Modelling the silica glass structure by the Rietveld method

A. Le Bail *

Université du Maine, Faculté des Sciences, Laboratoire des Fluorures, CNRS-URA 449, 72017 Le Mans , France

Abstract

To refine amorphous structures like crystalline ones is impossible. This statement needs now some reconsideration in the case of silica glass. Starting with a microstrained crystalline model deriving from the α-carnegieite structure, atomic coordinates refinements by the Rietveld method prove to be possible. The credibility of the study is supported by the simultaneous fit of neutron and X-ray diffraction data. The agreement R_χ factors are the best ever obtained with a small-size model built exclusively from [SiO_4] tetrahedra linked by corners. However it is concluded that 'best' remains insufficient.

1. Introduction

A molecular dynamics (MD) simulation [1] of the structure of silica glass was quoted [2] as representing probably the closest agreement with experiment. A discrepancy R_χ^N factor was defined by comparison of the observed and simulated neutron real space correlation functions for $T^N(r)$ ($R_\chi^N = 6.8\%$ $1 \leq r \leq 8$ Å with $Q_{max} = 22.88$ Å^{-1}, whereas $R_\chi^N = 9.1\%$ with $Q_{max} = 45.2$ Å^{-1}; see eq. (2) in Ref. [2]). Slightly better results are presented here from the polycrystalline Rietveld structure analysis technique [3]. An adaptation of this method to amorphous materials was first applied to multicomponent fluoride glasses [4]. It can be classified among the methods using periodic boundary conditions. Once the choice of a crystalline model is made, it is distorted mathematically by the application of a statistical isotropic microstrain which enhances progressively the short, medium and long range disorder. The

effect is to produce artificial amorphous-like powder diffraction patterns, thanks to a considerable line-broadening associated to microstrain. Then one can try to refine, in the usual least squares sense, the cell parameters and atomic coordinates of small models [5]. The method was considered [6] as a variation of the reverse Monte Carlo technique [7] (RMC). However it was not so widely adopted and few applications were performed [5]. The results presented here should bring out this procedure because glassy SiO_2 is concerned.

2. Methodology and results

Silica glass has been called quartz-like, cristobalite-like or tridymite-like and so on, although as good R_χ factors as above were never presented. Frequent controversies arose on this subject [6,8]. These 'quasi-crystalline' simulations were crude, by contrast with the present one for which the model changes to obtain the best agreement with experimental data. The modified Rietveld program used (ARITVE) is almost the original FORTRAN version.

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* Corresponding author. Tel: +33 43 83 33 46. Telefax: +33 43 83 35 06. E-mail: armel@one.univ-lemans.fr.

The full width at half maximum (FWHM) follows the Cagliotti law (FWHM $= [U \tan^2 \theta + V \tan \theta + W]^{1/2}$) able to take account of both instrumental resolution and sample broadening effects. The microstrain effect and an eventual size effect have variations proportional respectively to $\tan^2 \theta$ and $(1 + \tan^2 \theta)$. The V term needs not to be refined and should be fixed at the instrumental resolution value. Gaussian peak shape is used that could correspond physically to Gaussian microstrain distributions whose widths vary as the square of the distance from an arbitrary origin [5]. In fact, FWHM are so large that the profile shape is not very critical and a thousand reflections may overlap at a particular diffracting angle. The simultaneous fit of several diffraction patterns is allowed, X-ray together with neutron data if any, eventually with different (constant) wavelengths. Models tested in this study were all the crystalline silica forms and other tridimensional four connected nets including the denser of zeolites and clathrasils. When promising results were obtained for a particular model, a better agreement was searched by changing the space group of the model into the more direct maximal non-isomorphic subgroups or the isomorphic subgroups of lowest index [9].

The data simultaneously fitted in this study are the $S(2\theta)$ functions derived from the $Qi(Q)$ neutron diffraction data presented in Ref. [10] ($Q_{max} = 23.56$ Å^{-1}) and X-ray data in Ref. [11] ($Q_{max} = 16.0$ Å^{-1}). The final model was selected on the basis of the highest level of agreement among all the tested cases according to the conventional Rietveld profile reliability, R_p, on $S(2\theta)$ functions. Models based on dense forms of crystalline SiO_2 (α- or β-quartz, keatite, coesite) were rejected with $R_p > 12\%$ for both X-ray and neutron data. The best agreements were clearly obtained from cristobalite- and tridymite-like starting models with an advantage to the former. Large models could not be tested (the triclinic low tridymite [12] for instance). In the current version of the program, limits are 30 000 reflexions for each diffraction pattern (three maximum simultaneously) of which 12 000 could overlap, 70 atomic coordinates could be refined. Thermal displacement factors are considered as part of the disorder. The fit of some complete more recent neutron data ($Q_{max} > 45$ Å^{-1}) was impossible.
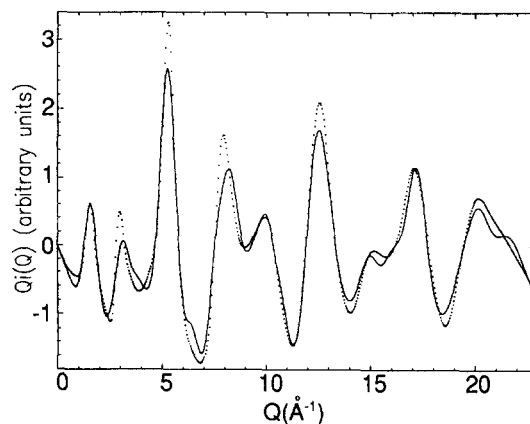

Fig. 1. Observed (dots) and calculated (line) neutron interference functions $Qi^N(Q)$.

The very simple model of the α-carnegieite structure [13], starting from the atomic coordinates given by Barth for its early description of high-cristobalite [14], was able to produce $R_p^N = 2.64\%$ and $R_p^X = 2.51\%$ after refinement of 13 parameters (six coordinates only). Lowering the symmetry from cubic ($P2_13$ space group) to orthorhombic ($P2_12_12_1$ space group) decreased these reliabilities to $R_p^N = 2.45\%$ and $R_p^X = 2.37\%$ for 27 refined parameters (18 coordinates; 16 237 reflexions for neutron data of which a maximum of 8444 could overlap at large angle, respectively 6133 and 4070 for X-rays). The improvement seems small but it was sufficient to lead to a significatively lower R_χ^N on $T^N(r)$ than for the MD

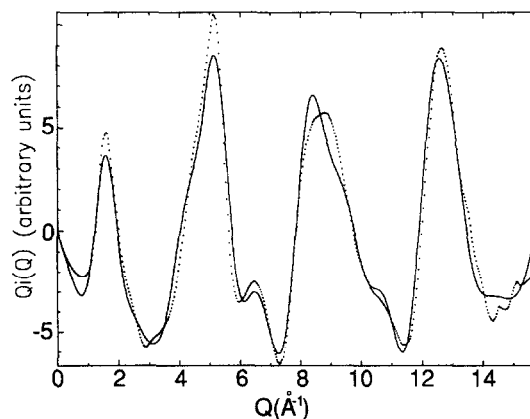
Fig. 2. Observed (dots) and calculated (line) X-ray interference functions $Qi^X(Q)/fe^2(Q)$.
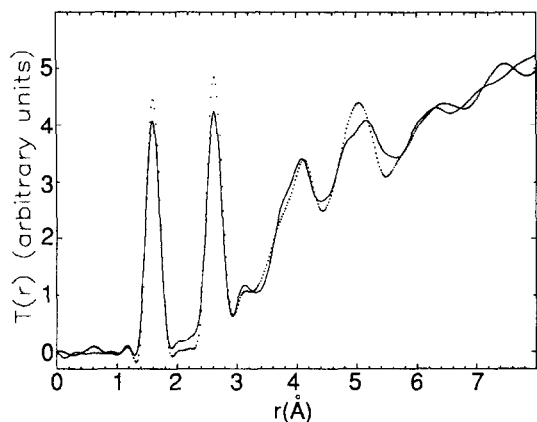
Fig. 3. Observed (dots) and calculated (line) neutron correlation functions $T^N(r)$.

Table 1
Refined parameters of the amorphous SiO_2 model in spacegroup $P2_12_12_1$

Atom	x	y	z
Si(1)	0.277(2)	0.275(2)	0.282(1)
Si(2)	0.009(1)	0.022(3)	0.016(3)
O(1)	0.125(3)	0.149(4)	0.152(3)
O(2)	0.635(4)	0.657(4)	0.061(5)
O(3)	0.065(4)	0.646(6)	0.654(7)
O(4)	0.670(3)	0.060(4)	0.621(4)

Lattice parameters: $a = 7.22(7)$ Å, $b = 7.09(6)$ Å and $c = 7.30(6)$ Å. V/molecule $= 46.7(2)$ Å³ with $Z = 4$. Halfwidth parameters for the simultaneous fit of diffraction data rebuilt at a fictitious 2θ scale: $U = 22(6)$, $V = 0.5$, $W = 5.2(1)$ (neutron, $\lambda = 0.35$ Å) and $U = 42(11)$, $V = 1.0$, $W = 15(1)$ (X-ray, $\lambda = 0.5$ Å). The number in parentheses denotes the estimated standard deviation in the last digit.

simulation [1,2], whereas this was not the case for the cubic model. The fits are shown in Fig. 1 for $Qi^N(Q)$ and in Fig. 2 for $Qi^X(Q)/fe^2(Q)$, according to the notation developed in Ref. [6]. In the case of neutron data, the results presented in Fig. 1 may be compared with a previous quasi-crystalline model of vitreous SiO_2 based on the β-cristobalite structure (fig. 17 in Ref. [6]), giving an idea of the improvement due to the refinement. The agreement on the neutron real space correlation function $T^N(r)$ was $R_\chi^N = 6.3\%$ (Fig. 3), i.e., 0.5% lower than for the best previous MD study for which no simultaneous fit of the X-ray data was presented.

The fact that an R_χ agreement factor may seem low or high for the same model depending on the data examined must be emphasized. Replacing $T(r)$ by $S(Q)$ in the R formula, one has $R_\chi^N = 4.32\%$ and $R_\chi^X = 3.60\%$, whereas for the $Qi(Q)$ data of Figs. 1 and 2 one obtains respectively 22.3% ($1 \leq Q \leq 22.88$ Å^{-1}) and 19.3% ($1 \leq Q \leq 15.72$ Å^{-1}). The Fourier transforms of these interference functions (using the same modification function $M(Q)$ as in Ref. [2]) are the differential correlation functions, $D(r)$, of which the $T(r)$ functions are deduced. The R_χ values obtained in the range $1 \leq r \leq 8$ Å are 22.1 and 19.3%, respectively, for $D^N(r)$ and $D^X(r)$. Better R_χ values were obtained when refining the X-ray data set alone or the neutron one; this is to be avoided. The model is small since 24 atoms are in the cell (of which six are independent). This may be compared with 648 independent atoms for the MD

simulation [1] in the P1 spacegroup. Lowering the symmetry from the actual $P2_12_12_1$ space group or enlarging the cell do not lead to a well conditioned problem. With more coordinates to refine, the process becomes unstable due to data scarcity. The introduction of constraints on distances, angles and cell volume or combination with RMC could improve a future version of the program.

The final atomic coordinates are given in Table 1 together with other refined parameters. An important value is the density: the well known measured $\rho_0 = 0.022065$ (SiO_2 units)/Å³ has to be compared with a calculated value of 0.0214(1). A view of the structure is shown in Fig. 4; its orientation allows one to recognize the typical cristobalite six-membered rings. The mean Si–O and O–O distances (1.61 and 2.63
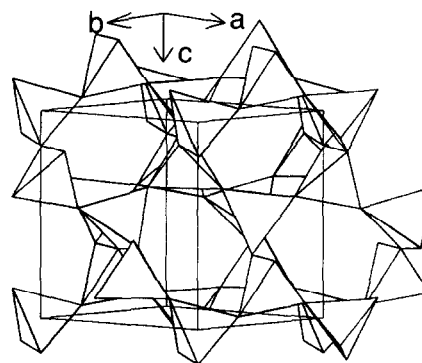

Fig. 4. View of the mean structure model for amorphous SiO_2. [SiO_4] tetrahedra are represented.

Å) and O–Si–O angle (109.5°) fit well the expected values [6] (respectively 1.608 ± 0.004 Å, 2.626 ± 0.006 Å and 109.7 ± 0.6°). There is however a significative deviation between the estimated [15] (144°) and calculated (157°) mean Si–O–Si angles. The mean is calculated from four values (151, 152, 153, 172°) of which one deviates much more. Consequently, the Si–Si mean distance (3.14 Å) is too large (experimental [10] 3.08 Å) and it is clear that the model needs further improvements.

3. Discussion and conclusion

An objection to crystal-based models is that they fail to specify the interconnecting materials [6]. The present model is a mean one and consequently it fails also to specify any exact local arrangement. In spite of its crystalline origin, the model is in agreement with the usual definition of a glassy or amorphous material: a solid in which the long-range ordering of the atoms is absent. Anyway, from a purely quantitative point of view, the fact is now that the closest agreement in the sense of R_χ on $T^N(r)$ is obtained with a very small mean model deriving from an early description of the high-cristobalite structure. By contrast with the RMC modelling [16] of SiO_2 (2596 atoms in a cubic box and P1 space group), there is no exception here to the fourfold oxygen coordination around the Si atoms and the model is built up exclusively from six-membered rings although this is unlikely to occur strictly in the real glass structure. The present refinement method is not as general as the RMC method: a reasonable starting approach of the final solution is required in order to apply least squares efficiently contrarily to RMC for which the procedure may start from a model just having the right density. Therefore the glass composition must be chosen to have at least one crystalline analogue suspected to present the same basic mean structure as the glass. On another hand, RMC fits will never be satisfying with a small volume box without a statistical disorder describer such as isotropic microstrain. All the models discussed here and competing for the closest agreement with experiments may be addressed the same criticisms: how significant are their cell parameters; is

the object to fit the data so as to obtain the best R-factor or fit, but to obtain the best physical model (how to define it?) that corresponds to the observed data; are the parameters describing the model providing a useful picture of silica glass.

It is not before obtaining $R_\chi < 1\%$ on $T(r)$ or $R_\chi < 2$–3% on $D(r)$ and $Qi(Q)$ functions that one should claim to have well described (may be) the structure of any amorphous material. So the conclusion will remain prudent, qualitative and not different from that of Hosemann et al. [17] stating: "there exist many similarities between the β-cristobalite and the silica glass". It is to be noted that the concept of high degree of microstrain is not far from the paracrystalline one [17], if not identical. These results may comfort works pointing out that "glasses come to order" [18].

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