

PARTIAL STRUCTURE FACTORS OF FLUORIDE GLASSES “ $\text{Pb}_2\text{M}_t^{\text{II}}\text{M}_t^{\text{III}}\text{F}_9$ ” BY NEUTRON DIFFRACTION

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Separation into partial structure factors has been performed from neutron experiments on “ $\text{Pb}_2\text{M}_t^{\text{II}}\text{M}_t^{\text{III}}\text{F}_9$ ” fluoride glasses making various substitutions for 3d transition metal ($\text{M}_t^{\text{II}} = \text{Mn}^{2+}$, Zn^{2+} ; $\text{M}_t^{\text{III}} = \text{Fe}^{3+}$, V^{3+} , Ga^{3+}). Three groups of pair contributions are obtained: ($\text{F}-\text{F}+\text{Pb}-\text{Pb}+\text{Pb}-\text{F}$), ($\text{M}_t-\text{F}+\text{M}_t-\text{Pb}$) and M_t-M_t , assuming a statistical repartition between M_t . A structural model is proposed built on corner shared M_tF_6 octahedra and close packing of large ions F^- and Pb^{2+} presenting some analogies with BaFeF_5 and ReO_3 structure types.

1. Introduction

The $\text{PbF}_2-\text{M}_t^{\text{II}}\text{F}_2-\text{M}_t^{\text{III}}\text{F}_3$ system authorizes a large extent of vitreous area and various 3d transition metal ion associations [1,2]. Structural information has been obtained by EXAFS studies of M_t and Pb local environment in glasses of composition “ $\text{Pb}_2\text{M}_t^{\text{II}}\text{M}_t^{\text{III}}\text{F}_9$ ” ($\text{M}_t^{\text{II}} = \text{Mn}^{2+}$, Zn^{2+} ; $\text{M}_t^{\text{III}} = \text{Fe}^{3+}$, Ga^{3+}) [3]. The M_t are found to be octahedrally coordinated and Pb^{2+} has eight to ten fluorine neighbours forming a very distorted polyhedra. First shell distances are well within the range of values generally observed for these coordinations in crystallized fluoride compounds so that if the Pb–F distances remain identical for all the glasses studied, the M_t –F distances lie between 1.89 Å (Ga–F) and 2.10 Å (Mn–F): this is not an especially good argument for an isomorphous substitution with a necessary conservation of distances. However, recent studies of the short range magnetic ordering by neutron diffraction [4,5] show that the M_t – M_t distances and interaction-type between magnetic species remain nearly the same up to 9 Å for glasses like “ $\text{Pb}_2\text{ZnFeF}_9$ ”, “ $\text{Pb}_2\text{MnGaF}_9$ ” and “ $\text{Pb}_2\text{MnFeF}_9$ ” where magnetic correlations depend only, respectively, on pairs Fe–Fe, Mn–Mn or (Mn, Fe)–(Mn, Fe). These results are not in contraction with the EXAFS ones, and examples are found in crystallized compounds of constant distances between M_t ions having different ionic radii (pyrochlore structure for instance). Neutron magnetic results were consistent with previous ^{19}F NMR ones [6], showing that M_t^{II} ions play a different role than M_t^{III} but do not confirm the hypothesis of an $\text{M}_t^{\text{II}}-\text{M}_t^{\text{III}}$ strict alternance: the 3d transition metals are organized in ramified chains built up from corner-shared octahedra and distances are coherent with a simple cubic lattice which could

be half occupied, the number of $M_t^{\text{II}}-M_t^{\text{II}}$ first neighbours being greater than $M_t^{\text{III}}-M_t^{\text{III}}$ ones [5].

The chemical behaviour of 3d transition metal and known M_t-M_t distances favoured the fact that our glasses could appear reasonably good candidates for isomorphous substitution in the sense of a medium range order. We present here the results of an attempt to determine some partial structure factors. The neutron diffraction spectra are those measured at 290 K in the previous magnetic study [5] (where only the 4–290 K difference spectra were analyzed); a “ Pb_2MnVF_9 ” glass is added, chosen for the interesting negative contribution due to the neutron scattering length of both Mn and V.

2. Experiment and data analysis

Intensities were recorded with the D2 diffractometer (I.L.L., Grenoble) at a wavelength $\lambda = 1.22 \text{ \AA}$ in the range of momentum transfer $Q = 0.4 - 9.1 \text{ \AA}^{-1}$ ($4\pi \sin \theta / \lambda$). The preparation of the glasses and the whole normalization procedure have been described in the previous study of the magnetic scattering contribution [5]. The nuclear interference function $I(Q)$ was derived from the normalized intensities $I_a(Q)$ with the usual formula:

$$I(Q) = [I_a(Q) - (\langle b^2 \rangle - \langle b \rangle^2)] / \langle b \rangle^2, \quad (1)$$

where $\langle b^2 \rangle = \sum_i c_i b_i^2$ and $\langle b \rangle = \sum_i c_i b_i$; c_i and b_i being respectively the atomic concentration and scattering length of element i . The reduced atomic distribution function $G(R)$ was calculated by the sine-Fourier transform of the reduced interference function extrapolated to the origin:

$$\begin{aligned} G(R) &= 4\pi R \rho_0 [g(R) - 1] \\ &= (2/\pi) \int_0^{Q_{\max}} Q [I(Q) - 1] M(Q) \sin QR \, dQ, \end{aligned} \quad (2)$$

where $M(Q)$ is the modification function due to Lorch [7] applied in order to remove truncation effects.

The separation into partial structure factors was made following the expression:

$$I(Q) - 1 = \sum_i \sum_j (c_i c_j b_i b_j / \langle b \rangle^2) [I_{ij}(Q) - 1]. \quad (3)$$

The glasses we have studied contain four to five elements and so the number of partial structure factors $I_{ij}(Q)$ would be ten or fifteen. We have only six equations like (3) for glasses of the same fundamental composition for which only the transition metals have been substituted. To the isomorphism hypothesis supported in the introduction, we must add, as an approximation, that M_t^{II} and M_t^{III} ions are statistically distributed on the same site although the previous neutron magnetic results show that this could not be considered as strictly true. In our opinion, the model proposed for the M_t organization

remains compatible with such an approximation because the particular arrangement between M_t^{II} and M_t^{III} could lead however to nearly the same partial distributions $M_t^{II}Pb$ and $M_t^{III}Pb$ or $M_t^{II}F$ and $M_t^{III}F$. The above hypothesis enable us to rewrite the expression (3) in the following form:

$$\begin{aligned}
 I(Q) - 1 = \frac{1}{\langle b \rangle^2} & \left\{ c_{M_t}^2 \bar{b}_{M_t}^2 (I_{M_t M_t} - 1) \right. \\
 & + 2c_{M_t} \bar{b}_{M_t} \left[c_{Pb} b_{Pb} (I_{M_t Pb} - 1) + c_F b_F (I_{M_t F} - 1) \right] \\
 & + \left[c_{Pb}^2 b_{Pb}^2 (I_{Pb Pb} - 1) + c_F^2 b_F^2 (I_{FF} - 1) \right. \\
 & \left. \left. + 2c_{Pb} c_F b_{Pb} b_F (I_{Pb F} - 1) \right] \right\}, \tag{4}
 \end{aligned}$$

where $\bar{b}_{M_t} = (\sum_i c_{M_{ti}} b_{M_{ti}}) / c_{M_t}$ and $c_{M_t} = \sum_i c_{M_{ti}}$. Eq. (4) shows evidence that three partial structure factor (or sum of partial) may be separated, i.e.

$$P_1 = c_{Pb} b_{Pb} (I_{M_t Pb} - 1) + c_F b_F (I_{M_t F} - 1),$$

$$P_2 = I_{M_t M_t} - 1,$$

$$P_3 = c_{Pb}^2 b_{Pb}^2 (I_{Pb Pb} - 1) + c_F^2 b_F^2 (I_{FF} - 1) + 2c_{Pb} c_F b_{Pb} b_F (I_{Pb F} - 1).$$

The weighting factors associated with these three partials for our six glasses are given in table 1, together with the \bar{b}_{M_t} . The system (over-determined) of linear equations has been solved following a least squares procedure. It is to be noted that, in fact, our six equations permit theoretically to decompose the partial P_2 in three terms for the pairs $M_t^{II}M_t^{II}$, $M_t^{III}M_t^{III}$, $M_t^{II}M_t^{III}$ and the partial P_1 in two terms involving M_t^{II} and M_t^{III} , and so the statistical repartition hypothesis for M_t would be unnecessary, but the difference in scattering length between Fe (0.954×10^{-12} cm) and Ga (0.72×10^{-12} cm) is weak and the determinant of such a system becomes too small as verified.

Table 1
Mean scattering length \bar{b}_{M_t} , weight factors of partials P_1, P_2, P_3 for " $Pb_2 M_t^{II} M_t^{III} F_9$ " glasses

Pb ₂	M _t ^{II}	M _t ^{III}	F ₉	\bar{b}_{M_t} (10 ⁻¹² cm)	P_2 $1/\langle b \rangle^2 c_{M_t}^2 \bar{b}_{M_t}^2$ (× 10 ²)	P_1 $2/\langle b \rangle^2 c_{M_t} \bar{b}_{M_t}$	P_3 $1/\langle b \rangle^2$
	Mn	V		-0.207	0.398	-0.250	3.928
	Mn	Ga		0.174	0.225	0.168	3.154
	Mn	GaFe (6:4)		0.220	0.353	0.208	3.074
	Mn	Fe		0.291	0.591	0.265	2.961
	ZnMn (6:4)	Fe		0.573	1.993	0.452	2.563
	Zn	Fe		0.762	3.214	0.549	2.340

3. Results and discussion

The six total interference functions $S(Q) - 1 = [I_a(Q) - \langle b^2 \rangle] / \langle b^2 \rangle$ (preferred to $I(Q) - 1$ for a best graphical representation because of large variations on $\langle b^2 \rangle$) are shown in fig. 1 and the corresponding reduced atomic distribution function $G(R)$ in fig. 2. Both are presented from A to F in an increasing order of \bar{b}_{M_i} and show the expected systematic evolution of peaks in intensity but also in position. The first peak of $G(R)$ at 2 Å is unresolved because of the proximity of a second peak at 2.7 Å and the broadening effect of the modification function $M(Q)$. This first peak can be attributed unambiguously to pairs M_i -F and, as expected, its contribution is larger in the case of "Pb₂ZnFeF₉" and appears to be negative in the case of "Pb₂MnVF₉". The second peak is coherent with F-F distances but also with Pb-F ones previously determined by EXAFS; its intensity increase regularly with the weighting factor $1/\langle b^2 \rangle$ of the sum of partials P_3 . Between 3.5 and 6 Å, two peaks are seen of almost equal intensity for "Pb₂ZnFeF₉", the first of them decreasing with \bar{b}_{M_i} and the second simultaneously increasing so that the region between 3.5 and 4.5 Å can be attributed to pairs M_i -Pb, M_i -F or M_i - M_i and the region between 4.5 and 6.0 Å to the sum P_3 . For larger distances, variations are less pronounced and peak attribution is uncertain.

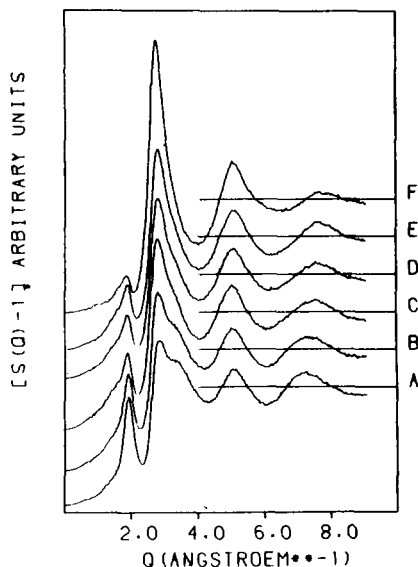


Fig. 1. Interference functions $S(Q) - 1$ for "Pb₂M_t^{II}M_t^{III}F₉" glasses with M_t^{II}M_t^{III} = ZnFe (A), Zn_{0.6}Mn_{0.4}Fe (B), MnFe (C), MnGa_{0.6}Fe_{0.4} (D), MnGa (E), MnV (F).

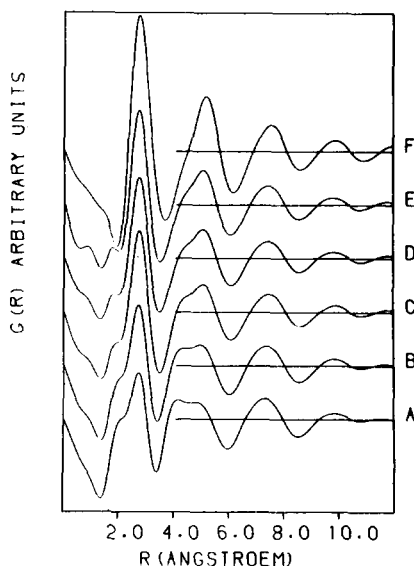


Fig. 2. Reduced atomic distribution function $G(R)$ for "Pb₂M_t^{II}M_t^{III}F₉" glasses with M_t^{II}M_t^{III} = ZnFe (A), Zn_{0.6}Mn_{0.4}Fe (B), MnFe (C), MnGa_{0.6}Fe_{0.4} (D), MnGa (E), MnV (F).

The partial reduced interference functions P_1 , P_2 , P_3 are shown in fig. 3 and the corresponding reduced atomic distribution in fig. 4. No constraint nor stabilization method has been applied in the resolution of the linear equations system (4) but it has been found necessary to realize a first separation with the three equations for which \bar{b}_{M_i} are the largest in order to obtain the more accurate partial P_2 (M_1-M_1). This is easily understood if we consider the weighting factors $W_{ij} = c_i c_j b_i b_j / \langle b \rangle^2$: the weight for M_1-M_1 is only 3.21% of the total in the "Pb₂ZnFeF₉" case and reduces to 0.23% in the most defavourable case of "Pb₂MnGaF₉" so the M_1-M_1 contribution is included in the error band consecutive to statistical noise and data treatment in the latter. The partial P_2 obtained in this way was smoothed and subtracted with the appropriate weight to the six equations; only partials P_1 and P_3 were then determined in a second solution of the system on the resulting equations. Of course, P_1 and P_3 for the first and second determination were compared and found almost identical but with less noise in the second case. Difficulties encountered to obtain the partial P_2 could be in some part the consequence of the above hypothesis (isomorphous substitution and statistical repartition for M_1) but results were in their favour: the unresolved peaks of the total reduced atomic distribution (fig. 2) appear very well separated on the three partials (fig. 4) and confirm the interpretation of the first four shells. The distances and coordination numbers (estimated with a mean value $\rho_0 = 0.0665$ atom/Å³)

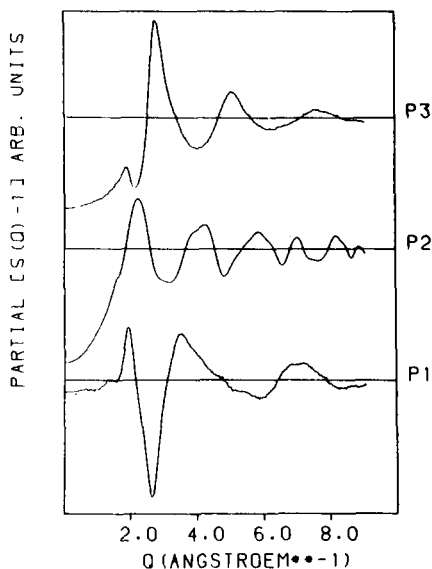


Fig. 3. Partial interference functions P_1 ($c_{Pb}b_{Pb} [I_{M_1Pb} - 1] + c_Fb_F [I_{M_1F} - 1]$), P_2 ($I_{M_1M_1} - 1$) and P_3 ($c_{Pb}^2b_{Pb}^2 [I_{PbPb} - 1] + c_F^2b_F^2 [I_{FF} - 1] + 2c_{Pb}c_Fb_{Pb}b_F [I_{PbF} - 1]$).

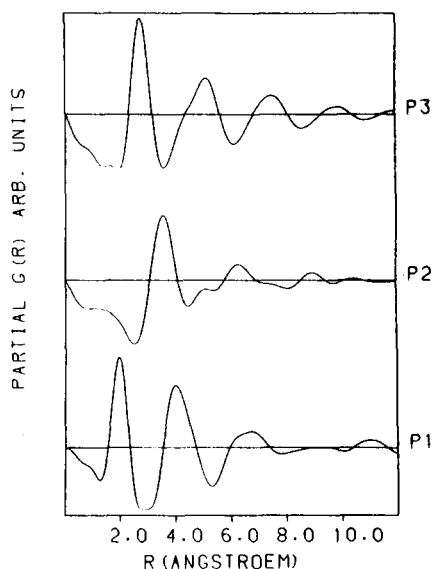


Fig. 4. Partial reduced atomic distribution functions P_1 ($0.145 G_{M_1Pb} + 0.922 G_{M_1F}$), P_2 ($G_{M_1M_1}$) and P_3 ($0.154 G_{FF} + 0.113 G_{PbF} + 0.021 G_{PbPb}$).

Table 2
Distances and coordination number for "Pb₂M_I^{II}M_I^{III}F₉" glasses

Partial	Pairs	Distances (Å)			Coordination numbers	
		This work	EXAFS	Magnetic correlations	This work	EXAFS
P_2	M_I-M_I	$\left\{ \begin{array}{l} 3.53 \\ 5.01 \\ 6.27 \\ 7.44 \end{array} \right.$	3.6 ± 0.1	3.62(AF)	3.0	
				5.08(F)	2.8	
				5.95(AF)	8.2	
				6.87(F)	8.6	
				8.21(AF)		
P_1	M_I-F	1.97	$\left\{ \begin{array}{l} 1.93 \text{ (Fe-F)} \\ 1.89 \text{ (Ga-F)} \\ 2.00 \text{ (Zn-F)} \\ 2.10 \text{ (Mn-F)} \end{array} \right.$		5.9 (M _I -F)	6 ± 1 (M _I -F)
						1.3 (F-M _I)
P_3	$\left. \begin{array}{l} M_I-F \\ M_I-Pb \end{array} \right\}$	4.01				
P_3	$\left. \begin{array}{l} (Pb-F, \\ F-F) \end{array} \right\}$	2.7	2.64 (Pb-F)		8.4	9 ± 2 (Pb-F)
	$\left. \begin{array}{l} (F-F, \\ Pb-F, \\ Pb-Pb) \end{array} \right\}$	$\left\{ \begin{array}{l} 4.20 \\ 5.11 \\ 7.51 \end{array} \right.$				

deduced of the three partials are given in table 2 together with previous EXAFS and neutron magnetic results.

For pairs M_I-M_I, the various results of table 2 are in well accordance but distances from magnetic correlations are certainly more accurate. The calculation of the mean value $\langle S_0 \cdot S_{R1} \rangle$ for first M_I-M_I neighbours is now possible by the ratio of $4\pi R^2 \rho(R) \langle S_0 \cdot S_R \rangle$ and $4\pi R^2 \rho(R)$, from respectively neutron magnetic measurements on "Pb₂MnFeF₉" glass and the M_I-M_I RDF (fig. 5), giving -0.5 which is to compare with -6.25 for perfect antiferromagnetic coupling between 5/2 spins. The curve $\langle S_0 \cdot S_R \rangle$ in fig. 6c was computed for a M_I-M_I RDF calculated with the same Q_{max} value (4.5 Å⁻¹) as for the magnetic RDF, it shows the negligible spin ordering of next nearest neighbours. The distance M_I-F of 1.97 Å agree with a mean value of EXAFS results and the M_I octahedral coordination is confirmed. The partial P₁ corresponds to 0.145 (I_{M_IPb} - 1) + 0.392 (I_{M_IF} - 1) so that the pairs M_IPb contribution is not negligible: the peak at 4.01 Å does not present large asymmetry and distance M_I-Pb is probably very close to that of a second fluorine shell for M_I. According to M_I-M_I distance, M_IF₆ octahedra are only corner-shared and a transition metal with three M_I neighbours at 3.6 Å would have twelve second fluorine neighbours near 4 Å. The first peak area of the partial P₃ gives 8.4 F-F neighbours if we use a coordination number of nine evaluated by EXAFS

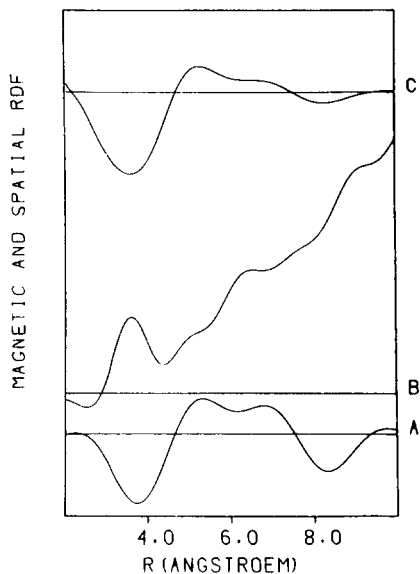


Fig. 5. Magnetic and spatial RDF for M_1-M_1 pairs. $4\pi R^2 \rho(R) \langle S_0 \cdot S_R \rangle$ (A); $4\pi R^2 \rho(R)$ (B); $\langle S_0 \cdot S_R \rangle$ (C).

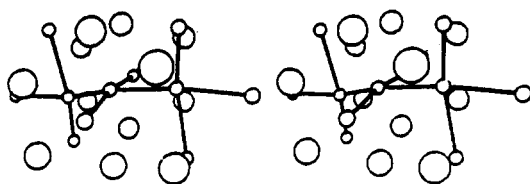


Fig. 6. Stereographic view of a possible model for M_1 and Pb^{2+} arrangement in " $Pb_2M_1^{II}M_1^{III}F_9$ " glasses.

for Pb-F; such a number is compatible with eight for a fluorine sharing two M_1F_6 octahedra or approximately nine for a fluorine sharing a PbF_9 polyhedra and an octahedra. The various contributions of P_3 are weighted as follows: $0.154 (I_{FF} - 1) + 0.113 (I_{PbF} - 1) + 0.021 (I_{PbPb} - 1)$ so that the Pb-Pb contribution is only 7.3% but the peaks of P_3 cannot be attributed unambiguously to one pair or another. Preliminary results of an X-ray diffraction study on these glasses, where Pb-Pb pairs largely dominate, give 4.2 Å for the Pb-Pb distance which corresponds well to the enhancement of the second peak of P_3 ; in fact, F-F or Pb-F distances could be also of this order on P_3 .

A glassy network model of distorted connected chains build up from corner sharing M_1F_6 octahedra, presenting some analogy with the ReO_3 type structure with half sites occupied, was proposed from the EXAFS and neutron magnetic studies [3-5]. Pb^{2+} was first thought to be in interstitial sites, this model can now be completed with the following considerations. For a composition

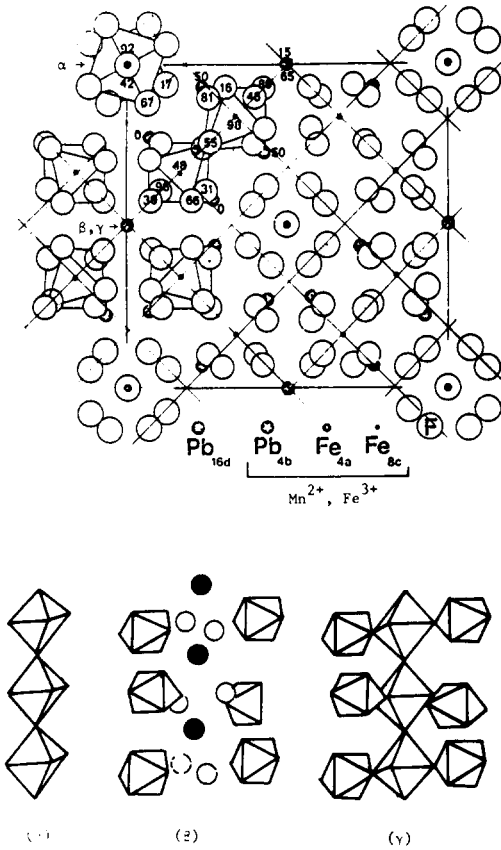


Fig. 7. $\text{Pb}_5\text{Fe}_3\text{F}_{19}$ structure ($\alpha + \gamma$ chains) and modification for BaFeF_5 type ($\alpha + \gamma$ chains)

$\text{Pb}_5\text{Fe}_3\text{F}_{19}$ close to the vitreous area limits, one can obtain a glass or a crystallized compound structurally closely related to BaFeF_5 [8]. Moreover, the main constituent appearing during a recrystallization process of glasses in all the vitreous domain has been identified as presenting fundamentally the same X-ray spectra as $\text{Pb}_5\text{Fe}_3\text{F}_{19}$ and a possibility of solid solution between M_i (M_i^{II} , M_i^{III}) is not excluded. If we consider the BaFeF_5 structure in an idealized point of view, $3/4$ of the Fe^{3+} are in an arrangement of corner shared octahedra occupying half the sites of the FeF_3 structure (ReO_3 -like); all the Ba^{2+} are situated on a site very close to that of F^- in FeF_3 so that Ba^{2+} and F^- form a face-centered cubic array $3/4$ occupied where $\text{Ba}-\text{Ba}$ direct contact is excluded. For their apparent simplicity (very few and well separated peaks) our partials P_1 and P_3 are compatible with such a model and also distances are coherent. Fig. 6 reproduces the previous model of M_i-M_i network and show how Pb^{2+} could be inserted; this model can be compared to the $\text{Pb}_5\text{Fe}_3\text{F}_{19}$ structure in fig. 7 (the BaFeF_5 type is obtained from $\text{Pb}_5\text{Fe}_3\text{F}_{19}$ by replacing

the Pb in 4b of β chains by Fe forming the γ chains) where Fe^{3+} have been joined to show the relation with the FeF_3 structure. The α chains are out of this description but, in our opinion, the isolated γ and α chains of BaFeF_3 must be interconnected and could not exist without defect on a large scale in glasses.

4. Conclusion

Lead transition metal fluoride glasses could be described in terms of relatively close packing of large ions F^- and Pb^{2+} excluding Pb–Pb direct contact with M_i inducing octahedral sites or in another way as a corner shared octahedral network with Pb^{2+} in interstitial sites. For the structural point of view, the common notion of “former” or “modifier” cannot be easily introduced here. The occurrence of disorder and the feasibility of these glasses is probably in large part the consequence of multiple possibilities for interconnecting octahedral chains and of some interchangeability between Pb^{2+} and F^- . A quasicrystalline modelisation is actually being performed in order to confirm the local order similitude in our glasses with fluoride compounds which crystallize near the vitreous domain.

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