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Topological Relationships and Building Blocks in Zintl Phases of the Composition $Ba_{n+1}(Mg,Li)_{2n}Si_{2(n+1)}$

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The structures of two novel Zintl phases, $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ and $BaMg_{0.1}Li_{0.9}Si_2$, are presented. Both compounds contain chains in *cis*−*trans* conformation. The silicon partial structure of $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ ($C2/m$; $a = 1212.0(1)$, $b = 459.78(4)$, $c = 1129.10(9)$ pm; $\beta = 91.77(2)°$; $Z = 1$) is built of unbranched, planar Si_6 chains while $BaMg_{0.1}Li_{0.9}Si_2$ ($Pnma$; $a = 725.92(5)$, $b = 461.36(3)$, $c = 1169.08(8)$ pm; $Z = 4$) consists of infinite Si_n chains. The compounds show all electronic and structural characteristics that are typical for the special subset of Zintl phases with highly charged planar anions. The structures of the new compounds, as well as that of $Ba_2Mg_3Si_4$, can be derived from the common parent type $BaMg_2Si_2$. It is shown that a comprehensive picture of a chemical twinning based on $BaMg_2Si_2$ can be derived.

Introduction

The novel compounds $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ and $BaMg_{0.1}Li_{0.9}Si_2$ were synthesized and characterized in the course of our current studies on ternary and quaternary silicides.[1,2] Our main interest in investigating Zintl phases is focused on a deeper understanding of the electronic structures and the structure-determining factors of polyanions in solids, at least within this class of compounds, but may well extend beyond. Although the Zintl−Klemm (ZK) concept[3−6] has been shown to be very successful in explaining the connectivity of the anionic substructures on the basis of simple electron−counting rules, it is not possible to predict specific crystal structures by the knowledge of stoichiometry alone because, in general, several structural solutions fit given overall electron number. Additional structure-directing parameters have to be evaluated to go beyond a pure prediction of the overall connectivity, and strategies should be developed for the synthesis of compounds with specific structural features in the solid state. Taking into account the strong relationship between structure and physical properties, it is highly desirable to be able to specifically change structures to optimize compounds having specific physical properties.

Quite recently, we were able to define a number of parameters that control certain local structural features in ternary Zintl phases M_xMg_yX (M = Ca, Sr, Ba; X = Si, Ge) with highly charged oligomeric or polymeric anions.[2,7−11] The most important factors are (1) the planarity of the anions and their eclipsed stacking, (2) the trigonal prismatic coordination of central parts of the anions by the larger cations M, (3) a coordination of terminal atoms of the anion by smaller Mg cations together with M in the form of a nearly square antiprism with Mg at the outer periphery, (4) the fact that the Mg cations stabilize higher charges and thus can determine the relative number of terminal groups in the Zintl anions, and (5) the influence of M and Mg on the conformation of unbranched chains.

The quaternary systems M/Mg/Li/Si seem to have been predestined for the study of different structure-determining factors: on one hand, the ratio Mg/Li allows us to explore the influence of the valence electron number; on the other hand, the ratio M/Mg allows us to use the different coordinative preferences of the cations, which have already been extensively studied.

Recently, we described the compound $Ba_2Mg_3Si_4$,[2,8] the structure of which was shown to be easily derived from the structure of $BaMg_2Si_2$[12,13] by simple geometrical transformations in the sense of a chemical twinning.[14] With $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$, another member of this series was characterized. This encouraged us to think about further possible structures and stoichiometries based on this formalism. Thus, a compound of the stoichiometry $BaM'Si_2$ (M′ = Li, Mg) was proposed,[2] and a correspondingly designed synthesis finally led to the discovery of the novel compound $BaMg_{0.1}Li_{0.9}Si_2$, which exhibits the predicted structure.

Experimental Section

Syntheses. All reagents and products were stored and handled in an argon-filled glovebox because of their sensitivity to oxygen and moisture. About 1 g amounts of the compounds $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ and $BaMg_{0.1}Li_{0.9}Si_2$ were prepared by direct synthesis from stoichiometric

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Table 1. Data Collection and Refinement Details for $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ and $BaMg_{0.1}Li_{0.9}Si_2$

formula	$Ba_6Mg_{5.2}Li_{2.8}Si_{12}$	$BaMg_{0.1}Li_{0.9}Si_2$
fw	1308.54	202.20
a (esd), pm	1212.0(1)	725.92(5)
b (esd), pm	459.78(4)	461.36(3)
c (esd), pm	1129.10(9)	1169.08(8)
β (esd), deg	91.77(2)	
V (esd), 10^6 pm^3	628.88(9)	391.54(5)
space group (No.); *Z*	*C*2/*m* (12); 1	*Pnma* (62); 4
density, g/cm^3	3.455	3.423
temp, K	298	298
λ, Å	0.710 69	0.710 69
μ(Mo Kα), cm^{-1}	99.4	105.7
R/R_w[a]	0.04/0.10	0.03/0.05

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (gP)^2 + kP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ and *k*, *g* = weights.

amounts of the pure elements (Mg pieces, Fluka 99.8%; Ba rods, Alfa 99.9%, additionally distilled under high vacuum; Si powder, Alfa 99.9%; Li rods, Alfa 99.9%) in sealed niobium ampules under vacuum. The stoichiometric mixtures of the elements were heated to 1120 K for 12 h. After the mixtures were cooled at a rate of ~50 K/h, brittle samples of silvery metallic luster were obtained. The products decomposed slowly under air and reacted violently with water, giving off pyrophoric gases. Differential thermal analyses led to the assumption that both compounds decompose peritectically above 1170 K. According to X-ray investigations on powdered samples, both $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ and $BaMg_{0.1}Li_{0.9}Si_2$ show minor impurities due to the presence of Ba_2LiSi_3.[15]

To investigate possible phase widths of the compounds, several samples with different Mg:Li contents were prepared. In X-ray investigations on the powders, we found varying contents of $BaMg_{0.1}Li_{0.9}Si_2$ and $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$, as well as different ternary and binary byproducts. In none of these cases, could we observe significant changes in the lattice parameters of $BaMg_{0.1}Li_{0.9}Si_2$ and $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ which would point to phase widths of the compounds.

Structural Studies. The data collection for $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ was performed on a bar-shaped single crystal (~0.1 × 0.02 × 0.02 mm) with an image-plate diffractometer (STOE IPDS) using monochromated Mo Kα radiation. The cell constants were determined on a four-circle diffractometer (STOE STADI4) using 74 reflections in the range $33.4° \leq 2\theta \leq 46.3°$ (Table 1). The observed Laue symmetry 2/*m* and the extinctions were consistent with the space groups *C*2/*m*, *C*2, and *Cm*. The structure of $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ was solved in the centrosymmetric group *C*2/*m* using direct methods.[16] The occurrence of quite large displacement parameters for the Mg sites was traced back to mixed Mg,Li occupancies. The further refinement of these occupancies, keeping the total occupancies fixed at unity, led to quite reasonable displacement parameters. An underoccupancy of the corresponding Mg sites is conceivable but may ruled out by the fact that lithium is essential for the synthesis of the compound. The final cycle of full-matrix, least-squares refinement with 505 observed reflections ($I > 2\sigma(I)$) and 44 variables (including all positional and anisotropic displacement parameters) converged at $R/R_w = 0.04/0.10$. The refined composition was found to be $Ba_6Mg_{5.2(3)}Li_{2.8(3)}Si_{12}$ (Tables 1 and 2).

Table 2. Positional Parameters (Esd's) and Isotropic-Equivalent Thermal Parameters (Esd's), pm^2, for $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$

atom	*x*	*y*	*z*	U_{eq}[a]	occ
Ba1	0	0	0	193(4)	1
Ba2	0.8574(1)	0	0.6257(1)	179(4)	1
Si1	0.5109(3)	0	0.7792(2)	190(7)	1
Si2	0.5692(3)	0	0.5791(3)	179(7)	1
Si3	0.3235(2)	0	0.8500(3)	179(7)	1
M1	0.7105(4)	0	0.9040(4)	218(17)	0.88(2) [Mg] 0.12(2) [Li]
M2	0.1319(6)	0	0.7128(6)	260(30)	0.44(2) [Mg] 0.56(2) [Li]

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Distances (Esd's), pm, in $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$[a]

atom pair	*d*	*n*	atom pair	*d*	*n*
Ba1−Si1	339.7(2)	4	Ba1− M1	364.0(4)	2
Ba1−Si3	353.6(2)	4	Ba1−M2	365.9(7)	2
Ba1−M1	362.5(4)	4			
Ba2−Si2	339.8(2)	2	Ba2−Si2	351.6(3)	
Ba2−Si1	339.9(2)	2	Ba2−M1	365.9(4)	
Ba2−M2	344.0(7)		Ba2−M2	372.6(6)	2
Ba2−Si3	345.5(2)	2	Ba2−M2	382.8(7)	
Ba2−Si2	349.8(2)	2			
Si1−Si2	238.8(4)		Si1−M2	284.0(5)	2
Si1−Si3	243.2(5)		Si1−Ba1	339.7(2)	2
Si1−M1	276.1(5)		Si1−Ba2	339.9(2)	2
Si2−Si1	238.8(4)		Si2−Ba2	339.8(2)	2
Si2−Si2	241.3(6)		Si2−Ba2	349.8(2)	2
Si2−M2	284.1(4)	2	Si2−Ba2	351.6(3)	
Si3−Si1	243.2(5)		Si3−M1	282.1(5)	
Si3−M2	275.1(7)		Si3−Ba2	345.5(2)	2
Si3−M1	275.3(3)	2	Si3−Ba1	353.6(2)	2
M1−Si3	275.3(3)	2	M1−M1	328.3(6)	2
M1−Si1	276.1(5)		M1−Ba1	362.5(4)	4
M1−Si3	282.1(5)		M1−Ba1	364.0(4)	2
M1−M2	327.5(7)	2			
M2−Si3	275.1(7)		M2−Ba2	344.0(7)	
M2−Si1	284.0(5)	2	M2−Ba1	365.9(7)	
M2−Si2	284.1(4)	2	M2−Ba2	372.6(6)	2
M2−M1	327.5(7)	2	M2−Ba2	382.8(7)	

[a] *n* denotes the frequency of the corresponding distance.

The data collection for $BaMg_{0.1}Li_{0.9}Si_2$ was performed for a disk-shaped single crystal (~0.18 × 0.12 × 0.04 mm) on a diffractometer with a CCD detector (Siemens SMART PLATFORM) using monochromated Mo Kα radiation. The data were integrated with the SAINT program[17] and corrected for Lorentz, polarization, air absorption, and absorption effects due to the path length through the detector face plate. The cell constants were determined on a four-circle diffractometer (STOE STADI4) using 112 reflections in the range $28.3° \leq 2\theta \leq 46.3°$ (Table 1). The observed Laue symmetry *mmm* and the extinctions were consistent with the space groups *Pnma* and $Pn2_1a$. The structure of $BaMg_{0.1}Li_{0.9}Si_2$ was solved in the space group *Pnma* using direct methods.[16] The occurrence of unusually small displacement parameters for the Li sites pointed to mixed Li,Mg occupancies. The corresponding refinement of the latter, keeping the total occupancy fixed at unity, led to very reasonable displacement parameters. As in case of $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$, an underoccupancy of the corresponding Mg sites is also possible but may ruled out again by the fact that lithium is essential for the synthesis of the compound. The final cycle of full-matrix, least-squares refinement based on 706 observed reflections ($I > 2\sigma(I)$) and 27 variables (including all positional and anisotropic displacement parameters) converged at $R/R_w = 0.03/0.05$. The refined composition was found to be $BaMg_{0.08(1)}Li_{0.92(1)}Si_2$ (Tables 1 and 4).

Results and Discussion

Both $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ and $BaMg_{0.1}Li_{0.9}Si_2$ are representatives of novel structure types (Figures 1 and 3). Their silicon partial structures are built of planar silicon anions (planar cis−trans−cis Si_6 chains and infinite cis−trans chains, respectively). The complete structures show all characteristics typical for compounds containing such anions.[2,8,18,19] Thus, the planar silicon

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Table 4. Positional Parameters (Esd's) and Isotropic-Equivalent Thermal Parameters (Esd's), pm^2, for $BaMg_{0.1}Li_{0.9}Si_2$

atom	x	y	z	U_{eq}[a]	occ
Ba	0.3695(1)	$^1/_4$	0.6382(1)	113(1)	1
Si1	0.9653(1)	$^1/_4$	0.3345(1)	117(2)	1
Si2	0.2911(1)	$^1/_4$	0.3408(1)	122(2)	1
M	0.8846(6)	$^1/_4$	0.5616(5)	126(17)	0.93(1) [Li] 0.08(1) [Mg]

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Distances (Esd's), pm, in $BaMg_{0.1}Li_{0.9}Si_2$[a]

atom pair	d	n	atom pair	d	n
Ba−Si1	336.6(1)	2	Ba−Si2	352.3(2)	
Ba−Si2	338.5(1)	2	Ba−M	363.2(4)	
Ba−Si1	346.9(1)	2	Ba−M	376.5(4)	2
Ba−Si2	350.6(1)	2	Ba−M	384.5(4)	
Ba−M	351.2(5)				
Si1−Si2	236.6(2)		Si1−M	282.6(3)	2
Si1−Si2	240.8(2)		Si1−Ba	336.6(1)	2
Si1−M	271.9(5)		Si1−Ba	346.9(1)	2
Si2−Si1	236.6(2)		Si2−Ba	338.5(1)	2
Si2−Si1	240.8(2)		Si2−Ba	350.6(1)	2
Si2−M	287.2(3)	2	Si2−Ba	352.3(2)	
M−Si1	282.6(3) 2	2	M−Ba	363.2(4)	
M−Si2	287.2(3)	2	M−Ba	376.5(4)	2
M−M	319.5(6)	2	M−Ba	384.5(5)	
M−Ba	351.2(5)				

units are stacked in an eclipsed way with stacking distances of about 450 pm, here, as in most other cases, directly reflected in one of the lattice constants. These distances are far greater than the Si−Si bond distances, which are in the range of 250 pm; however, they allow weak interactions between the π^* states of the highly charged Zintl anions, which stabilize the structures, and give rise to interesting physical properties such as strong anisotropies in the electrical conductivities. As expected, the cations, either calcium, strontium, and barium or magnesium and lithium, show clear preferences with respect to the coordination of specific silicon centers of the cluster anions. Terminal or isolated silicon atoms are always coordinated by Mg and Li, while M (M = Ca, Sr, or Ba) predominantly coordinates two- and trivalent Si centers. A nearly square arrangement of M atoms around the centers of Si−Si bonds in a trans conformation (e.g., zigzag chains) is a very common structural element. If two of the M atoms are exchanged by Li/Mg, a cis conformation of the Si−Si bond is preferred (cf. coordination of the Si_6 chains, Figure 1).

Figure 1a shows a perspective view of the crystal structure of $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$. Its silicon partial structure is built of planar Si_6 chains in cis−trans−cis conformations (Figure 1b). With bond lengths of 238, 241, and 243 pm and two bond angles of 118.8 and 128.1°, the geometry of the Si_6 unit has inversion symmetry and is very similar to that found in the structure of $Ba_2Mg_3Si_4$ (bond lengths 240, 243, and 244 pm; bond angles 117.8 and 128.2°), which is built of Si_6 chains and Si_2 dumbbells.[8] Applying a formal ionic view in the sense of the ZK concept, one would formulate $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ as $(Ba^{2+})_6(Mg^{2+})_{5.3}(Li^+)_{2.7}[Si_6^{12.65-}]_2$. Thus, the formal charge of the Si_6 chain lies between the values expected for a single- ($q = -14$) and a double-bonded system with $q = -12$. A partial-double-bond character would also be in accordance with the present bond lengths, being significantly smaller than the typical Si−Si single-bond lengths of about 250 pm, found in BaSi,[20] $BaMg_2Si_2$,[12,13] and Ba_5Si_3,[21] which clearly contain only single-bonded units. The general formulation for the charge of a (partially) double-bonded Si_6^q system is $q = -(14 - x)$ with $0 < x \leq 6$. For each x, there is a double-bond contribution to the total bonding because x electrons are taken out of the antibonding π orbitals (totally we have six orbitals of π symmetry). Within the simple molecular orbital (MO) picture of an isolated Si_6 cluster, x can only be an even number in order to result in a closed-shell system. For $x = 2$ (depopulation of π_6), we have one (Chart 1a), for $x = 4$ (depopulation of π_5 and π_6), two (Chart 1b), and for $x = 6$ (depopulation of π_4−π_6), three double bonds in the system (Chart 1c).

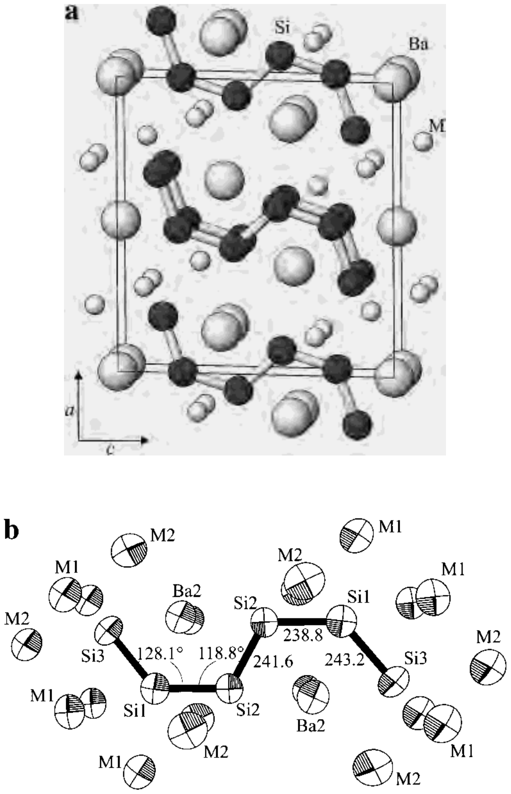
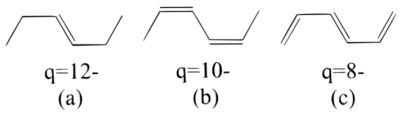


Figure 1. (a) Perspective view of the structure of $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ (b) ORTEP plot showing the conformation and coordination of the Si_6 unit with thermal vibrational (50%) ellipsoids.

Chart 1. Lewis Formulas of Si_6^q Clusters with Different Formal Charges q



The ecliptic packing of the clusters in the solid compound (along b) leads to an interaction of the π states and thus to a dispersion of the corresponding π bands. Because of this, the energy gaps found in the MO scheme of the isolated cluster disappear and restrictions in the choice of x no longer exist. For $x = 1.3$, the Fermi energy intersects the π bands, leading to a metallic behavior of the compound. Since both π_5 and π_6 bands are only partially occupied (Figure 2), we find an overall bond situation which is between those in Chart 1a−b and a single-bonded system or in other words a double-bond character delocalized over the silicon centers Si1−Si2−Si2−Si1.

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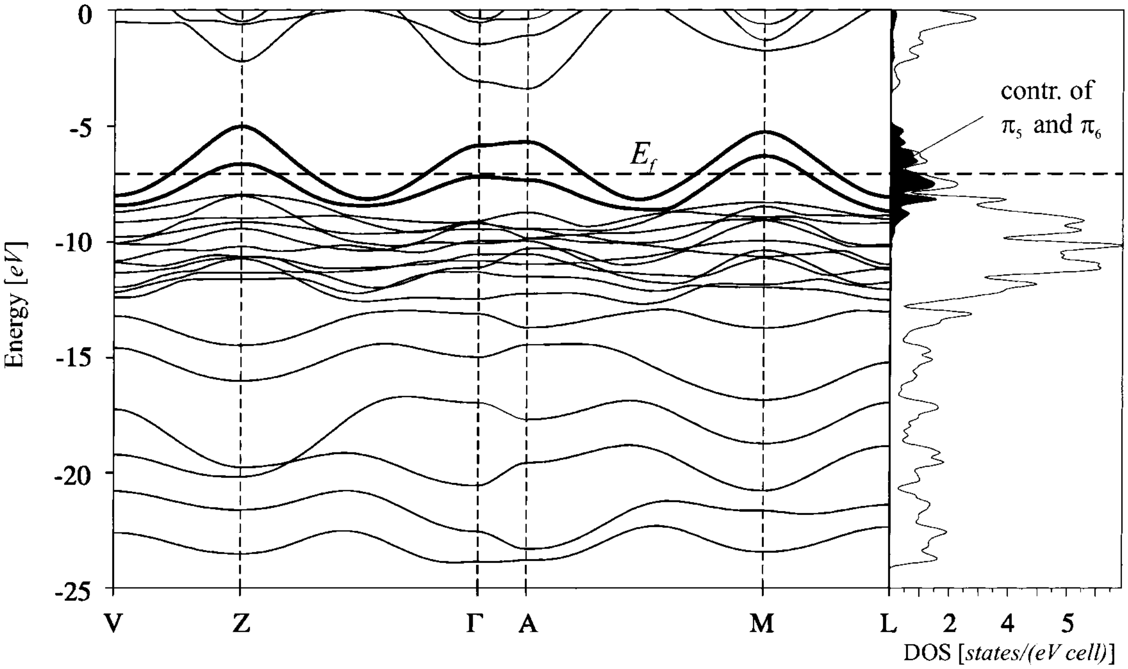

Figure 2. Electronic band structure and density of states (DOS) for $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ based on an extended Hückel (EH) band structure calculation.[25]

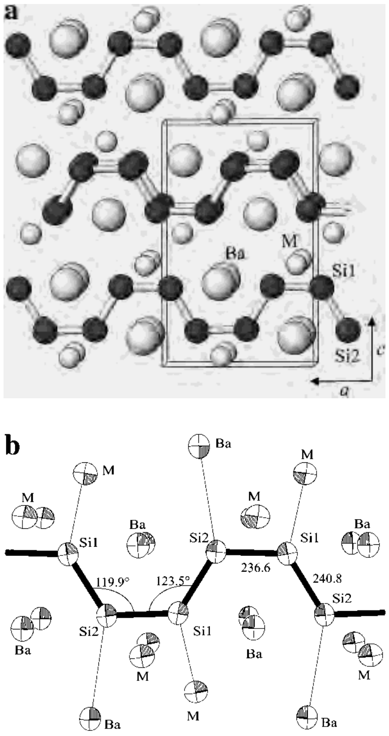

Figure 3. (a) Perspective view of the structure of $BaMg_{0.1}Li_{0.9}Si_2$. (b) ORTEP plot showing the conformation and coordination of the infinite cis−trans chain of silicon with thermal vibrational (50%) ellipsoids.

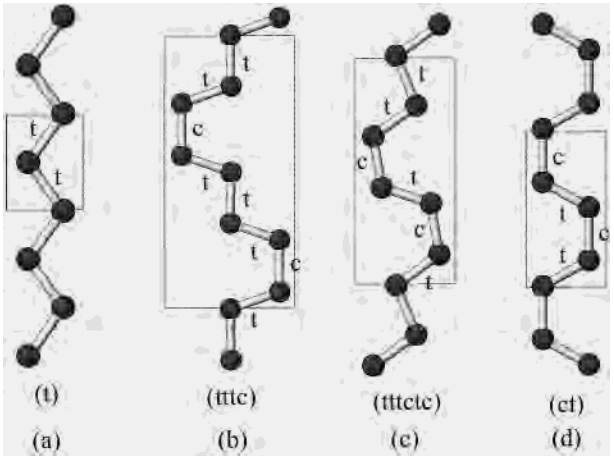

Figure 4. Conformations of known infinite silicon chains: (a) $(t)_n$ chain in MSi; (b) $(tttc)_n$ chain in $SrLaSi_2$; (c) (tttctc) chain in Ca_2LiSi_2; (d) (ct) chain in $BaMg_{0.1}Li_{0.9}Si_2$.

Figure 3a shows a perspective view of the crystal structure of $BaMg_{0.1}Li_{0.9}Si_2$. The silicon partial structure contains novel planar infinite Si chains of cis−trans conformations (Figure 3b). Each cis−trans chain shows two different Si−Si bond lengths of 237 and 242 pm. Again, the smaller value is found for the Si−Si bonds in cis conformations. Performing a formal charge transfer according to the ZK concept, $(Ba^{2+})_2(Mg^{2+})_{0.2}(Li^+)_{1.8}({}^1_\infty[Si_4{}^{6.2-}])$, we find that each Si atom of an infinite chain has a formal charge of $q = -1.55$. In the case of a polyethylene-like chain, one would expect values of $q = -1$ and $q = -2$ for a single-bonded chain like that in a BaSi complex. Thus, as in the $Si_6{}^{12.65-}$ chain, a partial-double-bond character is present. The Si−Si bond lengths compare quite well with those (238−239 pm) of the planar $Si_6{}^{10-}$ unit found in Ba_2LiSi_3.[15] With a formal charge of $q = -1.51$ per Si atom in the planar six-membered ring, the bond situation seems to be comparable to that in the cis−trans chain presented in this work. Quite recently, an infinite silicon chain having a similar conformation was reported in connection with the structure of the binary compound LaSi;[22] however, with values of 249−261 pm, the Si−Si bond lengths are significantly longer than those in the present compound.

Three other variants of infinite planar silicon chains are known: an all-trans or zigzag chain (Figure 4) seen in the monosilicides MSi (M = Ca, Sr, Ba), which crystallize in the CrB-type structure, and two planar chains of larger translation units containing Si−Si bonds in cis and trans conformations (Figure 4b,c) found in Ca_2LiSi_3[23] and $SrLaSi_2$,[24] respectively.

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Thus, the infinite cis−trans chain in $BaMg_{0.1}Li_{0.9}Si_2$ (Figure 4d) and the all-trans chain in MSi may be considered as two borderline cases of the smallest translation period. (Topologically, an all-cis conformation leads to isolated rings like the six-membered ring in Ba_2LiSi_3.[15] Consequently, an infinite all-cis chain is an infinitely large ring.) Between these two limiting cases, several intermediate conformations are conceivable, of which two are observed in Ca_2LiSi_3 and $SrLaSi_2$. All finite chains like the Si_6 chain in $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ may be regarded as fragments of such infinite chains.

The compound $BaMg_{0.1}Li_{0.9}Si_2$ was not found by chance but was found in a study based on a strong topological relationship among the crystal structures of $BaMg_2Si_2$, $Ba_2Mg_3Si_4$, and $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ from which the existence of a quaternary compound of the stoichiometry $BaM'Si_2$ ($M' = Li, Mg$) built of infinite cis−trans chains was predicted.[2] Thus, $BaMg_2Si_2$ can be viewed as the *parent structure* containing all the important structural features necessary for the compound family. A *glide separation* of different structure blocks (Figure 5; underlayed with grey) against each other together with an addition of an Si_2 unit in the resulting free space of the cation matrix leads to the real structures of $Ba_2Mg_3Si_4$ and $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ and to the hypothetical compound $BaM'Si_2$. Replacing Mg and Li by M′, one obtains the more general formulation $Ba_{n+1}M'_{2n}Si_{2(n+1)}$, including $[BaM'Si_2]_2$ ($n = 1$), $[Ba_6Mg_{5.2}Li_{2.8}Si_{12}]_{0.5}$ ($n = 2$, $M' = 65\%$ Mg), and $[Ba_2Mg_3Si_4]_2$ ($n = 3$, $M' = 100\%$ Mg). The Li/Mg ratio for M′ seems to be a free parameter which allows for each structure to adjust its optimum valence electron concentration. Phases with $n > 3$ are conceivable, but no evidence of their existence has yet been found. A series of syntheses for $BaM'Si_2$ with varying Li/Mg ratios led to the discovery of $BaMg_{0.1}Li_{0.9}Si_2$. As expected, the silicon partial structure is built of infinite cis−trans chains. The real structure differs only slightly from the expected structure, namely, with respect to the relative arrangement of the chains (Figure 5d). Thus, we find an orthorhombic structure and not the predicted monoclinic one.

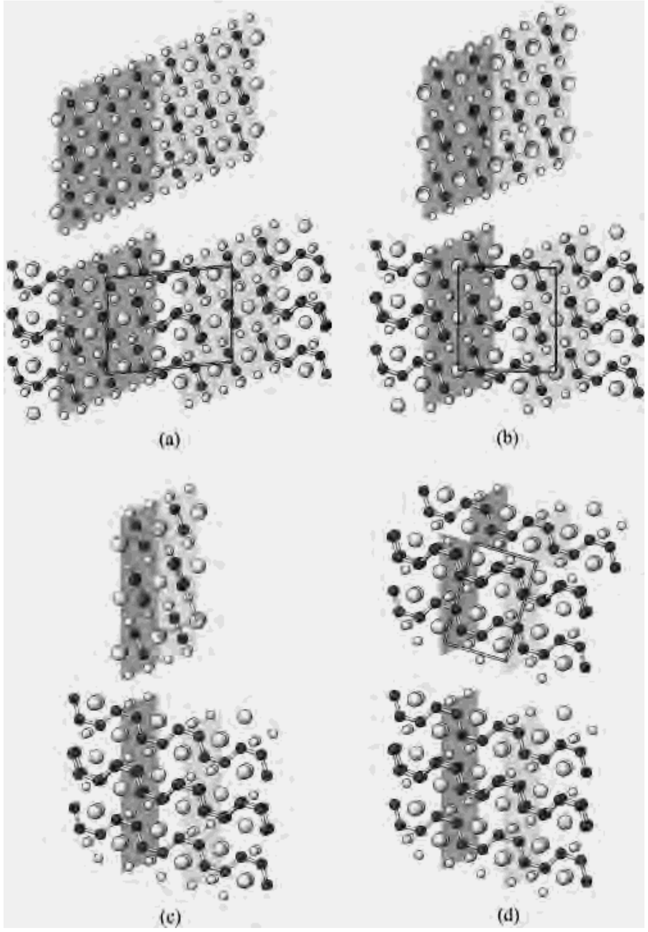

Figure 5. Topological relationship between the structures of $BaMg_2Si_2$ and (a) $Ba_2Mg_3Si_4$, (b) $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$, and (c) $Ba_2M_2Si_4$. Part d shows a comparison of the structures of $BaMg_{0.1}Li_{0.9}Si_2$ and the hypothetical compound $Ba_2M_2Si_4$. Key: black circles, Si; small white circles, Li/Mg; large white circles, Ba.

Conclusions

Nonpractitioners of solid-state chemistry often criticize the lack of *predictability* and *design* in solid-state synthesis. However, our strategy leading to the novel compound $BaMg_{0.1}Li_{0.9}Si_2$ shows that it is, in fact, possible to predict target structures successfully. The structures of the system $Ba_{n+1}(Mg,Li)_{2n}Si_{2(n+1)}$ ($n = 1-3$) represent a striking example of a topological relationship which may be described within the concept of *chemical twinning* formulated by Andersson and Hyde.[14]

Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) The EH band structure calculations[26] were performed with the MEHMACC[27] package. Using the standard parameters for Ba, Mg, Li, and Si[29] and the experimental valence electron (VE) number of 73.2 VE/formula unit for $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$, the results appeared to be independent if the statistically occupied M′ positions were treated as Li or Mg. The integration over the Brillouin zone was based on a set of 80 irreducible **k** points. The symmetry paths in reciprocal space used to represent the band structure of $Ba_6Mg_{5.2}Li_{2.8}Si_{12}$ were chosen according to ref 32 ($\Gamma(0, 0, 0)$; $A(0, 0, -{}^1/_2)$; $M(-{}^1/_2, {}^1/_2, {}^1/_2)$; $L(0, {}^1/_2, {}^1/_2)$; $V(0, {}^1/_2, 0)$; $Z(-{}^1/_2, {}^1/_2, 0)$].

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(29) Ba: $H_{ii}(6s) = -4.76$, $\zeta(6s) = 1.26$, $H_{ii}(6p) = -2.64$, $\zeta(6p) = 1.26$. Li: $H_{ii}(2s) = -5.4$, $\zeta(2s) = 0.65$, $H_{ii}(2p) = -3.5$, $\zeta(2p) = 0.65$. Mg: $H_{ii}(3s) = -9.0$, $\zeta(3s) = 1.38$, $H_{ii}(3p) = -4.5$, $\zeta(3p) = 1.38$. Si: $H_{ii}(3s) = -17.3$, $\zeta(3s) = 1.10$, $H_{ii}(3p) = -9.2$, $\zeta(3p) = 1.10$.[30,31]

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