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Zinc-lead ordering in equiatomic rare earth plumbides $REZnPb$ ($RE = La-Nd$ and $Sm-Tb$)

<https://doi.org/10.1515/znb-2018-0256>

Received December 6, 2018; accepted December 14, 2018

Abstract: The plumbides $REZnPb$ (RE =rare earth metals La–Nd and Sm–Tb) were synthesized by induction melting of the elements in sealed niobium ampoules. The samples were characterized by X-ray powder diffraction. The structures of the praseodymium and neodymium compound were refined from single-crystal X-ray diffractometer data: YPtAs type, $P6_3/mmc$, $a = 461.32(8)$, $c = 1658.00(3)$ pm, $wR2 = 0.0588$, 267 F^2 values, 12 variables for PrZnPb and $a = 460.12(3)$, $c = 1642.7(1)$, $wR2 = 0.0617$, 243 F^2 values, 12 variables for NdZnPb. The plumbides with $RE = La, Ce, Sm, Gd$ and Tb are isotypic while the Zintl phase EuZnPb crystallizes with the orthorhombic TiNiSi type, $Pnma$, $a = 796.6(2)$, $b = 482.53(9)$, $c = 822.9(2)$ pm. The zinc and lead atoms build up polyanionic networks: slightly puckered Zn_3Pb_3 layers in AA'BB' stacking sequence in the YPtAs type plumbides and a three-dimensional $[ZnPb]^{2-}$ network with distorted tetrahedral $ZnPb_{4/4}$ coordination in EuZnSn. The different crystal structures are a consequence of the valence electron count, i.e. 18 for EuZnSn and 19 for the hexagonal plumbides. The crystal chemical details and bonding peculiarities are discussed.

Keywords: crystal structure; intermetallics; plumbide; rare earth compounds.

1 Introduction

Of the rare earth (RE)-transition metal (T)-tetrel (tr) systems [1–9], those with lead have only scarcely been investigated. Although, meanwhile more than 240 $RE_xT_yPb_z$ plumbides are known [10–12] only few isothermal sections have completely been studied with respect to phase formation. Data have been published for the $RE-Ni-Pb$ systems with $RE = Y, La, Ce, Sm, Gd$ and Dy [13–18], the

$RE-Cu-Pb$ systems with $RE = Y, La, Ce, Nd, Sm, Gd$ and Dy [16, 17, 19], $La-Zn-Pb$ and $Tb-Zn-Pb$ [20].

The zinc containing systems comprise so far only 19 compounds, i.e. the series of zinc-rich phases $RE_7Zn_{21}Pb_2$ [21] und RE_2Zn_5Pb [22] both with $RE = La, Ce, Pr$, and Nd that both contain isolated lead atoms, La_5ZnPb_3 with Hf_5CuSn_3 type [23], the Cu_3Au type phase $LaZnPb_2$ [20], the solid solutions $La_{5.16}Zn_{1.4}Pb_{1.4}$ [20] and $La_{5.26}Zn_{0.4}Pb_{2.6}$ [24] which are derived from the Mo_5SiB_2 and Nb_5Sn_2Si types, $LaZn_{1.78}Pb_{0.22}$ with a disordered AlB_2 type [20] and the zinc-poor phase $\sim Tb_{10}ZnPb_9$ with a so far unknown structure [20].

In the present contribution we focus on the equiatomic plumbides $REZnPb$. The large and famous family of equiatomic $RETr$ tetrelides has intensively been studied since these compounds are interesting model systems for detailed investigations of the various magnetic ground states of the respective rare earth cation [25, 26]. For the $REZnPb$ series, so far, structural data have only been reported for $LaZnPb$ [20], $CeZnPb$ [27], $NdZnPb$ [28], $EuZnPb$ [29], and $YbZnPb$ [29]. While the $CeZnPb$ structure was refined from single crystal X-ray diffractometer data, the remaining plumbides were characterized on the basis of X-ray powder data. The YPtAs and LiGaGe types were correctly assigned to $LaZnPb$ [20], respectively $YbZnPb$ [29], while $NdZnPb$ [28] and $EuZnPb$ [29] were described with the $CaIn_2$, respectively KHg_2 types, with Zn/Pb statistics. Keeping the substantially different chemical potentials of lead and zinc in mind, complete Zn/Pb disorder is questionable. Herein we present the synthesis of the complete series of $REZnPb$ plumbides and report on the Zn/Pb ordering within the two-, respectively three-dimensional $[ZnPb]$ substructures.

2 Experimental

2.1 Synthesis

Starting materials for the syntheses of the $REZnPb$ plumbides were pieces of the rare earth elements (Smart Elements, >99.9%), zinc granules (Merck, >99.9%) and lead granules (ABCR, >99.5%). The moisture sensitive rare earth ingots were cut into smaller pieces under dry paraffin

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Table 1: Lattice parameters (Guinier powder data) of the equiatomic plumbides REZnPb (standard deviations in parentheses).

Compound	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	<i>V</i> (nm ³)	Space group	Reference
LaZnPb	466.4(1)	<i>a</i>	1699.2(4)	0.3201	<i>P</i> 6 ₃ / <i>mmc</i>	This work
LaZnPb	464.92(2)	<i>a</i>	1701.1(1)	0.3184	<i>P</i> 6 ₃ / <i>mmc</i>	[20]
CeZnPb	463.2(2)	<i>a</i>	1666.4(6)	0.3096	<i>P</i> 6 ₃ / <i>mmc</i>	This work
CeZnPb	463.7(2)	<i>a</i>	1669.6(6)	0.3109	<i>P</i> 6 ₃ / <i>mmc</i>	[27]
PrZnPb	461.6(1)	<i>a</i>	1653.1(3)	0.3050	<i>P</i> 6 ₃ / <i>mmc</i>	This work
NdZnPb	459.9(1)	<i>a</i>	1640.8(3)	0.3005	<i>P</i> 6 ₃ / <i>mmc</i>	This work
NdZnPb	458.8(2)	<i>a</i>	817.9(5)	0.1491	<i>P</i> 6 ₃ / <i>mmc</i>	[28]
SmZnPb	458.1(1)	<i>a</i>	1623.8(5)	0.2951	<i>P</i> 6 ₃ / <i>mmc</i>	This work
EuZnPb ^a	482.53(9)	796.6(2)	822.9(2)	0.3163	<i>Pmcn</i>	This work
EuZnPb	482.7(1)	796.8(2)	823.7(2)	0.3168	<i>Imma</i>	[29]
GdZnPb	455.1(1)	<i>a</i>	1604.2(3)	0.2877	<i>P</i> 6 ₃ / <i>mmc</i>	This work
TbZnPb	453.3(2)	<i>a</i>	1592.6(7)	0.2834	<i>P</i> 6 ₃ / <i>mmc</i>	This work

^aThe EuZnPb unit cell is listed in the non-standard setting *Pmcn* in order to facilitate comparison with the older literature data.

oil, repeatedly washed with dry cyclohexane and kept in Schlenk tubes prior to the reactions. Due to the low boiling temperatures of lead ($T=2013$ K) and zinc ($T=1180$ K) [30], the reactions were carried out in sealed tubes. Pieces of the three elements were weighed in the ideal atomic ratio of 1:1:1 and arc-welded [31] in niobium ampoules under an argon pressure of about 700 mbar. The argon gas was purified over silica gel, molecular sieves and titanium sponge at 870 K prior to use. The ampoules were placed in the water-cooled sample chamber of an induction furnace (type TIG 1.5/300, Hüttinger Elektronik, Freiburg) [32] and first heated rapidly to 1373 K and kept at this temperature for 5 min, followed by a decrease to 823 K. The last two steps were repeated three times and the samples were finally annealed at 823 K for 3 h. At the end the samples were quenched by switching off the power supply. The brittle polycrystalline samples are light grey and moisture sensitive. They rapidly deteriorate in moist air. The REZnPb plumbides were therefore kept in Schlenk tubes under dry argon prior to further investigations.

REZnPb samples have been obtained with $RE = \text{La-Nd}$ and Sm-Tb . Already the terbium sample showed impurity phases and attempts to synthesize compounds with the high-frequency melting technique for $RE = \text{Y, Dy and Lu}$ gave no hint for the existence of an equiatomic phase.

2.2 X-ray diffraction

The polycrystalline REZnPb samples were characterized by X-ray powder diffraction using the Guinier technique (Enraf-Nonius FR552 camera, imaging plate detector, Fujifilm BAS-1800) with $\text{CuK}\alpha_1$ radiation and α -quartz ($a=491.30$, $c=540.46$ pm) as an internal standard. The

lattice parameters (Table 1) were obtained from standard least-squares refinements. The experimental patterns were compared to calculated ones [33] to ensure correct indexing.

Small irregularly shaped single crystals were selected from the carefully crushed samples of PrZnPb and NdZnPb. The crystals were glued to glass fibres with bees

Table 2: Single crystal and structure refinement data for PrZnPb and NdZnPb; YPtAs type, space group *P*6₃/*mmc*, $Z=4$ and $T=293$ K.

Empirical formula	PrZnPb	NdZnPb
Formula weight, g mol ⁻¹	413.5	416.8
Unit cell dimension (single crystal data)		
<i>a</i> , pm	461.32(8)	460.12(3)
<i>c</i> , pm	1658.00(3)	1642.7(1)
Cell volume, nm ³	0.3056	0.3012
Calculated density, g cm ⁻³	8.99	9.19
Crystal size, μm^3	20×30×60	30×40×60
Diffractometer	IPDS II	Venture D8
Radiation	MoK α	MoK α
Transmission min/max	0.528/0.537	0.476/0.746
Detector distance, mm	70	40
Exposure time, s	1200	55
Absorption coefficient, mm ⁻¹	78.1	80.3
<i>F</i> (000), <i>e</i>	684	688
θ range, deg	5.1–33.3	2.48–32.1
Range in <i>hkl</i>	±7, ±7, ±25	±6, ±6, ±24
Total no. of reflections	3443	4557
Independent reflections/ R_{int}	267/0.0432	243/0.0301
Reflections with $I \geq 2 < \sigma(I)/R_o$	183/0.0136	222/0.0112
Data/parameters	267/12	243/12
Goodness-of-fit on F^2	1.74	2.25
$R1/wR2$ for $I \geq 2 < \sigma(I)$	0.0264/0.0554	0.0211/0.0604
$R1/wR2$ for all data	0.0448/0.0588	0.0251/0.0617
Extinction coefficient	98(14)	103(18)
Largest diff. peak/hole, $e \text{ \AA}^{-3}$	4.35/−3.60	2.22/−1.87

Table 3: Atomic coordinates and displacement parameters (pm^2) for $PrZnPb$ and $NdZnPb$: YPTAs type, space group $P6_3/mmc$.

Atom	Wyckoff position	x	y	z	U_{11}	U_{33}	U_{12}	U_{eq}
PrZnPb								
Pr1	2a	0	0	0	108(4)	109(4)	54(2)	109(3)
Pr2	2b	0	0	1/4	127(4)	99(4)	63(3)	118(3)
Zn	4f	1/3	2/3	0.16046(16)	126(5)	281(11)	63(3)	178(5)
Pb	4f	1/3	2/3	0.61387(4)	94(2)	123(3)	47(1)	104(2)
NdZnPb								
Nd1	2a	0	0	0	86(3)	93(4)	43(2)	88(2)
Nd2	2b	0	0	1/4	78(3)	84(4)	39(1)	80(2)
Zn	4f	1/3	2/3	0.16004(12)	111(4)	216(7)	55(2)	146(4)
Pb	4f	1/3	2/3	0.61326(2)	76(2)	105(3)	38(1)	86(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. $U_{11} = U_{22}$ and $U_{13} = U_{23} = 0$.

wax and additionally coated with a Paratone-N® film as moisture protection. They were first studied by Laue photographs on a Buerger camera (using white Mo radiation) to check their quality. Intensity data sets were collected on an IPDS-II (STOE) and a Venture D8 (Bruker) diffractometer at room temperature. Numerical absorption corrections were applied to both data sets. Details about the data collections and the crystallographic parameters are summarized in Table 2.

2.3 Structure refinements

The $PrZnPb$ and $NdZnPb$ data sets showed hexagonal lattices with high Laue symmetry and the systematic extinctions were compatible with space group $P6_3/mmc$, in agreement with earlier work on $CeZnPb$ [27]. The atomic

parameters of the cerium compound were taken as starting values and the structures were refined with anisotropic displacement parameters for all atoms using the Jana2006 package (full-matrix least-squares on F_o^2) [34]. Separate refinement of the occupancy parameters of all sites revealed full occupancy for all positions. The final difference Fourier synthesis revealed no residual peaks. The refined atomic positions, displacement parameters, and interatomic distances are given in Tables 3 and 4.

CCDC 1883472 ($PrZnPb$) and 1883473 ($NdZnPb$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4 EDX data and scanning electron microscopy

The $PrZnPb$ and $NdZnPb$ single crystals studied on the diffractometers were semi-quantitatively analysed by EDX in variable pressure mode with a Zeiss EVO® MA10 scanning electron microscope using PrF_3 , NdF_3 , Zn, and PbF_2 as standards. Measurements at several points of the irregularly shaped crystals showed only the respective three elements and gave no hint for impurity contributions, especially for niobium from the container material. The Paratone-N® coating prevented a quantification of the $RE:Zn:Pb$ ratios.

3 Crystal chemistry

The present study focused on the completion of the $REZnPb$ series. Our phase analytical studies showed that these plumbides form for $RE = La-Nd$ and $Sm-Tb$. The

Table 4: Interatomic distances (pm) for $PrZnPb$ and $NdZnPb$. All distances of the first coordination spheres are listed.

PrZnPb				NdZnPb			
Pr1:	6	Pb	326.5	Nd1:	6	Pb	324.3
	6	Zn	376.5		6	Zn	373.7
	2	Pr2	414.5		2	Nd2	410.7
	6	Pr1	461.3		6	Nd1	460.1
Pr2:	6	Zn	304.9	Nd2:	6	Zn	304.0
	6	Pb	349.1		6	Pb	347.9
	2	Pr1	414.5		2	Nd1	410.7
	6	Pr2	461.3		6	Nd2	460.1
Zn:	3	Pb	277.3	Zn:	3	Pb	276.5
	1	Zn	296.9		1	Zn	295.6
	3	Pr2	304.9		3	Nd2	304.0
	3	Pr1	376.5		3	Nd1	373.7
Pb:	3	Zn	277.3	Pb:	3	Zn	276.5
	3	Pr1	326.5		3	Nd1	324.3
	3	Pr2	349.1		3	Nd2	347.9

Standard deviations are equal or smaller than 0.1 pm.

Fig. 1: Course of the cell volume per formula unit for the series of $REZnSi$, $REZnGe$, $REZnSn$, and $REZnPb$ tetrelides. Literature data were taken from the Pearson data base [10].

course of the cell volume per formula unit is presented in Fig. 1 along with the literature data of the series $REZnSi$, $REZnGe$ and $REZnSn$ [10]. This plot shows four relevant features: (i) the cell volumes in the four series decrease with increasing atomic number as expected from the lanthanide contraction, (ii) in the europium compounds the RE element is divalent giving rise to a significant positive deviation from the smooth curve (the same holds true for $YbZnGe$ and $YbZnSn$), (iii) the volumes of the yttrium compounds are slightly smaller than those of the terbium compounds (for the $REZnPb$ series no representative with yttrium and the smaller rare earth elements has been observed), and (iv) the volumes increase from the $REZnSi$ to the $REZnPb$ series, a consequence of the increase of the covalent radius of the tetrel: Si (117 pm), Ge (122 pm), Sn (140 pm) and Pb (154 pm) [30].

The present investigation focused on the existence range of the $REZnPb$ plumbides as well as on the Zn/Pb ordering. Our X-ray powder and single crystal data clearly show that all of these plumbides are fully ordered (in contrast to the statistical descriptions for $NdZnPb$ [28] and $EuZnPb$ [29] based on powder diffraction data). In the following crystal chemical discussion we start with the hexagonal $YPtAs$ type [35] phases and refer to $NdZnPb$ when we quote interatomic distances. The unit cell of $NdZnPb$ is presented in Fig. 2. The zinc and lead atoms form ordered Zn_3Pb_3 hexagons that show a significant degree of puckering. The Zn–Pb distances of 277 pm are close to the sum of the covalent radii of 279 pm for Zn + Pb [30], indicating covalent Zn–Pb bonding within these layers. The layers of Zn_3Pb_3 hexagons show a stacking sequence $AA'BB'$. The layers A and A' as well as B and B' are related by the mirror planes perpendicular to the c axis at $z=1/4$ and $z=3/4$ (an equivalent description relates the layers through the inversion centres of space group $P6_3/mmc$). The layers A and B

Fig. 2: The crystal structure of $NdZnPb$. The puckered Zn_3Pb_3 hexagons and their stacking sequence are emphasized. Displacement ellipsoids of the zinc and lead atoms are drawn at 90% probability.

as well as A' and B' are related by the 6_3 screw axis. The $NdZnPb$ structure is reminiscent of the AlB_2 type structure. Indeed, the prototype $YPtAs$ is a superstructure of the arsitotype AlB_2 and the underlying group-subgroup relationship is discussed in review articles [36, 37].

The zinc atoms within the Zn_3Pb_3 network show a slight anisotropy, and this is also the case for $PrZnPb$ and the previously studied plumbide $CeZnPb$ [27]. The U_{33} displacement parameter is about two times larger than the U_{11} parameter. The zinc atoms of adjacent layers show a shorter Zn–Zn distance of 296 pm, slightly longer than the Zn–Zn distances (6×266 and 6×291 pm) in hcp zinc [38]. Thus, the formation of weak Zn–Zn bonding is a driving force for the puckering of the Zn_3Pb_3 layers. Nevertheless we need to discuss this feature in more detail. The puckering of the layers and the interlayer Zn–Zn bonding have been compared for the series $CeZnGe$ (373 pm Zn–Zn) $\rightarrow$ $CeZnSn$ (323 pm Zn–Zn) $\rightarrow$ $CeZnPb$ (305 pm Zn–Zn) [27]. On going from the germanide to the plumbide one observes increasing puckering paralleled by decreasing Zn–Zn distances. The even smaller value in $NdZnPb$ is a consequence of the lanthanide contraction.

The different orientation of the puckered Zn_3Pb_3 hexagons leads to drastic differences in the coordination of the two crystallographically independent neodymium sites. The Nd1 atoms have six closest lead neighbours (324 pm) and six further Nd1–Zn contacts (374 pm) while the Nd2 atoms have six closer contacts to zinc (304 pm) and much longer Nd2–Pb distances of 345 pm. The different hybridization of the two crystallographic rare earth

sites substantially influences the magnetic ground state as demonstrated for $CeZnPb$ [27].

Next we turn to the valence electron count of the $REZnPb$ plumbides. The trivalent rare earth elements and divalent zinc supply five valence electrons but plumbide formation can only accommodate four electrons, leading to a formulation $RE^{3+}Zn^{2+}Pb^{4-}e^-$. The excess electron can either fill the conduction band or allow metal-metal bonding (i.e. Zn–Zn in the present case). Keeping the comparison of $CeZnGe$, $CeZnSn$ and $CeZnPb$ in mind, notable Zn–Zn contacts only occur in the plumbide.

This peculiar behaviour is directly associated with the valence electron count (VEC) of the YPtAs type phases. The series $RENiP$, $RENiAs$ and $REPtAs$ have $VEC=18$ while the zinc series $REZnGe$, $REZnSn$ and $REZnPb$ [10] and the antimonides $REAuSb$ [39] have $VEC=19$. Especially the antimonide series shows pronounced Au–Au interlayer bonding with 298 pm Au–Au in $NdAuSb$ and this dimer formation is supported by the crystal orbital Hamilton population analyses.

The enhanced electron count of the zinc series leads to a facile hydride formation, exemplarily shown for $REZnSnH_{1.5}$ ($RE = Ce, Pr, Nd$) [40, 41], capturing the excess electron. Hydrogen incorporation leads to a flattening of the Zn_3Sn_3 hexagons along with drastic changes in the magnetic properties. To give an example, the Curie temperature increases from 4.8 K ($CeZnSn$) to 7.3 K ($CeZnSnH_{1.5}$) [40].

The YPtAs type is also formed for a variety of compounds with alkaline earth cations as well as with divalent europium and ytterbium: $CaGaGe$, $CaGaSn$, $SrGaGe$, $SrGaSn$, $BaGaGe$, $EuGaGe$, $EuGaSn$, $YbGaGe$ and $YbGaSn$ [10]. These tetrelides are the main group analogues to the transition metal compounds discussed above and we deal with $VEC=9$. The electron-precise $VEC=8$ compound is the Zintl phase $LiGaGe$ [42] where the Ga^- and Ge^0 entities build up a tetrahedral network with wurtzite type topology. An increase of the VEC through the divalent cations leads to a switch of the structure type to YPtAs, and the puckered $[GaGe]^{2-}$, respectively $[GaSn]^{2-}$, layers show a tendency to Ga–Ga contacts with distances of 300 pm in $YbGaSn$ [43], 318 pm in $EuGaSn$ [44] and 330 pm in $SrGaSn$ [45, 46]. These Ga–Ga distances are all longer than in gallium metal ($1 \times 244 + 6 \times 270\text{--}279$ pm Ga–Ga) [38]. Furthermore, the Zintl-related description seems to be too superficial. The bonding situation is more sophisticated since detailed electronic structure calculations for $EuGaSn$ [44] revealed essentially nonbonding Ga–Ga contacts.

Finally we turn to the Zintl phase $EuZnPb$. This plumbide was originally described with a KHg_2 type structure (space group $Imma$) with Zn/Pb statistics [29]. Since the lattice parameters determined by Merlo et al. [29]

Fig. 3: Experimental and simulated X-ray powder pattern ($CuK\alpha_1$ radiation) of $EuZnPb$. The three strongest reflections that violate the extinction conditions of a body-centered lattice (and thus manifest the Zn/Pb ordering of the TiNiSi type) are marked in magenta. The sample contains a small amount of residual lead. The 200 reflection is marked in green. The 111 reflection of lead overlaps with the triple around $2\theta = 31^\circ$.

compare well with our data, both samples apparently have the same composition. A solid solution $EuZn_{1-x}Pb_{1+x}$ towards higher zinc or lead content would lead to different cell parameters. In Fig. 3 we present the X-ray powder pattern of our $EuZnPb$ sample along with a simulation. The latter was performed with the $EuZnPb$ lattice parameters and the atomic parameters of TiNiSi type [47] $EuZnSn$ [48], space group $Pnma$. We clearly observe three stronger superstructure reflections 111, 102 and 311 which violate the body-centered lattice. The intensities of the calculated pattern perfectly match the experimental values and we can thus assume full Zn/Pb ordering, i.e. the TiNiSi type structure for $EuZnPb$. The sample contained a small amount of residual lead as impurity phase (marked by a green arrow within the powder pattern). The crystal chemistry of the europium-containing TiNiSi representatives has been discussed in detail and we refer to these reviews [36, 37, 49] for further reading.

References

- [1] G.-Y. Adachi, N. Imanaka, Z. Fuzhong in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 15, (Eds.: K. A. Gschneidner, Jr., L. Eyring), Elsevier Science B. V., Amsterdam, **1991**, chapter 99, pp. 61–190.
- [2] E. Dashjav, G. Kreiner, W. Schnelle, F. R. Wagner, R. Kniep, W. Jeitschko, *J. Solid State Chem.* **2007**, *180*, 636.
- [3] V. Babizhetskyy, B. Kotur, V. Levytskyy, H. Michor in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 52, (Eds.: J.-C. Bünzli, V. K. Pecharsky), Elsevier, Amsterdam, **2017**, chapter 298, pp. 1–263.
- [4] E. Parthé, B. Chabot in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 6, (Eds.: K. A. Gschneidner, Jr., L. Eyring), North-Holland, Amsterdam, **1984**, chapter 48, pp. 113–334.

- [5] P. S. Salamakha, O. L. Sologub, O. I. Bodak in *Ternary Rare-Earth-Germanium Systems*, in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 27, (Eds.: K. A. Gschneidner, Jr., L. Eyring), Elsevier Science B. V., Amsterdam, **1999**, chapter 173, pp. 1–223.
- [6] P. S. Salamakha in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 27, (Eds.: K. A. Gschneidner, Jr., L. Eyring), Elsevier Science B. V., Amsterdam, **1999**, chapter 174, pp. 225–338.
- [7] R. Pöttgen, *Z. Naturforsch.* **2006**, *61b*, 677.
- [8] R. V. Skolozdra in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 24, (Eds.: K. A. Gschneidner, Jr., L. Eyring), Elsevier Science, Amsterdam, **1997**, chapter 164, pp. 399–517.
- [9] R. Pöttgen, U. Ch. Rodewald in *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 38, (Eds.: K. A. Gschneidner Jr., V. K. Pecharsky, J.-C. Bünzli), Elsevier, Amsterdam, **2008**, chapter 237, pp. 55–103.
- [10] P. Villars, K. Cenzual, *Pearson's Crystal Data: Crystal Structure Database for Inorganic Compounds* (release 2018/19), ASM International®, Materials Park, Ohio (USA) **2018**.
- [11] L. Heletta, R. Pöttgen, *Z. Naturforsch.* **2018**, *73b*, 251.
- [12] L. Heletta, R. Pöttgen, *Z. Naturforsch.* **2018**, *73b*, 1015.
- [13] P. Salamakha, O. Zaplatynsky, *J. Alloys Compd.* **1997**, *260*, 127.
- [14] L. D. Gulay, *J. Alloys Compd.* **2000**, *313*, 144.
- [15] L. D. Gulay, *J. Alloys Compd.* **2002**, *347*, 124.
- [16] L. D. Gulay, *J. Alloys Compd.* **2003**, *348*, 146.
- [17] L. D. Gulay, *J. Alloys Compd.* **2003**, *349*, 201.
- [18] L. D. Gulay, M. Wolcyrz, *J. Alloys Compd.* **2001**, *315*, 164.
- [19] L. D. Gulay, *J. Alloys Compd.* **2005**, *392*, 165.
- [20] I. V. Oshchapovsky, V. V. Pavlyuk, *Visn. Lviv Derzh. Univ., Ser. Khim.* **2015**, *56*, 53.
- [21] N. T. Suen, S. Bobev, *Inorg. Chem.* **2013**, *52*, 12731.
- [22] N. T. Suen, S. Bobev, *Inorg. Chem.* **2013**, *52*, 9102.
- [23] A. M. Guloy, J. D. Corbett, *J. Solid State Chem.* **1994**, *109*, 352.
- [24] I. Oshchapovsky, V. Pavlyuk, G. Dmytriv, B. Harbrecht, *Acta Crystallogr.* **2014**, *E70*, i2.
- [25] A. Szytuła, J. Leciejewicz, *Handbook of Crystal Structures and Magnetic Properties of Rare Earth Intermetallics*, CRC Press, Boca Raton, **1994**.
- [26] S. Gupta, K. G. Suresh, *J. Alloys Compd.* **2015**, *618*, 562.
- [27] W. Hermes, U. Ch. Rodewald, B. Chevalier, S. F. Matar, V. Eyert, R. Pöttgen, *Solid State Sci.* **2010**, *12*, 929.
- [28] P. Salamakha, P. Demchenko, O. Sologub, O. Bodak, *Polish J. Chem.* **1999**, *73*, 885.
- [29] F. Merlo, M. Pani, M. L. Fornasini, *J. Less-Common Met.* **1991**, *171*, 329.
- [30] J. Emsley, *The Elements*, Oxford University Press, Oxford **1999**.
- [31] R. Pöttgen, Th. Gulden, A. Simon, *GIT Labor-Fachzeitschrift* **1999**, *43*, 133.
- [32] R. Pöttgen, A. Lang, R.-D. Hoffmann, B. Künnen, G. Kotzyba, R. Müllmann, B. D. Mosel, C. Rosenhahn, *Z. Kristallogr.* **1999**, *214*, 143.
- [33] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **1977**, *10*, 73.
- [34] V. Petříček, M. Dušek, L. Palatinus, *Z. Kristallogr.* **2014**, *229*, 345.
- [35] G. Wenski, A. Mewis, *Z. Kristallogr.* **1986**, *176*, 125.
- [36] R.-D. Hoffmann, R. Pöttgen, *Z. Kristallogr.* **2001**, *216*, 127.
- [37] R. Pöttgen, *Z. Anorg. Allg. Chem.* **2014**, *640*, 869.
- [38] J. Donohue, *The Structures of the Elements*, Wiley, New York, **1974**.
- [39] E. M. Seibel, L. M. Schoop, W. Xie, Q. D. Gibson, J. B. Webb, M. K. Fuccillo, J. W. Krizan, R. J. Cava, *J. Am. Chem. Soc.* **2015**, *137*, 1282.
- [40] W. Hermes, B. Chevalier, U. Ch. Rodewald, S. F. Matar, F. Weill, I. Schellenberg, R. Pöttgen, H. Lueken, M. Speldrich, *Chem. Mater.* **2011**, *23*, 1096.
- [41] B. Reker, B. Chevalier, O. Niehaus, U. Ch. Rodewald, R. Pöttgen, *Z. Naturforsch.* **2013**, *68b*, 1191.
- [42] W. Bockelmann, H. Jacobs, H.-U. Schuster, *Z. Naturforsch.* **1970**, *25b*, 1305.
- [43] J. R. Salvador, F. Guo, T. Hogan, M. G. Kanatzidis, *Nature* **2003**, *425*, 702.
- [44] T.-S. You, Yu. Grin, G. J. Miller, *Inorg. Chem.* **2007**, *46*, 8801.
- [45] A. Czybulka, B. Pinger, H.-U. Schuster, *Z. Anorg. Allg. Chem.* **1989**, *579*, 151.
- [46] M. J. Evans, Y. Wu, V. F. Kranak, N. Newman, A. Reller, F. J. Garcia-Garcia, U. Häussermann, *Phys. Rev. B* **2009**, *80*, 064514.
- [47] C. Brink Shoemaker, D. P. Shoemaker, *Acta Crystallogr.* **1965**, *18*, 900.
- [48] R. Pöttgen, *Z. Kristallogr.* **1996**, *211*, 884.
- [49] R. Pöttgen, D. Johrendt, *Chem. Mater.* **2000**, *12*, 875.