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# THERMAL ANALYSIS OF THE SYSTEM $NH_4NO_3/CsNO_3$ by MEANS OF X-RAY DIFFRACTION.

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## ABSTRACT

Series of x-ray diffraction patterns were measured while ammonium nitrate containing 2-10 weight % of $CsNO_3$ was cycled between -70/80 and -70/150°C. At room temperature, the samples with 4 - 10 % $CsNO_3$ consisted of phase V with minor amounts of phase IV. On cooling or heating phase IV changed into the neighboured phases V and II,resp.,without reappearing. In further experiment the transitions V/II/I between 40 and 50 and above 120°C were observed.

## INTRODUCTION

Dry ammonium nitrate (AN) crystallizes in four modifications:

$$V \underset{50- \ -29^{\circ}}{\overset{-8 \ - \ 0^{\circ}}{\rightleftharpoons}} IV \underset{44-53^{\circ}}{\overset{47-55^{\circ}}{\rightleftharpoons}} II \overset{125^{\circ}C}{\rightleftharpoons} I$$

tetragonal orthorhomb. tetragonal cubic

The phase behaviour is influenced by incorporating cesium ions. Contents of 4 or more % $CsNO_3$ are reported to stabilize phase II down to room temperature (ref.1). The DTA-diagrams show week double peaks between 30 and 40°C.

As in the case of pure AN, series of x-ray diffraction patterns were needed to identify reliably the phases involved in the transitions (ref.3), we extended our diffraction measurements to AN doped with $CsNO_3$ to study the influence of different cations on the phase changes.

## EXPERIMENTAL DETAILS

The energy dispersive x-ray diffraction patterns were measured with a tungsten tube and a Si(Li) semiconductor detector using an angle 2 theta of 10° (see ref.4). Angle dispersive patterns were obtained using a chromium tube and a Siemens Position Sensitive Proportional Counter (PSPC).

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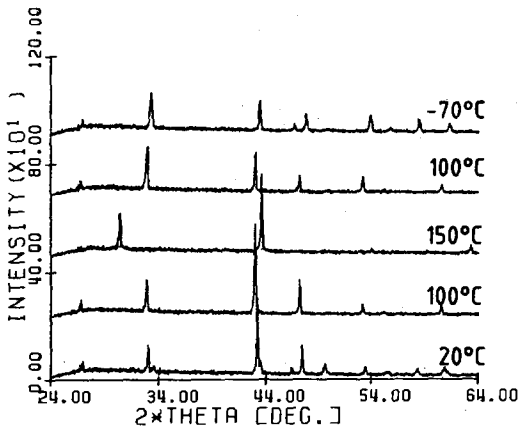


Fig. 1: Selected angle dispersive x-ray diffraction patterns

AN and 2-10% $CsNO_3$, reagent grade of Merck, were melted together and stored for a year before the measurements were made. The series were run with the following-temperature programs: 1. 20/150/-70/150 2. 20/-70/150/-70 3. 20/-70/80/-70 $^{o}C$. The different cycles were chosen,because the phase behaviour of pure AN depends on the temperature program (ref.3).

The energy dispersive series were performed with a heating rate of $2^{o}C$/min, measuring time 60 sec, whereas in the angle dispersive series stepwise heating was used with intervals of 2 $^{o}C$.

RESULTS AND DISCUSSION

Selected patterns of the angle dispersive series are shown in fig.1. The energy dispersive series were evaluated by the difference method (ref.4) yielding curves like those shown in fig. 2 and 3. In angle dispersive series, additionally, peak positions were fitted and lattice plane distances were calculated (fig.4).

The difference curves (fig.2-3) show the changing phase behaviour caused by the cesium ions. Compared with pure AN (ref.3) the addition of 2 weight% $CsNO_3$ lowers the temperature for the transition IV/II and rises the temperatures for the transitions IV/V and V/IV. With 4% $CsNO_3$ the transitions IV/V and V/IV are no longer observed. In the TG-like TXRA-curve a slight bent at about 40 $^{o}C$ indicates a phase transition IV/V.

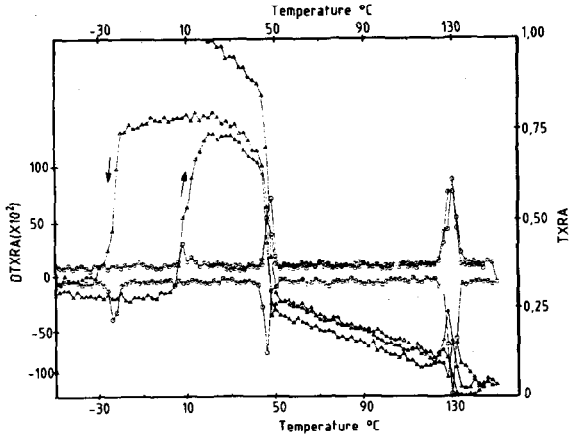


Fig. 2: Difference curves of $NH_4NO_3$ + 2% $CsNO_3$
o DTA-like curve, △ TG-like curve

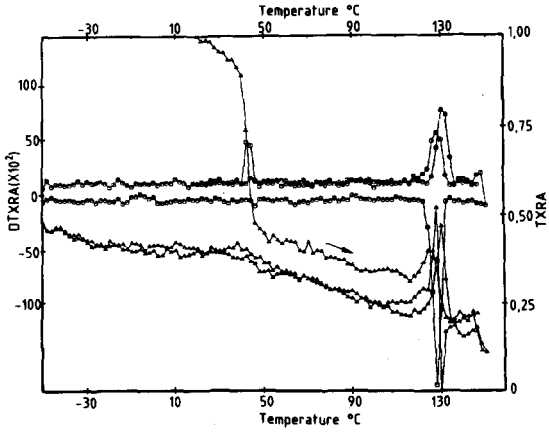


Fig. 3: Difference curves of $NH_4NO_3$ + 4% $CsNO_3$
o DTA-like curve, △ TG-like curve

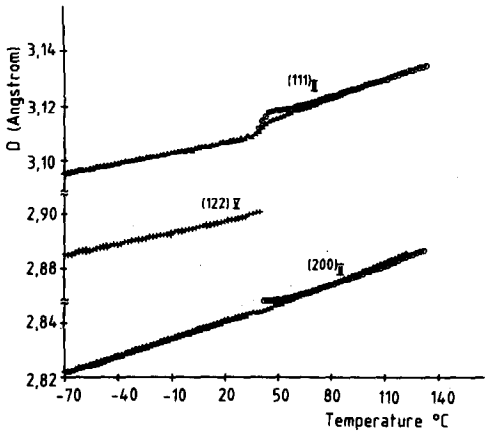


Fig. 4: Curves of calculated lattice plane distances

Forming the difference curves exclusively with peaks of phase V a clear step is observed caused by appearing and disappearing peaks between 40 and 50°C.

The diffraction patterns and the lattice plane distances d (fig.4) reveal that the samples with a content of 4 - 10 % consist at 20°C of phase V with minor portions of phase IV. Phase IV changes readily into the neighboured phases V and II on cooling and heating, respectively, without reappearing during further cycling. However, in contrast to literature (ref.1) there are phase changes V/II and II/V between 40 and 50°C. As both phases are very similar, the changes are small.

In contrast to pure AN (ref.3) the different maximum temperatures during cycling cause no different phase behaviour.

First evaluations do not correlate the results to the double peaks in DTA and DSC curves at about 40°C observed by Morand and in our own investigations.

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