Journal of Alloys and Compounds 618 (2015) 656–665

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

The Sr-poor part of the Sr–{Pd,Pt}–{Si,Ge} systems: Phase equilibria and crystal structure of ternary phases

V.V. Romaka [1], M. Falmbigl [2], A. Grytsiv, P. Rogl *

Institute of Physical Chemistry, University of Vienna, Währinger Str. 42, A-1090 Wien, Austria

ARTICLE INFO

Article history:
Received 5 July 2014
Received in revised form 17 August 2014
Accepted 18 August 2014
Available online 27 August 2014

Keywords:
Silicides
Germanides
Phase equilibria
Crystallography
X-ray diffraction
Electronic band structure

ABSTRACT

Phase relations have been established by electron probe microanalysis (EPMA) and X-ray powder diffraction (XPD) for the Sr-poor part of four ternary systems: Sr–{Pd,Pt}–Si at 900 °C and Sr–{Pd,Pt}–Ge at 700 °C. In the Sr–Pd–Si system the formation of the silicide $SrPdSi_3$ ($BaNiSn_3$-type) was confirmed and a small homogeneity region was found. Furthermore, two novel compounds were detected and their crystal structure was refined from X-ray powder patterns: $SrPd_{0.3}Si_{1.7}$ (AlB_2-type) and $SrPd_{5.9}Si_{6.1}$ (own-type). In the Sr–Pt–Si ternary system a novel compound with AlB_2-type was discovered ($SrPt_{0.3}Si_{1.7}$), whereas $SrPtSi_3$ with the $BaNiSn_3$-type was confirmed. Two more compounds were detected by EPMA, but their crystal structure remains unknown. In the Sr–{Pd,Pt}–Ge systems no new compounds were observed, but the existence of $SrPdGe_3$ and $SrPtGe_3$ (both adopt the $BaNiSn_3$ structure type), and $SrPt_4Ge_{12}$, crystallizing in the $LaFe_4Sb_{12}$ structure type, was corroborated. For selected ternary silicides the electronic structure was evaluated by DFT calculations.

1. Introduction

The need for thermoelectric materials, particularly those for waste heat recovery applications has triggered a worldwide concerted research activity to search for and characterize novel suitable candidates. Among the intermetallic clathrate family, Ge-based type-I clathrates are the most intensively studied compounds, several of which having a promising potential to serve in thermoelectric generator devices [1]. By careful tuning the electronic band gap, the authors have recently defined the quinary clathrate I, $Ba_8Ni_{0.22}Zn_{7.22}Ge_{37.12}Sn_{1.44}$, as so far the best n-type thermoelectric material for automotive applications (with the highest average figure of merit in the temperature range from 300 to 850 K) [2]. Whereas the barium based clathrates I have been extensively studied with respect to thermodynamic stability, phase relations, crystal chemistry, and thermoelectric properties, data on corresponding strontium clathrate systems are scarce. In a systematic approach the existence of clathrates has been investigated in the ternary systems Ba–TM–{Si,Ge}, where TM stands for a transition metal, and in most cases a ternary type I clathrate has been observed [3–21]. Hitherto only the systems Sr–{Ni,Cu,Zn}–{Si,Ge} have been studied revealing the formation of a type I clathrate for Cu [22] and Zn [23,24] and the absence of this structure in the ternary system Sr–Ni–{Si,Ge} at 900 °C (Si-system) and at 700 °C (Ge-system) [25,26]. No information is available for the remaining Sr-based transition metal combinations. The present paper intends to fill this gap covering a phase diagram study for four systems Sr–{Pd,Pt}–{Si,Ge} in the clathrate relevant region. Phase relations based on X-ray powder diffraction, SEM and EPMA data are provided, and crystal structural data on several ternary phases extracted from Rietveld refinements are presented. Furthermore for selected ternary silicides the electronic structure was evaluated by DFT calculations.

2. Experimental

For sample preparation the following components were used: strontium pieces with purity 99.5 mass%, Pd and Pt foils with purity better than 99.99 mass%, germanium and silicon pieces with purity better than 99.999 mass%. Oxygen sensitive strontium was cleaned and weighed under cyclohexane. For the preparation of the alloys the appropriate amounts of Sr (excess of 3 mass% was used to compensate evaporation losses), Pd/Pt and Si/Ge were melted in an electric arc-furnace under Ti-gettered argon with a non-consumable tungsten electrode on a water-cooled copper hearth for two times in order to achieve complete fusion and homogeneity. The obtained ingot was sealed in an evacuated quartz tube. Each ampoule was annealed at 700 °C (for Ge-systems) and 900 °C (for Si-systems) for 1 week. Finally, the samples were water quenched without breaking the ampoules.

X-ray powder diffraction data from the annealed specimens were collected with a Guinier-Huber image plate system (Cu $K\alpha_1$; $8° \leqslant 2\theta \leqslant 100°$). Precise lattice parameters were calculated by least-squares fits to indexed 2θ-values employing

---

* Corresponding author. Tel.: +43 1 4277 52456; fax: +43 1 4277 95245.
E-mail address: peter.franz.rogl@univie.ac.at (P. Rogl).

[1] On leave of absence from Lviv Polytechnic National University, Ukraine.

[2] Present address: University of Oregon, Eugene, USA.

http://dx.doi.org/10.1016/j.jallcom.2014.08.159
0925-8388/

Table 1
Crystallographic data and stability ranges of the binary phases ⩾50 at.% Si,Ge.

Compound	Structure type	Pearson symbol, space group no.	Temperature (melting point in °C and decomposition reaction)	Lattice parameters (nm)			Ref.
				a	*b*	*c*	
$SrSi_2$	$SrSi_2$	*cP*12, 213	1100	0.6715	–	–	[34]
SrSi	SrSi	*oI*40, 71	1150	1.298	0.489	1.803	[35]
	TlI	*oS*8, 63	1150	0.4826	1.1287	0.4042	[36]
$SrGe_2$	$BaSi_2$	*oP*24, 62	1015 (peritectic)	0.874	0.665	1.124	[37]
SrGe	TlI	*oS*8, 63	1165	0.482	1.139	0.4167	[38]
PdSi	FeAs	*oP*8, 62	901 (peritectic) 824 (eutectoid)	0.6154	0.5618	0.3387	[39]
Pd_2Si	Fe_2P	*hP*9, 189	1394	0.649	–	0.343	[40]
PtSi	FeAs	*oP*8, 62	1229	0.5595	0.3603	0.5932	[39]
PdGe	FeAs	*oP*8, 62	830	0.5782	0.3481	0.6259	[39]
$PtGe_2$	$CaCl_2$	*oP*6, 58	828 (peritectic)	0.5767	0.6185	0.2908	[41]
Pt_2Ge_3	Pt_2Ge_3	*oP*20, 62	879 (peritectic)	1.643	0.3378	0.6221	[41]
PtGe	FeAs	*oP*8, 62	1070	0.5733	0.3701	0.6088	[39]

Ge (for Si-containing samples) or Si (for Ge-containing samples) (a_{Ge} = 0.565791 nm; a_{Si} = 0.543107 nm) as internal standards using the CSD program package [27]. For crystal structure refinements we used the FullProf Suite program [28] and the standardization procedure was carried out with the program Structure Tidy [29]. The annealed samples were polished using standard procedures and chemical composition of phases was determined via a Zeiss Supra 55VP scanning electron microscope operated at 20 kV and equipped with an energy dispersive X-ray (EDX) spectrometer supported by the INCA software (Oxford Instruments). Standard deviations for the chemical compositions gained from electron probe microanalysis (EPMA) were smaller than ±1 at.%.

DFT (Density Functional Theory) electronic structure calculations for ternary compounds with experimentally determined structural parameters were performed with the Elk package [30] (an all-electron full-potential linearized augmented-plane wave code with LDA [31] exchange–correlation functional). VESTA [32] was used for crystal structure and volumetric data visualization.

3. Binary systems

For the binary systems we relied on the compilation in the Pauling File on binary phase diagrams [33]. A listing of the crystallographic data and stability ranges of the binary phases ⩾50 at.% Si,Ge is given in Table 1.

4. Results and discussion

4.1. The ternary system Sr–Pd–Ge at 700 °C

The Ge-rich part of this system is characterized by the formation of one ternary compound, τ_1-$SrPdGe_3$, which crystallizes in the $BaNiSn_3$ structure type [42] (Table 2). Besides this, hitherto another ternary phase at a Ge-content smaller than 50 at.%, is reported in the literature, $SrPd_2Ge_2$, which crystallizes in the $ThCr_2Si_2$-type and enters a superconducting state below 3.04 K [43]. Rietveld refinement results for $SrPdGe_3$ of our multiphase powder patterns are in excellent agreement with the reported crystallographic data from X-ray single crystal diffraction [42] and no indication for off-stoichiometry towards a Ge-richer composition is observed neither from Rietveld refinement nor from EPMA results (see Table 3). At 700 °C $SrPdGe_3$ is in equilibrium with Ge and with the binary compounds, $SrGe_2$ and PdGe (Fig. 1). Both phases exhibit no detectable solubility for the third element. Representative micrographs of both three-phase regions are shown in Fig. 2 on samples (a and b) annealed at 700 °C. Comparing the backscatter electron images in the as cast state with the annealed state, we observed no change of the microstructure besides grain growth. In contrast to the homologous Ba–Pd–Ge system [4], where a binary clathrate-type I $Ba_8Ge_{43}\square_3$ ($\square$ denotes a vacancy) [44] extends into the ternary $Ba_8Pd_xGe_{43-x-y}\square_y$ with x_{max} = 3.8 at 800 °C [4], no clathrate phase was observed.

4.2. The ternary system Sr–Pt–Ge at 700 °C

The investigation of the Ge-rich part (⩾50 at.% Ge) of the Sr–Pt–Ge system at 700 °C revealed the presence of two ternary phases: τ_1-$SrPtGe_3$, crystallizing in the $BaNiSn_3$ structure type [42] and the skutterudite τ_2-$SrPt_4Ge_{12}$, crystallizing in the $LaFe_4Sb_{12}$ structure type [45,46] (Table 2). The phase relations at 700 °C are plotted in Fig. 3 and the corresponding crystallographic and EPMA data of the samples are listed in Table 3. Whereas at the Sr-rich side the three-phase equilibrium (Ge) + $SrGe_2$ + τ_1 is equivalent to the Sr–Pd–Ge system, a different situation arises at the Pt-rich site due to the formation of τ_2-$SrPt_4Ge_{12}$. The comparison of the micrographs of the as cast and the annealed sample d (shown in Fig. 2) suggests a peritectoid formation of τ_2 according to the isothermal reaction τ_1 + (Ge) + $PtGe_2$ ⇔ τ_2. Whereas in as cast state the non-equilibrium phase $PtGe_2$ is clearly observed in the X-ray powder patterns as well as by EPMA, after annealing only the three equilibrium phases (Ge), τ_1, and τ_2 are found. The Rietveld refinements of multi-phase powder patterns revealed for both ternary compounds τ_1-$SrPtGe_3$ and τ_2-$SrPt_4Ge_{12}$ sound agreement with the reported crystal structures [42,45]. For the binary phases $SrGe_2$ and $PtGe_2$ the solubility of the third element remained below the detection limit of the EPMA (<0.5 at.%). Similar to the systems {Sr,Ba}–Pd–Ge also in this case the triangulation of the ternary phases corresponds to the equilibrium conditions in the Ba–Pt–Ge system [3] with the exception of the absence of any clathrate phase.

4.3. The ternary system Sr–Pd–Si at 900 °C

Phase equilibria in the Sr–Pd–Si ternary system at 900 °C are characterized by the formation of three ternary phases: τ_1-$SrPd_{0.3}Si_{1.7}$, isotypic with the AlB_2-type, τ_2-$SrPd_{1+x}Si_{3-x}$ ($0 \leqslant x \leqslant 0.3$), adopting the $BaNiSn_3$-type and τ_3-$SrPd_{5.9}Si_{6.1}$ crystallizing in a unique structure type (Table 2). No clathrate or skutterudite phases were found. The phase relations at 900 °C are plotted in Fig. 4 and the corresponding crystallographic and EPMA data of the samples are presented in Table 4 and Fig 5. The phase field triangulation in the ternary system Sr–Pd–Si is very similar to that of the system Ba–Pd–Si [5] except for the formation of the Ba-based clathrate phase and the crystal structure of the τ_3 phases. The crystal structure of τ_1-$SrPd_{0.3}Si_{1.7}$ was elucidated via Rietveld refinement (Fig. 1 in Supporting Information) and its crystallographic parameters are listed in Table 5. The crystallographic site 1*a* is fully occupied by Sr atoms, whereas the site 2*d* is occupied by a statistical mixture of Si and Pd atoms. Such structural peculiarity in AlB_2 type compounds was already found during the investigation