Chemistry of Metals and Alloys

Chem. Met. Alloys 16 (2023) 22-25
Ivan Franko National University of Lviv
http://publications.lnu.edu.ua/chemetal

$R_xZr_{2-x}Sb$ (R = La-Nd, Sm) compounds with UGeTe-type structure

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Received March 17, 2023; accepted June 29, 2023
https://doi.org/10.30970/cma16.0435

Five ternary compounds $R_xZr_{2-x}Sb$ (R = La-Nd, Sm; $x \approx 0.1$) were synthesized and their crystal structures were determined by X-ray powder diffraction (structure type UGeTe, Pearson symbol *tI*12, space group *I4/mmm*, $Z = 4$; $a = 4.1296(7)$, $c = 15.881(3)$ Å for $La_{0.08(2)}Zr_{0.92(2)}Sb$; $a = 4.1431(11)$, $c = 15.870(4)$ Å for $Ce_{0.114(19)}Zr_{0.886(19)}Sb$; $a = 4.1557(13)$, $c = 15.926(5)$ Å for $Pr_{0.14(2)}Zr_{0.86(2)}Sb$; $a = 4.1426(11)$, $c = 15.885(4)$ Å for $Nd_{0.136(18)}Zr_{0.864(18)}Sb$; $a = 4.1323(7)$, $c = 15.842(3)$ Å for $Sm_{0.104(16)}Zr_{0.896(16)}Sb$). The structure type UGeTe is a ternary ordered variant of the structure type La_2Sb. The structures are characterized by the existence of octahedral voids that may accommodate small atoms.

Rare-earth metals / Zirconium / Antimony / Intermetallic compound / X-ray powder diffraction / Crystal structure

Introduction

The amount of information available on the interaction of the components in the R–Zr–Sb (R = rare-earth metal) systems is rather limited. Phase equilibria have been studied for the systems with Ce [1], Sm [2], Gd [1], and Dy [3]. Two series of isostructural compounds have been reported [4,5]: R_3ZrSb_5 (R = La-Nd, Sm; structure type Hf_5CuSn_3, Pearson symbol *hP*18, space group $P6_3/mcm$), and RZrSb (R = Y, Gd-Tm, Lu; UGeTe, *tI*12, *I*4/*mmm*). For the GdZrSb compound a homogeneity range along the isoconcentrate 33.3 at.% Sb, extending from the equiatomic composition to the limiting composition $Gd_{0.095}Zr_{1.905}Sb$ (3.2-33.3 at.% Gd), was determined at 600°C [1]. A less extended domain was found for Dy at 800°C, 28-33.3 at.% [3]. An isostructural point compound of approximate composition $Ce_{0.08}Zr_{1.92}Sb$ was identified in the system Ce–Zr–Sb, which does not contain any equiatomic compound at 600°C [1]. A binary compound Zr_2Sb has been reported by some authors [4], and was in some cases assigned the structure type La_2Sb [6], which is a binary variant of the type UGeTe, but has not been observed in investigations of the binary phase diagram. In his study of the Sm–Zr–Sb diagram, the author [2] reported a compound Zr_2Sb with unknown tetragonal structure, dissolving up to 5 at.% Sm at 800°C. It seemed of interest to have a closer look at the phase diagrams of some of the R–Zr–Sb systems near the composition Zr_2Sb.

In this work we present results of the synthesis and structural characterization of the ternary compounds $R_xZr_{2-x}Sb$ (R = La-Nd, Sm; $x \approx 0.1$) with UGeTe-type structures.

Experimental details

The starting materials for the synthesis were the pure components: rare-earth metals (≥ 99.9 mass%), zirconium (≥ 99.99 mass%), and antimony (≥ 99.99 mass%). The initial compositions of the samples were $R_{2.67}Zr_{64}Sb_{33.33}$ ($R_{0.08}Zr_{1.92}Sb$, (R = La-Nd, Sm), by analogy with the composition of the compound $Ce_{0.08}Zr_{1.92}Sb$, found during the investigation of the phase equilibria in the ternary system Ce–Zr–Sb at 600°C.

The alloys were synthesized by arc-melting of the components in argon atmosphere and subsequent annealing in evacuated quartz ampoules at 600°C for 30 days. X-ray phase and structure analysis were performed using X-ray powder diffraction patterns, collected on a diffractometer STOE Stadi P (Cu $K\alpha_1$-radiation, angular range $6° \le 2\theta \le 110°$, step 0.015°) for the samples with Ce, Pr, Nd, and Sm, or DRON-2.0M (Fe $K\alpha$-radiation, angular range $30° \le 2\theta \le 90°$, step 0.05°) for the sample with La. Full-profile refinements of profile and structural parameters were carried out by the Rietveld method, using the program package FullProf Suite [7]. Atomic coordinates reported for the type-defining or related

compounds, were chosen as starting models for the refinements of the structural parameters. The compositions of selected phases were additionally analyzed by energy-dispersive X-ray spectroscopy (EDX), performed on a scanning electron microscope REMMA-102-02.

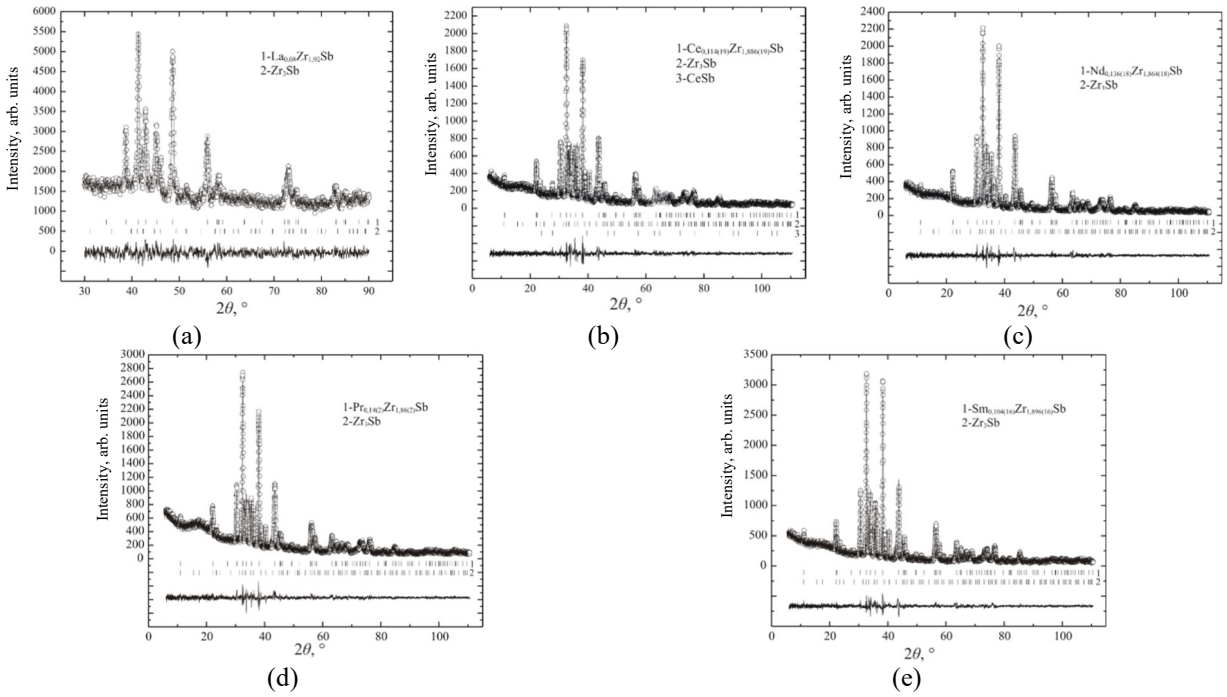

Fig. 1 Experimental (circles), calculated (lines), and difference (bottom) X-ray powder diffraction patterns of the samples $La_{2.67}Zr_{64}Sb_{33.33}$ (a), $Ce_{2.67}Zr_{64}Sb_{33.33}$ (b), $Pr_{2.67}Zr_{64}Sb_{33.33}$ (c), $Nd_{2.67}Zr_{64}Sb_{33.33}$ (d), $Sm_{2.67}Zr_{64}Sb_{33.33}$ (e). Vertical ticks show the positions of the reflections from the individual phases.

Table 1 Experimental details and crystallographic data for the ternary compounds $R_xZr_{2-x}Sb$ (R = La-Nd, Sm) (structure type UGeTe, Pearson symbol *tI*12, space group *I*4/*mmm*, Z = 4).

Composition	$La_{0.08}Zr_{1.92}Sb$	$Ce_{0.114}Zr_{1.886}Sb$	$Pr_{0.14}Zr_{1.86}Sb$	$Nd_{0.136}Zr_{1.864}Sb$	$Sm_{0.104}Zr_{1.896}Sb$
Content, mass %	73.8(19)	76.8(12)	82.0(13)	89.8(15)	79.1(10)
Unit-cell parameters:					
a, Å	4.1296(7)	4.1431(11)	4.1557(13)	4.1426(11)	4.1323(7)
c, Å	15.881(3)	15.870(4)	15.926(5)	15.885(4)	15.842(3)
Cell volume V, Å^3	270.82(8)	272.42(12)	275.05(15)	272.60(13)	270.51(8)
Density D_X, g/cm^{-3}	7.558	7.552	7.513	7.588	7.619
Preferred orientation:					
value [direction]	0.994(9) [010]	1.069(5) [010]	1.092(5) [010]	1.064(5) [010]	1.056(4) [010]
Profile parameters:					
U	-0.1(3)	1.72(8)	1.83(9)	1.22(6)	0.66(4)
V	1.5(3)	-0.37(6)	-0.39(6)	-0.26(5)	-0.13(3)
W	-0.41(7)	0.060(10)	0.054(12)	0.042(8)	0.019(4)
Shape parameter η	0.37(4)	0.172(15)	0.164(17)	0.357(13)	0.685(12)
Asymmetry parameters:					
P_1	0.05(6)	0.152(15)	0.08(2)	0.129(16)	0.089(11)
P_2	0.017(8)	0.047(3)	0.018(4)	0.036(3)	0.0457(15)
Reliability factors:					
R_B	0.0586	0.0315	0.0471	0.0438	0.0341
R_F	0.0394	0.0248	0.0269	0.0309	0.0271
R_p	0.0431	0.0738	0.0593	0.0730	0.0693
R_{wp}	0.0546	0.0983	0.0776	0.0979	0.0921
R_{exp}	0.0255	0.0825	0.0642	0.0833	0.0713
χ^2	4.60	1.44	1.48	1.39	1.73

All the synthesized alloys ($R_{2.67}Zr_{64}Sb_{33.33}$, R = La-Nd, Sm) were multiphase, containing a ternary compound with UGeTe-type structure as the main phase. Besides this phase, the samples contained a certain amount of the binary compound Zr_3Sb (Ni_3P, *tI*32, *I*-4) [8]. The sample with cerium in addition contained traces of the binary compound CeSb (NaCl, *cF*8, *Fm*-3*m*) [9]. Experimental, calculated and difference X-ray powder patterns for the samples $R_{2.67}Zr_{64}Sb_{33.33}$ (R = La-Nd, Sm) are shown on Fig. 1. Experimental details and crystallographic data for the UGeTe-type phases are listed in Table 1. The refined compositions of the ternary compounds agree with the compositions obtained by EDX analysis. The fact that the composition of the Ce-containing compound, $Ce_{0.114}Zr_{1.886}Sb$, differs from the composition at which it was first discovered, $Ce_{0.08}Zr_{1.92}Sb$, indicates that it has a certain homogeneity range along the isoconcentrate 33.3 at.% Sb, which is probably also true for the other compounds. It should, however, be noted that in all cases, besides the UGeTe-type phase, containing slightly more R than the nominal composition, not "Zr_2Sb" but Zr_3Sb was observed. The Sm-containing phase of similar composition with a = 6.567(7), c = 7.942(7) Å, reported at 800°C [2], was not detected in this study.

Results and discussion

The crystal structures of the ternary compounds $R_xZr_{2-x}Sb$ (R = La-Nd, Sm) belong to the tetragonal structure type UGeTe. Atom coordinates and isotropic displacement parameters are given in Table 2. The structures contain one site in Wyckoff position 4*e* occupied by a statistical mixture of R and Zr atoms, one site (4*c*) occupied by Zr atoms, and one site (4*e*) by Sb atoms. Refinements considering different distributions of the R atoms were less satisfactory. The unit cell and coordination polyhedra of the different sites are shown in Fig. 2, and interatomic distances between the atoms within the coordination polyhedra are listed in Table 3.

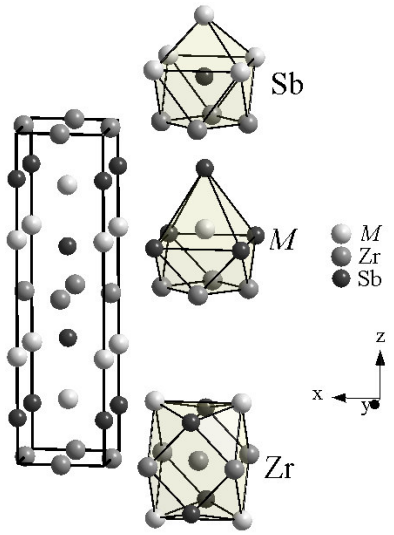

Fig. 2 Unit cell of the $R_xZr_{2-x}Sb$ compounds and coordination polyhedra.

Table 2 Atom coordinates and isotropic displacement parameters for the ternary compounds $R_xZr_{2-x}Sb$ (R = La-Nd, Sm) (UGeTe, *tI*12, *I*4/*mmm*).

Site / Wyckoff position	$La_{0.08}Zr_{1.92}Sb$ [a]	$Ce_{0.114}Zr_{1.886}Sb$ [b]	$Pr_{0.14}Zr_{1.86}Sb$ [c]	$Nd_{0.136}Zr_{1.864}Sb$ [d]	$Sm_{0.104}Zr_{1.896}Sb$ [e]
M / 4*e* (0 0 *z*)	z = 0.3253(4)	z = 0.32293(15)	z = 0.32299(15)	z = 0.32292(15)	z = 0.32289(14)
B_{iso}, Å^2	0.7(2)	0.70(7)	0.41(10)	0.50(10)	0.58(9)
Zr / 4*c* (0 ½ 0)					
B_{iso}, Å^2	0.7(2)	0.71(9)	0.66(10)	0.72(9)	0.42(8)
Sb / 4*e* (0 0 *z*)	z = 0.1357(3)	z = 0.13726(13)	z = 0.13757(13)	z = 0.13779(13)	z = 0.13785(12)
B_{iso}, Å^2	0.6(2)	0.38(7)	0.61(8)	0.61(7)	0.46(6)

M: [a] $La_{0.08(2)}Zr_{0.92(2)}$; [b] $Ce_{0.114(19)}Zr_{0.886(19)}$; [c] $Pr_{0.14(2)}Zr_{0.86(2)}$; [d] $Nd_{0.136(18)}Zr_{0.864(18)}$; [e] $Sm_{0.104(16)}Zr_{0.896(16)}$

Table 3 Interatomic distances in the ternary compounds $R_xZr_{2-x}Sb$ (R = La-Nd, Sm) (UGeTe, *tI*12, *I*4/*mmm*).

Atoms	δ, Å				
	$La_{0.08}Zr_{1.92}Sb$	$Ce_{0.114}Zr_{1.886}Sb$	$Pr_{0.14}Zr_{1.86}Sb$	$Nd_{0.136}Zr_{1.864}Sb$	$Sm_{0.104}Zr_{1.896}Sb$
M – 1 Sb	3.011(8)	2.947(4)	2.953(4)	2.941(4)	2.931(4)
– 4 Sb	2.9850(17)	2.9970(8)	3.0049(9)	2.9950(8)	2.9874(7)
– 4 Zr	3.458(6)	3.491(3)	3.502(3)	3.493(2)	3.4844(19)
Zr – 4 Zr	2.9201(3)	2.9296(5)	2.9385(6)	2.9293(5)	2.9220(3)
– 4 Sb	2.985(4)	3.0061(16)	3.0195(17)	3.0135(16)	3.0063(14)
– 4 M	3.458(6)	3.491(3)	3.502(3)	3.493(2)	3.4844(19)
Sb – 1 M	3.011(8)	2.947(4)	2.953(4)	2.941(4)	2.931(4)
– 4 M	2.9850(17)	2.9970(8)	3.0049(9)	2.9950(8)	2.9874(7)
– 4 Zr	2.985(4)	3.0061(16)	3.0195(17)	3.0135(16)	3.0063(14)

The atoms of the site M (statistic mixture of R and Zr atoms) and the Sb atoms are coordinated by square antiprisms with an additional atom above one of the square faces, $\underline{M}Zr_4Sb_5$ and $\underline{Sb}M_5Zr_4$, respectively. The Zr atoms are coordinated by cuboctahedra $\underline{Zr}M_4Zr_4Sb_4$, which are slightly elongated along the crystallographic direction [001].

The structure type UGeTe (*tI*12, *I*4/*mmm*) [10] is a ternary ordered variant of the binary structure type La_2Sb with the same symmetry (*tI*12, *I*4/*mmm*) [6]. The atom arrangements can be described as a stacking of layers of polyhedra along the crystallographic direction [001]: either separate layers of cuboctahedra around the Zr atoms, or interconnected layers (3D-framework) of capped square antiprisms around the Sb atoms (Fig. 3).

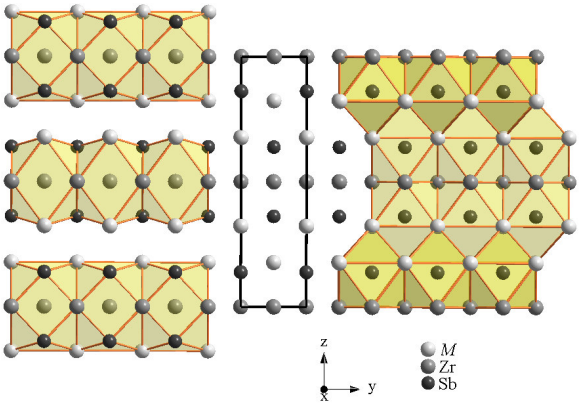

Fig. 3 Projection of the structure of the $R_xZr_{2-x}Sb$ compounds along the crystallographic direction [100], and stacking of the coordination polyhedra around Zr (left) and Sb (right) atoms.

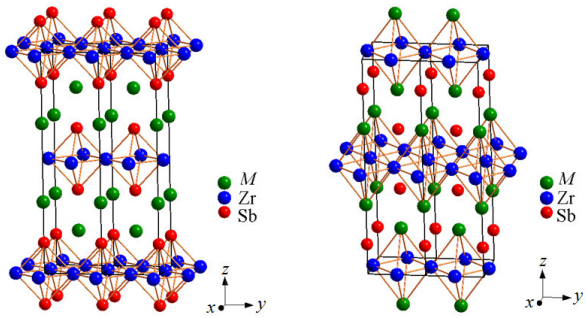

Fig. 4 Octahedral voids in the structures of the $R_xZr_{2-x}Sb$ compounds.

The structures of the UGeTe-type $R_xZr_{2-x}Sb$ compounds are characterized by the existence of relatively large octahedral voids with the centers in Wyckoff position 2*a* (0 0 0), surrounded by Zr and Sb atoms, and Wyckoff position 2*b* (0 0 ½), surrounded by Zr and R atoms, as shown in Fig. 4. The presence of these voids in the structures makes the discovered phases promising materials for possible incorporation of small atoms (see *e.g.* $Na_2Ti_2Sb_2O$ with $Sr_2CuO_2Cl_2$-type structure, *tI*14, *I*4/*mmm* [4]).

The newly synthesized ternary compounds $R_xZr_{2-x}Sb$ with light rare-earth metals (La, Ce, Pr, Nd, and Sm) expand the series of UGeTe-type compounds in the R–Zr–Sb systems, which had so far only been reported for cerium, in addition to yttrium and heavy rare-earth metals (Gd, Tb, Dy, Ho, Er, Tm, and Lu).

Conclusions

Five new ternary compounds $R_xZr_{2-x}Sb$ (R = La-Nd, Sm, $x \approx 0.1$) were synthesized and their crystal structures were refined from X-ray powder diffraction data. The structures belong to the structure type UGeTe, which is a ternary variant of the structure type La_2Sb. The structures are characterized by the existence of octahedral voids around the Wyckoff positions 2*a* and 2*b* of the space group *I*4/*mmm*. Further investigations are necessary to determine the homogeneity ranges, but it is likely that they are relatively narrow and do not include neither the binary border (compound not confirmed), nor the equiatomic composition, in systems where R is a light rare earth.

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