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Structure and ionic conductivity of nitrated lithium disilicate (LiSiON) glasses

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Abstract

Lithium disilicate is a critical glass forming composition as it is the basis of some glass-ceramics and it is also a model glass for the study of homogeneous and heterogeneous crystal nucleation. Incorporation of nitrogen in this glass significantly changes its structure and affects different properties. In this paper, nitrated lithium disilicate glasses were prepared by partial substitution of oxygen up to 6 atm % N/(N+O). The modification of the silicate glass structure with nitrogen has been confirmed by Fourier transform infrared reflection (FTIR) spectroscopy. ²⁹Si NMR and ⁷Li NMR have also been used to investigate the structural changes due to nitrogen incorporation. Substitution of oxygen by nitrogen with a higher coordination number (three) increases the connectivity of the glass. In fact, our NMR results indicate that nitrogen incorporation changes the Qⁿ distribution (n = average number of bridging oxygens to silicon) of the silicate structural units: SiNO₃, SiN₂O₂ and SiN₃O, whereas there is no detectable change in the Li environment.

We measured the ionic (Li^+) conductivity by impedance spectroscopy and found that the incorporation of nitrogen leads to a decrease in the activation energy for conduction, resulting in an increase of up to four-fold in the ionic conductivity of the most nitrated glass. We explained this high conductivity by the Anderson and Stuart model. This work provides renewed interest in improving and understanding the ionic conductivity in oxynitride glasses.

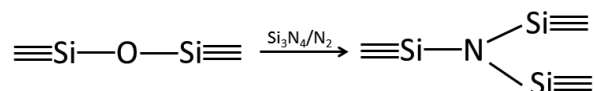
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1. Introduction

Lithium silicate glasses have been extensively studied for their interesting thermal, electrical, mechanical and structural properties [1-5], but also because these glasses present homogeneous (internal) nucleation in the volume [6, 7] serving as a model for crystallization studies. They are also the basis of some commercial glass-ceramics showing a numerous and relevant combination of properties [8, 9]. On the other hand, it has always been a fascinating idea for researchers to improve properties of any glass by different processing techniques and compositional changes. Nitridation of oxide glasses is known to improve various properties, such as chemical durability, mechanical strength and electrical conductivity over their counter oxide glasses due to changes in their chemical bonding and structure [10, 11]. In nitrated silicate glasses, oxygen atoms in the SiO_4 tetrahedra are partially replaced by nitrogen atoms. Accordingly, three coordinated nitrogen atoms in substitution to (two coordinated) oxygen results in a more connected structure than the corresponding oxide based silicate glasses, as we schematically show below:



The overall outcome due to the incorporation of nitrogen into the glass structure is the increase in crosslinking through bonding of nitrogen with three silicon atoms and hence, a more rigid glass network is formed. Moreover, the electronegativity of oxygen is higher than that of nitrogen. Consequently, Si-O is partially replaced by the more covalent Si-N bonding which favors the fast diffusion of the mobile Li^+ ion. Therefore, substitution of oxygen by nitrogen in glasses improves the electrical properties [12, 13]. According to some authors, the ionic conductivity increases due to the decrease of the electrostatic binding energy of the oxynitride glasses in comparison to oxide glasses [10, 12].

It is interesting to monitor the changes in the glass structure due to the substitution of oxygen by nitrogen using different techniques, such as ^{29}Si solid-state nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopies. These methods can be helpful to understand the possible arrangement of nitrogen atoms in the silicate network and provide information about structural changes which can help to describe the changes in the various properties of the oxynitride glasses.

Electrical properties of oxynitride glasses have been presented by different authors using structural and chemical bonding modification models due to the introduction of nitrogen by substitution of oxygen [12, 14, 15]. For instance, Reau *et al.* [12] have demonstrated an increase of Li^+ conductivity in lithium alumino silicate based oxynitride glasses with the increase in nitrogen content. Moreover, the conductivity and the activation energy for conduction of nitrated lithium alumino silicate and lithium silicate glass have been compared, and it was found that the conductivity of the last is higher than that of the lithium oxynitride aluminosilicate glasses. In another report, Muñoz *et al.* [15] have prepared oxynitride phosphate glasses by the ammonolysis process. Nitrogen incorporation resulted in a sharp increase in conductivity at low

content of nitrogen. The increase in the electrical conductivity is explained [15] through the structural changes in lithium environment, but also by the increase of coordination number (two to three) and the nature of bonding (Si-O to Si-N). The effect of nitrogen on the conducting mechanism in lithium phosphorous oxynitride glasses has also been studied by Mascaraque *et al.* [14]. They proposed that the decrease of the bridging (BO) to non-bridging (NBO) oxygen ratio observed in X-Ray photoelectron spectroscopy is directly linked to the increase of ionic conductivity

Li⁺ ion conductivity in silicate glasses is widely known. As a general rule, the activation energy decreases, and ionic conductivity increases with increasing the Li⁺ concentration. However, there are scarce reports on nitrated lithium silicate glasses and to the best of our knowledge; there is no report on the ionic conductivity in nitrated lithium disilicate, an important “model” glass. Thus, in this paper, we explore the influence of nitrogen on the ionic conductivity in a lithium disilicate glass. We discuss the structural changes in the silicate glass structure due to the incorporation of nitrogen using FTIR, and ²⁹Si and ⁷Li solid-state NMR. The difference in ionic conductivity in these oxynitride glasses is explained not only by taking into account modifications in the glass structure, but also by the nature of chemical bonding.

2. Experimental procedure

The Li₂O.2SiO₂ based oxynitride glasses were prepared by partial substitution of oxygen by nitrogen in the following atomic quantities: N/(N+O) = 0, 1.5, 3.0, 4.5 and 6.0. The glasses were prepared by melt-quenching in a glove box filled with nitrogen gas. The batches were made using reagent grade materials Li₂CO₃ (99% ACS Reagent, Aldrich), quartz, SiO₂ (99% ACS Reagent, Merck) and Si₃N₄ (99%, Merck). The mixture of raw materials was melted at 1300°C

for 2 h using a molybdenum crucible inside the glove box in a nitrogen atmosphere. Glass samples of approximately 50g were obtained by pouring the melts onto a molybdenum plate. The glasses were annealed at 400°C for 2 h to reduce the internal thermal stresses.

The glass transition (T_g) and crystallization temperatures (T_p) were determined from differential scanning calorimeter (DSC). The DSC experiments were performed using a Netzsch DSC 404 instrument from 30 to 1100 °C at a heating rate of 10 °C/min under air. Single glass pieces with 15 mg mass were inserted in a covered platinum crucible for the above-described experiment.

Fourier transform infrared (FTIR) reflection spectra of polished bulk glasses were recorded with a Bruker Tensor 27 FTIR spectrometer after 32 scans and recorded in the range of 400-2000 cm^{-1} .

High-resolution ^{29}Si and ^7Li -NMR spectra were obtained using a Varian Unity INOVA spectrometer under a magnetic field of 9.4 T using powdered samples. For the ^{29}Si -NMR experiments, the samples were spun at 5 kHz in 7 mm zirconia rotors. Typical experimental parameters were: $\pi/2$ -pulse duration of 3.3 μs , recycling delays of 150 s and 600 collected scans. For the ^7Li NMR experiments, samples were spun at 9 kHz in 4 mm silicon nitride rotors. Typical experimental parameters were: $\pi/2$ -pulses of 2.0 ms, recycle delays of 1000 s and collected 64 scans. The chemical shift standards were a kaolinite sample for ^{29}Si (-91.5 ppm concerning TMS) and LiCl 1M solution for ^7Li (0 ppm). The electrical conductivity was measured by impedance spectroscopy (IS) using a Solartron, SI1260 impedance meter. Rectangular shaped samples for conductivity were polished on parallel sides, and gold was sputtered on both surfaces for 3 minutes on each side. The electrical measurements were

performed in air with a two-point sample holder from 323 to 423 K with an applied voltage of 500 mV in the frequency range from 1 MHz to 1 Hz.

3. Results and discussion

3.1. Differential scanning calorimetry (DSC)

A typical DSC graph is shown in Fig. 1 for the lithium disilicate glass. The glass transition temperature (T_g) and crystallization peak temperature (T_p) are 457 °C and 655 °C, respectively. All glasses were annealed at 400 °C for 2 h, which is well below the glass transition temperature to avoid any crystallization process. T_g and T_p increased with the addition of nitrogen and are reported elsewhere [16].

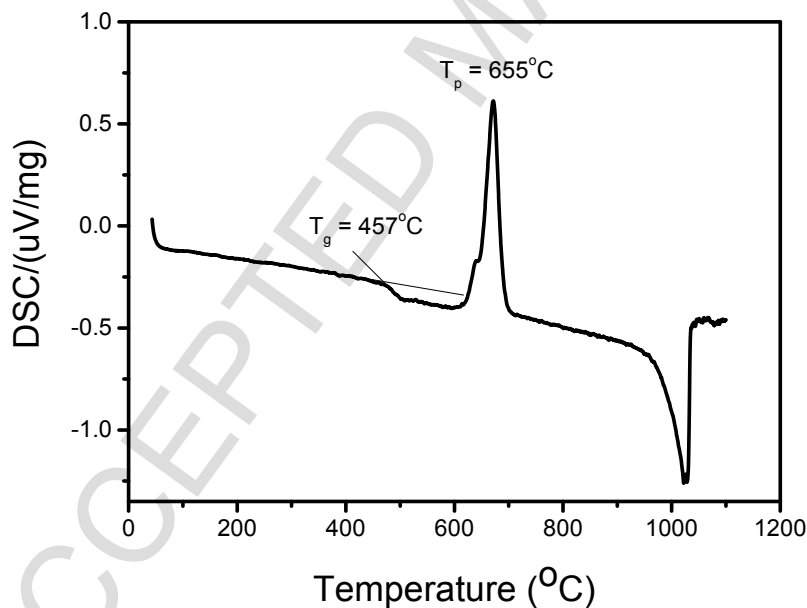


Fig. 1. Differential scanning calorimetry (DSC) thermogram of the lithium disilicate base glass (pure oxide glass).

3.2. Fourier transform infrared reflection (FTIR) spectroscopy

The results of FTIR spectroscopy tests are shown in Fig. 2 for the glasses containing 0, 3, 4.5 and 6 atm % N/(N+O). The glass spectra show reflection bands at 634, 666, 709, 823 and 979 cm^{-1} . The broad band centered at 666 cm^{-1} of the pure oxide glass gradually bifurcated into two bands at 634 and 709 cm^{-1} with the incorporation of nitrogen into the glass. This change in the spectral profile with the concentration of nitrogen confirms that there is a change in the nature of the bonds of the glass structure. The band at 666 cm^{-1} is assigned to the stretching vibration of Si-O-Si of tetrahedral $[\text{SiO}_4]$ units [17]. The introduction of nitrogen into the glass structure resulted in the development of two types of bands, Si-O and Si-N. The shift of the Si-O band is attributed to higher disorder or bond strain into the tetrahedral $[\text{SiO}_4]$ unit. The band at higher energy, 709 cm^{-1} , is assigned to Si-N stretching vibration [18, 19]. The spectral profiles of other bands are similar in all glasses. Bands at 823 and 979 cm^{-1} are also attributed to the stretching vibration of Si-O-Si [18]. The formation of Si-N bond in the glass structure may affect the glass properties. Moreover, the substitution of oxygen by nitrogen also results in an increase of the connectivity of the glass network through the bonding of nitrogen with three silicon atoms. Such increase in the connectivity may cause strain in the glass network.

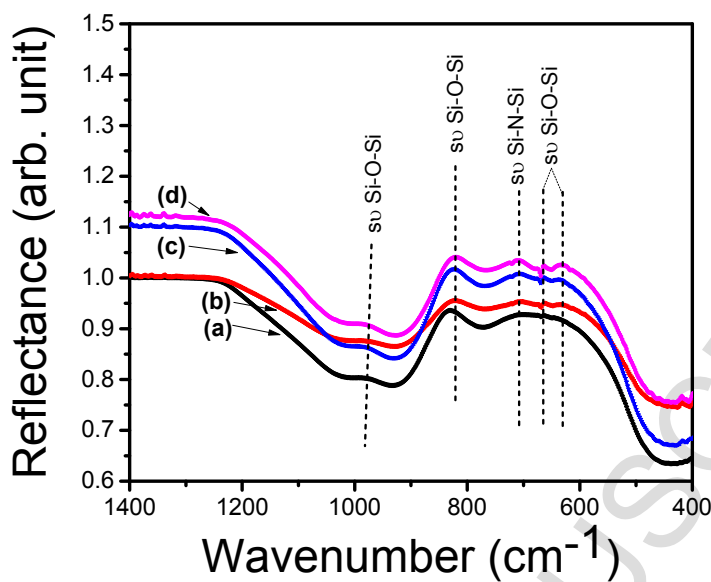


Fig. 2. FTIR spectra of the glass (a) 0, (b) 3, (c) 4.5 and (d) 6 atm % N/N+O.

3.3. ²⁹Si and ⁷Li solid-state nuclear magnetic resonance (NMR)

The ²⁹Si and ⁷Li solid-state NMR spectra of the set of the oxynitride glasses are shown in Fig. 3 and Fig. 4, respectively. The ²⁹Si-NMR spectra show gradual changes in the spectral profile of the nitrogenated glasses compared to the base glass. Least-square fittings of Gaussian functions were carried out to de-convolute the spectra. Three resonances can be identified in the nitrogen-free glass, with average isotropic chemical shifts δ_{iso} of -102ppm, -87ppm and -76ppm, corresponding to Q⁴, Q³ and Q² tetrahedral species, respectively [20-22]. The numbers 2, 3 and 4 in Q², Q³, Q⁴ are assigned as the average numbers of bridging oxygens to the silicon atoms. Fig. 3 shows that gradual incorporation of nitrogen to the lithium disilicate glass causes a general broadening of the spectral bands and an increase in the spectral intensity in the region of higher δ_{iso} . The incorporation of nitrogen in the glass structure creates SiO_{4-n}N_n structural units. The vertical bars in Fig. 3 locate the typical region for ²⁹Si- δ_{iso} for these structural units according to

literature data [23]. The increase in the spectral intensity on the left side of the spectra, between -80 ppm and -60 ppm, is consistent with the presence of SiN_2O_2 and SiN_3O but quantification of $\text{SiO}_{4-n}\text{N}_n$ species from these spectra is not possible due to the strong overlap between the resonances. ^7Li NMR was carried out in all glasses to determine the effect of nitrogen inclusion on the lithium sites. Fig. 4 shows the ^7Li NMR spectra for the 0 and 6 atm % of $\text{N}/(\text{N}+\text{O})$ glasses, which are identical ($\delta_{\text{iso}} = -0.16\text{ppm}$, $\text{FWHM} = 3.8\text{ ppm}$). This result supports the idea that nitrogen is bonded only to silicon atoms and not directly to lithium. Therefore, the structural environment of Li, which is determined essentially by the nearest non-bridging oxygens, is not affected by the addition of nitrogen.

Fig. 5 shows a schematic representation of the structural units described above, with three-fold coordinated nitrogen bonding only to Si, in substitution of O. On the other hand, there is still a possibility that the invariance of ^7Li -NMR spectra results from the combination of low concentration of N and the low intrinsic sensitivity of the ^7Li chemical shift to variations in more remote bonds. Muñoz *et al.* [15] have observed an increase in the chemical shift of the ^6Li NMR resonances with nitrogen in a lithium oxynitride phosphate (LiPON) glass which has been related to a decrease in the average Li^+ coordination number and to an increase in the covalent character of Li-O bonds. In contrary to Muñoz's report, we did not observe any chemical shift of the ^7Li in this study, which suggests that the environment of Li^+ is not affected due to the nitridation of the glasses.

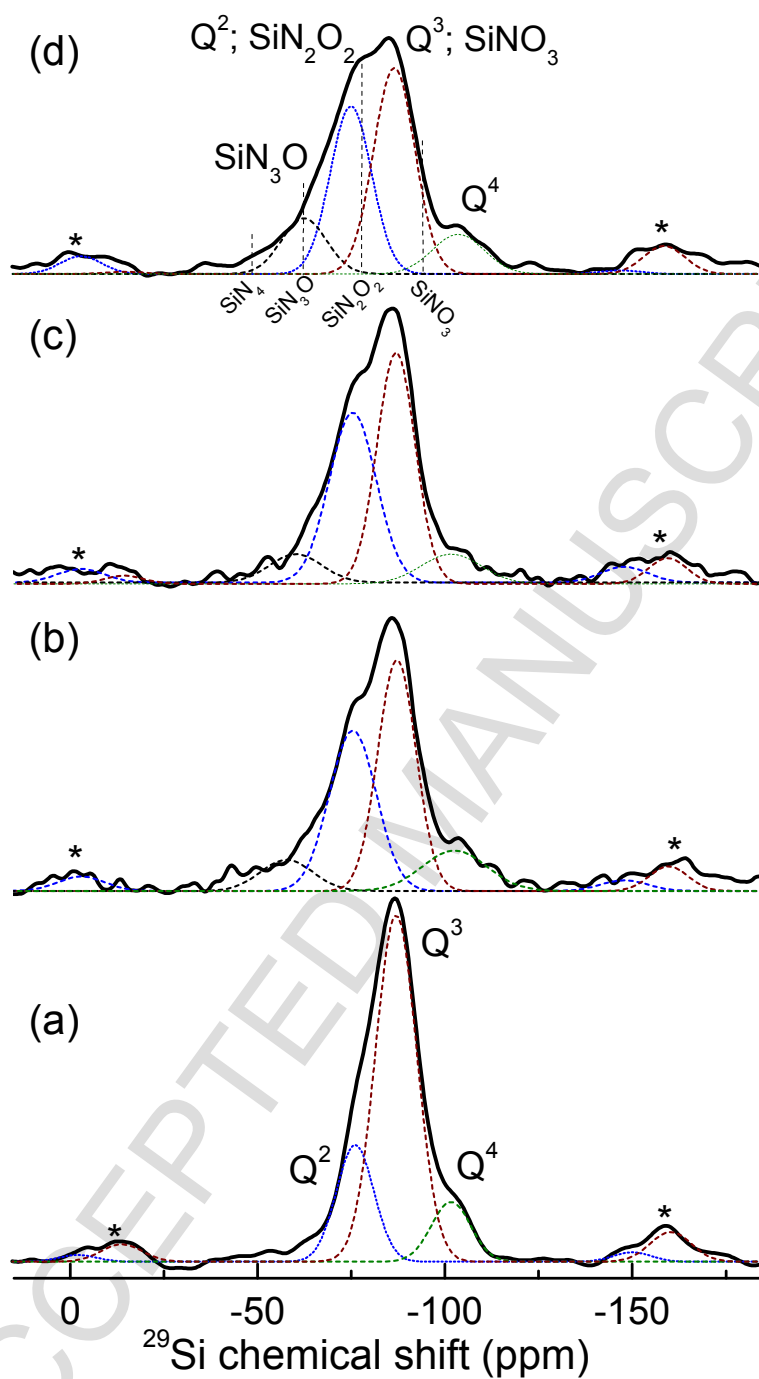


Fig. 3. ^{29}Si NMR spectra of the glass (a) 0, (b) 3, (c) 4.5 and (d) 6 atm % N/N+O. Dotted curves: least-square fitting of Gaussian functions. Vertical lines: typical chemical shift values expected for $\text{SiO}_{4-n}\text{N}_n$ units. Asterisks: spinning side-bands.

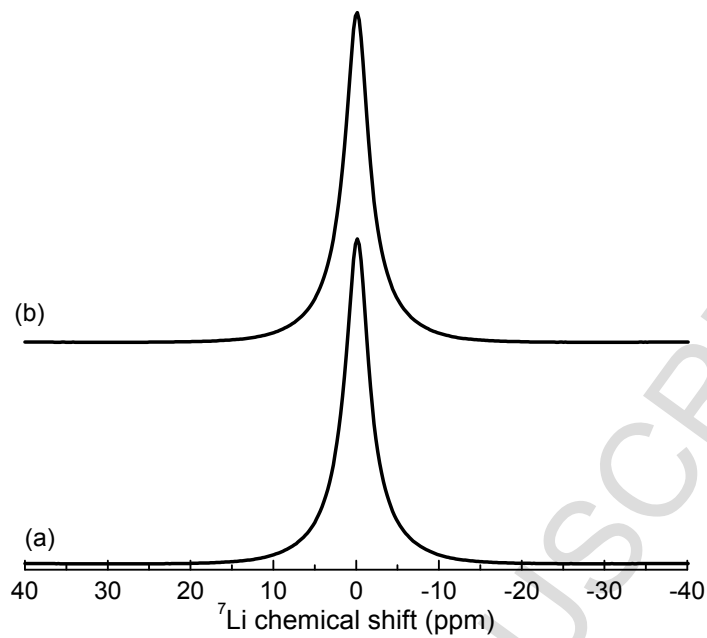


Fig. 4. ^7Li NMR spectra of the glass (a) 0 and (d) 6 atm % N/N+O.

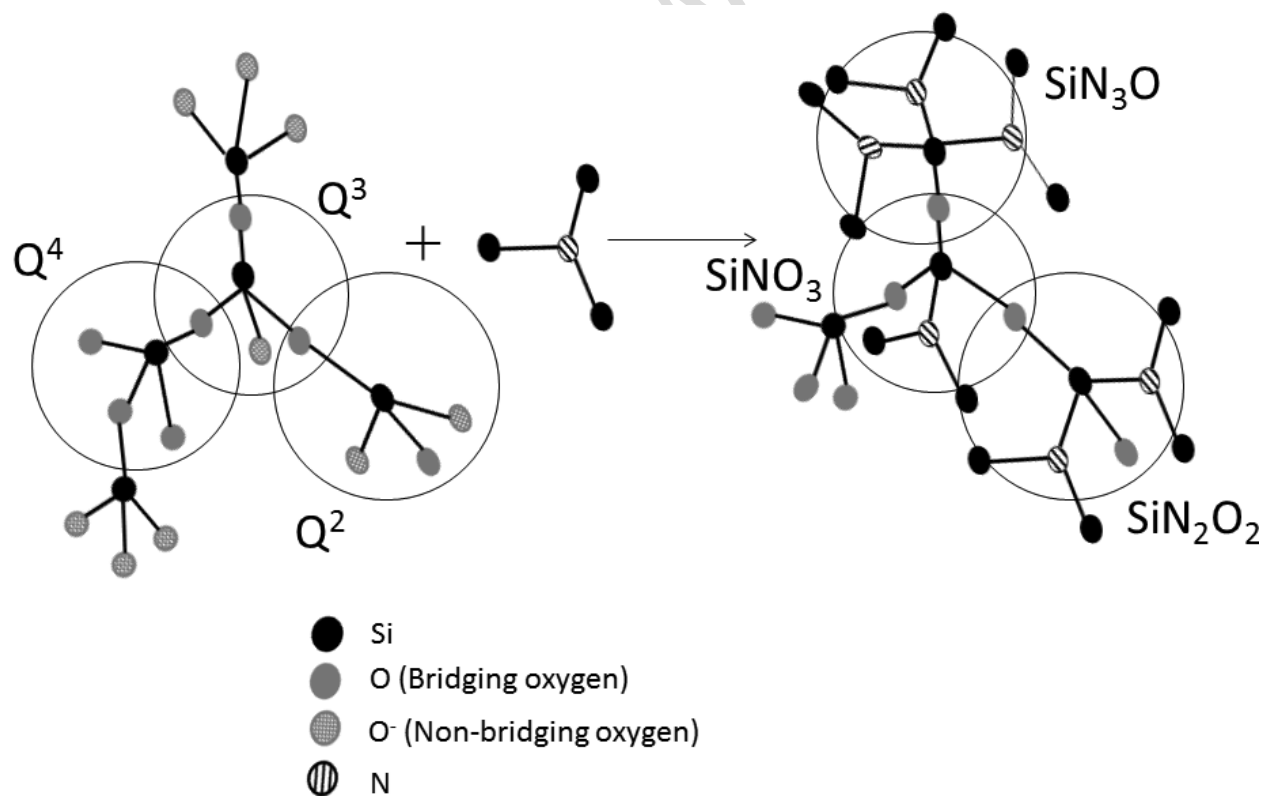


Fig. 5. Schematic representation of the structure of the oxynitride glass.

3.4. Ionic conductivity due to Li^+

Impedance spectroscopy data were collected and plotted in the impedance complex plane, the so-called Nyquist diagram. A single skewed semicircle, which passes through the origin of the complex plane, is found for all samples in the measured temperature range. The intersection at low frequency on the real axis corresponds to the resistance (R), or in the present case, where the geometrical factor has been taken into consideration, to the resistivity (ρ) of the sample. As an example, the Nyquist plots at room temperature are shown in Fig. 6, in which the real (Z') and imaginary (Z'') parts of impedance, were multiplied by S/l (S = area of the sample in contact with the electrode, l = thickness of the sample) to allow comparison between all samples.

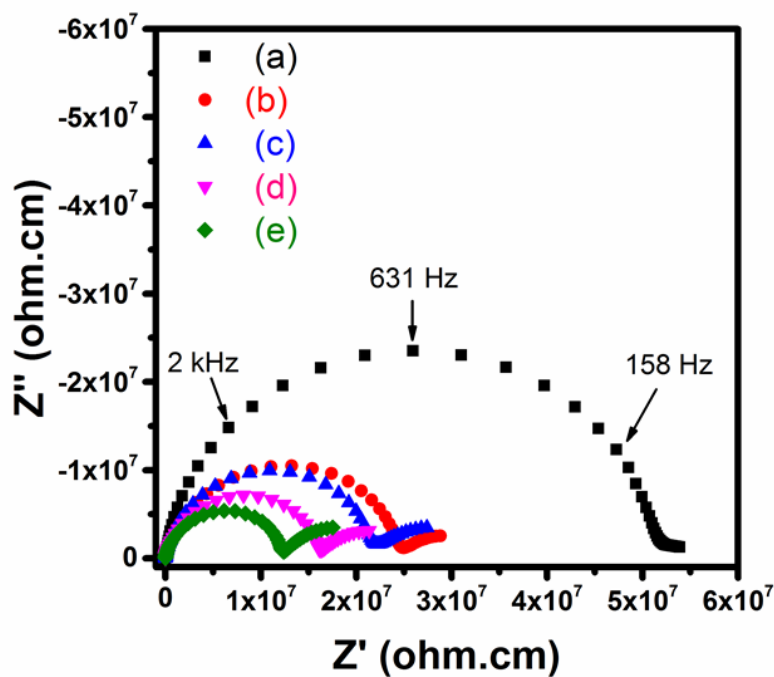


Fig. 6. Nyquist plot for samples containing (a) 0, (b) 1.5, (c) 3.0, (d) 4.5 and (e) 6.0 atm % N/(N+O).

Figure 6 shows that the resistivity (ρ) of the samples decreases with the nitrogen content. Using these plots, the ionic conductivity (σ) was calculated at different temperatures by $\sigma=1/\rho$. The ionic conductivity of glasses normally follows an Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

where σ_0 is a pre-exponential factor, E_a is the activation energy for Li^+ conduction, k is the Boltzmann constant, and T is the absolute temperature. Therefore, the ionic conductivity as a function of inverse temperature is plotted in Fig. 7. The activation energy was calculated from the slope of the linear regression (solid straight line) of the Arrhenius plot. Its evolution with the nitrogen content is shown in Fig. 8 along with the pre-exponential term σ_0 of expression (1)

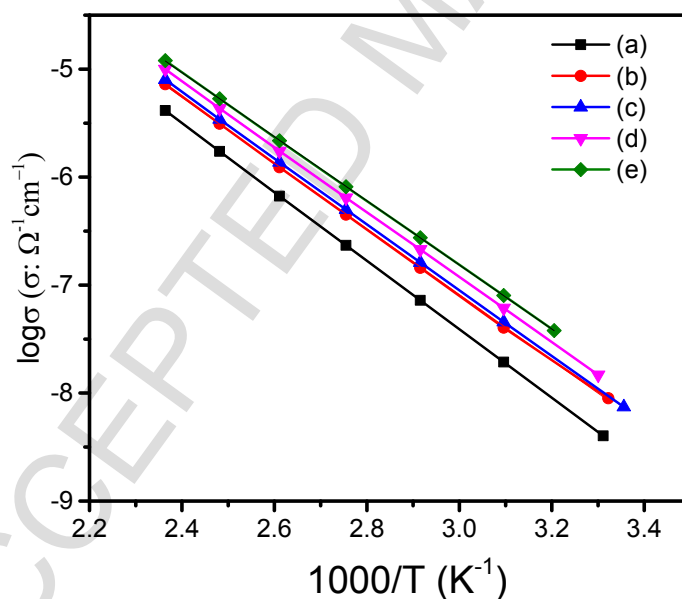


Fig. 7. Arrhenius plots of the oxynitride glasses containing (a) 0, (b) 1.5, (c) 3.0, (d) 4.5 and (e) 6 at % N/(N+O) as a function of inverse temperature.

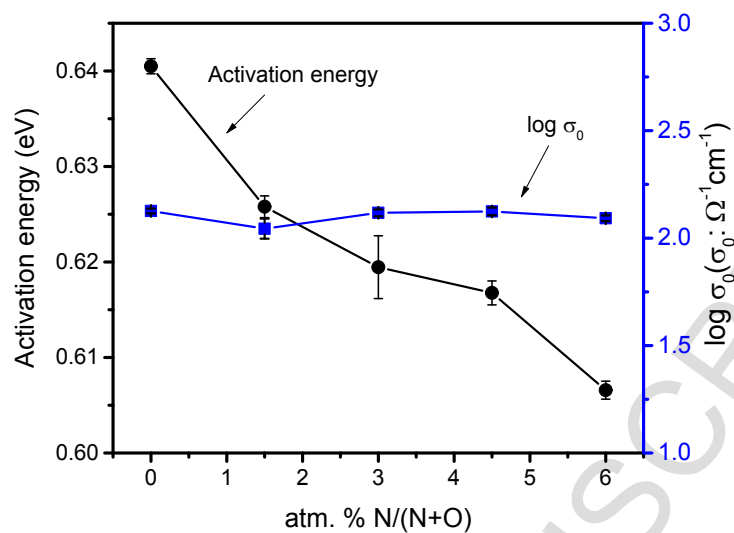


Fig. 8. The activation energy of the oxynitride glasses and the pre-exponential factor (σ_0) of the Arrhenius equation plotted as a function of N/(N+O). The bars indicate the mathematical error from the linear regression.

Figure 8 shows that the logarithm of the pre-exponential factor of the Arrhenius expression σ_0 , remains close to typical values of 2 found [24] and also calculated [25] for lithium ionic conductors. Therefore, the decrease of the activation energy as a function of nitrogen content leads to an increase in ionic conductivity at room temperature as shown in Fig. 9.

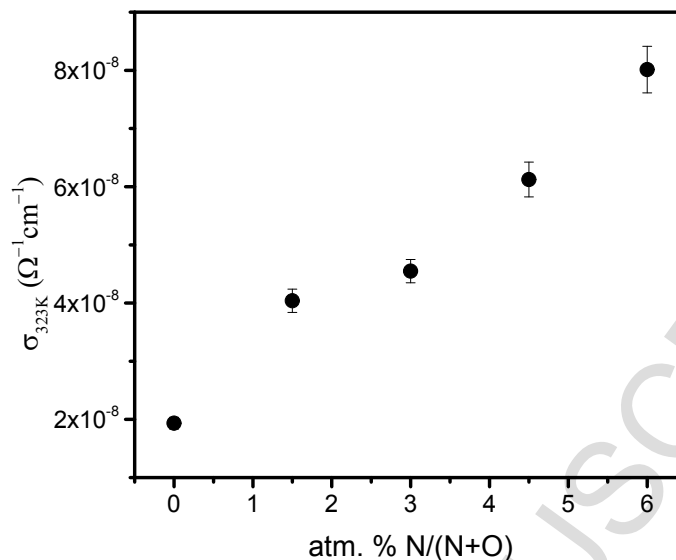


Fig. 9. Li^+ ionic conductivity of the oxynitride glasses at 323K as a function of N/(N+O).

An increase in ionic conductivity and decrease in the activation energy has already been observed in other oxynitride glasses [10, 11] and also in nitrated phosphate glasses [15]. This change in the ionic conductivity may be correlated to the structural changes in the glass matrix detected by FTIR spectroscopy and solid-state NMR techniques. In fact, the introduction of nitrogen changes the Q^n structure to SiO_3N , SiO_2N_2 , SiON_3 , as depicted in the Fig. 5. Moreover, the oxynitride glasses show more structural rigidity than the oxide glasses due to their higher structural connectivity as a result of the introduction of three coordinated nitrogen atoms, in substitution of two-coordinated oxygen atoms.

Munoz *et al.* [15] have studied the influence of the nitrogen content in the electrical conductivity of lithium phosphorus oxynitride glasses. They found that the ionic conductivity increases for low content of nitrogen ($\text{N/P} < 0.15$) and stabilizes for $\text{N/P} > 0.15$. They proposed that the increase in electrical conductivity for low nitrogen contents is due to the increase in the

amount of non-bridging oxygens. Moreover, the increased cross-linking density of the glass network results in the creation of conduction paths with lower activation energy. In case of high nitrogen contents, the increase in the covalent character of Li-O bonds as seen by ^6Li NMR may counteract the lithium mobility giving rise to a quite constant value of electrical conductivity. In another study of ionic conductivity in the glass system of Na-Si-O-N, Unuma *et al.* [26] have shown an increase in the conductivity upon nitridation. They explained this behavior by the fact that the Si-N bond has higher covalency than the Si-O bond. It results that the negatively charged electron cloud of anions may be more highly susceptible to deformation than that of pure oxide glass. Hence, the electrostatic force applied on a sodium ion would be reduced when the glass is nitrated and causes the reduction of the activation energy. The above studies show that it is not simple to infer the mechanism of the ionic conductivity increase in lithium disilicate oxynitride glasses. Therefore, we will use the model developed by Anderson and Stuart [27], which discusses the parameters affecting the activation energy for ionic conduction in a glassy ionic conductor.

According to this model, the activation energy (E_a) for ionic conduction depends on two terms, i.e. the network strain energy (E_s) and the electrostatic binding energy (E_b) as $E_a = E_s + E_b$. The strain energy (E_s) is the energy required to create a doorway for the mobile ion passing through the matrix and can be written as [27]

$$E_s = \frac{\pi}{2} G_o \lambda (r - r_d)^2 \quad (2)$$

where G_o is the (infinite frequency) shear modulus of the matrix, λ is the effective jump distance between the consecutive cation (Li^+) sites, r is the radius of the mobile cation and r_d is the doorway radius available in a certain glass composition. Thus, the strain energy is the energy necessary to enlarge the available doorway in a certain glass composition, in order to allow the

passage of the mobile ion. The value of r and r_d are constant for a given ion (in our case, Li^+) and a given glass composition. Since lithium environment is not changed by the introduction of nitrogen (Fig. 4), it can be concluded that r_d is also not affected by the presence of nitrogen.

Equation (2) demonstrates that the strain energy is directly proportional to the value of G_o . In oxynitride glasses, G_o increases with the increase of nitrogen content [29]. We have measured the values of G_o for all the glasses studied here and found 32.8, 33.1, 35.0, 35.4 and 35.7 GPa for 0, 1.5, 3, 4.5 and 6 at % N/(N+O) respectively. The values of G_o were determined using the pulse-echo technique from time-of-flight measurements conducted at room temperature with an estimated accuracy better than ± 1 GPa. Hence, because of an increase of G_o , the strain energy is gradually increased with the nitrogen content. **In an alternative interpretation, the strain energy (E_s) required to create a doorway for the diffusion of a mobile ion in a glassy matrix is correlated to the bulk modulus of the glass. Papathanassiou *et al.* [30, 31] have pointed out that the bulk modulus measured at infinitely high frequency governs the relaxation process of super-cooled liquids. They suggested that the Gibb's free energy for the diffusion of a species (e.g. Li^+) is proportional to the bulk modulus of the super-cooled liquid. In view of above argument, the strain energy can also be proportional to the bulk modulus of the glass.**

The electrostatic binding energy (E_b) is the energy required to remove a mobile cation from its non-bridging oxygen site and is given by the following relation [27, 28]

$$E_b = \frac{ZZ_0e^2}{\gamma} \left(\frac{1}{r+r_0} - \frac{2}{\lambda} \right) \quad (3)$$

where Z and Z_0 are the charges of the mobile ions and the corresponding counter ion (O^{2-}). r_0 is the ionic radius of the counter ion, oxygen. The covalency parameter, γ , indicates the degree of charge neutralization between the mobile ion and its immediate neighbors and is similar to the high-frequency limit of the dielectric permittivity (ϵ_∞) [27]. Since the introduction of nitrogen

into the glass structure increases the dielectric permittivity [26], E_b decreases with the increase of nitrogen content in the glass matrix.

According to this model, the increased bonding density and network reticulation caused by the formation of the Si-N bonds is the source of an increase of the term related to the network strain energy (E_s). Moreover, replacement of Si-O bonds by the more covalent Si-N causes a decrease in E_b . However, a decrease of activation energy (E_a) is experimentally observed with increasing nitrogen content. This decrease provides evidence that E_b is counteracted over E_s which leads to the effective decrease of E_a . After considering all possible contributions, the overall effect of nitration on ionic conductivity turns out to be positive.

In this study, the ^7Li NMR (Fig. 4) spectra did not show any structural change with nitrogen addition. Hence, we assume that all Li^+ ions are connected to oxygen before and after nitridation. However, with the introduction of nitrogen into the glass structure, the Li-O-Si-O units are substituted by Li-O-Si-N, which affects the Li-O bonds. Moreover, the combination of Si-N-Si bridge formation with silicon atoms in 4-fold coordination favors the delocalization of the negative charge of both oxygen and nitrogen atoms along the Li-O-Si-N of oxynitride structure. This charge delocalization mechanism withdraws negative charges from the coordination sites of Li and, thus, leads to weaker electrostatic interactions between glass network and the Li^+ ions. This situation favors Li^+ ion dissociation from the silicate structure, thus justifying the observed lower activation energy for conduction.

4. Conclusions

We prepared nitrided lithium disilicate glasses containing up to 6 atm % N/(N+O) by partial substitution of oxygen. The introduction of nitrogen in the -Si-N-Si-network was

evidenced by FTIR reflection spectroscopy and ^{29}Si solid-state NMR. A gradual change in the Q^n units of the silicate structure with the progressive substitution of oxygen was observed. The formation of structural units of SiNO_3 , SiN_2O_2 and SiN_3O with the addition of nitrogen is evidenced. Nitrogen provides higher connectivity through three coordinated nitrogen, rather than two coordinated oxygen with silicon. The partial substitution of oxygen in lithium disilicate glass decreases the activation energy of ionic conduction, which leads to an increase in the ionic conductivity. This is due to weaker electrostatic interactions between the lithium and oxygen ions. We believe this report provides insight into understanding the mobility of ions and electrical conductivity concerning modifications in the glass structure.

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Research Highlights

- Nitrided lithium disilicate glasses prepared by partial substitution of O₂ by N₂
- Incorporation of nitrogen decreases the activation energy for the conduction of Li⁺
- Increase in the ionic conductivity up to four-fold for the most nitrided glass
- Higher conductivity explained by the Anderson and Stuart model

