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Résumé – L'environnement local du fer dans des phosphates de potassium vitreux a été étudié par spectrométrie d'absorption X. Aux faibles concentrations en Fe^{2+} (< 5 % du fer total) la coordinence du Fe^{3+} est octaédrique. Aux concentrations élevées en Fe^{2+} (> 90 %), ce dernier présente également un environnement octaédrique. Dans les cas intermédiaires, une importante proportion de Fe^{3+} en coordinence tétraédrique est mise en évidence.

Abstract - Local environment of iron in potassium-phosphate glasses has been studied by X-ray absorption spectroscopy. At small Fe^{2+} concentration (< 5 % of total Fe), octahedral coordination is established for Fe^{3+}. At high Fe^{2+} concentration (> 90 %), Fe^{2+} is also sixfold coordinated. In intermediate cases, large amount of Fe^{3+} in tetrahedral environment is evidenced.

I – INTRODUCTION

Iron in phosphate glasses systems has been generaly reported in octahedral coordination for both Fe^{2+} and Fe^{3+}. Very conclusive works on this subject were made by Mössbauer spectroscopy (for a review, see /1/). Some evidence for tetrahedral iron was found only for very low (< 2 mol.%) Fe_2O_3 contents by others analytical methods /2-4/.

Following the EXAFS study of mixed valence tungsten phosphate glasses /5/, in which a strong dependence of the distortion of the oxygen polyhedra around tungsten as a function of the P_2O_5 content has been shown, glasses have been synthesized in the system K_2O-P_2O_5-Fe_2O_3 under reducing conditions /6/ with up to 38 mol.% of Fe_2O_3 ; they are characterized by variable concentrations of Fe^{2+}/Fe^{3+}. The aim of this work is to precise the local environment of iron in these glasses by X-ray absorption spectroscopy.

II – EXPERIMENTAL

The synthesis of the glasses has been performed by direct melting of the starting materials K_2CO_3, $(NH_4)_2HPO_4$ and Fe_2O_3 in quartz crucibles between 1300 and 1600 K. The fast decomposition of the diammonide phosphate insured the formation of a reducing atmosphere above the melt leading a partial reduction of the Fe^{3+} ion. The melt is cooled down by pouring on a brass platelet following a method described previously /5/.

The EXAFS spectra were recorded at the iron K absorption edge (7,120 eV) in LURE with the synchroton radiation of D.C.I. A value of 8991 eV for the maximum intensity at the K edge of copper was used as reference.

The EXAFS modulations were extracted using a standard method /7/. The structural parameters (coordination numbers N_j, interatomic distances R_j and mean square displacements σ_j) were obtained by fitting the partial functions $f_j(k)$ associated with the coordination sphere of order j, estimated by an inverse Fourier transform of F(R) in the interval (R_{min}, R_{max}) deduced from the modulus of F(R), by the relation /8, 9/ :

$$f_j(k) = (k/R_j)^2 \, N_j So^2(k) \, T_j(k) \, e^{-2\sigma_j^2 k^2} \, e^{-2(R_j-\Delta)/\lambda(k)} \, \sin(2kR_j + \varphi_j(k))$$

where λ is the electron mean free path, So^2 the multielectronic factor, φ_j the total phase shift and T_j the backscattered amplitude calculated by Teo and Lee /10/. Δ is taken equal to R_1.

III - CRYSTALLINE REFERENCES

Compounds containing Fe^{3+} ions in octahedral and tetrahedral coordination have been choosen as references. Their edge structure and Fourier-Transform are shown on figure 1 and 2 respectively.
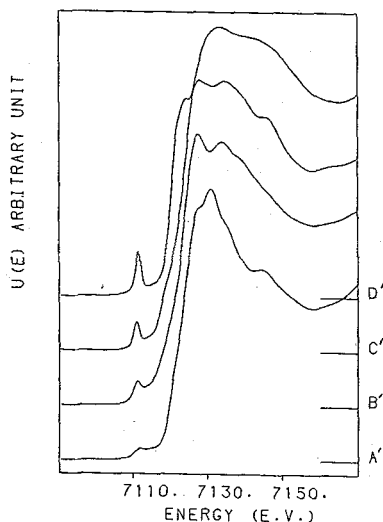

Figure 1 :
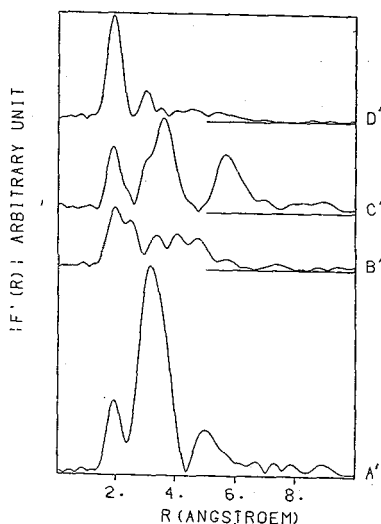Iron K-edge structures for the reference compounds (see table I)

Figure 2 :
Modulus of the Fourier transform of $k^3 \cdot \chi(k)$ EXAFS modulations (corrected for the phase shift of Fe-O pairs) for reference compounds.

As shown by CALAS et al /11/, the intensity of the prepeak corresponding to the 1s-3d transition can be related to the fourfold coordinated iron concentration inside the material. This result is well observed on the four edge structures (fig. 1) : from the distorted octahedral environment of Fe^{3+} ions in the hematite structure (A' on fig. 1) showing a small prepeak to the pure regular tetrahedral environment in $FePO_4$ compound characterized by a single intense prepeak, a progressive increase of the prepeak intensity is observed when going from the brown millerite structure of $Sr_2Fe_2O_5$ (50 % 4-fold coordinated iron) to the garnet structure of $Y_3Fe_5O_{12}$ (60 % of 4-fold coordinated iron).

Among the various definitions of edge position (peaks on derivatives, extrapolation from 1s → 4s feature), no method was able to give values within ± 1eV, although the 1s → 3d peak is centered at 7111.3 ± 0.2 eV. Thus we used the crude

position at half height of the edge crest, giving similar results excepted for $FePO_4$ which shows a very intense 1s → 4s transition.

The refined distances R_1 for the first coordination sphere (Fe-O pair) are given in table I for the reference compounds together with the other refined parameters (σ, So^2, N) and the Fe-O distances deduced from the structure determination by X-ray diffraction. For the $FePO_4$ compound, the Fe-O distance fitted by EXAFS is in good agreement with the standard one for a Fe^{3+} ion in tetrahedral symmetry. In the case of the brown-millerite type structure $Sr_2Fe_2O_5$, the EXAFS distance appears to be well centered on the mean Fe-O distance taking into account

TABLE I
Compositions and structural parameters.
In parenthesis are the numbers of oxygen neighbours.

Reference compounds	E_0 (eV)	Prepeak height	R (X-ray) (A)	R (EXAFS) (A)	σ (A)	N x S_o^2
D' $FePO_4$	7,121.2	0.162	1.88(4)	1.88	0.056	1.614
C' $Y_3Fe_5O_{12}$	7,122.6	0.092	1.872(4)-2.00(6)	1.89	0.085	1.700
B' $Sr_2Fe_2O_5$	7,122.7	0.050	1.87(4)-2.18(6)	1.95	0.090	1.867
A' α-Fe_2O_3	7,123.2	0.021	1.91(3)-2.06(3)	1.93	0.083	1.898

Glasses compositions

	K_2O	P_2O_5	Fe_2O_3	E_o (eV)	Prepeak height	R (EXAFS) (A)	σ (A)	Nx S_o^2
G	12	67	21	7,118.7	0.017	Fe-O 2.03	0.088	1.92
F	27	40	33	7,119.9	0.026	Fe-O 1.98	0.093	1.71
E	14	48	38	7,119.9	0.031	Fe-O 1.96	0.082	1.50
D	13	58	29	7,120.7	0.039	Fe-O 1.95	0.089	1.65
C	39	32	29	7,121.9	0.053	Fe-O 1.96	0.095	2.06
B	50	25	25	7,123.2	0.032	Fe-O 1.98	0.091	2.48
A	44	44	12	7,124.1	0.014	Fe-O 1.99	0.074	3.09

both polyhedra. In the garnet $Y_3Fe_5O_{12}$, the EXAFS distance R_1 is centered on the shortest Fe-O distances corresponding to the FeO_4 tetrahedras which are predominant and in the hematite Fe_2O_3, R_1 corresponds to the three shortest distances of the distorted octahedra around Fe^{3+} ions. Both last cases are characteristic of a larger distance distribution of the longest Fe-O distances. Taking into account the distribution of the scaling factor S_o^2 in the reference compounds, probably related to the polyhedra distortion, it appeared that any estimation of the coordination number in glasses could not be reliable.

IV - GLASSES

The edge energies (fig. 3) determined in the same way than for the reference compounds are reported in table I for all the studied compositions : they show a total shift of 5.4 eV which have been correlated to a change of the oxidation number of iron ions. The Fe^{2+} concentrations (c = $[Fe^{2+}]$ / $[Fe_{TOT}]$) have been determined by T.G.A. under oxygen stream and Mössbauer spectroscopy and compared to the one

TABLE II

Fe^{2+} concentrations estimated by T.G.A. (1)
Mössbauer (2) and Iron K-edge shift (3).
          (* : fixed value)

$K_2O-P_2O_5-Fe_2O_3$ glasses

Fe^{2+} concentration $C = [Fe^{2+}] / [Fe_{TOT}]$

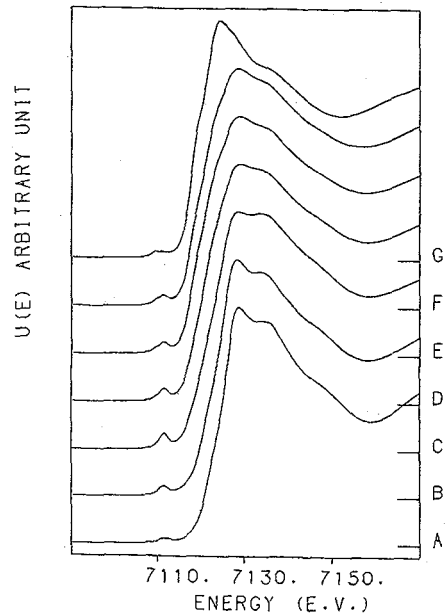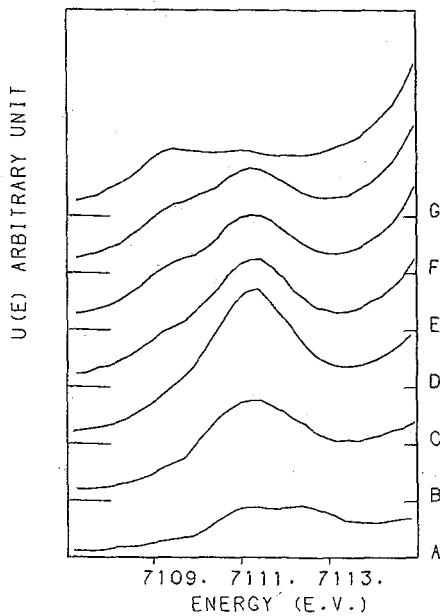| Sample	(1)	(2)	(3)
G	90	>90	90*
F	45	50	70
E	36	40	70
D	35	-	57
C	17	20	37
B	6	≈15	18
A	≈ 0	≈ 0	0*

Figure 3 :
Iron K-edge structures for
the glasses (see table I).

Figure 4 :
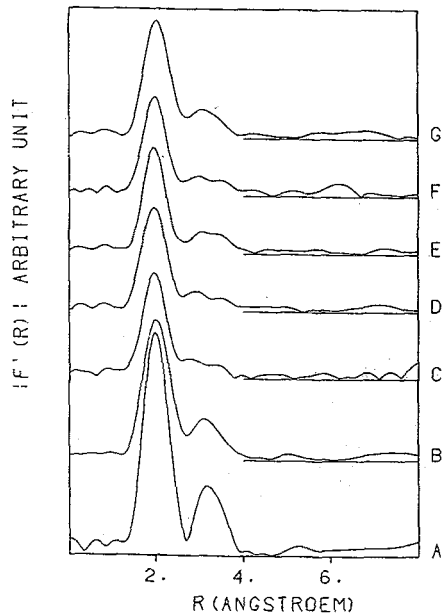Evolution of the iron K-edge
prepeak (1s-3d transition)
for the glasses

Figure 5
Modulus of the Fourier transform of
$K^3 \cdot \chi(K)$ EXAFS modulations (corrected
for the phase shift of Fe-O pairs)
for the glasses.

deduced from the edge shifts (table II), assuming a linear variation of the edge energy as a function of the Fe^{2+} concentration. The results of T.G.A. and Mössbauer spectrometry are in good agreement ; although less precise, the Fe^{2+} concentrations deduced from the edge shifts follow the same increasing order.

The prepeak, corresponding to the 1s-3d transition shown on figure 4A, is characteristic of Fe^{3+} ions in octahedral environment. As the Fe^{2+} concentration increases (fig. 4B, C, D), the increase of the relative intensities of the prepeak corresponds to the presence of Fe^{3+} ions in tetrahedral coordination. A direct comparison of the prepeak intensities given in table I, allow to estimate the concentration of tetrahedral iron ions to 50 % for the glass composition noted C.

Above 35 % of Fe^{2+}, a shoulder appears in the low energy range of the prepeak together with a decrease of the central peak intensity associated with the decrease of the Fe^{3+} ions in tetrahedral environment. For the glass containing more than 90 % of Fe^{2+} ions (fig. 4G), the prepeak results in a weak doublet similar to that of the first glass (fig. 4A) but shifted to the lower energies by 2 eV. It could be associated to Fe^{2+} ions in octahedral environment.

On the Fourier transform shown figure 5, the first oxygen neighbours are well visible. Good fits were always obtained considering only one shell. In sample A, the Fe-O distance agrees with the expected value for an octahedral coordination of Fe^{3+}, probably less distorted than in αFe_2O_3 as suggested by the high scaling factor S_o^2. Then the Fe-O distance decreases from sample B to D in accordance with the conclusion deduced from prepeak i.e. : the occurence of Fe^{3+} in tetrahedral sites. The decrease in the Fe-O distance is however weak but is naturaly hindered by the contribution of longer distances due to Fe^{2+}. This latter effect becomes dominant in sample K where however the Fe-O distance of 2.03 A appears to be very short for an octahedral coordination of Fe^{2+} ; note that the environment of Fe^{2+} in sixfold coordination is generaly much more distorted than the one of Fe^{3+} (distances are known ranging from 2.01 to 2.62 A, mean value being of the order of 2.18 A) EXAFS is dominated by the shortest ones. Preliminary Mössbauer results are consistent with a pure sixfold coordination of Fe^{2+} in sample G.

Second neighbours are well visible in fig. 5 ; sometimes, two peaks are present. It has been found possible to fit the contribution of the first one by P neighbours, giving distances Fe-P ranging from 3.01 to 3.19 A which are consistent with FeO_6 octahedras sharing corners with PO_4 tetrahedras as it has been observed in the phosphotungstate glasses /5/. The second peak was attributed to Fe-Fe pairs in samples D, E and F : the distances lie between 3.39 and 3.42; they are consistent with the distance between FeO_4 and FeO_6 polyhedra joined by corners in YIG (3.46 A).

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