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Use of potassium ferrocyanide as habit modifier in the size reduction and phase modification of ammonium nitrate crystals in slurries

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ABSTRACT

Ammonium nitrate (AN) is an inorganic crystalline compound used as a solid propellant oxidizer and as a nitrogenous fertilizer. The practical use of AN as solid propellant oxidizer is restricted due to the near room temperature polymorphic phase transition and hygroscopicity. A good deal of effort has been expended for last many years to stabilize the polymorphic transitions of AN, so as to minimize the storage difficulties of AN based fertilizers and to achieve more environmentally benign propellant systems. Also, particles with aspect ratio nearer to one are a vital requirement in fertilizer and propellant industries. In the present study AN is crystallized in presence of trace amount of potassium ferrocyanide ($K_4Fe(CN)_6$) crystal habit modifier and kept for different time intervals. And the effect of $K_4Fe(CN)_6$ on the habit and phase modification of AN was studied. Phase modified ammonium nitrate (PMAN) with a particle aspect ratio nearer to one was obtained by this method and the reasons for this modifications are discussed. The morphology changes were studied by SEM, the phase modifications were studied by DSC and the structural properties were studied by powder XRD.

1. Introduction

Interest in crystallization and in various ways of altering the shapes and structures of crystals has a long history considering the fact that an extraordinary range of physical and chemical properties of crystalline solid-state materials rely on their crystal form and size [1]. Among the important particle parameters, particle shape is particularly important as it significantly affects the physical and chemical characteristics including fluidity, solubility and electromagnetic characteristics of powder materials [2]. Numerous studies have been conducted on particle configuration control techniques for controlling chemical composition, size and size distribution, surface parameters and shape of particles. Also, many routes have been utilized to control the crystal growth and eventually modifying the morphology of crystals [3–5]. For crystal habit modification, crystals are grown in the presence of specific impurities or crystal habit modifiers and the face-specific interactions of these crystal habit modifiers result in the modification of the crystal habit. These crystal habit modifiers may be of very diverse characteristics such as multivalent cations, complexes, surface active agents, soluble polymers, biologically active macromolecules, fine particles of sparingly soluble salts, etc. [6–9].

Since long time, inorganic complexes are utilized as crystal habit modifier in the chemical industry, especially in the production of sodium chloride. Earlier investigators have crystallized sodium chloride in the presence of glycine, β-alanine and potassium ferrocyanide trihydrate [10]. Among these glycine and potassium ferrocyanide have reportedly exhibited significant effect on the habit modification and size reduction of sodium chloride [11]. The characteristic morphologies obtained by glycine and potassium ferrocyanide range from cubic out growth to octahedral crystals. Potassium ferrocyanide trihydrate (KFCT), $K_4[Fe(CN)_6]\cdot 3H_2O$, is a yellow coloured crystalline (monoclinic) compound with a solubility of ~27 g in 100 mL at room temperature. KFCT is known for its habit modification effect on different inorganic crystals and its anti-caking effects [6,12–14]. Also, a complex formation mediated mechanism for the crystal growth and morphological evolution of sodium chloride in the presence of KFCT is reported by earlier investigators [6]. In the present study, an innovative method to produce morphology and phase modified AN (PMAN) using KFCT as habit modifier is presented.

Ammonium nitrate (AN) is commonly used as fertilizer and its mixture with fuel oil as blasting agent [15]. As a nitrogenous fertilizer, it acts as a source of ammonia and nitrate ions, vital to the plant growth, whereas, in explosives and propellants, the nitrate ion acts as a source of oxygen. Recently, AN has received a new interest in the propellant field because of eco-friendly plumes, smokelessness and low sensitivity [16]. But the main difficulties in using AN as fertilizer or propellant oxidizer are the polymorphic phase tran-

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sitions and hygroscopicity. AN has five stable polymorphic forms between −18 and 169 °C at ambient pressure. Many studies have been carried out to stabilize these phase transitions, and most of the studies particularly concentrate on the stabilization of IV ↔ III transition, as it occurs near the room temperature. Another reason is, IV ↔ III (ordered orthorhombic ↔ disordered orthorhombic) transition occurring at 32 °C is accompanied by a volume change of 3.4% and the consequent density decrease. One of the other drawbacks of IV ↔ III transition is that, after this transition, the crystals fall to pieces and then cake together [17]. Hence, the IV ↔ III transition significantly influences the structure and quality of AN crystals, besides the density decrease. Earlier investigators have used cocrystallization of AN with different foreign salts to stabilize the near room temperature IV ↔ III phase transition. Most of the literature deals with the stabilization of IV ↔ III transition with potassium salts, where the K^+ ions replace some of the NH_4^+ ions and hence the stabilization is achieved. The disadvantage of this cocrystallization method is the amount of foreign salt required to stabilize the transition, which varies from 2 to 10% by weight [18,19]. Using a dye, acid magenta, as crystal habit modifier, morphology modification of AN is reported in the literature [3]. However, this habit modifier only modifies the morphology and not the IV ↔ III phase transition.

AN is considered to be one of the eco-friendly oxidizers used in the propellant industry. The percentage of oxidizer, in the propellant formulation, varies from 70 to 80% by weight depending on the energetic requirements and compatibility with the other ingredients. Because of the high percentage in the propellant formulation, the performance of the propellants (specific impulse and burning rate) varies with the oxidizer properties, and, in turn, the performance of the oxidizer varies with the particles' size and morphology [20]. Hence, in the present investigation, KFCT has been used to control the morphology of AN and, also, the effect of this method on the phase transition of AN is studied.

2. Materials and methods

AN and KFCT were of AR grade and used as obtained without further purifications in the experiments, from Thomas Baker (India) and CDH Chemical (India) respectively.

2.1. Crystallization

Saturated solution of AN was prepared by dissolving 12.5 g AN in 5 mL of distilled water at 80 °C. The solution was kept in a water bath and gently agitated (<50 rpm) for 30 min, after complete dissolution of the salt, different wt% of KFCT, say 0.1, 0.2, 0.3, 0.5 and 1%, was added to the solution. After the addition, agitation was continued for 15 min more and then the solution was cooled to room temperature and kept in ambient condition in a sealed container for 72 h. The agitation was stopped just before the container was removed from the hot water bath, i.e., before the crystallization begun, in order to avoid the mechanical milling or breakage effects [21]. After 72 h, the crystals were collected through filtration washed with methanol and analyzed under an optical microscope. The optical microscopic examinations showed some morphology modifications; however, all the samples were having a nearly same morphological evolution. Hence, the concentration of crystal habit modifier was optimized to the lowest, at 0.1 wt% of AN, and the time interval was varied from 48 to 240 h.

In a typical experiment, AN with optimized concentration of KFCT, 0.1% by wt of AN (0.0125 g), was prepared as explained above. Five such set of samples were prepared and the crystals were collected through filtration after 48, 96, 144, 192 and 240 h and washed with methanol and dried in desiccators under low pressure. In a second set of experiments the procedure was repeated without any additive and the dried samples were used for further analysis. Recrystallized samples mentioned here are obtained by dissolving 5 g AN in 2 mL distilled water by heating the solution to 80 °C on a waterbath, then cooled to room temperature and the crystals formed on cooling were filtered immediately.

2.2. Morphological (SEM) analysis

Scanning electron microscopy (SEM) images were obtained at 30× magnifications on a JSM 6360A scanning electron microscope and were used to understand the morphology of the AN particles. For SEM analysis the powder sample was put on a carbon tape and then coated with platinum using a sputter coater.

2.3. Thermal analysis

The differential scanning calorimetry (DSC) analyses of the vacuum dried samples were carried out on a Du Pont model 2000 DSC instrument at a heating rate of 5 °C/min. The AN samples collected, with and without KFCT modifier, after 48, 144 and 240 h were heated from RT to 100 °C and the first DSC thermogram of the samples was obtained. After one heating cycle, the samples were cooled to room temperature and again subjected for DSC from RT to 200 °C and the second thermograms were obtained. Thus, a minimum of two DSC runs were carried out for each samples and the results are presented. The thermal cycling of the samples conducted, other than on DSC instrument, were on a DTA instrument, calibrated with 4-nitrotoluene (51 °C), benzoic acid (122 °C) and cupric sulphate pentahydrate.

2.4. Structural (XRD) analysis

The AN samples were characterized by powder X-ray diffraction (PXRD) with a Bruker AXS D8 Advance XRD instrument to study the composition and structure of the compound. Each sample was scanned over a 2θ range of 10–70° with a sampling interval of 0.1°. The PXRD reflections were obtained at room temperature (25 °C). From the obtained PXRD patterns, the interplanar distances (d) were calculated by Bragg's equation and compared with the JCPDS-ICDD data.

3. Results and discussion

Production of spherical shaped particle is a vital requirement in propellant, textile, dairy, dyeing, food, fertilizer, paper, and pharmaceutical industries as the morphology modified particles exhibit distinct changes in optical activity, flow characteristics and shelf life [22]. The morphology of crystals depends on the growth rates of different crystallographic faces. The growth of a given face is governed by the crystal structure and defects on one hand and by environmental conditions on the other hand [23]. Usually AN crystallized from water, without any habit modifier, gives needle shaped particles, which is undesirable for chemical industry and especially for the propellant industry. When the crystals are formed by very slow growth, the crystal–liquid interface may be expected to display the equilibrium form for the crystal, and clear facets are formed, whereas, if more rapid growth is allowed, then this would tend to suppress the facet formation [24]. During solution crystallization the AN crystals were formed rapidly and hence the facet formation is not observed.

In the present study, when AN crystals were formed from its saturated solutions, in spite of having the crystal habit modifier in the solution, the AN crystals were of needle-like morphology. The needle-like morphology was similar to those of recrystallized samples. However, by keeping these AN crystals in solutions containing

KFCT modifier, for different time intervals, significant changes were observed in the morphology of AN crystals.

As explained in the experimental section, KFCT was added to the hot AN solution. After KFCT addition, the solution became pale greenish yellow in colour. This turbid greenish yellow solution after standing approximately for 24 h in a sealed container turned into transparent light green solution. On further standing the light green colour of the solution became deep bluish green and developed a bluish precipitate layer on top of the AN crystals. This bluish precipitate was readily getting suspended in the solution after slight shaking. As the standing time was increased from 48 to 240 h, the quantity of AN crystals retrieved by filtration from the solution was also reduced; simultaneously, the amount of bluish precipitate increased.

The colour change observed in the solutions during the addition time and on standing the solution might be due to the complex interaction between KFCT, AN and H_2O [25]. With the hydrogen ions in the solution, the KFCT might form a hexaaquairon(II) ion complex, $[Fe(H_2O)_6]^{2+}$, which can be oxidized to ferric by the ammonium nitrate solution with the formation of nitric oxide [26]. The light green colour of the solution is due to ferrous ion formation, which gets oxidized to ferric to give yellowish brown colour. These ferric or ferrous ions react with ferrocyanide to give the blue coloured precipitate. However, the concentration of hydroxide ion in ammonium nitrate solutions is extremely low. The dissociation equilibrium of hexacyanoferrate(II) is

$$Fe(CN)_6{}^{4-} \rightarrow Fe^{2+} + 6CN^- \quad (1)$$

where the water coordinated to the free iron(II) ion has been left out for simplicity. The equilibrium concentration of iron(II) under the given conditions can be estimated to about 1 μM. Ammonium ion is a weak acid and cyanide ion a weak base; in the concentrated ammonium nitrate solution iron(II) may be oxidized to iron(III):

$$3Fe^{2+} + NO_3{}^- + 4H^+ \rightarrow 3Fe^{3+} + NO + 2H_2O \quad (2)$$

followed by precipitation of Prussian blue:

$$Fe^{3+} + Fe(CN)_6{}^{4-} + K^+ \rightarrow KFe[Fe(CN)_6] \quad (3)$$

This latter process removes iron(III) ions from solution, then the second equilibrium is displaced to the right (le Châtelier's principle), and so is the first equilibrium.

We also expected the possible formation of nitritopentacyanoferrate(II) ions; however this possibility is ruled out as it is not stable in acidic solutions, where it is transformed to nitroprusside:

$$Fe(CN)_5NO_2{}^{4-} + 2H^+ \rightarrow Fe(CN)_5NO^{2-} + H_2O \quad (4)$$

and furthermore, these mixed complexes are orange red in colour.

These postulates and observations confirm that the AN in the solution is taking part in the formation of the blue precipitate, and because of this the quantity of AN was getting reduced and the quantity of blue precipitate was increasing. To isolate the blue precipitate from the solution (kept for 240 h), it was first filtered through a whatman (No. 40) filter paper and the AN crystals present were removed. The collected filtrate (deep blue in colour) was then centrifuged on micro-centrifuge tubes for 10 min at 10,000 rpm. The centrifugation procedure separated the blue precipitate and the residue obtained was collected and dried in desiccators under low pressure. Even after this procedure, the DTA analysis of the residue showed the presence of AN. However, after heating the residue up to 300 °C, the remaining compound obtained was brown coloured iron oxide (Fe_2O_3). This confirmed that the precipitate obtained after centrifuging contained both AN and the iron complex. As the isolation of the blue iron pigment itself is difficult, more studies may be required to understand the exact reaction behind this blue precipitate formation.

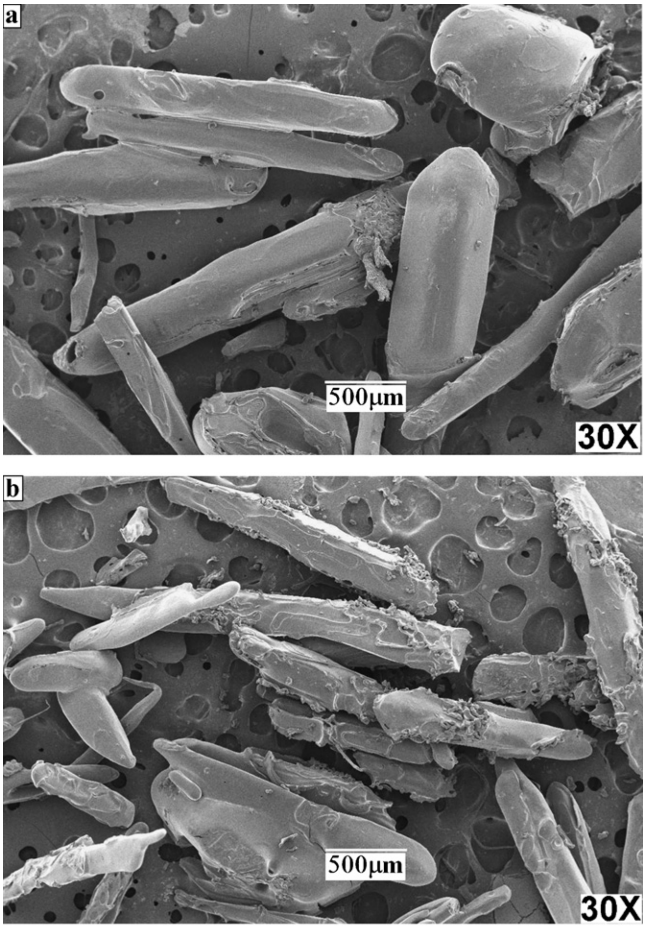

Fig. 1. SEM of AN crystals collected after 48 h (a) without KFCT and (b) with KFCT.

The crystals collected by filtration, from the solutions, after different time intervals were analyzed with SEM and the images are shown in Figs. 1–5. SEM images of both AN crystals without KFCT modifier and with modifier have been obtained, and the crystals obtained after same time period were grouped together and shown as (a) (without KFCT) and (b) (with KFCT). The crystals obtained after 48 h are shown in Fig. 1. Even though the general morphology is similar to that of the recrystallized samples, slight variations were observed in the morphology of AN crystals collected from solution containing KFCT. The crystals obtained after 96 h (the SEM images of crystals obtained after 96 h are shown in Fig. 2) were also showing slight morphological changes compared to the one obtained after 48 h. However, as the standing time (the SEM images of the samples filtered after 144 h are shown in Fig. 3) was increased to 144 h, the crystals started losing their needle-like nature and tend to break down into smaller crystals. Even though the morphology modifications were seen, the crystals obtained after 144 h were containing few particles with aspect ratio near to one and the general morphology of the crystals remained to be needle-like. With further increase in the reaction time of 192 h, the breaking down phenomena became more prominent (Fig. 4). The crystals collected after 48 and 96 h have an average size of 1000 µm, as compared to the crystals obtained after 192 h have an average size 100 µm. This shows that the 1000 µm crystals have broken down to smaller crystals of 100 µm size on standing in the solution with KFCT habit modifier. The crystals obtained after 240 h (Fig. 5) were of nearly spherical morphology and contained no needle shaped crystals. These observations point towards the occurrence of chemical milling of AN

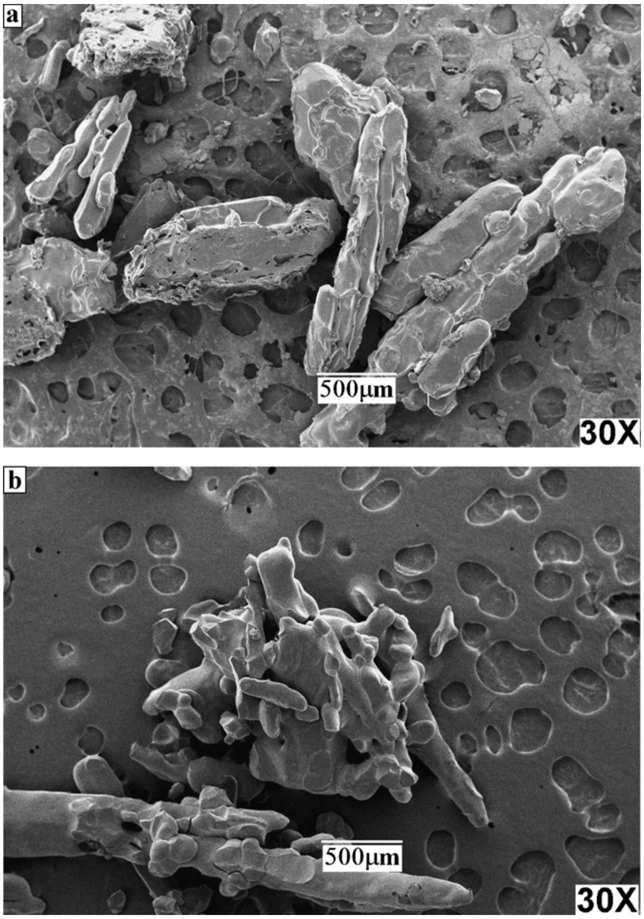

Fig. 2. SEM of AN crystals collected after 96 h (a) without KFCT and (b) with KFCT.

crystals in the solution, morphology modification and particles size reduction. However, the possibility that the complex is increasing the solubility of AN in solution and the crystals are dissolving back in the solution also cannot be ruled out.

When the AN crystals were kept in solution without habit modifier, only slight modifications were observed in the morphology. However, the crystals obtained after 240 h from the solution, without any habit modifier, were showing some morphological changes. This indicated that the KFCT may be acting as a catalyst for the habit modification or as an etching agent and this size reduction can be brought by keeping the crystals in its saturated solutions for longer periods. To confirm this, AN crystals were kept in solution for 30 days without any habit modifier and it has been observed that no appreciable size reduction occurs even after 30 days and, on the other hand, agglomeration of the particles has occurred and particle size increased. Thus, the possibility of KFCT participating in the size reduction mechanism is confirmed and such slight morphology variations might have occurred during the repetition of experiments.

To understand the phase transition behavior, thermal cycling studies of the AN samples were carried out in the temperature range of RT (room temperature) to 100 °C. The DSC thermograms of the AN samples obtained after different time intervals, without and with KFCT habit modifier, are shown in Figs. 6 and 7 respectively. The same samples were again subjected for DSC analysis for a temperature range of RT to 200 °C and the thermograms of AN without KFCT modifier are shown in Fig. 8 and with habit modifier are shown in Fig. 9. (The thermal cycling data acquired for the same are tabulated in Tables 1 and 2 and submitted as Supplemen-

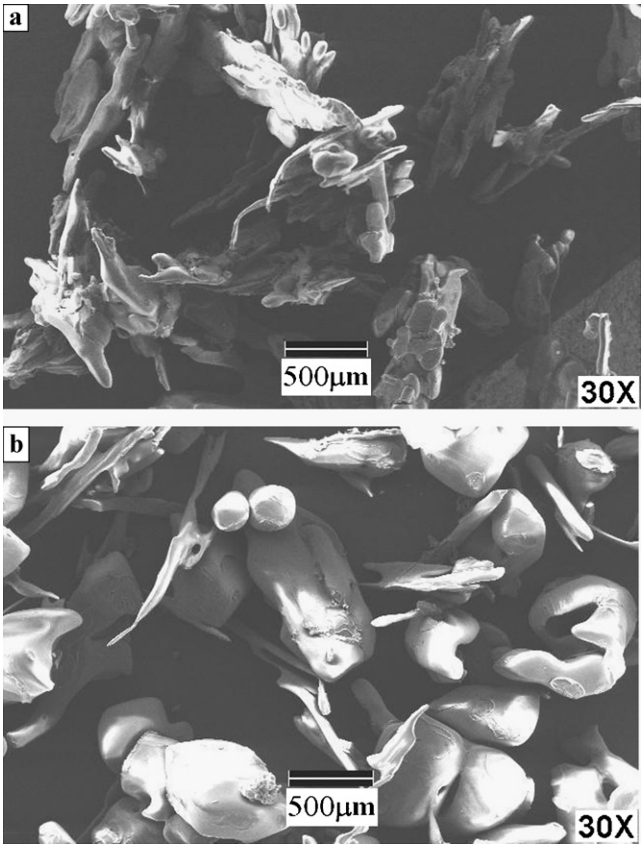

Fig. 3. SEM of AN crystals collected after 144 h (a) without KFCT and (b) with KFCT.

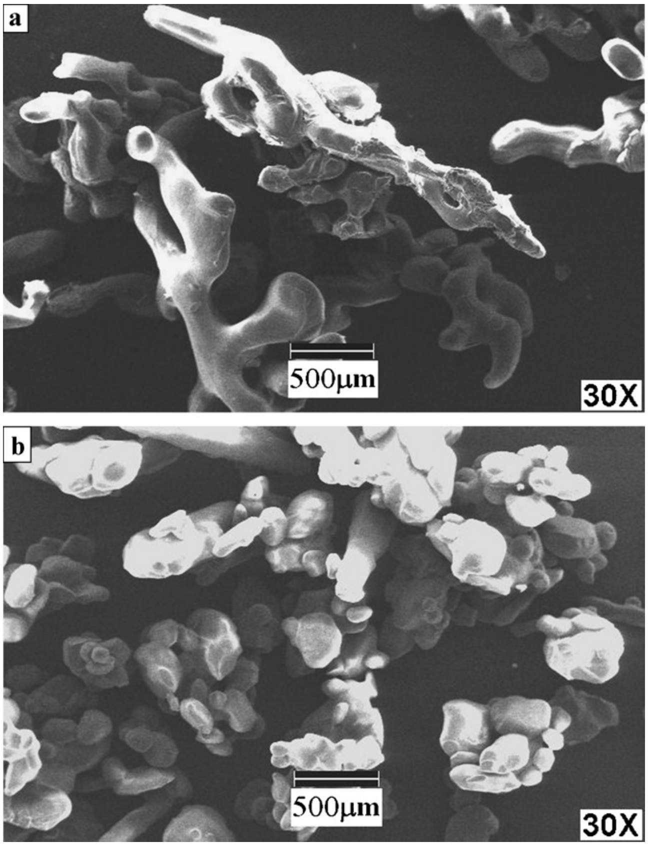

Fig. 4. SEM of AN crystals collected after 192 h (a) without KFCT and (b) with KFCT.

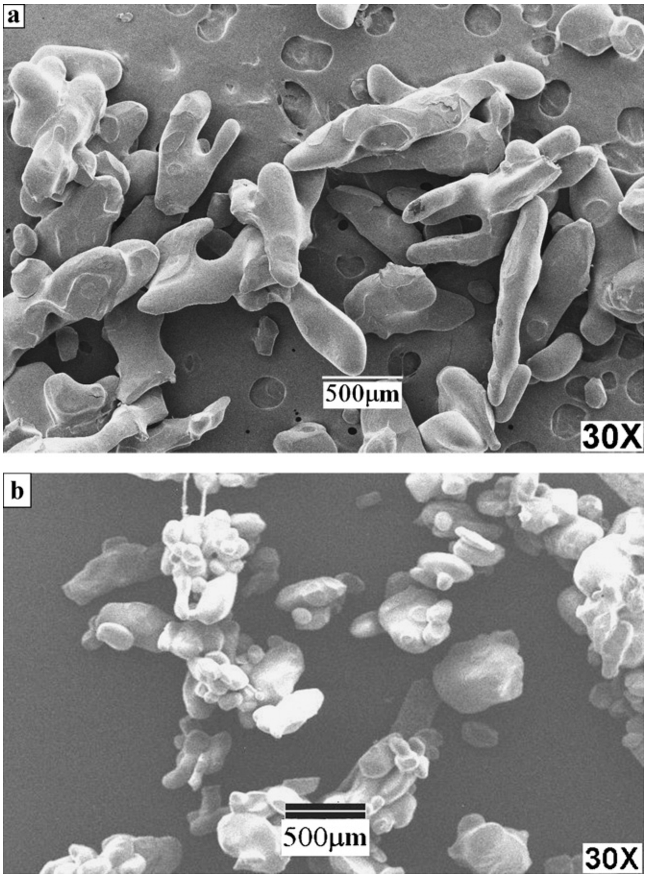

Fig. 5. SEM of AN crystals collected after 240 h (a) without KFCT and (b) with KFCT.

tary data.) The thermograms clearly point out that both AN, kept in solution with and without modifier, are phase modified and could withstand a minimum of two thermal cyclings.

However, our earlier studies revealed that recrystallized AN always shows a shift in IV ↔ III transition temperature at ∼50 °C, which falls back to 32 °C after one thermal cycling and the presence of trace amount of HAN contributes to this shift in transition [27]. Also, during the thermal cycling, some of the samples showed absence of the III ↔ II transition, which generally occurs at 84 °C. This anomaly is reported in the literature and said to have been influenced by the particle size [28]. Except this absence of III ↔ II peak exhibited by some samples, all other transitions were intact and behaved as reported in the case of pure AN.

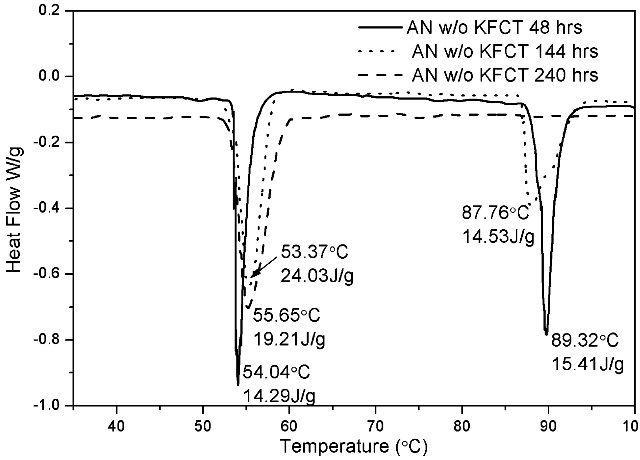

Fig. 6. DSC thermograms of AN without KFCT—temperature range RT to 100 °C.

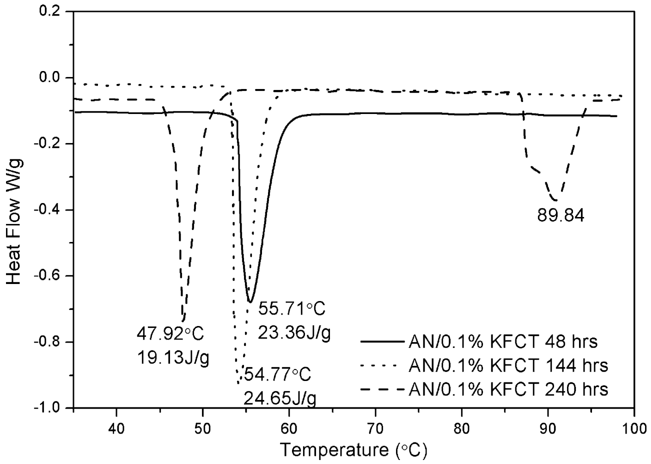

Fig. 7. DSC thermograms of AN with KFCT—temperature range RT to 100 °C.

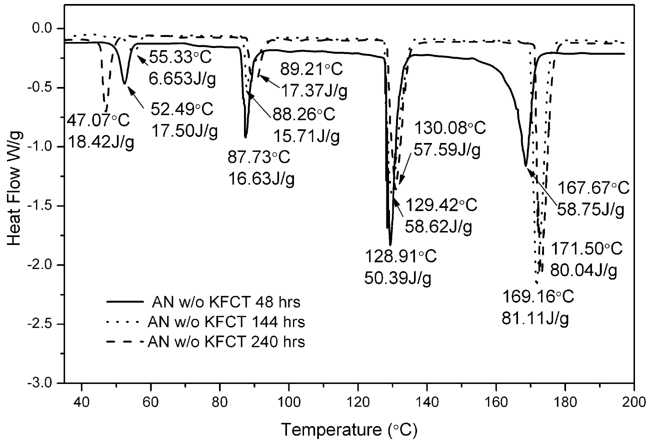

Fig. 8. DSC thermograms of AN without KFCT—temperature range RT to 200 °C.

To ascertain the thermal stability, all the AN samples were cycled between RT to 100 °C, in a DTA furnace, until the shifted transition at ∼50 °C is brought back to ∼32 °C. This showed that the samples remain stabilized for minimum of three cyclings, but some of the KFCT modified samples could maintain the IV ↔ III transition temperature at ∼50 °C up to eight thermal cyclings.

The powder XRD patterns obtained for the samples are shown in Figs. 10–14. The samples obtained after same time interval but with

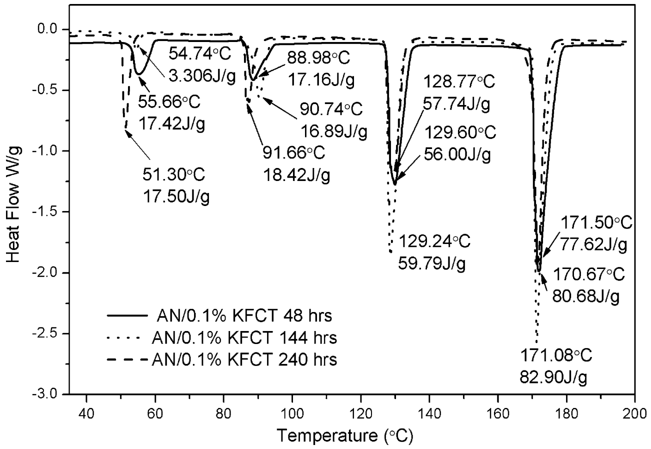

Fig. 9. DSC thermograms of AN with KFCT—temperature range RT to 200 °C.

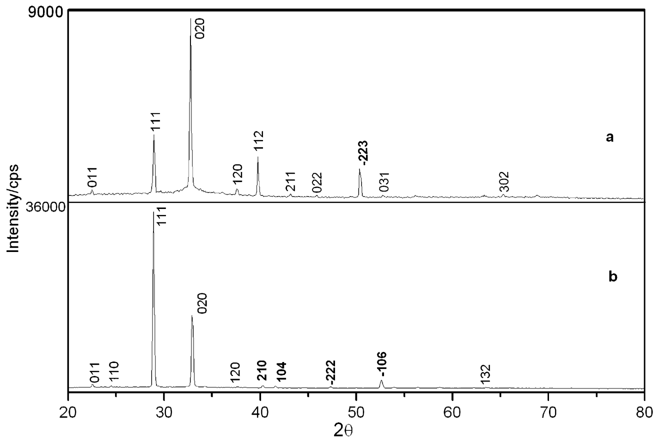

Fig. 10. Powder XRD of AN crystals collected after 48 h (a) without KFCT and (b) with KFCT.

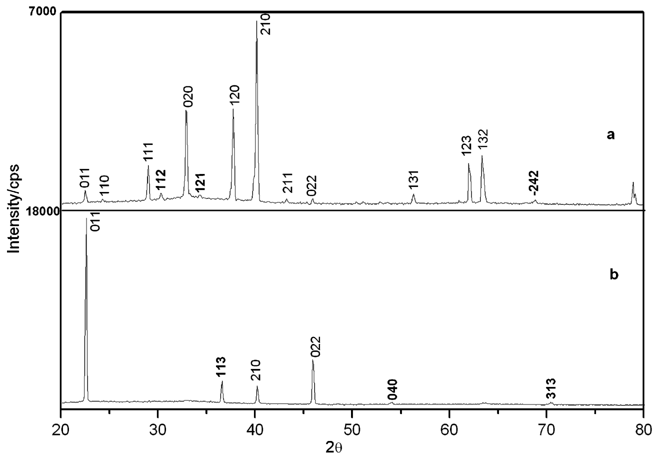

Fig. 11. Powder XRD pattern of AN crystals collected after 96 h (a) without KFCT and (b) with KFCT.

and without habit modifier are grouped together and shown as (a) (without KFCT) and (b) (with KFCT). The *d* values obtained from the powder XRD reflections were compared with the JCPDS-ICDD data of AN (JCPDS 8-452). The comparison revealed that some of the diffraction lines were not coinciding with the JCPDS-ICDD data of AN.

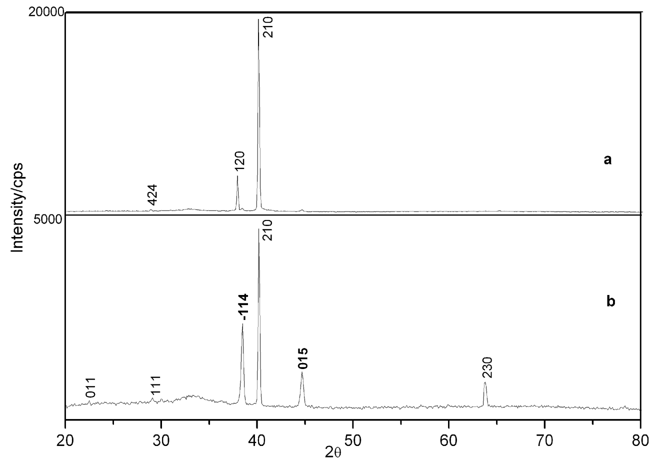

Fig. 12. Powder XRD pattern of AN crystals collected after 144 h (a) without KFCT and (b) with KFCT.

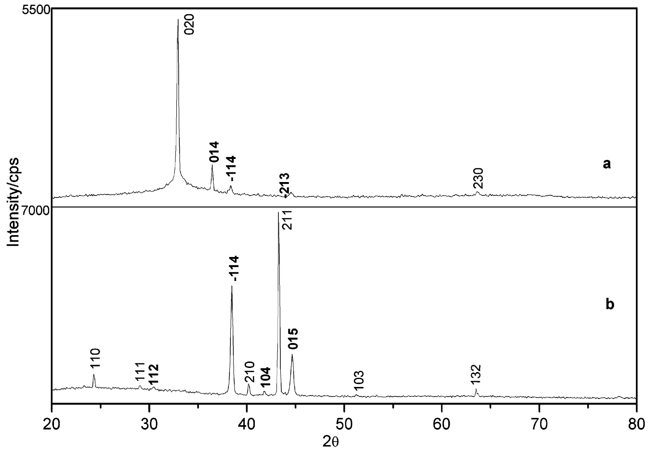

Fig. 13. Powder XRD pattern of AN crystals collected after 192 h (a) without KFCT and (b) with KFCT.

Further analysis of the powder XRD patterns revealed that the non-matching diffraction lines (with JCPDS-ICDD data of AN) seen in the powder XRD patterns were matching with the diffraction lines of hydroxylammonium nitrate (HAN). Even the recrystallized samples [27] were showing the diffraction lines which coincided with that of JCPDS-ICDD data of monoclinic HAN; however, the HAN signature was more prominent in the samples obtained in the present study. In the powder XRD diffractograms, most of the higher intensity peaks were of AN and few of the lower intensity peaks were corresponding to HAN reflections. The main AN peaks observed are 2.72 (0 2 0), 3.96 (0 1 1), and 3.08 (1 1 1), the peaks observed corresponding to HAN are 2.33 (−1 1 4), 1.81 (−2 2 3) and 2.02 (0 1 5). Even though the higher intensity diffraction lines were coinciding with JCPDS-ICDD data of AN, the intensity differed from one other. (The powder XRD analysis data are tabulated in Tables 3–7 and submitted as Supplementary data.)

We have seen that recrystallized samples also show a shift in temperature because of the presence of trace amount of HAN as impurity. However, the decomposition temperature of HAN is below 100 °C [29,30] and during the first thermal cycling (up to 100 °C) itself the HAN present in the recrystallized sample was getting decomposed off. In contrast, the PMAN obtained in the present study could withstand more number of thermal cyclings compared to the only one thermal cycling for recrystallized samples.

In the earlier investigations, where AN phase stabilized with potassium salts, the stabilization is achieved through a replacement

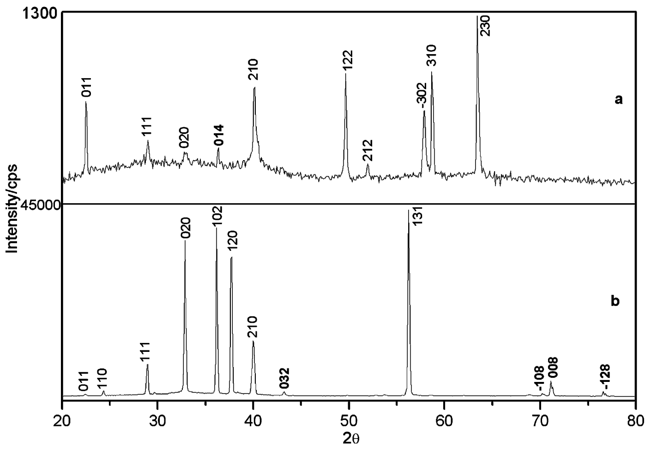

Fig. 14. Powder XRD pattern of AN crystals collected after 240 h (a) without KFCT and (b) with KFCT.

mechanism. The cation:anion radius ratio for AN is 0.76. When doped with potassium salts, some of the NH_4^+ is replaced by K^+ and the value of cation:anion ratio closely approaches 0.73. If the cation:anion ratio is below 0.73, the salts are stable in a six-fold coordinated NiAs structure [16]. The replacement mechanism is favoured only if the host cations have their cationic radii within ±15% of the cation being replaced. The NH_4^+ has a reported ionic radius of 1.48 Å and the replacement of this NH_4^+ by the $OHNH_3^+$ might be favoured in the present study. Another reason behind the stabilization effect could be, as the crystals were kept in their own saturated solutions for more time, HAN clusters have enough time to seek out the ideal sites, where it can locate itself or even form a weak networked structure with AN. Whereas in the recrystallized samples the crystals were precipitated and filtered immediately and, hence, HAN clusters might be getting randomly located. These randomly located HAN clusters were possibly getting decomposed off during the first thermal cycling, while the networked HAN clusters may require more thermal cyclings to get decomposed off. Hence, the HAN forming a weak networked structure with AN seems be the reason behind the exhibited higher stability.

4. Conclusions

Phase modified ammonium nitrate (PMAN) with a particle aspect ratio nearer to one has been synthesized by crystal habit modification route, using $K_4Fe(CN)_6$ as crystal habit modifier. AN crystals were kept in solutions containing KFCT habit modifier and a possible chemical milling of AN particles seems to be occurring in the solution. This chemical milling appears to be the reason behind the change in the needle morphology to smaller particles with aspect ratio nearer to one. Presence of HAN clusters was observed in the powder XRD pattern and, as an added advantage, these clusters were forming some networked structure with AN and seem to be modifying the IV ↔ III transition. The thermal cycling studies confirmed that the modified transition remains near 50 °C for a minimum of three cyclings. The crystal habit modification effect of $K_4Fe(CN)_6$ on AN is clearly seen in the morphology of AN crystals and this can be beneficial for the industrial crystallization of AN. The shift in the near room temperature phase transition will be a promising achievement for the rocket propellant industry as this will be helpful in the realization of more environmentally benign solid propellant systems. Also, in the fertilizer industry the storage of AN is a matter of concern because, after IV ↔ III transition (occurs around 32 °C), AN crystals fall to pieces and then cake together. PMAN has a IV ↔ III transition above 50 °C and this will avoid the possibility of a phase transition during the ambient storage conditions and hence the disintegration of physical properties of AN during storage can be abstained.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.04.073.

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