Electronic Supplementary Material (ESI) for RSC Advances.

The System Ce-Zn-Si for <33.3% at. Ce:

Phase Relations, Crystal Structures and Physical Properties

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Table S1. Crystallographic data of unary and binary boundary solid phases of the system Ce-Zn-Si.

Phase Temperature range (ºC)	Space group, Prototype	Lattice parameters (nm)			Comments
		a	b	c	
(δCe) 798-700 [1]	$Im\bar{3}m$ W	0.412	-	-	[1] -
(γCe) <726 [1]	$Fm\bar{3}m$ Cu	0.51610	-	-	[1]
(Zn) <420 [1]	$P6_3/mmc$	0.2665	-	0.4947	[1] -
(Si) <1414 [1]	$Fd\bar{3}m$ C (*Diamond*)	0.543110	-	-	[2]
$CeSi_2$ <1725 [3]	*Imma* α $GdSi_2$	0.4189(1) -	- -	0.4109(1)	$Ce_{37.4}Si_{62.6}$ [3]
$CeSi_2$ ~1575 [3] $Ce(Zn_xSi_{1-x})_2$	$I4_1/amd$ *O*2 α $ThSi_2$	0.4192(1) 0.4201(1) 0.42029(6)	- -	1.3913(5) 1.4312(7) 1.4258(4)	$Ce_{33.3}Si_{66.7}$ [3] x_{max}=0.32 at 800°C [4] x_{max}=0.30, at 600°C [this work]
CeSi <1630 [3]	*Pnma* FeB	0.8298(4) -	- -	0.3961(2)	$Ce_{49.9}Si_{50.1}$ [3]
Ce_5Si_4 <1500 [3]	$P4_12_12$ Zr_5Si_4	0.7936(1)	-	1.5029(5)	$Ce_{55.6}Si_{44.4}$ [3]
Ce_3Si_2 <1335 [3]	*P4/mbm* U_3Si_2	0.7780(6)	-	0.4367(6)	[3]
Ce_5Si_3 <1260 [3]	I4/mcm Cr_5B_3	0.7878(4)	-	1.067(1)	[3]
Ce_2Si_{3-x}	*Cmcm* V_2B_3	0.44035	2.48389	0.39517	x=0.3 [5]
$CeSi_5$ <827	*Immm* *$LaGe_5$*	0.37774839	0.60189(4)	0.92979(6)	[6] high pressure phase; 10GPa
Ce_2Si_7 <1127	*Cmmm* *Ce_2Si_7*	0.70893(7)	0.99644(7)	0.44868(4)	[6] high pressure phase; 10GPa
CeZn <825 [1]	$Pm\bar{3}m$ CsCl	0.3704(1) 0.37059(2)	- -	- -	[7] [8]
$CeZn_2$ <875 [1] $Ce(Zn_{1-x}Si_x)_2$	*Imma* $CeCu_2$	0.46393(8) 0.4583(3) 0.46417(6)	0.7544(1) 0.7568(5) 0.7596(7)	0.7506(1) 0.759(5) 0.7508(1)	[8] x_{max}=0.18 [4] x=0.05 at 600°C [this work]
$CeZn_3$ <820 [1]	*Cmcm* $CeZn_3$	0.4620(5) 0.46324(5)	1.0440(5) 1.0452(1)	0.6640(5) 0.66557(6)	[7] [8]
Ce_3Zn_{11} <840 [1]	*Immm* La_3Al_{11}	0.45215 0.45242(2)	0.88855 0.88942(3)	1.3463 1.34754(4)	[7] SC [8]
$Ce_{13}Zn_{58}$ <870 [1]	$P6_3/mmc$ $Gd_{13}Zn_{58}$	1.4638(1) 1.4616(1)	- -	1.4158(1) 1.4173(1)	[9] [8]
$CeZn_5$ <885 [1] $CeZn_{5+y}$	*P6/mmm* $CaCu_5$	0.54163(5) 0.54082(1) 0.54163(5)	- - -	0.42647(5) 0.42798(1) 0.42647(5)	[7] [8] 0.017≤y≤0.046 <885°C [10]
Ce_3Zn_{22} <960 [1]	$I4_1/amd$ Ce_3Zn_{22}	0.897(1) 0.8936(2)	- -	2.133(5) 2.1380(5)	[11] SC [8]
β Ce_2Zn_{17} <980 [1] 980-~750 [8]	$R\bar{3}m$ Th_2Zn_{17}	0.9090(5) 0.90916(4)	- - -	1.32844(7) 1.32861(1)	[7] [8]
α Ce_2Zn_{17} α$Ce_{1+x}Zn_{5+2x}$ <~750 [8]	$P6_3/mmc$ $TbCu_7$	0.9088(4) 0.52424(2)	- - -	0.8856(5) 0.44274(1)	[12] x=0.33 [8]
$CeZn_{11}$ <795 [1]	$I4_1/amd$ $BaCd_{11}$	1.0658(6) 1.06630(1)	-	0.6862(8) 0.686644(7)	[13] [8]

Table S2. Interatomic distances (<0.421 nm) in τ_5-$CeZn(Zn_{1-x}Si_x)_2$, x = 0.71 and τ_6-$CeZn_2(Si_{1-x}Zn_x)_2$, x = 0.30).

τ_5-$CeZn(Zn_{1-x}Si_x)_2$, x = 0.71						τ_6-$CeZn_2(Si_{1-x}Zn_x)_2$, x = 0.30		
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ce	M1 (2x)	0.31726		Ce (2x)	0.31726	Ce	M (8x)	0.31901
CN=21	M1 (4x)	0.31916		Ce (4x)	0.31916	CN=22	Zn1 (8x)	0.33555
	M2 (4x)	0.31940	M2	M1 (1x)	0.23975		M (2x)[a]	(0.40460)
	Zn3 (2x)	0.33470	CN=9	Zn3 (2x)	0.25263		Ce (4x)[a]	(0.41757)
	Zn3 (2x)	0.33714		Zn3 (2x)	0.25381	Zn1	M (4x)	0.25245
	M2 (1x)[a]	(0.40539)		Ce (4x)	0.31940	CN=12	Zn1 (4x)	0.29527
	Ce (2x)[a]	(0.41324)	Zn3	M2 (2x)	0.25263		Ce (4x)	0.33555
	Ce (2x)[a]	(0.41619)	CN=16	M2 (2x)	0.25381	M	M (1x)	0.24152
	Ce (2x)[a]	(0.42079)		Zn3 (4x)	0.29592	CN=9	Zn1 (4x)	0.25245
M1	M1 (2x)	0.23917		Ce (2x)	0.33470		Ce (4x)	0.31901
CN=9	M2 (1x)	0.23975		Ce (2x)	0.33714			

[a] Contribution of these atoms to the Dirichlet domain is less than 2%, which indicates rather weak bonding.

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