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The role of the fused silica stoichiometry on the intrinsic defects concentration

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Abstract

Silica is one of the reference materials for optical systems in Fusion Technology both in magnetic (ITER) and in inertial (NIF) confinement concepts. Its properties of interest (such as optical absorption, radioluminescence or mechanical properties) are closely related to the presence of defects which may be intrinsic to the material, generated by irradiation, or associated to impurities. In this work the types of intrinsic defects and their concentration as a function of stoichiometric deviations are studied using classical molecular dynamics. The Feuston–Garofalini potential is assessed in this study by analysing the obtained defects. The structural properties of defects found by computer simulations are characterized and compared with known defects in silica.

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1. Introduction

Due to its performance, vitreous silica is considered as a firm candidate to be used in different components in the future inertial and in magnetic confined fusion reactors [1–3]. This potential application renewed the interest in characterizing its behaviour under radiation. In recent years, the development of fused silica with high radiation resistance (from the optical point of view), at least to ionising radiation, has been possible [4]. However the cause of this resistance is not sufficiently clear. One possibility is the presence of impurities in the material [5].

Defects in silica determine its electrical, dielectric and optical properties that, together with its chemical inertness and thermal stability, are the main factors determining the great versatility of applications of this material. At the present time, there is abundant information on the different defects and their optical properties [6]. But, in spite of this vast accumulated knowledge, several uncertainties still exist and may have great technological importance. For example, it is not clear how the material stoichiometry or the content of impurities modify the main defect characteristics as well as its thermal and optical stability.

Molecular dynamics (MD) is a computer simulation technique that yields information on the atomic

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structure of the system and on its physical properties. It can be very useful in characterizing the behaviour of the material under extreme conditions not easily available in the laboratory though it requires some validation with experimental results. The objective of this work is the MD study of the defects that are formed in silica and their relationship with the material stoichiometry. Deviations from the exact stoichiometry SiO_2 is responsible for intrinsic defects in silica though its role in the morphology and relative concentration of the different defects is not clear. Information obtained in this paper is expected to be useful for the study of radiation defects in silica [7].

2. Interatomic potential and computer tools

The interatomic potential used for these simulations was the well known Feuston–Garofalini (FG) potential. This empirical potential was proposed in 1988 for vitreous silica [8] and revised in 1994 [9]. The FG potential uses a combination of 2- and 3-body terms to account for the mixed ionic-covalent nature of bonding in silica. Additionally it uses a small cut-off, which improves the reproduction of the medium-range scale of interest while maintaining its short-range nature. It was empirically fitted to experimental data obtained from neutron scattering and favours the Zachariasen model of tetrahedral amorphous structure of vitreous silica. The FG potential has been widely used to study a variety of properties under different conditions [10–13].

The MDCASK computer code used for the MD simulations presented in this work was constructed to study specifically radiation effects in materials [14]. This program is based on the MOLDY code developed by Finnis et al. [15] and later modified to run in parallel machines [16]. The time step selected in this work was 0.5 fs which is on the order of the vibrational frequency of vitreous silica [17]. This time step has been checked to generate stable and reproducible systems.

3. Material simulation

The different silicas studied in this paper were generated starting with the cubic β-cristobalite structure. This procedure includes two main parts. First, the cubic β-cristobalite structure is heated and maintained at 7000 K for 50000 steps of 0.5 fs. By using this procedure the long-range order characteristic of the crystalline structure disappear. Following this initial melting, the temperature is set at 6000 K in a new run. This second step is repeated for 5000 K, 4000 K, 3000 K, 2000 K 1000 K and 300 K. The output file in each run, containing positions and velocities, is used as input file in the following one. Periodic boundary conditions were used to reproduce an infinite lattice box. In each quenching run, the temperature was maintained constant by re-scaling the velocities of all the atoms in the system every 10 steps. This procedure has been previously used in similar studies [18,19,9]. The size of the simulated material was $8 \times 8 \times 8$ unit cells, which account for a total of 12288 atoms.

In order to obtain variations in the stoichiometry, the number of atoms in the initial β-cristobalite material was modified by introducing interstitials or vacancies. In addition to the case with exact stoichiometry SiO_2, eight different stoichiometries SiO_{2+x}, where x fluctuates from -0.074 to 0.080, were obtained. These materials represent a stoichiometry variation which oscillates nearly between −4% and 4%. The number and type of atoms added or eliminated in each case from the initial crystalline material is reported in Table 1.

Atoms were randomly eliminated from the initial crystalline material in order to create vacancies. The precaution of eliminating the same number of atoms in each set of 1000 atoms guaranteed uniform distribution of vacancies. The introduction of new atoms was a little more complicated since the location of new atoms too close to other atoms would give rise to high potential energy positions which should be avoided. The β-cristobalite may be seen as constructed by tetrahedrons $(SiO_4)^{-4}$ containing the Si atoms in its center and the O atoms in the corners being these last ones shared by two tetrahedrons. Regions of the unit cell out of these tetrahedrons were selected for introduction of new atoms.

4. Analysis of the materials

The atomic configuration of fused silica is, for short distances, very similar to that of β-cristobalite. In both configurations each silicon atom is placed in the center of a $(SiO_4)^{-4}$ tetrahedron being the O atoms in its corners. Each of these O atoms is shared by two tetrahedrons. In β-cristobalite this structure is repeated along the crystalline axis giving rise to a long-range order while in fused silica there

Table 1
Several materials with different stoichiometry SiO_{2+x} were prepared by introducing atoms or vacancies

	O atoms added	Si atoms added	x	Si5	O1	Si3	O3
Melting 4	−303		−0.0740	0	0	24	588
Melting 3		+157	−0.0738	3	1	18	614
Melting 2	−80		−0.0195	5	16	5	176
Melting 1		+40	−0.0193	10	15	4	181
Melting 0	0	0	0	22	67	2	87
Melting 5	+80		+0.0195	70	125	1	34
Melting 6		−40	+0.0197	63	130	0	33
Melting 7	+303		+0.0740	221	383	0	1
Melting 8		−157	+0.0797	210	418	0	0

Second and third columns show the number of atoms added in each case (negative number indicate creation of vacancies). The number of defects in each case is indicated in the last four columns. Each defect in this table corresponds to a defect concentration of 5.32×10^{18} defects/cm^3.

is a lack of long-range order. In fused silica tetrahedrons are connected through their corners but with a certain level of disorder [20].

Within this scheme, the simplest way to define defects is on the basis of the coordination number of each atom. Any atom that is not in the coordination number that corresponds to it, 2 for oxygen and 4 for silicon is considered a defect. In order to determine the coordination number, a cut off distance must be defined to discriminate between neighbours and non neighbours.

This cut off distance may be obtained from the pair distribution function $g(r)$. In the case of crystalline material, the peaks are very well defined even at long distances. In the case of fused material, the first peaks are well defined due to the short-range order but a nearly constant level is obtained for longer distances. From this function, it is easy to identify a value that discriminates between first and second neighbours. The value of 2.15 Å was selected as the cut off distance to identify first nearest neighbours.

Generally speaking, the defects that appear with a higher frequency are Si atoms bonded to 3 or 5 O atoms and O atoms bonded to 1 or 3 Si atoms. These defects will be named with the name of the atom followed by its coordination number, i.e., Si5, Si3, O1 and O3. The number of each kind of defect found after each run is reported in Table 1. As shown in this table, the materials with Si interstitial or O vacancies, i.e., negative values of x, contain a high number of Si3 and O3 defects. On the other hand, materials with added O interstitials or Si vacancies are rich in Si5 and O1 defects. Other defects are observed with a very low frequency. Usually these defects are a mixture of two of the four ones mentioned. With the help of a visualization tool it is possible to study the morphology of these types of defects. A scheme of these four defects is shown in Fig. 1.

The O1 defect (oxygen in coordination 1) gives rise to a tetrahedron disconnected in one of its vertices. A low atomic density is observed in the region of the disconnected atom. Additionally, the disconnected O atom, O1, reinforces its bonding with the Si causing that the Si–O1 distance is slightly lower than its usual value, 1.54 Å versus 1.60 Å. Simultaneously, the distance from the Si atom to the other three O atoms is slightly longer (1.64 Å). This change in the distances also gives rise to a variation in the O–Si–O angles. Usually, these angles are around 109.4°, which correspond to the angles for a regular tetrahedron. The angles O1–Si–O turned out to be slightly higher, 112° while the angles between any of the other three O atoms, O–Si–O result slightly lower, 106°. In other words, the Si atom moves towards the disconnected O atom.

The O3 defect consists of an oxygen atom in coordination 3 instead of 2. This oxygen atom is found in the plane defined by three O atoms as shown in Fig. 1. The distribution of Si–O–Si angles peaks at 120° instead of the usual 143–154° confirming this visual conclusion. Additionally, the Si–O distances are clearly longer than the usual one, 1.8 Å versus 1.65 Å.

The Si3 defect consists of a silicon atom in coordination 3 instead of 4. This defect is produced directly by an O vacancy. The other three O atoms form an equilateral triangle in whose center the Si is placed. This structure can be observed directly in Fig. 1 but it is also detected by the distribution of the O–Si–O angles for this type of defect which,

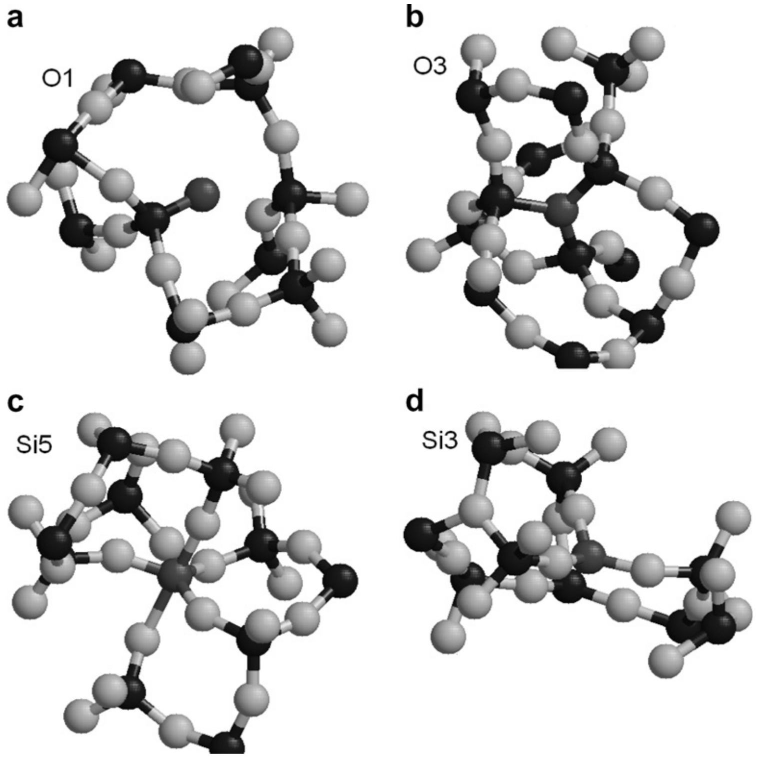

Fig. 1. Representation of the four most numerous defects found by molecular Dynamics in fused silica: (a) O1 defect (an oxygen atom with one neighbour silicon atom); (b) O3 defect (an oxygen atom with three neighbour silicon atom); (c) Si5 defect (a silicon atom with five neighbour oxygen atoms); (d) Si3 defect (a silicon atom with three neighbour oxygen atoms). Black spheres represent Si atoms, white spheres represent O atoms and gray spheres in the center of the figures represent the defective atom.

peaks at 120° confirming the triangle structure. In the distribution of distances a slightly shorter Si–O distance is also observed.

The Si5 defect consists of a Si atom shared by 5 O atoms instead of 4. The geometry of this defect is partially similar to that of the Si3 defect with three O atoms placed in the corners of an equilateral triangle and the Si atom in its center. The other two O atoms are almost aligned with the Si atom, being this one in the midpoint between both O, and in a direction normal to the plane that contains the other three O atoms and the Si atom. As a consequence, the distribution of O–Si–O angles produce peaks around 90°, 120° and 170°. The distribution of distances is also different to the usual one, being around 1.75 Å instead of 1.63 Å.

It is important to notice that the defect morphology described above, i.e., the coordination and distribution of distances and angles, is the same for the different prepared materials; the defect characteristics are always the same and independent of the material stoichiometry.

5. Discussion

The results show four types of preponderant defects whose concentration depends strongly on stoichiometry. Such dependence is not linear with x, at least in the studied range. As expected, the minimum total number of defects is observed in the exact stoichiometry SiO_2. It is interesting to note that results (number and type of defects) obtained by including interstitials are comparable with results obtained by producing vacancies provided that the resulting stoichiometry is the same in both cases. See for example melting 1 and melting 2 in Table 1.

The prevalence of O3 defects to Si3 defects is also noteworthy. See for example melting 4 in which 303 oxygen atoms (nearly 3.7%) are eliminated from the material, giving rise initially to an equal number of silicon atoms with coordination 3. During the melting, the system change in such a way that the O atoms are shared by 3 silicon atoms giving rise to the O3 defects and eliminating many of the Si3 defects. It is worth mentioning that very few defects associated to oxygen vacancies (ODC or E') are found in silica following irradiation experiments [21]. A similar process, though not as pronounced, takes place when Si vacancies are created. In melting 8, 157 Si atoms are eliminated giving rise initially to equal number of O1 defects. Many of these defects evolve towards the Si5 defects by sharing some of the available Si atoms between five O atoms.

It is difficult to compare these results with known defects in silica. One of the problems arises from the fact that it is not possible to know the ionization state of the defects obtained by MD. Si3 defects may correspond to the E' centers or to the oxygen deficient centers (ODC). The E' center is defined [22] as an unpaired electron in a dangling tetrahedral orbital of a silicon bonded to just three oxygen atoms. However, we can not make a distinction between ODCs and E' centers in these type of calculations, since no electronic effects are included. Calculations performed elsewhere [23] on the E' center foresee the planar configuration of this center as described in this work for the Si3 defect. On the other hand, O1 defects may find correspondence in the non binding oxygens (NBO). Once more it is not possible to distinguish between these and the NBOHC since the only difference is the ionization state.

Defects associated to Si atoms in coordination 5 or O atoms with coordination 3 are not found in the literature. There are other defects, well known in the literature as the peroxy radical (POR) or the interstitial O_2, that are not produced by simulation with this potential. Calculations by ab-initio methods probably would clarify these points as well as help in the comparison with data obtained experimentally.

6. Conclusions

The molecular dynamics code MDCASK has been used to produce vitreous silica with stoichiometric deviations. Four different defects that coincide with changes in the coordination number of O and Si atoms by one unit have been found in the resulting vitreous silica materials. An analysis of the number of defects produced during the several melting schemes shows the minimum number of defect for the exact stoichiometry SiO_2. A study of the defect morphology has been performed by measuring angles and distances in the defects. From the comparison of found defects with those reported in the literature, the capability of the Feuston–Garofalini interatomic potential for the study of defects needs to be revised since some defects, well known in the literature, are not reproduced while other defects, unknown experimentally, are created in the simulations.

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