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1998 J. Phys.: Condens. Matter 10 5475

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# Gas nucleation in a boron oxyfluoride glass by $^{11}\text{B}$ and $^{19}\text{F}$ NMR

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Received 16 December 1997, in final form 30 March 1998

**Abstract.** Nuclear magnetic resonance (NMR) of  $^{11}\text{B}$  and  $^{19}\text{F}$  is used in this study to monitor the structural evolution with temperature of the inorganic polymeric glass  $\text{BO}_{1.3}\text{F}_{0.4}$  whose vitreous transition temperature, determined by differential scanning calorimetry, is  $T_g = 333$  K. A local motion, essentially around the fluorine atoms, particularly on one kind of the fluorine atoms, is observed below  $T_g$ .

Above  $T_g$  this glass decomposes into a two-phase material—glass + gas; the origin of the formation of the gas is explained and the proportion gas/solid is followed when the temperature is varied.

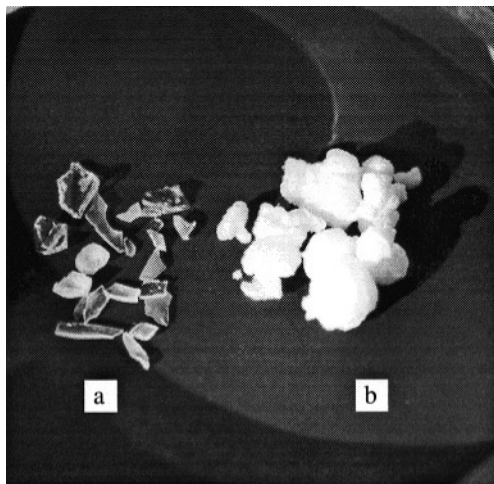
## 1. Introduction

In several previous papers [1–3] we have demonstrated the existence of a new family of glasses belonging to the boron–oxygen–fluorine system. These materials prepared in sealed silica tubes by reaction of  $\text{BF}_3$  on  $\text{B}_2\text{O}_3$  are called BOF glasses, but their real formula is  $\text{BO}_{(1.5-0.5x)}\text{F}_x$  with  $0 < x < 1$ . The composition of the vitreous transparent material is very dependent on the temperature  $T_d$  of the cold surface where the glasses are deposited by condensation of a vapour phase. For instance, the richest composition  $\text{BO}_{1.2}\text{F}_{0.6}$  is obtained for  $T_d = 260$  K. A temperature  $T_d = 223$  K would be necessary in order to condense the composition BOF.

Consequently, the main characteristic of these glasses is their low  $T_g$  ranging from the estimated value  $T_g = 233$  K for BOF ( $x = 1$ ) to  $T_g = 563$  K for  $\text{B}_2\text{O}_3$  ( $x = 0$ ). The low  $T_g$  is obviously related to the low dimensionality of the structures. The model which satisfies the results of ionic dynamics computer simulation (IDCS) and  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR corresponds to a cross linked chain lattice in which the ideal BOF ( $x = 1$ ) corresponds to 1D infinite chains of  $\text{BO}_{2/2}\text{F}$  interconnected triangles. The well known  $\text{B}_2\text{O}_3$  glass will correspond to  $x = 0$ , and in this case all the  $\text{BO}_3$  triangles are connected to form a 2D aperiodic lattice.

Another very important feature of these vitreous materials is illustrated by their foaming behaviour above  $T_g$ . It was suggested that these phase separation phenomena are due to  $\text{BF}_3$  isolated molecules which are formed into the viscous glass above  $T_g$  and which are trapped as bubbles in the vitreous matrix [2]. The result is the formation of a popcorn type glass as represented in figure 1. The glass below  $T_g$  is a transparent vitreous material but above

$T_g$ , its volume starts to grow spectacularly to form the white foaming glass containing  $\text{BF}_3$  bubbles portrayed on the right of figure 1.



**Figure 1.** Views of the  $\text{BO}_{1.3}\text{F}_{0.4}$  glass: (a) below  $T_g$ ; (b) after the transformations occurring when heated above  $T_g$ .

**Table 1.** Proportions and chemical shifts of the different fluorine atoms determined from a  $^{19}\text{F}$  MAS experiment (reference 0 ppm =  $\text{C}_6\text{F}_6$  and 1 ppm = 282 Hz).

	Schematic representation	$^{19}\text{F}$ proportion (%) ( $\pm 2$ ) R.T.	Position (ppm) ( $\pm 0.5$ )	
			R.T.	$T > T_g$
F1		68	48.0	49.5
F2		18	55.0	57.5
F3		2.5	24.2	24.2
F4		11.5	42.2	48

● Boron. ○ Fluorine. ● Oxygen.

A third characteristic of these materials, that is a general behaviour of boron compounds, is the tendency of the boron atom coordination to change from triangle  $\text{sp}^2$  to tetrahedron  $\text{sp}^3$  leading to very different  $^{11}\text{B}$  NMR spectra: in the first case the NMR line corresponding to the  $1/2 \rightarrow -1/2$  transition is broad and asymmetric and in the second case it becomes narrow and symmetrical.

In a previous structural investigation [3], we have identified that the fluorine atom in the structure was mainly situated in two configurations: the middle-chain F and the terminal F acting in pairs as chain termination extremities. Table 1 gives  $^{19}\text{F}$  NMR lines corresponding to four kinds of fluorine atom located in different environments. The difference in proportions, between these results and the ones given in [3], lies in the synthesis: the deposition temperature  $T_d$  is slightly changed because of a small difference in the length of a tube where the new formed glass deposits. The vitreous transition temperature  $T_g$  in the sample under investigation is 333 K.

The first objective of this paper is to investigate the dynamic phenomena which result, with increasing temperature, in the formation of  $\text{BF}_3$  molecules. The formation of  $\text{BF}_3$  molecules in the glassy matrix needs fluorine clustering in order to associate locally three F and one B atoms. As already shown, the only way to do this is to cross link the chains following two mechanisms.

The second objective of this contribution is to evaluate by  $^{19}\text{F}$  NMR the importance of the glass to gas phase separation in measuring the proportion of the  $\text{BF}_3$  molecules formed and trapped inside the glass. Indeed we are faced here with a very special and unique situation where a two phase material—gas ( $\text{BF}_3$ ) + glass( $\text{B}(\text{OF})$ )—contains in each phase the same atoms B and F which can be checked and measured by NMR.

## 2. Experimental procedure

The details of the sample preparation have been described in [2] and [3]. Variable temperature NMR spectra were obtained with a AM 300 Bruker spectrometer for static  $^{11}\text{B}$  experiments and with an MSL 300 Bruker spectrometer for static  $^{19}\text{F}$  and  $^{11}\text{B}$  and  $^{19}\text{F}$  magic angle spinning (MAS) experiments (emission frequencies 282 MHz and 96 MHz for  $^{19}\text{F}$  and  $^{11}\text{B}$  respectively). The temperatures were equilibrated by heating a dry air flow. For MAS experiments, the stabilization of the temperature is directly achieved by heating the bearing air.

## 3. Results and discussion

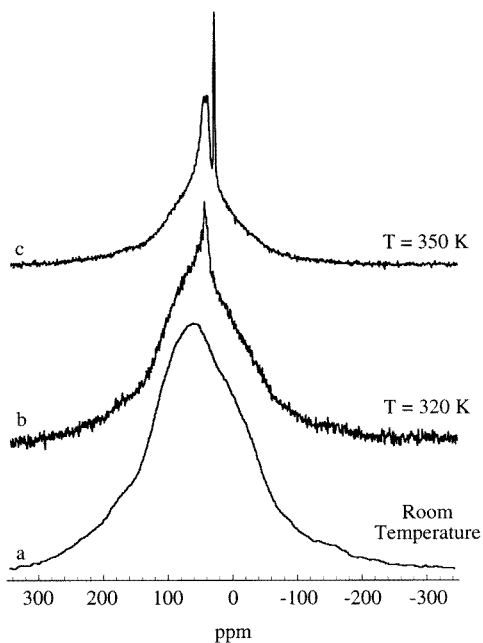
The material used in the present paper corresponds fairly well to the same chemical composition as that we previously studied at room temperature in [3] by  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR. It is the ' $\text{BO}_{1.3}\text{F}_{0.4}$  glass' deposited at room temperature (293 K) and whose vitreous transition temperature  $T_g$  occurs at 333 K. The temperature of the NMR experiments was then varied from 293 K to 373 K to cover the range spreading below and above  $T_g$ .

Figure 2 shows three static  $^{19}\text{F}$  spectra. Spectra 2(a) and 2(b) are the NMR response of the fluorine atoms below  $T_g$  and spectrum 2(c) corresponds to  $T > T_g$ . A progressive modification of the shape and of the number of individual lines can be noted on these three spectra.

In figure 3, three  $^{19}\text{F}$  MAS spectra can be observed at the same temperatures as in figure 2.

Figure 4 gives NMR spectra of the quadrupolar  $^{11}\text{B}$  (spin  $S = 3/2$ ) nucleus for a static sample. The lines correspond to the central transition between the  $m_s = 1/2$  and  $m_s = -1/2$  levels with selective irradiation. Two narrow lines referenced A and B, appear in the same temperature range in which the static  $^{19}\text{F}$  NMR linewidth is strongly affected.

For reasons of clarity, we only present two spectra above room temperature for the fluorine and for the boron. Nevertheless, we have recorded twelve spectra between 300 K



**Figure 2.**  $^{19}\text{F}$  static NMR spectra of the  $\text{BO}_{1.3}\text{F}_{0.4}$  glass at various temperatures (reference  $\text{C}_6\text{F}_6$ ).

and 370 K and we would like to emphasize three points.

(1) A narrow line (line A) comes out at  $T = 320 \text{ K} < T_g$  on  $^{11}\text{B}$  spectra and  $^{19}\text{F}$  spectra simultaneously.

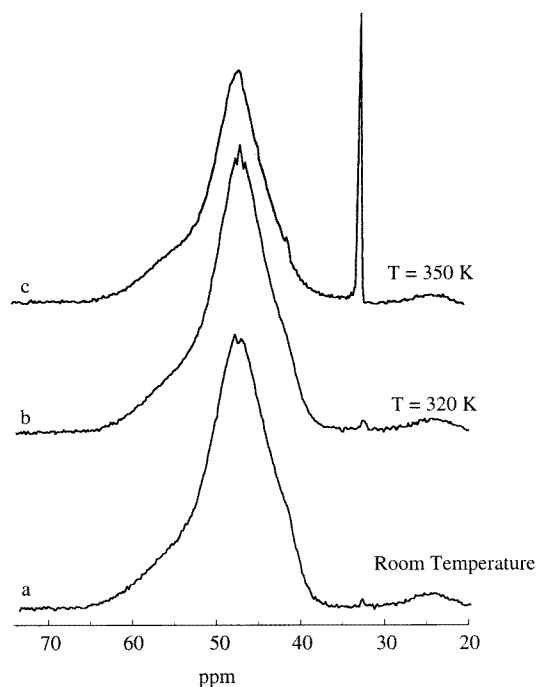
(2) A second still narrower line appears on  $^{11}\text{B}$  (line B) and  $^{19}\text{F}$  spectra as soon as  $T_g$  is reached and grows with increasing temperature.

(3) Another point to be emphasized is illustrated in figures 5(a) and 5(b): only the narrowest line appearing at  $T_g$  remains after the cooling down of the glassy sample to room temperature.

Figure 6 shows the variation of the half-height static width of the fluorine spectra between 293 and 373 K. A decrease of about 20 kHz occurs in that range of temperature on the global half-height line width accompanied by a progressive modification of its shape that becomes more and more Lorentzian as the temperature is increased.

Simultaneously with the change in the shape and the width of the static  $^{19}\text{F}$  spectra, the MAS  $^{19}\text{F}$  spectra reveal that the resonance frequencies of the different lines are progressively modified except for F3 atoms. Table 1 allows us to compare the frequency values at room temperature and above  $T_g = 333 \text{ K}$ . In contrast, except the rising of line A, the broad static  $^{11}\text{B}$  NMR spectra remain constant as the temperature is varied.

Before discussing these results let us recall the interactions to which the nuclei are sensitive. The  $^{19}\text{F}$  nucleus being a one half spin nucleus, it is sensitive to the chemical shift and the dipolar interactions between F-F and F-B.  $^{11}\text{B}$ , with  $S = 3/2$  spin value is named a quadrupolar nucleus; the most important interactions come from the quadrupolar one, from the dipolar one between two boron atoms and from the dipolar one between  $^{11}\text{B}$  and  $^{19}\text{F}$ . Moreover, the transition  $-1/2 \leftrightarrow I = +1/2$  is only sensitive to the second order



**Figure 3.** Three variable temperature  $^{19}\text{F}$  MAS spectra obtained with a spinning rate equal to 14.5 kHz (reference  $\text{C}_6\text{F}_6$ ).

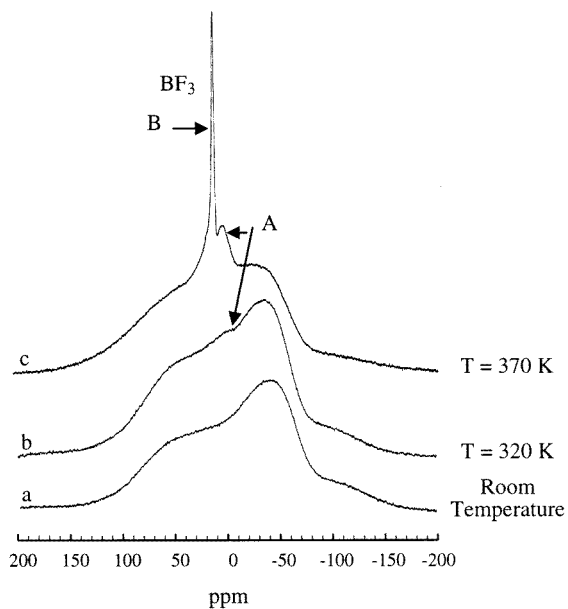
quadrupolar Hamiltonian part.

The progressive narrowing of the static line and the change into Lorentzian lineshape are in agreement with a motion of all the fluorine atoms which reduce the dipolar F–F and B–F interactions. Especially the position of the so-called F4 atoms is shifted by nearly 6 ppm toward the F1 position.

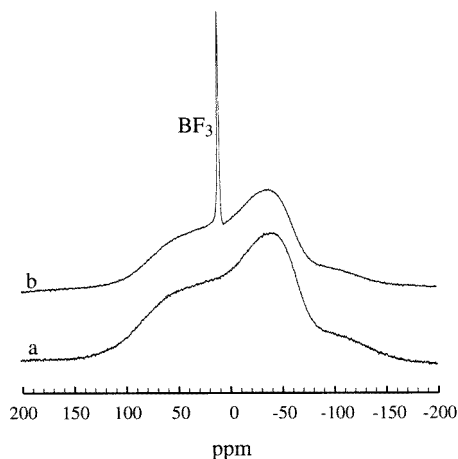
But in contrast to fluorine, the  $^{11}\text{B}$  broad static lines are only very weakly affected by increasing temperature. In spectra 4(b) and 4(c) the most intense component corresponding to the  $^{11}\text{B}$  in  $\text{BO}_3$  units is not at all modified. Nevertheless, the broad shoulder related to  $^{11}\text{B}$  in the  $\text{BO}_2\text{F}$  units at  $-110$  ppm is slightly attenuated due to the reduction of the  $^{11}\text{B}$ – $^{19}\text{F}$  dipolar interaction by the motion. This last result shows that the largest part of the boron atoms builds the rigid skeleton of the vitreous material made of linear chains of boron atoms [3].

It seems natural for the fluorine atoms that are essentially non-bridging to be more affected by the motion than the boron atoms. If the fluorine atoms are principally the mobile atoms, the dipolar interactions B–F and F–F will be averaged by the motion and the linewidths of dipolar origin will be reduced in  $^{11}\text{B}$  and  $^{19}\text{F}$  spectra. Concerning the quadrupolar interactions, as the boron is rigid, only that part of the electric field gradient due to fluorine will be partly averaged at the site of the boron and large second order quadrupolar effects will not be affected.

In figure 2, the  $^{19}\text{F}$  line emerging at 320 K corresponds to a more mobile species than the others that stay rigid at that temperature. In a similar way, the only kind of boron line that can be reduced by the motion of a fluorine atom are those whose central line is not broadened by the second order quadrupolar effect but only governed by weaker interactions



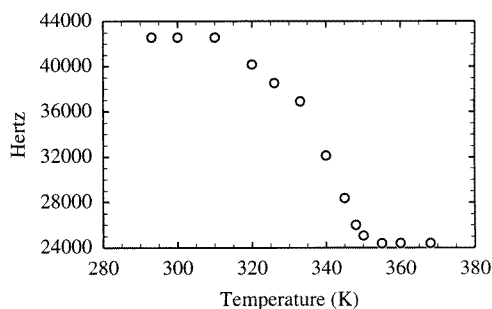
**Figure 4.**  $^{11}\text{B}$  static NMR spectra of the  $\text{BO}_{1.3}\text{F}_{0.4}$  glass at various temperatures (reference 0 ppm  $\text{Et}_2\text{OBF}_3$ ).



**Figure 5.** Room temperature  $^{11}\text{B}$  static NMR spectra before (a) and after (b) heating the sample to  $T = 370\text{ K}$  (reference 0 ppm  $\text{Et}_2\text{OBF}_3$ ).

such as the dipolar interaction or the chemical shift anisotropy.

In the case of the glassy compound  $\text{BO}_{1.3}\text{F}_{0.4}$ , one boron corresponds to this situation: it is the one that builds the tetrahedral  $\text{BO}_2\text{F}_2$  units, located in a more symmetrical site, at the centre of the tetrahedron made with two oxygen atoms and two fluorine atoms and therefore with a weak second order quadrupolar effect. The two first dipolar shoulders of that four-coordinated boron predicted by the IDCs, have also been observed at room temperature at  $\pm 18\text{ kHz}$  [4] on the room temperature static spectra [3]; the effect of the



**Figure 6.** Static  $^{19}\text{F}$  NMR linewidth variation with temperature for  $\text{BO}_{1.3}\text{F}_{0.4}$ .

motion by sufficiently reducing the linewidth, makes its amplitude large enough to let the central line emerge around 0 ppm, above the much broader and intense components due to  $\text{BO}_3$  and  $\text{BO}_2\text{F}$ : see figures 4(b) and 4(c).

The corresponding, narrow  $^{19}\text{F}$  line appears at about 43 ppm at 320 K, exactly at the position of the fluorine atoms called F4 whose existence was evidenced from MAS spectra at room temperature. As the three other kinds of fluorine atom were attributed to three-coordinated borons, the F4 fluorines were supposed to associate with the more symmetrical four-coordinated borons.

We confirm here by the results at 320 K that the  $^{19}\text{F}$  line appearing at 43 ppm is that of the F4 fluorine and that it belongs to the  $\text{BO}_2\text{F}_2$  unit. This strong mobility can be explained by the fact that to build  $\text{BO}_2\text{F}_2$ , two linear chains are needed and the F4 atoms are very probably those atoms around which the chains are rotating and tangling.

Figures 2(c) and 4(c) evidence the existence of a second new species (line B) containing boron and fluorine. It suddenly appears at  $T_g$ , it continues to grow when  $T$  increases and it is still observable after cooling to room temperature when the first narrow line (line A) is no longer visible below 320 K as shown in figure 5. The  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR lines of that species are particularly narrow over the whole studied range of temperature. This fact associated with a drastic change of the material, becoming white and foaming—see figure 1—leads to the idea of the formation of a gas that remains trapped in the material. The positions of these lines: 33 ppm for  $^{19}\text{F}$  (0 ppm for  $\text{C}_6\text{F}_6$ ) and 12 ppm for  $^{11}\text{B}$  (0 ppm for  $\text{Et}_2\text{OBF}_3$ ) correspond to the resonance position of the respective nuclei in the  $\text{BF}_3$  molecule, and allow us to conclude to the presence of the  $\text{BF}_3$  in material above  $T_g$ .

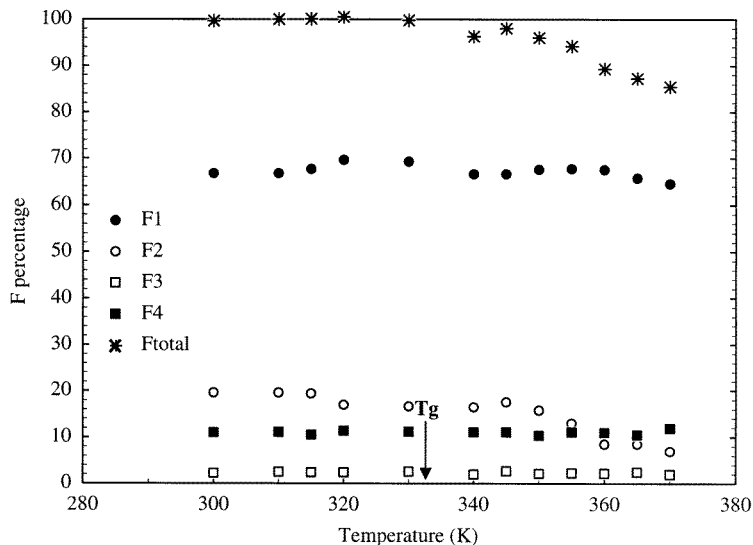
We already knew the behaviour of that family of materials in releasing  $\text{BF}_3$  when degradation occurs;  $^{11}\text{B}$  and  $^{19}\text{F}$  NMR investigations prove that the phenomenon takes place when  $T_g$  is reached and is irreversible.

At this stage of the discussion we can say that

- the line appearing at 320 K in static spectra corresponds to a fluorine and a boron that build the  $\text{BO}_2\text{F}_2$  unit,
- another informative line appearing at  $T > T_g$ , in each NMR spectrum corresponds to a fluorine and a boron that build the  $\text{BF}_3$  gas molecule and
- the line corresponding to  $\text{BO}_2\text{F}_2$  exists before  $T_g$  has been reached, but in contrast  $\text{BF}_3$  gas does not exist as long as the material has not been heated above  $T_g$ ; it is created at  $T_g$  and leads to an irreversible modification of the material.

Figure 7 shows the variation with the temperature of the concentration of the four kinds of fluorine atom F1, F2, F3 and F4 previously defined at room temperature, presented in



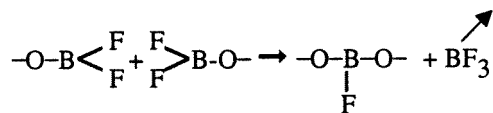


**Figure 7.** Variation with the temperature of the proportions of the four different fluorine atoms: F1, F2, F3, F4. Note the sum  $F1 + F2 + F3 + F4$  is constant below  $T_g$ , but decreases for  $T > T_g$ .

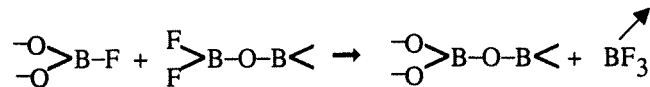
table 1. These qualitative results have been obtained from 12 variable temperature  $^{19}\text{F}$  MAS spectra (figure 3) in which the anisotropic dipolar and chemical shift interactions are strongly reduced by rotating the sample at 14.5 kHz.

At each investigated temperature the proportion of the four basic F1, F2, F3 and F4 atoms was calculated with a precision of about 2%. Figure 7 clearly exhibits constant proportions for F1, F3 and F4 in the temperature range, and a decrease of the F2 proportion from about 18% at room temperature to about 7% at 370 K. From these results, we can conclude that only one kind of fluorine atom, the F2 species, contributes to the formation of the  $\text{BF}_3$  gas. We recall the F2 atoms have been attributed to the very broad MAS line corresponding to a high level of structural disorder.

When three or four fluorine atoms are near neighbours as is the case for the F2 atoms, the motion related to the increasing temperature previously described may favour the destruction of the B–F and B–O bonds and the appearance of  $\text{BF}_3$  molecular isolated species. Two ways are possible:



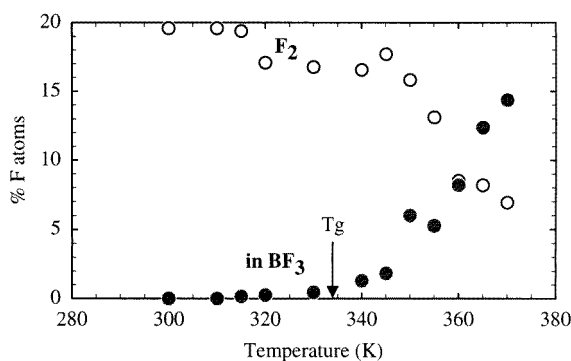
**Scheme 1.**



**Scheme 2.**

This process is not reversible. One part of the  $\text{BO}_{1.3}\text{F}_{0.4}$  glass is then progressively destroyed and tends to the more stable  $\text{B}_2\text{O}_3$  composition that would be reached if all the fluorine atoms were able to leave the glass. An important part of the  $\text{BF}_3$  gas molecules is trapped in the material, giving to this its particular foaming aspect.

For the NMR experiments we used a rotor carefully filled and closed to obtain a good rotation, so that no  $\text{BF}_3$  gas could escape from the NMR coil and the change in the proportion of fluorine atoms belonging to the  $\text{BF}_3$  gas could be followed. Figure 8 shows this evolution together with that of the F2-type atom quantity. As expected no modification occurs below  $T_g$ . For  $T > T_g$  the F2-type atoms progressively transform into fluorine atoms building the  $\text{BF}_3$  gas molecules.



**Figure 8.** Evolution with temperature of the percentage of F2 fluorine atoms and of the proportion of fluorine atoms belonging to  $\text{BF}_3$  gas.

The other fluorine atoms are also affected by the thermal motion but, the presence of at least three fluorine atoms being necessary in a very near neighbourhood to create  $\text{BF}_3$ , these remain bound to the boron atom skeleton of the linear chains:  $\text{O-B-O-B-O-B-}$ . Particularly the F4-type atoms of the  $\text{BO}_2\text{F}_2$  units produce modified NMR spectra with temperature only because of the motion and do not participate in making  $\text{BF}_3$  gas.

#### 4. Conclusion

The modification of the NMR spectra with temperature variations in the family of glassy compounds  $\text{BO}_{1.4-0.5x}\text{F}_x$  is explained in terms of motion in the whole study range and of a structural modification for  $T > T_g$ , giving rise to a two phase system: solid + gas.

With this variable temperature dynamical study, the attributions of the different kinds of fluorine and boron atom, established at room temperature from structural considerations alone, are entirely confirmed.

Finally the chemical phenomena occurring above the vitreous transition are fully described: only one kind of fluorine atom, the F2 atoms, creates the  $\text{BF}_3$  gas.

#### References

- [1] Boussard-Pledel C, Fonteneau G and Lucas J 1995 *J. Non-Cryst. Solids* **188** 147
- [2] Boussard-Pledel C, Fonteneau G, Le Floch M and Lucas J 1997 *Mater. Res. Bull.* **32** 805
- [3] Boussard-Pledel C, Le Floch M, Fonteneau G, Lucas J, Sihbandhit S, Shao J, Angell C A, Emery J and Buzare J 1997 *J. Non-Cryst. Solids* **209** 247
- [4] Jager C and Haubenreisser U 1985 *Phys. Chem. Glasses* **5** 152