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High resolution nuclear magnetic resonance study of the mobility in solid cryolite, Na_3AlF_6, from room temperature up to 300 °C

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RÉSUMÉ

Nous présentons dans ce travail, l'évolution en température des spectres haute résolution solide (MAS) de ^{27}Al, ^{23}Na et ^{19}F dans la cryolite solide (Na_3AlF_6), de 20 à 300°C. Les évolutions des déplacements chimiques et des largeurs de raie, nous ont permis pour chacun des noyaux de caractériser la mise en mouvement et de donner une image plus précise de la mobilité des espèces dans le solide. Ces mesures ont été complétées, pour le sodium, par des expériences de "2D d'échange" qui permettent d'accéder aux constantes d'équilibre des échanges chimiques.
Mots clés: RMN/MAS/température/cryolithe/échanges.

ABSTRACT

This work describes the temperature evolution of ^{27}Al, ^{23}Na and ^{19}F MAS spectra in solid cryolite (Na_3AlF_6), from room temperature up to 300°C. The description of ionic mobility in the solid is derived from chemical shifts and line-widths evolution for each nucleus with temperature. Exchange two-dimensional experiments on ^{23}Na directly detect Na mobility and equilibrium constants can be measured.
Keywords : NMR/MAS/temperature/cryolite/mobility/exchanges

INTRODUCTION

The industrial interest of liquid cryolite (Na_3AlF_6) in the aluminium production, has motivated numerous studies of its liquid phase[1]. In the solid state there exist a very high ionic mobility in the high temperature phase β-Na_3AlF_6 (T>550°C). From NMR measurements of lineshape and relaxation times, Spearing et al.[2] have shown that the reorientation of the [AlF_6] octahedra can be observed at lower temperature (α-

Na_3AlF_6) at least 150°C below the phase transition at 550°C, together with an important diffusional exchange of ^{23}Na.

We report a high resolution MAS NMR study of the mobility of ^{19}F, ^{23}Na and ^{27}Al from room temperature up to 300°C and evidence motion with frequencies from Hz to kHz, using one and two-dimensional experiments.

EXPERIMENTAL PROCEDURE

Sample was finely ground natural handpicked cryolite from Ivigtut, Greenland. All NMR data were collected on a BRUKER DSX400 (9T) operating at 104.2, 105.8 and 376.2 MHz for ^{27}Al, ^{23}Na and ^{19}F respectively. Chemical shifts are referenced to room temperature 1M solutions of $Al(NO_3)_3$, NaCl and $CFCl_3$. Variable temperature Magic Angle Spinning (MAS) NMR spectra were collected using a Bruker double bearing 4 mm MAS probe spinning at 5 kHz. Temperatures were controlled to within ±5°C. 2D exchange experiments were acquired with a non-selective $\pi/2$ pulse of 36 μs, using fluorine decoupling during t_1, t_m and t_2 evolution times.

RESULTS AND DISCUSSION

Structure and NMR characterisation of Natural Cryolite at Room Temperature:

At room temperature, cryolite (α-Na_3AlF_6) has a fluoride perovskite structure, consisting in alternating [AlF_6] and [NaF_6] octahedra, with interstitial [NaF_8] [3]. A transition occurs at 550°C from the monoclinic (α-Na_3AlF_6) to orthorhombic form (β-Na_3AlF_6).

As reported previously [2] the ^{27}Al MAS spectrum consists in a symmetric peak (-1 ppm, $\nu_Q = 200$ kHz) attributed to the [AlF_6] octahedra. The ^{23}Na MAS spectrum is composed of two peaks, one symmetric ([NaF_6], 1 ppm, ν_Q = 240 kHz) and the second with a typical second order quadrupolar shape ([NaF_8], -12.5 ppm, ν_Q = 700 kHz). The ^{19}F MAS spectrum presents two distinct broad lines : one at -143 ppm (width: 23 kHz) attributed to the two FNa_3Al crystallographic sites, and a second at -230 ppm (width 26 kHz) corresponding to the FNa_4Al site.

Temperature evolution of ^{27}Al, ^{23}Na and ^{19}F MAS spectra:

^{23}Na: from RT up to 300°C the linewidth of both contributions decrease from 700 to 450 Hz and 900 to 700 Hz for [NaF_6] and [NaF_8] respectively. At the same time the two line get slightly closer in chemical shift before merging at higher temperature [2]. This behaviour is understood as testifying the beginning of the Na mobility that will be clearly evidenced in the two-dimensional experiments described below.

^{19}F: the evolution with temperature of the ^{19}F spectra is characterised by the collapse of the two lines at ~200°C due to chemical exchange (fig. 1). At 300°C, only remains a much sharper line with well-defined spinning sidebands. At this temperature the exchange rate between the different sites is much higher than 43 kHz : the frequency separation of the two lines at room temperature.

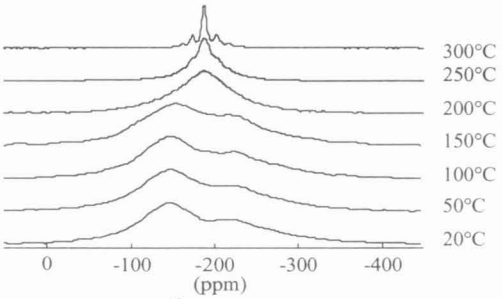

Figure 1 : Evolution of ^{19}F MAS NMR spectra with temperature

^{27}Al: Above 200°C, the line-width decreases drastically from 1250 Hz (200°C) to 450 Hz (300°C). This evolution can be correlated with the increase mobility of fluorine described above : the fluorine motion averages the dipolar interactions, which broadened the signal at room temperature.

^{23}Na 2D exchange experiments:

2D exchange experiments [3] are based three evolution periods (figure 2) : (1) encoding of the initial chemical shift position - t_1 , (2) exchange or mixing period - t_m and (3) acquisition of the final chemical shift position - t_2. The spectra are acquired for a given t_m value by regularly sampling the t_1 evolution period. In the final

spectrum obtained by Fourier transforming long t_2 and t_1 the off diagonal intensity (cross peaks) is characteristic of the Na atoms that exchanged their positions during the mixing time t_m. The equilibrium constant of the exchange process is measured from the analysis of cross peak intensities build-up as a function of the mixing time.

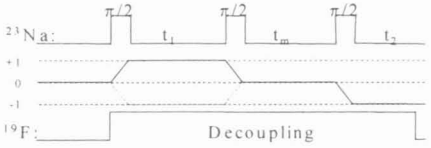

Figure 2 : 2D exchange spectroscopy pulse program

For sodium in cryolite, if we consider the two site chemical exchange $Na_{VI} \underset{k_2}{\overset{k_1}{\rightleftarrows}} Na_{VIII}$ the amplitude of the cross peak Na^{VI} => Na^{VIII} ($I_{NaVI=>NaVIII}$) is given by:

$$Na_{VI} \xrightarrow{k_1} Na_{VIII} \text{ exchange: } I = \frac{a\, k_2 \left[1 - e^{-(k_2+k_1)t_m}\right]}{k_2 + k_1\, e^{-(k_2+k_1)t_m}} I_{Na_{VI}} \qquad (1)$$

where a is a constant, t_m is the mixing time and I_{NaVI} is the amplitude of the corresponding Na_{VI} diagonal peak. The population of each Na site are measured from the volume of each Na corresponding peak (diagonal or cross-peak).

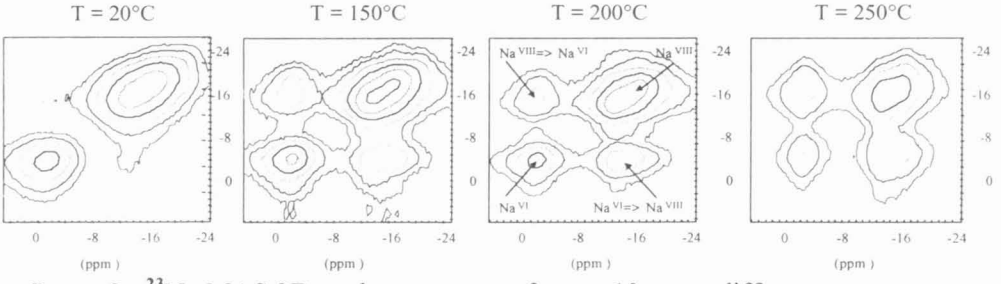

figure 3 : ^{23}Na MAS 2D exchange spectra for t_m =10 ms at different temperatures

The most significative spectra are presented in figure 3 with the spectra acquired at RT, 150, 200 and 250°C for a mixing time of 10 ms. The cross peak intensities (~null at RT for t_m=10 ms) grow with increasing temperature evidencing the progressive

increase of exchange between the Na_{VI} and Na_{VIII} sites. At 200°C the exchange rate obtained by fitting experimental results of equ. 1 is in the order of k_1=353 s^{-1} and k_2=128 s^{-1}.

CONCLUSION

These preliminary results show that the ionic mobility in cryolite (α-Na_3AlF_6) that clearly evidence from 200°C in the lineshapes and linewidth of ^{27}Al, ^{19}F and ^{23}Na one dimensional spectra can even be traced at lower temperature with two dimensional exchange experiments on ^{23}Na.

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REFERENCES

1 V. Lacassagne, C. Bessada, B. Ollivier, D. Massiot, P. Florian et J.-P. Coutures (1997) *C. R. Acad. Sci.Paris, t. 325,* Série II *b*, 91-98.
2 D.R. Spearing, J.F. Stebbins and I. Farnan (1994) *Phys.Chem.Minerals* 21, 373.
3 F.C. Hawthorne and R.B. Ferguson (1975) *Canadian Mineralogist* 13, 377.
4 K. G. Orrell (1995) Encyclopedia of Nuclear Magnetic Resonance. David M. Grant and Robin K. Harris, Wiley, Chichester, 4850 p.