UDC 548.736.4+546.669:546.747:546.28 doi: 10.33609/2708-129X.88.11.2022.3-10

CRYSTAL STRUCTURE OF THE NEW GERMANIDE $Pr_3Co_2Ge_{7.36}$

B. Belan[1], M. Dzevenko[2], J. Stępień-Damm[3], R. Gladyshevskii[1]

Dedicated to the memory of Prof. Oksana Bodak

[1]Department of Inorganic Chemistry, Ivan Franko National University of Lviv,
6 Kyryla i Mefodia Str., 79005 L'viv, Ukraine
[2]Kruty Heroes Lviv Lyceum with intensive military and physical training,
68 Pasichna Str., 79038 L'viv, Ukraine
[3]Institute of Low Temperature and Structure Research, Polish Academy of Sciences,
P. O. Box 1410, 50–950 Wrocław 2, Poland
e-mail: bohdanabelan@gmail.com

The structure of $Pr_3Co_2Ge_{7.36}$ (*Cmmm*, *a* = 4.236 (1), b = 25.994(5), c = 4.272(1) Å, *Z* = 2) can be considered as a partly disordered derivative of the $La_3Co_2Sn_7$ type. The Ge positions in the Pr_4Ge_8 cuboctahedra of the $AuCu_3$-type slabs are conveniently described by two partly occupied sites, one of which is split. The Co and Ge atoms are characterized by square-antiprismatic, cubooctahedral, and trigonal-prismatic coordination.

Key words: praseodymium, cobalt, germanium, crystal structure, single crystal method.

INTRODUCTION. Intermetallic compounds formed in the ternary systems *RE*-Co-Ge (*RE* = rare earth metals) have attracted considerable scientific interest due to various crystal structures and interesting physical properties. On the other hand, the most effective way to find new compounds is to study in detail the isothermal sections of the corresponding systems. Therefore, our main scientific interest is focuses on the investigation of *RE*-Co-Ge ternary systems. Some of the *RE*-Co-Ge systems have been studied only for searching of new compounds, for example the La-Co-Ge system [1]. The isothermal section have been constructed for other systems. Particularly, the isothermal sections of the ternary systems Ce-Co-Ge [2, 3], Pr-Co-Ge [4], Nd-Co-Ge [5], Sm-Co-Ge [6], and Eu-Co-Ge [7] have been constructed in whole concentration range. The majority of these systems are characterized by formation of rather large number of compounds. Thus, 11 ternary compounds have been found in the Ce-Co-Ge system, 13 ternary compounds – in the Pr-Co-Ge system, 16 compounds – in the Nd-Co-Ge system, 18 compounds – in the Sm-Co-Ge system, and only three compounds – in the Eu-Co-Ge system. However, crystal structures are determined only for a few of them. During the study of the Pr-Co-Ge system, we have found the new ternary compound. Herein we present the results of the crystal structure determination of $Pr_3Co_2Ge_{7.36}$, which is the new representative of $La_3Co_2Sn_7$ structure type.

EXPERIMENT AND DISCUSSION OF THE RESULTS. The sample with composition $Pr_{22.72}Co_{18.18}Ge_{59.1}$ was melted under an argon atmosphere in an arc furnace, and annealed at 870 K under vacuum for 350 h. Single crystals were selected from the sample by mechanical fragmentation. They exhibit metallic lustre whereas the ground powders are dark grey.

The crystal structures of the compound were investigated by X-ray single-crystal diffraction. The reflections intensities were measured with graphite-monochromatized Mo *K*α radiation on an KM4CCD diffractometer at 293(2) K. The structures were solved by direct methods and refined by the SHELXL-97 program package [8] with anisotropic atomic displacement parameters. The composition of the investigated single crystal was analyzed in a scanning electron microscope with an EDAX Genesis XM4 spectrometer. The experimentally determined composition of the grain of is close to the composition calculated from the structure refinements.

The crystallographic data and details on the data collection for $Pr_3Co_2Ge_{7.36}$ are listed in Table 1. The structure was refined in space group *Cmmm* with anisotropic atomic displacement parameters. A final electron-density difference map was flat and did not reveal any significant residual peaks. The majority of the crystallographic positions are fully occupied. The exception is the positions Ge4, Ge5 and Ge6, which are occupied only on 0.215, 0.287 and 0.361 accordingly. Due to such low occupation if these positions the U_{iso} has been calculated instead of anisotropic displacement parameters. Final atomic positional and displacement parameters of $Pr_3Co_2Ge_{7.36}$ compound are presented in Table 2.

Table 1.

Crystal data and structure refinement details for $Pr_3Co_2Ge_{7.36}$.

Empirical formula	$Pr_3Co_2Ge_{7.36}$
Formula weight	524.36
T, K	293(2)
Space group	*Cmmm*
Pearson code	*OC*24,72
Unit cell dimensions, Å	a = 4.236(1), b = 25.994(5), c = 4.272(1)
Volume, Å^3	470.4(2)
No. formula units per unit cell	2
Calculated density, g·cm^{-3}	7.404
Absorption coefficient, mm^{-1}	40.553
F(000), *e*	910
Crystal color	metallic
θ range for data collection	10.60–30.50
Index ranges	$-3 \le h \le 6$, $-35 \le k \le 34$, $-5 \le l \le 6$

Table 1.

Measured reflections	3325
Independent reflections / R_{int}	422 / 0.1888
Reflections with $I > 2\ \sigma(I)$ / R_{σ}	311 / 0.0892
Data / restraints / parameters	422 / 0 / 31
Goodness-of-fit on F^2	1.170
Final $R1$ / $wR2$ [$I > 2\ \sigma(I)$]	0.0760 / 0.1900
Final $R1$ / $wR2$ (all data)	0.0975 / 0.2044
Largest diff. peak / hole, e Å^{-3}	3.391 / –4.018

Table 2.

Atomic coordinates and thermal displacement parameters for $Pr_3Co_2Ge_{7.36}$.

Atom	Wyckoff Site	G	x	y	z	U_{eq}, Å^2	U_{iso}, Å^2
Pr1	4*j*	1	0	0.31584(6)	0.5	0.0161(6)	
Pr2	2*a*	1	0	0	0	0.0145(7)	
Co	4*i*	1	0	0.13092(15)	0	0.0180(9)	
Ge1	4*j*	1	0	0.09140(13)	0.5	0.0190(8)	
Ge2	4*i*	1	0	0.22086(13)	0	0.0159(7)	
Ge3	4*i*	1	0	0.40856(13)	0	0.0203(8)	
Ge4	4*j*	0.215(1)	0	0.4480(6)	0.5		0.015(2)
Ge5	4*j*	0.287(1)	0	0.4734(4)	0.5		0.015(2)
Ge6	2*c*	0.361(2)	0.5	0	0.5		0.015(2)

Atom	U_{11}	U_{22}	U_{33}	$U_{12} = U_{13} = U_{23}$
Pr1	0.0190(9)	0.0208(10)	0.0086(8)	0
Pr2	0.0178(10)	0.0168(11)	0.0088(9)	0
Co	0.0218(16)	0.0221(19)	0.0099(13)	0
Ge1	0.0267(15)	0.0220(16)	0.0082(11)	0
Ge2	0.0167(13)	0.0199(14)	0.0111(11)	0
Ge3	0.0201(14)	0.0260(18)	0.0149(12)	0

The interatomic distances (δ), the values of interatomic distances reductions from the sum of atomic radii and coordination numbers of atoms for $Pr_3Co_2Ge_{7.36}$ listed in Table 3 (values of the atomic radii are taken from [9]: *r*(Pr) = 1.828 Å, *r*(Co) = 1.253 Å, *r*(Ge) = 1.220 Å). The majority of interatomic distances are in good agreement with the sum of atomic sizes. Some Ge-Ge interatomic distances are rather short and another one are rather long in comparison with the sum of the respective atomic radii.

Table 3.

Interatomic distances (δ), *Δ* values (*Δ* = 100(Σ*r* – δ)/ Σ*r*, where Σ*r* is the sum of the respective atomic radii) of $Pr_3Co_2Ge7.36$ compound (alternative positions are italicized).

Atoms		δ, Å	*Δ*, %	Atoms		δ, Å	*Δ*, %
Pr1	4 Ge2	3.156(1)	3.4	Ge2	1 Co1	2.338(5)	-5.8
	2 Ge1	3.209(3)	5.0		2 Ge2	2.604(3)	6.3
	2 Ge3	3.220(3)	5.3		4 Pr1	3.156(1)	3.4
	2 Ge2	3.265(3)	6.6		2 Pr1	3.265(3)	6.6
	4 Co1	3.311(2)	6.9	Ge3	2 Co1	2.354(2)	-5.0
	1 Ge4	3.435(16)	11.3		*2 Ge4*	*2.369(7)*	*-3.0*
	2 Pr1	4.025(2)	9.2		*2 Ge5*	*2.721(7)*	*10.3*
Pr2	*4 Ge6*	*3.008(1)*	*-1.3*		4 Ge1	3.008(1)	18.9
	8 Ge5	*3.087(2)*	*1.3*		2 Pr2	3.184(3)	4.3
	4 Ge3	3.184(3)	4.3		*2 Ge6*	*3.196(3)*	*23.7*
	4 Ge1	3.195(3)	4.6		2 Pr1	3.220(3)	5.3
	8 Ge4	*3.298(6)*	*7.6*	Ge4	2 Ge1	2.353(7)	-3.7
	2 Co1	3.403(4)	9.5		2 Ge3	2.369(7)	-3.0
Co	1 Ge2	2.338(5)	-5.8		1 Ge4	2.703(22)	9.7
	2 Ge3	2.354(2)	-5.1		4 Pr2	3.298(6)	7.6
	2 Ge1	2.370(2)	-4.3		1 Pr1	3.435(16)	11.3
	4 Pr1	3.311(2)	6.9	Ge5	2 Ge1	2.706(7)	9.8
	1 Pr2	3.403(4)	9.5		2 Ge3	2.721(7)	10.3
Ge1	*2 Ge4*	*2.353(7)*	*-3.7*		4 Pr2	3.087(2)	1.26
	2 Co1	2.370(2)	-4.3	Ge6	4 Pr2	3.008(1)	-1.3
	2 Ge5	*2.706(7)*	*9.8*		4 Ge1	3.183(3)	23.3
	4 Ge3	3.008(1)	18.9		4 Ge3	3.196(3)	23.7
	2 Ge6	*3.183(3)*	*23.3*				
	2 Pr2	3.195(3)	4.6				
	2 Pr1	3.209(3)	5.0				

The projection of the crystal structure of $Pr_3Co_2Ge_{7.36}$ on the *ab* plane and the coordination polyhedral (CP) of the atoms are shown in Fig. 1. It must be noted that some coordination polyhedrons are rather unusual due to partial occupation of crystallographic positions and some disordered of the structure in comparison with the structure of prototype $La_3Co_2Sn_7$. Moreover, the Ge4, Ge5 and Ge6 atoms are too close and cannot be in one region simultaneously. Therefore, only one of these atoms can be in one region, respectively, or the Ge4, or the Ge5 or the Ge6 atom is included to coordination polyhedra as well (such positions are marked in Table 3 with italics). Additionally, only the Ge6 atoms are indicated in Fig. 1 and 2 for clarity. The coordination polyhedra for the Pr atoms have from 17- and 20-vertices and consist of the atoms of all sorts. The coordination sphere of the Pr1 atoms consist of 11 germanium atoms, four cobalt and two praseodymium atoms, which form of a very irregular polyhedron. The Pr2 atoms are surrounded by 12 Ge atoms and two Co atoms. Eight germanium atoms form distorted square prism (if the Ge6 atoms are taken) with four additional germanium atoms on the side faces. The one cobalt atom is located above each of the square bases of this prism. The Co atoms are surrounded by five germanium atoms and five praseodymium atoms. The CP can be described as pyramid with quadrangular base with additional atoms. The coordination number of the germanium atoms are ranges from 8 to 12. The Ge1 and Ge3 have similar coordination polyhedral, which can be described as tetragonal prism with four additional atoms opposite sides. The Ge1 and Ge3 atoms are surrounded by four praseodymium atoms, two cobalt and six germanium, two of which are two Ge 4 or two Ge5 or two Ge6. The CP of the Ge2 atoms is tricapped trigonal prism, which consist of all three types of atoms. The CP of Ge 4 atoms are similar to the CP of the Co atoms. The tetragonal antiprism is the CP of the Ge5 atoms. The Ge6 atoms are surrounded of by four Pr and eight Ge atoms.

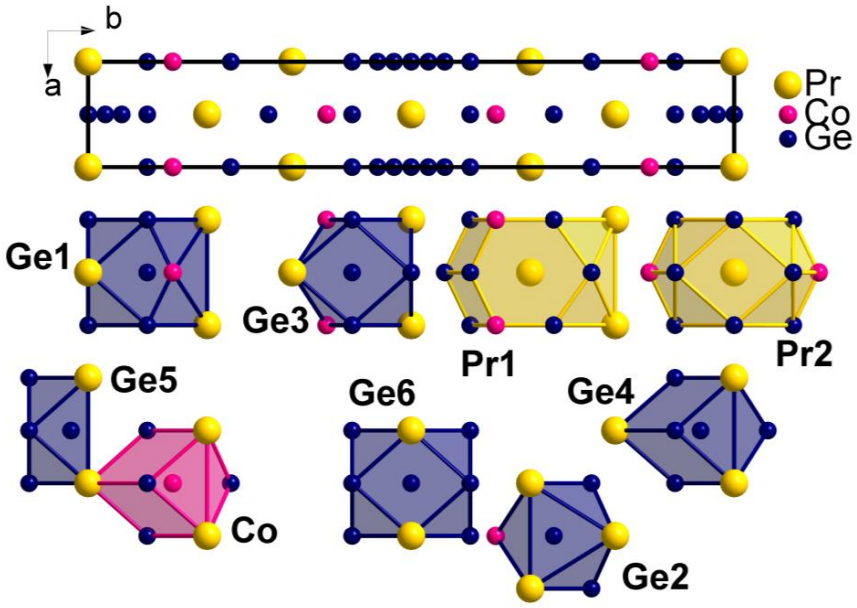

Fig. 1. A projection of the $Pr_3Co_2Ge_{7.36}$ unit cell on *ab* plane and a view of the coordination polyhedra of the atoms.

The structure of $Pr_3Co_2Ge_{7.36}$ can be considered as a partly disordered derivative of the $La_3Co_2Sn_7$ type. The main difference between these structures is in the additional position of the Ge atoms. The (2*c*) position of Ge6 atoms in the structure of our compound is partially occupied and two additional split positions (4*j*) of Ge 4 and Ge5 atoms are partially occupied as well. All these three postion can be considered as displacement of some Ge atoms from (2*c*) in (4*j*) with simultaneous splitting.

The $Pr_3Co_2Ge_{7.36}$ structures can be described as packing of two types polyhedra with the Pr in the center (Fig.2). First polyhedral is cuboctahedra [Pr2(Ge_{12})] similar to the $AuCu_3$-type slabs with two partly occupied sites of Ge atoms, one of which is split. The second one is slightly distorted hexagonal prism [Pr1(Co_4Ge_{10})] with two additional germanium atoms opposite the side faces.

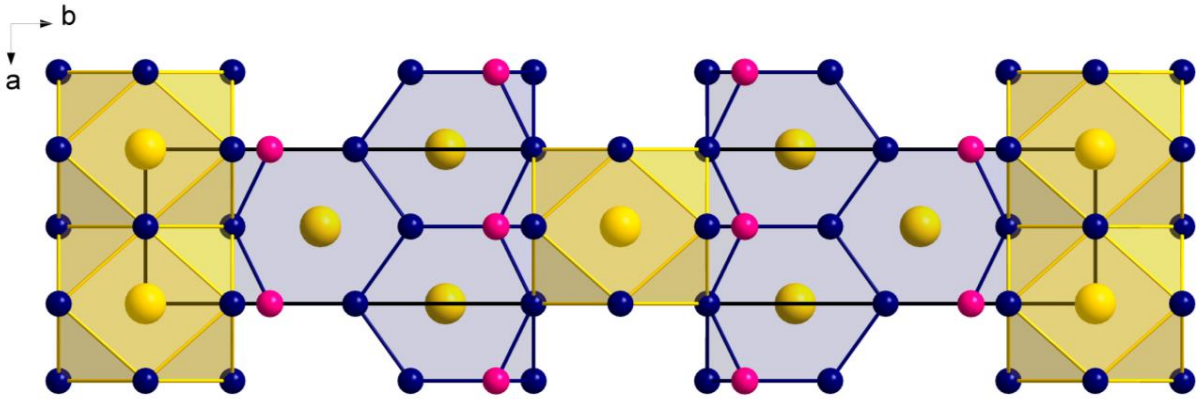

Fig. 2. Packing of [Pr2(Ge_{12})] (yellow) and [Pr1(Co_4Ge_{10})] (blue) slabs in the $Pr_3Co_2Ge_{7.36}$ structure.

CONCLUSIONS. The crystal structure of ternary compound $Pr_3Co_2Ge_{7.36}$ have been investigated in detail using single crystal X-ray data for the first time. This compound is disordered derivative of the $La_3Co_2Sn_7$-type structure.

ACKNOWLEDGMENTS. This study was performed under the research project of Ivan Franko National University of Lviv "New substances, materials, types of matter and approaches to energy saving and environmental protection", state registration number: 0121U113567 (21-01-2022).

КРИСТАЛІЧНА СТРУКТУРА НОВОГО ГЕРМАНІДУ $Pr_3Co_2Ge_{7.36}$

Б. Белан[1]*, М. Дзевенко[2], Ю. Степень-Дамм[3], Р. Гладишевський[1]

[1]Львівський національний університет імені Івана Франка, вул. Кирила і Мефодія, 6, Львів 79005, Україна
[2]Львівський ліцей з посиленою військово-фізичною підготовкою імені Героїв Крут, вул. Пасічна, 68, Львів 79000, Україна
[3]Інститут низькотемпературних і структурних досліджень, Польська академія наук, П. О. Бокс 1410, Вроцлав 2, 50–950, Польща
**e-mail: bohdanabelan@gmail.com*

Потрійну систему Pr-Co-Ge досліджували і раніше. Так, було побудовано ізотермічний переріз діаграми її стану в повному концентраційному інтервалі та знайдено існування 13 тернарних сполук. Однак, кристалічну структуру досліджено лише для кількох із них. Під час більш детального дослідження системи Pr-Co-Ge знайдено нову потрійну сполуку $Pr_3Co_2Ge_{7,36}$ та встановлено її кристалічну структуру методом монокристалу. Зразок синтезовано методом електродугового плавлення. Монокристал відібрано зі зразка, відпаленого за температури 870 K впродовж 350 год. Масив експериментальних інтенсивностей **відбить** отримано на автоматичному монокристальному дифрактометрі KM4CCD (MoKα-проміння). Структуру визначено прямими методами за допомогою комплексу програм SHELX-2018/3. Параметри теплового зміщення усіх атомів уточнено в анізотропному наближенні. Кристалічну структуру сполуки $Pr_3Co_2Ge_{7.36}$ (*Cmmm*, a = 4,236 (1), b = 25,994(5), c = 4,272(1) Å, Z = 2) можна розглядати як частково невпорядкований варіант структури типу $La_3Co_2Sn_7$. Більшість кристалографічних позицій в структурі дослідженої сполуки є повністю зайнятими. Винятком є позиції Ge4, Ge5 і Ge6, які зайняті лише на 0,215, 0,287 і 0,361 частки відповідно. Більшість міжатомних відстаней добре узгоджуються з сумою атомних розмірів, за винятком деяких відстаней Ge-Ge, одні з яких є дещо коротшими, а інші дещо довшими порівняно із сумою відповідних атомних радіусів. Координаційні поліедри атомів є типовими для подібних структур, проте вони є дещо відмінні від відповідних поліедрів атомів у структурі прототипу $La_3Co_2Sn_7$. Це можна пояснити деякою розупорядкованістю структури сполуки $Pr_3Co_2Ge_{7.36}$ та наявністю розщеплених позицій атомів германію. Координаційні поліедри атомів празеодиму мають 17 і 20 вершин і складаються з атомів усіх сортів. Координаційний поліедр атомів кобальту можна описати як піраміду з чотирикутною основою, побудованою з атомів празеодиму, з п'ятьма додатковими атомами германію навпроти усіх граней. Координаційне число атомів германію коливається від 8 до 12.

Структуру сполуки $Pr_3Co_2Ge_{7.36}$ можна представити як упаковку двох видів поліедрів, побудованих навколо атомів празеодиму. Перший поліедр – це кубоктаедри, подібні до відповідних у структурі типу $AuCu_3$ з двома частково зайнятими положеннями атомів Ge, **одне з яких розщеплене**. Інший поліедр – це злегка спотворена гексагональна призма з двома додатковими атомами германію навпроти бічних граней.

Ключові слова: празеодим, кобальт, кристалічна структура, метод монокристалу.

REFERENCES

1. Villars P., Cenzual K., Eds. *Pearson's Crystal Data: Crystal Structure Database for Inorganic Compounds* (release 2018/19). ASM International®, Materials Park, Ohio (USA), 2018.
2. Konyk M. B., Bodak O. I., Ternary Ce-Co-Ge system. *J. Alloys Compd.* 1998. **267**: 189–191.
3. Belan B. D., Stepen Damm J., Gladyshevskii R. E., Bodak O. I. The new structure type $Ce_5Co_4Ge_{13}$. *Chem. Met. Alloys*. 2008. **1**: 43–45.
4. Fedyna M. Thesis, University of Lvov. 1988 [in Russian].
5. Salamakha P. Thesis, University of Lvov. 1989 [in Russian].
6. Mruz O. Thesis, University of Lvov. 1988 [in Russian].
7. Oniskovets (Belan) B. D., Pavlyuk V. V., Bodak O. I. Eu-Co-Ge system. Dopov. Akad. Nauk Ukr. RSR, Ser. B. 1985. **10**: 40–41 [in Russian].
8. Sheldrick G. M., SHELX-97 – WinGX Version. Release 97–2. University of Göttingen, Germany, 1997.
9. Emsley J. *The Elements, 2nd ed.* Clarendon Press, Oxford. 1991.

Стаття надійшла 05.12.2022.