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Letter

Preparation and characterization of ternary Nd–Pr–Sb alloys

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Abstract

Ternary Nd–Pr–Sb alloys were studied using X-ray powder diffraction and optical and electron microscopy. $(Nd, Pr)_2Sb$ (tI12 – La_2Sb type), $(Nd, Pr)_4Sb_3$ (cI28 – anti-Th_3P_4 type), (Nd, Pr)Sb (cF8 – NaCl type) and $(Nd, Pr)Sb_2$ (oC24 – $SmSb_2$ type) show complete solubility between Nd and Pr. The variation of the lattice parameters as a function of the Nd to Pr ratio was determined. In addition, the alloy $Nd_{0.475}Pr_{0.475}Sb_{0.05}$ was investigated by differential thermal analysis (DTA). The results obtained confirm a previous thermodynamic prediction of the Nd–Pr–Sb phase equilibria.

1. Introduction

Rare earth compounds with the pnicogens and, in particular, with antimony have been described as promising substances for several technological applications (for instance, as superconductors having high critical temperatures [1]). A review on the various (structural, magnetic, electronic) properties of these compounds is presented in ref. 2. Moreover, these substances form a well-defined group of very stable phases, which are also interesting from a general point of view.

An accurate description of the phase diagrams of the lanthanide pnictides may therefore be worthwhile. However, experimental information on these systems is poor because of several experimental difficulties: the high or very high melting temperatures of the compounds, the high volatility of the pnicogens and the high reactivity of the elements involved and of the compounds. Therefore, these systems constitute a case in which a combination of experimental work, calculation and correlation techniques may be especially useful to select crucial measurements and to obtain a thermodynamic optimization of the data. The ternary Nd–Pr–Sb system was considered in ref. 3. Optimized thermodynamic descriptions of the Nd–Sb and Pr–Sb systems were calculated and, on the basis of certain assumptions, the ternary system was predicted. In this paper, we present the results obtained from an experimental investigation of the ternary alloys carried out to verify the assumed and predicted data.

2. Literature data on the Nd–Pr–Sb system

The Nd–Sb and Pr–Sb phase diagrams have been studied previously [4, 5]. The following phases are formed in both systems (R ≡ Nd, Pr): congruently melting RSb and the peritectic decomposing compounds R_2Sb, R_5Sb_3, R_4Sb_3 and RSb_2 (crystal structure data relevant to these phases are summarized in Table 1, which also includes data obtained in this work).

The enthalpies of formation of the Nd–Sb and Pr–Sb phases have been determined previously [7, 18]. High-temperature e.m.f. measurements have been carried out on the Sb-rich regions of both systems [19–21].

Using the phase diagram data and the enthalpy of formation data, optimized thermodynamic descriptions of the Nd–Sb and Pr–Sb systems were calculated by the least-squares method [3] using the procedure first described in ref. 22 and subsequently improved upon in refs. 23 and 24.

These data were combined for the calculation of the ternary Nd–Pr–Sb system [3], using Toop's extrapolation formula [25] to obtain ternary thermodynamic functions from the binary ones, with the assumption that no ternary compound exists and ideal complete mutual solution behaviour is given by the corresponding binary Nd and Pr antimonides.

Ideal solution formulae were used for the three (Nd, Pr) binary phases: liquid, α-(Nd, Pr) and β-(Nd, Pr).

The Nd–Pr phase diagram [26] shows complete mutual solubility in the α and β solid phases and in the liquid state (with very narrow two-phase fields).

The predicted liquidus surface is shown in Fig. 1.

3. Experimental details

The metals employed were Nd and Pr of 99.9 mass.% nominal purity and Sb of 99.99 mass.% purity. The alloys were prepared by induction melting mixtures of the elements in small tantalum crucibles (sealed by welding under argon).

The samples were examined using X-ray diffraction methods (photographic Debye camera with Fe Kα

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TABLE 1. Solid phases

Phase	Pearson symbol/prototype	Lattice parameters (pm)	Comments and refs.
$(Nd_{1-x}Pr_x)_2Sb$	tI12 La_2Sb	$a=451.0$ $c=1761$	$x=0$, [6]
		$a=452.0$ $c=1763$	$x=0.125$, this work
		$a=452.8$ $c=1761.9$	$x=0.5$, this work
		$a=452.6$ $c=1767.7$	$x=0.625$, this work
		$a=453.3$ $c=1765$	$x=0.75$, this work
		$a=455$ $c=1782$	$x=1.0$, [5]
		$a=454.0$ $c=1774$	[7]
$(Nd_{1-x}Pr_x)_4Sb_3$	cI28 anti-Th_3P_4	$a=940.6$	$x=0$, [8]
		$a=938.0$	[9]
		$a=937.1$	[4]
		$a=942.5$	$x=0.25$, this work
		$a=943.6$	$x=0.5$, this work
		$a=945.3$	$x=0.75$, this work
		$a=945.8$	$x=1$, [8]
		$a=936$	[9]
		$a=945$–948	[7]
		$a=935$	[5]
$Nd_{1-x}Pr_xSb$	cF8 NaCl	$a=633$	$x=0$, [10]
		$a=633.8$	[11]
		$a=632.1$	[12]
		$a=634.0$	This work
		$a=634.8$	$x=0.25$, this work
		$a=635.3$	$x=0.4$, this work
		$a=636.1$	$x=0.5$, this work
		$a=636.4$	$x=0.6$, this work
		$a=637.0$	$x=0.75$, this work
		$a=636.6$	$x=1$, [13]
		$a=636.0$	[14]
		$a=637.5$	[15]
		$a=637.7$–638.2	[7]
		$a=638$	[5]
		$a=638$	This work
$(Nd_{1-x}Pr_x)Sb_2$	oC24 $SmSb_2$	$a=620.7$ $b=609.8$ $c=1808.1$	$x=0$, [16]
		$a=623.0$ $b=606.3$ $c=1789.2$	[17]
		$a=622.3$ $b=610.6$ $c=1812.6$	This work
		$a=623.3$ $b=611.0$ $c=1815.9$	$x=0.25$, this work
		$a=623.5$ $b=611.3$ $c=1814.5$	$x=0.25$, this work

(*continued*)

TABLE 1. (*continued*)

Phase	Pearson symbol/prototype	Lattice parameters (pm)	Comments and refs.
		$a=623.9$ $b=611.8$ $c=1815.5$	$x=0.5$, this work
		$a=624.4$ $b=612.1$ $c=1817.4$	$x=0.61$[a], this work
		$a=623.0$ $b=606.4$ $c=1789.2$	$x=1$, [17]
		$a=626.7$ $b=612.5$ $c=1818.0$	[7]
		$a=626$ $b=612$ $c=1816$	[5]

[a]The reported composition is that obtained by microprobe analysis.

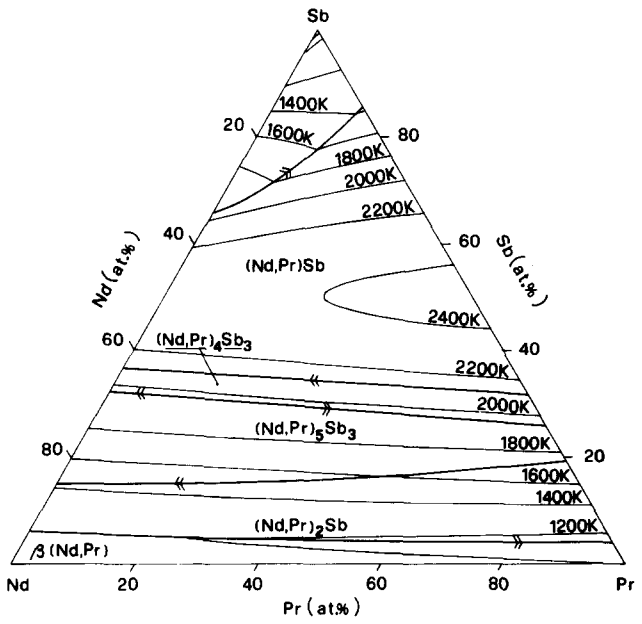

Fig. 1. Predicted liquidus surface of the Nd–Pr–Sb system [3].

radiation and diffractometer with Cu Kα radiation). Lattice parameters were obtained by least-squares fitting to the Nelson–Riley function.

Specimens of the different alloys were examined under an optical microscope and a scanning electron microscope after dry polishing and etching in air or in a very dilute ethanol solution of HNO_3.

In a few cases a semiquantitative microanalysis of the phases was carried out (using an energy dispersive X-ray microanalyser). The intensities, corrected for atomic number, absorption and fluorescence, were compared with those of standards.

4. Results and general remarks

In agreement with the assumptions made, no ternary phase, but only a ternary extension of the binary phases, was observed. Continuous solid solutions between the isostructural binary compounds were generally noted. The lattice parameter data of these phases are reported in Table 1.

In the graph shown in Fig. 2, which gives the average atomic volume as a function of the rare earth composition, very small deviations from linearity are ob-

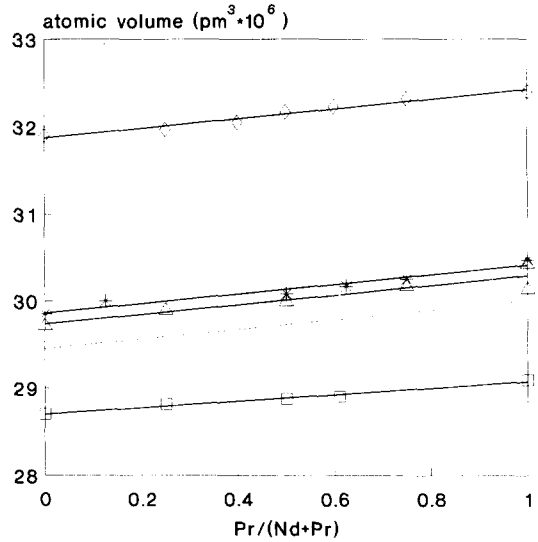

Fig. 2. (Nd, Pr)$_x$Sb$_y$ phases: *, $(Nd_{1-x}Pr_x)_2Sb$; △, $(Nd_{1-x}Pr_x)_4Sb_3$; ◇, $Nd_{1-x}Pr_xSb$; □, $(Nd_{1-x}Pr_x)Sb_2$. Average atomic volume *vs.* rare earth composition. The experimental points were obtained in this work. The broken line (interpolated values) refers to the $(Nd, Pr)_5Sb_3$ phase.

served and all the lines are nearly parallel (the different packing efficiency of the various structures is also apparent).

In regions easily accessible to experimental examination, the results of differential thermal analysis (DTA) were found to be in good agreement with the computed values. For example, an alloy with the composition $Nd_{0.475}Pr_{0.475}Sb_{0.05}$ was found to be very close to the predicted valley joining the two binary R-rich eutectics (see Fig. 1). The main thermal effects observed on heating were at 1090 and 1170 K, in comparison with the values of 1082 and 1169 K computed for an alloy on the eutectic valley at the composition $Nd_{0.478}Pr_{0.478}Sb_{0.044}$, corresponding to the eutectoidal ($\beta R \rightarrow \alpha R + R_2Sb$) and eutectic ($L \rightarrow \beta R + R_2Sb$) reactions respectively.

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