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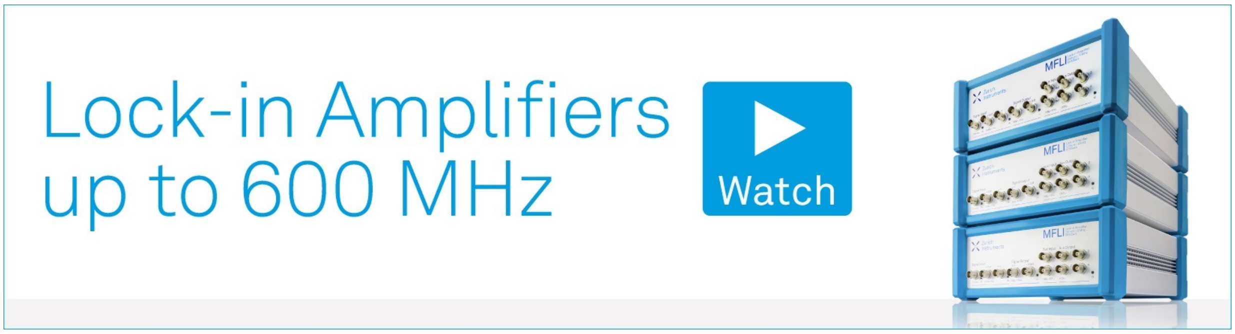

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ABSTRACT

The dielectric properties of alkali and alkaline earth-modified silicate glasses were characterized in the frequency range where electronic and ionic polarizabilities contribute to permittivity. From the Clausius–Mossotti (CM) model, dielectric polarizability of each cation-oxygen constituent was determined from the permittivity and molar volume. The silicon–oxygen polarizability of silica glass (5.24 Å^3) is significantly higher than that of crystalline quartz (4.87 Å^3), suggesting that additional polarization modes contribute to glass permittivity. A full range of alkali species (Li, Na, K, Rb, and Cs) were then added as glass network modifiers through a series of binary silicate glasses, and the silicon–oxygen polarizability increased to 5.38 Å^3. A similar trend was observed for alkaline-earth aluminosilicate glasses in which the polarizability increased with the addition of cationic modifiers to 5.89 Å^3. CM analysis provides a method to explore the fundamental relationship between the glass structure and its unique polarization response in the microwave frequency range. Microwave permittivity values are predicted over broad compositional ranges for alkali and alkaline earth-modified silicate glasses using the CM relationship.

The drive toward faster data transmission in 5G telecommunications has deepened interest in characterization and prediction of electrical properties at microwave and mm-wave frequencies. Glass and glass-ceramics are important materials for high-frequency packaging, transmission lines, and filters where the dielectric permittivity and loss are important design parameters. Silicate glass compositions are tailored to optimize processing and physical properties through the addition of alkali and alkaline earth elements, which act as network modifiers in the prototypical tetrahedral network of pure vitreous silica. A key question is then how such glass modifiers influence the cumulative electronic and ionic polarizability, and ultimately the dielectric permittivity and loss, at microwave frequencies.

Polarizability models to estimate the refractive index at optical frequencies may be applied to understand the relationship between the glass structure and dielectric properties at lower frequency (i.e., microwave and mm-wave) where there is additional ionic polarization.[1,2] The dielectric permittivity is fundamentally related to the dipole density and polarizability as described through the Clausius–Mossotti (CM) equation.[3] Permittivity is predicted from the polarizability of constituent cations and anions as shown by the following equation:

$$\varepsilon_r' = \frac{\left(3V_m + 8\pi\alpha_D^T\right)}{\left(3V_m - 4\pi\alpha_D^T\right)}, \tag{1}$$

$$V_m = \frac{MW}{\rho N_A}, \tag{2}$$

where ε_r' is the relative permittivity, V_m is the molar volume (Å^3), MW is the molecular weight, ρ is the glass density, N_A is Avogadro's number, and α_D^T is the total dielectric polarizability.

The CM model has been applied to crystalline oxides and fluorides, and the permittivity is accurately predicted from individual cation and anion polarizabilities.[4] In this case, the polarizability of each ion contributes to the total polarization according to the following equation:

$$\alpha_D^T(M_xO_y) = x\alpha_D(M) + y\alpha_D(O), \tag{3}$$

where the total polarizability α_D^T is the sum of individual metal cation $\alpha_D(M)$ and oxygen anion $\alpha_D(O)$ polarizabilities.

In previous work on oxide and fluoride crystalline structures, a comprehensive table of ion polarizabilities was generated through permittivity and molar volume data from over 150 compounds.[4] The polarizability of the oxygen anion (2.01 Å^3), silicon (0.87 Å^3), and

TABLE I. Predicted and measured permittivity for crystalline and amorphous silica.

	Clausius–Mossotti calculation			Microwave measurement[5,6]
	Density (g/cm^3)	Polarizability (Å^3)	Calculated permittivity	Measured permittivity
Quartz	2.65	4.87[4]	4.55	4.54
Fused silica	2.20	4.87	3.50	3.82
		5.24	3.82	3.82

alkali cations (Li = 1.20 Å^3 to Cs = 7.43 Å^3) was determined from known oxygen stoichiometry and cation coordination of silicate minerals.

An example CM calculation is shown in Table I, and there is close agreement between the calculated and measured permittivity values for crystalline quartz. However, the predicted permittivity of fused silica when calculated using the quartz polarizability value is substantially lower than the measured permittivity value. A higher polarizability estimation (5.24 Å^3) is required to match the CM calculation with the measured permittivity for fused silica. The additional polarizability within the silica glass is attributed to additional ion motions in the low frequency vibrational density of states as compared to the acoustic phonon in the crystalline counterpart.[7–9]

There are significantly fewer dielectric polarizability studies below optical frequencies for amorphous materials than for crystalline materials. The relationship between the structure and dielectric polarization for alkali aluminosilicate glass was determined from low frequency dielectric data (frequency <1 MHz), where it was found that conductivity and space charge polarization play a significant role in the electrical response.[10] The dielectric response of silica over a wide range of modified oxide glasses was explored through THz time-domain spectroscopy.[11] It was shown that through the CM model, ionic polarization provided a significant contribution to the overall permittivity in the THz frequency range and that polarizability increased significantly with modifier additions into the silicate network.

In this study, the microwave dielectric properties of alkali and alkali earth-modified silica glass were characterized over a wide compositional range. An alternative approach to quantify glass permittivity is introduced in the following equation, wherein the total polarizability is the sum of constituent oxide polarizabilities,

$$\alpha_D^T(glass) = \sum_M X_M \alpha_D(M - O), \tag{4}$$

where X_M is the cation mole fraction and α_D (M − O) is the polarizability of individual metal cation species with coordinated oxygen anions. Note that Eqs. (3) and (4) are similar in the way that both cations and anions contribute to the overall polarizability; however, they differ because Eq. (4) combines the contributions as a single cation–anion unit. Both bridging and non-bridging oxygens (NBOs) introduced into the glass structure with alkali and alkaline earth modification are accommodated by Eq. (4).

The permittivity of alkali and alkali earth-modified silica glass can be estimated from Eq. (1) through the total polarizability [Eq. (4)] and the molar volume [Eq. (2)]. This approach has been applied to the index of the refraction calculation of $NaAlSi_3O_8$–$CaAl_2Si_2O_8$ glass mixtures.[1] The electronic polarizabilities of the metal-oxides were found to be an accurate predictor of the refractive index and dielectric permittivity of amorphous structures. A similar approach will be explored to quantify polarizability in the microwave frequency range.

The binary alkali silicate glasses shown in Table II were batched with target compositions of 5 and 10 mol. % alkali oxides, with the balance being silica. This table reports the analyzed compositions determined by a combination of inductively couple plasma optical emission and flame-emission spectroscopies (ICP-OES/FES). All glasses were melted in 2 kg batches from industrial quality sand, alumina, and alkali carbonate raw materials. Each composition was melted twice to achieve better homogeneity. The batch materials were initially melted in Pt crucibles at 1650 °C for six hours, and the melts were poured into cold water to quench. The resulting glass cullet was dried overnight to remove water. The glass cullet was then remelted in Pt

TABLE II. Alkali silicate glass compositions measured by ICP-OES/FES (balance SiO_2).

Sample	Li_2O mol. %	Na_2O mol. %	K_2O mol. %	Rb_2O mol. %	Cs_2O mol. %	Density (g/cm^3)
Li-5	4.88					2.209
Li-10	10.06					2.280
Na-5		4.90				2.231
Na-10		10.02				2.287
K-5			4.87			2.245
K-10			9.83			2.297
Rb-5				5.01		2.389
Rb-10				9.77		2.567
Cs-5					5.00	2.523
Cs-10					9.82	2.805

crucibles at 1650 °C for six hours and poured onto a steel plate to form glass patties. The glass patties were annealed between 450 °C and 600 °C overnight at their predicted annealing points to reduce thermal stress. Upon visual inspection, only Li-10 glass had an opalescent color, while all other glasses were optically transparent. Subsequent scanning electron microscopy (SEM) analysis showed Li-5, Na-5, and Na-10 glasses to be phase separated at the ∼10 to ∼100 nm scale. All glasses in this study can be treated as a homogeneous dielectric medium because the microwave wavelengths are significantly larger than the phase separated regions. In addition, the composition differences between phase separated regions were small and will not affect the overall dielectric properties. Bulk densities were determined by the Archimedes method and are also given in Table II.

The alkaline earth-modified glasses shown in Table III were made from 99.99% purity SiO_2, 99.98% purity Al_2O_3, 99.9% purity $CaCO_3$, and 99.992% MgO powders. These compositions were melted in covered Pt90/Rh10 crucibles at 1600 °C in a Globar furnace for 12–16 h, and then the glass was poured on a metal table and rolled with a metal roller. The roller served to break the glass into small pieces that were then re-melted at 1650 °C for 6 h again in covered Pt90/Rh10 crucibles. This double melting process helps to ensure good glass homogeneity. After the second melt, the glasses were poured into patties. The poured glass patties were annealed at 700 °C for 2 h and then cooled to room temperature at 2 °C/min. These glasses showed no evidence of visible phase separation or gaseous inclusions. Glasses were checked in a polariscope for any evidence of residual stress and confirmed the absence of any significant residual stress after annealing.

Dielectric measurements of sheet glass samples were performed on a split post dielectric resonator.[6] Samples were measured in the fundamental $TE_{01\delta}$ mode at 9.95 GHz. The actual measurement frequency with the loaded sample will be slightly less than 9.95 GHz depending on the sample thickness and the magnitude of the real part of complex permittivity. For clarity, all the dielectric data presented below are reported as being measured at nominally 10 GHz.

For evaluating polarizabilities in the alkaline earth aluminosilicate system, the silica, alumina, and alkaline earth-oxide components (CaO or MgO) in the ternary glasses were each modeled using a single polarizability value. These polarizabilities were allowed to vary freely as fitting parameters, and residual error between the measured and calculated permittivities [via Eqs. (1) and (4)] was minimized by least squares regression over all the aluminosilicate glasses in the ensemble. The use of a single polarizability value for Al–O species follows from the supposition that the effects of Al–O on permittivity were largely concentrative in nature (i.e., varies with proportion in the glass composition) but that its polarizability did not vary significantly as a function of composition due to similarities in the local environment around Al—at least across the series of glasses in the current study.

TABLE III. Calcium and magnesium aluminosilicate glass compositions.

	Composition (oxide mol. %)			
Sample	CaO	Al_2O_3	SiO_2	Density (g/cm^3)
CAS-23	23.42	22.59	53.99	2.522
CAS-26	26.18	24.93	48.89	2.713
CAS-27	27.39	26.07	46.54	2.720
CAS-34	33.87	32.12	34.02	2.780
	MgO	Al_2O_3	SiO_2	
MAS-20	20.14	19.71	60.15	2.573
MAS-25	25.2	25.7	49	2.713
MAS-27	27.4	26.92	45.68	2.721

Table IV summarizes the cation–anion polarizabilities deduced from Eq. (4) for the glass compositions shown in Table II. Calculations involve solving linear equations from the permittivity values of the two stoichiometries in each alkali-silica glass system. Silica polarizability was independent of the type and mole fraction of modifier. As in the crystalline oxides, polarizability monotonically increases with the alkali atomic number.[4]

The predicted permittivities for each of the alkali-silicate glasses are shown in Table V from the polarizability values from Table IV with good agreement between measured and CM calculated permittivity values. The dielectric loss values generally increased with the alkali cation size, and the results are consistent with previous microwave measurements of borosilicate glass with modifying oxides.[12]

A similar approach was pursued for calculating polarizabilities for glasses in the alkaline-earth aluminosilicate system. Table VI summarizes the cation–anion polarizabilities from the glass compositions shown in Table III.

All the amorphous oxide polarizabilities shown in Table VI are larger than the corresponding crystalline polarizabilities from the study by Shannon,[4] suggesting that the open glass structure allows for a larger ionic polarization response. As expected, the larger calcium ion will also have a higher polarizability contribution than the magnesium cation. The polarization values of silicon oxide and aluminum oxide are alike as they play similar roles as part of the tetrahedral network. The average silica and alkaline earth values in Table VI were used to estimate the CM permittivity values in Table VII. There is general agreement between the calculated and measured permittivity values. The dielectric loss values followed a similar trend as the alkali-silicates where the loss increases the with cation size for the alkaline-earth compositions.

A comparison of the Si–O polarizability values for crystalline and amorphous silicates is shown in Table VIII. For crystalline silicates, the Si–O polarizability of 4.87 A^3 is identical for quartz, orthosilicates, metasilicates, and feldspars.[4] Glass has higher cation–anion polarizability for species including silicon, alkali, and alkaline earth cations, suggesting that a larger ion dipolar response is possible in more open glass structures. The polarizability error was estimated to be 1% for crystalline silica compounds,[4] and the error for the amorphous silica compounds is also estimated to be in the 1% range.

For crystalline silicates, the silicon–oxygen coordination is tetrahedral and the cation–anion polarizabilities are independent of the composition or phase. Structural data for glassy binary alkali silicate show that the Si–O bond distance does not change with the type of alkali or concentration of alkali cations in the glass;[13] however, the

TABLE IV. Polarizability values for metal oxide constituents in alkali-modified silica glass.

	Si–O	Li–O	Na–O	K–O	Rb–O	Cs–O
Polarizability Å^3	5.38	5.60	8.84	10.73	12.33	14.42

TABLE V. Comparison of measured and calculated permittivity values for alkali silica glass.

	Cation%		Clausius–Mossotti Calculation		Measured at 10 GHz	
Composition	R–O	Si–O	Total polarizability	Permittivity	Permittivity	Loss tangent
Composition	R–O	Si–O	Total polarizability	Permittivity	Permittivity	Loss tangent
Li-5	0.098	0.902	5.40	4.17	4.19	0.005
Na-5	0.098	0.902	5.69	4.40	4.37	0.008
K-5	0.097	0.903	5.91	4.55	4.59	0.008
Rb-5	0.100	0.900	6.08	4.68	4.69	0.009
Cs-5	0.100	0.900	6.26	4.81	4.83	0.009
Li-10	0.201	0.799	5.44	4.65	4.64	0.008
Na-10	0.200	0.800	6.02	5.08	5.07	0.012
K-10	0.197	0.803	6.47	5.34	5.33	0.013
Rb-10	0.195	0.805	6.76	5.56	5.54	0.013
Cs-10	0.196	0.804	7.12	5.80	5.83	0.012

TABLE VI. The polarizabilities of metal oxides calculated from the alkaline-earth alumina silica glass system.

	Si–O	Al–O	Mg–O	Ca–O
Polarizability Å^3	5.89	5.49	11.71	14.75

TABLE VIII. Polarizability of silicon oxide in a range of crystal and glass structures.

Silica form	Polarizability Å^3
Crystalline SiO_2, Li_2SiO_3, $MgSiO_4$[4]	4.87
Fused silica	5.24
Alkali modified silica	5.36
Silica with alkaline earth and alumina	5.89

Si–O–Si angle does increase as the ionic radii of the alkali cations on the order of Li > Na > K,[14] which seems to have little impact on the polarizability in the binary system studied here. The polarizability of alkali-modified silica is very close to that of fused silica. Since there are 90% and 95% silica in the binary system, alkali modifier effects on the Si–O polarizability is limited. The big differences between the binary system (alkali-modified silica) and the ternary system (alkaline earth aluminosilicate) could be explained by the chemical compositions, especially the effect from alumina. In the ternary system, the vast majority of alumina remains four coordinated,[15] and it links through bridging oxygens with silica or other alumina tetrahedra to form the network structure for the glass. The Al/Si ratio is the lowest in MAS-20, which is 0.66, to the highest in CAS-34, which is 1.89. In a completely chemically ordered system obeying Lowenstein's rule, one would expect each Si to be connected to four Al via the four bridging oxygens connecting to it, and vice versa if Al/Si = 1. In reality, such perfect mixing rarely exists,[16,17] and moreover, linkages like Al–O–Al cannot be avoided in glasses with Al/Si >1. As a result, statistically speaking, each Si tetrahedron in the ternary system studied here would be expected to connect to more than two Al tetrahedra on average, which may have a profound impact on the ionic polarizability in the system.

TABLE VII. Comparison of measured and calculated permittivity values for calcium and magnesium aluminosilicate glasses.

	Cation %			Clausius–Mossotti calculation		Measured at 10 GHz	
Composition	Ca–O	Al–O	Si–O	Total polarizability	Permittivity	Permittivity	Loss tangent
CAS-23	19.1	36.85	44.04	7.43	7.05	7.17	0.009
CAS-26	21	39.91	39.13	7.59	7.47	7.40	0.009
CAS-27	21.7	41.36	36.92	7.65	7.53	7.53	0.008
CAS-34	25.6	48.62	25.75	7.96	8.10	8.08	0.009
	Mg–O	Al–O	Si–O				
MAS-20	16.8	32.93	50.25	6.74	5.89	5.81	0.007
MAS-25	20.1	40.92	39.02	6.89	6.42	6.37	0.008
MAS-27	21.6	42.42	35.99	6.98	6.58	6.68	0.008

A primary goal of this work was to link glass chemistry and the structure to dielectric properties at microwave frequencies. The Clausius–Mossotti approach was applied to amorphous silicates, where ionic polarizability and the molar volume were used to predict the permittivity. It was found that the cation-oxygen polarizability increased with the atomic number and valence of the glass modifier. Polarizability values ranged from 5.60 Å^3 to 14.42 Å^3 for the alkali series. Similar trends were seen for alkaline earth modifiers where the polarizability for Mg–O was 11.71 Å^3 and Ca–O was 14.75 Å^3.

Unlike crystalline silicates, a single Si–O polarizability value is not possible for silicate glass. It was found instead that the coupled silicon–oxygen polarizability is only constant within a specific glass system. The Si–O polarizability was independent of the amount and type of alkali species within a glass with the same cation species. The silica environment is the same for all alkali modifiers in the sense that some of the tetrahedral network is connected to non-bridging oxygen, allowing for higher mobility and polarizability. Individual cation and anion polarizabilities were not calculated because it is assumed that the polarizability of bridging oxygen (i.e., oxygen connecting two tetrahedra) will differ from that of non-bridging oxygen (NBO). The NBO species are attached to one silica tetrahedron and charge balanced by the alkali cation. In the aluminosilicate glasses, aluminum will also typically enter the network as a tetrahedral species (i.e., predominantly four-coordinated), surrounded by bridging oxygens, and is locally charge-compensated by nearby alkali or alkaline earth ions. When both the modifier (M_2O or MO) and Al_2O_3 are present in equimolar proportions—for example, the alkaline earth aluminosilicate glass compositions (MO/Al_2O_3 close to 1) considered in this study (Table III)—a maximal degree of polymerization is achieved in the mixed aluminosilicate network, and there is no "excess" modifier in the composition to go toward the substantial creation of NBO on Si. Next steps in this work will entail analysis of glasses in the aluminosilicate space with higher Si/Al ratios and venturing into the peralkaline composition space where Si-NBO is also present in the network structure.

The additional polarization modes found in the microwave frequency range for glass are the probable cause for the higher dielectric loss values found in modified silica glass when compared to quartz and fused silica. The results have significant consequences in the selection of glass compositions for high frequency applications.

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DATA AVAILABILITY

The data that support the findings of this study are available within this article.

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