THERMOCHEMICAL APPROACH OF THE PRECIPITATION OF METALLIC PARTICLES IN "LiNaPON GLASSES"

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Abstract Nitrogen as N³⁻ gives nitrido-phosphate glasses a reducing character which makes it possible to observe redox reactions inducing in situ precipitation of metallic particles of silver or copper. From a thermodynamic approach, a calorimetric study has been undertaken to explore the energetics of "LiNaPON glasses". High-temperature solution calorimetry has been very useful in elucidating the energetics of a series of "LiNaPON oxynitride glasses". The standard enthalpy of formation was measured as $-961.88 \pm 3.86 \text{ kJ.mol}^{-1}$ for a 9 wt.% nitrogen containing LiNaPON glass. These values constitute a first set of energetic data necessary to achieve further thermodynamic studies on nitrido-phosphates.

INTRODUCTION

The reducing character of nitride-type compounds has been demonstrated in many types of reactions. For example, $\text{LnEu}^{\text{II}}\text{SiO}_3\text{N}$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$) ^{1,2} may be prepared from trivalent $\text{Eu}^{\text{III}}\text{O}_3$ europium oxide and an excess of silicon nitride Si_3N_4 , which enables the reduction of europium to a divalent state Eu^{II} . Molecular nitrogen is also produced in the reaction between AlN and TiO_2 , leading to the formation of TiN and an intermediate pseudobrookite phase ³ $(\text{Al,Ti}^{\text{III}})_2\text{Ti}^{\text{IV}}\text{O}_5$. Previous studies have shown that nitrido-phosphate glasses manifested the same reducing properties ^{4,5}. Starting from MnO_2 and Fe_2O_3 oxides, divalent manganese and iron are stabilized in such glasses by heating at 700 °C under nitrogen atmosphere. In those cases, the reduction does not reach the metallic state, but with easily reducible oxides, as silver or copper oxides, we observe the following redox reaction:

The purpose of this study lies in the preparation of glass-metal composites by precipitating small metallic particles throughout the matrix. Therefore, we have controlled the reduction phenomenon from a chemical point of view and undertaken, in a first attempt, a calorimetric study of "LiNaPON glasses" to predict which oxide may be reduced spontaneously.

EXPERIMENTAL PROCEDURES

*** Preparation of "LiNaPON glasses"**

Oxide base glass $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3$ was prepared as a starting material by mixing powders of commercial NaPO_3 , Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ in suitable amounts and melting in air in a platinum crucible ^{1,2}. $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3$ was nitrated by melting the crushed glass in a vitreous carbon boat at 973 K under an anhydrous ammonia flow. Starting from the same phosphate base glass, a series of nitrated glasses $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{(3-3x/2)}\text{N}_x$ was prepared with progressive nitrogen content by using different nitridation times. The redox reactions were carried out after mixing of silver or copper oxides with an oxynitride glass composition. The mixtures were heated for 1 hour at a chosen temperature in pure nitrogen to avoid the presence of oxygen giving rise to the reaction: oxynitride glass + $\text{O}_2 \rightarrow$ oxide glass + $\text{N}_2^{\uparrow}$.

*** Calorimetry**

Whereas thermodynamic results concerning phosphates are given in the literature, no data characterize the energies of formation of nitrido-phosphates, despite the preparation of many novel compositions these two last decades. The high volatility of " P_2O_5 " (sublimes as low as 823 K) can explain why no thermodynamic advances have been made in the knowledge of their formation and stability. Recently, high-temperature solution calorimetry has been very useful in elucidating the energetics of nitride and oxynitride materials ^{6,7}. A sodium molybdate melt of composition $3\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ has been proven to be very effective for nitride calorimetry. We have developed this methodology to the calorimetry of phosphorus oxynitrides and, in particular, a series of

"LiNaPON glasses" has been studied. High temperature oxidative drop solution calorimetry into a $3\text{Na}_2\text{O} \cdot 0.4\text{MoO}_3$ molten solvent was performed in a Calvet type twin calorimeter described in detail by Navrotsky⁸. 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^{6,7}. This reaction includes the oxidation and the dissolution of the nitride, 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. Further details of the experimental procedure are provided in previous papers⁶⁻¹⁰.

RESULTS AND DISCUSSION

Starting from Ag_2O and CuO oxides, we have shown experimentally the *in situ* precipitation of Ag and Cu particles in mixed alkaline phosphorus oxynitride glasses: $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{(3-3x/2)}\text{N}_x$ ¹¹⁻¹³. In a first step, the stability of silver Ag^+ and copper Cu^{2+} cations has been verified in the corresponding oxide glass composition $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3$. The study of a mixture $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3 + 0.225 \text{Ag}_2\text{O}$ by DTA under nitrogen atmosphere and by XRD does not reveal (or very little) reduction of Ag_2O to metallic silver, even at temperatures higher than those required to dissociate silver oxide. We observe in Figure 1, for a sample heat treated at 700 °C under nitrogen and quenched, that nearly all the silver content is stabilized in the glass as Ag^+ species. A very little part of Ag_2O is transformed into metallic Ag by self-dissociation at low temperatures (< 320 °C), as indicated by the yellowish color of the glass.

FIGURE 1. XRD pattern of a mixture oxide glass $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3 + 0.225 \text{Ag}_2\text{O}$ heated at 700°C under nitrogen.

FIGURE 2. XRD pattern of a mixture oxynitride glass $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{2.46}\text{N}_{0.36} + 0.225 \text{Ag}_2\text{O}$ heated at 700°C under nitrogen.

This phenomenon is negligible compared to the intense diffraction peaks of Ag observed in Figure 2 when a mixture $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{2.46}\text{N}_{0.36}$ oxynitride glass + 0.225 Ag_2O is heated under the same conditions. The reduction of Ag_2O , with formation of silver metal, is unambiguously related to the presence of nitrogen N^{3-} into the glass. A same conclusion follows for the study of the reduction of CuO in a mixture $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{2.61}\text{N}_{0.26}$ + 0.225 CuO , but in this case, it is necessary to heat the mixture above the melting temperature of the glass (600°C) to avoid any crystalline phases.

Using the method of drop solution calorimetry, we have measured the energetics of nitrido-phosphate glasses in the series $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{(3-3x/2)}\text{N}_x$ in which x ranged from x = 0 to x = 0.57. The results obtained for this series as well as the values of endothermic ΔH_{ds} ($\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3$, glass) and exothermic ΔH°_f ($\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3$, glass) are given in Table 2. The enthalpies of formation ΔH°_f of those oxynitride glasses follow from their experimental ΔH_{ds} values and this general thermochemical cycle:

$$\Delta H^\circ_f (\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{(3-3x/2)}\text{N}_x) = \Delta H_{28} = -\Delta H_{27} + 1/4 (\Delta H_{23} - \Delta H_{13} - \Delta H_{24} - \Delta H_{14}) - 1/2 (\Delta H_6 + \Delta H_8) + x/2 \Delta H_7 - 3x/4 \Delta H_9 \quad (11)$$

In Figure 3, a plot of the enthalpies of drop solution and enthalpies of formation of the "LiNaPON" series versus nitrogen atomic content x displays a linear correlation of equation:

$$\Delta H^\circ_f (\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{(3-3x/2)}\text{N}_x) = \Delta H^\circ_f (\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3) + 441.7 x \quad (12)$$

FIGURE 3. Linear correlation between the enthalpies of formation and the increasing N/O substitution represented by x in $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{3-3x/2}\text{N}_x$ glass

	ΔH drop solution	ΔH° formation
eutectic $\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_3$	60.74 ± 1.41	-1218.49 ± 3.75
$\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{2.79}\text{N}_{0.14}$	-8.70 ± 0.08	-1149.89 ± 3.47
$\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{2.61}\text{N}_{0.26}$	-59.23 ± 1.26	-1100.09 ± 3.69
$\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{2.46}\text{N}_{0.36}$	-94.11 ± 1.35	-1065.82 ± 3.72
$\text{Li}_{0.5}\text{Na}_{0.5}\text{PO}_{2.14}\text{N}_{0.57}$	-199.37 ± 2.07	-961.88 ± 4.04

TABLE 2. A summary of the enthalpies obtained

The enthalpies of formation of the glasses become less exothermic with increasing nitrogen/oxygen substitution. This linear trend parallels trends in T_g , hardness and density^{4,11,14}. The energetic destabilization relative to the elements, when increasing nitrogen/oxygen substitution, is seen in many other nitrides compared to corresponding oxides^{6,7}. It reflects not only the stronger N_2 triple bond ($945 \text{ kJ}\cdot\text{mol}^{-1}$) compared to the O_2 double bond ($498 \text{ kJ}\cdot\text{mol}^{-1}$), but also the major role played in the solid by specific bonding factors, as P-N and P-O bond strengths.

Silver and copper oxides have been shown to reduce to Ag and Cu metals by nitrogen N^{3-} in several nitrido-phosphate glass compositions at temperatures lower than 973 K ¹¹⁻¹³. A rational thermodynamic approach of this reduction phenomenon should allow to predict which oxide will spontaneously reduce into a vitreous phosphorus oxynitride matrix. Therefore, we have mentioned in a first attempt a qualitative thermocycle interpreting the reduction of silver oxide Ag_2O in contact with nitrogen N^{3-} :

The enthalpy of reaction ΔH_{13} is calculated from the enthalpies ΔH_{14} to ΔH_{17} , which correspond to drop solution calorimetry and literature results. Depending of the magnitude of ΔH_{13} , redox reactions will be observed. If ΔH_{13} is strongly exothermic,

then the reduction of the metal will be obvious. Complementary experiments are envisaged to progress in this determination.

SUMMARY

In this work, we have shown the possibility to reduce metallic particles of silver and copper into a nitrido-phosphate matrix. The knowledge of the enthalpies of formation of LiNaPON glasses constitutes a first result necessary to achieve further promising thermodynamic studies such as the prediction of redox reactions.

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