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Structure of MgO/CaO sodium aluminosilicate glasses: Raman spectroscopy study

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ABSTRACT

Understanding the composition dependence of the atomic structure of multicomponent aluminosilicate glasses is a challenging problem. Aluminum has a crucial influence on the structure-property relations in these systems, but there are still questions regarding its local structural environment. Here, we present results detailing the network structure of twenty quaternary MgO/CaO-Na_2O-Al_2O_3-SiO_2 glasses upon Al_2O_3-for-SiO_2 and MgO-for-CaO substitutions using room temperature and in situ high-temperature Raman spectroscopy. The Raman spectra reveal that the Mg-containing glasses violate the Al-avoidance at lower Al_2O_3 concentration than the Ca-containing glasses. Furthermore, the alkaline earth ions acting as charge-compensators for tetrahedral aluminum are found to have a similar effect on the network structure (Q^n speciation and Al/Si mixing), while they affect the network differently when they are in a modifying role. Increasing cation field strength allows for stabilization of networks with a larger distribution of bond angles.

1. Introduction

Oxide glasses are synthesized by making use of at least one network-former (such as SiO_2, GeO_2, B_2O_3, or P_2O_5), which forms a continuous three-dimensional network, that is typically mixed with one or more network-modifying oxides (such as alkali or alkaline earth oxides). Understanding of the atomic structure of oxide glasses has advanced substantially in recent decades, primarily due to significant improvements in experimental methods and theoretical calculations [1–4]. Also, qualitative structure-property correlations in various glass systems have been demonstrated [1,5–16]. However, quantitative understanding of such correlations is still lacking for most multi-component glass-forming systems.

Silica (SiO_2) and alumina (Al_2O_3) are the two most important network-forming oxides for industrial glasses and also the two most abundant in natural magmatic liquids. Under ambient pressure conditions, Si^{4+} is in tetrahedral coordination in aluminosilicate glasses, while Al^{3+} can adopt various coordination states and thus possess different structural roles [1]. Early studies demonstrated the more complicated impact of Al_2O_3 on viscosity compared to that of SiO_2 [17,18]. A dual structural role of aluminum was suggested to explain this observation, i.e., Al^{3+} can act either as a network-former in tetrahedral coordination or in a charge compensating role in five- or six-fold coordination [19]. It is now well established that Al^{3+} is stabilized in tetrahedral coordination (Al^{IV}) when associated with charge balancing cations (such as Na^+ and Ca^{2+}) [1,20]. In the ideal case, addition of Al_2O_3 to an alkali silicate or alkaline earth silicate glass thus leads to the removal of network-modifying cations from their original role in the network until no more non-bridging oxygen (NBO) atoms remain [21]. When the concentration of Al_2O_3 exceeds that of the network-modifying oxides, Al^{3+} can no longer be charge balanced in tetrahedral configuration and some excess Al^{3+} is forced into higher coordination number as a means of charge-balancing additional Al tetrahedra [22–24]. Most such peraluminous glass systems exhibit a preference for the formation of five-fold over that of six-fold coordinated Al^{3+} [22,25,26]. We note that an alternative hypothesis is that Al^{IV} can be incorporated, even in peraluminous compositions, without the need for a charge-balancing cation through association with a three-coordinated oxygen [27]. A three-coordinated oxygen is shared by three tetrahedral network cations as found in crystalline $CaAl_4O_7$. Such oxygen triclusters have been found in molecular dynamics simulations [28], with additional evidence from viscosity data in the vicinity of the charge-balanced join [29] and nuclear magnetic resonance (NMR) studies on a calcium aluminate glass [30].

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The ability of a modifier to charge-compensate Al^{3+} is affected by its size and valence. While the structure of aluminosilicate glasses modified solely by sodium oxide is essentially equivalent to the ideal case with no Al^{V} or Al^{VI} present in peralkaline compositions, the structure of glasses modified by alkaline earth cations, such as Mg^{2+} and Ca^{2+}, is more complex since two charges are confined in the same position. The smaller ionic radius of Mg^{2+} in comparison with Ca^{2+} also causes it to have a different local environment, which affects the aluminosilicate network [31,32]. While the coordination number of Ca^{2+} is believed to be around six to seven [33,34], the local environment of Mg^{2+} is significantly different. Previous work has reached different conclusions and reported the presence of four-, five-, and six-fold coordinated Mg^{2+} [35–43]. The role of Mg^{2+} appears to be between a traditional network modifier and network former, but the detailed structural and topological role of Mg^{2+} remains relatively poorly understood, and its impact on the physical properties is therefore still unclear [44]. The modifier type also affects the mixing of Si^{4+} and Al^{3+} tetrahedra. Al—O—Al structural units have been found to be energetically unfavorable, which is termed Al-avoidance [45]. However, the fraction of Al—O—Al appears to increase with increasing Mg/Ca and Al/Si ratios [46,47]. Moreover, while much work has been done on the ternary alkali aluminosilicate and alkaline earth aluminosilicate systems [1], significantly less attention has been devoted to the more complicated quaternary alkali-alkaline earth aluminosilicate systems [46,48–50]. In these systems, the alkali and alkaline earth cations compete with each other in their interactions with the network forming units. A better understanding of the structural and topological roles of network modifiers and formers is important to provide the link between microscopic structure and the macroscopic properties.

In this study, we investigate the change in network structure upon Al_2O_3-for-SiO_2 and MgO-for-CaO substitutions in sodium aluminosilicate glasses (Fig. 1) using room temperature and in situ high-temperature Raman spectroscopy measurements to detect structural changes at ambient conditions and as a function of temperature. This investigation thus seeks to improve the understanding of the role of Al^{3+} in the silicate network in the presence of both alkali and alkaline earth cations and on the nature of the influence of these cations.

2. Experimental methods

2.1. Sample preparation

We prepared two sets of sodium aluminosilicate glasses with either calcium or magnesium (in mol%): $(76 - x)SiO_2 – xAl_2O_3 – 16Na_2O – 8RO$ with $x = 0$, 2.7, 5.3, 8, 10.7, 13.3, 16, 18.7, 21.3, and 24 for R = Ca and Mg [51,52]. We included 0.15 mol% SnO_2 as fining agent in all compositions. The batch materials (SiO_2, Al_2O_3, Na_2CO_3, $CaCO_3$, MgO, and SnO_2) were first thoroughly mixed for 60 min using a ball mill. The mixed batch materials were then melted in a covered Pt crucible for 5 h in air at a temperature between 1450 and 1600 °C depending on composition. In order to ensure chemical homogeneity, the melts were first quenched in water, and then the resulting glass pieces were crushed and remelted for 6 h at 1650 °C and finally poured onto a stainless steel plate in air. The homogeneity of the samples was subsequently confirmed through inspection under cross polarized light, showing no evidence of phase separation. The glasses were annealed for 2 h at their respective annealing points. The chemical compositions of the final glasses were determined using x-ray fluorescence and are reported in Table 1. The analyzed compositions were within 0.5 mol% of the nominal ones. All figures and calculations in this paper are made using the analyzed compositions, which are accurate within ± 0.1 mol %.

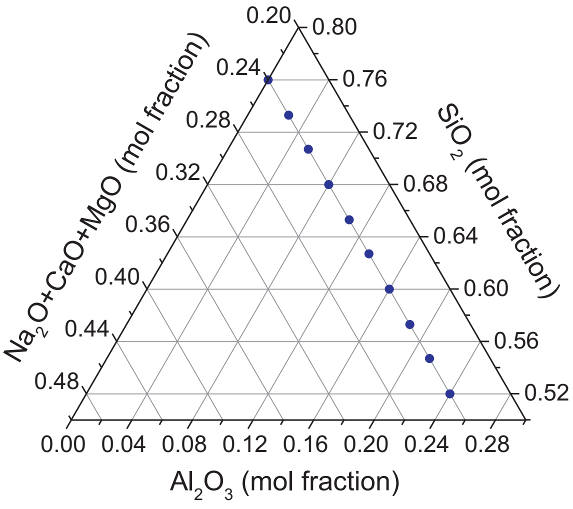

Fig. 1. Ternary molar diagram (SiO_2-Al_2O_3-[Na_2O + CaO + MgO]) showing the investigated glass compositions in this study.

Table 1
Analyzed chemical compositions (in mol%) of the twenty investigated aluminosilicate glasses as determined using x-ray fluorescence. The results are accurate within ± 0.1 mol %.

Glass		Chemical composition (mol%)					
R	x	SiO_2	Al_2O_3	Na_2O	MgO	CaO	SnO_2
Mg	0	75.8	0.1	15.6	8.1	0.2	0.2
Mg	2.7	73.7	2.7	15.7	7.6	0.1	0.2
Mg	5.3	70.9	5.3	15.7	7.9	0.1	0.2
Mg	8	68.1	8.0	15.7	8.0	0.1	0.2
Mg	10.7	65.3	10.7	15.7	8.0	0.1	0.2
Mg	13.3	62.8	13.3	15.8	7.9	0.1	0.2
Mg	16	59.9	16.0	15.8	8.1	0.1	0.2
Mg	18.7	56.6	18.6	15.6	8.9	0.1	0.2
Mg	21.3	54.6	21.3	15.8	8.0	0.1	0.2
Mg	24	52.0	24.0	15.8	8.0	0.1	0.2
Ca	0	75.9	0.0	15.7	0.1	8.1	0.2
Ca	2.7	73.2	2.7	15.8	0.1	8.1	0.2
Ca	5.3	70.7	5.3	15.8	0.1	7.9	0.2
Ca	8	68.1	8.0	15.7	0.1	7.9	0.2
Ca	10.7	65.2	10.7	15.8	0.1	8.0	0.2
Ca	13.3	62.6	13.3	15.8	0.1	8.1	0.2
Ca	16	59.8	16.0	15.8	0.1	8.1	0.2
Ca	18.7	57.2	18.7	15.7	0.1	8.2	0.2
Ca	21.3	54.2	21.3	15.7	0.1	8.4	0.2
Ca	24	51.8	24	15.8	0.1	8.1	0.2

2.2. Raman spectroscopy

Raman spectra were collected both at room temperature and in situ at higher temperatures. To do so, glass samples were optically polished to a thickness of 50–80 μm with two parallel top and bottom surfaces. Grinding and polishing were done using 600 grit SiC sand paper and cerium oxide slurry. The evolution of the glass structure as a function of temperature was monitored by heating up the polished thin samples in a Linkham TS1500 heating stage from room temperature to approximately 100 °C above the glass transition temperature (T_g) of each composition. T_g has been determined in a parallel study based on viscosity measurements [53].

Raman spectra were collected through the top fused quartz window of the Linkham TS1500 in air [54]. A LabRAM HR800 Raman microscope (Horiba Jobin Yvon) was used to carry out the in situ high-temperature light scattering experiments by using a 532 nm Verdi V2 DPSS green laser as the probing light source. In all experiments, a heating rate of 50 °C/min was used. After each temperature was reached, Raman spectra were collected after the temperature inside the heating stage had stabilized for 5 min. Following Refs. [55,56], we have removed the spectral background by fitting a second order