Thermochemistry of Phosphorus Oxynitrides: PON and LiNaPON Glasses

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High-temperature solution calorimetry has been very useful in elucidating the energetics of many oxide materials. Recently, a sodium molybdate melt, $3Na_2O \cdot 4MoO_3$, has been shown to be very effective for nitride calorimetry. This methodology has now been used to determine the energetics of formation of phosphorus oxynitride PON samples and of a series of LiNaPON oxynitride glasses. Enthalpies of formation from the elements at 298 K are −371.71 ± 4.45 and −356.14 ± 3.98 kJ mol^{-1} for β-cristobalite and amorphous PON, respectively, and −961.88 ± 3.86 kJ mol^{-1} for a 9 wt % nitrogen-containing LiNaPON glass. The β-cristobalite energy of amorphization is −15.57 ± 5.97 kJ mol^{-1}. A linear relation, $\Delta H_f^\circ(Li_{0.5}Na_{0.5}PO_{(3-3x/2)}N_x) = \Delta H_f^\circ(Li_{0.5}Na_{0.5}PO_3) + 441.7x$, was found between the enthalpies of formation of the glasses and their atomic nitrogen content, x ($0 \leq x \leq 0.57$). The magnitude of the energetics of nitrogen/oxygen substitution within PON and LiNaPON glasses has been correctly evaluated by using N−N, O−O, P−N, and P−O bond strengths. The in-situ precipitation of metallic particles from corresponding oxides in LiNaPON glasses has been predicted from high-temperature solution calorimetry results and appropriate thermodynamic cycles. These results constitute the first set of energetic data on nitridophosphates.

Introduction

Phosphates and silicates show similar structural arrangements based upon XO_4 (X = P, Si) tetrahedral networks. The similarity between phosphates and silicates is clearly illustrated if we consider the following charge-balanced substitution:

$$P^{5+} + N^{3-} = Si^{4+} + O^{2-} \tag{1}$$
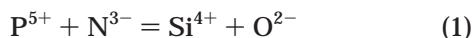
Starting from SiO_2, a PON phosphorus oxynitride formula is derived. PON is isoelectronic with SiO_2 and is its chemical analog.[1−7] It is possible to introduce nitrogen progressively into phosphate glasses with the formation of mixed $P(O,N)_4$ tetrahedra,[8−15] as discussed below in the study of LiNaPON glasses. The properties of phosphate glasses are significantly modified by substituting nitrogen for oxygen. Increasing nitrogen substitution results in a decrease in the thermal expansion coefficient, an increase of the glass transition temperature, density, and refractive index, and an improvement in the hardness and chemical durability of the glass.[8,12,16] Furthermore, nitrogen incorporation as N^{3-} gives the glass a reducing character which makes possible the in-situ precipitation of metallic Ag and Cu particles from the corresponding oxides, making potentially interesting optical glasses.[8] A qualitative thermodynamic approach has been used to predict which oxides may reduce into nitridophosphate glasses.[17]

Whereas the energetics of silica and silicates are relatively well established[18,19] and several thermody-

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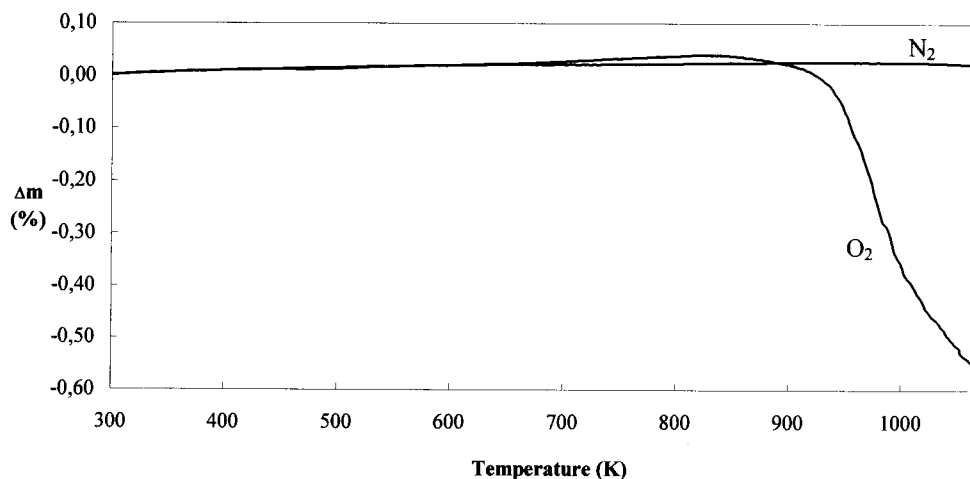(19) Navrotsky, A. *Phys. Chem. Miner.* **1997**, *24*, 222.

Figure 1. Thermogravimetric analysis of the β-cristobalite PON phase under oxygen and nitrogen flow (heating rate is 1 K min^{-1}).

namic data concerning phosphates are given in the literature,[20,21] no data characterize the energies of formation of nitridophosphates, despite the preparation of many novel compositions these past two decades.[16,22,23] The high volatility of P_2O_5 (subliming as low as 823 K) makes thermodynamic measurements difficult by conventional high-temperature equilibration techniques. High-temperature oxide melt solution calorimetry has been very useful in elucidating the energetics of many classes of oxide materials.[18,19] Recently, a sodium molybdate melt of composition $3Na_2O\cdot4MoO_3$ has been proven to be very effective for nitride calorimetry.[24-27] Here we extend this methodology to the calorimetry of phosphorus oxynitrides. The enthalpies of formation of crystalline (β-cristobalite polymorph) and amorphous PON have been determined.[28] A series of LiNaPON glasses has also been studied. These are interesting because of their low glass transition and melting temperatures.

Experimental Methodology

Preparation and Characterizations of PON. PON may be prepared, following Sommer,[29] by reacting urea or melamine with a phosphorus precursor such as phosphoric acid, phosphorus oxide (P_4O_{10}), ammonium phosphate, or urea phosphate. We used melamine [$(NCNH_2)_3$] and ammonium dihydrogenphosphate ($NH_4H_2PO_4$) as reactants.[8] This process enables the preparation of large quantities of X-ray amorphous PON powder. Crystalline β-cristobalite PON was obtained after heating the amorphous powder in an evacuated silica glass ampoule at temperatures between 973 and 1073 K for

several days. This time is required to achieve complete crystallization. The purity of the samples was confirmed by chemical analysis of nitrogen, according to a previously described procedure.[30] The thermal stability of both amorphous and crystalline phases was examined by thermogravimetry. The study was carried out on a Setaram TG92 DTA/TGA analyzer under an oxygen or nitrogen atmosphere, at a heating rate of 1 K min^{-1}. Under oxygen, the β-cristobalite polymorph persists to 923 K (Figure 1). Above this temperature, PON oxidizes into P_2O_5, which sublimes immediately, thus explaining the dramatic weight loss observed. A comparison of thermal behavior under O_2 and N_2 flow in Figure 1 suggests that a slight oxidation phenomenon, characterized by a weight gain, may intervene at temperatures as low as 623−673 K. Under an inert atmosphere, β-cristobalite PON persists to 1073 K. Figure 2 shows that, under an oxygen atmosphere, amorphous PON starts to oxidize into P_2O_5 as low as 523 K, thus generating a weight gain. P_2O_5 remains stable until 823 K, above which a competition between PON oxidation and P_2O_5 sublimation is observed. Under an inert atmosphere, thermal decomposition of amorphous PON becomes significant only above 1023 K.

Preparation of LiNaPON Glasses. Oxide base glass $Li_{0.5}Na_{0.5}PO_3$ was prepared as a starting material by mixing powders of previously dehydrated (773 K) sodium metaphosphate ($NaPO_3$), Li_2CO_3, and $NH_4H_2PO_4$ in stoichiometric amounts and melting in air in a platinum crucible.[8,17] This eutectic composition (T_m = 749 K for $Li_{0.5}Na_{0.5}PO_3$, compared to T_m = 936 K for $LiPO_3$ and 893 K for $NaPO_3$) was chosen mainly to increase the reactivity in flowing ammonia at the chosen nitridation temperature (973 K) because of a lower viscosity of the liquid. The range of reaction temperatures is limited at high temperature (above 1073 K) by reduction phenomena which result in phosphorus loss. $Li_{0.5}Na_{0.5}PO_3$ was nitrided by melting the crushed glass in a vitreous carbon boat at 973 K under an anhydrous ammonia flow. Starting from the same phosphate glass batch, a series of nitrided glasses $Li_{0.5}Na_{0.5}PO_{(3-3x/2)}N_x$ was prepared with progressive nitrogen enrichment depending on nitridation time. We noticed an apparent saturation at x = 0.57 after a treatment of 20 h at 973 K, corresponding to a maximum nitrogen content of 9 wt %.

Calorimetry. High-temperature oxidative drop solution calorimetry into a $3Na_2O\cdot4MoO_3$ molten solvent was performed in a Calvet-type twin calorimeter described in detail by Navrotsky.[18,19] The solvent was prepared from $Na_2MoO_4\cdot2 H_2O$ and MoO_3, dehydrated and liquefied at 973 K, and quenched to room temperature by pouring into a graphite dish. The melt

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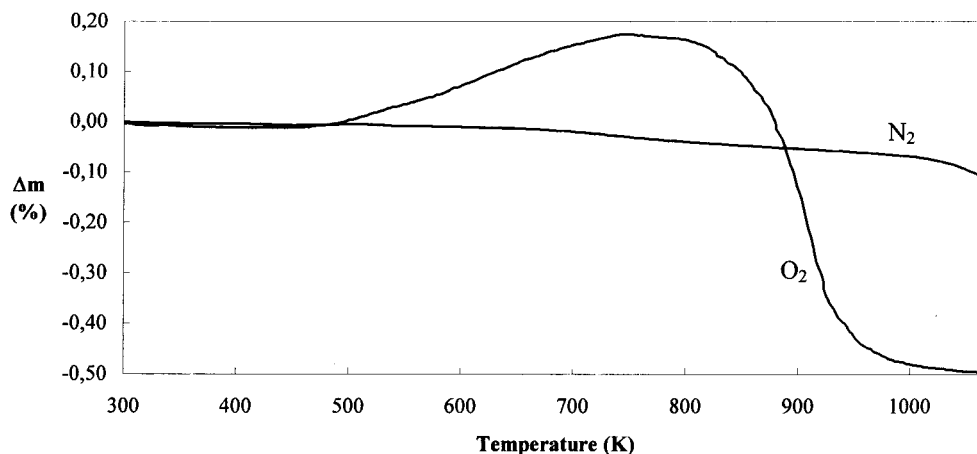
Figure 2. Thermogravimetric analysis of the amorphous PON phase under oxygen and nitrogen flow (heating rate is 1 K min^{-1}).
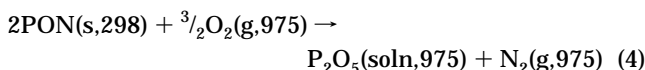
does not quench to a glass, so the entire batch was ground to a powder to homogenize it before it was loaded into the calorimetric crucibles. Because a DTA analysis had revealed that PON phases persist in a nitrogen atmosphere but oxidize in oxygen at calorimetric temperature (975 K), we decided to flush the calorimetric system with pure argon (at ~90 cm^3 min^{-1}) to prevent any oxidation of the product before reaching the molten solvent. Oxygen gas was used only for bubbling through the solvent (at ~5 cm^3 min^{-1}) to stir the melt and oxidize the oxynitride sample once it reached the solvent. In an Ar-filled glovebox, phosphorus oxynitride samples were pressed into pellets of 5–10 mg and kept in small screw-top glass vials. When a stable baseline signal was achieved, a sample vial was quickly opened and a pellet was dropped from room temperature into liquid $3Na_2O\cdot4MoO_3$ at 975 K in the calorimeter. The calorimetry utilizes a redox reaction between MoO_3 in the melt and N^{3-}, which supplies a rapid pathway for elimination of N^{3-} as N_2 gas. An illustration is given with the oxynitride composition PON, where P is in the +5 oxidation state:

$$2PON(s,298) + 3MoO_3(\text{in melt},975) \rightarrow$$
$$P_2O_5(\text{soln},975) + 3MoO_2(s,975) + N_2(g,975) \quad (2)$$
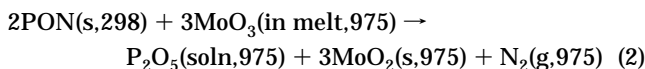
Any molybdenum dioxide dissolved in the melt is subsequently oxidized to MoO_3 by bubbling O_2 through the solvent:

$$3MoO_2(s,975) + {}^3/_2O_2(g,975) \rightarrow 3MoO_3(\text{in melt},975) \quad (3)$$
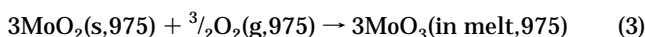
Combination of the reactions (2) and (3) yields

$$2PON(s,298) + {}^3/_2O_2(g,975) \rightarrow$$
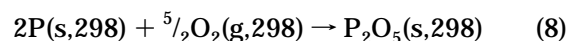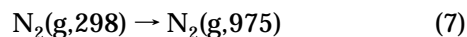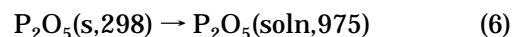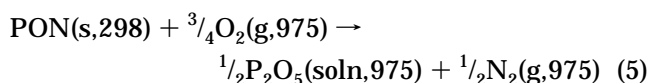$$P_2O_5(\text{soln},975) + N_2(g,975) \quad (4)$$

This reaction includes the oxidation and the dissolution of the oxynitride and represents the heat effect measured through oxidative drop solution calorimetry (ΔH_{ds}). Resulting enthalpies of formation (ΔH_f° oxynitride) and enthalpies of drop solution of the oxides necessary for the calculations were obtained by appropriate thermodynamic cycles, as shown below. Further details of the experimental procedure are provided in previous papers.[25–27]
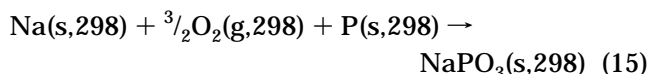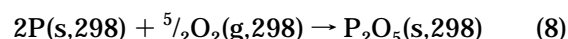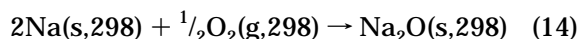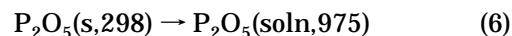
Results

PON. Drop solution calorimetry was first performed on β-cristobalite PON samples, yielding an average enthalpy of drop solution $\Delta H_{ds} = \Delta H_5 = -460.95 \pm 3.27$ kJ mol^{-1}. The enthalpy of formation of PON is determined using this value and the following thermodynamic cycle:

$$PON(s,298) + {}^3/_4O_2(g,975) \rightarrow$$
$${}^1/_2P_2O_5(\text{soln},975) + {}^1/_2N_2(g,975) \quad (5)$$

$$P_2O_5(s,298) \rightarrow P_2O_5(\text{soln},975) \quad (6)$$

$$N_2(g,298) \rightarrow N_2(g,975) \quad (7)$$

$$2P(s,298) + {}^5/_2O_2(g,298) \rightarrow P_2O_5(s,298) \quad (8)$$

$$O_2(g,298) \rightarrow O_2(g,975) \quad (9)$$

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$$P(s,298) + {}^1/_2O_2(g,298) + {}^1/_2N_2(g,298) \rightarrow$$
$$PON(s,298) \quad (10)$$
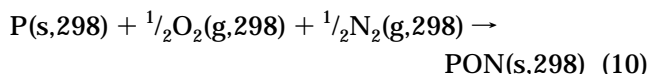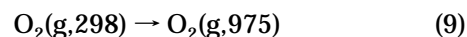
$$\Delta H_f^\circ(PON) = \Delta H_{10} =$$
$$-\Delta H_5 + {}^1/_2(\Delta H_6 + \Delta H_7 + \Delta H_8) - {}^3/_4\Delta H_9 \quad (11)$$

As P_2O_5 sublimes near 823 K, it is not possible to evaluate ΔH_6 directly. We have access to this enthalpy by measuring, for example, the enthalpy of drop solution of sodium metaphosphate ($NaPO_3$) in the same melt. ΔH_6 is determined through the thermochemical cycle:

$$NaPO_3(s,298) \rightarrow {}^1/_2Na_2O(\text{soln},975) +$$
$${}^1/_2P_2O_5(\text{soln},975) \quad (12)$$

$$Na_2O(s,298) \rightarrow Na_2O(\text{soln},975) \quad (13)$$

$$P_2O_5(s,298) \rightarrow P_2O_5(\text{soln},975) \quad (6)$$

$$2Na(s,298) + {}^1/_2O_2(g,298) \rightarrow Na_2O(s,298) \quad (14)$$

$$2P(s,298) + {}^5/_2O_2(g,298) \rightarrow P_2O_5(s,298) \quad (8)$$

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$$Na(s,298) + {}^3/_2O_2(g,298) + P(s,298) \rightarrow$$
$$NaPO_3(s,298) \quad (15)$$
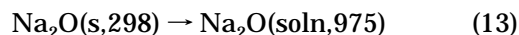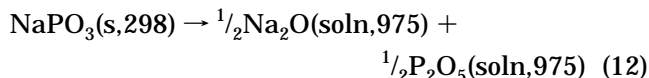
$$\Delta H_6 = 2\Delta H_{12} - \Delta H_{13} - \Delta H_{14} - \Delta H_8 + 2\Delta H_{15} =$$
$$-148.31 \pm 6.03 \text{ kJ mol}^{-1} \quad (16)$$

ΔH_{13} has been measured by dissolving sodium carbonate (Na_2CO_3) under the same conditions, using the following

Table 1. Data Used in Thermodynamic Cycles To Determine the Enthalpy of Formation from Drop Solution Calorimetry (All Values Are in kJ mol^{-1})

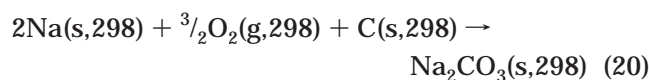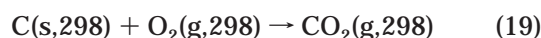|	ΔH drop solution	$\Delta H°$ formation	ref
P_2O_5	$\Delta H_6 = -148.31 \pm 6.03^a$	$\Delta H_8 = -1504.9 \pm 0.5$	35
$NaPO_3$	$\Delta H_{12} = 75.68 \pm 0.34^b$ (14)	$\Delta H_{15} = -1220.054$	20
Na_2CO_3	$\Delta H_{17} = 133.76 \pm 0.61^b$ (15)	$\Delta H_{20} = -1130.77 \pm 0.21$	33
Na_2O	$\Delta H_{13} = -217.56 \pm 4.25^a$	$\Delta H_{14} = -417.98 \pm 4.2$	33
CO_2	$H_{975} - H_{298} = 32.05$	$\Delta H_{19} = -393.52 \pm 0.05$	33
Li_2O	$\Delta H_{23} = -90.3 \pm 2.5^{26}$	$\Delta H_{24} = -598.73 \pm 2.1$	33

^{a} Calculated using thermodynamic cycles described in the text.
^{b} Measured. Uncertainty is 2 standard deviations of the mean; the number in parentheses is the number of experiments performed.

thermodynamic cycle:

$$Na_2CO_3(s,298) \rightarrow Na_2O(soln,975) + CO_2(g,975) \quad (17)$$

$$CO_2(g,298) \rightarrow CO_2(g,975) \quad (18)$$

$$Na_2O(s,298) \rightarrow Na_2O(soln,975) \quad (13)$$

$$2Na(s,298) + {}^1\!/_2O_2(g,298) \rightarrow Na_2O(s,298) \quad (14)$$

$$C(s,298) + O_2(g,298) \rightarrow CO_2(g,298) \quad (19)$$

$$2Na(s,298) + {}^3\!/_2O_2(g,298) + C(s,298) \rightarrow$$
$$Na_2CO_3(s,298) \quad (20)$$

$$\Delta H_{13} = \Delta H_{17} - \Delta H_{14} - \Delta H_{18} - \Delta H_{19} + \Delta H_{20} =$$
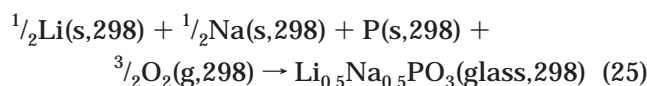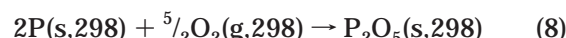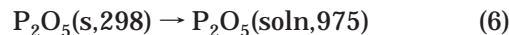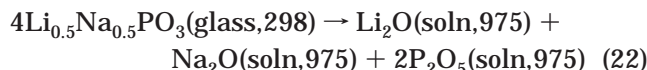$$-217.56 \pm 4.25 \text{ kJ mol}^{-1} \quad (21)$$

We note that the enthalpy of drop solution of P_2O_5 (a very acidic oxide) and the enthalpy of drop solution of Na_2O (a very basic oxide) are both strongly exothermic. This reflects the ability of the solvent both to provide oxide ions (to convert P_2O_5 into $2PO_4^{3-}$) and to absorb oxide ions (probably by converting $Mo_2O_7^{2-}$ species to MoO_4^{2-} species), making the solvent suitable for dissolution of a variety of oxides. These trends in enthalpies of solution in oxide melts are similar to these seen previously for the system $Na_2MoO_4-MoO_3$[31] and for a variety of oxides in several molten oxide solvents.[32]

Heat contents $H_{975}-H_{298}$ of N_2, O_2, and CO_2 are respectively $\Delta H_7 = 20.65$, $\Delta H_9 = 21.84$, and $\Delta H_{18} = 32.05$ kJ mol^{-1}.[33] From the enthalpy values gathered in Table 1, which result from both our experiments and the literature, we calculate the standard enthalpy of formation of cristobalite PON from the elements at 298 K, as $\Delta H_f°(PON) = -371.71 \pm 4.45$ kJ mol^{-1}.

Similar thermodynamic cycles are used to determine the energetics of amorphous PON. From the enthalpy of drop solution $\Delta H_{ds} = -476.52 \pm 2.59$ kJ mol^{-1}, we deduce an enthalpy of formation of -356.14 ± 3.98 kJ mol^{-1}.
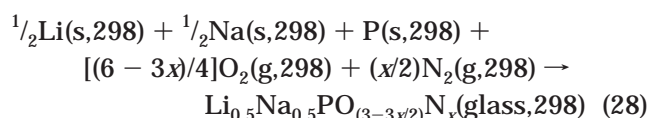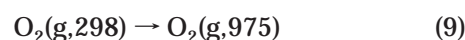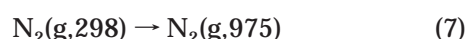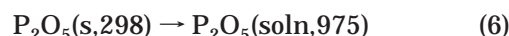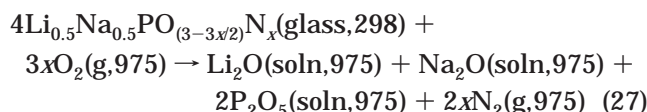
LiNaPON. Using the same method of drop solution calorimetry, we measured the energetics of nitridophosphate glasses of the series $Li_{0.5}Na_{0.5}PO_{(3-3x/2)}N_x$ ($0 \le x \le 0.57$).

(31) Navrotsky, A.; Kleppa, O. J. *Inorg. Chem.* **1967**, *6*, 2119.
(32) Navrotsky, A. MSA Presidential Address. *Am. Miner.* **1994**, *79*, 589.
(33) Chase, M. W.; et al. *JANAF Thermochemical Tables*, 3rd ed.; Journal of Physical and Chemical Reference Data; American Chemical Society: Washington, DC, 1985; Vol. 14, Suppl. 1).

The $Li_{0.5}Na_{0.5}PO_3$ ($x = 0$) enthalpy was evaluated from the thermochemical cycle based on the reactions:

$$4Li_{0.5}Na_{0.5}PO_3(glass,298) \rightarrow Li_2O(soln,975) +$$
$$Na_2O(soln,975) + 2P_2O_5(soln,975) \quad (22)$$

$$Li_2O(s,298) \rightarrow Li_2O(soln,975) \quad (23)$$

$$Na_2O(s,298) \rightarrow Na_2O(soln,975) \quad (13)$$

$$P_2O_5(s,298) \rightarrow P_2O_5(soln,975) \quad (6)$$

$$2Li(s,298) + {}^1\!/_2O_2(g,298) \rightarrow Li_2O(s,298) \quad (24)$$

$$2Na(s,298) + {}^1\!/_2O_2(g,298) \rightarrow Na_2O(s,298) \quad (14)$$

$$2P(s,298) + {}^5\!/_2O_2(g,298) \rightarrow P_2O_5(s,298) \quad (8)$$

$${}^1\!/_2Li(s,298) + {}^1\!/_2Na(s,298) + P(s,298) +$$
$${}^3\!/_2O_2(g,298) \rightarrow Li_{0.5}Na_{0.5}PO_3(glass,298) \quad (25)$$

$$\Delta H_{25} = -\Delta H_{22} + {}^1\!/_4(\Delta H_{23} + \Delta H_{13} + \Delta H_{24} +$$
$$\Delta H_{14}) + {}^1\!/_2(\Delta H_6 + \Delta H_8) \quad (26)$$

The values of endothermic $\Delta H_{ds}(Li_{0.5}Na_{0.5}PO_3,glass) = \Delta H_{22}$ and exothermic $\Delta H_f°(Li_{0.5}Na_{0.5}PO_3,glass) = \Delta H_{25}$, as well as the results obtained for the LiNaPON glasses series, are reported in Table 2. The enthalpies of formation $\Delta H_f°$ of those oxynitride glasses follow from their experimental ΔH_{ds} values and the following general thermochemical cycle:

$$4Li_{0.5}Na_{0.5}PO_{(3-3x/2)}N_x(glass,298) +$$
$$3xO_2(g,975) \rightarrow Li_2O(soln,975) + Na_2O(soln,975) +$$
$$2P_2O_5(soln,975) + 2xN_2(g,975) \quad (27)$$

$$Li_2O(s,298) \rightarrow Li_2O(soln,975) \quad (23)$$

$$Na_2O(s,298) \rightarrow Na_2O(soln,975) \quad (13)$$

$$P_2O_5(s,298) \rightarrow P_2O_5(soln,975) \quad (6)$$

$$2Li(s,298) + {}^1\!/_2O_2(g,298) \rightarrow Li_2O(s,298) \quad (24)$$

$$2Na(s,298) + {}^1\!/_2O_2(g,298) \rightarrow Na_2O(s,298) \quad (14)$$

$$2P(s,298) + {}^5\!/_2O_2(g,298) \rightarrow P_2O_5(s,298) \quad (8)$$

$$N_2(g,298) \rightarrow N_2(g,975) \quad (7)$$

$$O_2(g,298) \rightarrow O_2(g,975) \quad (9)$$

$${}^1\!/_2Li(s,298) + {}^1\!/_2Na(s,298) + P(s,298) +$$
$$[(6-3x)/4]O_2(g,298) + (x/2)N_2(g,298) \rightarrow$$
$$Li_{0.5}Na_{0.5}PO_{(3-3x/2)}N_x(glass,298) \quad (28)$$

$$\Delta H_f°(Li_{0.5}Na_{0.5}PO_{(3-3x/2)}N_x) = \Delta H_{28} =$$
$$-\Delta H_{27} + {}^1\!/_4(\Delta H_{23} + \Delta H_{13} + \Delta H_{24} + \Delta H_{14}) +$$
$${}^1\!/_2(\Delta H_6 + \Delta H_8) + (x/2)\Delta H_7 - (3x/4)\Delta H_9 \quad (29)$$

Discussion

PON. PON and SiO_2 enthalpies of formation from the elements may not be compared directly in the sense that

Table 2. Enthalpies of Drop Solution and Formation from the Elements at 298 K (kJ mol^{-1})

		N/P	ΔH drop solution	ΔH^o formation
PON	β-cristobalite	1	-460.95 ± 3.27^a (12)	-371.71 ± 4.45
PON	amorphous	1	-476.52 ± 2.59^a (7)	-356.14 ± 3.98
eutectic $Li_{0.5}Na_{0.5}PO_3$		0	$\Delta H_{22} = 60.74 \pm 1.41^a$ (8)	$\Delta H_{25} = -1218.49 \pm 3.75$
$Li_{0.5}Na_{0.5}PO_{2.79}N_{0.14}$		0.14	-8.70 ± 0.08^a (6)	-1149.89 ± 3.47
$Li_{0.5}Na_{0.5}PO_{2.61}N_{0.26}$		0.26	-59.23 ± 1.26^a (6)	-1100.09 ± 3.69
$Li_{0.5}Na_{0.5}PO_{2.46}N_{0.36}$		0.36	-94.11 ± 1.35^a (6)	-1065.82 ± 3.72
$Li_{0.5}Na_{0.5}PO_{2.14}N_{0.57}$		0.57	-199.37 ± 2.07^a (9)	-961.88 ± 4.04

^{a} Measured. Uncertainty is 2 standard deviations of the mean; the number in parentheses is the number of experiments performed.

Table 3. Enthalpies of SiO₂ and PON Phases Relative to Their Stable Polymorph at 298K. All Values Are in kJ Mol^{-1}

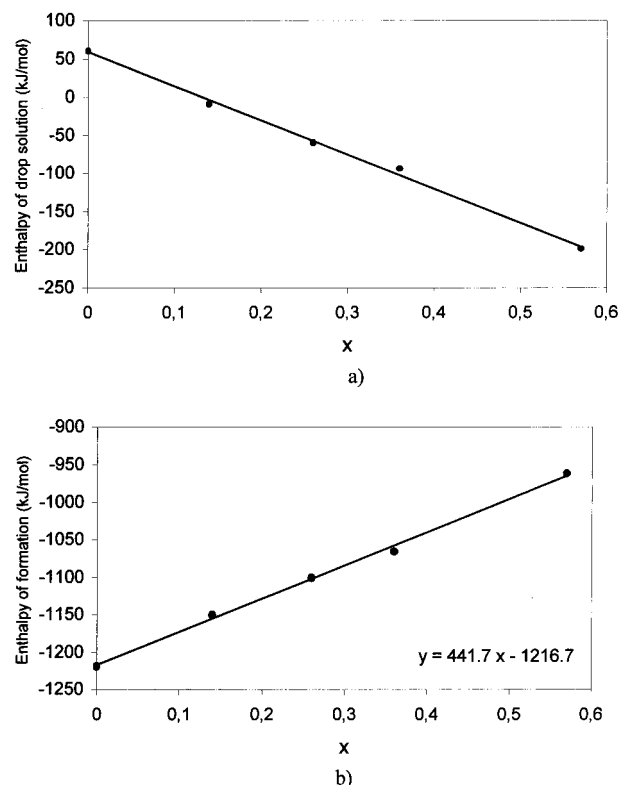|	polymorph	ΔH^o	ref
SiO_2	quartz	0	35
	cristobalite	2.3 ± 2.3	35
	coesite	2.9 ± 2.3	35
	tridymite	3.2 ± 2.6	35
	moganite	3.4 ± 1.6	36
	glass	9.1 ± 2.3	35
	stishovite	49.4 ± 2.3	35
PON	cristobalite	0	this work
	amorphous	15.6 ± 6.0	this work

a)

b)

Figure 3. Linear correlation between (a) the enthalpies of drop solution and (b) the enthalpies of formation and the increasing N/O substitution represented by x in $Li_{0.5}Na_{0.5}PO_{3-3x/2}N_x$ glass. Error bars are of the size of symbols chosen.

PON is an oxynitride and SiO_2 an oxide material. Standard enthalpies of formation obtained for nitrides are often small in magnitude, sometimes an order of magnitude smaller than those of the corresponding oxides.[25-27] Furthermore, the β-cristobalite polymorph is a low-temperature phase for PON and, in contrast, a high-temperature phase for SiO_2. Interest lies in the comparison of the energetic difference between PON polymorphs, as compared in Table 3 with values for silica polymorphs. The close similarity between SiO_2 and PON structures, and the small energy differences between SiO_2 polymorphs suggest that similar relations may hold for PON. The enthalpy of formation of amorphous PON is less exothermic than that of β-cristobalite PON (Table 2), illustrating the fact that an amorphous phase is thermodynamically less stable than the crystalline material. The present ΔH_f^o data give an enthalpy of amorphization of the (presumably most stable) cristobalite polymorph of PON, as 15.57 ± 5.97 kJ mol^{-1}. The enthalpy of vitrification of quartz SiO_2 is 7.00 kJ mol^{-1}, while that of cristobalite SiO_2 is 6.09 kJ mol^{-1}.[34] These new data on PON show a similarity with SiO_2 though the range in energy between the most stable crystalline polymorph and the glass (or amorphous phase for PON) is about 2 times larger for PON than for SiO_2. Nevertheless, this enthalpy of amorphization of PON is still small compared to that of most other oxides.[18] Measurements on other PON polymorphs are in progress. The study of the energetics of quartz or moganite PON will require the preparation of relatively large quantities of samples (50–100 mg) under pressure.

LiNaPON. Figure 3 shows the enthalpies of drop solution and enthalpies of formation of the LiNaPON series versus nitrogen atomic content, x. A linear

(34) Navrotsky, A.; Hon, R.; Weill, D. F.; Henry, D. J. *Geochim. Cosmochim. Acta* **1980**, *44*, 1409. Weill, D. F.; Hon, R.; Navrotsky, A. In *Physics of Magmatic Processes;* Hargraves, R. B., Ed.; Princeton University Press: Princeton, NJ, 1980; pp 49–92.

relation gives values of

$$\Delta H_f^o(Li_{0.5}Na_{0.5}PO_{(3-3x/2)}N_x) = \Delta H_f^o(Li_{0.5}Na_{0.5}PO_3) + 441.7x = (-1218.49 \pm 3.75) + 441.7x \quad (30)$$

The enthalpies of formation of the glasses become less exothermic when increasing the nitrogen/oxygen substitution. This linear trend parallels trends in T_g, hardness, and density. The energetic destabilization relative to the elements, when increasing the nitrogen/oxygen substitution, is seen in many other nitrides compared to corresponding oxides.[25-27]

We evaluated quantitatively the contribution of N–N, O–O, P–N, and P–O bond strengths in the energetics of nitrogen/oxygen substitution. Calculations are illustrated below for $Li_{0.5}Na_{0.5}PO_{2.14}N_{0.57}$ and PON. Starting from the oxygen/nitrogen substitution

$$Li_{0.5}Na_{0.5}PO_{2.14}N_{0.57} + 0.43O_2 \rightarrow Li_{0.5}Na_{0.5}PO_3 + 0.285N_2 \quad (31)$$
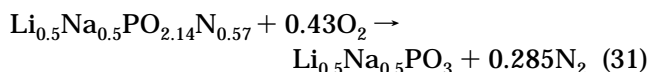
the enthalpy of reaction at 298 K is obtained from standard enthalpy values in Table 2:

$$\Delta H_{\text{oxidation}} = \Delta H_f^o(\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3) -$$
$$\Delta H_f^o(\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{2.14}\text{N}_{0.57})$$
$$= -1218.49 + 961.88 =$$
$$-256.61 \text{ kJ mol}^{-1} \quad (32)$$

From bond energies given in Table 4, the energetic contribution of N_2 and O_2 bonds is equal to

$$0.285E_{\text{N}-\text{N}} - 0.43E_{\text{O}-\text{O}} = -55.12 \text{ kJ mol}^{-1} \quad (33)$$

Thus, the oxynitride is less stable energetically than simple formation of N−N versus O−O bonds would imply. If we consider N−N, O−O, P−N, and P−O bond strengths, the difference in bond energies (neglecting any effects of cations and structure) would become

$$\Delta E = 0.285E_{\text{N}-\text{N}} + 0.86E_{\text{P}-\text{O}} - 0.43E_{\text{O}-\text{O}} -$$
$$0.57E_{\text{P}-\text{N}} = -218.69 \text{ kJ mol}^{-1} \quad (34)$$

This is of a similar magnitude as the observed enthalpy change (-256.61 kJ mol^{-1}). Another example is the oxidation of crystalline PON:

$$2\text{PON} + {}^3/_2\text{O}_2 \rightarrow \text{P}_2\text{O}_5 + \text{N}_2 \quad (35)$$

The enthalpy of this oxidation reaction at 298 K is

$$\Delta H_{\text{oxidation}} = \Delta H_f^o(\text{P}_2\text{O}_5) - \Delta H_f^o(\text{PON})$$
$$= -1504.9 - 2(-371.71) =$$
$$-761.48 \text{ kJ mol}^{-1} \quad (36)$$

A similar approach in the calculation with, first, only N−N and O−O bond strengths gives

$$E_{\text{N}-\text{N}} - {}^3/_2E_{\text{O}-\text{O}} = -197.79 \text{ kJ mol}^{-1} \quad (37)$$

Again, the oxynitride is even less stable than predicted from N−N and O−O bond strengths alone. Considering P−N and P−O bonds, as well as N−N and O−O, we obtain an energetic difference ΔE:

$$\Delta E = E_{\text{N}-\text{N}} + 3E_{\text{P}-\text{O}} - {}^3/_2E_{\text{O}-\text{O}} - 2E_{\text{P}-\text{N}} =$$
$$-761.19 \text{ kJ mol}^{-1} \quad (38)$$

These experimental and calculated values agree well.

In both examples, LiNaPON glass and PON, the magnitude of the enthalpy of oxidation is predicted correctly when N−N, O−O, P−N, and P−O bonds are considered. Thus nitridophosphate stability reflects not only the much stronger N_2 triple bond compared to the O_2 double bond in the gas but also the somewhat stronger P−N bond compared to the P−O bond in the solid. The same kind of calculations may be applied to other nitride systems.
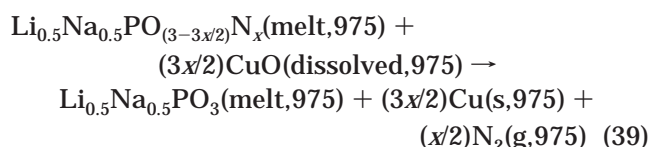
The properties of phosphate glasses are significantly modified by substituting nitrogen for oxygen in the glass network. In particular, nitrogen gives the glass a reducing character which makes it possible to observe redox reactions. This property induces the in-situ precipitation of metallic particles. Silver (Ag_2O) or copper (CuO) oxides have been shown to reduce to Ag and Cu metal by nitrogen N^{3-} in several nitridophosphate glass compositions at temperatures lower than 973 K.[8,9,17] A

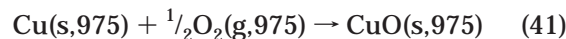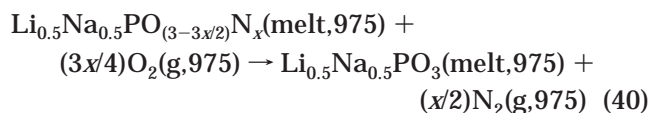**Table 4. Bond Dissociation Energies[a,21]**

bond	energy (kJ mol^{-1})	bond	energy (kJ mol^{-1})
N−N	945.33 ± 0.59	P−N	617.1 ± 20.9
O−O	498.36 ± 0.17	P−O	599.2 ± 12.6

[a] Note: bond strengths are given for diatomic molecules.

rational thermodynamic approach to this reduction phenomenon should allow one to predict which oxide will spontaneously reduce in a vitreous phosphorus oxynitride matrix. A thermodynamic reaction interpreting the reduction of dissolved copper oxide CuO in contact with nitrogen N^{3-} can be written as

$$\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{(3-3x/2)}\text{N}_x(\text{melt},975) +$$
$$(3x/2)\text{CuO}(\text{dissolved},975) \rightarrow$$
$$\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3(\text{melt},975) + (3x/2)\text{Cu}(\text{s},975) +$$
$$(x/2)\text{N}_2(\text{g},975) \quad (39)$$

The enthalpy of this reaction can be computed by the following thermodynamic cycle with $\Delta H_{39} = \Delta H_{40} - (3x/2)(\Delta H_{41} + \Delta H_{42})$:

$$\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{(3-3x/2)}\text{N}_x(\text{melt},975) +$$
$$(3x/4)\text{O}_2(\text{g},975) \rightarrow \text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3(\text{melt},975) +$$
$$(x/2)\text{N}_2(\text{g},975) \quad (40)$$

$$\text{Cu}(\text{s},975) + {}^1/_2\text{O}_2(\text{g},975) \rightarrow \text{CuO}(\text{s},975) \quad (41)$$

$$\text{CuO}(\text{s},975) \rightarrow \text{CuO}(\text{dissolved},975) \quad (42)$$

ΔH_{40} is obtained from the heat of formation data and, neglecting ΔC_p terms, is equal to $-441.7x$ kJ mol^{-1}. Enthalpy of formation ΔH_{41} is obtained from the literature[37] as -150.7 kJ mol^{-1}, and enthalpy of solution ΔH_{42} at 975 K (not known) has been estimated in the range $-20 \leq \Delta H_{42} \leq 20$ kJ mol^{-1}. These values then approximate ΔH_{39} as $-140.0 \leq \Delta H_{39} \leq -105.8$ kJ mol^{-1} for $x = 0.57$ (Table 2). Because for reaction (39) ΔS is positive because gas is produced, it is clear that this reaction is strongly favored. However, a partial molar entropy of solution term needs to be added to the free energy ΔG_{39} to consider the reduction of the oxide in the melt at low concentration. This term is on the order of $-RT\ln(y)$, where y represents the mole fraction. With, for example, 1 mol % oxide in the glass at 975 K, the contribution to ΔG_{39} would be $-RT \ln(0.01)$ or $+37.3$ kJ. Estimated ΔG_{39} is listed in Table 5.

Ag_2O is itself thermodynamically unstable with respect to Ag + O_2 above 500 K.[38] The ability of the O_2 produced to further oxidize the N^{3-} would clearly make the reduction of Ag_2O in contact with a nitridophosphate glass or melt even more thermodynamically favorable.

Calculations have been performed for other oxides to anticipate which oxide can be fully reduced to the metallic state in LiNaPON glasses. We have also

(35) Robie, R. A.; Hemingway, B. S. *Thermodynamic Properties of Minerals and related Substances at 295.15K and 1 Bar (10^5 Pa) Pressure and at Higher Temperatures*; U.S. Geological Survey Bulletin 2131; U.S. Government Printing Office: Washington, DC, 1995.
(36) Petrovic, I.; Heaney, P. J.; Navrotsky, A. *Phys. Chem. Miner.* **1996**, *23*, 119.
(37) Barin, I. *Thermochemical Data of Pure Substances*; VCH: New York, 1989.
(38) Kubaschewski, O.; Evans, E. L. L. *Metallurgical[a] Thermochemistry*; Pergamon Press: London, 1958.

Table 5. Calculation of the Possibility To Reduce Oxides in LiNaPON Glasses (All Values Are in kJ mol⁻¹)

oxide/metal	enthalpy of formation ΔH_{41} at 975 K[37]	ΔH_{39} at 975 K[a]	ΔG_{39} at 975 K[b]
PdO/Pd	−86.3	−195.1 to −160.9	−157.8 to −123.6
CuO/Cu	−121.7	−164.8 to −130.6	−127.5 to −93.3
PbO/Pb	−182.6	−112.7 to −78.5	−75.4 to −41.2
CoO/Co	−201.1	−96.9 to −62.7	−59.6 to −25.4
NiO/Ni	−203.1	−95.2 to −61.0	−57.9 to −23.7
CdO/Cd	−225.4	−76.2 to −42.0	−38.9 to −4.7
FeO/Fe	−234.8	−68.1 to −33.9	−30.8 to +3.4
MoO_2/Mo	−540.5	−29.3 to −12.2	+8.0 to +25.1
WO_2/W	−541.9	−28.7 to −11.6	+8.6 to +25.7
ZnO/Zn	−318.0	+3.0 to +37.2	+40.3 to +74.5
MnO/Mn	−351.2	+31.4 to +65.6	+68.7 to +102.9
Cr_2O_3/Cr	−1057.6	+43.9 to +55.3	+81.2 to +92.6
TiO_2/Ti	−898.0	+123.6 to +140.7	+160.9 to +178.0
Ti_2O_3/Ti	−1429.6	+150.0 to +161.4	+187.3 to +198.7
Al_2O_3/Al	−1600.8	+198.8 to +210.2	+236.1 to +247.5
SrO/Sr	−556.9	+207.3 to +241.5	+244.6 to +278.8
MgO/Mg	−569.5	+218.1 to +252.3	+255.4 to +289.6

[a] $\Delta H_{39} = -441.7x - (3x/2)(\Delta H_{41} + \Delta H_{42})$ with $-20 \leq \Delta H_{42} \leq 20$ kJ mol⁻¹ where $x = 0.57$. [b] $\Delta G_{39} = \Delta H_{39} - RT \ln(y)$ with $R = 8.31441$ J mol⁻¹ K⁻¹ where $T = 975$ K and $y = 1$ mol %.

considered the glass composition $Li_{0.5}Na_{0.5}PO_{2.14}N_{0.57}$ to model our predictions. Results are gathered in Table 5. Enthalpies of formation at 975 K, ΔH_{41}, have been calculated from literature data.[37] Enthalpies of solution at 975 K, ΔH_{42}, were approximated in the range $-20 \leq \Delta H_{42} \leq 20$ kJ mol⁻¹. Negative ΔG_{39} values, including the enthalpy of solution term, indicate the possibility to reduce a given oxide to the metal in LiNaPON glasses. Our estimations show that the reaction is strongly favored for palladium, copper, lead, cobalt, and nickel oxides. Because of their concentrations in the melt (1 mol %), CdO and FeO are right at the edge of reducibility. Other oxides listed in Table 5 are not reduced to the metal in LiNaPON glasses.

These calculations show the reducing nature of the environment in nitridophosphate glasses. The present determination of the enthalpies of formation of PON and LiNaPON glasses constitutes the first measured thermochemical parameters for nitridophosphates. They clearly are promising for interpreting the structure and reactivity in these materials.