

New intermetallic phase and subnitride with Ba, Li, Na

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In recent years numerous metal-rich nitrides of alkaline-earth metals, particularly of Ba in combination with Na, have been discovered [1]. Extending this chemistry to the heavier homologues of Na proved unsuccessful; however, Li emerged as the most promising candidate for a further development of this area, as we found several new subnitride phases in presence of this element.

A detailed knowledge of the relevant intermetallic systems is needed to open up this field of research. Two binary compounds in the Na–Ba system (Na_2Ba and NaBa) and one compound in the Li–Ba system (BaLi_4) are known. In contrast, no miscibility exists in the solid-state Li–Na system. Ternary compounds were previously unknown in the Na–Li–Ba system as well. Herein, we report the first such compound, together with a first Li–Ba subnitride.

$\text{Li}_{13}\text{Na}_{29}\text{Ba}_{19}$ formed from the elements at 670 K crystallizes in a new structure type of cubic symmetry [2]. The main feature of this structure is a Li_{26} cluster formed from four interpenetrating icosahedra (Fig. 1). In that cluster, a central Li_4 tetrahedron is capped by 4, 6, and 4×3 Li atoms above its faces, edges, and vertices, respectively. Such anti-Mackay-type Li_{26} clusters have been predicted to be stable in the gas phase, and isostructural Ar_{26} and Ba_{26} species have been postulated on the basis of the cluster distribution in mass spectra of the gaseous elements.

In the solid state, the M_{26} cluster of γ -brass (Cu_5Zn_8) is well-known, however, it is composed of at least two different atoms types. Similarly, the M_{26} cluster of Ag_4Li_9 contains both Ag and Li atoms. To our knowledge, $\text{Li}_{13}\text{Na}_{29}\text{Ba}_{19}$ is the first example of a solid with homoatomic M_{26} clusters.

The 4+4 atoms at the center of the Li_{26} cluster define what is known as a tetrahedron star (TS; Fig. 1(a)). Additional capping of the TS by 6 Li atoms and 4 Li_3 triangles results in four interpenetrating centered Li_{13} icosahedra, (I; Fig. 1(b)). The structures of numerous crystalline and quasicrystalline intermetallic phases can be systematized on the basis of TS and I. Icosahedral Li_{13} fragments are found in the binary compound BaLi_4 , where they share faces to form infinite chains. Distorted I surround Na atoms in the structures of Na_2Ba and NaBa .

The TS is composed of 5, and I of 20 (slightly distorted) face-sharing tetrahedra. This type of close packing of tetrahedra in intermetallic structures was recognized by Frank and Kasper early on. Their approach can also be used to describe the local environment of the Na and Ba atoms in $\text{Li}_{13}\text{Na}_{29}\text{Ba}_{19}$. While the Na atoms are icosahedrally coordinated, larger Frank-Kasper-type polyhedra with 15–17 vertices surround the Ba atoms. In the crystal structure of $\text{Li}_{13}\text{Na}_{29}\text{Ba}_{19}$, the Na and Ba atoms lie between the Li_{26} clusters, which form a face-centered cubic array (A sites).

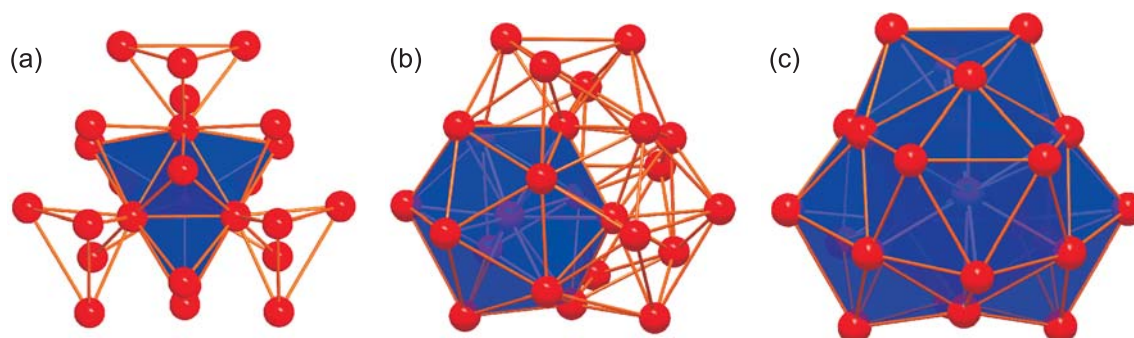


Figure 1: (a) ‘Tetraederstern’ (TS) and (b) icosahedral (I) fragments of the Li_{26} cluster (c) in $\text{Li}_{13}\text{Na}_{29}\text{Ba}_{19}$.

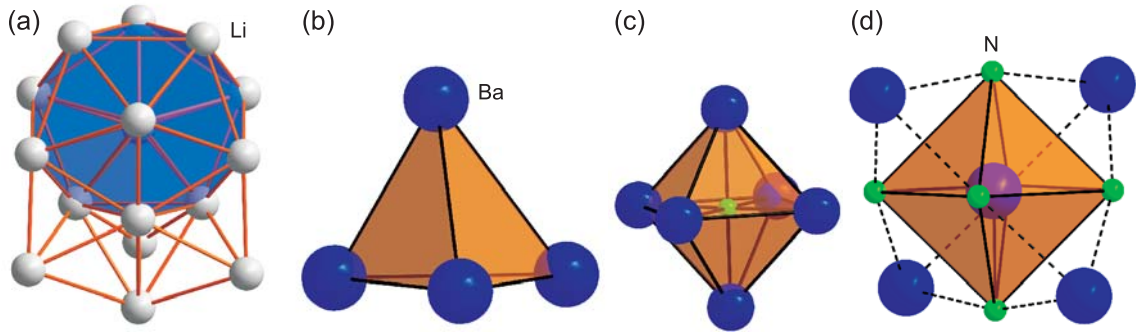


Figure 2: Structural fragments in (a) $\text{Li}_{80}\text{Ba}_{39}\text{N}_9:\text{Li}_{17}$ cluster, (b) Ba_4 tetrahedron, (c) Ba_6N octahedron, and (d) Ba_5N_6 cluster.

All of the octahedral (O sites) and half of the tetrahedral (T sites) voids are filled by $\text{BaBa}_4\text{Na}_{12}$ polyhedra, as in the LiAlSi structure type, corresponding to a filled zinc blende or rock salt structure. The resulting formulation of $(\text{Li}_{26})_4^{\text{A}} (\text{BaBa}_4\text{Na}_{12})_4^{\text{O}} (\text{BaBa}_4\text{Na}_{12})_4^{\text{T}} \cong \text{Li}_{13}\text{Na}_{12}\text{Ba}_5$ accounts for only 5 of 19 Ba and 12 of 29 Na atoms per formula unit. The remaining Na and Ba atoms fill the rest of space in the unit cell, resulting in a polytetrahedral packing.

The Li_{26} clusters are surrounded by a larger cage of 28 Ba atoms, which consists of 16 triangles and 12 pentagons. All of the pentagons are capped from the inside by peripheral Li atoms of the Li_{26} cluster and from the outside by Na atoms. These capping Na and Li atoms form the only Li–Na contact in the structure, in which the remaining Li and Na atoms are completely separated, consistent with the immiscibility of the two elements in solid state.

The question remains whether the Li_{26} clusters in $\text{Li}_{13}\text{Na}_{29}\text{Ba}_{19}$ represent the upper limit of icosahedron-based Li clusters. In principle, polytetrahedral packing could be continued to yield larger anti-Mackay-type clusters, such as Li_{45} comprising 13 interpenetrating Li_{13} icosahedra, analogous to the M_{45} clusters in $\text{Mg}_2\text{Al}_5\text{Cu}_6$ and $\text{Mg}_2\text{Zn}_{11}$. According to calculations for gas-phase Li clusters, structural strain increases with cluster size, such that Mackay-type icosahedral clusters, followed by fcc-based face centered clusters are predicted to form before converging to the bulk bcc structure of metallic lithium.

Single crystals of the first Li–Ba subnitride $\text{Li}_{80}\text{Ba}_{39}\text{N}_9$ were obtained from Ba, $\text{Ba}(\text{N}_3)_2$, and Li in closed Ta containers at 670 K followed by slow cooling to room temperature [3]. Its crystal structure is best described as a packing of four different fragments. Again centered Li_{13} icosahedra with additional lithium atoms present the backbone of the structure, forming an fcc-type arrangement (A sites, Fig. 2(a), and Fig. 3). Half of the tetrahedral voids in the A packing are filled by Ba_4 tetrahedra (B sites, Fig. 2(b)), so that the AB packing corresponds to the zinc blende structure type. The remaining tetrahedral voids in the A packing are filled in an ordered way by subnitride clusters Ba_6N (C sites, Fig. 2(c)) and Ba_5N_6 (D sites, Fig. 2(d)). So, the overall composition can be written as $A_8B_8C_6D_2 \cong \text{Li}_{160}(\text{Ba}_4)_8(\text{Ba}_6\text{N})_6(\text{Ba}_5\text{N}_6)_2 \cong \text{Li}_{80}\text{Ba}_{39}\text{N}_9$. The packing of the four fragments can also be regarded as an ordered variant of the fluorite structure type. The Ba–Li framework exhibits interatomic distances as in the related intermetallic phases.

Isolated octahedral Ba_6N units in $\text{Li}_{80}\text{Ba}_{39}\text{N}_9$ are very similar to those in $\text{Na}_{16}\text{Ba}_6\text{N}$. In contrast, the Ba_5N_6 unit is observed for the first time. Here, the central barium atom is surrounded by an octahedron of nitrogen atoms, which is, in turn, capped on every second face by four additional barium atoms in a tetrahedral fashion (Fig. 2(d)). Since each of the six nitrogen atoms has close contacts to two lithium atoms of the neighboring lithium clusters, the overall composition of this novel subnitride cluster may be written as $\text{Li}_{12}\text{Ba}_5\text{N}_6$.

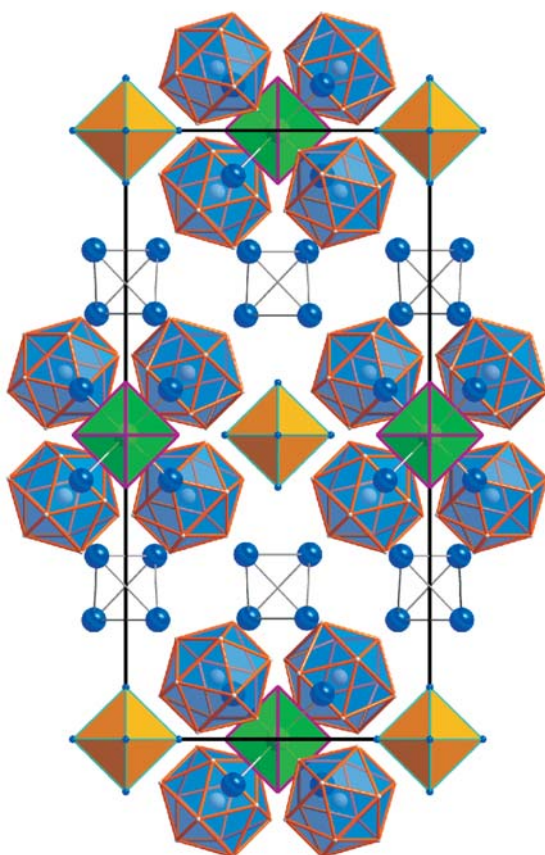


Figure 3: Location of Ba_4 (*B*), Ba_6N (*C*), and Ba_5N_6 (*D*) fragments in the crystal structure of $Li_{80}Ba_{39}N_9$. The tetragonal unit cell is outlined.

Thus, $Li_{80}Ba_{39}N_9$ is the first example of a subnitride with nitrogen atoms bonded to both alkali and alkaline earth metal atoms. None of the previously known Na–Ba based subnitrides contain a Na–N bonding contact. The only examples of bonding between the nonmetal atoms and metal atoms of two different types in subnitrides or suboxides are $Na_nBa_{14}CaN_6$, $(Sr_{0.48}Ba_{0.52})N$, and $Rb_{2.59}Cs_{8.37}O_3$, however, featuring the same valency. $Li_{80}Ba_{39}N_9$ is the first example of a metal-rich nitride in which both the mono- and divalent metal atoms are bonded to the nitrogen atoms. Both new metal-rich phases involving Li and Ba, the intermetallic compound $Li_{13}Na_{29}Ba_{19}$ and the subnitride $Li_{80}Ba_{39}N_9$, appear to represent just a tip of an iceberg, with more compounds to follow.

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- [3] *Smetana, V., V. Babizhetskyy, G. Vajenine and A. Simon.* *Inorganic Chemistry* **45**, 10786–10789 (2006).