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Interaction behaviour of neodymium and silver with elements of Group IVa at 600°C

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Abstract

Phase equlibria have been established in the ternary Nd–Ag–Ge(Sn) systems over the whole concentration region and in the ternary Nd–Ag–Pb system within 0–33 at.% Nd for an isothermal section at 600°C. Seven ternary intermetallic compounds of silver and neodymium have been observed: NdAg$_2$Ge$_2$, Nd$_2$AgGe$_6$, NdAg$_{1.1}$Ge$_{0.9}$, Nd$_6$Ag$_8$(Ge)Sn$_8$ and NdAgSn(Pb).

Keywords: Ternary intermetallic compounds; Rare earth compounds; Nd–Ag–Pb system; Nd–Ag–Sn system; Nd–Ag–Ge system; Isothermal sections

1. Introduction

The influence of the third component on the character of the interaction in ternary systems formed from rare earths, transition metals and Group IVa elements is of substantial interest and therefore the subject of our continued studies. Recently we reported on the isothermal sections of the Nd–Ag–Si system at 600°C [1] and the Nd–Ag–Ge system at 800°C [2]. In this paper we present results of X-ray investigation of the Nd–Ag–Ge(Sn) systems at 600°C over the whole concentration region and the Nd–Ag–Pb system at 600°C within 0–33 at.% Nd.

The binary boundary systems Ag–Ge(Sn,Pb), Nd–Ge(Pb) and Nd–Ag are described in Ref. [3]. The Nd–Sn system was reinvestigated by Weitzer et al. [4] employing X-ray powder techniques and magnetic susceptibility measurements up to 600 K and 6 T. Crystallographic data of the elements and the binary phases occurring in the Nd–Ag–Ge(Sn,Pb) ternary system are listed in Table 1.

2. Experimental details

The ternary samples used to derive the phase relations in the ternary section at 600°C, each with a total weight of 0.5 g, were synthesized by arc-melting proper weightings of the constituent elements under high purity argon on a water-cooled copper hearth. The starting materials were used in the form of ingots of high purity metals (99.9 at.%). The samples were remelted twice under a low electric current. The alloys were afterwards sealed in evacuated quartz tubes and annealed for 250 h at 600°C; after heat treatment the samples were quenched by submerging the silica tubes in cold water.

The isothermal section was constructed using X-ray powder film data obtained by the Debye–Scherrer technique with non-filtered CrK radiation (RKD-57.3 cameras). Lattice constants were determined from the powder patterns (DRON-3 diffractometer, Cu Kα radiation). The crystal structure of the ternary compounds was investigated by a powder X-ray diffraction method (DRON-4.07 diffractometer, Cu Kα radiation). Structure determination was performed using the DBWS.25 program package [6].

The sensitivity of the ternary compounds of tin and lead with respect to moisture recommended handling of the specimens in Ar-controlled glove-box systems.

3. Results and discussion

3.1. The Nd–Ag–Ge system

Four ternary compounds are observed in the Nd–Ag–Ge system at 600°C (see Fig. 1(b)). The

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Table 1
Crystallographic data of the elements and binary boundary phases in Nd–Ag–T systems (T = Ge, Sn, Pb)

Phase	Pearson symbol	Paced group	Prototype	Lattice parameter (nm)			Volume (nm^3)	Comments	Ref.
				a	*b*	*c*			
βNd	cI2	*Im3m*	W	0.413			0.074	883 to 863°C	[3,5]
αNd	hP4	$P6_3/mmc$	α-La	0.36582		1.17966	0.1367	<863°C	[3,5]
Ag	cF4	*Fm3m*	Cu	0.40853			0.0682	<961°C	[3,5]
Ge	cF8	*Fd3m*	$C_{diamond}$	0.56580			0.1811	<780°C	[3,5]
Ge	tI4	$I4_1/amd$	Sn_{white}	0.4884		0.2692	0.0642	<780°C	[3,5]
βSn	tI4	$I4_1/amd$	Sn_{white}	0.58318		0.31818	0.1082	232 to 13°C	[3,5]
αSn	cF8	*Fd3m*	$C_{diamond}$	0.64892			0.2733	<13°C	[3,5]
Pb	cF4	*Fm3m*	Cu	0.49507			0.1213	<178	[3,5]
$Nd_{14}Ag_{51}$	hP65	*P6/m*	$Gd_{14}Ag_{51}$	1.2814		0.9432	1.5487	<1025°C	[3,5]
$NdAg_2$	oI12	*P6/mmm*	AlB_2	0.4789		0.7060	0.1619	825 to 635°C	[3,5]
$NdAg_2$	oI12	*Imma*	$CeGu_2$	0.4774	0.7027	0.8153	1.1506	<620°C	[3,5]
NdAg	cP2	*Pm3m*	CsCl	0.3714			0.0512	<920°C	[3,5]
Nd_5Ge_3	hP16	$P6_3/mcm$	Mn_5Si_3	0.875		0.655	0.2810	<1580°C	[3,5]
Nd_5Ge_4	oP36	*Pnma*	Sm_5Ge_4	0.785	1.510	0.794	0.9412	<1490°C	[3,5]
NdGe	oC8	*Cmcm*	CrB	0.422	1.097	0.404	0.1870	<1397°C	[3,5]
β-$NdGe_{2-x}$	tI12	$I4_1/amd$	α-$ThSi_2$	0.423		1.415’	0.6551	1483 to 828°C	[3,5]
α-$NdGe_{2-x}$	oI12	*Imma*	α-$GdSi_2$	0.422	0.417	1.403	0.2469	<828°C	[3,5]
$Ag_xSn_{1-x}(\xi)$	hP2	$P6_3/mmc$	Mg	0.29386		0.47860	0.0413	<724°C	[3,5]
Ag_3Sn	oP8	*Pmmm*	Cu_3Ti	0.59680	0.47802	0.51843	0.1478	<480°C	[3,5]
Nd_5Sn_3	hP16	$P6_3/mcm$	Mn_5Si_3	0.91181		0.67354	0.4935	<1660°C	[4]
Nd_5Sn_4	oP36	*Pnma*	Sm_5Ge_4	0.82166	1.588	0.83809	1.094	<1558 ± 10°C	[4]
$Nd_{11}Sn_{10}$	tI84	*I4/mmm*	$Ho_{11}Ge_{10}$	1.18440		1.76122	2.4707	<1396 ± 4°C	[4]
NdSn	Unknown							<1257 ± 4°C	[4]
Nd_3Sn_5	Unknown							<1140°C	[4]
$NdSn_2$	oC12	*Cmmm*	$ZrGa_2$	0.44404	1.59193	0.45628	0.3225	<1180°C	[4]
Nd_3Sn_7	oC20	*Cmmm*	Ce_3Sn_7	0.44990	2.57881	0.45846	0.5317	<1145°C	[4]
Nd_2Sn_5	oC28	*Cmmm*	Ce_2Sn_5	0.45688	3.51188	0.46139	0.7403	<1135°C	[4]
$NdSn_3$	cP4	*Pm3m*	$AuCu_3$	0.47061			0.10423	<1150°C	[4]
$NdPb_3$	cP_4	*Pm3m*	$AuCu_3$	0.4852			0.11423		[3,5]

$NdAg_{0.7}Ge_{1.3}$ phase of AlB_2 type which exists at 800°C [2] does not appear at 600°C.

3.2. The Nd–Ag–Sn system

Phase equilibria in the Nd–Ag–Sn system at 600°C are characterized by the existence of two ternary compounds and one liquid phase field (Fig. 1(c)).

The crystal structure of the RAgSn (R = La, Ce, Sm, Gd–Lu) compounds was investigated earlier [5]. In the present work this isotypic series is complemented by two novel members: NdAgSn and PrAgSn. Rietveld full-matrix full-profile refinement of the X-ray powder data of the NdAgSn compound based on the structural model of $CaIn_2$ type [7] confirmed the atom order and site occupation in the $P6_3/mmc$ space group and proved isotypism with the above-mentioned structure type. As seen from Fig. 2(a), observed and calculated intensities are in good agreement. The PrAgSn phase was found to crystallize in the same structure type ($CaIn_2$, space group $P6_3/mmc$, $a = 0.4767(3)$, $c = 0.7673(5)$ nm).

The crystal structure determination of the $Nd_6Ag_8Sn_8$ compound was performed by Rietveld full-matrix full-profile refinement of the X-ray powder diffraction pattern on the basis of the $Gd_6Cu_8Ge_8$ structure type. Employing the set of atomic parameters derived for the $Gd_6Cu_8Ge_8$ type [8], convincing agreement was found between the experimentally observed and calculated X-ray intensities (Fig. 2(b)). Room temperature X-ray patterns of the $R_6Ag_8Sn_8$ samples where R = La, Ce, Pr, Sm revealed a close resemblance to the pattern of $Nd_6Ag_8Sn_8$, and all were completely indexed on the basis of an orthorhombic unit cell [9].

3.3. The Nd–Ag–Pb system

A partial isothermal section of the Nd–Ag–Pb phase diagram at 600°C is shown in Fig. 1(d). The phase relations for the Pb-rich concentration region are characterized by the presence of one ternary compound and one liquid phase region.

Crystallographic data of the ternary compounds of the Nd–Ag–Si(Ge,Sn,Pb) systems are listed in Table 2.

The systems under discussion are characterized by the following peculiar alloying behavior features of Group IVa elements with silver and neodymium:

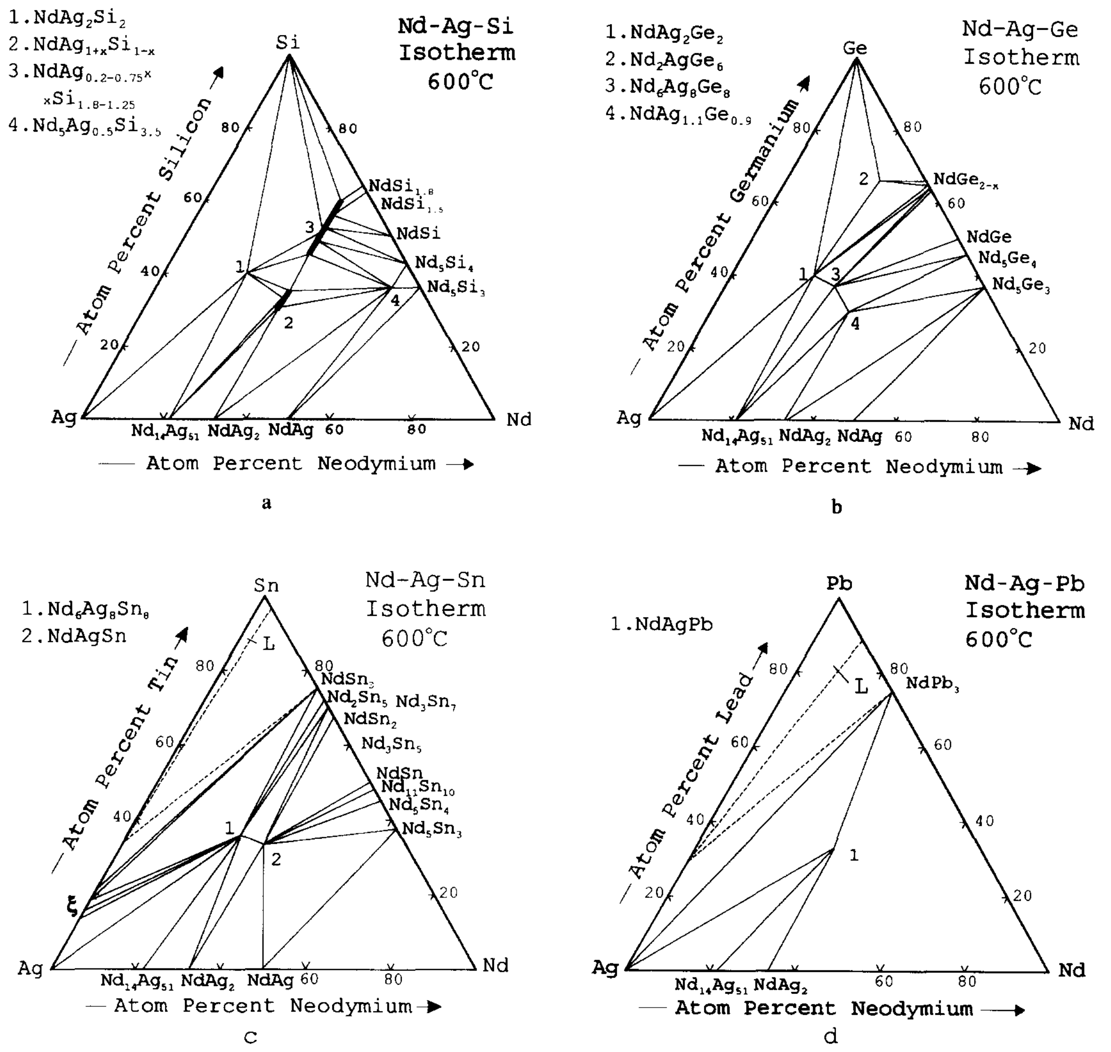

Fig. 1. Isothermal sections of Nd–Ag–T systems at 600°C: (a) Nd–Ag–Si, (b) Nd–Ag–Ge, (c) Nd–Ag–Sn, (d) Nd–Ag–Pb.

Table 2

Crystallographic data of the ternary Nd–Ag–T compounds (T = Si, Ge, Sn, Pb)

Compound	Structure type	Space group	Lattice parameters (nm)			Ref.
			a	*b*	*c*	
$NdAg_2Si_2$	$CeGa_2Al_2$	*I4/mmm*	0.4250(4)		1.0757(1)	[1]
$NdAg_{0.2-0.75}Si_{1.8-1.25}$	α-$ThSi_2$	$I4_1/amd$	0.4209(1)– –0.4223(1)		1.4979(8)– –1.4508(11)	[1]
NdAgSi	$A1B_2$	*P6/mmm*	0.4211(1)		0.4146(2)	[1]
$Nd_5Ag_{0.5}Si_{3.5}$	Sm_5Ge_4	*Pnma*	0.7645(2)	1.5040(3)	0.7881(2)	[1]
$NdAg_2Ge_2$	$CeGa_2Al_2$	*I4/mmm*	0.4244(1)		1.0978(2)	[2][a]
Nd_2AgGe_6	Ce_2CuGe_6	*Amm2*	0.4271(1)	0.4117(1)	2.1517(5)	[2][a]
$Nd_6Ag_8Ge_8$	$Gd_6Cu_8Ge_8$	*Immm*	1.4636(5)	0.7082(3)	0.4407(1)	[9][a]
$NdAg_{1.1}Ge_{0.9}$	Fe_2P	*P62m*	0.7339(1)		0.4329(1)	[2][a]
$Nd_6Ag_8Sn_8$	$Gd_6Cu_8Ge_8$	*Immm*	1.54051(2)	0.73378(1)	0.46321(3)	[9][a]
NdAgSn	$CaIn_2$	$P6_3/mmc$	0.47523(2)		0.75980(3)	[a]
NdAgPb	$CaIn_2$	$P6_3/mmc$	0.47994(2)		0.76735(1)	[a]

[a] This work.

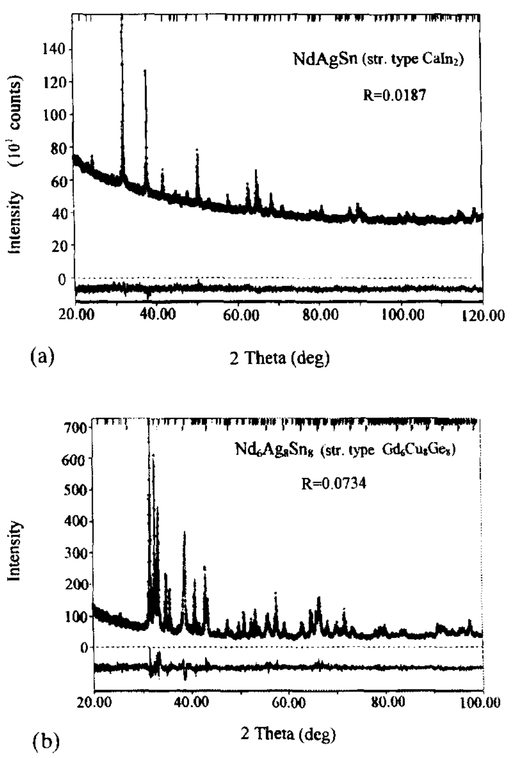

Fig. 2. Comparison of observed and calculated X-ray powder profiles of (a) NdAgSn and (b) $Nd_6Ag_8Sn_8$ compounds.

- the formation of only a small number of ternary phases;
- the formation of isotypic compounds limited to neighbouring elements in the SiGeSnPb series (see Table 3);
- the crystallization of equiatomic compounds (NdAgSi, NdAgSn, NdAgPb) or of compounds close to the equiatomic composition ($NdAg_{1.1}Ge_{0.9}$) involving different structure types: AlB_2, $CaIn_2$ and Fe_2P.

Table 3
Isotypic compound formation in ternary Nd–Ag–Si(Ge,Sn,Pb) systems

Structure type	Si	Ge	Sn	Pb
$CeGa_2Al_2$	+	+	–	–
$Gd_6Cu_8Ge_8$	–	+	+	–
$CaIn_2$	–	–	+	+

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