packard 3457A. Laser-welded tantalum ampoules (diameter 2 mm, length ∼15 mm) and Pt−PtRh thermocouple thermocoax were used in a homemade 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 $\cdot$min^{-1} and cooled at 1 °C$\cdot$min^{-1}.

X-ray Diffraction and Structure Refinement. Several irregularly shaped single crystals were selected from sample A and 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_α radiation by oscillation of the crystal around the ω axis. The starting atomic parameters derived via direct methods using the program SIR 97[10] were subsequently refined with the program SHELX-97[11] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for Ba atoms within the WinGX program package[12] in the space group $I\bar{4}2d$. The positions of the Li atoms were found in difference Fourier maps according to reasonable interatomic distances between found and new, proposed atoms. Details of the crystal structure investigation are summarized in Tables 1 and 2.

X-ray powder diffraction patterns were obtained on a powder diffractometer STOE STADI P with Mo $K_{\alpha 1}$ radiation, using capillaries sealed under dried argon to avoid hydrolysis. The unit cell parameters were refined with the help of the WinCSD program package[13] from powder data as $a = 16.343(2)$ Å, $c = 32.702(7)$ Å. The correct indexing of the X-ray patterns was ensured through intensity calculations taking the atomic positions from the refined single-crystal structure of $Ba_{19}Li_{44}$. The powder of elemental Si (6N, $a_{Si} = 5.43102$ Å) was used as an external standard.

Temperature-dependent investigations were performed on a Guinier−Simon camera[14] with Cu $K_{\alpha 1}$ radiation.

Results and Discussion

As the result of our thermal and X-ray diffraction study of the Ba−Li system, some details were added to the established phase equilibrium system (Figure 1). In the present work, samples were heated first to 250 °C and then cooled very slowly (1 °C$\cdot$h^{-1}) to 120 °C. Thanks to this procedure, identification of the second compound $Ba_{19}Li_{44}$ in the Ba−Li system was made possible. Owing to kinetic reasons in both samples, $Ba_{19}Li_{44}$ was detected with different amounts of $BaLi_4$ and Ba. By heating the sample with the composition $BaLi_2$, two peaks were observed in the DTA study: at 126(2) °C $Ba_{19}Li_{44}$ undergoes a peritectoidal decomposition to Ba and $BaLi_4$ (according to temperature-dependent Guinier measurement[14]) and at 156(2) °C $BaLi_4$ melts incongruently (in agreement with the previously reported phase diagram[8]).

$Ba_{19}Li_{44}$ crystallizes in a new structure type of tetragonal symmetry. Its crystal structure can be regarded as an fcc packing of Ba_6 and $(BaBa_3Ba_{1/4})_4$ fragments with icosahedron-based polytetrahedral Li_{19} clusters and Li triangles filling the tetrahedral voids of the packing. The structure can be described as a complicated variant of the chalcopyrite structure type.[15] The packing of the different Ba and Li polyhedra in $Ba_{19}Li_{44}$ is presented in Figure 2. Ba_6 octahedra (A, Figure 3a) and units of four centered Ba tetrahedra connected through a common vertex (B, Figure 3b) (positions of Cu and Fe in the structure of $CuFeS_2$, respectively) comprise the basis of the structure. One-half of the tetrahedral voids in the AB packing are filled with Li_{19} clusters (C, Figure 4). These clusters, interconnected by Li triangles (D), which fill the remaining tetrahedral voids, represent the Li network of this structure. The packing $(AB)(CD)_2$ corre-

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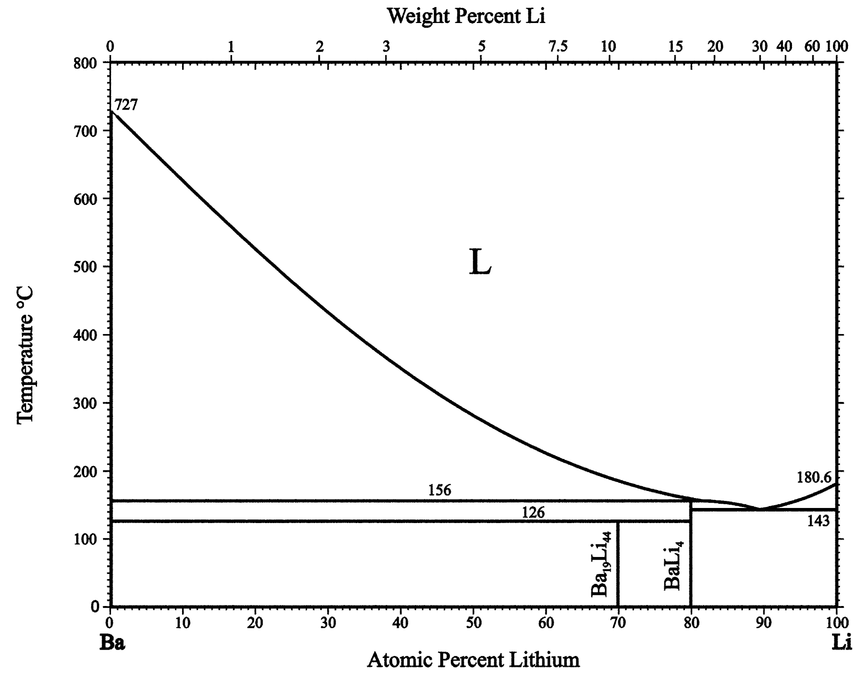

Figure 1. Equilibrium phase diagram of the Ba−Li system[8] complemented with the new compound $Ba_{19}Li_{44}$.

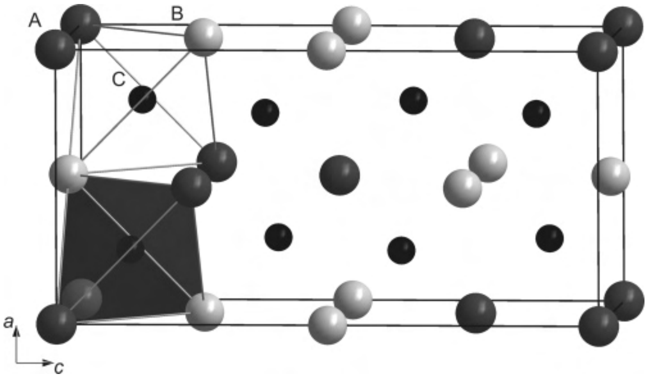

Figure 2. Location of Ba_6 (A), Ba_{17} (B), and Li_{19} (C) fragments in the crystal structure of $Ba_{19}Li_{44}$, tetrahedra outlined.

sponds also to the packing of atoms in CaF_2.[16] In general, the structure can be regarded as $A_4B_4C_8D_8 \cong (Ba_6)_4{}^A(Ba_9Ba_{8/2})_4{}^B(Li_{19})_8{}^C(Li_3)_8{}^D \cong Ba_{19}Li_{44}$.

The structure of $Ba_{19}Li_{44}$ has many similarities with that of the known Ba−Li subnitride $Li_{80}Ba_{39}N_9$.[17] Their unit cell parameters are similar; however, in contrast to the subnitride, a volume increase ($\Delta V = +1.9\%$, compared to the elements) is observed for $Ba_{19}Li_{44}$, much like in the other binary Ba−Li compound $BaLi_4$.[9] Ba atoms in both phases form similar polyhedra: empty Ba_6 octahedra ($Ba_{19}Li_{44}$, d_{Ba-Ba} = 4.3968(1)−4.4428(1) Å) and N-centered octahedra ($Li_{80}Ba_{39}N_9$,[17] d_{Ba-Ba} = 3.9321−3.9353 Å), as well as complexes of four centered Ba tetrahedra connected through common vertices $Li_{12}Ba_{17}$ ($Ba_{19}Li_{44}$, d_{Ba-Ba} = 4.2096(1)−4.2730(1) Å) and $Li_{12}Ba_{17}N_6$ ($Li_{80}Ba_{39}N_9$,[16] 4.1156−4.1315 Å). Ba atoms from these clusters form an infinite 3D network (Figure 5) connected via common edges. A further similarity of $Ba_{19}Li_{44}$ and other Li−Ba phases shows up in polytetrahedral Li_n clusters. These are Li_{17} in $Li_{80}Ba_{39}N_9$, Li_{26} in $Li_{13}Na_{29}Ba_{19}$,[18] and infinite rows of face-sharing centered Li_{13} icosahedra in $BaLi_4$.[9]

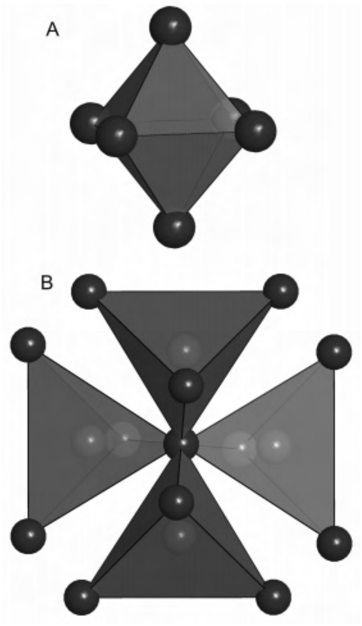

Figure 3. Structural fragments of Ba in $Ba_{19}Li_{44}$: Ba_6 octahedron (A) centered at 0, 0, 0; Ba_{17} cluster (B) (according to $(BaBa_3Ba_{1/4})_4$) at 1/2, 1/2, 0.

Each of the Li clusters in $Ba_{19}Li_{44}$ is formed by two centered, interpenetrating icosahedra and contains 35 close-packed tetrahedra. The Li_{19} cluster was predicted to be stable in the gas phase[19] and is one of the six most stable Li anti-

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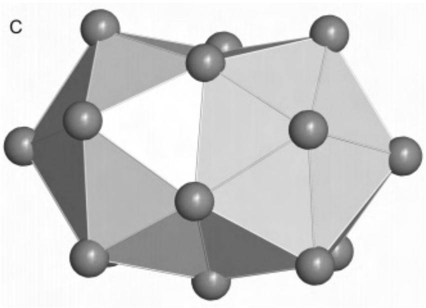

Figure 4. Li_{19} polytetrahedral cluster (C) centered at 1/4, 3/4, 1/8.

Mackay clusters.[20,21] Ba_{19}[22] and Ar_{19}[23] have been found for the gaseous elements. In the solid state, the 19-atom double icosahedron is known[24,25] but is formed of different atom types. This cluster is also often a structural subunit in many decagonal phases.[26,27]

All Li atoms in the structure have coordination number 12. Endohedral Li−Li distances for clusters are in the range 2.87(3)−3.44(2) Å, distances in Li triangles are 3.25(3) and 3.71(3) Å. The Ba atoms form Frank−Kasper polyhedra on the basis of tetrahedra (in part highly distorted) with coordination numbers 14, 15, and 16. The Ba−Li interatomic distances (3.78(2)−4.30(2) Å) are in the range for other known Ba−Li intermetallic compounds.

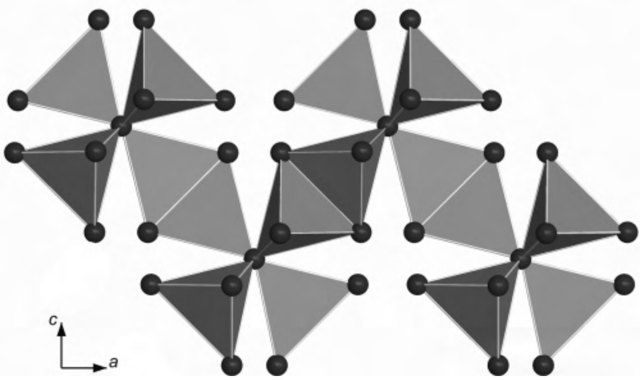

Figure 5. Infinite 3D network of Ba_{17} clusters (according to $Ba_9Ba_{8/2}$).

Conclusion

The new intermetallic compound $Ba_{19}Li_{44}$, synthesized from the elements, has an exceptionally complex structure and very large unit cell for binary compounds. Its crystal structure, investigated by single-crystal and powder X-ray diffraction analysis, can be described as a complicated variant of the chalcopyrite structure type and contains icosahedron-based polytetrahedral clusters typical for Li-rich phases. Thermal behavior of this compound was also characterized. According to DTA and Guinier measurements, $Ba_{19}Li_{44}$ undergoes peritectoid decomposition at 126 °C to $BaLi_4$ and Ba.

Supporting Information Available: Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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