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Synthesis and properties of new filled skutterdites and their related compounds

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For the purpose of synthesizing new types of intermetallic compounds having interesting structural and/or physical properties, the use of high-pressure and high-temperature reactions is a promising choice. Recently, a new germanide, $LaGe_5$, has been discovered by the reaction of constituent elements under 5 GPa and 1200 C. It had a novel sp^3-Ge covalent network, and showed superconductivity with a critical temperature $Tc = 7.0$ K. In the present work, we have investigated reactions of Ge and light rare earth elements, and obtained new germanides having the $LaGe_5$ structure. We have also tried to prepare new skutterudite compounds containing Ge in the 15 group element network.

[New germanides] Mixtures of Ln and Ge having different atomic ratios were melted with an Ar-filled arc furnace, where Ln = La, Ce, Pr, and Nd. The products were ground in an Ar-filled glove box, and then put into h-BN cells (5 mm in inner diameter and 5 mm in depth). Each cell was placed in a carbon tube heater, and was put in a pyrophyllite cube ($20 \times 20 \times 20 mm^3$). The cube was pressed and heated in a multi-anvil press at different pressures and temperatures. After the reaction, the cube was quenched to room temperature, and then the pressure was gradually released. Products obtained by the high-pressure treatment were examined by X-ray powder diffraction measurement. All the reactions gave germanides with the $LaGe_5$ structure, which are listed in Table 1. Two of them, $PrGe_5$ and $NdGe_5$, are new compounds. Single crystals of $LnGe_5$ with Ln = Ce, Pr, and Nd were first obtained in this work and their structures were determined by single X-ray crystal analysis. From the chemical analysis, La, Ce, and Nd compounds were found to be stoichiometric. Only for $PrGe_5$, the existence of Ge defect was suggested. These germanides except for the La compound were metallic but did not show superconductivity below to 2 K. This would be due to the influence of f electrons on rare earth ions.

[Skutterudite] Mixtures of Ln (= La and Lu), Ru, and Sb (and Ge) were placed in h-BN cells (3 mm in inner diameter and 4 mm in depth). Each cell was wraped in Ta foil, and was placed in an MgO octahedron as a pressure medium. The MgO cell was pressed and heated in a multi anvil press at different pressures and temperatures as the same manner mentioned above. In the Lu-Ru-Sb system, the compound with the skutterudite structure was not obtained even by the reaction under 7 GPa. In La-Ru-Sb-Ge system, a skutterudite compound was obtained. The lattice constant of it was slightly smaller than that of $LaRu_4Sb_{12}$. The chemical analysis of this compound is now under investigation.

Table 1 Cell constants and preparation conditions of germanides with $LaGe_5$ type structure

	comp. from EPMA	lattice constants (Å)	conditions
$LaGe_5$	1 : 4.97	$a = 4.0290(6)$, $b = 6.307(1)$, $c = 9.978(2)$	5 GPa 1200 °C
$CeGe_5$	1 : 4.96	$a = 4.000(1)$, $b = 6.188(2)$, $c = 9.854(1)$	5 GPa 1300 → 950 °C
$PrGe_5$	1 : 4.59	$a = 3.994(7)$, $b = 6.224(7)$, $c = 9.87(2)$	5 GPa 1600 °C
$NdGe_5$	1 : 5.00	$a = 3.977(5)$, $b = 6.180(5)$, $c = 9.825(4)$	5 GPa 1200 → 900 °C