

## Effect of Crystallization on the Electrical Conductivity of Lithium Disilicate Glasses

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### I. Introduction.

Lithium disilicate (LS2) glass is one of the few known stoichiometric glasses presenting homogeneous nucleation. Its nucleation and growth rates have been measured by more than one author [1-4] and, therefore, the nucleation and growth curve as a function of temperature is 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 a material containing a crystalline phase randomly dispersed in a vitreous matrix. Lithium disilicate is defined as a "stoichiometric" glass since both the crystalline and glassy phases present the same chemical composition. In the case of lithium disilicate, the electrical conductivity of the glassy phase is three orders of magnitude higher than that of the LS2 crystal [5 and this work]. Thus, partially crystallized lithium disilicate is a material possessing interesting electrical properties, particularly when studied by a.c. impedance spectroscopy. This technique, which allows for the separation of electrical phenomena with different time constants, has been widely employed in the study of ceramics to separate, for instance, grain and grain boundary effects. Applying this technique to the investigation of oxygen conductivity in zirconia, Kleitz and co-authors [6-7] proposed the blocking effect model to explain the role of grain boundaries in such ceramics.

The effect of devitrification on the ionic diffusion of lithium disilicate glass has already been studied [5], while impedance spectroscopy has been applied to monitor surface crystallization in an  $\text{AgPO}_3$  glass [8]. This work discusses the evolution of electrical conductivity in lithium disilicate glass according to the duration of single-stage heat treatment, as well as an interpretation of the impedance diagrams obtained in light of the blocking effect model. Our assumptions are further supported by an analysis of the relaxation frequency. The crystalline phase is characterized by X-ray analysis and its morphology is investigated by electron microscopy. The crystalline volume fraction of a heat-treated sample is also determined.

### II. Experimental.

- a) 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 hours. The glass was finally quenched in an 14 mm diameter stainless steel mould and then annealed at 390°C for 24 hours.
- b) Heat treatments: 1.5 to 2.0 mm thick (14 mm diameter) tablets were cut from the initial glass cylinder. These tablets were heat-treated at 454°C  $\pm$  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, the growth rate is very low at this temperature, resulting in glass-ceramics composed of a large number of small crystals randomly dispersed in the glassy matrix.

c) Characterization: The results of a chemical analysis indicated 19.3 weight % of  $\text{Li}_2\text{O}$  and 80.0 weight % of  $\text{SiO}_2$ , which corresponds to a molar composition of 0.33  $\text{Li}_2\text{O}$  0.67  $\text{SiO}_2$ .

An X-Ray analysis revealed that the only crystalline phase present in the heat-treated samples was lithium disilicate, which was detected starting from the 10<sup>th</sup> day of heat treatment at 454°C.

Images of the crystals in the vitreous matrix were obtained by electron microscopy (Fig. 1) and revealed crystals in an ellipsoidal morphology, which is a characteristic of lithium disilicate nucleated at this temperature [4,10]. Volume fractions of crystalline phase of 15% and 24% were calculated, by contrast, for samples heat-treated for 20 and 25 days, respectively.

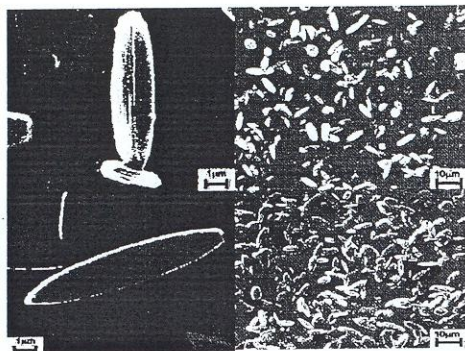


Figure1. Electron microscopy of lithium disilicate nucleated at 454 °C for different periods of time.

d) 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. Measurements were taken from 100 to 280°C, using an HP4192A impedance analyzer with an available frequency range of 5Hz-13Mhz. Impedance data are presented in the so-called Nyquist diagram – the opposite of the imaginary part of Z at the y axis and the real part of Z at the x axis. In addition to the samples' resistance, this representation allowed us to determine the relaxation frequency at the apex of each semi-circle. The impedance data were treated using a software program proposed by Kleitz and Kennedy [9], which calculates the best fit to the semi-circle by the minimum square-method, as well as the relaxation frequency ( $f_0$ ) using a property proposed by Cole-Cole [9], in addition to the decentralization angle ( $\alpha\pi/2$ ).

### III. Results

Figure 2 shows, as an example, impedance diagrams obtained at a temperature close to 155°C for the annealed glass and samples heat-treated during the different periods of time. A second semi-circle is observed starting from the 20<sup>th</sup> day of heat treatment.

In the case of the Nyquist diagram showing two semi-circles, the high frequency semi-circle is attributed to the vitreous matrix and the second semi-circle is attributed to the ionic blocking effect due to the dispersed crystalline phase. The corresponding resistance ( $R$ ) values and the relaxation frequencies ( $f_0$ ) were extracted from the impedance diagrams. The electrical conductivity ( $\sigma$ ), calculated from the samples' resistance ( $\sigma = 1/R \cdot l/S$ ,  $l$  is the thickness and  $S$  the electrode area  $l/S$  being the geometric factor), and the relaxation frequencies are presented in an Arrhenius plot (Figs. 3 to 6). In the case of diagrams presenting two semi-circles, the conductivity and relaxation frequency relating to each of the semicircles are presented separately. For the sake of comparison, the electrical conductivity and relaxation frequencies of crystalline lithium disilicate is also shown in Figure 5 and 6, respectively.

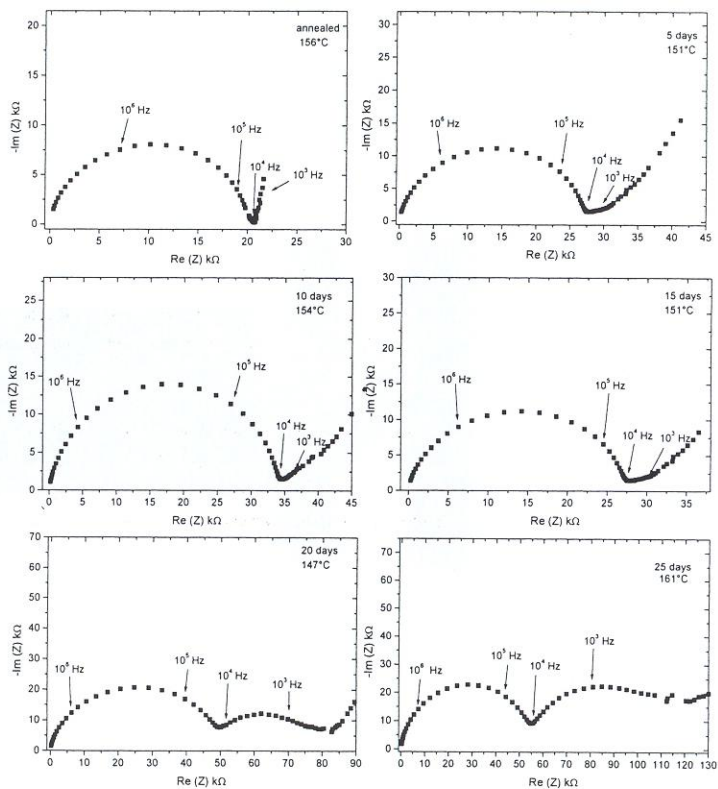


Figure 2. Nyquist diagram for samples heat-treated at 454°C for different periods of time and for a crystalline lithium disilicate sample.

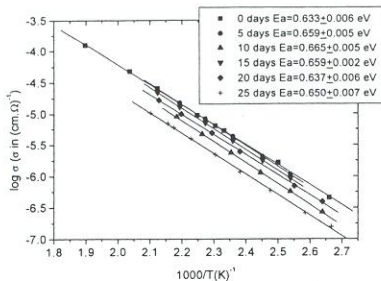


Figure 4. Arrhenius plot of relaxation frequencies for the same samples as those in Fig 3 (high frequency semi-circles). Corresponding activation energies (eV) are also presented.

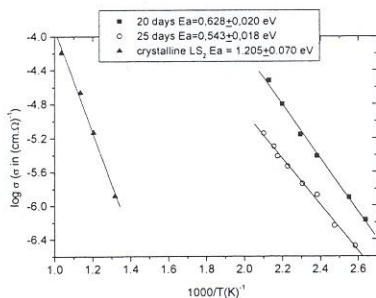


Figure 3. Arrhenius plot of electrical conductivity (high frequency semi-circles or vitreous matrix) for the annealed sample and samples heat-treated at 454°C for different periods of time. Activation energies for conduction (eV) are also presented. All the straight lines have a correlation coefficient higher than 0,999.

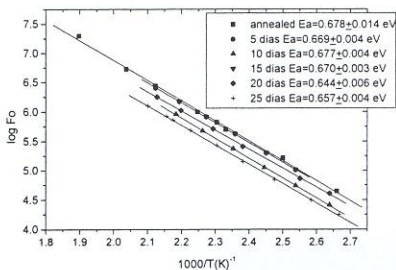
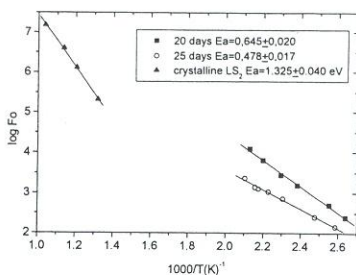


Figure 5. Electrical conductivity – data of the low frequency semi-circle obtained from samples heat-treated for 20 and 25 days at 454°C and of crystalline lithium disilicate.

Figure 6. Arrhenius plot of relaxation frequency – Data of the low frequency semi-circle for the same samples as those in Fig 5.



#### IV. Discussion

Figure 2 shows that a second semicircle in the impedance diagrams appears for samples heat-treated for 20 and 25 days at 454°C. In this case, the high frequency semicircle (HFSC) is indisputably due to the vitreous matrix.

This hypothesis is confirmed when the relaxation frequency (independent of the geometrical factor [11,12]) of HFSC obtained from heat-treated samples is compared with the relaxation frequency of the annealed glass (Fig. 4). It can be seen that, while the relaxation frequency values show a tendency to decrease with increasing periods of heat treatment, these values remain close to the relaxation frequency of the annealed glass, which is characteristic of the glassy phase, with no influence from crystals. The activation energies for electrical conduction (Fig. 3) are consistent with those found by other authors [13,14] for lithium disilicate glass. These observations confirm that the HFSC is related to the electrical properties of the vitreous matrix. In a similar diagram obtained from AgPO<sub>3</sub> glass, the HFSC was also attributed to the vitreous phase [8].

The low frequency semi-circle (LFSC), which clearly appears for samples heat-treated for 20 and 25 days, 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 [6,7]. 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 this study, 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 cause the appearance of a second semicircle (LFSC), the small number of existing crystals in those samples suffices to produce a blocking effect and to cause the electrical conductivity in the vitreous matrix to decrease.
- 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 semi-circle (LFSC),

