Chemistry of Metals and Alloys

Chem. Met. Alloys 13 (2020) 55-60
Ivan Franko National University of Lviv
www.chemetal-journal.org

Crystal structure of the ternary compound $La_2Ge_{3.03}Bi_{0.81}$

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Received November 20, 2020; accepted December 29, 2020; available on-line January 4, 2021
https://doi.org/10.30970/cma13.0405

The new ternary intermetallic compound $La_2Ge_{3.03}Bi_{0.81}$ was synthesized, and its crystal structure was determined by X-ray powder diffraction (structure type $Pr_2Ge_{3.26}Bi_{0.62}$, Pearson symbol *oS*36, space group *Cmcm*, a = 4.2289(3), b = 31.915(2), c = 4.4379(3) Å, Z = 4). The structure is characterized by partial disorder of Bi and Ge atoms, which form a statistical mixture on one site, and by positional disorder of Ge atoms, modeled by split positions. The structure type $Pr_2Ge_{3.26}Bi_{0.62}$ is a member of the linear intergrowth structure series composed by AlB_2-type (triple slabs of trigonal prisms) and CaF_2-type (double slabs of "half octahedra") fragments in the ratio 3:2.

Lanthanum / Germanium / Bismuth / X-ray powder diffraction / Crystal structure

Introduction

The phase diagram of the ternary system La–Ge–Bi has not yet been investigated. However, the existence and crystal structure of a ternary compound with high La content has been reported: $La_5Ge_{1.2}Bi_{1.8}$ (structure type Y_2HfS_5, Pearson symbol *oP*32, space group *Pnma*, a = 12.814, b = 9.604, c = 8.437 Å) [1].

In the Ge-rich part of other R–Ge–Bi systems (R = Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho), ternary compounds of general composition $R_2(Ge_{1-x}Bi_x)Ge_{3-y}$ are known. Their crystal structures belong to three related structure types: $Pr_2Ge_{3.26}Bi_{0.62}$ (R = Pr, Nd, Sm), $Gd_2Ge_{3.38}Bi_{0.42}$ (R = Gd, Tb), and $Gd_2Sn_{0.82}Ge_{2.94}$ (R = Y, Dy, Ho) [2]. Crystallographic data for the ternary $R_2(Ge_{1-x}Bi_x)Ge_{3-y}$ compounds are summarized in Table 1.

The structure types $Pr_2Ge_{3.26}Bi_{0.62}$ and $Gd_2Ge_{3.38}Bi_{0.42}$ are ternary variants of the binary type $TbGe_2$ (*oS*24, *Cmmm*) [3], whereas the structure type $Gd_2Sn_{0.82}Ge_{2.94}$ [4] is a ternary variant of the $DyGe_{1.85}$ type (*oS*24, *Cmc*2$_1$) [5]. All the ternary types are characterized by partial disorder of the different *p*-element atoms (Ge and Bi, or Ge and Sn), and by disordered vacancies on other Ge-atom sites. The occurrence of vacancies is accompanied by positional disorder, which was modeled by split positions during the structure refinements.

The aim of the present work was to refine the crystal structure of the new ternary compound $La_2Ge_{3.03}Bi_{0.81}$ (structure type $Pr_2Ge_{3.26}Bi_{0.62}$), which was found during an investigation of the phase equilibria in the ternary system La–Ge–Bi at 600°C.

Table 1 Crystallographic data for ternary compounds $R_2(Ge_{1-x}Bi_x)Ge_{3-y}$ [2].

Compound	Structure type	Pearson symbol	Space group	Unit-cell parameters, Å		
				a	*b*	*c*
$Pr_2Ge_{3.26}Bi_{0.62}$	$Pr_2Ge_{3.26}Bi_{0.62}$	*oS*36	*Cmcm*	4.147	31.279	4.303
$Nd_2Ge_{3.24}Bi_{0.56}$	$Pr_2Ge_{3.26}Bi_{0.62}$	*oS*36	*Cmcm*	4.1204	31.070	4.2592
$Sm_2Ge_{3.28}Bi_{0.52}$	$Pr_2Ge_{3.26}Bi_{0.62}$	*oS*36	*Cmcm*	4.0733	30.715	4.2047
$Gd_2Ge_{3.38}Bi_{0.42}$	$Gd_2Ge_{3.38}Bi_{0.42}$	*oS*32	*Cmcm*	4.0404	30.444	4.1629
$Tb_2Ge_{3.48}Bi_{0.28}$	$Gd_2Ge_{3.38}Bi_{0.42}$	*oS*32	*Cmcm*	4.0052	30.213	4.1210
$Y_2Ge_{3.50}Bi_{0.22}$	$Gd_2Ge_{2.94}Sn_{0.82}$	*oS*32	*Cmcm*	4.128	30.08	3.934
$Dy_2Ge_{3.52}Bi_{0.18}$	$Gd_2Ge_{2.94}Sn_{0.82}$	*oS*32	*Cmcm*	4.1120	29.917	3.9234
$Ho_2Ge_{3.54}Bi_{0.16}$	$Gd_2Ge_{2.94}Sn_{0.82}$	*oS*32	*Cmcm*	4.0951	29.799	3.9159

Experimental

An alloy of nominal composition $La_{34}Ge_{52}Bi_{14}$ was synthesized from high-purity metals (La ≥ 99.85 mass%, Ge ≥ 99.999 mass%, Bi ≥ 99.98 mass%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using a tungsten electrode. To achieve high efficiency of the interaction between the components, the sample was melted twice. After the synthesis, the alloy was wrapped into tantalum foil, sealed in a quartz ampoule under vacuum, and annealed at 600°C for 720 h. Finally, the ampoule with the sample was quenched into cold water. The weight loss did not exceed 1 % of the total mass, which was approximately 1 g.

X-ray powder diffraction patterns were obtained at room temperature on a diffractometer STOE Stadi P equipped with a linear position-sensitive detector (Cu $K\alpha_1$ radiation, angular range $4° \leq 2\theta \leq 106°$, step 0.015°). The phase analysis of the sample, which was carried out using the WinXPOW program package [6], revealed the presence of a new ternary compound with the general formula $La_2(Ge_{1-x}Bi_x)Ge_{4-y}$. The positions and intensities of the diffraction peaks of the new compound and the similarity of the X-ray powder diffraction pattern with powder patterns calculated for known ternary phases $R_2(Ge_{1-x}Bi_x)Ge_{3-y}$ (see Table 1) indicated possible formation of a phase with the structure type $Pr_2Ge_{3.26}Bi_{0.62}$ or $Gd_2Ge_{3.38}Bi_{0.42}$.

The crystal structure was refined by the Rietveld method using the FullProf Suite program package [7], starting from the atom coordinates reported for $Pr_2Ge_{3.26}Bi_{0.62}$. The following parameters were refined: scale factor, three cell parameters, 2θ-shift parameter, six profile parameters (pseudo-Voigt profile), eight positional, five displacement, four occupational parameters, and one texture parameter. In total 29 parameters were included in the final cycles of the refinement. The background was defined using the Fourier filtering technique. Experimental, calculated and difference X-ray powder diffraction patterns are presented in Fig. 1; experimental details and crystallographic data for the ternary compound $La_2Ge_{3.03}Bi_{0.81}$ are listed in Table 2.

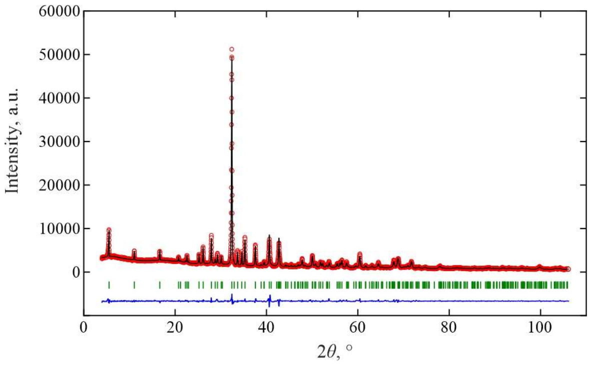

Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $La_{34}Ge_{52}Bi_{14}$ (Cu $K\alpha_1$ radiation). Vertical bars indicate the positions of the reflections of the ternary compound $La_2Ge_{3.03}Bi_{0.81}$.

The composition of the new ternary compound was in addition determined by local X-ray spectral analysis performed on a scanning electron microscope TESCAN Vega3 LMU equipped with an energy-dispersive X-ray analyzer Oxford Instruments Aztec ONE with a detector X-Max^{N}20: $La_{2.0(1)}Ge_{3.0(2)}Bi_{0.8(2)}$.

Table 2 Experimental details and crystallographic data for the ternary compound $La_2Ge_{3.03}Bi_{0.81}$.

Phase		$La_2Ge_{3.031(18)}Bi_{0.812(6)}$
Structure type		$Pr_2Ge_{3.26}Bi_{0.62}$
Pearson symbol		*oS*36
Space group		*Cmcm*
Unit-cell parameters:	*a*, *b*, *c*, Å	4.2289(3), 31.915(2), 4.4379(3)
Cell volume *V*, Å^3		598,96(7)
Formula units per cell *Z*		4
Density D_X, g cm^{-3}		7.441
Preferred orientation:	value / [direction]	0.913(3) / [101]
Profile parameters	*U*	0.306(9)
	V	0.076(5)
	W	0.0193(8)
Shape parameter		0.745(7)
Asymmetry parameters		0.0714(19), 0.0217(7)
Reliability factors:	R_B	0.0380
	R_F	0.0340
	R_p	0.0408
	R_{wp}	0.0570
	χ^2	5.73

Results and discussion

The crystal structure of the ternary compound with refined composition $La_2Ge_{3.031(18)}Bi_{0.812(6)}$ belongs to the orthorhombic structure type $Pr_2Ge_{3.26}Bi_{0.62}$. Positional atom coordinates, isotropic displacement parameters, and site occupancies for $La_2Ge_{3.03}Bi_{0.81}$ are given in Table 3. The structure has two sites occupied by La atoms, five sites occupied by Ge atoms alone, and one site occupied by a statistical mixture of Ge and Bi atoms. The main features of the refined structure are the partial disorder of Ge and Bi atoms, and positional disorder of Ge atoms, which was modeled by three partially occupied sites: position 4*c* (Ge3B), which is 62 % occupied, position 4*a* (Ge3C) 11 % occupied, and the split position 8*f* (site Ge3A) 6 % occupied. The refined separation within the split site Ge3A is 1.26(5) Å. The distance from the "central" site Ge3B to the nearest positions of the sites Ge3A and Ge3C are 0.593(13) and 1.202(4) Å, respectively. It follows that neighboring positions of the sites Ge3A, Ge3B, and Ge3C cannot be occupied simultaneously, and the occupancy of site Ge3A cannot exceed 50 %. The total occupancy of sites Ge3A, Ge3B, and Ge3C cannot exceed the sum 2×occ.(Ge3A) + 1×occ.(Ge3B) + 1×occ.(Ge3C) = 1. Full occupation of sites Ge3B or Ge3C, or 50 % occupation of site Ge3A, would correspond to the formula $La_2(Bi,Ge)Ge_3$. The presence of ~16 % Ge vacancies, distributed over the sites Ge3B, Ge3A, and Ge3C, gives the refined composition $Gd_2(Bi_{0.812(6)}Ge_{0.188(6)})Ge_{2.843(18)}$, and the vacancies are probably responsible for the partly disordered arrangement of the Ge atoms. The content of the unit cell and the coordination polyhedra of the atoms in the structure of $La_2Ge_{3.03}Bi_{0.81}$ are shown in Fig. 2. The interatomic distances within the coordination polyhedra are listed in Table. 4.

Table 3 Atomic coordinates, site occupancies, and isotropic displacement parameters for $La_2Ge_{3.031(18)}Bi_{0.812(6)}$ ($Pr_2Ge_{3.26}Bi_{0.62}$, *oS*36, *Cmcm*, a = 4.2289(3), b = 31.915(2), c = 4.4379(3) Å).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
La1	4*c*	0	0.44179(8)	¼	0.76(9)
La2	4*c*	0	0.83289(10)	¼	0.71(9)
Ge1	4*c*	0	0.08973(17)	¼	0.78(15)
Ge2	4*c*	0	0.63938(18)	¼	1.23(17)
Ge3A (occ. = 0.058(5))	8*f*	0	0.0109(19)	0.1191(18)	1.0
Ge3B (occ. = 0.619(10))	4*c*	0	0.0145(3)	¼	1.0
Ge3C (occ. = 0.108(9))	4*a*	0	0	0	1.0
M (0.812(6)Bi + 0.188(6)Ge)	4*c*	0	0.24973(6)	¼	1.07(8)

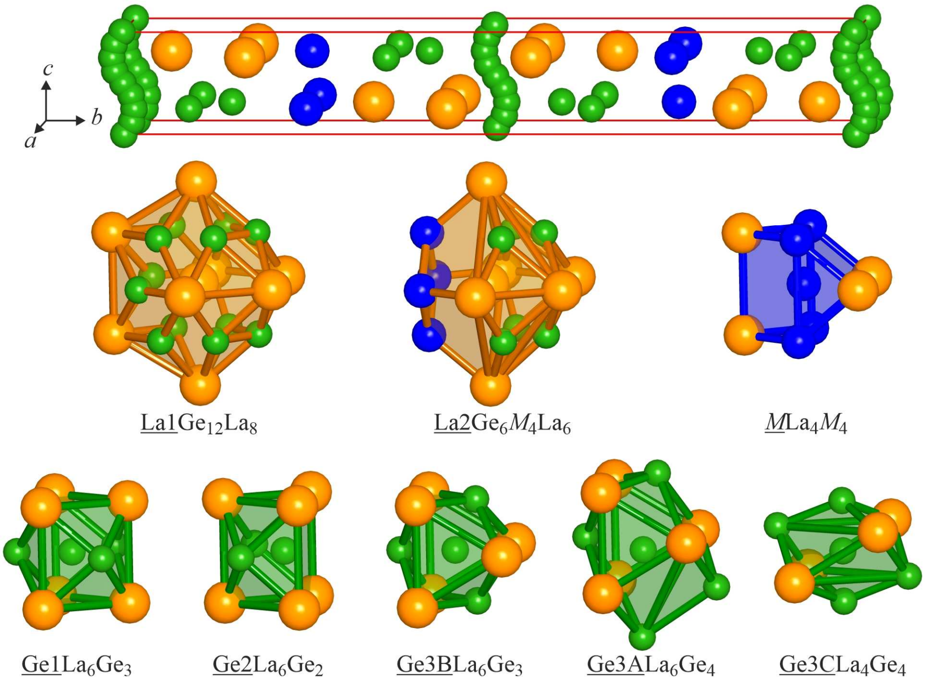

Fig. 2 Cell content and coordination polyhedra of the atoms in the structure of $La_2Ge_{3.03}Bi_{0.81}$.

Table 4 Interatomic distances (*δ*) within the coordination polyhedra and coordination numbers (CN) in the structure of $La_2Ge_{3.03}Bi_{0.81}$ ($Pr_2Ge_{3.26}Bi_{0.62}$, *oS*36, *Cmcm*).

Atoms		*δ*, Å	CN
La1	– 2 Ge3B (*2 Ge3A, 2 Ge3C*) [a]	3.139(7) (*3.11(5), 3.025(2)*) [a]	20
	– 4 Ge1	3.226(2)	
	– 4 Ge3B (*2 Ge3A, 2 Ge3C*) [a]	3.368(4) (*3.07(3), 3.025(2)*) [a]	
	– 2 Ge2	3.411(5)	
	– 2 La2	4.068(3)	
	– 2 La1	4.229(3)	
	– 2 La1	4.328(3)	
	– 2 La1	4.438(3)	
La2	– 4 Ge2	3.190(2)	16
	– 2 Ge1	3.320(5)	
	– 2 M [b]	3.393(3)	
	– 2 M [b]	3.446(3)	
	– 2 La1	4.068(3)	
	– 2 La2	4.229(3)	
	– 2 La2	4.438(3)	
M [b]	– 4 M [b]	3.065(3)	8
	– 2 La2	3.393(3)	
	– 2 La2	3.446(3)	
Ge1	– 1 Ge3B (*1 Ge3A, 1 Ge3C*) [a]	2.401(11) (*2.59(6), 3.071(5)*) [a]	9
	– 2 Ge2	2.642(5)	
	– 4 La1	3.226(2)	
	– 2 La2	3.320(5)	
Ge2	– 2 Ge1	2.642(5)	8
	– 4 La2	3.190(2)	
	– 2 La1	3.411(5)	
Ge3B	– 1 Ge1	2.401(11)	9
	– 2 Ge3B	2,404(5)	
	– 4 La1	3.139(7)	
	– 2 La1	3.368(4)	
Ge3A	– 1 Ge1	2.59(6)	10
	– 2 La1	3.07(3)	
	– 2 La1	3.11(5)	
	– 1 Ge3A	3.276(18)	
	– 1 Ge3A	3.450(18)	
	– 1 Ge1	3.61(6)	
	– 2 La1	3.82(3)	
Ge3C	– 2 Ge3C	2.219(15)	8
	– 2 Ge1	3.071(5)	
	– 4 La1	3.025(2)	

[a] alternative interatomic distances to the sites Ge3A and Ge3C are indicated in italics; [b] M = 0.812(6)Bi + 0.188(6)Ge.

The polyhedra shown for the atom sites La1 and Ge1 include Ge atoms from the site Ge3B, which represents a “central” position among the sites Ge3A, Ge3B, and Ge3C. In Table 4 the primary list of interatomic distances assumes occupation of site Ge3B alone, in accordance with the presented polyhedra, and the alternative distances (involving sites Ge3A or Ge3C instead of Ge3B), which may occur due to the positional disorder, are indicated in parentheses. The coordination polyhedra of the La atoms on site La1 are 20-vertex Frank-Kasper polyhedra of composition $\underline{La1}Ge_{12}La_8$, which can be described as pentagonal prisms Ge_{10} with two additional Ge and eight La atoms. The La atoms on site La2 center square antiprisms Ge_4M_4 with six additional Gd and two Ge atoms, forming 16-vertex polyhedra $\underline{La2}Ge_6M_4La_6$. The closest coordination environment for the statistical mixture of Bi and Ge atoms on site M consists of four La and four M atoms forming a *gyrobifastigium* $\underline{M}La_4M_4$, built by joining two mutually perpendicular trigonal prisms of composition La_2M_4 through a square face (La_4). The coordination polyhedra of the Ge atoms are trigonal prisms Gd_6 with two (Ge2) or three (Ge1, Ge3B) additional Ge atoms above the rectangular faces. The coordination polyhedra of the Ge atoms on the sites Ge3A and Ge3C differ from those of the Ge atoms on the "central" site Ge3B. A shift of the Ge atoms from the center of the trigonal prism towards one of rectangular faces leads to the formation of a deformed trigonal prism with four additional atoms for the site Ge3A. Further displacement of the Ge atoms leads to the formation of an eight-vertex polyhedron La_4Ge_4, which can be described as a deformed square prism, for the site Ge3C.

The structure of the ternary compound $La_2Ge_{3.03}Bi_{0.81}$ belongs to the family of linear intergrowth structures composed by AlB_2- and CaF_2-type slabs [8] and contains triple layers of trigonal prisms, separated by double slabs of "half octahedra". It is closely related to the structures of other ternary compounds $R_2(Ge_{1-x}Bi_x)Ge_{3-y}$, which also belong to this family of linear intergrowth structures. The structure type $Gd_2Ge_{3.38}Bi_{0.42}$, reported for the compounds with R = Gd and Tb, differs from the structure type $Pr_2Ge_{3.26}Bi_{0.62}$, reported for the compound with R = La, Pr, Nd, and Sm, by the modeling of the positional disorder of the Ge atoms in the central prism layers, which is described by three partially occupied sites in the $Pr_2Ge_{3.26}Bi_{0.62}$-type structures and by two partially occupied sites in the $Gd_2Ge_{3.38}Bi_{0.42}$-type structures. The positional disorder of the Ge atoms in the structures of the $Gd_2Ge_{2.94}Sn_{0.82}$-type compounds with R = Y, Dy, and Ho is modeled by two partially occupied sites, similarly as in the $Gd_2Ge_{3.38}Bi_{0.42}$-type structures. However, the structure types $Gd_2Ge_{3.38}Bi_{0.42}$ and $Gd_2Ge_{2.94}Sn_{0.82}$ differ by the way of stacking of the consecutive AlB_2-type layers within the triple slab. In $Gd_2Ge_{3.38}Bi_{0.42}$, the layers are stacked so that all prism axes are parallel, as in the parent structure AlB_2, whereas in $Gd_2Ge_{2.94}Sn_{0.82}$ the prism axes in consecutive layers are mutually perpendicular, as in the structure type α-$ThSi_2$.

The orthorhombic structure types $Pr_2Ge_{3.26}Bi_{0.62}$, $Gd_2Ge_{3.38}Bi_{0.42}$, and $Gd_2Ge_{2.94}Sn_{0.82}$ have the same space group and similar cell parameters: two short parameters a and c (~4 Å) and a much larger parameter b (stacking direction). They are derived from binary structure types of rare-earth germanides [9]: $TbGe_2$ (*oS*24, *Cmmm*) [10] and $PrGe_{1.91}$ (*oS*36, *Cmmm*) [11] with mutually perpendicular trigonal prism axes in consecutive AlB_2-type layers, and $DyGe_{1.85}$ (*oS*24, *Cmc*2$_1$) [12] and $YGe_{1.82}$ (*oS*28, *Cmcm*) [13] with parallel prism axes in consecutive layers.

The ternary structure types $Pr_2Ge_{3.26}Bi_{0.62}$, $Gd_2Ge_{3.38}Bi_{0.42}$, and $Gd_2Ge_{2.94}Sn_{0.82}$ are characterized by Ge vacancies and positional disorder of the Ge atoms occupying the central prism layers, which was modeled by splitting the Ge-atom position in a direction perpendicular to the prism axes. A correlation was observed between the structures of the ternary compounds $R_2(Ge_{1-x}Bi_x)Ge_{3-y}$ and the Ge deficiency y. The compounds with 16-21 % vacancies on the Ge sites are described by the structure type $Pr_2Ge_{3.26}Bi_{0.62}$ (R = La, Pr, Nd, Sm), those with 9-14 % vacancies by the structure type $Gd_2Ge_{3.38}Bi_{0.42}$ (R = Gd, Tb). The stacking variant $Gd_2Ge_{2.94}Sn_{0.82}$ (R = Y, Dy, Ho) was observed for 5-7 % vacancies.

Conclusions

The new ternary compound $La_2Ge_{3.03}Bi_{0.81}$ was synthesized and its crystal structure determined by X-ray powder diffraction. The structure belongs to the structure type $Pr_2Ge_{3.26}Bi_{0.62}$, which is a member of the family of linear intergrowth structures composed by AlB_2- and CaF_2-type slabs in the ratio 3:2.

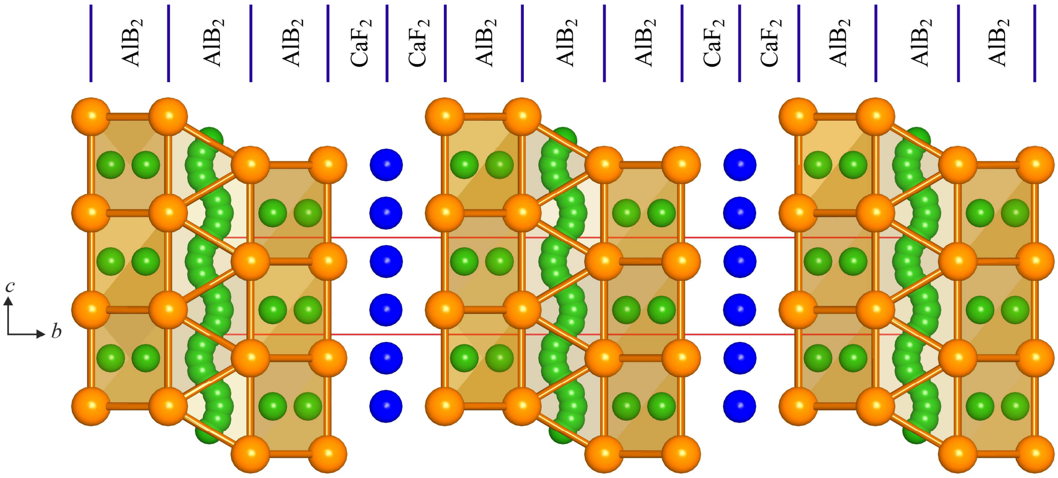

Fig. 3 Intergrowth of AlB_2- and CaF_2-type slabs in the structure of $La_2Ge_{3.03}Bi_{0.81}$ along the crystallographic direction [010]. Yellow circles: La, grey circles: Ge, blue circles: 0.812(6)Bi + 0.188(6)Ge.

Acknowledgment

This work was carried out under the grant of the Ministry of Education and Science of Ukraine No. 0118U003609.

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