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A reverse Monte Carlo study of a titanosilicate glass

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Abstract. Neutron scattering measurements with isotopic substitution of Ti have been carried out on a $\text{K}_2\text{O}-\text{TiO}_2-2\text{SiO}_2$ glass using ^{46}Ti and ^{48}Ti isotopes. The total structure factors and the first difference function (giving all the partial pair correlation functions centred on Ti) were fitted by the reverse Monte Carlo (RMC) technique to generate a three-dimensional structural model of this glass. Information was obtained on the medium-range ordering around Ti. The structure determined with RMC indicates a non-homogeneous distribution of Ti in the glass in agreement with the available scattering data.

1. Introduction

A better knowledge of the structure of glasses is necessary to understand their physico-chemical properties. Important information on local and medium-range order in glasses can be obtained from the distribution functions extracted from neutron and x-ray scattering. Furthermore, using x-ray anomalous scattering [1] or isotopic substitution with neutron scattering [2–4], it is possible to probe selectively the environment of one specific element. In order to extract more structural information, modelling techniques are necessary. Monte Carlo and molecular dynamics simulations were widely used to provide some insight into glass structures [5–7]. These methods rely on the use of interatomic potentials and the development of three-body terms allows more realistic representations to be obtained. Since it becomes difficult to justify the addition of more terms to potential functions, it is not clear how interatomic potentials can be improved. Although good qualitative agreement is generally obtained between simulations and experimental results, it is more difficult to reproduce quantitatively the data. The reverse Monte Carlo (RMC) approach [8] offers the possibility to obtain a quantitative fit of the experimental data as no potential functions are used. This technique is particularly appealing for the study of multicomponent glasses where the determination of potential functions is difficult.

In this paper we present a reverse Monte Carlo simulation of a $\text{K}_2\text{O}-\text{TiO}_2-2\text{SiO}_2$ glass studied by neutron diffraction with isotopic substitution of Ti. The first difference function which gives the weighted sum of all the Ti-centred pair functions was used in the fitting process, which allows the environment around this element to be constrained. The three-dimensional structural model created by RMC is consistent with the neutron experimental data. The analysis of the RMC configuration provides information on the silicate network and on the medium-range order (MRO) around Ti.

2. The RMC method

The RMC method has been extensively described elsewhere [9] and only a brief outline will be given. The basis for RMC simulation is the Metropolis Monte Carlo algorithm but, instead of the energy of a set of N atoms, the RMC technique samples the quantity χ :

$$\chi_k^2 = \sum_k \sum_i \frac{[F_k^c(Q_i) - F_k^e(Q_i)]^2}{2\sigma_k^2(Q_i)} \quad (1)$$

where F^e are the experimental data with i points, F^c are the corresponding quantities that are calculated with the atomic coordinates, and σ is a parameter taking into account the experimental errors. The sum over k indicates that different data sets can be used simultaneously during the procedure. These data can be from various sources: neutron scattering (including isotopic substitution), x-ray scattering (including anomalous scattering), EXAFS. The atomic configuration is thus optimized only by comparison with the experimental data. This allows a model to be obtained that agrees quantitatively with the available data (in contrast to most of the Monte Carlo or molecular dynamics simulations).

The procedure consists of moving an atom randomly and then calculating the new F^c and the new χ^2 factor. If χ^2 is improved, the displacement is accepted; if not, the displacement is accepted with a probability $\exp(-(\chi_n^2 - \chi_o^2)/2)$, where χ_n and χ_o are, respectively, the new and the old configuration. This latter condition allows a wider solution space to be sampled, by avoiding only a refinement of the initial configuration.

Table 1. Parameters for the initial configuration used in the RMC simulation.

Types of atom	Number	Density (atoms \AA^{-3})
Si	200	0.01075
O	700	0.03224
K	200	0.0484
Ti	100	0.06448

3. The initial configuration

A crystal structure can be used as the starting configuration; however there is no crystalline $\text{K}_2\text{O-TiO}_2\text{-2SiO}_2$. A random configuration was thus generated with the following steps (see also table 1).

- Si atoms were randomly introduced with a density of $0.01075 \text{ atoms } \text{\AA}^{-3}$. A hard-sphere Monte Carlo simulation (HSMC) was run to constrain each Si to be linked to four Si between 2.9 and 3.4 \AA .

- O atoms were added in the middle of each Si-Si bond (density of $0.03224 \text{ atoms } \text{\AA}^{-3}$), giving a three-dimensional network of SiO_4 tetrahedra. A constraint was then imposed to preserve these structural units.

- O atoms were added to reduce the connectivity of the network and K atoms were introduced in proximity to non-bridging bonds. This simulates the introduction of K_2O (density of $0.0484 \text{ atoms } \text{\AA}^{-3}$).

- The previous step was repeated to introduce TiO_2 . This gives a model in agreement with the experimental atomic density ($\rho = 0.0645 \text{ atoms } \text{\AA}^{-3}$). The Ti site can be

determined without ambiguity by neutron scattering (see below). As RMC is used to obtain information on MRO, the local environment around Ti was constrained by running a HSMC simulation. Distances of closest approach between two types of atom were also imposed, based on the experimental correlation functions and the distances found in crystalline references (table 2).

We thus created a cubic box with edges, L , equal to 26 \AA ($\rho = N/L^3$). The configuration contains 1200 atoms and periodic boundary conditions were used. During the simulation, the SiO_4 and TiO_5 polyhedra were maintained and the constraints on closest approach distances were applied.

Table 2. Distances of closest approach (in \AA) between two types of atom determined from the radial distribution functions and from crystalline references.

	Si	O	K	Ti
Si	2.6	1.4	2.9	2.6
O		2.3	2.3	1.5
K			2.9	2.9
Ti				2.9

4. Neutron scattering data

Neutron scattering measurements were carried out on the SANDALS diffractometer at the ISIS spallation neutron source (UK) on a $\text{K}_2\text{O-TiO}_2\text{-2SiO}_2$ glass [10]. Isotopic substitution of Ti allows a first difference function (sum of all the Ti-centred partial pair correlation functions) and a second difference function (only the Ti-Ti partial correlation function) to be calculated.

Data for the ^{46}Ti sample and the first difference were used in a first step. When a reasonable agreement was achieved, the data for the ^{48}Ti and ^{mix}Ti samples were added. We did not use the second-difference data (giving the Ti-Ti pairs only) as this signal is subject to large statistical and systematic errors. Only Q -space data were fitted because some features related to the MRO (first sharp diffraction peak, FSDP) do not give an apparent contribution in r -space.

5. RMC results and discussion

In figure 1, the sets of experimental data are compared with the RMC simulations. An excellent agreement is obtained for the first difference describing the environment of Ti. The total structure factors are also well fitted despite some small differences in the intensity of the low- Q part. The variations in the low- Q region arise from the differences in the Ti neutron scattering length for each sample ($^{48}\text{Ti} = -6.003 \text{ fm}$, $^{mix}\text{Ti} = -1.713 \text{ fm}$, $^{46}\text{Ti} = 2.577 \text{ fm}$). The shape of the first sharp diffraction peaks, which is linked to the MRO in the glass, is well reproduced for all structure factors.

In table 3, the coordination numbers for Si, K and Ti are compared to those obtained by fitting the neutron data with Gaussian functions. A good agreement is obtained, except for K where the RMC model gives a coordination number of five instead of eight. The K-centred partials are mainly contained in the total structure factors where they are buried by the partials related to the silicate network (O-O, Si-O). In consequence, the potassium

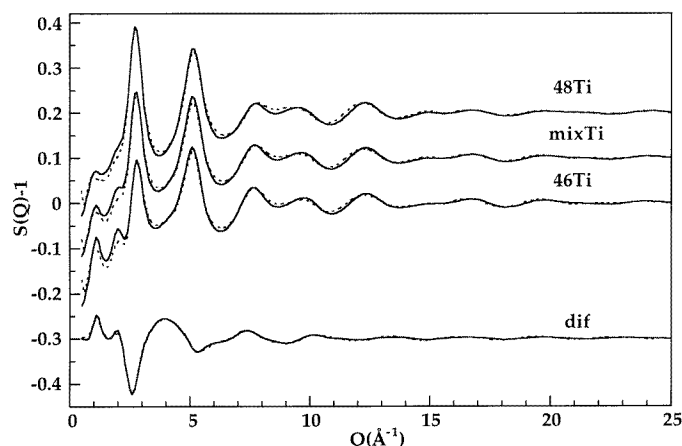


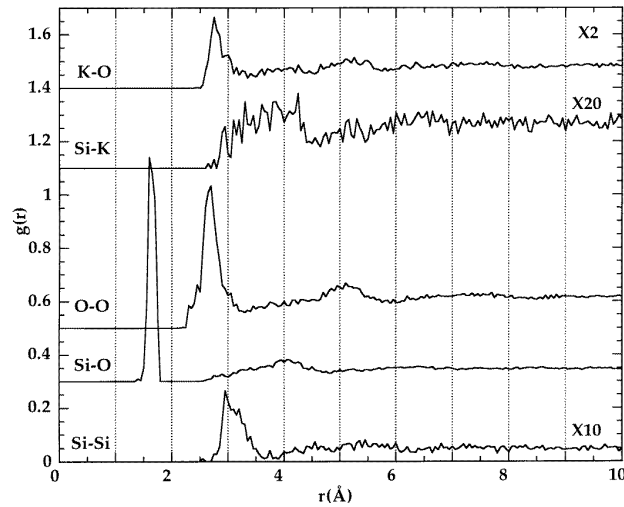
Figure 1. Comparison between the total experimental structure factors (solid curves) and the RMC fits (dotted curves) for the glasses containing ^{48}Ti , ^{46}Ti and ^{mix}Ti (equal mixture of ^{46}Ti and ^{48}Ti) and for the first difference of Ti (dif) which is the sum of all the Ti-centred partial structure factors.

Table 3. Coordination numbers determined by RMC modelling compared to those calculated by Gaussian fitting [10] of the correlation function (total and first difference).

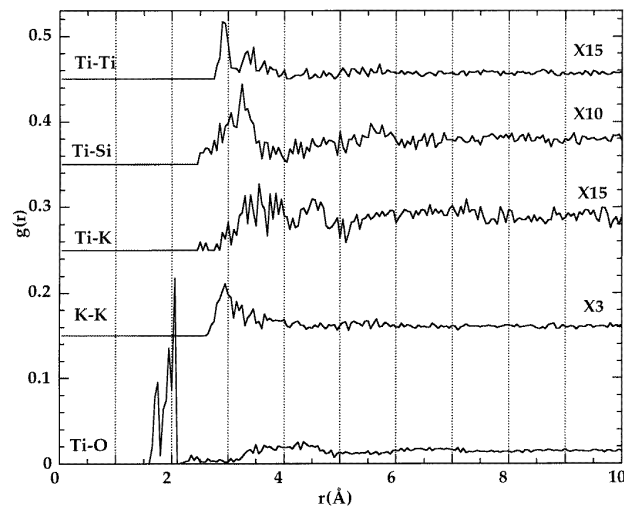
Pairs $i-j$	Interval to calculate N_{RMC} (Å)	N_{RMC}	$N_{neutron}$
Si-O	0-1.8	3.96	3.98
O-Si	0-1.8	1.13	1.12
Ti-O	0-2.05	4.72	4.85
O-Ti	0-2.05	0.67	0.12 + 0.58
O-O	0-3	5.59	4.9
K-O	0-3.5	5.05	7.8

environment is poorly constrained in the RMC model, which explains a low apparent coordination number.

The Ti-O partial dominates the first difference function, $G_{Ti-\alpha}(r)$ (figure 2). Analysis of the $G_{Ti-\alpha}(r)$ function indicates that Ti atoms occur at the centre of a square-based pyramid: four oxygens at 1.96 Å form the square base and one (titanyl) oxygen at 1.68 Å the apex [10]. Before starting the RMC simulation, the local environment around Ti was constrained to reproduce this site: one oxygen below 1.75 Å and four oxygens between 1.75 and 2.05 Å. The comparison with the experimental data indicates that the first Ti-O distances after the RMC simulation are slightly shifted to a higher value (about 0.04 Å). First Si neighbours around Ti are located at 3.26 Å, close to the values of 3.2 Å observed in crystalline titanosilicate references. In contrast the Ti-K distances are widely spread. This suggests that K atoms are in more distorted sites than Ti or Si atoms in agreement with their compensating role in the structure around the titanyl oxygen. The Ti-Ti distribution can be compared with the second difference function obtained experimentally (figure 3). With the RMC simulation a first intense peak is obtained near 3 Å. This peak is probably due to the constraint of closest approach fixed at 2.9 Å for the Ti-Ti pair and this distance is not meaningful. However the first experimental Ti-Ti distance at 3.5 Å (the peak at 2 Å is a spurious feature arising from an incomplete subtraction of the Ti-O correlation) is roughly



(a)



(b)

Figure 2. Partial correlation functions for the RMC model: (a) g_{K-O} , g_{Si-K} , g_{O-O} , g_{Si-O} , g_{Si-Si} ; (b) g_{Ti-Ti} , g_{Ti-Si} , g_{Ti-K} , g_{K-K} , g_{Ti-O} . The functions were multiplied by the weighting factors corresponding to the ^{46}Ti glass and then shifted for clarity.

reproduced by the RMC simulation. A homogeneous distribution of Ti in the glass gives a first Ti–Ti distance of 6.1 Å. The RMC model supports thus a non-random distribution of Ti in the structure with a low first Ti–Ti distance (compared to a value larger than 4 Å in silicate crystals containing fivefold coordinated titanium). These small Ti–Ti distances indicate that, in contrast to silicate crystals, the TiO_5 polyhedra are linked together by sharing a corner, with an average Ti–O–Ti angle of $126 \pm 10^\circ$. Edge sharing is avoided due to the strong Ti–Ti repulsion. Moreover, a number of 2.4 Ti neighbours is obtained with RMC, which agrees with an estimate of two derived from the second difference function by Gaussian fitting [10]. The RMC model indicates that 1.8 Si atoms are present on average around the Ti atoms,

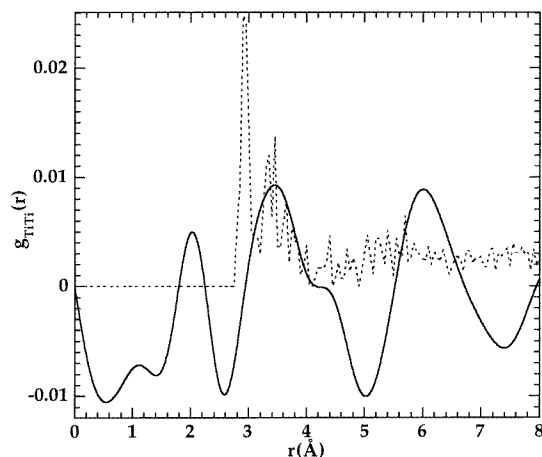


Figure 3. Comparison of the experimental distribution of Ti (solid curve) obtained directly from the second-order difference and the RMC modelling (dotted curve). A first Ti–Ti distance of 2 Å is unphysical and the peak observed on the experimental curve is probably due to an incomplete subtraction of the Ti–O correlation.

which indicates that the 4 O of the square base participate in the polymerization of the network by a corner linkage either with another TiO_5 pyramid or with an SiO_4 tetrahedron. The short Ti=O (titanyl) bond is non-bridging, and the charge compensation of this bond is ensured by potassium atoms. Figure 4 represents a slice of about 10 Å into the RMC configuration. The inhomogeneous structure of the glass can be visualized with the presence of Ti-rich regions and Si-rich regions. The distribution of K atoms is also non-homogeneous but an association with Ti or Si atoms is not clear. The structure modelled by RMC is not unique. In particular, the choice of the initial configuration is of great importance. Starting with a random configuration gives a more disordered model consistent with the available experimental data and the constraints applied. It is thus important to note that the real glass almost certainly presents more structural ordering than that observable in this RMC model.

The bond angle distributions for Si–O–Si and O–Si–O are given in figure 5. The O–Si–O distribution shows a maximum close to the value expected for a regular SiO_4 tetrahedron at 109.3° . The O–Si–O angles are widely distributed though a weak maximum can be observed near 150° , close to recent calculations on SiO_2 [11].

With the atomic coordinates of each atom, all the partial pair correlation functions can be calculated (figure 2). Si atoms were constrained to remain in tetrahedral sites; however a small fraction of Si (<2%) has an unusual configuration (1, 2 or 5 O neighbours). Si–O and O–O partials dominate the total correlation function at high r . They can be used to assign the 4 and 5 Å peaks to Si–O and O–O correlations, respectively. Similar values have been found in vitreous SiO_2 [12] and are also in good agreement with molecular dynamics simulations on alkali silicate glasses [7]. Mozzi and Warren [12] also indicated a first Si–Si distance at 3.1 Å which is close to the 3 Å peak in the Si–Si partial. On average, Si atoms are linked with 2.8 Si and 0.9 Ti, giving a total coordination number for second neighbours of 3.7. This seems to indicate that the glass has a three-dimensional network. There is no NMR measurements on this glass but an NMR study on a potassium trisilicate glass [13] indicates that the predominant species is Q^3 (Q^3 and Q^4 are predominant in the RMC model). Despite its high coordination number, titanium acts thus as a network former in the structure.

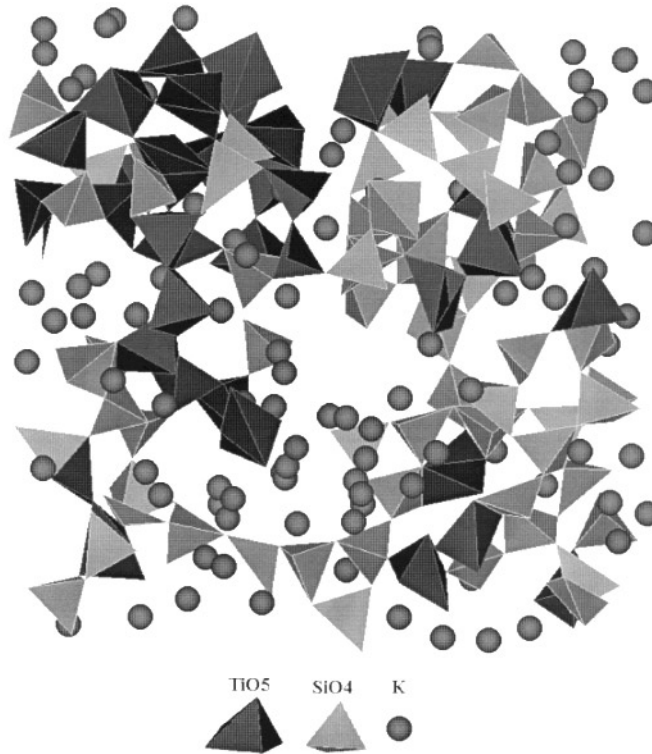


Figure 4. Representation of the glass structure modelled by RMC for a slice (about 10 Å) in the configuration of 1200 atoms.

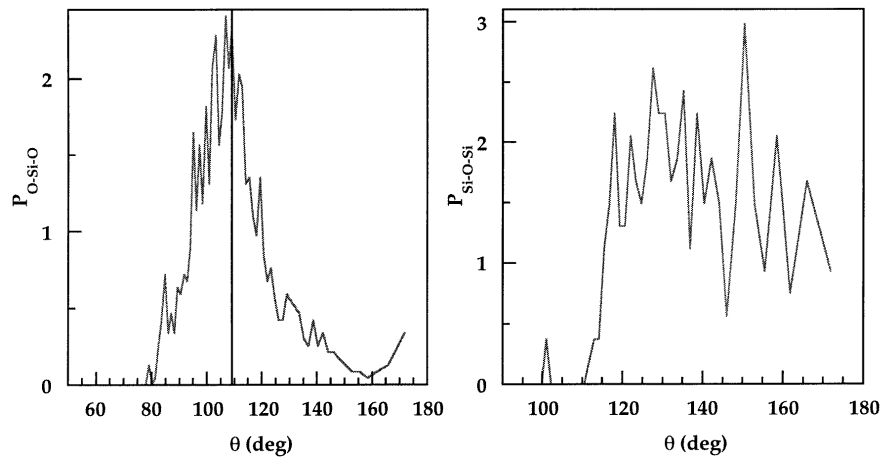


Figure 5. RMC distributions of O-Si-O (left) and Si-O-Si (right) bond angles.

The K-O partial function presents a maximum at 2.8 Å in agreement with K-O distances determined by EXAFS [14, 15] but as mentioned earlier the coordination number of five is low. The lack of structural data on the medium-range order around potassium is illustrated in the K-K partial function. A first K-K distance at 3 Å is observed. This value seems

short compared to the K–K distances existing in crystalline silicate [16] (4 Å) or molecular dynamic simulations of a potassium silicate glass [7] (~3.75 Å). However, similar distances (3.2 Å) are found in crystalline $K_2Ti_2O_5$ which contains five-coordinated titanium [17]. Furthermore a distance of 3 Å is close to the limit imposed by the constraint of closest approach between two potassium atoms (fixed at 2.9 Å). This indicates that atoms generally tend to reach this lower limit because atomic displacements are facilitated (there are fewer steric constraints when the ‘spheres’ have smaller radii).

A modelling of this multicomponent glass using atomic potentials would be a tedious task to correctly reproduce the MRO around Ti. Although a common use of RMC and other simulating techniques (Monte Carlo, molecular dynamics) is necessary to obtain thermodynamic stable structures consistent with the experimental data sets, the separate use of RMC can help us to understand the glass structure. Despite a low statistic (box size limited to 26 Å, 100 Ti atoms), the RMC model confirmed some experimental results (direct corner linkage between Ti polyhedra, presence of about 2 Si and 2 Ti second neighbours around a Ti atom, non-random distribution of Ti).

6. Conclusions

Using the RMC technique, the structure of a potassium titanosilicate glass has been modelled by fitting neutron scattering data obtained using isotopic substitution on Ti. The model reproduces the local environment of each species in the glass and gives structural three-dimensional information that allows a better understanding of the medium-range order around Ti. The distribution of Ti is broadly consistent with the experimental second difference. The RMC simulation is in agreement with an inhomogeneous glass structure with some regions enriched in Ti and some regions enriched in Si. This heterogeneous structure may provide a key to understand the unusual thermodynamic properties of this glass.

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