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.

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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.
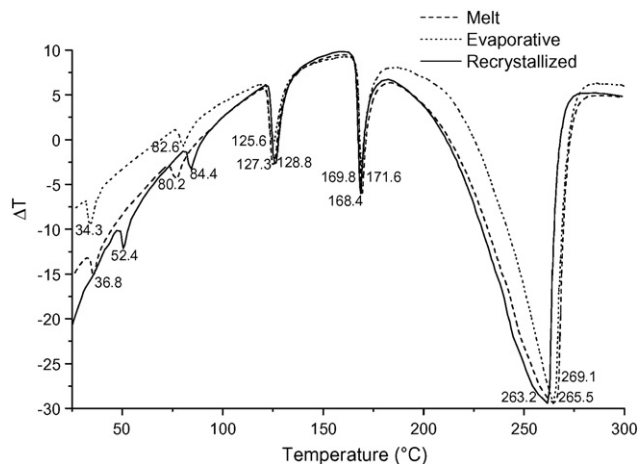
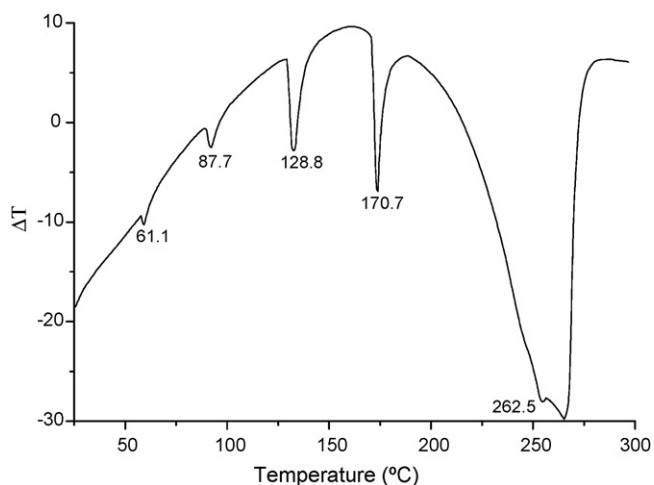**Fig. 1.** DTA of the differently crystallized samples.

Fig. 2. DTA of recrystallized sample with moisture content 5.6%.

The only anomaly observed in the present study from the reported AN transition path is the absence of 84 °C peak in few cases (Fig. 3). The absence of 84 °C peak in those cases can be attributed to the dependability of transition path on the particle size, as reported elsewhere [16]. The sample with a particle size near 0.06 mm more likely undergo the transition path IV ↔ II, as compared to the bigger particles (<2 mm) which undergo the IV ↔ III ↔ II transition path. All the samples melted at ∼170 °C before decomposing (at around 260 °C). The comparison of DTA results are compiled in Table 2.

The AN samples, especially the recrystallized samples, were subjected to thermal cycling between 25 and 100 °C. The thermal cycling analysis shows that after heating the sample up to 100 °C, the transition observed at 55 °C in the recrystallized samples has been shifted back to 32 °C (shown in Fig. 4), while the
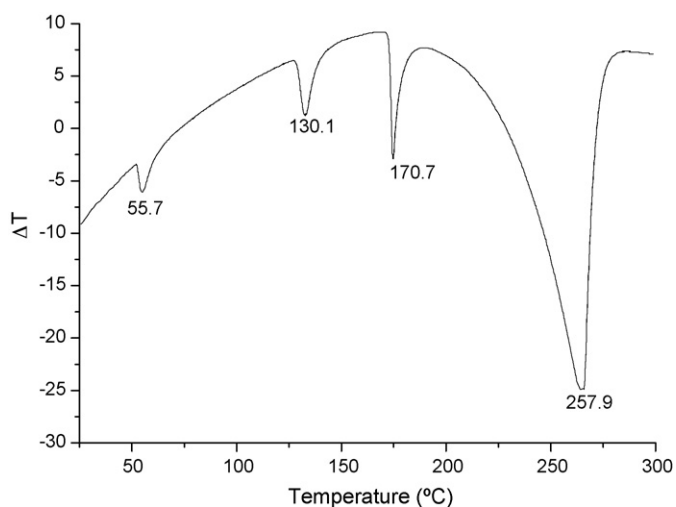

Fig. 3. DTA of IV ↔ II transition in AN.

Table 2
Comparison of transition temperature of different samples

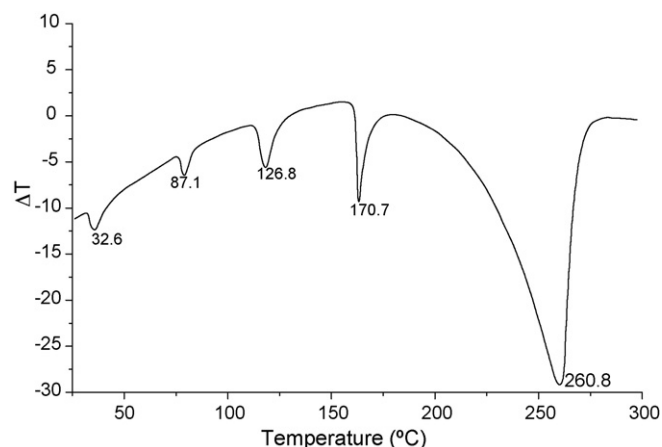| Sample	Transition temperature (°C)			
	IV ↔ III	III ↔ II	II ↔ I	Melt
Recrystallized	52.4	84.4	127.3	169.8
Evaporated	34.3	80.2	125.6	168.4
Melt	36.8	82.6	128.8	171.6
After one thermal treatment				
Recrystallized	32.6	87.1	126.8	170.7

Fig. 4. DTA of recrystallized sample after one thermal treatment.

other transition including the one at 84 °C remained unaltered. This observation shows that after one thermal cycle the AN crystals loose their stabilized behaviour and behave in the same way as the melt or evaporative crystallized samples.

The X-ray powder diffraction data of the samples, obtained at room temperature is shown in Table 3 and the XRD patterns of the crystals are shown in Fig. 5. Interesting results were seen, when the patterns were compared with the JCPDS-ICDD data. The recrystallized sample exhibits the presence of hydroxylammonium nitrate (HAN) along with the AN peaks. The corresponding HAN peaks observed in recrystallized sample are 3.89 (1 1 0), 2.86 (0 2 2), 2.46 (0 1 4), 2.37 (2 0 0), 2.24 (2 1 0) and 1.57 (1 0 6). The evaporated and melt crystals were exhibiting the sharp reflections of AN (JCPDS 8-452) phase IV peaks, confirming that these structures are composed of well crystallized AN particles. The peaks of AN at d values 2.72 (0 2 0) Å, 3.09 (1 1 1) Å, 2.48 (1 0 2) Å, 2.49 (2 1 0) Å and 3.95 (0 1 1) Å, corresponding to phase IV are seen intact in their XRD patterns.
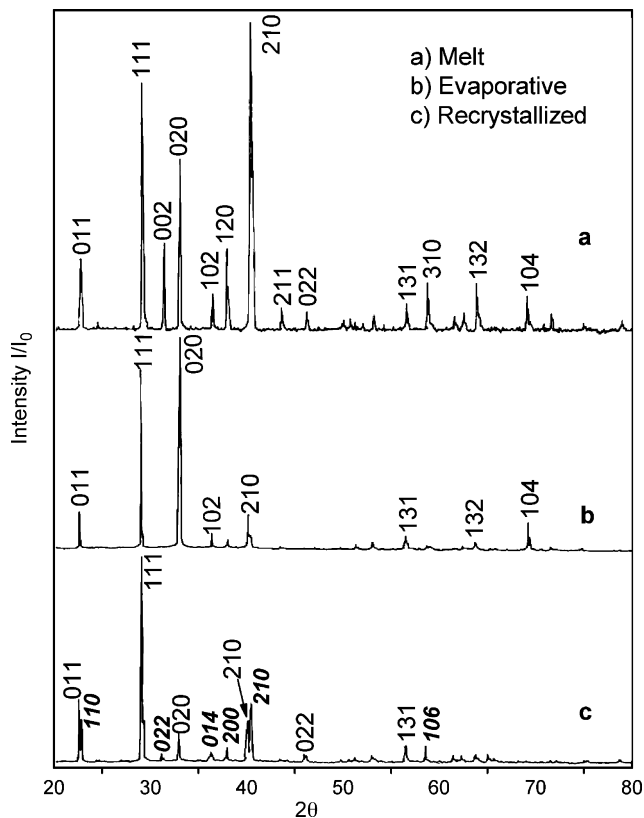
It is well known that the presence of impurities can dramatically affect the nucleation, morphology and chemical properties of the crystals. The observations show that the presence of HAN as impurity in the crystal lattice of AN might be the reason behind the stabilization effect observed in recrystallized samples. HAN is also a propellant oxidizer and usually its aqueous solution is used as liquid oxidizer. HAN is a crystalline compound with monoclinic structure and has a high affinity for moisture [24]. The stability of crystalline HAN or HAN solution at higher temperatures is much lower. The compound starts melting at 48 °C and decomposes below 100 °C [25]. Considering this point, we have observed earlier that the stabilization effect is present for only one thermal cycle and after that the recrystallized sample also behaves as evaporated or melt crystallized samples. This behaviour of recrystallized crystals may be because of the fact that the HAN present in the crystals is decomposing off at higher temperatures and only pure AN remains after the thermal cycling. In this case the HAN may be acting as a stabilizing impurity. A set of other experimental techniques such as NMR, FTIR, etc., were employed to identify the presence of HAN but these techniques were unable to identify the species as the amount present in AN samples seems to be very low or below the detection limit. The XRD patterns of the AN samples obtained after one thermal treatment were showing the sharp reflections of AN(IV) crystals, similar to the evaporated and melt crystallized samples. The XRD pattern of heated sample is shown in Fig. 6 and the d values are compiled in Table 4. This once again confirms that the HAN present in the sample has decomposed off at higher temperatures and only pure AN remains after the thermal cycling.

It is well known that potassium salts are used to produce phase stabilized ammonium nitrate (PSAN) [11]. To produce the PSAN, the
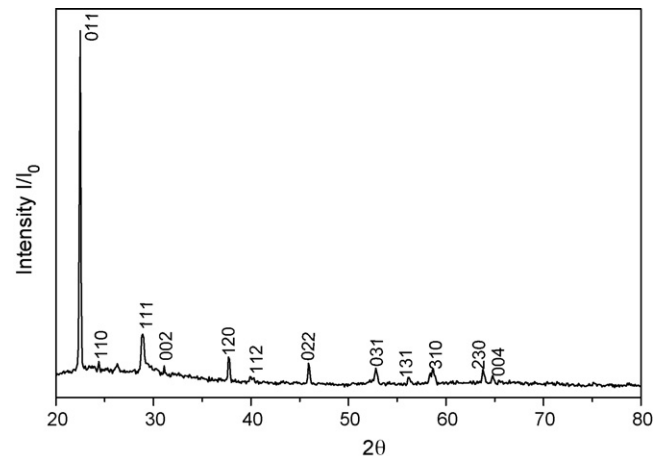
Table 3
Comparison of *d* values with ASTM data

ASTM				Recrystallized		Evaporated		Melt	
AN		HAN		*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
d (Å)	*I*	*d* (Å)	*I*						
3.96	65	3.89515	52	3.93565	13	3.95088	9	3.91624	28
3.66	2	2.86061	100	3.89489	6	3.08579	25	3.64593	2
3.087	100	2.46619	3	3.06167	100	2.72221	100	3.07096	86
2.879	10	2.37601	8	2.86173	2	2.48177	2	2.87774	29
2.722	75	2.24303	10	2.71366	7	2.38237	2	2.71478	51
2.485	10	2.08294	8	2.47089	2	2.25834	8	2.47327	10
2.38	8	1.97364	<1	2.3722	4	2.09085	<1	2.38095	30
2.26	45	1.82616	1	2.24803	4	1.83631	<1	2.24022	100
2.249	2	1.77377	<1	2.2424	5	1.78474	<1	2.08464	7
2.094	2	1.71848	<1	2.08571	<1	1.73142	1	1.96908	4
1.978	4	1.57267	<1	1.97634	1	1.63374	4	1.82694	2
1.835	2	1.50325	2	1.83012	<1	1.58108	1	1.80242	2
1.786	4	1.49323	<1	1.78224	<1	1.5719	<1	1.72764	6
1.769	<1	1.46832	<1	1.72672	1	1.49468	<1	1.63077	7
1.73	4	1.43583	2	1.62893	4	1.46644	1	1.5768	13
1.631	6	1.3177	<1	1.57663	2			1.51036	3
1.578	6	1.26472	<1	1.51087	1			1.49003	5
1.513	2			1.49314	1			1.46328	15
1.492	2			1.46309	2				
1.464	2								
1.461	2								

cocrystallization method is usually employed and this is attained by the replacement of NH_4^+ ions in AN by the K^+ ions in the potassium salts. In the present study, the replacement mechanism may not be happening because after one thermal treatment the modified transition in recrystallized AN which occurs at 55 °C shifts back to 32 °C. This shows that HAN clusters might be present as impurity in the crystal lattice of AN and forcing the modification in the transition temperature. The *d* values of monoclinic HAN found in the XRD of

Fig. 6. XRD pattern of recrystallized sample after one thermal treatment.

recrystallized AN sample confirms the presence of HAN clusters. The presence of K^+ ions in the unit cell of AN explains the reason behind higher stability range and number of thermal treatment the potassium salt stabilized PSAN could withstand.

Table 4
XRD reflections of recrystallized AN after heating

d (Å)	Intensity
3.94689	100
3.64368	10
3.38460	9
3.08574	17
2.87229	9
2.38322	11
2.25674	6
1.97473	9
1.73176	8
1.63746	6
1.57097	8
1.45712	8
1.43703	6

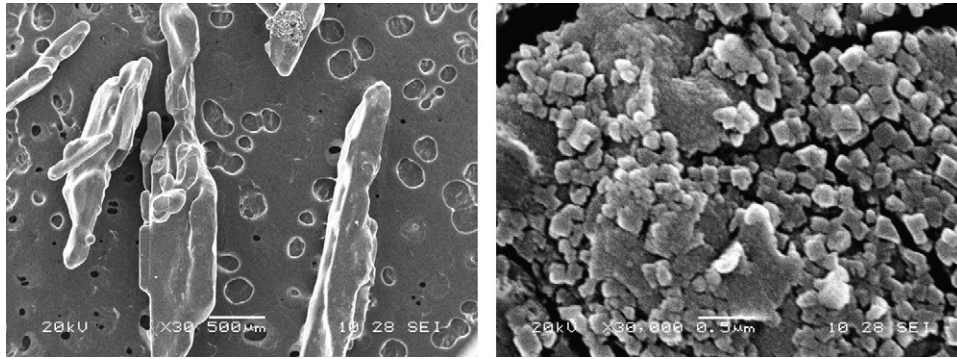**Fig. 5.** XRD patterns of differently crystallized samples.

Fig. 7. SEM of recrystallized sample.

The SEM images of the crystals at different magnification are shown in Figs. 7–9. The images were taken at different magnifications varying from 30× to 30,000×. There was no single crystal present in the evaporated and melt crystallized samples, so small pieces were taken out from the bulk and used for the SEM analysis. For the recrystallized samples the images were taken at a higher magnification of 30,000×. To understand the difference, images of evaporated and melt crystallized samples were taken at 300× and 2000×, respectively.

The crystal surfaces exhibited different growth patterns at higher magnifications. The crystals obtained by the recrystallization method were of needle shape (at 30×) and at higher magnification it became evident that the needlelike superstructure of the crystals synthesized by recrystallization (Fig. 7), consisted of small cube like particles. While the evaporative (Fig. 8) or melt crystallized (Fig. 9) samples were not showing this type of particle agglomeration. The evaporated sample showed rounded corners

at 300×. The melt crystallized sample surface showed a sheet like surface with cracks on it. Both the crystal surfaces were containing holes and cracks as seen in the SEM images.

The crushing strength was determined by simple finger test, in which a granule can be classified as soft, medium hard or hard. Crushing strength also seems to vary with the mode of crystallization. The recrystallized sample, as said earlier, consists of small agglomerated particles and hence disintegrates into small pieces on applying small amount of pressure. Comparatively, the melt crystallized samples were showing highest crushing strength by way of hardness while the samples were being crushed, on mortar and pestle, for the moisture uptake analysis. The friability of the particles in turn depends upon the crushing strength and hence gets affected by the mode of crystallization.

The moisture absorption characteristics of the samples obtained by using constant humidity solution at different time intervals are shown in Figs. 10–12. The percentage moisture absorbed (by
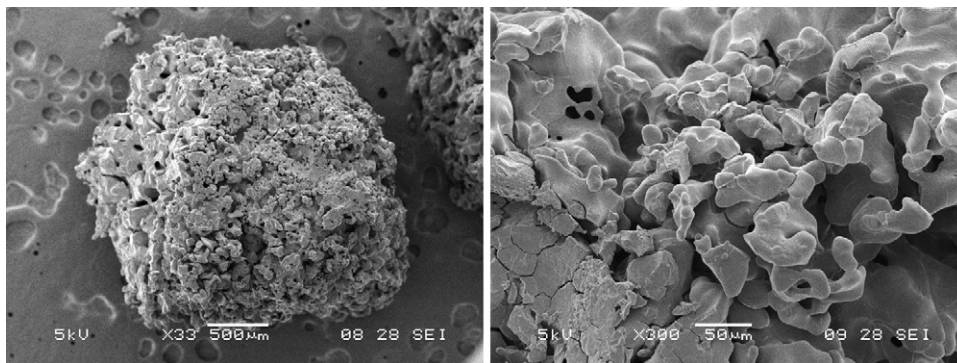

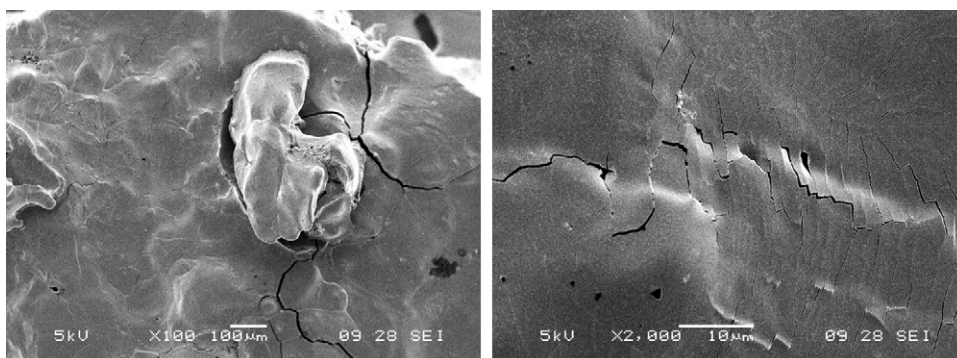**Fig. 8.** SEM of evaporative crystallized sample.

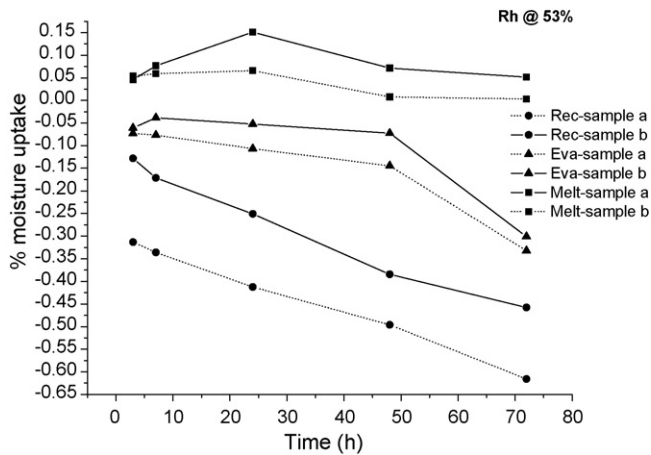**Fig. 9.** SEM of melt crystallized sample.
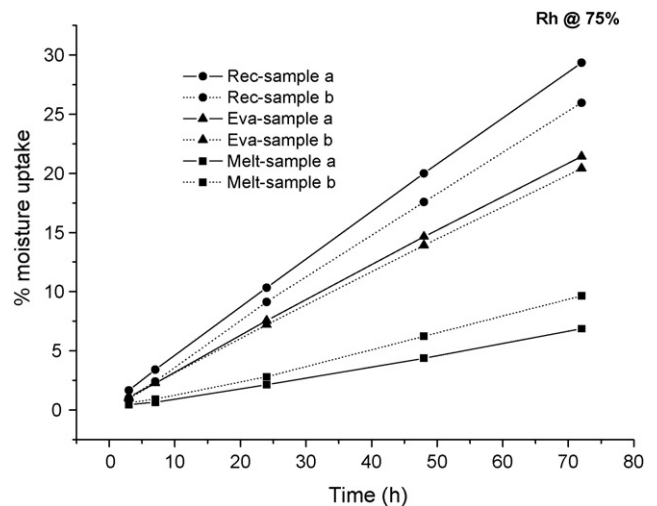
Fig. 10. Moisture absorption at 53%.

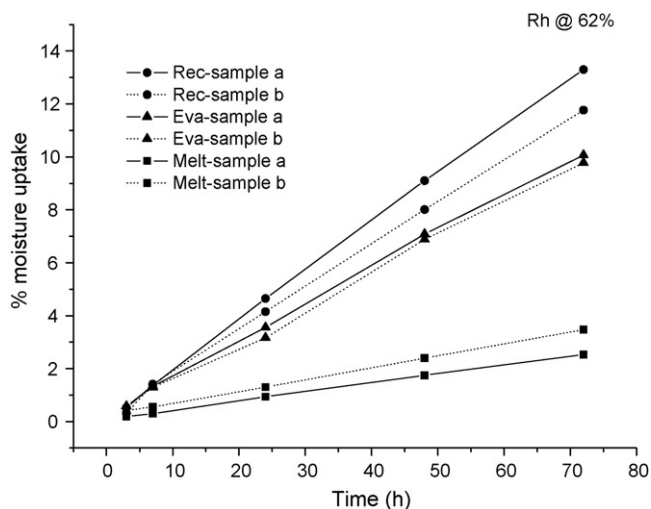**Fig. 12.** Moisture absorption at 75%.

Fig. 11. Moisture absorption at 62%.

which remains more or less the same even after 72 h. However, the evaporated and recrystallized samples continue to loose moisture. These observations may be explained as, the recrystallized crystals might be holding maximum amount of moisture as they have been crystallized from water. The recrystallized samples are loosing this moisture present in the crystals because the critical relative humidity (CRH) of AN is 55–60% at 30 °C. The melt and evaporated crystals might be containing less moisture to loose and this trend is reflected in the figures. The melt sample has lowest moisture as it was prepared by melting the AN around 180 °C and hence looses little moisture at 53. Whereas, the evaporative samples have more moisture compared to melt crystallized product and hence has more moisture to loose at RH 53%. This is even more with the samples recrystallized from water and hence the trend of loosing more moisture from these samples compared to melt and evaporative crystallized samples. The trend of moisture absorption rate remains as for melt > evaporative > recrystallized or moisture loss at 53% RH varies in the order recrystallized > evaporative > melt.

The moisture uptake characteristics observed at 62% RH (Fig. 11) and 75% RH (Fig. 12) are entirely different from the one observed at 53% RH. The moisture uptake values are shown in Table 5. This seems to be because both the relative humidities used for the experiment are above the CRH of AN. All the samples were showing the

weight) is plotted against time of exposure. Fig. 10 shows that the melt crystallized sample has taken up highest amount of moisture in 3 h compared to the other two samples at 53% RH. The moisture uptake by melt sample stops at 24 h and it starts loosing the moisture at this point. At 48 h the sample reaches a saturation limit

Table 5
Moisture uptake at different humidity levels

Sample	Time (h)	Moisture uptake (wt%)					
		@53		@62		@75	
		1	2	1	2	1	2
Recrystallized	3	−0.31341	−0.12809	0.52556	0.31531	1.67687	1.02761
	7	−0.3358	−0.17109	1.36515	1.41526	3.41504	2.40986
	24	−0.41229	−0.2506	4.64264	4.15308	10.33	9.13995
	48	−0.49624	−0.38461	9.1057	8.01219	19.99227	17.58151
	72	−0.61563	−0.45756	13.29892	11.7673	29.34708	25.95442
Evaporated	3	−0.07279	−0.06095	0.583	0.57844	1.09741	0.98146
	7	−0.07669	−0.03843	1.33658	1.29533	2.28045	2.26946
	24	−0.10659	−0.05234	3.55583	3.16335	7.55641	7.21334
	48	−0.14428	−0.07222	7.08291	6.88202	14.64091	13.92066
	72	−0.3321	−0.3008	10.06523	9.77821	21.42409	20.40322
Melt	3	0.04607	0.05393	0.19293	0.42892	0.47242	0.61276
	7	0.0768	0.0595	0.29516	0.54984	0.66572	0.94473
	24	0.15123	0.06591	0.9376	1.30012	2.14556	2.81264
	48	0.07161	0.00799	1.7469	2.39179	4.37591	6.23064
	72	0.05158	0.00332	2.53015	3.47076	6.87629	9.65268

uptake of moisture at these two relative humidities. But the recrystallized sample was showing a higher uptake than the other two. It is evident from the SEM images that, the recrystallized sample is in an agglomerated form of small (<0.5 μm) cube like particles and this might have given more surface area to take up the moisture. The evaporated sample also has a porous crystalline structure which allows the higher moisture uptake. The melt sample has a plane sheet like surface which in turn prevents the intrusion of moisture and hence it has absorbed less moisture compared to the other two samples.

As AN is used as a fertilizer and propellant oxidizer, the bulk storage and handling properties have much interest. The recrystallized samples have got a higher IV ↔ III transition temperature (~55 °C) and hence can be stored under ambient conditions as the temperature fluctuations during the storage may not go above this transition temperature. Also the CRH of AN is around 55–60% and therefore handling of AN below this relative humidity will not be of much problem. The IV ↔ III transition may not be happening in these recrystallized samples and this greatly reduces the caking tendency and the loss of mechanical strength which is observed after IV ↔ III transition.

4. Conclusions

The crystallization method is the main factor which influences the near room temperature (IV ↔ III) phase transition of AN. The pure AN has a IV ↔ III transition at 32 °C and the presence of very trace amount of HAN shifts this transition to 52 °C, which is observed only in the recrystallized samples. The HAN present in the recrystallized sample decomposes after one thermal cycling and the remaining AN behaves as the evaporated and melt samples and shows the same XRD reflections. The moisture content seems to have very minor influence on the IV ↔ III transition. The crystallization methods found to have influenced even the moisture uptake at constant humidity conditions. The SEM images showed that the recrystallized crystals are composed of small cube like particles making it more vulnerable to moisture uptake. The above findings also prove that the dependency of the IV ↔ III transition on the parameters such as thermal history, number of previous transformations and moisture is very less compared to the crystallization method. Thus, it is evident that the mode of crystallization is the foremost important parameter affecting the near room temperature IV ↔ III transition and other characteristics of AN.

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