Chemistry of Metals and Alloys

Chem. Met. Alloys 1 (2008) 352-359
Ivan Franko National University of Lviv
www.chemetal-journal.org

$Pr_4Al_3Ge_3$, a new member of the structural series with linear intergrowth of AlB_2- and W-type slabs

Evgen GLADYSHEVSKII[1], Nataliya SEMUSO[1]*, Roman GLADYSHEVSKII[1], Karin CENZUAL[2], Jean-Louis JORDA[3]

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv,*
Kyryla i Mefodiya St. 6, UA-79005 Lviv, Ukraine
[2] *Département de Chimie Minérale, Analytique et Appliquée, Université de Genève,*
Quai Ernest Ansermet 30, CH-1211 Geneva, Switzerland
[3] *SYMME Polytech' Savoie, Chemin de Bellevue 5, F-74944 Annecy le Vieux, France*
* *Corresponding author. Tel.: +38 032 2394163; e-mail: nakonechna_n@franko.lviv.ua*

Received November 28, 2008; accepted December 29, 2008; available on-line March 19, 2009

The structure of praseodymium aluminum germanide $Pr_4Al_3Ge_3$ has been determined by single-crystal X-ray diffraction. The refined composition is $Pr_4Al_{3.117(3)}Ge_{2.883(3)}$, M_r = 857.01(8), *oS*20, (63) *Cmcm–c*^{5}, *a* = 4.161(1), *b* = 26.261(8), *c* = 4.373(1) Å, *Z* = 2, D_x = 5.96 Mg m^{-3}, *R* = 0.012, *wR* = 0.015 for 304 independent reflections with $F > 3\sigma(F)$. Four sites in Wyckoff position 4*c* are occupied by Pr(1), Pr(2), Al, and Ge, respectively, and a fifth position 4*c* by a statistical mixture of Al and Ge with a ratio close to 1:1. The compound is characterized by a homogeneity range extending from 26.6 to 30.6 at.% Ge at a constant Pr content of 40 at.%. Isotypic compounds have been found for $R_4Al_3Ge_3$, where *R* = Ce, Nd, or Sm. This new structure type can be considered as an intergrowth of slabs cut from three simple structure types: AlB_2, its ternary substitution variant LiBaSi, and W, following the sequence -LiBaSi-AlB_2-LiBaSi-W-, with eight slabs in the translation unit. The axes of the trigonal prisms in the AlB_2-type slab are rotated by 90° with respect to those in the neighboring LiBaSi-type slabs, as in the α-$ThSi_2$ type and the intergrowth structure $TbGe_2$. The structure of $Pr_4Al_3Ge_3$ is also related to the structures of binary borides V_2B_3, Ta_3B_4, V_5B_6, and CrB, and the ternary aluminum germanide $Ba_3Al_2Ge_2$, which altogether form a structural series with different ratios of intergrown AlB_2- (LiBaSi-) and W-type slabs.

Alumogermanide / Rare-earth metal / Single-crystal X-ray diffraction / Crystal structure / Structural series

Introduction

Five ternary compounds are known in the Pr-Al-Ge system: $PrAl_2Ge_2$ ($CaAl_2Si_2$-type structure, Pearson symbol *hP*5, space group $P\bar{3}m1$) [1], $Pr_2Al_3Ge_4$ ($Ba_2Cd_3Bi_4$, *oS*36, *Cmce*) [2], Pr_2AlGe_6 (La_2AlGe_6, *mS*36, *C*2/*m*) [3], $PrAl_{1.5}Ge_{0.5}$ (AlB_2, *hP*3, *P*6/*mmm*) [4], and PrAlGe (LaPtSi, *tI*12, $I4_1md$) [4,5]. The latter two alumogermanides are characterized by significant homogeneity ranges ($PrAl_{1.55-1.48}Ge_{0.45-0.52}$ and $PrAl_{1.42-0.98}Ge_{0.58-1.02}$). In other *R*-Al-Ge systems, where *R* = La, Ce, Nd, Sm, Eu, and Gd, compounds isotypic to those mentioned above are formed [6-8]. To date, the Pr-rich part of the Pr-Al-Ge system has not been investigated and the aim of the present work is to study the formation of phases in the system in the range 33.3-45.0 at.% Pr, determine their crystal structures and search for isotypic compounds in related systems.

Experimental

Alloys containing 35.0, 37.5, 40.0, 42.5, and 45.0 at.% Pr and equiatomic amounts of Al and Ge were prepared by arc melting under an argon atmosphere. The following starting elements were used: Pr 99.9%, Al and Ge 99.99%, and the weight losses were less than 2%. The samples were annealed in evacuated quartz tubes at 1073 K for 500 h and quenched into cold water. Preliminary phase analysis was carried out using diffraction patterns recorded with a Debye-Scherrer camera (diameter 53.7 mm) using Cr *K* radiation. The formation of a new compound of approximate composition $Pr_4Al_3Ge_3$ was observed, and its crystal structure was determined from single-crystal X-ray diffraction. A single crystal was selected from an alloy, which after additional annealing at 1073 K for 1000 h had been crushed into metallic gray platelets. Diffraction data were collected on an Enraf-

Nonius CAD-4 automatic diffractometer. The programs used to solve and refine the structure were all from the MolEN system [9]. Crystal data, experimental and refinement details are given in Table 1.

To determine the homogeneity range of the phase $Pr_4Al_3Ge_3$, samples containing 40 at.% Pr and 25-35 at.% Ge were prepared. To check for the possible formation of isotypic compounds in systems with other rare-earth metals, $R_4Al_3Ge_3$ alloys with R = La, Ce, Nd, Sm, Eu, and Gd were synthesized. The conditions for sample preparation were the same as described above. The purities of the rare-earth metals were 99.9% for La and Ce, 99.87% for Nd, Sm, Eu, and Gd. Cell parameters were refined by the program LATCON [10] from diffraction patterns recorded using a diffractometer DRON-2.0 (Fe $K\alpha$ radiation, Si standard). Theoretical patterns were computed with the program LAZY PULVERIX [11].

Table 1 Crystal data, data collection and refinement.

Nominal composition	$Pr_{40}Al_{30}Ge_{30}$
Refined composition	$Pr_4Al_{3.117(3)}Ge_{2.883(3)}$
M_r	857.01(8)
Space group	*Cmcm* (# 63)
a (Å)	4.161(1)
b (Å)	26.261(8)
c (Å)	4.373(1)
V (Å^3)	477.8(4)
Z	2
D_x (Mg m^{-3})	5.96
Radiation type, wavelength (Å)	Mo $K\alpha$, 0.71073
Number of reflections for cell parameters	16
θ range for cell parameters (°)	7-20
μ (mm^{-1})	29.61
F(000)	737
Temperature (K)	293
Crystal size (mean radius, mm)	0.035
Crystal color	metallic gray
Scan method	ω-2θ
Absorption correction	empirical (ψ scans)
T_{min}-T_{max}	0.849-0.997
Number of measured reflections	2788
Number of independent reflections	448
Number of reflections with $F > 3\sigma(F)$	304
R_{int}	0.026
θ_{max} (°)	30
Range of h, k, l	$-5\rightarrow5, -36\rightarrow36, -6\rightarrow6$
Number of standard reflections	3
Frequency of standard reflections (min)	120
Intensity decay (%)	0.4
Refinement on	F
R	0.012
wR	0.015
S	0.49
Number of reflections used in refinement	304
Number of parameters refined	20
$(\Delta/\sigma)_{max}$	0.9×10^{-3}
$\Delta\rho_{max}$ (e Å^{-3})	1.41
$\Delta\rho_{min}$ (e Å^{-3})	0.56
Extinction coefficient	$3.1(2)\times10^{-7}$
Scattering factors from	*International Tables for X-ray Crystallography* (1974, Vol. IV)

Results

Fractional atomic coordinates, displacement parameters and relevant interatomic distances for $Pr_4Al_3Ge_3$ (*oS*20, *Cmcm*) are presented in Tables 2 and 3. The atomic positional parameters were standardized with the program STRUCTURE TIDY [12]. The atoms are distributed over five sites 4*c*, two of which are occupied by Pr, two others by Al and Ge, respectively, and the remaining one by a statistical mixture of Al and Ge ($M = Al_{0.558(4)}Ge_{0.442(4)}$). Consequently, the cell contains eight Pr atoms and approximately six Al and six Ge atoms, the refined composition being $Pr_4Al_{3.117(3)}Ge_{2.883(3)}$ ($Z = 2$). The Pr-Al, Pr-Ge, and Pr-*M* interatomic distances are similar to the sums of the metallic radii of the corresponding atoms [13]. The shortest distances between Pr atoms exceed the sum of the metallic radii by 4.6-11.1%, whereas those between Al and *M* or Ge are shorter by 11.5-12.6%. The shortening observed for the latter indicates a tendency towards covalent type of bonding.

Figs. 1 and 2 show projections of the structure of $Pr_4Al_3Ge_3$ and the coordination polyhedra of the different sites. It can be seen that the coordination polyhedron of the site Pr(1) is a 20-vertex polyhedron, a deformed hexagonal prism with all faces capped by additional atoms. The site Pr(2) is surrounded by 17 atoms, which form a pentagonal prism with all faces capped. The Al and Ge atoms are situated at the centers of trigonal Pr_6 prisms with three additional atoms located opposite the rectangular faces.

The $Pr_4Al_3Ge_3$ (or $Pr_4Al_2(Al,Ge)_2Ge_2 \equiv Pr_2Al(Al,Ge)Ge$) compound is characterized by a constant content of Pr, whereas the Al and Ge content was found to vary within the range $Pr_4Al_{3.34\text{-}2.94}Ge_{2.66\text{-}3.06}$ at 1073 K. Within the homogeneity range the cell parameters change linearly. With increasing Ge content the *a* parameter remains almost constant, 4.159-4.163 Å, whereas the *b* and *c* parameters decrease from 26.303 to 26.237 Å and from 4.384 to 4.364 Å, respectively. The cell volume decreases from 479.5 to 476.5 $Å^3$ (Fig. 3). The main contraction is observed along the zigzag chains formed by the site occupied by a statistical mixture of Al and Ge, i.e. the site where the substitution takes place. A relatively high displacement parameter is observed for the mixed

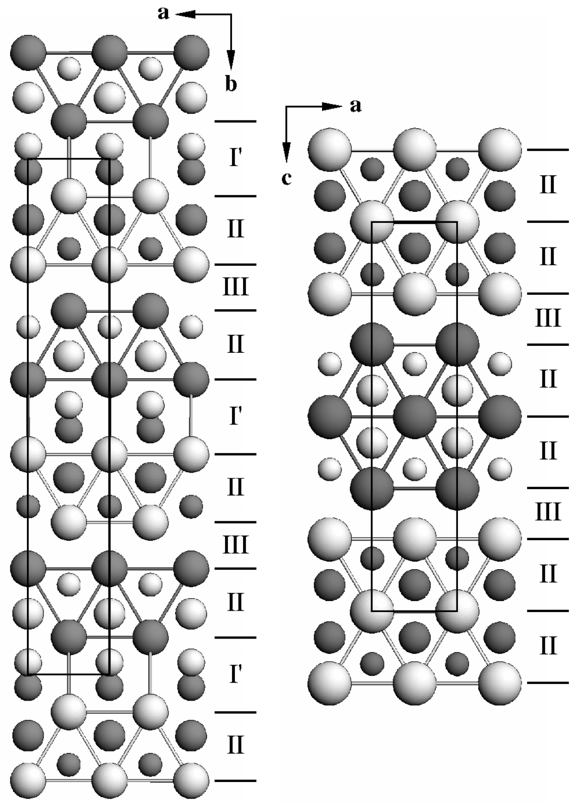
Table 2 Fractional atomic coordinates, equivalent and anisotropic displacement parameters ($Å^2$) in the structure of $Pr_4Al_3Ge_3$ (*Cmcm*, $a = 4.161(1)$, $b = 26.261(8)$, $c = 4.373(1)$ Å; $U_{eq} = ⅓ \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$, $U_{12} = U_{13} = U_{23} = 0$).

Site	Wyckoff position	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}
Pr(1)	4*c*	0	0.42758(2)	¼	0.0062(1)	0.0050(2)	0.0079(2)	0.0058(2)
Pr(2)	4*c*	0	0.79475(1)	¼	0.0060(1)	0.0062(2)	0.0062(2)	0.0056(2)
Al	4*c*	0	0.11809(8)	¼	0.0058(5)	0.0048(9)	0.0039(9)	0.0090(9)
$Al_{0.558(4)}Ge_{0.442(4)}$	4*c*	0	0.02370(5)	¼	0.0110(3)	0.0162(7)	0.0089(5)	0.0079(6)
Ge	4*c*	0	0.67423(3)	¼	0.0076(1)	0.0048(3)	0.0097(3)	0.0083(4)

Table 3 Interatomic distances (Å) in the structure of $Pr_4Al_3Ge_3$ (standard uncertainties are less than 5 on the last digit).

Pr(1)	– 4 Al	3.248	Al	– 1 *M*	2.479
	– 2 *M*	3.271		– 2 Ge	2.549
	– 4 *M*	3.278		– 2 Pr(2)	3.166
	– 2 Ge	3.454		– 4 Pr(1)	3.248
	– 2 Pr(2)	4.063			
	– 2 Pr(1)	4.161	*M*	– 1 Al	2.479
	– 2 Pr(1)	4.373		– 2 *M*	2.516
	– 2 Pr(1)	4.386		– 2 Pr(1)	3.271
Pr(2)	– 4 Ge	3.127		– 4 Pr(1)	3.278
	– 1 Ge	3.165			
	– 2 Al	3.166	Ge	– 2 Al	2.549
	– 4 Pr(2)	3.824		– 4 Pr(2)	3.127
	– 2 Pr(1)	4.063		– 1 Pr(2)	3.165
	– 2 Pr(2)	4.161		– 2 Pr(1)	3.454
	– 2 Pr(2)	4.373			

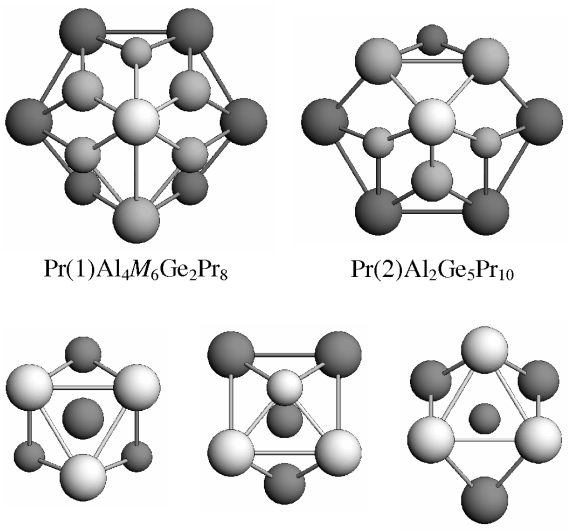
$M = Al_{0.558(4)}Ge_{0.442(4)}$



Pr$_4$Al$_3$Ge$_3$, *oS*20
(63) *Cmcm* – c^5
a = 4.161 Å
b = 26.261 Å
c = 4.373 Å

Ba$_3$Al$_2$Ge$_2$, *oI*14
(71) *Immm* – j^2ia
a = 4.34 Å
b = 5.09 Å
c = 19.82 Å

Fig. 1 Projections of the structures of Pr$_4$Al$_3$Ge$_3$ and Ba$_3$Al$_2$Ge$_2$ (Pr and Ba atoms large, Al atoms medium, Ge atoms small).



Pr(1)Al$_4M_6$Ge$_2$Pr$_8$ Pr(2)Al$_2$Ge$_5$Pr$_{10}$

AlPr$_6M$Ge$_2$ MPr$_6$AlM_2 GePr$_7$Al$_2$

Fig. 2 Coordination polyhedra in the structure of Pr$_4$Al$_3$Ge$_3$ (Pr atoms large, Al atoms medium, Ge atoms small).

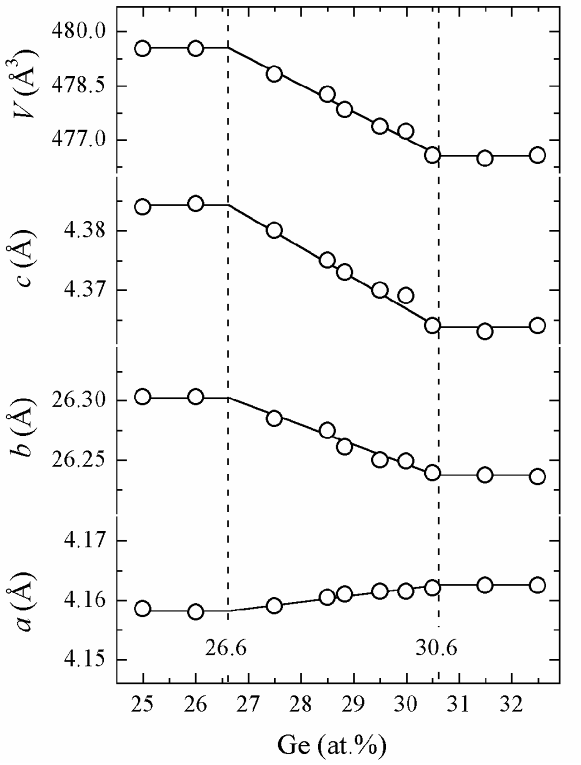


Fig. 3 Cell parameters in the homogeneity range of the compound Pr$_4$Al$_3$Ge$_3$.

site in the direction between the chains. It may be mentioned that no superstructure reflections were observed for the equiatomic Al/Ge ratio 1:1. The alloys containing 25.0, 31.5, 32.5, and 35.0 at.% Ge were multiphase samples; the diffraction pattern of the latter did not contain the lines characteristic of Pr$_4$Al$_3$Ge$_3$.

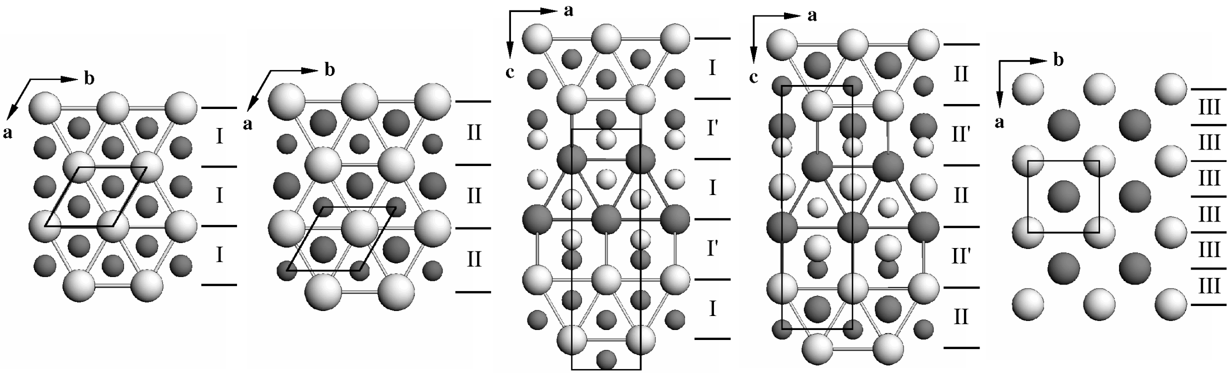
The phase analysis of the R_4Al$_3$Ge$_3$ samples prepared from R = La, Ce, Nd, Sm, Eu, and Gd showed that isotypic compounds form with Ce, Nd, and Sm. The unit-cell parameters decrease linearly with decreasing ionic radii R^{3+} of the rare-earth element (Table 4). The alloys containing La, Eu, and Gd were multiphase samples and their diffraction patterns did not reveal any phase with Pr$_4$Al$_3$Ge$_3$-type structure.

Discussion

The structure of Pr$_4$Al$_3$Ge$_3$ belongs to class 10, trigonal prismatic, according to the classification proposed by Kripyakevich [14], which is based on the coordination polyhedra around the smallest atoms. In an ideal case, when the R-R and R-X distances are equal to the sum of the corresponding atomic radii, structures with trigonal prismatic coordination XR_6 form for $k = r_X/r_R = 0.528$. For larger values of k,

Table 4 Cell parameters for compounds with $Pr_4Al_3Ge_3$-type structure (space group *Cmcm*).

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
$Ce_4Al_3Ge_3$	4.1918(8)	26.366(5)	4.3860(7)	484.7(1)
$Pr_4Al_3Ge_3$	4.1615(6)	26.249(4)	4.3690(6)	477.2(1)
$Nd_4Al_3Ge_3$	4.1432(8)	26.132(4)	4.3544(7)	471.4(1)
$Sm_4Al_3Ge_3$	4.0988(5)	25.899(3)	4.3037(6)	456.9(1)



AlB_2, *hP*3
(191) *P*6/*mmm* – *da*
a = 3.005 Å
c = 3.257 Å

LiBaSi, *hP*3
(187) $P\bar{6}m2$ – *eda*
a = 4.38 Å
c = 4.85 Å

α-$ThSi_2$, *tI*12
(141) $I4_1/amd$ – *ea*
a = 4.134 Å
c = 14.375 Å

LaPtSi, *tI*12
(109) $I4_1md$ – a^3
a = 4.2490 Å
c = 14.539 Å

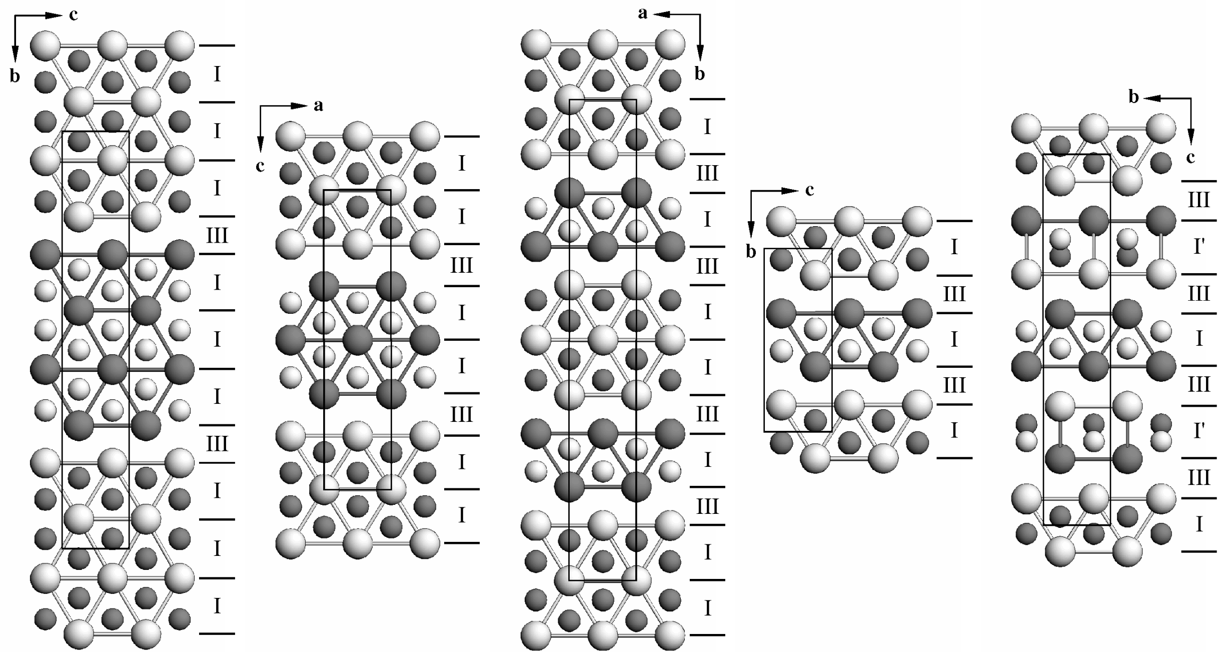
W, *cI*2
(229) $Im\bar{3}m$ – *a*
a = 3.155 Å

Fig. 4 Projections of the structures of AlB_2, LiBaSi, α-$ThSi_2$, LaPtSi, and W (Al, Ba, Th, La, and W atoms large, Li and Pt atoms medium, B and Si atoms small).

structures with coordination number 8 and coordination polyhedra in form of square antiprisms (0.64) or cubes (0.732) are more stable. For smaller values of *k*, structures with coordination number 6, but with coordination polyhedra with a smaller size, octahedron (0.414), are formed. For a compound of composition $Pr_4Al_3Ge_3$, an average value of $k = 0.77$ for *X* (Al and Ge) can be calculated from the values of the atomic radii listed in [13], however, the distances between *R* atoms observed in the structure are longer, and those between *X* atoms shorter, than the sum of the tabulated metallic radii, so that an effective value of $k = 0.60$ may be considered, which is closer to the ideal value for trigonal prismatic structures.

Class 10 in the classification by Kripyakevich has the largest number of representatives among intermetallic compounds and is subdivided into several groups. In the first group the whole space is filled exclusively by trigonal prisms. The trigonal prisms can be differently filled and/or arranged, and consequently deformed, for different representatives of this group. When the axes of the trigonal prisms are all parallel, the hexagonal structure type AlB_2 [15] is realized. In this type the *X* (B) atoms, which are situated at the centers of the trigonal prisms, form graphite-like isolated 6^3 nets. In the hexagonal structure of LiBaSi [16], the *X* (Li and Si) atoms adopt an ordered arrangement in the nets. In these structures the trigonal prisms share rectangular faces to form infinite slabs, which are interconnected via common bases. In Fig. 4 one-prism-thick slabs are cut from AlB_2 and LiBaSi in a different way: perpendicular to the [210] direction. When neighboring slabs of prisms are rotated by 90° with respect to each other (the prism axes become perpendicular), the *X* atoms form a three-dimensional framework, characteristic of the structures of tetragonal α-$ThSi_2$ [17] and LaPtSi [18]. In the latter structure the atoms centering the trigonal prisms are ordered. Blocks formed by two consecutive one-prism-thick slabs can be considered, neighboring blocks being shifted by ½ ½ *z* with respect to each other. The translation unit in the stacking direction contains four slabs (or two blocks). It is interesting to note that two other compounds identified in the Pr-Al-Ge system, $PrAl_{1.5}Ge_{0.5}$ and PrAlGe, crystallize with AlB_2- and LaPtSi-type structures, respectively.

Structures in which the space is filled by trigonal prisms and segments characteristic of other simple structure types belong to the second group of types with trigonal prismatic coordination. Transition metal borides such as orthorhombic CrB [19], V_5B_6 [20,21], Ta_3B_4 [22], and V_2B_3 [20,23], are representatives of this group. Their structures can be considered as built up from slabs of trigonal prisms with parallel prism axes, separated by slabs with empty tetrahedra and square pyramids (Fig. 5). These thin slabs correspond to half the translation unit of the cubic W type (see Fig. 4), in which the high-temperature modification of praseodymium, β-Pr, crystallizes. Other types of borides in which trigonal-prism slabs are separated by



V_2B_3, $oS20$
(63) $Cmcm - c^5$
$a = 3.0599$ Å
$b = 18.429$ Å
$c = 2.9839$ Å

Ta_3B_4, $oI14$
(71) $Immm - j^2ia$
$a = 3.13$ Å
$b = 3.29$ Å
$c = 14.0$ Å

V_5B_6, $oS22$
(65) $Cmmm - j^3i^2a$
$a = 2.975$ Å
$b = 21.25$ Å
$c = 3.058$ Å

CrB, $oS8$
(63) $Cmcm - c^2$
$a = 2.969$ Å
$b = 7.858$ Å
$c = 2.932$ Å

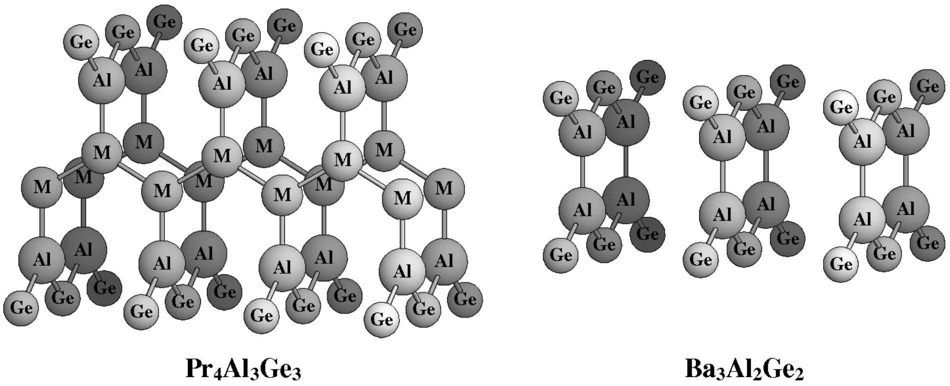
MoB, $oS22$
(141) $I4_1/amd - e^2$
$a = 3.105$ Å
$c = 16.97$ Å

Fig. 5 Projections of the structures of V_2B_3, Ta_3B_4, V_5B_6, CrB, and MoB (V, Ta, Cr, and Mo atoms large, B atoms small).

two or more such W-type slabs are also known (see [12]). In the CrB type (antitype to α-TlI [24]), individual AlB_2-type slabs are separated by W-type slabs, whereas in Ta_3B_4 and V_2B_3, double and triple AlB_2-type slabs, respectively, are separated by W-type slabs. The structure of V_5B_6 contains single and double trigonal prism slabs and can, therefore, also be considered as an intergrowth of CrB- and Ta_3B_4-type slabs. Among these structure types adopted by binary borides, only Ta_3B_4 has a known ternary substitution variant, $Ba_3Al_2Ge_2$ [25], among aluminum gemanides. The double slabs of trigonal prisms in orthorhombic $Ba_3Al_2Ge_2$ can be considered as cut from LiBaSi, the ternary substitution variant of AlB_2 (see Fig. 1).

In the structure of $Pr_4Al_3Ge_3$, as in the structure of V_2B_3, blocks of three consecutive slabs of trigonal prisms are separated by W-type slabs. However, differing from V_2B_3, consecutive slabs in the blocks are rotated by 90° with respect to each other, as in the α-$ThSi_2$- and LaPtSi types. These blocks contain ordered and disordered slabs, the disordered ones being located between two ordered slabs. In AlB_2 and α-$ThSi_2$ each X atom is connected to three other X atoms, however, in V_2B_3 and $Pr_4Al_3Ge_3$ only 2/3 of the X atoms have three B, Al, or Ge atoms capping the trigonal prisms. The remaining X atoms have a V or Pr atom capping one of the prism faces. In $Pr_4Al_3Ge_3$, the distribution of Al and Ge is ordered in the outer layers so that each Ge atom is connected to two Al atoms, the third atom of the triangle being a Pr atom, whereas each Al atom is surrounded by two Ge atoms and one atom from the mixed site M in the central slab of trigonal prisms. It may be noted that once the atoms are ordered like this in the outer layers, there is no possibility to order the Al and Ge atoms in the central slab so that each Al has three Ge and each Ge has three Al neighbors. The same arrangement of Al and Ge atoms as in the outer slabs of trigonal prisms is observed in all the slabs in $Ba_3Al_2Ge_2$. No Ge-Ge contacts occur in this structure, whereas Al-Al contacts occur in both structures. If we assume that Ge-Ge contacts are also not favored in $Pr_4Al_3Ge_3$, then the homogeneity range of the phase can be formulated as $Pr_4Al_{3+x}Ge_{3-x}$. The substructures formed by the small atoms in the closely related structures of $Pr_4Al_3Ge_3$ and $Ba_3Al_2Ge_2$ are shown in Fig. 6. Similar blocks consisting of three consecutive slabs of trigonal prisms with their prism axes rotated by 90° are observed in the binary structure type $TbGe_2$ [26]. The α-$ThSi_2$-type blocks are, however, separated by CaF_2-type segments in this structure. A closely related structure was reported for $PrGe_{1.91}$ [27], where partial disorder was observed in the central prism slab and the CaF_2-type segments.

The structures of the borides and alumogermanides shown in Figs. 1, 4 and 5 form a linear heterogeneous



$\mathbf{Pr_4Al_3Ge_3}$ $\mathbf{Ba_3Al_2Ge_2}$

Fig. 6 Substructures formed by Al and Ge atoms in the structures of $Pr_4Al_3Ge_3$ and $Ba_3Al_2Ge_2$ ($M = Al_{0.558(4)}Ge_{0.442(4)}$).

Table 5 Members of the structural series $R_{(m+m')+n}X_{2(m+m')}$ with different ratios of linearly intergrown AlB_2- (m), LiBaSi- (m'), and W- (n) type slabs.

Structure type	Number of slabs in the translation unit			Ratio $(m+m')/n$	R content (at.%)
	m	m'	n		
AlB_2	1	0	0	∞	33.3
LiBaSi	0	1	0		
α-$ThSi_2$	4	0	0		
LaPtSi	0	4	0		
V_2B_3	6	0	2	3	40.0
$Pr_4Al_3Ge_3$	2	4	2		
Ta_3B_4	4	0	2	2	42.9
$Ba_3Al_2Ge_2$	0	4	2		
V_5B_6	6	0	4	1.5	45.4
CrB	2	0	2	1	50.0
MoB [28]	4	0	4		

homologous series. Their compositions can be represented by the generalized formula $R_{m+n}X_{2m}$, where m and n are the relative numbers of slabs cut from the AlB_2 (LiBaSi) and W structures, respectively (Table 5). A decrease of the ratio m/n corresponds to an increase of the R content from 33.3 to 50.0 at.% for structures with a single separating W-type slab. A binary variant of the $Pr_4Al_3Ge_3$ type is not yet known.

Conclusions

The structure of the $R_4Al_3Ge_3$ compounds where R = Ce, Pr, Nd, or Sm, belongs to a new structure type of intermetallic compounds, which was determined on the compound with praseodymium. The $Pr_4Al_3Ge_3$ type is a member of the linear structural series where AlB_2- and/or LiBaSi-type slabs are intergrown with W-type slabs. Other representatives of this series are the ternary alumogermanide $Ba_3Al_2Ge_2$ and some binary borides.

References

[1] O.S. Zarechnyuk, A.A. Muravyova, E.I. Gladyshevskii, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* (8) (1970) 753-756.

[2] J.T. Zhao, E. Parthé, *Acta Crystallogr. C* 47 (1991) 1781-1784.

[3] J.T. Zhao, K. Cenzual, E. Parthé, *Acta Crystallog. C* 47 (1991) 1777-1781.

[4] E.I. Gladyshevskii, N.Z. Nakonechna, K. Cenzual, R.E. Gladyshevskii, J.-L. Jorda, *J. Alloys Compd.* 296 (2000) 265-271.

[5] J.T. Zhao, E. Parthé, *Acta Crystallogr. C* 46 (1990) 2276-2279.

[6] I. Melnyk, S. Pikus, N. Semus'o, R. Gladyshevskii, *Arch. Mater. Sci.* 25 (2004) 113-131.

[7] I. Melnyk, S. Pikus, V. Kuprysyuk, N. Semuso, R. Gladyshevskii, *Arch. Mater. Sci.* 26 (2005) 279-301.

[8] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data, Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, 2007.

[9] C.K. Fair, *MolEN, an Interactive Intelligent System for Crystal Structure Analysis*, Enraf-Nonius, Delft, 1990.

[10] D. Schwarzenbach, *Program LATCON: Refine Lattice Parameters*, University of Lausanne, Lausanne, 1966.

[11] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* 10 (1977) 73-74.

[12] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cenzual, R. Gladyshevskii, *TYPIX. Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types*, Springer-Verlag, Berlin, 1993/1994.

[13] E. Teatum, K. Gschneidner, J. Waber, *Los Alamos Report LA-2345*, US Department of Commerce, Washington DC, 1960.

[14] P.I. Kripyakevich, *Structure Types of Intermetallic Compounds*, Nauka, Moscow, 1977 (in Russian).

[15] W. Hofmann, W. Jäniche, *Naturwissenschaften* 23 (1935) 851.

[16] H. Axel, K.H. Janzon, H. Schäfer, A. Weiss, *Z. Naturforsch. B* 23 (1968) 108-109.

[17] G. Brauer, A. Mitius, *Z. Anorg. Allg. Chem.* 249 (1942) 325-339.

[18] K. Klepp, E. Parthé, *Acta Crystallogr. B* 38 (1982) 1105-1108.

[19] R. Kiessling, *Acta Chem. Scand.* 3 (1949) 595-602.

[20] K.E. Spear, P.W. Gilles, *High Temp. Sci.* 1 (1969) 86-97.

[21] H. Bolmgren, T. Lundström, L.E. Tergenius, S. Okada, I. Higashi, *J. Less-Common Met.* 161 (1990) 341-345.

[22] R. Kiessling, *Acta Chem. Scand.* 3 (1949) 603-615.

[23] Y. Yu, L.E. Tergenius, T. Lundström, S. Okada, *J. Alloys Compd.* 221 (1995) 86-90.

[24] L. Helmholz, *Z. Kristallogr.* 95 (1936) 129-137.

[25] A. Widera, B. Eisenmann, H. Schäfer, K. Tuban, *Z. Kristallogr.* 31 (1976) 1592-1595.

[26] P. Schobinger-Papamantellos, D.B. de Mooij, K.H.J. Buschow, *J. Less-Common Met.* 144 (1988) 265-274.

[27] I.A. Savysyuk, *Thesis*, Ivan Franko National Univ. Lviv, 2000.

[28] R. Kiessling, *Acta Chem. Scand.* 1 (1947) 893-916.