# Li diffusion in $\beta$ -eucryptite studied by high-temperature static <sup>6</sup>Li NMR

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### Abstract

The relaxation processes of <sup>6</sup>Li in polycrystalline  $\beta$ -eucryptite were studied by hightemperature static NMR from room temperature up to 973K. The spectra revealed three diffusion processes, which were attributed to the motion of three distinct crystallographic Li in the structural channels. In the temperature range up to 973K there is no evidence for cross-channel motion of Li ions.

# 1 Introduction

Beta-eucryptite (LiAlSiO<sub>4</sub>) is a subject of continuing interest, because of its onedimensional superionic conductivity due to lithium ion transport in the structural channels [6]. It also exhibits near-zero overall thermal expansion [4, 5, 10]. The symmetry and extinction of the main reflections in single crystal X-ray patterns indicates that at ambient temperatures  $\beta$ -eucryptite has the high-quartz space group  $P6_422$  or  $P6_222$  [14, 15].

The Larmor frequency of the spin I=1 nucleus <sup>6</sup>Li is about 2.6 times smaller than <sup>7</sup>Li and it has much lower natural abundance (7.5%). <sup>6</sup>Li has also a lower quadrupole moment. Because of its smaller quadrupolar interaction, the <sup>6</sup>Li shift may more closely approximate the isotropic chemical shift and provide a better measure of the Li bonding environment. In aqueous solution, the Li chemical shift is almost constant regardless of concentration, presumably because of tight Li-H<sub>2</sub>O bonding and shielding of Li<sup>+</sup> ions by water molecules.

Boyce et al. (1979) examined both the ionic conductivity and the line narrowing in  $\beta$ -eucryptite applying a one-dimensional theory and using <sup>7</sup>Li NMR data. They calculated an activation energy of 0.42 eV for Li motion along the channels in betaeucryptite. However, there was no mention of cross-channel diffusion, which it is assumed has not been observed.

In 1981, Brinkmann et al. studied relaxation rates of <sup>6</sup>Li and <sup>7</sup>Li in single crystals of  $\beta$ -eucryptite at temperatures up to 760K [2]. These authors showed that two diffusion processes occur: diffusion along the structural channels and hopping of Li ions between different channels. They have calculated activation energies of 0.1 eV for the processes dominant from 125K to 400K and 0.6eV for the processes dominant from 400K to 760K. In a continuation of this work, the same authors studied relaxation of <sup>7</sup>Li by paramagnetic impurities in  $\beta$ -eucryptite in Schweickert et al. (1983) [11]. They have proposed a model explaining the influence of paramagnetic impurities on the T<sub>1</sub> relaxation time. The 1-D cooperative motion of Li ions along the structural channels was discussed once again.

In 1983, Renker et al. studied Li ionic diffusion by quasi-elastic neutron experiments [8]. They showed that ionic diffusion mainly happens along the crystallographic channels parallel to [001] and confirmed a jump-distance of c/3.

Xu and Stebbins, in 1995, studied the correlation between <sup>6</sup>Li NMR chemical shifts and coordination number [16]. They quoted a chemical shift of 0.2 ppm for <sup>6</sup>Li in eucryptite.

The aim of this work was to study Li ion mobility in  $\beta$ -eucryptite by <sup>6</sup>Li static high-temperature NMR. We look here at the temperature dependence of the <sup>6</sup>Li NMR line structure and of the relaxation of <sup>6</sup>Li in  $\beta$ -eucryptite.

## 2 Experiment

#### 2.1 Sample synthesis

 $\beta$ -eucryptite was synthesised from Li<sub>2</sub>CO<sub>3</sub> (EUROSO-TOP 94.99%), Al<sub>2</sub>O<sub>3</sub> (Aldrich 99.99%) and SiO<sub>2</sub> (Aldrich 99.99%) powders in the molar ratio 1:1:2. Lithium carbonate was enriched with <sup>6</sup>Li. The mixture was sintered at 1373K for 15 hours and, after grinding, resintered at 1573K for 24 hours and at 1373K for another 24 hours. X-ray powder analysis showed that the final material consisted of pure  $\beta$ -eucryptite.

#### 2.2 NMR measuraments

**High-temperature static NMR** Static <sup>6</sup>Li NMR spectra were collected using a Chemagnetics Infinity spectrometer equipped with a 9T magnet operating at 56.33MHz for <sup>6</sup>Li. Powdered samples were placed in 8 mm sample holders and loaded into a home-built high-temperature probe. The measurements were made at 293K, 400K, 488K, 534K, 583K, 629K, 679K, 733K, 753K, 763K, 773K, 783K, 793K, 823K, 853K, 873K, 923K and 973K. After each temperature was reached, the sample was held between 5 and 10 minutes for the temperature to equilibrate. Conventional NMR spectra were acquired with an averaging of 100-200 transients with a recycle interval of 5 sec. (293K-673K) and 1 sec. (673K-973K). The typical radiofrequency field strength was approximately  $\omega_1/2\pi=25$  kHz. We used saturation recovery experiments [3] to measure T<sub>1</sub> from 293K to 673K and inversion recovery experiments [3] from 673K to 973K.

Temperature calibration on the probe was performed beforehand and showed a non-linear offset of the temperature of the thermocouple from the furnace temperature. Using this calibration all the temperatures were re-calculated and the absolute error is  $\pm$  3K. All the temperatures quoted are calibrated temperatures. MAS NMR A <sup>6</sup>Li MAS NMR spectrum was collected using a Chemagnetics Infinity spectrometer with 9.4 T magnet, operating at 58.87 MHz for <sup>6</sup>Li. The powdered sample was placed in a 4 mm sample holder. A conventional Chemagnetics MAS probe was used. The measurements were made at room temperature. Single pulse NMR spectra were acquired by the averaging of 20 transients, and a typical rediofrequency field strength of 50 kHz.

# 3 Results and analysis

### 3.1 Li motion

Figure 1 presents <sup>6</sup>Li static NMR spectra for  $\beta$ -eucryptite from room temperature up to 973K. From room temperature up to about 500 K, there is one resolvable peak with a pronounced shoulder. From about 500K to 973K, there are three distinct



Figure 1: <sup>6</sup>Li NMR spectra of  $\beta$ -eucryptite recorded at  $B_0 = 9 T$  as a function of temperature in Kelvin.

peaks contributing to the overall line shape. We assign these peaks to the three distinct crystallographic Li in the structural channels in  $\beta$ -eucryptite as follows: peak 1 - Li<sub>1</sub>, peak 2 - Li<sub>2</sub> and peak 3 - Li<sub>3</sub>, following the neutron data of Sartbaeva et al. (2004) [9]. Since Li<sub>2</sub> and Li<sub>3</sub> are in the same channels, the peaks display almost identical chemical shifts (Figure 2). Li<sub>1</sub> ions are in the primary channels, with Li<sub>2</sub> and Li<sub>3</sub> in the secondary channels.

Knowing the number of each Li atom in the unit cell [7, 13, 9] (Li<sub>1</sub> - 3 atoms, Li<sub>2</sub> - 3 atoms, Li<sub>3</sub> - 6 atoms) we have constrained the area of peak 3 to be twice the area of peaks 1 and 2. This constraint was employed in order to preserve



Figure 2: Fitting of three <sup>6</sup>Li resonances for the spectrum collected at 534K. Red circles are data at 534K, triangles - fitted peak 1, diamonds - fitted peak 2, open squares - fitted peak 3, blue line - fitting of the spectrum and purple line - difference between data and fitting.

the stoichiometric proportions of the compound. All the peaks were fitted with a Gaussian function (Figure 2). The fitting of all spectra starting from 488K showed a good fit using this model.

A very pronounced feature of the <sup>6</sup>Li spectra is that there is no cross-channel motion up to 973K. The three peaks do not overlap with temperature, and the fitting remains very good up to the highest temperatures measured, without deviations. This is consistent with the neutron diffraction analysis, which we have performed previously [9] on  $\beta$ -eucryptite, where there was no evidence for cross-channel motion of Li ions up to 873K. This is also consistent with the data by Boyce et al. (1979), where only 1-D motion of Li ions was seen [1].



Figure 3: Dependence of fitted width on temperature. Peaks 1 and 2 have relatively similar widths; peak 3 is approximately twice as wide as peaks 1 and 2.

The widths of all three fitted peaks decrease with temperature smoothly with

similar trends (Figure 3). The narrowing of the linewidth, which arises from dipolar interactions, can be related to the correlation time  $\tau_c$  of the motion causing the narrowing, which is in our case the Li diffusion.

Line narrowing in  $\beta$ -eucryptite has been reported previously. Boyce et al. [1] observed a single line narrowing process around 550K with an activation energy of 0.42 eV.

To confirm the chemical shifts for all three <sup>6</sup>Li resonances, we used the <sup>6</sup>Li MAS spectra, which was collected at room temperature. Xu and Stebbins (1995) showed that the chemical shift for <sup>6</sup>Li in  $\beta$ -eucryptite is equal to 0.2ppm [16]. Figure 4 is a <sup>6</sup>Li MAS spectrum for  $\beta$ -eucryptite at room temperature. As the MAS



Figure 4: <sup>6</sup>Li MAS NMR spectrum for  $\beta$ -eucryptite recorded at B<sub>0</sub>=9.4T at room temperature.

spectrum was collected with only 20 seconds recycle interval, there is a possibility that the sample was not fully relaxed. This differential relaxation may account for the intensity of peak 1 in the MAS spectrum being smaller than that observed in the static spectra.

The position of the maximum of peak 1 from the static NMR spectra changes slightly with temperature. The overall change is no more than 1 ppm. However, peak 2, which is assigned to  $\text{Li}_2$  in the secondary channel, changes position significantly with increasing temperature (Figure 5). The overall change is about 3 ppm. The position of peak 3, which was assigned to  $\text{Li}_3$ , was difficult to fit, owing to the peak being very broad. Since the errors were relatively large, further calculations on peak 3 were not possible.

The furnace polarity may introduce a shift of the whole spectrum, which may be as large as 3 ppm. However, the relative shifts of  $Li_1$  and  $Li_2$  do not correlate in this manner, demonstrating that the effect of the furnace polarity on the spectra is not significant.



(b)

Figure 5: Isotropic chemical shifts,  $\delta$ , for a) Li<sub>1</sub> and b) Li<sub>2</sub> as a function of temperature.

### 3.2 Spin-lattice relaxation time

We have measured the spin-lattice relaxation time by both saturation recovery and inversion recovery experiments. The temperature dependence of  $T_1$ , the longitudinal relaxation constant, is presented in Figure 6. With temperature,  $T_1$  decreases very rapidly from about 4 sec. at room temperature to about 30 ms at 773K. Around 680K it passes through a minimum and starts increasing with a further temperature increase. The estimated activation energy for Li motion from room temperature up to 670K is 0.3 eV. This was obtained by fitting a line for  $ln(T_1)$  versus inverse temperature between 289 K and 680 K, the gradient of which gives us the activation energy for Li<sup>+</sup> diffusion.

Brinkmann et al. [2] reported two thermally activated processes with an activation energy of 0.1 eV for the process dominant from 125K to 400K and 0.6 eV for the process dominant from 400K to 760K. Schweickert et al. [11] reported an activation energy equal to 0.3 eV. Boyce et al. (1979) showed activation energy of 0.42 eV for Li motion in beta-eucryptite. These data are in rough agreement with our data for Li cooperative motion, as our activation energy is equal to 0.3 eV.



Figure 6: <sup>6</sup>Li spin-lattice relaxation time for  $\beta$ -eucryptite in logarithmic scale.

Assuming that the relative jump of Li ions in the channels is the inter-site distance c/3, where c is the  $\beta$ -eucryptite cell parameter along the z-axis [9], it is possible to calculate the relative diffusivity rate  $D_{1D}$  at the temperature of the T<sub>1</sub> minimum by

$$D_{1D} = \frac{1}{2} \cdot \nu \cdot d^2 \tag{1}$$

where  $\nu$  is the inverse correlation time,  $\tau_c$ . We have already estimated that  $T_1$  is a minimum at 680K, so at 680K  $\tau_c=1.77 \times 10^{-8}$  s and  $D_{1D}$  at 680K is equal to  $2.37 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$ . This value of the diffusivity rate is in good agreement with previously reported values for Li ionic diffusion calculated from D.C. conductivity measurements in vanadates [12].

Using

$$\tau_c = \tau_0 \cdot exp \frac{\Delta E}{kT} \tag{2}$$

where  $\Delta E$  is the activation energy equal to 0.3 eV, T is the temperature, k is the Boltzman constant and  $\tau_0$  is a time at infinite temperature, we can estimate the correlation time  $\tau_c$  at any given temperature. The prefactor  $\tau_0$  is equal to



Figure 7: Dependence of correlation time  $\tau_c$  for Li motion in beta-eucryptite on temperature.

 $3.81 \times 10^{-9}$  s. This is in good agreement with Boyce et al. (1979) [1], where the prefactor was equal to  $2 \times 10^{-9}$  s. Figure (7) shows correlation time,  $\tau_c$ , for the Li motion along the structural channels of  $\beta$ -eucryptite versus temperature, described by equation (2).

# 4 Conclusions

The fact that all three peaks can be observed up to 973K showed that there is no cross channel diffusion in the structure. This agrees with the neutron data [9] and previous NMR data [1].

Starting from room temperature up to 500K, <sup>6</sup>Li NMR spectra showed one broad peak with a pronounced shoulder (Figure 1). As the temperature increased, three relatively sharp peaks appeared and persisted up to 973K. The three peaks were assigned to three crystallographic Li in the channels of  $\beta$ -eucryptite.

During the fitting of the spectra, the area of peak 3 (representing  $Li_3$ ) was constrained to be twice the area of the other two peaks. This was done to maintain the right stoichiometric proportions of the compound. The fit was very successful and allowed us to calculate the chemical shifts of peak 1 and 2. All three peaks showed line narrowing with increasing temperature.

One-dimensional diffusivity rate,  $D_{1D}$  was calculated for Li motion along the channels with the prefactor  $\tau_0$  equal to  $3.81 \times 10^{-9}$  sec.

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