Journal of the European Ceramic Society **17** (1997) 1967–1970
© 1997 Elsevier Science Limited
Printed in Great Britain. All rights reserved
PII: S0955-2219(97)00066-6
0955-2219/97/$17.00 + 0.00

In-situ Precipitation of Metallic Silver and Copper Within a Phosphorus Oxynitride Glass Matrix by Involving the N^{3-}/N^0 Redox Couple

A. Le Sauze, E. Gueguen, R. Marchand and Y. Laurent

Laboratoire des "Verres et Céramiques", UMR CNRS 6512, Université de Rennes I, F35042 Rennes Cedex, France

Abstract

The presence of nitrogen as N^{3-} in anionic network gives the phosphorus oxynitride glass medium a reducing character which has been used to obtain precipitates of metallic silver and copper particles from the corresponding oxides. In the case of Ag_2O, the reduction phenomenon can be characterized by the temperature of reduction (Tr) which is not directly related to the Tg value. © 1997 Elsevier Science Limited.

1 Introduction

Low melting points and high thermal expansion coefficients have, for many years, made phosphate glasses attractive to a specific field of applications, namely the sealing to high-expansion, low-melting point alloys or metals such as aluminum.[1] Unfortunately, their poor chemical durability has often limited their practical use.[2]

Different approaches have been used to improve this characteristic. Improvement in durability was obtained by substitution within the vitreous network of multivalent cations, such as alkaline-earth or aluminum, for alkaline cations. However, the high thermal expansion and low melting point were often unfavorably affected by these additions. Another possibility to increase the cross-linking within the vitreous network exisits in the incorporation of chemically bonded nitrogen. This solution induces a significant increase in the chemical durability without significant reduction in the thermal expansion coefficient.[3]

On the other hand, the presence of N^{3-} in the anionic network gives the phosphorus oxynitride glass medium a reducing character. In a previous work, Boukbir and Marchand have shown the possibility of stabilizing divalent Fe^{II} or Mn^{II} in a nitrided phosphate glass starting from trivalent iron oxide or tetravalent manganese oxide, according to the following oxido-reduction reactions.[4]

$$0{\cdot}7NaPO_3 + 0{\cdot}15Fe_2^{III}O_3 + 0{\cdot}3PON \xrightarrow{700°C} Na_{0{\cdot}7}Fe^{II}_{0{\cdot}3}PO_{2{\cdot}85}N_{0{\cdot}2}(\text{glass}) + 0{\cdot}05N_2\uparrow$$

$$0{\cdot}7NaPO_3 + 0{\cdot}3Mn^{IV}O_2 + 0{\cdot}3PON \xrightarrow{700°C} Na_{0{\cdot}7}Mn^{II}_{0{\cdot}3}PO_3N_{0{\cdot}1}(\text{glass}) + 0{\cdot}1N_2\uparrow$$

In this work, phosphorus oxynitride glass matrices were used to precipitate *in situ* metallic silver and copper, according to the general scheme:

$$(6/n)M^{n+} + 2N^{3-}(\text{glass}) \rightarrow (6/n)M\downarrow + N_2\uparrow \qquad (M = Ag, Cu)$$

2 Sample Preparation

There are well two well known ways to produce phosphorus oxynitride glasses : either by melting a base glass mixed with nitride[5] or oxynitride such as phosphorus oxynitride PON[6] or by remelting a glass frit under anhydrous ammonia.[7,8]

In the first method, the batch materials were mixed dry, then heated at 700°C in a nitrogen atmosphere in a vitreous carbon crucible. In order to obtain homogeneous glasses, each sample was systematically crushed, remelted and finally cooled rapidly by a translating motion of the furnace.

In the second method, $NaPO_3$ and $Li_{0{\cdot}5}Na_{0{\cdot}5}PO_3$ were nitrided by remelting the crushed glass at 700°C in flowing anhydrous ammonia. After crushing, the resulting glass was reheated at 700°C in a nitrogen atmosphere.

Lastly, the oxydo-reduction reactions were carried out by 1 h heating, at a chosen temperature, oxynitride glass and silver or copper oxide (Ag_2O, Cu_2O, CuO) in a nitrogen atmosphere.

3 Thermodynamic Approach of the Reduction Phenomenon

Assimilation of the phosphorus oxynitride glass with PON allows the characterization of the reduction of an oxide MO_x by the general equation:

$$(6/n)MO_x + 4PON \xrightarrow{700^\circ C} 6/nMO_{(x-n)} + P_4O_{10} + 2N_2 \uparrow \tag{1}$$

where $0 < n \leq x$.

The case $n = x$ corresponds to the reduction up to metallic state, otherwise an intermediate oxidation state is considered. In all cases, the standard free energy variation ΔG^o of the reaction may be expressed as a function of the standard free energy of formation ΔG_f^o of PON: $\Delta G^o = 4[A - \Delta G_f^o(PON)]$. 'A' is a numerical value which can be calculated from tables using Kirschoff's formula for each couple MO_x/M or $MO_x/MO_{x'}$. These 'A' values at 700°C, when M = Fe or Mn, are given in Table 1 as well as the sign of Δ_G^o for the corresponding reaction. The sign is given by the qualitative observations of Boukbir and Marchand.[4]

In the absence of thermodynamic data concerning PON, estimation of its standard free energy of formation at 700°C gives the following result:

$$-504\cdot 1\ kJ\,mol^{-1} < \Delta G_f^o(PON) < -479\cdot 2\ \mathrm{kJ\,mol^{-1}}$$

This result lets us predict with a good approximation the reduction or not of a given metal oxide when the corresponding calculated 'A' value will be outside the interval (−504·1, −479·2) kJ mol^{-1}. The 'A' value for CuO and Cu_2O enables the prediction of their reduction into metal at 700°C, which will be verified experimentally. Calculations cannot be done with silver oxide because thermodynamic data do not exist beyond 500 K (227°C) due to dissociation above this temperature.

Table 1. 'A' values calculated at 700°C for reaction (I) with M = Fe or Mn

Redox couple	A *(kJ mol^{-1})*	ΔG^o
Fe_2O_3/FeO	−504·1	<0
MnO_2/MnO	−693·9	<0
FeO/Fe	−440·8	>0
Fe_2O_3/Fe	−462·0	>0
MnO/Mn	−264·5	>0
MnO_2/Mn	−479·2	>0

4 Experimental Results

4.1 Silver oxide reduction

Silver oxide does not dissociate in the presence of a phosphate glass medium, several oxide glass compositions containing Ag^+ have been prepared without any silver reduction. When Ag_2O is added to the eutectic $Li_{0\cdot5}Na_{0\cdot5}PO_3$ glass composition it does not form metallic silver as clearly shown in Fig. 1. Moreover, DSC study shows that at low temperatures ranging from 320 to 400°C formation of crystalline Ag_3PO_4 occurs. Above 400°C and up to 700°C absence of any crystallization peaks means that silver is stabilized and enters the glass composition as Ag^+.

On the contrary, the X-ray powder pattern of a mixture $Li_{0\cdot35}Na_{0\cdot35}PO_{2\cdot4}N_{0\cdot3} + 0\cdot225\ Ag_2O$, heated at 700°C, reveals unambiguously that the presence of N^{3-} in the phosphorus oxynitride glass has induced silver oxide reduction into silver metal.

The reaction is:

$$\underset{\text{glass}}{Li_{0\cdot35}Na_{0\cdot35}PO_{2\cdot4}N_{0\cdot3}} + 0\cdot225Ag_2O \xrightarrow{700^\circ C} \underset{\text{glass}}{Li_{0\cdot35}Na_{0\cdot35}PO_{2\cdot625}N_{0\cdot15}} + 0\cdot45Ag\downarrow + 0\cdot075N_2\uparrow \tag{2}$$

From a quantitative viewpoint, a good correlation between experimental and calculated values of remaining nitrogen after reaction (1·45/1·57 wt%) supports eqn (2).

In the same way, a DTA study of the starting mixture shows that reduction of silver oxide within the $Li_{0\cdot35}Na_{0\cdot35}PO_{2\cdot4}N_{0\cdot3}$ glass matrix is characterized by an exothermic peak at Tr ~355°C (Tr = reduction temperature), i.e. at a temperature slightly higher than the corresponding glass transition temperature (Tg = 310°C). In order to correlate or not, Tg and Tr, different phosphorus oxynitride glasses have been used as a reducing medium. The results, listed in Table 2, evidence that the temperature of reduction Tr depends on the nature of the glass but not directly on its Tg value.

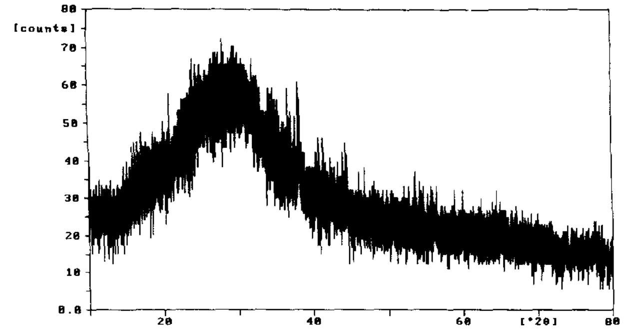

Fig. 1. XRD powder pattern of $Li_{0.5}Na_{0.5}PO_3 + 0{\cdot}225$ Ag_2O mixture heated at 700°C.

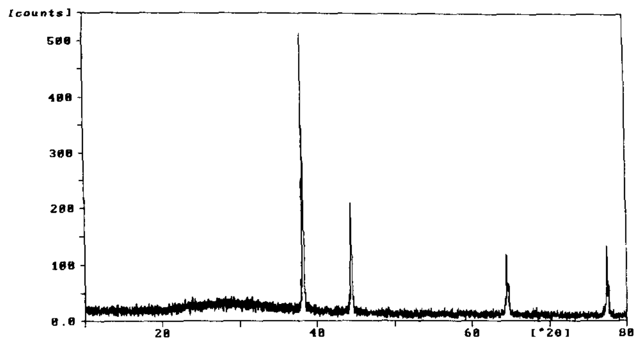

Fig. 2. XRD powder pattern of $Li_{0.35}Na_{0.35}PO_{2.4}N_{0.3} + 0{\cdot}225$ Ag_2O mixture heated at 700°C.

A TG-DTA study also enables also the determination of the weight loss due to the release of molecular nitrogen verification of the good correlation between experimental and calculated results. Figure 3 illustrates the silver oxide reduction within a glass matrix of composition $Li_{0.5}Na_{0.5}PO_{2.55}N_{0.3}$ (Tg = 306°C, Tr = 370°C).

With very low Ag_2O starting contents (1 wt%), X-ray diffraction does not give access to the reduction phenomenon but the resulting composite can be studied by scanning electron microscopy. SEM images of Figs 4 and 5 reveal that the silver particles are essentially regrouped in holes generated by bubbles of released dinitrogen. They exist either as isolated particles below 1 μm in size (Fig. 4) or as aggregates (Fig. 5).

4.2 Copper oxide reduction

Contrary to the case of Ag_2O, the existence of intermediate states does not allow assessment of an accurate reduction temperature of the copper oxides Cu_2O and CuO within the vitreous medium. However, at 700°C, an $Li_{0.35}Na_{0.35}PO_{2.4}N_{0.3}$ glass melt mixed with Cu_2O or CuO oxides gives rise to the precipitation of metallic copper, identified by X-ray diffraction, according to the preceding thermodynamic conclusions. The reactions are:

$$\underset{\text{glass}}{Li_{0.35}Na_{0.35}PO_{2.4}N_{0.3}} + 0{\cdot}225Cu_2O \xrightarrow{700°C} \underset{\text{glass}}{Li_{0.35}Na_{0.35}PO_{2.625}N_{0.15}} + 0{\cdot}45Cu \downarrow + 0{\cdot}075N_2 \uparrow \tag{3}$$

$$\underset{\text{glass}}{Li_{0.35}Na_{0.35}PO_{2.4}N_{0.3}} + 0{\cdot}225CuO \xrightarrow{700°C} \underset{\text{glass}}{Li_{0.35}Na_{0.35}PO_{2.625}N_{0.15}} + 0 \cdot 225Cu \downarrow + 0 \cdot 075N_2 \uparrow \tag{4}$$

Nitrogen contents of the resulting glass–metal composites are in good agreement with the calculated values, as shown in Table 3.

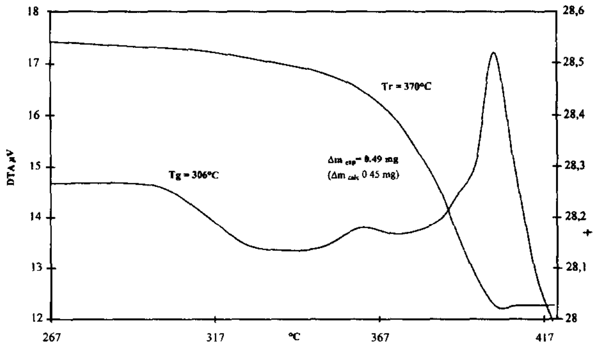

Fig. 3. TG-DTA thermogram of the $Li_{0.5}Na_{0.5}PO_{2.55}N_{0.3}$ $+0 \cdot 225Ag_2O$ mixture under inert atmosphere.

Table 2. Reduction temperature Tr of silver oxide within different phosphorus oxynitride glass matrices

Group	*No.*	*Formula*	*Tg(°C)*	*Tr(°C)*
1	1	$NaPO_{2.7}N_{0.2}$	320	410
	2	$NaPO_{2.55}N_{0.3}$	335	408
	3	$NaPO_{2.22}N_{0.52}$	374	403
	4	$Na_{0.7}PO_{2.4}N_{0.3}$	361	408
2	5	$Na_{0.7}Mn_{0.3}PO_{2.7}N_{0.3}$	380	387
	6	$Na_{0.6}Mn_{0.4}PO_{2.6}N_{0.4}$	425	391
	7	$Na_{0.5}Mn_{0.5}PO_{2.5}N_{0.5}$	440	397
	8	$Na_{0.6}Mn_{0.55}PO_{2.75}N_{0.4}$	455	386
3	9	$Li_{0.7}PO_{2.7}N_{0.2}$	390	377
4	10	$Li_{0.35}Na_{0.35}PO_{2.4}N_{0.3}$	310	355
	11	$Li_{0.5}Na_{0.5}PO_{2.55}N_{0.3}$	306	370
	12	$Li^{0}{}_{.5}Na_{0.5}PO_{2.25}N_{0.5}$	337	363

Table 3. Experimental and calculated nitrogen contents after Cu_2O and CuO reduction at 700°C in a 'LiNaPON' glass matrix, according to eqns (3 and 4)

		Nitrogen content (wt.%) experiment/calculation	*N/P atomic ratio experiment/calculation*
eqn (3)	Cu_2O	1·95/1·84	0·16/0·15
eqn (4)	CuO	2·10/2·10	0·15/0·15

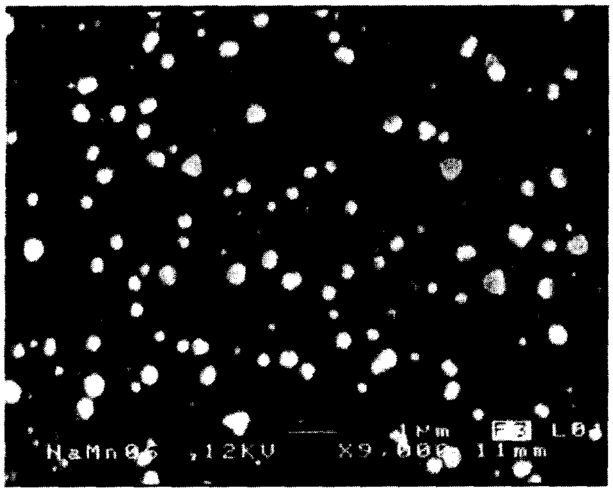

Fig. 4. SEM micrograph of isolated silver metal particles precipitated from a $Na_{0 \cdot 5}Mn_{0 \cdot 5}PO_{2 \cdot 55}N_{0 \cdot 5}$ glass composition at

Fig. 5. SEM micrograph of metallic silver aggregates precipitated from a $Na_{0 \cdot 5}Mn_{0 \cdot 5}PO_{2 \cdot 55}N_{0 \cdot 5}$ glass composition at 700°C.

5 Conclusions

Substitution of nitrogen for oxygen in a phosphate glass network significantly modifies the physical and chemical properties. On the other hand, nitrogen gives the glass a reducing character which makes possible oxido-reduction reactions with a corresponding release of molecular nitrogen, according to the general scheme:

$$(6/n)M^{n+} + 2N^{3-} \rightarrow (6/n)M \downarrow + N_2 \uparrow$$

In situ precipitation of metallic particles of silver and copper from corresponding oxides has been studied mostly in the low-melting $Li_{0 \cdot 35}Na_{0 \cdot 35}PO_{2 \cdot 4}N_{0 \cdot 3}$ glass composition. We have shown that the temperature of reduction is first related to the stability of the P-N bonds and does not depend closely on the Tg value.

References

1. Wilder, J. A., *Journal of Non-Cryst. Solids*, 1980, **38–39**, 879.
2. Gray, P. E. and Klein, L. C., *Glass Technol.*, 1983, **24**, 202.
3. Larson, R. W. and Day, D. E., *Journal of Non-Cryst. Solids*, 1986, **88**, 97.
4. Boukbir, L. and Marchand, R., *Rev. Int. Hautes Tempér. Refract., Fr.*, 1990, **26**, 143.
5. Reidmeyer, M. R. and Day, D. E., *Journal of Am. Ceram. Soc.*, 1985, **68**, C188.
6. Boukbir, L. and Marchand, R., *Rev. Chem. Min.*, 1986, **23**, 343.
7. Marchand, R., *C.R. Acad. Sci. Paris*, 1982, **294**, 91.
8. Marchand, R., *Journal of Non-Cryst. Solids*, 1983, **56**, 173.