LOCAL ENVIRONMENT OF Zr IN BARYUM FLUOROZIRCONATE GLASSES : THE EXAFS POINT OF VIEW

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Résumé – L'étude EXAFS de l'environnement (coordinence, distance moyenne M-F) des ions Zr^{4+} dans les phases vitreuses du système BaF_2-ZrF_4 montre que ces ions adoptent une coordinence comprise entre 7 et 8. De nombreux composés cristallisés adoptant les diverses coordinations connues dans la cristallochimie des fluorures de zirconium ont servi de référence.

Abstract – EXAFS studies (coordination number, mean M-F distance) for Zr^{4+} ions in vitreous phases of BaF_2-ZrF_4 system lead to a coordination number between 7 and 8. Numerous crystallized compounds involving the various C.N. known in crystal chemistry of zirconium fluorides were used as references.

I - INTRODUCTION

Due to their high potentiality for middle infra-red applications, fluorozirconates have given rise to a number of studies. Fundamental structural works have been performed essentially on binary BaF_2-ZrF_4 glasses:
- this binary system can be seen as the best known and the simplest of all glass-forming ones.
- the crystal structure of numerous baryum fluorozirconates is known (1)
- the crystal chemistry of zirconium in fluoride medium has been extensively described : the coordination number (C.N.) of Zr^{4+} varies from 6 to 8 but 7 and 8 are the most usual C.N. (1).

Some controversy still exists on the Zr^{4+} coordination in fluorozirconates glasses ; for the most extensively studied glass "$BaZr_2F_{10}$" sixfold (2) and eightfold (3) coordination is concluded from RAMAN investigations, neutron and X-ray studies (4-6) always lead to large Zr-F distance (2.08 to 2.09 A) with 6.6 to 7.4 first neighbours.

The present study gives the E.X.A.F.S. point of view on this problem.

II - EXPERIMENTAL CONDITIONS

The crystalline compounds were obtained by solid state reaction from baryum and zirconium fluorides (7). The glasses used in this investigation were prepared from melt of same fluorides mixture by quenching from 750°C to 175°C.

E.X.A.F.S. spectra were recorded on the D.C.I. synchroton source of LURE in ORSAY on powdered samples; the data treatment is described in (8).

III - RESULTS AND DISCUSSION

In crystallized fluoride medium, the zirconium polyhedra are often distorted and the large alkaline or alkaline earth ions ,when present, are located in large vacancies.

1) References compounds . The refined parameters for references are given in Table I and the zirconium environments are shown in Figures 1 :

* Li_2ZrF_6 (9). The structure is built with regular isolated octahedra

* $\alpha-BaZrF_6$. The coordination number of zirconium is 7; the structure results from infinite zig-zag $(ZrF_6)_n$ chains (1).

* $\beta-BaZr_2F_{10}$ (10). 2 ZrF_7 polyhedra share a edge to form Zr_2F_{12} entities which are connected by corners leading to $(Zr_2F_{10})_n$ chains

* $\beta-BaZrF_6$ (11). Each ZrF_8 polyhedron shares 2 edges leading to linear ZrF_6 chains.

* $\alpha-ZrF_4$ (high temperature form, (1)). The network is built on ZrF_8 dodecahedra sharing corners and edges.

* $\beta-ZrF_4$ (12). The tridimensional structure comes from connection by corners of ZrF_8 Archimede antiprisms.

TABLE I :Refinement parameters for crystalline compounds for Zr at K absorption edge

Compounds	CN	R(A) EXAFS	R(A) RX	$\sigma_j(A)$	S^2_o	$\Delta E_o(ev)$
Li_2ZrF_6	6	2.034	2.016	0.070	0.486	+12
$\alpha-BaZrF_6$	7	2.031	2.082	0.077	0.387	+3
$\beta-BaZr_2F_{10}$	7	2.083	2.05	0.112	0.551	+11
$\beta-BaZrF_6$	8	2.046	2.126	0.095	0.375	+8
$\alpha-ZrF_4$	8	2.122	2.108	0.080	0.488	+11
$\beta-ZrF_4$	8	2.114	2.116	0.075	0.517	+12.5

Figure 2 shows that Zr-F distance obtained by simulation of E.X.A.F.S. spectra is always lower than the mean Zr-F X-ray value especially for a wide and asymmetrical distribution. The Zr-F distance obtained for Li_2ZrF_6 leads us to modify the zirconium phase shift because the six Zr-F distances have to be identical and no difference between E.X.A.F.S. and X-ray values is allowed.

2) Vitreous compositions . Figure 3 shows that we can see only the first coordination shell. The variation of Zr-F distances is related to the glass ZrF_4 content (Table II). Figure 4 makes a comparison of glass Zr-F distances with those of crystallized compounds sorted by coordination number : the conclusion is that in these glasses C.N. is between 7 and 8.

TABLE II : Refinement parameters for ZrF_4 based glasses.
* calculated from mean value of S^2_o for crystallized references (Table I)

Glasses	CN*	R(A) EXAFS	R(A) RX	$\sigma_j(A)$	S^2_o	$\Delta E_o(ev)$
ZBLA	6.6	2.088		0.093	0.398	+11
$Ba_2Zr_3F_{16}$	6.8	2.079	2.11 (4)	0.090	0.406	+12
$BaZr_2F_{10}$	7.1	2.079	2.08 (6)	0.103	0.426	+10
$BaZr_3F_{14}$	8.1	2.095	2.11 (4)	0.110	0.484	+17

When the ZrF_4 content increases C.N. increases ; 2 explanations can be invoked :
* The ratio of 7-fold and 8-fold coordinated zirconium varies to fit the stoechiometric Zr/F ratio.
* The polyhedra connecting scheme varies (corner sharing, edge sharing).

The diversity of coordination and linkage in zirconium fluoride chemistry supports the two hypothesis, but, if we cannot choose clearly, we can say that in these glasses the existence of significative contribution of octahedral coordination for zirconium (as claimed by RAMAN investigators (2)) is excluded.

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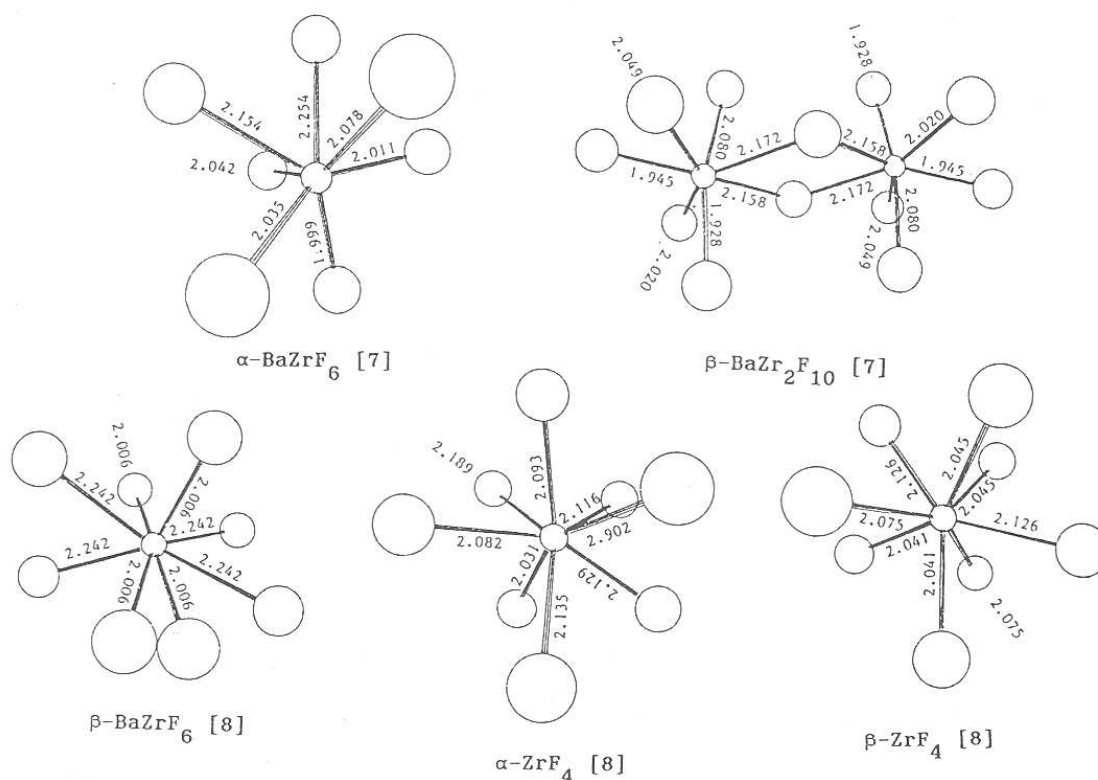(12) R. D. BURBANK and F. N. BENSEY, U.S.A. At. Energ. Com. Rept. K-1280 (1956)

Figure 1 : Main ZrF_n polyhedra in crystallized references

Figure 2 :

Histogram of Zr-F distances
in crystallized references.
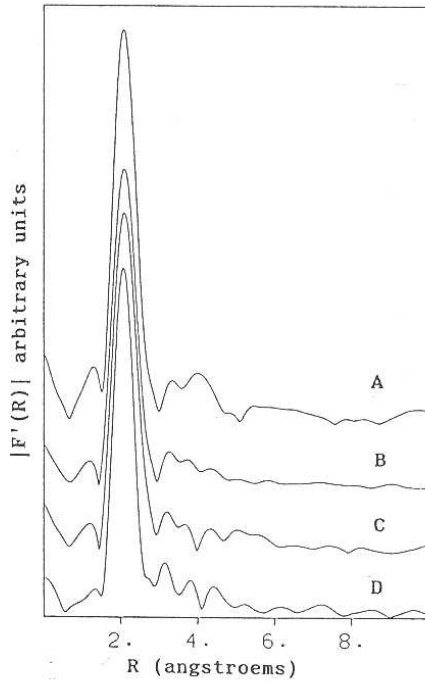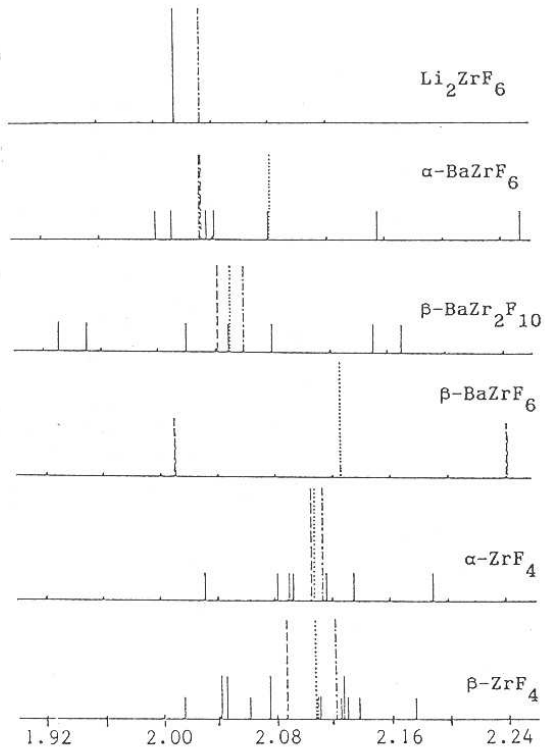........ X-ray
------- simulated EXAFS
-·-·-·- real EXAFS

Figure 3 :
Zr K absorption edge – |F'(R)| modulus
ZBLA (A), "BaZr$_3$F$_{14}$" (B),
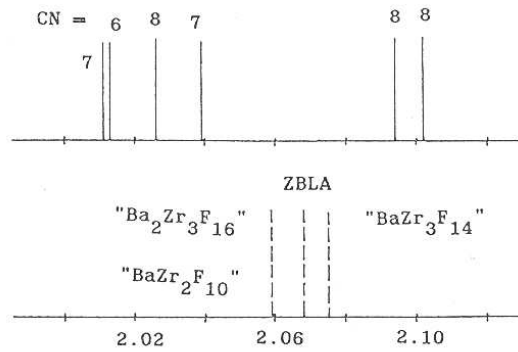"BaZr$_2$F$_{10}$" (C), "Ba$_2$Zr$_3$F$_{16}$" (D)

Figure 4 :
Relations between coordination number
and distance Zr-F
——— crystallized references
--------- studied glasses