

## The properties and crystallization of $\text{LiNbO}_3$ in lithium niobophosphate glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 9723

(<http://iopscience.iop.org/0953-8984/7/50/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:43

Please note that [terms and conditions apply](#).

# The properties and crystallization of $\text{LiNbO}_3$ in lithium niobophosphate glasses

E B de Araujo, J A C de Paiva and A S B Sombra

Laboratório de Ótica Não-Linear e Ciência dos Materiais, Departamento de Física, Universidade Federal do Ceará, Caixa Postal 6030, 60450-Fortaleza-Ceará, Brazil

Received 31 May 1995

**Abstract.** Lithium niobophosphate glasses  $[(x\text{Nb}_2\text{O}_5 \cdot (0.5 - x)\text{P}_2\text{O}_5) \cdot 0.5\text{Li}_2\text{O}]:y\text{Fe}_2\text{O}_3$  were studied using infrared spectroscopy and x-ray powder diffraction. The use of the two techniques gives new information about the structure of niobium phosphate glasses and glass ceramics. It was observed that under heat treatment phosphorus–oxygen groupings of different degrees of complexity, like  $\text{LiPO}_3$ ,  $\text{Li}_4\text{P}_2\text{O}_7$  and  $\text{Li}_3\text{PO}_4$ , were formed. Ferroelectric  $\text{LiNbO}_3$  crystals were also detected for  $x = 0.1$  niobium content samples

## 1. Introduction

In recent years, optical glasses containing  $\text{Nb}_2\text{O}_5$  have been of great interest to scientists due to their use as nonlinear photonic materials [1, 2], and as laser glasses of high stimulated emission parameters [3].

However, unlike for silicates and phosphates, very little work has been done on niobate glasses. The role played by  $\text{Nb}_2\text{O}_5$  in the glass structure, the coordination state of  $\text{Nb}^{5+}$ , and the interaction with other elements in the glass network is still a subject under study in the literature.

Many authors have studied the coordination of Nb atoms in glass networks. Rachkovskaya and Bubkova [4] have studied glasses composed of  $\text{P}_2\text{O}_5$ – $\text{Nb}_2\text{O}_5$ – $\text{V}_2\text{O}_5$ – $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$ – $\text{Nb}_2\text{O}_5$ – $\text{TiO}_2$ – $\text{Fe}_2\text{O}_3$  by infrared spectroscopy and found evidence of the existence of  $\text{NbO}_4$  and  $\text{NbO}_6$  units. Fukumi and Sakka [5], using Raman spectroscopy, confirmed that there are  $\text{NbO}_6$  polyhedra in the glass network of  $\text{K}_2\text{O}$ – $\text{Nb}_2\text{O}_5$ – $\text{SiO}_2$ .

Oliveira *et al.*, using thermally stimulated depolarization currents and Mössbauer spectroscopy, studied the effect of iron doping and associated vacancies in  $\text{P}_2\text{O}_5$ – $\text{PbO}$ – $\text{Nb}_2\text{O}_5$ – $\text{K}_2\text{O}$ – $\text{Fe}_2\text{O}_3$  glasses [6].

Recently, Komatsu [7] proposed the use of glasses containing ferroelectric crystals as a new type of nonlinear optical glass. Lithium niobate,  $\text{LiNbO}_3$ , is a ferroelectric material with a high Curie temperature of 1210 °C and a high value for the nonlinear susceptibility associated with second-harmonic generation, and is widely used for optical devices like wave guides [8].

This paper describes experiments in which lithium niobophosphate glasses  $[(x\text{Nb}_2\text{O}_5 \cdot (0.5 - x)\text{P}_2\text{O}_5 \cdot 0.5\text{Li}_2\text{O}]:y\text{Fe}_2\text{O}_3$ , with  $0 \leq x \leq 0.5$  and  $y = 0.02$ , were prepared and studied using infrared spectroscopy and x-ray diffraction with the aim of understanding the formation processes of niobophosphate glass and glass ceramics. Ferroelectric  $\text{LiNbO}_3$  and lithium phosphates of different degrees of complexity were obtained during heat treatments. Structures such as isolated  $\text{PO}_4^{3-}$  tetrahedra for the orthophosphate  $\text{Li}_3\text{PO}_4$ , two

tetrahedra joined together for the pyrophosphate  $\text{Li}_4\text{P}_2\text{O}_7$  and long chains or rings of  $\text{PO}_4^{3-}$  complexes for the metaphosphate  $\text{LiPO}_3$  were detected in our samples, depending on the heat treatment. Such glasses and glass ceramics containing microcrystallites of ferroelectric materials formed in a controlled crystallization process would be interesting candidates for new optical nonlinear glasses or glass ceramics.

## 2. Experimental procedure

### 2.1. Glass preparation

Initial compositions of the studied samples are given in table 1. Samples were prepared from reagent grade ammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and niobium oxide ( $\text{Nb}_2\text{O}_5$ ) with iron oxide  $\text{Fe}_2\text{O}_3$  as an impurity, by mixing reagents in appropriate proportions and heating them in platinum crucibles in an electric furnace. To prevent excessive boiling and consequent loss of mass, the water and ammonia in  $\text{NH}_4\text{H}_2\text{PO}_4$  were removed by pre-heating the mixture at 200 °C for several hours before the fusion. The mixture was subsequently melted at 1150 °C for 1 h. The melt was then poured into a stainless steel mould and pressed between two stainless steel plates. The mould and plates were pre-heated to 300 °C. The glasses are  $\{(x\text{Nb}_2\text{O}_5 \cdot (0.5 - x)\text{P}_2\text{O}_5) \cdot 0.5\text{Li}_2\text{O}\} : y\text{Fe}_2\text{O}_3$  with  $0 \leq x \leq 0.5$  and  $y = 0.02$ ; see table 1.

Table 1.  $\{(x\text{Nb}_2\text{O}_5 \cdot (0.5 - x)\text{P}_2\text{O}_5) \cdot 0.5\text{Li}_2\text{O}\} : y\text{Fe}_2\text{O}_3$  glass system compositions with 'x' and 'y' molar fractions ( $0 \leq x \leq 0.5$  and  $y = 0.02$ ).

Sample	$\text{Li}_2\text{O}$	$\text{P}_2\text{O}_5$	$\text{Nb}_2\text{O}_5$	$\text{Fe}_2\text{O}_3$
A	50	50	-	-
B	50	50	-	2
C	50	40	10	2
D	50	30	20	2
E	50	20	30	2
F	50	10	40	2
G	50	-	50	2

Losses in  $\text{Li}_2\text{O}$  and  $\text{P}_2\text{O}_5$  (which are the more volatile) for our experimental procedure are around 1 mol% and 0.5 mol% respectively, measured by chemical gravimetric methods. A comparable loss is also reported in the literature for lithium phosphate glasses [9], where loss in  $\text{Li}_2\text{O}$  is around 1 to 5 mol%. Because of the low loss the results are discussed in terms of the starting compositions of the samples (table 1).

According to the x-ray powder diffraction (XRD) spectra, samples with  $x$  ranging between zero and 0.2 only exhibit an amorphous phase, whereas samples with  $x > 0.2$  exhibit an additional crystalline phase (see figure 1).

### 2.2. Infrared spectroscopy

The infrared spectra (IR) were measured using KBr pellets made from a mixture of powder for each glass composition. The pellet thickness varied from 0.5 to 0.6 mm. The IR spectra were measured from 1400 to 400  $\text{cm}^{-1}$  with a Perkin Elmer 283-B spectrometer.

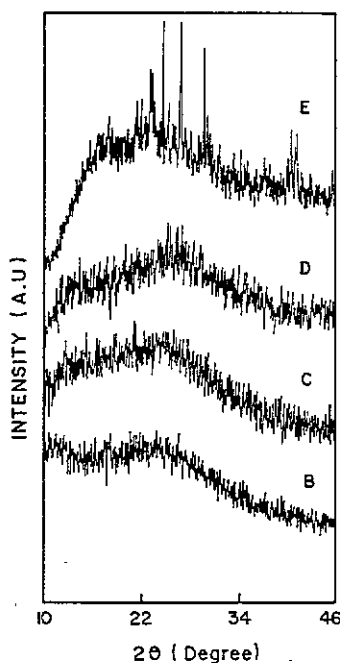


Figure 1. The x-ray powder diffraction pattern of samples B, C, D and E (see table 1).

### 3. Results and discussion

Figure 1 shows the x-ray powder diffraction pattern of samples B, C, D and E. One can observe that samples with  $x$  ranging between zero and 0.2 show only an amorphous phase, whereas samples with higher  $x$  values show a crystalline phase in addition to the amorphous phase.

In the present work we use the results of the literature [10–12] to interpret the IR spectra of the phosphate glasses.

According to Muller [10], the absorption of the P=O group is around 1282–1205  $\text{cm}^{-1}$  in polymeric phosphate chains. The stretching bands of P–O<sup>-</sup> (NBO—non-bridging oxygen) are around 1150/1050 and 950/925  $\text{cm}^{-1}$ . Absorptions at 800/720  $\text{cm}^{-1}$  are due to P–O–P vibrations (BO—bridging oxygen). The bands below 600  $\text{cm}^{-1}$  are due to the bending mode of the PO<sub>4</sub> units in phosphate glasses.

Spectrum A in figure 2 shows the IR spectra of the basic lithium phosphate glasses. The bands at 1250  $\text{cm}^{-1}$  (P=O), 1085  $\text{cm}^{-1}$  and 890  $\text{cm}^{-1}$  (P–O<sup>-</sup>) and 770  $\text{cm}^{-1}$  and 480  $\text{cm}^{-1}$  (P–O–P) are present. The presence of the iron as an impurity does not change the phosphorus absorptions much (spectrum B, figure 2).

However with the substitution of P<sub>2</sub>O<sub>5</sub> by Nb<sub>2</sub>O<sub>5</sub> (spectra C and D in figure 2) strong changes can be found. The resonances associated to the bridging oxygen (P–O–P) around 770  $\text{cm}^{-1}$  and 480  $\text{cm}^{-1}$  disappear and a new resonance around 600  $\text{cm}^{-1}$  appears (spectrum D, figure 2). The absence of an infrared absorption band near 1250  $\text{cm}^{-1}$  in the glasses C and D indicates the absence of the P=O double bond. The resonances associated with the non-bridging oxygen (P–O<sup>-</sup>) also decrease with the presence of the Nb<sub>2</sub>O<sub>5</sub>. This is an indication that the niobium oxygen octahedra are using the NBO associated with phosphorus to form the glass network structure.

According to the Mössbauer results reported in the literature, the niobium ion occupies an octahedral site in the glass network [6]. This is in good agreement with the IR data

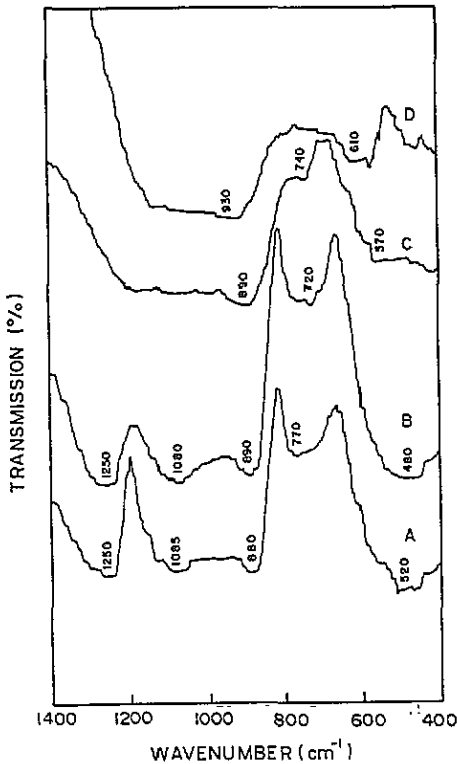


Figure 2. The infrared spectra of the samples A, B, C and D (see table 1). The transmission scales has been displaced vertically for clarity.

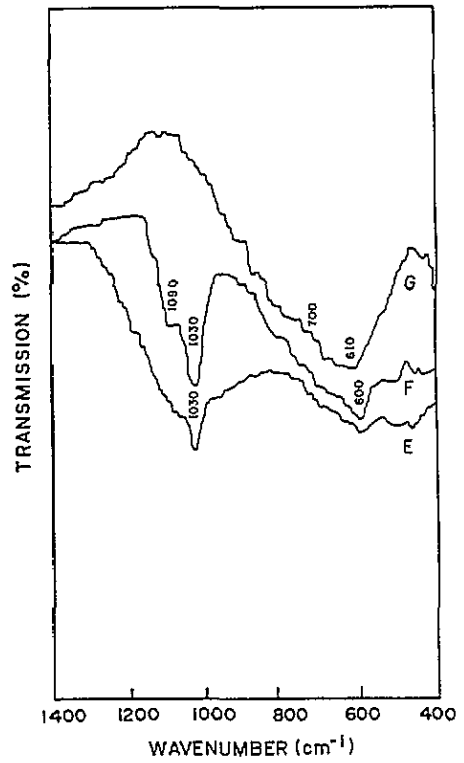


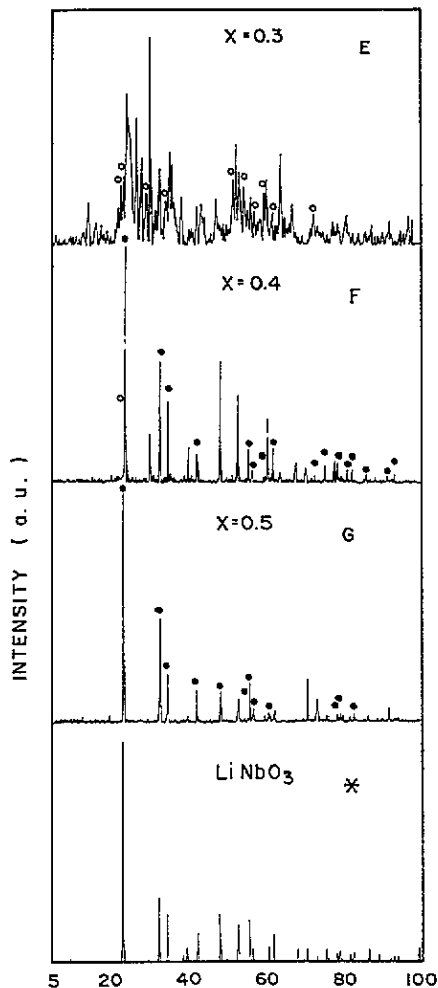
Figure 3. The infrared spectra of the glass ceramics E, F and G (see table 1).

reported in the literature [13], where  $\text{NbO}_6$  octahedra exhibit absorption bands around 700 and  $610/620 \text{ cm}^{-1}$ . In our glass a broad band around  $600 \text{ cm}^{-1}$  is clear in spectrum D, figure 2.

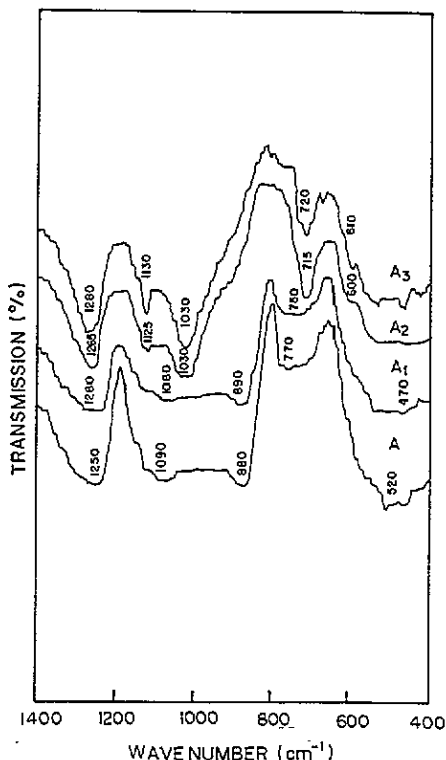
Figure 3 shows the infrared spectra of the samples E, F, G which are glasses with the presence of a crystalline phase. In this situation, the IR spectra is strongly modified. In spectra E and F, where we have the presence of  $\text{P}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$ , there are three major absorptions around  $1030 \text{ cm}^{-1}$ ,  $1090 \text{ cm}^{-1}$  and  $600 \text{ cm}^{-1}$ . The last one is probably associated with the formation of  $\text{NbO}_6$  octahedra. The absorptions around  $1030 \text{ cm}^{-1}$  and  $1090 \text{ cm}^{-1}$  are associated with the  $\nu_3$  antisymmetric stretching vibration of the  $\text{PO}_4$  tetrahedra. Results reported in the literature show that in the  $\text{Li}_3\text{PO}_4$  crystal this absorption ( $\nu_3$ ) is represented by two bands of unequal intensity around  $1093 \text{ cm}^{-1}$  and  $1038 \text{ cm}^{-1}$  and  $\nu_4$  is around  $600 \text{ cm}^{-1}$  [14]. This doubling of  $\nu_3$  may be due to some deformation of the  $\text{PO}_4$  tetrahedron, or to vibrational coupling between anions in the same unit cell, or both.

The existence of these absorptions in our glass ceramic is an indication of the existence of the crystalline phase  $\text{Li}_3\text{PO}_4$ . Figure 4 shows the x-ray powder diffraction of the samples E, F and G. The crystallization of  $\text{Li}_3\text{PO}_4$  is quite clear in sample E and decreases with the increase of LBN crystallization.

In spectrum G, figure 3, where we do not have  $\text{P}_2\text{O}_5$ , absorptions associated with the  $\text{PO}_4$  tetrahedra disappear completely. The absorptions around  $700 \text{ cm}^{-1}$  and  $610 \text{ cm}^{-1}$  in spectra G are in good agreement with the IR spectra of the glass ceramics of  $\text{LiNbO}_3$  (LBN)



**Figure 4.** The x-ray powder diffraction patterns at room temperature for the glasses (table 1) (E)  $x = 0.3$ , (F)  $x = 0.4$ , (G)  $x = 0.5$ , (\*) crystalline LiNbO<sub>3</sub>, (●) LiNbO<sub>3</sub>, (○) Li<sub>3</sub>PO<sub>4</sub>.



**Figure 5.** The infrared spectra of glass A, and samples A1, A2 and A3 which are glass A which has been heat treated (in air) at 300 °C for 2 h, 4 h and 9 h respectively.

reported in the literature [13]. These reported results show that both glassy and crystalline LiNbO<sub>3</sub> exhibit only two absorption bands at 700 and 610/620 cm<sup>-1</sup> [13]. These bands have been assigned to the  $\nu_3$  mode in the corner-shared NbO<sub>6</sub> octahedron [13]. All this behaviour is confirmed by x-ray diffraction. In figure 4 one can see that the crystallization of LBN is taking over the crystallization process. In spectrum E of figure 4 one can identify the presence of Li<sub>3</sub>PO<sub>4</sub>. If one increases the niobium concentration to  $x = 0.4$  the LBN crystalline phase increases. In spectrum G of figure 4 the lithium niobate is easily identified if one compares with figure 4(\*) which is the x-ray powder diffraction pattern from a crystalline LBN reference sample. To have a confirmation of the nature of the absorptions  $\nu_3$  (1030/1090 cm<sup>-1</sup>) and  $\nu_4$  (600 cm<sup>-1</sup>) associated to the PO<sub>4</sub> tetrahedra, we start from glass A (0.5Li<sub>2</sub>O–0.5P<sub>2</sub>O<sub>5</sub>), non-heat treated with a subsequent treatment to

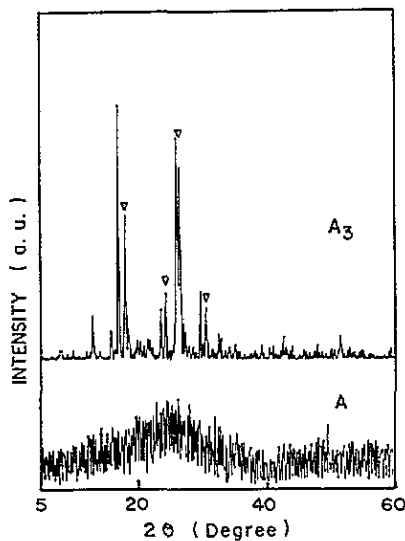


Figure 6. The x-ray powder diffraction patterns at room temperature for the glasses (see table 1) (A) without heat treatment and (A3) heat treated in air at 300 °C for 9 h (▽  $\text{LiPO}_3$ ).

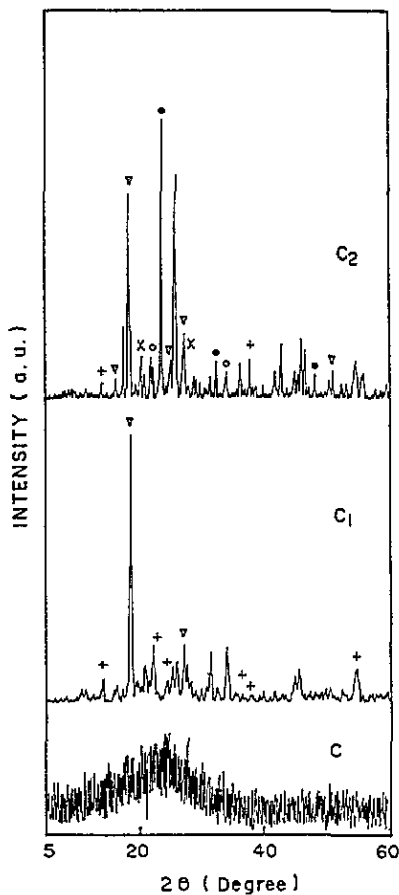


Figure 7. The x-ray powder diffraction patterns at room temperature for the glasses (see table 1) (C) without heat treatment, (C1) heat treated in air at 500 °C for 1 h and (C2) heat treated in air at 700 °C for 1 h (●  $\text{LiNbO}_3$ ; ○  $\text{Li}_3\text{PO}_4$ ; ▽  $\text{LiPO}_3$ ; ×  $\text{Li}_4\text{P}_2\text{O}_7$ ; +  $\text{Fe}_2\text{O}_3$ ).

produce crystallization. Figure 5 shows IR spectra of glass A (spectrum A, figure 5) and heat-treated glasses for different preset periods of time to obtain a glass ceramic. Spectra A1, A2 and A3 are obtained from sample A, heat treated at 300 °C in air, for 2 h, 4 h and 9 h, respectively. In spectrum A of figure 5 one can see the basic absorptions of the phosphate glass. In the process of crystallization the absorptions change only in shape and intensity. However, new absorptions appear around 1030  $\text{cm}^{-1}$  and 600  $\text{cm}^{-1}$  (see spectrum A3, figure 5). This is a clear indication that during the heat treatment there is a crystallization of the glass, with the phosphorus in a tetrahedral geometry  $\text{PO}_4$ .

Figure 6 shows the x-ray powder diffraction of samples A and A3 (the same samples as figure 5) where for sample A3 one can identify the  $\text{LiPO}_3$ , which consists of long chains or rings of  $\text{PO}_4$  tetrahedra sharing corners. According to the theory of disordered rearrangement, the average length of a  $(\text{PO}_3)_n$  chain should decrease with the increase of the degree of overheating of the metaphosphate melts, and consequently one can expect the appearance in the melt of anionic complexes of  $\text{PO}_4^{3-}$  and  $\text{P}_2\text{O}_7^{4-}$  that could lead to

the formation of Li<sub>3</sub>PO<sub>4</sub> and Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. For the orthophosphate Li<sub>3</sub>PO<sub>4</sub> the basic element is a tetrahedron of PO<sub>4</sub><sup>3-</sup>, and for the pyrophosphate Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub> one has two tetrahedra joined together. The fusion temperatures for LiPO<sub>3</sub>, Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and Li<sub>3</sub>PO<sub>4</sub> are 700 °C, 915 °C and 1250 °C respectively [15].

In order to understand the crystallization process in the niobophosphate glass we start a heat treatment in the niobium doped samples. In figure 7 one has the x-ray diffraction of the sample C ( $x = 0.1$ ) and samples C1 and C2, which are sample C which has had heat treatment in air for 1 h at 500 °C and 700 °C respectively. In sample C1 only the metaphosphate LiPO<sub>3</sub> is present. With heat treatment at higher temperature, the (LiPO<sub>3</sub>)<sub>x</sub> chains are broken down, leading to the formation of units of Li<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and Li<sub>3</sub>PO<sub>4</sub>, as expected. In sample C2 one can identify LBN and LiPO<sub>3</sub> with the formation of certain amount of pyrophosphate and orthophosphate as expected. A little of Fe<sub>2</sub>O<sub>3</sub> was also detected. Figure 8 shows the IR spectra of the same samples. For sample C2 the absorptions at 1030, 1149, 950, 900 and 700 cm<sup>-1</sup> are associated with the PO<sub>4</sub> tetrahedra [16]. The modes of NbO<sub>6</sub> are not so clear for these spectra.

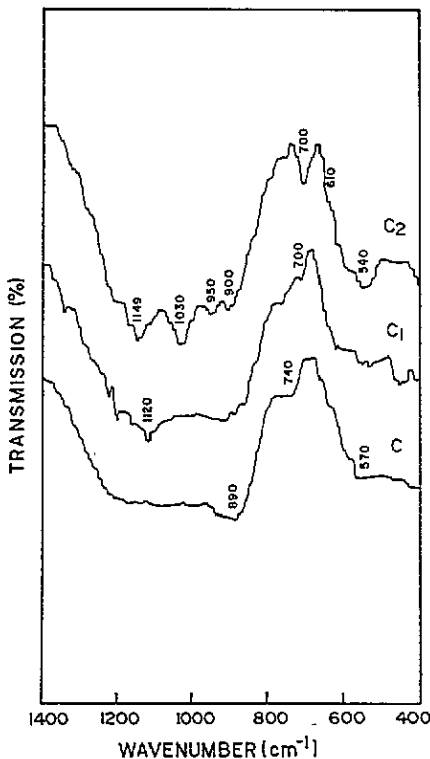


Figure 8. The infrared spectra of glass C and samples C1 and C2 which are glass C heat treated (in air) for 1 h at 500 °C and 700 °C respectively.

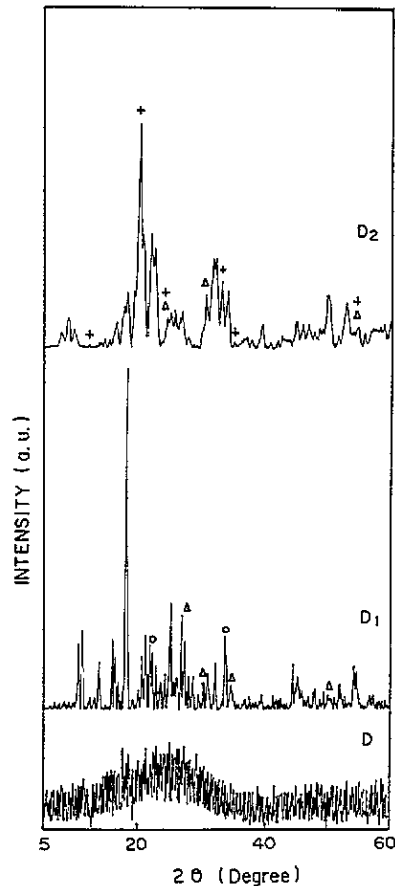


Figure 9. The x-ray powder diffraction patterns at room temperature for the glasses (see table 1) (D) without heat treatment, (D1) heat treated in air at 500 °C for 1 h and (D2) heat treated in air at 700 °C for 1 h (○ Li<sub>3</sub>PO<sub>4</sub>; Δ FeNbO<sub>4</sub>; + Fe<sub>2</sub>O<sub>3</sub>).



For the last glass of our set (glass D,  $x = 0.2$ ) the formation of LBN was not observed. In figure 9 one has sample D and samples D1 and D2 which are sample D which has had heat treatment for 1 h at 500 °C and 700 °C respectively. For this sample, the iron (in spite of the low concentration) is more effective in the crystallization process. Structures of  $\text{Fe}_2\text{O}_3$  and  $\text{FeNbO}_4$  were detected.

The next step of the experimental work is to prepare transparent niobophosphate glass ceramic composed essentially of ferroelectric  $\text{LiNbO}_3$  crystals by means of controlled heat treatment of the niobate glass for optical applications.

#### 4. Conclusion

Lithium niobophosphate glasses of the family  $[(x\text{Nb}_2\text{O}_5 \cdot (0.5 - x)\text{P}_2\text{O}_5) \cdot 0.5\text{Li}_2\text{O}] : y\text{Fe}_2\text{O}_3$  were studied using infrared and x-ray powder diffraction. The precipitation behaviour of ferroelectric  $\text{LiNbO}_3$  crystals was confirmed by x-ray powder diffraction. The crystallization processes of phosphorus–oxygen groupings of different degrees of complexity, such as  $\text{LiPO}_3$ ,  $\text{Li}_4\text{P}_2\text{O}_7$  and  $\text{Li}_3\text{PO}_4$ , were observed.

The IR results suggest that the increase of the ratio  $\text{Nb}_2\text{O}_5/\text{P}_2\text{O}_5$  leads the niobium to sites of octahedral symmetry and consequently to the formation of ferroelectric  $\text{LiNbO}_3$ , as seen by x-ray diffraction analysis. The study of the niobophosphate glass containing ferroelectric crystals is very important in view of recent optoelectronic and nonlinear optical device applications.

#### Acknowledgments

This work was partly sponsored by FINEP, CNPq (Brazilian agencies). We gratefully acknowledge the Centro de Tecnologia da UNIFOR (Universidade de Fortaleza) for the use of their laboratories for sample preparation.

#### References

- [1] Vogel E M 1989 *J. Am. Ceram. Soc.* **72** 719  
Vogel E M, Kosinski S G, Krol D M, Jackel J L, Friberg S R, Oliver M and Powers J D 1989 *J. Non-Cryst. Solids* **107** 244
- [2] Sombra A S B 1993 *Solid State Commun.* **88** 305; 1990 *Opt. Quantum Electron.* **22** 335; 1994 *Braz. J. Phys.* **24** 480
- [3] Samuneva B, Kvalchev St and Dimitrov V 1991 *J. Non-Cryst. Solids* **129** 54
- [4] Rachkovskaya G E and Bubkova N M 1987 *J. Non-Cryst. Solids* **90** 617  
Jazouli A E, Broche R, Viala J C, Olazcuaga R, Delmas C and de Flem G 1982 *Ann. Chim. Fr.* **7** 285
- [5] Fukumi K and Sakka S 1988 *J. Mater. Sci.* **23** 2819
- [6] de Oliveira C J et al 1993 *J. Mater. Sci.* **28** 4305
- [7] Komatsu T et al 1991 *J. Non-Cryst. Solids* **135** 105
- [8] Abouelleil M M and Leonberger F J 1989 *J. Am. Ceram. Soc.* **72** 1311
- [9] Choudari B V R et al 1991 *J. Non-Cryst. Solids* **128** 18
- [10] Muller K P 1969 *Glastechn. Ber.* **42** 83
- [11] Mogus Milankovic A and Day D E 1993 *J. Non-Cryst. Solids* **162** 275
- [12] Corbridge D E and Lowe E J 1954 *J. Chem. Soc. Part I* 493
- [13] Tatsumisago M, Hamada A, Minami T and Tanaka M 1983 *J. Non-Cryst. Solids* **56** 423
- [14] Tarte P 1967 *J. Inorg. Nucl. Chem.* **29** 915
- [15] Bamishev A F, Voronko Yu K, Osiko V V and Sobol A A 1984 *Sov. Phys.-Dokl.* **29** 50
- [16] Nyquistand R A and Kagel R O 1971 *Infrared Spectra of Inorganic Compounds* (New York: Academic)