Journal of Solid State Chemistry 238 (2016) 88–102

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Single crystal studies of binary compounds Ta/Ga – A system with experimental and crystallographic peculiarities

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ARTICLE INFO

Article history:
Received 19 November 2015
Received in revised form
4 March 2016
Accepted 7 March 2016
Available online 8 March 2016

Keywords:
Synthesis
Single crystals
Structure analysis
Tantalum
Gallium
Intermetallics

ABSTRACT

We report on single crystal growth and characterisation of binary intermetallics Ta_xGa_y. Single crystals were obtained from mixtures of the elements which were handled under various conditions. Several new compounds were identified. The highest Ga-content is found for the new binary phases Ta_6Ga_{31} and Ta_8Ga_{41}. Both compounds evolve as intergrown crystals. Ta_8Ga_{41} belongs to the V_8Ga_{41} type ($R\bar{3}$, $Z=3$, $a=14.311$ Å, $c=15.344$ Å), Ta_6Ga_{31} to the triclinic Mo_6Ga_{31}-type ($P\bar{1}$, $Z=2$, $a=9.697$ Å, $b=9.698$ Å, $c=14.879$ Å, $\alpha=87.18°$, $\beta=80.83°$, $\gamma=85.18°$). $TaGa_3$ bases on the tetragonal $TiAl_3$-type ($I4/mmm$, $Z=2$, $a=3.769$ Å, $c=8.718$ Å) but shows stacking faults leading to an increased Ta content $Ta_{1+x}Ga_{3-x}$. This interpretation is supported by the structure model of an orthorhombic superstructure with an idealized composition Ta_2Ga_5 ($Cmcm$, $Z=4$, $a=3.769$, $b=31.37$, $c=3.770$ Å). $Ta_{2-x}Ga_{5+x}$ ($x\approx 0.38$) is a representative of the Mn_2Hg_5-type ($P4/mbm$, $Z=2$, $a=9.3213(13)$, $c=2.7572(6)$ Å). Ta_4Ga_5 represents a new compound with a novel crystal structure ($P4/mbm$, $Z=16$, $a=11.793(2)$, $c=16.967(3)$ Å). The complex structure contains polyhedra with coordination numbers between 11 and 14. Ta_3Ga_2 ($P4_2/mnm$, $Z=2$, $a=6.8382(4)$, $c=3.4963(2)$ Å) belongs to the U_3Si_2 type. For the composition Ta_5Ga_3 three different structure types were confirmed but with some differences. The tetragonal W_5Si_3 type ($I4/mcm$, $Z=4$, $a=10.2199(7)$, $c=5.1121(4)$ Å) is a stoichiometric binary compound, the hexagonal Mn_5Si_3-type ($P6_3/mcm$, $Z=2$, $a=7.7023(4)$, $c=5.3062(3)$ Å) contains a small amount of oxygen ($Ta_5Ga_3O_{0.4}$) and in the tetragonal Cr_5B_3-type ($I4/mcm$, $Z=4$, $a=6.5986(9)$, $c=11.931(2)$Å) one of the *Ga*-sites shows a significant underoccupation of 40% ("$Ta_{2.2}Ga$"). Compositions were confirmed by EDX measurements.

1. Introduction

Investigations on binary intermetallic systems are an old topic in inorganic chemistry and many binary diagrams including the binary compounds are listed in the literature [13]. On a first view the situation seems to be clear as the experimental challenge for the study of binary systems is limited. A simple combination of the elements with subsequent heating and cooling is the easiest way to explore binary systems. Problems results from three reasons (at least) dealing with kinetic reasons as there are phase transitions, peritectic compounds and low reactivity. While phase transitions and peritectic decompositions are general phenomena for intermetallics an incomplete reaction must be considered, if a low-melting metal is combined with a high-melting one.

With Ga as the low-melting metal there emerges another aspect because of its position between metals and semi-metals. Therefore, on the one hand gallium acts in intermetallics as a typical metal with a great influence of size effects and valence electron concentration on stability and crystal structures. On the other hand theoretical calculations and an appropriate analysis of the bonding properties have shown, that many Ga-rich intermetallics have a significant covalent interaction between the Ga-atoms [4].

The system Ta/Ga is a typical example for this situation. Strategies to avoid incomplete reactions by kinetic reasons are long reaction times and/or high dilutions. Furthermore, an activation can be achieved by addition of a third element. This changes the reactivity and might enables the formation of single crystals, but on the other hand small amounts might be included into the product. For our investigation on the system Ta/Ga we applied high dilutions of Ta in an excess of Ga and varied the temperature program (temperature, dwelling time, cooling rate). The excess of Ga was removed by dil. HCl and the residue investigated by means

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http://dx.doi.org/10.1016/j.jssc.2016.03.014
0022-4596/

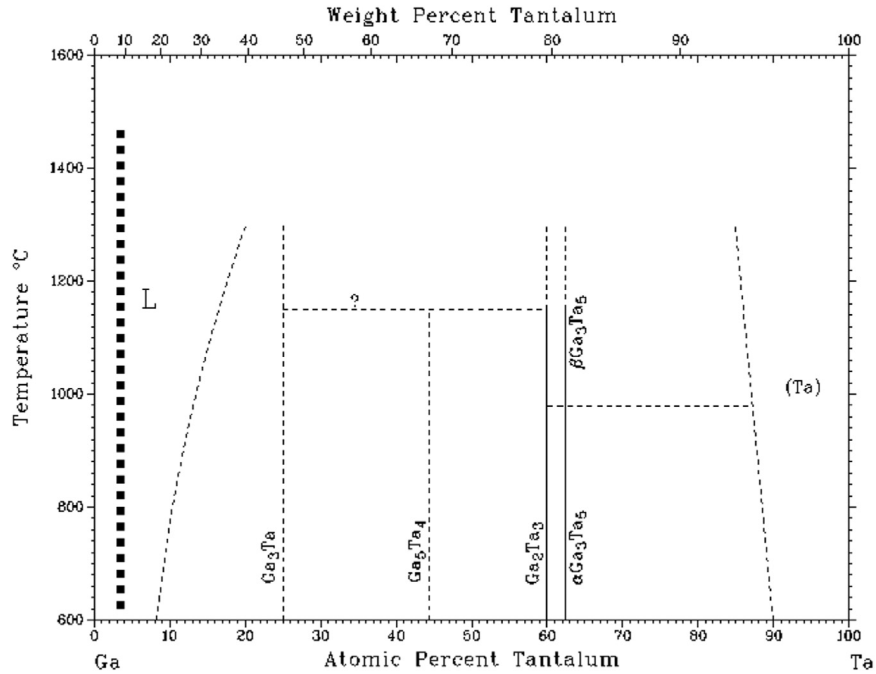

Fig. 1. Phase diagram Ta/Ga according to Okamoto [1], dotted lines are tenative, the bold dotted line represents the conditions for our syntheses.

of X-ray diffraction (powder, single crystal) and energy-dispersive X-ray spectroscopy (EDX). This approach results usually in multiphase products (see below).

Fig. 1 shows the binary phase diagram Ta-Ga according to Okamoto [1]. This diagram bases on the work of Meissner and Schubert [5]. It displays four binary compounds: $TaGa_3$, Ta_4Ga_5, Ta_3Ga_2 and two forms of Ta_5Ga_3. The many dotted lines, which represent estimated data, show, that well-defined melting points are unknown and the formation of compounds probably takes place by peritectic reactions and/or sub-solidus reactions. A detailed view to the data bases [2,3] and the literature yielded additional information but also some inconsistencies. Interestingly, there are no single crystal investigations at all on binary compounds Ta-Ga. An overview on the work on binary compounds is given in Table 1. The knowledge bases mainly on three systematic investigations of the binary system Ta/Ga [4–6] and several selected contributions in combination with other systems [8–11]. The compounds $TaGa_3$ Ta_3Ga_2 and Ta_5Ga_3 (Mn_5Si_3-type, W_5Si_3-type) are quite well established and described by several authors. Only one contributions deals with the compounds $TaGa_2$, Ta_4Ga_5, Ta_6Ga_5, and Ta_5Ga_3 (Cr_5B_3-type).

According to literature $TaGa_3$ is the Ga-richest compound. It was assigned to a $TiAl_3$-type [5,6]. Meissner and Schubert reported on a tetragonal compound with a composition $TaGa_3$ [5]. This was confirmed by Popova and Putro [6]. Interestingly, Meissner and Schubert [5] described the similarity to the $TiAl_3$ type but pointed out, that the direction [001] is not clearly defined, so they only communicated a c/a ratio for the subcell. Brown carried out a complete investigation of the system Ta/Ga. Brown [7] described a compound $TaGa_2$ with a tetragonal-primitive unit cell with lattice parameters of $a=11.778$ Å and $c=16.927$ Å. No detailed structure parameters were given. The existence of a compound $TaGa_2$ which has been mentioned by Gladyshevskii et al. [9], has never been confirmed by other investigations. Meissner and Schubert mentioned a compound $Ta_{\sim 4}Ga_{\sim 5}$, but no structural details were given and the compound was not confirmed by other authors. Ta_6Ga_5 was synthesized under high pressure conditions by Popova et al. [6]. The compound was not confirmed by other authors. Ta_3Ga_2 was assigned to the U_3Si_2-type by several investigations [5–8]. Two forms of Ta_5Ga_3 were described by different authors. It is assumed, that the hexagonal Mn_5Si_3-type is stabilized by impurities (i.e. oxygen). A third form of Ta_5Ga_3 (tetragonal Cr_5B_3 type) was only found in one experiment [11]. Nowotny et al. described for formation of the Cr_5B_3 type below 950 °C, while the W_5Si_3 structure is formed above 1000 °C. (It should be mentioned that the two forms of Ta_5Ga_3 listed in the phase diagram refer to the types W_5Si_3 and Mn_5Si_3).

Table 1
Overview on binary compounds of the system Ta-Ga.

Compound	Space group	Structure type	Reference
$TaGa_3$	*I4/mmm*	$TiAl_3$	[5,6]
$TaGa_2$	*tP*	–	[7,9] [a]
Ta_4Ga_5		–	[5,7] [a]
Ta_6Ga_5	*P6₃/mmc*	Ti_6Sn_5	[7]
Ta_3Ga_2	*P4/mbm*	U_3Si_2	[5–8]
Ta_5Ga_3/$Ta_5Ga_3O_x$	$P6_3/mcm$	Mn_5Si_3	[5,7,9]
Ta_5Ga_3	*I4/mcm*	W_5Si_3	[5–7,9–11]
Ta_5Ga_3	*I4/mcm*	Cr_5B_3	[11]

[a] Brown [7] described $TaGa_2$ with the same tetragonal unit cell as it was found for Ta_4Ga_5; Meissner and Schubert [5] communicated for Ta_4Ga_5 a complex pattern without indexing.

2. Experimental

2.1. Syntheses

Single crystals of binary compounds Ta_xGa_y were obtained by slow cooling of binary mixtures of the elements. The Ta:Ga ratio was typically about 1:30, i.e. the experimental conditions are far away from the conventional investigation of a binary phase diagram (and accordingly the validity of the phase rule). Therefore, we have added a mark to the Ta-Ga phase diagram in Fig. 1, that shows the compositions used in our experiments. We expect, that we obtain our single crystals as peritectic compounds, which are formed from the Ga-rich melt. This may also include metastable compounds according to the kinetics of formation. As a simple