

published by Ural Federal University eISSN 2411-1414 <u>chimicatechnoacta.ru</u>

Structural and physico-chemical properties of selected glasses in the $(Ca_{1-x}Mg_x)O-Al_2O_3$ system

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Abstract

Oxide glasses and melts are of interest in many fields of science and technology. The structural and physico-chemical properties of C12A7, C11M1A7, C10M2A7, C9M3A7, and C8M4A7 glasses (C = CaO, M = MgO and A = Al_2O_3) were studied for the first time. It was shown by Al K-edge XANES spectroscopy that Al is in fourfold coordination in all studied glass samples with increasing Q^4/Q^2 ratio in the C12A7-C8M4A7 composition range. The coordination number of Ca was found to be between 6 and 7 in all studied glasses by Ca K-edge XANES spectroscopy. From the thermodynamic point of view there is no composition dependence, within experimental uncertainty, of the heat capacity in the C12A7-C8M4A7 composition range. In contrast, the enthalpy of formation from the constituent solid oxides at 298.15 K was found to be greater for C8M4A7 than for C12A7 glasses. A decrease of density, molar volume and glass transition temperature was observed for increasing MgO content. In addition to the experimental investigation, classical molecular dynamics simulations were conducted using a recently optimized Born-Mayer-Huggins potential. It was found that the simulations present a good estimation of the structural properties (local surroundings of Ca and Mg) and some of the thermodynamic properties (heat capacity of glasses and liquids), but overestimate the values of the coordination number of Al and the other thermodynamic properties (density and enthalpy of formation from oxides at 298.15 K).

Key findings

 \bullet Al is in fourfold coordination in all the studied glass samples, with increasing the Q4/Q2 ratio in the C12A7-C8M4A7 composition range.

• There is no excess composition dependence, within experimental uncertainty, of the heat capacity in the C12A7-C8M4A7 composition range in the 370-830K temperature interval.

• The enthalpy of formation from constituent oxides at 298.15 K was found to be greater for C8M4A7 than for C12A7 glasses.

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1. Introduction

Multicomponent oxide glasses and melts are materials used in many scientific areas. They are applied in the cement industry [1,2], in the production of optics [3,4] and glass-ceramics [5,6], and they are also very important from a fundamental point of view in Earth science and planetology [7,8]. It is well known that there are different oxide glass families: silicates, borates, chalcogenides, phosphates, halides [8]. In addition, there is one more family – aluminate glasses that are usually considered to belong to silicate glasses. In aluminate glasses Al is only a network former, which allows better understanding of the role of Al in glasses. The most detailed information about structural properties of aluminate glasses is summarized in [9]. The majority of existing data are presented for glasses and melts in the CaO-Al₂O₃ binary system. Additional information is presented for the SrO-Al₂O₃ and BaO-Al₂O₃ binary systems. It is also noted that it is impossible to synthesize glasses in the MgO-Al₂O₃ binary system even using fast-quench methods [9], since Mg²⁺ forms a very stable spinel with alumina (MgAl₂O₄), which is always crystallized from melt. However, MgO is one of the widespread substances in the Earth's mantle; therefore, it is critically important from a fundamental point of view to study glasses and melts containing MgO.



Accompanying information

Article history Received: 09.04.25 Revised: 25.04.25 Accepted: 25.04.25 Available online: 05.05.25

Keywords

calcium-magnesium-aluminate glasses; CAM; structural properties; thermodynamic properties; classical molecular dynamics

Funding

The study was conducted under the state assignment of Lomonosov Moscow State University (project no 121031300039-1).

Supplementary information

Supplementary materials: **CREAD**

Transparent peer review: **CREAD**

Sustainable Development Goals



In the CaO-Al₂O₃ binary system it is possible to synthesize glasses for compositions ranging from C3A (Ca₃Al₂O₆) to CA (CaAl₂O₄) [9]. Moreover, glasses close to the C12A7 (Ca12Al14O33) composition are easy to quench, and their preparation does not need sophisticated laser-melting techniques. The structure of glasses in calcium-aluminate system are well-known [10-13] in the literature. Aluminium is only a network former and is in tetrahedral coordination with the number of bridging oxygens varying between 2 (often noted Q² in the literature) and 4 (Q⁴) for C3A and CA, respectively [11]. Calcium in glasses evolves from a regular 6-fold coordination for C3A glass up to 7-fold for CA [12]. From the thermodynamic point of view glasses in the C3A-CA range are also well studied [14-17]. There are a thermodynamic assessment of the CaO-Al₂O₃ system [14], high-quality data on heat capacity of C3A [15] and C12A7 [16] glasses, enthalpy of solution in lead-borate solvent at 985 K of CA glass [17] and enthalpy of formation from oxides of C12A7 glass [16].

There is a series of experimental and calculated investigations of glasses in the CaO-MgO-Al₂O₃-SiO₂ quaternary system [18-25] in the literature, but for the CaO-MgO-Al₂O₃ ternary system (without SiO₂) very limited data was found [26]. However, using the Calphad approach, low-dimensional systems should be studied from the beginning, starting from the unary, binary and ternary glasses. In addition, in the recent works [27,28] the need of high-quality experimental data to predict the reactivity of amorphous substances using thermodynamic and kinetic modeling was shown.

Summarizing the above, in this work we focus on glasses in the (Ca_{1-x}Mg_x)O-Al₂O₃ ternary system for the following reasons: i) their structural and physico-chemical properties have not been reported in the literature; ii) these are pure aluminate glasses (without any other glass-forming oxides); iii) it is possible to synthesize glasses by classical quenching, since the base of the glasses is CaO-Al₂O₃ system; and iv) replacing CaO by MgO allows us to investigate the impact of MgO content on structural and physico-chemical properties of glasses. Thus, the aim of this work is to investigate the structural and physico-chemical properties of glasses in the (Ca_{1-x}Mg_x)O-Al₂O₃ ternary system.

2. Experimental Section

2.1. Starting materials

The following raw materials supplied by Alfa Aesar were used in this work: CaCO₃ (>99.95%), *α*-Al₂O₃ (>99.9%) and MgO (>99.95%). The purity of calcium carbonate and magnesium oxide is declared as a metal base. All chemicals were used as such without further purification.

2.2. Glass synthesis

The studied glasses were synthesized by the classical method of melting and quenching in water. The starting materials (powders of CaCO₃, MgO and α -Al₂O₃ in appropriate amounts) were dried in a muffle furnace in air for 12 h at 573 K, 573 K and 1273 K, respectively. After that, they ARTICLE

The mixture was calcined at 1273 K for 1 hour to remove traces of water and CO₂. The furnace temperature was then increased to 1873 K (which corresponds to a temperature 50-250 K above the liquidus temperature of the mixture, depending on the target composition), and the sample was kept for 2 h to obtain a homogeneous melt. The glasses were quenched by immersing the bottom of the crucible in cold water for approximately 10-15 sec. The resulting glass was then ground in a mechanical agate mortar, and the obtained powder was remelted again at the same temperature of 1873 K. This procedure was repeated three times to ensure the sample was homogeneous. To verify the absence of crystalline phases, powder X-ray diffraction (powder XRD) analysis was performed. The results showed no evidence of any crystalline phases in the samples, confirming that the resulting samples are amorphous (see Figure S1). The photo of the synthesized glasses is presented in Figure S2 in the supplementary information.

The chemical composition of all glasses was determined by the X-ray fluorescence method. Fused bed samples were produced using 67/33 lithium meta-borate / tetraborate as fluxing agent and a Katanax X300 automatic fluxer. The chemical composition was measured in a Panalytical Zetium spectrometer using the standard calibration. The results are reported in Table 1. In addition to the target oxides, in the whole final glass samples a small amount (around 0.3 mol.%) of SiO₂ was found, which could get into the samples from the agate mortar.

All resulting glasses had a yellowish color, which is associated with the presence of Pt⁴⁺ trapped in the samples from the crucible material [29]. To determine the amount of dissolved platinum in the studied glasses, a wet chemical analysis of the samples was carried out using inductively coupled plasma mass spectrometry (ICP-MS ELAN DRC II). Standard samples of platinum (Carl Roth) were used for calibration. According to the results of the analysis, the amount of platinum did not exceed 0.02 wt.% in all the samples.

Glasses in the binary $CaO-Al_2O_3$ and the ternary CaO-Al₂O₃-MgO systems were selected for our study corresponding to the C12A7-"M12A7" section (cement notation: C = CaO, M = MgO and $A = Al_2O_3$). Five glass compositions were chosen for the investigation: C(12-n)M(n)A7, where n is 0, 1, 2, 3 and 4 (Figure S3). The C12A7 (n = 0) glass sample is an amorphous analogue of the mineral mayenite $(Ca_{12}Al_{14}O_{33\pm x})$, the labelling of the samples with magnesium corresponds to different amounts of CaO replaced by MgO in the C12A7 sample (*n* = 1; 2; 3; 4).

2.3. Al and Ca K-edge XANES spectroscopy

Al and Ca K-edge X-ray absorption near edge structure (XANES) spectroscopy measurements were performed on the LUCIA beamline at the SOLEIL synchrotron facility (Saint-Aubin, France). For the Al edge, a KTP monochromator was used for all measurements with a calibrated energy using an Al foil as a reference.

Name	<i>x</i> , % *					M. m/mal
	CaO	MgO	Al ₂ O ₃	SiO ₂	Σ**	- <i>M</i> , g/moi
C12A7	62.9 (63.2)	0 (0)	36.5 (36.8)	0.4 (0)	99.8 (100)	72.99 (72.98)
C11M1A7	57.2 (57.9)	6.3 (5.3)	36.1 (36.8)	0.3 (0)	99.9 (100)	71.80 (72.15)
C10M2A7	52.0 (52.6)	11.4 (10.5)	36.2 (36.8)	0.3 (0)	99.9 (100)	71.02 (71.32)
C9M3A7	46.5 (47.4)	16.7 (15.8)	36.4 (36.8)	0.3 (0)	99.9 (100)	70.26 (70.49)
C8M4A7	11 3 (12 1)	210(211)	36 4 (36 8)	03(0)	00.0 (100)	69 45 (69 66)

Table 1 Composition (in mol.%) and molar mass (g/mol) of studied glasses. The aimed compositions and molar masses are in brackets.

* Determined by X-ray fluorescence.

** Some additional traces of Fe₂O₃, ZrO₂, P₂O₅ were also experimentally found.

The spectra were collected in the 1540-1660 eV range with a step of 0.2 eV and a counting time of 400 ms. From 6 to 18 spectra were recorded for each studied sample.

The Ca K-edge XANES spectra were collected using a Si-(111) double-crystal monochromator calibrated at 4966 eV with a metallic Ti foil and checked with calcite CaCO₃, perovskite CaTiO₃, and wollastonite CaSiO₃ as calcium references. The spectra were collected in the region from 3970 to 4200 eV with a step of 0.2 eV and a counting time of 400 ms. Three scans were acquired for each sample with their subsequent averaging. All XANES spectra at the Al and Ca K-edge were acquired in fluorescence mode using a 60 mm² mono-element silicon drift diode detector (Bruker).

All XANES spectra were averaged and normalized using the Larch software [30]. The normalization parameters were kept the same for all samples. For the Ca K-edge, in addition to the position of the main edge, particular attention was given to the analysis of the pre-edge peak. After the background subtraction the pre-edge peaks were fitted using a sum of pseudo-Voigt functions. The analysis of the pre-edge features (position, relative intensity) gives information about Ca surroundings.

2.4. Density measurements

The density of the glass pieces was measured using the Archimedes method. Toluene was used as an immersion liquid. The glass pieces were balanced in both air and toluene, and since the toluene density and its variations with temperature are precisely known, the density of the studied samples (d_s) was calculated using Equation 1:

$$d_s = d_t \cdot \frac{m_a}{m_a - m_t},\tag{1}$$

where m_a and m_t are the weight of sample in air and toluene, respectively, d_t – density of toluene. Before each set of experiments a standard sapphire sample with a mass close to 1 g was measured to check the correct value of density (3.987 g/mL). For each composition at least 10 glass pieces were measured. The uncertainty of this method is 0.001 g/mL, and detailed information about this technique is presented elsewhere [31].

2.5. Glass transition temperature measurements

The glass transition temperature (T_g) of the studied glasses was experimentally measured by differential scanning calorimetry (DSC calorimeter LABSYS evo, Setaram). The measurements were conducted from room temperature to 1823 K at 10 K/min heating rate in Ar atmosphere in Pt/Rh crucibles using glass powder amounts of around 30 mg. The glass transition temperature T_g was determined as the middle of the glass-transition range. The temperature calibration of the calorimeter was performed in the 853-1673 K temperature range using high purity K_2SO_4 (solid-solid transition; melting point), CaF₂ (melting point) and NaCl (melting point). The experimental uncertainty of these measurements was estimated as ± 5 K. The software Calisto from Setaram was used to treat the obtained raw data.

2.6. Heat capacity measurements

The isobaric heat capacity (C_p) of the studied glasses was measured using differential scanning calorimetry (DSC Calvet Pro, Setaram). This equipment is a high-precision Tian-Calvet type calorimeter with a 3D Calvet sensor and a thermopile with more than 600 thermocouples. The measurements were conducted below the glass transition temperature in the 370-830 K temperature range at a 10 K/min constant heating rate in Ar atmosphere. The powder glass samples were placed in Al₂O₃ crucible with amounts ranging from 60 to 100 mg. The heat capacity of each sample was measured at least 3 times, and the result was obtained by averaging of these data. Before the experiments, the baseline (empty crucibles) and a reference sample (one crucible with high-purity sapphire cylinder of around 300 mg) were measured to calibrate the equipment. The experimental uncertainty of these measurements was estimated as $\pm 3\%$ in the whole temperature range. The software Calisto from Setaram was used to treat the obtained raw data.

2.7. High temperature drop-solution calorimetry

The enthalpy of dissolution of C8M4A7 glass sample in a lead borate solvent ($n(PbO) / n(B_2O_3) = 2$; 30.00 ± 0.05 g) was measured by high temperature drop-solution calorimetry. The experiments were carried out using a commercial isoperibol Tian-Calvet calorimeter Alexsys 1000 (Setaram, France). The measurements were conducted at 1073 K with 5-15 mg of individual glass pellets under atmospheric pressure (the rate of artificial air flow was 10 mL/min). To enhance the dissolution process, dry air ($x(H_2O) < 5 \cdot 10^{-40}$ %) was bubbled through the solvent at a rate of 5 mL/min. This ensured constant mixing and maintained a high oxygen

fugacity in the melt, helping to preserve the oxidation state of the dissolved oxides. The experiments were carried out in two independent lead borate solvents. Prior to each series of experiments, the calorimeter was calibrated by dropping 4-17 mg of high-purity alumina pellets (99.95% from NIST) into an empty platinum crucible placed inside the calorimeter. The calibration factors were determined with uncertainties of less than $\pm 1\%$. Heat increments between the room temperature and the temperature inside the calorimeter (1073 K) were calculated using the Standard Reference Material equation [32]. After the experiments, the enthalpy of formation of C8M4A7 glass with respect to the constituent single oxides in their crystalline reference state was calculated. Detailed information about the experimental procedure is described in our recent article [16]. The Calisto software from Setaram was used to record the output signals and integrate the heat flux curves from the calorimeter.

3. Molecular Dynamics Simulations

The structural and physico-chemical properties of studied glasses were calculated by using classical molecular dynamics (MD) simulations. To describe the interatomic interaction, the Born-Mayer-Huggins potential (see Equation 2), which works well for oxide systems, was chosen, in which the parameter D was assumed to be o for all interaction pairs:

$$u(r_{ij}) = \frac{q_i q_j}{r_{ij}} + A_{ij} exp\left(\frac{\sigma_{ij} - r_{ij}}{\rho_{ij}}\right) - \left(\frac{C_{ij}}{r_{ij}}\right)^6 - \left(\frac{D}{r_{ij}}\right)^8, \quad (2)$$

where i, j represent different ions, and r_{ij} is the interatomic distance between two ions of types i and j. The first term corresponds to a long-range Coulomb interaction. The second term represents a repulsion of particles, while the last two terms are the contribution of dipole attraction.

The parameters for CaO and Al_2O_3 were taken from [33] and for MgO from [34]. For the pairs Ca-Mg, Ca-Al and Mg-Al, we only took into account the Coulomb term in Equation 2.

The simulations were carried out using the LAMMPS software package [35]; the total number of atoms was 10 005 atoms (C12A7: Ca - 2035, Al - 2374, O - 5596; C11M1A7: Ca - 1865, Mg - 170, Al - 2374, O - 5596; C10M2A7: Ca - 1696, Mg - 339, Al - 2374, O - 5596; C9M3A7: Ca - 1526, Mg - 509, Al - 2374, O - 5596; C8M4A7: Ca - 1357, Mg - 678, Al - 2374, O - 5596). All the calculations were performed in the NPT ensemble at atmospheric pressure. The equations of motion were numerically solved within the Verlet algorithm in the velocity form using a time step of 1 fs. The initial atom positions were chosen randomly. For all glass compositions, the system was first heated up to 3000 K and equilibrated during 100 ps for complete melting. The system was then quickly cooled (quenched) to the required temperature with a cooling rate of 10¹¹ K/s, and equilibrated again at this new temperature for 100 ps to reach equilibrium. Last but not least, the properties calculation stage was then performed during 200 ps. Averaging of the obtained properties over time at the last stage gave estimates of the structural and physico-chemical properties (all stages were also conducted at the NPT ensemble).

At the production stage different properties of the glasses were calculated. From the structural point of view, the pair correlation function ($g_{ij}(r)$) was determined (see Equation 3):

$$g_{ij}(r) = \frac{N}{V} \frac{n_{ij}(r)}{4\pi r_{ij}^2 \Delta r'},$$
(3)

where $n_{ij}(r)$ represents the mean number of particles j in a spherical shell of radius r and thickness Δr centered on particle i (i, j – Ca, Mg, Al and O species).

Using the resulting pair correlation functions $(g_{iO}(r))$, the coordination numbers of Ca, Mg and Al atoms (CN_{iO}) were determined. To do this, a numerical integration of the pair correlation function to the first minimum (r_{min}) was performed:

$$CN_{i0} = 4\pi\rho x_0 \int_0^{r_{min}} r^2 g_{i0}(r) dr,$$
 (4)

where ρ is the calculated density, and x_0 is the concentration of O atoms (N_0/N). Since only the nearest neighbours (oxygen atoms) were taken into account in the calculation, integration was carried out to the first minimum (r_{min}) of the corresponding partial pair correlation function.

For the thermodynamic properties, the enthalpy of the studied glasses was calculated using Equation 5:

$$H(T,P) = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2 + \frac{1}{2} \sum_{i< j=1}^{N} u(r_{ij}) + P_{ext}V,$$
 (5)

where P_{ext} is the pressure exerted on the virtual surface inside which the atoms are located, and *V* is the volume of the cell. Since the absolute value of enthalpy has no physical meaning, calculations at different temperatures (the temperature step is 100 K) were used to obtain the heat content between the two temperatures, which can be compared to the actual experimental data. The heat capacity at constant pressure C_p was calculated as the temperature derivative of enthalpy as a function of temperature at constant pressure:

$$C_p(T,P) = \left(\frac{\partial H(T,P)}{\partial T}\right)_p.$$
(6)

In addition to the heat content, the enthalpy of formation from the constituent solid oxides were calculated. For that, additional simulations for crystalline CaO (NaCl structure type), Al_2O_3 (corundum structure type) and MgO (NaCl structure type) at 300 K were conducted with 10648, 7680, and 10648 atoms, respectively. The enthalpy of formation from oxides was calculated as a difference between the enthalpy of studied glasses at 300 K and the enthalpy of constituent solid oxides considering the molar fraction of the latter in the glasses.

The density of studied glasses in this work was calculated directly as the inverse volume of the system at atmospheric pressure. The glass transition temperature was found as a sharp jump in the calculated density and a bend in the heat content data.

4. Results and Discussions

4.1. Al surroundings

The results of the Al K-edge XANES spectroscopy measurements are presented in Figure 1. In all spectra there are three main peaks at around 1565, 1568.5 and 1582.5 eV. The absorption peak A at around 1565 eV corresponds to a 1s-3p transition. The energy position of this peak is related to an Al coordination in the structure. The ^[4]Al/^[6]Al ratios of many aluminosilicates and aluminum oxide minerals were discussed in [36,37] in detail. The second peak B at around 1568.5 eV and a weak feature B1 are related to multiple scattering in the medium-range order [38]. The last broad peak C at around 1582.5 eV corresponds to a multiple scattering from the nearest neighbors of the AlO₄ tetrahedra. A presence of this peak indicates that Al is present in the fourfold coordination [38].

Analyzing the position of the absorption peak A (1565 eV) and taking into account the relevant literature data [36,37], we may conclude that in all the samples Al is in fourfold coordination. Additional evidence is the presence of a broad peak C (1582.5 eV) at the Al K-edge XANES spectroscopy.

Similar spectra were found in the literature [11,13] for a pure binary C12A7 glass. The positions of all peaks are identical to those observed in our work. In the article [11], the authors found a correlation between the ratio of relative intensity of peaks A and B at the Al K-edge XANES spectroscopy and the ratio of bridging and non-bridging oxygens in the glass composition: a more intense peak B indicates more non-bridging oxygens in the glass.

This dependence was also observed for other glasses in the CaO-Al₂O₃ system such as C₃A, C1₂A₇ and CA [11]. In a C1₂A₇ glass, it was indirectly shown that Al has surroundings between Q² and Q⁴ [11,12]. Analyzing the ratio of peaks A and B of our studied samples, we may notice that for the C8M4A₇ sample (purple curve) peak B has the lowest relative intensity, which means that in the series C1₂A₇-C8M4A₇ (with increasing the Ca replacement by Mg) the number of bridging oxygens is increasing.

In addition to the experimental investigation of the Al surroundings, classical molecular dynamics simulations were conducted (see Equation 4). As a result, the coordination number of Al varies between 4.6 and 4.7 (depending on composition) at 300 K for all studied glasses, which is in a poor agreement with the experiment findings. The calculated bond length of Al-O was 1.75 Å. At higher temperature

(2000 K) the coordination number of Al in the melts decreases to 4.3-4.5 (depending on composition) and continues to slightly decrease with increasing temperature.

4.2. Ca surroundings

The results of the Ca K-edge XANES spectroscopy measurements are presented in Figure 2. In all the spectra a main absorption peak at around 4051 eV is observed, corresponding to the 1s-np transition. In addition, at lower energy the pre-edge peak at around 4040 eV is visible, corresponding to a 1s-3d transition [39] together with a shoulder at around 4045 eV which was observed in all the spectra. In Figure 3 the pre-edge region of normalized Ca K-edge XANES spectra of the studied glasses are presented. The presence and the relative intensity of the pre-edge peak are related to the Ca surroundings.

We obtained Ca K-edge XANES spectra of C12A7 glass that are similar to those available in the literature [12,13]. It is well known that in the absence of the pre-edge peak, Ca is in octahedral coordination (like in the C3A crystal [12]). The appearance of this pre-edge peak corresponds to a break in the symmetric octahedral structure and leads to increasing of the local surroundings of Ca like in the CaO-Al₂O₃ and CaO-Al₂O₃-SiO₂ systems [11–13].



Figure 1 Normalized Al K-edge XANES spectra of studied glasses.



Figure 2 Normalized Ca K-edge XANES spectra of studied glasses.



Figure 3 Pre-edge region of normalized Ca K-edge XANES spectra of studied glasses.

The relative intensity of pre-edge peak for all the studied glasses in this work is the same within experimental uncertainty, which means that the coordination number of Ca in all the samples is ranging between 6 and 7.

From classical MD simulations, the calculated coordination number of calcium (see Equation 4) was found to be in the 6.1-6.3 range (depending on composition), which is an excellent estimation compared to the experimental data. The bond length of Ca-O is higher than that of Al-O (since Al is a network former) and equal to 2.27 Å. At 2000 K the coordination number of Ca in the melts is 6.5 to 6.7 (depending on composition) and decreases with temperature.

4.3. Mg surroundings

Due to experimental difficulties, we were not able to experimentally determine the atomic surroundings of Mg. However, using classical molecular dynamics, we calculated the coordination number of Mg in all the studied glasses (see Equation 4). The result varies between 5.4-5.8 (depending on composition) at room temperature with a bond length of Mg-O that equals 2.12 Å. This result is in a good agreement with the data for the other glass systems containing MgO [25,40]. The results obtained by Shimoda et al. [41] using ²⁵Mg NMR spectroscopy, which contradict other literature data, showed that Mg is in an octahedral coordination. However, in another work of the same authors, it is stated that Ca atoms have a coordination of $7\div8$ [42]. Thus, the results of their work qualitatively confirm that the coordination number of Ca in glasses is greater than the coordination number of Mg.

Based on these results, we can conclude that the parameters of BMH potential used in this work describe well the structural properties of non-crystalline phases in the threecomponent CaO-Al₂O₃-MgO system. In addition, at high temperature (2000 K), the coordination number of Mg in the melts varies in the 5.5-5.6 range (depending on composition) and slightly decreases with temperature.

4.4. Density and glass transition temperature

The density of the studied glasses was experimentally measured by the Archimedes method. The results are presented in Table 2 and in Figure S4. For the C12A7 glass, a good agreement with the literature data from [43] (d = 2.909 g/mL) was found. However, in another article of the same authors [11] the reported density value is significantly lower (d = 2.657 g/mL). The origin of this big difference is unknown, but we propose that in paper [11] the column of density (Table 1) is a misprint, since the glass synthesis details are the same in both papers. It is also interesting to mention that we found close values of the density of glasses among the literature data in the CaO-MgO-Al₂O₃-SiO₂ quaternary system with low (~4 mol.%) SiO₂ content [21].

A decreasing density from C12A7 to C9M3A7 samples was observed in the samples. For the last glass of the series, C8M4A7, the result is different; however, it is difficult to draw any conclusion as the uncertainty ranges overlap for the samples C9M3A7 and C8M4A7. The measured data were used to calculate the molar volume (Table 2 and Figure S5). Again, a decrease in molar volume of glass was found upon replacement of CaO by MgO in the C12A7 glass sample.

In addition to the experimental investigation, the density of glasses was calculated by classical molecular dynamics. The results are also presented in Table 2. The calculated density is overestimated by ~10% compared to the experimental observations for all samples. This result was somehow expected, since for the MD simulations the parameters for CaO were used from [33], which represent a minor adjustment of the parameters as compared to the previous paper of the same authors [44].

Table 2 Density (g/mL), molar volume (mL/mol) and glass transition temperature (K) of studied glasses. The experimental uncertainties for d and T_g are in brackets.

Nomo	<i>M</i> , g/mol * -	d, g/mL		V_m , mL/mol		- T V
Name		exp	calc **	exp	calc **	<i>I</i> g, K
C12A7	72.99	2.919(2)	3.19	25.0	22.9	1120(5)
C11M1A7	71.80	2.914(1)	3.18	24.6	22.7	1103(5)
C10M2A7	71.02	2.911(1)	3.20	24.4	22.3	1091(5)
C9M3A7	70.26	2.909(2)	3.20	24.2	22.0	1078(5)
C8M4A7	69.45	2.913(3)	3.20	23.8	21.8	1070(5)

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* Composition of glass sample was determined by X-ray fluorescence.

** Calculated by classical molecular dynamics simulation.

Alvares et al. [44] did show that the specific volume of solid CaO was underestimated by ~12% using their optimized potential (which means that density is overestimated), as compared to the available experimental data. It is therefore not surprising that we observed a similar behavior in this work. However, it should be noted that the molar volume calculated by MD (see Table 2) has the same trend for C12A7-C8M4A7 series compared to the experimental data: V_m decreases with increasing replacement of Ca by Mg in C12A7 glass.

The glass transition temperature was experimentally determined by DSC, and the results are presented in Table 2 and Figure S6. The raw DSC curves of studied samples are presented in Figure S7. A good agreement of the obtained T_g for the C12A7 glass with literature data [11,43] was observed. A linear decrease of the glass transition temperature with increasing MgO content was found.

The glass transition temperature obtained by classical molecular dynamics simulations for all the studied glasses was found to be between 1300 and 1400 K (see Figure S8 and Figure S9). The final value is higher than the value found by DSC (see Table 2), which was expected, due to the fast cooling rate in MD.

4.5. Heat capacity

Differential scanning calorimetry was used to measure the isobaric heat capacity of C12A7, C10M2A7 and C8M4A7 glasses in the 370–830 K temperature range. The results are presented in Figures 4 and 6 and in Tables S1–S3. In addition to the data obtained in this work, the heat capacity of the C12A7 glass measured in the range of 10–350 K by low-temperature adiabatic calorimetry [16] is also added in Figure 4 for comparison.



Figure 4 Heat capacity of a C12A7 glass measured by DSC in this work (green triangles). Blue squares – heat capacity of a C12A7 glass obtained by low-temperature adiabatic calorimetry (literature data [16]). Purple dashed line – Voronin's model (Planck-Einstein functions) with the parameters from [16], dark red line – Voronin's model (Planck-Einstein functions) with the parameters obtained in this work (Table 3).

As can be seen for the C12A7 glass the results obtained by DSC in this work (green triangles in Figure 4) and by low-temperature adiabatic calorimetry [16] (blue squares in Figure 4) are in agreement with each other, which shows the validity of the experimental approach.

In addition to experimental data two calculated curves were added in Figure 4. The purple dashed line is obtained using Voronin's model to determine the heat capacity as a function of temperature. It corresponds to a combination of Planck-Einstein functions [45] using parameters from our previous article [16], in which a numerical optimization was conducted for the low-temperature adiabatic calorimetry data (10-350 K) only. As can be seen in Figure 4, this model does not predict new experimental data at a higher temperature (> 600 K) within experimental uncertainty. Thus, in this work a new optimization of parameters was carried out, including both the low-temperature data [16] and the new data obtained by DSC in this work. Detailed information about Voronin's model [45] and the optimization procedures are presented in our previous paper [16]. As a result, a new set of parameters of Voronin's model for C12A7 glass was generated, and the parameters are listed in Table 3. The numerical values are provided with an additional number of significant digits to enable the most precise reproduction of the calculation results of this study. The thermodynamic functions $(C_p, S^{\circ}(T)-S^{\circ}(O), H^{\circ}(T) H^{0}(0)$) were calculated using the parameters from Table 3 and Equations 1–3 from [16] and are presented in Table S4.

The differences between the experimental heat capacity of C12A7 obtained by DSC in this work (see Table S1), those obtained by adiabatic calorimetry (see Table S1 in [16]) and calculated by Equation 1 from [16] as well as those calculated using the parameters from Table 3 for C12A7 glass sample are shown in Figure 5. The deviations for almost all points obtained by adiabatic calorimetry in our previous work [16] are less than 0.4% for T > 50 K, and 2% from 10 to 50 K. However, using this new set of parameters of Voronin's model from Table 3, the differences of C_p data measured by DSC in this work and the calculated values using the model are less than experimental uncertainty. Thus, we believe that the new parameters of the Planck-Einstein equation adequately describe all experimental data.

In addition to the C12A7 glass sample, the heat capacity of C10M2A7 and C8M4A7 glasses were measured by DSC in the 380-830 K temperature range. The results are presented in Figure 6 and listed in Tables S2–S3 in the Supplementary Information file.

Table 3 A new set of parameters of Voronin's model (combinationof Planck-Einstein functions) for C12A7 glass

Parameter	Value	Parameter	Value
α_1	0.048±0.002	$ heta_3$, К	268±5
$ heta_1$, K	71±1	$lpha_4$	1.205±0.017
α2	0.225±0.013	$ heta_4$, К	549±10
$ heta_2$, K	140±3	α_5	0.944±0.026
α3	0.785±0.015	$ heta_5$, K	1115±19



Figure 5 Differences between experimental heat capacity (Table S1 (this work) and Table S1 in [16])) and that calculated by Equation 1 from [16] and parameters from Table 3 for C12A7 glass sample.

No composition dependence, within the experimental uncertainty, on C_p was found upon replacement of CaO by MgO in the C(12-n)M(n)12A7 glass up to 4 magnesia molecules in the glass composition.

In addition to the experimental investigation, classical molecular dynamics simulations were conducted to calculate the heat capacity of these glasses (see Equation 6). The results are also presented in Figure 6. As we can see, the absolute value of C_p for all the glasses and the main trend (close C_p value for C12A7, C10M2A7 and C8M4A7 glasses) are in excellent agreement with the results obtained by DSC. Thus, we can conclude that the parameters of the BMH potential used in this work give excellent results for estimation of heat capacity of the glasses.

In addition to the heat capacity of glasses, the heat capacity of studied samples in the liquid state was calculated by classical molecular dynamics simulations. The results from 1400 to 2300 K (T_g found by MD is slightly higher than 1300 K, see above) are also presented in Figure 6. As we can see, the heat capacity values for C12A7 (112.4 J/(mol·K)), C10M2A7 (113.6 J/(mol·K)) and C8M4A7 (115.5 J/(mol·K)) liquids are close to each other and are in good agreement with Gurvich estimation (113 J/(mol·K)) [46], which may indirectly confirm that the parameters of the BMH potential used in this work give good results for estimation of heat capacity of the liquids.

4.6. High-temperature drop-solution calorimetry

To determine the enthalpy of dissolution of the C8M4A7 sample, high-temperature drop-solution calorimetry was used. The raw data of the experiment (solvent, number of drops, mass of sample, mass of solvent, room temperature, calorimeter temperature, enthalpy of drop solution for each drop) are summarized and listed in Table S5 in the Supplementary Information file.

To check if the drop-solution experiments were carried out at infinitely diluted solution, the dependence of the enthalpy of dissolution of C8M4A7 glass *vs* the mole fraction of the dissolved sample in the lead borate solvent $(30\pm0.05 \text{ g})$ was plotted and presented in Figure 7. Analyzing the obtained results, a composition dependence of the heat effect on the total amount of the studied sample in the lead borate solvent was observed. Therefore, the found dependence was fitted by linear regression and extrapolated to zero concentration of the sample in solvent to obtain the enthalpy of dissolution of C8M4A7 in lead borate solvent at 1073 K. Thus, the final value was accepted as 29.5±1.4 kJ/mol (the confidence interval corresponds to the two standard deviation).

To calculate the enthalpy of formation from the constituent oxides of C8M4A7 glass sample, a thermochemical cycle was used (Table 4).



Figure 6 Heat capacity of C12A7, C10M2A7 and C8M4A7 glasses measured by DSC (colored solid lines) and calculated heat capacity of C12A7, C10M2A7 and C8M4A7 glasses / liquids by classical molecular dynamics (dashed lines). Black solid line – estimation of heat capacity of liquid C12A7, C10M2A7 and C8M4A7 samples by Gurvich [46] (since suggested C_p of liquid CaO and MgO are the same [46], the estimated heat capacity for all studied samples is also the same).



Figure 7 The dependence of the enthalpy of dissolution *vs* mole fraction of the dissolve C8M4A7 glass sample in the lead borate solvent at 1073 K (m_{solv} =30.00±0.05 g).

Except for the enthalpy of dissolution of C8M4A7 glass in the lead borate solvent at 1073 K experimentally measured in this work, the data for pure oxides (CaO, Al₂O₃, MgO) in their crystalline state were taken from the literature [47,48] (these results were obtained in the same conditions as those for our C8M4A7 glass). The final value of the enthalpy of formation from oxides of glassy C8M4A7 was found to be 20.6 \pm 2.6 kJ/mol.

Since it is impossible to synthesize the M12A7 glass sample because of too high liquidus temperature in the MgO-Al₂O₃ system and immediate crystallization of stable crystalline MgAl₂O₄, we cannot obtain a variation of the enthalpy of formation from oxides at 298.15 K for the whole series. The conclusion is that the value of $\Delta_{\rm f} H_{\rm ox}(298.15)$ of C12A7 glass (the value was taken from [16]) increases with increasing replacement of CaO by MgO up to 4 atoms Mg in the glass composition (Figure 8).

In addition to experimental investigation of the enthalpy of formation from oxides, FactSage (version 8.3) estimation [49] for the liquid / glass state and classical molecular dynamics simulations were conducted, and the results are also presented in Figure 8 (green and red curves, same respectively). We found the trend of $\Delta_{\rm f} H_{\rm ox}(298.15)$ increasing with increasing replacement of CaO by MgO up to 4 atoms Mg in the glass composition. However, it should be noted that the absolute values of the enthalpy of formation from oxides are significantly shifted compared to the data obtained experimentally by the dropsolution calorimetry. This discrepancy in absolute value of $\Delta_{\rm f} H_{\rm ox}(298.15)$ may be explained, since the parameters of the BMH potential was set up by fitting the local structures (mainly the partial radial distribution functions) taken from DFT-based ab initio molecular dynamics simulations (see [33,34]) and the energy of the ab initio MD was not taken as a constraint for the fitting. Thus, we may conclude that the used parameters of the BMH potential give the correct trend in the enthalpy of formation from oxides but not the correct absolute values. In addition, we may conclude that the thermodynamic databases in Calphad are inaccurate, and the data we found experimentally can be further used to improve them.

4.7. Summary of the most important findings of the current study

An experimental and theoretical study on the C(12-n)M(n)A7 glasses (n <= 4) were performed to determine their structural and physico-chemical properties using XANES spectroscopy, various calorimetric techniques and classical molecular dynamics simulations. The key findings are:

• a good agreement on structural, dynamic and thermodynamic properties of C12A7 glass with the literature data [11-13,16,43] was observed;

- Al is in fourfold coordination in all studied glass samples. The Q^4/Q^2 ratio is increasing in the C12A7-C8M4A7

composition range, which was confirmed by Al K-edge XANES spectroscopy;

Table 4 Thermochemical cycle for calculation of the enthalpy of formation from pure solid oxides of the C8M4A7 glass sample at 298.15 K from drop-solution calorimetry. The number of drops is presented in round brackets.

CaO $_{(cr, 298.15)} \rightarrow$ CaO $_{(diss, 1073)}$	$\Delta H_1 = -7.08 \pm 2.31$ kJ/mol [47]
MgO $_{(cr,\ 298.15)}\rightarrow$ MgO $_{(diss,\ 1073)}$	$\Delta H_2 = 42.09 \pm 0.41$ kJ/mol [48]
$\alpha\text{-Al}_2O_3\ _{(\mathrm{cr},\ 298.15)}\rightarrow Al_2O_3\ _{(\mathrm{diss},\ 1073)}$	$\Delta H_3 = 120.12 \pm 0.17$ kJ/mol [48]
$\begin{array}{c} (\text{CaO})_{0.421}(\text{MgO})_{0.211}(\text{Al}_2\text{O}_3)_{0.368 \text{ (gl,}} \\ & _{298.15)} \rightarrow \\ (\text{CaO})_{0.421}(\text{MgO})_{0.211}(\text{Al}_2\text{O}_3)_{0.368 \text{ (diss,}} \\ & _{1073)} \end{array}$	ΔH ₄ = 29.5±1.4 kJ/mol [this work] (12)
$\begin{array}{l} \text{0.421CaO}_{(cr, 298.15)} + \text{0.211MgO}_{(cr, 298.15)} \rightarrow \\ \text{(CaO)}_{0.421}(\text{MgO})_{0.211}(\text{Al}_2\text{O}_3)_{0.368} \text{ (gl,} 298.15) \end{array}$	$\Delta_{\rm f} H_{\rm ox, 298.15}({\rm C8M4A7, gl}) *$
$\Lambda_{cH_{constant}}(C8M4A7, gl) = 0.421\Lambda H_{c} + 0$	$211\Lambda H_{0} + 0.368\Lambda H_{0} - \Lambda H_{0}$

 $\Delta_{\rm f} H_{\rm ox,298.15}(\rm C8M4A7, gl) = 0.421\Delta H_1 + 0.211\Delta H_2 + 0.368\Delta H_3 - \Delta H_4$ = 20.6 ± 2.6 kJ/mol

* The result was found by assuming the aimed composition of C8M4A7 glass (see Table 1). Taking into account the composition determined by XRF (Table 1) leads to a change in $\Delta_{\rm f}H_{\rm ox,298.15}$ (C8M4A7, gl) by 0.1 kJ/mol.



Figure 8 Enthalpy of formation from oxides of C12A7-C8M4A7 solid solution at 298.15 K: blue circle – experimental data obtained by drop-solution calorimetry in this work, black circle – experimental data obtained by drop-solution calorimetry in [16], green solid curve – FactSage (version 8.3) estimation [49], red solid curve – classical molecular dynamics simulation obtained in this work.

• the coordination number of Ca was found to be between 6 and 7 in all studied glasses by Ca K-edge XANES spectros-copy;

• the published parameters of interaction potentials for classical molecular dynamics simulations were used in this work to simulate the glass properties numerically. The calculated results give a good estimation on structural properties of glasses at room temperature for Ca and Mg (CN(Ca): 6.1-6.3 and CN(Mg): 5.4-5.8) and a poor estimation for Al

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• the density and molar volume decrease in the C12A7-C8M4A7 composition range;

the interaction potential from the literature for classical MD simulations used in this work give a ~10% overestimated values of the density of glasses at room temperature;
 a linear decrease in the glass transition temperature in

the C12A7-C8M4A7 composition range was observed;

• the replacement of CaO by MgO in C12A7 glass influences to a greater extent the enthalpy term in the Gibbs free energy;

• there is no excess composition dependence, within experimental uncertainty, of the heat capacity in the C12A7-C8M4A7 composition range in the 370-830 K temperature range;

• an optimized set of parameters of Voronin's model (combination of Planck-Einstein functions) adequately describes all experimental C_p data of C12A7 glass sample;

• the used parameters of the BMH potential give excellent results for the estimation of heat capacity of the glasses and good estimation of heat capacity of the liquids;

• the enthalpy of formation at 298.15 K was found to be greater for C8M4A7 than for C12A7 glasses with respect to the constituent oxides. The glasses become less stable when MgO is added to their composition;

• the calculated enthalpy of formation from oxides obtained by FactSage (version 8.3) estimation [49] and classical molecular dynamics simulations has the same trend, but the absolute values are significantly shifted compared to the data obtained experimentally by drop-solution calorimetry.

5. Limitations

The main limitation of this study is in the experimental investigation of the Mg local surroundings. Due to the very low intensity of Mg K-edge XANES spectra, it takes significantly more time to collect a good spectrum, compared to the spectra for Ca and Al. Thus, in this work the local surroundings of Mg was estimated only by classical molecular dynamics simulation. In the future it would be interesting to measure the coordination number of Mg by experimental methods and to compare the obtained results with the values found in this article by MD simulations.

6. Conclusions

In this work, we studied the structural and physico-chemical properties of glasses in the $(Ca_{1-x}Mg_x)O-Al_2O_3$ ternary system using different experimental techniques and classical molecular dynamics simulations. To sum up, the replacement of CaO by MgO in the C12A7 glass leads to increasing Q⁴/Q² ratio, decreases the density and glass-transition temperature, increases the enthalpy of formation from oxides at 298.15 K, with constant, within the experimental uncertainty, Ca surroundings and heat capacity of the glasses in the 370–830 K temperature range. The newly determined high-quality experimental data may be further used for the construction of physico-chemical models of glasses and liquids containing CaO, MgO and Al₂O₃, which may be of interest in various fundamental and applied fields.

Supplementary materials

This manuscript contains supplementary materials, which are available on the corresponding online page. Figure S1: Powder XRD data of studied glasses; Figure S2: Photo of synthesized glasses; Figure S3: Compositions of studied glasses; Figure S4: Experimental density of studied glasses at room temperature; Figure S5: Molar volume of studied glass at room temperature, calculated from the experimental density; Figure S6: Glass transition temperature of studied glasses, as measured by DSC; Figure $\mathbf{S7:}$ The raw DSC curves of studied samples for glass transition temperature determination; Figure S8: Temperature dependence of density of C12A7, C10M2A7 and C8M4A7 glasses, obtained by classical molecular dynamics simulations; Figure S9: Temperature dependence of heat content of C12A7, C10M2A7 and C8M4A7 glasses, obtained by classical molecular dynamics simulations; Table S1: Experimental molar heat capacity of glassy C12A7 sample per 1 mole of formula unit of glass; Table S2: Experimental molar heat capacity of glassy C10M2A7 sample per 1 mole of formula unit of glass; Table S3: Experimental molar heat capacity of glassy C8M4A7 sample per 1 mole of formula unit of glass: Table S4: Smoothed thermodynamic properties of C12A7 glass; Table S5: Heat effects after drops of studied C8M4A7 glass in lead borate solvent from room temperature to calorimetry temperature.

Data availability statement

The data presented in this study are available in this article and in Supplementary materials.

Acknowledgments

The authors acknowledge SOLEIL for provision of synchrotron radiation facilities (proposal ID #20221616) and would like to thank Nicolas Trcera and other LUCIA staff for assistance in using the beamline. Also, the authors acknowledge Alexander Pisch, Noel Jakse and Daniel R. Neuville for their help in conducting experiments and MD simulations.

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Conflict of interest

The authors declare no conflict of interest.

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