Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Solid State Chemistry 179 (2006) 2472–2478
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Preparation, crystal structure and chemical bonding analysis of the new binary compounds Rh_4Ga_{21} and Rh_3Ga_{16}

Magnus Boström*, Yurii Prots, Yuri Grin

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany

Received 25 March 2006; accepted 27 April 2006
Available online 9 May 2006

Abstract

The two new binary compounds Rh_4Ga_{21} (space group *Cmca* (*Cmce*), $a = 40.135(6)$ Å, $b = 6.470(2)$ Å, $c = 6.473(1)$ Å, Pearson symbol *oC*136) and Rh_3Ga_{16} (space group *Ccca* (*Ccce*), $a = 30.424(7)$ Å, $b = 6.476(2)$ Å, $c = 6.468(2)$ Å, Pearson symbol *oC*76) were synthesised and their crystal structures were solved from single-crystal X-ray diffraction data. From a topological point of view, both these two crystal structures and the crystal structure of $PdGa_5$ can be described either as inhomogeneous intergrowth structures containing three different kinds of segments, or as built up by layers of capped square antiprisms condensed via their capping atoms. Bonding analysis with bonding indicators revealed that the crystal structures of Rh_4Ga_{21} and Rh_3Ga_{16} have to be considered as framework polyanions formed by covalently bonded gallium atoms with embedded rhodium cations.

Keywords: Binary compound; Rhodium; Gallium; Crystal structure; Electron localization function; Electron localizability indicator

1. Introduction

Four binary phases are known in the Rh–Ga system; RhGa (CsCl type, Pearson symbol *cP*2) [1], $Rh_{10}Ga_{17}$ (prototype, *tP*108) [2], $RhGa_3$ ($IrIn_3$ type [3], *tP*16) [4] and Rh_2Ga_9 (prototype, *mP*22) [5,6]. No phase diagram has hitherto been published. In course of a systematic investigation of Ga- and Al-rich compounds of Ir, several new phases were found [6,7]. This encouraged an investigation of the chemically related Rh–Ga system, of which the first results are the subject of the present work.

2. Experimental

Single crystals of Rh_4Ga_{21} were prepared in a Ga-rich self-flux containing 0.0538 g Rh (99.9%, Chempur) and 0.952 g Ga (99.999%, Chempur), hence having the nominal composition $Rh_{3.7}Ga_{96.3}$. The elements were sealed inside an evacuated quartz tube already prepared with a quartz wool filter on a support of small pieces of crushed quartz glass according to the high-temperature centrifugation aided filtration technique (HTCAF) [8,9]. The sample was heat treated at 300 °C for 18 days before the melt was removed from the solid using a centrifuge operating at 2000*g*, without significantly decreasing the temperature of the sample.

Single crystals of Rh_3Ga_{16} were prepared analogously from 0.0239 g Rh and 1.003 g Ga (nominal composition $Rh_{1.6}Ga_{98.4}$), but cooled down from 900 °C at the rate of 5 °C/h down to 150 °C, where the sample was kept for 18 days before the melt was removed.

X-ray powder diffraction patterns of the powdered single crystals were collected with a Huber Imaging Plate Guinier Camera 670 using Cu$K\alpha_1$ radiation ($\lambda = 1.54059$ Å) for Rh_3Ga_{16} and Co$K\alpha_1$ radiation ($\lambda = 1.78897$ Å) for Rh_4Ga_{21}. Silicon ($a = 5.43119(1)$ Å) and LaB_6 powder ($a = 4.15692(1)$ Å), respectively, were added as internal standard to the samples. The lattice parameters were refined from the powder data with the program CELLREF [10].

Single crystals with well-exhibited faces were isolated and parts of them were used for the X-ray diffraction experiment. Single-crystal X-ray diffraction data were

*Corresponding author. Fax: +49 351 4646 4002.
E-mail address: bostroem@cpfs.mpg.de (M. Boström).

0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2006.04.045

collected on a Rigaku Mercury CCD diffraction system employing Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The measured data sets were corrected for absorption using multi-scans in the Laue-class *mmm*. Relevant details for the data collection and handling are summarized in Table 1.

The crystal structures of Rh_4Ga_{21} and Rh_3Ga_{16} were solved by direct methods with the Shelxs97 program [11]. The refinement was performed using the program Jana2000 [12]. The refined parameters were scale factor, atomic coordinates, anisotropic displacement parameters, extinction coefficient and a twinning factor for Rh_3Ga_{16}.

The TB–LMTO–ASA program package [13] with exchange correlation potential (LDA) according to Barth and Hedin [14] was used for quantum chemical calculations. Because of the clear similarity between the crystal structures of Rh_3Ga_{16} and Rh_4Ga_{21}, the calculations were made only for the latter. The radial scalar-relativistic Dirac equation was solved to obtain the partial waves. A calculation within the atomic sphere approximation (ASA) includes corrections for the neglect of partial waves of higher order and interstitial regions [15], hence no addition of empty spheres was found to be necessary. The radii of the atomic spheres used in the calculations were: r(Rh1) = 1.609 Å, r(Rh2) = 1.630 Å, r(Ga1) = 1.543 Å, r(Ga2) = 1.537 Å, r(Ga3) = 1.579 Å, r(Ga4) = 1.581 Å, r(Ga5) = 1.605 Å, r(Ga6) = 1.597 Å, r(Ga7) = 1.571 Å. A basis set containing the Rh(5*s*, 5*p*, 4*d*) and Ga(4*s*, 4*p*) orbitals was employed for the self-consistent calculations with the Rh(4*f*) and Ga(4*d*) functions being downfolded. The electron localization function (ELF, η) was evaluated according to [16] within the TB–LMTO–ASA program package with an ELF module already implemented. To gain a deeper insight in the chemical bonding, the topology of ELF was analysed with the program Basin [17]. The electron density was integrated in basins which were bound by zero flux surfaces in the ELF gradient. This method, analogous to the procedure proposed by Bader [18] for charge calculations from electron densities resulted in electron counts for each basin, which revealed basic information for the description of the bonding situation.

Table 1
Crystallographic information and data handling for Rh_4Ga_{21} and Rh_3Ga_{16}

Crystal data		
Chemical formula	Rh_4Ga_{21}	Rh_3Ga_{16}
Crystal system	Orthorhombic	
Space group	*Cmca* (*Cmce*)	Ccca (*Ccce*)
Z	4	4
a (Å)[a]	40.135(6)	30.424(7)
b (Å)[a]	6.470(2)	6.476(2)
c (Å)[a]	6.473(1)	6.468(2)
V (Å^3)[a]	1681	1274
Density calc. (g cm^{-3})	7.41	7.42
Crystal form	Irregular	
Crystal size (mm^3)	$0.050 \times 0.040 \times 0.020$	$0.040 \times 0.030 \times 0.015$
Colour	Grey metallic	
Absorption coefficient (mm^{-1})	36.8	37.0
Data collection		
Diffraction system	Rigaku AFC7 Mercury CCD	
Radiation, λ (Å)	Mo$K\alpha$, 0.71069	
No. of measured reflections	6820	2858
Range of $h\,k\,l$	$-43 \leqslant h \leqslant 57$ $-9 \leqslant k \leqslant 9$ $-8 \leqslant l \leqslant 8$	$-41 \leqslant h \leqslant 41$ $-8 \leqslant k \leqslant 7$ $-6 \leqslant l \leqslant 8$
Absorption correction	Multi-scan	
T_{min}/T_{max}	0.523	0.541
R_{int}	0.055	0.045
Refinement		
Refinement on	F	
No. of independent reflections	1286	759
No. of independent observed reflections	967	565
Observation criterion	$I > 3\sigma(I)$	
No. of reflections used in refinement	1286	759
No. of parameters refined	62	47
Weighting scheme	Unit	
$R(F)_{all}$, w$R(F)_{all}$, $R(F)_{obs}$	0.053, 0.046, 0.036	0.076, 0.061, 0.060
GOF_{all}	1.0	5.0
$\Delta\rho_{max}$, $\Delta\rho_{min}$, (e Å^{-3})	2.0, −1.8	6.2, −1.9
Extinction model	Gaussian isotropic	—
Extinction coefficient	0.051(2)	—

[a]Cell parameters from powder diffraction data with internal standard.