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ACTUAL KNOWLEDGE OF 3d TRANSITION METAL FLUORIDE GLASSES STRUCTURE

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In 1978 MIRANDAY (1,2) prepared a new family of fluoride glasses characterized by their high content of 3d transition metal fluorides. We report here the actual conclusions of structural investigations by quantitative methods , coordination geometry and bond distances by E.X.A.F.S., neutron and X-ray diffraction . The study is restricted to three general formulations in ternary systems :

I - "$Pb_2M^{II}M^{III}F_9$"

II - "$A^{II}M^{II}M^{III}F_7$" with $A^{II} = Pb^{2+}, Ba^{2+}$

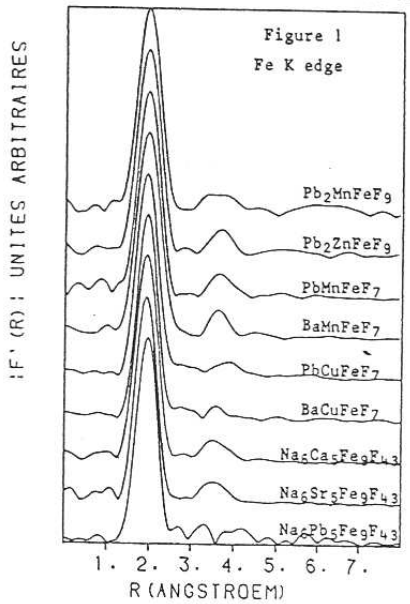
III - "$Na_6A_5{}^{II}M_9{}^{III}F_{43}$" with $A^{II} = Ca^{2+}, Sr^{2+}, Pb^{2+}$

$M^{II} = Mn^{2+}, Zn^{2+}, Cu^{2+}$ and $M^{III} = V^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}$.

E.X.A.F.S. (3)

In the glasses I,II and III, the Fe-F mean distance is found identical : 1.927±0.007 Å (mean of 9 samples, fig. 1). This holds also for the Ga-F distance :1.897±0.014 Å (8 samples). Typically, the accuracy on coordination numbers deduced from EXAFS is not good ; errors may be of about 20% or more in highly disordered systems. We obtain 6.0±1. and 5.5±1. respectively for Fe^{3+} and Ga^{3+} but the distances M-F are in very good agreement with those commonly observed for such cations octahedrally coordinated in fluoride crystallized compounds. For Zn^{2+} in glasses I and II, octahedral coordination is also established by the mean Zn-F distance (1.991±0.022 Å on 4 samples), very different from that found in crystallized $CaZnF_4$ for tetrahedral coordination (≃ 1.9 Å). The possibility of coordination higher than 6 is known for Mn^{2+}, in such a case the polyhedron is always distorted. In $MnCrF_5$, Mn^{2+} has 7 fluorine neighbours between 2.018 and 2.434 Å . By EXAFS, only the two nearest neighbours at 2.018 Å are evident and this is a classical result due to the high sensitivity of the method to large distribution of distances. On 8 samples of glasses I and II the mean Mn-F distance is 2.091±0.017 Å with

Fig. 1, 2 - Fourier transform of $k^3\chi(k)$ EXAFS modulations corrected for phase shift.



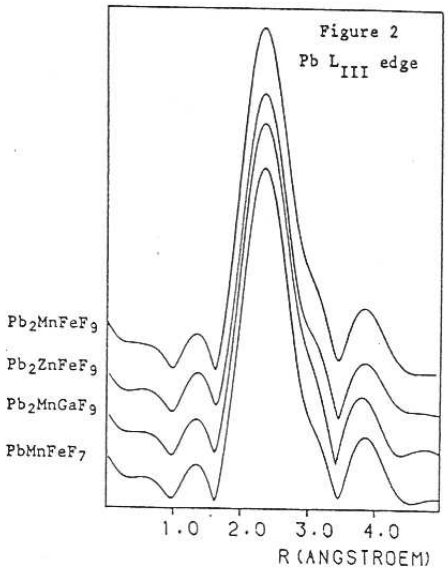


Fig. 3 - $4\pi R^2\rho(R) \langle \vec{S}_0 . \vec{S}_R \rangle$ for "$PbMnFeF_7$"(A), "Pb_2MnFeF_9"(B), "$Na_6Sr_5Fe_9F_{43}$"(C) (Qmax = 4.5 $Å^{-1}$).

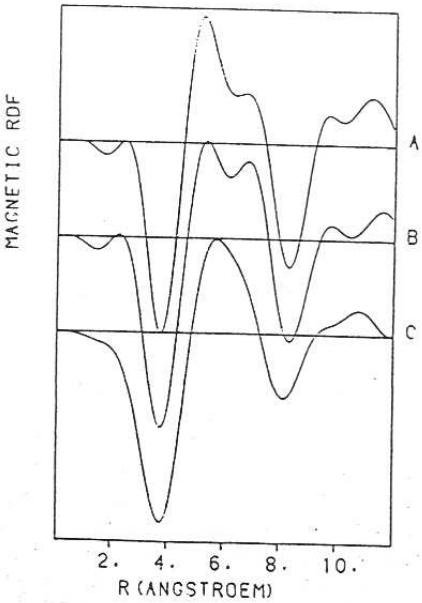
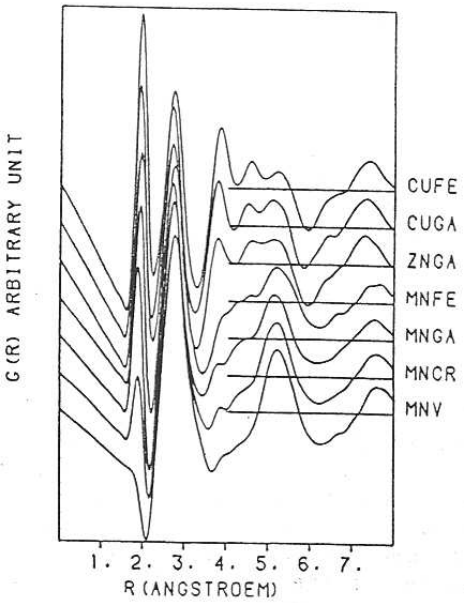


Fig. 4 - Reduced atomic distributions functions of "$PbM^{II}M^{III}F_7$" glasses (neutrons, Qmax = 22 A^{-1}).



N = 6.0±0.6 . This excludes the possibility of coordination higher than 6 in important proportions in glasses. Jahn-Teller effects are found in fluoride materials for Cu^{2+} and leads to an octahedral distortion (generally 4 short distances at ∼ 1.9 Å and 2 long at ∼ 2.26 Å . In glass II, the Cu-F distance is found at 1.906±0.008 Å (4 samples) in good agreement with such a distortion but the longer distances are not detected.

Pb^{2+} gives similar results in glass I and II . Distorted polyhedra are seen in crystallized materials like PbF_2-α and $Pb_5Fe_3F_{17}$. EXAFS gives an idea of the shortest Pb-F distances (2.32 Å). A special treatment with asymetrical distribution of distances was applied to the above reference compounds in order to calculate the true mean Pb-F distance. The same calculation gives 2.63 ± 0.01 Å for all glasses and a coordination number of the order of 9 (fig. 2). Ba^{2+} environment appears also distorted, EXAFS gives only the mean distance of closest neighbours (5 fluorines at 2.69 Å). of course the coordination is more probably larger than (or equal to) 8.

Second neighbours in the environment of cations contribute so weakly that no serious interpretation is possible.

Neutron Magnetic Diffraction (4, 5)

Some glasses containing Mn^{2+} and/or Fe^{3+} exhibit spin glass behaviour (6, 7). The pure magnetic scattering was isolated by substracting data recorded in the paramagnetic domain from those collected below (or near) the spin freezing temperature. The problem with such measurements is that exists an infinity of solutions. One of them is obtained with the hypothesis that there is no correlation between the magnetic moment direction and that of the interatomic vector. The data may then be Fourier transformed giving the magnetic correlation function. Results obtained in this way are very similar for glasses I, II and III (fig. 3) : the correlation is antiferromagnetic between first neighbours. The mean M-M distance (M = magnetic ion) is 3.6 ± 0.1 Å which is in good agreement with an hypothesis of corner linking between MF_6 octahedra.

Neutron Nuclear Diffraction (8)

With classical diffraction methods, the situation becomes very complicated because 10 partial pair correlation functions contribute to the RDF. For V-containing glasses the problem is reduced to 6 partials. The negative contribution of Mn allows the localization of Mn-F pairs. The 4 partials involving Fe^{3+} are separated with the hypothesis of isomorphous substitution between Fe^{3+} and V^{3+} (highly supported by the crystallochemical behaviour of these ions). Glasses I, II and III were all investigated using these above possibilities. The M-F distances and coordinations deduced from neutron data are in good agreement with EXAFS data . Figure 4 shows G(R) for glasses II based on Pb^{2+} following an increasing order of the M mean scattering length. A systematical evolution is observed which indicates structural organization remains basically the same for various substitution between M (essentially the same features are observed for Ba based glasses). The case of "$BaMnM^{III}F_7$" (M^{III}= Fe^{3+}, V^{3+}) is shown (fig. 5) as an illustration of the separation in two sets of contributions by the isomorphous substitution method. Owing to the fact that pairs involving F largely dominate in weight, the interpretation of the reduced atomic distribution of "$BaMnVF_7$" gives 5.9 F neighbours at 2.12 Å from Mn (first negative peak) ; the large positive peak at 2.75 Å is due predominantly to

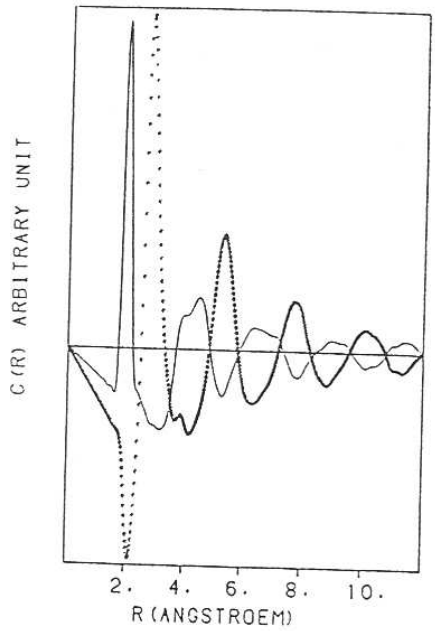


Fig. 5

The two contributions obtained from "$BaMnMF_7$" (M = Fe, V), weighted as : 86.3FeF + 11.4FeBa + 10.4FeFe - 8.1FeMn (——) ; 94.5FF + 25.1FBa - 17.8MnF - 2.4MnBa + 1.7BaBa + 0.8MnMn (∘∘∘) ; neglecting V Neutrons, Qmax = 22 $Å^{-1}$).

Fig. 6

Reduced atomic distributions functions of "Pb_2MnMF_9" glasses (M = Ga, V ; X-ray, Qmax = 7.8 $Å^{-1}$).

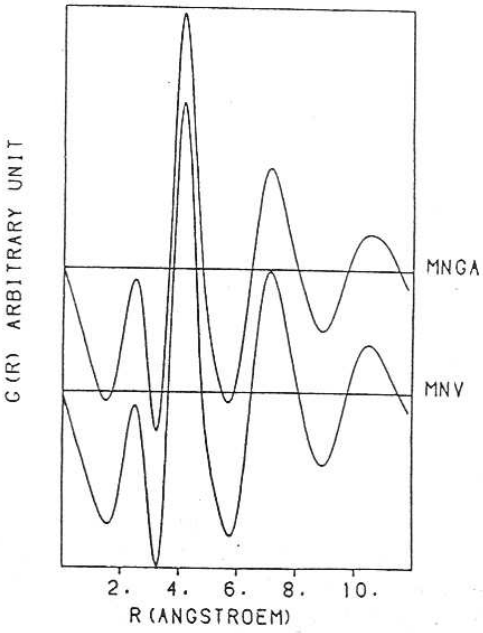
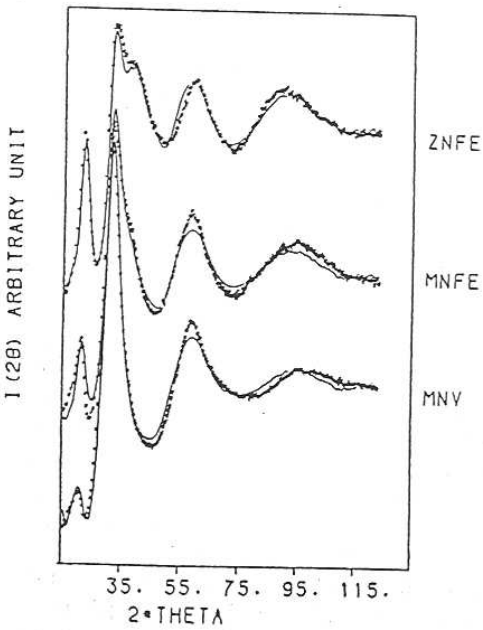


Fig. 7

Observed (∘∘∘) and simulated (——) interference functions of "$Pb_2M^{II}M^{III}F_9$" glasses (neutrons, λ = 1.22 Å).



F-F pairs but contains also Ba-F. The sum of the 4 partials involving Fe shows 6.1 F neighbours at 1.93 Å. The two overlapping peaks between 3.5 and 5 Å are coherent with the two sets of Fe-F distances expected for tilted corner sharing octahedra (3.90 and 4.45 Å in rhomboedral FeF_3 with Fe-F-Fe angle near 150°), but Fe-Ba pairs must also contribute in this domain.

X-Ray Diffraction (9)

Practically, this method gives almost only one additional information to the above results : an idea of the mean Pb-Pb distance in high containing Pb^{2+} glasses I. In fact, the most intense peak at 4.20 Å on the fig. 6 must contains also Pb-M and Pb-F contributions if one considers the weights (%) of the principal contributing pairs : 46 Pb-Pb, 20 Pb-M , 24 Pb-F (in "Pb_2MnVF_7" at Q = 8 A^{-1}).

Simulation of Diffraction Data (9)

The easiest way to test structural models for our rather complicated glasses was to proceed by quasi-crystalline simulation. For some glasses, crystalline materials are known with the same composition ($BaMnFeF_7$, $BaCuFeF_7$ for the type II) or with analogous ones (Ba_2CoFeF_7, $KPbCr_2F_7$, $NaBaFe_2F_7$, $BaFeF_5$, $Pb_5Fe_3F_{17}$ for the type I and III). A new method was constructed that allows the simulation of data in reciprocal space and allows the refinement of the atomic positions in the cell of the starting model.

For glasses I the best results are obtained with the structural model of $KPbCr_2F_7$. Fig. 7 shows the fit obtained simultaneously on neutron interference functions of 3 glasses with the same parameters (only changing the scattering length of M) assuming a statistical repartition of M . This result supports the hypothesis of a nearly isomorphous substitution of 3d cations. It was then possible to separate three sets of partials : (F-F + Pb-F + Pb-Pb) which is constant for the three glasses, (M-F + M-Pb) and (M-M). The weight of the last partial is only 3 % in the best case and contained large deviations but the two others show good agreement with the simulated data. The reduced atomic distribution functions are shown fig. 8 and 9. Reliability factors are respectively 11.1 and 22.7 % from 0 to 12 Å (simulation based on the $BaFeF_5$ structure gives significantly higher reliabilities : 22.8 and 29.0 %). In this model, MF_6 octahedra are only linked by corners ; F^- and Pb^{2+} are in a close packed arrangement (prohibiting Pb-Pb direct contact).

For glasses II a satisfying result is obtained for "$BaCuFeF_7$" using the model of crystallized $BaCuFeF_7$ (fig. 10). In this model, each MF_6 octahedron is linked to three others at corners and to another one by edge ; the F^- and Ba^{2+} are in a nearly hexagonal close packed . At this time, such an organization does not work for "$BaMnM^{III}F_7$" glasses (M^{III} = Fe^{3+}, V^{3+}). We are now testing the $BaMnFeF_7$ structure in which the occurence of edge sharing between octahedra is reduced.

Glasses III have not yet been simulated . Their composition is close to that of glasses I, so the $KPbCr_2F_7$ or $NaBaFe_2F_7$ models may accurately describe their behavior.

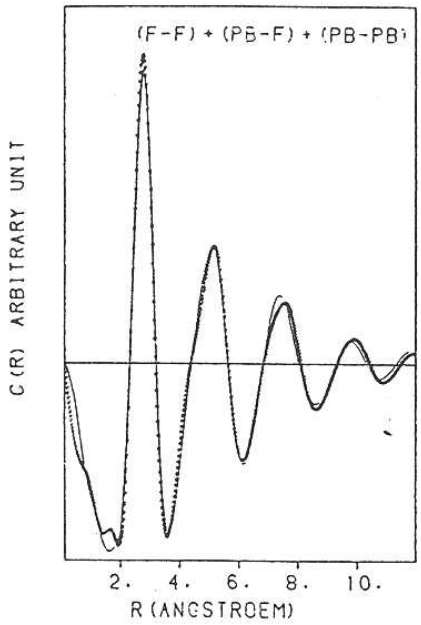


Fig. 8

Experimental (ooo) and simulated (——) partial reduced atomic distribution function of "$Pb_2M^{II}M^{III}F_9$" glasses weighted as : 53.5FF + 39.2PbF + 7.3PbPb (neutrons, Qmax = 9.2 $Å^{-1}$).

Fig. 9

id. fig. 8 - 73,0MF + 27.0 MPb.

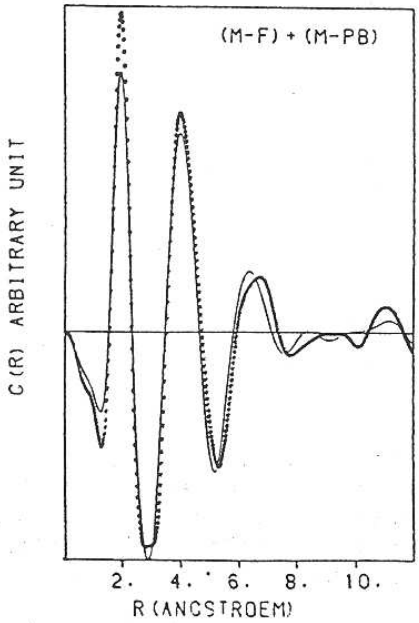
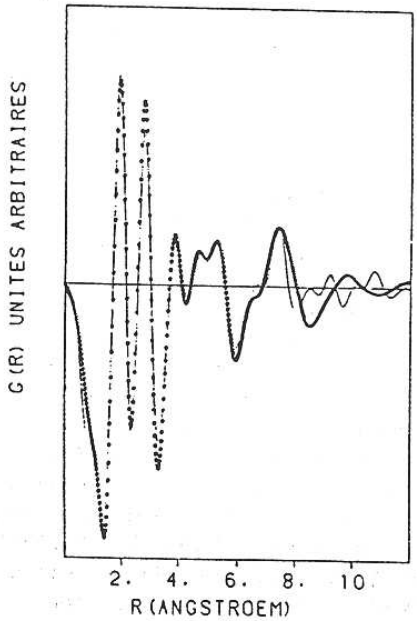


Fig. 10

Observed (ooo) and simulated (——) total reduced atomic distribution functions of "$BaCuFeF_7$" glass : modelisation starting from crystallized $BaCuFeF_7$.



CONCLUSION

MF_6 octahedra are the basic structural units of 3d transition metal fluoride glasses. They are predominantly linked by corners but the possibility of edge sharing is not excluded for the high M containing glasses II. Results of modelling show that locally the organization may be similar to that of some crystallized phases. Close packing between F^- and large cations induced by the vicinity of their ionic radii, with M in octahedral holes, may be the common denominator of glasses I, II and III. They could be also described by an octahedral random network with large cations in intersticial sites. The notion of former and modifier probably does not apply here in a structural sense.

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