Articles

Equiatomic Quaternary Rare Earth Element Zinc Pnictide Oxides RZnPO and RZnAsO

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The twelve phosphide oxides RZnPO (R = Y, La−Nd, Sm, Gd−Tm) and the nine arsenide oxides (R = Y, La−Nd, Sm, Gd−Dy) have been prepared by reaction of the rare earth elements, ZnO, and phosphorus or arsenic, respectively, in a NaCl/KCl flux. The compounds RZnPO (R = Y, Pr, Nd, Sm, Gd−Tm) crystallize with a new trigonal rhombohedral structure type, determined from single-crystal X-ray diffractometer data of NdZnPO: $R\bar{3}m$, $a = 397.7(1)$ pm, $c = 3097.5(5)$ pm, $Z = 6$. The other eleven compounds are isotypic with ZrCuSiAs ($P4/nmm$, $Z = 2$). This tetragonal structure was refined from single-crystal X-ray data of LaZnPO ($a = 404.0(1)$ pm, $c = 890.8(2)$ pm) and NdZnAsO ($a = 403.0(1)$ pm, $c = 894.9(4)$ pm). In both structure types rare earth element−oxygen layers alternate with zinc−pnictogen layers. The rare earth element atoms have four oxygen and three (NdZnPO) or four (LaZnPO, NdZnAsO) pnictogen neighbors. The zinc atoms have tetrahedral pnictogen coordination. The arsenide oxides as well as the tetragonal phosphide oxides LaZnPO and CeZnPO are black, while the other (trigonal) phosphide oxides are transparent. The more metallic character of the tetragonal compounds is ascribed to their more delocalized chemical bonding, as is indicated by their higher coordination numbers, which in part also result through significant Zn−Zn bonding.

Introduction

In recent years some 60 quaternary pnictide oxides with the composition 1:1:1:1 have been reported, including the actinoid- and copper-containing compounds UCuPO,[1] ThCuPO,[2] and ThCuAsO,[2] as well as the series of lanthanoid (Ln) compounds LnFePO,[3] LnRuPO,[3,4] LnOsPO,[4] LnCoPO,[3] and LnMnPnO, with Pn = P, As, Sb.[4,5] Compounds with zinc at the positions of the transition elements were reported most recently.[4,6] All of these compounds crystallize with the very simple "filled" PbFCl-type structure, first reported for ZrCuSiAs,[7] where the silicon positions correspond to the oxygen positions of the quaternary pnictide oxides. We have now explored the stability range of this structure type for the zinc-containing series. In the course of this investigation, we prepared eleven compounds LnZnPnO with Pn = P, As. In addition we found ten compounds LnZnPO, which crystallize with a new trigonal structure type. This paper presents a full account of our work. A brief preliminary report has already been given at a conference.[8]

Materials and Methods

Sample Preparation, Properties, and Lattice Constants. The starting materials for the preparation of the new quaternary compoundswere ingots of the rare earth elements (all with nominal purities of ≥99.9%), ZnO (Merck, ultrapure), and red phosphorus (Hoechst, Knapsack, ultrapure). The arsenic (Ventron, 99%) was purified by fractional sublimation[9] prior to the reactions. Filings of the rare earth metals were prepared under dry (Na) paraffin oil, which was washed away by repeated treatment with dry *n*-hexane. The filings were only briefly exposed to air prior to the reactions.

The title compounds, the tetragonal as well as the trigonal, were prepared by reaction of stoichiometric mixtures of the rare earth elements, ZnO, and red phosphorus or arsenic, respectively, in a salt flux (1:1 NaCl/KCl). In all cases, 0.5 g of the mixed components and 2 g of the NaCl/KCl flux were annealed in evacuated sealed silica tubes for 1 day at 500 °C, followed by 7 days at 800 °C, and then quenched in air. The salt matrix was dissolved in water.

The crystals of all compounds have the shape of platelets. The trigonal platelets are relatively thicker than the tetragonal ones. The crystals of the trigonal compounds RZnPO (R = Y, Pr, Nd, Sm, Gd−Tm) are transparent with brownish color, and their powders are yellow-ocher, whereas the crystals with tetragonal symmetry (including LaZnPO and CeZnPO) have metallic luster, and their powders are black. All samples are stable on air for long periods of time.

The lattice constants of the quaternary pnictide oxides (Table 1) were determined by least-squares fits of the Guinier powder data using Cu Kα_1 radiation and α-quartz ($a = 491.30$ pm, $c = 540.46$ pm) as an internal standard.

Structure Determinations. Single crystals of NdZnPO, LaZnPO, and NdZnAsO were examined in Buerger precession cameras to establish their suitability for the structure determination. Intensity data

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* Corresponding author.

(1) Kaczorowski, D.; Albering, J. H.; Noël, H.; Jeitschko, W. *J. Alloys Compd.* **1994**, *216*, 117.

(2) Albering, J. H.; Jeitschko, W. *Z. Naturforsch.* **1996**, *51b*, 257.

(3) Zimmer, B. I.; Jeitschko, W.; Albering, J. H.; Glaum, R.; Reehuis, M. *J. Alloys Compd.* **1995**, *229*, 238.

(4) Nientiedt, A. T.; Zimmer, B. I.; Wollesen, P.; Jeitschko, W. *Z. Kristallogr. Suppl.* **1996**, *11*, 101.

(5) Nientiedt, A. T.; Jeitschko, W.; Pollmeier, P. G.; Brylak, M. *Z. Naturforsch.* **1997**, *52B*, 560.

(6) Wollesen, P. Ternäre und quaternäre Antimonide der Lanthanoide und Actinoide mit Übergangsmetallen. Dissertation, Universität Münster, Germany, 1996.

(7) Johnson, V.; Jeitschko, W. *J. Solid State Chem.* **1974**, *11*, 161.

(8) Nientiedt, A. T.; Jeitschko, W. *Z. Kristallogr. Suppl.* **1997**, *12*, 135.

(9) Geach, G. A.; Jeffery, R. A.; Shelton, R. J. *J. Chem. Soc. (London)* **1950**, 1207.

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Table 1. Cell Dimensions of Quaternary Pnictide Oxides with Trigonal NdZnPO- and Tetragonal ZrCuSiAs-Type Structures[a]

	a (pm)	*c* (pm)	*c*/*a*	*V* (nm^3)
	NdZnPO-Type			
YZnPO	388.3(1)	3031.9(7)	7.808	0.3959
PrZnPO	398.6(1)	3105.4(4)	7.791	0.4273
NdZnPO	397.7(1)	3097.5(5)	7.789	0.4243
SmZnPO	394.8(1)	3074.9(6)	7.789	0.4151
GdZnPO	391.8(1)	3054.8(6)	7.797	0.4061
TbZnPO	390.4(1)	3044.7(9)	7.799	0.4019
DyZnPO	389.1(1)	3032.4(6)	7.793	0.3976
HoZnPO	388.2(1)	3024.9(6)	7.792	0.3948
ErZnPO	386.8(1)	3015.0(6)	7.795	0.3907
TmZnPO	385.9(1)	3007.9(6)	7.795	0.3879
	ZrCuSiAs-Type			
LaZnPO	404.0(1)	890.8(2)	2.2050	0.14539
CeZnPO	401.3(1)	882.4(2)	2.1989	0.14210
YZnAsO	394.3(1)	884.3(3)	2.2427	0.13748
LaZnAsO	409.5(1)	906.8(3)	2.2144	0.15206
CeZnAsO	406.9(1)	899.5(3)	2.2106	0.14893
PrZnAsO	404.7(1)	896.3(1)	2.2147	0.14680
NdZnAsO	403.0(1)	894.9(4)	2.2206	0.14534
SmZnAsO	400.3(1)	890.3(2)	2.2241	0.14266
GdZnAsO	397.6(1)	889.4(3)	2.2369	0.14060
TbZnAsO	395.7(1)	884.1(2)	2.2343	0.13843
DyZnAsO	394.7(1)	883.8(1)	2.2392	0.13769

[a] Standard devitations in the least significant digits are given in parentheses throughout the paper.

Table 2. Crystallographic Data of NdZnPO, LaZnPO, and NdZnAsO[a]

empirical formula	NdZnPO	LaZnPO	NdZnAsO
space group	$R\bar{3}m$ (No. 166)	$P4/nmm$ (No. 129)	$P4/nmm$ (No. 129)
a^b (pm)	397.6(1)	403.8(1)	402.9(1)
c^b (pm)	3095.5(5)	889.6(1)	894.7(1)
V (nm^3)	0.4238(1)	0.1451(3)	0.1452(3)
Z	6	2	2
fw	256.58	251.25	300.53
T (°C)	21	21	21
λ (pm)	71.07	71.07	71.07
ρ_{calcd} (g/cm^3)	6.025	5.739	6.867
μ (cm^{-1})	273	233	372
$R(F)$	0.010	0.016	0.015
$R_W(F)$	0.012	0.017	0.015

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$; $R_w = ((\sum(\sigma(F))^{-2}||F_o| - |F_c||^2)/(\sum(\sigma(F))^{-2}|F_o|^2))^{1/2}$. [b] These lattice constants were obtained on the four-circle diffractometer. For the calculations of the interatomic distances, the lattice constants obtained from the Guinier powder patterns (Table 1) were used.

Table 3. Atomic Parameters of NdZnPO, LaZnPO, and NdZnAsO[a]

		occupancy	*x*	*y*	*z*	B_{eq}
		NdZnPO, $R\bar{3}m$				
Nd	6*c*	1.0011(8)	0	0	0.381 18(1)	0.338(3)
Zn	6*c*	0.989(2)	0	0	0.196 17(2)	0.661(7)
P	6*c*	1.001(4)	0	0	0.113 65(4)	0.47(1)
O	6*c*	1.07(1)	0	0	0.305 2(1)	0.53(4)
		LaZnPO, $P4/nmm$				
La	2*c*	1.000(1)	$1/4$	$1/4$	0.138 70(5)	0.470(3)
Zn	2*b*	1.000(3)	$3/4$	$1/4$	$1/2$	0.82(1)
P	2*c*	0.992(6)	$1/4$	$1/4$	0.664 6(2)	0.63(2)
O	2*a*	1.05(1)	$3/4$	$1/4$	0	0.71(5)
		NdZnAsO, $P4/nmm$				
Nd	2*c*	0.998(1)	$1/4$	$1/4$	0.130 32(5)	0.425(3)
Zn	2*b*	1.014(3)	$3/4$	$1/4$	$1/2$	0.88(1)
As	2*c*	1.009(3)	$1/4$	$1/4$	0.676 32(9)	0.62(1)
O	2*a*	1.01(1)	$3/4$	$1/4$	0	0.57(5)

[a] The occupancy parameters were obtained in separate series of least-squares cycles. In the final cycles, the occupancy parameters were assumed to be ideal. The last column contains the equivalent isotropic thermal parameters B_{eq} ($\times 10^{-4}$, pm^2), as defined by $B_{\text{eq}} = 8\pi^2 U_{\text{eq}}$, where U_{eq} is one-third of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Interatomic Distances in the Structures of NdZnPO, LaZnPO, and NdZnAsO[a]

			NdZnPO (New Trigonal Structure Type)					
Nd:	1O	235.4	Zn:	3P	240.9	P:	3Zn	240.9
	3O	237.6		1P	255.6		1Zn	255.6
	3P	307.0		3Zn	293.5		3Nd	307.0
	3Zn	359.5		3Nd	359.5	O:	1Nd	235.4
	3Nd	374.9					3Nd	237.6
	6Nd	397.7						
			LaZnPO (Tetragonal ZrCuSiAs-Type Structure)					
La:	4O	236.8	Zn:	4P	249.6	P:	4Zn	249.6
	4P	335.2		4Zn	285.7		4La	335.2
	4La	377.7		4La	380.0	O:	4La	236.8
	4Zn	380.0						
	4La	404.0						
	1P	422.4						
			NdZnAsO (Tetragonal ZrCuSiAs-Type Structure)					
Nd:	4O	232.8	Zn:	4As	255.9	As:	4Zn	255.9
	4As	333.4		4Zn	284.9		4Nd	333.4
	4Nd	368.2		4Nd	387.3	O:	4Nd	232.8
	4Zn	387.3						
	4Nd	403.0						
	1As	406.3						

[a] All distances shorter than 440 pm (Ln−Ln, Ln−Zn, Ln−Pn, Ln−O), 390 pm (Zn−Zn, Zn−Pn), 335 pm (Zn−O, Pn−Pn, Pn−O), and 280 pm (O−O) are listed. The standard deviations are all equal to or less than 0.1 pm with the exception of one Nd−O distance in NdZnPO that is 0.3 pm.

were collected on a four-circle diffractometer with graphite-monochromated Mo Kα radiation, a scintillation counter with pulse-height discrimination, and background counts at both ends of each $\theta/2\theta$ scan. Empirical absorption corrections were made from ψ scan data. Additional details of the data collections and structure refinements are listed in Table 2.

The crystals of LaZnPO and NdZnAsO showed tetragonal symmetry and were found to be isotypic with the previously reported compounds NdMnPnO (Pn = P, As, Sb).[5] Rhombohedral symmetry was observed for NdZnPO. The positions of the neodymium atoms of this new structure type were located by Patterson synthesis,[10] and the other atomic sites were obtained through difference Fourier syntheses.

The structures were refined by a full-matrix least-squares program using atomic scattering factors corrected for anomalous dispersion as provided by the program.[11] Parameters correcting for isotropic secondary extinction were refined and applied to the calculated structure factors. The weighting schemes reflected the counting statistics. In each case the occupancy parameters were refined in a series of least-squares cycles together with the thermal parameters, while the scale factors were held constant. These occupancy parameters are listed in Table 3. It can be seen that they did not greatly deviate from the ideal values. Therefore, in the final least-squares cycles the ideal occupancy parameters were resumed. All atoms were refined with anisotropic thermal parameters. The positional parameters of LaZnPO and NdZnAsO were transformed to the setting as described for the prototype ZrCuSiAs[7] and the parameters of NdZnPO were standardized using the program STRUCTURE TIDY.[12] The atom parameters and interatomic distances are summarized in Tables 3 and 4. The anisotropic displacement parameters are available as Supporting Information.

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(10) Sheldrick, G. M. *SHELXS-86: Program for the Solution of Crystal Structures;* University of Göttingen: Gottingen, Germany, 1986.

(11) Frenz, B. A. & Associates Inc. *SDP Structure Determination Package;* College Station, TX, 1985.

(12) Gelato, L. M.; Parthé, E. *J. Appl. Crystallogr.* **1987**, *20*, 139.

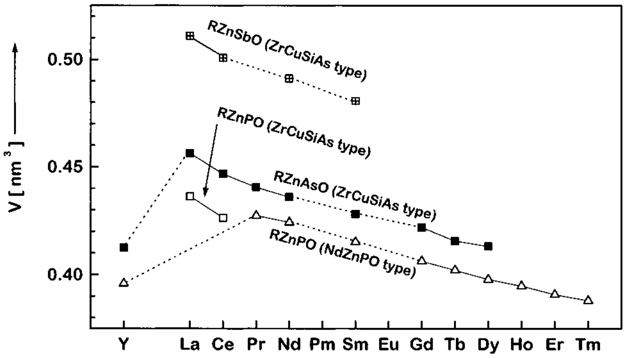

Figure 1. Cell volumes of rare earth element zinc pnictide oxides with NdZnPO ($Z = 6$)- and ZrCuSiAs ($Z = 2$)-type structure. To facilitate comparisons, the cell volumes of the tetragonal ZrCuSiAs-type compounds are multiplied by 3. The data for the antimonide oxides are taken from ref 4.

Discussion

The new rare earth element zinc pnictide oxides RZnPO and RZnAsO as well as the earlier reported corresponding compounds with antimony[4] RZnSbO crystallize with two different structure types (Figure 1). For the phosphorus-containing compounds RZnPO we find the tetragonal ZrCuSiAs-type structure for R = La, Ce, while a new trigonal structure type is now established for R = Y, Pr, Nd, Sm, Gd−Tm. The arsenic-containing compounds RZnAsO as well as the corresponding compounds with antimony RZnSbO are all isotypic with ZrCuSiAs. With the neodymium compounds NdZnAsO (tetragonal) and NdZnPO (trigonal) we have examples where both structure types were refined. They are therefore well-suited for a comparison of both structure types and their near-neighbor environments (Figures 2 and 3). Both structures have a layered character, and this is also reflected in the shapes of the crystals, which are platelets. In both structures the zinc and phosphorus or arsenic atoms, respectively, form polyanionic two-dimensionally infinite networks, which are separated from each other by cationic layers of the composition NdO. These layers reflect the trigonal and tetragonal symmetry of the structures (Figure 2).

The neodymium atoms in the trigonal (tetragonal) structure have four (four) oxygen and three phosphorus (four arsenic) neighbors, respectively. It is remarkable that in both structures the more electronegative oxygen atoms are all at one side of the coordination shell of the neodymium atoms, while the three phosphorus or four arsenic atoms are at the other side (Figure 3).

In both structures the zinc atoms have four pnictogen atoms as closest neighbors forming tetrahedra. In addition, the zinc atoms have three (in the trigonal) or four zinc neighbors (in the tetragonal structure) at the marginally bonding distances of 293.5 and 284.9 pm, respectively (Table 4). We will return to these below.

The phosphorus and arsenic atoms of both structures have four zinc neighbors all at one side of their coordination shells with three (in the trigonal) and four neodymium atoms (in the tetragonal structure) at the other side. The arrangement of these neighbors around the phosphorus and arsenic atoms is similar to the coordination polyhedra of the neodymium atoms. These polyhedra may be designated as monocapped octahedra and trigonal antiprisms, respectively (Figure 3).

The environments of the oxygen atoms are similar in both structures: distorted tetrahedra of neodymium atoms. The average Nd−O distance of 237.1 pm in the trigonal compound NdZnPO is greater than the Nd−O distances of 232.8 pm in the tetragonal compound NdZnAsO. This difference may possibly be rationalized by considering the other neighbors of the neodymium atoms. In the trigonal compound they have (in addition to the oxygen atoms) three (relatively strongly

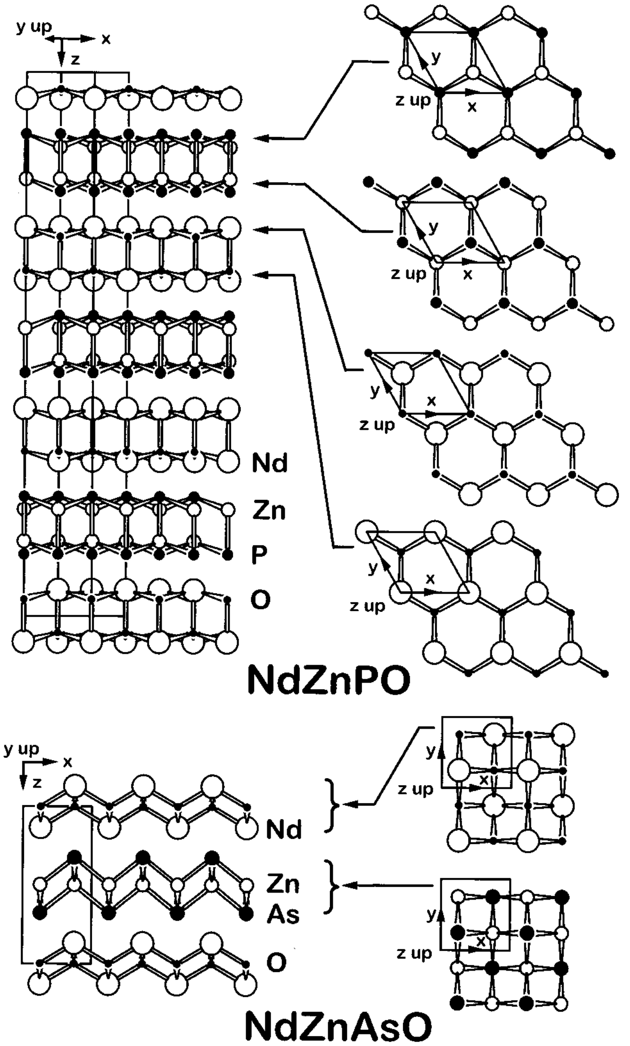

Figure 2. Crystal structures of the trigonal (space group $R\bar{3}m$) and the tetragonal ($P4/nmm$) rare earth element zinc pnictide oxides with the compounds NdZnPO and NdZnAsO as examples. The right-hand parts of this figure show projections of the Nd−O and Zn−Pn layers along z.

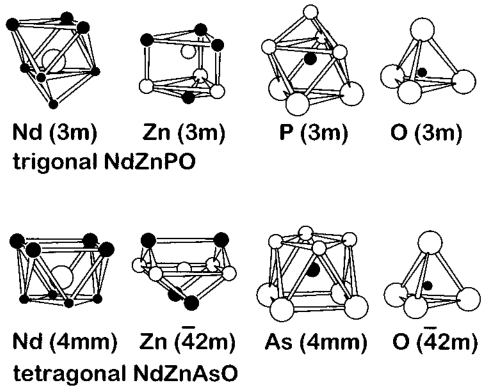

Figure 3. Near-neighbor environments in the trigonal compound NdZnPO and in NdZnAsO with the tetragonal ZrCuSiAs-type structure. The site symmetries are indicated in parentheses.

bonded) phosphorus neighbors at 307.0 pm, whereas in the tetragonal compound they have four arsenic neighbors at 333.4 pm.

For the rationalization of chemical bonding we can start from a simple model using oxidation numbers (formal charges), where the bonding electrons are counted at the partner with the higher electronegativity. Neither the trigonal nor the tetragonal compounds have any P−P, As−As, P−O, As−O, or O−O bonds. Hence, these electronegative atoms can be assigned their usual oxidation numbers: As^{3-}, P^{3-}, and O^{2-} in agreement with the octet rule. Then the metal atoms also obtain their normal oxidation numbers: 3+ for the rare earth elements and 2+ for zinc. The cell volumes of the cerium coumpounds do not deviate from the smooth function of the cell volumes found for the compounds with the typically trivalent rare earth elements (Figure 1). Thus, cerium does not show any tendency to become tetravalent in the three tetragonal compounds CeZnPnO (Pn = P, As, Sb).

The fine-tuning of this simple bonding model should account for the fact that the trigonal compounds RZnPO (R = Y, Pr, Nd, Sm, Gd−Tm) are transparent, whereas all tetragonal compounds (including LaZnPO and CeZnPO) are black. They might be metallic conductors, or they might be semiconducting like elemental silicon, which is also black. Unfortunately, the crystals of all compounds prepared by us were too small to determine their electrical conductivity. However, the optical properties clearly indicate that the tetragonal crystals have a smaller band gap and thus that they have more metallic character than the trigonal ones.

We now focus our attention to the differences between the two crystal structures. The oxygen atoms are well-embedded in the RO layers, and although these layers are different in the two structures, these layers are ionic in character, and we believe that they are not primarily responsible for the different band gaps of the two structures. Thus, we look for the differences in the ZnP, ZnAs, and ZnSb layers. We note that the more metallic, tetragonal structure occurs for all arsenides and antimonides, and certainly these elements have a smaller electronegativity and are more metallic than phosphorus. This leads us to a comparison of the coordination numbers, since the more metallic elements are known to have a tendency for higher coordination numbers, especially in intermetallics, which have broad bands. Indeed we find higher coordination numbers in the tetragonal structure for all atoms except for the oxygen atoms (Table 4 and Figure 3). Possibly the most important difference can be seen in the higher coordination number of the zinc atoms in the tetragonal structure caused by the stronger Zn−Zn interactions. In the transparent trigonal structure of NdZnPO, the zinc atoms have three zinc neighbors with the rather long Zn−Zn distance of 293.5 pm. Because the zinc atoms have the more electronegative phosphorus atoms as their main bonding partners, they will have mostly engaged their valence electrons in zinc−phosphorus bonding, and little Zn−Zn bonding is to be expected in this transparent compound. In contrast, the Zn−Zn distances of 284.9 pm in NdZnAsO are shorter, and they are close to the average Zn−Zn bond distance of 277.8 pm in the hexagonally close-packed stucture of elemental zinc.[13] Therefore, we believe that the more metallic, tetragonal pnictide oxides are stabilized by weak Zn−Zn bonds. However, since the Zn−Zn distances are rather large, the splitting between bonding and antibonding Zn−Zn bands will be small or it may not occur at all. In either case the Zn−Zn interactions might well be responsible for the semiconducting or metallic properties of the tetragonal phosphide oxides LaZnPO and CeZnPO as well as the arsenide and antimonide oxides. Certainly, band structure calculations are required for a more quantitative understanding of these interesting simple compounds.

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Supporting Information Available: Listings of crystallographic data and the anisotropic displacement parameters for all atoms of NdZnPO, LaZnPO, and NdZnAsO (2 pages). Ordering information is given on any current masthead page.

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(13) Donohue, J. *The Structures of the Elements*; Wiley: NewYork, 1974.