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Effect of method of crystallization on the IV–III and IV–II polymorphic transitions of ammonium nitrate

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ABSTRACT

A study has been undertaken on the effect of crystallization method on the IV ↔ III transition of ammonium nitrate (AN). AN is crystallized in three different ways, viz. recrystallization, evaporative crystallization and melt crystallization. When the samples were crystallized from saturated aqueous solution, ideal crystals were formed, which behaved differently from the crystals formed from the other methods. The DTA examination of the crystals showed that the crystals have different transition behaviour. The moisture uptake of the samples determined were found to have influenced by the mode of crystallization. The samples were further analyzed by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The present study showed that the parameters like thermal history, number of previous transformations and moisture content have a very negligible influence on the IV ↔ III transition of AN as compared to the method of crystallization.

1. Introduction

The interest in understanding the physical and thermal properties of ammonium nitrate (AN) has a long history and is motivated by the wide use of this material as fertilizer and blasting agent [1]. Irrespective of its drawbacks, such as phase transitions, low performance and low burning rate, AN has gained a new interest in the propellant field because of eco-friendly plumes, smokelessness and low sensitivity [2]. AN has five stable polymorphic forms between −18 and 169 °C. Since long time there is an interest on more fundamental understanding of the phase transitions of AN, particularly the IV ↔ III transition observed near the room temperature. Even though the polymorphic transition of AN has undergone numerous investigations [3–9], its actual behaviour remains unanswered. Better understanding of these transitions and its reasons will help in developing better ways to stabilize the phases. The crystallographic data and stability range of various phases of AN are given in Table 1 [3,10].

Solid-state polymorphic transitions have a profound influence on the processing and storage of some crystalline powders. A number of experimental techniques have been employed to study the phase transition depending on the characteristic properties of the compound under investigation. This has increased the complexity in determining the actual behaviour of AN. Since DTA is the most simple and clear method to understand the phase transition, we have employed the same for the phase transition analysis of AN.

The transition at 32 °C is of much importance because it involves a change in volume of ∼3.84% and at this temperature the ordered orthorhombic phase IV changes to disordered phase III orthorhombic [11]. The earlier studies pointed out that the IV ↔ III transition temperature may be influenced/affected by moisture [12], mode of crystallization [13], thermal history of the sample [14], number of previous transformations and heating mode [15], grain size [16], experimental technique, etc. The IV ↔ III transition is reported to have occurred anywhere between 32 and 55 °C [11]. A number of investigators believe that the IV ↔ III transition proceeds via a dissolution or solvent mediated mechanism [17], but this mechanism seems to be highly debatable [18,19]. One of the factors which affect the performance of fertilizers and propellant oxidizers is moisture content present or absorbed during storage. By determining moisture absorption characteristics the humidity at which the material starts absorbing significant amount of moisture can be found out. In the present investigation, an attempt has been made to understand the influence of crystallization method on the IV ↔ III transition temperature and the moisture absorption characteristics.

2. Experimental

AR grade AN was used for the experiments. Crystallization of AN was carried out by three different methods, viz. recrystallization, evaporative crystallization and melt crystallization.

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Table 1
Crystallographic phase information of ammonium nitrate

Phase	Structure	Crystal ordering	Stability range (°C)
V	Tetragonal	Ordered	Below −17
IV	Orthorhombic	Ordered	−17 to 32.25
III	Orthorhombic	Disordered	32.25–84.2
II	Tetragonal	Disordered	84.2–125.5
I	Cubic	Disordered	125.5–169.6

2.1. Crystallization

2.1.1. Recrystallization from water

2.5 g AN was dissolved in 1 ml distilled water by heating the solution to 80 °C on a waterbath. After 30 min heating and complete dissolution, the solution was slowly cooled to room temperature with gentle agitation. The resulting crystals were collected through filtration, washed with methanol, and stored in a desiccator and used for further analysis. In another experiment rapid recrystallization was done by dipping the hot saturated AN solution at 80 °C in to an ice bath kept at −10 °C. The crystals formed were of needlelike morphology and behaved similarly to those obtained via slow cooling.

2.1.2. Evaporative crystallization

Aqueous solution containing 3 g/ml AN was evaporated to dryness and the crystals obtained were collected, and stored in a desiccator before use.

2.1.3. Melt crystallization

Five grams of AN was kept at 180 °C until it completely melted, then cooled to room temperature, the crystals were collected, dried and analyzed.

2.2. Crushing strength

The crushing strength of the samples was determined by finger test, used for the quick field measurement, as explained elsewhere [20].

2.3. DTA analysis

The DTA analyses were carried out at a heating rate of 5 °C/min on a TA instruments SDT2960, to understand the phase behaviour of differently crystallized AN samples. Before running the DTA, all the samples, unless stated otherwise, were kept in a desiccator under low pressure in presence of a desiccant for at least 24 h. No special drying was done for any of the samples.

2.4. Thermal cycling

The AN samples obtained via different crystallization methods were heated from 25 to 100 °C, at a heating rate of 2 °C/min, in a DTA furnace. After one heating cycle, the samples were cooled to room temperature and again subjected to DTA analysis.

2.5. Structural (XRD) and morphological (SEM) analysis

X-ray diffraction (XRD) patterns were obtained from a Panalytical X'Pert Pro-MPD instrument. The interplanar spacing (d) was calculated by Bragg's equation and the obtained d values were compared with the ASTM data.

The morphology of the AN particles was studied by scanning electron microscopy (SEM) using a JEOL JSM-6360A instrument.

2.6. Moisture absorption characteristics

Moisture absorption characteristics of the AN samples were determined by using constant humidity chambers, created with special saturated salt solutions [21]. Three different relative humidities (RH) at 53%, 62% and 75% were used to find out the moisture absorption characteristics. Moisture absorption studies were done by keeping accurately weighed quantities of crushed and sieved particles in the size of 105–250 μm of AN in the constant humidity chamber and recording the increase in weight at different intervals. The experiments were repeated to ensure the reproducibility of the results.

3. Results and discussion

Ideal crystals with needlelike morphology were formed from recrystallization method as the crystals slowly grow from its saturated solution. The evaporative and melt crystallization techniques gave samples in a bulk form and no single crystal could be seen.

The DTA of AN samples crystallized by different methods are shown in Fig. 1. In the recrystallized samples, the IV ↔ III transition occurs around 52 °C. On the other hand, the melt crystallized and evaporative crystallized samples showed the IV ↔ III transition around 34 and 36 °C, respectively. The other transitions, viz. III ↔ II, II ↔ I were not affected, thus showing that, the transition route is not altered but the IV ↔ III transition temperature in the recrystallized sample has been shifted to a higher temperature. All the samples were showing the III ↔ II transition peak in the range 80–84 °C as expected and this small shift in temperature is not uncommon in the literature. This in turn also proves that the transition occurred around 55 °C in recrystallized samples is of IV ↔ III transition and does not correspond to IV ↔ II or a metastable transition as reported by some earlier literature. Nor have we observed any exothermic peak between 55 and 84 °C, attributable to a reverse II ↔ III transition [13].

Some of the earlier papers state that the IV ↔ III transition is influenced by the amount of moisture content present in the crystals [7,22,23]. But in the present study, a few samples were analyzed for their moisture content by Karl Fisher method before doing the DTA analysis. Even when the moisture content of the recrystallized samples was as high as 5.6%, the IV ↔ III transition occurred around 55 °C (Fig. 2). This clearly shows that, the postulate which says, IV ↔ II transition occurs at 55 °C only when the moisture content is less than 0.01% and in other cases the IV ↔ III transition will occur at 32 °C, is debatable. Experiments conducted on AN slurries [18] further confirm our observations.

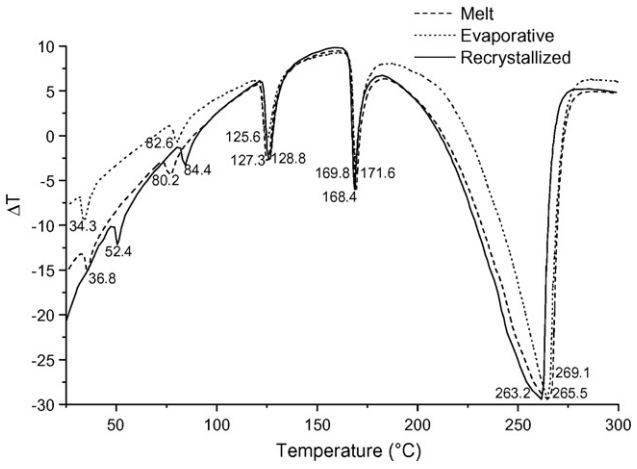

Fig. 1. DTA of the differently crystallized samples.