

## A Structural Investigation of Phosphorus Oxynitride Glasses

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Phosphorus oxynitride glasses, containing up to 10 wt% nitrogen were prepared as bulk samples by nitridation in molten state—700°C—under ammonia flow of  $(\text{NaPO}_3)_x$  sodium phosphate. The structure of glasses has been investigated using  $\text{Pb}^{2+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Eu}^{3+}$  as local probes. Nitrogen is inserted between two or three phosphorus atoms of the metaphosphate-like chains. The environment of modifier ion is uniquely oxygenated. It results in a reinforcement of the modifier ion–oxygen bond. © 1990 Academic Press, Inc.

### INTRODUCTION

Introduction of chemically bonded nitrogen within oxide glasses results in a large modification of chemical and physical properties of these materials. Substitution of trivalent nitrogen for divalent oxygen leads to the formation of  $\text{Si}(\text{O},\text{N})_4$  or  $\text{P}(\text{O},\text{N})_4$  tetrahedral units in silicate and phosphate glasses inducing alteration of some chemical bonds and larger ramification of the network former as suggested by Mulfingher (1).

Various techniques such as IR (2–5), Raman (6), NMR (6, 7), and XPS (4, 8–11) spectroscopies allow the determination of the configuration of structural features existing in the nitrogen glasses. This paper reports for the first time a structural investigation using  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$ , and  $\text{Pb}^{2+}$  as local probes. Up to now, such a method has not been considered due to the more or less dark

color of the samples. Meanwhile oxynitride phosphate glasses with a good optical quality can be obtained even doped by luminescent species. They belong to the Na–P–O–N system and have the general formula  $\text{NaPO}_{3-3x/2}\text{N}_x$  ( $0 \leq x \leq 0,51$ ).

The structural investigation is based on a simultaneous analysis of the absorption properties of  $\text{Nd}^{3+}$  and  $\text{Pb}^{2+}$  and the emission properties of  $\text{Eu}^{3+}$ .

This strategy initially suggested by T Izumitani *et al.* (12) was successfully used to analyze some structural aspects of the sodium borate glasses. The results were strongly confirmed by a detailed structure investigation of borate glasses using  $\text{Eu}^{3+}$  fluorescence line narrowing (13).

Obviously the probe ions are located in various multiple sites. The purpose of this paper is to detect the effects of introduction of nitrogen in the glasses, with a unique assumption: the location of nitrogen within the

phosphate groups does not change with the nature of the probe ions.

## I. Nd<sup>3+</sup>, Eu<sup>3+</sup>, and Pb<sup>2+</sup> as Structural Probes

### I.1. Calculation of the Judd–Ofelt Parameters from Neodymium Absorption Measurements

The absorption of Nd<sup>3+</sup> has been studied in the context of the Judd–Ofelt theory (14, 15).

The line strength of the forced electric-dipole transition between the  $J$  manifold  $\langle (SL)J |$  and the terminal manifold  $| (S'L')J' \rangle$  of neodymium  $4f$  states can be expressed by

$$S_{ed} = \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle (SL)J || U^{\lambda} || (S'L')J' \rangle|^2,$$

where the three terms  $\langle || U^{\lambda} || \rangle$  are the doubly reduced unit tensor operators in the intermediate coupling approximation. The Judd–Ofelt parameters contain two types of terms (16): (i) the crystal field parameters  $A_{t,p}$  (with  $t$  odd) which are the odd parity terms in the crystal field expansion. They depend on the site symmetry of the probe ion and (ii) the  $\Sigma(t, \lambda)$  parameters which contain the radial part of the  $4f$  wave functions and the energy gap between  $4f$  and admixing levels with opposite parity. These parameters can be considered as a measure of the amount of covalency of the rare earth–ligand bond.

As a general rule  $\Omega_2$  has been demonstrated to be related to the probe–ligand covalency (17). Thus the lowest values of  $\Omega_2$  are found for fluoride glasses and the highest for sulfide or oxysulfide glasses (18). A list of relevant examples is given in Table I.

In order to separate the respective contributions of  $A_{t,p}$  and  $\Sigma(t, \lambda)$ , two types of complementary measurements were carried out on the same glasses, involving Pb<sup>2+</sup> absorption and Eu<sup>3+</sup> fluorescence.

TABLE I

RANGE OF JUDD–OFELT  $\Omega_2$  INTENSITY PARAMETERS FOR Nd<sup>3+</sup> IN DIFFERENT GLASS TYPES (18)

	$\Omega_2(10^{-20}\text{cm}^2)$
Fluoroberyllates	0.1–1.7
Fluorozirconates	1.8–2.0
Fluorohafnates	1.3
Fluoroaluminates	0.6–2.4
Phosphates	2.9–6.7
Oxysulfides	8.2
Sulfides	6.6–9.4

### I.2. Absorption Spectra of Pb<sup>2+</sup>

In oxide glasses the concept of optical basicity introduced by Duffy and Ingram (19) is related to the ability of the former oxygen atoms to donate some of their negative charge to the modifier metal ions. It can be deduced from the position of the absorption band corresponding to the  $^1S_0 \rightarrow ^3P_1$  transition of Pb<sup>2+</sup>. As pointed out by Reisfeld (20) this band is red shifted with the increasing covalency of the Pb–O bond and consequently of the  $\Sigma(t, \lambda)$  terms.

### I.3. Europium Fluorescence Spectra

In glasses Eu<sup>3+</sup> usually occupies sites with low symmetry. Its emission spectrum may include electric dipole emission lines such as  $^5D_0 \rightarrow ^7F_{0,2,4,6}$  whose intensities dramatically rise with the degree of asymmetry of the probe environment. On the other hand, the  $^5D_0 \rightarrow ^7F_1$  transition which is of the magnetic dipole type is always observed and its intensity is independent of the site symmetry. Therefore it is generally admitted that the ratio of the emission intensities,

$$R = \frac{I_{5D_0 \rightarrow 7F_2}}{I_{5D_0 \rightarrow 7F_1}},$$

is an asymmetry factor for the Eu<sup>3+</sup> sites (21). Accordingly the variation of  $R$  versus glass composition reflects the variation of the  $A_{t,p}$  terms ( $t$  odd).

## II. Experimental Procedure

### II.1. Glass Preparation

Several methods have been described to introduce nitrogen in phosphates. Phosphorus oxynitride glasses were prepared for the first time by melting alkaline phosphates  $(\text{MPO}_3)_n$  in ammonia (22, 23). Nitrogen-containing phosphate glasses were also obtained by doping a melt with metal nitrides (Al, Mg, Ca) (24, 25) or by using PON phosphorus oxynitride as a nitrogen source (26).

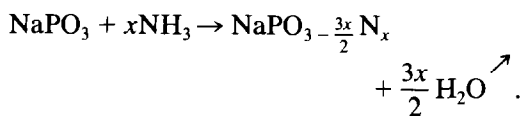
The investigated glasses were prepared from  $(\text{NaPO}_3)_n$  phosphate using ammonia as a nitrogen source. This procedure allows to bring a progressive amount of nitrogen in the material without changing all other parameters.

Two ways—a priori—enabled us to obtain the doped samples:

—the addition of  $\text{Nd}_2\text{O}_3$ ,  $\text{PbO}$ , or  $\text{Eu}_2\text{O}_3$  oxide to a previously nitrated glass and the melting of the mixture and

—the nitridation of the previously doped sodium phosphate.

This second way gave the best results. Thus, doped phosphorus oxynitride glasses, containing up to ~10 wt% nitrogen, were prepared as bulk samples by nitridation—in the molten state, at 700°C, under ammonia flow—of  $(\text{NaPO}_3)_n$  reagent grade sodium phosphate, in a vitreous carbone crucible, according to the reaction scheme



The nitridation time was between several hours and 48 hr depending on the required nitrogen concentration. At the end of the preparation, a nitrogen flow was kept for 1 hr before the furnace temperature was decreased to room temperature.

The nitrogen content was measured by chemical analysis of nitrogen as  $\text{NH}_3$  with an accuracy of about 1%. The compositions

TABLE II

COMPOSITIONS OF THE INVESTIGATED GLASSES

Europium-doped glasses	0.99 $\text{NaPO}_3$ , 0.01 $\text{Eu}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.70}\text{N}_{0.20}$ , 0.01 $\text{Eu}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.52}\text{N}_{0.32}$ , 0.01 $\text{Eu}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.25}\text{N}_{0.50}$ , 0.01 $\text{Eu}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.16}\text{N}_{0.56}$ , 0.01 $\text{Eu}_2\text{O}_3$
Lead-doped glasses	0.9999 $\text{NaPO}_3$ , 0.0001 $\text{PbO}$
	0.9999 $\text{NaPO}_{2.235}\text{N}_{0.51}$ , 0.0001 $\text{PbO}$
Neodymium-doped glasses	0.995 $\text{NaPO}_3$ , 0.005 $\text{Nd}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.61}\text{N}_{0.26}$ , 0.01 $\text{Nd}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.535}\text{N}_{0.310}$ , 0.01 $\text{Nd}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.25}\text{N}_{0.50}$ , 0.01 $\text{Nd}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.27}\text{N}_{0.52}$ , 0.01 $\text{Nd}_2\text{O}_3$
	0.99 $\text{NaPO}_{2.205}\text{N}_{0.530}$ , 0.01 $\text{Nd}_2\text{O}_3$

of the investigated samples are collected in Table II.

### II.2. Spectroscopic Measurements

All the spectroscopic measurements were carried out at room temperature. The absorption spectra were recorded by transmission using a Cary 17 spectrometer.

The  $\text{Nd}^{3+}$  absorption was studied on 2-mm-thick samples whose parallel sides were carefully polished using diamond powder. The  $\text{Pb}^{2+}$  absorption spectra were recorded on very thin glasses (<0.5 mm); moreover in this case a grating with optical density of 2 was interposed on the reference beam due to the strong absorptivity of the samples.

The Judd–Ofelt parameters were calculated from the intensities of the absorption bands, as previously described (13, 27). A computerized least-squares program yields the best fit values for  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$ , from the observed  $S_{\text{ed}}$  line strengths of the various  $^4\text{I}_{9/2} \rightarrow ^2\text{S}+^1\text{L}_J$  absorption transitions.

The  $S_{\text{ed}}$  values are calculated using the equation

$$\int k(\lambda) d\lambda = N \frac{8\pi^3 e^2 \bar{\lambda}}{3hc(2J+1)n} \frac{1}{9} \frac{(n^2+2)^2}{9} S_{\text{ed}}$$

where  $\int k(\lambda) d\lambda$  is the experimental integrated absorbance of the transition;  $N$ , the

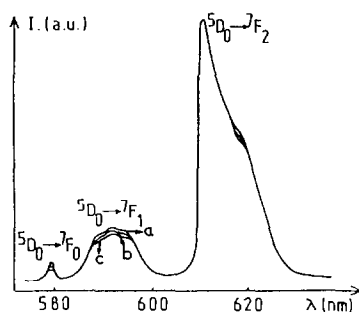


FIG. 1. Matching of the  $\text{Eu}^{3+}$  emission spectra in the  $\text{NaPO}_3 - \frac{x}{2}\text{N}_x$ :  $\text{Eu}^{3+}$  glasses for various compositions from  $x = 0$  to  $x = 0.51$  (a,  $x = 0$ ; b,  $x = 0.23$ ; c,  $x = 0.51$ ) ( $\lambda_{\text{exc}} = 380 \text{ nm}$ ,  $T = 80 \text{ K}$ ).

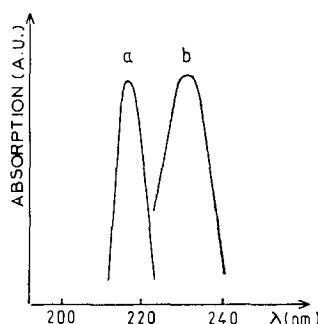


FIG. 2.  $^1\text{S}_0 \rightarrow ^3\text{P}_1$  absorption band for the  $\text{Pb}^{2+}$  probe in glasses with composition a,  $\text{NaPO}_3$ ; and b,  $\text{NaPO}_{2.235}\text{N}_{0.510}$ .

rare earth ion concentration;  $\bar{\lambda}$ , the average wavelength of the absorption band; and  $n$ , the bulk refractive index at the  $\lambda$  wavelength.

The  $\text{Eu}^{3+}$  emission spectra were recorded under a xenon lamp excitation at 392 nm using a H.R.S.2 Jobin-Yvon monochromator and a R 928 Hamamatsu photomultiplier. The spectra were corrected by taking into account the specific response curve of the detection device.

### III. EXPERIMENTAL RESULTS

Figure 1 shows the  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  ( $J = 0, 1, 2$ )  $\text{Eu}^{3+}$  emission spectra for glasses without nitrogen or containing various proportions of nitrogen.

The location, intensity, and profile of  $\text{Eu}^{3+}$  emission lines are exactly the same whatever the nitrogen rate. As a consequence  $\text{Eu}^{3+}$  environment is quite identical in pure oxygen and oxynitride glasses. Obviously  $R$  remains constant.

This behavior is different from the situation generally observed in various pure oxide systems for which the least composition variation induces a marked change of  $R$  (see, e.g., Refs. 13 and 38).

Figure 2 illustrates the red shift of the absorption band maximum corresponding to the  $^1\text{S}_0 \rightarrow ^3\text{P}_1$   $\text{Pb}^{2+}$  transition for the  $\text{NaPO}_3$

and  $\text{NaPO}_{2.235}\text{N}_{0.510}$  glasses taken as examples. From this spectrum the optical basicity  $\Lambda$  obtained for the free-nitrogen phosphate ( $\Lambda = 0.48$ ) is very close to the theoretical value calculated using relations given by Duffy and Ingram (19) ( $\Lambda = 0.52$ ). The red shift resulting from the introduction of nitrogen in glasses reveals a reinforcement of the lead-ligand bond covalency.

Table III lists the Judd-Ofelt parameters deduced from the neodymium absorption spectra. The  $^4\text{I}_{9/2} \rightarrow ^2\text{G}_{7/2}$ ,  $^4\text{G}_{5/2}$  transitions have the highest intensity as illustrated in Fig. 3. They are the most sensitive of the  $\Omega_2$  variations due to the larger value of the involved reduced matrix element  $\langle\langle U^{(2)} \rangle\rangle$  (29).

A fair agreement between observed and calculated oscillator strengths is obtained for all the transitions (Table III).

The  $\Omega_2$  parameter of  $\text{NaPO}_3$  agrees with those generally found for phosphate glasses (18). The value calculated for the nitrogen-richest sample is one of the highest obtained for this class of materials (18).

### IV. DISCUSSION

The former network of  $\text{NaPO}_3$  glasses is made up of quasi-infinite  $(\text{PO}_3)_\infty$  chains. Nitrogen replaces oxygen in P-O-P bridging

TABLE III  
MEASURED AND CALCULATED OSCILLATOR STRENGTHS FOR NEODYMIUM-DOPED GLASSES WITH  
COMPOSITION  $\text{NaPO}_3\text{-}_{3x/2} \text{N}_x$

Transition $^4I_{9/2}$	0		0.26		0.31		0.50		0.52		0.53	
	$f_{\text{calc}}$ ( $10^{-6}$ )	$f_{\text{obs}}$ ( $10^{-6}$ )	$f_{\text{calc}}$ ( $10^{-6}$ )	$f_{\text{obs}}$ ( $10^{-6}$ )	$f_{\text{calc}}$ ( $10^{-6}$ )	$f_{\text{obs}}$ ( $10^{-6}$ )	$f_{\text{calc}}$ ( $10^{-6}$ )	$f_{\text{obs}}$ ( $10^{-6}$ )	$f_{\text{calc}}$ ( $10^{-6}$ )	$f_{\text{obs}}$ ( $10^{-6}$ )	$f_{\text{calc}}$ ( $10^{-6}$ )	$f_{\text{obs}}$ ( $10^{-6}$ )
$\rightarrow ^4F_{3/2}$	1.08	0.97	1.16	1.04	1.35	1.22	1.77	1.63	1.92	1.74	1.99	1.78
$\rightarrow ^4F_{5/2}, ^2H_{9/2}$	3.48	3.64	3.93	4.10	4.50	4.69	5.67	5.90	6.15	6.42	6.41	6.74
$\rightarrow ^4F_{7/2}, ^4S_{3/2}$	3.63	3.48	4.17	4.02	4.72	4.56	5.85	5.66	6.35	6.11	6.63	6.34
$\rightarrow ^4G_{5/2}, ^2G_{7/2}$	8.08	8.07	10.3	10.3	12.7	12.7	16.3	16.3	17.9	17.9	18.3	18.3
$\rightarrow ^4G_{7/2}, ^4G_{9/2}$	2.85	2.79	3.25	3.26	3.82	3.81	4.92	4.80	5.36	5.35	5.54	5.38
$^2K_{13/2}$												
$\Omega_2$ ( $10^{-20} \text{ cm}^2$ )	2.44		3.53		4.44		5.63		6.24		6.34	
$\Omega_4$ ( $10^{-20} \text{ cm}^2$ )	2.88		3.03		3.57		4.75		5.15		5.32	
$\Omega_6$ ( $10^{-20} \text{ cm}^2$ )	3.44		3.97		4.49		5.54		6.01		6.28	

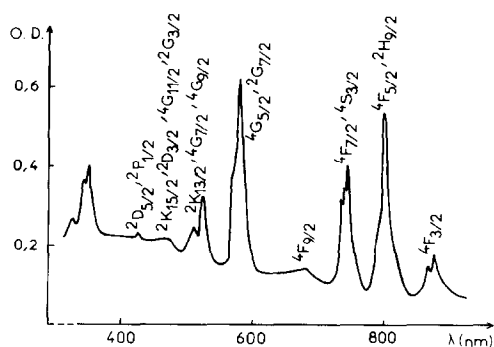
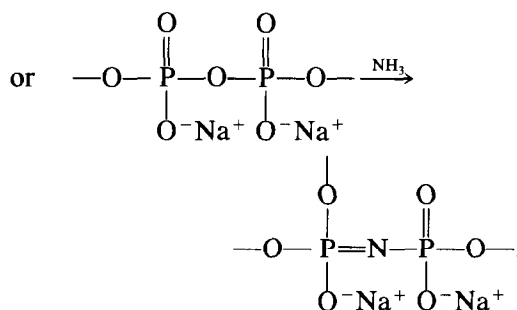
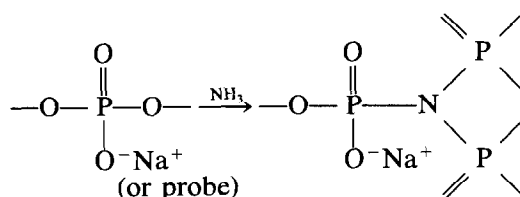


FIG. 3. Absorption spectrum of a neodymium-doped glass with composition  $0.99 \text{NaPO}_{2.61}\text{N}_{0.26}$ ,  $0.01 \text{Nd}_2\text{O}_3$ .

and P = O nonbridging sequences, with creation of cross-linked chains through  $\text{P}(\text{O},\text{N})_4$  tetrahedra.

As demonstrated by Bunker *et al.* (6), nitrogen can be bonded either to three phosphorus atoms via three single bonds or to two phosphorus atoms via one double bond and one single bond, according to the following mechanisms:



This atomic distribution was corroborated by a more recent XPS investigation (10): the  $\text{N}_{1s}$  electron spectrum can be decomposed in two Gaussians located at energies very close to those found in the  $\text{P}_3\text{N}_5\text{H}_x$  compound where a similar situation exists for nitrogen (31).

As regards to the present investigation, the introduction of nitrogen in phosphate glasses results in

(i) a large increase of the  $\text{Nd}^{3+} \Omega_2$  Judd-Ofelt parameter,

(ii) a red shift of the  $\text{Pb}^{2+} ^1S_0 \rightarrow ^3P_1$  absorption band,

(iii) a striking identical  $\text{Eu}^{3+}$  fluorescence spectrum, whatever the nitrogen content.

This last property reveals not only an identical  $\text{Eu}^{3+}$  site distribution, but also a pure oxygenated environment of the probe ions. This conclusion is in agreement with a previous Na NMR investigation showing

clearly the insensitivity of the position and intensity of the  $^{23}\text{Na}$  NMR spectra to the nitrogen content (6).

In contrast, the large variations observed in (i) and (ii) can be related to the nature of the bond between the probe and the oxygen-nearest neighbors. They suggest the following mechanism. Replacing O by N leads to the creation of mixed  $\text{P}(\text{O},\text{N})_4$  tetrahedral units—mainly  $\text{PO}_3\text{N}$  and  $\text{PO}_2\text{N}_2$ —at the expense of  $\text{PO}_4$  groups. The existence of strong P–N and P=N bonds within these new tetrahedral units induces a weakening of the phosphorus-oxygen bonds within the same  $\text{P}(\text{O},\text{N})_4$  groups and consequently a reinforcement of the antagonistic sodium–oxygen bonds.

## V. CONCLUSIONS

The use of  $\text{Nd}^{3+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Eu}^{3+}$  as local structural probes allows us to explain the consequences of nitrogen introduction in the  $\text{NaPO}_3$  sodium phosphate glasses, in agreement with previous investigations.

Nitrogen atoms replace oxygen in the phosphate network. They are bonded to two or three phosphorus atoms but they are never located in a chain-ending site. Such an atomic distribution which involves a pure oxygenated environment for the modifier ions is demonstrated by two different spectroscopies:  $^{23}\text{Na}$  NMR and  $\text{Eu}^{3+}$  fluorescence.

In addition, the covalent character of the bond between sodium ions and nonbridging oxygen of phosphate groups increases with the nitrogen content. Such a tendency was evidenced by both  $\text{Pb}^{2+}$  and  $\text{Nd}^{3+}$  spectroscopies.

These conclusions can explain the changes in physical properties such as thermal expansion or softening temperature, which were observed by previous authors, as a result of

(i) the creation of strong phosphorus–nitrogen bonds in the tetrahedral groups,

(ii) the increase of crosslinking between the phosphate chains, and

(iii) the higher oxygen–sodium bond covalency, as it is clearly deduced from the present study.

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