

EXPERIMENTAL CAPABILITY OF HIGH RESOLUTION O¹⁷ USING DOUBLE ROTATION ON CRYSTALLINE SODIUM ENNEAGERMANATE

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Abstract. We have studied sodium enneagermanate crystal using both magic angle spinning (MAS) and double rotation (DOR) at two magnetic field strengths. Using equation for the total shift observed at two field strengths, the chemical shift is uniquely determined together with a product of the quadrupolar coupling constant ($C_Q = e^2qQ/h$) and the quadrupolar asymmetry parameter (η). We demonstrate a computer simulation that uses the isotropic shifts and quadrupolar products as constraints and provides simulations of overlapped magic-angle spinning line shapes. In this way the quadrupolar parameters, C_Q and η , are determined separately for each crystallographic site of crystalline sodium enneagermanate. High resolution DOR spectra of oxygen-17 nuclei in sodium enneagermanate crystal illustrate the experimental capabilities. Crystalline studies of sodium enneagermanate is one of the structural data for confirming the correlations between the measured ¹⁷O quadrupolar coupling parameters and the oxygen environment. The result of these studies should provide insight to further investigation using ¹⁷O solid state NMR to study the structure of other oxide glasses and as well as other germanate-based glasses.

Keywords: sodium enneagermanate crystal, magic angle spinning (MAS), double rotation (DOR), oxygen-17 (O¹⁷), nuclear magnetic resonance (NMR)

Abstrak. Sampel kristal sodium enneagermanate telah dikaji dengan menggunakan penspinan sudut ajaib (MAS) dan putaran berganda (DOR) pada dua medan magnet yang berbeza. Jumlah anjakan kimia yang dicerap pada dua medan magnet telah digunakan untuk mengira anjakan kimia isotropik berserta dengan nilai pemalar gandingan ($C_Q = e^2qQ/h$) dan parameter tak simetri empat kutub (η). Nilai anjakan kimia isotopik dan pemalar gandingan itu telah digunakan dalam komputer simulasi untuk menentukan bentuk spektra penspinan sudut ajaib. Melalui kaedah tersebut parameter C_Q dan η , telah ditentukan untuk setiap fasa kristal sampel sodium enneagermanate. Kaedah putaran berganda (DOR) telah menunjukkan keupayaan yang sangat tinggi dengan memperlihatkan spektrum oksigen-17 resolusi tinggi, untuk menentukan struktur unit yang terdapat dalam sampel kristal sodium enneagermanate. Kristal sodium enneagermanate telah dikaji untuk menentukan hubungan yang berlaku di antara parameter gandingan empat kutub ¹⁷O dengan kedudukan kekisi oksigen didalam sampel. Hasil yang diperolehi ini pula boleh digunakan untuk kajian yang selanjutnya untuk menentukan struktur kaca oksida yang lain dan kaca yang berasaskan germanate dengan menggunakan kaedah ¹⁷O keadaan pepejal resonan magnet nukleus.

Kata kunci: kristal sodium enneagermanate, penspinan sudut ajaib, putaran berganda, oksigen-17 (O¹⁷), resonan magnet nukleus

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1.0 INTRODUCTION

Oxygen is a major constituent of many important compounds including minerals, glasses and inorganic solids, so ^{17}O solid state nuclear magnetic resonance (NMR) spectroscopy should have considerable potential for investigating the structures of such materials. The potential of oxygen-17 solid-state nuclear magnetic resonance (NMR) [1-3] as a probe of structure in solids has been greatly enhanced with the recent development of solid-state techniques such as double rotation (DOR) [4], dynamic angle spinning (DAS) [5-8] and multiple-quantum magic-angle spinning (MQ-MAS) [9], which provide high-resolution NMR spectra of quadrupolar nuclei in solids.

The techniques of MAS [10-14], dynamic-angle spinning (DAS) and double rotation (DOR) were developed to overcome the broadening induced by broadening from the first-order chemical shift and second-order quadrupolar interactions. The total isotropic shift (δ_{obs}) observed for a resonance in DOR (or DAS) is the sum of two isotropic components;

$$\delta_{\text{obs}} = \delta_{\text{iso}}^{\text{CS}} + \delta_{\text{iso}}^{2\text{Q}} \quad (1)$$

where the first term is the isotropic chemical shift and the second is the field-dependent isotropic second-order quadrupolar shift. The isotropic chemical shift (in ppm) is field-independent and equal to one-third of the trace of the chemical shift tensor. For a nucleus with spin I , the isotropic quadrupolar shift of the central transition is

$$\delta_{\text{iso}}^{2\text{Q}} = \frac{3}{40} \left(\frac{C_{\text{Q}}}{\nu_{\text{L}}} \right)^2 \frac{[I(I+1) - \frac{3}{4}]}{I^2 (2I-1)^2} \left(1 + \frac{\eta^2}{3} \right) \times 10^6 \quad (2)$$

The quadrupolar asymmetry parameter (η) describes the deviation of the local electric field gradient from cylindrical symmetry, while the quadrupolar coupling constant ($C_{\text{Q}} = e^2 q Q / h$) reflects the magnitude of the gradient. With DOR, the lines are narrowed and the maxima of the resonance occur at the positions of the total isotropic shifts for each magnetically inequivalent species.

Since the isotropic second-order quadrupolar shift is inversely proportional to the square of ν_{L} (Larmor frequency of the nucleus), the contributions of $\delta_{\text{iso}}^{\text{CS}}$ and $\delta_{\text{iso}}^{2\text{Q}}$ to the total shift can be determined by performing DOR experiments in two different magnetic fields. As field strength increases, the observed isotropic shift (in ppm) must move to a higher frequency since the isotropic chemical shift remains the same and the isotropic second-order quadrupolar shift is less negative (*see* Eqs. 2). The isotropic chemical shift and the quadrupolar product for each site is defined as P_{Q} , given by

$$P_{\text{Q}} \equiv C_{\text{Q}} \sqrt{\left(1 + \frac{\eta^2}{3} \right)} \quad (3)$$

Substituting the relevant constants for oxygen-17 and the two field strengths into Eqs. (2) yields the following set of simultaneous equations:

$$\delta_{\text{iso}}^{\text{CS}} = \delta_{\text{obs}}^{11.7\text{T}} + 1.30524 P_{\text{Q}}^2 \quad (4)$$

$$\delta_{\text{iso}}^{\text{CS}} = \delta_{\text{obs}}^{14.1\text{T}} + 0.90776 P_{\text{Q}}^2 \quad (5)$$

The shifts values are all in units of ppm while P_{Q} is given in megahertz (MHz). These two equations may be solved for $\delta_{\text{iso}}^{\text{CS}}$ and P_{Q} , and the results were used to place constraints upon the simulations of MAS line shapes at both field strengths.

X-ray single-crystal structure studies of sodium enneagermanate $\text{Na}_4\text{Ge}_9\text{O}_{20}$ have been reported [15-17]. The structure of the $2\text{Na}_2\text{O} \cdot 9\text{GeO}_2$ crystal [15] is shown in Figure 1. The unit cell contains four formula units and the structure of $\text{Na}_4\text{Ge}_9\text{O}_{20}$ is built up of $[\text{GeO}_6]$ octahedra and chains of $[\text{GeO}_4]$ tetrahedra coupled together to form a three-dimensional network with no NBO (non bridging oxygen). Five Ge atoms per formula unit are in tetrahedral coordination with oxygen and four are in octahedral coordination.

There are five O sites in the structure: O2, O4, O5, O1 and O3 with occupancy equal to 1 [15,17] with Ge-O-Ge bridging bond angles of 98.1° , 116.5° , 116.9° , 121.1° , and 130.6° , respectively, as shown in Figure 1(d to h). The O2 site is unique to the sodium enneagermanate crystal, connecting three Ge (GeO_6 octahedra) with each other, forming a three-dimensional network (Fig. 1d). The O3 site is a normal BO, connecting $[\text{GeO}_4]$ tetrahedra. Three other types of O sites (O1, O4, O5), with both $^{[4]}\text{Ge}$ and $^{[6]}\text{Ge}$, are present in the structure. The $[\text{GeO}_4]$ tetrahedra and $[\text{GeO}_6]$ octahedra share corners with each other, forming a three-dimensional network.

As part of a program aimed at determining the utility of ^{17}O NMR for investigating sodium germanate system [18], we have exploited the field dependence of the DOR spectra of oxygen-17 to uniquely determine values for the isotropic chemical shifts experienced at crystallographically distinct oxygen sites in sodium enneagermanate and to see more clearly the presence of BO and NBOs, and to extend the database on ^{17}O NMR measurements in order to know better the relationships between C_{Q} and the intertetrahedral bond angle, $\text{Ge}-\hat{\text{O}}-\text{Ge}$. These studies should also provide insight to future investigation using ^{17}O solid state NMR to study the structure of other oxide glasses and as well as other germanate-based glasses.

2.0 EXPERIMENTAL PROCEDURES

2.1 Chemical Aspects

The oxygen-17 labeled enriched germanium dioxide (Ge^{17}O_2) as starting materials were enriched to ca. 10% in ^{17}O by direct synthesis using H_2^{17}O , as described previ-

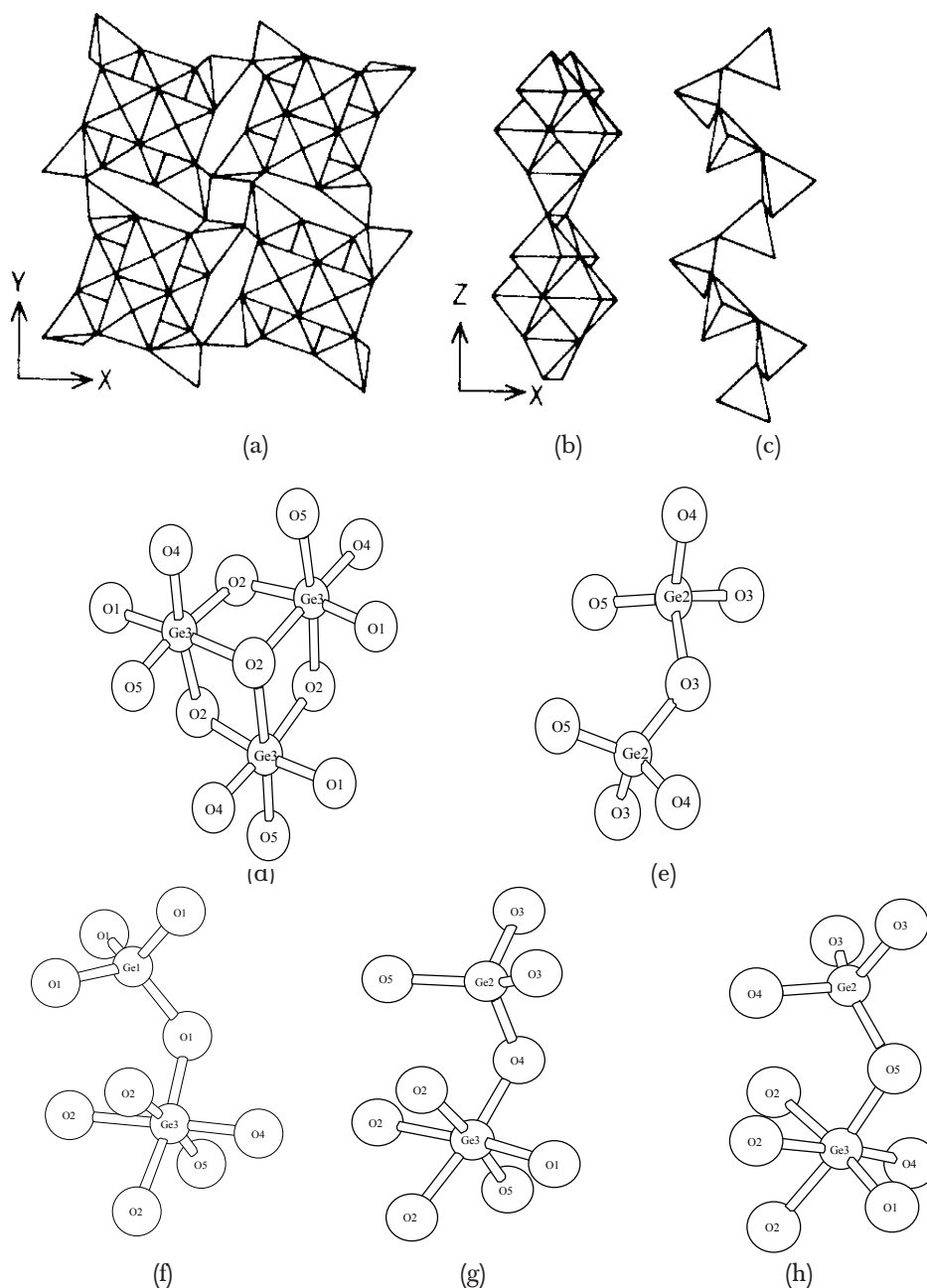


Figure 1 The structure of sodium enneagermanate ($\text{Na}_4\text{Ge}_9\text{O}_{20}$). (a) The connection of chains and spirals in $\text{Na}_4\text{Ge}_9\text{O}_{20}$. (b) Ge_4O_{16} groups connected with four-coordinated Ge atoms forming chains of the composition $(\text{Ge}_5\text{O}_{16})_n$. (c) $[\text{GeO}_4]$ tetrahedra sharing two corners forming a spiral. There are five O sites in the structure; (d) O2 site is unique, connecting three Ge ($[\text{GeO}_6]$ octahedra) with each other, (e) O3 site is a normal BO, connecting $[\text{GeO}_4]$ tetrahedra. Three other types of O sites (O1, O4, O5), with both $^{[4]}\text{Ge}$ and $^{[6]}\text{Ge}$, are present in the structure (f, g and h)

ously [18]. The synthesis of isotopically enriched germanium dioxide (Ge¹⁷O₂) was carried out by reaction between 1.0 ml H₂¹⁷O and 1.0 ml germanium (IV) tetraethoxide at room temperature for 24h. This produced a white gel which was dried at room temperature under nitrogen, then heated to 300°C under nitrogen. The sample of Na₄Ge₉O₂₀ glass were prepared from unenriched Na₂GeO₃ and Ge¹⁷O₂ by melting the mixture under nitrogen at 1100°C for 4h in a platinum tube and then were crystallized at 650°C for 10h. The phase identities of this material was confirmed by powder X-ray diffraction.

2.2 Nuclear Magnetic Resonance Spectroscopy

¹⁷O NMR spectra were obtained with different NMR spectrometers operating at 8.45T, 11.7T and 14.4T corresponding to ¹⁷O frequencies of 48.8, 67.8 and 81.3 MHz respectively. Static and magic angle spinning (MAS) NMR spectra at 48.8 MHz were obtained using a 4 mm outside diameter Bruker MAS probe. All the ¹⁷O MAS NMR experiments at these fields were done with sample spinning rates of ~14 kHz. Since the line widths are very broad, relatively fast spinning speeds (>12kHz) were necessary in order to remove the spinning sidebands from the main peak. ¹⁷O MAS NMR spectra at 81.3 MHz were obtained using a 4 mm outside diameter CMX probe at a spinning speed of 12 kHz. Static and MAS spectra were recorded using a spin-echo pulse sequence, (90°-τ-180°-acquire), with τ the delay time between pulses, adjusted according to rotor spinning speed (ν_r, kHz), to be a whole number of rotor periods, (n/ν_r). The pulse width was ~1.3 μs (90°), corresponding to a 3.8 μs 90° pulse width for the H₂O reference with a recycle delay of typically 5s. Chemical shifts are reported in parts per million (ppm) from an external standard sample of tap water (H₂¹⁷O, natural abundance). Line broadenings in the range of 200–500 Hz for static and 100–200 Hz for MAS ¹⁷O NMR spectra were applied.

A DOR spectrum, while technically more demanding, is acquired in a one-pulse NMR experiment, which provides high-resolution spectra with fewer signal acquisitions than in the MAS experiment. The DOR probes used for these experiments were home built using a design detailed in reference [4]. The sample in a small rotor is spun inside a larger rotor whose spinning axis is inclined at the magic angle θ₁ = 54.74° with respect to the external field. The small rotor has its spinning axis oriented at higher order magic angle θ₂ = 30.56° with respect to the spinning axis of the larger rotor (Figure 2). Fourier transformation of a conventional one-dimensional FID gives the high resolution spectrum immediately. Comparison of spectra obtained at a variety of spinning speeds can help in the assignment of sidebands arising from the larger (outer) rotor.

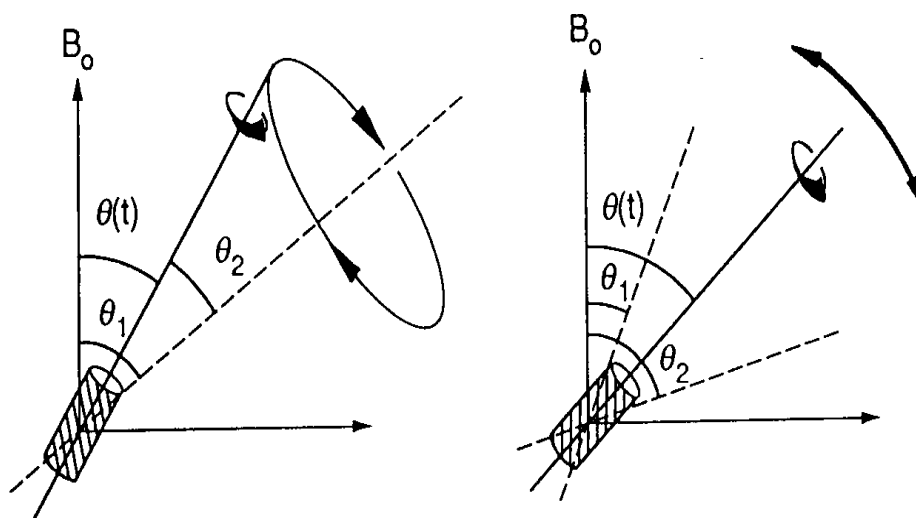


Figure 2 Schematic representation of the approaches for averaging second order interactions double rotation (DOR)

3.0 RESULTS AND DISCUSSION

Figure 3 shows the ^{17}O static NMR spectra of an enriched sample of crystalline $\text{Na}_4\text{Ge}_9\text{O}_{20}$ ($2\text{Na}_2\text{O} \cdot 9\text{GeO}_2$), obtained at different magnetic field strengths. At both fields, the static spectrum is quite broad and featureless and does not lead to a ready identification of the various nonequivalent oxygen sites. However, the ^{17}O MAS NMR spectrum of this phase clearly shows only two resolved peaks (Figure 4). The sum of the intensity of peak 2 and its side-bands is almost four times that of peak 1 and its respective side-bands, thus peak 2 almost certainly corresponds to 4 of the crystallographically near-equivalent oxygens O1, O3, O4, O5 in this system. In Figure 4 we show measurements at two different magnetic fields, together with the computer simulation. Values for the nuclear quadrupole coupling constant, C_Q , electric field gradient tensor asymmetry parameter (η), and isotropic chemical shift (δ_i) for each type of oxygen are given in Table 1.

Crystallographically inequivalent oxygen sites give rise to individual narrow lines in the DOR spectra at 14.1 T, as shown in Figure 5. Due to the presence of many peaks in the DOR spectra, isotropic shifts are distinguished from spinning sidebands by performing experiments at two or more spinning speeds. The spinning sidebands arise from the larger (outer) rotor. The DOR spectrum of sodium enneagermanate is consistent with a crystal structure having five inequivalent oxygens sites as shown in Figure 1. The observed isotropic shifts (δ_{obs}) for the resonances in the DOR spectra of crystalline sodium enneagermanate obtained at 11.7 T (67.8 MHz), and at 14.1 T (81.3 MHz) are given in Table 1.

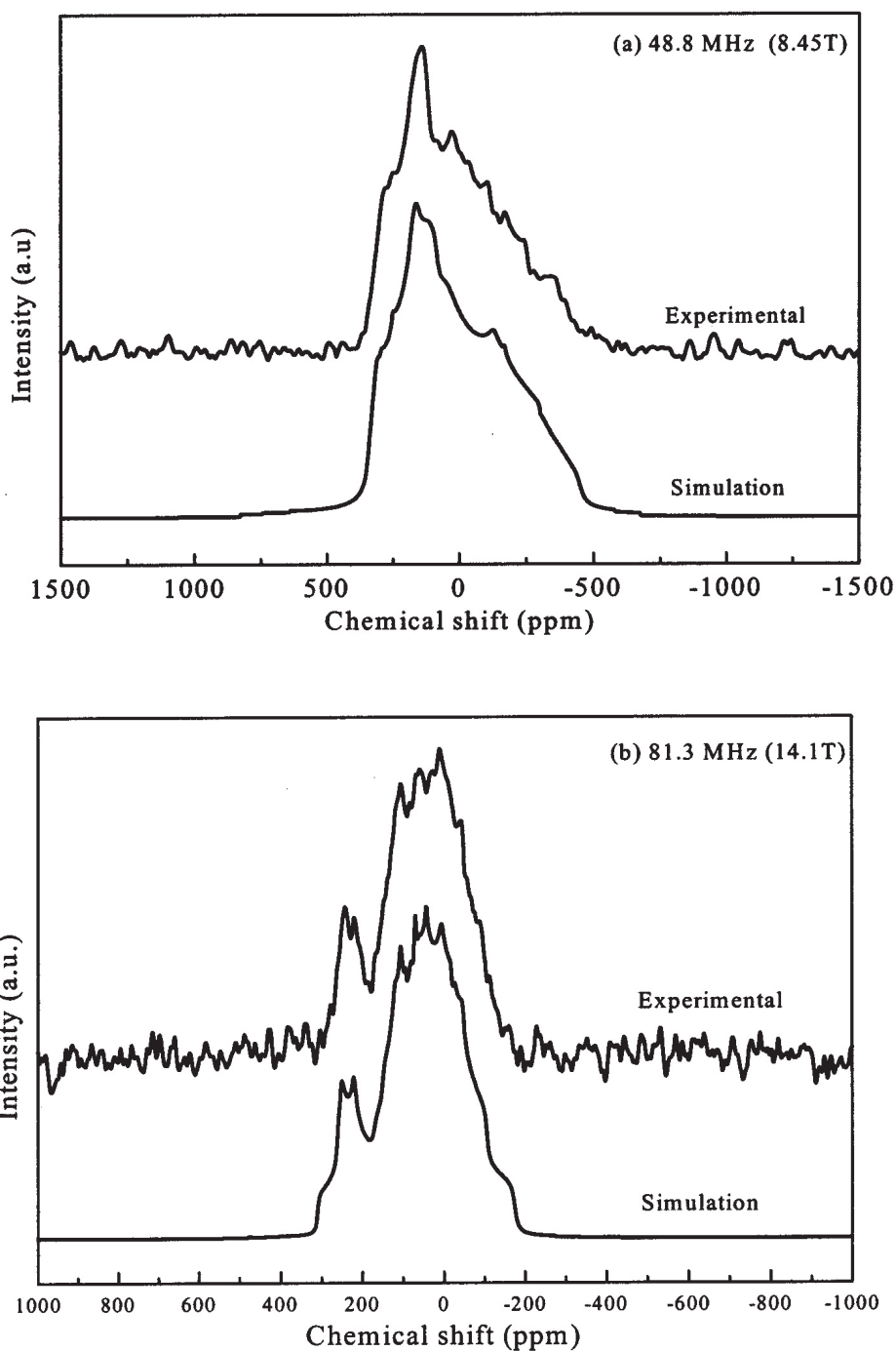


Figure 3 Experimental and simulated ^{17}O static NMR spectra of sodium enneagermanate obtained at 48.8 and 81.3 MHz respectively, without considering chemical shift anisotropy (CSA) in simulation

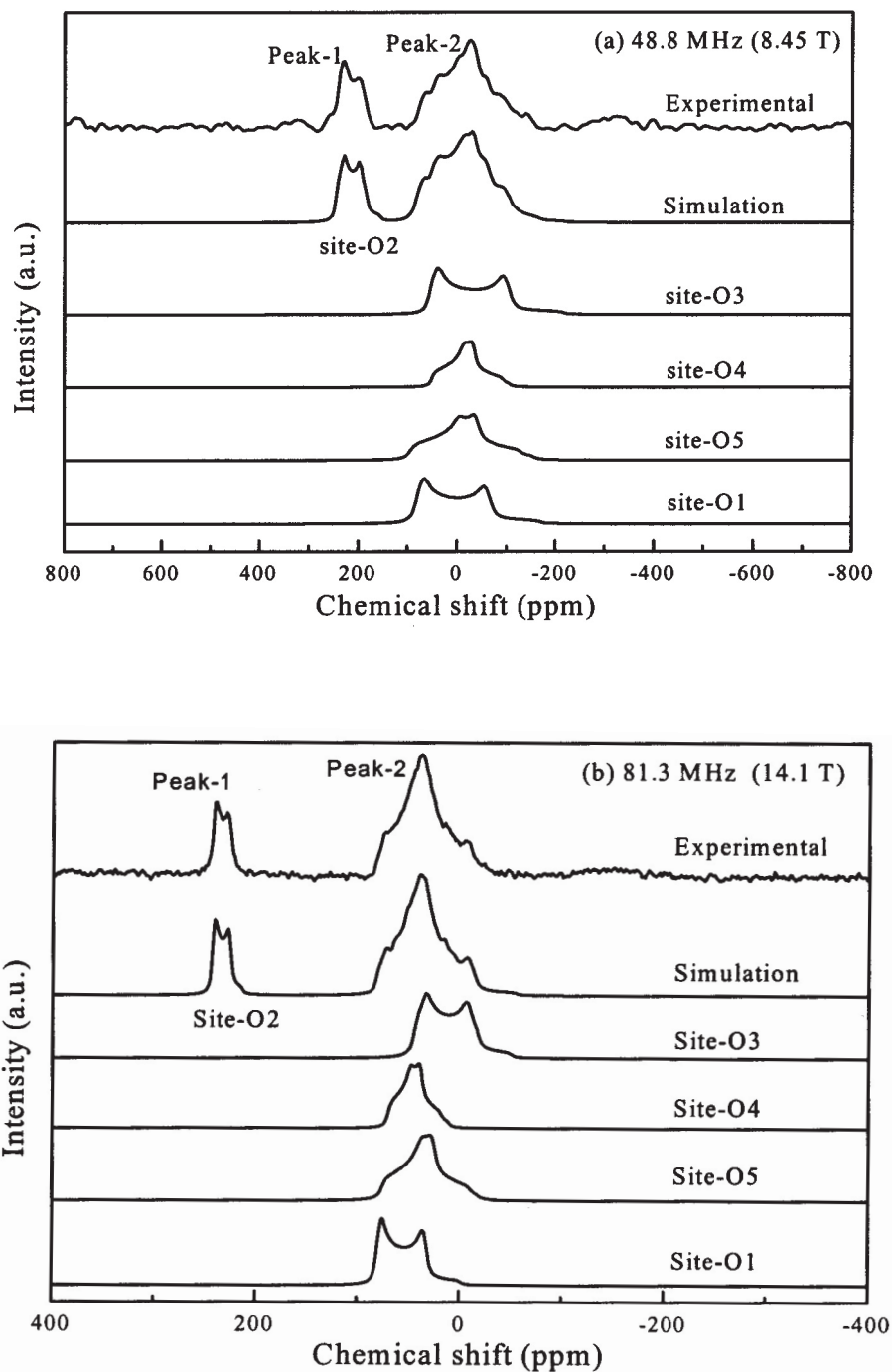


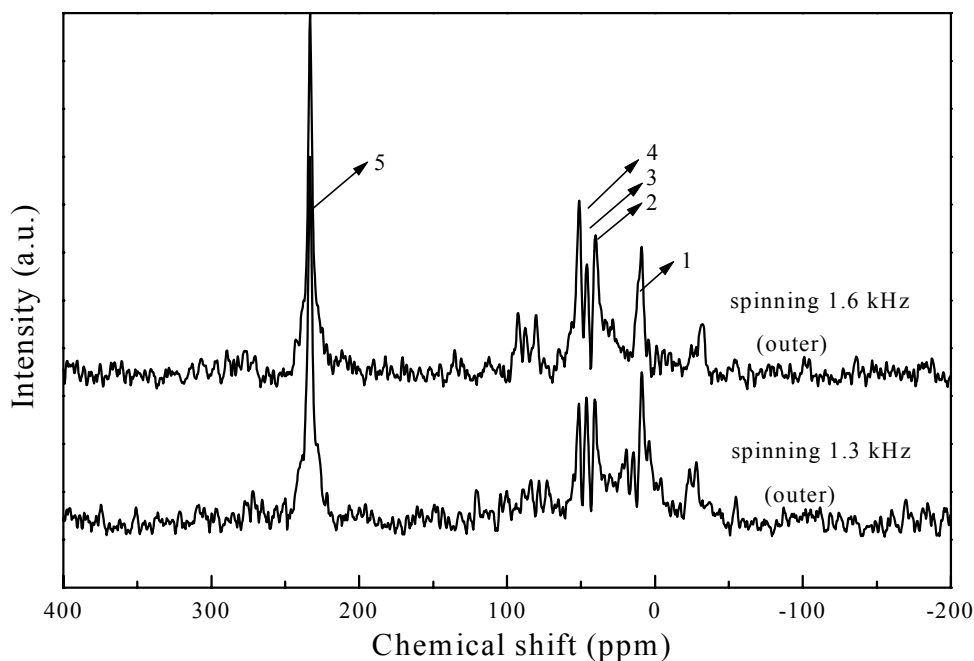
Figure 4 Experimental and simulated ^{17}O MAS NMR spectra of sodium enneagermanate obtained at 48.8 and 81.3 MHz. The sample spinning speed was 14 kHz

Table 1 ¹⁷O MAS NMR parameter; nuclear quadrupole coupling constants C_Q, asymmetry parameters (η), and isotropic chemical shifts (δ_i) for crystalline sodium enneagermanate [Na₄Ge₉O₂₀]

O Site	C _Q , MHz	η (0.1)	δ _i , ppm	δ _{obs} (ppm) 67.8* MHz	DOR 81.3 MHz	A-Ô-A angle(°)	Rel. int.
O2 (BO)	3.9 (±0.1)	0.2	250 (±2)	226.2 (±1)	235 (±1)	98.1	1
O4 (BO)	4.6 (±0.5)	0.7	67 (±2)	34.2 (±1)	44 (±1)	116.5	1
O5 (BO)	5.5 (±0.5)	0.8	72 (±2)	23.1 (±1)	38 (±1)	116.9	1
O1 (BO)	6.4 (±0.5)	0.1	87 (±2)	30.9 (±1)	48 (±1)	121.2	1
O3 BO)	6.7 (±0.5)	0.2	50 (±2)	-11.8 (±1)	7 (±1)	130.6	1

Note: The ¹⁷O static parameters (not shown) are somewhat in error because of the neglect of chemical shift anisotropy in the simulations.

* ¹⁷O DOR measurement at 11.7T were done by Dr. L. Bull and Dr. A. Samoson at Institute des Materiaux de Nantes, Laboratoire de Chimie des Solides, 2 rue de la Houssiniere, B.P. 32229, 44322 Nantes, Cedex 3, France.

**Figure 5** ¹⁷O DOR NMR spectra of sodium enneagermanate obtained at a magnetic field strength of 14.1 T (81.3 MHz)

Equations (eqs 4 and 5) may be solved for δ_{iso}^{CS} and P_Q , and the results were used to place constraints upon the simulations of MAS line shapes at both field strengths. The calculated line shapes are compared to the original MAS spectra in Figure 4. The best-

fit quadrupolar parameters and the isotropic chemical shift for each site are shown in Table 1.

The high-frequency “doublets” (with C_Q values of ~ 3.9 MHz) are assigned to the bridging oxygen sites and the other four lower frequency resonances to the other bridging oxygen sites. This assignment is in accord with the empirical relationship observed between the magnitude of the nuclear quadrupolar coupling constant and ionicity of the cation-oxygen bond [19,20]. According to Timken et al. [21] non bridging oxygens coordinated to divalent cations may be considered to be more ionic in nature than bridging oxygens, resulting in less π -orbital contribution to the electric field gradient and consequently smaller values of the quadrupole coupling constant.

In this crystalline compound, it is difficult to extract the quadrupole interaction parameters from the ^{17}O MAS NMR spectra alone, since accurate simulation of the line shapes of all the different O sites is not possible. The procedure adopted here is therefore to extract the quadrupole interaction parameters from the DOR measurement and then use them to simulate the MAS data which should provide accurate, undistorted quantitative information. The best simulations of the different oxygen sites are shown in Figure 4 and the parameters used summarised in Table 1. Although the simulations are not perfect they provide much less ambiguous estimates of the NMR interaction parameters than could be achieved from static NMR spectra. In the simulated MAS NMR spectra reasonably close agreement is achieved although some discrepancies do exist for example in the static NMR spectrum (Figure 3). There could be various reasons for this, for instance in the static case chemical shift anisotropy should be included. It is apparent from this data that an approach using parameters obtained by DOR experiments to aid simulation of MAS NMR spectra will provide accurate relative intensities in sodium enneagermanate crystalline materials. These spectra illustrate that the quadrupole interaction can be a very useful discriminator of structural units as it is largely on the basis of the differing C_{QS} that the four different units are distinguished here. These results illustrate that the combination of MAS and DOR and static experiments can provide significant structural detail on the sodium enneagermanate crystal.

Assignments of the five ^{17}O resonances to the five crystallographically distinct oxygen sites is based on the empirical correlation [22] that the ^{17}O quadrupolar coupling constant, C_Q , increases with increasing $A-\hat{\text{O}}-A$ angle ($A \equiv \text{Si, Ge}$), while the ^{17}O quadrupolar asymmetry parameter, η , decreases with increasing $A-\hat{\text{O}}-A$ angle [2,3,23]. Also useful is the variation of the isotropic chemical shift, δ_{iso} and bond angle based on observation of crystalline silicate systems and germania polymorphs. One of the oxygen sites (O2) in sodium enneagermanate is distinguished by its small C_Q (3.9 MHz) and the large δ_{iso} values (250 ppm). These are extreme values compared with those in all known silicates [2,8,23-27]. From the crystal structure as shown in Figure

1(d) and value of η (which is ~ 0.2 very close to an axially symmetric environment) the signal near 250 ppm must correspond to the crystallographic site O2 (98.1°). The O site with the biggest bridging angle, O3 (130.6°), is assigned to the resonance near 50 ppm. In this case (Figure 1(e)), the O3 site is a normal BO ($^{[4]}\text{Ge-O-}^{[4]}\text{Ge}$), and its δ_{iso} and C_Q values are both in the range of normal BO in other silicates. The remaining three crystallographic sites are unique to sodium enneagermanate, containing mixed four-fold and six-fold coordinated Ge (Figure 1(f-h)), and may be partially assigned by assuming that the site with bridging bond angle, O1 (121.2°) is assigned to the resonance near 87 ppm, which has the smallest asymmetry parameter and biggest quadrupolar coupling constant. The remaining two sites, with almost identical bridging bond angles, O4 (116.5°) and O5 (116.9°), could correspond to the peaks near 67 and 72 ppm, respectively, on the basis of their quadrupolar coupling parameters. However, the distinction between these two sites (O4 and O5) is uncertain.

In the silicate system, as already discussed by Xue et al.[2], the different types of O sites can be distinguished by one or both of the two parameters. NBO are characterized by small C_Q values (approximately 2.3 MHz). The δ_{iso} values of NBO are very sensitive to the type of network-modifying cations, and a larger cation causes a more positive δ_{iso} . BO and $^{[4]}\text{Si-O-}^{[4]}\text{Si}$ sites have similar C_Q values (4.5-5.7 MHz), which are intermediate between those of NBO and $^{[3]}\text{O}$ (Rutile- SiO_2). It has also been shown previously [2,8] that the δ_{iso} and C_Q values of BO are relatively insensitive to the type of network modifiers compared with those of NBO.

Finally, from the MAS simulations at the two fields, the values for the asymmetry parameter, η , at each of the four sites in sodium enneagermanate were determined (Table I). This provides additional information above and beyond the coupling product, P_Q . It also allows us to determine with greater precision the value of the actual quadrupolar coupling constants C_Q , giving a quantitative description of the strength the field gradient at each site. Further, O2 sites in the sample have asymmetry parameters near zero, indicating that the x and y gradients are of approximately the same strength.

4.0 CONCLUSION

By performing field-dependent ^{17}O DOR and magic angle spinning (MAS) experiments, we have resolved and assigned all five oxygen sites in sodium enneagermanate crystal. The results we have presented above indicate that solid state ^{17}O nuclear magnetic resonance spectroscopy can be used to determine in many cases the isotropic chemical shifts, nuclear quadrupole coupling constants and electric field gradient (efg) tensor asymmetry parameters for each of the types of non-equivalent oxygen in germanate based glasses. Crystalline studies of sodium enneagermanate is one of the structural data for confirming the correlations between the measured ^{17}O quadrupolar coupling parameters and the oxygen environment. These results also

provide a check on the correlations between the Ge- \hat{O} -Ge bond angle and ^{17}O quadrupolar parameters, although a larger database is needed in the alkali germanate system to further refine the application of ab initio or Townes-Dailey approaches to ^{17}O electric field gradient tensor calculations in silicates so that these can be used in germanates. The result of these studies should provide insight to future investigation using ^{17}O solid state NMR to study the structure of other oxide glasses as well as other germanate-based glasses.

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