Convenient Route for the Synthesis of Transition-Metal Pnictides by Direct Reduction of Phosphate, Arsenate, and Antimonate Precursors†

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Received March 27, 1997. Revised Manuscript Received July 21, 1997⊗

Several transition-metal phosphates, arsenates, and antimonates undergo direct reduction in hydrogen at relatively low temperatures (400−1050 °C) to the corresponding phosphides, arsenides, and antimonides, providing a convenient route for the synthesis of transition-metal pnictides. We have synthesized by this route a variety of binary transition-metal phosphides (MoP, WP, Fe_2P, Ni_2P, FeP, RuP), arsenides (NiAs, CoAs), and antimonides ($NiSb_2$, $CoSb_3$). We could not however synthesize pnictides of manganese, vanadium, and gallium by this route, suggesting that the method is applicable only to those metals that are less electropositive than hydrogen, that is, those metals whose binary oxides are reducible by hydrogen to the metallic state.

Introduction

Solid-state chemistry, for the most part, is concerned with synthesis and characterization of inorganic solids of the kind, M_xX_z, $M_xM_y'X_z$, etc., containing metallic (M, M′) and nonmetallic (X) elements.[1] The nonmetallic elements are usually drawn from the periodic groups 14, 15, 16, and 17, the corresponding solid compounds being the tetrelides, pnictides, chalcogenides, and halides. Among these solids, metal oxides have traditionally attracted major attention,[2] not surprisingly because oxygen is the most reactive constituent of the earth's atmosphere and most of the metals in the periodic table form stable oxides relatively easily, with large negative free energies of formation.[3] Investigations of metal oxides over the past 3 decades or so have provided a wealth of new materials and new knowledge of importance to both materials science and condensed matter physics, the most widely known among them being the high-T_c superconducting cuprates.[4] Progress with other families of solids containing non-oxide anions have been relatively tardy, mainly because of the difficulties associated with synthesis of these materials. Basic research into non-oxide transition-metal compounds is especially attractive in view of the possibility of novel structures and electronic properties that have no parallel among the oxide analogues.[5]

Among the non-oxide solids, transition-metal pnictides constitute a distinct family exhibiting several unique structures and properties. A special feature of pnictide (phosphide, arsenide, and antimonide) structures is that, besides normal valence compounds containing X^{3-} anions, polyanionic compounds containing X−X bonds as well as polycationic compounds containing M−M bonds are common.[5,6] NiAs, MnP, pyrite, marcasite, arsenopyrite, and skutterudite are some of the well-known structure types among transition-metal pnictides. Examples for almost every type of electronic property can be found among members of this family.[5] Thus, MnP and FeP are metallic ferromagnets, while the d^6 low-spin pyrites, PtX_2 (X = P, As, Sb), are diamagnetic semiconductors; the isostructural $AuSb_2$ (d^7) is metallic and even superconducting. The low-spin d^6 $NiAs_2$ and $NiSb_2$ marcasites are semiconducting as expected, but the d^5 arsenopyrites (distorted marcasites) $CoAs_2$ and $CoSb_2$ would have been metallic but for a structural distortion arising from the highest occupied band of d_{xy} parentage which would be half-filled in the undistorted structure.[5] The skutterudite ($CoAs_3$) structure, which is unique to the pnictide family containing cyclic $X_4{}^{4-}$ anions, is related to the ReO_3 structure.[7] As such, it is not surprising to find stuffed derivatives of this structure, RM_4X_{12} (R = rare earth),[8] members of which exhibit superconducting ($LaFe_4P_{12}$),[9] ferromagnetic (UFe_4P_{12}),[10] and thermoelectric properties ($LaFe_{4-x}Co_xSb_{12}$);[11] the latter are potential candidate

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[†] Contribution No. 1269 from the Solid State and Structural Chemistry Unit.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

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S0897-4756(97)00175-0 CCC: $14.00

Table 1. Synthesis of Transition-Metal Pnictides by Reduction of Phosphate, Arsenate, and Antimonate Precursors

precursor	synthesis conditions	pnictide	structure type and lattice parameters (Å)
$MoOPO_4$	800 °C, H_2, 1 h	MoP	WC, hexagonal, $a = 3.214(2)$, $c = 3.198(2)$
$MoO_2HPO_4 \cdot H_2O$	870 °C, H_2 + Ar, 1 h	MoP	
$W_2O_3(PO_4)_2$	800 °C, H_2, 2 h	WP	MnP, orthorhombic, $a = 5.729(1)$, $b = 3.250(5)$, $c = 6.220(1)$
$NH_4FePO_4 \cdot H_2O$	800 °C, H_2 + Ar, 7 h	FeP	MnP, orthorhombic, $a = 5.185(4)$, $b = 5.788(1)$, $c = 3.096(1)$
$NH_4CoPO_4 \cdot H_2O$	980 °C, H_2 + Ar, 2 h	Co_2P	anti-$PbCl_2$, orthorhombic, $a = 5.666(1)$, $b = 6.301(9)$, $c = 3.528(2)$
$NH_4NiPO_4 \cdot H_2O$	820 °C, H_2 + Ar, 2 h	Ni_2P	Fe_2P, hexagonal, $a = 5.863(2)$, $c = 3.377(7)$
$NH_4MnPO_4 \cdot H_2O$	1000 °C, H_2 + Ar, 3 h	no phosphide	
$FePO_4$	1000 °C, H_2 + Ar, 9 h	Fe_2P	Fe_2P, hexagonal, $a = 5.876(1)$, $c = 3.454(1)$
$RuP_2O_7 \cdot 2H_2O$	600 °C, H_2, 6 h	RuP	MnP, orthorhombic, $a = 5.499(2)$, $b = 3.160(1)$, $c = 6.100(3)$
$VOPO_4 \cdot 2H_2O$	1000 °C, H_2, 3 h	no phosphide	
$GaPO_4$	1000 °C, H_2, 3 h	no phosphide	
$NH_4NiAsO_4 \cdot CH_3CN \cdot 2H_2O$	400 °C, H_2, 2 h	NiAs	NiAs, hexagonal, $a = 3.618(1)$, $c = 5.037(2)$
$CoAs_2O_6$	420 °C, H_2 + Ar, 6 h	CoAs	MnP, orthorhombic, $a = 3.470(1)$, $b = 5.862(1)$, $c = 5.287(1)$
$CoSb_2O_6$	600 °C, H_2, 6 h	$CoSb_2$	FeAsS (arsenopyrite), orthorhombic, $a = 6.486(6)$, $b = 6.353(6)$, $c = 6.516(6)$
$NiSb_2O_6$	500 °C, H_2, 6 h	$NiSb_2$	FeS_2 (marcasite), orthorhombic, $a = 5.177(2)$, $b = 6.295(3)$, $c = 3.827(2)$
$CoSb_3O_9$	575 °C, H_2, 6 h	$CoSb_3$	$CoAs_3$ (skutterudite), cubic, $a = 9.017(2)$

materials for thermoelectric power generation and refrigeration.

We believe that nonavailability of a rapid and convenient synthetic route is a major reason for the tardy progress of research in this area. A common method employed for the synthesis of pnictides is the direct reaction between the constituent elements in evacuated and closed containers at elevated temperatures.[12] In view of the problems associated with the direct elemental reaction route, which include volatility of nonmetallic constituents, slow diffusion and long reaction duration, incomplete reaction, and formation of mixture of phases,[12,13] we considered it important to explore alternate synthetic routes that would avoid these problems. One such route would be the direct redution of metal oxoanion precursor compounds such as $M_x(XO_y)_z$ ($X =$ P, As, Sb) to the desired pnictide.[14,15] We explored this route at some length, and our investigations have revealed that a surprisingly large number of transition-metal phosphates, arsenates, and antimonates undergo direct reduction in hydrogen at not so very high temperatures (400−1050 °C) to yield the corresponding pnictides. Our results, which are described in this paper, show that hydrogen reduction of oxoanion precursors not only provides a convenient route for the synthesis of a wide variety of transition-metal pnictides but also opens up new avenues for exploring the solid-state chemistry of several families of transition-metal non-oxide solids. Our method appears to be complementary to that described by Kaner and co-workers[16] for the synthesis of non-oxide solids. Their method is based on highly exothermic metathetical (exchange) reactions that enable synthesis of thermally stable pnictides such as ZrP, GaP, and GaAs, among others.

Experimental Section

We investigated the formation of pnictides by direct reduction of several phosphate, arsenate, and antimonate precursors in hydrogen. The precursor compounds (Table 1) were prepared by standard methods reported in the literature.[17] In addition, the following new precursors were also prepared: $RuP_2O_7 \cdot 2H_2O$,[18] $NH_4NiAsO_4 \cdot CH_3CN \cdot 2H_2O$,[18] and $CoSb_3O_9$.[19] We investigated the course of reduction reactions of every precursor by thermogravimetric (TG, Cahn TG-131 system) in flowing hydrogen or hydrogen:argon (1:1) mixture (12 mL/min) at a heating rate of 2 °C/min. Bulk samples were prepared by reducing ~1 g quantities of the precursor in a tubular furnace at temperatures determined by thermogravimetry. The reduction products were characterized by EDX analysis using JEOL JSM 840A scanning electron microscope and powder X-ray diffraction (XRD) using JEOL JDX-8P X-ray diffractometer and Cu Kα radiation. Unit-cell parameters were derived by least-squares refinement of powder XRD data using PROSZKI program.[20] We list in Table 1 the precursors, the product pnictides, conditions for their synthesis together with their lattice parameters.

Results and Discussion

TG investigations showed that several transition-metal phosphates undergo facile reduction in hydrogen at 650−1050 °C to the corresponding phosphides. For example, $MoOPO_4$ was reduced at 800 °C to MoP directly (Figures 1a and 2a). The observed weight loss in TG (38.57%) corresponded to the reaction, $MoOPO_4 + 5H_2 \rightarrow MoP + 5H_2O$ (calculated weight loss, 38.66%), indicating that the reduction to the phosphide was quantitative. Powder XRD showed that the reduction product was indeed MoP having the WC structure.[21] The

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[12] (a) von Schnering, H. G. In *Encyclopedia of Inorganic Chemistry*; King, R. B. Ed. John Wiley & Sons: Chichester, 1994; Vol. 6, pp 3110−3115. (b) Kjekshus, A. *Acta Chem. Scand.* **1971**, *25*, 411. (c) Kjekshus, A.; Rakke, T.; Andersen, A. F. *Acta Chem. Scand.* **1974**, *28*, 996.

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[14] To our knowledge, reduction of $Fe_2P_2O_7$ to FeP seems to be the only definitive report in the literature of hydrogen reduction of a phosphate to a phosphide. See: von Schnering, H. G.; Hönle, W. *Chem. Rev.* **1988**, *88*, 243.

[15] Electrolytic reduction of fused salts containing alkali-metal phosphates/arsenates and transition-metal oxides and/or chlorides is known to yield transition-metal phosphides and arsenides. See: Wold, A.; Bellavance, D. In *Preparative Methods in Solid State Chemistry*; Hagenmuller, P., Ed.; Academic Press: New York, 1972; pp 279−307.

[16] (a) Wiley, J. B.; Kaner, R. B. *Science* **1992**, *225*, 1093. (b) Gillan, E. G.; Kaner, R. B. *Chem. Mater.* **1996**, *8*, 333−343.

[17] (a) $MoOPO_4$: Kierkegaard, P.; Westerland, M. *Acta Chem. Scand.* **1964**, *18*, 2217. (b) $MoO_2HPO_4 \cdot H_2O$: Kierkegaard, P. *Acta Chem. Scand.* **1960**, *14*, 657. (c) $NH_4MPO_4 \cdot H_2O$ (M = Mn, Fe, Co, Ni): Carling, S. G.; Day, P.; Visser, D. *Inorg. Chem.* **1995**, *34*, 3917. (d) $FePO_4$: Standard X-ray Diffraction Powder Patterns, NBS Monograph 25, Section 15; U.S. Department of Commerce, 1978; p 33. (e) $VOPO_4 \cdot 2H_2O$: Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Rich, S. M. *Inorg. Chem.* **1982**, *21*, 3820. (f) $GaPO_4$: Mooney, R. C. L. *Acta Crystallogr.* **1956**, *9*, 728. (g) $CoAs_2O_6$: Taylor, J. B.; Heyding, R. D. *Can. J. Chem.* **1958**, *36*, 597. (h) $CoSb_2O_6$: Standard X-ray Diffraction Powder Patterns, NBS Monograph 25, Section 5; U.S. Department of Commerce, 1967; p 26.

[18] $RuP_2O_7 \cdot 2H_2O$ was prepared by direct reaction of RuO_2 and $NH_4H_2PO_4$ in the required proportion in air at 600 °C. $NH_4NiAsO_4 \cdot CH_3CN \cdot 2H_2O$ was prepared by refluxing a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (10 mmol), $H_3AsO_4 \cdot 3H_2O$ (10 mmol) and concentrated NH_3 (200 mmol) in 60 mL of CH_3CN for 3 days.

[19] $CoSb_3O_9$ was prepared by reacting $CoC_2O_4 \cdot 2H_2O$ and Sb_2O_3 in the stoichiometric proportion at 1000 °C for 24 h. Powder XRD pattern of the phase revealed a trirutile structure similar to that of $CoSb_2O_6$.

[20] Losocha, W.; Lewinski, K. *J. Appl. Crystallogr.* **1994**, *27*, 437.

[21] Rundqvist, S.; Lundström, T. *Acta Chem. Scand.* **1963**, *17*, 37.

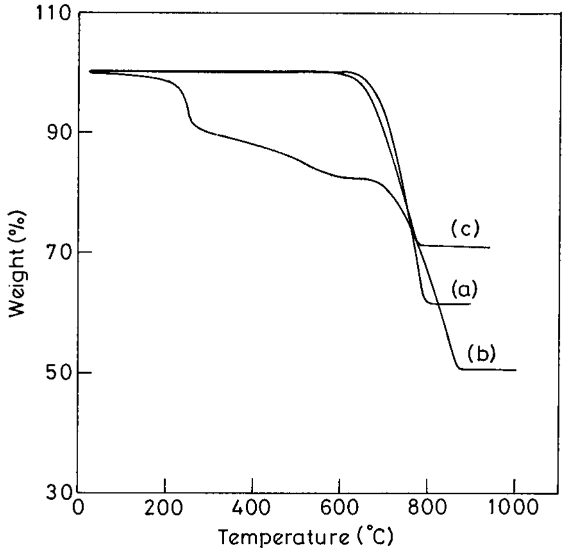

Figure 1. Thermogravimetric curves for the reduction of (a) $MoOPO_4$, (b) $MoO_2HPO_4{\cdot}H_2O$, and (c) $W_2O_3(PO_4)_2$.

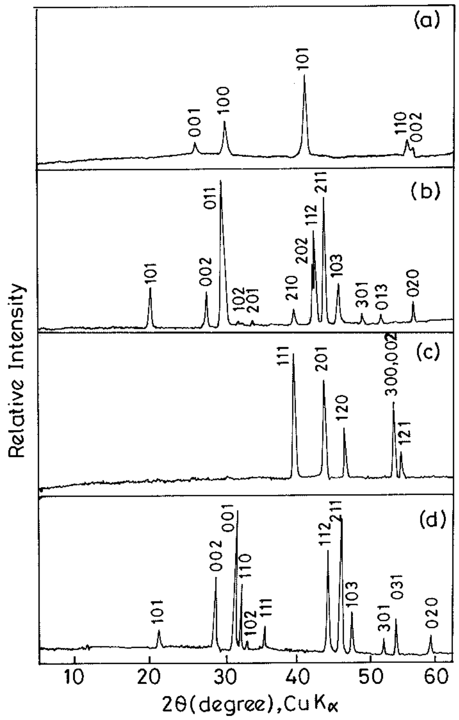

Figure 2. Powder XRD patterns of (a) MoP, (b) WP, (c) Ni_2P, and (d) RuP.

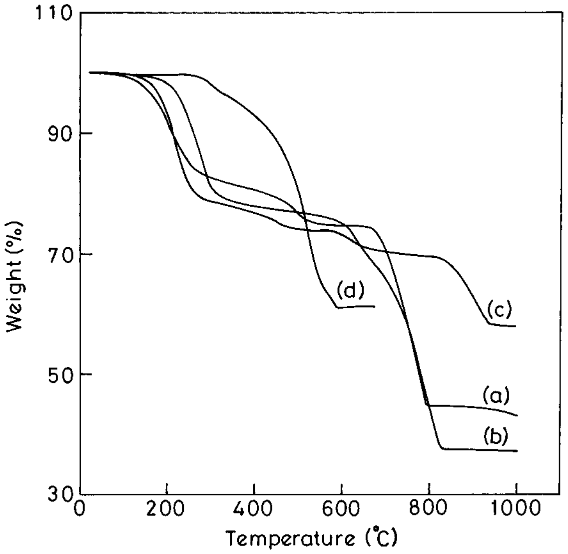

Figure 3. Thermogravimetric curves for the reduction of (a) $NH_4FePO_4{\cdot}H_2O$, (b) $NH_4NiPO_4{\cdot}H_2O$, (c) $NH_4MnPO_4{\cdot}H_2O$, and (d) $Ru_2P_2O_7{\cdot}2H_2O$.

hexagonal lattice parameters of the sample prepared by us (a = 3.214(2); c = 3.198(2) Å) are in agreement with the values of MoP reported in the literature.[21] MoP could also be prepared starting from $MoO_2HPO_4{\cdot}H_2O$ (Figure 1b). Similarly, WP having the MnP structure could be obtained by the reduction of W_2O_3 $(PO_4)_2$ at 800 °C (Figures 1c and 2b). The elemental ratios of MoP and WP as determined by EDX analysis were 1:1 within a relative error of 2%.

Next, we investigated the formation of first-row transition-metal phosphides from precursor phosphates of the general formula $NH_4MPO_4{\cdot}H_2O$ (M = Mn, Fe, Co, Ni). While we obtained FeP from $NH_4FePO_4{\cdot}H_2O$, we could obtain only Ni_2P and Co_2P by the reduction of the corresponding nickel and cobalt phosphates. Reduction of $FePO_4$ on the other hand yields Fe_2P. From the TG data (Figure 3a), the reaction sequence for the formation of FeP from $NH_4FePO_4{\cdot}H_2O$, for example, could be written as follows:

$$NH_4FePO_4{\cdot}H_2O \rightarrow FeHPO_4 + NH_3 + H_2O \quad (1)$$

$$FeHPO_4 \rightarrow {}^1/_2Fe_2P_2O_7 + {}^1/_2H_2O \quad (2)$$

$$^1/_2Fe_2P_2O_7 + {}^7/_2H_2 \rightarrow FeP + {}^7/_2H_2O \quad (3)$$

EDX analysis and powder XRD data showed that the products were single-phase phosphides having the expected stoichiometry and structure, the lattice parameters (Table 1) being in agreement with the values reported in the literature.[22] Reduction of $RuP_2O_7{\cdot}H_2O$ yielded RuP instead of the expected RuP_2 (Figures 2d and 3d):

$$RuP_2O_7 + {}^{17}/_2H_2 \rightarrow RuP + P + {}^3/_2H_2 + 7H_2O \quad (4)$$

It is significant that for Co_2P, Ni_2P, Fe_2P, and RuP, the precursor phosphate compositions do not match with the product phosphides, indicating that part of phosphorus is lost during the reduction process.

Interestingly, we could not obtain a manganese phosphide by reduction of $NH_4MnPO_4{\cdot}H_2O$ (Figure 3c). Also, both $VOPO_4{\cdot}2H_2O$ and $GaPO_4$ did not yield phosphides on reduction up to 1000 °C. Our inability to prepare phosphides of manganese, vanadium, and gallium is significant. The implication of this result is discussed later.

We could readily synthesize a number of transition metal arsenides and antimonides as well by the reduction route. For example, $NH_4NiAsO_4{\cdot}CH_3CN{\cdot}2H_2O$ and $CoAs_2O_6$ undergo facile reduction around 400 °C in hydrogen to yield the well-known NiAs (Figure 4a) and CoAs. Similarly, we could synthesize $CoSb_2$ and $NiSb_2$ possessing the arsenopyrite and marcasite structures,

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(22) (a) FeP: Kjekshus, S. K. *Acta Chem. Scand.* **1972**, *26*, 1276. (b) Co_2P: Standard X-ray Diffraction Powder Paterns, NBS Monograph 25, Section 18; U.S. Department of Commerce, 1981; p 32. (c) Ni_2P: Nowotny, H.; Henglein, E. *Z. Phys. Chem.* **1938**, *40*, 281. (d) Fe_2P: Fujii, H.; Komura, S.; Takeda, T.; Okamoto, T.; Ito, Y.; Akimitsu, J. *J. Phys. Soc. Jpn.* **1979**, *46*, 1616.

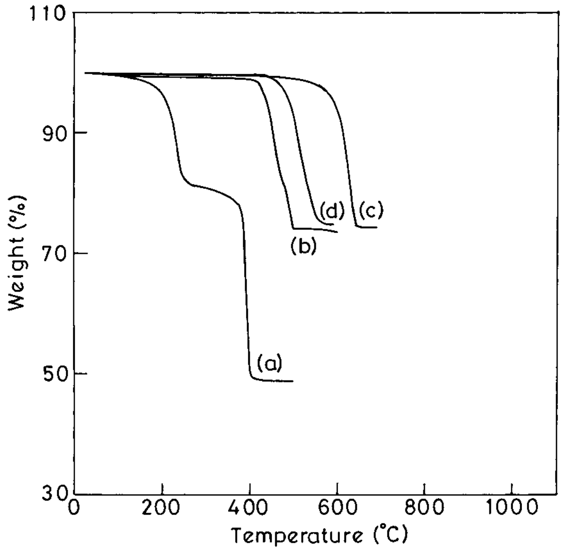
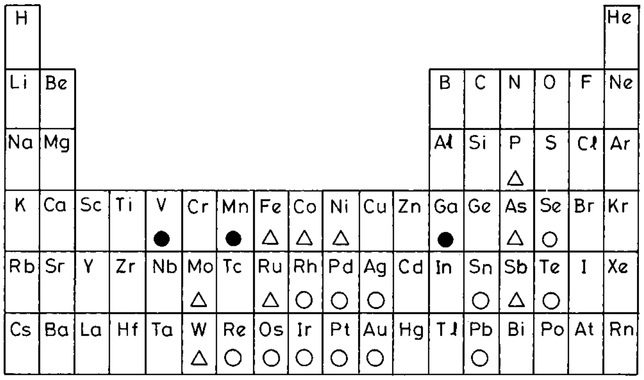


Figure 4. Thermogravimetric curves for the reduction of (a) $NH_4NiAsO_4 \cdot CH_3CN \cdot 2H_2O$, (b) $NiSb_2O_6$, (c) $CoSb_2O_6$, and (d) $CoSb_3O_9$.

respectively,[5] by the reduction of trirutile-like $CoSb_2O_6$ and $NiSb_2O_6$ precursor antimonates. Reduction of arsenates and antimonates occurs at relatively low temperatures (400−650 °C) to yield the pnictides and clean single-phase products could be prepared within a few hours, whereas syntheses of these phases by direct reaction route require several days of repetitive reaction in closed systems at higher temperatures.[12] We could also synthesize $CoSb_3$ possessing the skutterudite structure[5] by reduction of a new precursor, $CoSb_3O_9$. Again, single-phase $CoSb_3$ was obtained at 575 °C within a few hours. We believe this result is quite significant because of the recently discovered thermoelectric materials based on the skutterudite structure.[11]

The following general observations could be made on the basis of the data given in Table 1. We see that in general arsenates and antimonates undergo reduction at much lower temperatures (400−650 °C) than phosphates (700−1050 °C). This is not surprising in view of the fact that pentavalent arsenates and antimonates are oxidizing agents, whereas phosphates are stable toward reduction.[23] Another important observation is that while most of the phosphates investigated yield phosphides on reduction, there are three exceptions, namely $VOPO_4 \cdot 2H_2O$, $NH_4MnPO_4 \cdot H_2O$, and $GaPO_4$, which do not yield phosphides on reduction up to 1000 °C. This result is significant because it gives an insight into the thermodynamics of the reduction process. When electrons and protons (hydrogen) are pumped into the precursor phosphates at elevated temperatures, it is likely that the electrons first go to the lowest unoccupied (LUMO-like) states which are essentially derived from the metal d orbitals. Simultaneously, oxide ions would be removed by the protons, destabilizing the anionic P(V) states; accordingly, P(V) becomes susceptible to reduction. Electron-rich M and P species thus formed in situ during the reduction process eventually transforms to the appropriate phosphide under the reaction condition. We therefore believe that addition of electrons to metal-like LUMO states is an essential first step that triggers reduction of the phosphate in the precursor. A similar process would be operative for the reduction of the arsenates and antimonates as well, except that the latter are more easily reducible than the phosphates. These considerations also explain why phosphates like $GaPO_4$, $VOPO_4 \cdot 2H_2O$, and $NH_4MnPO_4 \cdot H_2O$ do not undergo reduction to phosphides; Ga (III), V(III), and Mn(II) cannot be reduced by hydrogen to lower oxidation states. Accordingly, the reduction route is applicable to the synthesis of pnictides of only those transition metals whose binary oxides are reducible by hydrogen; MoO_3, WO_3, FeO, CoO, and NiO are reducible to the metallic state by H_2, while MnO, V_2O_3, and Ga_2O_3 are not.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P △	S	Cl	Ar
K	Ca	Sc	Ti	V ●	Cr	Mn ●	Fe △	Co △	Ni △	Cu	Zn	Ga ●	Ge	As △	Se ○	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo △	Tc	Ru △	Rh ○	Pd ○	Ag ○	Cd	In	Sn ○	Sb △	Te ○	I	Xe
Cs	Ba	La	Hf	Ta	W △	Re ○	Os ○	Ir ○	Pt ○	Au ○	Hg	Tl	Pb ○	Bi	Po	At	Rn

Figure 5. Periodic table of elements showing the applicability of oxoanion precursor reduction route for the synthesis of metal−nonmetal compounds. Open triangles denote metals and nonmetals for which the route has been found applicable; open circles denote metals and nonmetals for which the route is likely to be applicable but not investigated; filled circles denote metals for which phosphate reduction does not yield phosphide.

We believe that the results of this paper have a much wider significance in the light of the relative stabilities of oxoanions of nonmetallic elements of groups 14 (Si, Ge, Sn), 15 (P, As, Sb), 16 (S, Se, Te), and 17 (Cl, Br, I). It is generally known from the standard reduction potential data[24] that the stability of XO_y^{n-} (X = nonmetallic element) anions decreases as we move from left to right and from top to bottom in the periodic table, SiO_4^{4-} being most stable and IO_4^- least stable (highly oxidizing). Accordingly, we suggest that the method described in this paper could be extended to the synthesis of transition-metal chalcogenides (especially selenides and tellurides) and even tetrelides (stannides and plumbides). Further work to realize these objectives is in progress. Finally, we indicate in a periodic table (Figure 5) the metals and nonmetals whose binary and ternary compounds could be synthesized by hydrogen reduction of oxoanion precursors.

Acknowledgment. We thank Professor C. N. R. Rao for encouragement and support. We also thank the Indo-French Centre for the Promotion of Advanced Research, New Delhi and the Department of Science & Technology, Government of India, for financial support.

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[23] Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Oxford University Press: Oxford, 1991; p 337.

[24] Reference 3, p D:158.