

## Structural Investigation of Glasses Belonging to the $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$ System\*

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The structure of glasses [with composition  $0.855(x\text{Na}_2\text{O}-y\text{Nb}_2\text{O}_5-z\text{P}_2\text{O}_5)-0.145\text{Ln}_2\text{O}_3$ ;  $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}$ , and  $x + y + z = 100$ ] has been investigated by Raman scattering and optical spectroscopy using  $\text{Nd}^{3+}$  and  $\text{Eu}^{3+}$  as local structural probes. For the niobium-poor glasses ( $y < 12.5$ ) octahedral  $\text{NbO}_6$  groups are inserted within modified metaphosphate chains. In contrast the network former of the niobium-rich glasses ( $y > 12.5$ ) contains chains of  $\text{NbO}_6$  octahedra sharing common corners. An intermediate situation seems to occur for  $y \approx 12.5$  which preserves the Nasicon-type structure with all oxygen atoms common to  $\text{NbO}_6$  and  $\text{PO}_4$  groups. © 1988 Academic Press, Inc.

### I. Introduction

Due to their particular physical chemical properties, niobium oxide-based glasses appear quite attractive in various fields of material science. They can be used, for instance, for the elaboration of the  $\text{MNbO}_3$  ( $M = \text{Li}, \text{Na}$ ) glass ceramics (1-3) or as neodymium laser materials with a low optical pumping threshold and a very narrow emission bandwidth (4). Yet, such glasses have so far been poorly investigated.

In a recent study the vitreous domains of the  $M_2\text{O}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$  ( $M = \text{Li}, \text{Na}$ ) systems have been well-defined (5). They are quite similar whatever the alkali element considered, either Li or Na (Fig. 1). The lithium- and niobium-rich glasses exhibit good ionic conductivity which can reach  $10^{-2} \Omega^{-1} \text{cm}^{-1}$  at  $300^\circ\text{C}$  for the molar composition  $50\text{Li}_2\text{O}-24\text{Nb}_2\text{O}_5-26\text{P}_2\text{O}_5$  with an activation energy  $\Delta E = 0.45 \text{ eV}$ .

To provide better insight into the structure of those glasses a detailed investigation was carried out by Raman scattering and optical spectroscopy using  $\text{Eu}^{3+}$  and  $\text{Nd}^{3+}$  as local structural probes. The present pa-

\* Dedicated to Professor A. Rabenau on the occasion of his 65th anniversary.

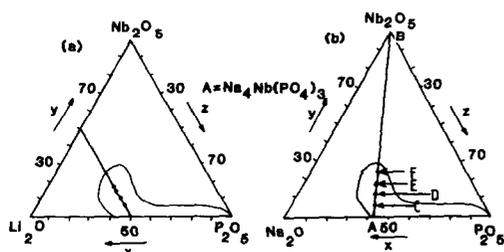


FIG. 1. Vitreous domain (hatched) in the  $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$  system. Glass compositions investigated for  $\text{Na}/\text{P} = 4/3$  (AB); C,  $y = 6$ ; D,  $y = 12.5$  ( $\text{Na}_4\text{Nb}(\text{PO}_4)_3$ ); E,  $y = 18$ ; F,  $y = 24$ .

per reports results obtained for rare-earth oxide-doped sodium glasses belonging to the  $\text{Na}_2\text{O}-\text{Nb}_2\text{O}_5-\text{P}_2\text{O}_5$  system with  $\text{Na}/\text{P} = 1.33$ , i.e., on the AB line of Fig. 1. This line includes the compound  $\text{Na}_4\text{Nb}(\text{PO}_4)_3$  for which a reversible glass-crystal transition was pointed out (6).

## II. Experimental

As mentioned, the glasses investigated had molar compositions  $0.855 (x\text{Na}_2\text{O}-y\text{Nb}_2\text{O}_5-z\text{P}_2\text{O}_5)-0.145 \text{Ln}_2\text{O}_3$  with  $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}$ ,  $x + y + z = 100$ , and  $x/z = \frac{4}{3}$ . The  $y$  values were 6, 12.5, 18, and 24.

Optically inactive lanthanum was introduced for the Raman scattering and diffuse reflectance investigations in order to allow useful comparisons in terms of structural information for the lightly neodymium- or europium-doped glasses.

The glasses were prepared according to a procedure previously reported (5). Their thermal behavior was investigated using differential thermal analysis and classical X-ray diffraction (XRD) techniques. As an example, the vitreous transition and recrystallization temperatures of the rare-earth free glass corresponding to  $y = 12.5$  were found to be 430 and 570°C, respectively. Recrystallization of the glasses led to  $\text{Na}_4\text{Nb}(\text{PO}_4)_3$ , the XRD spectrum of which can be indexed assuming a monoclinic cell with

parameters consistent with a Nasicon-type structure (6). For  $y = 6$  the same phase is also found among the recrystallization products, whereas the XRD patterns corresponding to the recrystallized niobium-rich glasses ( $y = 18$  and  $y = 24$ ) are complex but don't include the characteristic lines of  $\text{Na}_4\text{Nb}(\text{PO}_4)_3$ .

The Raman spectra were recorded at room temperature using a Jobin-Yvon spectrophotometer coupled with an Ar laser Spectra Physics 2560. Samples in the form of pressed pellets ( $\phi = 13$  mm, thickness = 1.5 mm) were prepared from ground glasses.

Reflectance diffuse spectra and absorption spectra of the neodymium-doped samples were determined at room temperature using a Cary 17 spectrophotometer.

The fluorescence of  $\text{Nd}^{3+}$  and  $\text{Eu}^{3+}$  was recorded using a Jobin-Yvon monochromator and a Varian VPM 159A photomultiplier. Steady-state emission spectra were obtained with a Xe lamp excitation. The lifetime of the  $\text{Nd}^{3+} {}^4F_{3/2}$  level was deduced from the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  fluorescence decay after a pulsed nonselective excitation in the  ${}^4G_{5/2}$  and  ${}^2G_{7/2}$  levels. The source was a rhodamine 590 solution excited by a nitrogen laser; the photomultiplier was connected to a PAR M 162 boxcar averager.

## III. Raman Scattering Investigation

The Raman spectra of the investigated glasses are shown in Fig. 2. Band assignment can be made on the basis of previous data characterizing either sodium phosphate glasses (7, 8) or the Nb-O bonds in crystals (9-12).

For the composition close to the sodium phosphate ( $y = 6$ ), the bands at 725 and 1145  $\text{cm}^{-1}$  can be assigned, respectively, to  $\gamma_{\text{SPO}_4}$  and  $\gamma_{\text{SPO}_2}$  vibrations of metaphosphate chains. Introduction of niobium gives rise to an intense band at 900  $\text{cm}^{-1}$  and to

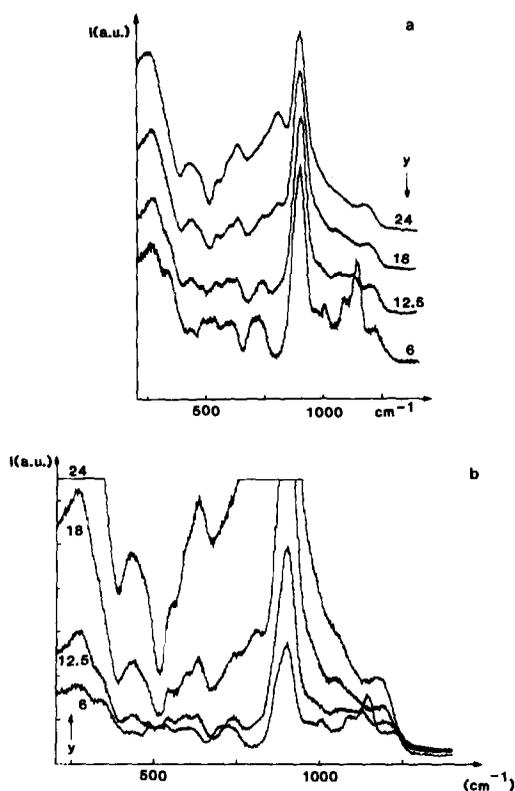


FIG. 2a. Raman spectra of the  $0.855(x\text{Na}_2\text{O}-y\text{Nb}_2\text{O}_5-z\text{P}_2\text{O}_5)-0.145\text{La}_2\text{O}_3$  glasses ( $x/z = 1.33$ ;  $y = 6, 12.5, 18, \text{ and } 24$ ).

FIG. 2b. Comparison of the band intensities of the investigated glass spectra.

several weaker bands at 630, 450, and 260  $\text{cm}^{-1}$ .

As the amount of niobium present in the glasses increases, the intensities of these new bands are enhanced, in particular that at 900  $\text{cm}^{-1}$ . On the contrary the bands at 1145 and 725  $\text{cm}^{-1}$  weaken gradually, indicating a modification in the metaphosphate chains.

The new bands characterize Nb–O bonds in octahedral sites: the first two frequencies represent the Nb–O stretching mode, thus demonstrating the existence of a distribution of Nb–O lengths in the NbO<sub>6</sub> groups. The vibration at 900  $\text{cm}^{-1}$  corresponds to a short Nb–O bond ( $d_{\text{Nb-O}} \approx 1.77 \text{ \AA}$ ), that at

630  $\text{cm}^{-1}$  is equivalent to the mode characterizing equatorial Nb–O bonds found in  $\alpha\text{-NbPO}_5$  ( $d_{\text{Nb-O}} \approx 1.97 \text{ \AA}$ ). In agreement with Ref. (11) the band at 450  $\text{cm}^{-1}$  probably involves O–Nb–O and O–P–O coupled modes. The remaining band located at 260  $\text{cm}^{-1}$  can be associated with various O–Nb–O bending modes. Such a band was also found in some ferroelectric materials with tungsten–bronze structures (12) in which the NbO<sub>6</sub> groups share common corners.

From those results it appears that the introduction of increasing amounts of Nb<sub>2</sub>O<sub>5</sub> in the phosphate glasses initially breaks the metaphosphate chains and progressively develops a new network former structure constituted mainly by chains of NbO<sub>6</sub> octahedra sharing common corners.

An intermediate structure seems to occur for the glass corresponding to a formulation Na<sub>4</sub>Nb(PO<sub>4</sub>)<sub>3</sub> ( $y = 12.5$ ), the crystallization of which leads to a Nasicon-type arrangement. Each NbO<sub>6</sub> unit is surrounded in this material by six PO<sub>4</sub> groups.

#### IV. Investigation of the Diffuse Reflectance Spectra

The diffuse reflectance spectra have been recorded and compared to those of crystalline materials. Figure 3 gives the spectra of the glasses as well as those of crystallized

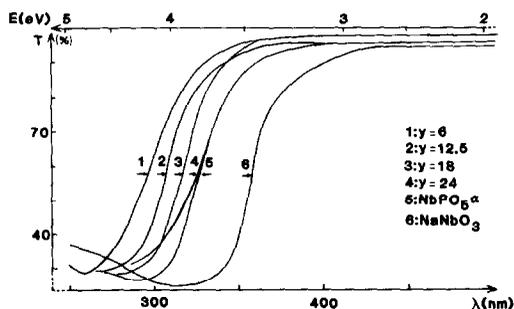
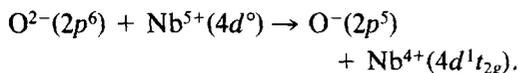


FIG. 3. Comparison of the diffuse reflectance spectra of niobium crystallized oxides with those of the investigated glasses.

TABLE I  
 ABSORPTION THRESHOLD OF  $O^{2-} \rightarrow Nb^{5+}$  ELECTRONIC TRANSFER IN NIOBIUM CRYSTALLIZED  
 COMPOUNDS AND IN THE INVESTIGATED GLASSES

		Glass 0.855 (xNa <sub>2</sub> O-yNb <sub>2</sub> O <sub>5</sub> -zP <sub>2</sub> O <sub>5</sub> )-0.145 Ln <sub>2</sub> O <sub>3</sub>					
		y = 6	y = 12.5	y = 18	y = 24	NbPO <sub>5</sub>	NaNbO <sub>3</sub>
E (eV)	P/Nb	6.715	3	1.953	1.358	1	0
	Eu	3.90	3.76	3.65	3.54	3.49	3.29
	La	3.85	3.78	3.57	3.42		

$\alpha$ -NbPO<sub>5</sub> and NaNbO<sub>3</sub>. The strong absorption observed at high energy results from the formal electronic transfer:



The values of the corresponding absorption thresholds  $E$  are given in Table I.

It is worthwhile to analyze the electronic transfer for the crystallized phases as a function of their crystal structure. The structure of NaNbO<sub>3</sub> (14) involves NbO<sub>6</sub> groups sharing their corners in the three space directions. The  $\alpha$ -NbPO<sub>5</sub> lattice is built up by chains of NbO<sub>6</sub> octahedra sharing four out of six oxygen atoms with PO<sub>4</sub> groups (15). The increase of the charge transfer energy  $E$  from NaNbO<sub>3</sub> to  $\alpha$ -NbPO<sub>5</sub> results from the strengthening of the ionic character of the Nb-O bonds due to the presence of the strong covalent PO<sub>4</sub> groups.

As previously pointed out (under Section III) niobium is present in the glasses as NbO<sub>6</sub> octahedra. These groups share some of their oxygen atoms with PO<sub>4</sub> groups. For glasses with low niobium content the Nb-O bonds have a relatively strong ionic character due to competition with many PO<sub>4</sub> tetrahedra, leading to a high  $E$  value. As a consequence, as niobium content increases and the relative number of PO<sub>4</sub> groups is lowered,  $E$  is expected to decrease. For the niobium-richest glasses the absorption

threshold is close to that of  $\alpha$ -NbPO<sub>5</sub>, which is consistent with the presence of corner-sharing NbO<sub>6</sub> groups.

## V. Use of Nd<sup>3+</sup> and Eu<sup>3+</sup> as Local Structural Probes

### 1. Investigation Method

The Nd<sup>3+</sup> absorption of the neodymium-doped glasses has been investigated in the scope of the Judd-Ofelt theory (16, 17).

The Judd-Ofelt parameters  $\Omega_2$ ,  $\Omega_4$ , and  $\Omega_6$  are related to:

(i) the odd crystal field coefficients  $A_{t,p}$  which depend on the local site symmetry, and

(ii) the  $\theta(t, \lambda)$  parameter which can be considered as measuring the degree of covalency of the rare earth-ligand bond.

From the neodymium absorption spectra one can calculate the  $\Omega_\lambda$  parameters.  $\Omega_2$  is the most sensitive to the neodymium-ligand bond covalency. For instance,  $\Omega_2$  decreases strongly for glasses by introduction of fluorine but increases in presence of sulfur (18).

Once the  $\Omega_\lambda$  parameters have been calculated, the radiative decay probability of the  $^4F_{3/2}$  level may be determined and compared with the experimental one. In order to separate the respective contributions of  $A_{t,p}$  and  $\theta(t, \lambda)$ , the europium fluorescence has been

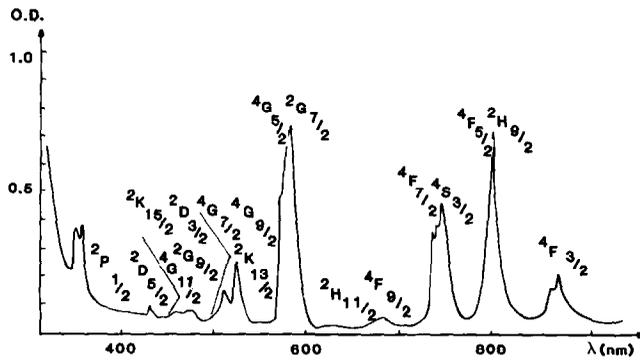


FIG. 4. Nd<sup>3+</sup> absorption spectrum of the  $y = 12.5$  neodymium-doped glass (thickness = 0.364 cm).

analyzed as a complementary measurement.

When Eu<sup>3+</sup> occupies low symmetry sites, which occurs generally in glasses, its emission spectrum may contain electric-dipole lines such as those corresponding to  ${}^5D_0 \rightarrow {}^7F_{0,2,4,6}$ . But, on the other hand, the  ${}^5D_0 \rightarrow {}^7F_1$  transition which is of magnetic dipole nature is always observed and its intensity is independent of the site symmetry. Therefore, it is generally accepted that the  $R = {}^1S_0 \rightarrow {}^7F_2 / {}^1S_0 \rightarrow {}^7F_1$  ratio represents a real asymmetry parameter for the Eu<sup>3+</sup> site (19).

### 2. Nd<sup>3+</sup> Absorption and Emission Spectra

As an example, Fig. 4 shows the absorption spectrum of the  $y = 12.5$  glass containing  $0.5 \times 10^{20}$  Nd<sup>3+</sup> cm<sup>-3</sup>. The observed bands correspond to various transitions between the ground state  ${}^4I_{9/2}$  and excited levels. The  $\Omega_\lambda$  parameters calculated for the various glasses are listed in Table II. The variation of  $\Omega_2$  as a function of the Nb<sub>2</sub>O<sub>5</sub> content is given in Fig. 5.  $\Omega_2$  increases with higher niobium concentration reaching  $6.8 \pm 0.3 \times 10^{-20}$  cm<sup>2</sup> for the glass corresponding to  $y = 24$ . Note that this value is one of the highest so far obtained for phosphate glasses. It indicates a high covalency of the Nd-O bonds. Figure 6 shows the neodymium  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  emission spectrum under broadband excitation. The wavelength of

the emission maximum and the effective bandwidth are given in Table II. The intensity of the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  emission for both niobium-richest glasses is about twice that of the two others.

The decay curves of the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  Nd<sup>3+</sup> emission have been recorded between 50 and 1500  $\mu$ sec. They are of exponential nature whatever the glass composition. The radiative lifetime and the corresponding measured radiative desexcitation probability  $A_{rad}$  are given in Table II. These data agree fairly well with the theoretical values calculated from the Judd-Ofelt theory.

TABLE II

RADIATIVE PROPERTIES OF THE NEODYMIUM-DOPED GLASSES WITH COMPOSITION  $0.855(x\text{Na}_2\text{O}-y\text{Nb}_2\text{O}_5-z\text{P}_2\text{O}_5)-0.145\text{Nd}_2\text{O}_3$  ( $x + y + z = 100$ ;  $N_{\text{Nd}^{3+}} \approx 0.5 \times 10^{20}$  IONS  $\times$  cm<sup>-3</sup>)

	$y = 6$	$y = 12.5$	$y = 18$	$y = 24$
Judd-Ofelt intensity parameters				
$\Omega_2 \pm 0.3 \times 10^{-20}$ cm <sup>2</sup>	4.9	5.7	6.5	6.8
$\Omega_4 \pm 0.3 \times 10^{-20}$ cm <sup>2</sup>	5.0	4.7	4.3	4.4
$\Omega_6 \pm 0.3 \times 10^{-20}$ cm <sup>2</sup>	5.4	4.9	4.9	4.7
<sup>4</sup> F <sub>3/2</sub> lifetime				
Measured: $\tau_M \pm 10$ $\mu$ sec	340	321	314	292
Calc. $\tau_{rad} \pm 10$ $\mu$ sec	352	320	302	276
Emission probability				
Measured $1/\tau_M \pm 100$ sec <sup>-1</sup>	2940	3115	3185	3425
Calc. $A_{rad} \pm 100$ sec <sup>-1</sup>	2845	3080	3320	3620
Emission wavelength				
$\lambda_p \pm 2$ nm	1056	1056	1058	1058
Effective line width				
$\Delta\lambda_{eff} \pm 0.5$ nm	23.6	24	25	25.4

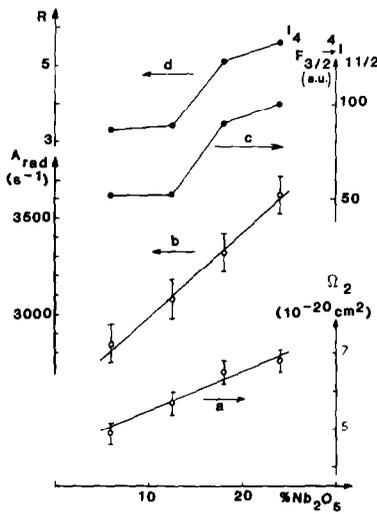


FIG. 5. Variations as a function of the  $\text{Nb}_2\text{O}_5$  content of: (a) the  $\Omega_2$  Judd parameter for  $\text{Nd}^{3+}$ ; (b) the  $\text{Nd}^{3+}$  radiative emission probability  $A_{\text{rad}}$ ; (c) the  $\text{Nd}^{3+} \ ^4F_{3/2} \rightarrow \ ^4I_{1/2}$  emission intensity, (d) the  $\text{Eu}^{3+}$  intensity ratio

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

### 3. $\text{Eu}^{3+}$ Emission Spectra

As an example, Fig. 7 gives the  $\text{Eu}^{3+} \ ^5D_0 \rightarrow \ ^7F_1$  ( $J = 0, 1, 2$ ) emission spectrum under broad excitation recorded at 300 K for the  $y = 12.5$  glass. The intensity of the  ${}^5D_0 \rightarrow \ ^7F_2$  transition is stronger than that of the two other lines. Figure 5 gives the variation of the intensity ratio  $R$  of  $\text{Eu}^{3+}$  with  $\text{Nb}_2\text{O}_5$  content. For low  $y$  values  $R$  is about 3.5

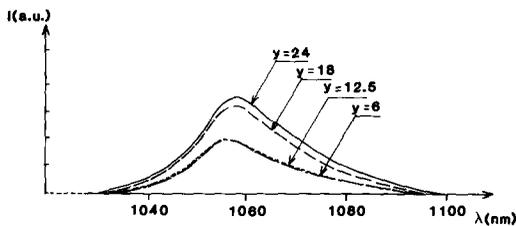


FIG. 6. Spectra of the  $\text{Nd}^{3+} \ ^4F_{3/2} \rightarrow \ ^4I_{1/2}$  emission for the neodymium-doped glasses ( $x/z = 1.33$ ;  $y = 6, 12.5, 18, \text{ and } 24$ ).

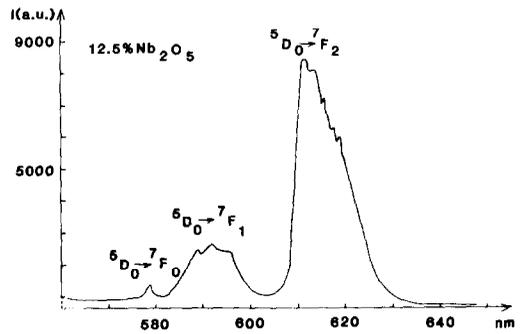


FIG. 7.  ${}^5D_0 \rightarrow \ ^7F_j$  ( $J = 0, 1, 2$ ) emission spectrum for the 0.855 ( $50 \text{ Na}_2\text{O}-12.5\text{Nb}_2\text{O}_5-37.5\text{P}_2\text{O}_5$ )-0.145  $\text{Eu}_2\text{O}_3$  glass (broad excitation at 392 nm;  $T = 300 \text{ K}$ ).

whereas it reaches 5.5 for the niobium-rich glasses ( $y = 18$  and  $y = 24$ ).

### 4. Discussion

The substitution of  $\text{PO}_4$  tetrahedra for  $\text{NbO}_6$  octahedra tends to strengthen the rare earth–oxygen bond in the glass lattice. This evolution is clearly illustrated by the increase of  $\Omega_2$  with niobium content. The variation of the  $\text{Nd}^{3+} \ ^4F_{3/2} \rightarrow \ ^4I_{1/2}$  emission intensity illustrates the existence of two types of glasses: those with a low niobium oxide content ( $y < 12.5$ ) and those with a higher one ( $y = 18$  and  $24$ ).

The  $R$  variation deduced from the europium emission spectra supports the same conclusion: a significant increase of the asymmetry of the europium site is observed when  $y$  rises from 12.5 to 18. This evolution can be explained by the replacement of almost regular  $\text{PO}_4$  groups by more or less distorted  $\text{NbO}_6$  octahedra which may modify the oxygen surrounding of the rare earth.

### VI. Conclusions

The structural evolution of glasses with molar compositions  $0.855 (x\text{Na}_2\text{O}-y\text{Nb}_2\text{O}_5-z\text{P}_2\text{O}_5)-0.145 \text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}$ , and  $x + y + z = 100$ ) can be understood by considering the material having a medium

composition ( $y = 12.5$ ). It has been shown that the network former of such a glass seems to keep the Nasicon structure in which all oxygen atoms are common between NbO<sub>6</sub> and PO<sub>4</sub> polyhedra. In the niobium-poor glass ( $y = 6$ ) corner-sharing NbO<sub>6</sub> groups are inserted within modified metaphosphate chains. As recrystallization of this glass gives rise to formation of Na<sub>4</sub>Nb(PO<sub>4</sub>)<sub>3</sub>, a partial demixion cannot be excluded. On the other hand, the network former of the niobium-rich glasses appears to be made up of chains containing NbO<sub>6</sub> octahedra sharing corners. As a consequence the cages of the covalent skeleton accommodating rare-earth ions appear to be more and more distorted at higher niobium concentrations.

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