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Effect of ZrO_2 on the structure and properties of soda-lime silicate glasses from molecular dynamics simulations

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ABSTRACT

Zirconia-containing soda-lime silicate glasses with compositions of $xZrO_2$-(75-x)SiO_2-15Na_2O-10CaO, where x = 0, 1, 3, 5 and 7, were studied using classical molecular dynamics (MD) simulations to understand the effect of ZrO_2/SiO_2 substitution on the short-, medium-range glass structures, and properties such as ionic diffusion and mechanical behaviors of these glasses. Local environments of Zr^{4+} and other cations such as bond distance and cation-oxygen coordination number as a function of composition were systematically analyzed from pair distribution function and bond angle distribution calculations. It was found that Zr—O bond distance is around 2.12 Å and zirconium coordination number is around 6, forming slightly distorted [ZrO_6] octahedron, with both showing little changes with composition. Silicon maintains perfectly four-fold coordinated with a Si—O bond distance of 1.61 Å throughout the glass series. Medium-range structural information (e.g., Q_n distribution, network connectivity and polyhedral linkages) was also studied as a function of ZrO_2 substitution. It was found that [ZrO_6] enters the glass-forming network through corner-sharing with [SiO_4]. Both Na^+ and Ca^{2+} act as charge compensators of [ZrO_6] with slightly higher preference of the latter. Addition of zirconia was found to impact the properties of the glasses: it increases both the low and high temperature diffusion energy barriers of modifier cations and increases the elastic moduli of the glasses. These changes of properties can be explained by the enhanced glass network due to zirconia incorporation.

1. Introduction

Addition of zirconia (ZrO_2) significantly alters the chemical and physical properties of silicate glasses: it increases density, chemical durability, and glass transition temperature while decreases thermal expansion coefficient [1,2]. As a result, zirconia is added in silicate or borosilicate based nuclear waste glasses to enhance properties such as chemical durability and mechanical strength or introduced unintentionally in glasses from the zirconia-based refractory material which forms the walls of glass melter and from powders generated during spent fuel reprocessing [1,3]. The changes of glass properties with addition of zirconia are commonly explained by the strengthening of the glass network due to corner-sharing of [ZrO_6] octahedra with [SiO_4] tetrahedra in the glass-forming networks [4–6]. However, the exact structural role of zirconia in oxide glasses is still controversial: for example, the preference of charge compensators around negatively charged $[ZrO_6]^{2-}$ are unclear and difficult to elucidate from experiments; zirconia is sometimes categorized as a modifier [6,7] or an intermediate [5,8], instead of a glass former. Thus, a detailed study of the local environments of zirconium ions in glasses and associated medium-range structural characteristics are important for understanding the composition-property relations of these glasses.

Chemical durability is one of the most fundamental but important properties of glasses for industrial and technological applications. This is especially true for glasses as matrixes for nuclear waste disposal where long-term stability is desirable. Addition of ZrO_2 has been reported to improve the chemical durability of silicate glasses in both neutral pH environment and in alkali-enriched basic environments [2,9]. Fisher et al. [1] found that addition of up to 4 mol% of ZrO_2 in soda-lime silicate glasses dramatically decrease the leaching rates (tested for 28 days) of glasses in distilled water, while this effect saturates for glasses with higher ZrO_2 concentrations (up to 12 mol%) where no additional decrease of leaching rates was observed. Cailleteau et al. [10] and Bergeron et al. [11], however, discovered that even though initial dissolution rate drops significantly with increasing ZrO_2 concentration (up to 8 mol%) in soda-lime borosilicate glasses, these glasses experience a higher degree of long-term corrosion. This was explained by the fact that zirconia inhibits/delays the formation of hydrated porous silica-rich alteration layer that controls the residual dissolution rate [11].

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Experimental structural characterization from techniques such as X-ray absorption spectroscopy (XAS) and solid-state nuclear magnetic resonance (NMR) have been used to obtain local structural environment of zirconium in bulk and corroded silicate glasses. Several XAS studies found that zirconium ions (Zr^{4+}) enter the silicate glass mainly as six-fold coordination e.g., sodium-lithium borosilicate glasses with addition of ZrO_2 (up to 5.7 mol%) [12], soda-lime borosilicate glasses with up to 8 mol% zirconia [13], and French models of inactive nuclear waste glasses [4], although a small amount of seven-fold coordinated zirconium was suggested in high-zirconia borosilicate glasses [14]. The Zr—O distance was found to be about 2.09 Å and $[ZrO_6]$ octahedra are corner-shared with $[SiO_4]$ tetrahedra. Pèlegrin et al. [15] studied the evolution of Zr environments during glass alteration with XAS. It was found that Zr changes from 6-fold to higher coordination under (silica) saturated conditions, while no changes are observed in near saturated conditions [15]. Angeli et al. [16] studied zirconium environment using nuclear magnetic resonance (NMR) and found that zirconium ions sit in 6-coordinated octahedra and form Si—O—Zr bonds in both pristine glass and the alteration gel. Therefore, corner-sharing of $[ZrO_6]$ species with $[SiO_4]$ is the main structural motif in these glasses and critical to understand the physical and chemical properties. It is known that zirconia has limited solubility in silicate glasses. Zirconia solubility is found to be 12.3 mol% in soda-lime silicate glasses [1], and the low solubility of ZrO_2 in both silicate glasses and borosilicate glasses often causes glass devitrification, defects in glasses, and waste-form cracking [3]. Hence, it is critical to study the relationship between glass structural evolution caused by addition of ZrO_2 and its properties such as density, glass transition temperature, solubility in silicate/borosilicate glasses and chemical durability.

Molecular dynamics (MD) simulation is an effective method of studying the structure and structure-property correlation in glass materials, and it provides a direct observation of atomic level structural information, which is usually difficult to obtain from experimental methods [17]. MD simulations of soda-lime silicate glasses were reported by Cormack and Du [18] and it was found that both sodium and calcium ions play the role of modifiers to break the Si—O—Si linkages and create non-bridging oxygen bonds, while calcium ions have a better defined first coordination shell with higher percentage of non-bridging oxygen. Amorphous zircon ($ZrSiO_4$) has been studied using MD simulations by Du et al. [19], where addition of ZrO_2 leads to polymerization of silicon-oxygen network and formation of Zr-riched region. Structure of $42CaO$-$48SiO_2$-$10ZrO_2$ glass was studied using MD by Montorsi et al. [20] and Zr ions are found to be in distorted octahedral sites, corner-sharing with $[SiO_4]$ tetrahedra. Connelly et al. [3] found that ZrO_2 changes the coordination of boron and the polymerization of the glass network in two sodium-lithium borosilicate glasses with MD simulation; additionally, a possible method of predicting the solubility limits of oxides within glasses was proposed. Ferlat et al. [6] have combined MD simulation with XAS to study a sodium alumina borosilicate glass with ZrO_2 added and perfectly regular $[ZrO_6]$ octahedra were observed.

This study was inspired by experimental studies of ZrO_2-containing glasses [2,7,10,11,21], where detailed glass formation behaviors, physical properties such as corrosion rate and others were systematically measured experimentally. The purposes of this paper are to study the structural evolution and property change of soda-lime silicate glasses as a function of zirconia concentration by MD simulation with a set effective partial charge potentials. The goals are to study the effect of ZrO_2 on local environment and medium-range structure of the glasses, to analyze dynamic properties of the ions to better understand the chemical durability of glasses, and to calculate bulk, shear and Young's moduli to investigate the relationships between glass structure and properties.

Table 1
Glass composition, density, cell size and number of Zr atoms for structural analysis.

Glass	Composition (mol%)				Experimental density (g/cm^3) [2]	Simulation cell info	
	Na_2O	CaO	ZrO_2	SiO_2		Cell size (Å)[a]	No. of Zr
0Zr	15	10	–	75	2.4753	55.01	0
1Zr	15	10	1	74	2.5061	55.96	40
3Zr	15	10	3	72	2.5716	54.87	124
5Zr	15	10	5	70	2.6425	54.75	208
7Zr	15	10	7	68	2.7025	54.96	288

[a] All simulation cells were in cubic shape. Total numbers of atoms in the simulation cells for structural analysis and diffusion analysis were 11,996 and 5998, respectively.

2. Simulation details

2.1. Glass generation and structural analysis

Glass composition, density, cell size and number of Zr atoms of glasses from MD simulations are listed in Table 1, where 0Zr, 1Zr, 3Zr, 5Zr and 7Zr represent different molar percentages of zirconia substitution of silica in the glass composition.

The interatomic interactions are described by the Born model of solids using partial charge pairwise potentials. The covalent character of the bond is described by the partial charge on the ions. The short-range interaction has the Buckingham form and detailed description can be found in previous papers [22,23]. The parameters including atomic charges and Buckingham potential parameters were obtained from previous work [19,24,25] and are listed in Table 2.

Molecular dynamics simulations were performed with DL_POLY 2.20 program developed at Daresbury Laboratory in the UK [26]. The initial atom positions were generated randomly with experimental density in a cubic simulation box. Three random configurations for each composition were generated and simulated through a melt-quench process. The cutoff distance used was 8 Å for the short-range interactions, and 10 Å for long-range interactions, which were calculated using the Ewald sum method with a relative precision of 1×10^{-6}. Integration of motion equations was carried out using the Verlet Leapfrog algorithm with a time step of 1 femtosecond (fs). After initial relaxation at 300 K at zero pressure, the temperature was increased to 6000 K. The glasses were melted at 6000 K and the temperature was gradually reduced with a cooling rate of 1.4 K/ps. At each temperature, the system was run under canonical ensemble (constant number, volume and temperature (NVT)) for 200 picosecond (ps), which is followed by equilibration under canonical ensemble (constant number, volume and energy (NVE)) for another 200 ps. At 300 K, the trajectory was recorded every 50 steps of the last 40,000 steps under NVE ensemble for final structural analysis.

Cutoff distances of first coordination shell for coordination number analysis and bond angle distribution analysis are presented in Table 3. The cutoff values were obtained as the first minimum of partial correlation functions. Detailed introduction of structural analysis methods such as pair distributions functions (PDF), bond angle distribution (BAD), coordination number (CN) and Q_n distribution can be found in a

Table 2
Atomic charges and Buckingham potential parameters [19,24,25].

Pairs	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV Å^6)
$O^{-1.2}$—$O^{-1.2}$	2029.2204	0.343645	192.580
$Si^{2.4}$—$O^{-1.2}$	13,702.9050	0.193817	54.681
$Na^{0.6}$—$O^{-1.2}$	4383.7555	0.243838	30.700
$Ca^{1.2}$—$O^{-1.2}$	7747.1834	0.252623	93.109
$Zr^{2.4}$—$O^{-1.2}$	17,943.3840	0.226627	127.650