



# Elastic and structural properties of low silica calcium aluminosilicate glasses from molecular dynamics simulations

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## ABSTRACT

The elastic constants and the structural of low silica calcium aluminosilicate glasses with a low content of silica (5–25 mol%) and  $[\text{CaO}]/[\text{Al}_2\text{O}_3] = 2$ , are investigated using molecular dynamics simulations. In particular, their elastic constants are calculated using two methods: a standard approach at zero temperature and another method designed to work at finite temperature. We show that while they both reproduce qualitatively the experimental behavior, only the method taking temperature into account provides a quantitative agreement with the experimental values. Therefore, taking temperature into account in the determination of elastic constants seems necessary to give a satisfactory account of the mechanical properties of these materials. In accordance with the experimental results, our molecular dynamics calculations show values of elastic constants that decrease with increasing amount of silica in the vitreous network. Then, the structure of the glasses is analyzed in term of pair distribution functions, oxygen kinds, and the parameter of short-range order, and discussed in correlation with the available experimental data. An overall good agreement is obtained with the calculated structure and the experimental data.

## 1. Introduction

The mechanical and structural properties of glass are considered as one of the fundamental problems of condensed matter physics and chemistry because they can help to understand how macroscopic properties emerge from microscopic characteristics [1–4]. It is known that certain glassy compositions can be obtained from  $\text{CaO}-\text{Al}_2\text{O}_3$  without the existence of any strong network formers in glass state networks such as  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$  or  $\text{P}_2\text{O}_5$  [5]. Pioneer works [6,7] have reported that the addition of a high content of  $\text{SiO}_2$  to the calcium aluminate glasses enhances their glass-forming ability but also deteriorate the optical properties owing to the stretching motion of the  $\text{Si}-\text{O}$  bonds. Adding a low amount of silica to calcium aluminate leads to low silica calcium aluminosilicate (LSCAS) glasses,  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , which present a high potential for technological applications [8,9]. This chemical composition achieves easily a glassy state by the conventional quenching technique where the  $\text{CaO}$  content is substantially broadened (around 60%–70% of  $\text{CaO}$ ) [9]. It is important to note that the tellurite [10], phosphate [11], and aluminosilicate [9] glasses system can

dissolve a relatively large modifier content compared to pure silica glass [12]. Ternary  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  glasses are used in many applications such as: glass fibers, gems and printed circuit boards [13,14]. Furthermore, the chemical durability, thermo-mechanical properties and infrared transparencies of LSCAS glasses make them very attractive for near- and mid-infrared laser applications [15,16].

As far as the structure of alkaline earth-aluminosilicate glasses is concerned, it has long been known that the three-dimensional structure consists of the interpenetration of the two networks of formers, consisting respectively of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra, in which the  $\text{Si}-\text{O}$  and  $\text{Al}-\text{O}$  bonds are highly covalent.

Extra framework cations such as  $\text{Ca}$  can act either as charge compensator and/or modifier, depending on the ratio  $[\text{CaO}]/[\text{Al}_2\text{O}_3]$  and silica amount. The geological glasses are a good example of multi-component systems with a significant extent of topological and chemical disorder where the ratio  $[\text{CaO}]/[\text{Al}_2\text{O}_3]$  plays an important role [9]. Despite the important number of studies devoted to aluminosilicate glasses in this field [9] and references therein, the detailed mechanisms at the molecular scale as well as their connection with the macroscopic

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properties have not been well understood yet.

The presence of a modifier such as calcium together with the formers of the LSCAS glasses drives the transformation of the bridging oxygens (BO) into nonbridging oxygens (NBOs) increasing the extent of depolymerization. MD has led to a better understanding of the relationship between chemical composition and mechanical properties in silicate glasses (see [1]). In LSCAS glasses, Hwa [17] showed that the nature of chemical bonds plays an essential role in the elastic properties of glasses, and that ionic bonds have a decisive effect on the structure of these systems. For that, the main subject of the present work is to calculate the elastic constants of LSCAS to correlate them with the structural properties. Modeling and simulation techniques can be used to understand how glasses properties are linked to the microscopic scale. MD simulations are generally applied in the field of glasses to get structural and mechanical properties with a very good accuracy [18,19]. To investigate the elastic constants of LSCAS glasses, we have used two methods; the minimization energy at zero temperature (Zero-T) and a second one that allows to calculate the elastic constants at finite temperature (FT) using a script treating the output from the LAMMPS package [20]. The reliability of the two methods to calculate these parameters has been evaluated comparing our results with those measured using Brillouin light scattering (BLS) spectroscopy [21]. Our second objective is to understand the structural changes in LSCAS glasses with the evolution of the silica content, and to compare our results with available experimental data.

This paper is structured as follows. Section II presents a brief description of the interatomic potential used together with the simulation technique and explains the methods for preparing the glass samples and for determining the elastic constants. Section III.A shows our detailed results on elastic constants determined by the two methods Zero-T and FT. In Section III.B, we present the effects of the addition of silica on the LSCAS glass structures. The results will be then discussed in Section IV, especially the relationship between the structural and elastic properties for various loading of SiO<sub>2</sub> in the LSCAS, in connection with the literature. The last section summarizes the findings of this work.

## 2. Methods

### 2.1. Simulation procedure

The quality of molecular dynamics results is strongly dependent on the choice of the interatomic potential form and on the successful fitting of the parameters to the aimed systems [22]. The Born–Mayer–Huggins potential [23] is quite adapted to investigate the glassy states because it contains a so-called repulsive term in addition to the Coulomb and dispersive terms. Silicate [1] and aluminosilicate [18,19] glasses properties have been successfully recovered using this potential formula:

$$U_{ij}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + f_0(b_i + b_j) \exp\left(\frac{(a_i + a_j) - r_{ij}}{(b_i + b_j)}\right) - \frac{C_i C_j}{r_{ij}^6} + \frac{D_i D_j}{r_{ij}^8} \quad (1)$$

where  $r_{ij}$  is the interatomic distance between atoms  $i$  and  $j$ ,  $f_0$  is a standard force that equals to 0.0434 eV. So, we recognize the ionic contribution in the first term, and the covalent contribution in the second one. Parameters ( $a$ ,  $b$ ,  $c$ ,  $D$ ) are a set of fitting constants that characterize the different species of the material. The two terms on the right-hand side in the potential formula represent the dipole–dipole and dipole–quadrupole dispersion energies, respectively.

The effective charges for the constituents are  $q_{Al} = 1.8$  for aluminum,  $q_{Si} = 2.4$  for silicon,  $q_{Ca} = 1.2$  for calcium, and  $q_O = -1.2$  for oxygen. For the rest, we use the parameters developed by Bouhadja et al. [19] as shown in Table 1. The parameters  $D_{ij}$  are set to be null as proposed in the original version of the potential [19]. The simulation is performed using periodic boundary conditions and an integration time step of 1 fs. The short-range interaction cutoff has been fixed to 8.0 Å.

**Table 1**

Two-body coefficients for Bouhadja's potential.

	$A = f_0(b_i + b_j)$ (eV)	$(b_i + b_j)$ (Å)	$(a_i + a_j)$ (Å)	$C = c_i c_j$ eV/Å <sup>6</sup>	$D = D_i D_j$ eV/Å <sup>12</sup>
Si–Si	0.0012	0.0460	1.4408	25.1873	0.0
Si–O	0.0070	0.1560	2.5419	46.2930	0.0
O–O	0.0120	0.2630	3.6430	85.084	0.0
Ca–Ca	0.0035	0.0800	2.3440	20.9856	0.0
Ca–Si	0.0027	0.0630	1.8924	22.9907	0.0
Ca–O	0.0077	0.1780	2.9935	42.2556	0.0
Al–Al	0.0029	0.0680	1.5704	14.0498	0.0
Al–Ca	0.0032	0.0740	1.9572	17.1710	0.0
Al–Si	0.0025	0.0570	1.5056	18.8116	0.0
Al–O	0.0075	0.1640	2.6067	34.5747	0.0

The coulomb interaction is computed with a cutoff of 12 Å, using an Ewald summation method with a desired relative error in the forces of less than 10<sup>−6</sup> eV/Å.

Both isothermal–isobaric NPT (with zero pressure) and canonical NVT ensembles have been used during our MD simulations. The system, consisting of 4000 atoms, was firstly thermalized at a high temperature ( $T = 4000$  K) over 10<sup>6</sup> steps using the NPT ensemble. This process is followed by another equilibration at the same temperature using NVT during 10<sup>5</sup> steps. These two equilibration steps are applied on the initial structure, in which the atom positions are distributed in different regions of the cell to form a steady liquid state independently of the initial configuration (memory losing process). To obtain a glassy state, the liquid undergoes a rapid cooling step to low temperature (300K) using the barostat NPT with a cooling rate of 10<sup>12</sup> K/s. Finally, to relax the glassy state configurations, we ran relaxation simulations during 10<sup>5</sup> steps using the NVT ensemble at 300 K. Therefore, the structure results presented in this work are obtained at 300 K. Also, the compositions of calcium aluminosilicate glasses in mol % are reported in Table 2.

### 2.2. Elastic constant calculations

The elastic constants  $C_{\alpha\beta}$  of a system are obtained from the second derivatives of the free energy,  $F$ , with respect to small strain deformations  $\epsilon$  [24].

$$C_{\alpha\beta} = \frac{1}{V} \frac{\partial^2 U}{\partial \epsilon_\alpha \partial \epsilon_\beta} \quad (2)$$

where  $V$  is the volume of the system.  $U$  is associated to the potential calculated by the Eq. (1). The  $\alpha$  and  $\beta$  indices correspond here to the so-called contracted rating and have values ranging from 1 to 6.

#### 2.2.1. Zero temperature (Zero-T)

The elastic constants of the investigated glasses have been computed by means of a Newton-Raphson energy [25] at a constant pressure. In a first step, we have estimated the derivative by deforming the used simulation box into one of its six directions using the change in the volume and/or shape, and/or boundary conditions for the simulation box and computing the change in the stress tensor [1]. To that end, the simulated MD-structure is in a local potential energy minimum and the system pressure tensor is near the specified exterior tensor. So, it is useful to have the possibility to determine Zero-T elastic constants,

**Table 2**

Summary of the compositions of calcium aluminosilicate glasses (mol.%).

Sample	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	[CaO]/[Al <sub>2</sub> O <sub>3</sub> ]
LSCAS25	50.00	25.00	25.00	2.00
LSCAS20	53.30	26.70	20.00	2.00
LSCAS15	56.70	28.30	15.00	2.00
LSCAS10	60.00	30.00	10.00	2.00
LSCAS05	63.30	31.70	05.00	2.00

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