SOLID SOLUTIONS BASED ON THE M_5X_3 BINARY COMPOUNDS IN THE M–{Si, Ge}–Sb TERNARY SYSTEMS (M – Ti, Zr, Y; X – Si, Ge, Sb)

A. Yu. Kozlov, V. V. Pavlyuk

Department of Inorganic Chemistry, Ivan Franko L'viv National University, Kyryla i Mefodiya str. 6, UA-79005 Lviv, Ukraine

ABSTRACT

The solid solutions based on M_5X_3 binary compounds in Ti–{Si, Ge}–Sb, Zr–Si–Sb and Y–{Si, Ge}–Sb ternary systems at 400°C were found (str. type Mn_5Si_3, space group $P6_3/mcm$). The crystal structure of $Ti_5Si_{2.76}Sb_{0.24}$ (a=0.7500 nm, c=0.5182 nm) and $Ti_5Ge_{2.26}Sb_{0.74}$ (a=0.7604(5) nm, c= 0.5260(3) nm) was investigated by single-crystal X-ray analysis. Continuous solid solutions between Y_5Si_3–Y_5Sb_3 and Y_5Ge_3–Y_5Sb_3 compounds were investigated by powder X-ray analysis. The solid solution $Zr_5Si_xSb_{3+y}$ (x=0-1, y=0-1) is formed by interstitial of atoms of Si in trigonal antiprisms which are formed by Zr atoms in 6g sites in Zr_5Sb_3 (str. type Mn_5Si_3, space group $P6_3/mcm$) binary compound or substitution of atoms of Sb in 2b sites by Si atoms in Zr_5Sb_4 (str. type Ti_5Ga_4, space group $P6_3/mcm$) binary compound.

INTRODUCTION

The long history of the chemical flexibility of Mn_5Si_3 – type M_5X_3 compounds and their interstitial derivatives has been described in a review [1]. Pearson's 1991 handbook [2] lists ~175 binaries and ~290 combinations of elements that crystallize in this structure type. The formation of 'pseudobinary' compounds by substitution or interstitial of atoms based on M_5X_3 compounds were determined during investigations of the transition metal–{Si, Ge}–Sb ternary systems. The formation of the solid solutions $Ti_5Si_{3-x}Sb_x$ (x=0-0.24) and $Ti_5Ge_{3-x}Sb_x$ (x=0-0.8) were determined earlier [3, 4]. The formation of 'pseudobinary' compounds by substitution in the $Zr_5(Al, Ga, In)_{3-x}Sb_x$, $Ti_5Ga_{3-x}Sb_x$ and $Hf_5In_{3-x}Sb_x$ systems (x~1.5) were investigated as a possible way to oxidative resistance and stability [5]. We report the results of the investigations of the solid solutions based on the M_5X_3 binary compounds in the {Ti, Zr. Y}–{Si, Ge}–Sb ternary systems.

EXPERIMENTAL

The samples with the a total mass of about 1 g were prepared by arc melting of pure metals (the purity of the ingredients was better than 99.999 at.%) in a high-purity argon atmosphere with Ti as a getter. All alloys were remelted twice to ensure homogeneity. The ingots were annealed at 400°C in quartz ampoules under vacuum during 720 h an subsequently quenched in cold

water. The weight loses during the sample preparation were less than 1% of the total mass. Phase analysis was carried out using X-ray powder diffraction (diffractometr DRON-2.0, FeK_α radiation). The crystal structures of the ternary compounds were refined using the X-ray powder and single crystal diffraction data, obtained on Siemens D5000 diffractometer (CuK_α radiation) and DARTCH-1 automatic diffractometer (Mok_α radiation), respectively. All procedures, including indexing, refinement of lattice and atomic parameters and calculations of interatomic distances were performed with SHELXL-97 [6], DBWS-9411 [7], CSD [8] and FULLPROF [9] software.

RESULTS AND DISCUSSION

Solubility of the Si or Ge in binary compound Ti_5Sb_3 with Yb_5Sb_3 structure type was not observed. Limited solid solutions based on the Ti_5Si_3 and Ti_5Ge_3 with the Mn_5Si_3 structure type were observed and investigated in the Ti–{Si, Ge}–Sb systems [3]. The crystal structure of these solid solutions were investigated by single-crystal and powder X-ray analysis. Crystallographic parameters, atomic and isotropic thermal displacement parameters for composition $Ti_5Si_{2.76}Sb_{0.24}$ and $Ti_5Ge_{2.26}Sb_{0.74}$ are shown in table 1.

Table 1. Crystallographic data, atomic and isotropic thermal displacement parameters for composition $Ti_5Si_{2.76}Sb_{0.24}$ and $Ti_5Ge_{2.26}Sb_{0.74}$

Composition	$Ti_5Si_{2.76}Sb_{0.24}$	$Ti_5Ge_{2.26}Sb_{0.74}$
Space group	$P6_3/mcm$	
Person symbol	hP16	
a, (nm)	0.7500(1)	0.7604(5)
c,(nm)	0.5182(1)	0.5260(3)
V, (nm^3)	0.2524(7)	0.2634(5)
F (000)	414	440
Calculated density (g/cm^3)	5.967(3)	6.22(1)
Radiation and wavelengh	MoKα 0.71073	MoKα 0.71069
Diffractometer	KM-4	DARTCH-1
Number of unique reflections	141	183
Goodness-of-fit	1.432	1.050
R(F), wR(F^2)	0.0501, 0.1107	0.0623, 0.1121

Atom	Site	x/a		y/b	z/c	$B_i \times 10^2$	
		$Ti_5Si_{2.76}Sb_{0.24}$	$Ti_5Ge_{2.26}Sb_{0.74}$			$Ti_5Si_{2.76}Sb_{0.24}$	$Ti_5Ge_{2.26}Sb_{0.74}$
Ti (1)	6g	0.2461(3)	0.2463(6)	0	1/4	1.2(1)	0.79(10)
Ti (2)	4d	1/3		2/3	0	0.9(1)	0.48(8)
Si* (Ge*)	6g	0.6066(3)	0.6078(3)	0	1/4	1.1(1)	0.82(6)

Si*=92Si+8Sb; Ge*=75Ge+25Sb

Y–Si–Sb and Y–Ge–Sb ternary systems are characterize by formation of the continuous solid solutions between isostructural binary compounds Y_5Si_3 (Y_5Ge_3) and Y_5Sb_3 (str. type Mn_5Si_3). The crystal structure of these solid solutions were investigated by powder X-ray analysis (Siemens D5000 diffractometer CuK_α radiation). The experimental X-ray diffraction patterns together with calculated and difference diffraction profiles for $Y_5Si_{2.6}Sb_{0.4}$ (a), $Y_5Si_{0.8}Sb_{2.2}$ (b) compounds are shown in figure 1.

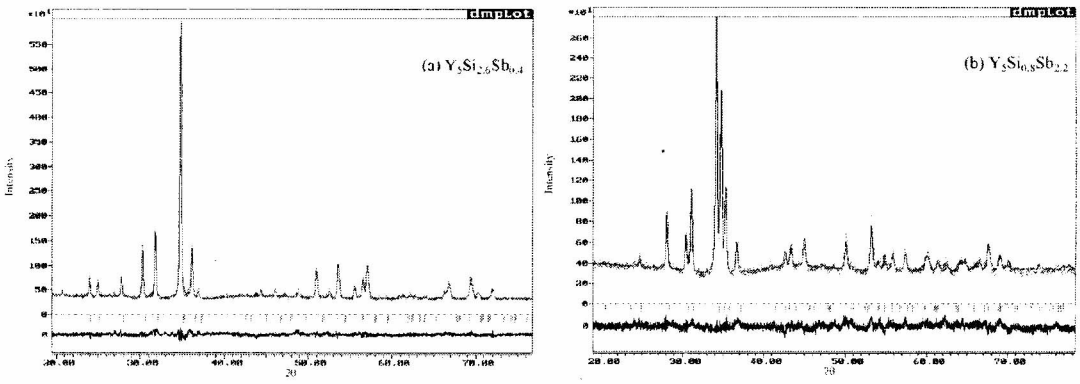

Figure 1. The experimental X-ray diffraction patterns together with calculated and difference diffraction profiles for $Y_5Si_{2.6}Sb_{0.4}$ (a), $Y_5Si_{0.8}Sb_{2.2}$ (b) compounds.

The composition dependences of the unit cell parameters for the $Y_5Si_{3-x}Sb_x$ and $Y_5Ge_{3-x}Sb_x$ solid solutions ($0 \le x \le 3$) are shown in figure 2. The lattice parameters for alloys from continuos solid solutions are listed in table 2.

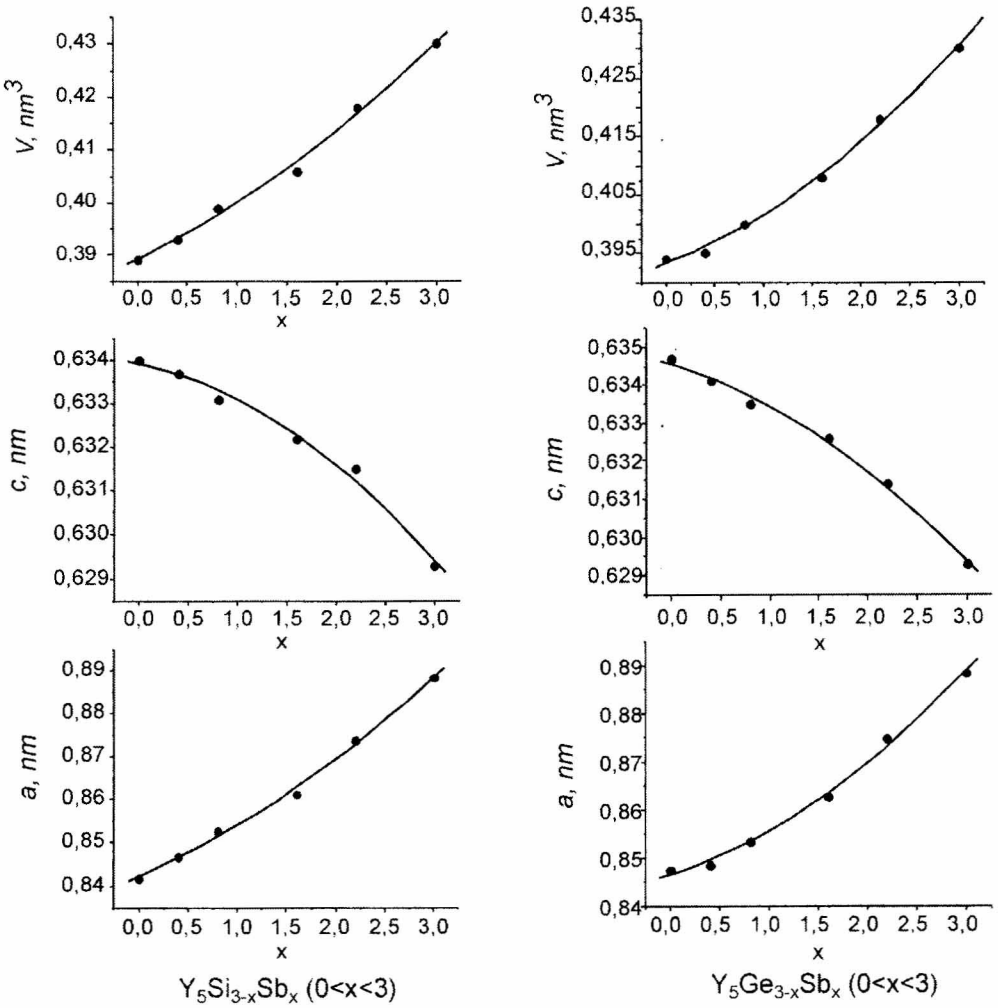

Figure 2. The composition dependences of the unit-cell parameters for the $Y_5Si_{3-x}Sb_x$ and $Y_5Ge_{3-x}Sb_x$ solid solutions ($0 \le x \le 3$).

Table 2. The lattice parameters of $Y_5Sb_{3-x}Si_x$ and $Y_5Ge_{3-x}Sb_x$ ($0 \le x \le 3$)

Samples	Lattice parameters, nm		V, nm^3	Samples	Lattice parameters, nm		V, nm^3
	a	c			a	c	
Y_5Si_3	0.8418(3)	0.6340(2)	0.389(1)	Y_5Ge_3	0.8475(2)	0.6347(3)	0.394(2)
$Y_5Sb_{0.4}Si_{2.6}$	0.8467(5)	0.6337(3)	0.393(3)	$Y_5Sb_{0.4}Ge_{2.6}$	0.8485(3)	0.6341(5)	0.395(4)
$Y_5Sb_{0.8}Si_{2.2}$	0.8526(2)	0.6331(4)	0.399(2)	$Y_5Sb_{0.8}Ge_{2.2}$	0.8534(4)	0.6335(4)	0.400(3)
$Y_5Sb_{1.6}Si_{1.4}$	0.8612(4)	0.6322(3)	0.406(2)	$Y_5Sb_{1.6}Ge_{1.4}$	0.8626(3)	0.6326(2)	0.408(2)
$Y_5Sb_{2.2}Si_{0.8}$	0.8739(2)	0.6315(3)	0.418(1)	$Y_5Sb_{2.2}Ge_{0.8}$	0.8747(5)	0.6314(3)	0.418(3)
Y_5Sb_3	0.8883(3)	0.6293(2)	0.430(2)	Y_5Sb_3	0.8883(3)	0.6293(2)	0.430(2)

During the investigation of the Zr–Si–Sb system at 400°C the solid solution based on the Zr_5Sb_3 binary compound was determined. The Zr_5Si_3 compound with Mn_5Si_3 structure type was not determined at annealing temperature.

The solid solution $Zr_5Si_xSb_{3+y}$ (x=0-1, y=0-1) is formed by interstitial of atoms of Si in trigonal antiprisms which are formed by Zr atoms in 6g sites in Zr_5Sb_3 (str. type Mn_5Si_3, space group $P6_3/mcm$) binary compound or substitution of atoms of Sb in 2b sites by Si atoms in Zr_5Sb_4 (str. type Ti_5Ga_4, space group $P6_3/mcm$) binary compound. Crystallographic parameters, atomic and isotropic thermal displacement parameters from $Zr_5Si_xSb_{3+y}$ solid solution for composition Zr_5Sb_3, Zr_5SiSb_3 and Zr_5Sb_4 are shown in table 3.

Table 3. Crystallographic parameters, atomic and isotropic thermal displacement parameters from $Zr_5Si_xSb_{3+y}$ (x=0-1, y=0-1) solid solution for composition Zr_5Sb_3, Zr_5SiSb_3 and Zr_5Sb_4

Formula	Zr_5Sb_3	Zr_5SiSb_3	Zr_5Sb_4
Space group	$P6_3/mcm$		
Person symbol	hP16	hP18	hP18
Lattice parameters			
a, (nm)	0.8422(3)	0.8538(2)	0.8603(4)
c, (nm)	0.5696(2)	0.5815(3)	0.5912(5)
V, (nm^3)	0.350(2)	0.367(2)	0.379(3)
R_{BRAGG}, (%)	7.34	6.21	7.89

Atom	Site	x/a			y/b	z/c	B_{iso} 10^2		
		Zr_5Sb_3	Zr_5SiSb_3	Zr_5Sb_4			Zr_5Sb_3	Zr_5SiSb_3	Zr_5Sb_4
Zr1	6g	0.2434(3)	0.2595(3)	0.2784(4)	0	1/4	0.88(3)	0.96(5)	1.08(5)
Zr2	4d	1/3			2/3	0	0.68(5)	0.73(5)	0.87(6)
Sb	6g	0.6052(4)	0.6074(2)	0.6127(3)	0	1/4	0.58(6)	0.52(3)	0.64(7)
Si^a (Sb^b)	2b	–	0		0	0		1.20(4)	0.71(5)

Si^a – atoms of Si in Zr_5SiSb_3 compound; Sb^b – atoms of Sb in Zr_5Sb_4 compound

Projection of the unit cell for compounds (a) Zr_5Sb_3 (str. type Mn_5Si_3), (b) Zr_5Sb_4 (str. type Ti_5Ga_4) and (c) Zr_5SiSb_3 (str. type Hf_5CuSn_3), on the XY plane are shown in figure 3.

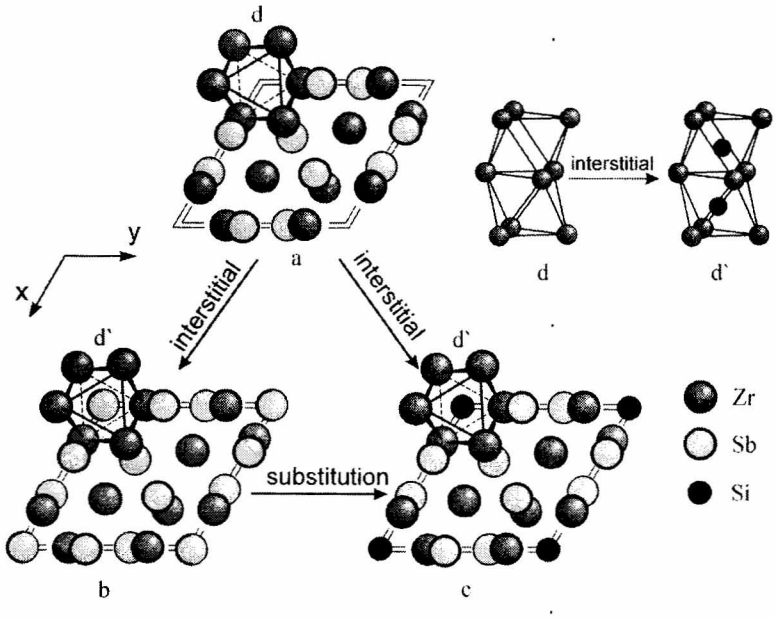

Figure 3. Projection of the unit cell for compounds (a) Zr_5Sb_3 (str. type Mn_5Si_3), (b) Zr_5Sb_4 (str. type Ti_5Ga_4) and (c) Zr_5SiSb_3 (str. type Hf_5CuSn_3), on the XY plane; (d) and (d`) – trigonal antiprisms which are formed by Zr atoms in 6g sites.

REFERENCES

[1] J. D. Corbett, E. Garcia, A. M. Guloy, W. -M. Hurng, Y. -U. Kwon, E. A. Leon-Escamilla, Chem. Mater. 10 (1998) 2824.

[2] P. Villars, L. D. Calvert, Pearson's Handbook of Crystallographic Data for Intermetallic Phases, 2nd Edition, American Society for Metals International, Metals Park, OH, 1991.

[3] A. Kozlov, V. Pavlyuk, Visn. L'viv Univ. Ser. Khim., 41, (2002) 27.

[4] A. Yu. Kozlov, V. V. Pavlyuk, VIII International Conference on Crystal Chemistry of Intermetallic Compounds, Ukrain, Lviv, September 25-28, (2002) 68.

[5] H. Boller, E. Parthe, Acta Cryst. 16 (1963) 830.

[6] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement. University of Göttingen, Germany, 1997.

[7] R. A. Young, A. Sakthivel, T. S. Moss, C. O. Paria-Santos, Program DBWS-9411 for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns, Georgia Institute of Technology, Atlanta, GA, (1995) 60.

[8] L. G. Akselrud, P. Yu. Zavalii, Yu. N. Grin, V. K. Pecharsky, B. Baumgartner, E. Wolfel, Mater. Sci. Forum, 133-136 (1993) 335.

[9] J. Rodriguez-Carvajal, in: Cong. Int. Union of Crystallography, Tolouse, Satellite Meeting on Powder Diffraction (1990) 127