Ba$_4$Si$_3$Br$_2$: A Double Salt of Barium Bromide and Barium Silicide Containing a Novel Cyclotrisilicide Unit

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Dedicated to Professor Hans-Georg von Schnering on the occasion of his 70th birthday

Abstract: A new compound of the composition Ba$_4$Si$_3$Br$_2$ was obtained by reacting BaSi with a melt of BaBr$_2$. Ba$_4$Si$_3$Br$_2$ may be described as a double salt between a Zintl phase and a halide. The structure was determined by single-crystal X-ray diffraction ($P2_1c$, $a = 1504.1(2)$, $b = 884.5(1)$, $c = 880.2(1)$ pm, $\beta = 101.93(2)°$, $R = 0.041$ $R_w = 0.079$). The crystal structure contains isolated barium cations and bromide anions as well as novel singly bonded cyclotrisilicid units. The electronic structure has been studied by linear Muffin tin orbital (LMTO) band structure calculations, which reveal semiconducting behavior with a band gap of about 0.1 eV, and by an analysis of the electron localization function.

Keywords: cluster compounds · double salts · electron localization function · silicides · Zintl phases

Introduction

Zintl phases make up a class of solid compounds between metals and semimetals that are situated electronically amid intermetallic and insulating valence compounds. A great deal of research has been carried out on Zintl phases of silicon over the last few decades. Thus, a rich variety of, in some cases, completely new homoatomic silicon arangements and oligomeric clusters, so-called *Zintl anions*, has been established.[1] There is an increasing interest in the chemical reactions of Zintl phases, not least because of luminscence phenomena. While the search for novel Zintl phases has led to a large number of novel compounds with interesting properties, the rich chemical potential of this class of compounds was hardly been explored. About 70 years ago, E. Zintl showed that it is possible to dissolve binary phases like Na$_4$Sn$_9$ or Na$_4$Pb$_9$ in liquid ammonia.[2] The intensively colored solutions contain polyanions of the type E$^{n-}_x$ (E = Sn, Pb), which were later called Zintl anions. A large number of Zintl phases have been studied with respect to their reactions in different solvents. In some cases the dissolution was enhanced by the addition of crown ethers or cryptants, which readily form complexes with the counterions.[3–9] Only a limited number of isolated polyanions have been crystallized from solutions and studied by X-ray diffraction methods. In nearly all cases the charge per atom n/x of the homonuclear clusters E$^{n-}_x$ is below one; the huge set of known Zintl anions with $n/x > 1$ could not be stabilized in solutions.

Quite recently we reported on the existence of the compounds Ba$_3$E$_2$I (E = Si, Ge),[10, 11] which may be understood as double salts between the Zintl phases Ba$_2$E[12, 13] and BaI$_2$.[14] The basic idea behind these investigations was the use of salt melts instead of organic solvents as reaction media for Zintl anions. The formation of double salts is a first step in this direction and restricts the mobility of Zintl anions in the salt melt. Thus, it may be considered as further chemical proof for the validity of the term *Zintl anion* in the sense of a chemical species whose existence is not bound to a specific crystal structure. By exploring the reactivity of the Zintl phase BaSi[15, 16] in a BaBr$_2$ melt,[17] we were able to synthesize the novel compound Ba$_4$Si$_3$Br$_2$. Ba$_4$Si$_3$Br$_2$ can be understood with respect to its stoichiometry as a double salt of BaSi and BaBr$_2$. However, the silicon partial structure in Ba$_4$Si$_3$Br$_2$ differs totally from the infinite zigzag chain in BaSi; instead of the silicon chain, a finite variant in the form of a three-membered ring of silicon is realized. Thus, we synthesized the first cyclotrisilicide anion,[*] similar to the substituted cyclotrisilanes R$_6$Si$_3$ that have been investigated quite intensively, both experimentally as well as theoretically, since the discovery of the first derivative, hexa-2,6-dimethylphenylcyclotrisilane, by

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[*] The compound Ba$_2$NiSi$_3$[18] is built of silicon trimers which are not isolated. There are short Ni−Si contacts of 242.6 pm, which are interpreted as covalent interactions. Thus, the anionic substructure has to be described as infinite [NiSi$_3$]$^{4-}$ chains.

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Masamune et al. in 1982.[19] With the help of band structure calculations and an analysis of electron localization function (ELF[20, 21]), we show, apart from the geometric viewpoint, that, in fact, a single bonded cyclic Si_3 unit is present in $Ba_4Si_3Br_2$.

Experimental Section

Syntheses: All reagents and products were stored and handled in an argon-filled glove box because of their sensitivity to oxygen and moisture. $Ba_4Si_3Br_2$ was prepared by reaction of stoichiometric amounts of barium (Ba rods, ALFA 99.9%, additionally destilled under high vacuum), silicon (Si powder, ALFA 99.9%), and barium bromide ($BaBr_2$ beads, Aldrich 99.999%) at 1270 K for 8 h in sealed niobium ampoules under vacuum, followed by cooling down at a rate of 50 K per h. The resulting brittle black material shows a dark metallic luster. It decomposes slowly in air but reacts violently with water with evolution of pyrophoric gas. According to differential thermal analysis (DTA), $Ba_4Si_3Br_2$ decomposes peritectically above 1090 K. Decomposition and reformation of $Ba_4Si_3Br_2$ was shown to be reversible by DTA and X-ray powder methods. However, the decomposition product could not be identified to date. All samples of $Ba_4Si_3Br_2$ were found to be fairly phase-pure with only minor impurities. We suppose that the latter are identical with the unknown decomposition product.

Structural studies: The data collection for $Ba_4Si_3Br_2$ was performed on a bar-shaped single crystal ($\approx 0.06 \times 0.02 \times 0.02$ mm) on a diffractometer with a CCD detector (Siemens smart platform) and monochromated $Mo_{K\alpha}$ radiation. The data were integrated by using the SAINT program[22] and corrected for Lorentz factor, polarization, air absorption, and absorption arising from the path length through the detector faceplate.[23] The cell constants were determined on a four-circle diffractometer(STOE STADIP) using 91 reflections in the range $27.1° \leq 2\Theta \leq 42.9°$(Table 1). The observed Laue symmetry *2/m* and the extinctions are consistent with the space group $P12_1/c1$. The structure of $Ba_4Si_3Br_2$ was solved by direct methods.[24] The final cycle of full-matrix least-squares refinement with 4761 observed reflections ($I > 2\sigma(I)$) and 82 variables (including all positional and anisotropic displacement parameters) converged at $R/R_w = 0.04/0.08$. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), (fax: (+49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-411640.

Theoretical studies: The band structure calculations on $Ba_4Si_3Br_2$ were performed using the tight-binding linear Muffin tin orbital method in the atomic sphere approximation (TB-LMTO-ASA[25]). The calculations are based on density functional theory (DFT) with a local exchange-correlation potential from Barth and Hedin,[26] and an additional nonlocal exchange-correlation potential from Perdew and Wang.[27] The radii of the overlapping Muffin tin spheres in the ASA approximation are chosen following the suggestions outlined by Jepsen and Andersen.[28] The basis set consists of Si-3(s,p), Ba-6s, Ba-5d, Br-4p, and 1s partial waves for interstitial spheres with Br-5s, Ba-6p, and 2p partial waves of the interstitial atoms folded down into the tails of the resulting muffin tin orbitals.[29] The Br-4s function is

treated as a core function. The energy expansion parameters $E_{v,RL}$ were chosen at the centers of gravity of the occupied part of the partial state densities. The k space integrations were performed on a set of 266 irreducible k points. The distribution of the electron localization function (ELF)[20, 21] was calculated from the LMTO wavefunction and visualized by the program GRAPA.[30]

Table 1. Crystallographic data for $Ba_4Si_3Br_2$.

empirical formula	$Ba_4Si_3Br_2$
formula weight [amu]	793.45
temperature [K]	293(2)
$\lambda(Mo_{K\alpha})$[Å]	0.71073
crystal system	monoclinic
space group	$P2_1/c$ (no. 14)
volume [10^6 pm^3]	1145.6(2)
unit cell dimensions	
a [pm]	1504.1(2)
b [pm]	884.5(1)
c [pm]	880.2(1)
β [°]	101.93(2)
Z	4
ρ_{calcd} [g cm^{-3}]	4.601
$\mu(Mo_{K\alpha})$ [mm^{-1}]	20.786
absorption correction	empirical[23]
cystal size [mm]	$0.06 \times 0.02 \times 0.02$
θ range [°]	$1.38 \leq \theta \leq 32.03$
index ranges	$-22 \leq h \leq 22$ $-13 \leq k \leq 13$ $-13 \leq 1 \leq 13$
reflections collected	16608
independent reflections	3984
R_{int}[a]	0.0845
min./ max. transmission	0.6813/0.3685
refinement method	SHELXL97,[241] full-matrix least-squares on F^2
R/R_w[b,c] [$I > 2\sigma(I)$]	0.041/0.079
R/R_w (all data)	0.068/0.089

[a] $R_{int} = \Sigma |F_o^2 - F_c^2|/\Sigma F_o^2$. [b] $R = \Sigma(w(|F_o - F_c|)/\Sigma F_o$. [c] $R_w = (\Sigma(w(|F_o^2 - F_c^2|)^2)/\Sigma w(F_o^2)^2)^{1/2}$. $w = 1/\sigma^2(F_o^2) + (gP)^2 + kP)$, $P = Max(F_o^2, 0) + 2 F_c^2/3$, k, g = weights.

Results and Discussion

The structure of the double salt $Ba_4Si_3Br_2$ is built of isolated barium cations, bromide anions, and novel cyclotrisilicide units (Figure 1). However, there is a clear partitioning into a saltlike barium bromide (SB) and Zintl-phase-like barium silicide blocks (ZB). The halogenide partial structure is a two-dimensional (2D) block with dimensions of about 480 pm, and the thickness of the 2D block of the Zintl phase is about 1010 pm.

Table 2. Atomic coordinates and displacement parameters[a] [pm^2] for $Ba_4Si_3Br_2$ (all sites are fully occupied).

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Ba1	0.3491(1)	0.1776(1)	0.1193(1)	153(2)	143(2)	144(2)	−5(2)	−2(2)	−18(2)	152(1)
Ba2	0.1479(1)	0.5569(1)	0.8737(1)	158(2)	174(2)	205(2)	−28(2)	31(2)	−6(2)	180(1)
Ba3	0.6687(1)	0.1641(1)	0.2363(1)	248(3)	168(2)	188(2)	30(2)	99(2)	57(2)	193(1)
Ba4	0.0436(1)	0.2096(1)	0.0203(1)	137(2)	131(2)	133(2)	5(2)	23(2)	12(2)	134(1)
Br1	0.3670(1)	0.5066(1)	0.9477(1)	223(4)	171(4)	179(4)	1(3)	48(3)	17(3)	190(2)
Br2	0.4928(1)	−0.1400(1)	0.1339(1)	198(4)	233(4)	257(4)	88(3)	51(3)	32(3)	229(2)
Si1	0.1995(1)	0.1328(2)	0.8022(2)	122(10)	130(9)	151(9)	27(7)	5(8)	−5(7)	138(4)
Si2	0.1868(2)	0.9307(2)	0.9924(2)	142(10)	133(9)	115(9)	14(7)	11(8)	−5(8)	132(4)
Si3	0.0870(2)	0.5622(2)	0.2399(2)	179(11)	169(10)	122(9)	6(8)	−4(8)	21(8)	162(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The components of the anisotropic displacement tensor are defined for $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*)]$.
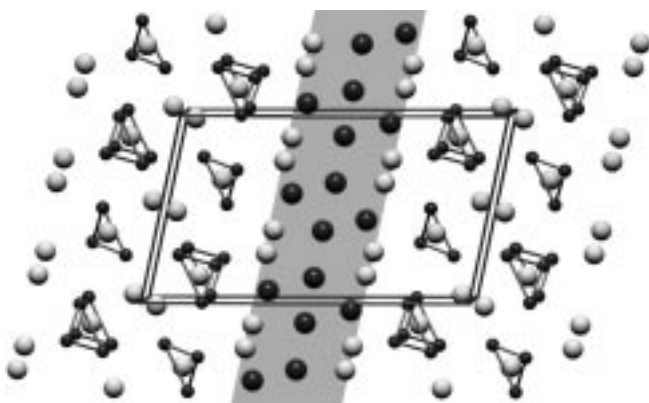
Figure 1. Structure of $Ba_4Si_3Br_2$ (perspective view). The saltlike structure block (SB) is underlaid in gray (small black spheres: Si; large black spheres: Br; large white white spheres: Ba).

Considering a simple charge-transfer model, from the cationic to the anionic substructures, the Zintl–Klemm concept, $(Ba^{2+})_4(Br^-)_2(Si_3^{6-})$ results. Thus, the cyclic Si_3 unit should carry a formal charge of -6 and the cyclotrisilicide anion is valence isoelectronic to S_3 and is expected to be bonded by three single bonds. From a stoichiometric point of view $Ba_4Si_3Br_2$ may be considered as *double salt* between $BaBr_2$ and the Zintl phase $BaSi$. Indeed, we find the silicon centers have a formal charge of -2, and thus expect a silicon sublattice built of divalent silicon just like in the Zintl phase $BaSi$.[15, 16] However, unlike $BaSi$, in which an infinite zigzag chain of silicon is realized, a cyclic Si_3 system occurs. This is not surprising, because our earlier investigations have shown that the bonding of such highly charged Zintl anions may easily rearrange; such rearrangement is induced by only slight changes of the cation characteristics.[31–34]

The Si–Si bond lengths of 239.9, 241.2, and 248.4 pm in the cyclotrisilicide unit (Figure 2) are comparable to those of other singly bonded clusters of silicon found in Zintl phases of
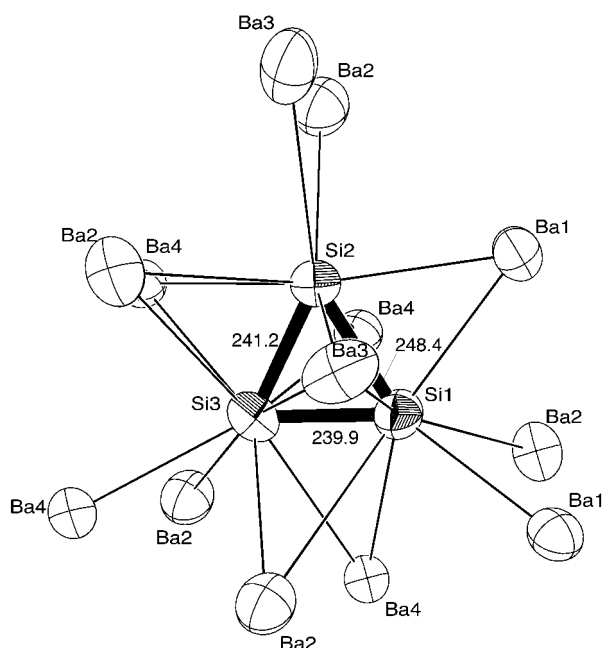
silicon (237–256 pm).[35, 36] The distances in the hitherto known substituted cyclotrisilanes range from 238 to 255 pm in the case of hexa-2,6-dimethylphenylcyclotrisilane and hexa-*tert*-butylcyclotrisilane.[37] Cyclotrisilane itself has not been synthesized up to now but ab initio studies predict Si–Si bond lengths of 233 pm.[38] The large discrepancy to the values found for the substituted cyclotrisilanes was attributed to ligand–ligand interactions.[39] The elongation of the Si–Si bonds in Si_3H_6 by 0.1–0.15 Å compared to those in Si_3^{6-} might be due to the high negative charge per silicon atom. Figure 2 shows the barium coordination of the Si_3 system. The Si–Ba distances in the first coordination sphere range from 322.7 to 374.6 pm (Table 3). The latter are comparable to those found in binary barium silicides[12, 15, 16, 35, 40, 41]. The triangular face of the Si_3 unit is bicapped from below and above by barium

Table 3. Selected atomic distances (esd) [pm] for $Ba_4Si_3Br_2$.

Atom pair	d	Atom pair	d	Atom pair	d
Ba1–Si1	322.7(2)	Ba4–Si2	331.7(2)	Si3–Si1	239.9(3)
Ba1–Br1	328.1(1)	Ba4–Si1	334.5(2)	Si3–Si2	241.2(3)
Ba1–Br2	329.3(1)	Ba4–Si3	336.5(2)	Si3–Ba4	336.5(2)
Ba1–Si2	329.4(2)	Ba4–Si1	339.1(2)	Si3–Ba4	342.5(2)
Ba1–Br1	331.5(1)	Ba4–Si3	342.5(2)	Si3–Ba2	352.8(2)
Ba1–Si1	346.0(2)	Ba4–Si3	360.0(2)	Si3–Ba4	360.0(2)
Ba1–Br2	353.0(1)	Ba4–Si3	365.6(2)	Si3–Ba2	362.4(2)
Ba1–Br2	359.5(1)	Ba4–Si2	366.1(2)	Si3–Ba2	362.4(2)
				Si3–Ba4	365.6(2)
Ba2–Br1	325.5(1)	Si1–Si3	239.9(3)	Si3–Ba3	374.6(2)
Ba2–Si2	348.0(2)	Si1–Si2	248.4(3)		
Ba2–Si2	352.6(2)	Si1–Ba1	322.7(2)	Br1–Ba3	325.3(1)
Ba2–Si3	352.8(2)	Si1–Ba4	334.5(2)	Br1–Ba1	328.1(1)
Ba2–Si3	362.4(2)	Si1–Ba3	334.9(2)	Br1–Ba1	331.5(1)
Ba2–Si3	362.4(2)	Si1–Ba4	339.1(2)	Br1–Ba3	332.2(1)
		Si1–Ba1	346.0(2)	Br1–Br2	384.1(1)
Ba3–Br1	325.3(1)			Br1–Br2	384.3(2)
Ba3–Br1	332.2(1)	Si2–Si3	241.2(3)		
Ba3–Si1	334.9(2)	Si2–Si1	248.4(3)	Br2–Ba1	328.1(1)
Ba3–Si2	335.9(2)	Si2–Ba1	329.4(2)	Br2–Ba3	337.0(1)
Ba3–Br2	337.0(1)	Si2–Ba4	331.7(2)	Br2–Br2	345.7(2)
Ba3–Br2	364.6(2)	Si2–Ba3	336.0(2)	Br2–Ba1	353.0(1)
Ba3–Si2	371.9(2)	Si2–Ba2	352.6(2)	Br2–Ba1	359.5(1)
Ba3–Si3	374.6(2)	Si2–Ba4	366.1(2)	Br2–Ba3	364.6(2)
Ba3–Br2	375.1(2)	Si2–Ba3	371.9(2)	Br2–Ba3	375.1(2)

Figure 2. Coordination of the cyclotrisilicide unit in $Ba_4Si_3Br_2$.

Table 4. Selected angles of the Si_3 unit in $Ba_4Si_3Br_2$.

Atoms	Angle
Si3-Si1-Si2	59.18(8)
Si3-Si2-Si1	58.65(8)
Si1-Si3-Si2	62.17(9)

cations (Ba3, Ba4; see Figure 2). In addition, the two shorter Si–Si bonds (Si1–Si3 and Si2–Si3) are each bridged by two further Ba cations, and the longer Si1–Si2 bond by only one additional Ba cation. This lack of coordinating cations is compensated by a slight shift of the two Ba caps towards the singly bridged Si–Si bond. The sensitivity by which the bond lengths of the Si_3 unit react to such slight changes of the local coordination supports impressively the above-mentioned arguments towards a fairly soft and polar-

izable kind of Zintl anion. Finally, each silicon vertice is coordinated by two additional terminal barium cations. This geometry is strongly reminiscent of the structures of the carbonyl-bridged clusters of transition metals.[42] Contrary to how it may appear from Figure 1, there is no ecliptical or partial ecliptical stacking of Si_3^{6-} ions. Ecliptical stacks of Zintl anions are observed in all silicides with planar anions and an incomplete π filling. Thus, also from packing considerations a full π system, that is a σ-bonded anion is expected.

The structure of the saltlike $BaBr_2$ block poses some questions. As a main structure element we find a flattened octahedron built of bromide anions (Figure 3a, $d(Br1-Br1)$
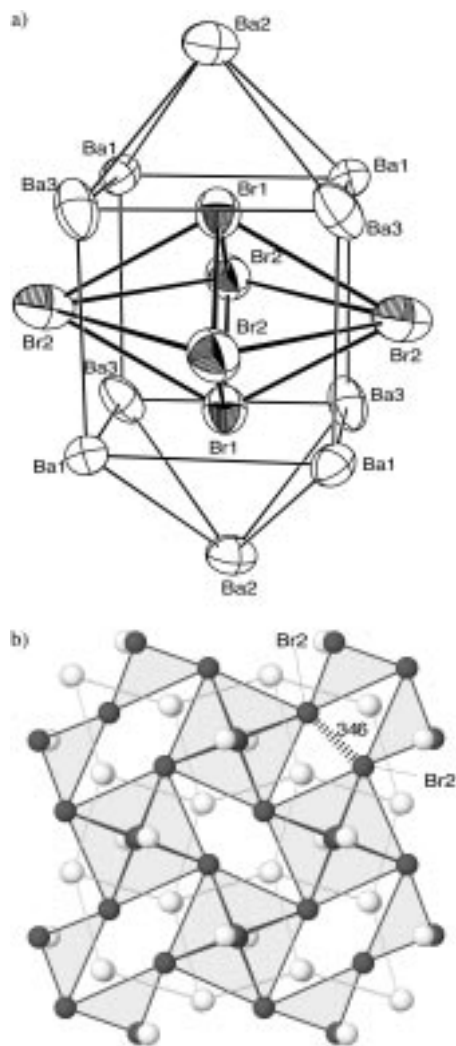
Figure 3. Br_6 units in the saltlike structure block of $Ba_4Si_3Br_2$ (a), view of the structure block with Br_6 units highlighted (b).

$= 391.9$ pm, $d(Br1-Br2) = 384.1 - 406$ pm, $d(Br2-Br2) = 481.2 - 485.8$ pm), the faces of which are capped by barium cations forming a cube (Ba–Ba $451.1 - 473.8$ pm). The topology of the saltlike block may formally be derived by vertex sharing of the octahedra with neighboring units (Figure 3b). The shortest Br–Br distance of 345.7 pm is found between the equatorial Br2 anions of neighboring Br_6 octahedra. This value is 25 pm shorter than the smallest Br–Br distance in

$BaBr_2$, but is still comparable to values found in bromides of rare-earth metals (337 pm in $GdBr_3$,[43] 352 pm in $PrBr_3$[44, 45]). The topology of the saltlike block is strongly reminiscent of the intermetallic $CuAl_2$ structure type,[46] but the distribution of barium and bromide ions over the atomic sites is quite different from that of copper and aluminum ions. While the equatorial Br2 anions are surrounded in a trigonal-prismatic fashion by barium cations, the apical Br1 anions are coordinated only partly by a square of barium cations. Thus, the coordination of the latter by cations is unbalanced leading to a direct neighborhood of Br2 anions as part of its first coordination sphere. Such a coordination may be explained under the assumption of the presence of additional cations in the bromide octahedron. A detailed view of the structure shows that there are four equivalent tetrahedral vacancies with distances of about 255 pm to bromide anions. Eligible cations would be Li^+ or H^+. Taking into account that only half of the vacancies could be occupied at the same time, a formula $Ba_4Si_3Br_2E$ results. Since we made sure that our starting materials were free of lithium, and given the fact that the synthesis gives nearly quantitative amounts of $Ba_4Si_3Br_2$, the presence of Li^+ may be excluded. On the other hand, neither ^{1}H NMR measurements nor chemical analysis give any hints to the presence of hydrogen in our samples.[*] Thus, based on our data, we propose that the distorted bromine octahedra are empty. Comparisons with other halides show that such an unbalanced cation coordination is not unusual. For instance, in $CdBr_2$,[47] which is a layered structure that may formally be derived from a hexagonal closed packing of bromide anions with Cd ions occupying only 1/2 of the octahedral sites, layers of edge-sharing empty Br_6 octahedra occur, and the structures of $PrBr_3$[44, 45] or $LaBr_3$[44, 45] exhibit pillars of face-sharing empty Br_6 octahedra.

To gain a deeper insight into the bonding, we performed TB-LMTO-ASA band structure calculations on $Ba_4Si_3Br_2$. According to the calculation the compound is expected to be a semiconductor with a band gap of about 0.1 eV. Figure 4 shows contributions of the Br-4p in states to the total density of states (DOS). We find a weak dispersion of the bromine states, due to the different ligand field of the two bromine sites, but all Br contributions are well below the Fermi energy level. Thus, there is no evidence for covalent interactions between Br centers, which may be considered as Br^- ions, and the formal ionic picture, $(Ba^{2+})_4(Br^-)_2(Si_3^{6-})$, seems to be a good approximation of the electronic configuration. This is also supported by an analysis of the electron localization function (ELF) based on the electronic wavefunction that was gained from the LMTO calculation. Figure 5 shows the distribution of the ELF in the main plane of the Si_3 unit, and in cuts perpendicular to the different Si–Si bonds. In the main plane, the core of the silicon atoms are clearly recognized together with the attractors of the three Si–Si bonds. The maximum of the longer bond is less extended than those of the other two bonds. This is also reflected in
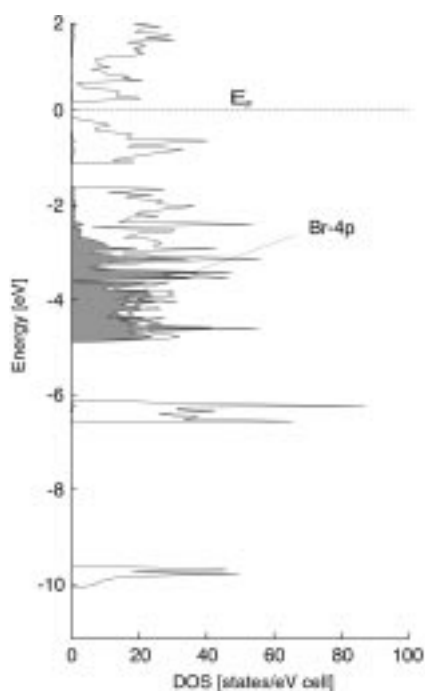
Figure 4. Electronic density of states (DOS) of Ba$_4$Si$_3$Br$_2$ based on a LMTO band structure calculation. Contributions of Br-4p orbitals to the DOS are underlaid in gray.
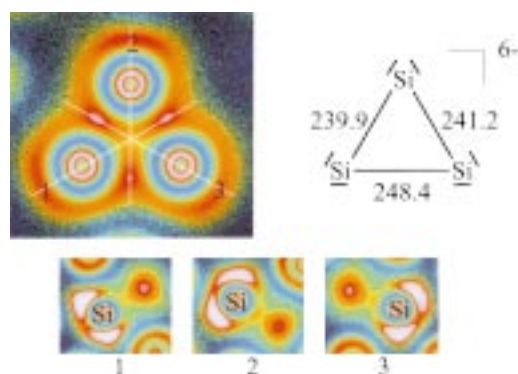

Figure 5. Distribution of the ELF in sections through the cyclotrisilicide unit in Ba$_4$Si$_3$Br$_2$ compared with a possible Lewis formula.

sections perpendicular to the bonds. Each of them shows a rotationally symmetric ELF distribution in the bond region which supports the picture of a singly bonded system. Furthermore, one can clearly recognize the attractors of the two lone pairs of electrons at each Si atom. Hence, the ELF distribution shows all features which are consistent with the Lewis formula of a cyclic Si$_3^{6-}$ system (Figure 5).

Conclusion

We present a novel representative of a *double salt* between halides and Zintl phases of silicon. The crystal structure combines structural features of both halides and silicides, arranged in separated two-dimensional blocks. For the first time a cyclotrisilicide unit was found in a solid which represents an anionic derivative of the intensively studied substitued cyclotrisilanes.

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