J. Am. Chem. Soc. **1995,** *117,* 6637−6638

High-Resolution Solid State ^{19}F MAS NMR Study of Ionic Motion in α-PbF_2

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Received February 6, 1995

There is considerable current interest in materials that show solid electrolyte behavior, driven largely by an increasing need for alternative economical and environmentally-friendly energy devices. Solid electrolytes have found uses in a range of applications, including batteries, fuel cells, sensors, and electrochemical cells.[1] Fluorine ionic conductors are, to date, the best anionic conductors, due to the small size of the fluoride anion and its single charge. Many fluorine ionic conductors show considerable disorder on the fluorine sublattice. Diffraction studies of these materials provide a long-range representation of the structure, in which, unless there is considerable ordering of the defects, the local structure can often be obscured.[2] ^{19}F magic angle spinning (MAS) NMR would, in principle, appear to be an ideal method to probe the local order and motion of the fluorine sublattice. There have, however, been few applications of ^{19}F MAS NMR to study fluoride-containing materials, since the large gyromagnetic ratio of the ^{19}F nucleus, and its 100% natural abundance, result in strong dipolar coupling between ^{19}F nuclei, which is not always completely removed by MAS. Broad, featureless spectra are generally observed in the absence of MAS. Activation energies for fluorine motion can be extracted from these "wideline" spectra,[2,3] but resonances from individual sites are not typically resolved. With the development of high-speed MAS probes, this homonuclear coupling can be substantially removed, and a limited number of high-resolution spectra of inorganic fluorides have been reported.[4] In this paper we report, for the first time, the use of very fast MAS NMR to study fluoride ion motion in fluorides. Individual crystallographic sites are resolved for the solid electrolyte α-PbF_2 and are assigned on the basis of their $^{207}Pb-^{19}F$ *J* coupling. A resonance from mobile fluoride ions is observed, and the correlation time for fluoride ion motion is determined.

α-PbF_2 adopts the $PbCl_2$ structure.[5] This structure has two crystallographically distinct fluorine sites, F(1) and F(2). F(1), which is coordinated to four lead atoms, has a smaller spread of Pb−F bond lengths (from 2.45 to 2.64 Å) and a smaller average Pb−F bond length of 2.52 Å. In contrast, F(2), which is coordinated to five lead atoms, has Pb−F bond lengths that vary from 2.41 to 3.03 Å and an average Pb−F bond length of 2.77 Å. α-PbF_2 is a moderate anion conductor, with a conductivity between 3.9×10^{-6} and $5.3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 100 °C.[6] The conduction mechanism of α-PbF_2 remains, to date, ambiguous due to the conflicting results of a number of groups. Mahajan et al. report that conduction occurs via vacancies in the fluorine lattice,[7] while others report that conduction occurs via fluoride ion interstitials (Frenkel defects).[6,8]

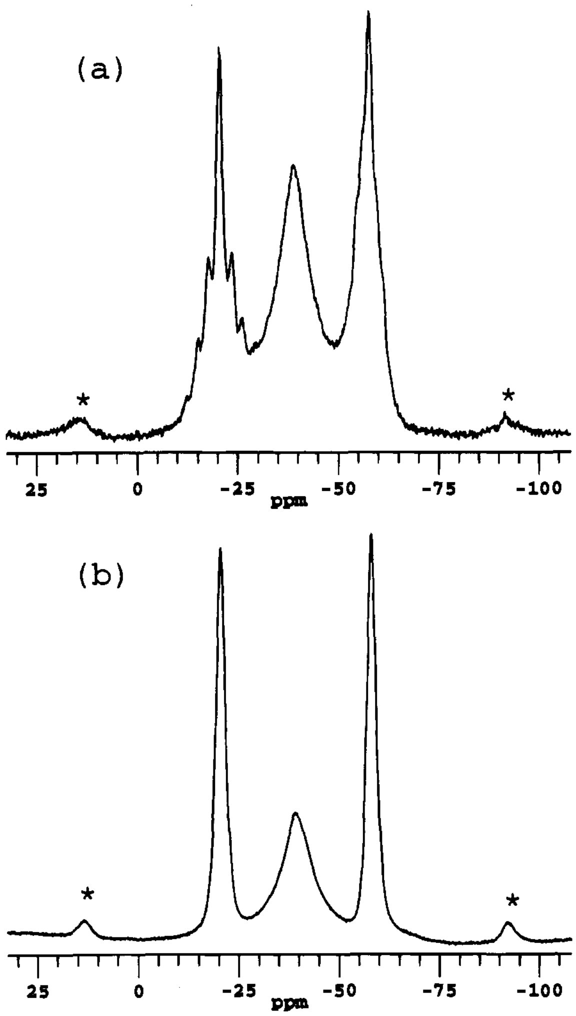

Figure 1. (a) ^{19}F MAS NMR spectrum of α-PbF_2 collected at a spinning speed of 22.5 kHz. (b) ^{207}Pb-decoupled ^{19}F MAS NMR spectrum of α-PbF_2, collected at a spinning speed of 20.3 kHz. The ^{207}Pb resonance of PbF_2 was first located and was found to resonate at −2715 ppm from an external reference of $Pb(NO_3)_2$ at 0 ppm. The ^{207}Pb decoupling frequency was then set on-resonance. All the spectra were acquired on a Chemagnetics 360 MHz NMR spectrometer, at operating frequencies for ^{19}F and ^{207}Pb of 338.75 and 75.12 MHz, respectively. ^{19}F spectra were referenced to CCl_3F at 0 ppm. The asterisks indicate spinning sidebands.

The room temperature spectrum of α-PbF_2,[9] collected at a spinning speed of 24.2 kHz, is shown in Figure 1a. Three resonances are observed at −20.5, −39.0, and −57.7 ppm. The resonances at −20.5 and −57.7 ppm are split into multiple peaks. The resonance at −20.5 ppm is a septet with a splitting between peaks of 1.0 kHz. Individual peaks cannot be as clearly resolved for the resonance at −57.7 ppm. On reducing the spinning speed, the line widths of the resonances increase, and at a spinning speed of 15 kHz, the fine structure of the resonance at −20.5 ppm is no longer visible. The fine structure arises from *J* coupling to the 22.6% abundant $I = {}^1/_2$ nucleus ^{207}Pb and is removed when the ^{19}F spectrum is acquired under conditions of ^{207}Pb decoupling (Figure 1b).

The resonances at −20.5 and −57.7 ppm can be assigned to the two crystallographically distinct sites, F(1) and F(2), for

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[1] West, A. R. *J. Mater. Chem.* **1991,** *1,* 157−162.
[2] Linford, R. G.; Hackwood, S. *Chem. Rev.* **1981,** *81,* 327−364.
[3] Gordon, R. E.; Strange, J. H. *Faraday Symp.* **1979,** *13,* 153−160.
[4] For example: Clark, J. H.; Goodman, E. M.; Smith, D. K.; Brown, S. J.; Miller, J. M. *J. Chem. Soc., Chem. Commun.* **1986,** 657−658. Kreinbrink A. T.; Sazavsky, C. D.; Pyz, J. W.; Nelson, D. G. A.; Honkonen, R. S. *J. Magn. Reson.* **1990,** *88,* 267−276.
[5] Boldrini, P.; Loopstra, B. O. *Acta Crystallogr.* **1967,** *22,* 744−745.
[6] Liang, C. C.; Joshi, A. V. *J. Electrochem. Soc.* **1975,** *122,* 466−470.
[7] Mahajan, M.; Rao, B. D. N. *Chem. Phys. Lett.* **1971,** *10,* 29−30.
[8] Kennedy, J. H.; Miles, R.; Hunter, J. *J. Electrochem. Soc.* **1973,** *120,* 1441−1446.
[9] Lead fluoride used in this study was obtained from Johnson Matthey and has a nominal purity of 99.9%. X-ray powder diffraction showed that only the α phase was present. No further heat or pressure treatments were applied to the sample prior to acquisition of the NMR spectra.

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fluorine in the α-PbF_2 structure. The $^{207}Pb-^{19}F$ *J* coupling is likely to be larger for ^{19}F nuclei in site F(1) than for those in F(2), due to the shorter Pb−F(1) internuclear distances. In addition, a smaller range of Pb−F(1) distances will result in a smaller range of coupling constants for *J* coupling to the four lead atoms in the F(1) first coordination sphere; hence, the coupling is more likely to be resolved. We therefore assign the resonance at −20.5 ppm to F(1). The larger range of Pb−F distances for F(2) results in sufficiently large differences in the *J* couplings that the individual peaks cannot be resolved. Five magnetically inequivalent environments are possible for F(1): $F(^{207}Pb)_x(Pb)_{4-x}$ (where Pb represents lead nuclei with $I = 0$; $x = 0-4$), which give rise to a singlet, doublet, triplet, quartet, and quintet for $x = 0-4$ respectively. Given the natural abundance for ^{207}Pb, probabilities for the occurrence of each of these environments of 35.8, 41.9, 18.4, 3.6, and 0.3, respectively, can be calculated. Thus, a nonet with intensities 0.02:0.45:4.7:21.9:45.1:21.9:4.7:0.45:0.02 is predicted. The outermost satellites of this multiplet have such small intensities that they are unlikely to be detected experimentally. The calculated intensities of the inner seven peaks of the nonet are close to those measured by deconvoluting the septet (assuming seven equally spaced resonances) of 1.5:7:17:49:17:7:0.2. Differences between the measured and calculated intensities may arise from small differences in *J* couplings for the different Pb−F bonds; this will result in asymmetrical peak shapes for the outer transitions and lead to errors in intensities obtained from the deconvolution of the resonance. The $^{207}Pb-^{19}F$ *J* coupling for F(1) is given by twice the separation of peaks in the multiplet and is therefore 2.0 kHz. This is close to the *J* coupling of 2.15 kHz observed in a single crystal ^{19}F NMR study of β-PbF_2.[10]

The resonance at −39.0 ppm occurs halfway between fluorine sites F(1) and F(2). No spinning sidebands are observed for this resonance, and therefore, the fluorine ions that contribute to this resonance must have a reduced ^{19}F dipolar coupling. No $^{207}Pb-^{19}F$ *J* coupling is visible. These observations suggest that this resonance arises from a subset of mobile fluoride ions that are hopping rapidly between fluorine sites F(1) and F(2). Since the resonance at −39 ppm lies halfway between those from F(1) and F(2), there must be an equal contribution of mobile fluoride ions from each site. The frequency of the jumps between the two sites must be greater than the frequency separation of the two resonances, i.e., >12.6 kHz, for the two resonances of the mobile F(1) and F(2) ions to coalesce. Thus, the time constant, τ_c, for the jump process is $<3.6 \times 10^{-5}$ s. Of the total number of fluorine ions, 32 ± 2%, as determined by integration of the spectrum, are mobile. The line width of this resonance at half-height is 4 kHz, which is much larger than the line widths of the peaks in the F(1) multiplets (which are only 1.0 kHz). This suggests that the mobile fluoride ions are in the so-called intermediate regime of motion, and thus the time constant of the motion can be directly estimated from the line width, assuming that the motion represents the dominant source of line broadening.[11] Given this assumption, we can calculate a value for τ_c of $\leq 1.6 \times 10^{-5}$ s. The intensity of the resonance decreases dramatically with the length of the evolution period, τ, in spectra acquired using a rotationally-synchronized spin echo pulse sequence, which confirms that the resonance arises from ^{19}F nuclei in the intermediate regime.[12] For example, the intensity decreases to 9% of the total intensity for a value of τ of 52 μs. Variable temperature studies, currently in progress, are consistent with the above assignments of the resonances. The intensity of the resonance at −39 ppm decreases with temperature and at 6 °C can no longer be detected. On raising the temperature, the intensity of the resonance increases, and at 230 °C, only the resonance at −39 ppm can be observed.[13] The effect of sample preparation and impurity dopant level on the mobility of the fluoride anions is currently being investigated.

The value for τ_c obtained by ^{19}F MAS NMR at room temperature is significantly smaller than the value of 3.0×10^{-4} s at 263 K obtained by wideline ^{19}F NMR by Mahajan et al., but it is consistent with the rapid line narrowing of the ^{19}F resonance that was observed from 263 to 370 K.[7] τ_c calculated from our data represents the correlation time for a jump from F(1) to F(2) and vice versa, while those from the wideline data represent the time constant for a jump between any two unspecified fluorine sites. Since we are able to see resolved *J* coupling, this rules out the possibility that a significant concentration of fluoride ions are undergoing jump processes involving only identical crystallographic sites. For example, if one F(1) ion jumps to another F(1) site, the spin states of the ^{207}Pb nuclei in its local coordination sphere, or the number of ^{207}Pb nuclei, will alter for most jumps, and an averaging of the *J* coupling pattern will result if the frequency of the motion is of the order of or larger than the *J* coupling. This motion may also account for the small discrepancies between the calculated and measured F(1) *J* coupling pattern.

Fluoride ions with $\tau_c \leq 1.6 \times 10^{-5}$ s are most likely to be those close to a defect, while ions in the slow regime are more distant. The lack of any other resonances which could be assigned to interstitial fluorine ions, and the observation of a resonance intermediate in frequency between the resonances of the rigid fluorine ions, suggest that the motion does not involve interstitial ions but, more probably, anion vacancies.

In conclusion, the ^{19}F MAS NMR spectra reported in this paper cannot be described by a coalescence of two resonances with a single correlation time; they can only be explained by a minimum of two rates of ^{19}F motion. Of all the fluorine ions, 32 ± 2% are in the so-called intermediate regime of motion ($\tau_c \leq 1.6 \times 10^{-5}$ s), while the remaining fluorine ions are in the slow regime. The presence of two regimes of fluorine motion was not detected in a previous ^{19}F wideline NMR study.[7] This study demonstrates the potential of high-speed ^{19}F MAS for studying fluorine ion mobility in moderate fluoride ion conductors; it is hoped that ^{19}F MAS will prove particularly useful as a method for determining the fluorine sites responsible for conduction, particularly when the fluorine ion motions approach time scales similar to those determined by the separation of ^{19}F chemical shifts, or when there is a large range of fluoride ion motions.

Acknowledgment. The solid state NMR spectrometer was funded by a grant from the National Science Foundation (CHE-9405436). Partial support of this research by the National Science Foundation, through the National Young Investigator Program (DMR 9458017), is gratefully acknowledged.

JA950385Z

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[10] Sears, R. E. J.; Guo, Q. Zh.; Mackey, H. J. *J. Chem. Phys.* **1984**, *80*, 5448−5452.

[11] Abragam A. *The Principles of Nuclear Magnetism*; Oxford University Press: Oxford, 1961.

[12] Spiess, H. W.; Sillescu, H. *J. Magn. Reson.* **1981**, *42*, 381−389.

[13] Wang F.; Grey C. P., unpublished results.