Intermetallic *RE*PtZn Compounds with TiNiSi-type Structure

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The equiatomic rare earth compounds *RE*PtZn (*RE* = Y, Pr, Nd, Gd–Tm) were synthesized from the elements in sealed tantalum tubes by high-frequency melting at 1500 K followed by annealing at 1120 K and quenching. The samples were characterized by powder X-ray diffraction. The structures of four crystals were refined from single-crystal diffractometer data: TiNiSi type, *Pnma*, a = 707.1(1), b = 430.0(1), c = 812.4(1) pm, $wR2$ = 0.066, 602 F^2, 21 variables for $PrPt_{1.056}Zn_{0.944}$; a = 695.2(1), b = 419.9(1), c = 804.8(1) pm, $wR2$ = 0.041, 522 F^2, 21 variables for $GdPt_{0.941}Zn_{1.059}$; a = 688.2(1), b = 408.1(1), c = 812.5(1) pm, $wR2$ = 0.041, 497 F^2, 22 variables for $HoPt_{1.055}Zn_{0.945}$; a = 686.9(1), b = 407.8(1), c = 810.4(1) pm, $wR2$ = 0.061, 779 F^2, 20 variables for ErPtZn. The single-crystal data indicate small homogeneity ranges $REPt_{1\pm x}Zn_{1\pm x}$. The platinum and zinc atoms build up three-dimensional [PtZn] networks (265 – 269 pm Pt–Zn in ErPtZn) in which the erbium atoms fill cages with coordination number 16 (6 Pt + 6 Zn + 4 Er). Bonding of the erbium atoms to the [PtZn] network proceeds *via* shorter *RE*–Pt distances, *i. e.* 288 – 293 pm in ErPtZn.

Key words: Intermetallics, Rare Earth Compounds, Crystal Structure

Introduction

A huge number of equiatomic intermetallic *RETX* compounds (*RE* = rare earth metal, *T* = transition metal, *X* = element of the 3rd, 4th, or 5th main group) has been synthesized and structurally characterized in the last forty years. The basic crystallographic data of the phases are compiled in the Pearson data base [1]. Most of these phases crystallize with the hexagonal ZrNiAl [2 – 4] or orthorhombic TiNiSi [5] structure types. The size of the *T* and *X* atoms and the valence electron concentration have an important influence on the structure and physical properties of the compounds [6].

The *T* and *X* atoms build up three-dimensional [*TX*] polyanionic networks with substantial covalent *T*–*X* bonding. This has been manifested by electronic structure calculations for diverse representatives of both structure types [7 – 9, and refs. cited therein]. Recent investigations on related equiatomic compounds have shown that the *X* positions within the covalently bonded networks can be substituted by magnesium [10], cadmium [11, 12], and even zinc [11, 13]. The resulting compounds show covalent *T*–Mg, *T*–Cd, and *T*–Zn bonding within the [*TX*] networks [14]. Substitution of the *X* position by divalent magnesium, cadmium or zinc leads to a decrease of the valence electron concentration, and one can effectively modify the physical properties while keeping the crystal structure. To give an example, in going from EuAuGe [15] *via* EuAuIn [16] to EuAuZn [13], the magnetic ordering temperature changes from 34 *via* 21 to 51 K.

Of the compounds with divalent magnesium, cadmium and zinc, the zinc-containing compounds have only scarcely been studied. Few intermetallic compounds *RE*NiZn and *RE*PdZn [11, 17 – 19] with ZrNiAl-type structure as well as some KHg_2 / TiNiSi-type compounds with copper, silver and gold as transition metal component [20, 21] have been reported. The first investigations of the properties of such materials showed interesting magnetic behavior. CeNiZn [18] is an intermediate-valent cerium compound, EuAuZn [13] orders ferromagnetically at the comparatively high Curie temperature of 51.1 K, and YbPtZn [22] shows an onset of a heavy fermion state which orders magnetically at 1.35 K. CePtZn [23, 24] is a dense Kondo system, and its antiferromagnetic ordering has been detected at T_N = 1.7 K. SmPtZn [25] shows a comparatively high Curie temperature of 48 K. The Laves phase $EuRh_{1.2}Zn_{0.8}$ [26] orders ferromagnetically at 95 K, and magnetocaloric investigations have shown that $EuRh_{1.2}Zn_{0.8}$ has a quite high normal-

Table 1. Lattice parameters of the equiatomic *RE*PtZn (*RE* = Y, La–Nd, Sm–Lu) compounds.

Compound	*a* (pm)	*b* (pm)	*c* (pm)	*V* (nm^3)	Ref.
YPtZn	695.0(2)	414.0(1)	813.3(1)	0.2340	This work
LaPtZn	719.2(2)	438.4(1)	816.0(3)	0.2568	[24]
CePtZn	707.4(2)	436.0(1)	810.4(1)	0.2499	[24]
CePtZn	706.89(19)	435.08(15)	809.71(16)	0.2490	[23]
PrPtZn	707.2(2)	430.4(1)	810.8(3)	0.2467	This work
$PrPt_{1.056}Zn_{0.944}$[a]	707.1(1)	430.0(1)	812.4(1)	0.2470	This work
NdPtZn	703.7(2)	428.1(1)	812.1(1)	0.2447	This work
SmPtZn	701.5(2)	422.0(1)	811.1(3)	0.2401	[25]
EuPtZn	727.8(3)	443.7(1)	781.7(3)	0.2524	[13]
GdPtZn	696.9(3)	418.8(1)	809.1(4)	0.2362	This work
$GdPt_{0.941}Zn_{1.059}$[a]	695.2(1)	419.9(1)	804.8(1)	0.2349	This work
TbPtZn	695.9(2)	414.7(1)	812.7(2)	0.2345	This work
DyPtZn	691.52(9)	411.21(7)	811.9(2)	0.2309	This work
HoPtZn	688.4(2)	408.4(1)	811.4(2)	0.2281	This work
$HoPt_{1.055}Zn_{0.945}$[a]	688.2(1)	408.1(1)	812.5(1)	0.2282	This work
ErPtZn	687.0(2)	407.9(2)	811.1(3)	0.2273	This work
ErPtZn[a]	686.9(1)	407.8(1)	810.4(1)	0.2270	This work
TmPtZn	687.2(2)	406.0(1)	809.6(3)	0.2259	This work
YbPtZn	684.2(1)	405.7(1)	810.3(1)	0.2249	[22]
LuPtZn	681.6(2)	402.0(1)	812.9(2)	0.2227	[22]

[a] Single crystal data.

ized relative cooling power of 103 J K^{-1}T^{-1} for ΔH = 5 T, classifying it as an interesting material for cooling applications.

In continuation of our phase analytical studies on the *RE*AuZn series [13, 21] we have now investigated the corresponding platinum-based compounds. The synthesis protocols and the complete structural characterization of the equiatomic *RE*PtZn (*RE* = Y, Pr, Nd, Gd–Tm) compounds are reported herein.

Experimental Section

Synthesis

Starting materials for the preparation of the *RE*PtZn (*RE* = Y, Pr, Nd, Gd–Tm) samples were ingots of the rare earth elements (Johnson Matthey, smart elements, or Kelpin), platinum powder (Degussa-Hüls), and zinc granules (Merck), all with stated purities better than 99.9 %. The rare earth metal ingots were cut into smaller pieces and arc-melted [27] to buttons under an argon atmosphere of *ca.* 800 mbar. The argon was purified before with molecular sieves, silica gel, and titanium sponge (900 K). Subsequently, the rare earth buttons, the platinum powder and the pieces of the zinc granules (1 : 1 : 1 atomic ratio) were sealed in tantalum tubes under an argon pressure of 800 mbar. The tubes were then placed in a water-cooled sample chamber of a high-frequency furnace (Hüttinger Elektronik, Freiburg, Germany, Typ TIG 2.5/300) under flowing argon [28], heated up to 1500 K for about 5 min and then annealed at 1120 K for another 4 h, followed by quenching. The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of ±30 K. The samples did not react with the tantalum tube. The gray polycrystalline *RE*PtZn samples are stable in air over months.

EDX data

Semiquantitative EDX analyses on the crystals investigated on the diffractometer and on the bulk samples were carried out by use of a Zeiss EVO® MA10 scanning electron microscope in variable pressure mode with the rare earth trifluorides, platinum and zinc as standards. The bulk samples were previously embedded in a methylmetacrylate matrix, and the surface was polished with diamond and silica paste. The surface remained unetched for the EDX measurements. The experimentally observed compositions were close to the ideal ones. No impurity elements heavier than sodium (detection limit of the instrument) were found.

X-Ray diffraction

The *RE*PtZn samples were characterized by Guinier patterns (imaging plate detector, Fuji-film BAS-1800 readout system) with Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30 and c = 540.46 pm) as the internal standard. The orthorhombic lattice parameters (Table 1) were refined by a least-squares routine. Proper indexing was ensured through intensity calculations [29].

Small irregularly shaped single crystals of *RE*PtZn (*RE* = Pr, Gd, Ho, Er) were isolated from the crushed samples. They were glued to quartz fibers and investigated on a Buerger precession camera (white Mo radiation, Fuji-film imaging plate) in order to check the quality for intensity data collection. The data sets were collected at room temperature by use of two four-circle diffractometers (CAD4) with graphite-monochromatized MoK_α (AgK_α) radiation and a scintilla-

Table 2. Crystallographic data and structure refinements of *RE*PtZn (*RE* = Pr, Gd, Ho, Er) with space group *Pnma*, $Z = 4$.

Refined composition	$PrPt_{1.056}Zn_{0.944}$	$GdPt_{0.941}Zn_{1.059}$	$HoPt_{1.055}Zn_{0.945}$	ErPtZn
Molar mass, g mol^{-1}	408.50	409.93	432.52	427.72
Crystal size, μm^3	$20 \times 30 \times 40$	$20 \times 25 \times 50$	$20 \times 35 \times 50$	$20 \times 40 \times 50$
Lattice parameters	Table 1	Table 1	Table 1	Table 1
Calculated density, g cm^{-3}	11.00	11.53	12.59	12.50
Radiation	MoK_α	AgK_α	AgK_α	MoK_α
λ, pm	71.073	56.086	56.086	71.073
Absorption coeff., mm^{-1}	87.8	50.4	58.3	108.0
Transm. ratio, max / min	0.309 / 0.221	0.267 / 0.236	0.302 / 0.180	0.517 / 0.211
F(000), e	679	676	711	704
θ-range, deg.	3 – 35	3 – 26	3 – 26	3 – 40
Range in *hkl*	± 11, ± 6, ± 13	± 10, ± 6, ± 12	± 10, ± 6, ± 12	± 12, ± 7, ± 14
Total no. reflections	4079	3508	5053	5344
Independent reflections / R_{int}	602 / 0.122	522 / 0.068	497 / 0.101	779 / 0.095
Reflections with $I \geq 2\sigma(I)$ / R_σ	518 / 0.052	439 / 0.035	414 / 0.039	628 / 0.042
Data / ref. parameters	602 / 21	522 / 21	497 / 22	779 / 20
Goodness-of-fit on F^2	1.158	1.065	1.143	1.071
$R1$ / $wR2$ for $I \geq 2\sigma(I)$	0.031 / 0.063	0.026 / 0.039	0.022 / 0.038	0.027 / 0.057
$R1$ / $wR2$ for all data	0.040 / 0.066	0.040 / 0.041	0.034 / 0.041	0.040 / 0.061
Extinction coefficient	0.0023(3)	0.0050(3)	0.0104(4)	0.0043(3)
Largest diff. peak / hole, e Å^{-3}	3.42 / −4.81	2.36 / −3.11	2.26 / −2.31	3.47 / −4.15

Table 3. Atomic coordinates and anisotropic displacement parameters (pm^2) for *RE*PtZn (*RE* = Pr, Gd, Ho, Er). All atoms lie on Wyckoff sites 4*c* (*x* 1/4 *z*). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. $U_{12} = U_{23} = 0$.

Atom	*x*	*z*	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
$PrPt_{1.056(5)}Zn_{0.944(5)}$							
Pr	0.03090(8)	0.69141(7)	72(3)	100(3)	95(2)	−7(2)	89(1)
Pt	0.26488(6)	0.38785(5)	80(2)	89(2)	118(2)	18(1)	96(1)
0.944(5) Zn + 0.056(5) Pt	0.64969(17)	0.43158(14)	156(6)	106(6)	93(6)	−27(4)	118(4)
$GdPt_{0.941(5)}Zn_{1.059(5)}$							
Gd	0.03479(8)	0.68823(7)	90(2)	108(2)	106(2)	−6(2)	101(2)
0.941(5) Pt + 0.059(5) Zn	0.25936(6)	0.38357(5)	88(2)	90(2)	105(2)	8(2)	94(1)
Zn	0.64377(18)	0.43485(17)	132(6)	102(5)	97(5)	−9(4)	111(3)
$HoPt_{1.055(5)}Zn_{0.945(5)}$							
Ho	0.04194(6)	0.68525(7)	31(2)	89(2)	70(2)	−5(2)	63(1)
0.983(5) Pt + 0.017(5) Zn	0.25193(5)	0.37774(6)	42(2)	79(2)	96(2)	14(1)	73(1)
0.927(4) Zn + 0.073(4) Pt	0.63836(14)	0.43577(15)	88(5)	97(5)	71(6)	−11(4)	85(4)
ErPtZn							
Er	0.04238(6)	0.68441(5)	62(1)	64(1)	72(1)	−4(1)	66(1)
Pt	0.25150(5)	0.37723(4)	67(1)	55(1)	77(1)	4(1)	66(1)
Zn	0.63627(17)	0.43711(14)	86(4)	64(4)	68(4)	−4(3)	73(2)

tion counter with pulse height discrimination. Scans were taken in the $\omega/2\theta$ mode. Empirical absorption corrections were applied on the basis of ψ-scan data, accompanied by spherical absorption corrections. Details on the crystallographic data are given in Table 2.

Structure refinements

The four diffractometer data sets showed primitive orthorhombic lattices, and the extinction conditions were compatible with space group *Pnma*, in agreement with our previous results on CePtZn [23] and EuPtZn [13]. The atomic parameters of the europium compound were taken as starting values, and the four structures were refined using SHELXL-97 [30] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all sites. The occupancy parameters were refined in separate series of least-squares cycles in order to check for deviations from the ideal composition. Only for ErPtZn all sites were fully occupied within two standard deviations. Similar to the series of *RE*AuZn compounds [21], for the remaining three crystals we also observed small degrees of Pt/Zn mixing, which led to the refined compositions listed in Table 2. In the final cycles these mixed occupancies were refined as least-squares variables. The refined positional parameters and interatomic distances (exemplarily for ErPtZn) are listed in Tables 3 and 4.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe,

Table 4. Interatomic distances (pm) in the structure of ErPtZn. All distances within the first coordination shells are listed. Standard deviations are all equal or smaller than 0.2 pm.

Er:	1 Pt	287.6	Pt:	2 Zn	265.0
	2 Pt	291.3		1 Zn	267.0
	2 Pt	293.4		1 Zn	268.8
	1 Zn	313.7		1 Er	287.6
	2 Zn	314.1		2 Er	291.3
	2 Zn	316.3		2 Er	293.4
	1 Zn	343.6	Zn:	2 Pt	265.0
	2 Er	359.6		1 Pt	267.0
	2 Er	366.7		1 Pt	268.8
				2 Zn	295.1
				1 Er	313.7
				2 Er	314.1
				2 Er	316.3
				1 Er	343.6

76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-423114 ($PrPt_{1.056}Zn_{0.944}$), CSD-423117 ($GdPt_{0.941}Zn_{1.059}$), CSD-423116 ($HoPt_{1.055}Zn_{0.945}$), and CSD-423115 (ErPtZn).

Discussion

The series of equiatomic *RE*PtZn intermetallics has been completely characterized on the basis of powder X-ray diffraction data. The members with *RE* = Y, Pr, Nd, and Gd–Tm have been synthesized for the first time. These *RE*PtZn compounds were prepared at high temperatures, *i. e.* 900 [13], 920 [23], 1070 [22, 24, 25], and 1120 (this work) K, followed by quenching. These samples all crystallize with the orthorhombic TiNiSi-type [5] structure. With the exception of EuPtZn [13], the cell volumes decrease from the lanthanum to the lutetium compound as expected from the lanthanoid contraction. Due to the presence of divalent europium atoms, EuPtZn shows a positive deviation from this smooth curve (Fig. 1). The cell volume of YPtZn fits in between TbPtZn and DyPtZn. Similar to the series of *RE*AuZn compounds [21], we obtained no *RE*PtZn representative with scandium.

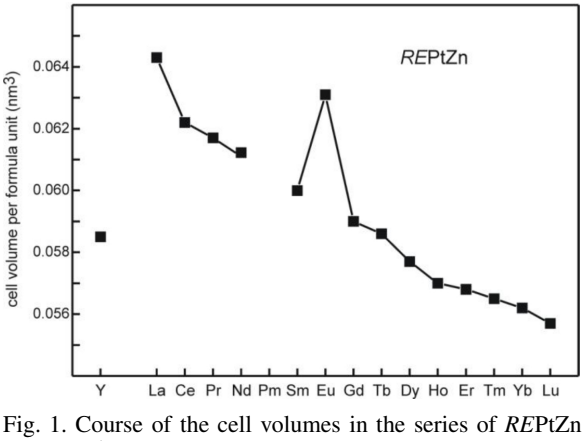

Fig. 1. Course of the cell volumes in the series of *RE*PtZn compounds.

Annealing of the *RE*PtZn samples towards lower temperatures (from 1070 K to r. t. at a rate of 2 K h^{-1}) leads to hexagonal phases with ZrNiAl-type structure. However, there are distinct differences when compared with the *RE*PdZn series [11, 13, 19]. For the *RE*PtZn samples we observed distinct deviations from the ideal 1 : 1 : 1 composition either through platinum vacancies or strong Pt/Zn mixing. Detailed studies on these low-temperature phases are in progress.

Quenching of the *RE*PtZn samples from high temperature might induce structural disorder. This is readily understandable for the TiNiSi type (space group *Pnma*), which is an ordered ternary version of KHg_2 (space group *Imma*) [31]. Full platinum-zinc ordering has only been observed for the ErPtZn crystal. All other investigated crystals showed small homogeneity ranges, for $HoPt_{1.055(5)}Zn_{0.945(5)}$ even both 4*c* sites were refined with mixed occupancies. Thus, small homogeneity ranges can be expected for all *RE*PtZn samples. The mixing observed here for the $REPt_{1\pm x}Zn_{1\pm x}$ samples is slightly smaller than for the $REAu_{1\pm x}Zn_{1\pm x}$ compounds [21]. The lattice parameters of the single crystals and of the bulk powders agree well (Table 1). The Pt/Zn mixing has only little influence.

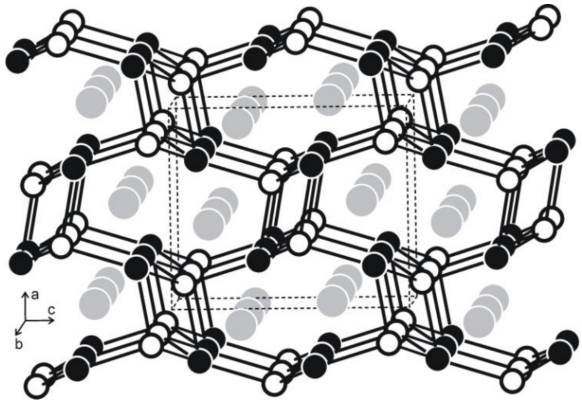

Fig. 2. View of the ErPtZn structure approximately along the *b* axis. Erbium, platinum, and zinc atoms are drawn as medium grey, black filled and open circles, respectively. The three-dimensional [PtZn] network is emphasized.

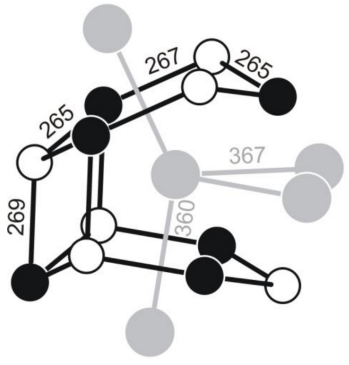

Fig. 3. Near-neighbor coordination of the erbium atoms in ErPtZn. Erbium, platinum, and zinc atoms are drawn as medium grey, black filled and open circles, respectively. The puckered Pt_3Zn_3 hexagons are emphasized, and relevant interatomic distances are indicated.

As an example for the *RE*PtZn series we discuss the ErPtZn structure, where no mixing was observed. In Fig. 2 we present a view of the ErPtZn structure approximately along the *b* axis. The platinum and zinc atoms build up a three-dimensional [PtZn] network with Pt–Zn distances ranging from 265 to 269 pm, slightly longer than the sum of the covalent radii [32] of 254 pm. Within the network the platinum atoms have distorted tetrahedral zinc coordination and *vice versa*. These $PtZn_{4/4}$, respectively $ZnPt_{4/4}$ tetrahedra share common corners within the network.

The TiNiSi-type structure of ErPtZn derives from the well known AlB_2 structure. The erbium atoms take the aluminum position, and the platinum and zinc atoms order on the boron network. The resulting Pt_3Zn_3 hexagons are strongly puckered, leading to the erbium coordination shown in Fig. 3. The platinum atoms are the nearest neighbors to erbium. The five short Er–Pt distances range from 288 to 293 pm, close to the sum of the covalent radii of 286 pm [32]. The puckering of the Pt_3Zn_3 hexagons leads to interlayer Pt–Zn distances of 269 pm. Between the layers we observe formation of Pt_2Zn_2 rhombs in a ladder-type arrangement. The platinum atoms as the most electronegative components of ErPtZn show a maximum distance (401 pm) within these rhombs. By contrast, we observe somewhat shorter Zn–Zn distances of 295 pm, which compare with the longer Zn–Zn distances in *hcp* zinc (6×266 and 6×291 pm) [33]. Each erbium atom has four nearest erbium neighbors at 360 (2×) and 367 (2×) pm, only slightly longer than in *hcp* erbium (6×356 and 6×347 pm) [33].

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