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Reverse Monte Carlo and Rietveld modelling of the NaPbM$_2$F$_9$ (M = Fe, V) fluoride glass structures

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Abstract

Fluoride glasses with a nominal composition of NaPbM$_2$F$_9$ (M = Fe, V, assuming isomorphous replacement) have been structurally modelled through the simultaneous simulation of their neutron and X-ray diffraction patterns by a reverse Monte Carlo (RMC) model and by a Rietveld for disordered materials (RDM) method. Models and methods are discussed and compared. Models are consistent with an expected network of interconnected [MF$_6$] polyhedra. Those polyhedra are exclusively octahedral by the RDM method, and both trigonal prisms and octahedra, which are more or less distorted, by the RMC approach. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Glasses in the NaF/PbF$_2$/MF$_3$ systems with high content of 3d cations (M^{III} = Cr^{3+}, Fe^{3+}, V^{3+}, Ga^{3+}) were prepared first by Miranday et al. [1,2]. These 3d cations are well known for presenting exclusively a sixfold coordination in crystallized fluoride compounds. Optical absorption spectra early confirmed the [MF$_6$] octahedra presence in the glasses. EXAFS measurements suggested that M–F mean distances and polyhedra regularity were quite similar either in crystallized fluorides or in glasses [3]. There is little doubt that the transition metal fluoride glasses (TMFG) are structurally related to the fluoroaluminate ones (with AlF$_6$ octahedra) but they should not be

confused with the fluoroberyllates glasses (BeF$_4$ tetrahedra) or the heavy metal fluoride glasses (HMFG) like fluorozirconates [4] (with ZrF$_6$ to ZrF$_9$ possible polyhedra). Previous structural studies of TMFG, which represents now a quite large family of fluoride glasses, have concerned mainly the A^{II}F$_2$/M^{II}F$_2$/M^{III}F$_3$ systems (A^{II} = Ba^{2+}, Pb^{2+}; M^{II} = Mn^{2+}, Zn^{2+}, Cu^{2+}; M^{III} as above) by EXAFS [5], neutron magnetic and nuclear diffraction [6–8], Raman [9,10] and EPR [11–14]. Few structural modelling were undertaken, which is understandable because of the study of these multicomponent glasses which is a real challenge. However, modelling was first attempted by applying a Rietveld for disordered materials (RDMs) method on a series of Pb$_2$M^{II}M^{III}F$_9$ glasses [15], assuming isomorphous substitution for the transition metals (M^{II} = Mn/Zn and M^{III} = Fe/V), a practice relatively well accepted at least when 3d elements are concerned [16]. Isotopic

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substitution in TMFG is unfortunately hardly possible because one of the best 3d candidates (Ni) does not lead to wide glassy domains. The atom pair Fe/V is particularly convenient for isomorphous replacement in fluoride materials due to a large difference in the neutron scattering lengths ($0.954/-0.0382 \times 10^{-12}$ cm), and because crystal chemistry arguments (see below) well support this choice. Molecular dynamics (MD) simulation on amorphous fluoride samples (GaF_3 and $BaGaF_5$) prepared by chemical vapour deposition (CVD) was not found very convincing when the resulting X-ray distribution functions were compared with the observed ones [17]; MD studies on fluoroaluminate glasses were also published [18], leading in one case to 2/3 [AlF_6] octahedra and 1/3 [AlF_7] polyhedra, a hardly believable result regarding the usual sixfold coordination behaviour of aluminium in fluorides.

The aim of the present study is to perform the first application of the RMC method [19–22] to the octahedral network-based TMFG glasses, selecting the nominal $NaPbM_2F_9$ compositions (M = Fe, V). The results will be compared to those obtained by the RDM method (recently applied to glassy SiO_2 [23]).

2. Experimental

In order to apply the RDM method to glasses, one should dispose of crystalline-based starting models presenting the same composition or at least the same formulation as the material to be modelled. During the recrystallization study inside the vitreous domain in the systems NaF/PbF_2/MF_3 (M = Fe, V), one phase was identified with the $NaPbM_2F_9$ composition and its structure was determined ab initio [24] from powder diffraction data, in spite of the absence of suitable single crystal. The structure of $NaPbM_2F_9$ is built up from linear intercrossed chains of corner-linked [MF_6] octahedra. It is worth noting that some Na/Pb disorder was suggested to be present in this crystalline phase. Some years later, the structure of a polytype of $NaPbFe_2F_9$ was determined from single crystal data with a tripled cell parameter c: $KCaAl_2F_9$ disclosed together with two isotypical compounds $KCaFe_2F_9$ and $KCaV_2F_9$ [25]. The $KCaAl_2F_9$ crystal structure presented some anomalies and difficulties in refinements which were suggested to be due to possible microtwinning and/or defaults in the stacking sequence with parts presenting possibly the $NaPbFe_2F_9$ structure-type. On the other hand, a lot of other enneafluorides are known which present a highly flexible structure deriving from a common basis built up from isolated staircase double chains of [MF_6] octahedra differently oriented ($NaBaFe_2F_9$ [26], $KPbCr_2F_9$ [27], Ba_2ZnAlF_9 with Zn/Al disorder [28]). With neighbouring compositions, the $Ba_7CuFe_6F_{34}$ structure [29] belonging to the Jarlite types as well as the $BaTiF_5$ structure [30] were also considered as possible model candidates.

Owing to this abundance of crystal structures which could serve as starting models by using the RDM method, it was decided to study glasses having exactly the $NaPbM_2F_9$ composition. Glasses were prepared by melting the anhydrous fluoride mixtures in a dry box (inert atmosphere), then the melt, in a covered platinum crucible, were cast and rolled in a bronze mould heated at 200°C. Neutron data were recorded at ILL (Grenoble) on the D4 instrument for M = Fe and V ($\lambda = 0.703$ Å) [31]. X-ray data were recorded on a Siemens D500 diffractometer with Cu Kα radiation, normalized and rebuilt by interpolation as corresponding to $\lambda = 0.703$ Å for the modelling purposes.

The expected isomorphous replacement between Fe^{3+} and V^{3+} is well supported by the crystal chemistry in fluorides in general and in particular for the compounds listed in Table 1, most of these crystal structures being used in the present RDM modelling. As a rule, when a Fe^{3+}-based crystalline fluoride exists, the isostructural equivalent V^{3+} material can be prepared too, with generally no more than 1% variation in cell dimensions. The mean usual interatomic distances are 1.935 and 1.950 Å, respectively, for Fe–F and V–F bonds in octahedra. These considerations apply exclusively to fluoride compounds because Fe^{3+} and V^{3+} cations may present a quite different behaviour in oxides having a less pronounced ionic character than fluorides.

Table 1
Cell parameters comparison between some Fe- and V-based isostructural compounds

	a	b	c	α	β	γ	Ref.
FeF_3	5.196	5.196	13.33	90	90	120	[32]
VF_3	5.170	5.170	13.40	90	90	120	[32]
$NaPbFe_2F_9$	7.308	12.559	7.640	90	93.06	90	[24]
$NaPbV_2F_9$	7.274	12.570	7.628	90	92.63	90	This work
$NaBaFe_2F_9$	7.371	17.533	5.475	90	91.66	90	[26]
$NaBaV_2F_9$	7.372	17.555	5.491	90	91.60	90	[32]
$KCaFe_2F_9$	12.758	7.468	23.23	90	90	90	[25]
$KCaV_2F_9$	12.778	7.481	23.28	90	90	90	[25]
$BaFeF_5$	14.919	14.919	15.218	90	90	90	[32]
$BaVF_5$	14.97	14.97	15.06	90	90	90	[32]

3. Results of RMC modelling

The model consists of 1950 atoms in a cubic box (30.12 Å length for corresponding to the number density $\rho_0 = 0.07135$ as determined from the glass density). The initial positions were generated from a random filling of the box by the M atoms first, then the Na, the Pb and the F atoms were successively inserted. Positions at this filling stage were accepted, if minimal predefined interatomic distances were respected. Then, during the RMC simulation runs, distances (Å) of closest approach were applied too: $\Delta_{NaNa} = 3.15$, $\Delta_{NaPb} = 3.25$, $\Delta_{NaFe} = 3.05$, $\Delta_{NaF} = 2.05$, $\Delta_{PbPb} = 3.35$, $\Delta_{PbFe} = 3.25$, $\Delta_{PbF} = 2.15$, $\Delta_{FeFe} = 3.05$, $\Delta_{FeF} = 1.73$ and $\Delta_{FF} = 2.28$. The $[MF_6]$ coordination was constrained to occur with a maximum M–F distance equal to 2.15 Å. The neutron diffraction data of $NaPbM_2F_9$ (M = Fe, V) glasses and the X-ray data for M = Fe were simulated as $F(Q)$ data, the total coherent scattering functions (TSF)

$$F(Q) = [I_{coh}(Q) - \langle f^2 \rangle]/\langle f \rangle^2,$$

where the $\langle f^2 \rangle$ and $\langle f \rangle^2$ terms are the usual mean diffusion factors, depending on Q (X-ray) or not (neutron). About 16 million accepted moves were completed before the sixfold constraint was fulfilled, the last of the 300 octahedra was particularly long to be obtained. The whole process took 720 h CPU on a DEC-ALPHA AXP 4620.

The R factors calculated as $100 * \sum |I_{obs} - kI_{calc}| / \sum |I_{obs}|$ (%) (according to the definition $I(Q) = F(Q) + 1$, k being a scale factor) are 1.42%, 1.29% and 1.72%, respectively, for the Fe- and V-based neutron data and the Fe-based X-ray data. The observed and calculated $F(Q)$ curves are shown in Fig. 1.

4. Results of RDM modelling

Using the Rietveld method for glass modelling supposes that one accepts the idea that a selected crystal structure may represent a mean model for a glass. The disorder should be viewed as statistically introduced by microstrain effects leading to line broadening on the diffraction pattern. When testing a model by the RDM method, the data fitted become

$$S(2\theta) = I_{coh}(2\theta)/\langle f^2 \rangle.$$

The ideal situation is to start from a crystallized structure presenting exactly the glass composition. The cell volume may be adjusted for corresponding to the measured glass density. A preliminary test consists in looking at the starting agreement between observed and calculated $S(2\theta)$ selecting some standard line broadening parameters (they can be easily adjusted by hand) and refining the scale factors. In case of non-ideal composition, for instance modelling a $NaPbFe_2F_9$ glass starting from coordinates of $KCaAl_2F_9$, after cell adaptation, the best would be to refine first the F atom coordinates, expecting adjustment of Pb–F ($\sim$2.50 Å), Na–F ($\sim$2.35 Å) and Fe–F ($\sim$1.93 Å) distances replacing, respectively, the K–F ($\sim$2.80 Å), Ca–F ($\sim$2.40 Å) and Al–F ($\sim$1.81 Å) ones (one should try Pb/Na permutation too and also some statistical disorder). The next step, if some convergence
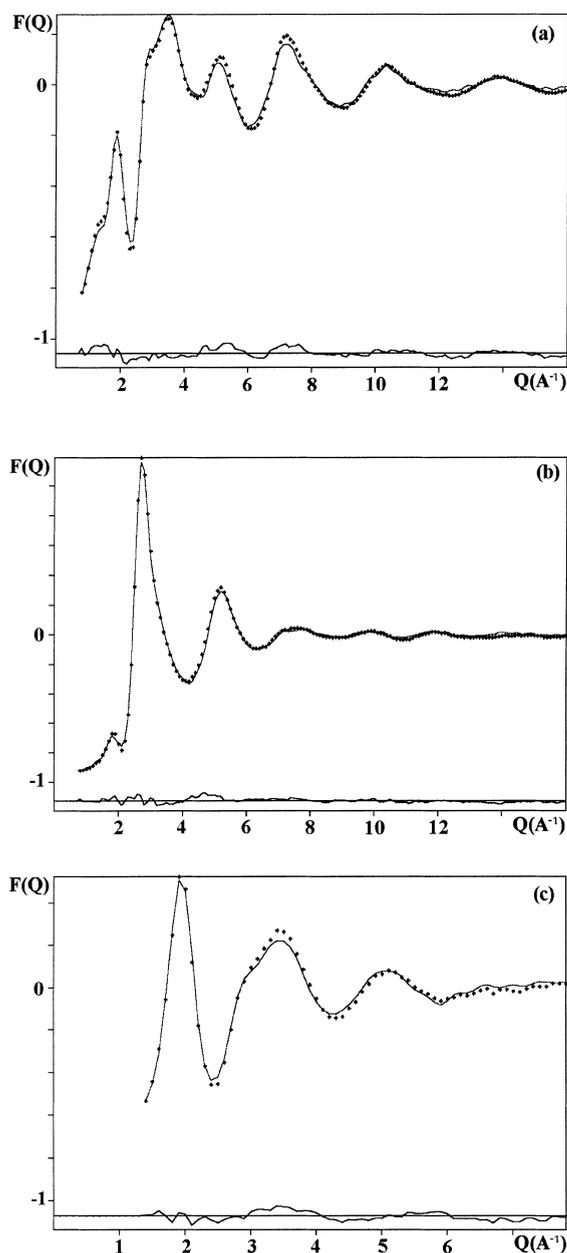
Fig. 1. Experimental (dots) and RMC simulated (solid line) TSF of NaPbM$_2$F$_9$: (a) neutron data for M = Fe, (b) neutron data for M = V, (c) X-ray data for M = Fe.

has been obtained, is to refine all atomic coordinates. This supposes that a maximum of independent diffraction data have been collected. The RDM software (program name: ARITVE) used in

this study is limited to 75 refinable coordinates. Testing a model with this complexity would require the largest possible number of oscillations on diffraction data, say at least a total of 25 bumps which could correspond to three independent structure factors, each of them exhibiting eight or nine oscillations. Finally, the line-broadening parameters could be refined and even the cell parameters. The process converges, or does not, with agreement factors specific to the models.

Depending on the initial model tested, these strategies were applied for modelling the title materials. Usually, both the neutron patterns with M = Fe and V were fitted first simultaneously up to some agreement (in the range 4–120°(2θ)). Then the X-ray data were added and it was generally observed that the previous agreement factor R on the neutron data increased before reaching a new equilibrium value, whereas the X-ray R factor decreased. In the present case, the X-ray data are highly dependent on atom pairs involving the Pb atom (mainly Pb–F and Pb–Pb pairs) whereas the F–F contribution is dominant for both neutron data together with the Fe–F contribution for NaPbFe$_2$F$_9$. The contribution of the four partial structure factors involving the V atom (V–Na, V–Pb, V–V and V–F) is almost negligible on the NaPbV$_2$F$_9$ neutron data, explaining the large differences in the two neutron TSF. Calculations by the RDM method were on a PC Pentium 100 MHz, each model needed a few hours for being completed. At the stage of fitting the two neutron datasets only (M = Fe, V), it was concluded that most of the models were able to provide R factors smaller than 2% or 3% (Table 2), as low as the RMC ones, even lower in a few cases. However, adding the X-ray data made a difference between the RDM models with an advantage to those deriving from the crystalline forms of NaPbFe$_2$F$_9$ and KCaAl$_2$F$_9$ followed by the KPbCr$_2$F$_9$ and NaBaFe$_2$F$_9$ models. With a non-exact composition, the Ba$_7$CuFe$_6$F$_{34}$ and BaTiF$_5$ models are not to be considered seriously but were able to produce fits of the experimental data as well as the two previous models, whereas the Ba$_2$ZnAlF$_9$ model gives a distinctly worst fit. In the early study of Pb$_2$M^{II}M^{III}F$_9$ glasses by the RDM method [15], the KPbCr$_2$F$_9$ model was retained as the best,

Table 2
Results from the RDM fits[a]

Model [Ref]	R (%) N only	R (%) N and RX	Number of x, y, z parameters	Reflections number	Cell volume and ρ_0	Z
$NaPbFe_2F_9$ [24]	1.87	2.00 Fe (N)	14	7484	707.5	4
	2.21	2.43 V (N)		7484	0.07350	
		5.07 Fe (RX)		1002		
$KCaAl_2F_9$ [25]	1.31	2.44	57	11878	2098.4	12
	1.86	1.97		11878	0.07434	
		5.22		1685		
$KPbCr_2F_9$ [27]	1.53	2.09	23	7745	698.2	4
	1.78	2.56		7745	0.07448	
		5.54		1086		
$NaBaFe_2F_9$ [26]	1.12	2.79	39	15721	732.6	4
	1.11	2.79		15721	0.07098	
		5.53		2104		
Ba_2ZnAlF_9 [28]	2.45	4.13	23	8045	728.0	4
	2.18	4.14		8045	0.07143	
		7.69		1122		
$BaTiF_5$ [30]	1.40	1.68	27	8376	1527.7	16
	2.18	2.20		8376	0.07331	
		5.10		1166		
$Ba_7CuFe_6F_{34}$ [29]	1.13	2.58	37	15825	1456.2	2
	1.24	2.87		15825	0.06592	
		5.51		2170		

[a] Reliabilities on $S(2\theta)$ are defined as $R = 100 * \sum |S_{obs} - kS_{calc}| / \sum |S_{obs}|(\%)$ in the ranges 4–120°(2θ) (neutron data) and 8–52°(2θ) (X-ray). The observed number density is $\rho_0 = 0.07135$.

however most of the crystalline structures tested in the present study were unknown at this date. The best model as suggested by RDM is considered to be that derived from the crystallized $NaPbFe_2F_9$ phase because of the lowest R factors obtained with the lowest number of x, y, z refined parameters, although the calculated density is 3% too high (Table 2). The observed and calculated $S(Q)$ curves are shown in Fig. 2. A view of the tridimensional octahedral network is shown in Fig. 3. The starting and RDM-refined atomic coordinates are gathered in Table 3.

5. Discussion

5.1. Solid state chemistry considerations on models

At first glance, the RMC model does not present two identical polyhedra and the [MF_6]

(M = Fe, V) polyhedral chains are zigzagging with *trans* or *cis* connections. A few rings with 3, 4, 5 or 6 [MF_6] polyhedra sharing corners have been built up by the Monte Carlo process and 92 of the 300 [MF_6] units share at least one edge with another such unit (12 of them share 2 edges and 2 share 3 edges). It should be kept in mind that the RMC constraint to have [MF_6] polyhedra should not have necessarily led to regular octahedra. A model built up from [MF_6] trigonal prisms (unknown for Fe^{3+} and V^{3+} in fluorides) could have been proposed by the RMC method as well. Indeed, a large majority of more or less distorted octahedra have been built but a few trigonal prisms (TP) have occurred (Fig. 4). A visual examination of each of the 300 [MF_6] entities by a three-dimensional capable virtual reality modelling language (VRML) viewer, allows to estimate that 20 of them are near of TP, 25 are quite irregular polyhedra (intermediate between TP and octahedra), the rest being
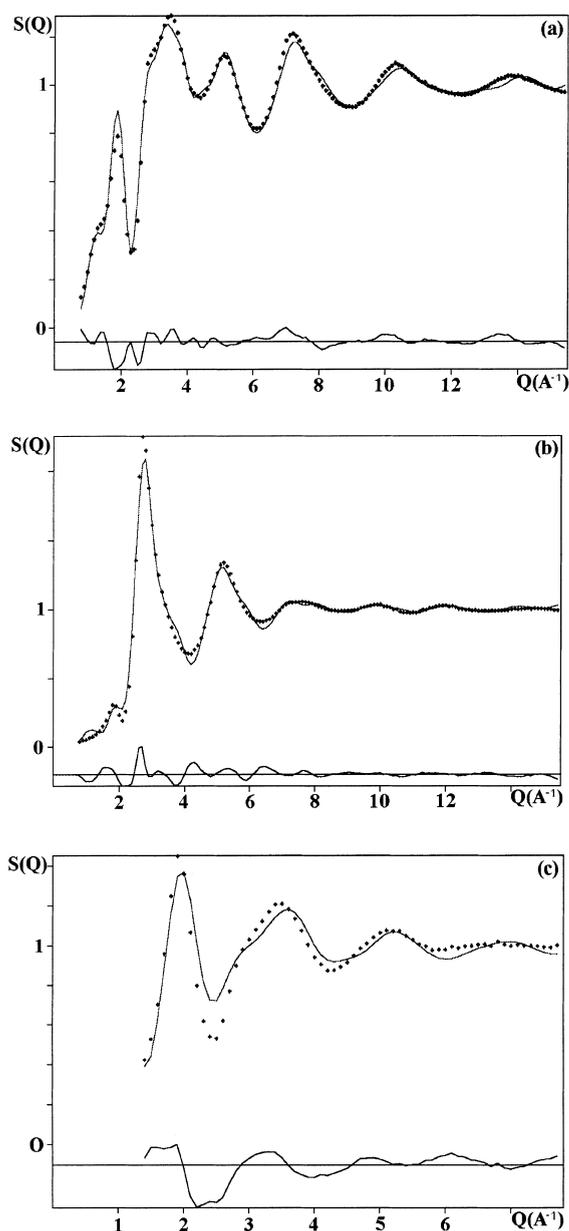
Fig. 2. Experimental (dots) and RDM simulated (solid line) TSF of $NaPbM_2F_9$: (a) neutron data for M = Fe, (b) neutron data for M = V, (c) X-ray data for M = Fe. Model based on the $NaPbFe_2F_9$ crystal structure.

acceptable more or less distorted octahedra (very few being really regular). The way octahedra are linked in the RMC model is dominantly by corners. In fact among fluoride crystal structures with

formulation $A_2M_2F_9$, none present any established $[MF_6]$ octahedra edge sharing. However, edge sharing occurs as a fraction of the octahedra interlinks in crystallized compounds as $BaZnFeF_7$ [33], $BaCuFeF_7$ [34] or $BaMnFeF_7$ [35] (with larger 3d-cation/F ratio) and also $BaTiF_5$ [30] (with smaller ratio); it is thus admittable that edge sharing could occur in the title glasses. Rings delimited by F–F edges with 3, 4, 5 and 6 octahedra sharing corners are the only known in 3d transition metal fluoride crystal chemistry. One can find some of them in the RMC model but zigzagging chains are the main arrangement. A strange cluster of five edge sharing octahedra has been built (Fig. 5) which is really unknown for 3+ charged 3d cations in fluorides which show only binuclear edge sharing, whereas a trinuclear unit has been described for Cu^{2+} in $Ba_6Cu_{11}F_{34}$ [36]. The counterpart of such a denser zone is that five isolated octahedra exist in the RMC model.

The Na and Pb coordinations are much less restricted than the Fe and V ones in fluorides with, respectively, 6–9 and 7–12 possible fluorine neighbours, with various possible polyhedra shapes for each coordination, regular or not. Thus, there could not have been any constraint on the Na–F and Pb–F atom pairs. Table 4 gives the details of the Na–F, Pb–F and Fe–Fe statistics of neighbours for the RMC and first RDM models.

The RDM best model is of course consistent with crystal chemistry. The $[MF_6]$ polyhedra, which are all octahedra contrarily to the RMC model, present the expected mean M–F distance and are not excessively distorted (Fig. 4). If we accept the idea that obtaining low R discrepancy factors by RDM fits could indicate that the glass may present locally a distorted, but analogous, arrangement as in the crystalline model, then we should conclude that several such different models may be present in the glass because similar fits have been obtained with quite different models. Models from RMC and Rietveld studies present similitudes in the sense that one observes predominantly chains of $[MF_6]$ octahedra sharing corners. The Rietveld models are limited by the existence of only two or three different types of crystallographically independent octahedra. It is amazing to observe the agreement quality on the
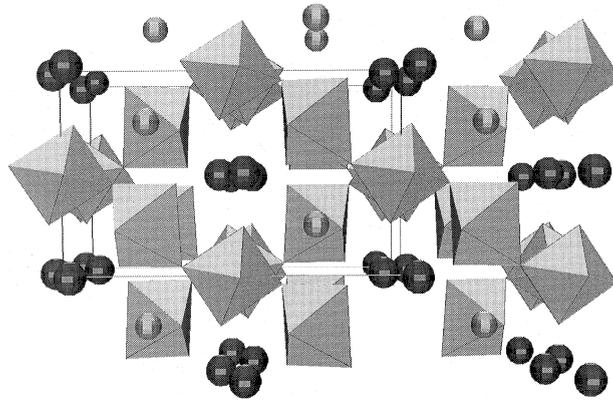
Fig. 3. Projection along the c-axis of the RDM refined model for the $NaPbM_2F_9$ glasses (M = Fe, V). The starting model is that of the $NaPbFe_2F_9$ crystal structure. The M atoms in $[MF_6]$ octahedra are at $z = 0$ or $1/2$, Na atoms are shown as spheres alternating along c with some $[MF_6]$ octahedra (at $z = 0$ or $1/2$). Pb atoms are shown as spheres at the corners and centre of the cell (at $z = 1/4$ and $3/4$).

Table 3
Atomic coordinates corresponding to the best RDM model[a]

Atom	Site	x		y		z	
Na	4c	1/4	(1/4)	1/4	(1/4)	0	(0)
Pb	4e	0	(0)	0.044	(0.027)	1/4	(1/4)
Fe/V(1)	4d	1/4	(1/4)	1/4	(1/4)	1/2	(1/2)
Fe/V(2)	4b	0	(0)	1/2	(1/2)	0	(0)
F(1)	8f	0.257	(0.256)	0.033	(0.041)	0.947	(0.976)
F(2)	8f	0.227	(0.207)	0.169	(0.194)	0.304	(0.280)
F(3)	8f	0.046	(0.082)	0.160	(0.153)	0.576	(0.578)
F(4)	8f	0.045	(0.039)	0.353	(0.345)	0.458	(0.463)
F(5)	4e	0	(0)	0.532	(0.527)	1/4	(1/4)

[a] In parentheses are the original starting coordinates [24] from the $NaPbFe_2F_9$ crystal structure. Space group C2/c: a = 7.442 (7.308) Å, b = 12.553 (12.559) Å, c = 7.621 (7.640) Å, β = 96.44 (93.06)°, V = 707.5 (700.2) Å^3.

neutron data associated to such small box volumes (see Table 2).

5.2. Comparing RMC and RDM methods

One can think about what would happen if the ten partial structure factors had been experimentally available. It is not possible to assert that the actual models proposed by either the RMC or the RDM methods would lead necessarily to low R factors on the lacking structure factors without any adjustment. Fitting without the X-ray data by the RDM method has clearly shown that the less the data, the best the fit and the less the model is reliable. The RMC final result produces a closest approach to the three datasets than the RDM which has difficulties to model the X-ray

data. There are large differences in model size and consequently in the number of free parameters in the two methods. Obtaining the quality of the fits as shown on Fig. 2 by the Rietveld refinement of only 14 atomic coordinate parameters may be considered as convincing that the model reflects some local reality in the glass, owing to the fact that the glass truly recrystallizes into it. The first Rietveld method application to glass structure modelling [15] was published 12 years ago, well before the first RMC one [19]. Both methods are based on models using periodic boundary conditions (leading thus to some sort of 'triperiodic glasses'). The model for the RMC method is usually described with the P1 space group and the cell is large otherwise no acceptable fit can be expected. The model for the RDM method has to
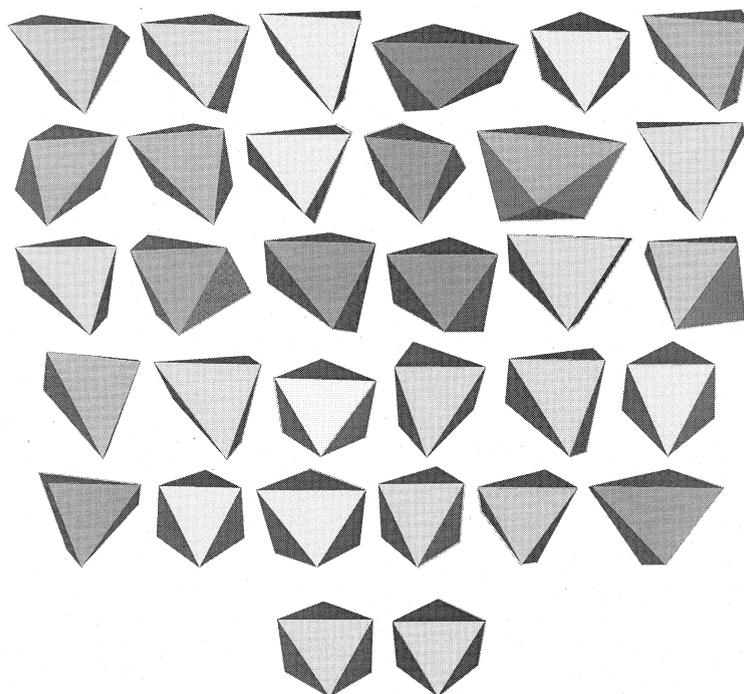
Fig. 4. Selected [MF$_6$] polyhedra. Some (10%) of the most regular octahedra and trigonal prisms are shown together with the most irregular ones built by the RMC process. At the bottom are the two different (but almost regular) [MF$_6$] octahedra of the RDM model derived from the NaPbFe$_2$F$_9$ crystal structure.
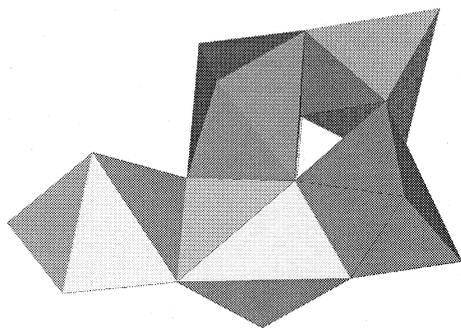
Fig. 5. A cluster of five [MF$_6$] polyhedra linked by edges as found in the RMC model.

be generally much smaller in volume and can use space groups with any symmetry. A powder diffraction pattern from the RMC result could be calculated exactly in the same way as by the RDM method. The problem is to build a special program for the simulation of powder patterns in case of P1 space group with cell parameters of

30 Å or more. The reflection number for Q up to 25 Å^{-1} would be probably larger than 10^6. There is no serious difficulty to code a program doing that, but this was not realized in the present study (30 000 reflections maximum are allowed per pattern in the present RDM ARITVE software [37]).

cIs it possible to take the best RDM model and to build a starting RMC model with it, extending the size by doubling (or more) the cell dimensions? In the present case, and even if the sixfold constraint is maintained, the response is yes. A demonstration reconciling RMC and RDM methods is to be published elsewhere [38] by using three very different examples, previously modelled by both RMC and RDM methods (glassy SiO$_2$ [23] and ZnCl$_2$ [39] and the title compound).

It cannot be excluded that two different users may obtain different results trying to model the same glass from the same data. By the RMC

Table 4
Neighbours (N) statistics of Na–F, Pb–F and Fe–Fe pairs as obtained by RMC and RDM methods

N	Na–F		Pb–F		Fe–Fe	
	RMC	RDM	RMC	RDM	RMC	RDM
0					5	
1					10	
2					54	4
3					96	
4	1				88	4
5	7				38	
6	17		2		8	
7	39		16		1	
8	42	4	38			
9	30		38			
10	12		42	4		
11	2		12			
12			2			
Total	150	4	150	4	300	8
Cutoff (Å)	3.2	3.2	3.50	3.50	4.30	4.30
Average N	7.75	8	8.97	10	3.44	3

method, various strategies are possible for building the starting model but generally a random number generator is used. Thus, it is excluded that two starting configurations could be identical so that the final results will never be exactly the same. By the RDM method, it is easy to reduce to various false minima by using different strategies (in fact, even the 'best' final results presented here are to be considered as the lowest false minima I have found).

At the present stage, both RMC and RDM methods, and probably others, are able to fit satisfactorily the neutron and X-ray data. But we are still not very sure that the corresponding models really represent possible local arrangements for the glass. In the present study, full data would have consisted in 10 partial structure factors and we had only three really independent ones. This study is thus highly contestable. Are we more happy with a ∼2000 atoms model by RMC modelling than with a 50 or 150 atoms model of which 9 or 20 only are really crystallographically independent by the RDM method? Well, the truth is that the modeller may be embarrassed with both of them. All that can be concluded is that both are quite different but fit as well (an advantage has to be given to the RMC method which usually is able to fit per-

fectly); this should discredit all further attempts of modelling glass structures but in fact this simply reflects the impossibility to propose a unique model for a material by definition built up from much more different configurations than we could reasonably introduce. If a large number of these arrangements lead to quite similar short and medium range order, then testing some of them will produce relatively good fits. It was emphasized in the RDM study of glassy SiO_2 [23] that reliability factors R_I which may seem low (1–2%) when estimated from the $I(Q) = [F(Q) + 1]$ data, may become less satisfying when estimated from the $F(Q)$ data which oscillate around zero. For the present study, the RMC R_F values drop to 11.1%, 7.3% and 13.6%, whereas the RDM best model gives 14.1%, 12.9% and 43.9%, respectively, for the Fe and V-based neutron data and Fe-based X-ray data. From such values it is clear that modelling has progress to make, requiring accuracy better than 1% on the experimental data. Such accuracy was certainly not attained for the X-ray pattern, much more difficult to normalize than neutrons patterns. It has to be noted that the neutron patterns, in addition to the usual data reduction, were corrected for paramagnetism as a consequence of the Fe^{3+} and V^{3+} presence in the glasses.

6. Conclusion

From this study, expectations for a unique structure representation for the $NaPbM_2F_9$ (M = Fe, V) fluoride glasses from the RDM or RMC methods are disappointed. Several models which may seem very different to a crystallographer's eyes have led by the RDM method to similar diffraction data fits because they are in fact characterized by similar mean short and medium range orders. The RMC model may be considered as combining the various special arrangements (plus others) characterizing the crystalline-derived models tested by the RDM method. A tridimensional network built up from corner sharing $[MF_6]$ octahedra was expected from crystal chemistry considerations before to start the study. Such a network characterizes the $NaPbFe_2F_9$ crystal structure which is quite different from that of $KPbCr_2F_9$ and of the other related enneafluorides having a mono-dimensional character drawn by infinite isolated staircase double chains of corner sharing octahedra. In fact, RDM as well as RMC results tend to show that locally the $KPbCr_2F_9$ configuration cannot be ruled out. The contrast between the 1950×3 free atomic coordinates implicit in the RMC model and the 14 coordinates refined by the RDM method for the $NaPbFe_2F_9$ crystalline structure-derived model is not reflected by a proportionally large difference in fit quality (though the effective number of free parameters by the RMC method is much less than 5850, due to constraints on interatomic distances together with the fixed density). This suggests that the RDM method could be improved maybe by the introduction of constraints on interatomic distances and of a Monte Carlo process which would allow one to describe small cells in the $P1$ space group. With such a modification, the 14 parameters of the model designed here as the best would extend to 52×3 by a method combining RMC and RDM, leading very probably to some R factor improvement. On the other hand, the presence of $[MF_6]$ trigonal prisms in the RMC result is theoretically nonsense regarding fluoride crystal chemistry, but can we really exclude their presence in glass structures? A new RMC modelling with a more drastic constraint in order to build exclusively octahedra should be undertaken. Application of RMC and RDM methods to TMFG fluoride glasses even more concentrated in $[MF_6]$ octahedra is in preparation for the selected typical compositions $BaMnMF_7$ and $PbMnMF_7$ (M = Fe, V) (66% of the cations in sixfold coordination against 50% in the title glasses). More edge sharing is to be expected in these glasses as suggested by the corresponding crystal structures in which up to 50–100% octahedra share at least one edge with another octahedron.

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