Multiple Quantum Magic Angle Spinning NMR Detection of Impurity Phases in Na_2HfO_3

J. V. Hanna,*,[†] M. E. Smith,*,[‡,§] and H. J. Whitfield[⊥]

Contribution from the CSIRO Division of Coal and Energy Technology, P.O. Box 136, North Ryde, NSW 2113, Australia, CSIRO Division of Materials Science and Technology, Private Bag 33, Rosebank MDC Clayton, Victoria 3169, Australia, Department of Physics, University of Kent, Canterbury, Kent CT2 7NR, U.K., and Department of Applied Physics, Royal Melbourne Institute of Technology, Box 2476W, Melbourne, Victoria 3001, Australia

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Abstract: One-dimensional ^{23}Na magic angle spinning (1D-MAS) NMR spectra obtained at 9.4 and 14.1 T from Na_2HfO_3 reveal three distinct sodium sites with widely differing NMR interaction parameters which can be accurately and unambiguously extracted. On exposure to atmospheric H_2O and CO_2 minor (~5%) impurities can be detected by 1D-MAS. Complete resolution of the different sites is possible by use of the recently introduced two-dimensional multiple quantum technique which is used for the first time here to detect minority phases. The reaction mechanism is further elucidated by obtaining an alternative perspective from ^{17}O MAS NMR which reveals an amorphous HfO_2-related phase is also formed during the decomposition process.

Introduction

NMR spectroscopy of solids has developed into an important characterization probe offering an atomic scale perspective on materials. The resolution of structurally distinct sites is central to most work. Magic angle spinning (MAS) is widely applied to remove the first-order anisotropic broadenings (proportional to the second-order Legendre polynomial $P_2(\cos\theta)$).[1] For quadrupolar nuclei (nuclear spin $I > {}^1/_2$) the interaction of the nuclear electric quadrupole moment (eQ) and the electric field gradient (which has a maximum component eq) can complicate spectral interpretation, and when second-order perturbations become important terms proportional to both $P_2(\cos\theta)$ and $P_4(\cos\theta)$ are present (P_4 corresponds to the fourth-order Legendre polynomial).[2,3] Spinning about a single fixed axis alone cannot simultaneously remove both these terms. Hence for the central (${}^1/_2$, $-{}^1/_2$) transition some narrowing occurs under MAS but there is residual broadening from the $P_4(\cos\theta)$ term.[3,4] This often results in the NMR spectra of such systems being characterized by overlapping resonances from different sites. If sufficient second-order quadrupolar structure is present it is still often possible to accurately deconvolute the line shape extracting the NMR interaction parameters for the different sites, particularly if advantage is taken of the inverse magnetic field dependence (in Hz) of the second-order quadrupole perturbation.[5,6] For such spectra, although the isotropic chemical shift (δ_{iso}) contains the most direct spectral evidence for identifying different sites, the quadrupolar coupling constant C_Q ($=e^2qQ/h$) and the asymmetry parameter η are also very useful parameters for characterization. There is now considerable interest in understanding the relation between the quadrupolar parameters and the nature of the site symmetry, with for example some detailed studies of compounds with well-defined structures existing for ^{23}Na.[7,8]

Although MAS partially removes second-order quadrupole effects, complete spectral resolution of different sites is often desirable for unambiguous interpretation. The requirement to remove both P_2 and P_4 terms has lead to the development of some sophisticated sample reorientation techniques that make the spinning axis time-dependent. These include dynamic angle spinning where the rotation axis is moved between two angles[9] and double angle rotation where the direction of the spinning axis is made a continuously varying function of time.[10] There are examples where both these sequences have achieved very much enhanced spectral resolution but both suffer from mechanical drawbacks that preclude their general usage. A very recent suggestion has proposed the utilization of a two-dimensional experiment that excites a multiple quantum (MQ) transition, and monitors the time evolution of this MQ transition under the influence of chemical shift and quadrupolar interactions. After an evolution time τ, the MQ coherence is reconverted back to observable (single quantum) magnetization and detected under conventional MAS conditions. This experiment requires the efficient excitation of a specific MQ coherence from the manifold of satellite transitions existing for $I > {}^1/_2$ nuclei (although it should be noted that some excitation of all coherences will, in general, occur), while the phase cycling implemented within the pulse sequence selects the appropriate coherence order. MAS is used to remove the P_2 anisotropy from all interactions (i.e. chemical shift, dipolar, and quadrupolar). This experiment was initially proposed as a three-pulse sequence;[11] however, significant improvements in sensitivity and implementation have been achieved with a two-pulse adapta-

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[†] CSIRO Division of Coal and Energy Technology.

[‡] CSIRO Division of Materials Science and Technology.

[§] University of Kent.

[⊥] Royal Melbourne Institute of Technology.

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tion.[12,13] Optimization of this experiment is achieved when $\pm m$ coherences are simultaneously excited and symmetrically reconverted back to single quantum coherence, thus producing pure absorption 2D NMR spectra. Initial studies on some model compounds have produced very significant improvements in spectral resolution, which are apparent in the 2D NMR data of $Na_2C_2O_4$, Na_2SO_4 and Na_2HPO_4 (^{23}Na), $KMnO_4$ (^{55}Mn) and Ca-A zeolite and Linde-13X faujasite (^{27}Al),[11] the aluminophosphate molecular sieves $AlPO_4$-11, and VPI-5 (^{27}Al)[12] and $RbNO_3$ (^{87}Rb).[13] In this 2D data the f_2 projection is the normal MAS spectrum and the P_4 terms refocus at $t_2 = R(I,m)t_1$ resulting in the isotropic information skewed in the 2D plot parallel to a gradient of R.[11−13] A very recent ^{23}Na MQ-MAS study of some model crystalline compounds[14] has shown that if the data produced by direct double Fourier transformation are sheared[13,14] it is possible to obtain a two-dimensional data set where the mean frequencies in the two directions of the sheared data depend only on combinations of the isotropic chemical and quadrupole shifts. Hence from these two values the isotropic chemical shift and quadrupole interaction parameters can be deduced that can be used to constrain the fit to the normal one-dimensional MAS spectrum from which quantitative data can be obtained.[14]

In this present study the NMR interaction parameters for ^{23}Na in Na_2HfO_3 are reported from multiple magnetic field MAS spectra. This compound has three well-defined sodium sites and comparison is made to the isostructural Na_2ZrO_3 where solid state NMR results have been previously reported.[15] Some samples could be accurately simulated but others showed small but significant discrepancies. This resulted from some minor (~5%) impurity phase that is unambiguously revealed by spectral subtraction. This emphasizes the sensitivity of precise second-order quadrupolar line shapes for detection of minor amorphous phases that are absent in conventional X-ray diffraction. A very similar observation has been reported for both ^{23}Na and ^{27}Al in $NaAl(CO_3)_2{\cdot}2H_2O$ formed on carbonation of Bayer liquor.[16] The complete separation of all the distinct resonances is achieved here by the 2D-MQ technique which represents the first time this MQ approach has been used for applications other than single phase, model compounds. The nature of the other phases observed is elucidated by deliberately encouraging structural breakdown by heating at 80 °C in the ambient atmosphere.

Adoption of a multinuclear magnetic resonance approach allows an alternative perspective to be gained on the structure, here through ^{17}O MAS studies. Ionic oxides enriched in ^{17}O have been shown to produce high-resolution MAS NMR spectra.[15,17] As ^{17}O exhibits a substantial chemical shift range any ambiguity in the identification of different phases and sites is often more straightforward from ^{17}O NMR than from other nuclei (e.g. ^{29}Si). In simple metal oxides it is often the most effective NMR probe. For example, nanocrystalline rutile and anatase are readily distinguished[18] and nanoscale phase separation in TiO_2−SiO_2 gels is readily observed.[19] The ability to probe amorphous oxides is a very important asset of ^{17}O MAS NMR. The pervasive nature of oxygen in the present sample should mean that it provides an important alternative view on the breakdown products.

Experimental Details

$Hf(OPr)_4{\cdot}PrOH$ (1.75 g) was dissolved in 20 cm^3 of toluene with enough anhydrous Na_2CO_3 added to produce the correct final stoichiometry of Na_2HfO_3. Then 1 g of H_2O mixed with 8 cm^3 of 2-propanol was added dropwise in a few minutes to this mixture with stirring which was continued for 4 h. The solvents were then allowed to evaporate under a stream of nitrogen at 20 °C until a dry powder formed. This powder was then ground and heated at 950 °C for 1 h. X-ray powder diffraction using a Siemens type F diffractometer employing Ni-filtered Cu radiation showed a single crystalline phase of Na_2HfO_3. For an ^{17}O-enriched sample the same procedure was followed except that the water used for the hydrolysis was 10 atomic % ^{17}O-enriched. To accelerate the reaction with the atmosphere the powder was placed in an open silica container at 80 °C for 15 h.

NMR spectra were accumulated on a Bruker MSL 400 spectrometer (equipped with a 9.4T magnet) operating at a ^{23}Na frequency of 105.8 MHz. Two experiments were performed using a 4-mm double-bearing (DB) MAS probe spinning at 15 kHz. 1D MAS experiments used 0.7 μs small tip angle pulses (~15°) with a recycle delay of 3 s. The 2D-MQ experiment employed the two-pulse sequence described in ref 12. The first pulse of 5.1 μs corresponding to a "liquid" 270° pulse was used to excite the triple quantum coherence and a "liquid" 90° pulse (1.7 μs) was used to convert the ± 3 quantum coherence back to observable magnetization. The spacing between the pulses was incremented 256 times by 8.3 μs; 72 scans per increment were used. The phase between consecutive slices of the 2D data set was incremented by 30° using the standard TPPI method for obtaining phase-sensitive 2D data.[20] (Note that for a triple quantum coherence a 30° phase increment is effectively 90°.) An additional ^{23}Na MAS NMR spectrum was accumulated at 158.6 MHz on a Varian VXR-600 spectrometer using a 5-mm DB-MAS probe with short 1.5-μs (~30°) pulses and a 5-s recycle delay with other conditions similar to those used at 9.4 T. Spectra were externally referenced to a 1 M aqueous NaCl solution at 0 ppm.

^{17}O MAS NMR spectra were accumulated at 54.242 MHz on an MSL 400 using a 7-mm DB MAS probe spinning at ~5 kHz. Short 1.5-μs pulses (~30°) were used with a 5-s recycle delay. Total accumulation times varied from 2 to 15 h depending on the line width and the number of sites present. An external shift reference of H_2O at 0 ppm was used.

Results and Discussion

The ^{23}Na MAS NMR spectrum obtained at 9.4 T (Figure 1a) is highly structured showing a number of singularities in the powder pattern from the three overlapping resonances. It is very similar in form to that previously reported for the isostructural Na_2ZrO_3.[15] To confirm the deconvolution an additional spectrum was run at 14.1 T (Figure 1f). In altering the field, the changes are as expected for a second-order quadrupolar line shape. The two sites with the smaller quadrupolar interactions are much more completely resolved at the higher field (Figure 1f). This resolution is a result of the increased chemical shift dispersion and the decreased quadrupolar broadening. The differing frequency scales of Figures 1a and 1f demonstrates how the high field reduces the frequency spread of such spectra with the total extent of the centerband reduced from 120 ppm at 9.4 T to 54 ppm at 14.1 T, almost exactly the expected B_o^{-2}-dependence (in ppm), thus confirming the dominance of second-order quadrupole effects in determining these line shapes. Simulations were performed using the Bruker POWDER program and the results of the complete simulation are shown in Figure 1(b) corresponding to 9.4 T. The fit was performed using the parameters from Na_2ZrO_3[15] as the starting

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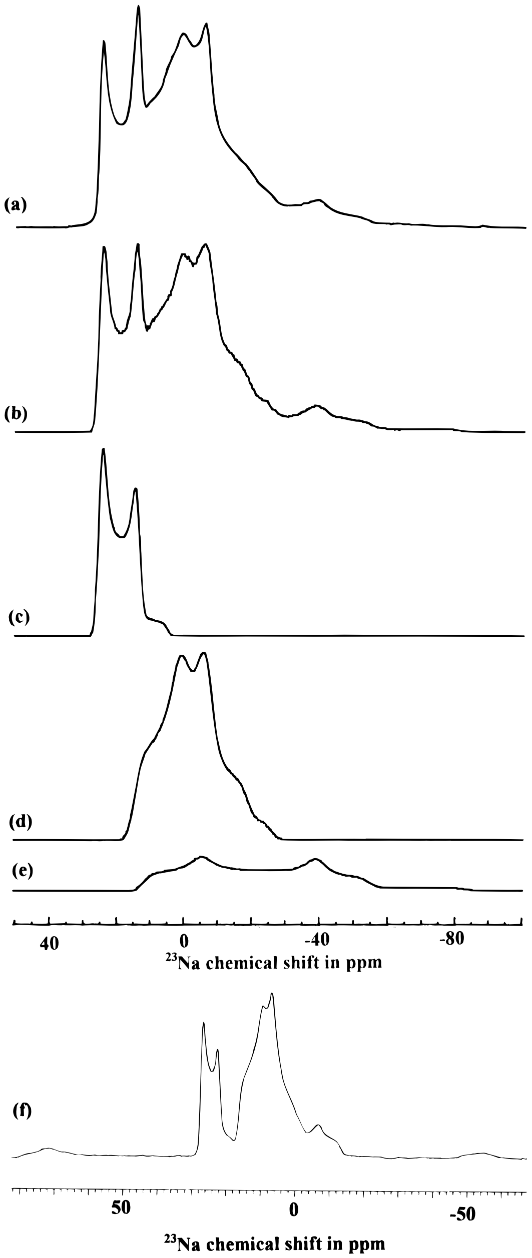

Figure 1. ^{23}Na MAS NMR spectra of Na_2HfO_3 at 9.4 T: (a) experimental, (b) complete simulation and the individual site components (c) S2, (d) S1, and (e) S3, together with (f) the experimental data at 14.1 T.

Table 1. ^{23}Na NMR Interaction Parameters Deduced from Centerband Simulations

site	C_Q (MHz)	η	δ_{iso} (ppm)	Δ^a (Hz)	intensity (%)
1	2.64 ± 0.02	0.62 ± 0.05	15.75 ± 0.15	420	57
2	2.05 ± 0.02	0.05 ± 0.05	28.75 ± 0.15	250	21
3	4.25 ± 0.02	0.32 ± 0.03	19.0 ± 0.10	500	22

[a] Δ is the Gaussian broadening used.

point and then varying these until the best fit of both the 9.4 and 14.1 T data was achieved by only allowing the magnetic field to vary. The data at two fields allow an unambiguous fit to be obtained despite the significant spectral overlap. The NMR interaction parameters are summarized in Table 1 and the three individual components at 9.4 T are shown in Figures 1c−e. The large variation in C_Q demonstrates its sensitivity as a structural probe. The two smaller values of C_Q corresponding to sites S1 and S2 are typical of ^{23}Na in inorganic materials, whereas the magnitude of C_Q for S3 (4.25 MHz) is one of the largest C_Q's reported for ^{23}Na.[7,8] There is also a noticeable variation in the isotropic chemical shift of ~13 ppm between the sites.

A single crystal structure determination of Na_2HfO_3 has not yet been reported; however, the X-ray powder pattern is very similar to that of Na_2ZrO_3 and has been indexed in terms of the same structure.[21] It is highly likely that polytypism of the form observed in Na_2ZrO_3 also occurs for Na_2HfO_3. Our NMR results are well explained by assuming our preparation is isostructural with the monoclinic form of Na_2ZrO_3 with space group *C*2/*c* which has a distorted sodium chloride structure. Layers form that are stacked up the *c*-axis with alternate cation layers containing either only sodium or sodium and hafnium. Three sodium sites occur in the ratio 2:1:1 for the sites designated S1, S2, and S3. From the spectral intensities obtained from the simulations it is possible to assign the site with the largest intensity with $C_Q = 2.64$ MHz to S1. This assignment is unambiguous although the agreement of the intensities is not as good as it superficially appears to be because of the varying amounts of magnetization appearing in the centerband due to the different C_Q's,[22] which was discussed previously in detail with respect to Na_2ZrO_3.[15] The three sodium sites are all octahedrally coordinated by oxygens as nearest neighbors. S1 and S2 also have identical next nearest neighbors with six sodiums in the plane and a triangle of one sodium and two hafniums in the layers above and below. However, there is quite a large change of δ_{iso} so this cannot be used to assign which two resonances are similar. The assignment of the sodium sites in Na_2ZrO_3 was on the basis of the variation of the nearest neighbor Na−O bond lengths being related to C_Q with the variation in bond length being S3 > S1 > S2. This agrees with the assignment of the site S1 with the $C_Q = 2.64$ MHz resonance as it has the intermediate site distortion.[21] Then the two extremes can be assigned as S2 and S3 with the $C_Q = 2.05$ MHz and $C_Q = 4.25$ MHz resonances, respectively.

In some Na_2HfO_3 samples that have been synthesized for some time it was observed that significant discrepancies (of the order of 5%) existed between the experimental and simulated ^{23}Na MAS NMR spectra (compare Figures 1b and 2a), despite great care being exercized in ensuring that no distortions were introduced by the NMR experiment. Figure 2a represents a typical case where the downfield singularity of the S1 resonance appears larger and broader, and the only observable singularity of the S3 resonance is not as well defined. These are small, but nevertheless significant differences in comparison to the MAS NMR spectrum of a fresh Na_2HfO_3 sample given in Figure 2b. The series of ^{23}Na 2D-MQ NMR spectra given in Figure 3 clearly demonstrates the origins of these observed discrepancies, and illustrates the utility of the 2D-MQ technique for detection of minor impurities. The three sodium sites of Na_2HfO_3 are clearly displayed in the ^{23}Na 2D-MQ spectra of Figures 3a and b. Although the data are skewed, enhanced resolution is obtained, thus clearly resolving the S1, S2, and S3 sites. The mean position along the horizontal (f_2) axis is given by eq 12b in ref 14, and using the interaction parameters for three sites given in Table 1 for Na_2HfO_3 gives mean positions of −2, 19, and −23 ppm in very close agreement with the data of Figure 3a. This indicates how the single-field MQ MAS data provide a useful check on the NMR interaction parameters. The very narrow width of the contours for these sites suggests a very highly ordered Na_2HfO_3 network exists in the initially synthesized product where negligible chemical shift dispersion

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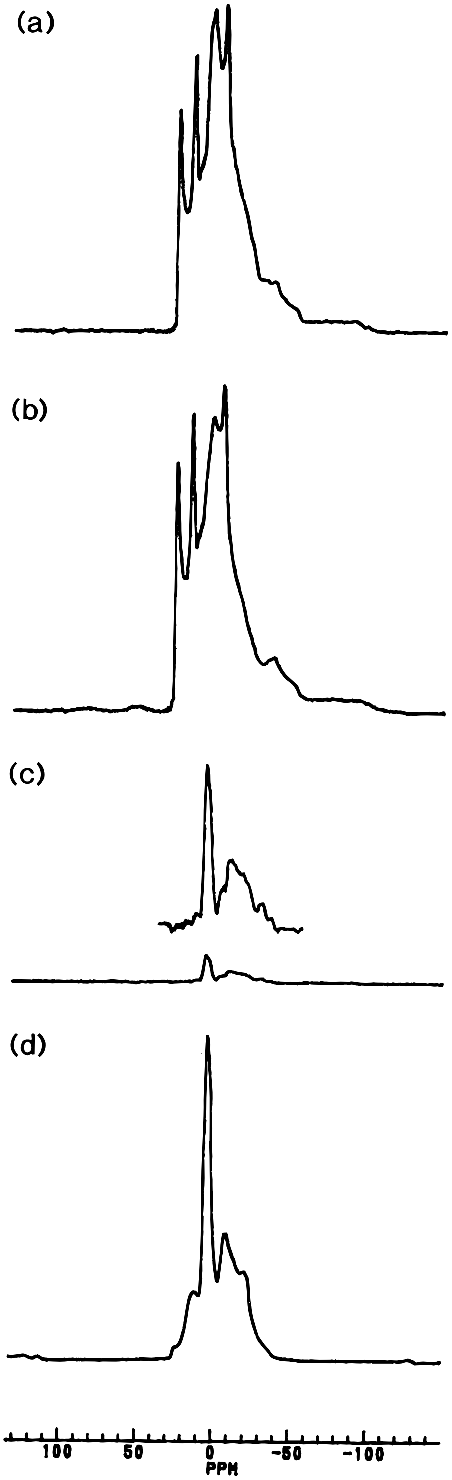

Figure 2. ^{23}Na MAS NMR spectra at 9.4 T of Na_2HfO_3: (a) exposed to the atmosphere, (b) a fresh sample, (c) the difference of (a) and (b) showing the impurity phase (including a vertical expansion), and (d) after heating at 80 °C for 18 h.

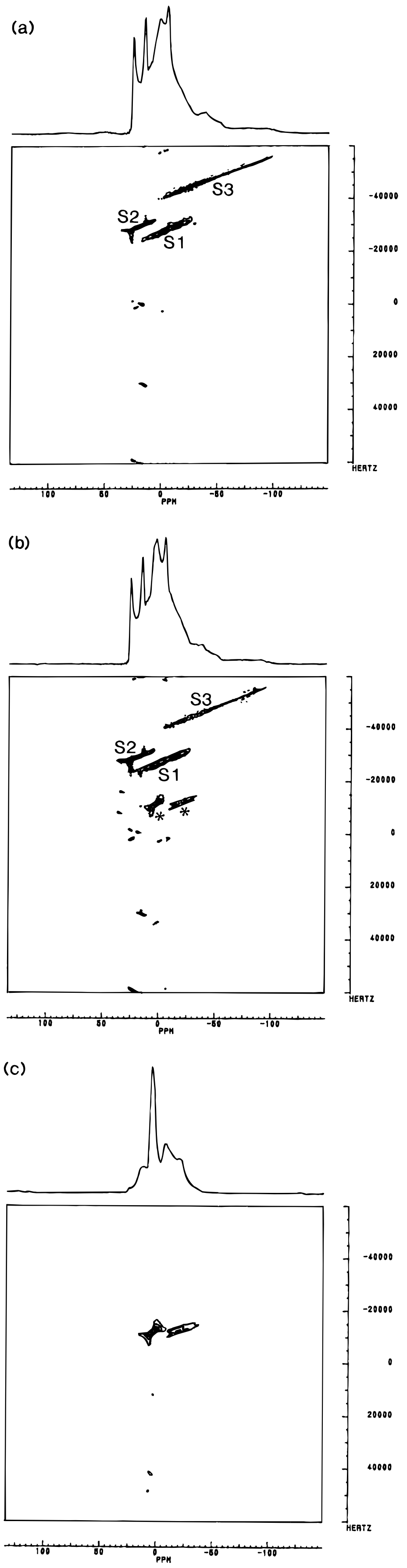

Figure 3. 2D-MQ ^{23}Na MAS NMR spectra: of (a) freshly prepared Na_2HfO_3, (b) Na_2HfO_3 exposed to the atmosphere, and (c) after heating at 80 °C for 18 h.

and/or distribution of electric field gradients appears to influence these ^{23}Na resonances. From the 2D-MQ NMR spectrum of Figure 3b, it is evident that exposure of this highly ordered material to the atmosphere induces some transformation of the structure reflected in the sodium environments; in this spectrum the same three sodium environments are still present; however, decomposition products (marked with asterisks) have now become apparent. In principle it would be possible from a sheared data set for the NMR interaction parameters to be deduced[14] that could then be used to fit the one-dimensional ^{23}Na MAS NMR spectrum (Figure 2a). However, so far this approach has only been successfully demonstrated on highly crystalline model compounds where individual sites have a single well-defined set of interaction parameters, whereas here the second phase is structurally poorly defined and probably noncrystalline and there is likely to be some spread of interaction parameters. Hence for quantitative analysis of these sites there is no advantage of such an approach over simple direct spectral subtraction. It is estimated from the difference spectrum (Figure 2c) that these decomposition products detected by the 2D-MQ technique are present at the ~5 mol % level. This subtraction of 1D MAS NMR spectra is performed after scaling the undistorted spectral features of Figures 2a and 2b to be equal, yielding the spectrum of Figure 2c. Quantitative estimates cannot be deduced from the 2D-MQ data as non-uniform excitation of the MQ transitions, and the nonsymmetrical reconversion of the ±3 quantum coherences back to an observable single quantum coherence (both of which are strongly governed by the quadrupole parameters of each site and the rf field strength) led to strongly non-quantitative intensities.[12,13,23]

The transformation reaction can be accelerated by heating the sample at 80 °C for periods >10 h, after which the whole sample decomposes. This is observed with the 2D-MQ technique which shows that the initial decomposition products marked with asterisks in Figure 3b now completely dominate the ^{23}Na MQ NMR spectrum in Figure 3c. The 1D MAS NMR spectrum of Figure 2d (and f_2 projection of Figure 3c) of completely decomposed Na_2HfO_3 closely resembles the subtraction spectrum observed in Figure 2c, indicating that the trace impurities (formed as a function of time exposed to the atmosphere) and those formed after accelerated reaction are similar sodium species. Only ^{23}Na NMR static line shapes of Na_2CO_3 have been reported,[24] but MAS line shapes from hydrated Na_2CO_3[25] resemble those observed here. This evidence suggests that structural deterioration has proceeded via hydrolysis[26] and carbonation[27] of Na_2HfO_3 with atmospheric H_2O and CO_2 which can be important reactions of oxides in the atmosphere. XRD analyses of the fully decomposed Na_2HfO_3 provided no evidence of a crystalline phase existing in this product. With the variable composition (e.g. water content) and ill-defined, noncrystalline nature of this phase(s) accurate fitting of the MAS NMR spectrum to sites with well-defined NMR interaction parameters is not merited. XRD of the sample corresponding to Figure 2a indicated that the sample was still single-phase Na_2HfO_3. Small amounts of poorly ordered components are often preferentially lost against the background of the majority crystalline phase from conventional XRD while NMR can detect and accurately quantify them, as was demonstrated recently for $NaAl(CO_3)_2{\cdot}2H_2O$.[16]

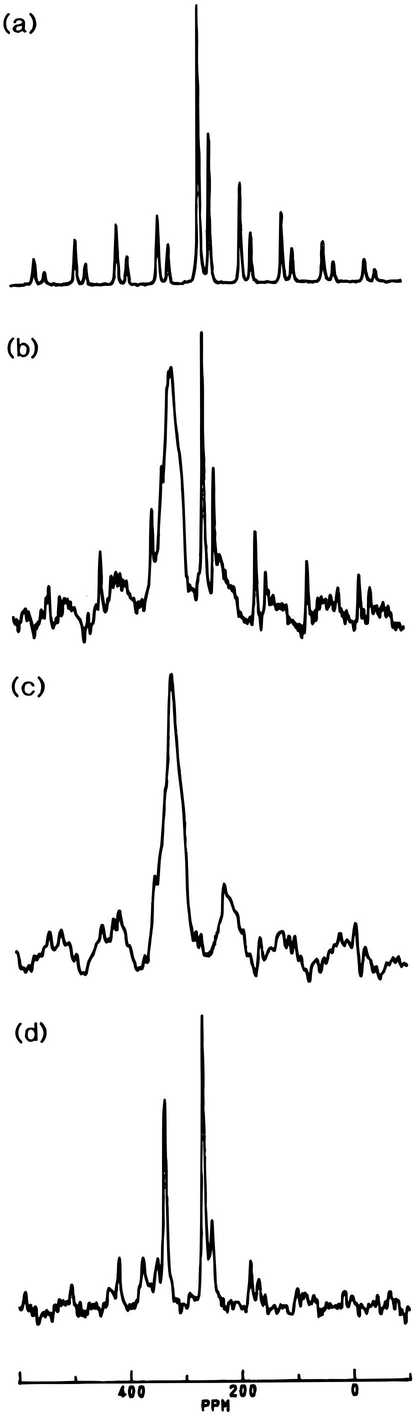

Figure 4. ^{17}O MAS NMR spectra: of (a) Na_2HfO_3 and then heated at 80 °C for (b) 6 h and (c) 18 h, with (d) crystalline HfO_2 shown for comparison.

For an alternative perspective on the decomposition reaction an ^{17}O-enriched sample of Na_2HfO_3 was synthesized that gave two centerbands at 258.4 and 239.8 ppm, together with extensive sideband manifolds that are due to chemical shift anisotropy of the central ($^1/_2$, $-^1/_2$) transition, in the ratio 2:1 (Figure 4a). There are three oxygen sites in the structure all coordinated by four sodium ions and two hafnium ions, so it must be more subtle effects that make two of these resonances coincident. The orientation of these coordination octahedra and the variation in the bond lengths are more similar for sites O(1) and O(3) so that these are assigned to the resonance at 258.4 ppm on the basis of the intensity. On heating at 80 °C for 6 h, in addition to the Na_2HfO_3 resonances a much broader line at ~320 ppm is observed indicating some reaction (Figure 4b). Then after 18 h the Na_2HfO_3 resonances are completely eliminated leaving only the broad resonance and accompanying sidebands (Figure 4c). Crystalline monoclinic HfO_2 is shown for comparison (Figure 4d) with the two resonances at 336 and 267 ppm. The advantages of ^{17}O NMR in probing structures is illustrated here as the shift range of oxygen is very large so that it is straightforward to identify the chemical bonding. The shift indicates that the oxygen is still bonded to hafnium in one of the decomposition phases but is not disordered monoclinic HfO_2. It also suggests that oxygen has not been exchanged out of the framework into the carbonate phase as evidenced by the absence of a quadrupolar broadened resonance with δ_{iso} at ~200 ppm (with a main singularity at ~100 ppm) which would be characteristic of a carbonate species.[28] (Note that the spectra

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in Figure 4 have all been acquired with a common MAS rate of ∼5 kHz. For a decomposed sample of Na_2HfO_3 higher MAS rates were used that would have narrowed a resonance with a large C_Q (∼7 MHz) characteristic of a carbonate species, but still no sign of signal in the region of 100 ppm was observed.) The line width also provides important information. In such ionic systems ^{17}O NMR resonances are usually very narrow as residual second-order quadrupolar effects are very small so that line broadening is a result of chemical shift dispersion which is associated with structural disorder.[18,19] The relatively large line width observed here indicates disorder hence the difficulty of XRD identifying the decomposition phases.

The combination of 1D- and 2D-MQ MAS NMR spectra have unequivocally shown the reaction of Na_2HfO_3 with atmospheric moisture and CO_2 to form a hydrated sodium carbonate and HfO_2-related phase, both of which are disordered as they gave no sharp XRD pattern. Even the very early stages of reaction, when these phases are very minor constituents, can be readily detected by NMR methods.

Conclusion

Second-order quadrupolar-broadened ^{23}Na MAS NMR spectra from Na_2HfO_3 can be accounted for by three distinct sodium sites. The spectra are sensitive to the formation of small amounts of secondary phases. The 2D-MQ NMR method shows significantly enhanced resolution and can detect separate resonances from the minor sodium-containing phase. ^{23}Na and ^{17}O NMR used in conjunction show that the poorly ordered decomposition products are a hydrated sodium carbonate and HfO_2-related phase. This NMR approach offers a very powerful methodology for characterizing such solid state chemistry.

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