

The effect of mixing methods on the phase transition of ammonium nitrate

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Abstract

A study has been undertaken on the effect of mixing methods on the IV ↔ III transition of ammonium nitrate (AN). Potassium chloride (KCl) and monoammonium phosphate (MAP) were mixed with ammonium nitrate (AN) by different mixing methods. The results of differential scanning calorimetry (DSC) showed that the crystals have different transition behaviour. When the samples were mixed by mechanical mixing method, the temperature of IV ↔ III transition was increased. For the solution mixing method, the IV ↔ III transition of AN-8%KCl mixture was disappear, while the IV ↔ III transition temperature of AN-MAP mixture was reduced to a lower temperature. The morphology changes and structural properties were further analyzed by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The present study showed that mixing methods, additives, thermal cycling and hydrogen-bond have an important influence on the IV ↔ III transition of AN.

Keywords : ammonium nitrate, potassium chloride, monoammonium phosphate, phase transition

1. Introduction

Ammonium nitrate is widely used as a high nitrogen fertilizer and a major component in energetic material and civil explosives¹⁻³. However, there are several drawbacks that limited its application, such as phase transitions, low burning rate and hygroscopic. AN can exist in five polymorphic forms (designated as phases V, IV, III, II and I) under ambient pressure, these solid phases of samples exhibit different physical and thermodynamic properties such as solubility, specific volume and heat capacity^{4,5}. The IV ↔ III transition occurs near the room temperature, the phase IV ($\rho = 1.72 \text{ gcm}^{-3}$) to phase III ($\rho = 1.66 \text{ gcm}^{-3}$) can cause variation in density and volume change (3.8%), after this transition, the crystals have a porous structure and cracked crystals with poor mechanical strength and unwanted burning behavior⁶. These problems affect the application of AN. The main difficulty in stabilizing the phase arises because of the sensitivity of the phase to a diverse range of variables. In particular, the problems associated with the phase transition at 32 °C have been

addressed by developing phase stabilized AN (PSAN). The phase stabilized AN (PSAN) is a mixture of AN and several weight percent of additives. PSAN exhibits very little density and volume change on thermal cycling. This effect is achieved by suppressing the IV ↔ III transition, or modifying the morphology. PSAN is widely used in the field of industrial explosive and propellant now for the its low cost, chemical stability, low sensitivity to friction and to shock, as well as its low polluting characteristics.

The earlier studies pointed out that the IV ↔ III transition temperature may be influenced by moisture, mode of crystallization, thermal history of the sample, number of previous transformations, heating mode and grain size, etc⁷⁻¹¹. Anuj A. Vargeese⁸ et al. assumed crystallization method was the main factor that influences the near room temperature (IV ↔ III) phase transition of AN; Hong Bo Wu¹⁰ et al. observed that the transition path and temperature of AN particles can be changed by the addition of KNO₃; R.N. Brown¹¹ et al. assumed that the transformations IV ↔ III only take place in the

presence of moisture. Tu Lee¹²⁾ et al. assumed that co-crystallization may become a solid-state modification method in the areas of propellants and explosives. Jo Takeuchi¹³⁾ proved that proton transfer in the ammonium nitrate system enhances the internal electrostatic interaction, resulting in an ionic form with remarkable stability even in the gas phase.

The IV↔III phase transition of AN has made certain achievements under laboratory conditions (low content of the additive, ideal crystals, mild process). However, in the actual application process, the interaction between AN and additives, thermal cycle, the different mixing methods etc will have a huge impact on the AN crystals. In addition, some modification methods are complex and time-consuming, improving the IV↔III phase transition temperature by the simple method is significant for the production of AN. KCl is one of suppressor agent in mine safety explosive, it is used to reduce the energy release of AN to ensure stable detonation. MAP is a raw material in compound fertilizer. They are often mixed with AN in actual production. To better know which factor play an important role on phase transition of AN in the actual application process, the IV↔III phase transition of AN-KCl and AN-MAP mixtures was analyzed, with an emphasis on analysis the effect of mixing methods on the IV↔III transition.

2. Experimental

2.1 Preparation of modified ammonium nitrate sample

AN, KCl and MAP were of AR grade and obtained without further purifications in the experiments, from Kailong Chemical (China) and Huarui Chemical (China) respectively.

2.1.1 Mechanical mixing method

To prevent moisture absorption, AN, additives and the mill pot were preheated at 80°C for 0.5h. 600 g AN was mixed with different wt% of additives by ball mill at a speed of 120 r min⁻¹ for 0.5h, then stored in a desiccator before use.

2.1.2 Solution mixing method

Saturated solution of AN was prepared by dissolving 25 g AN in 10 mL of distilled water at 80°C. The solution was kept in a water bath for 30 min, after complete dissolution of the salt, different wt% of additives were added to the solution, the samples are shown in Table 1. After heating and complete dissolution, the solution was slowly cooled to room temperature with gentle agitation^{8),14)}. The agitation was stopped just before the solution was cooled to the room temperature. The solution kept in ambient condition in a sealed container for 72 h. The resulting crystals were collected through filtration, then stored in a desiccator and used for further analysis. The water content of the mixtures was identified using a Sartorius-MA35, and the moisture was maintained at approximately 0.06% to ensure the consistency of the experiment.

Table 1 Table 1 Composition of different samples

Material	Mixing method	content [%]	AN [g]	Additive [g]	Mass [g]
AN/KCl	machinery	15	25	3.75	28.75
AN/KCl	machinery	20	25	5.00	30.00
AN/KCl	solution	10	25	2.50	27.50
AN/KCl	solution	15	25	3.75	28.75
AN/NH ₄ H ₂ PO ₄	machinery	25	25	6.25	31.25
AN/NH ₄ H ₂ PO ₄	machinery	30	25	7.50	32.50
AN/NH ₄ H ₂ PO ₄	solution	25	25	6.25	31.25
AN/NH ₄ H ₂ PO ₄	solution	30	25	7.50	32.50

2.2 DSC thermal analysis

The phase transition of the modified AN was determined by using a DSC 1 instrument that produced by Mettler-Toledo. The samples obtained via different mixing methods were heated from 20°C to 200°C in a sealed crucible, at a scan rate of 5°C min⁻¹ and using N₂ as the atmosphere. All the samples were dried in a vacuum desiccator before use.

2.3 SEM analysis

The SEM uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The morphology of the modified AN particles was studied by using a JSM 6360A scanning electron microscope. The powder sample was put on a carbon tape and then coated with platinum using a sputter coater.

2.2 XRD analysis

The crystal structure of the modified AN was identified by using a X-ray diffraction (Bruker AXS D8). The interplanar spacing (d) was calculated by Bragg's equation and the obtained d values were compared with the American Society for Testing and Material (ASTM) data. The scanning was conducted in a continuous mode over a 2θ range from 10.00° to 85.00° with a step size of 0.05° were compared with the ASTM data. The XRD measurements were carried out with Cu Ka radiation at 30 kV and 40 mA.

3. Results and analysis

3.1 DSC thermal analysis results

The results of DSC are shown in Table 2 and the DSC curve of AN is shown in Figure 1. The AN exhibited four endothermic peak, the first endothermic peak occurs around 38.68°C is the result of the IV to III phase change, the second (87.55 °C) is the III to II phase change, the third at 127.88 °C is II to I phase change, the last is the melting point of AN at 158.33°C^{16),17)}. The DSC curves of modified AN (mechanical mixing method) are shown in Figure 2-3. The IV↔III phase transition of the AN-15%KCl mixture occurs around 48.30°C. When the content of KCl reached to 20%, the temperature was increased to 52.16°C. For the MAP, the IV↔III phase transition occurs around 46.83°C (MAP: 25%) and 49.84°C (MAP: 30%). The other transitions, viz. III↔II, II↔I were not affected, and the transition route is not altered but the IV↔III transition

Table 2 Comparison of transition temperature of different samples

Material	Mixing method	content [%]	IV↔III [°C]	III↔II [°C]	II↔I [°C]
AN			38.68	87.55	127.88
AN/KCl	machinery	15	48.30	88.63	122.08
AN/KCl	machinery	20	52.16	91.80	126.88
AN/NH ₄ H ₂ PO ₄	machinery	25	46.83	83.88	122.77
AN/NH ₄ H ₂ PO ₄	machinery	30	49.83	89.25	122.77

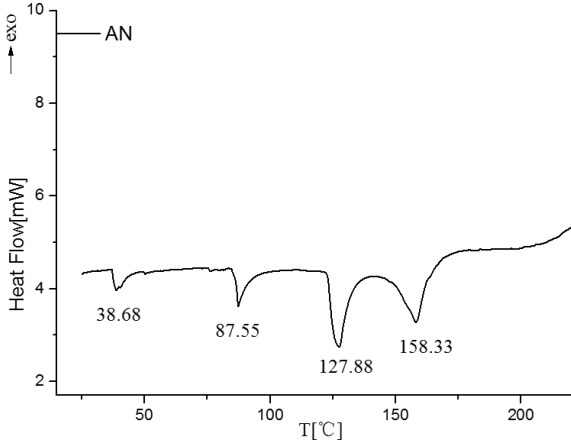


Figure 1 DSC curve of neat AN

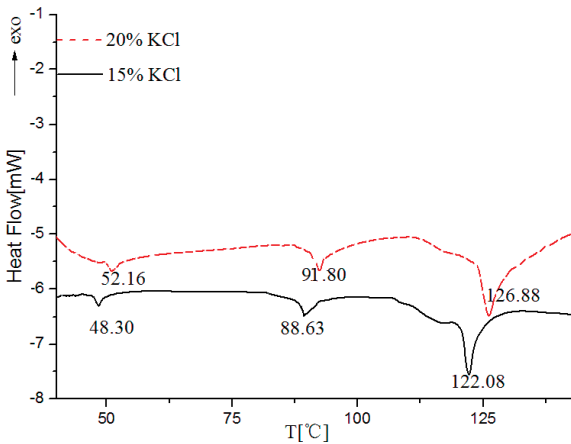


Figure 2 DSC curve of AN/KCl (mechanical mixing)

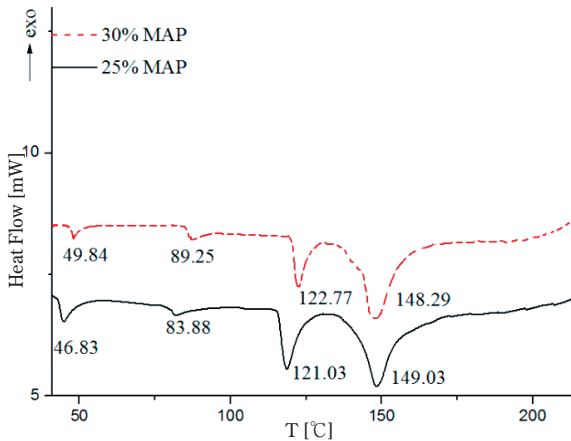


Figure 3 DSC curve of AN/NH₄H₂PO₄ (mechanical mixing)

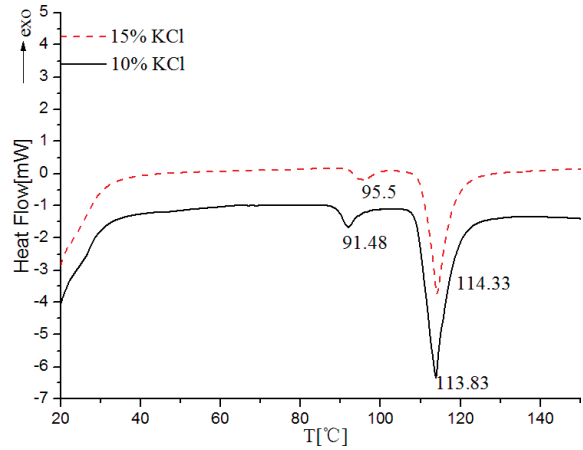


Figure 4 DSC curve of AN/KCl (solution mixing)

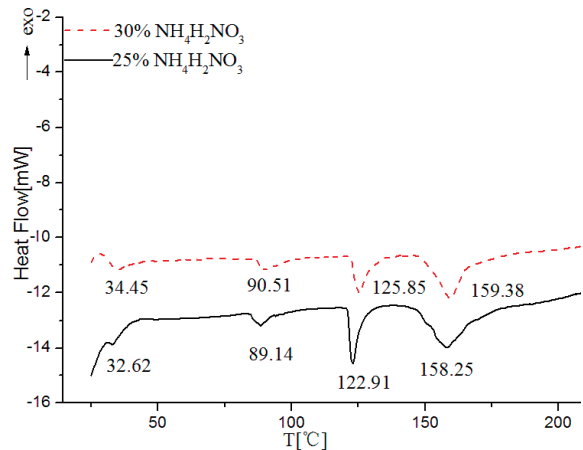


Figure 5 DSC curve of AN/NH₄H₂PO₄ (solution mixing)

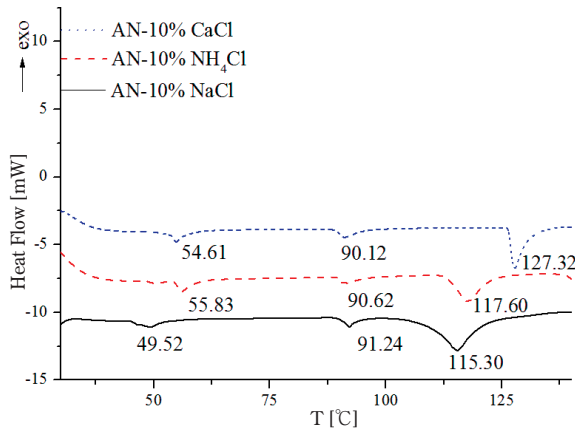
temperature has been shifted to a higher temperature. This in turn also proves that the transition occurred around 48.30°C (KCl: 15%) or 46.83°C (MAP: 25%) is the IV↔III transition rather than the IV↔II phase transition or a metastable transition.

The DSC curves of modified AN (solution mixing method) are shown in Figure 4–5. As shown in Figure 4, the IV↔III phase transition was disappear, the III↔II transition occurs around 91.48°C (KCl: 10%) and 95.5°C (KCl: 15%). While it should be noted that the IV↔III phase transition of AN-MAP mixtures has been shifted to a low temperature, the transition occurred around 32.62°C (MAP: 25%) and 34.45°C (MAP: 30%), the III↔II phase transition occurs around 89.14°C (MAP: 25%) and 90.51°C (MAP: 30%). The results are compiled in Table 3.

For the solution mixing method, the re-crystallization is the main reason impact the IV↔III phase transition. In the re-crystallization process, the size of the additives, pH, and viscosity will affect the ammonium nitrate crystals. In order to compare the effect of cations on the IV↔III phase transition of AN, the AN-10% sodium chloride (NaCl), AN-10% ammonium chloride (NH₄Cl) and AN-10% calcium chloride (CaCl₂) samples were prepared for the DSC analysis, the results are shown in the Table 3. Unlike AN-10% KCl, the IV↔III phase transition still exists. As it shown in the Figure 6, the III↔II transition occurred around 40.52°C (AN-NaCl), 55.83°C (AN-NH₄Cl) and 54.61°C (AN-CaCl₂), it can be concluded that the cations

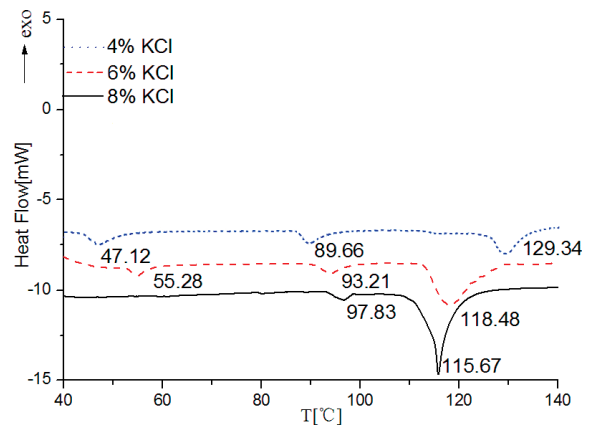
Table 3 Comparison of transition temperature of different samples

Material	Mixing method	content [%]	IV↔III [°C]	III↔II [°C]	II↔I [°C]
AN			38.68	87.55	127.88
AN/KCl	solution	10		91.48	113.83
AN/KCl	solution	15		95.50	114.33
AN/NH ₄ H ₂ PO ₄	solution	25	32.62	89.14	122.91
AN/NH ₄ H ₂ PO ₄	solution	30	34.45	90.51	125.85
AN/NaCl	solution	10	49.52	91.24	115.30
AN/NH ₄ Cl	solution	10	55.83	90.62	117.60
AN/CaCl ₂	solution	10	54.61	90.12	127.32

**Figure 6** DSC curve of AN/additives mixtures (solution mixing)

played a significant role in the re-crystallization process.

The room temperature phase (AN-IV) is ordered with an orthorhombic crystal structure (Pmmn), the NH₄⁺ and NO₃⁻ are arranged in columns along the b axis with a periodicity equal to the unit cell length. The nitrate ions lie in the ac plane and each is hydrogen bonded to 4 ammonium ions. There are infinite hydrogen-bonded [H(1).....O(1)=2.05Å] chains parallel to the a axis. These chains are linked by some weaker hydrogen bonds [H(2).....O(1)=2.16Å] to form infinite sheets parallel to (001)⁽¹⁸⁾⁻²⁰⁾. In AN-III, NO₃⁻ moieties are ordered, the strong two-dimensional hydrogen-bond network which occurs in the phase IV structure is broken systematically along one direction and becomes a one-dimensional chain (with a weaker O.....H interaction) in the phase III form^(21),22). In KCl-NH₄NO₃ samples, K⁺ ion radius is 133pm, the NH₄⁺ is 143pm, the size of the atom Δr = 7% (Δr < 15%), the cation:anion ratio is below 0.73, the salts are stable in a six-fold coordinated NiAs structure⁽¹⁸⁾. For the Na⁺ ions, Ca⁺ ions, the size of the atom is not suitable for the ion exchange. In the re-crystallization process, K⁺ ions will replace NH₄⁺ ions in the crystal lattice and form a solid solution because of their similar ionic radius, thereby reducing weaker hydrogen bonds [H(2).....O(1)=2.16Å]. This could cause the disappearance of phase IV with the increase in additive content. It can be known from Figure 7, when the mixtures contain 4% KCl, the IV↔III transition occurred around 47.12°C, with the KCl reaching 8%, the IV↔III transition was disappeared. Importantly, we found the

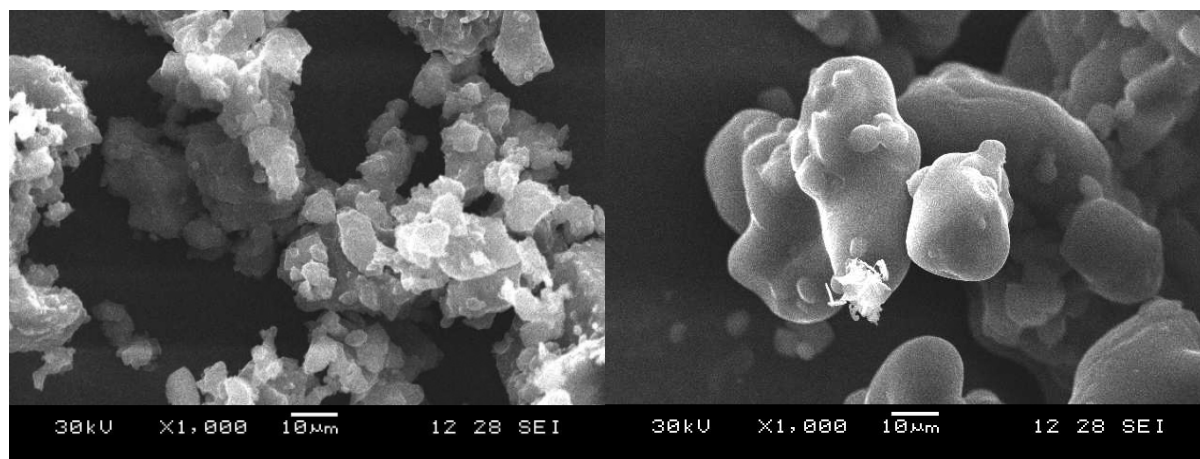
**Figure 7** DSC curve of AN/KCl (solution mixing)

temperature of II↔I transition was decreased with the increase of the additive.

The I phase was stable in the temperature range of 125.2-169°C, in the cubic symmetry the NO₃⁻ ions are in free rotation and the NH₄⁺ ions are comparatively free to diffuse in the lattice⁽²³⁾⁻²⁵⁾. Form II is tetragonal with a space group P421m, in this form the NO₃⁻ ions are no longer in free rotation and each NO₃⁻ ion is rotating in its own plane^(26),27). For this phase transition, it needs an energy barrier hindering the free rotation of the NO₃⁻ ions and the translational diffusion of the NH₄⁺ ions begins to operate. Harri Kiiski⁽²⁸⁾ reported that phase transition is accompanied by a distortion of the lattice from cubic to tetragonal and the barrier is probably an hydrogen bonding bond and it is expected to be of the order of 5 to 10 kcal mol⁻¹. Cationic substitution may affect the hydrogen bonds of AN, but II↔I transition of AN-10% NaCl mixtures was also decreased to 115.30°C. The ionic radius of chloride and the rotating nitrate group are 1.90 and 2.35Å with equivalent symmetry, Hendricks⁽²⁹⁾ et al. think chloride could replace nitrate in cubic AN for the similar radius. The temperature of II↔I transition was decreased with the increase of the additive, we thought hydrogen bonding and ion exchange may play an important part in the interaction of ammonium ion with the additive.

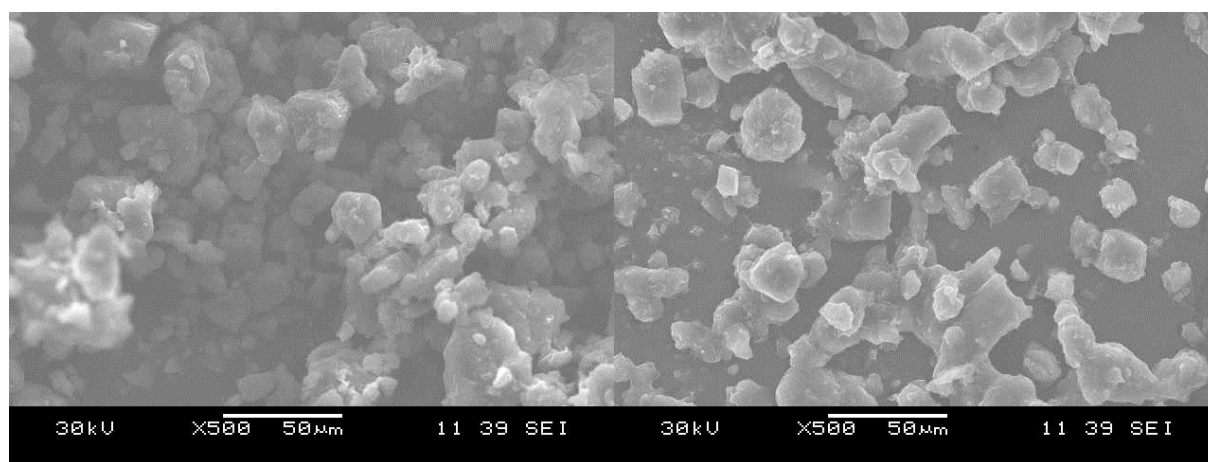
It should be noted that the AN-KCl and AN-MAP mixtures (mechanical mixing method) can't make the IV↔III phase transition disappearance, but it can increase the IV↔III phase transition around to 50°C. The IV↔III phase transitions of AN can be raised to a higher temperature by a simple method, it is significant for the production of AN. It is well known that the presence of impurities can dramatically affect physical properties of the crystals in the process of mechanically mixing and the growth of crystal morphology is governed by the crystal structure and defects, environmental conditions, growth rates, etc. Under the action of external energy, the friction and energy exchange between particles can cause variation in crystal structure^(6),30). We think the mechanical mixing methods can improve the temperature of IV↔III phase change perhaps due to thermal cycling or macroscopic stress.

To better understanding the impact of macroscopic



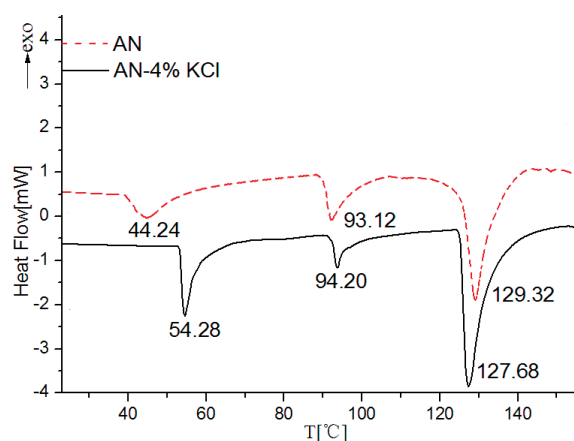
(A) AN/ KCl mixtures (mechanical mixing)

(B) AN/ KCl mixtures (solution mixing)

Figure 8 SEM of AN/15% KCl mixtures(A) AN/NH₄H₂PO₄ mixtures (mechanical mixing)(B) AN/NH₄H₂PO₄ mixtures (solution mixing)**Figure 9** SEM of AN/25% NH₄H₂PO₄ mixtures

stress on the crystal morphology, the SEM was carried out. The SEM images of the crystals at different magnification are shown in Figures 8–9. For the mechanical mixing method, under the action of external stress and friction, the crystal had a certain degree of broken. The crystals started losing their nature and tend to break down into smaller crystals. In Figures 8 (A) and Figures 9 (A), the sample showed smaller and irregular, the specific surface area of AN will increase with the particle size becomes smaller, the friction between the particles will become more intense. Since the sample through preheated at 80°C for 0.5h, the energy exchange between the particles will form a “hot spots” —small isolated regions of crystal at a much higher temperature. Once the particles separated, the local temperature of the crystal will decrease. That means the crystal undergoing many thermal cycles in mechanical mixing process. R.N. Brown¹¹⁾ et al. assumed that repeated cycling between 0 and 140°C may cause the IV↔III transition temperature to rise or eventually this transition was replaced by a IV↔II transition. The result is consistent with literature¹¹⁾ and previous results of DSC analysis.

Some of the earlier papers state that the IV ↔ III transition is influenced by the hydroxylammonium nitrate (HAN) present in the crystals^{8), 31)}. The stabilization effect

**Figure 10** DSC curve of AN and AN/KCl (solution mixing)

is present for only one thermal cycle, this behaviour of crystals may be due to the fact that the HAN present in the crystals is decomposing off at higher temperatures and only pure AN remains after the thermal cycling. But in the present study, a few samples were analyzed for the thermal cycle before doing the DSC analysis. In the Figure 10, after 10 times thermal cycle (20–120°C) the stabilization effect is still present, although there just a little change in the IV↔III transition temperature. We think the stabilization effect maybe is influenced by the number of

thermal cycling and the HAN isn't only parameter influence the IV↔III transition.

3.2 XRD Characterization

The X-ray powder diffraction data of modified AN (mechanical mixing method) obtained at room temperature is shown in Table 4, the XRD patterns of the crystals are shown in Figure 11–12, the crystals were exhibiting the sharp reflections of AN (JCPDS 8-452) phase IV peaks. The peaks of AN at *d* values 2.72 (020), 3.09 (111), 3.96 (011) and the standard spectra of XRD was 17.90°, 22.43°, 28.9°, 32.88°, and 39.85°. When KCl and MAP were added as additive to AN respectively, no difference of the main feature peaks was seen in the Figure 10. The main peaks of AN-KCl mixtures were 18.25°, 22.76°, 29.20°, 31.36°, 40.41°, the main peaks of AN-MAP mixtures were 18.16°, 22.64°, 29.13°, 31.24°, 33.07°, 40.01°, the small angle offset maybe is cause by the crystal defects or macroscopic stress in the mechanical mixing process. The mixtures were in IV phase, the mechanical mixing method has little effect on phase transition.

For the solution mixing method, the X-ray diffraction data is shown in Table 5, the XRD pattern of the crystals is shown in Figure 1. The AN-KCl mixture was in III phase, this result is consistent with previous results of DSC analysis. In the re-crystallization process, K⁺ ions replace NH₄⁺ ions in the crystal lattice and form a solid solution because of their similar ionic radius, thereby reducing weaker hydrogen bonds [H(2).....O(1)=2.16Å]. This could cause the disappearance of phase IV with the

Table 4 Comparison of *d* values with ASTM data

AN(ASM)		AN		AN-KCl		AN-MAP	
D [Å]	I	D [Å]	I	D [Å]	I	D [Å]	I
4.95	45	4.87	8.4	4.86	16.4	4.88	30.7
3.96	65	3.86	26.7	3.91	38.6	3.92	49.6
3.66	2	3.03	25.6	2.85	14.5	3.25	3.7
3.09	100	2.83	3.8	2.70	100	3.07	100
2.88	10	2.67	100	2.46	6.6	2.71	55.9
2.72	75	2.45	3.2	2.37	7.7	2.46	9.7
2.48	10	2.35	3.6	2.23	57.5	2.25	38.9
2.38	8	2.24	12.5	1.78	2.0	2.23	10.1
2.26	45	1.72	3.8			1.72	2.3

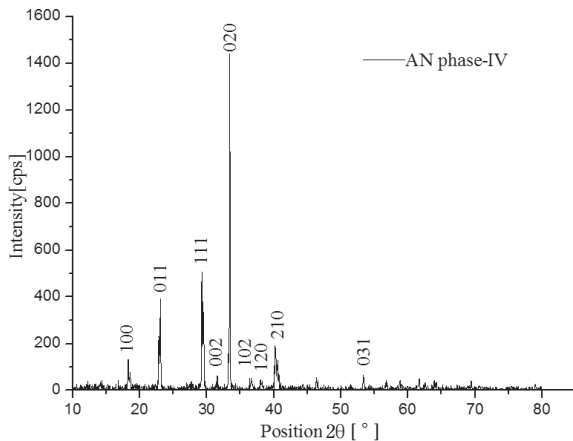


Figure11 XRD patterns of neat AN

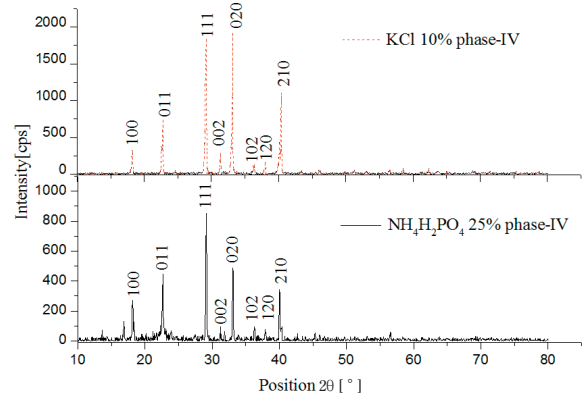


Figure12 XRD of different samples (mechanical mixing)

increase in additive content³²⁾. It should be noted that the peaks of NH₄Cl and potassium nitrate (KNO₃) were found instead of KCl, the ion exchange is not only has an important impact on the phase transition but also in the mine safety explosive. KCl is one of suppressor agent in mine safety explosive, in the process of detonation, under the action of high temperature and high pressure, KNO₃ and NH₄Cl will interact with each other and generate NH₄NO₃ and KCl. The result of ion exchange were to generate the molecular level of KCl⁶⁾, this is an important significance for the mine explosive safe use. While the MAP-NH₄NO₃ mixtures were in phase IV and III. Unlike KCl, the size of the ion is not suitable, anionic mixed into the crystal by electric balance, so only a small amount of MAP into the crystal. In addition, MAP is a weak acid, hydrogen ions can promote the decomposition of AN and influence the formation of hydrogen bond. Structural defects will decrease the transition energy and lower the transition temperatures, the AN exhibited IV↔III↔II↔I

Table 5 Comparison of *d* values with ASTM data

AN-III(ASM)		AN-MAP		AN-KCl	
D [Å]	I	D [Å]	I	D [Å]	I
5.34	10	5.26	20.1	5.17	7.4
4.55	20	4.88	23.6	4.48	26.4
3.91	55	4.48	3.0	3.92	13.9
3.4	70	3.92	53.3	3.86	100
3.25	90	3.87	29.1	3.36	54.1
3.20	30	3.72	11.4	3.22	61.5
2.93	12	3.36	15.9	3.19	66.1
2.91	8	3.22	17.5	2.90	10.9
2.85	40	3.19	16.8	2.81	27.2
2.63	100	3.06	100	2.61	52.7
2.55	8	2.94	1.9	2.53	6.6
2.42	35	2.91	1.7	2.40	27.9
2.33	18	2.86	9.8	2.31	24.1
2.29	35	2.82	4.9	2.27	7.1
2.26	45	2.71	91	2.25	35.3
1.92	16	2.64	2.8	1.93	8.2
1.49	16	2.40	23.7		
		2.31	6		
		2.25	21.6		
		1.46	3.4		

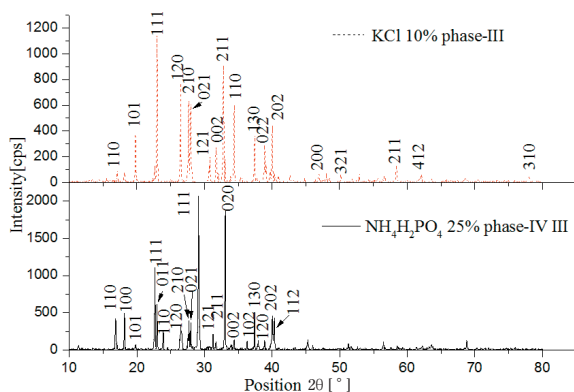


Figure 13 XRD of different samples (solution mixing)

transitions^{18),30)}. So the solution mixing method is not suitable for the AN-MAP mixtures.

4. Conclusion

To better understand the effect of mixing methods on the phase transition of Ammonium Nitrate, the IV \leftrightarrow III transition of AN-KCl and AN-MAP mixtures were analyzed. The following conclusions can be drawn :

(1) For the mechanical mixing method, the friction, heat exchange and thermal cycle have an important influence on the IV \leftrightarrow III transition of AN. To produce PSAN, the co-crystallization method is usually employed, but the process is complex and time-consuming. Improving the IV \leftrightarrow III phase transition temperature by the simple mechanical mixing is significant for the production of AN.

(2) KCl added to AN, some of the NH_4^+ is replaced by K^+ thereby reducing weaker hydrogen bonds, this could cause the disappearance of phase IV. But for AN-MAP mixtures, crystal defects decrease the transition energy and lower the IV \leftrightarrow III transition. The cations played a significant role in the re-crystallization process.

(3) According to the results, it is evident that in the actual production process, different mixing method is important parameter affecting the IV \leftrightarrow III phase transition for the different additives.

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References

- 1) K. Othmer, "Encyclopedia of Chemical Technology", Wiley, New York (1992).
- 2) P. S. Valery, Y. Viacheslav, and I. L. Anton, *Propell. Explos. Pyrot.*, 4, 269–280 (2005).
- 3) X. R. Li and H. Koseki, *Sci. Tech. Energetic Materials.*, 66, 431–435 (2005).
- 4) L. Filipescu, D. Fatu, T. Coseac, M. Mocioi, and E. Segal, *Thermochim. Acta.*, 97, 229–241 (1986).
- 5) J. H. Michael and E. Walter, *Propell. Explos. Pyrot.*, 22, 143–147 (1997).
- 6) C. X. Lu, Z. L. Liu, and O. Q. Ni, "Arms Industry Press", Beijing, (1994).
- 7) K. Fujisato, H. Habu, A. Miyake, and K. Hori, *Sci. Tech. Energetic Materials.*, 75, 28–36 (2014).
- 8) A. V. Anuj, S. J. Satyawati, and V. N. Krishnamurthy, *J. Hazard. Mater.*, 161, 373–379 (2009).
- 9) I. Klimova, T. Kaljuvee, L. Bebder, A. Trikkel, and R. Kuusik, *J. Therm. Anal. Calorim.*, 105, 13–26 (2011).
- 10) H. B. Wu and K. C. Chak, *Atmos Environ.*, 42, 313–322 (2008)
- 11) R. N. Brown and A. C. McLaren, *P. Roy. Soc. Lond. B. Bio.*, 266, 329–343 (1962).
- 12) L. Tu, J. W. Chen, L. L. Hung, L. Y. Tsung, Y. C. Tsai, S. L. Cheng and S. W. Lee, *Chem. Eng. J.*, 225, 809–817 (2013).
- 13) J. Takeuchi, Y. Masuda, R. Clack and K. Takeda, *Jpn. J. Appl. Phys.*, 52, 5 (2013).
- 14) A. V. Anuj, S. J. Satyawati, and V. N. Krishnamurthy, *J. Hazard. Mater.*, 180, 583–589 (2009).
- 15) I. Dellien, *Thermochim. Acta.*, 55, 181–191 (1982).
- 16) M. Nagatani, T. Seiyama, M. Sakiyama, H. Suga, and S. Seki, *B. Chem. Soc. Jpn.*, 40, 1833–1844 (1967).
- 17) J. C. Oxley, J. L. Smith, E. Rogers, and M. Yu, *Thermochim. Acta.*, 384, 23–45 (2002).
- 18) C. S. Choi and J. E. Mapes, *Acta Cryst.*, 28, 176–185 (1972).
- 19) D. W. Jeams, M. T. Carrick, and W. H. Leong, *Chem. Phys. Lett.*, 28, 117–119 (1974).
- 20) C. S. Choi and H. J. Prask, *Acta Cryst.*, 38, 2324–2328 (1982).
- 21) R. J. Davey, A. J. Ruddick, P. D. Guy, B. Mitchell, S. J. Maginn, and L. A. Polywka, *J. Phys. D: Appl. Phys.*, 24, 176–185 (1991).
- 22) G. Y. Zeng and J. H. Zhou, *J. Energ. Mater.*, 4, 400–403 (2007).
- 23) Y. Shinnaka, *J. Phys. Soc. Jpn.*, 14, 1073–1083 (1959).
- 24) M. T. Riggan, R. R. Knispel, and M. M. Pintar, *J. Chem. Phys.*, 56, 2911–2918 (1972).
- 25) S. Yamamoto and Y. Shinnaka, *J. Phys. Soc. Jpn.*, 37, 732–734 (1974).
- 26) B. W. Lucas, M. Ahtee, and A. W. Hewat, *Acta Crystallogr.*, 35, 1038–1041 (1979).
- 27) M. H. Brooker, *J. Chem. Phys.*, 68, 67–73 (1978).
- 28) K. Harri, "Properties of Ammonium Nitrate based fertilizers University of Helsinki", Finland (1978).
- 29) S. B. Hendricks, E. Posnjak, and F. C. Kracek, *J. Amer. Chem. Soc.*, 54, 2766–2786 (1932).
- 30) C. S. Choi, H. J. Prask, and E. Prince, *J. Appl. Cryst.*, 13, 403–409 (1980).
- 31) B. W. Lucas, M. Ahtee, and A. W. Hewat, *Acta Cryst.*, 26, 2005–2008 (1980).
- 32) C. Oommen and S. R. Jain, *J. Therm. Anal. Calorim.*, 55, 903–918 (1998).