

INFRARED SPECTRUM OF CRYSTALLINE AND GLASSY PYROPHOSPHATES : PRESERVATION OF THE PYROPHOSPHATE GROUP IN THE GLASSY STRUCTURE

M. GABELICA-ROBERT and P. TARTE

Chemistry Institute, University of Liège, B-4000 Sart-Tilman, LIEGE (Belgium)

ABSTRACT

Two families of pyrophosphates, namely $M^I M^{III} P_2 O_7$ and $M_2^I M^{II} P_2 O_7$ have been synthesized and investigated by IR spectroscopy, the emphasis being put on the antisymmetric and symmetric frequencies of the P-O-P bridge. These bands are still present in the spectra of the glasses obtained by rapid quenching of the corresponding melts. This strongly suggests that, contrarily to expectations, the pyrophosphate group is essentially conserved in the glassy structure. This interpretation is supported by the investigation of glassy phases whose composition extend from meta- to ortho-phosphate.

INTRODUCTION

The vibrational spectrum of the pyrophosphate group exhibits 2 bands, the so-called "bridge stretching frequencies", which are generally located in the 960-900 and 800-700 cm^{-1} regions, for the antisymmetric and symmetric stretching modes, respectively (ref. 1). The simultaneous occurrence of these bands may be considered as a good indication of the existence of pyrophosphate groups in an unknown structure and accordingly, we have applied this method to the search of pyrophosphate groups in glassy structures.

EXPERIMENTAL

Two families of pyrophosphates, namely $M_2^I M^{II} P_2 O_7$ ($M^I = Na$ or K ; $M^{II} = Mg, Co, Zn...$) and $M^I M^{III} P_2 O_7$ ($M^I = Li, Na...Cs, Ag, Tl$; $M^{III} = Ga, Fe$) were found to give glasses by melting at an appropriate temperature (between 800 and 1200°C, depending on the chemical composition), followed by rapid quenching. For the purpose of comparison, we have also synthesized 2 series of glasses of variable composition, namely $(NaFeP_2 O_7)_{(1-x)}(Na_4 P_2 O_7)_x$ in which the pyrophosphate composition is maintained throughout, and glasses whose composition is going progressively from an ortho- to a pyro- and then to a metaphosphate. The IR spectra were registered on a Beckman 4250 spectrophotometer by the conventional KBr disc technique. We have checked by X-ray diffractometry that the glasses were free from crystalline

inclusions.

RESULTS AND INTERPRETATION

Pyrophosphate glasses $M^I Fe^{III} P_2 O_7$

The IR spectra of crystalline and glassy $NaFeP_2 O_7$ are represented in Fig. 1.

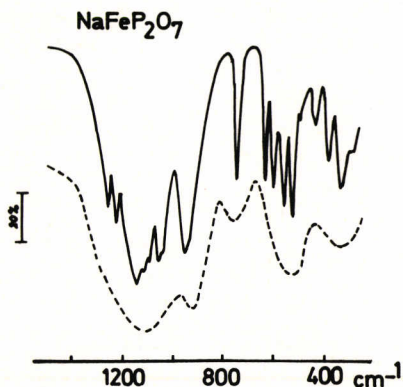


Fig. 1. IR spectrum of $NaFeP_2 O_7$, crystal (full line) and glass.

After its X-ray powder diagram, $NaFeP_2 O_7$ is monoclinic, but its structure is still unknown (ref. 2), and a detailed interpretation of the spectrum is impossible. Nevertheless, a comparison with the spectra of similar $NaM^{III} P_2 O_7$ pyrophosphates ($M^{III} = Al, Ga, Cr, In$) (ref. 3) leads to the following assignments :

1250-1000 cm^{-1} region : stretching vibrations of the terminal PO_3 groups

940 cm^{-1} : antisymmetric stretch of the P-O-P bridge

735 cm^{-1} : symmetric stretch of the bridge

650-450 cm^{-1} : bending vibrations of the terminal PO_3 groups

450-250 cm^{-1} : the absorption in this region is due, at least in part, to translational motions of the Fe cation.

Now, it is clear from Fig. 1, that the same absorption regions are present in the IR spectrum of glassy $NaFeP_2 O_7$, but we shall restrict the discussion to the most interesting point, namely the preservation of the 2 bands characteristic of the bridge stretching modes, which are now observed at about 922 and 755 cm^{-1} .

Similar results have been obtained with the whole series of $M^I FeP_2 O_7$ pyrophosphates : all of them, either crystalline or vitreous, exhibit the 2 bands characteristic of the bridge stretching modes. Thus, we have good reasons to believe that the pyrophosphate group has been preserved when going from the crystal to the corresponding glass.

Pyrophosphate glasses of varying composition $(NaFeP_2 O_7)_{(1-x)}(Na_4 P_2 O_7)_x$

The composition of these glasses is intermediate between $NaFeP_2 O_7$ and $Na_4 P_2 O_7$.

Their P/O ratio is that of a pyrophosphate, but they do not necessarily correspond to a definite compound. Their IR spectra are somewhat modified according to their chemical composition (Fig. 2), but the 2 bands characteristic of the P-O-P bridge are again observed in a narrow frequency range : $922-895\text{ cm}^{-1}$ and $755-740\text{ cm}^{-1}$ for the antisymmetric and symmetric modes, respectively.

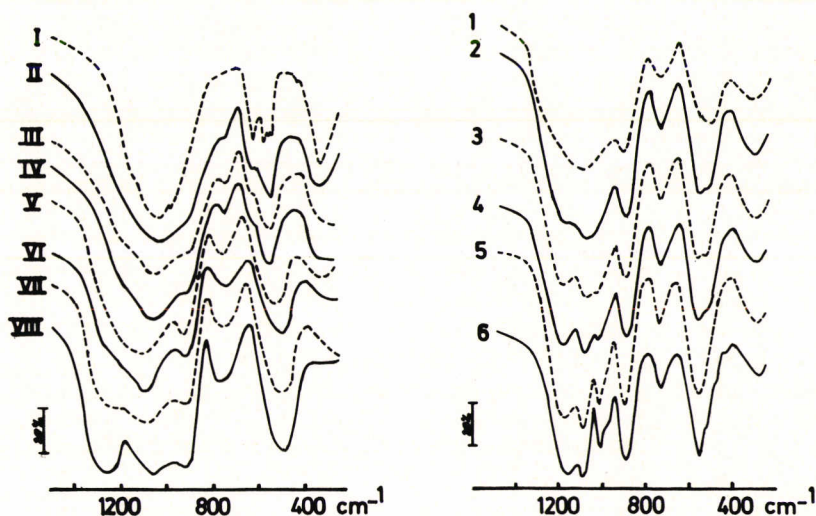


Fig. 2. (right). IR spectra of glasses in the $\text{NaFeP}_2\text{O}_7/\text{Na}_4\text{P}_2\text{O}_7$ series.

Molar compositions : 1, 1/0 ; 2, 4/1 ; 3, 2/1 ; 4, 1/1 ; 5, 2/3 ; 6, 2/5.

Fig. 3. (left). IR spectra of glasses in the ortho ($\text{Na}_3\text{Fe}_2\text{P}_3\text{O}_{12}$) - pyro (NaFeP_2O_7) - meta ($\text{NaFeP}_4\text{O}_{12}$) phosphate series. Molar compositions : I, oxy-ortho $\text{Na}_4\text{Fe}_2\text{P}_3\text{O}_{12.5}$; II-V, ortho/pyro with the following molar compositions : II, 1/0 ; III, 2/1 ; IV, 1/1 ; V, 0/1 ; VI-VIII : pyro/meta : VI, 2/1 ; VII, 1/1 ; VIII, 0/1.

Glasses of ortho- to meta-phosphate composition (Fig. 3)

A glass (containing a small quantity of a non-identified crystalline phase) of oxy-orthophosphate composition $\text{Na}_4\text{Fe}_2\text{P}_3\text{O}_{12.5}$ exhibits no bands in the 900 and 750 cm^{-1} regions. Such bands appear as weak shoulders in the spectrum of the glassy orthophosphate, and increase in intensity when going from the ortho- to the pyro-phosphate composition (spectra II-V of fig. 3). This evolution adds support to the statement that these bands are really due to the pyrophosphate group.

The spectral changes in the pyro- to meta-phosphate series are less clear-cut, because both pyro- and meta-phosphate compositions give bands in the 900 and 750 cm^{-1} regions ; but the metaphosphate glass is characterized by a strong absorption in the 1300 cm^{-1} region ; this absorption is typical of metaphosphate chains, and its lack in the spectrum of the pyrophosphate glass is a good indication that this latter does not contain important amounts of chain structures.

Glasses of the type $M_2^{I,III}P_2O_7$

These spectra will not be discussed and we shall just point out that, here again, the analogies between the spectra of the crystalline and glassy phases strongly suggest that the pyrophosphate group is essentially preserved in the glassy structure (ref. 4).

DISCUSSION

It is fair to consider that, in a glass corresponding to a pyrophosphate composition, the PO_4 tetrahedra are distributed into isolated PO_4 , P_2O_7 groups and $(PO_3)_n$ chains of variable length. The results presented in this paper strongly suggest that the pyrophosphate group is the predominant structural unit in these glasses.

This conclusion brings up the problem of the stability of such glasses : some of them are fairly stable, a property which is generally observed for chain or tridimensional structures. This condition may be fulfilled, at least in part, if some of the trivalent cations are located on tetrahedral sites in the glassy structure (against an octahedral coordination in the crystal). So far, we have no proof of this tetrahedral coordination ; but it is probably significant that $M^{I,III}P_2O_7$ glasses can be obtained only with trivalent cations which have a strong tendency to form tetrahedral groups, namely Ga and Fe ; no glass was obtained with In or Cr, whose tendency to form tetrahedral groups is small to negligible.

ACKNOWLEDGEMENTS

The authors greatly acknowledge the financial support given to their laboratory by the "Fonds National de la Recherche Scientifique" and by the "Fondation de Bay" (University of Liège).

REFERENCES

- 1 See for example : A.N. Lazarev, Vibrational Spectra and Structure of Silicates Consultant Bureau, N.Y. 1972
M. Gabelica-Robert, Doctorate Thesis, University of Liège, 1980.
- 2 J.P. Gamondès, F. d'Yvoire and A. Boullé, C.R. Acad. Sci. Paris, C 272 (1971) 49-52.
- 3 M. Gabelica-Robert and P. Tarte, to be published.
- 4 M. Gabelica-Robert, to be published.