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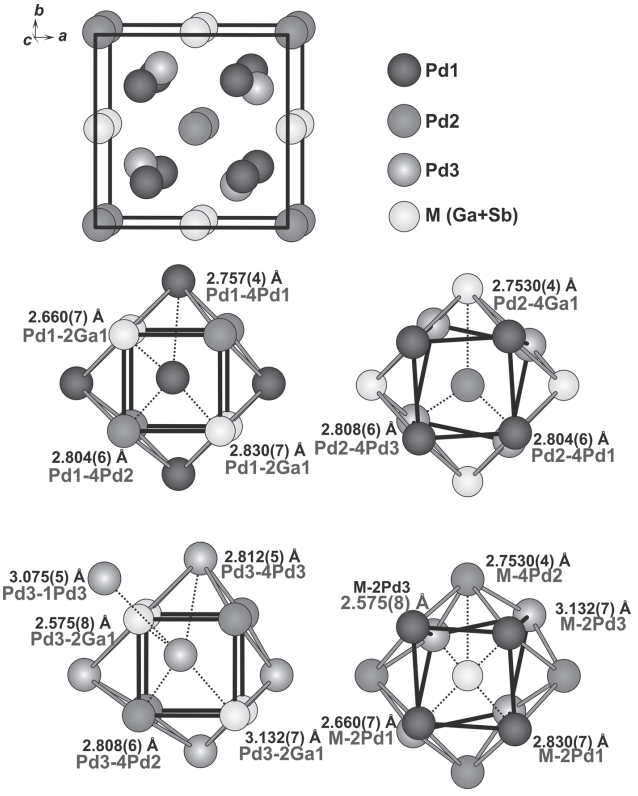
Crystal structure of $Ga_{0.62(3)}Sb_{0.38(3)}Pd_3$



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Abstract

$Ga_{0.62(3)}Sb_{0.38(3)}Pd_3$, tetragonal, $P4/mbm$ (no. 127), $a = 5.5036(2)$ Å, $c = 7.9990(3)$ Å, $V = 242.29(3)$ Å^3, $Z = 4$, $R_p = 0.0168$, $R_{wp} = 0.0291$, $T = 295$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Sample, setting:	Grey powder, transmission geometry
Wavelength, μ:	Cu $K_{\alpha 1}$ radiation, (1.54056 Å), 214.6 mm^{-1}
Diffractometer, scan mode:	Huber Guinier G670, step scan (0.005°)
2θ range / data points:	21–100.3°, 15861
Profile function:	Pseudo-Voigt
No(*hkl*), *N*(*param*):	82, 22
Programs:	WinCSD [6], Diamond [7]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	B_{iso}*/B_{eq}
Pd1	0.2345(6)	0.7345(6)	0	1.7(2)
Pd2	0	0	0.252(1)	1.53(13)
Pd3	0.3024(7)	0.8024(7)	0.5	1.74(13)
Ga1[a]	0.5	0	0.241(1)	1.5(2)
Sb1[b]	0.5	0	0.241(1)	1.5(2)

[a]Occupancy: 0.62(3), [b]Occupancy: 0.38(3).

Source of materials

New palladium compound with gallium and antimony, $Ga_{0.62(3)}Sb_{0.38(3)}Pd_3$, was synthesized from elemental palladium (granules, ChemPur, 99.95%), gallium (pellets, ChemPur, 99.9999%) and antimony (shots, ChemPur, 99.9999%) by arc melting in a glove box (Ar atmosphere; O_2 and H_2O content below 1 ppm). Sample with a nominal composition $Ga_{14}Sb_{11}Pd_{75}$, placed in alumina crucible and evacuated quartz glass tube, was annealed at 1123 K (48 h) and then at 773 K (408 h) and subsequently quenched in water. For the XRPD analysis the sample was filed and additionally annealed at 773 K for 24 h to remove residual strain. According to the obtained results, formation of the new ternary phase was detected.

Experimental details

The crystal structure of $Ga_{0.62(3)}Sb_{0.38(3)}Pd_3$ was refined from XRPD data.

Comment

$Ga_{0.62(3)}Sb_{0.38(3)}Pd_3$ crystallizes in the Pt_3Ga structure type [1]. There is no binary phase with composition 3:1 in the Ga–Pd

system [2], while Pt_3Al and Pt_3Ga exist in three modifications [3] – high temperature cubic (Cu_3Au-type structure, $Pm\bar{3}m$, $cP4$), intermediate (U_3Si-type structure, $I4/mcm$, $tI16$) and low temperature (Pt_3Al-type structure, $P4/mbm$, $tP16$). The new ternary phase behaves similar to the binary platinum representative. Preliminary information on this phase was presented in [4].

Coordination environments of Pd1, Pd2, Ga1/Sb1 may be described as distorted tetragonal prisms with four additional atoms centering side faces (CN = 12). In the case of Pd3, the coordination polyhedron is also a distorted tetragonal prism, but with five additional atoms – four are situated opposite side faces and one is centering an edge (CN = 13).

In the crystal structure of $Ga_{0.62(3)}Sb_{0.38(3)}Pd_3$ the interatomic Pd–Pd distances are not significantly increased in comparison with elemental palladium (by 0.6% for Pd1, 2.3% for Pd2, 2.5% for Pd3). Thus, palladium atoms are not well isolated. This feature does not allow to consider the title compound as a good potential catalytic material for the selective semi-hydrogenation of acetylene [5].

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