© 2010 The Chemical Society of Japan Bull. Chem. Soc. Jpn. Vol. 83, No. 4, 323–327 (2010)

BCSJ Award Article

Preparation and Structures of Lanthanoid Germanides, $PrGe_{3.36}$, $NdGe_{3.25}$, and $TmGe_3$ with Double Square Ge-Mesh Structures

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A series of lanthanoid trigermanides of Pr, Nd, and Tm has been prepared by high-pressure (3–5 GPa) and high-temperature (1200 °C) reactions. $TmGe_3$ crystallizes in an orthorhombic unit cell (*Cmcm*, No. 63) with $a = 3.990(1)$ Å, $b = 20.488(5)$ Å, $c = 3.8794(8)$ Å, and $V = 317.2(1)$ Å^3. It is isotypic with the $DyGe_3$ structure composed of Ge zig-zag chains and Tm situated between double square Ge-meshes. $PrGe_{3.36}$ crystallizes in an orthorhombic unit cell (*Cmmm*, No. 65) with $a = 4.062(4)$ Å, $b = 21.43(3)$ Å, $c = 4.212(6)$ Å, and $V = 366.6(8)$ Å^3. The structure is principally the same to the $DyGe_3$ structure but contains an additional Ge site. The site is partially occupied, and is situated on the square mesh. Each Ge atom in the site is coordinated by five Ge atoms in the chain and in the mesh. $NdGe_{3.25}$ is isotypic with $PrGe_{3.36}$ and has lattice constants of $a = 4.073(1)$ Å, $b = 20.961(6)$ Å, $c = 4.254(1)$ Å, and $V = 363.2(2)$ Å^3. The magnetic susceptibilities of $PrGe_{3.36}$ and $NdGe_{3.25}$ follow the Curie–Weiss law with the effective magnetic moments $\mu_{\text{eff}} = 3.60$ and $3.57\,\mu_B$, respectively, implying the oxidation states of Pr and Nd are 3+.

Lanthanoid (Ln) ions with medium-sized radii such as Y^{3+}, Er^{3+}, Ho^{3+}, Tb^{3+}, and Gd^{3+} form the $DyGe_3$ structure.[1–6] The structure contains two types of Ge subunits as shown in Figure 1.[1] One is a zig-zag chain and the other is a layer composed of double square meshes. Dy ions and the Ge chains are situated between the layers. The space group is *Cmcm* and the double meshes are stacked along the *b* axis. The chains extend along the *c* axis corresponding to the diagonal direction of the meshes. The lattice constants of the *a* (4.0278(5) Å) and *c* (3.8997(5) Å) axes of $DyGe_3$ are very similar but not the same, because the mesh is slightly distorted from the regular square net.

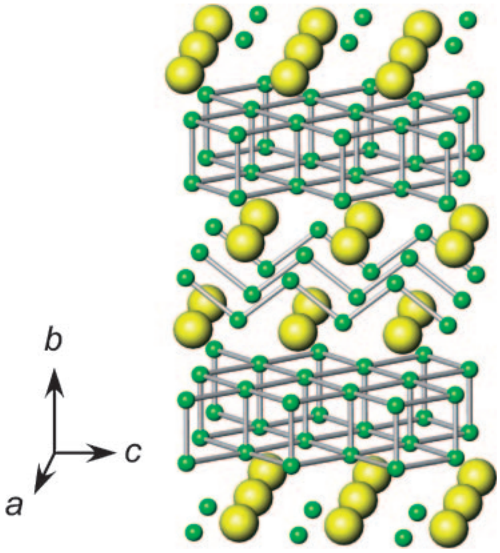

Figure 1. The crystal structure of $DyGe_3$. The yellow and green balls represent Dy and Ge atoms, respectively. It has a layer structure composed of Dy^{3+} ions, double square Ge-meshes, and Ge-chains.

Light lanthanoid elements do not form the $DyGe_3$ structure. For these elements, only the compounds with compositions of $LnGe_x$ with $x \leq 2$ have been reported by reactions under ambient pressure. However, in our recent studies, Ge rich compounds were obtained by high-pressure and high-temperature reactions, such as $LnGe_5$, Ln = La, Ce, Pr, Nd, and Sm with the $LaGe_5$ structure, and $CeGe_3$ with the Cu_3Au structure.[7–9] The former has a tunnel structure composed of Ge–Ge covalent network containing uncommon 8-coordinated Ge atoms.

We are interested in the structures of Ge networks in lanthanoid germanides formed under high pressure. In the present study, we have investigated the reactions of Pr, Nd, and Tm with Ge and successfully prepared three new germanides $PrGe_{3.36}$, $NdGe_{3.25}$, and $TmGe_3$ with the aid of high-pressure and high-temperature conditions. They have the $DyGe_3$ structure (for Tm), and its closely related structures (for Pr and Nd).

Experimental

The new lanthanoid germanides were prepared as follows: Pr (Nilaco 99.9%) and Tm (Nilaco 99.7%) were reacted with Ge (Mitsuwa Pure Chemical 99.999%) in a molar ratio of 1:3 in an arc

Published on the web March 18, 2010; doi:10.1246/bcsj.20090310

Table 1. Crystallographic Data and Details on the Structure Determination of $PrGe_{3.36}$, $NdGe_{3.25}$, and $TmGe_3$

Formula	$PrGe_{3.36}$	$NdGe_{3.25}$	$TmGe_3$
Formula weight	384.98	380.32	386.7
Space group	*Cmmm* (No. 65)	*Cmmm* (No. 65)	*Cmcm* (No. 63)
a/Å	4.062(4)	4.073(1)	3.990(1)
b/Å	21.43(3)	20.961(6)	20.488(5)
c/Å	4.212(6)	4.254(1)	3.8794(8)
V/Å^3	366.6(8)	363.2(2)	317.2(1)
Z	4	4	4
Crystal size/mm^3	0.03 × 0.04 × 0.08	0.06 × 0.06 × 0.10	0.08 × 0.10 × 0.16
Diffractometer	Rigaku Raxis-Rapid	Rigaku Raxis-Rapid	Rigaku Raxis-Rapid
Radiation (graphite monochromated)	Mo Kα	Mo Kα	Mo Kα
μ(Mo Kα)/mm^{-1}	39.98	40.07	55.55
2θ limit	54.9	54.9	54.9
No. of observed unique reflections	276	274	236
No. of variables	23	23	18
$R1$, $wR2$[a)]	0.032, 0.072	0.052, 0.124	0.039, 0.094
Goodness of fit, S[b)]	1.17	1.16	1.14

a) $wR2 = \{\sum((F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2\}^{1/2}$. b) $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o is the number of reflections and N_v is the total number of parameters refined.

furnace. Mixtures of $LnGe_2$ and Ge were obtained. The mixtures were put in h-BN cells and reacted at 3–5 GPa and 1200 °C for 0.5 to 1 h. After quenching to room temperature, the pressure was slowly decreased to ambient pressure. For the Nd system, Nd (Nilaco 99.9%) and Ge in a molar ratio of 1:2 were reacted in the arc furnace to obtain $NdGe_2$. The obtained $NdGe_2$ and Ge were mixed in a molar ratio of 1:1. The mixture was reacted under the same conditions as those for Pr and Tm compounds. Details of the high-pressure synthesis are described elsewhere.[10]

Powder X-ray diffraction (XRD) measurement of the products was performed with a MacScience M18XHF diffractometer with graphite-monochromated Cu Kα radiation. Single-crystal X-ray analysis was performed with a Rigaku R-AXIS diffractometer equipped with an imaging plate area detector with graphite-monochromated Mo Kα radiation. Single-crystal structure analysis was performed with the SHELX-97 crystallographic software package.[11] Chemical compositions of the products were determined with an electron probe microanalyzer (EPMA) (JEOL JCMA-733). Magnetic susceptibility measurements were performed with a SQUID magnetometer (Quantum Design MPMS-5) in a 5000-Oe field.

Crystallographic data have been deposited with Inorganic Crystal Structure Database: Deposition number (CSD number) 380433 ($NdGe_{3.25}$), 380434 ($PrGe_{3.36}$), and 380435 ($TmGe_3$). These CIF files can be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax (+49)7247-808-666, e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD number.

Results and Discussion

Synthesis and Structures of $PrGe_{3.36}$ and $NdGe_{3.25}$. Reactions of mixtures of $LnGe_2$ and Ge in a molar ratio of 1:1 at 3 GPa and 1200 °C yielded unknown phases in the Pr– and Nd–Ge systems. These compounds show XRD patterns very similar to that of $DyGe_3$. To confirm the compositions of these compounds, we performed chemical analysis by EPMA. It was found that the compounds with a formula represented by $LnGe_x$ $x \approx 3$ were obtained. They have narrow homogeneity ranges with $2.90 < x < 3.36$ for Pr and $2.95 < x < 3.15$ for Nd, showing that they are nonstoichiometric compounds.

Single crystals of the compounds were obtained and we performed single-crystal structure analysis. The crystallographic data are summarized in Table 1. It was found that the space group of both crystals (*Cmmm*) is different from that of $DyGe_3$. The atomic coordinates and thermal displacement parameters are listed in Table 2. Selected bond distances are listed in Table 3. Both compounds have a closely related structure to the $DyGe_3$ structure, however difference Fourier synthesis clearly showed that there is an additional Ge site between the layers. We refined the occupancy of this site as well as its coordination and thermal displacement parameters. The resulting compositions were $PrGe_{3.36}$ and $NdGe_{3.25}$. The compositions determined by structure analysis are within the composition ranges determined by the chemical analysis.

Considering the fact that occupancies of the additional Ge sites are close to the inverse of natural numbers ($0.36 \approx 1/3$ for Pr and $0.25 = 1/4$ for Nd; see Table 2), these compounds can possibly form superstructures. We examined the X-ray diffraction data for these compounds but no superspots indicating the existence of any superstructures were observed.

The refined crystal structure of Pr and Nd compounds is shown in Figure 2. The structure is similar to that of $DyGe_3$ in Figure 1. The lanthanoid ions are situated between double square Ge-meshes. The Ge chains extend along the diagonal direction of the meshes. The additive Ge4 site caps on the square mesh and bonds to Ge atoms in the chains. In $PrGe_{3.36}$ and $NdGe_{3.25}$, only about one third and one fourth of the sites are occupied, respectively. The Ge network in these compounds becomes three-dimensional through the Ge4 site.

The Ge–Ge bond lengths in the layer are 2.926 Å (Ge2–Ge3) for intra-mesh and 2.421 and 2.433 Å (Ge2–Ge2 and Ge3–Ge3, respectively) for inter-mesh in $PrGe_{3.36}$. The large bond distances like the Ge2–Ge3 length are commonly observed in layered germanides e.g., $DyGe_3$, UGe_2, $LaGe_5$, etc.[1,7,12] The bond lengths for inter-mesh (Ge2–Ge2 and Ge3–Ge3) are similar to those in $DyGe_3$. The slight difference in length for

Table 2. Atomic Coordinates and Thermal Displacement Parameters for $PrGe_{3.36}$, $NdGe_{3.25}$, and $TmGe_3$[a)]

	x	*y*	*z*	*Ocp.*	U_{11}	U_{22}	U_{33}	*U*eq
$PrGe_{3.36}$								
Pr	0	0.33303(4)	1/2	1.0	0.0070(4)	0.0096(4)	0.0084(4)	0.0083(3)
Ge1	0	0.21426(8)	0	1.0	0.0086(7)	0.0180(9)	0.0101(8)	0.0122(4)
Ge2	1/2	0.44350(9)	1/2	1.0	0.0113(9)	0.0107(9)	0.089(2)	0.0371(7)
Ge3	0	0.44322(9)	0	1.0	0.104(2)	0.0115(9)	0.0101(9)	0.0418(8)
Ge4	1/2	0.3972(2)	0	0.387(9)	0.008(2)	0.014(2)	0.012(2)	0.011(1)
$NdGe_{3.25}$								
Nd	0	0.33265(5)	1/2	1.0	0.0088(7)	0.0116(7)	0.0158(7)	0.0121(5)
Ge1	0	0.2124(1)	0	1.0	0.011(1)	0.021(1)	0.015(1)	0.0158(6)
Ge2	1/2	0.4426(1)	1/2	1.0	0.014(2)	0.016(2)	0.154(5)	0.061(2)
Ge3	0	0.4413(2)	0	1.0	0.169(6)	0.016(2)	0.018(2)	0.068(2)
Ge4	1/2	0.4038(5)	0	0.25(1)	0.012(5)	0.017(5)	0.016(5)	0.015(3)
$TmGe_3$								
Tm	0	0.08170(3)	1/4	1.0	0.0028(5)	0.0066(5)	0.0131(6)	0.0075(4)
Ge1	1/2	−0.0400(1)	1/4	1.0	0.0030(9)	0.0110(9)	0.011(1)	0.0084(5)
Ge2	1/2	0.18851(9)	1/4	1.0	0.0050(9)	0.007(1)	0.020(1)	0.0107(5)
Ge3	0	0.19073(9)	−1/4	1.0	0.12(1)	0.007(1)	0.016(1)	0.0116(5)

a) U_{12}, U_{23}, and U_{13} for all compounds are 0.

Table 3. Selected Bond Distances/Å for $PrGe_{3.36}$, $NdGe_{3.25}$, and $TmGe_3$

$PrGe_{3.36}$		$NdGe_{3.25}$		$TmGe_3$	
Pr–Ge1	3.097(3) × 4	Nd–Ge1	3.092(1) × 4	Tm–Ge1	2.9106(8) × 4
Pr–Ge2	3.119(3) × 2	Nd–Ge2	3.076(3) × 2	Tm–Ge1	3.194(2) × 2
Pr–Ge3	3.164(3) × 2	Nd–Ge3	3.115(2) × 2	Tm–Ge2	2.961(2) × 2
Pr–Ge4	3.233(3)	Nd–Ge4	3.300(5)	Tm–Ge3	2.958(2) × 2
Ge1–Ge1	2.544(3) × 2	Ge1–Ge1	2.577(3) × 2	Ge1–Ge1	2.541(3) × 2
Ge1–Ge4	2.387(6)	Ge1–Ge4	2.434(10)		
Ge2–Ge2	2.421(5)	Ge2–Ge2	2.405(6)	Ge2–Ge3	2.474(2)
Ge2–Ge3	2.926(3)	Ge2–Ge3	2.945(6)	Ge2–Ge3	2.7830(4) × 4
Ge2–Ge4	2.328(3)	Ge2–Ge4	2.278(4)		
Ge3–Ge3	2.433(3)	Ge3–Ge3	2.463(6)		
Ge3–Ge4	2.258(3)	Ge3–Ge4	2.183(4)		

the two inter-mesh bonds is reflected by the fact that the square mesh is not completely flat. Each Pr ion is surrounded by four Ge1, two Ge2, and two Ge3 atoms with distances from 3.097 to 3.164 Å. The bond lengths in $NdGe_{3.25}$ are almost the same.

The major difference from the $DyGe_3$ structure is in the stacking manner of the Ge chains. Figure 3 shows a projection of the two structures ($DyGe_3$ and $PrGe_{3.36}$) perpendicular to the *b* axis to compare the relative position of adjacent Ge chains. Note that the Ge chains run along the *a* axis in $PrGe_{3.36}$, but along the *c* axis in $DyGe_3$. In the projection of $DyGe_3$ on the *ab* plane (Figure 3a), the chains are stacked in a staggered manner; the successive Ge chains along the *b* axis are mutually shifted by 1/2 *a*, but there is no shift along the *c* axis (Figure 3b). In contrast, in the projection of $PrGe_{3.36}$ on the *bc* plane (Figure 3c), the chains are stacked on the successive chains, but are shifted along the *a* axis (Figure 3d). The orientation of the adjacent chains is therefore opposite in $PrGe_{3.36}$, but is the same in $DyGe_3$ as shown in Figures 3b and 3d.

The thermal displacement parameters of the Ge2 and Ge3 sites composing the double mesh are rather large. This should be related to the partial occupancy of the Ge4 site. Insertion of the additional Ge atoms causes the relaxation of atomic positions for Ge2 and Ge3 sites. The interatomic distances involving the Ge4 atom are substantially short (e.g., 2.258 Å for Ge3–Ge4 distance in $PrGe_{3.36}$). This should be connected to the relaxation of the Ge2 and Ge3 sites as well as to the partial occupancy of the Ge4 site. If Ge2/Ge3 atom has a neighboring Ge4 atom, the position of Ge2/Ge3 atom should shift along diagonal direction of the mesh. Since the Ge4 sites are randomly occupied, the averaged position of the Ge2 and Ge3 are not changed but the thermal ellipsoids are elongated along the diagonal direction of the mesh.

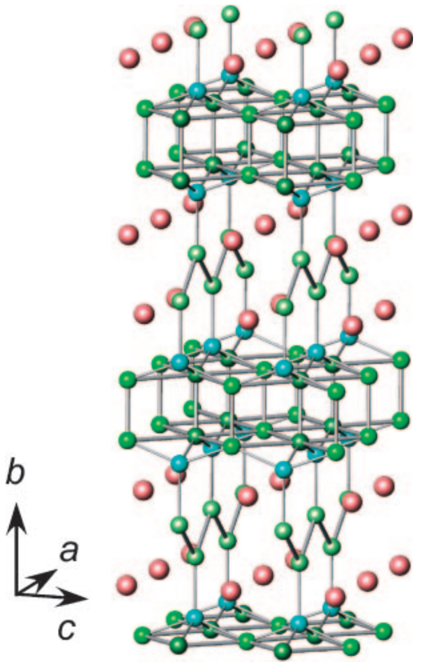

Figure 2. The crystal structure of $PrGe_{3.36}$ and $NdGe_{3.25}$. Red balls are lanthanoid ions. Light blue, light green, and green balls are the Ge1, Ge2, and Ge3 sites, respectively. Blue balls are the additional Ge site not fully occupied.

A germanide having similar short Ge–Ge distances is reported. $ErGe_{2.16}$ has a closely related structure to UGe_2 having a layered structure composed of single square Ge-mesh and Ge chains.[13] In $ErGe_{2.16}$, additional Ge atoms are inserted in the UGe_2 structure. The Ge atoms are situated on a site between layers, and have the same structural features as the Ge4 site in $PrGe_{3.36}$ and $NdGe_{3.25}$. The structures of $PrGe_{3.36}$, $NdGe_{3.25}$, and $ErGe_{2.16}$ are therefore the same except for the number of meshes composing the layer. The Ge–Ge bond distances involving the additional Ge atoms are 2.10 to 2.18 Å in $ErGe_{2.16}$ and 2.183 to 2.278 Å in $NdGe_{3.25}$.

Synthesis and Structure of $TmGe_3$. The product obtained by the reaction of a 1:3 mixture at 5 GPa and 1200 °C for 30 min was a mixture of $TmGe_{2.16}$, Ge, and an unknown phase. By increase of the Ge content up to 1:5, we obtained a mixture of the unknown phase and Ge. The XRD pattern of the phase was very similar to that of $DyGe_3$, but we could not determine the space group from the powder chart due to the low crystallinity.

We therefore performed single-crystal analysis, and confirmed that the unknown phase is $TmGe_3$ isotypic with $DyGe_3$. The crystallographic data and atomic coordinates and thermal displacement parameters for $TmGe_3$ are listed in Tables 1 and 2. Selected bond distances are listed in Table 3.

The Ge1 site composes the Ge zig-zag chain, and the Ge2 and Ge3 form the double square meshes. We checked the difference Fourier map but no remarkable peaks indicating the existence of additional atom positions were observed. Chemical analysis by EPMA shows that the composition of this compound is $TmGe_{2.9}$, suggesting no additional Ge in this germanide.

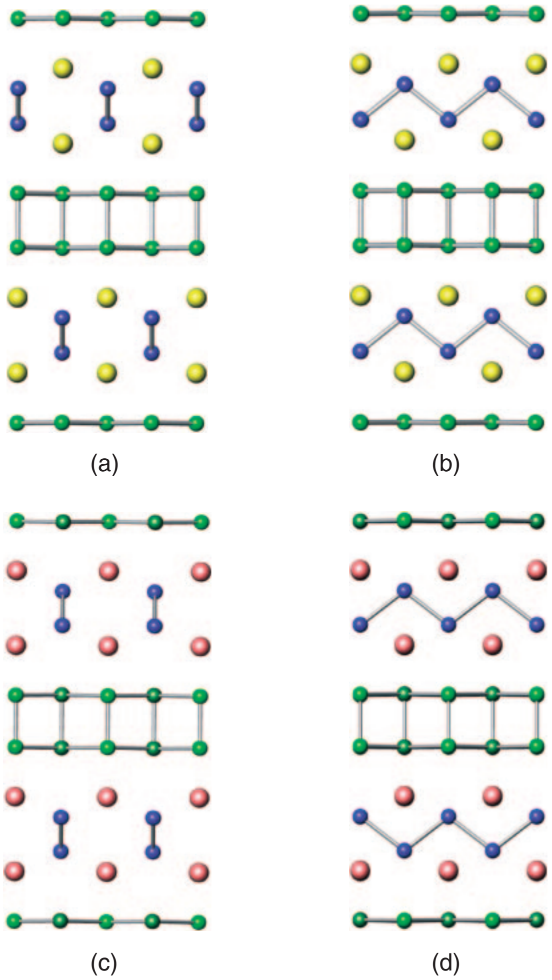

Figure 3. Comparison between the structures of $DyGe_3$ and $PrGe_{3.36}$. (a) Projection on the *ab* plane of $DyGe_3$. Yellow balls are Dy ions. Blue and green balls are Ge atoms. (b) Projection on the *bc* plane of $DyGe_3$. (c) Projection on the *bc* plane of $PrGe_{3.36}$. Red balls are Pr ions. Green and blue balls are Ge atoms. (d) Projection on the *ab* plane of $PrGe_{3.36}$. For clarity, the additional Ge4 sites in $PrGe_{3.36}$ are not displayed.

Each Tm ion is surrounded by ten Ge atoms with distances ranging 2.911 to 3.194 Å, shorter than the Pr– and Nd–Ge distances because of the smaller ionic radius of Tm. The Ge1–Ge1 distance of 2.541 Å in the Ge chain is very similar to those in Pr and Ge germanides. In contrast, the Ge2–Ge3 distances of 2.783 and 2.474 Å for intra- and inter-meshes are substantially smaller than the corresponding distances in $PrGe_{3.36}$ and $NdGe_{3.16}$. The elongation of the Ge–Ge distances in $PrGe_{3.36}$ and $NdGe_{3.25}$ should be due to the additional Ge atoms as well as to the large ionic radii of the guest ions.

Magnetic Properties. The magnetic susceptibility measurements for Pr and Nd germanides showed that both compounds obey the Curie–Weiss law from room temperature down to 20 and 4 K, respectively. The effective magnetic moments were calculated to be 3.60 and 3.57 μ_B for Pr and Nd compounds, respectively. Those values agree well with the theoretical values for Pr^{3+} (3.58 μ_B) and Nd^{3+} (3.62 μ_B), showing the lanthanoid ions in these compounds are trivalent. Below 20 K, samples of $PrGe_{3.36}$ showed a ferromagnetic transition, but the saturated magnetic moment was too small to consider the transition is due to $PrGe_{3.36}$. We have to prepare and use single crystals for more detailed study of the magnetic properties of $PrGe_{3.36}$.

Conclusion

We prepared three new binary germanides, $PrGe_{3.36}$, $NdGe_{3.25}$, and $TmGe_3$ using high-pressure (≥3 GPa) and high-temperature (1200 °C) reactions. $TmGe_3$ is isotypic with $DyGe_3$ having a double square Ge-mesh structure. One-dimensional Ge chains and Tm ions are sandwiched between the meshes. Pr and Nd compounds have principally the same double mesh structure but contain additional Ge atoms in the interlayer region. The oxidation states of Pr^{3+} and Nd^{3+} are confirmed by magnetic susceptibility measurements.

We are grateful to Mr. Yasuhiro Shibata of Hiroshima University for his help with the EPMA measurements. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, Grant Nos. 16037212, 16750174, 18750182, 18027010, and 20550178.

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