Short Communications

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The thermal transformations in solid ammonium nitrate containing potassium and caesium ions. By S. SRINI-

VASAN, *Department of Physics, Indian Institute of Technology, Madras* 600036, *India*

The four solid–solid phase transformations in NH_4NO_3 and its solid solutions, $K_x(NH_4)_{1-x}NO_3$ are studied by differential thermal analysis and X-ray diffraction. The formation of the cubic phase (nearest to the melting point) is attributed to the onset of rotational disorder of the NO_3^- ions.

Introduction

It has been shown by different experimental techniques (Hendricks, Posnjak & Kracek, 1932; Brown & McLaren, 1962) that solid ammonium nitrate exists in five different crystallographic forms below its melting point of 165°C. The transition temperatures

$$V \xrightarrow{-19\,^\circ C} IV \xrightarrow{32\,^\circ C} III \xrightarrow{84\,^\circ C} II \xrightarrow{125\,^\circ C} I .$$

The crystallographic data of all the phases except III, which is obtained only when the crystal has a large quantity of occluded mother liquor are given in Table 1 (normally a crystal in phase IV transforms directly to phase II at 84°C).

The structures of phase V (Amoros, Aresse & Canut, 1962) and phase IV (Choi, Mapes & Prince, 1972) show that there is hydrogen bonding. The N–H···O bond length is 2·88 Å in phase V and 2·94 Å in phase IV.

The mechanism of the transitions in potassium nitrate (Yanagi, 1965) and rubidium nitrate (Salhotra, Subba Rao & Venkateswarlu, 1969) have been investigated with studies made on their solid solutions with nitrates of other cations (of different sizes). The present work is a similar attempt on the transitions in ammonium nitrate.

Coates & Crewe (1961) found from X-ray powder diagrams that ammonium nitrate forms solid solutions with potassium nitrate (K$^+$ ion radius 1·33 Å; NH$_4^+$ ion radius 1·48 Å). We find that it forms solid solutions with caesium nitrate (Cs$^+$ ion radius 1·69 Å). The thermal transitions of mixed crystals $K_x(NH_4)_{1-x}NO_3$ ($x_{max}=0\cdot4$) and $Cs_x(NH_4)_{1-x}NO_3$ ($x_{max}=0\cdot1$) were studied by X-ray (oscillation and Weissenberg) methods and by differential thermal analysis.

Experimental results

X-ray diffraction

Needle-shaped crystals of pure and mixed crystals of ammonium nitrate were prepared by slow evaporation of aqueous solutions containing stoichiometric proportions of the salts. Zero and higher-layer Weissenberg pictures taken by mounting the crystals along the needle axis (the [100] direction) showed that they belong to the space group *Pmmn* (of phase IV). The crystals containing Cs$^+$ ions

showed a slight increase in all the lattice parameters, but no systematic study was made of these increases.

On heating, they transformed at $\sim 80°C$ to phase II: Hendricks *et al.* (1932) eliminated all other space groups except *P4bm* and *P$\bar{4}$2$_1$m* from the minimum NH$_4$–O distances (assumed by them to be 2·6 Å). Rotation pictures were taken about the needle axis (the [100] of phase IV transformed as a twofold axis of phase II) and the 0*kl* reflexions indexed. The absence of 0*k*0 (k=odd) reflexions showed the space group to be *P$\bar{4}$2$_1$m*. The calculated atomic parameters N (of NH$_4$) 0,0,0·5; N (of NO$_3$) 0,0·5,0·01; O(1) 0,0·5,0·25 and O(2) 0·631, $-0\cdot131,0\cdot885$, agreed well with the intensities observed.

Differential thermal analysis

The D.T.A. was carried out in a Netzsch thermal analyser with alumina powder as reference sample, and the transitions were recorded during heating. The rapid sublimation of the salt above 150°C did not permit the cooling part to be studied.

In the $K_x(NH_4)_{1-x}NO_3$ system, $x>0\cdot05$, phase II did not appear, the transformation occuring directly from IV to I. With increasing values of x, the transformation temperature decreased, becoming 110°C at $x=0\cdot4$. In the $Cs_x(NH_4)_{1-x}NO_3$ system for $x=0\cdot1$, the IV $\rightarrow$ II transformation was shifted upwards by 5°C and phase I did not appear; the crystal melted at $\sim 160°C$. At lower concentra-

Table 1. *Crystallographic data for the polymorphs of ammonium nitrate*

Phase	System and space group	Cell dimensions (Å)	Source
V	Tetragonal *P*4$_2$*	$a=5\cdot74$ $c=4\cdot89$	Amoros *et al.* (1962)
IV	Orthorhombic *Pmmn*	$a=5\cdot745$ $b=5\cdot438$ $c=4\cdot942$	Choi *et al.* (1972)
II	Tetragonal *P$\bar{4}$2 m*	$a=5\cdot76$ $c=4\cdot96$	Present work
I	Cubic (CsCl type)	$a=4\cdot40$	Hendricks *et al.* (1932) Shinnaka (1959)

*Pseudocell. True cell has dimensions $\sqrt{2}a$ and $2c$.

tions, the phase I transition was shifted to temperatures above 125 °C.

Discussion

Brown & McLaren (1962) measured the proton magnetic resonance line widths of polycrystalline ammonium nitrate and explained the low values due to 'nil' intra-NH$_4$ contribution which they interpreted as evidence of free rotation of the NH$_4^+$ ion. The libration amplitudes of the hydrogens obtained by Choi et al. (1972) from neutron diffraction also suggest a nearly free rotation producing spherical symmetry for the cation. As in alkali nitrates, the foreign cations may thus be expected to enter the lattice substitutionally.

In phases IV and II, steric hindrance prevents any large amplitude oscillation of the nitrate ion. On the other hand, in phase I (Shinnaka, 1959), X-ray studies provide evidence for hindered rotation of the nitrates. The absence of phase II in crystals containing K$^+$ ions is traceable to the onset of rotational disorder of the NO$_3^-$ ions, when they have the symmetry of phase II. The cation–oxygen distance in phase II, $\sim 3 \cdot 0$ Å, is larger than the maximum K–O distance (for eightfold coordination in the phase II structure) (International Tables for X-ray Crystallography, 1968), $2 \cdot 98$ Å. This is found to be true in trigonal phase I of potassium nitrate (Tahvonen, 1949), where anion rotation is present for the K–O distance $2 \cdot 96$ Å for sixfold coordination (max. K–O distance $2 \cdot 91$ Å). The rotation stops when the distance decreases to $2 \cdot 88$ Å (Shinnaka, 1962) in trigonal phase III. Likewise, the delayed onset of phase I in crystals containing Cs$^+$ ions, is due to the Cs–O distances varying from $3 \cdot 0$–$3 \cdot 59$ Å (International Tables for X-ray Crystallography, 1968).

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The computation of radial distribution functions for glassy materials. Errata.

By J. H. KONNERT and J. KARLE, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375, U.S.A.

Corrections are given to equations (5), (6), (8) and (15) in the paper by Konnert & Karle [Acta Cryst. (1973). A29, 702–710].

In a previous paper of the above title (Konnert & Karle, 1973), the term $2r/\pi$ on the right-hand side of equation (5) should be replaced by $r/[(2\pi)^{1/2}]$ and l_{ij}^{-1} should be inserted after the summation sign, the right-hand sides of equations (6) and (8) should be multiplied by Δs and $(\Delta s)^2$ respectively, and the term ϱ_0 in equation (15) should be replaced by $4\pi r \varrho_0$. The symbol Δs represents the interval between successive points in the summation.

Reference

KONNERT, J. H. & KARLE, J. (1973). Acta Cryst. A29, 702–710.