$Mg_5Pd_{10}Si_{16}$ und $Mg_5Pt_{10}Si_{16}$, Magnesium-Platinmetall-Silicide mit Tetraedern und gekappten Tetraedern aus Silicium-Atomen

$Mg_5Pd_{10}Si_{16}$ and $Mg_5Pt_{10}Si_{16}$, Magnesium Platinum Metal Silicides with Si_4 Tetrahedra and Si_{12} Truncated Tetrahedra

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Platinum Metal Silicide, Magnesium, Crystal Structure

The ternary silicides $Mg_5Pd_{10}Si_{16}$ and $Mg_5Pt_{10}Si_{16}$ have been prepared by reaction of magnesium with the binary platinum-metal silicides in sealed tantalum containers (Pt-compound: 1200 °C, 3 d, up 20 °/h, down 5 °/h; Pd-compound: 1000 °C, 2 d, up and down 50 °/h). In the case of the Pd-compound contact with the tantalum had to be avoided by using a boron nitride crucible. The isotypic compounds crystallize in the cubic space group $F\bar{4}3m$ with 4 formula units per unit cell. The crystal structures were determined from single crystal data, lattice constants from Guinier patterns. The following data were obtained: a = 1258.81(8) pm for $Mg_5Pd_{10}Si_{16}$ and a = 1256.94(9) pm for $Mg_5Pt_{10}Si_{16}$. Short distances in the three-dimensional platinum-metal silicon network indicate strong, covalent Pd(Pt)-Si-bonding (d(Pd-Si) = 240.2 to 256.1 pm; d(Pt-Si) = 237.1 to 258.5 pm). In addition, homonuclear bonding seems to be important, resulting in the formation of Si_4-tetrahedra (d(Si-Si) = 250.4 pm ($Mg_5Pd_{10}Si_{16}$) and 255 pm ($Mg_5Pt_{10}Si_{16}$)), empty Si_{12}-polyhedra with the shape of truncated tetrahedra (d(Si-Si): 234.5 and 248.2 pm ($Mg_5Pd_{10}Si_{16}$); 236 and 248.2 pm ($Mg_5Pt_{10}Si_{16}$)), and Mg-centered $Pd(Pt)_{10}$-clusters with the shape of adamantane (d(Pd-Pd) = 282.3 pm; d(Pt-Pt) = 284.5 pm). Furthermore, Mg_4-tetrahedra with Mg-Mg-distances of 360 pm are formed. The structure may be described by an expanded cubic "close" packing of $MgPd(Pt)_{10}$-units in which the Si_4-tetrahedra occupy the octahedral holes while the Si_{12}-polyhedra and the Mg_4-tetrahedra reside in one half of the tetrahedral holes each.