Lanthan-Triel/Tetrel-ide $La(Al,Ga)_x(Si,Ge)_{1-x}$. Experimentelle und theoretische Studien zur Stabilität intermetallischer 1 : 1-Phasen

Lanthanum Triel/Tetrel-ides $La(Al,Ga)_x(Si,Ge)_{1-x}$. Experimental and Theoretical Studies on the Stability of Intermetallic 1:1 Phases

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Systematic studies of the phase formation at the binary sections LaSi – LaGa and LaGe – LaAl have been carried out by means of synthetic, crystallographic and bond theoretical methods. The high-temperature forms of the two binary monotetrelides LaSi and LaGe crystallize with the FeB structure type, whereas LaGa forms the related CrB type and LaAl the significantly different CeAl type. Starting from LaSi/LaGe, the FeB type (orthorhombic, space group *Pnma*, $Z = 4$, $a = 839.2(1)/842.7(1)$, $b = 399.9(1)/412.3(1)$, $c = 606.2(2)/612.2(1)$ pm, $R1 = 0.0356/0.0298$) remains stable only down to a valence electron number per *M* atom (*M* = Si, Ge, Al, Ga) of 6.9 ($LaGa_{0.10}Si_{0.90}$: $a = 840.14(7)$, $b = 404.12(12)$, $c = 608.5(2)$ pm, $R1 = 0.0513$; $LaAl_{0.15}Ge_{0.85}$: $a = 845.40(7)$, $b = 414.08(13)$, $c = 614.08(14)$ pm, $R1 = 0.0213$). In the system $LaGa_xSi_{1-x}$, the stability range of the CrB type (orthorhombic, space group *Cmcm*, $Z = 4$) starts at a gallium proportion of 25 % ($LaGa_{0.25}Si_{0.75}$: $a = 450.03(8)$, $b = 1140.5(2)$, $c = 406.05(6)$ pm, $R1 = 0.0163$) and extends to the border compound LaGa (v. e./$M = 6$). The CrB type also occurs in the system La-Al-Ge, but is in this case only formed around the 1 : 1 composition in between $LaAl_{0.42}Ge_{0.58}$ ($a = 455.90(12)$, $b = 1161.1(3)$, $c = 418.05(9)$ pm, $R1 = 0.0474$) and $LaAl_{0.61}Ge_{0.39}$ ($a = 454.89(10)$, $b = 1168.8(2)$, $c = 420.41(11)$ pm, $R1 = 0.0447$). These stability ranges, the variations of several key geometric parameters such as the *M*-*M* distances or the heights of the trigonal prisms, and the main aspects of the chemical bonding in these lanthanum monometallides are analyzed using FP-LAPW band structure methods. The structure of the new compound La_2Al_2Ge (V_2B_3 structure type, orthorhombic, space group *Cmcm*, $a = 416.69(4)$, $b = 2719.7(4)$, $c = 450.46(5)$ pm, $Z = 2$, $R1 = 0.0458$) combines the structural elements of the CrB/FeB structure family (two-bonded *M* atoms) with the trigonally planar bonded *M* atoms of the $ThSi_2$ type in a fully ordered Al and Ge atom distribution and thus without phase width.

Key words: Lanthanum, Gallium, Aluminum, Tetrelides, Band Structure Calculation