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Phase equilibria and crystal structures in the system Ce–Zn–Si

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ABSTRACT

Phase relations in the system Ce–Zn–Si have been determined for the isothermal section at 800 °C using electron microprobe analysis and X-ray powder diffraction. Phase equilibria are characterized by extended solid solutions along the section $CeSi_2$–$CeZn_2$, which form a structurally related sequence of structure types: $Ce(Zn_xSi_{1-x})_2$ ($\alpha ThSi_2$-type, $0 \le x \le 0.32$), τ_2-$Ce(Zn_xSi_{1-x})_2$ (AlB_2-type, $0.36 \le x \le 0.76$) and $Ce(Zn_{1-x}Si_x)_2$ ($CeCu_2$-type, $0 \le x \le 0.18$). Silicon stabilizes the ternary compound τ_1-$Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$, ($0.28 \le x \le 0.98$) for which the crystal structure was derived from X-ray diffraction data for a single crystal of $Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$ ($x = 0.28$; unique structure type, *Pbam*; $a = 1.55722(3)$ nm, $b = 1.71942(3)$ nm, $c = 0.44772(1)$ nm; $R_F = 0.029$). The structure of $Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$ can be considered as an arrangement of slightly distorted building blocks of Cu_3Au-type ($Zn[Ce_4Zn_8]$) and $BaAl_4$-type ($Ce[Ce_2Zn_{10}M_4]$ and $Ce[Ce_2Zn_{13}M_2]$), arranged in form of a zig-zag string of face-sharing units…Cu_3Au–$BaAl_4$–$BaAl_4$–$BaAl_4$–Cu_3Au… running parallel to the *b*-axis. Structural analyses proved isotypism for homologous $La_7Zn_{21}(Zn_{1-x}Si_x)_2$ ($x = 0.27$), $Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$-type, *Pbam*; $a = 1.56817(2)$ nm, $b = 1.72923(3)$ nm, 0.450887(7) nm; X-ray single crystal data and $La(Zn_xSi_{1-x})_2$, ($x = 0.56$, AlB_2-type, P6/*mmm*, $a = 0.42775(4)$ nm, $c = 0.42832(4)$ nm; X-ray powder data). The structure types of the ternary compounds τ_3-$Ce(Zn_xSi_{1-x})$, $0.17 \le x \le 0.23$, and τ_4-$Ce_{40}Zn_{37}Si_{23}$ (in at.%) are still unknown.

1. Introduction

Zinc-based alloys with rare-earth metals are used in several engineering applications and are employed to replace cast iron because of similar properties and higher machinability [1]. Rare earths (RE) improve the mechanical performance, tensile strength, hardness and also the corrosion resistance by removing impurities from the grain boundaries of their alloys with zinc [2]. Silicides may find applications as contact materials or in optoelectronic devices or simply as grain refiners [3]. As far as high strength lightweight alloys for automotive applications are concerned [4], the Ce–Zn system is an important part of the multinary Mg-based alloy system Mg–Zn–Mn–RE–(Si). Besides the compound CeZnSi, which has been reported [5] to be paramagnetic within the temperature range of 77–300 K, no phase diagram has yet been established for the system Ce–Zn–Si. Therefore the present work intends to provide detailed information on phase equilibria and crystal structures in the Ce–Zn–Si system and some attempts to explore the homologous system La–Zn–Si.

2. Experimental

Samples were prepared from cerium ingots (Alfa Aesar, purity >99.9 mass%), lanthanum ingots (Auer Remy, 99.9 mass%) zinc granules (Alfa Aesar, >99.9 mass%), Ni foil (Alfa Aesar, >99.8 mass%) and silicon pieces (Alfa Aesar, 6 N). Zinc drops were purified in an evacuated quartz tube by heating them at ~750 °C, below the boiling point of Zn (907 °C). Cerium and lanthanum ingots were mechanically surface cleaned before use.

Samples for ternary phase analysis were prepared from intimate blends of powders of arc melted master alloys $CeSi_x$ or $LaSi_x$ (various *x*; powdered under cyclohexane) and fine Zn-filings in proper compositional ratios. These blends were cold compacted in a steel die without lubricants, vacuum-sealed in quartz tubes, heated from 420 °C to 800 °C at the rate of 1 °C/min and then annealed at this temperature for 4 days. After water quenching the samples were re-powderized under cyclohexane in order to ensure homogeneity. The samples were once again cold compacted and annealed at 800 °C for 7 days and subsequently water quenched.

X-ray powder diffraction data were collected from each alloy in as cast and annealed state employing a Guinier-Huber image plate system with monochromatic $CuK_{\alpha 1}$ radiation ($8° < 2\theta < 100°$).

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Table 1
Crystallographic data of unary and binary boundary solid phases of the system Ce–Zn–Si[a].

Phase, temperature range (°C)	Space group, prototype	Lattice parameters (nm)			Comments
		a	*b*	*c*	
(δCe)	$Im\bar{3}m$	0.412	–	–	[11]
798–700 [11]	W		–	–	–
(γCe)	$Fm\bar{3}m$	0.51610	–	–	[11]
<726 [11]	Cu		–	–	
(Zn)	$P6_3/mmc$	0.2665	–	0.4947	[11]
<420			–		–
(Si)	$Fd\bar{3}m$	0.543110	–	–	[22]
<1414 °C	C (*Diamond*)		–	–	–
$CeSi_2$	*Imma*	0.4189(1)	–	0.4109(1)	$Ce_{37.4}Si_{62.6}$[b] [13]
<1725 °C [13]	α $GdSi_2$		–		
$CeSi_2$	$I4_1/amd$	0.4192(1)	–	1.3913(5)	$Ce_{33.3}Si_{66.7}$[b] [13]
~1575 °C [13]	α$ThSi_2$	–	–	–	
$Ce(Zn_xSi_{1-x})_2$		0.4201(1)		1.4312(7)	$x_{max} = 0.32$[c] [This work]
CeSi	*Pnma*	0.8298(4)	–	0.3961(2)	$Ce_{49.9}Si_{50.1}$[b] [13]
<1630 °C [13]	FeB		–		
Ce_5Si_4	$P4_12_12$	0.7936(1)	–	1.5029(5)	$Ce_{55.6}Si_{44.4}$[b] [13]
<1500 °C [13]	Zr_5Si_4		–		
Ce_3Si_2	*P4/mbm*	0.7780(6)	–	0.4367(6)	[13]
<1335 °C [13]	U_3Si_2		–		
Ce_5Si_3	*I4/mcm*	0.7878(4)	–	1.067(1)	[13]
<1260 °C [13]	Cr_5B_3		–		
Ce_2Si_{3-x}	*Cmcm*	0.44035	2.48389	0.39517	$x = 0.3$ [14]
	V_2B_3		–	–	–
$CeSi_5$	*Immm*	0.37774839	0.60189(4)	0.92979(6)	[15]
<827 °C	$LaGe_5$				High pressure phase; 10 GPa
Ce_2Si_7	*Cmmm*	0.70893(7)	0.99644(7)	0.44868(4)	[15]
<1127 °C	Ce_2Si_7				High pressure phase; 10 GPa
CeZn	$Pm\bar{3}m$	0.37059(2)	–	–	[12]
<825 [11]	CsCl				
$CeZn_2$	*Imma*	0.46393(8)	0.7544(1)	0.7506(1)	[12]
<875 [11]	$CeCu_2$				
$Ce(Zn_{1-x}Si_x)_2$		0.4583(3)	0.7568(5)	0.759(5)	$x_{max} = 0.18$[c] [This work]
$CeZn_3$	*Cmcm*	0.46324(5)	1.0452(1)	0.66557(6)	[12]
<820 [11]	$CeZn_3$				
Ce_3Zn_{11}	*Immm*	0.45242(2)	0.88942(3)	1.34754(4)	SC [12]
<840 [11]	La_3Al_{11}				
$Ce_{13}Zn_{58}$	$P6_3/mmc$	1.4638(1)	–	1.4158(1)	[23]
<870 [11]	$Gd_{13}Zn_{58}$	1.4616(1)	–	1.4173(1)	[12]
$CeZn_5$	*P6/mmm*	0.54082(1)	–	0.42798(1)	[12]
<885 [11]	$CaCu_5$				
$CeZn_{5+x}$					$0.09 \le x \le 0.29$ [24]
		0.54163(5)	–	0.42647(5)	$x = 0.09$
		0.54069	–	0.42757	$x = 0.29$
Ce_3Zn_{22}	$I4_1/amd$	0.897(1)	–	2.133(5)	[25]
<960 [11]	Ce_3Zn_{22}	0.8936(2)	–	2.1380(5)	SC [12]
β Ce_2Zn_{17}	$R\bar{3}m$	0.90916(4)	–	1.32861(1)	[12]
<980 [11]	Th_2Zn_{17}		–		
980–~750 [12]					
α Ce_2Zn_{17}	$P6_3/mmc$	0.9088(4)	–	0.8856(5)	[26]
	Th_2Ni_{17}				
α$Ce_{1-x}Zn_{5+2x}$	$P6_3/mmc$	0.52424(2)	–	0.44274(1)	$x = 0.33$ [12]
<~750 [12]	$TbCu_7$				
$CeZn_{11}$	$I4_1/amd$	1.06630(1)		0.686644(7)	[12]
<795 [11]	$BaCd_{11}$				
τ$_1$-$Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$	*Pbam*	1.55722(3)	1.71942(3)	0.44772(1)	$x = 0.28$ [This work] SC
	$Ce_7Zn_{21}(Zn_{1-x}Si_x)_2$	–			$(0.28 \le x \le 0.98)$ [This work]
τ$_2$-$Ce(Zn_{1-x}Si_x)_2$	*P6/mmm*	0.4223	–	0.4238	$x = 0.50$ [5]
	AlB_2	0.41827(2)	–	0.42747(2)	[This work] SC at $x = 0.56$
			–		$(0.36 \le x \le 0.76)$ [This work]
		0.41315(7)	–	0.4295(2)	$x = 0.36$ [This work]
		0.4421(2)		0.38960(3)	$x = 0.76$ [This work]
τ$_3$-$Ce(Zn_xSi_{1-x})$	Unknown	–	–	–	$(0.17 \le x \le 0.23)$
τ$_4$-$Ce_{40}Zn_{37}Si_{23}$	Unknown	–	–	–	at.%

[a] For the Ce–Zn compounds only data from our recent investigation [12] are listed essentially consistent with the literature data [27].
[b] Composition reported [13].
[c] x_{max} – maximum solubility at 800 °C [This work].