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# Monitoring crystallization in lithium silicate glass-ceramics using $^{7}Li \rightarrow {}^{29}Si$ cross-polarization NMR

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ABSTRACT

Quantification of the crystalline versus amorphous fraction is an important objective for the structural characterization of glass-ceramics. Owing to its well-documented ability of differentiating between crystalline and amorphous materials and its inherently quantitative character, magic-angle-spinning solid state nuclear magnetic resonance (MAS-NMR) spectroscopy is an excellent method for this objective. For the technologically important lithium disilicate glass-ceramics, the applicability of $^{29}Si$ MAS-NMR is, however, seriously impeded by poor signal to noise ratios and extremely long spin–lattice relaxation times (on the order of magnitude of hours). The detection sensitivity problem can be overcome by magnetization transfer from $^{7}Li$ nuclei to the $^{29}Si$ spins ($^{7}Li \rightarrow {}^{29}Si$ cross-polarization). While this method is inherently non-quantitative owing to the influence of various relaxation processes involved, we show that it can be successfully calibrated to yield quantitatively reliable crystalline fractions that are similar to those determined by alternative methods (optical microscopy and X-ray powder diffraction). In addition, this method can be used to detect very low (~1%) crystallized volume fractions.

## 1. Introduction

Owing to their relatively high fracture toughness (2.0–2.7 MPa × $m^{1/2}$) and flexural strength (350–400 MPa), good chemical durability and low mass density, lithium disilicate glass-ceramics are among the top choices for transparent armor applications and restorative dentistry [1–5]. Their technological value arises from all the above positive combinations of properties plus the possibility of being prepared in opaque, translucent or transparent form, their easy formability into complex shapes and their moderate cost. The large aspect ratios of lithium disilicate crystals grown within the glassy matrix produce a microstructure ideal for crack deflection and toughening. Dental restorations fabricated with lithium disilicate based glass-ceramics currently represent a multimillion Euro market.

The development of new or improved lithium disilicate glass-ceramics requires a solid understanding of their mechanisms of crystallization, the rates of crystal nucleation and growth involved, and their impact on the nano- and microstructural organization. While X-ray diffraction methods remain the standard-bearer experimental tool for phase identification and structural characterization of well-ordered materials with high crystallinity, they are less well-suited for studying the *early nucleation* stages. Here modern magnetic resonance techniques offer powerful element-selective, inherently quantitative insights into structure and dynamics at the atomic scale [6]. For example, high-resolution $^{6/7}Li$ and $^{29}Si$ NMR have been widely applied for monitoring the formation of lithium disilicate-based glass ceramics [7–21]. While most of the results obtained indicate that stoichiometric disilicate glass transforms directly into the crystalline compound, there have been also some reports of metastable $Li_2Si_2O_5$ (and lithium metasilicate) precursor phases [9,12]. Furthermore, off-stoichiometric and/or $P_2O_5$-containing glasses – used in commercial glass-ceramics – result in the additional formation of crystalline phases of lithium metasilicate, lithium phosphate and quartz, accompanied by compositional changes in the residual glass matrix [7,15,20,21]. An accurate quantification of the crystalline content of lithium silicate glass-ceramics is severely hampered, however, by the low natural abundance of the $^{29}Si$ isotope and its relatively small gyromagnetic ratio ($\gamma = -5.319 \times 10^{6}\ T^{-1}\ rad\ s^{-1}$), resulting in low detection sensitivity. This problem is severely compounded by extremely long $^{29}Si$ spin–lattice relaxation times [8,21] – both for the glassy and the crystalline component – necessitating signal accumulation times on the order of one week per sample for building up sufficient signal to noise ratios suitable for quantitative analyses.

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In principle, significant gains in signal-to-noise ratio (and hence reduction in overall measurement time) may be achieved by means of cross-polarization (CP) methods, where the large magnetization of highly abundant nuclei with large magnetic moments is channeled to weakly abundant and/or low-gamma nuclei, and the signal is acquired under conditions of MAS (e.g. CPMAS-NMR) [22]. While the overwhelming majority of such applications involve magnetization transfer from $^1$H to $^{13}$C nuclei, we have recently reported analogous $^7$Li → $^{29}$Si cross-polarization experiments, resulting in significant signal-to-noise gains and spectral editing opportunities in the spectroscopy of various crystalline binary lithium silicides [23,24]. Part of the signal-to-noise benefit arises from the fact that in $^7$Li → $^{29}$Si cross-polarization the recycle delay used for signal accumulation depends on the spin–lattice relaxation time of the magnetization source nuclei (here $^7$Li), which in general relax much faster than the $^{29}$Si nuclei. On the other hand a serious drawback of cross-polarization methods is their generally non-quantitative character. Signal amplitudes generated by cross-polarization are affected by the influence of various superimposed relaxation processes involving the two spin systems and their surroundings, making it difficult to relate signal intensities to spin populations [25]. This complication is particularly serious for spin systems containing quadrupolar nuclei such as $^7$Li, where population transfers among the different Zeeman levels during the MAS rotor period can interfere with spin locking [26–29].

In this contribution, we have addressed this challenge, developing a reliable $^7$Li → $^{29}$Si cross-polarization procedure for measuring crystallized volume fractions in lithium disilicate glass-ceramics. We validate our procedure by comparison with more established methods (optical microscopy and X-ray powder diffraction analyses) and discuss the advantages and limitations of the various methods to be used.

## 2. Fundamental concepts and methodology

Fig. 1 shows the pulse sequence used for the $^7$Li → $^{29}$Si CPMAS experiments in the present study. First, transverse $^7$Li magnetization is prepared by a 90° pulse, which is subsequently fixed in the rotating frame by applying a 90° phase-shifted $B_1$ field. In this “spin locked” state, the $^7$Li nuclei precess with their nutation frequency around the direction of the applied $B_1$ field perpendicular to the direction of the external magnetic field. During the “contact time” period $t_c$ the $^7$Li and $^{29}$Si spins are simultaneously irradiated at their respective resonance frequencies. The radio frequency irradiation amplitudes $B_1$ of both spin species are chosen such that their respective precession frequencies in the doubly rotating frame are matched, following the Hartmann–Hahn condition [30], modulated by magic-angle spinning as given by [29]

$$\omega_1\left({}^{29}\mathrm{Si}\right) = \omega_1\left({}^{7}\mathrm{Li}\right) \pm n\omega_r \tag{1}$$

where $\omega_1(^{29}\mathrm{Si})$ and $\omega_1(^7\mathrm{Li})$ are the effective nutation angular frequencies of $^{29}$Si and $^7$Li and $\omega_r$ is the angular rotor frequency. For spin-1/2 nuclei such as $^{29}$Si $\omega_1$ is given by the product of $\gamma(^{29}\mathrm{Si}) \times B_1(^{29}\mathrm{Si})$ where $\gamma(^{29}\mathrm{Si})$ is the gyromagnetic ratio of the $^{29}$Si recipient nuclei. In the case of the quadrupolar $^7$Li nuclei, the analogous situation $\omega_1(^7\mathrm{Li}) = \gamma(^7\mathrm{Li}) \times B_1(^7\mathrm{Li})$ holds only true if it is large compared to the quadrupolar angular frequency $\omega_Q(^7\mathrm{Li}) = 3C_Q / 2I(2I - 1)$, where $C_Q$ and I are the $^7$Li quadrupolar coupling constant and the spin quantum number (3/2), respectively. This situation corresponds to the non-selective excitation of all 2I Zeeman transitions. In the opposite extreme case, which corresponds to the selective excitation of the $m = 1/2 \leftrightarrow m = -1/2$ Zeeman transition, the effective nutation frequency is equal to $\omega_1 = (I + 1/2)\gamma B_1$. In the case of $^7$Li, for which typical $C_Q$ values are measured on the order of ~100 kHz, neither of these extremes is realized. As a result, an orientational distribution of nutation frequencies is observed, whose average adopts an intermediate value between the above extreme cases. As these distributions of nutation frequencies result in distributions of Hartmann–Hahn matching conditions, which are additionally modulated further by MAS according to Eq. (1), it is advantageous to subject the amplitude of the $^7$Li spin-lock field to a linear ramping function [31]. With the $^{29}$Si and $^7$Li nuclei precessing with equal frequencies in the doubly rotating frame during the contact time period, magnetization transfer occurs via the $^7$Li–$^{29}$Si magnetic dipole–dipole interaction between proximal nuclei, resulting in a significant boost of the $^{29}$Si detection sensitivity. As discussed for the more common case of $^1$H → $^{13}$C CPMAS the optimal value chosen for the contact time, $t_c$, depends on the interplay of three competing rate constants (see Fig. 1) [25]: the cross-relaxation rate $T_c^{-1}$ governing the magnetization transfer between the two spin systems, (2) the rotating frame spin–lattice relaxation rate of the source nuclei, $T_{1\rho}^{-1}(^7\mathrm{Li})$, describing the dispersal of their spin-locked magnetization, and (3) the rotating-frame spin lattice relaxation rate of the recipient nuclei, $T_{1\rho}(^{29}\mathrm{Si})$, describing the analogous process for the $^{29}$Si magnetization created by $^7$Li → $^{29}$Si cross-relaxation during the contact time. While the first process favors increasing $^{29}$Si magnetization buildup with increasing contact time, the latter two processes lead to signal diminution with increasing $t_c$. As a result, an optimum contact time exists, for which

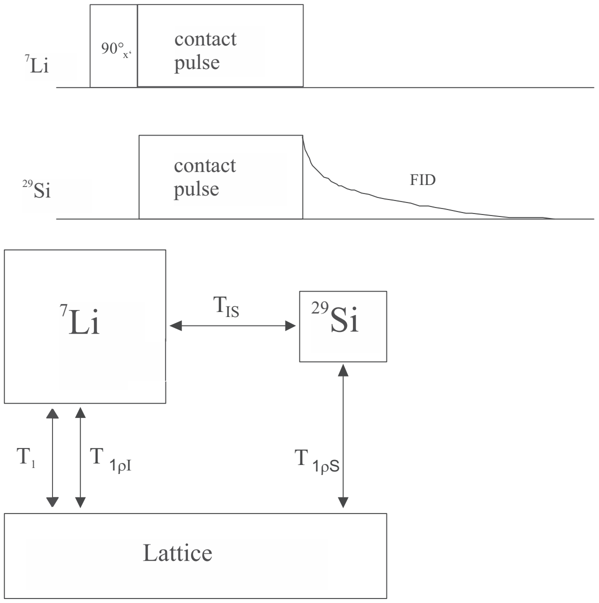

**Fig. 1.** Pulse sequence of the cross-polarization experiment and scheme illustrating the relaxation processes involved.

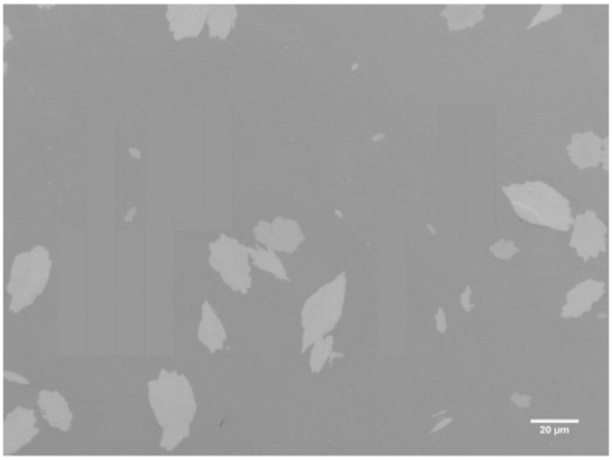

**Fig. 2.** Optical micrograph of a lithium disilicate glass-ceramic obtained by annealing glassy lithium disilicate for 90 h at 500 °C.