

PHASE TRANSITIONS OF AMMONIUM NITRATE DOPED WITH ALKALI NITRATES STUDIED WITH FAST X-RAY DIFFRACTION

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Dried samples of ammonium nitrate (AN) containing 1, 3, 5 mol% KNO_3 , RbNO_3 and CsNO_3 were investigated with temperature resolved X-ray diffraction. The samples were cycled with 2 temperature programs from -70° to 100° and -70° to 150°C , resp. DSC measurements were made for comparison.

KNO_3 extends the stability range of phase III. The supercooling observed with the transitions II/III and III/IV was so severe that the phases III and IV could be skipped leading to the transitions II/IV and III/V. No hindered nucleation was observed on heating.

RbNO_3 gives dried AN the properties of the humid nitrate. Phase III appeared on heating but was skipped on cooling, when the sample had been heated to 150°C . Hindered nucleation was observed.

CsNO_3 stabilizes the phases II and V. No strong hysteresis or supercooling was observed.

Keywords: ammonium nitrate, phase transformation

Introduction

Ammonium nitrate (AN) crystallizes in five different phases at normal pressure. The transitions observed under storage conditions cause serious problems for certain applications. Therefore numerous attempts have been made to influence the phase behaviour by incorporating alkali ions into the lattice.

Especially the system AN/ KNO_3 was frequently investigated with DSC and X-ray diffraction [1-6]. It was found that the potassium ion extends the stability range of phase III from 84°C to higher and from 32 to lower temperatures. With 4 weight% KNO_3 phase III becomes the stable phase at room temperature.

Less information is available on the system AN/ RbNO_3 . DTA measurements showed no influence of Rb^+ on the phase transitions [6].

In the system AN/CsNO₃ contents of 4 or more weight% CsNO₃ are reported to stabilize phase II down to room temperature. The measured DTA diagrams contained weak peaks between 30° and 40°C [6]. X-ray diffraction revealed that at room temperature AN with 4–10 weight% CsNO₃ consisted mainly of phase V with minor amounts of phase IV. Transitions of the phases II/V were observed between 40° and 50°C [7].

As in the case of ammonium nitrate several phases may occur in a temperature range, the identification of the phases participating in a transition is required to avoid ambiguities. Therefore temperature resolved X-ray diffraction was used for a new systematic approach to elucidate remaining ambiguities. Samples containing 1, 3 and 5 mol% of KNO₃, RbNO₃ and CsNO₃ were investigated. For comparison DSC measurements were performed.

Experimental

The measuring system described elsewhere [8] consists of an X-ray diffractometer equipped with a chromium tube and combined with a low temperature device. With a fast position sensitive proportional counter series of more than 200 angle dispersive diffraction patterns per day can be measured, while the samples are heated and cooled linearly or stepwise with a freely programmable temperature controller within a range of –100° to 300°C. In this way the phases in the samples can be monitored vs. temperature or time.

In the measurements an angular range of 2 theta from 22–62 degrees was scanned with 30 degrees per minute. The samples were heated and cooled in steps of 5°C. As the phase sequences may depend from passing the transition I/II at 125°C, the measurements were performed with two different temperature programs 20°/100°/–70°/100°C and 20°/150°/–70°/150°C.

DSC-diagrams were measured with a DuPont 990 Thermoanalyzer with a heating rate of 5 deg/min for a more accurate determination of the transition temperatures.

The samples were obtained by melting dry AN with 1, 3, 5 mol% of KNO₃, RbNO₃, CsNO₃, dried at 70°C with P₂O₅ under reduced pressure and stored for 2 months.

Evaluation

A Gaussian profile was fitted to the peaks in the diffraction patterns yielding peak position, intensity and peak width. The phases were identified by a reason-

able fit of the elementary cell using the lattice plane distances $d(hkl)$ calculated from the peak positions.

The series were evaluated by a difference procedure described elsewhere [9]. In the difference procedure diffraction patterns are subtracted, and the absolute sums of the difference patterns correlating with the changes in the patterns are plotted against temperature.

$$DY(T_i) = \sum_{j=1}^N |X_j(T_i) - X_j(T_{i-1})| ; i = 2, \dots, M$$

N = number of channels
 j = index channel no.
 x_j = content j -th channel of i -th pattern
 T_i = independent variable e.g. temperature

$$Y(T_i) = \sum_{j=1}^N |X_j(T_i) - X_j(T_i)|$$

If the differences are formed with neighboured patterns, a DSC-like curve $DY(T_i)$ results. Formed constantly with the same pattern, e.g. the very first one, a TG-like curve $Y(T_i)$ is obtained.

Results and discussion

$NH_4NO_3 + KNO_3$

The results of the diffraction series are presented in Figs 3 and 4 for the different temperature programs. Low phase concentrations are indicated by brackets. The corresponding DSC results are found in Table 1. Figures 1 and 2 enclose typical difference curves $DY(T)$ and $Y(T)$ used for the evaluation.

On cycling until $150^\circ C$ increasing amounts of potassium extend the stability range of phase III, as it is known from literature. The stabilization is not very expressed with 1 mol% KNO_3 . The phase behaviour is similar to humid ammonium nitrated, where phase III appears on heating but is skipped on cooling.

With 3 and 5 mol% phase III is already stable at room temperature. On heating, the phase transition III/II is shifted towards higher temperatures, whereas the transitions II/I and I/II are not influenced.

On cooling, a strong hysteresis is observed for the transition II/III. With 1 mol% the supercooling is so strong that the samples reach the stability range of phase IV at about $45^\circ C$ changing into this phase without further delay. Increasing the percentage of potassium reduces the supercooling so that phase III appears already at $70^\circ C$.

On further cooling AN+1 mol% KNO_3 changes from IV to V as expected, whereas the samples with 3 and 5% change directly into phase V below -25°C skipping phase IV.

Table 1 DSC-results of AN/ KNO_3

mol% KNO_3	Phase transition temperatures / $^\circ\text{C}$									
	20 \rightarrow 100		100 \rightarrow -60			-60 \rightarrow 100				
1.0	34	93	70	46	-34	-8	48	94		
3.0					-31	-6	26	100<		
5.0					-31	-4	18	100<		
mol% KNO_3	20 \rightarrow 150		150 \rightarrow -60			-60 \rightarrow 150				
1.0	40	100	128	125	46	-32	-8	49	106	129
3.0	103	128	125	44	-30	-2	35	108	133	
5.0	111	129	125	42	-28	+1	23	114	134	

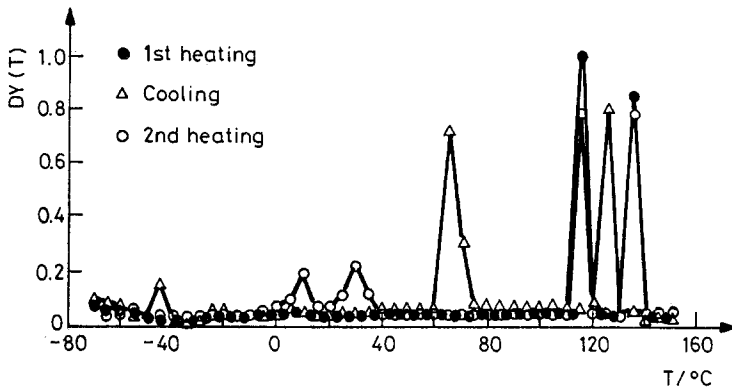


Fig. 1 Difference diagram $DY(T)$ of AN+5 mol% KNO_3 ($20^\circ/150^\circ/-70^\circ/150^\circ\text{C}$)

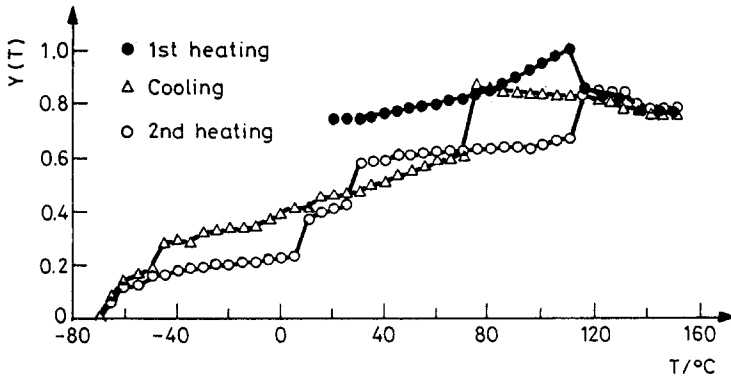


Fig. 2 Difference diagram $Y(T)$ of AN+5 mol% KNO_3 ($20^\circ/150^\circ/-70^\circ/150^\circ\text{C}$)

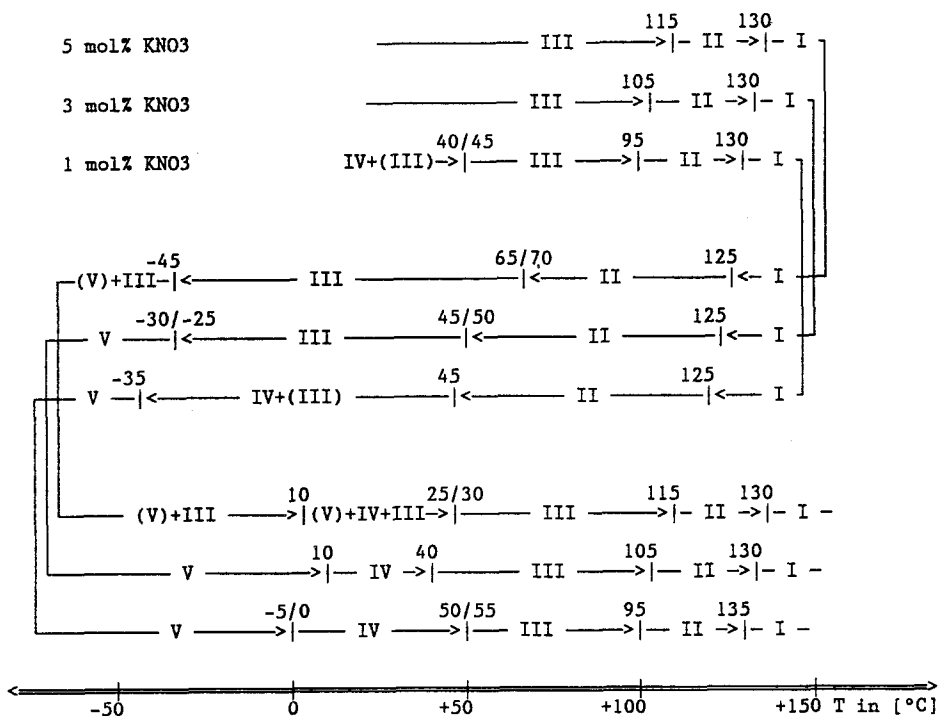


Fig. 3 Path diagrams of AN/KNO₃ (20°/150°/-70°/150°)

On reheating phase IV appears in all cases from 0° to 10°C before changing into phase III at temperatures, which are lowered with increasing potassium concentration. The further reheating cycle corresponds to the first heating of the sample.

Cycling until 100°C the sample with 1 mol% KNO₃ changes on cooling into phase III. A retarded phase transition II/III or skipping phase III is not observed, because the sample doesn't reach phase I before. Phase III changes into phase IV at temperatures slightly above 0°C followed by the transition IV/V. However, when the transition is retarded, the sample changes into the phases IV and V in the same temperature range below 0°C. The transitions observed with 3 and 5 mol% correspond to cycling until 150°C described above.

The data observed in both cycles suggest that nucleation problems lead to the strong supercooling of phase II and the delayed appearance of phase III. Nucleation problems should also be the reason that the formation of phase IV nuclei is hindered, when phase III is cooled. Therefore phase IV is skipped and a direct transition III/V is observed.

On reheating the easier formation of phase IV nuclei from phase V leads to the reappearance of phase IV even with the samples containing 5 mol% KNO_3 .

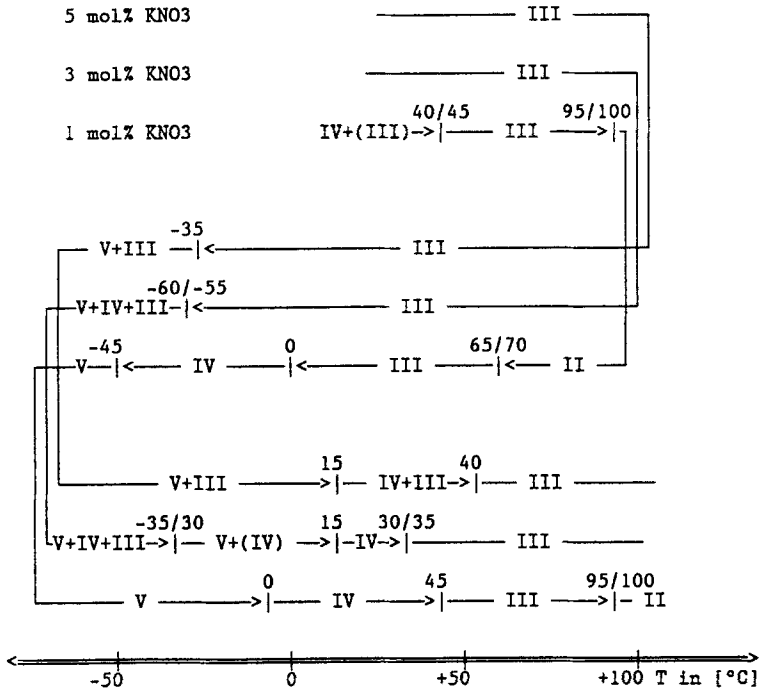


Fig. 4 Path diagrams of AN/KNO_3 ($20^{\circ}/100^{\circ}/-70^{\circ}/100^{\circ}\text{C}$)

This result explains, why phase III is not stabilized reliably with the investigated concentrations of potassium, though a part of the sample remains in phase III throughout the lower temperature range.

The transition temperatures in Table 1 obtained with DSC correspond principally to the diffraction experiments. On cooling, however, a constant transition temperature at 46°C suggests that even with higher concentrations of potassium the sample changes directly from II into IV due to the cooling rate of 10 deg/min, whereas an average rate of 0.5–1.0 deg/min was performed during the diffraction experiments.

$\text{NH}_4\text{NO}_3+\text{RbNO}_3$

On cycling until 150°C the diffraction series show a simpler pattern than with KNO_3 (Figs 5–6). On heating the transitions IV/III/II/I occur at 55° , 95° and 135°C independently from the rubidium content. A smaller part of the sam-

ple, which decreases with the rubidium content, changes at 55°C directly into phase II, as it is known from pure dry ammonium nitrate.

On cooling phase III is skipped so that the sequence I/II/IV/V is observed. On reheating phase V changes into IV at temperatures decreasing with the rubidium content. This is the only transition temperature, which is influenced by the rubidium concentration. The further reheating corresponds to the first heating.

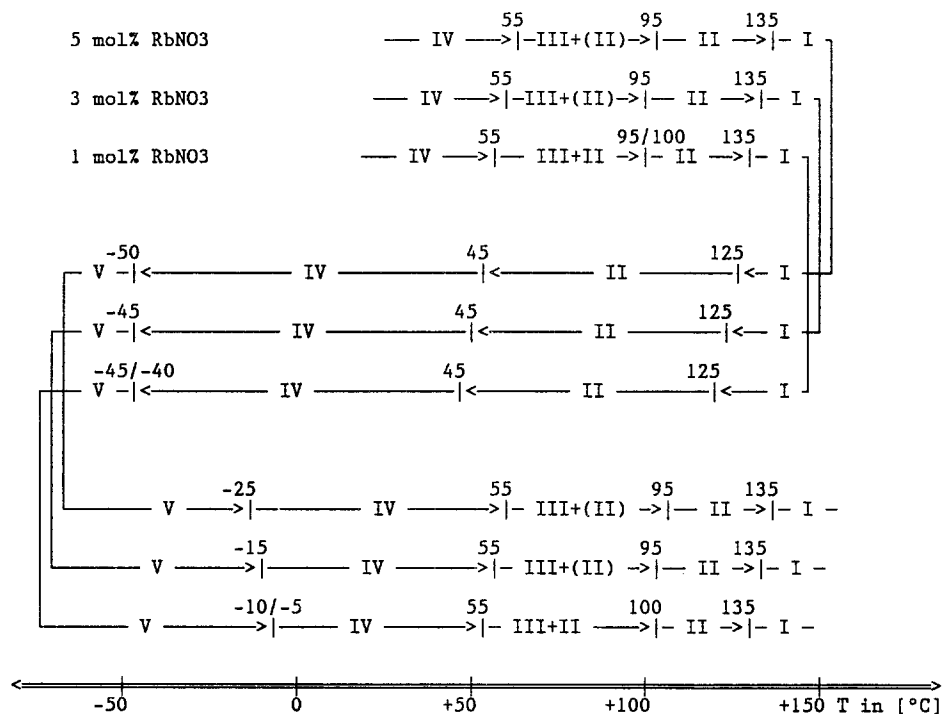


Fig. 5 Path diagrams of AN/RbNO₃ (20°/150°/-70°/150°C)

The DSC data in Table 2 are in agreement with the diffraction data, if the slight temperature differences are neglected.

Cycling until 100°C corresponds to heating to 150°C with the exception of the cooling cycle, where phase II changes partially at about 60°C into phase III, whereas the other part changes at about 45°C into phase IV. Phase III disappears at -10°C changing into phase IV and also into phase V, before all the phase IV changes into V at about -50°C.

The DSC data in Table 2 agree with the diffraction data, as far as the sequence is concerned. The temperatures deviate, because of the poor temperature

resolution with the measurements performed in 5°C steps and because of the different cooling rate, which leads to stronger supercooling with the DSC.

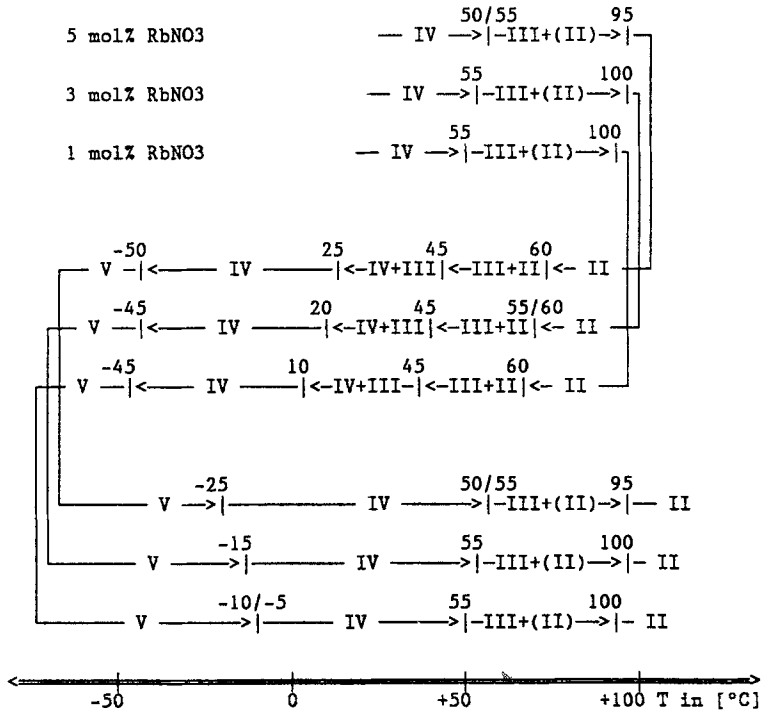


Fig. 6 Path diagrams of AN/RbNO₃ (20°/100°/-70°/100°C)

Table 2 DSC-results of AN/RbNO₃

mol%	Phase transition temperatures /°C									
	20 → 100		100 → -60			-60 → 100				
1.0	47	87	56	35	-24	-39	-16	42	88	
3.0	46	85	50	32	-29	-40	-22	45	85	
5.0	44	82	60	38	-26	-46	-30	49	80	
	20 → 150		150 → -60			-60 → 150				
1.0	49	83	127	124	48	-40	-10	51	85	131
3.0	49	86	127	124	47	-43	-24	51	84	129
5.0	49	84	126	124	47	-49	-39	51	86	130

Phase III appearing on heating was not expected. It is skipped on cooling after cycling to 150°C. This reminds to the phase behaviour of humid ammonium nitrate.

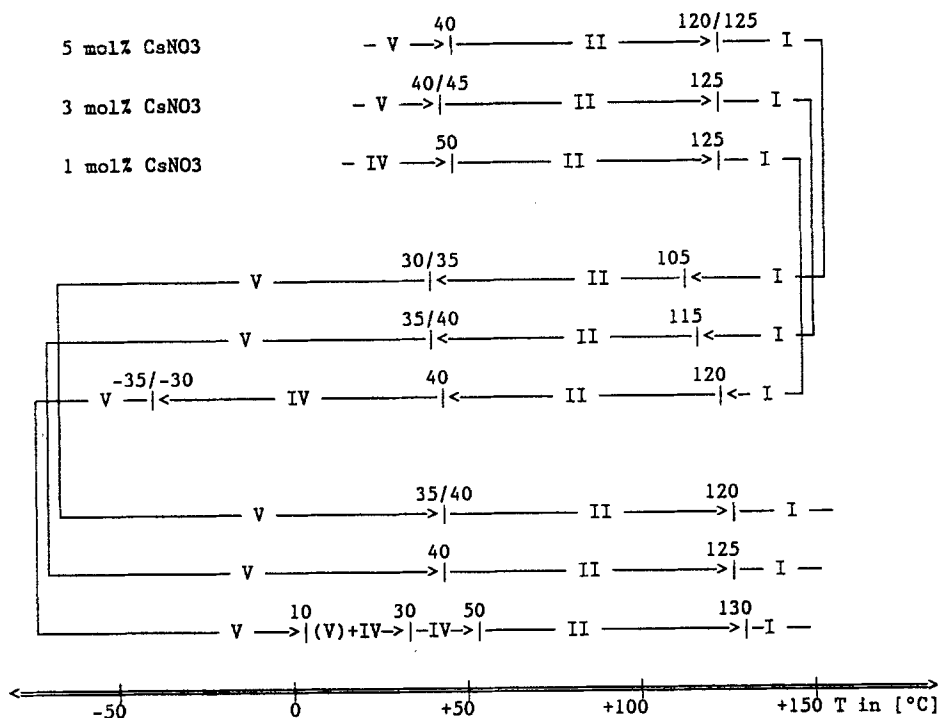


Fig. 7 Path diagrams of AN/CsNO₃ (20°/150°/-70°/150°C)

The data suggest that the formation of phase III nuclei is inhibited, when the sample passed the transition II/I. Without passing II/I nuclei of phase III can be formed, so that a part of the sample changes into phase III at about 60°C. Obviously this part again reveals hindered nucleation so that the transition to phase IV is delayed allowing a minor part of the sample to change directly into phase V.

NH₄NO₃+CsNO₃

The results of the diffraction series in Fig. 7 show a simple pattern, as phase III does not occur and phase IV is only observed in the sample containing 1 mol% CsNO₃. On heating the transition into phase II and the following transition II/I is lowered with increasing cesium concentration. The same effects are observed on cooling, when the reciprocal transitions occur with a hysteresis of about 10°C. The results of cycling to 100°C are not shown separately, as they agree with cycling to 150°C.

In the sample with 1 mol% the phases II and V are not yet completely stabilized, so that the sample exists at room temperature in phase IV before changing into II. On cooling the sample still changes into IV at about 40°C. An interesting detail became visible in the 100°C cycle, when phase II changed into phase V on cooling, before a small part continued to change into phase IV.

In contrast to the samples with KNO₃ and RbNO₃ no large hysteresis and no strong supercooling was observed. Obviously no hindered nucleation occurs, when the similar structures of phase II and V change into each other.

Table 3 DSC-results of AN/CsNO₃

mol%	Phase transition temperatures /°C											
	20 → 100			100 → -60			-60 → 100					
CsNO ₃												
1.0	44	48		42	38		40	44	48			
3.0	36	40		40	36		36	40				
5.0	32	36		34	30		32	36				
	20 → 150			150 → -60			-60 → 150					
1.0	40	44	48	129	123	45	41	38	40	44	48	126
3.0	36	40		122	116	40	36		36	40		122
5.0	32	36		118	109	35	30		32	36		118

In the DSC measurements (Table 3) a double peak occurred reproducibly in the range of 33°–48°C on heating and cooling. Diffraction patterns performed in this range with a temperature interval of 0.5°C detected only the phase transition II/V.

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Zusammenfassung — Trockene Ammoniumnitratproben (AN) mit einem Gehalt von 1, 3 bzw. 5 mol% KNO₃, RbNO₃ und CsNO₃ wurden mittels Röntgendiffraktion in Abhängigkeit von der Temperatur untersucht. Die Proben durchliefen 2 Temperaturprogramme (von 70° auf 100° und von -70° auf 150°C). Zum Vergleich wurden DSC-Messungen durchgeführt.

KNO_3 erweitert den Stabilitätsbereich der Phase III. Die Unterkühlung bei den Übergängen II/III und III/IV war so ausgeprägt, daß man die Phasen III und IV überspringen konnte, um die direkten Phasenübergänge II/IV und III/V zu erhalten. Beim Erhitzen wurde keine behinderte Keimbildung beobachtet.

RbNO_3 verleiht trockenem AN die Eigenschaften von feuchtem Nitrat. Phase III tritt zwar beim Erhitzen auf, wird aber beim Abkühlen ausgelassen, wenn die Probe zuvor auf 150°C erhitzt wurde. Es wurde eine behinderte Keimbildung beobachtet.

CsNO_3 stabilisiert die Phasen II und V. Es wurde keine ausgeprägte Hysterese oder Unterkühlung beobachtet.