Chemical Twinning in Zintl Phases[†]

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In the systems Ba/Mg/(Si, Ge), two new ternary Zintl phases with the compositions $BaMg_4Si_3$ and $BaMg_4Ge_3$ were found and structurally characterized. Both compounds are isotypic and crystallize with a new structure type [$BaMg_4Si_3$, *P*4/*mmm*, $Z = 1$, $a = 4.6115(9)$ Å, $c = 8.615(2)$ Å; $BaMg_4Ge_3$, *P*4/*mmm*, $Z = 1$, $a = 4.6335(8)$ Å, $c = 8.746(2)$ Å]. The anionic partial structure is built of X_2^{6-} dumbbells and isolated X^{4-} ions (X = Si, Ge), and the structure can be described according to the Zintl−Klemm-Busmann concept with the formulation $(Ba^{2+})(Mg^{2+})_4[X_2^{6-}][X^{4-}]$. The $BaMg_4X_3$ structure can also be described as a result of the fusion of the structures of Mg_2X and $BaMg_2X_2$. In this regard, $BaMg_4Si_3$ and $BaMg_4Ge_3$ are very striking examples of chemical twinning.

Introduction

One of the most important and demanding tasks for a chemist is to ascertain the essential features of structure−property relationships. A very simple structure can be described in several ways. The chemist has to choose the best one, depending on which microscopic feature he wants to point out. For example, rock salt has a very simple structure but it can be described in at least three different ways: as two interpenetrating fcc networks of sodium and chlorine, as an fcc packing of sodiums with the octahedral holes occupied by chlorines and vice versa, and as edge-sharing octahedra of sodium filled with chlorines and vice versa. All descriptions are equivalent, but each one points out a different characteristic of the rock salt structure. The different descriptions should be simple and general; thus, they should show as many relationships as possible to related structures, and they should be useful in explaining physical properties.[1] Andersson and Hyde[1,2] as well as Parthé,[3] in their pioneering work, have shown that complex structures can be described by combining simple building blocks in a manner that is reminiscent of the twinning of crystals, though on a smaller scale. This approach is called “chemical twinning”[1] or intergrowth.[3] The building blocks, which are part of the unit cells, are combined according to “twinning laws” as translation, reflection, and rotation.[1]

We have collected some examples where this simple approach can be used in describing the structures of Zintl phases.[4,5] In this work, we will report a very beautiful and illustrative example of “chemical twinning” using the two new Zintl phases $BaMg_4Si_3$ and $BaMg_4Ge_3$, which crystallize in a novel structure type.

The new phase $BaMg_4X_3$ extends the hitherto known ternary compounds BaMgX,[6,7] $BaMg_2X_2$,[8,9] $Ba_5Mg_{18}X_{13}$,[10] and $Ba_2Mg_3Si_4$[11] of the system Ba/Mg/X (X = Si, Ge) by one other interesting representative.

Experimental Section

The compounds were synthesized from the pure elements (Mg pieces, Fluka, 99.8%; Ba rods, Alfa, 99.9%; Si powder, Alfa, 99.99%; Ge lumps, Alfa, 99.9999%), which were sealed under argon atmosphere in niobium ampules and transferred to a furnace under vacuum.

$BaMg_4Si_3$ decomposes peritectically above 1300 K to $Ba_5Mg_{18}Si_{13}$ and a melt of Mg/Si. Consequently, pure phase material was not produced from stoichiometric amounts of the elements. The maximum yield of crystalline $BaMg_4Si_3$ is obtained by cooling a melt of the composition Ba:Mg:Si = 1:2:4 from 1350 K at 50 K 1 h. The XRD powder pattern indicates the presence of $BaSi_2$, apart from the main product $BaMg_4Si_3$. The brittle material has a silvery metallic luster and is sensitive to air and moisture.

$BaMg_4Ge_3$ decomposes peritectically above 1180 K to $Ba_5Mg_{18}Ge_{13}$ and a melt of Mg/Ge. The highest yield of $BaMg_4Ge_3$ is obtained by heating a stoichiometric mixture of the elements up to 1120 K. After the system is cooled at about 200 K/h, a brittle material having a silvery metallic luster is produced. The XRD powder pattern indicates the presence of traces of $BaMg_2Ge_2$, apart from the main product $BaMg_4Ge_3$. The product is exceptionally sensitive to air and moisture and decomposes in a few seconds to a yellow-orange powder, which probably contains amorphous GeO.

The single crystals of $BaMg_4Si_3$ and $BaMg_4Ge_3$ (black fragments with a metallic luster) were examined on STOE IPSD and STADI4 four-circle diffractometers, respectively, both operating with graphite monochromators and Mo Kα radiation. The diffraction data were collected in the angular ranges $5° < 2\theta < 50°$ (oscillation method, $\varphi = 0-181°$, $\Delta\varphi = 1.0°$) and $2° < 2\theta < 60°$ ($\omega-\theta$ scan, 40 steps, $\Delta\omega = 0.03°$), respectively. The diffraction data of $BaMg_4Ge_3$ were empirically corrected for absorption (ψ scan). The Laue symmetry is 4/*mmm*, and there are no systematic extinctions allowing for the space groups *P*4*mm*, *P*422, $P\bar{4}2m$, $P\bar{4}m2$, and *P*4/*mmm*. The refinement of the unit cell yielded the following lattice parameters: $a = 4.6115(9)$ Å, $c = 8.615(2)$ Å for $BaMg_4Si_3$ and $a = 4.6335(8)$ Å, $c = 8.746(2)$

[†] Dedicated to Prof. Dr. Peter Böttcher on the occasion of his 60th birthday.

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Table 1. Crystallographic Data for $BaMg_4Si_3$ and $BaMg_4Ge_3$

chem. formula	$BaMg_4Si_3$	$BaMg_4Ge_3$
fw	318.85	452.35
space group	*P*4/*mmm* (No. 123)	*P*4/*mmm* (No. 123)
a, Å	4.6115(9)	4.6335(8)
b, Å	4.6115(9)	4.6335(8)
c, Å	8.615(2)	8.746(2)
cell vol. $Å^3$	183.21(6)	187.77(7)
Z	1	1
temp., K	298	298
wavelength, Å	0.710 73	0.710 73
ρ_{calcd}, $g\cdot cm^{-3}$	2.890	4.000
abs coeff, mm^{-1}	6.135	17.282
reliability factors[a]		
$R(F_o)$	0.017	0.022
$R_w(F_o^2)$	0.040	0.054

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2/\sum w(F_o^2)]^{1/2}$.

Table 2. Wyckoff Sites, Atomic Coordinates, and Equivalent Isotropic Displacement Parameters ($Å^2$) for $BaMg_4Si_3$

atom	Wyckoff site	*x*	*y*	*z*	*U*(iso)
Ba	1*a*	0	0	0	0.0108(4)
Mg	4*i*	0	$^1/_2$	0.3176(2)	0.0121(5)
Si(1)	1*b*	0	0	$^1/_2$	0.0103(7)
Si(2)	2*h*	$^1/_2$	$^1/_2$	0.1426(2)	0.0099(5)

Table 3. Selected Interatomic Distances (Å) for $BaMg_4Si_3$

Ba−Si(2)	3.4847(9)	×8	Mg−Si(2)	2.755(2)	×2
Ba−Mg	3.579(2)	×8	Mg−Si(1)	2.790(1)	×2
Si(1)−Mg	2.790(1)	×8	Mg−Mg	3.142(4)	
Si(2)−Si(2)	2.458(4)		Mg−Mg	3.2608(6)	×4
Si(2)−Mg	2.755(2)	×4	Mg−Ba	3.579(2)	×2
Si(2)−Ba	3.4847(9)	×4			

Table 4. Wyckoff Sites, Atomic Coordinates, and Equivalent Isotropic Displacement Parameters ($Å^2$) for $BaMg_4Ge_3$

atom	Wyckoff site	*x*	*y*	*z*	*U*(iso)
Ba	1*a*	0	0	0	0.0149(2)
Mg	4*i*	0	$^1/_2$	0.3188(2)	0.0164(4)
Ge(1)	1*b*	0	0	$^1/_2$	0.0134(3)
Ge(2)	2*h*	$^1/_2$	$^1/_2$	0.14723(6)	0.0138(2)

Table 5. Selected Interatomic Distances (Å) for $BaMg_4Ge_3$

Ba−Ge(2)	3.5204(6)	×8	Mg−Ge(2)	2.7602(9)	×2
Ba−Mg	3.625(1)	×8	Mg−Ge(1)	2.8070(8)	×2
Ge(1)−Mg	2.8070(8)	×8	Mg−Mg	3.170(3)	
Ge(2)−Ge(2)	2.576(1)		Mg−Mg	3.2764(6)	×4
Ge(2)−Mg	2.7602(9)	×4	Mg−Ba	3.625(2)	×2
Ge(2)−Ba	3.5204(6)	×4			

Å for $BaMg_4Ge_3$. The structure of $BaMg_4Si_3$ was solved in *P*4/*mmm* using direct methods and refined by full-matrix least-squares F^2. The structure of $BaMg_4Ge_3$ was refined in *P*4/*mmm* (full-matrix least-squares F^2) using the parameters of the isotypic $BaMg_4Si_3$. All atoms were anisotropically refined and the displacement parameters are all satisfactory in both structures. The final refined agreement parameters for the $BaMg_4Si_3$ and $BaMg_4Ge_3$ structures are given in Table 1. Atomic coordinates and selected interatomic distances are listed in Tables 2−5.

Structure and Discussion

$BaMg_4Si_3$ and $BaMg_4Ge_3$ are isotypic and crystallize within a novel structure type (Figure 1). The anionic partial structure is built of X_2 dumbbells and isolated X ions (X = Si, Ge). According to the Zintl−Klemm−Busmann concept,[12,13] $BaMg_4X_3$ can be described by the formulation $(Ba^{2+})(Mg^{2+})_4[X_2^{6-}][X^{4-}]$.

The dumbbells, formally X_2^{6-}, show a cation coordination (Figure 2a) comparable to that found in the structure of $BaMg_2X_2$ (X = Si, Ge).[8,9] The center of the X−X bond is coordinated by a square of Ba atoms. Together with magnesium, a distorted square antiprism Ba_4Mg_4 is formed around the X atoms of the dumbbells. This basic building unit is quite typical for the coordination of terminal silicon or germanium atoms in even more extended Zintl anions found in compounds of the phase systems EA/Mg/(Li)/(Si, Ge).[4,5,10,11] At 2.46 and 2.58 Å, the X−X distances are in the range of typical single-bond lengths for silicon and germanium, respectively. The isolated X atoms, formally X^{4-}, are coordinated by eight magnesium atoms, forming a cube (Figure 2b), as in the structure of Mg_2X.[14−17] Again the strong preference of magnesium for the coordination of highly charged silicon or germanium centers is evident. From a number of investigations, we already know that magnesium acts quite differently on Zintl anions than the heavier alkaline-earth metals Ca, Sr, and Ba. Thus, it is not surprising that, compared to the valence isoelectronic compounds Ba_5X_3 (Cr_5B_3 type; X = Si, Ge),[18,19] a novel structure type is realized in $BaMg_4X_3$, just because of the different functionalities of the cation types.

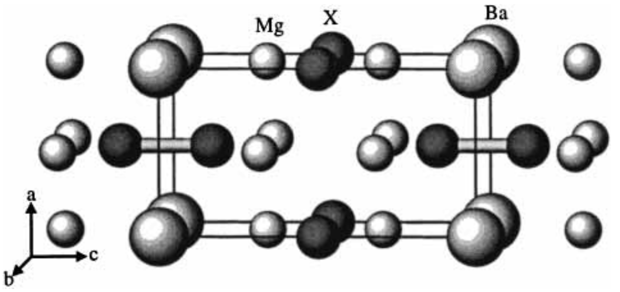

Figure 1. Perspective view of the structure of $BaMg_4X_3$ (X = Si, Ge).

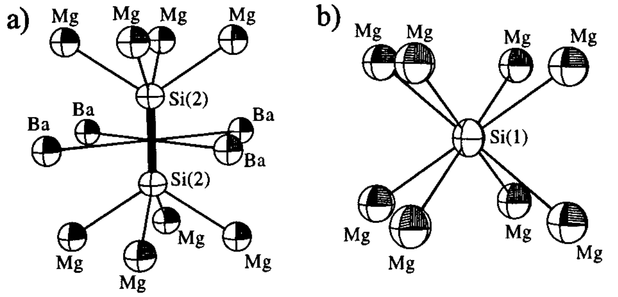

Figure 2. Coordination of the Si_2^{6-} dumbbells (a) and isolated Si^{4-} anions (b) in $BaMg_4Si_3$.

Although both structures of Ba_5X_3 and $BaMg_4X_3$ are built of X_2 dumbbells and isolated X atoms, $BaMg_4X_3$ shows a much greater relationship to the structures of $BaMg_2X_2$ and Mg_2X than to that of Ba_5X_3. Actually, it is possible to derive the structures of $BaMg_4X_3$ just by fusing the structures of $BaMg_2X_2$ and Mg_2X (Figure 3). The lengths of the tetragonal *a* axes of $BaMg_2X_2$ and $BaMg_4X_3$ are nearly identical (4.65 and 4.61 Å for the Si compounds; 4.67 and 4.63 Å for the Ge compounds), and the values for the *c* axes of $BaMg_4X_3$ (8.62 and 8.75 Å observed for the Si and Ge compounds, respectively) calculated

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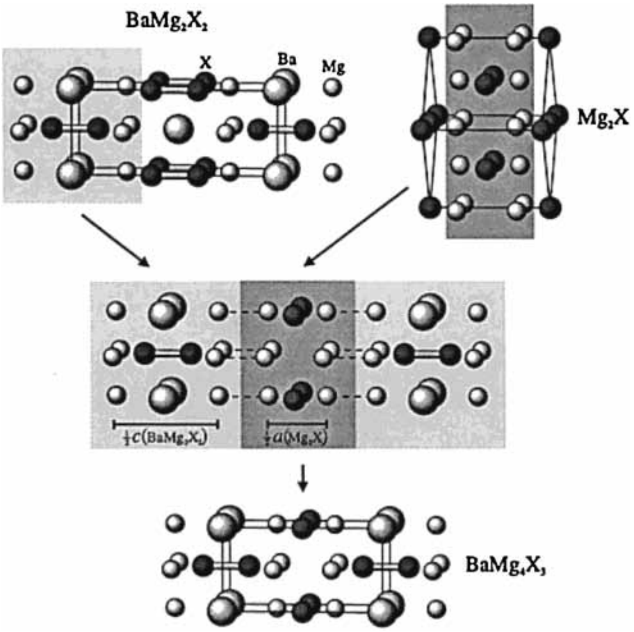

Figure 3. The $BaMg_4X_3$ structure (X = Si, Ge) showing chemical twinning. The marked sections of the $BaMg_2X_2$ and Mg_2X structures (top) fuse together, retaining the original dimensions (middle) and forming the daughter structure $BaMg_4X_3$ (bottom).

by adding the lattice parameters of $BaMg_2X_2$ and Mg_2X according to $c(BaMg_4X_3) = {}^1/_2a(Mg_2X) + {}^1/_2c(BaMg_2X_2)$ (leading to 8.71 and 8.86 Å, respectively) are equal within 0.1 Å to those observed. The discrepancy is due to a slight compression of the Mg_2X block along the c axis (a/a'=1.03, compared with 1.0 for cubic Mg_2X). Thus, $BaMg_4X_3$ is a very nice example of chemical twinning in the sense of the descriptions of Andersson and Hyde,[1,2] and Parthé.[3]

The “chemical twinning” reported for $BaMg_4Si_3$ and $BaMg_4Ge_3$ is a very beautiful example of how Nature can form complex structures by combining simple building blocks. The fusion of these building units retains the original distances, and it is possible to calculate the new lattice parameters simply by adding the original lengths of the parent structures. The structure of $BaMg_4Si_3$ and $BaMg_4Ge_3$ is the almost perfect topological fusing of the structures of Mg_2Si and $BaMg_2Si_2$ and of Mg_2Ge and $BaMg_2Ge_2$, respectively. Mg_2X and $BaMg_2X_2$ can be called the *parent structures* of $BaMg_4X_3$ (X = Si, Ge), which is therefore the *daughter structure*. We have shown that the “chemical twinning” approach is very powerful and intuitive and it can be used for predicting new structures.[4]

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

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