

Ionic blocking effect in partially crystallized lithium disilicate

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A lithium disilicate glass was heat treated at 454 °C, the temperature of maximum nucleation rate, up to 25 days. At this temperature the growth rate is negligible, and therefore these thermal treatments lead to a glassy matrix in which ellipsoidal crystals of about the same size were randomly dispersed. Crystallized volume fraction (α) of up to 20% was reached. Electrical conductivity of glassy, partially crystallized, and 100% crystallized lithium disilicate was then measured by impedance spectroscopy. The crystallized surface layer was eliminated by polishing in order to solely analyze the effect of bulk crystals. The complex plane plots of impedance data showed one or two semicircles depending on (α). The high frequency semicircle represents the vitreous matrix while the low frequency one was ascribed to the blocking effect imposed to the lithium ions by the existing crystals in the partially crystallized samples. This hypothesis was confirmed by the analysis of the relaxation frequency related to each one of the semicircles and by comparison to the relaxation frequency of lithium disilicate glass and crystal. Results show that the blocking effect produces a second semicircle in the impedance diagram starting from a crystallized volume fraction of 15%. © 2006 American Institute of Physics. [DOI: 10.1063/1.2345465]

I. INTRODUCTION

Lithium disilicate— $0.33\text{Li}_2\text{O}-0.66\text{SiO}_2$ or simply L2S—glass is one of the few known stoichiometric glasses which nucleate homogeneously. Its nucleation and growth rates have been measured by more than one author¹⁻⁴ and, therefore, the nucleation and growth rate curves as a function of temperature are already known. This collection of data is helpful to predict heat treatments in order to obtain glass ceramics with different crystallized volume fractions. Partially crystallized lithium disilicate is then composed by a vitreous matrix in which a crystalline phase of the same chemical composition is randomly dispersed.

In the case of lithium disilicate, the electrical conductivity of the glassy phase is more than three orders of magnitude higher than that of the L2S crystal (^{this work},⁵). Thus, partially crystallized lithium disilicate presents interesting electrical properties, particularly when studied by ac impedance spectroscopy, a powerful technique which allows for the separation of electrical phenomena with different time constants. This technique has been widely employed in the investigation of ceramics to separate, for instance, grain and grain boundary effects. It has also been applied to the characterization of ferroelectric single crystals⁶ and ceramics^{7,8} and to monitor surface crystallization in a AgPO_3 glass.⁹ Other applications of impedance spectroscopy include the investigation of amorphous phase separation¹⁰ and glass sintering.¹¹

The effect of devitrification on the ionic diffusion of lithium disilicate glass has already been studied by Kanert et al.,⁵ even though the effect investigated by those authors with *in situ* measurements seems to be mainly due to the surface crystallization. In contrast, this work discusses the

evolution of electrical conductivity in lithium disilicate glass according to the crystalline volume fraction of single-stage heat treated samples. An interpretation of the impedance diagrams is proposed in light of the blocking effect model, developed for zirconia based ceramics.^{12,13} Our assumptions are further supported by an analysis of the relaxation frequencies of both crystalline and glassy phases as well as partially crystallized glasses. The crystalline phase was characterized by x-ray analysis, its morphology was revealed by electron microscopy, while the crystallized volume fraction was determined by optical microscopy.

II. EXPERIMENT

Glass synthesis. Glassy lithium disilicate was synthesized using appropriate amounts of lithium carbonate and silica with 99% or higher purity as starting reagents. The powder was melted in a platinum crucible at 1550 °C for 3 h. The glass was finally quenched in a 14 mm diameter stainless steel mould and then annealed at 390 °C for 24 h to release internal stresses formed on cooling. This heat treatment is necessary since the nonannealed glass is very fragile and could not be cut into the required shape for the electrical measurements.

Heat treatments. 1.5–2.0 mm thick (14 mm diameter) tablets were cut from the initial glass cylinder using a diamond-impregnated saw. These tablets were heat treated at (454 ± 1) °C for different periods of time: 5, 10, 15, 20, and 25 days. This temperature was chosen because it corresponds to that of the maximum nucleation rate.¹⁻⁴ Moreover, at this temperature, the growth rate is negligible, resulting in glass ceramics composed of a large number of same sized crystals randomly dispersed in the glassy matrix.

Characterization. The results of a chemical analysis indicated 19.3 wt. % of Li_2O and 80.0 wt. % of SiO_2 , which

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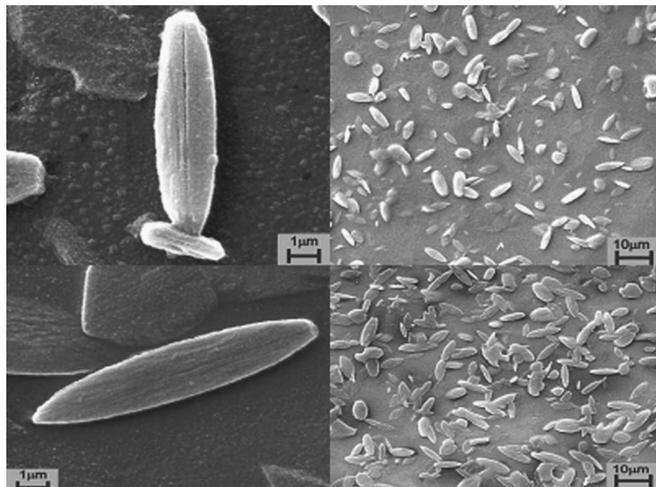


FIG. 1. Electron microscopy of lithium disilicate nucleated at 454 °C for 20 (up) and 25 days (down). Crystallized volume fractions are 15% and 24%, respectively.

corresponds to a molar composition of $0.33\text{Li}_2\text{O}-0.67\text{SiO}_2$. X-ray analysis, not shown here, revealed that the only crystalline phase present in the heat-treated samples was lithium disilicate, which was detected starting from the tenth day of heat treatment at 454 °C. Lithium disilicate glass transition temperature T_g obtained by differential scanning calorimetry (DSC) with a heating rate of 10 °C/min is 453 °C.

Impedance spectroscopy. After being heat treated, the samples' surface crystallization was eliminated by polishing. Gold electrodes were then deposited by sputtering on both parallel faces. Samples with sputtered platinum electrodes were also analyzed. Measurements were taken from 100 to 280 °C, using an HP4192A impedance analyzer with an available frequency range of 5 Hz–13 MHz. Impedance data are presented in a complex plane plot, the so-called Nyquist diagram. In addition to the samples' resistance (R), read at the low frequency intercept of the semicircle with the real axis, this representation allowed us to determine the relaxation frequency at the apex of each semicircle. The impedance data were treated using a software program proposed by Kleitz and Kennedy,¹⁴ which calculates R by the best fit of the semicircle from the minimum square-method; the relaxation frequency (f_0); and the decentralization angle ($\alpha\pi/2$) is calculated using a property proposed by Cole-Cole.¹⁴ The electrical conductivity (σ) was then calculated using the relation $\sigma=l/(SR)$, l/S being the samples' geometrical factor, l is the sample's thickness, and S the electrode area.

III. RESULTS

Images of the crystals in the vitreous matrix were obtained by electron microscopy (Fig. 1) and revealed crystals of about 10 μm with the characteristic ellipsoidal morphology^{4,15} of lithium disilicate nucleated at this temperature. Volume fractions of crystalline phase of 15% and 24% were calculated, in contrast, for samples heat treated at 454 °C for 20 and 25 days, respectively.

Figure 2 shows, as an example, impedance diagrams obtained at temperatures close to 155 °C for the annealed glass

and samples heat treated at 454 °C for different periods of time, as indicated. Impedance data of the annealed glass show, as expected, only one semicircle followed by a spike due to ionic conduction and electrode polarization. However, impedance diagram of samples heat treated at 454 °C for 5 and 10 days shows a valley between the semicircle and the electrode spike, which clearly indicates the presence of an additional phenomenon in this frequency range. This phenomenon evolves to a second semicircle for samples heat treated for 20 and 25 days. The Arrhenius plot of electrical conductivity of the vitreous matrix—or high frequency semicircle (HFSC) of annealed glass and heat treated samples—is shown in Fig. 3. Electrical conductivity of the vitreous matrix is very close to that of the annealed glass, but diminishes with increasing the heat-treatment time, i.e., with the crystallized volume fraction. Nevertheless, the sample heat treated for 10 days presents lower electrical conductivity than samples heat treated for 5 and 15 days. The relaxation frequency, shown in Fig. 4, presents the same trend as the electrical conductivity, including the nonexpected behavior observed for the 10 day heat treated sample. Finally, to confirm that the second or low frequency semicircle (LFSC) is not an artifact, due, for instance, to uncontrolled phenomena at the gold electrodes, platinum electrodes were evaporated in the 25 day heat treated samples. The corresponding impedance data, obtained at 153 °C (Fig. 5), show similar distribution frequency as in the case of the sample measured with gold electrode (Fig. 2). This confirms that LFSC is not dependent on the nature of the electrode and is due only to samples' bulk phenomena.

IV. DISCUSSION

The lithium disilicate electrical conductivity and activation energies in Fig. 3 are consistent with those found by other authors,^{16,17} which confirms that the HFSC is related to the electrical properties of the vitreous matrix. In a similar diagram obtained from AgPO_3 glass, the HFSC was also attributed to the vitreous phase.⁹ Nevertheless, the electrical conductivity of the vitreous matrix, or HFSC, diminishes as the crystallized volume fraction increases, Fig. 3. This effect is attributed to current constriction caused by the ellipsoidal crystals in the glassy phase. Yet not enough to produce a second semicircle until the 15th day of heat treatment, this effect is already detectable by a valley between the HFSC and the electrode spike (Fig. 2). One could argue that this decrease in electrical conductivity could be due to a change in the geometrical factor of glassy phase, as the crystallized volume fraction increases. Although the total volume of crystals is known, we cannot define l and S values for the crystallized or remained glassy phase and therefore, the geometrical factor of both phases are not accessible in partially crystallized samples. Thus, to avoid any misinterpretation due to the geometrical factor, we also determined and plotted the relaxation frequency, which is a material's intrinsic characteristic, independent of samples' geometrical factor.^{18,19}

Figure 4 shows that relaxation frequencies taken from the HFSC, yet diminishes slightly (less than half order of magnitude) as the crystallized volume fraction increases, are

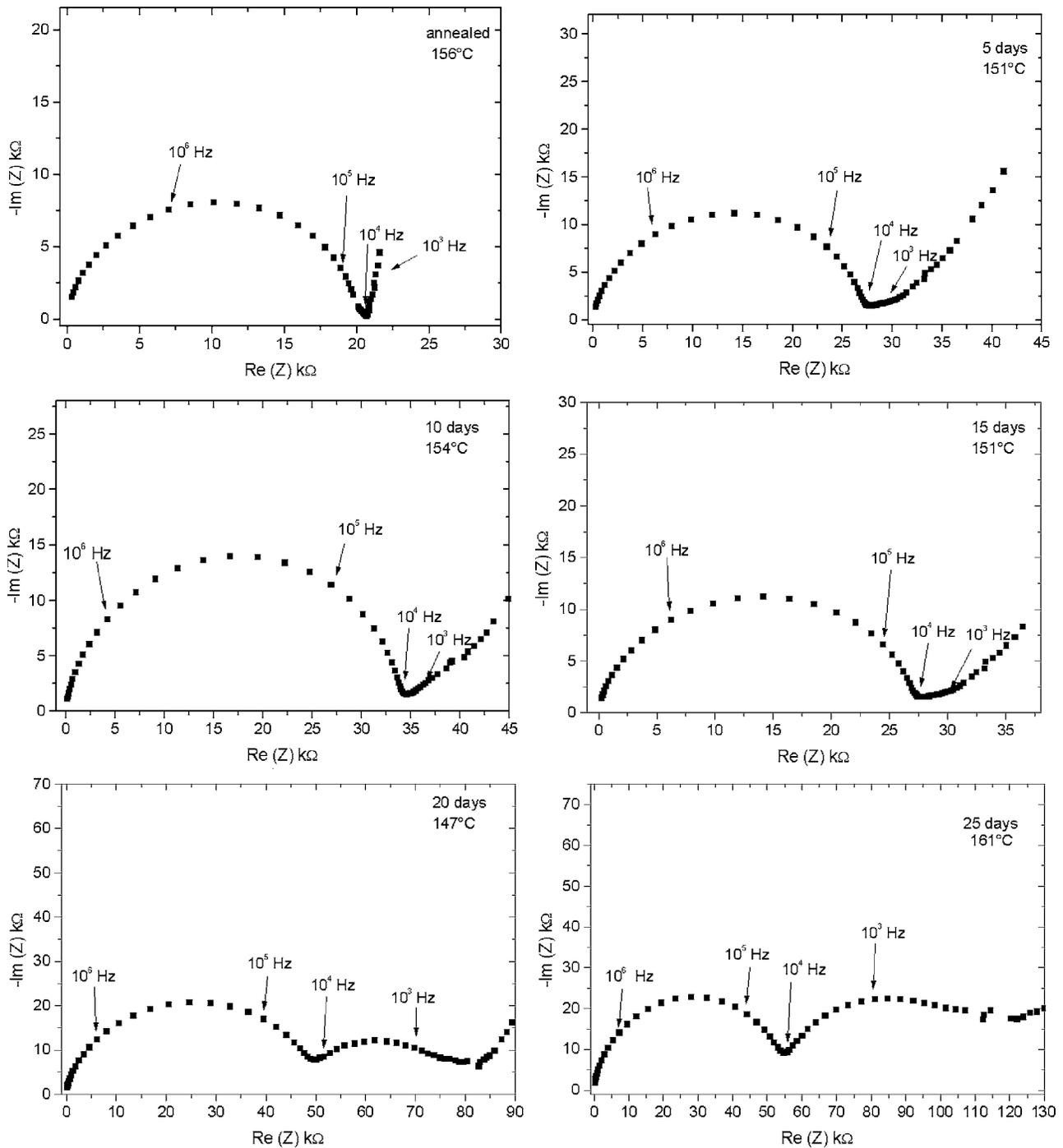


FIG. 2. Complex plane plot of impedance data, for an annealed glass and samples heat treated at 454 °C for indicated periods of time. Temperature inside graphs indicates measurement temperature. Frequency corresponding to some points is also specified. Gold sputtered electrodes were deposited in both samples' faces.

very close to that of annealed sample. This corroborates the assumption that the HFSC describes the vitreous matrix electrical properties. The decrease in vitreous matrix relaxation frequency confirms that the presence of crystals in the vitreous matrix affects its electrical properties even if a second semicircle is not observable. The activation energy found for relaxation frequency is slightly higher than that of electrical conductivity. This was also observed for lithium borosilicate glasses²⁰ and may be attributed to the fact that the semicircles are nonideal, i.e., they present a decentralization angle due to a constant phase element (CPE).

The nonexpected behavior of the 10 day heat-treated sample, whose electrical conductivity and relaxation frequency are lower than those found for the 5 and 15 day heat-treated samples, is ascribed to the orientation of ellipsoidal crystals. According to the micrographs shown in Fig. 1, one might expect that crystals could be less perpendicular to the ac electric field, leading to a less pronounced blocking effect, as seen in Fig. 2. Also, it is sensible that the current constriction effect caused the observed increase in the sample's resistance (and therefore the decrease in electrical conductivity), when compared to the 5 and 15 day heat-treated

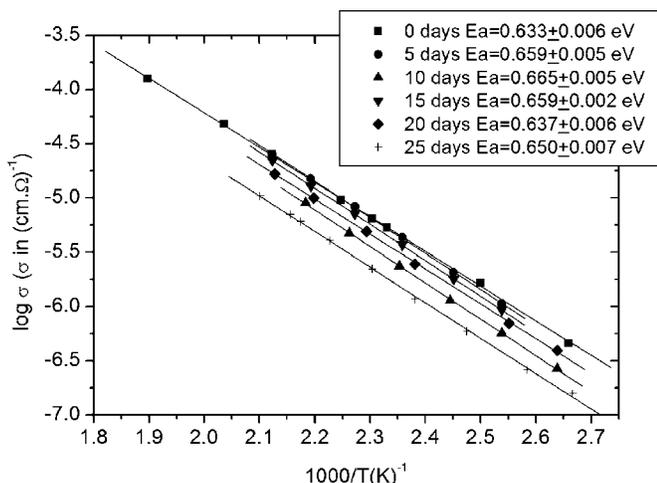


FIG. 3. Arrhenius plot of electrical conductivity (high frequency semicircles or vitreous matrix) for the annealed sample and samples heat treated at 454 °C for different periods of time. Activation energies for conduction (eV) are also presented. All the straight lines have a correlation coefficient higher than 0.999.

samples. Nevertheless, the precise origin of the increase in the vitreous matrix resistance of the 10 day heat-treated sample still remains unclear.

In the case of the complex plane showing two semicircles, the high frequency semicircle is thus unambiguously attributed to the vitreous matrix. We first envisaged ascribing the second semicircle to the lithium disilicate crystals. Therefore, the electrical conductivity (Fig. 6) and relaxation frequency (Fig. 7) of the LFSC were plotted together with data of a completely crystallized lithium disilicate. Values of electrical conductivity and activation energy of completely crystallized lithium disilicate agree with previously published data.²¹ However, it is clearly seen (Figs. 6 and 7) that the second semicircle cannot be ascribed to the lithium disilicate crystals, since neither the electrical conductivity nor the relaxation frequency of this LFSC is compatible with those from lithium disilicate crystals, which shows, besides, a different activation energy of both electrical conductivity and relaxation frequency.

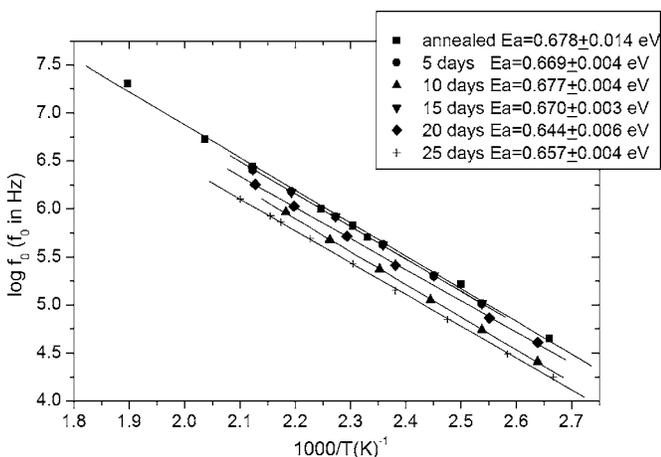


FIG. 4. Arrhenius plot of relaxation frequencies (F_0) (HFSC) for the same samples as those in Fig. 3 (high frequency semicircles). Corresponding activation energies E_a (eV) are also presented.

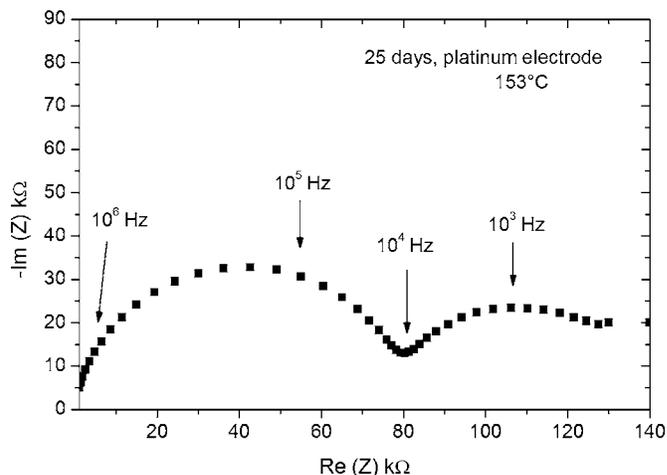


FIG. 5. Complex plane plot of impedance data of sample heat treated at 454 °C for 25 days measured with platinum electrodes. Data were taken at 153 °C. The frequency distribution is very similar to that obtained with the same sample, gold electrodes (Fig. 2).

Accordingly, the low frequency semicircle, which cannot be predicted by the effective medium theory,¹³ clearly appears for samples heat treated for 20 and 25 days and is attributed here to a blocking effect imposed on the lithium ions by the presence of lithium disilicate crystals. This blocking effect has already been described in oxygen-conducting materials such as zirconia.^{12,13} In this ceramic material, the blocking effect on the oxygen ions is caused by grain boundaries or by a second, isolating phase such as alumina or pores introduced into samples. In the case of the present study the blocking effect is due to the constriction of current lines around the “blockers” or lithium crystals. Thus, the presence of the blocking effect is corroborated by the following observations:

- (i) The electrical conductivity of the vitreous matrix decreases as the heat-treatment time increases (Fig. 3). Although the amount of crystalline phase in samples heat treated for less than 20 days is insufficient to

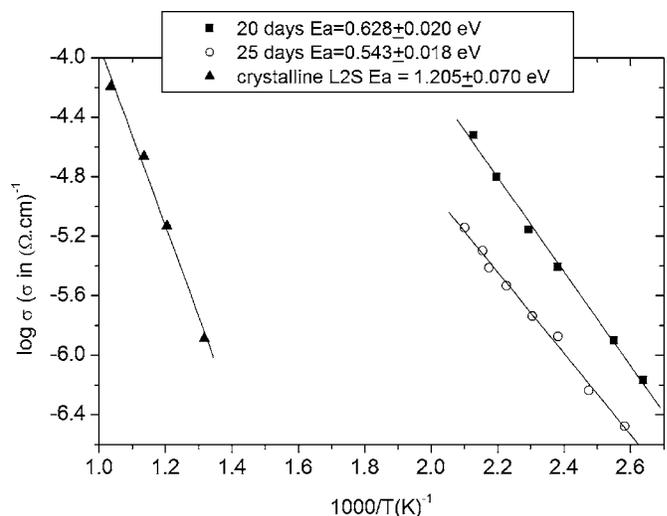


FIG. 6. Arrhenius plot of electrical conductivity of crystalline lithium disilicate and of data from the low frequency semicircle obtained from samples heat treated for 20 and 25 days at 454 °C.

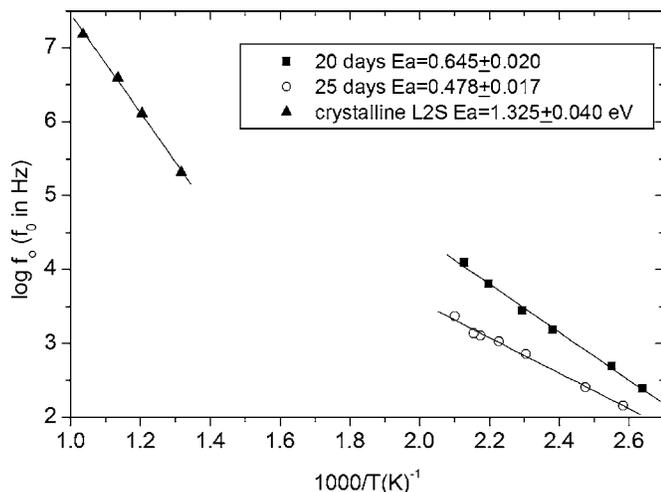


FIG. 7. Arrhenius plot of relaxation frequency of crystalline lithium disilicate and of data from the low frequency semicircle, for same samples as those in Fig. 6.

cause the appearance of a second semicircle (LFSC), the existing crystals in those samples suffice to produce a blocking effect and consequently a current constriction that cause the decrease in the electrical conductivity of the vitreous matrix.

- (ii) The values of electrical conductivity, activation energy (Fig. 5), and relaxation frequency of crystalline lithium disilicate differ greatly from those found for the second semicircle (LFSC), confirming that this LFSC cannot be attributed to the electrical properties of crystalline lithium disilicate.
- (iii) The ratio between electrical conductivities of glassy matrix and crystalline phase is higher than 10^3 , which is a condition for the blocking effect to be present.^{12,13}
- (iv) The activation energy of both HFSC and LFSC for partially crystallized L2S is similar, indicating that both phenomena are provoked by the same ionic species, which is also a statement of the ionic blocking model.

V. CONCLUSION

When heat treated at 454 °C, lithium disilicate, in its vitreous matrix, shows randomly dispersed crystals with an electrical conductivity at least 10^3 times lower than the

glassy phase. These crystals produce an ion-blocking effect in the vitreous matrix, which is confirmed by a reduction in the electrical conductivity of the vitreous matrix when the crystallized volume fraction is increased, as a consequence of longer heat-treatment times. This blocking effect is more noticeable when a second semicircle at low frequencies appears in the impedance diagram, starting from the 20th day of heat treatment, or 15% of crystallized volume fraction. In the case of glass ceramics where the geometrical parameter of each phase is undefined, the analysis of relaxation frequency instead of electrical conductivity proved a helpful and accurate tool to avoid misinterpretation of the results.

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- ¹P. F. James, *Phys. Chem. Glasses* **15**, 95 (1974).
- ²E. G. Rowlands and P. F. James, *Phys. Chem. Glasses* **20**, 1 (1979).
- ³J. Deubener, R. Brückner, and M. Steritzke, *J. Non-Cryst. Solids* **163**, 1 (1993).
- ⁴E. D. Zanotto and M. L. G. Leite, *J. Non-Cryst. Solids* **202**, 145 (1996).
- ⁵O. Kanert, R. Küchler, D. Suter, G. N. Shannon, and H. Jain, *J. Non-Cryst. Solids* **274**, 202 (2000).
- ⁶D. C. Sinclair and A. R. West, *Phys. Rev. B* **39**, 13486 (1989).
- ⁷D. C. Sinclair and A. R. West, *J. Appl. Phys.* **66**, 3850 (1989).
- ⁸N. Hirose and A. R. West, *J. Am. Ceram. Soc.* **79**, 1633 (1996).
- ⁹Y. Grincourt, D. Coppo, J. L. Souquet, and M. Duclot, *Phys. Chem. Glasses* **36**, 123 (1995).
- ¹⁰M. O. Prado, A. A. Campos Jr., P. C. Soares Jr., A. C. M. Rodrigues, and E. D. Zanotto, *J. Non-Cryst. Solids* **332**, 166 (2003).
- ¹¹R. Mucillo, E. N. S. Mucillo, Y. V. França, C. Fredericci, M. O. Prado, and E. D. Zanotto, *Mater. Sci. Eng., A* **352**, 232 (2003).
- ¹²M. Kleitz, L. Dessemmond, and M. C. Steil, *Solid State Ionics* **75**, 107 (1995).
- ¹³M. Kleitz and M. C. Steil, *J. Eur. Ceram. Soc.* **17**, 819 (1997).
- ¹⁴M. Kleitz and J. H. Kennedy, in *Fast Ion Transport in Solids*, edited by P. Vashista, J. N. Mundy, and G. K. Shenoy (Elsevier, New York, North-Holland, Amsterdam, 1979), pp. 185–188.
- ¹⁵L. L. Burgner, M. C. Weinberg, P. Lucas, P. C. Soares Jr., and E. D. Zanotto, *J. Non-Cryst. Solids* **255**, 264 (1999).
- ¹⁶L. L. Hench, S. W. Frieman, and D. L. Kinser, *Phys. Chem. Glasses* **12**, 58 (1971).
- ¹⁷A. Kone, M. Ribes, and J. L. Souquet, *Phys. Chem. Glasses* **23**, 18 (1982).
- ¹⁸*Impedance Spectroscopy*, edited by J. R. MacDonald (Wiley, New York, 1987), pp. 13–14.
- ¹⁹S. Lanfredi and A. C. M. Rodrigues, *J. Appl. Phys.* **86**, 2215 (1999).
- ²⁰L. F. Maia and A. C. M. Rodrigues, *Solid State Ionics* **168**, 87 (2004).
- ²¹I. D. Raistrick, C. Ho, and R. A. Huggins, *J. Electrochem. Soc.* **123**, 1469 (1976).