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Note on the Phase Transition II'–IV in the Ammonium Rich End of the Mixed Crystals Series $(NH_4)_xK_{1-x}NO_3$

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With 3 figures in the text

Abstract

The transition curve II'_A–IV_A in the range NH_4NO_3–$(NH_4)_{0.75}K_{0.25}NO_3$ was determined. A single phase II' of ammonium rich mixed crystals was observed in the complete miscibility range from x = 1 to 0.918 (x = molar fraction of ammonium nitrate). From x = 0.913 to 0.750 two phases occur simultaneously: II'_A ammonium rich and II_K as undercooled potassium rich phase. The stable phase at room temperature III_A forms readily on cooling. The complete miscibility range of phase III_A extends over the whole range studied here. Hence homogenization of the formerly unmixed crystals sets in, by ion diffusion in the solid state.

Zusammenfassung

Die polymorphen Umwandlungstemperaturen II'_A–IV_A wurden in der Mischkristallreihe NH_4NO_3–$(NH_4)_{0,75}K_{0,25}NO_3$ bestimmt. Am ammoniumreichen Ende wurde eine homogene Kristallphase II'_A beobachtet, die sich über den Interwall x = 1 bis 0,918 erstreckt (x = Molarfraktion des Ammoniumnitrats). In dem Bereich x = 0,918 bis 0,750 werden zwei nicht mischbare Phasen beobachtet, und zwar: II' als ammoniumreichere und II_K als kalireichere Phase. Die stabile Phase III_A bildet sich beim Abkühlen auf Zimmertemperatur leicht. Bei dieser Phase erstreckt sich die vollständige Mischbarkeit über den ganzen, hier untersuchten Bereich. Deshalb tritt sofort nach der polymorphen Umwandlung die Homogenisierung der vorher entmischten Phasen auf durch Ionen Austausch im festen Zustande.

INTRODUCTION

The complete phase diagram of the two-component system NH_4NO_3-KNO_3 was studied by WALLERANT (1905). The literature on the metastable transitions in this system is not abundant. Important studies on KNO_3 were made by KRACEK (1930), MIEKK-OJA (1946), SAWADA, NOMURA and FUJII (1958), SAWADA, NOMURA and ASAO (1961) and SHINNAKA (1962). The mixed crystals

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of the potassium rich end of the system had been dealt with by YANAGI and SAWADA (1963) and KAWABE, YANAGI and SAWADA (1965). The II′–IV transition of NH_4NO_3 was studied by BOWEN (1926), HENDRICKS, POSNJAK and KRACEK (1932), AMOROS, ALONSO and CANUT (1958), SHINNAKA (1956 and 1959). See also M. DE SÁENZ, TESSORE and LEONE (1970, this volume).

The influence of KNO_3 on the II′–IV transition of ammonium nitrate has, to our knowledge, not been submitted to study. TESSORE (1965) observed a transition temperature of $41 \pm 1°$ C for $x = 0.94$ (personal communication). The nomenclature used at present for the different modifications of ammonium and potassium nitrate is given in the sketch of the phase diagramm (fig. 1). The suffix A or K is used to differentiate phases, which have the same denomination in the K rich end or the ammonium rich end, by their crystallographic properties (e.g. II_A-tetragonal and II_K-rhombic).

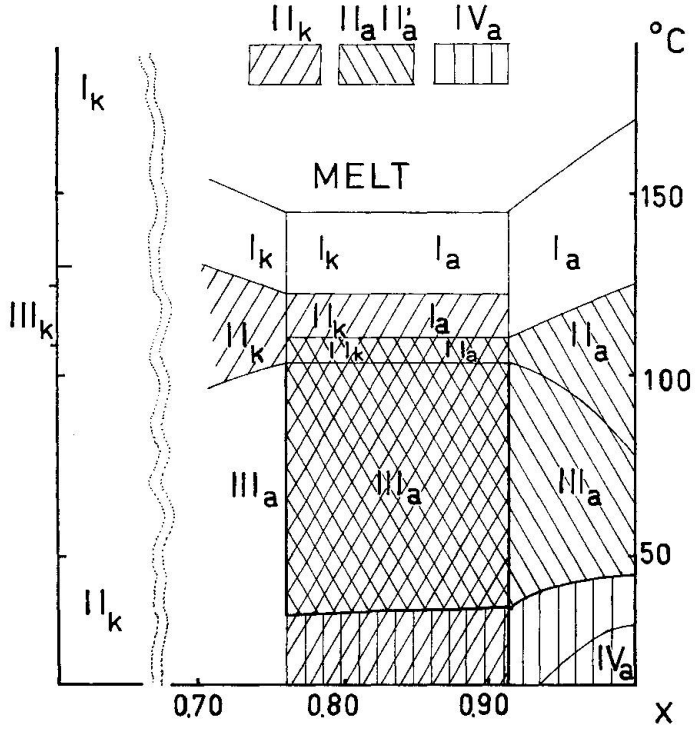

Fig. 1. Stable phase diagram of the system NH_4NO_3–KNO_3 at its ammonium rich end according to WALLERANT including some data from KRACEK; EARLY and LOWRY and from YANAGI and SAWADA. The names of the stable phases are given in the diagram, the limits of the stability fields of the stable phases are drawn with thin lines. The striated areas represent the occurrence of each phase in the metastable phase diagram, as determined in this paper. The names of the phases are given at the top of the graph. Transition curves belonging to the metastable phase diagram are drawn in thick lines. (For more details on the metastable potassium rich phases see YANAGI and SAWADA, 1963.)

EXPERIMENTAL

Determinations were made with the Dialux polarizing microscope (Leitz) using the thermostatic heating stage (Leitz 1437). Samples of different composition were prepared by dissolving proportional quantities of both compounds in distilled water (NH_4NO_3 Merk A. R. or Prolabo Rhône-Poulenc P.A.). The maximum absolute error in the molar fraction x of NH_4NO_3 in the mixture of both salts was 0.0005. A drop of the solution was evaporated on a microscope slide and fused rapidly on a heating stage at 170° C. It was then

transferred to the thermostatic heating stage of the microscope and allowed to cool down to 60° C. The temperature of the stage was noted. The maximum estimated error in the determination of the transition temperature is ± 2° C.

RESULTS

The graph given in fig. 2 represents the transition temperatures of the II'_A–IV_A transition of the ammonium rich phase. An inflection if observed at $x = 0.918$ dividing the graph into two zones: the zone of complete miscibility for phase II'_A up to $x = 1$, and the zone of partial miscibility where II'_A coexists with II_K. In this range the compostion of the ammonium rich phase changes only very little with the total increase of K content of the system. At the

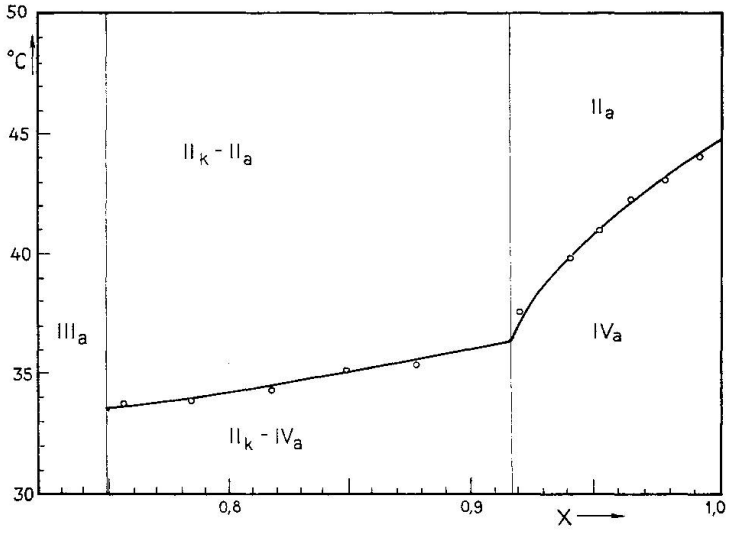

Fig. 2. II'–IV transition curve for the ammonium rich phase in the system $(NH_4)_xK_{1-x}NO_3$. A considerable difference is noted in the slope of the complete miscibility area and that of partial miscibility.

temperatures given in the graph, phase IV_A forms with the same composition as formerly II'_A. Almost immediately unstable phase IV transforms into the stable phase III_A and immediately the undercooled potassium rich phase will be found to transform as well. By this procedure, in the compositional range $x = 0.918$ to $x = 0.750$ two types of crystals of modification III_A, having different compositions, will form. (It is not surprising that the potassium rich phase should only transform after the ammonium rich one does so. As II_K transforms only with difficulty into III_A it can be considerably undercooled below its range of stability. As soon as the transition IV–III occurs in the ammonium rich phase, its crystals act like seeds, causing the immediate transformation II_K–III_A.)

Phase III_A is however completely miscible in the compositional range studied here. Under the microscope it can be observed how homogenization of the formerly unmixed crystals sets in and proceeds by diffusion. As the change in composition is accompanied by a considerable change in the refractive in-

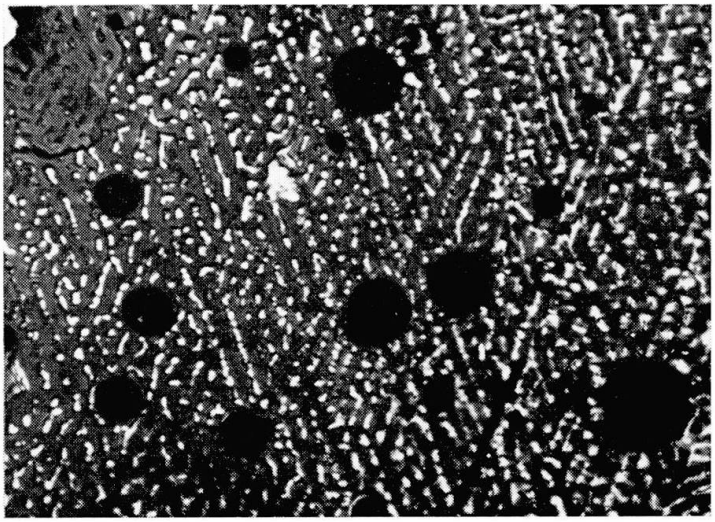

Fig. 3a. Crystals II_K (light coloured) and II_A (dark) cooled metastably down to 60° C. x = 0.85, parial miscibility range (compare fig. 1). The black spots are air bubbles taken as reference.

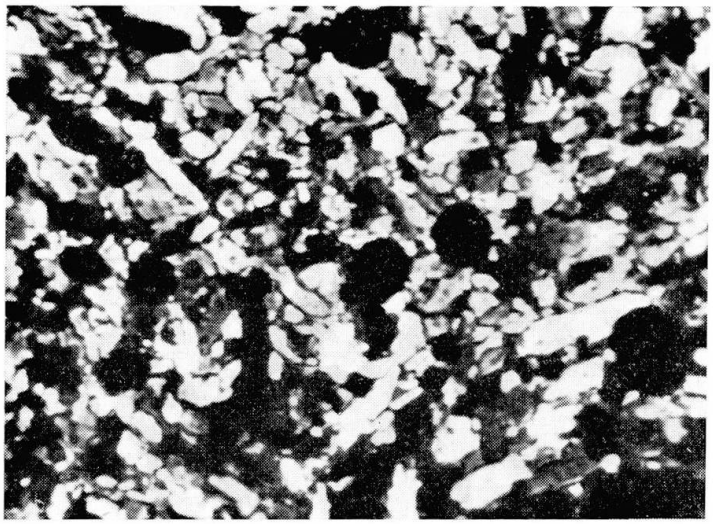

Fig. 3b. The crystal transformed into the completely miscible phase III_A stable at that temperature. The outlines of the crystals are somewhat diffuse owing to changes in the refractive index in the homogenization of the formerly unmixed crystals and also to the very rapid recrystallization.

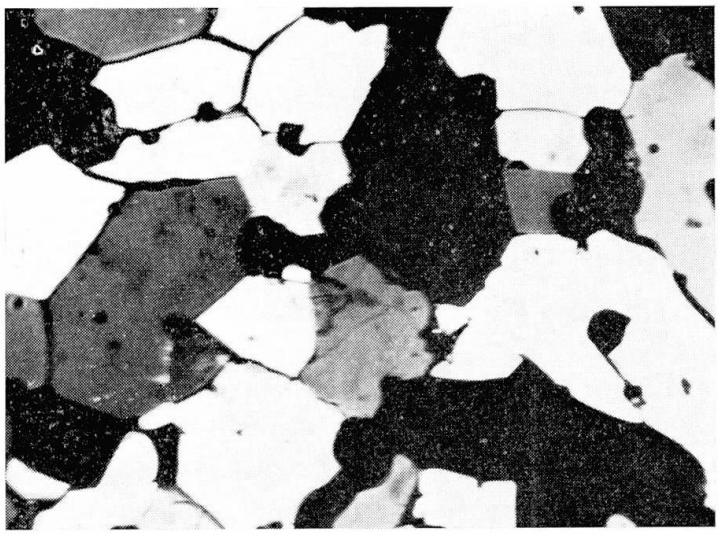

Fig. 3c. The same zone after annealing at 80° C for 18 hours. The now uniform crystals have developed nearly idiomorphic outlines and have grown considerably in size. (Width of the photographs: 0.5 mm.)

dices and birefringence, the whole sample has the aspect of a stirred liquid. Owing to considerable ion mobility recrystallization starts also immediately, and after some length of time rather large idiomorphic crystals of phase III_A will have grown.

As observed above, the presence of III_A formed from II_K will also act as a seed causing the direct stable transition II_A–III_A to occur. This happens if the sample is maintained for some length of time in the stability range of III_A. $II_K \rightarrow III_A$ will occur and $II_A \rightarrow III_A$ follows immediately. In this case the transition II'_A–IV_A cannot, of course, be observed. Under the microscope the two transitions of either example are seen to expand as circular fronts over the slide. Usually the stable transition follows close behind the metastable one. The cooling speed is important in regulating the relative rate of both transitions. From the phase diagram in fig. 1 it could be expected not to meet at all phase IV for the higher K concentrations. As just explained, it is however observed that phase IV forms metastably. This fact can easily be explained by the similarity of the structures of II_A and IV_A. Certainly the ease of crystallization of phase IV_A from II_A is much greater than that of the rather complex structure of III_A. Thus it is not surprising to find this modification outside its stability range (compare GOLDSMITH, 1955).

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REFERENCES*)

KAWABE, U., YANAGI, T. and SAWADA, S. (1965). Dielectric and X-ray studies of KNO_3-series mixed crystals. J. Phys. Soc. Japan *20*, 2059–2073.

KRACEK, F. C. (1930): The polymorphism of potassium nitrate. J. Phys. Chem. *34*, 225–247.

MIEKK-OJA, H. (1941): Kalorimetrische Untersuchungen über Umwandlungen in $NaNO_3$ and KNO_3. Ann. Acad. Sci. Fenn. A 11, 65 pp.

SÁENZ, I. M. DE, TESSORE, J. C. and LEONE, R. (1970): Optical study of the phase transitions of ammonium nitrate and of its proerties in the range 15–90° C (Phase IV, III, II' and II). Schweiz. Mineral. Petrogr. Mitt. *50/2*, 209–220.

SAWADA, S., NOMURA, S. and ASAO, Y. (1961): Dielectric behaviour of KNO_3 in the ferroelectric phase III. J. Phys. Soc. Japan *16*, 2486–2494.

SAWADA, S., NOMURA, S. and FUJII, S. (1958): Ferroelectricity in the phase III of KNO_3. J. Phys. Soc. Japan *13*, 1549.

SHINNAKA, Y. (1962): X-ray study on the disordered structure above the ferroelectric Curie point in potassium nitrate. J. Phys. Soc. Japan. *17*, 1073–1083.

YANAGI, T. and SAWADA, S. (1963): Ferroelectricity in the $(NH_4)_xK_{1-x}NO_3$ mixed Crystal. J. Phys. Soc. Japan *18*, 1228–1229.

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*) For other references see M. de SÁENZ, TESSORE and LEONE (1970, this volume).