JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 2, February 2010, p. 375 - 379

$Li_2O \cdot 2SiO_2$ glass structure simulation using molecular dynamics simulation

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Knowledge of various types of solid structure presents both a theoretical interest, fundamental and practical. If current experimental methods can characterize the structure of crystalline solids, the information is limited to more simple system in case of vitreous solids. The explanation lies in the lack of order at distance characteristic for glasses. In the last two or three decades, the method of molecular dynamic was remarked among the theoretical simulation method of some oxide glasses. In the present paper the structure of lithium disilicate glass obtained by the method of molecular dynamic is presented. Complementary, the method of radial distribution for internuclear distances of different component atom pairs is used. The obtained results are compared to reference data.

(Received November 28, 2009; accepted February 18, 2010)

Keywords: Glass, Lithium disilicate, Simulation, Structure, Temperature

1. Introduction

A first use of the molecular dynamics simulation (MDS) method in silicate systems was proposed by Woodcock and col. [1] for SiO_2 glass. In the following decades the studies extended to more complex silicate systems. Depending on the chemical composition, the model represents a system consisting of a particular number of atoms. For example, for the metasilicate glasses in the R_2O-SiO_2 system (R = Li, Na, K), in the paper [2] a number of 108 atoms was used, while in the paper [3] a number of 864 atoms was used (144 – Si, 432 – O, 288 – Na). In the paper [3] is presented a detailed analysis of the melt simulated structure and $Na_2O \cdot SiO_2$ and $Na_2O \cdot 2SiO_2$ glasses. In order to describe interatomic interactions of different ion pairs, Born-Mayer type [3] potential functions were used.

The results obtained by Inoue and Yasui [2] suggest the presence of chain-type silicate formations for the studied glasses, with alkali ions placed in interstitials positions of the chains. IR and Raman calculated spectra are similar to the experimental data.

Recent works, cited in the paper [4], revealed that the interatomic forces described through more refined methods (for example, by three-body terms) may reproduce a more accurate model of the melt and of the SiO_2 glass.

The information obtained directly from the molecular dynamics model require additional calculations in order to be corroborated with the laboratory experimental techniques and quantum chemistry calculations. For this purpose, the molecular orbital methods are fit to correlate the structure and the electronic state of every local structure (position). In this way a number of small clusters for SiO_2 glass [4] was studied. Their structure and properties can be explained because SiO_2 local structure is similar to the structure of the crystalline phase, at interatomic bonding scale. Other results obtained through dynamic simulation for the glass in binary and ternary silicate or non-silicate systems are available in the papers [5-7].

An application of dynamic simulations method for a lithium disilicate glass is presented in this paper. The aim of the study is to highlight a possible change in the glass basicity with the temperature.

2. Theoretical basis

The dynamic model is based on the potential functions PPFs (pair potential functions) which describe the interatomic interactions. According to different authors as Born-Mayer (BM), Pauling (PA) etc., explicit relations for PPFs can be used.

The molecular dynamics simulation (MDS) consist in solving the motion equations for a system of atoms interacting between themselves due to an interatomic potential. For the structures with a pronounced covalent character, as it is for vitreous silica, in order to describe the interactions between the atoms i and j, which are placed at the distance r_{ij}, in the technique MDS is used a modified Born-Mayer-Huggins potential.

The form of BM relation which describes the potential between different pairs of atoms V_{ij}, is:

$$V_{ij} = A_{ij}\exp\left(\frac{-r_{ij}}{\rho}\right) + \frac{Z_i \cdot Z_j \cdot e^2}{4\pi\varepsilon_0 r_{ij}} \quad (1)$$

$$A_{ij} = \left(1 + \frac{Z_i}{n_i} + \frac{z_j}{n_j}\right) \cdot b \cdot \exp\frac{\sigma_i + \sigma_j}{\rho} \quad (2)$$

where r_{ij} is the internuclear distance between the atoms i and j; Z – electric charge; σ – distance parameter which depends on ion radius; n – number of electrons in the valence layer; b and ρ – constants.

The molecular dynamics method [8, 9] simulates the glass structure considering that the interaction forces between the atoms are known. These forces are considered to come from a particular type of potential.

It is possible to solve the newtonian equations for the movement of particle system by knowing the analytical formula for the interaction forces. In other words, if we know the initial ions positions and initial velocities it is possible to calculate the positions and velocities at a later time. The ions are considered to be distributed in a cube whose sides depend on the glass density and on the number of ions, and the velocities are considered to correspond to Maxwell's velocity distribution for a given temperature.

3. Results and discussion

This paper describes the simulation of lithium disilicate glass (LS_2) structure through molecular dynamics, for three different temperatures. The Born Mayer [10] potential was used in the simulation and a number of 1792 atoms was considered: 768 oxygen atoms, 512 silicon atoms and 512 lithium atoms.

The elementary cell dimension was deduced as a function of atoms number and the real density of glass and is equal to 2,34 g/cm^3.

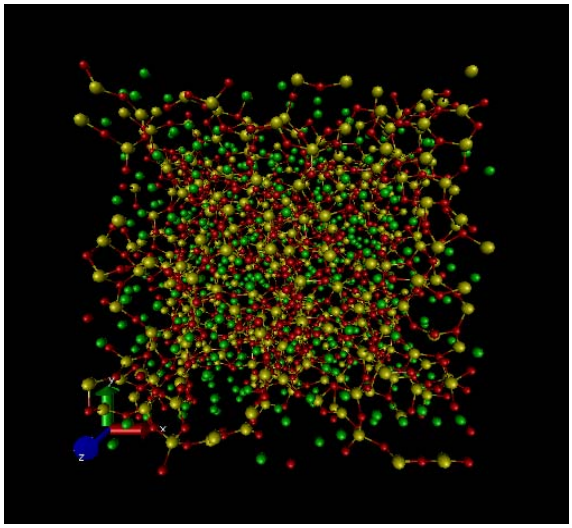

Fig. 1. System image at 3000K.

The simulation started from a random configuration at the initial temperature of 3000 K. The system evolved for 30000 iterations, the final configuration is considered as the initial for the temperature of 1000 K. The process repeated until a temperature of 300 K.

Images of the LS_2 glass structure for three temperatures: 3000 K, 1000 K and 300 K are presented in the figures 1-3.

Also as a result of molecular dynamics simulation of lithium disilicate structure, the radial distribution functions calculated for six ion pairs were obtained. Two of these functions are presented in the figures 4 and 5. In the table 1, the first three radius of the coordination spheres for the ion pairs Si-O have been evidentiated and they were obtained at three different temperatures at which the computer simulation was carried out.

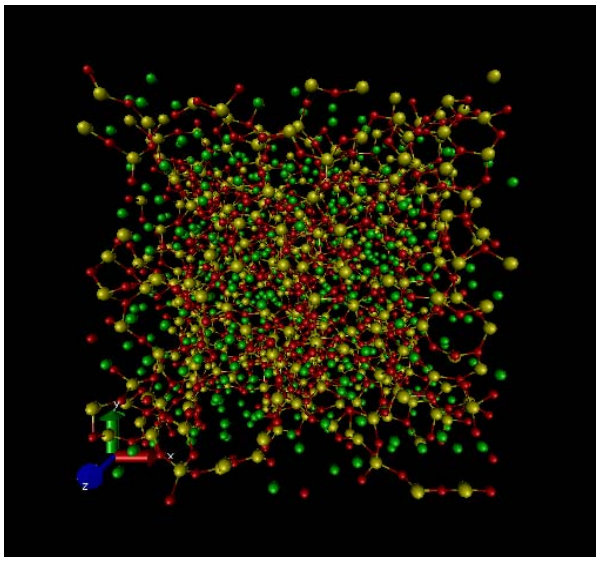

Fig. 2. System image at 1000K.

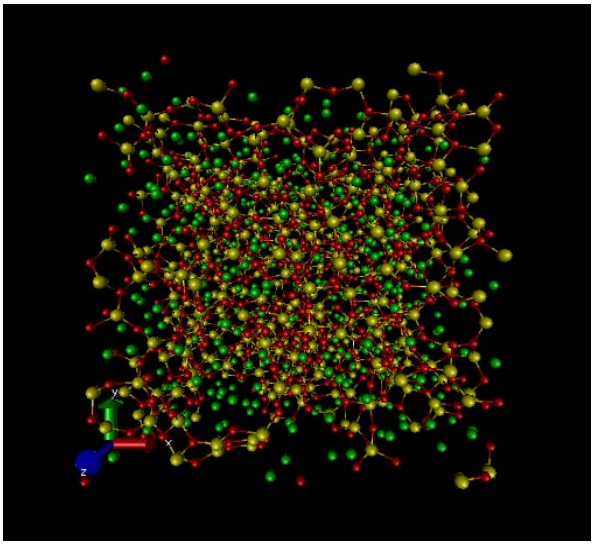

Fig. 3. System image at 300K

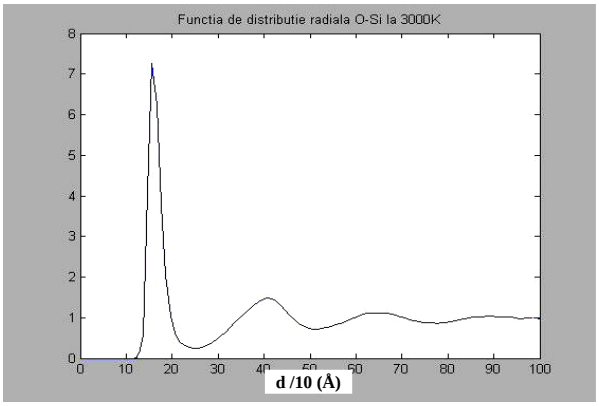

Fig. 4. The radial distribution function O-Si at 3000K, for lithium disilicate, LS_2.

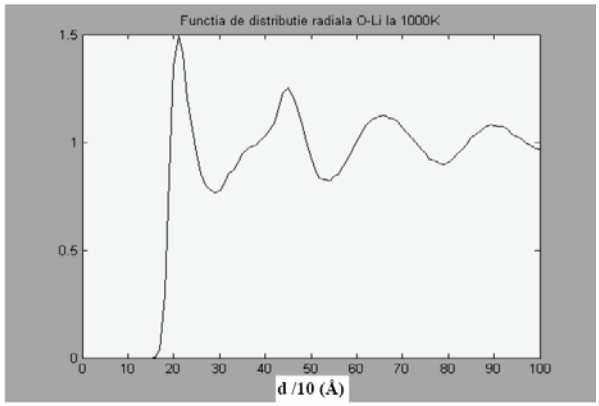

Fig. 5. The radial distribution function O-Li at 1000K, for lithium disilicate, LS_2.

Table 1. The radius of the first three coordination spheres for the Si-O ion from lithium disilicate, obtained at three different temperatures at which the computer simulation for the LS_2 glass structure was carried out.

Ion pairs	Temperature (K)								
	3000			1000			300		
	The radius of the first three coordination spheres (Å)								
	I	II	III	I	II	III	I	II	III
Si-O	1,76	4,78	6,65	1,694	4,805	6,68	1,615	4,12	6,42

The literature reports a series of results obtained for the oxide system Li_2O-SiO_2 glasses, using the molecular dynamics method. Generally, this structure simulation method is presented in correlation with the results obtained through X-ray diffraction or neutrons diffraction. This type of experiment allows us to set the curves and the electronic radial distribution functions by processing the resulted data, and from these functions we obtained a series of internuclear distances at small and medium-range distance (up to a limit of 0.5-1 nm). The results obtained through the two methods are close and this fact represents the validation degree of the dynamic modeling. In the case that discrepancies arise, the adjustment of some coefficients involved in calculus algorithm is effectuated. Such coefficients usually have values placed in a range depending on how they were determined. Following this (possible) fitting, the molecular dynamics method shows its potential by presenting a three-dimensional structural model, the internuclear distances and angles between the bonding orbitals are a function of the chemical composition and the thermal history of the respective glass.

For a glass with the composition of lithium metasilicate ($Li_2O{\cdot}SiO_2$), Inoue and Makishima [11] have applied the molecular dynamics method on a cell representing a cube with the side of 16.6740 Å, containing a number of 432 atoms (72 Si, 216 O, 144 Li), the glass density is considered to be 2.32 g/cm^3. In order to describe the interatomic potential the Born-Mayer relation was used (as we did in this paper). The potential parameters were calculated ab initio for clusters with the SiO_4Li_4 and $Si_2O_7Li_6$ composition, referring to the Si-O, Si-Si and O-O pairs (in the paper were considered the interactions between 6 pairs of atoms: Si-O-(Si), Si-O··(Li), Li··O, Si-Si, O-O, Li··Li). In these conditions the electric charges for Si, O and Li were, respectively +2.6/-1.533/+1.

A number of MD results related to Li_2O-SiO_2 system for glasses with the composition from Table 2 are presented in a recent paper [12] . The number of cells in this simulation is 3600 atoms.

Table 2. Compositions of xLi_2O-$(100-x)SiO_2$ glasses, density and informations on simulation cells.

Name	Composition	The number of atoms in simulation cells			Cell size (Å)	Density (g/cm^3)
	x Li_2O	O	Si	Li		
SiO_2	0	2000	1000	0	35.66	2.20
LS15	15	2200	1020	360	36.60	2.258
LS20	20	2160	960	480	36.13	2.283
LS25	25	2100	900	600	35.67	2.306
LS30	30	2040	840	720	35.21	2.330
LS33,3	33,3	2000	800	800	34.89	2.346
LS40	40	1920	720	960	34.42	2.346

In the paper [10] are presented the results obtained on disilicate glasses in different binary systems with different alkali oxides. In the table 3 [10] the data for lithium disilicate glass are centralized. These data were obtained through molecular dynamics method and are presented in the second and third columns in Table 2. In the last two columns are presented the internuclear distance values for the considered atoms pairs, which were obtained by processing the experimental data.

Table 3. Comparison between bond length (Å) and the coordination number between brackets) obtained through different methods for LS_2 glass.

Ion pair	Bond length (Å) / The coordination number			
	Molecular dynamics (MD) [11]	Another MD	Neutron diffraction	Extended X-ray Absorption Fine Structure (EXAFS)
Si-O	1.612(4.0)	1.62	1.63 (3.9) 1.625 (3.8) 1.60 (3.88)	1.613
O-O	2.621	2.61	2.66 2.655 2.62	-
Si-Si	3.126	3.01	3.04 2.96	-
Li-O	1.95(3.7)	2.00	1.97 (3.2) 1.963 (2.16) 1.88 (3.63)	-

In the simulation which was effectuated in this paper, were obtained the values presented as a function of temperature in Table 4.

Table 4. Simulated values through MD for LS_2 glass.

Internuclear distance type	Temperature, K		
	3000	1000	300
Si-O	1.76	1.694	1.615
O-O	2.9	2.9	2.9
Si-Si	3.1	3.1	3.1
Li-O	2.0	2.1	2.1
Si-Li	3.0	3.0	3.0
Li-Li	2.7	2.8	2.9

A comparison between the Tables 3 and 4 shows the very good data correspondence, which demonstrates the viability and the potential of simulation method used.

Also, for the medium-range internuclear distance d = d(Si-O) is pointed out an increase as the system temperature is increasing. The increase of medium-range distance d(Si-O) shows an emphasis of ionic character of Si-O bond, because of a stronger deformation of the electronic cloud. The final result is an increase of local basicity for SiO_4 tetrahedra and finally for LS_2 glass. The final effect is the increase of glass basicity with the temperature.

4. Conclusions

The molecular dynamics method was used to simulate the structure at three different temperature for the lithium disilicate glass.

The radial distribution functions for different atom pairs were also calculated for the considered temperatures.

Values were determined for the main internuclear distances between the vitreous system atoms. The results were compared with the values from the literature data and it was observed a very good data agreement.

Through its potential, the molecular dynamics simulation (MDS) method shows the way in which different glass steric characteristics change with the temperature variation. In this way it is possible to obtain informations regarding the variation of glass basicity with their thermal history.

References

[1] L. V. Woodcock et al., J. Chem. Phys. **65**, 1565, (1976).
[2] H. Inoue, I. Yasui, Phys. Chem. Glass. **28**, 63, (1987).
[3] B. Hatalova, M. Liska, J. Non-Cryst. Sol. **146**, 218, (1992).
[4] Y. Benino, K. Hirao, N. Soga, J. Non-Cryst. Sol. **183**, 23 (1995).
[5] F. Gan, G. N. Greaves, W. Smith, R. Winter, J. Non-Cryst. Solids, **293-295**, 539 (2001).
[6] O. Gedeon, S. Charvatova, J. Machacek, Advanced Materials Research, **39-40**, 65 (2008).

[7] G. G. Boiko, G. V. Berezhnoi, Advanced Materials Research, **39-40**, 49 (2008).
[8] E. Roțiu, Modelling of some structural processes in glass, Ph. D. Thesis, Bucharest, (1999).
[9] Y. Akasaka, H. Inoue, I. Yasui, J. Non-Cryst. Solids, **150**(1-3), 92 (2002).
[10] A. Abrahamson, Phys. Rev. **178**, 76 (1969).
[11] H. Inoue, A. Makishima, Phys. Chem. Glasses **37**(3), 116 (1996).
[12] Jincheng Du, L. Rene Corrales, J. Non-Cryst. Sol., **325**, 3255 (2006).

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