

Phase Transitions in KNO_3 Studied by Variable-Temperature ^{15}N Magic-Angle Spinning NMR Spectroscopy

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The phase transitions within the three phases of potassium nitrate (α -, β -, and γ - KNO_3) have been investigated in detail by variable-temperature (VT) ^{15}N magic-angle spinning (MAS) NMR spectroscopy employing 98% ^{15}N -enriched KNO_3 . The stability of the metastable γ - KNO_3 phase is found to be highly influenced by the thermal history of the sample, i.e., by the number of heating cycles into the high-temperature β - KNO_3 phase at 160°C . Furthermore, the spectral appearance for the room-temperature α - KNO_3 phase is found to change after excursions of the sample into the high-temperature β - KNO_3 phase, an observation similar to that made in a recent VT synchrotron X-ray powder diffraction study. © 1999 Academic Press

INTRODUCTION

Potassium nitrate KNO_3 , an important chemical with many industrial uses, exhibits a number of different phases at atmospheric pressure (1). On heating, the room-temperature phase α - KNO_3 is converted to β - KNO_3 at approximately 127°C (400 K). On cooling of β - KNO_3 this phase has been observed to transform into a metastable phase γ - KNO_3 at about 124°C (397 K) (1). On further cooling, the metastable γ - KNO_3 phase is reported to transform to α - KNO_3 at approximately 100°C (373 K). However, the lifetime of γ - KNO_3 and its transition temperature back to α - KNO_3 strongly depends on the thermal history of the KNO_3 sample and on the cooling rate (1,2).

In a recent investigation Christensen *et al.* (2) employed variable-temperature synchrotron X-ray powder diffraction to monitor the phase transitions for KNO_3 in an elegant manner and with special attention being paid to the γ to α -phase transition. Furthermore, the temperature dependence of this transition and of the existence of the γ phase was studied in detail and shown to be strongly affected by the thermal history of the sample. In addition, their study revealed that a number of reflections observed for the α - KNO_3 starting material disappeared after the sample had been heated through the first cycle into the β -phase. Several other methods have been employed to study the transitions

and structure of the different phases for KNO_3 . These include X-ray diffraction (XRD) (1,3,4), neutron diffraction (5), Raman spectroscopy (6), acoustic emission, and microscopic observations (7). The Raman work suggests the presence of disordered NO_3^- groups on alternating lattice sites in the α phase. This observation was used to explain the unexpected results of the neutron diffraction studies that the NO_3^- groups are approximately 1° off the ab plane (5).

Solid-state NMR spectroscopy has proven a useful tool in studies of phase transitions for organic and inorganic solids because even small changes in crystal structures and/or molecular dynamics are reflected as changes in the parameters for the anisotropic interactions, e.g., the shielding tensor elements (spin $I = 1/2$ nuclei) or quadrupole coupling parameters (spin $I > 1/2$ nuclei). In high-resolution magic-angle spinning (MAS) NMR spectroscopy, where complete averaging of the chemical shielding anisotropy for spin $I = 1/2$ nuclei is often observed, phase transitions may be detected solely from abrupt changes in the isotropic chemical shifts. For example, this is the case in the recent solid-state ^{15}N NMR study of the phase transitions in ammonium nitrate (8,9).

Prompted by the synchrotron powder XRD study (2) we report here the results of a variable-temperature (VT) ^{15}N MAS NMR investigation of the phase transitions in KNO_3 . Special attention has been paid to the observation of the metastable γ - KNO_3 phase and the transitions involving this phase. Finally, the initial detection and disappearance of some anomalous reflections in the synchrotron XRD patterns of α - KNO_3 following temperature cycling between the α and β phase (2) also attracted our interest during the VT MAS NMR study.

EXPERIMENTAL

^{15}N -enriched (99% ^{15}N) K^{15}NO_3 was purchased from Isotec Inc. and used without further purification. ^{15}N MAS NMR spectra was recorded on a Varian XL-300 spectrometer using a homebuilt 7 mm VT high-speed MAS NMR probe capable of operating in the temperature range of

approximately -120°C (153 K) to 210°C (483 K). The stator design is quite similar to that described elsewhere (10); however, the VT stator is produced from ceramic materials. K^{15}NO_3 was packed into a 7-mm o.d. (5 mm i.d.) Si_3N_4 rotor (11.5 mm long sample volume) by inserting it between 2-mm layers of unlabeled KNO_3 at the top and bottom to reduce magnet inhomogeneity and the temperature gradient over the sample along the rotor axis. The ^{15}N MAS NMR spectra were acquired employing a spinning frequency of 3.3 kHz, a pulse width of $14\ \mu\text{s}$ corresponding to a flip angle of 90° , a spectral width of 50 kHz, and an acquisition time of 81 ms. The ^{15}N T_1 relaxation time for the α - KNO_3 phase was found to be on the order of hours, while for the β - KNO_3 phase it is somewhat shorter. Thus only one scan was acquired for each spectrum or at each temperature and at least a 30-min repetition delay was used between acquisition of spectra. The observed ^{15}N line widths are extremely narrow and are approximately 10 Hz for the α -phase and 13 Hz for the β -phase. Line positions are referenced to the $^{15}\text{NH}_4^+$ resonance for an external sample of NH_4NO_3 at 24°C (297 K).

Heating the sample was done by employing hot air-bearing gas only to the stator; i.e., the air-drive gas is kept at ambient temperature for all VT experiments. For this purpose we used a homebuilt heater and VT control system, based on a microprocessor CAL 3200 Autotune temperature controller, an instrumentation which will be described in detail elsewhere. Using this setup the temperature of the air-bearing gas, which is monitored just 3 cm from the inlet to the stator, can be maintained within $\pm 0.2^\circ\text{C}$. However, since we have shown earlier that frictional heating caused by MAS can greatly influence the temperature of the sample (11), we have measured the actual sample temperature within $\pm 1^\circ$ by calibration with a sample of $\text{Pb}(\text{NO}_3)_2$ (12). Experiments with $\text{Pb}(\text{NO}_3)_2$, performed under identical conditions as for K^{15}NO_3 reveal that the temperature gradient along the rotor axis for the restricted K^{15}NO_3 sample volume increases from 0.2 to 2.0 K in the temperature range from 21°C (294 K) to 110°C (383 K). In the temperature range from 110°C (383 K) to 130°C (403 K) we observe the temperature gradient to be approximately 2.5 K.

RESULTS AND DISCUSSION

The ^{15}N MAS NMR spectrum at ambient temperature (24°C) for a “fresh” sample of K^{15}NO_3 , i.e., taken directly from the sample container of the supplier, is shown in Fig. 1a. This spectrum of α - KNO_3 appears with its main peak at 360.5 ppm (line width of about 10 Hz) and a significant shoulder to high frequency, the shoulder almost assumes the character of an additional line at approximately 361.1 ppm. It may be argued that the shoulder is caused by a temperature gradient within the sample similar to the

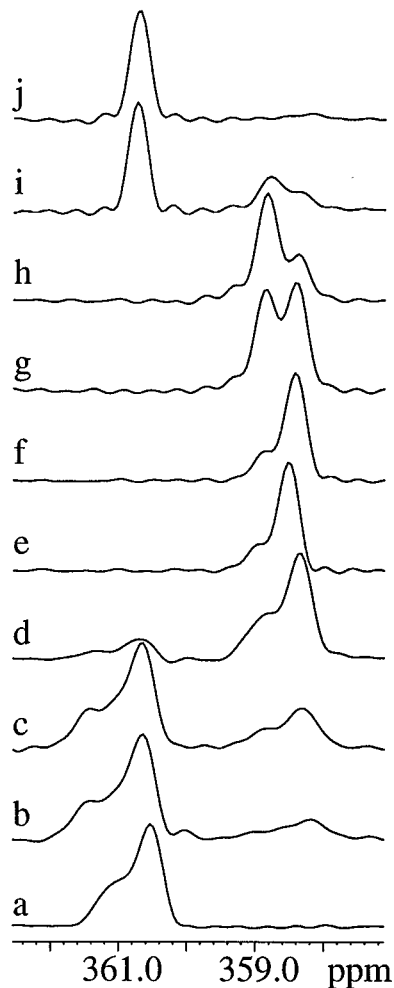


FIG. 1. Variable-temperature ^{15}N MAS NMR spectra of K^{15}NO_3 at (a) ambient temperature (24°C), (b) 119°C , (c) 125°C (d) 131°C , (e) 159°C , (f) after 2 min at 125°C , (g) after 30 min at 125°C , (h) after 90 min at 125°C , (i) 119°C , and (j) 113°C . The spectra (a)–(d) are obtained for K^{15}NO_3 during the first heating cycle, i.e., for a sample taken directly from the container. The spectra (e)–(j) are from the third heating cycle of K^{15}NO_3 .

^{207}Pb spectra observed in certain circumstances for $\text{Pb}(\text{NO}_3)_2$ (12,13). However, on heating the α - KNO_3 sample to 125°C we observe from the spectra in Figs. 1a–1c that the main peak changes its frequency by only approximately 0.25 ppm to its new resonance position at 360.75 ppm. Simultaneously we note that the shoulder appears more as a discrete peak at the high temperatures with a resonance position of 361.8 ppm. The observation of a negligible temperature dependence for the $^{15}\text{NO}_3^-^{15}\text{N}$ chemical shift from ambient to 125°C excludes a temperature gradient within the sample to be the cause for the observation of the shoulder in this temperature range. Similarly, inhomogeneity in the static magnetic field can be excluded as the cause for the observation of the shoulder. The reason is that following three cycles of the KNO_3 sample between the α - KNO_3 phase at ambient temperature and the high-temperature

β -KNO₃ phase (160°C) (*vide infra*), the resonance for the α -KNO₃ phase appears *without* a shoulder, with a line width of 10 Hz and at a resonance position identical to that of the main peak for a fresh sample. This is apparent from the spectra in Figs. 1i–1j.

During the first heating cycle of the fresh KNO₃ sample the temperature interval observed for the complete α to β -phase transition is quite broad (114–137°C) as manifested by the intensity changes observed in the ¹⁵N MAS NMR spectra shown in Figs. 1b–1d (119–131°C). In this temperature interval a new resonance for the β -KNO₃ phase emerges at approximately 358.3 ppm in the spectrum along with an associated shoulder similar to that observed in the ambient temperature spectrum for the fresh sample. The largest change in the intensity ratio for the two phases occurs in the midst of the temperature interval, i.e., at about 125°C. Following the first heating/cooling cycle for the sample, the α to β -KNO₃ phase transition observed during the second heating of the sample occurs in the somewhat reduced interval of 119–131°C. For the highest temperature (160°C) employed to the β -KNO₃ phase in this study the ¹⁵N resonance position for the main peak (358.6 ppm) and its small shoulder (359.0 ppm) has changed only slightly compared to the position at the temperature of the α to β -phase transition (125°C).

Upon slow cooling of the β -KNO₃ phase we have succeeded in lowering the temperature to about 125°C without observation of a noticeable change of the β -KNO₃ phase composition in the ¹⁵N MAS NMR spectrum. Following the first heating/cooling cycle, the spectrum obtained upon cooling to 125°C and after 2 min at this temperature (during the second and third cycle) is quite similar to that of β -KNO₃ at 159°C, as shown in Fig. 1f. Keeping the sample at 125°C for 30 min and then extending the period to 90 min, the ¹⁵N MAS NMR spectra recorded at these intervals (Figs. 1g and 1h, respectively) show a dramatic change in that a new resonance appears with increasing intensity at 359.0 ppm at the expense of the β -KNO₃ resonance at 358.6 ppm. A metastable γ phase of KNO₃ has been observed by other methods upon cooling of β -KNO₃. In particular, we note the recent synchrotron powder XRD study (2), which paid special attention to observing the γ -KNO₃ phase by cooling β -KNO₃. The spectral changes observed at 125°C upon cooling of the β -KNO₃ phase propose that the resonance appearing at 359.0 ppm arises from the metastable γ -KNO₃. The resonance for the γ -KNO₃ phase appears with a line width of about 10 Hz and without a shoulder to high frequency as observed in the case of the α - and β -KNO₃ phase. On the other hand, in all experiments we never observed the resonance for the γ -KNO₃ phase as a single narrow resonance but always accompanied by a low-intensity shoulder on its low-frequency side, i.e., corresponding to the position of the β -KNO₃ phase.

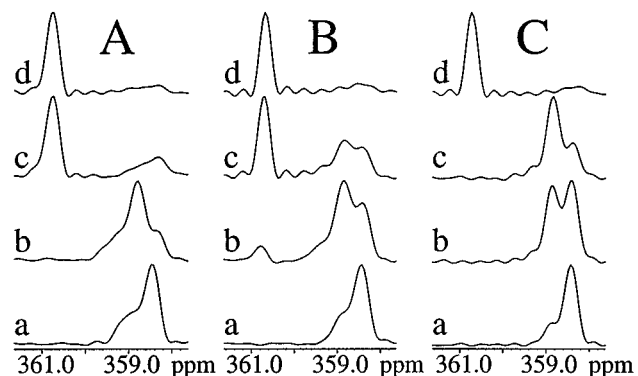


FIG. 2. The effect of the thermal history on the stability of the γ -phase of KNO₃. For all heating cycles the sample was heated from 24 to 160°C before cooling. The γ -phase is observed at 359.0 ppm, i.e., 0.4 ppm to higher frequency from the resonance of β -KNO₃. (A) A first heating cycle with spectra recorded at (a) 159°C, (b) after 2 min at 125°C, (c) after 30 min at 125°C, and (d) after 30 min at 119°C. (B) A second heating cycle with spectra recorded at (a) after 2 min at 125°C, (b) after 30 min at 125°C, (c) after 90 min at 125°C, and (d) after 30 min at 119°C. (C) A third heating cycle with spectra recorded at (a) after 2 min at 125°C, (b) after 30 min at 125°C, (c) after 90 min at 125°C, and (d) after 30 min at 119°C.

The appearance of the spectra for the β - to γ -KNO₃ phase transition depends somewhat on the numbers of heating cycles (24°C → 150°C → 24°C, i.e., α - to β - to γ - to α -KNO₃ phase transitions) for the sample, as illustrated in Fig. 2. First, we note that the observed temperature for the β - to γ -KNO₃ phase transition is not affected by the thermal history of the sample; i.e., we observe a constant temperature of 125°C for the transition independent of the numbers of heating cycles. However, the rate of the β - to γ -phase transformation as well as the stability of γ -KNO₃ are found to be highly affected by the thermal history of the sample. In Fig. 2 the three columns labeled A, B, and C each show some of the spectra observed during the first, second, and third heating cycle, respectively. Each column corresponds to the spectral changes observed under identical conditions upon cooling the sample after 60 min at 160° to 125°C and then to 119°C: (a) β -KNO₃, after 2 min at 125°C, (b) β - and γ -KNO₃ after 30 min at 125°C, (c) α -, β -, and γ -KNO₃, after 90 min at 125°C, and (d) 30 min at 119°C. From the lowest row of spectra at 125°C (a) in Fig. 2 we find that during the first heating cycle β -KNO₃ converts to γ -KNO₃ almost instantly following cooling to 125°C, which may be realized from Fig. 2A(b). Furthermore, with an increasing number of heating cycles for the sample (B and C) the high-frequency shoulder (359.0 ppm) for the β -KNO₃ resonance at 358.4 ppm becomes less predominant. A similar observation has been made for the α -KNO₃ phase at 24°C (not shown). Moreover, during the first cycle (Fig. 2A) γ -KNO₃ is seen to survive at the temperature of 125°C for only a short time since after 30 min α -KNO₃ appears as the main phase (Fig. 2A(c)). As seen from Fig. 2A(c) the γ - to α -phase

transition is basically complete after keeping the sample at 125°C for 30 min.

The influence of the thermal history of the sample on the rate and “purity” of the phase transformation and on the stability of the $\gamma\text{-KNO}_3$ phase is clearly observed from comparison of the spectra in the three columns (A, B, and C) of Fig. 2. From these spectra we conclude that the β - to $\gamma\text{-KNO}_3$ phase transition at 125°C becomes slower but also more “clean” with an increasing number of heating cycles. For example, while all three phases (α , β , and γ) are clearly observed to coexist during the transformation for the second cycle 125°C (Fig. 2B(b)), $\gamma\text{-KNO}_3$ can be observed as a nearly pure phase during the third cycle (C). Following 90 min at 125°C of the third cycle (Fig. 2C(c)), no changes in the appearance of the spectrum were observed for the next 60 min. Thus, the stability of the $\gamma\text{-KNO}_3$ phase also improves with the numbers of heating cycles for the sample. However, by lowering the temperature within the sample from 125°C by just a few degrees, an abrupt transformation of $\gamma\text{-KNO}_3$ to $\alpha\text{-KNO}_3$ takes place immediately. For example as shown in Fig. 2C(d), $\alpha\text{-KNO}_3$ is obtained as an almost pure phase in less than 30 min after a drop of the temperature to 119°C . We should note that for all three heating cycles *pure* $\alpha\text{-KNO}_3$ is observed only when the sample is cooled to about 115°C .

Using other experimental methods, earlier studies have shown that the $\gamma\text{-KNO}_3$ phase is stable from about 124°C down to a temperature range between 115° and 110°C (1,3,4,14). Furthermore, it has been observed that $\gamma\text{-KNO}_3$ is stable at 91°C and that it is possible for $\gamma\text{-KNO}_3$ to exist even at room temperature for about 30 min before converting to the $\alpha\text{-KNO}_3$ phase (1). We have succeeded in keeping $\gamma\text{-KNO}_3$ in a state of stable condition only at a temperature of about 125°C (and only after three heating cycles) using the sample container of a 7-mm o.d. (5 mm i.d.) MAS rotor. Even fast lowering of the sample temperature from 160°C to the range $119\text{--}113^\circ\text{C}$, as proposed to be an efficient method of isolating $\gamma\text{-KNO}_3$ (2), appeared unsuccessful under our experimental conditions. As shown above and illustrated in Fig. 2, we observe that the stability of $\gamma\text{-KNO}_3$ at 125°C increases as the sample is heat-cycled through the different phases for a number of times. In this context we note that Christensen *et al.* (2) observed the temperature interval for the appearance of $\gamma\text{-KNO}_3$ to decrease on continuing cycling through the different phases, i.e., from the range of $115\text{--}97^\circ\text{C}$ to the range of $115\text{--}104^\circ\text{C}$ for 3 cycles. Also, we should point out that in our experiments we always observe $\gamma\text{-KNO}_3$ along with the $\beta\text{-KNO}_3$ phase present in different amounts. The observation of the coexistence of all three KNO_3 phases (α , β , and γ) from our NMR experiments in the course of the phase transformation at 125°C differs from the recent synchrotron XRD study (2), where the coexistence of only the γ - and α -phase of KNO_3 has been observed.

Finally, we return to the somewhat strange NMR observation of a high-frequency shoulder for the ^{15}N resonance of a fresh $\alpha\text{-KNO}_3$ sample and the corresponding anomalous reflections similarly observed in the synchrotron XRD pattern (2) for a fresh sample. In the synchrotron powder XRD study (2) it is observed that the crystallinity of $\alpha\text{-KNO}_3$ changes when heated to the high-temperature $\beta\text{-KNO}_3$ phase. Thus, we suppose that the observed change in crystallinity is responsible for the disappearance of the shoulder in the ^{15}N MAS NMR spectrum of $\alpha\text{-KNO}_3$ following one or more heating cycles. In the Raman study of $\alpha\text{-KNO}_3$ (6) it is suggested that disordered NO_3^- groups exist on alternating lattice sites which are present for the α -phase. This observation may explain why neutron diffraction studies (5) observed that the NO_3^- groups are approximately 1° off the *ab* plane for the α phase. This angle has been shown to increase with temperature (5). The supposition of disordered NO_3^- groups on alternating lattice sites in $\alpha\text{-KNO}_3$ may be a possible explanation why we observe a shoulder for a fresh sample of $\alpha\text{-KNO}_3$. In addition, our observations show that the disorder of the NO_3^- groups only takes place for a fresh sample of KNO_3 .

CONCLUSION

The three phases α -, β -, and $\gamma\text{-KNO}_3$ and their mutual phase transformations have been successfully monitored using variable-temperature ^{15}N MAS NMR spectroscopy. The influence of the thermal history on the appearance of the different phases and on the phase transformations are clearly illustrated. However, a better understanding and a convincing explanation of these phenomena is still required. For example, the changes of the α phase when KNO_3 is heated to the high-temperature phase a number of times still need to be accounted for. Our observations support the supposition that $\alpha\text{-KNO}_3$ undergoes changes in crystallinity when heated to the high-temperature phase a number of times.

The metastable $\gamma\text{-KNO}_3$ phase has been successfully observed at 125°C but it is found not to survive at lower temperatures even though the literature claims this not to be the case. The stability of $\gamma\text{-KNO}_3$ at 125°C was found to depend strongly on the thermal history of the sample and it was found that all three phases coexist during the transition from the β -phase to the α -phase.

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