

STRUCTURE OF BARIUM FLUOROZIRCONATE GLASSES A QUASI-CRYSTALLINE MODELLING OF "BaZr₂F₁₀"

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INTRODUCTION

Structural investigations of fluorozirconate glasses have progressed considerably since the first contribution using Raman and I.R. spectroscopy [1]. Two papers have recently examined the state of the art in this field [2, 3]; they agree in the conclusion that some uncertainties remain even on the basic structural unit.

Following the study of the BaF₂-ZrF₄ glass-forming system by EXAFS [4], an attempt is made in this contribution to provide accurate data with high real space resolution by neutron diffraction. The only previously reported neutron study was for the composition BaF₂-2 ZrF₄ by the time of flight method [5]. We present here the analysis of this composition by the variable 2θ method and also the study of 2 BaF₂-3 ZrF₄, BaF₂-3 ZrF₄ and BaF₂-2 HfF₄ glasses.

Various models have been suggested to account for the structure of these glasses, some of them by Molecular Dynamics simulation (see the review in [3]). They are not easy to compare, because a criteria that could precisely define the degree of fitting is never given; moreover, a comparison in the reciprocal space with the experimental data is never provided. A modelling of the "BaZr₂F₁₀" glass structure is presented in detail in this work which satisfies the latter requirements.

NEUTRON DIFFRACTION RESULTS

Intensities were recorded with the D4 diffractometer (I.L.L. Grenoble) at a wavelength $\lambda = 0.497 \text{ \AA}$ in the range of momentum transfer $0.4 \leq Q \leq 22.9 \text{ \AA}^{-1}$ ($4\pi \sin\theta/\lambda$). The nuclear interference function $I(Q)$ was derived from the intensities $I_a(Q)$ (normalized in a classical way [6]) following the usual formula :

$$I(Q) = [I_a(Q) - (\langle b^2 \rangle - \langle b \rangle^2)] / \langle b \rangle^2$$

The reduced interference functions $[I(Q)-1]$ are shown Figure 1a, extrapolated to $Q = 0$. The curve corresponding to "BaZr₂F₁₀" glass is in good agreement with that of Etherington et al [5,7] measured by the neutron time of flight method, but has less statistical noise. The isomorphous substitution (Hf for Zr) used in the previous X-ray diffraction study of "BaZr₂F₁₀" [8] appears to be confirmed here owing to the weak variation between the coherent scattering length of Zr and Hf (respectively 0.716 and 0.77.10⁻¹² cm) and the similarities among Fig. 1a, B and C. However, all the interference functions of Fig. 1a are quite similar despite of the large variations in the Zr/Ba ratio.

The reduced atomic distribution functions $G(R)$ (Figure 1b) were determined according to :

$$G(R) = (2/\pi) \int_0^{Q_{max}} Q \cdot [I(Q)-1] \cdot M(Q) \cdot \sin Q \cdot R \cdot dQ,$$

where $M(Q)$ is the modification function due to Lorch [9], applied in order to remove truncation effects. The crystal chemistry of Barium-Zirconium fluorides allows the unambiguous interpretation of the first two peaks for any composition in Figure 1b as follows : Zr-F first neighbour near 2.1 Å and a mixture of F-F and Ba-F correlations near 2.6 Å. The third peak near 4 Å cannot be clearly assigned but is most probably due to second neighbours Zr-F, F-F, and Ba-F because these pairs largely dominate both the weight (the sum is >85%) and the number of neighbours; in view of the clear increase of this peak with the Zr concentration, one might be tempted to attribute it mainly to Zr-F second neighbours.

It is not possible to obtain an accurate mean coordination number for Zr because of severe overlapping of the first two peaks. The various methods used and also some human influence may explain the relatively broad range of values proposed until now. We used two peak fitting techniques on the radial distribution function (RDF) : a pure gaussian shape for Zr-F and (F-F, Ba-F) peaks (i) and another determination with the more realistic constraint that F-F and Ba-F distances cannot be shorter than 2.3 Å (ii). Results are shown in Table 1 and compared with previous ones obtained by diffraction or EXAFS on the same glasses. Considering these various results it is clear that the zirconium may adopt either a C.N. of 7 or 8 (or a mixture) but cannot be strictly in octahedral coordination as stated in the first Raman study [1] (note that ZrF₆ octahedra encountered in crystal chemistry are generally only weakly distorted, the largest mean Zr-F distance being 2.02 Å in Li₂ZrF₆ [10]).

QUASI-CRYSTALLINE MODELLING OF "BaZr₂F₁₀"

The method was described elsewhere [11] and we recall here only its peculiarities. Strictly speaking, the mean local arrangement is expected to be modelled by a crystalline cell, the long range order being mathematically destroyed by the introduction of a Gaussian local strain distribution varying as the square of the distance (the width of the Gaussian distribution is refined). The interference function is then fitted as the summation over all contributing hkl reflections

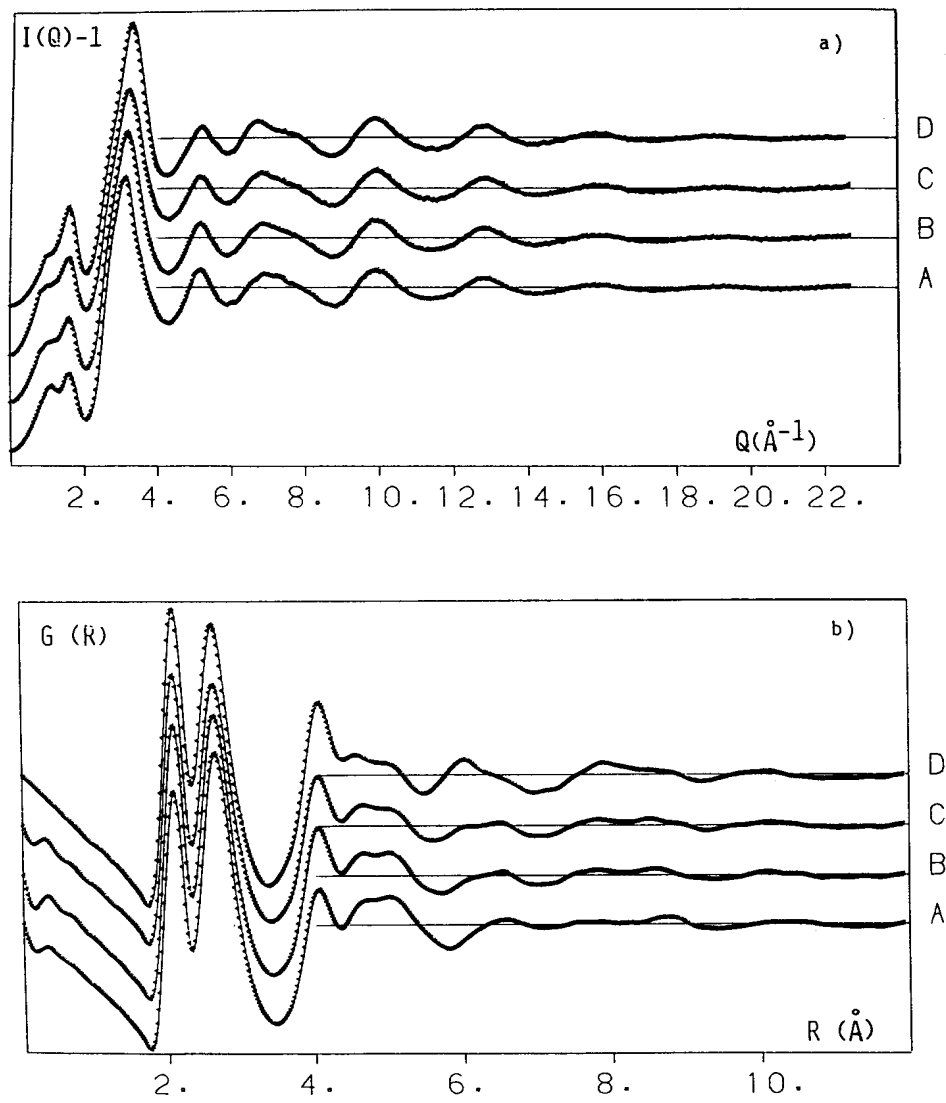


Fig.1 : Neutron interference functions $I(Q)-1$ (a) and reduced atomic distribution functions $G(R)$ (b) for glasses " $\text{Ba}_2\text{Zr}_3\text{F}_{10}$ " (A), " $\text{BaZr}_2\text{F}_{10}$ " (B), " $\text{BaHf}_2\text{F}_{10}$ " (C) and " $\text{BaZr}_3\text{F}_{14}$ " (D)

broadened according to the strain value. A procedure analogous to the Rietveld method [12] allows the refinement of the positional parameters in the starting model. The principal advantage is that the experimental data (interference functions) themselves are fitted, on which the range $Q < 5 \text{ \AA}^{-1}$ is particularly sensitive to the medium range order. This point is especially important since generally the differences between various models of the same glass are in the medium range order; we think that a comparison between observed and calculated interference functions is required for any modelling, and not only between the RDF's. Another advantage of such a refinement is that both the $G(R)$ observed and simulated functions are affected in the same way by truncation effects when Fourier transforming. The principal disadvantage is that the final model can just be a limited modification of the starting model; different models may give more or less satisfying results.

In the case of " $\text{BaZr}_2\text{F}_{10}$ ", a good starting model is the recently determined structure of $\beta\text{-BaZr}_2\text{F}_{10}$ [13]; it is characterized by a three-dimensional network of ZrF_7 polyhedra connected by corners (2) and edges (1). We also tried a model derived from TlZrF_8 [14], replacing Tl by Ba with half occupation of the site (ZrF_8 polyhedra sharing corners (4) and edges (1) in disconnected sheets). The neutron and X-ray ($\text{CuK}\alpha$) interference function were fitted. Results are detailed in Table 2 and Figure 2, with notations from A to E which are used in the following comments.

A - This is the starting model; from ρ_0 it is clear that the glass is more dense than its crystalline polymorph. On Figure 2c-A, it may be seen that the (F-F; Ba-F) distances are shorter in the glass than in $\beta\text{-BaZr}_2\text{F}_{10}$. Another important point concerns the cation-cation first neighbours lying at the mean values of 4.96 Å (2Ba-Ba), 4.35 Å (8Ba-Zr; 4Zr-Ba) and 3.82 Å (3Zr-Zr) in the crystal which are inconsistent with the X-ray diffraction results in Fig. 2d-A, where the most intense peak in $G(R)$ is at smaller value (4.2 Å).

B - We first tried to fit the neutron spectra only and immediately obtained a result which appears to be excellent (Fig. 2a,c in B). In fact, if this model is applied to the X-ray case, the fit is clearly not as good (Fig. 2b,d in B).

C - The parameters were then refined by simultaneously fitting the neutron and X-ray spectra. The X-ray curves shows a spectacular amelioration (compare B and C in Figure 2b,d) but the previous quality of the neutron fit is deteriorated. However, ρ_0 has almost reached practically the expected value.

D - At this stage, the only way to expect some amelioration, if staying in the same model, is to increase the number of degrees of freedom either by using another less symmetrical space group or by suppressing the symmetry center in the starting space group. The best fit was obtained with the latter approach using the Cc space group. The number of refined parameters increases by a factor of two, but this seems to be justified by the gain in the agreement factors R. The fit is almost perfect in the X-ray case and very good for neutrons; in fact, ρ_0 is now too high.

E - This is the best fit obtained using the structure TlZrF_8 as a starting model. If the agreement appears reasonably good,

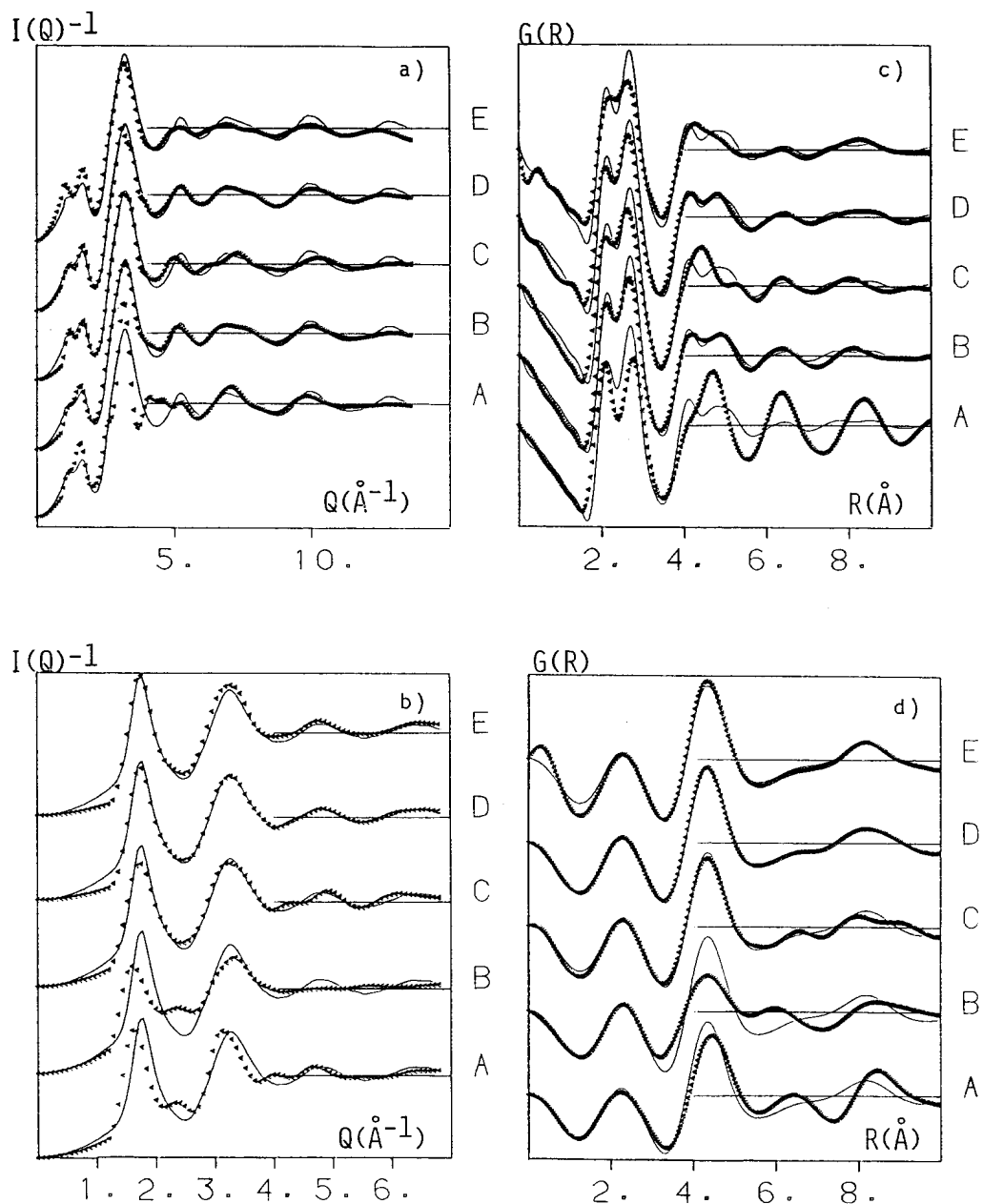


Fig.2 : Observed (---) and simulated (.....) interference functions $I(Q)-1$ (a : neutron ; b : X-ray) and reduced atomic distributions functions $G(R)$ (c : neutron ; d : X-ray) for the "BaZr₂F₁₀" glass. The notation from A to E follows table 2.

especially for the X-ray data, the mean atomic density is quite too low. This may be a consequence of the bidimensional character of the structure. Attempts to lower the degree of symmetry, with a full occupation of some sites by Ba were not successful and the R factors immediately increase significantly.

The conclusion, based on considerations about R factors and ρ_0 , is that the best actual model obtained by this method of modelling is the mean local arrangement noted in D above. Comparisons between the main mean distances of the starting and refined models D and E (respectively β -BaZr₂F₁₀ and TlZrF₈ type) are shown Table 3; stereographs of the structures are presented Figure 3 (Positional and cell parameters can be obtained on request from the authors).

DISCUSSION AND CONCLUSIONS

We will discuss only the model derived from β -BaZr₂F₁₀ since it seems to be the "best". The Zr coordination number increases from 7 to 7.5 but 1.5 F are distinctly at longer distances. The mean distances for Ba-F and F-F first neighbours show a clear decreasing trend; the Ba C.N. of 10 seems to be reasonable if compared to 15.5 which was estimated in [5]. The edge sharing distance between the two ZrF₇ and ZrF₈ polyhedra is very short but more clearly separated from the corner sharing ones than it was in the crystalline phase. The first Ba-Ba and Zr-Ba distances have significantly decreased if compared to β -BaZr₂F₁₀. Comparison of Figure 3a and 3b shows that the price to paid to improve the fit is the distortion of the model. It must be noted that some distances are unreasonable, in particular, two F are found 1.34 Å apart (in the proportion of 1/32 of the F-F pairs) and one Ba-F distance is 2.06 Å; some relaxation, according to an appropriate interatomic potential could suppress such defects.

Can we really conclude that the mean local organization in the glass is not very different from β -BaZr₂F₁₀? This is not so evident for two reasons: first, the final model shows some important and systematic evolutions, particularly with respect to the F-F, Ba-F and cation-cation distances which are all shorter in the glass (but this is consistent with the higher density). Second, the fact that the model agrees relatively well in both real and reciprocal space on both neutron and X-ray measurements is not sufficient to prove that another model could not succeed equally well. The ideal case would be to obtain a good fit on all the partial pair contributions; they are not however available for the bariums fluorozirconate glasses. Some additional information could be obtained by anomalous X-ray dispersion at wavelengths near the zirconium absorption K-edge, such work is in progress.

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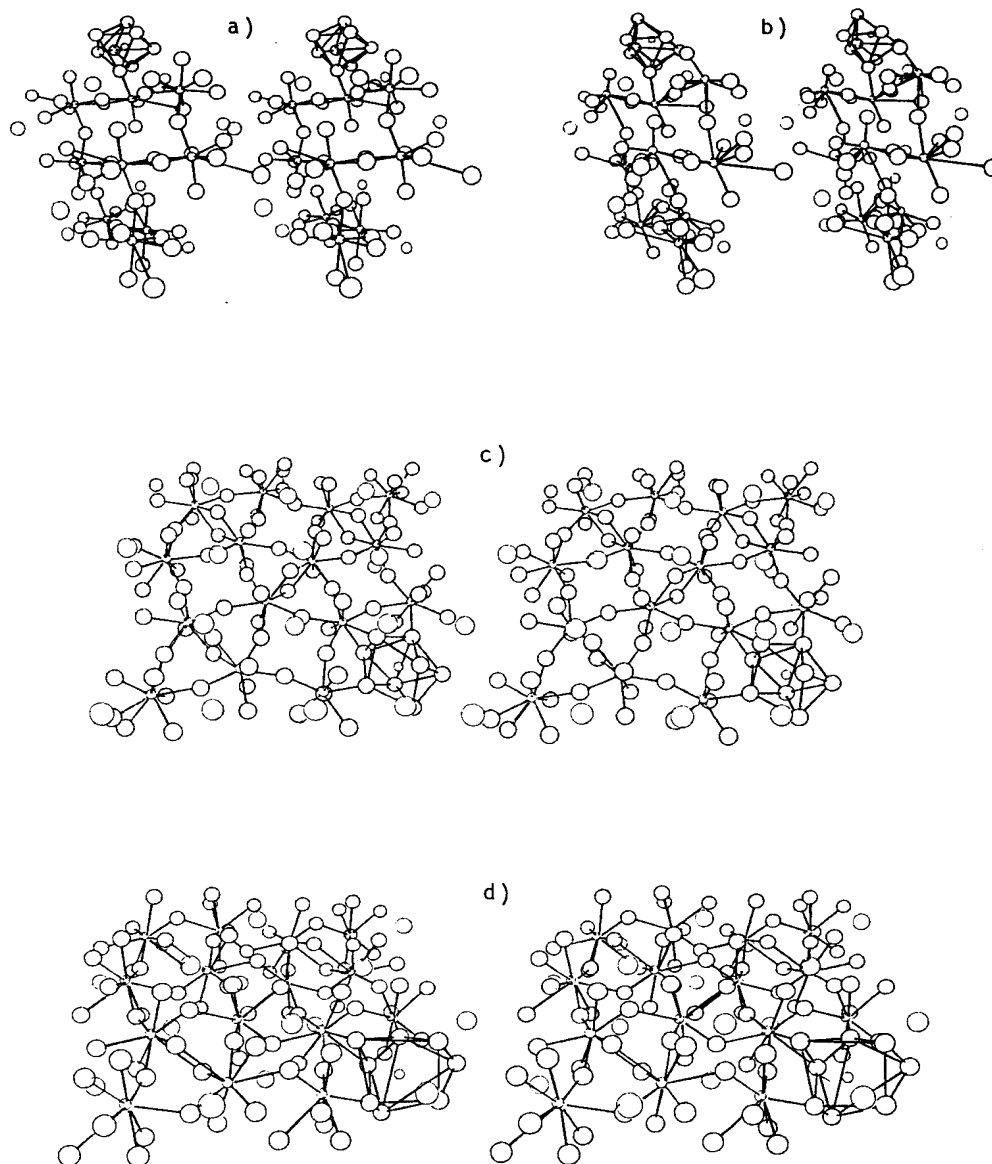


Fig. 3 : Stereoscopic view of the starting (a) and final model (b) in the β -BaZr₂F₁₀-type, and respectively the same in c and d for the TiZrF₈-type (only one sheet at $x = 0.5$ is shown)

Table 1 :

Results on Zr-F mean distances (first line) and coordination numbers (C.N., second line) compared to previous works (last column)

Glass	this work			EXAFS [10]	Neutron (") X-ray (")	
	max G(R)	fit i	RDF ii			
BaZr ₃ F ₁₄	2.08	2.09	2.10	2.10	2.11[15]	2.20[16]"
		6.3	6.9	8.1	8.35 "	
BaHf ₂ F ₁₀	2.07	2.08	2.09		2.08[8]	
		6.2	6.9		7.7 "	
BaZr ₂ F ₁₀	2.07	2.08	2.09	2.08	2.08[8]	2.09"[5,17,18]
		6.5	7.3	7.1	7.4""	6.8"" ; 6.6""
Ba ₂ Zr ₃ F ₁₆	2.07	2.08	2.09	2.08	2.10[15]	2.20""[16]
		6.4	7.0	6.8	7.39""	

Table 2

Reliabilities defined as $R = 100 \times [\sum (\text{obs}-\text{cal})^2 / \sum \text{obs}^2]^{1/2}$ (%) determined in the ranges $1 < Q < 14 \text{ \AA}^{-1}$ (neutron) ; $1.3 < Q < 6.9 \text{ \AA}^{-1}$ (X-ray) and $1 < R < 12 \text{ \AA}$.
For the glass, ρ_0 is $0.071 \text{ at. \AA}^{-3}$. The number of refined xyz parameters was 18 (A,B,C) ; 37(D) and 21(E).

Model	Neutrons			X-ray			ρ_0
	I(Q)	I(Q)-1	G(R)	I(Q)	I(Q)-1	G(R)	
β -BaZr ₂ F ₁₀							
Starting A	10.1	34.8	59.7	13.0	42.3	44.2	0.0669
C2/c N B	4.2	13.1	17.7	15.4	50.1	52.9	0.0667
N+X C	5.6	17.8	27.2	6.3	18.7	16.7	0.0719
Cc N+X D	3.7	13.3	16.0	3.8	14.2	8.8	0.0763
TlZrF ₅							
N+X E	5.9	20.8	27.0	6.4	22.2	12.6	0.0558

Table 3

Mean distances (up to 6 Å for some pairs) and numbers of neighbours in parenthesis

	Model			
	β -BaZr ₂ F ₁₀		TlZrF ₅	
	Starting	Refined (Cc)	Starting	Refined
Zr-F	2.05(7)	2.08(6)	2.03(4)	2.12(4)
	3.38(1)	2.74(1.5)	2.19(4)	2.74(4)
	3.74(2)	3.19(2)	3.68(2)	3.30(1)
	4.35(9)	4.05(9)	4.21(10)	4.23(7)
Ba(Tl)-F	2.78(10)	2.58(10)	3.15(12)	3.02(10)
	3.41(1)	3.80(3)	4.21(4)	4.16(4)
F-F	2.71(6.3)	2.57(7.1)	2.64(6.6)	2.58(4.6)
Zr-Zr	3.82(3)	3.25(1)	3.68(1)	4.20(5)
	5.37(3)	3.94(1)	4.19(4)	4.67(2)
	5.83(2)	4.75(4)		
		5.50(4)		
Ba(Tl)-Ba(Tl)	4.96(2)	4.38(2)	4.09(4)	4.08(3)
Zr-Ba(Tl)	4.35(3)	4.17(4)	4.19(6)	4.12(1.5)
	5.55(1)	5.09(0.5)		4.72(1.5)
	5.89(1)	5.67(1.5)		

REFERENCES

- [1] R.M. Almeida, J.D. Mackenzie, *J. Chem. Glasses* 11 74 (1981)
- [2] Y. Kawamoto, *Mat. Sci. Forum*, 6 417 (1985)
- [3] A.C. Wright, Proc. NATO ARW on Halide Glasses for I.R. fiberoptics Vilamoura, Portugal (1986) in press.
- [4] B. Boulard, A. Le Bail, J.P. Laval and C. Jacoboni, Proc. "EXAFS and Near Edge Structure IV" - Fontevraud, France (1986). In press *J. de Physique*.
- [5] G. Etherington, C.N.J. Wagner, R. Almeida and J. Faber, Symp. on neutron scattering., eds. M.S. Lehmann, W. Saenger, G. Hildebrandt and H. Dachs, Reports Hahn-Meitner Institut Berlin, HMI-B411, 64 (1984).
- [6] A. Le Bail, C. Jacoboni and R. De Pape, *J. Non Cryst. Solids* 74 205 (1985).
- [7] C.N.J. Wagner, *J. Non Cryst. Solids* 76 29 (1985).
- [8] G. Etherington, L. Keller, A. Lee, C.N.J. Wagner and R.M. Almeida, *J. Non Cryst Solids* 69 69 (1984).
- [9] E.A. Lorch, *J. de Phys.* C2 229 (1969).
- [10] G. Brunton, *Acta Cryst.* B29 2294 (1973).
- [11] A. Le Bail, C. Jacoboni and R. De Pape, *J. de Physique*, Coll. C8 163 (1985).
- [12] H.M. Rietveld, *J. Appl. Cryst.* 2 65 (1969).
- [13] J.P. Laval, to be published
- [14] D. Avignat, I. Mansour, R. Chevalier and J.C. Cousseins *J. Sol. State Chem.*, 38, 121 (1981).
- [15] R. Coupe, D. Louer, J. Lucas, A.J. Leonard, *J. Am. Ceram. Soc.* 66 145 (1983).
- [16] H. Inoue, H. Hasegawa and I. Yasui, *Phys. chem. glasses* 26 74 (1985).
- [17] R.M. Almeida, *Mat. Sci. Forum* 6 427 (1985)
- [18] R.M. Almeida and J.D. Mackenzie, *J. de Physique*, Coll C8 75 (1985).