THERMOCHEMICAL MODELLING AND AB INITIO MOLECULAR DYNAMICS SIMULATIONS OF CALCIUM ALUMINATE GLASSES

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Simple thermodynamic model, without any adjustable parameter, and ab initio molecular dynamics (MD) were used for the structural study of binary calcium aluminate glass xCaO·(1 - x)Al_2O_3, x = 1/3, 1/2, and 2/3. Both methods provided mutually comparable quantitative results in a reasonable agreement with the accessible experimental data and previous results of classical MD simulation. The obtained compositional trends are in agreement with the concept of the increase of Al/O coordination number (accompanied with formation of Al-triclusters) with the decreasing CaO content in the per-aluminous region.

INTRODUCTION

Calcium aluminate glasses are of interest from a fundamental structural point of view because of the lack of any of the traditional glass forming oxide [1]. They are also of technological interest because they have ultra low optical losses, making them attractive candidates for the low loss optical fibers. In addition, they have excellent mechanical properties. Calcium aluminate glass fibers have been therefore proposed for use for reinforcement of cement composites [2]. Latest challenge in the application of calcium aluminate glass is preparation of the transparent armors [3].

Structure of calcium aluminate glasses and melts was intensively studied during the last decade. Due to the developments of the experimental techniques the local structures of both glasses and melts were investigated by Raman spectroscopy, Nuclear Magnetic Resonance (NMR), and Neutron Diffraction (ND). The experimental results were also complemented with classical Molecular Dynamics (MD) simulations. The crucial task of the structural investigations was the coordination of aluminum by oxygen, namely in per-aluminous compositional region, i.e. for xCaO·(1 - x)Al_2O_3 where $x < 0.5$. In per-alkaline region, $x > 0.5$, it was found aluminum is close to be four-coordinated, i.e. the structure is dominated by AlO4 tetrahedra. Whereas in per-aluminous region, $x < 0.5$, the Al/O coordination number smoothly increases with an increasing Al_2O_3 content, i.e. the structure is composed with tetragonal, pentagonal, and hexagonal Al-polyhedra, different proportions of the above coordination polyhedra were found by different experimental/theoretical methods. In general, wider distributions of polyhedra can be observed for melts at higher temperatures. In addition, the average coordination does not reach six even for x going to zero [4].

The aim of the paper resides in the complementation of the structural studies with *ab-initio* MD and a simple Thermodynamic Model (TM). The following compositions are studied: the extreme case $CaAl_2O_4$ (CA), with stoichiometry corresponding to the fully polymerized 3D network of AlO_4 tetrahedra; the per-alkaline composition $Ca_2Al_2O_5$ (C_2A); and the per-aluminous composition $CaAl_4O_7$ (CA_2).

COMPUTATIONAL DETAILS

Ab initio molecular dynamics

The *ab initio* MD calculations using the Hellmann-Feynman forces of the bulk calcium aluminate systems were performed with help of the Vienna ab-initio simulation package VASP [5]. 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). The projector augmented wave (PAW) pseudopotentials [6] were used. The pseudopotentials can be found in the VASP pseudopotential PAW_PBE database under the following designation: Al, Ca_sv, and O_s. The potential energy calculations were performed with a default plane-wave cut-off (283 eV). Brillouin-zone sampling was restricted to the Γ-point only.

The CA_2 and CA systems were simulated by *ab initio* MD. Both systems contained 84 atoms: 28 Al, 7 Ca, and 49 O for CA_2, and 24 Al, 12 Ca, and 48 O for CA. The MD glasses were prepared in a similar way as it was done in our previous works [7-10]. Atoms were randomly placed into the cubic computational box adjusted to the temperature dependent experimental densities of the studied systems (Table 1). Then, the systems were thermodynamically equilibrated and structurally relaxed for 2 picoseconds (ps) at 5000 K. After that, the temperature was decreased to 4000 K, 2500 K, 1000 K, and finally to 300 K. At each temperature the systems relaxed for 20 ps. Temperature was rescaled in every 20 time-steps. The time-step of the numerical integration of the equations of motion was set to 0.002 ps. Atom positions were recorded in every 20th time-step to be later used in calculations of radial distribution functions (RDF) and coordination numbers.

Table 1. Experimental densities of MD simulated calcium aluminates. The values are compiled from [3, 11, 1].

	CA_2		CA	
Temperature (K)	Density (g/cm^3)	Box length (Å)	Density (g/cm^3)	Box length (Å)
300	2.98	10.047	2.88	10.303
1000	2.98	10.047	2.88	10.303
2500	2.80	10.258	2.70	10.526
4000	2.48	10.681	2.38	10.978

Thermodynamic model

The thermodynamic model of Shakhmatkin and Vedishcheva [12-14] was used for oxide glasses and melts. The systems were considered as ideal solution of the components given by stoichiometry of the equilibrium phases of the pertinent $CaO–Al_2O_3$ phase diagram. The equilibrium constants were determined from the standard Gibbs energies of formation of the corresponding crystalline phases [15] in the usual thermodynamic manner. This model supposes that Gibbs energies of crystalline phases can be applied even at the molten state when Gibbs energies of the corresponding liquids are not at hand. The strong feature of the model is the absence of any adjustable parameter in the computation of the equilibrium composition.

The mean Al/O and O/Al coordination numbers were calculated as the weighed sums of the calculated equilibrium compositions using the coordination fractions of each phase as presented in Tables 2 and 3.

Table 2. Coordination fractions, x_i, of aluminum in the different equilibrium crystalline phases. Data taken from [16].

Number	Composition	Collection code	x_4	x_5	x_6
1	C		0	0	0
2	A		0	0	1
3	C_3A	1841	1/2	1/2	0
4	CA	41661	1	0	0
5	CA_2	44519	1/2	1/2	
6	CA_2	34487	1/2	1/2	
7	CA_2	27264	1/2	1/2	
8	CA_2	16191	1/2	1/2	
9	CA_2	14270	1/2	1/2	
10	CA_6	34394	2/12	1/12	9/12

Table 3. Fractions of oxygen coordinations, x_i, by aluminum in the different equilibrium crystalline phases. Data taken from [16].

Number	Composition	Collection code	x_1	x_2	x_3	x_4
1	C		0		0	0
2	A		0		0	1
3	C_3A	1841	5/6	1/6	0	0
4	CA	41661	0	1	0	0
5	CA_2	44519	0	5/7	2/7	0
6	CA_2	34487	0	5/7	2/7	0
7	CA_2	27264	0	5/7	2/7	0
8	CA_2	16191	0	5/7	2/7	0
9	CA_2	14270	0	5/7	2/7	0
10	CA_6	34394	0	0	11/19	8/19

RESULTS AND DISCUSSION

Three independent MD simulations were carried out for both CA2 and CA systems. The resulting internal pressures of the systems were approximately -5 ± 17 kbar for CA_2 and -15 ± 13 kbar for CA. Results of CA simulations can be directly compared with experimental radial distribution functions (RDF), obtained by both neutron and X-ray diffractions [17] (Figure 1). MD results are very close to ND data (within the limit of 3-σ statistics). As far as the MD simulations are *ab-initio* (without empirical adjustable parameter) we can suppose the same quality in other studied systems, where the experimental RDFs are not available. Moreover, because the total RDF is straightforwardly connected with the coordination numbers we can anticipate the same reliability of the analysis of the coordination polyhedra distributions obtained from all of our MD simulations. Total RDFs together with their decompositions to the partial pair RDFs of CA and CA_2 glasses at 300 K are presented in Figures 2 and 3, respectively. It is worth noting that the smooth courses of the total RDFs were obtained due to averaging of three independent MD simulations. This fact is also emphasized by the relatively large error bars seen in both figures. The details of the partial pair RDF analyses can be quantified in terms of the coordination numbers (Table 4). The visible shifts in the average coordination numbers can be mostly attributed to the compositional changes, i.e. to the higher relative abundance of calcium cations in the CA system. The more detailed structural insight can be gained from the coordination polyhedra analysis (Tables 5-7). The prevalence of the Al/O 4-coordination was confirmed for CA. On the other hand a significant amount of 5-coordinated aluminum was found in contradiction with a purely stoichiometric view, predicting only 4-coordinated state of aluminum. The increased number of 5-coordinated aluminum cations is found in CA_2 glass in harmony with the expectation. The higher average coordination numbers of alumina is directly connected with the increasing number of 3-coordinated oxygen atoms, co called Al-triclusters (Table 6).

Figure 4 is an example of the application of TM to the $CaO–Al_2O_3$ system for 300 K and 3000 K. The unrealistic high temperature of 3000 K is used just to emphasize the temperature effect on the compositional distribution. The regular mixing of the following components is supposed: CaO (C), Al_2O_3 (A), $Ca_3Al_2O_6$ (C_3A), $CaAl_2O_4$ (CA), $CaAl_4O_7$ (CA_2), $CaAl_{12}O_{19}$ (CA_6). The equilibrium concentrations of the individual components were used for the following coordination analyses of the CA, CA_2, and C_2A systems. Figures 5 and 6 presents the calculated temperature dependences of the average Al/O and O/Al coordination numbers.

Table 4. Average coordination numbers. The cut-off distances correspond to the first local minima of particular pair RDFs. The *p*-level represents the probability of error involved in accepting the hypothesis about the existence of a difference (two-tailed t-test for the independent samples).

Pair	cut-off (A)	CA_2	CA	*p*-level
Al–Al	3.86	6.7 ± 0.4	5.4 ± 0.2	0.0073
Al–Ca	4.27	2.6 ± 0.1	4.1 ± 0.3	0.0012
Al–O	2.41	4.4 ± 0.1	4.2 ± 0.1	0.0705
Ca–Ca	4.67	2.4 ± 0.3	4.5 ± 0.4	0.0019
Ca–O	3.11	6.8 ± 0.4	6.1 ± 0.2	0.0535
O–O	3.42	9.2 ± 0.3	8.3 ± 0.1	0.0079
O–Al	2.41	2.5 ± 0.1	2.1 ± 0.1	0.0080
O–Ca	3.11	1.0 ± 0.1	1.5 ± 0.1	0.0036

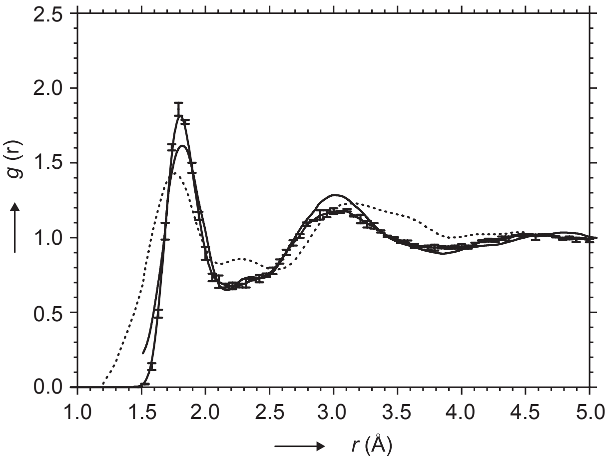

Figure 1. Total experimental and simulated RDFs of CA melt. Legend: X-ray (dotted) and neutron (thin solid) scattering, a levitated sample at 2100 K [17]; and this simulation at 2500 K (thick solid).

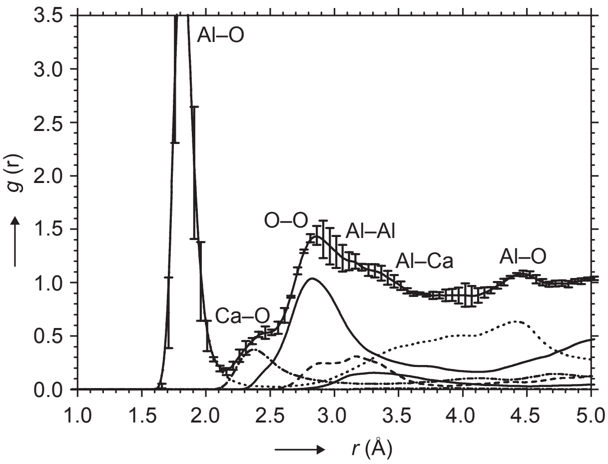

Figure 2. Total RDF (thick solid line), and partial RDFs (thin lines) of CA_2 glass at 300 K. Legend: Al–O (dotted), Ca–O (dash-dotted), O–O (solid), Al–Al (dashed), Al–Ca (solid).

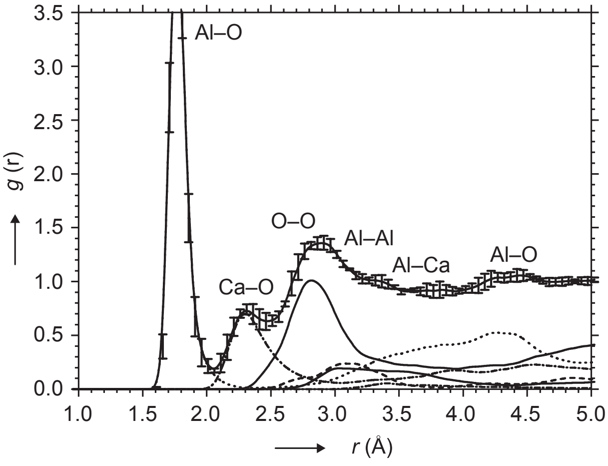

Figure 3. Total RDF (thick solid line), and partial RDFs (thin lines) of CA glass at 300 K. Legend: Al–O (dotted), Ca–O (dash-dotted), O–O (solid), Al–Al (dashed), Al–Ca (solid).

As the glass transition temperatures of CaO–Al_2O_3 glasses are close to 1100 K, it is reasonable to take the average Al/O coordination number at this temperature as those realized in glasses; they reach the value of 4.20, 4.27, and 4.75 for C_2A, CA, and CA_2 glass, respectively. Similarly, the values of 1.82, 2.12, and 2.56 can be found for the O/Al average coordination numbers.

Comparing the results of *ab-initio* MD and TM obtained for Al/O coordination numbers shows excellent agreement for CA system (4.2 ±0.1 versus 4.27). On the other hand some discrepancy was found for CA_2 system (4.4 ±0.1 versus 4.75). The TM results obtained for the studied glasses are close to those obtained by classical MD (4.2, 4.4, and 4.7, respectively) [19]. However, the classical MD results were obtained from just one configuration and therefore some deviations in particular values can be expected.

Most of the experimental results in per-alkaline region, including the CA composition, indicate the Al/O coordination number is close to four. However, the detail inspection shows that the experimental coordination numbers suffer with quite a large experimental error (estimated to ±0.2), e.g. for 38 mole% Al_2O_3 various experimental results are in the range from 3.97 to 4.8 [4]. Within these limits, we can state both of our results, MD and TM, are in quantitative agreement with experimental ones. On the other side the compositional

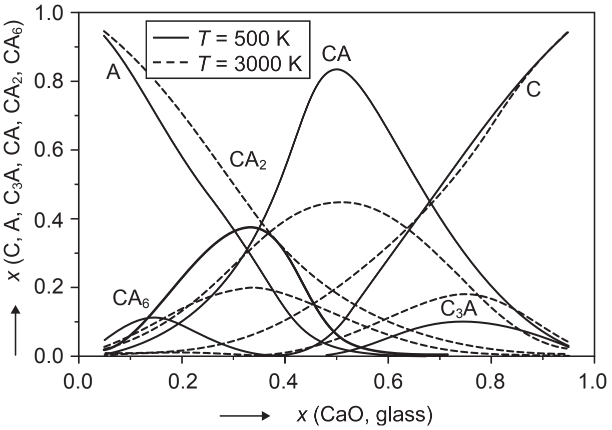

Figure 4. Equilibrium composition of the CaO–Al_2O_3 system at 300 K and 3000 K calculated by the thermodynamic model.

Table 5. Coordination number Al/O. Cut-off distance = 2.41 Å.

CN	CA_2 (%)	CA (%)	*p*-level
4	60 ± 9	76 ± 5	0.0546
5	38 ± 10	23 ± 6	0.0898
6	2 ± 2	1 ± 1	0.4818

Table 6. Coordination number O/Al. Cut-off distance = 2.41 Å.

CN	CA_2 (%)	CA (%)	*p*-level
0	0 ± 0	1 ± 1	0.2879
1	2 ± 2	12 ± 2	0.0036
2	46 ± 4	61 ± 4	0.0101
3	50 ± 3	25 ± 3	0.0005
4	2 ± 2	1 ± 2	0.5734

Table 7. Coordination number Ca/O. Cut-off distance = 3.11 Å.

CN	CA_2 (%)	CA (%)	*p*-level
4	0 ± 0	3 ± 4	0.2761
5	11 ± 15	17 ± 7	0.5642
6	23 ± 4	52 ± 20	0.0695
7	43 ± 12	24 ± 11	0.1133
8	20 ± 9	2 ± 2	0.0277
9	3 ± 2	2 ± 2	0.5734

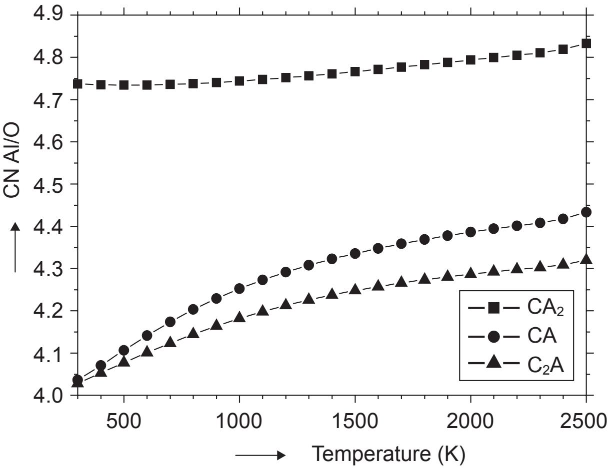

Figure 5. Calculated temperature dependences of the average Al/O coordination numbers in the glassy CA_2, CA, and C_2A systems (TM model).

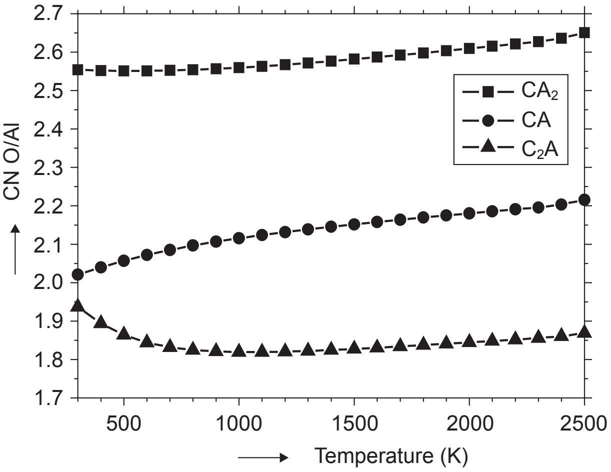

Figure 6. Calculated temperature dependences of the average O/Al coordination numbers the glassy CA_2, CA, and C_2A systems (TM model).

trends observed by both MD and TM are in agreement with the concept of the increase of Al/O coordination number (accompanied with formation of Al-triclusters) with the decreasing CaO content in the per-aluminous region.

CONCLUSION

Simple thermodynamic model, without any adjustable parameter, and ab-initio Molecular dynamics were used for the structural study of binary calcium aluminate system. Both methods provided mutually comparable results in a reasonable agreement with the available experimental data and the previous results of classical MD simulations.

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TERMODYNAMICKÝ MODEL A *AB INITIO* MOLEKULOVÁ DYNAMIKA HLINITOVÁPENATÝCH SKEL

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Binární hlinitovápenaté sklo, $x\mathrm{CaO}\cdot(1 - x)\mathrm{Al_2O_3}$, $x = 1/3$, 1/2, a 2/3, bylo studováno pomocí jednoduchého termodynamického modelu, který neobsahuje žádné nastavitelné parametry, a také pomocí *ab initio* molekulové dynamiky. Obě metody poskytly vzájemně srovnatelné kvantitativní výsledky, které byly v dobré shodě s dostupnými experimentálními daty a s předchozími klasickými simulacemi MD. Obdržené trendy jsou v souladu s představou o růstu koordinačního čísla Al/O (spojeného s tvorbou hlinitých triklastrů) při současném poklesu obsahu CaO v koncentrační oblasti od 0 do 50 mol% CaO (per-aluminous region).