STRUCTURE OF SILICATE OXYNITRIDE MELT DOPED WITH SCANDIUM, YTTRIUM AND LANTHANUM: A MD DFT SIMULATION

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The MD DFT simulations of three oxynitride systems (Mg–M–Si–O–N, M = Sc, Y, La, 20 eq.% of N) were carried out. The results in the form of RDF and a coordination number were compared with the available experimental data and a good agreement was found. The main features of the experimental total RDFs were identified by means of the partial RDF originating from the simulations. Calculated coordination numbers of anions and cations were compared with the experimental data measured on both glasses and crystalline phases. It was confirmed that MD DFT can be used for bulk simulations of multicomponent glassy oxynitride systems with quite reasonable results. Some discrepancies in Si-O and Si-N distances were attributed mainly to higher temperature and limited size of the systems.

INTRODUCTION

Oxynitride glasses occur as grain-boundary phases in nanostructured silicon nitride ceramics and dramatically influence its mechanical strengths [1, 2]. Therefore, the investigation of their structure and properties is lead not only by the theoretical interest but primarily by the strong technical impact. In early studies related to the refining of glass melts, small concentrations of nitrogen in silicate glasses were reported to increase their softening temperature, viscosity and resistance to devitrification [2, 3]. However, till now the relationship between physical properties and the structure of oxynitride glass is not fully understood [4, 5].

Atoms in oxynitride glasses are usually considered to be cations and anions. The amount of the particular ion can be alternatively quantified by the equivalent percentage, which expresses the relative contribution of the cationic/anionic charge. For example, the concentration of nitrogen expressed in equivalent percents yields

$$\text{eq.\% of N} = \frac{3[N]}{2[O] + 3[N]} \qquad (1)$$

where [N] and [O] are atomic concentrations, 2 and 3 are valences. Similarly, eq.% of O or eq.% of cations can be expressed as well. It was found that the glass forming region for oxynitride glasses is quite narrow and rarely exceeds 25 eq.% of N [2].

If nitrogen is substituted for oxygen the silicate structure becomes stiffer due to higher valency (-III) of nitrogen. In principle, three bonding possibilities should be considered:

a) $\equiv$Si–N(-Si$\equiv$)$_2$ b) $\equiv$Si–N$^-$–Si$\equiv$ c) $\equiv$Si–N^{-2} (2)
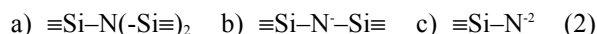
The case a) reflects the situation in glassy and crystalline systems with no alkali or alkali-earth modifier. When a modifier is added, the cases b) and c) will happen in the structure. Simultaneously, with formation of b) and c) type structures the non-bridging oxygens (e.g. $\equiv$Si–O$^-$) are formed in this case. ^{15}N MAS-NMR and neutron diffraction show that in sodium-silicate (20 mol.% Na$_2$O) glasses with 4 at.% of N [3] the cases a) and b) predominate. ^{29}Si MAS-NMR measurements revealed that a silicon atom binds more than one nitrogen atom very unwillingly, at least for the measured system (20 eq.% of N, 80 eq.% of O, 20 eq.% of Mg, 20 eq.% of La, 60 eq.% of Si) [4]. It was suggested [6] that, while Mg is a network modifier in oxide systems and is usually 6-coordinated, in oxynitride glasses it acts as a network former (or intermediate), being 4-coordinated. As a rule of thumb, cationic modifiers (such as column III elements and lanthanides) with higher cationic field strength (CFS) increase strength of the silicate structure [4, 7].

In many cases, MD simulations help with interpretation of the experimental data [8, 9]. Recently, experimental investigations on oxynitride glasses were com-

pleted with atomistic computer simulations [10-12]. However, molecular dynamics simulations with empirical force fields are seldom able to describe interatomic polar covalent bonds with an acceptable accuracy. It seems that the most difficult task is the deriving of interatomic potential functions describing correctly the first coordination spheres of the network-forming atoms, e.g. N, B, P, Al, Si. Thus, in comparison with classical simulations of oxynitride glasses [10-12], more precise and more promising simulations can be performed with atomic forces calculated with help of density functional theory (MD DFT) [13]. Despite such simulations comprise only about a hundred particles and only a short time interval can be studied, typically tens of picoseconds, it was shown that even such limited calculations suffice for establishing of the short range ordering (SRO) of atoms in amorphous systems [14, 15]. Atomistic simulations enable to calculate various physico-chemical properties of the studied system and they can be directly compared with the experimental results e.g. radial distribution functions (RDF), structure factor, distribution of Q-species, diffusion and viscosity coefficients, elastic moduli, IR spectrum, etc.

The aim of this study is to perform MD DFT simulations of silicate oxynitride systems containing magnesium and the column III elements - scandium, yttrium, and lanthanum. Our work follows the extensive experimental research carried out by Lofaj and co-workers [4, 5, 16].

COMPUTATIONAL DETAILS

The composition of the simulated systems Mg–M––Si–O–N (M = Sc, Y, La) were as follows: 21.33 eq.% of Mg, 20.00 eq.% of M, 58.67 eq.% of Si, 80.00 eq.% of O, 20.00 eq.% of N. It corresponds to 42.1 mol.% of MgO, 13.2 mol.% of M_2O_3, 38.2 mol.% of SiO_2, and 6.6 mol.% of Si_3N_4. The systems were simulated in cubic computational cells with periodic boundaries. The box volumes were determined by the experimental densities of the corresponding glasses (table 1). The total number of ions in each computational box was 118 (10 N, 60 O, 16 Mg, 10 M, and 22 Si).

The simulation procedure consisted from preparation of reasonably chemically ordered systems which were used as input for MD DFT simulation. The classical MD was used for this initiation procedure and only the yttrium containing system was subjected to above procedure. The other two systems were prepared for MD DFT simulation start by replacement of yttrium atoms by scandium or lanthanum followed by geometry relaxation performed by MD DFT. Thus the simulation procedure may be decomposed in the following detailed steps:

1) The positions of atoms in a simulation cell were randomised at 5000 K during 10000 steps using classical MD with time step of 0.001 ps.
2) The randomised structure entered the classical MD simulation [17]. The system was cooled down to 300 K to obtain the structure of "some chemical order".
3) The obtained ion positions were taken as an input for a MD DFT simulation using Hellmann-Feynman forces. The time-step of a numerical solution of the equations of motions was set to 0.001 ps. The system was relaxed for 7.5 ps at 4000 K and was treated as an NVT ensemble. The temperature was scaled at each 0.05 ps.
4) Up to now, only the system with Y was simulated. For other two studied systems, at this point, the Y ions were replaced by Sc/La. All ion coordinates were linearly rescaled according to the room temperature densities of Sc/Y/La oxynitride glasses (table 1).
5) Additional MD DFT runs (5 ps) were performed for Sc and La systems with a temperature scaling followed by NVE relaxations for 3 ps. As an example, the time evolutions of temperature, total energy, and potential energy for Sc system are shown in figure 1.
6) The temperature of all systems were numerically rescaled to 2000 K. Temperature was scaled for 2.5 ps
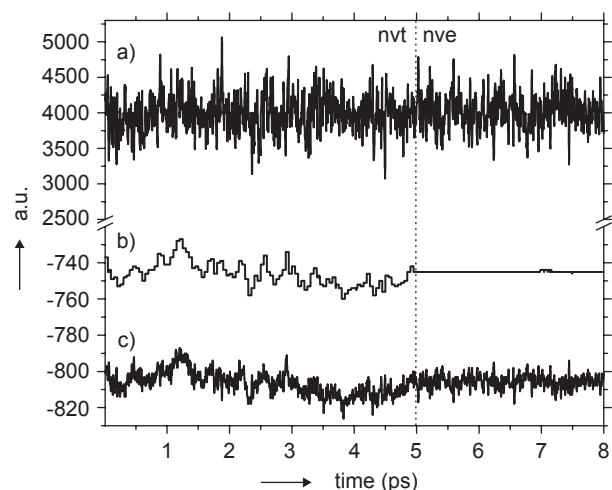

Figure 1. Temperature (K) - (a), total energy (eV) - (b), and potential energy (eV) - (c) evolutions in Sc-system at 4000 K. The dotted line separates the constant temperature (NVT) and the following constant total energy (NVE) modes.

Table 1. Room temperature densities [4] of studied Mg–M–Si––O–N (M = Sc, Y, La) oxynitride systems.

M	Density (g/cm³)	Simulation box size (Å)
Sc	3.096	11.109
Y	3.545	11.196
La	3.972	11.348

in MD DFT run (NVT) to ensure no temperature drift would be observed after switching the temperature scaling off.

7) Finally, 2.5 ps runs were completed under constant total energy conditions (NVE). During the runs the radial distribution functions were collected every 0.05 ps. The radial step of 0.057 A was used for RDF accumulation.

The MD DFT calculations of the bulk oxynitride systems were performed using the Vienna ab-initio simulation package VASP [18]. The valence-electron wavefunctions were expanded in plane waves. The Kohn-Sham equations of density-functional theory (DFT) were solved using generalized gradient approximation (GGA) adapted by Perdew, Burke and Ernzerhof (PBE). All-electron wave functions were used to describe the electron-ion interaction as derived from ultrasoft pseudopotentials [19] via projector augmented wave technique (PAW). The potential energy calculations in scandium, yttrium and lanthanum systems were performed with plane-wave cut-offs of 250 eV, 213 eV, and 250 eV, respectively. The cut-offs correspond to the maxima of the minimal values recommended for DFT molecular dynamics among atoms present in the oxynitride systems. Brillouin-zone sampling was restricted to the Γ-point only.

RESULTS

No remarkable energy drifts of NVE ensembles were observed both at 4000 K and 2000 K. The total energy was perfectly conserved and therefore the timestep of 0.001 ps seems to be quite reasonable even at the highest used temperature (figure 1). Moreover, the potential energies were also kept constant what may serve as an indication that the major structural rearrangements faded out. The interpretation of hereafter presented results presumes that the short range ordering in the oxynitride systems is formed very quickly at an extremely high temperature and does not depend on a simulation time scale too much. This assumption is in harmony with the results of classical MD simulations [9]. Using of the above assumption enables significant time shortening of the performed MD DFT simulations. The reason for performing as short as possible simulations dwells in enormous computational demands of DFT. The size of a simulated system represents even more limiting factor, because the DFT algorithm scales as N^3, where N is the number of particles.

The snapshot of the simulated Sc-system is presented in figure 2. Such images may be useful for the first inspection of the structure, e.g. provide an initial hint on homogeneity and/or warn of the unusual coordinations. It is seen that the atoms in the Sc-system are reasonably distributed without a visible separation of the nitrogen phase. Although not presented here, other systems (Y- and La-) offer similar pictures.

As the snapshots are not suitable for the quantitative analyses, a comparison of the simulated and the experimental RDFs is given in figure 3. Experimental data for scandium and lanthanum oxynitride systems (20 eq.% of N, 80 eq.% of O, 60 eq.% of Si, 20 eq.% of
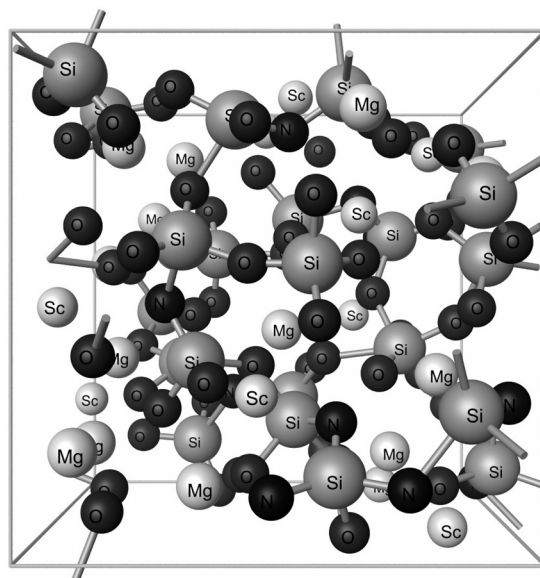

Figure 2. Structure of the simulated Sc-system.

Table 2. Positions of the maxima of the first peaks of pair RDFs. Average bond length (Å) in some common crystalline nitrides are denoted with asterisk [23].

System	N-					O-						
	N	O	Mg	M	Si	O	Mg	M	Si	Mg–Mg	M–M	Si–Si
Sc	3.06	2.83	2.17	2.11	1.78	2.67	2.00	2.11	1.67	3.28	3.55	3.00
Y	2.85	2.85	2.07	2.41	1.79	2.69	2.02	2.30	1.68	3.13	3.97	3.02
La	2.89	2.84	2.16	2.50	1.76	2.78	1.99	2.44	1.70	3.29	3.97	3.01
Sc*			2.13	2.22	1.73							
Y*				2.43								
La*				2.57								

Mg, 20 eq.% of M) were obtained by neutron diffraction at room temperature [16]. The yttrium system was not measured. Positions of the maxima of peaks corresponding to the particular X-Y pairs, summarized in table 2, are depicted in the figure 3 to identify the main contributions. The peaks of RDFs are not clearly separated what embarrasses the determination of the local structure of glassy systems. However, the main features can be identified on both the simulated and experimental RDFs. The simulated RDFs reveal similar behaviour as the experimental ones; however, the peaks coming from simulations are broader due to the higher temperature. The peaks of the first maxima are systematically shifted to a longer radius (about 4.3 %) and their right-hand shoulder is contributed by Mg–O/N (and M–O/N in case of Sc-system).
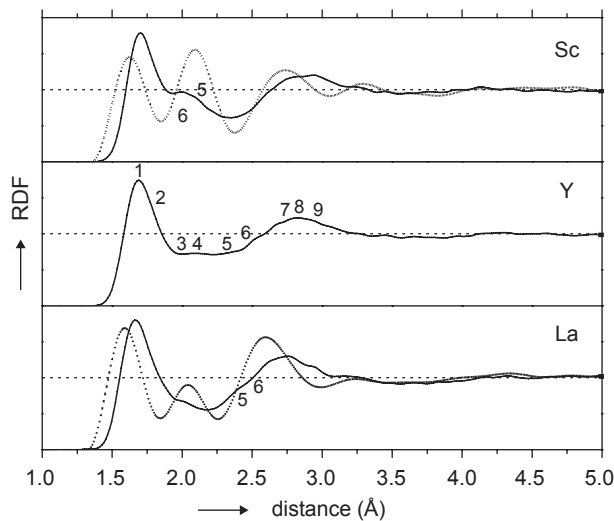

Figure 3. Total radial distribution functions of the scandium, yttrium, and lanthanum systems. DFT MD results are sketched by the solid lines; experimental results [16] by the dashed lines. The main features of the curves were identified with help of the simulated pair RDFs as follow: 1 Si–O, 2 Si–N, 3 Mg–O, 4 Mg–N, 5 M–O, 6 M–N, 7 O–O, 8 N–O and N–N, 9 Si–Si. For the sake of simplicity, only M–O and M–N peaks are marked in Sc- and La-systems.

In case of the Sc- and La-systems, one unstable N–N bond (of length 1.6 A) was observed in several atomic configurations. However, such arrangement is highly unstable in a system with a low content of nitrogen. In the amorphous $SiO_2 \cdot Si_3N_4$ system, there was observed much higher willingness of N towards formation of N–N bonds [13].

Coordination numbers were obtained by the integration of the pair RDFs up to their first local minima. The obtained results, including upper integration bounds, are presented in table 3. As expected, the partial coordination M–O increases with the increasing ionic diameters of column III elements. Scandium, yttrium, and lanthanum cations are coordinated by 6.6, 7.5, and 8.9 anionic neighbours, respectively. However, the number of coordinating nitrogen anions is not monotonous. The highest amount of nitrogen is coordinated to scandium, that is the smallest among the studied modificators. Then abrupt drop of the number of N around Y is observed followed by the expected increase in case La due to the increase of the ion size. The magnesium coordination sphere remains unchanged in all systems studied. This contains less than one nitrogen anion within 5.6 total neighbouring anions. The coordination sphere of a silicon atom remains approximately the same for all systems. Silicon binds 4.1 anions from which 0.8 are N. The coordination number of nitrogen is very close to 4. Most of nitrogen atoms are connected to two silicon atoms. For M and Mg, nitrogen slightly prefers bonding to magnesium. The coordination number of oxygen is roughly 3.5. Vast majority of oxygen atoms are non-bridging oxygens.

DISCUSSION

The simulated and the experimental total RDFs reveal similar features. Peaks of the experimental RDFs can be identified with help of MD simulation. On the other hand, some striking discrepancies arise when a quantitative comparison is required. While the peak widening of simulated RDFs can be attributed to the

Table 3. Coordination numbers and the first local minimum distances (Å) (in parentheses) of X–Y pairs.

System	Si–N	Si–O	M–N	M–O	Mg–N	Mg–O
Sc	0.7 (2.33)	3.5 (2.33)	1.3 (3.16)	5.4 (3.11)	0.8 (3.05)	4.7 (2.83)
Y	0.9 (2.29)	3.2 (2.35)	0.7 (3.30)	6.9 (3.19)	0.8 (3.07)	4.9 (2.85)
La	0.8 (2.32)	3.3 (2.32)	0.9 (3.34)	7.8 (3.46)	0.9 (3.00)	4.8 (2.89)

System	N–Si	N–M	N–Mg	O–Si	O–M	O–Mg
Sc	1.5 (2.33)	1.3 (3.17)	1.3 (3.06)	1.3 (2.33)	0.9 (3.11)	1.3 (2.83)
Y	2.0 (2.30)	0.6 (3.30)	1.3 (3.08)	0.9 (2.35)	1.1 (3.19)	1.3 (2.85)
La	1.8 (2.33)	0.9 (3.35)	1.4 (3.01)	1.2 (2.32)	1.3 (3.46)	1.3 (2.89)

influence of higher temperature, the 0.07-Å-drift of the first peak belonging to Si–O and Si–N pairs can be discussed such way only partly. Probably, a coincidence of more effects happens during a calculation. Among them, size of the system, incompleteness of a wave function basis set and premises of DFT should play a certain role. The over-coordinated silicon atoms are considered to be another important factor influencing Si–O distance. At this point, additional testing is to be carried out. We have tested the DFT methodology implemented in the VASP programme on silicate clusters: H_4SiO_4, $H_6Si_2O_7$, H_5SiO_3N, $H_7Si_2O_6N$, and $H_9Si_3O_9N$ (table 4). We have found our results to be in agreement with post Hartree-Fock quantum calculations [20, 21]. It seems that the Si–O and Si–N distances are usually rather longer in clusters than in a bulk material. We can speculate the main contribution, which prolongs the first RDF peak, to be the size of a simulation box. On the other hand, no difference in the first peak positions of the large (6000 atoms) and small (117 atoms) $Na_2O \cdot 2SiO_2$ glassy systems modeled with empirical Buckingham potentials was observed [22].

Average interatomic distances correspond to the first maxima of the pair RDFs (table 2). Except for M–X lengths no significant differences among the simulated systems were found (up to 5 %). Thus, the major changes are caused by the increasing ionic diameter of Sc, Y, and La ions. The calculated M–N distances are in good agreement with the tabulated values of crystalline nitrides [23].

An additional piece of information to the experimental results offers the analysis of coordination numbers (table 3). There are some common features throughout the systems. In all systems, the coordination number of silicon slightly exceeds four. Not only SiO_4 tetrahedra but also SiO_5 trigonal bi-pyramids were

observed in the simulated oxynitride melt. Such unusual units are believed to act as intermediates of high temperature transport processes in a melt [24, 9]. Number of over-coordinated silicon atoms decreases with the increasing ionic radius of M. Similar behaviour was observed in potassium-, rubidium- and caesium-silicate glasses modelled by classical MD simulations [25, 9] and by ^{29}Si MAS-NMR [24]. Larger cations are weakly bound to the silicate network, decrease rigidity and viscosity [5] of the structure. Therefore, high-temperature diffusive processes proceed more readily and formation of SiO_5 defects is suppressed [25].

A silicon atom is mostly bound to three oxygen atoms and one nitrogen atom. It seems consistent with the published results [5] where SiO_3N units dominate in the structure of oxynitride glass.

The crystalline Si_3N_4 phases contain only 3-coordinated nitrogen. However, in the oxynitride systems presented in this study, the coordination number of nitrogen is very precisely four, as it is in ionic crystalline nitrides [23]. It is not surprising if we consider chemical composition of systems contained a huge amount of MgO and M_2O_3. Nitrogen atoms bind approximately 1.8 silicon atoms. The formation of $\equiv Si–N^-–Si\equiv$ and $\equiv Si–N^{2-}$ units is preferred (see figure 2). It is in agreement with the present-day concept of the nitrogen role in the silicate structure [2, 7]. Nearly all oxygen atoms are non bridging oxygens (NBO), bridging oxygens (BO) form only lesser part of the structure. The equivalent binary metasilicate system ($MgO \cdot SiO_2$, i.e. 40 eq.% of Mg, 60 eq.% of Si, 100 eq.% of O) contains 2/3 of NBO and 1/3 BO.

Differences in coordination numbers throughout the systems do not seem to be conclusive enough. Larger M cations prefer oxygen in their coordination spheres, i.e. N/O ratio decreases. On the other hand, N/O ratio in the Mg coordination sphere is invariant with respect to a column III cation diameter. In most cases, the coordination number of Mg in crystalline magnesium oxides and silicates is 6. On the other hand, it equals 4 in magnesium nitrides. Therefore, the calculated average value 5.6 proves to be a superposition of these two values. The coordination number of Mg approaching 6 is in contradiction with ref. [6] which claims Mg atoms play rather a network forming than a network modifying role. Our simulations witness Mg to be a network modifier in oxynitride systems. Coordination number of Sc in crystalline materials [23] ranges from 5 to 8; the most frequent coordination number is 6. Y ranges from 6 to 7; mostly 7. La ranges roughly from 6 to 9, mostly 8. The calculated values slightly exceed tabulated data. It is quite common and can be explained by disordering in the oxynitride structure.

Table 4. Si–O and Si–N bond lengths (Å) in some oxynitride clusters. a) Our results obtained by DFT; b) RHF simulation [21]; c) experimental data cited in [20]; d) HF simulations cited in [20].

	Si–NBO	Si–BO	Si–N
$Si(OH)_4$	1.649[a]		
	1.643[d]		
$(HO)_3SiOSi(OH)_3$	1.647[a]	1.622[a]	
	1.650[d]	1.624[d]	
	1.657[b]	1.591[b]	
$H_3SiOSiH3$		1.633[d]	
		1.634[c]	
$(HO)_3SiNH_2$	1.654[a]		1.711[a]
$(HO)_3SiNHSi(OH)_3$	1.653[a]		1.721[a]
	1.660[b]		1.691[b]
$N[Si(OH)_3]_3$	1.652[a]		1.746[a]
	1.660[b]		1.719[b]

CONCLUSION

The DFT MD simulations of three oxynitride systems (Mg–M–Si–O–N, M = Sc, Y, La, 20 eq.% of N) were carried out. The results in the form of RDF and a coordination number were compared with the available experimental data and the good agreement was found. The main features of the experimental total RDFs were identified by means of the partial RDF originating from the simulations. Coordination numbers of anions and cations were calculated and compared with the available data measured on both glasses and crystalline phases. This work confirmed that DFT MD can be used for bulk simulations of multi-component glassy oxynitride systems with quite reasonable results. Some discrepancies in Si–O and Si–N distances were attributed mainly to higher temperature and limited size of the simulated systems.

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STRUKTURA KŘEMIČITÝCH OXYNITRIDOVÝCH TAVENIN DOPOVANÝCH SKANDIEM, YTRIEM A LANTANEM: MD DFT SIMULACE

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Byla provedena MD DFT simulace třech oxynitridových systémů (Mg–M–Si–O–N, M = Sc, Y, La, 20 eq.% N). Výsledky ve formě RDF a koordinačních čísel byly srovnány s dostupnými experimentálními daty a byla zjištěna dobrá shoda. Hlavní píky experimentálních RDF byly identifikovány pomocí parciálních RDF získaných ze simulací. Vypočítaná koordinační čísla aniontů a kationtů byla srovnána s experimentálními daty naměřenými u skel i krystalických fází. Bylo potvrzeno, že metoda MD DFT může být použita pro modelování vícesložkových skelných oxynitridových systémů, a to s rozumnými výsledky. Zjištěné nesrovnalosti v délkách vazeb Si–O a Si–N byly připsány hlavně vyšší teplotě a omezené velikosti simulovaných systémů.