Phase equilibria in the ternary system Yb–Cr–Sb at 500°C

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The isothermal section of the phase diagram of the ternary system Yb–Cr–Sb was constructed in the whole concentration range at 500°C using X-ray powder diffraction data. The binary compounds of the systems Yb–Sb and Cr–Sb do not dissolve the third component. The existence of the ternary compound $YbCrSb_3$ (structure type $CeCrSb_3$, Pearson symbol $oP20$, space group *Pbcm*, unit-cell parameters $a = 12.926(3)$, $b = 6.141(1)$, $c = 5.990(1)$ Å) was confirmed.

Ytterbium / Chromium / Antimony / X-ray powder diffraction / Phase diagram / Crystal structure

Introduction

Several ternary systems *R*–Cr–Sb (*R* is a rare-earth metal) have been studied with the aim to find ternary compounds. A series of ternary rare-earth chromium antimonides with the general formula $RCrSb_3$ was first discovered for the early rare earths La, Ce, Pr, Nd, and Sm [1], and subsequently extended to the late rare earths Gd, Tb, Dy [2], and Yb [3]. The crystal structure of the $RCrSb_3$ compounds belongs to the orthorhombic structure type $CeCrSb_3$ (space group *Pbcm*, Pearson symbol $oP20$).

The binary systems that delimit the ternary system Yb–Cr–Sb have been studied in the whole concentration range and the corresponding phase diagrams constructed [4].

Five binary compounds were found in the system Yb–Sb [5,6]. It was later established that the correct composition of the low-temperature polymorph α-Yb_5Sb_4 is $Yb_{11}Sb_{10}$ [7], and the phase reported as Yb_5Sb_2 was identified as the low-temperature polymorph of Yb_5Sb_3 [8]. The transformation temperature of α-$Yb_{11}Sb_{10}$ into β-$Yb_{11}Sb_{10}$ is 1040°C and that of α-Yb_5Sb_3 into β-Yb_5Sb_3 is 1350°C. The phases $YbSb_2$ and Yb_4Sb_3 melt congruently at 880 and 1570°C, respectively, whereas the phases YbSb, $Yb_{11}Sb_{10}$, and Yb_5Sb_3 melt incongruently at 820, 1400, and 1540°C. An additional phase, $Yb_{16}Sb_{11}$, was reported within a study of isotypic compounds [9].

The phase diagram of the system Cr–Sb was evaluated in [10] and the existence of two binary compounds was established already in the first phase diagram investigation in 1907 [11]. The compound CrSb melts congruently at 1113°C and has a small homogeneity range of up to 3 at.%, whereas $CrSb_2$ forms *via* a peritectic reaction at 718°C and has no significant homogeneity range.

No binary compounds form in the system Yb–Cr [12].

In this work we present the results of an investigation of the ternary system Yb–Cr–Sb at 500°C.

Experimental

The samples, approximately 1 g each, were synthesized by arc melting metals with a nominal purity of more than 99.9 mass% under an argon atmosphere, using Ti as a getter and a tungsten electrode. To achieve high efficiency of the interaction between the components, the samples were melted twice. To ensure the homogeneity, they were annealed in evacuated silica ampoules at 500°C for two months, and finally quenched in cold water.

Phase analysis and structure refinements were carried out using X-ray powder diffraction data collected at room temperature on an automatic diffractometer DRON-2.0M (Fe *K*α-radiation, $\lambda = 1.93801$ Å, angular range $15° \leq 2\theta \leq 120°$, step 0.05°). Phase analysis was performed by comparing the experimental patterns with theoretical patterns of the metals, and binary and ternary compounds [13], using the program PowderCell [14]. The profile and structural parameters were refined by the Rietveld method, using the program package WinCSD [15].

Results and discussion

The phase analysis of the alloys confirmed the existence of five compounds in the binary system Yb–Sb ($YbSb_2$, YbSb, $Yb_{11}Sb_{10}$, Yb_4Sb_3, Yb_5Sb_3), two compounds in the system Cr–Sb ($CrSb_2$, CrSb), and the absence of compounds in the system Yb–Cr at 500°C. Unit-cell parameters of the binary compounds, refined from X-ray powder diffraction data of ternary samples, are listed in Table 1. Comparing the unit-cell parameters of the binary compounds obtained here with those reported in the literature, we can assume that no significant solid solubility of the third component in the binary phases exists.

The isothermal section of the phase diagram of the ternary system Yb–Cr–Sb at 500°C is shown in Fig. 1. It contains 11 single-phase, 20 two-phase and 10 three-phase fields. The ternary compound $YbCrSb_3$ is in equilibrium with four binary compounds: $YbSb_2$, YbSb, $CrSb_2$, and CrSb. The binary compounds $Yb_{11}Sb_{10}$, Yb_4Sb_3, and Yb_5Sb_3 all form equilibria with elementary Cr. The binary compound CrSb forms equilibria with $YbCrSb_3$ and two of the binary compounds of the Yb–Sb system: YbSb and $Yb_{11}Sb_{10}$. The binary compound $YbSb_2$ is in equilibrium with $CrSb_2$, and both form equilibria with $YbCrSb_3$.

Table 1 Unit-cell parameters of the binary compounds in the Yb–Cr–Sb system at 500°C.

Compound	Structure type	Pearson symbol	Space group	a, Å	b, Å	c, Å
$YbSb_2$	$ZrSi_2$	$oS12$	$Cmcm$	4.548(2)	16.700(8)	4.272(2)
YbSb	NaCl	$cF8$	Fm-$3m$	6.088(1)	–	–
$Yb_{11}Sb_{10}$	$Ho_{11}Ge_{10}$	$tI84$	$I4/mmm$	11.920(2)	–	17.202(3)
Yb_4Sb_3	Th_3P_4	$cI28$	I-$43d$	9.363(3)	–	–
Yb_5Sb_3	Yb_5Sb_3	$oP32$	$Pnma$	12.376(5)	9.721(4)	8.332(4)
$CrSb_2$	$FeAs_2$	$oP6$	$Pnnm$	6.037(2)	6.868(2)	3.2627(9)
CrSb	NiAs	$hP4$	$P6_3/mmc$	4.1234(5)	–	5.4692(8)
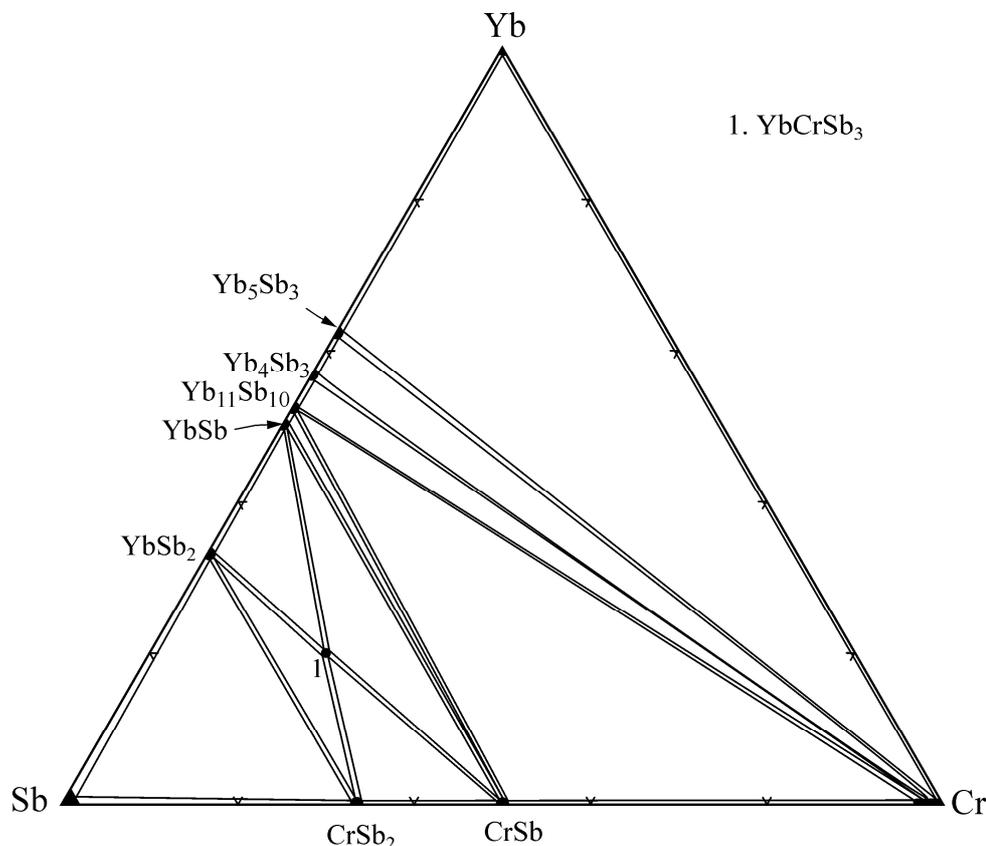
Fig. 1 Isothermal section of the phase diagram of the system Yb–Cr–Sb at 500°C.

The existence of the ternary compound of fixed composition $YbCrSb_3$ at 500°C was confirmed and the cell parameters refined to $a = 12.926(3)$, $b = 6.141(1)$, $c = 5.990(1)$ Å. The crystal structure was refined by the Rietveld method on powder diffraction data collected at room temperature, starting from the atom coordinates of the structure type $CeCrSb_3$ [1]. The sample of nominal composition $Yb_{20}Cr_{20}Sb_{60}$, used for the refinement, appeared to be slightly deficient in antimony since it contained three phases: $YbCrSb_3$, $YbSb_2$ [16], and $CrSb_2$ [17]. Cr-vacancies had been detected in the Nd-analogue [18], however, refinement of the site occupancies in the structure of $YbCrSb_3$ showed no significant deviation from unity. Only the scale factors and unit-cell parameters were refined for the secondary phases.

Experimental details and crystallographic data of the individual phases are given in Table 2. The atomic coordinates of the structure of $YbCrSb_3$ are listed in Table 3 and the interatomic distances in Table 4. Fig. 2 shows the content of the unit cell and the coordination polyhedra of the different sites. The data are in good agreement with the refinement on single crystal from 2005 [3].

The ytterbium atoms are coordinated by nine antimony atoms (1 Sb1, 4 Sb2, and 4 Sb3) forming a coordination polyhedron that can be described as a monocapped square antiprism (coordination number CN = 9). The chromium atoms have distorted octahedral coordination formed by six antimony atoms (4 Sb1 and 2 Sb2) (CN = 6). The antimony atoms from the site Sb1 are located inside distorted trigonal prisms formed by one ytterbium, one antimony (Sb2) and four chromium atoms (CN = 6). The atoms from the site Sb2 have irregular seven-vertex coordination polyhedra formed by four ytterbium, one antimony (Sb1) and two chromium atoms (CN = 7). The atoms from the site Sb3 are characterized by eight-vertex polyhedra composed by four ytterbium atoms forming a distorted tetrahedron and four antimony atoms (Sb3) forming a square (CN = 8).

Comparing the isothermal section of the phase diagram of the ternary system Yb–Cr–Sb at 500°C investigated here, with the isothermal sections of the phase diagrams of the systems {La,Er}–Ti–Sb at 800°C [19] and {Ce,Gd}–Zr–Sb at 600°C [20], it can be seen that the diagrams of the early and late rare-earth elements differ significantly. For example, in the systems with late rare earths no (Er–Ti–Sb) or single compounds (Gd–Zr–Sb, Yb–Cr–Sb) form at the selected temperature, whereas in the systems with early rare earths the interaction between the components is apparently more complex and leads to the formation of two (La–Ti–Sb) or four (Ce–Zr–Sb) ternary compounds.

Table 2 Experimental details and crystallographic data for the individual phases in the sample $Yb_{20}Cr_{20}Sb_{60}$.

Compound		$YbCrSb_3$	$YbSb_2$	$CrSb_2$
Content, mass%		63.9	15.8	20.3
Structure type		$CeCrSb_3$	$ZrSi_2$	$FeAs_2$
Pearson symbol		$oP20$	$oS12$	$oP6$
Space group		$Pbcm$	$Cmcm$	$Pnnm$
Cell parameters:	a, Å	12.926(3)	4.548(2)	6.037(2)
	b, Å	6.141(1)	16.700(8)	6.868(2)
	c, Å	5.990(1)	4.272(2)	3.2627(9)
Cell volume V, Å^3		475.5(3)	325.5(3)	135.3(1)
Formula units per unit cell Z		4	4	2
Calculated density D_X, g/cm^3		8.245(5)	8.499(8)	7.253(7)
Radiation and wavelength, Å			Fe $K\alpha$, 1.93736	
FWHM parameters:	U		0.536	
	V		-0.083	
	W		0.065	
Number of reflections		235	94	74
Reliability factors:	R_B	0.099	0.121	0.098
	R_F	0.150	0.152	0.155
	R_p		0.046	
	R_{wp}		0.061	

Table 3 Atom coordinates in the structure of YbCrSb$_3$ ($B_{ov} = 0.6$ Å^2)

Site	Wyckoff position	x	y	z
Yb1	4d	0.3109(9)	0.016(3)	¼
Cr1	4c	0.902(4)	¼	0
Sb1	4d	0.080(1)	0.143(3)	¼
Sb2	4d	0.212(1)	0.473(3)	¼
Sb3	4c	0.513(2)	¼	0
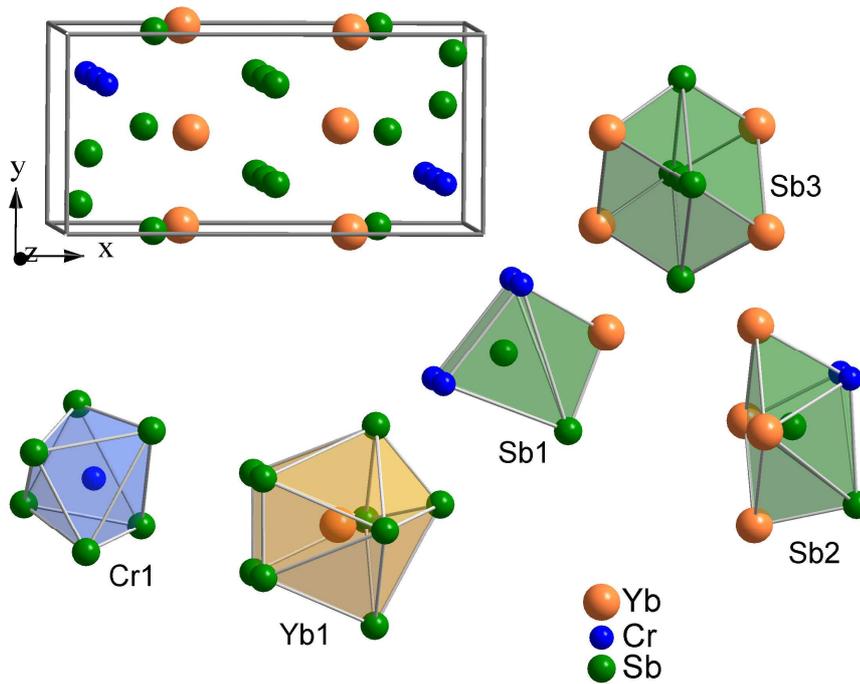
Fig. 2 Unit cell of YbCrSb$_3$ and coordination polyhedra.

Table 4 Interatomic distances (δ) and coordination numbers (CN) in the structure of YbCrSb$_3$.

Atoms		δ, Å	CN	Atoms		δ, Å	CN
Yb1	− 2 Sb3	3.213(12)		Sb2	−2 Cr1	2.583(15)	
	− 2 Sb2	3.214(4)			−1 Sb1	3.123(14)	
	− 2 Sb2	3.23(2)	9		−2 Yb1	3.214(4)	7
	− 2 Sb3	3.234(12)			−1 Yb1	3.23(2)	
	− 1 Sb1	3.278(13)			−1 Yb1	3.33(2)	
	− 1 Sb2	3.33(2)		Sb3	−2 Sb3	2.9949(4)	
Cr1	− 2 Sb2	2.583(15)			−2 Sb3	3.0715(5)	8
	− 2 Sb1	2.760(9)	6		−2 Yb1	3.213(12)	
	− 2 Sb1	2.88(2)			−2 Yb1	3.234(12)	
Sb1	− 2 Cr1	2.760(9)					
	− 2 Cr1	2.88(2)	6				
	− 1 Sb2	3.123(14)					
	− 1 Yb1	3.278(13)					

Conclusions

The ternary system Yb–Cr–Sb at 500°C is characterized by the existence of one ternary compound with point composition YbCrSb$_3$.

The differences in size, electronic structure and electronegativity between the elements that form the system Yb–Cr–Sb prevent the formation of any significant solid solutions on the basis of the binary compounds.

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