Solid-state NMR studies of $^{17}$O-enriched pyrophosphates

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Abstract

For the first time, $^{17}$O NMR studies were performed on $^{17}$O-enriched crystalline pyrophosphates (magnesium-, sodium- and barium-pyrophosphate) by means of triple-quantum magic-angle spinning (3QMAS) and double-rotation (DOR) in the high external field of 17.6 T. Oxygen atoms in bridging positions (P–OB–P) exhibit a significant higher quadrupole coupling constant compared to oxygen atoms in terminal positions (P–OT). With increasing cationic radius a higher value of the chemical shift of the terminal oxygen atoms is observed.

$^{17}$O NMR spectroscopy meets the problem that the natural $^{17}$O abundance is only 3.7\%\,/, the magnetogyric ratio is low ($\gamma/2\pi = 5.77\text{MHz}\,/\text{T}^{-1}$) and the quadrupolar interaction of the spin-5/2-nuclei broadens the signal. It requires the enrichment of the framework by $^{17}$O and the application of narrowing techniques-like double-rotation (DOR), multiple-quantum magic-angle spinning (MQMAS), or satellite transition (ST) MAS [5]. These narrowing techniques and high magnetic fields are the base of numerous recent $^{17}$O NMR studies in inorganic materials [6–8]. For some inorganic materials-like zeolites [9] or phosphorous glasses [10], correlations between structural and $^{17}$O NMR parameters could be found. Already Schramm et al. [11] established for inorganic oxides an empirical correlation between the ionicity of the metal–oxygen bonding and the quadrupole coupling constant $C_q$. But only very few $^{17}$O NMR studies of crystalline phosphates exist until now [12,13], and no $^{17}$O NMR studies on crystalline polyphosphates are known to us. Pyrophosphates are the simplest polyphosphates and have therefore been chosen for the present study, in order to investigate, whether relations exist between structural and $^{17}$O NMR parameters.

The present study shows the usefulness and the limitations of the application of the solid-state $^{17}$O NMR to some more crystalline materials, which were enriched in $^{17}$O during the synthesis. A $^{17}$O NMR-comparison between solid sodium pyrophosphate and sodium pyrophosphate in aqueous solution (which can be investigated at natural abundance of $^{17}$O) showed that the investigation

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of a solution does not give information about the solid material [14].

2. Materials and methods

2.1. Preparation

The synthesis of the investigated samples was performed by using water 20% enriched in $^{17}$O. Like $^{17}$O-enriched water all sources of $^{17}$O are very expensive, therefore a suitable synthesis had to fulfill the following conditions: (i) low-scale (mg) synthesis to provide the filling of a 4 mm probe (ca. 150 mg); (ii) stoichiometric reaction to avoid losses of enriched material; (iii) no use of natural abundant oxygen containing reactants to protect the starting level of losses of enriched material; (iv) absence of impurities as (acid) monophosphates $\text{Me}_2\text{P}_{(n+2)}\text{O}_7$ with ($0 < x < 2$) or polyphosphates $\text{Me}_2\text{P}_{(n+2)}\text{O}_{(3n+1)}$ with $n > 2$.

Preliminary synthesis experiments using simple direct exchange between non-enriched pyrophosphates and $\text{H}_2^{17}$O failed as solid–gas reaction as well as in aqueous solution. Therefore it was indispensable to prepare the $^{17}$O-enriched pyrophosphates starting from enriched phosphoric acid. Exploiting the volatility of $\text{HCl}$ the stoichiometric hydrolysis reaction of $\text{PCl}_3$

$$4\text{H}_2^{17}\text{O} + \text{PCl}_3 \rightarrow \text{H}_3\text{P}_{17}\text{O}_4 + 5\text{HCl} \uparrow$$

yields pure, viscous phosphorous acid $\text{H}_3\text{P}_{17}\text{O}_4$. The second step was the introduction of the cation, the obvious use of (non-enriched) oxides and hydroxides is not feasible because of the depletion of $^{17}$O. The way out was the use of metals (Mg, Ba) or azide (Na$_3$N) according to

$$2\text{Mg} + 2\text{H}_3\text{PO}_{17}\text{O}_4 \rightarrow \text{Mg}_2\text{P}_{2}^{17}\text{O}_7 + 2\text{H}_2 \uparrow + \text{H}_2^{17}\text{O} \uparrow,$$

$$2\text{Ba} + 2\text{H}_3\text{PO}_{17}\text{O}_4 \rightarrow \text{Ba}_2\text{P}_{2}^{17}\text{O}_7 + 2\text{H}_2 \uparrow + \text{H}_2^{17}\text{O} \uparrow,$$

$$4\text{Na}_3\text{N} + 2\text{H}_3\text{PO}_{17}\text{O}_4 \rightarrow \text{Na}_4\text{P}_{2}^{17}\text{O}_7 + 2\text{H}_2 \uparrow + \text{H}_2^{17}\text{O} \uparrow + 6\text{Na}_2 \uparrow.$$  

Even in the mg-scale the hydrolysis of $\text{PCl}_3$ as well as metal–acid reactions are very violent and bring along the danger of losses of material. As a last step, the volatile reaction products were expelled by heating, the loss of $1/8$ of the used $\text{H}_3^{17}\text{O}$ is acceptable. In order to have all reactions at any time under control, the consecutive steps were frequently practiced using non-enriched materials. The identity and purity of the final products were checked by liquid state $^{31}$P-NMR spectroscopy as well as by XRD powder diffraction. Carefully prepared samples contained >95% of the expected crystalline pyrophosphate [14].

2.2. Crystal structures of pyrophosphates

Pyrophosphates are the simplest examples of polyphosphates consisting of two PO$_4$-tetrahedrons connected via a P–O–P–P bridge. The negative charge of the P$_2$O$_7^{3-}$-anion is compensated by univalent and bivalent cations. The crystal structures of the pyrophosphates under investigation are well known and were determined using X-ray diffraction by Leung and Calvo [15] for Na$_4$P$_2$O$_7$, Calvo [16,17] for $\alpha$-$\beta$-Mg$_2$P$_2$O$_7$, and ElBelghitti et al. [18] for $\sigma$-Ba$_2$P$_2$O$_7$.

From these X-ray data, the angles of the P–O–P–P bridge can be derived: 127.5° (Na$_4$P$_2$O$_7$), 144.0° ($\alpha$-Mg$_2$P$_2$O$_7$) and 180.0° ($\beta$-Mg$_2$P$_2$O$_7$), respectively. For $\sigma$-Ba$_2$P$_2$O$_7$, the two bond angles 130.0° and 134.0° are given. A detailed view on the crystal structures can be found in Ref. [18].

2.3. NMR experiments

$^{17}$O NMR and $^{31}$P NMR experiments were performed on Bruker Avance 750 and Bruker MSL 500 spectrometers operating at a field of $B_0 = 17.6$ and 11.7 T, respectively. MAS-spectra were recorded at spinning frequencies varying in the range from 4 to 30 kHz. For DOR experiments a DOR probe purchased by the Institute of Chemical Physics in Tallinn and for MQMAS experiments 4 mm Bruker MAS probes were used. $^{17}$O NMR and $^{31}$P chemical shifts are related to external standard references (see [19]). In $^{31}$P MAS NMR-experiments a preparation-pulse-width of 0.5μs was used. $^{17}$O MAS NMR experiments were performed with nutation frequencies between 80 and 120 kHz. The $\pi$-filter pulse sequence [20] including States [21] was applied for triple-quantum magic-angle spinning (3QMAS) experiments. The time in F1 dimension was increased in steps of the reciprocal spinning frequency to avoid spinning sidebands. The programs XfShear [22] and DORFIT [23] were used for the shearing of the 2D 3QMAS-spectra and simulation of the anisotropic lineshape, respectively. DOR spectra were acquired with odd side-band suppression [24], nutation frequency of 25 kHz and rotation frequency of the external rotor between 900 and 1400 Hz. For referencing of the MQMAS spectra we used the shift convention given in Ref. [25].

3. Results

3.1. Characterization of the $^{17}$O-enriched pyrophosphates by $^{31}$P NMR

In the case of Na$_4$P$_2$O$_7$ and Mg$_2$P$_2$O$_7$, the $^{17}$O-enriched material (Fig. 1) and the shielding tensors obtained from the spectra were compared with corresponding results from polyphosphates obtained by a usual synthesis [2]. We found a good agreement (see Table 1). The quantitative analysis of the $^{31}$P NMR spectra yields only for sodium pyrophosphate another unknown phase with a concentration of about 4%. This was also confirmed by X-ray diffraction data of all materials [14], which were compared with data from the literature [26].

3.2. $^{17}$O NMR of sodium pyrophosphate, Na$_4$P$_2$O$_7$

The $^{17}$O DOR NMR spectrum of the crystalline $^{17}$O-enriched sodium pyrophosphate consists of three signals
The relative intensities of the signals at 71.0, 75.8, and 101.1 ppm are 50%, 35%, and 15%, respectively.
The 3QMAS experiment (Fig. 3a) yield a lower resolution and only two signals at 87.1 and 90.5 ppm.
Quadrupole parameter and the isotropic value of the chemical shift were determined by a fit of the MAS spectrum (Fig. 2c) taking into account the shift values obtained by DOR and 3QMAS. It results a mean quadrupole coupling constant of $C_{qcc} = 3.9$ MHz for the terminal oxygen atoms and a value of 7.3 MHz for the bridging oxygen atoms (Table 2).

### 3.3. 17O NMR of magnesium pyrophosphate, $\alpha/\beta$-Mg$_2$P$_2$O$_7$

$^{17}$O MAS NMR spectra were measured in the temperature range 188–375 K (Fig. 3), but no significant variations of the spectra upon temperature change could be observed [14]. The fit of the 3QMAS spectra (see Fig. 4b), which were measured at room temperature, yield only one signal with the parameters $\delta_{\text{iso}} = 83.7$ ppm, $C_{qcc} = 5.15$ MHz, and $\eta_{\text{r}} = 0.41$. $^{17}$O DOR experiments in the fields of $B_0 = 17.4$ T (Fig. 2b) and $B_0 = 11.7$ T [14] also yield only one signal with $\delta_{\text{iso}} = 83.7$ ppm and $P_Q = 5.29$. The quadrupole parameter $P_Q$ is defined as $P_Q = C_{qcc}(1 + \eta_{\text{Q}}^2/3)^{1/2}$.

### 3.4. 17O NMR of barium pyrophosphate, $\sigma$-Ba$_2$P$_2$O$_7$

The $^{17}$O 3QMAS NMR spectrum of Ba$_2$P$_2$O$_7$ (Fig. 5) shows the strong signal of terminal oxygen atoms (O$_T$) with an isotropic shift at $\delta_{\text{3QMAS}} = 147.6$ ppm, the weak signal at $\delta_{\text{3QMAS}} = 157.8$ ppm, and a very weak signal with $\delta_{\text{3QMAS}} = 150.8$ ppm. The latter were assigned to bridging oxygen atoms (O$_B$). For the signal O$_T$ we obtain an isotropic chemical shift $\delta_{\text{iso}} = 141.3$ ppm and a coupling constant $C_{qcc} = 4.19$ MHz. For the signals O$_B$ we obtain $\delta_{\text{iso}} = 142.9$ ppm and $C_{qcc} = 7.25$ MHz. The intensity of the signal O$_T$ corresponds to the 6.2-fold of the intensity of the signals O$_B$. The intensity was determined from the isotropic projection, in which the very weak signal is superimposed over the strong signal. The quadrupole parameter of the very weak signal (Figs. 2a and 5) could not be obtained from the 3QMAS slice. We combined the DOR position of this signal with the 3QMAS data, in order to obtain the isotropic chemical shift and the parameter $P_Q$ (see Table 2).

It is remarkable that the symmetry axis of signal O$_T$ in the 3QMAS spectrum of Ba$_2$P$_2$O$_7$ (Fig. 5) has a slope of one which corresponds exactly to the slope of the axis of

### Table 1

$^{31}$P shielding tensors of $^{17}$O-enriched pyrophosphates

<table>
<thead>
<tr>
<th>Phosphate</th>
<th>$\sigma_{\text{iso}}$ (ppm)</th>
<th>$\Delta\sigma$ (ppm)</th>
<th>$\eta_{\text{r}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$-Mg$_2$P$_2$O$_7^{17}$O</td>
<td>13.4(14.0)</td>
<td>−95.0(−98.0)</td>
<td>0.35(0.38)</td>
</tr>
<tr>
<td>$\beta$-Mg$_2$P$_2$O$_7^{17}$O</td>
<td>19.6(20.0)</td>
<td>−110.9(−128.0)</td>
<td>0.25(0.38)</td>
</tr>
<tr>
<td>Na$_4$P$_2$O$_7^{17}$O</td>
<td>18.6(19.1)</td>
<td>−103.0</td>
<td>0.00</td>
</tr>
<tr>
<td>$\sigma$-Mg$_2$P$_2$O$_7^{17}$O</td>
<td>−2.1(−1.5)</td>
<td>−130.6(125.9)</td>
<td>0.00(0.00)</td>
</tr>
<tr>
<td>$\beta$-Mg$_2$P$_2$O$_7^{17}$O</td>
<td>−2.7(−2.7)</td>
<td>−130.6(125.9)</td>
<td>0.00(0.00)</td>
</tr>
<tr>
<td>Ba$_2$P$_2$O$_7^{17}$O</td>
<td>8.6</td>
<td>−121.1</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
<td>−103.8</td>
<td>0.30</td>
</tr>
</tbody>
</table>

The data of pyrophosphates obtained by usual synthesis [2] are given in brackets.
the chemical shift. This hints to a distribution of isotropic values of the chemical shift. Without such a distribution we should find the symmetry axis parallel to the isotropic axis (see [14]).

4. Discussion

The DOR spectrum of sodium pyrophosphate (Fig. 2c), consists of two strong signals at 71.0 and 75.8 ppm and one weak signal at 101.1 ppm with intensities of 50%, 35%, and 15%, respectively. Dividing the sum of the stronger signals by the weaker signal gives $85/15 \approx 5.7$. This agrees well, in the limits of the experimental error, with the relation $6/1$ of terminal to bridging oxygen atoms, which can be derived from the crystallographic structure of sodium pyrophosphate [15]. The non-equivalent terminal oxygen atoms do not significantly vary with respect to P–O$_T$ bonding lengths [15]. But differences in the coordination of the four

Fig. 2. $^{17}$O DOR and MAS NMR ($v_{rot} = 30$ kHz) spectra of: Ba$_2$P$_2$O$_7$ (a), Mg$_2$P$_2$O$_7$ (b) and Na$_4$P$_2$O$_7$ (c) at $T = 293$ K ($B_0 = 17.4$ T).

Fig. 3. Temperature dependent $^{31}$P und $^{17}$O MAS NMR spectra of $\alpha$-/\$\beta$-Mg$_2$P$_2$O$_7$ at $v_{rot} = 10$ kHz ($B_0 = 11.7$ T).
non-equivalent sodium ions can explain the two signals of terminal oxygen atoms. The $^{23}$Na DOR spectrum consists of four signals with identical intensity [14]. Na(1), Na(2), and Na(3) are similarly coordinated to all terminal oxygen atoms [15]. But Na(4) has a stronger coordination to one of the both PO$_4$-tetrahedra [15]. The higher sodium coordination of one of the both PO$_4$-tetrahedra explains the two signals of terminal oxygen atoms. The assignment of the weak signal at 101.1 ppm to bridging oxygen atoms is supported by their large range of spinning sidebands that is connected with the larger quadrupole coupling constant (see Table 2).

Magnesium pyrophosphate has different phases. At the lower temperature ($T = 188\,\text{K}$) is the $\alpha$-phase, at room temperature ($T = 293\,\text{K}$) we have both phases, whereas at higher temperature ($T = 375\,\text{K}$) only the $\beta$-phase exists. $^{31}$P MAS NMR studies [14] confirmed that at room temperature for spinning frequencies $n_{\text{rot}} \leq 10\,\text{kHz}$ the concentration of both phases are about equal. Calvo determined the P–OB–P angle of 144$^\circ$ for the $\alpha$-phase [16] and of 180$^\circ$ for the $\beta$-phase [17]. Thus we would expect two OB-signals at room temperature and different OB-signals at $T = 214\,\text{K}$ ($\alpha$-phase) and at $T = 330\,\text{K}$ ($\beta$-phase). But all $^{17}$O DOR and $^{17}$O 3QMAS spectra of magnesium pyrophosphate in this temperature range show only the signal of terminal oxygen atoms.

IR studies [27] show the occurrence of a symmetric bonding vibration of the P–OB–P bridge which hints to a non-linear diphosphate group. The given P–OB–P angle of 180$^\circ$ for $\beta$-Mg$_2$P$_2$O$_7$ [17] can explained as a value obtained by a motion average over the two angles (180$^\circ$ – $\Delta^\circ$ and (180 + $\Delta^\circ$). The line narrowing by MAS fails, if the jump frequency between two positions becomes about equal to the MAS frequency. This could explain the absence of the OB signal in the spectra.

The significant difference of the barium pyrophosphate spectra with respect to those of sodium or magnesium pyrophosphate is the strong broadening of the signal of terminal oxygen atoms in the $^{17}$O DOR spectrum (see Fig. 2a). This can be explained by a distribution of isotropic values of the chemical shift in the following way: The P–P axis of the P$_2$O$_7^-$ ions has a $C_3$-symmetry [18]. Three bridging oxygen positions with an occupation of 1/3

<table>
<thead>
<tr>
<th>Phosphate</th>
<th>Cation radius (pm)</th>
<th>$\delta_{\text{iso}}$ (ppm) O$_T$</th>
<th>$\delta_{\text{iso}}$ (ppm) O$_B$</th>
<th>$C_{\text{iso}}$ (MHz) O$_T$</th>
<th>$C_{\text{iso}}$ (MHz) O$_B$</th>
<th>$\eta_Q$ O$_T$</th>
<th>$\eta_Q$ O$_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$P$_2$O$_7$</td>
<td>72</td>
<td>82.9</td>
<td>—</td>
<td>5.27</td>
<td>—</td>
<td>0.40</td>
<td>—</td>
</tr>
<tr>
<td>Na$_4$P$_2$O$_7$</td>
<td>102</td>
<td>85.7(1) 134.3</td>
<td>3.90(1) 7.30</td>
<td>0.60(1) 0.55</td>
<td>0.60(2) 0.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba$_2$P$_2$O$_7$</td>
<td>132</td>
<td>141.3 142.9(1) 134.9(2)</td>
<td>4.19 7.25(1) 6.82(2)</td>
<td>0.26 0.15(1)</td>
<td>0.10(2) 0.00(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$P$_Q$—parameter ($\eta_Q = 0$ assumed).
exist for the P-O-P angles of 130° and 134° [18]. This causes a distortion of the symmetry of the terminal oxygen atoms. The resulting distribution of isotropic values of the chemical shift broadens the signal in the DOR spectrum and causes the tilting of the symmetry of the O_T signal in the two-dimensional 3QMAS spectrum (see Fig. 5).

Our 17O NMR studies of low silicate zeolites (Si/Al = 1) [9] yield a correlation between the isotropic value of the chemical shift δ_iso and the Si–O–P–Al bond angle α: δ_iso/ppm = −0.65α/° + 134.0. For these zeolites the chemical shift increases, if the bond angle decreases. The tendency is opposite for the bridging oxygen atoms of the sodium and barium pyrophosphate (see Table 2). There is also no correlation between shift values and bond angles, if we compare the data of the pyrophosphates under study with data obtained from Na2–P2O5 glasses [10]. Thus, a correlation between the isotropic value of the 17O chemical shift and the oxygen bond angle could not be found for phosphates.

Turner et al. [28] observed in alkaline earth oxides that the value of the 17O-chemical shift rises with increasing cation radius. For the cation radii of the two alkaline-earth pyrophosphates examined here Turner et al. [28] give the values r(Mg) = 65 pm and r(Ba) = 135 pm, respectively. The corresponding values of the 17O-chemical shift determined here, are δ_iso(Mg) = 82.9 ppm and δ_iso(Ba) = 141.3 ppm, respectively. Thus, this trend is also observable on the terminal oxygen atoms of the two examined alkaline-earth pyrophosphates (Mg3P2O7 und Ba2P2O7), but much weaker than in alkaline-earth oxides.

As already shown in our investigations of LSX zeolites [9] the increasing value of isotropic chemical shift with increasing mass-to-charge ratio of the cation can be explained as follows: A charge transfer between the terminal oxygen atoms O_T of the pyrophosphate anions and the facing cations is the larger, the smaller the distance is between the terminal oxygen atoms and the cations. Since the distance increases with rising cation radius, a smaller charge transfer from the terminal oxygen atoms to the cations takes place with increasing radius of the cation. This smaller charge transfer results in a strengthened electron charge at the oxygen atom and causes a larger chemical shift (increase of δ).

5. Conclusions

The identity and purity of all 17O-enriched pyrophosphates were checked by liquid state 31P NMR spectroscopy as well as by XRD powder diffraction. XRD confirmed that the amount of impurities is smaller than 5%. The determined values of the 31P shielding tensor of 17O-enriched Na4P2O7 and Mg2P2O7 agree with those determined in the natural pyrophosphates. The chemical shift of the terminal oxygen atoms of the examined alkaline earth pyrophosphates shifts with rising cation radius to larger ppm-values and thus, shows a simple dependence on the inserted cation. The quadrupole coupling constants of the terminal oxygen atoms are significantly smaller than those of the bridge oxygen atoms. Compared with the isotropic 3QMAS-spectra the DOR spectra exhibit a higher resolution.

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References