

Combining the Reverse Monte Carlo and the Rietveld Glass Structure Modelling Methods

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Abstract The Reverse Monte Carlo (RMC) method involves usually at least one thousand atoms, and modelling may start from random atomic positions. The Rietveld for disordered material (RDM) method needs a crystal structure as a starting mean model, with hardly more than 25 independent atoms. The two methods are reconciled when a satisfying RDM model, enlarged by multiplying the cell axes, is subjected to random moves by the RMC method. Three examples are presented : glassy SiO_2 , ZnCl_2 and NaPbM_2F_9 ($M = \text{Fe}, \text{V}$). Coordinations were constrained (SiO_4 and ZnCl_4 tetrahedra ; MF_6 octahedra), so that the final RMC models keep essentially the crystal structure features of the RDM starting models, being the phases in which devitrify the glasses, in all cases.

1. Introduction

The Reverse Monte Carlo [1] method (RMC) is now widely used [2] for structural modelling. RMC produces glass structure models tending to the very best fit of diffraction data, almost in a systematical way. The composition and density are required, minimal/maximal interatomic distances should be known, and coordination numbers are welcome when dealing with network glasses. Model size involves at least 1000 atoms. Modelling may start from random atomic positions. In case of network glasses, the building of a model satisfying the coordination constraint requirements (for instance, a 4-connected three-dimensional network for SiO_2 or ZnCl_2) may become tedious and require a final by-hand intervention. The models tend to present non-requested features such as tetrahedra edge sharing, pending oxygen atoms, exception to the expected coordination. On the other hand, the Rietveld for disordered material [3] method (RDM) needs a crystal structure as a starting mean model, so that the coordination constraints are respected *ab initio*. Glasses or nanocrystalline material diffraction data are fitted using microstrain effects on line broadening. Model size involves less than 25 independent atoms of which the coordinates are refined.

How to reconcile both methods, that lead to quite different models, is the aim of the present paper. Is examined the behaviour of RDM models, enlarged to nearly one thousand atoms or more (by multiplying the cell edges), and submitted to random moves by the RMC method. Three examples are presented : glassy SiO_2 , ZnCl_2 and NaPbM_2F_9 ($M = \text{Fe}, \text{V}$), all previously submitted to RMC [4-6] and RDM [3,7,6, respectively] modelling, but not simultaneously to both methods.

2. Methodology and results

Both RMC and RDM methods are based on models using periodic boundary conditions (leading thus implicitly to some sort of "three-periodic glasses"). The model for the RMC method is usually described with the P1 space group and the cell (generally a cube) is large,

otherwise no acceptable fit can be expected. The model for the RDM method has generally to be 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 covering an interference function with a maximum value of Q up to 25 Å⁻¹ would be probably larger than 10⁶ ("only" 60000 reflections maximum are allowed per pattern in the present RDM ARITVE software [8]).

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, or a nanocrystalline material. The disorder is statistically introduced by microstrain effect, leading to strong line broadening on the diffraction pattern. If the mean RDM small models were physically sound, then they should be able to represent good starting configurations for RMC modelling, that would really introduce locally the disorder treated statistically in RDM modelling. It was thus decided to enlarge some previously established RDM models, so as to build starting RMC configurations to be tested. In all cases presented hereafter, some initial coordinations were constrained during the Monte Carlo process (SiO₄ and ZnCl₄ tetrahedra; MF₆ octahedra), so that the final RMC models were obtained from small random atom moves, keeping essentially the crystal structure features of the RDM starting models. Table 1 summarizes the test conditions. With the RMC method, the neutron and X-ray data were simulated as F(Q) data, the total coherent scattering functions (TSF) $F(Q) = [I_{\text{coh}}(Q) - \langle f^2 \rangle] / \langle f \rangle^2$, 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). In order to characterize the fit quality, a reliability Rp factor was calculated as $100 * \sum |I_{\text{obs}} - kI_{\text{calc}}| / \sum |I_{\text{obs}}|$ (%) (according to the definition $I(Q) = F(Q) + 1$, k being a scale factor). The RDM final models were selected among many possibilities [3, 6, 7] as those providing the best Rp reliability factor. Testing a model by the RDM method, the data fitted become : $S(2\theta) = I_{\text{coh}}(2\theta) / \langle f^2 \rangle$. The Rp values obtained for the previous RDM and RMC (starting from random configurations) models and those corresponding to the present study (RMC starting from the enlarged RDM models) are compared in Table 2.

Table 1

Conditions for building the RMC models from the RDM ones

	ZnCl ₂	SiO ₂	NaPbM ₂ F ₉
Initial RDM model	δ-ZnCl ₂ [9]	carnegieite [10]	NaPbFe ₂ F ₉ [11]
Axes enlarged	ax6, bx4, cx6	ax4, bx4, cx4	ax3, bx2, cx3
Total atom number in RMC modelling	1728	1536	936
RMC constraints	[ZnCl ₄]	[SiO ₄]	[MF ₆]

Table 2Final reliabilities R_p (%). N = neutron, X = X-ray ; M = Fe, V.

	ZnCl ₂	SiO ₂	NaPbM ₂ F ₉
RDM	2.40 (N)	2.45 (N) 2.37 (X)	2.00 (N, Fe) 2.45 (N, V) 5.07 (X, Fe)
RMC - random	0.76 (N)	unavailable, see Ref. [4]	0.77 (N, Fe) 1.00 (N, V) 1.14 (X, Fe)
RMC from RDM starting models	1.09 (N)	1.48 (N) 2.00 (N)	0.81 (N, Fe) 1.22 (N, V) 1.75 (X, Fe)

ZnCl₂ - A RMC study of glassy ZnCl₂ has already been published [5]. We used the same neutron data [12] as in this previous work. Because in this early study, the model was small (324 atoms), a much larger one was built here with 1950 atoms in a cubic box with $L = 39.906 \text{ \AA}$. Strategy is quite important when using RMC, and the normal way for imposing a 4-

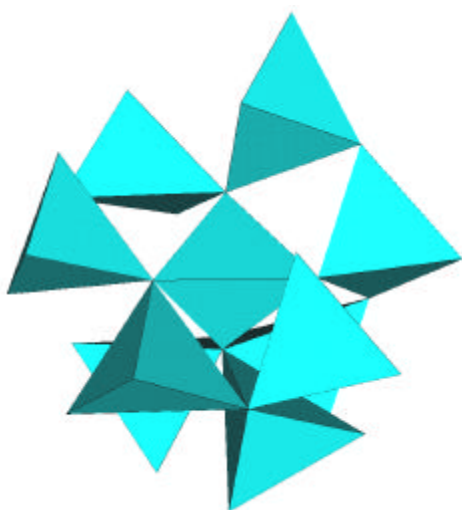


Fig. 1. A central [ZnCl₄] tetrahedra sharing Cl atoms with 9 other tetrahedra : the biggest cluster built up by the "classic" RMC approach, without [ClZn₂] coordination constraint.

connected three-dimensional network is first to fill randomly the box with Zn atoms, respecting a shortcut distance; constraining a [ZnZn₄] fourfold coordination by a RMC run without diffraction data; adding the Cl atoms at the Zn-Zn midpoints (ensuring corner sharing) and finally running RMC with diffraction data. Another approach was deliberately used here, in order to verify if a good fit would be obtained also when edge sharing could occur between [ZnCl₄] tetrahedra. The model was built up by filling first the box with 650 Zn atoms, at random, but respecting a 3.1 \AA shortest Zn-Zn distance. Then, the chlorine atoms were added at random, with 1.9 \AA and 3.0 \AA respectively as shortest Zn-Cl and Cl-Cl interatomic distances. The RMCA program was then run without diffraction data, in order to increase these shortest Zn-Zn, Zn-Cl and Cl-Cl distances to 3.4 , 2.05 and 3.2 \AA , respectively, adding the constraint that four Cl atoms should be found in the range 2.05 - 2.65 \AA around a Zn atom. Ensuring that all the Zn atoms form [ZnCl₄] tetrahedra took quite long (several days on a Pentium-II 333MHz). Then, the RMCA program was run against the neutron diffraction data, obtaining finally an excellent agreement with $R_p = 0.76 \%$ (Table 2). Looking accurately to this model reveals that the systematic sharing of exactly two Zn atoms by Cl atom is far from being realized, as shown in Table 3. One tetrahedron among 650 is isolated and clusters were built of which the biggest

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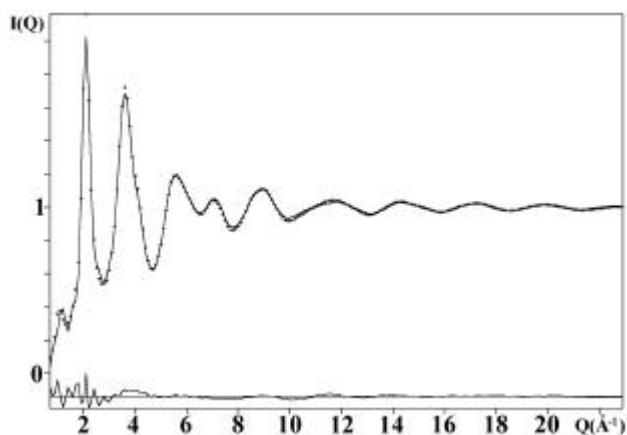


Fig. 2. Observed (+++) and calculated (—) interference function corresponding to the RMC modelling of glassy ZnCl_2 , starting from the $\delta\text{-ZnCl}_2$ RDM model. The difference function is in the lower part. $R_p = 1.09\%$.

edge and 2 tetrahedra share 2 edges. So that, the RMC method was unable to ensure naturally the expected tetrahedra corner sharing exclusivity. Nevertheless, the fit is almost perfect. On the other hand, the ZnCl_2 RDM model [7] ($R_p = 2.40\%$), built up from the $\delta\text{-ZnCl}_2$ structure [9], corresponds to a perfect 4-connected three-dimensional network. It was expanded to 1728 atoms before to realize the RMC approach (Table 1), obtaining finally the expected low reliability value $R_p = 1.09\%$. The observed and calculated interference functions are shown in fig. 2, and the structure model is represented in fig. 3.

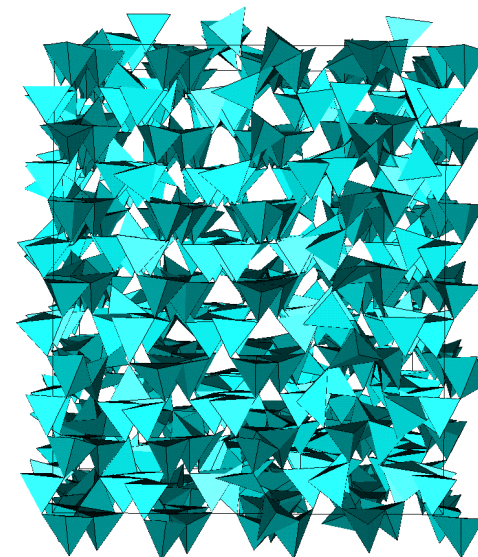


Fig. 3. Projection of the RMC model for glassy ZnCl_2 , starting from the $\delta\text{-ZnCl}_2$ RDM model. The distorted triangular tunnels are finger print of the starting model.

N	NT
0	1
1	4
2	18
3	82
4	157
5	201
6	129
7	52
8	5
9	1

Table 3

Repartition of neighbouring $[\text{ZnCl}_4]$ tetrahedra in the final "classic" RMC model for ZnCl_2 , starting from a pseudo random configuration. NT is the number of tetrahedra sharing N chlorine atoms with other tetrahedra. A perfect 4-connected 3D net would have corresponded to $\text{NT} = 650$ for $\text{N} = 4$.

SiO₂ - The glassy SiO_2 RMC model published in Nature [4] is not a perfect 4-connected 3D network, the average Si coordination is slightly less than 4 oxygen atoms. In the RDM model [3], each oxygen atom is exactly shared by two Si atoms in tetrahedral coordination. That RDM model is based on the α -carnegieite structure, starting from the atomic coordinates given by Barth for its early description of high-cristobalite [10]. It was selected for the reason that it corresponds to a distinctly best fit among all the tested MX_2 possible crystalline

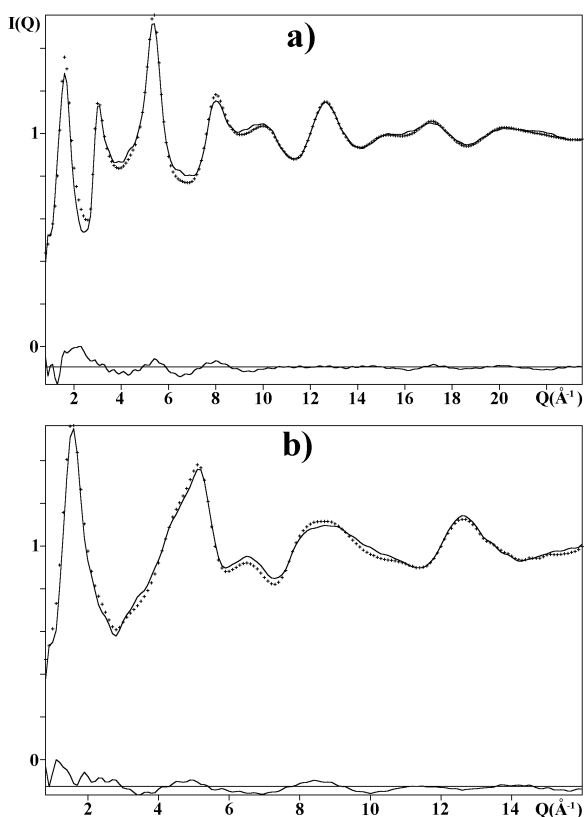


Fig. 4. Observed (+++) and calculated (—) interference functions corresponding to the RMC modelling of glassy SiO_2 , starting from the α -carnegieite RDM model. The difference functions are in the lower parts. a) Neutrons, $R_p = 1.48\%$; b) X-ray, $R_p = 2.00\%$.

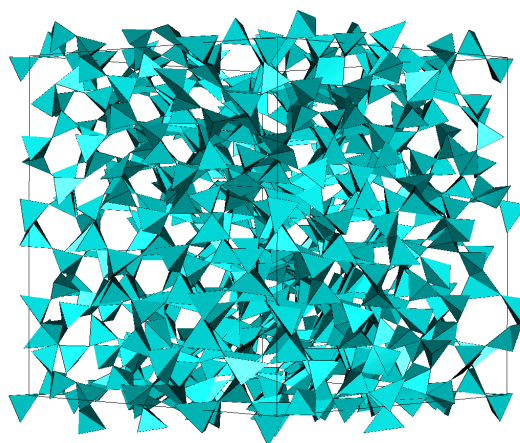


Fig. 5. Projection of the RMC model for glassy SiO_2 , starting from the α -carnegieite RDM model. The distorted hexagonal tunnels are finger print of the starting high-cristobalite-like model (α -carnegieite).

structures. Fitting both neutron and X-ray diffraction data by RMC, using a model based on the RDM model, extended to 1536 atoms, led to the final R_p values gathered in Table 2. It should be emphasized that constraints on interatomic distances were applied during the RMC process, in order to maintain the initial RDM model connectivity scheme. This approach produces a new RMC model for glassy SiO_2 with exclusively 6-membered rings. It is quite different from the model built by a "classic" RMC approach [4] (with random starting model) leading to the occurrence of 4-, 5-, 6-, 7-, and 8-membered rings. Figures 4 and 5 show respectively the interference functions and a projection of the final RMC model derived from the RDM one.

NaPbM_2F_9 ($M = \text{Fe}, \text{V}$) - The best RDM model [6] was proposed to be the $\text{NaPbFe}_2\text{F}_9$ crystal structure [11], disclosed during the recrystallization study inside the vitreous domain in the $\text{NaF/PbF}_2/\text{FeF}_3$ system. The crystal structure is built up from linear intercrossed chains of corner-linked $[\text{MF}_6]$ octahedra. It is worth noting that some Na/Pb disorder was suggested to be present in the crystalline phase. A $\text{NaPbFe}_2\text{F}_9$ polytype was synthesized later, and its structure was determined from single crystal data, showing a tripled cell parameter c : KCaAl_2F_9 disclosed together with two isotypical compounds KCaFe_2F_9 and KCaV_2F_9 [13]. 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 adopting possibly the $\text{NaPbFe}_2\text{F}_9$ structure-type. Data presented here for the RMC/RDM study are two neutron patterns (for $M = \text{Fe}$ and V) and an X-ray one. The expected isomorphous replacement between Fe^{3+} and V^{3+} is well supported by the crystal chemistry in fluorides in general. As a rule, when a Fe^{3+} -based fluoride exists, the isostructural equivalent V^{3+} material can be prepared too, with generally no more than 1% variation in cell dimension. The mean usual interatomic distances are 1.935 and 1.950 Å respectively for Fe-F and V-F atom pairs 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. The random RMC model [6] consisted of 1950 atoms in a cubic box (30.12 Å length for corresponding to the number density $\rho_0 = 0.07135 \text{ atom}/\text{Å}^3$, 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 successively were inserted. Positions at this filling stage were accepted if minimal predefined interatomic distances were respected. The MF_6 coordination was constrained to

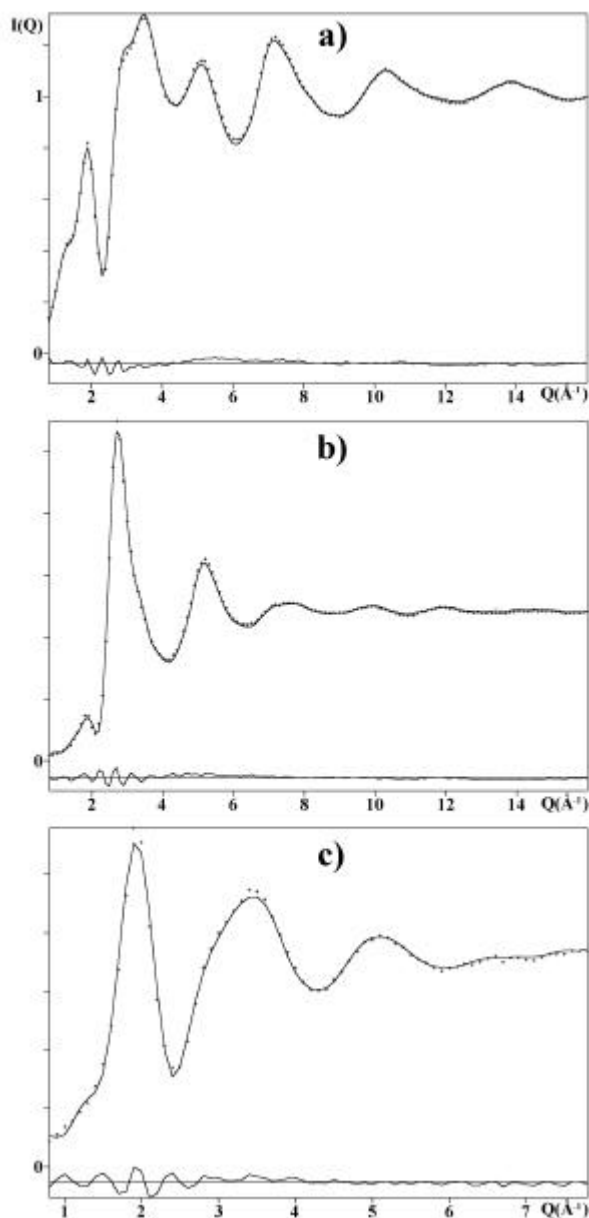


Fig. 6. Observed (+++) and calculated (—) interference functions corresponding to the RMC modelling of glassy NaPbM_2F_9 ($M = \text{Fe}, \text{V}$), starting from the $\text{NaPbFe}_2\text{F}_9$ RDM model. The difference functions are in the lower parts. a) Neutron, $M = \text{Fe}$ and $R_p = 0.81 \%$; b) Neutron, $M = \text{V}$ and $R_p = 1.22 \%$; c) X-ray, $M = \text{Fe}$ and $R_p = 1.75 \%$.

occur with a maximum M-F distance equal to 2.15 Å. The RMC model did not present two identical polyhedra and the $[\text{MF}_6]$ ($M = \text{Fe}, \text{V}$) polyhedral chains were zigzagging with trans or cis connections. A few rings with 3, 4, 5 or 6 $[\text{MF}_6]$ polyhedra sharing corners were built up by the Monte Carlo process and 92 of the 300 $[\text{MF}_6]$ 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 $[\text{MF}_6]$ trigonal prisms (unknown for Fe^{3+} and V^{3+} in fluorides) could have been proposed by the RMC method as well (this is not the same for distorted tetrahedra which continue to look like tetrahedra, or possibly square plane if distances allow it). Indeed, a large majority of more or less distorted octahedra were built, but a few trigonal prisms have occurred. A visual examination of each of the 300 $[\text{MF}_6]$ entities by a three-dimensional capable VRML (Virtual Reality Modelling Language) viewer, allowed one to estimate that 20 of them were close to trigonal prisms (TP), 25 were quite irregular polyhedra (intermediate between TP and octahedra), the rest being acceptable as more or less distorted octahedra (very few being really regular). The way octahedra were linked in the RMC model was predominantly by corners. In fact among fluoride crystal structures with formulation $\text{A}_2\text{M}_2\text{F}_9$, none presents any established $[\text{MF}_6]$ octahedra edge sharing. However edge sharing occurs for a fraction of the octahedra interlinks in crystallized compounds such as BaZnFeF_7 [14], BaCuFeF_7 [15] or BaMnFeF_7 [16] (with larger 3d-cation/F ratio) and also BaTiF_5 [17] (with smaller ratio). It is thus admissible that edge sharing could occur in the NaPbM_2F_9 glasses. On the other hand, the presence of $[\text{MF}_6]$ trigonal prisms in the RMC result is unfounded in the context of fluoride crystal chemistry. So

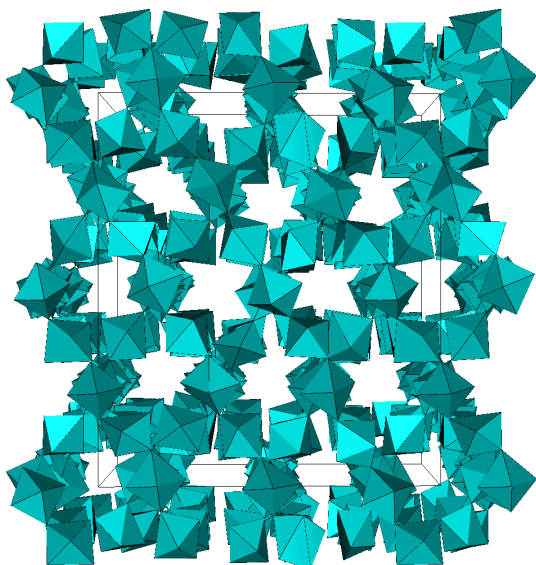


Fig. 7. Projection of the RMC model for NaPbM_2F_9 ($M = \text{Fe}, \text{V}$) fluoride glasses, starting from the $\text{NaPbFe}_2\text{F}_9$, RDM model. The distorted intercrossed chains of $[\text{MF}_6]$ octahedra are finger print of the starting model.

that a RMC modelling based on the selected RDM model, showing exclusively corner-sharing octahedra, seemed appropriate, in order to validate it by modelling involving a much larger number of atoms. The RDM model was extended to 936 atoms (Table 1), and the RMC application produced soon acceptable R_p values (Table 2). Fig. 6 and 7 show respectively the interference functions and a projection of the final model on which the linear intercrossed chains of corner-linked $[\text{MF}_6]$ octahedra are still well recognized.

3. Conclusion

It has been shown that a satisfying RDM model may constitute a starting model for a RMC simulation. The RDM best models correspond to crystal structures in which the glasses devitrify, in all three cases. Quantitative agreement with the experimental

data is a prerequisite for a modelling credibility. The possibility to build quite different models with similarly good agreement, as shown in this paper, has significant bearing on the confidence one can put into the interpretation of scattering data from amorphous structures : uniqueness is not ensured for these network glasses. Those three dimensional structures are simply models that are consistent with the data and constraints. In other words, the RDM best model is one structure in the group of possible RMC solutions, the most ordered. RMC tends to produce the most disordered structure if the starting configuration is random. Finally, if the starting model is a RDM optimized configuration, the RMC resulting structure may look very ordered, almost crystalline.

Both methods have pro and con. Testing a model by RDM is fast, but finding a model having the exact glass composition can be a problem. Obtaining convergence by RMC may be quite long when drastic constraints are imposed, however, the model size brings more credibility than for the generally small RDM models. Nevertheless, appropriate strategy is essential for succeeding in building models consistent with knowledge (absence of edge sharing, strict coordinations and so on). Such a strategy is not always easy to establish with the current existing RMC code. For instance, if you wish only octahedra, a sixfold coordination constraint will not avoid the occurrence of trigonal prisms too.

It is expected that confidence in RDM modelling will increase as a consequence of the present study, showing that a good RDM model is always an excellent RMC candidate, reconciling both methods.

Acknowledgments. Drawings of RMC models were made by using GLASSVIR [18].

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