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The rare earth transition metal phosphide oxides LnFePO, LnRuPO and LnCoPO with ZrCuSiAs type structure

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Abstract

The compounds LnFePO (Ln = La–Nd, Sm, Gd), LnRuPO (Ln = La–Nd, Sm, Gd) and LnCoPO (Ln = La–Nd, Sm) crystallize with the tetragonal ZrCuSiAs type structure ($P4/nmm$, $Z = 2$), which was refined from single-crystal X-ray data of PrFePO ($a = 391.13(6)$ pm, $c = 834.5(2)$ pm, $R = 0.026$) and CeRuPO ($a = 402.6(1)$ pm, $c = 825.6(2)$ pm, R = 0.018). The refinement of the occupancy parameters showed the oxygen position to be fully occupied in both compounds. The oxygen content of the samples was also proven by EDAX analyses. The structures of the compounds SmFePO and LaCoPO were refined by Rietveld analyses of X-ray powder data.

Keywords: Rare earth metals; Transition metal phosphide oxides; Crystal structure

1. Introduction

The ZrCuSiAs type structure is relatively simple with only two formula units in the primitive tetragonal cell and only two variable positional parameters. It was first described as a "filled" PbFCl type structure some twenty years ago [1]. The analogous atom distribution was found for the compounds LaOAgS [2,3], LaOCuS [4] and more recently for BiOCuSe [5], ThCuPO [6], ThCuAsO [6] and UCuPO [7]. Ternary compounds with this atomic arrangement were also reported, with $HfCuSi_2$ as the first example [8]. Other examples with this structure include $CaMnBi_2$ [9], $LnNiSb_2$ [10], $UCuAs_2$ [11], the series $UTPn_2$ (T = Fe, Co, Ni, Cu; Pn = P, As, Sb, Bi) [12] and $ATSb_2$ (A = Ln, U; T = Fe, Co, Ni, Pd, Cu, Ag, Au) [13–15]. With the phosphide oxides reported herein there are more than one hundred representatives with the atomic arrangement of ZrCuSiAs and $HfCuSi_2$.

2. Sample preparation, properties and lattice constants

Filings of the rare earth metals (all with nominal purities > 99.9 %) were prepared under dried paraffin oil. They were washed with dried n-hexane under argon to remove the oil. The transition metals (iron and cobalt from Merck: "reinst"; ruthenium from Degussa: 99.9%) were used in the form of powders and the red phosphorus was of semiconductor quality (Hoechst, Knapsack: "ultrapure"). The compounds SmFePO, PrCoPO, NdCoPO and SmCoPO were first obtained from a tin flux as byproducts in preparations of the corresponding LnT_2P_2 compounds with $ThCr_2Si_2$ type structure. At that time [16] these compounds were assumed to be ternary phases of the composition 1:1:1, because their Guinier powder patterns showed perfect agreement with a PbFCl type structure [17–19]. Later the yield was improved by deliberately adding oxygen in the form of the corresponding rare earth or transition metal oxides Ln_2O_3, Fe_2O_3, Co_3O_4 and RuO_2. The compounds can be prepared without the tin flux, however, they were obtained with higher purity and with better crystals from the tin flux with 75 at% tin. The samples were annealed in evacuated sealed silica tubes for 2 h at 600°C, followed by 10 d at 900°C. The tin-rich matrix of the samples was dissolved in cold, slightly diluted hydrochloric acid, which attacks the quaternary phosphide oxides at a lower rate.

These compounds are stable in air for long periods of time. They are slowly dissolved in hydrochloric acid.

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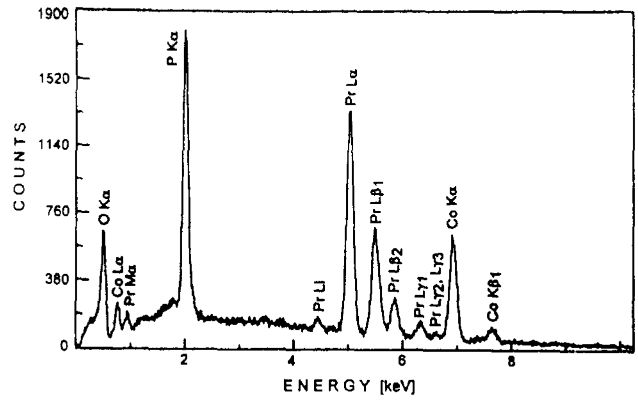

Fig. 1. Energy dispersive X-ray emission spectrum of PrCoPO.

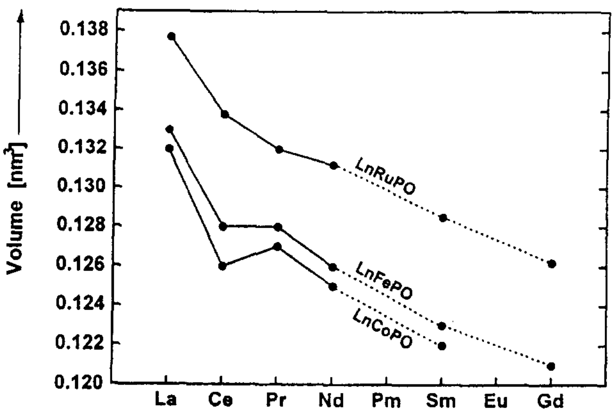

Fig. 2. Cell volumes of the tetragonal phosphide oxides LnFePO, LnRuPO and LnCoPO.

The powders are black. Well crystallized samples have a metallic lustre. The crystals have the form of platelets and those of the iron containing compounds have a golden tint.

Samples of GdFePO, CeCoPO, PrCoPO, SmCoPO and GdRuPO were investigated in a scanning electron microscope by energy dispersive X-ray emission analysis with a windowless detector. None of these samples showed impurity elements such as nitrogen or silicon and the oxygen Kα peaks were well resolved. As an example the spectrum of PrCoPO is shown in Fig. 1.

The compounds were characterized by their Guinier powder patterns using α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as a standard. The lattice constants (Table 1) were obtained by least-squares fits of these data. The lattice constants, calculated from the four-circle and from the powder diffraction data, were in good agreement with those of the Guinier powder patterns. The volume plot (Fig. 2) reflects the expected lanthanoid contraction.

3. Structure refinements

Single crystals of PrFePO and CeRuPO were investigated on a CAD4 four-circle diffractometer. They showed the tetragonal high Laue symmetry 4/*mmm*. The only systematic extinctions occured for the *hk*0 reflections, which were present only with $h + k = 2n$. This suggested the space group *P*4/*nmm* (No. 129), which was found for the isotypic compounds ZrCuSiAs [1] and UCuPO [7], and this was proven to be correct during the structure refinements. The data were recorded with graphite monochromated Mo-Kα radiation using a scintillation counter with pulse-height discrimination. Background counts were taken at both ends of each $\theta/2\theta$ scan. An absorption correction was made from ψ-scan data.

For the structure refinements the positional parameters for the metal atoms were taken from UCuPO [7]. The positions of the phosphorus and the oxygen atoms were obtained by difference Fourier syntheses. A full-

Table 1
Lattice constants of the tetragonal compounds LnFePO, LnRuPO (Ln = La–Nd, Sm, Gd) and LnCoPO (Ln = La–Nd, Sm)[a]

Compound	*a* (pm)	*c* (pm)	*c*/*a*	*V* (nm³)
LaFePO	395.70(9)	850.7(4)	2.150	0.1332
CeFePO	391.9(1)	832.7(3)	2.125	0.1279
PrFePO	391.13(6)	834.5(2)	2.134	0.1277
NdFePO	389.95(5)	830.2(3)	2.129	0.1262
SmFePO	387.8(1)	820.5(1)	2.116	0.1234
GdFePO	386.1(3)	812.3(7)	2.104	0.1211
LaRuPO	404.7(1)	840.6(1)	2.077	0.1377
CeRuPO	402.6(1)	825.6(2)	2.051	0.1338
PrRuPO	401.8(1)	817.4(3)	2.034	0.1320
NdRuPO	400.86(5)	816.7(2)	2.037	0.1312
SmRuPO	399.35(5)	805.8(2)	2.018	0.1285
GdRuPO	397.9(1)	797.4(2)	2.004	0.1262
LaCoPO	396.78(9)	837.9(3)	2.112	0.1319
CeCoPO	392.13(7)	821.9(4)	2.096	0.1264
PrCoPO	392.24(8)	822.4(2)	2.097	0.1265
NdCoPO	390.84(5)	817.2(2)	2.091	0.1248
SmCoPO	388.17(7)	807.3(2)	2.080	0.1216

[a] Standard deviations in the place values of the least significant digits are listed in parentheses throughout the paper.

Table 2
Crystallographic data for PrFePO and CeRuPO

	PrFePO	CeRuPO
Space group	$P4/nmm$	$P4/nmm$
Lattice constants	Table 1	Table 1
Formula units per cell	$Z = 2$	$Z = 2$
Formula weight	243.73	288.16
Calculated density (g cm^{-3})	6.34	7.15
Crystal size (mm^3)	0.04 × 0.05 × 0.01	0.09 × 0.07 × 0.02
Scan range (2θ)	4°–90°	4°–80°
Range in h, k, l	±7, ±7, +16	±8, ±8, −16 to +6
Total no. of reflections	2180	2687
Data after averaging	368	297
Inner residual	$R_i = 0.043$	$R_i = 0.021$
Data with $I > 3\sigma(I)$	238	288
No. of variables	12	12
Conventional residual	$R = 0.026$	$R = 0.018$
Weighted residual	$R_w = 0.029$	$R_w = 0.025$

matrix least-squares programme was used with atomic scattering factors [20], corrected for anomalous dispersion [21]. The weighting scheme accounted for the counting statistics and a parameter correcting for isotropic secondary extinction was optimized as a least-squares parameter. Further details are summarized in Table 2.

To verify the compositions of the compounds, especially the oxygen content, we refined occupancy parameters together with the thermal parameters with fixed scale factors. The results were as follows: Pr 0.9993(7); Fe 1.002(2); P 0.976(3); O 0.986(7); Ce 1.006(2); Ru 0.988(2); P 0.990(7); O 0.98(2). Thus, the deviations from the full occupancies were minor, and the ideal values were resumed during the final least-squares cycles. The positional parameters were transformed to the setting as described for the prototype ZrCuSiAs [1]. The results of the refinements are summarized in Tables 2 and 3. The crystal structure and the near-neighbour environments of PrFePo are shown in Fig. 3.

The powder diffraction patterns of SmFePO and LaCoPO (Fig. 4) were recorded on a Stoe STADI/P focussing, monochromatic beam diffractometer using Cu-Kα_1 radiation with a rotating sample in the symmetric transmission mode. The data for SmFePO (with the corresponding values for LaCoPO in parentheses) were collected with a linear photosensitive detector, a step width of 0.02° (0.02°) in 2θ and a constant counting time of 130 s (75 s) per step in a 2θ range from 17° (18°) to 95° (95°). For the refinements the RIETAN program [22] was used. The isotropic thermal parameters of SmFePO could be refined, whereas the thermal parameters of LaCoPO were fixed at the values obtained for SmFePO. The refinements resulted for SmFePO (LaCoPO) in profile residuals of $R_{wp} = 0.013$ (0.023) and $R_p = 0.009$ (0.018) and structure residuals of $R_{Int} = 0.055$ (0.041) and $R_F = 0.033$ (0.025). The positional parameters for both compounds are shown in Table 4.

4. Discussion

The crystal structure of the compounds reported here is rather simple with eight atoms in the tetragonal cell and only two variable positional parameters. In discussing the near-neighbour coordinations (Table 5)

Table 3
Atomic parameters as obtained from the single-crystal data refinements of PrFePO and CeRuPO[a]

Atom	$P4/nmm$	x	y	z	$B_{11} = B_{22}$	B_{33}	B_{eq}
Pr	2c	1/4	1/4	0.14830(7)	0.342(7)	0.50(1)	0.394(4)
Fe	2b	3/4	1/4	0.5	0.31(2)	0.49(3)	0.37(1)
P	2c	1/4	1/4	0.6396(3)	0.36(4)	0.61(7)	0.44(2)
O	2a	3/4	1/4	0	0.5(1)	0.5(1)	0.51(6)
Ce	2c	1/4	1/4	0.14716(4)	0.456(6)	0.537(8)	0.482(3)
Ru	2b	3/4	1/4	0.5	0.246(6)	0.513(8)	0.336(4)
P	2c	1/4	1/4	0.6419(2)	0.37(2)	0.43(4)	0.39(1)
O	2a	3/4	1/4	0	0.63(8)	0.63(8)	0.66(4)

[a] The anisotropic displacement parameters are defined by $\exp[-0.25(h^2a^{*2}B_{11} + \cdots)]$. For symmetry reasons the values B_{12}, B_{13} and B_{23} are all equal to zero. The last column contains the equivalent thermal parameters B_{eq} ($\times 10^{-4}$, in units of pm^2).

Table 4
Atomic parameters resulting from the powder data refinements of SmFePO and LaCoPO

Atom	*P*4/*nmm*	*x*	*y*	*z*	B (pm^2 × 10^{-4})
Sm	2c	1/4	1/4	0.1482(7)	0.7(2)
Fe	2b	3/4	1/4	0.5	0.9(4)
P	2c	1/4	1/4	0.642(4)	1.0(6)
O	2a	3/4	1/4	0	0.9(1.2)
La	2c	1/4	1/4	0.155(1)	0.8[a]
Co	2b	3/4	1/4	0.5	0.8[a]
P	2c	1/4	1/4	0.617(6)	0.9[a]
O	2a	3/4	1/4	0	0.9[a]

[a] The isotropic displacement parameters of LaCoPO were not varied during the least-squares refinements.

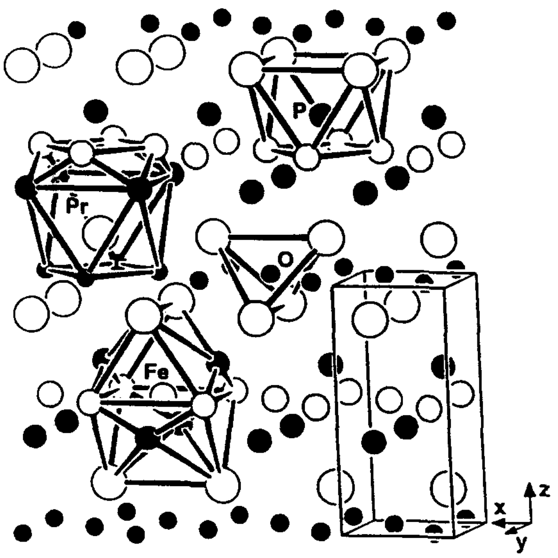

Fig. 3. Crystal structure and coordination polyhedra of PrFePO.

we will, for simplicity, refer to PrFePO. The praseodymium atoms are coordinated by four phosphorus and four oxygen atoms forming a distorted square antiprism. Four iron atoms, situated outside the square formed by phosphorus atoms, may also be considered as part of the coordination sphere of a praseodymium atom. In addition there are eight praseodymium atoms outside the triangular faces formed by the phosphorus and oxygen atoms of that coordination polyhedron at distances of 371.1 and 391.1 pm. However, in view of the fact that the praseodymium atoms are the most electropositive components of this compound, and therefore have largely transferred their valence electrons to the other atoms, the Pr–Pr bonding will be rather weak at best.

The iron atoms are tetrahedrally coordinated by four phosphorus atoms. That coordination is augmented by four iron atoms at 276.6 pm forming a square. These Fe–Fe distances might be considered as weakly bonding, as it is known also for the transition metal-transition metal interactions of the closely related $ThCr_2Si_2$ type phosphides [23–27]. In addition to the phosphorus and iron neighbours the coordination polyhedron of the iron atom contains four praseodymium atoms at a practically nonbonding distance of 352.7 pm.

The environment of a phosphorus atom consists of a square antiprism formed by four praseodymium and four iron atoms. There are no P–P bonds: the shortest P–P distances in PrFePO are 361 pm.

The oxygen atoms have only four praseodymium neighbours at 231.4 pm in tetrahedral arrangement. This distance is only slightly shorter than the average

Table 5
Interatomic distances in PrFePO, SmFePO, CeRuPO and LaCoPO[a]

		PrFePO	SmFePO	CeRuPO	LaCoPO
Ln	4O	231.4(1)	228.9(4)	235.1(1)	237.1(5)
	4P	328.4(2)	324(2)	333.7(1)	339(3)
	4T	352.7(1)	347.7(5)	354.1(1)	350.6(7)
	4Ln	371.1(1)	366.5(6)	374.3(1)	382.3(8)
	4Ln	391.1(1)	387.8(1)	402.6(1)	396.8(1)
T	4P	227.6(2)	226(2)	232.9(1)	221(2)
	4T	276.6(1)	274.2(1)	284.7(1)	280.6(1)
	4Ln	352.7(1)	347.7(5)	354.1(1)	350.6(7)
P	4T	227.6(2)	226(2)	232.9(1)	221(2)
	4Ln	328.4(2)	324(2)	333.7(1)	339(3)
O	4Ln	231.4(1)	228.9(4)	235.1(1)	237.1(5)

[a] All distances shorter than 400 pm (coordination of the rare earth atoms) and 390 pm (coordination of the transition elements) are listed. The shortest P–P, P–O and O–O distances are all greater than 320, 350 and 270 pm, respectively.

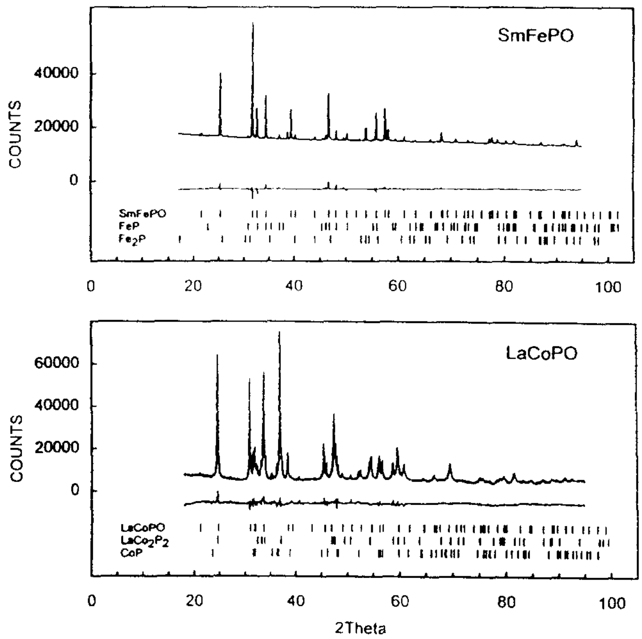

Fig. 4. X-ray powder diffraction patterns of SmFePO and LaCoPO. Also shown are the difference plots of the observed and the calculated patterns as well as the peak positions of SmFePO and LaCoPO and the impurity phases FeP, Fe_2P, $LaCo_2P_2$ and CoP.

O1–Pr distance of 234.2 pm in A-Pr_2O_3 [28], where the O1 atoms are also tetrahedrally coordinated by praseodymium atoms.

Most compounds reported here may be rationalized with oxidation numbers according to the formula $Ln^{+3}T^{+2}P^{-3}O^{-2}$. Nevertheless, the chemical bonding is certainly not purely ionic. In addition to the bonding between the heteropolar atoms at least some bonding transition metal–transition metal interactions may be assumed, as already discussed above. The volume plot (Fig. 2) indicates mixed or intermediate (III/IV) valence for the cerium atoms in the iron- and cobalt-containing compounds, while almost no deviation from the smooth curve is observed for the cerium compound in the LnRuPO series. This behaviour is paralleled in the series LnT_4P_{12} and LnT_4As_{12}, where again the cerium compounds show relatively large deviations from the smooth volume plot of the trivalent rare earth compounds when T = Fe, while the deviations are smaller for T = Ru and Os [29]. A higher valency for the cerium atoms in the compounds LnTPO might be favoured if the oxygen atoms were at least partially substituted by nitrogen atoms. It might be possible to prepare the corresponding nitrides; however, for CeCoPO our EDAX analysis definitely did not show any significant nitrogen content.

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