Phase equilibrium and oscillation of crystal-structure parameters of ammonium perchlorate in the polymorphic transition region

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Abstract. Polymorphism of crystalline materials is a part of their structural-phase changes at any type (thermal, baric, etc) of impacts. There are at least two known types of polymorphic transitions, i.e. enantiotropic and monotropic. As is well known, ammonium perchlorate (AP) is revealed to have the polymorphous transition of the first kind within 511–517 K and the data on the isotropic change of thermal expansion coefficients in the pressed AP are analyzed. In this paper, qualitative results on the changes in the diffraction pattern of x-rays reflected from crystals are obtained to perform detailed analysis of the polymorphous transition in AP under atmospheric pressure. The structure of AP crystals at final temperatures was thoroughly investigated with the help of the x-ray diffractometer within 150 and 550 K. Changes recorded in the diffraction pattern indicate changes in the crystalline structure, phase composition, and oscillation of the structural state in AP. Crystallographic models of two modifications of AP, i.e. orthorhombic and cubic, are developed to perform precise, standard-free phase and structural analyses. The full-profile analysis (quantum simulation combined with the differential Fourier-transforms) used to process x-ray patterns. So, the polymorphous transition is proved to be incomplete in AP under atmospheric pressure until its complete decomposition. A simple exponential model is proposed for description of the phase equilibrium process in AP.

1. Introduction

Nowadays, studying oxidizer–fuel energetic compositions continues to be relevant. This is due to both their combustion heat that is greater than that of individual explosives and their explosive decomposition that takes place in the case of insignificant degradation and sometimes even improvement of detonation parameters.

Ammonium perchlorate (AP) is the main oxidizer of composite explosives (mixed) [1–6] and many solid propellants [7, 8]. It is stable, non-hygrosopic, rather efficient, and intrinsically safe in handling. It serves as the basis for the formation of type II composite explosives (oxidizer–fuel), i.e. AP–Al mixtures. Properties of these mixtures were studied in detail by many investigators [1–8] though detailed data on the process how the structure of an oxidizing component in the mixture changes under thermal impact are presented in the literature poorly. We find no data on the analysis of oscillation and AP phase-equilibrium parameters in the transition region order–disorder. Parameters of the inherent thermal expansion of AP crystals
Anisotropic investigations can reveal a qualitatively different nature of the AP structure variation under thermal impact as in this case it is possible to trace changes in the unit cell parameters and to distinguish each contributions into the pattern of changes in the crystalline-structure thermal expansion and oscillation. From the standpoint of physics and mathematics, processes observed in materials subjected to external factors are primarily described by equations of state and kinetics equations.

In the paper, we study changes in the AP structure under thermal impact and gives detailed analysis of processes observed in the region of polymorphous transitions and results of these investigations are presented.

The goal of this effort are as follows:

- anisotropic study of the AP crystalline structure oscillation in the polymorphous transition region;
- analysis of phase equilibrium under thermal impact;
- anisotropic determination of inherent expansion coefficients within 150–550 K.

Two modifications of AP are currently known, i.e. orthorhombic [9] and cubic ones [10], figure 1. The orthorhombic–cubic polymorphic transition of NH$_4$ClO$_4$ (II)—NH$_4$ClO$_4$ (I) was observed by authors of paper [11] at $T_p = 513$ K (in different publications $T_p$ from 511 to 517 K [12]).

The unit cell parameters of each of the modifications shown in table 1.

In paper [13], AP structure was studied, but accuracy of given x-ray diffraction analysis was too low and the x-ray image was strongly distorted and misfits the high-precision analysis of the AP structure ($a = 9.202(6)$ Å; $b = 5.815(4)$ Å; $c = 7.449(5)$ Å; $V = 398.593$ Å$^3$). Both polymorphous types are ionic crystals wherein ClO$_4^-$ group serves as the anion and NH$_4^+$—as the cation.
Table 1. The unit cell parameters known polymorphic modifications of AP, where \( Z \)—the number of formal gross units; \( \rho \)—density; \( R_f \)—R-factor of model is a measure of the agreement between the crystallographic model and the experimental x-ray diffraction data.

| \( T \) (K) | Phase | Type | Group | \( a \) (\( \text{Å} \)) | \( b \) (\( \text{Å} \)) | \( c \) (\( \text{Å} \)) | \( V \) (\( \text{Å}^3 \)) | \( Z \) | \( R_f \) | \( \rho \) (g/cc) | Ref. |
|------------|-------|------|-------|----------------|----------------|----------------|----------------|------|------|-------------|-----|
| 293        | \( \alpha \) | rhombic | Pnma  | 9.2          | 5.82           | 7.45           | 398.9          | 4    | 0.08 | 1.948       | [9] |
| 513        | \( \beta \) | cubic  | F-43m | 7.63         |                | 444.195        |                | 4    | —    | 1.757       | [10]|

2. Experiment details

Before analyzing oscillation and phase equilibrium parameters in the region of polymorphous transition, it is reasonable to perform structural determination and to estimate volume and linear expansion of crystals under thermal impact. For this purpose, we used the x-ray diffraction analysis with the help of the x-ray powder diffraction apparatus having the low-, and high-temperature add-on unit. The method of anisotropic determination of thermal expansion is borrowed from [14].

To identify structural changes the diffraction system with the x-ray long-focus (F12x0.4) tube with the maximum power of 2200 W was used. The anode of the x-ray tube is made of copper. The working radiation K-series of the \( K_{\alpha 1} \), \( K_{\alpha 2} \) and \( K_{\beta} \) for copper corresponds to wavelengths 1.5406, 1.5444 and 1.3920 \( \text{Å} \) (working quantum energy is about 8 keV). The goniometer diameter was 520 mm. For registration of x-ray radiation used semiconductor detector with the thermoelectric cooling uses the Peltier effect. To prevent reflexes overlapping and to increase informativity of x-ray images, energy line \( K_{\alpha 2} \) and \( K_{\beta} \) are separated with the help of both hardware (filters, detectors) and also software.

Calibration is performed under normal conditions in accordance with the known position of reflexes, \( 2\theta \), of the AP having the orthorhombic structure [9]. This study used the following kinetic parameters of the diffraction system operation:

- heating and cooling rate—10 K/min;
- exposure—12 min.

The pattern how diffraction data change depending on the thermal impact within 150–550 K is given in figures 2 and 3.

Changes observed in x-ray images with time suggest structural changes in the AP crystal. First of all, changes indicate of the thermal expansion (compression) of crystals and polymorphous transition in the range > 514 K.

3. Analysis of experimental data

Thermal expansion of AP crystals in the anisotropic approximation was determined through redetermination of the AP structure (unit cell parameters) under thermal impact. This redetermination was made in succession for each phase with the fixation at the initial state of the Debye–Waller thermal scattering parameters and also independent coordinates of atoms. The Rietveld method [15] was used for the initial processing then the use was made of the method of quantum simulation combined with the differential Fourier transforms over the grid [16].

Figure 4 presents the results of the changes in the parameters of the AP unit cell under thermal impact within 150–550 K.

From figure 4 it is obvious that parameter \( a \) is the main contributor to changes in the volume of the AP unit cell primarily due to the force interaction inside a cell and the anion misorientation. For the same reason, changes in parameter \( b \) turned out to be the least. Therefore, volume variations can be characterized as non-equilibrium.
Figure 2. Changes of \([hkl]\) main groups under heating within 150–550 K \((a)\); in the range of polymorphous transition 500–550 K \((b)\).

Figure 3. Changes of AP reflexes position under cooling 550–500 K.

The averaged variation in the AP structure by thermal effects can be characterized by relative values of volume and density, figure 5.
Figure 4. Curves demonstrating relative changes in unit cell parameters $a$, $b$, and $c$ of the $\alpha$-AP: (a) within 150–550 K; (b) in the range of polymorphous transition ($> 514$ K).

Figure 5. Changes in the unit cell volume and density crystallite $\alpha$-AP: (a) in the range of 150–550 K; (b) in the range of polymorphous transition $\alpha \rightarrow \beta$ ($> 514$ K).

In figures 4 and 5, oscillation of the unit cell parameters in the region of $\beta$ phase disengagement ($T > 490$ K) is obviously observed. It should be noted that the beginning of the process of oscillation precedes the beginning of the polymorphic transition ($\Delta T \approx 11$ K).

Under cooling, parameters are varying practically according to the linear law, see figure 4(b), and again changes are mainly observed in parameter $a$ and less observed in parameter $b$. Figure 6 demonstrates that density of AP after its thermal treatment increases ($\approx 0.8 \%$). Under normal
Table 2. Variation of AP phase-composition under thermal impact (error ±1 %).

|       | Heating          | Cooling         |
|-------|------------------|-----------------|
| $T$ (K) | 493 503 508 513 518 523 533 543 553 | 533 518 493 293 |
| $\alpha$-AP (%) | 100 100 100 100 96.1 78.0 52.7 46.9 46.9 | 50.6 51.9 100 100 |
| $\beta$-AP (%) | — — — — 3.9 22.0 47.3 53.1 53.1 | 49.4 48.1 — — |

conditions, before heat exposure ($T = 293$ K, $P = 1$ atm; here and after, we will denote all parameters at this state by superscript 293) the ratio $\rho/\rho^{293}$ is 1.0, see figure 5(a), after thermal treatment, this ratio was equal to 1.08, see figure 6(b). Probably due to removal of inherent stresses striving to the intracrystalline energy minimum. As AP is a non-hygroscopic material and forms no hydrates [11, 12] then during heating with the subsequent slow cooling, energy relaxation was very likely to take place and this caused the packing and ordering factor to increase due to the removal of microdistortions and inherent stresses of a crystal.

According to x-ray diffraction analysis under thermal impact, the temperature of the $\alpha$–$\beta$ phase transition onset falls within 513–518 K, figure 3. Further, the smooth increase of the AP $\beta$-phase content is observed to take place. So, above 513 K, the composition of samples has two phases.

The quantitative x-ray phase analysis (table 2) was performed using the method of quantum simulation combined with the differential Fourier transformations [16] on the basis of the constructed models. This approach prevents non-physical solutions and enhances computational accuracy compared to the Rietveld method [15] and this is by no means unimportant for molecular and composite ionic crystal.

A complete polymorphic transition $\alpha \rightarrow \beta$ AP is not observed according to the results of quantitative x-ray phase analysis. Therefore, let us analyze indications of the phase equilibrium in the system $\alpha$–$\beta$ AP (see table 2).

The phase equilibrium indicates the physical and chemical stability of the system of several structural modifications of one material in certain thermodynamic conditions that are shown in figure 7 for AP. Phase equilibrium versus thermodynamic parameters is described by a simple exponential model, figure 7: $w_\beta = n \exp(-e^{-k(T-T_p)})$, where $w_\beta$ is the mass fraction of the $\beta$-AP phase; $T$ is the temperature; $n$, $k$ and $T_p$ are coefficients: $n$ is the limit content of the isolated $\beta$-AP phase; $T_p$ is the temperature of the high-intensity process $\beta$-AP phase isolation; and $k$ is the coefficient of $\beta$-AP phase isolation rate.

Model parameters for the case with AP: $n = 53.40 \%$ ($\sigma = 0.25910$); $T_p = 522.48$ K ($\sigma = 0.07943$); $k = 0.208$ ($\sigma = 0.00543$); and goodness of fit: $\chi^2 = 0.11671; R^2 = 0.99981$ ($R^2$ is the coefficient of determination, which shows the correlation with experiment). As we can see, the model adequately describes parameters of the AP phase-equilibrium within the temperature range from 150 to 550 K. So, it can be applied to analyze the AP state in mixtures of energetic materials (EM).

Results of the quantitative x-ray diffraction analysis show that the rate of the direct polymorphous transition is seriously lower than that of the reverse one (during cooling) and, thus, metastability of the $\beta$-AP can be characterized as strongly pronounced.

Additionally, the thermal expansion coefficient was anisotropically estimated by the formula: $\alpha = 1/S \times (\partial S/\partial T)_p \approx (S_1 - S_0)/(|(T_1 - T_0)S_0|$, where $S$—structural characteristic (volume or cell parameter) and $T$—temperature. Index 0—the initial state, 1—the final state.

Comparison between our results and those from paper [17] (table 3) reveals difference in the determination of the linear expansion coefficient.
Figure 6. Changes in the crystall structure of α-AP under cooling: (a) unit cell parameters; (b) unit cell volume and density crystallite.

Figure 7. Changes in the phase composition of the thermal effects of AP.

In paper [17], thermal expansion was investigated of pressed samples that are probably strongly grain-oriented and this resulted in sufficient (≈ 65 times) growth of the thermal expansion coefficient during the polymorphous transition in comparison with the mean value of this coefficient prior to this transition. Here we studied AP crystals and inherent values of the thermal expansion coefficients. Discrepancies in values of the thermal expansion coefficient may be evidence of the fact that gas (Cl₂, H₂O, O₂ and N₂O) liberation contributed to the
growth of pressed samples size. This process affects the imaginary thermal expansion coefficient while this is not observed in the case of true thermal expansion coefficient. In physically gas liberation has no influence on the position of reflexes in the AP x-ray image. So, when comparing the maximum values, it is important to take into account the grain orientation influence and the gas liberation contribution to the thermal growth of samples. In turn, the grain orientation is a structural parameter that characterizes the crystal orientation being dependent on the initial state of the sample, i.e. a molded article (pressed, rolled, stamped), powder, or a thin film.

4. Findings
Qualitative results on the changes in the diffraction pattern of x-rays under heating are obtained and they indicate changes in the crystalline structure, phase composition, and oscillation of the structural state in AP. Ammonium perchlorate is revealed to have the polymorphous transition of the first kind within 511–517 K in accordance with earlier results [12].

The developed crystallographic models of two modifications of AP and the full-profile analysis (quantum simulation combined with the differential Fourier-transforms) were used for high-precision processing of x-ray patterns, which helped to determine that phase equilibrium takes place at \( T > 540 \) K in the AP sample at the level of 53% \( \beta \)-AP. So, the polymorphous transition is proved to be incomplete in AP until its complete decomposition.

Changes in unit cell parameters and in the inherent thermal expansion coefficient are studied in the anisotropic approximation. Parameter a is revealed to be the main contributor to changes in the volume of the AP unit cell. So, changes in the volume can be characterized as non-equilibrium. The isolated \( \beta \)-phase of AP is noted to influence oscillation of the thermal expansion coefficient of the sample. The limiting oscillation amplitude in the case with the random-orientation powder is \( 5.7 \times 10^{-4} \) K\(^{-1}\) in contrast to \( 65 \times 10^{-4} \) K\(^{-1}\) in the case with the grain-oriented briquette.

5. Conclusion
Development of composite EM of specified performance requires certain issues to be resolved. One of these issues is the composite EM developed to have a needed feature set and stable performance parameters. Knowing that properties of composite EM depend not only on their components, but also on the structure and properties of these components, it is of critical importance to study these characteristics in order to understand materials response to different impacts.

In the paper, we have considered anisotropic thermal expansion within 150–550 K of AP being the main component of solid propellants. Special features in the structure changes in the

| Table 3. Anisotropic values of AP thermal expansion. |
|---------------------------------------------------|
| **Average** (to \( T = 500 \) K) | **Maximum** (at \( T > 500 \) K) |
| Notation | \( \alpha \times 10^4 \) (K\(^{-1}\)) | Notation | \( \alpha \times 10^4 \) (K\(^{-1}\)) |
| \( \alpha_a \) | 0.74 | \( \alpha_a \) | 2.8 |
| \( \alpha_b \) | 0.40 | \( \alpha_b \) | 5.7 |
| \( \alpha_c \) | 0.49 | \( \alpha_c \) | 1.6 |
| \( \alpha_V \) | 1.7 | \( \alpha_V \) | 4.0 |
| \( \alpha_l \) | \( \approx 1 \) [17] | \( \alpha_l \) | \( \approx 65 \) [17] |
polymorphous transition region are demonstrated. Regularities in anisotropic changes of the AP structure under thermal impact are stated, as well as the oscillation character for seven parameters of the structure, i.e. four parameters of the unit cell, microdistortion, sizes of the coherent scattering region, and crystallite density.

The obtained results will allow us to characterize behavior of pressed AP and also AP being a component of the rocket propellant inside a mixture in response to thermal impact.

References
[1] Vadhe P P, Pawar R B, Sinha R K, Asthana S N and Subhananda Rao A 2008 *Combust., Explos. Shock Waves* **44** 461–77
[2] Dolgoborodov A Yu, Streletskii A N, Makhov M N, Kolbenev I V and Fortov V E 2007 *Russ. J. Phys. Chem. B* **1** 606–11
[3] Gogulya M F, Makhov M N, Brazhnikov M A, Dolgoborodov A Yu, Arkhipov V I, Zhigach A N, Leipunskii I O and Kuskov M L 2008 *Combust., Explos. Shock Waves* **44** 198–212
[4] Gogulya M F, Makhov M N, Dolgoborodov A Yu, Brazhnikov M A, Arkhipov V I and Shchetinin V G 2004 *Combust., Explos. Shock Waves* **40** 82–95
[5] Dolgoborodov A Yu, Kirilenko V G, Brazhnikov M A, Shevchenko A A and Teselkin V A 2014 Proc. 12th Zababakhin Sci. Readings (Snezhinsk: VNIITF)
[6] Zhigach A N, Leipunskiy I O, Berezkina N G, Pshechenkov P A, Zotova E S, Kudrov B V, Gogulya M F, Brazhnikov M A and Kuskov M L 2009 *Combust., Explos. Shock Waves* **45** 35–47
[7] Sarner S 1969 *Chemistry of Rocket Fuels* (Moscow: Mir)
[8] Pivkina A N, Frolov Yu V and Ivanov D A 2007 *Combust., Explos. Shock Waves* **43** 60–5
[9] Smith H G and Levy H A 1962 *Acta Crystallogr.* **15** 1201
[10] Herrmann K and Ilge W Z 1930 *Z. Kristallogr., Mineral. Petrogr., Abt. A* **75** 41
[11] Stull D R and Prophet H 1971 *JANAF Thermochemical Tables* (Washington: NBS37)
[12] Ivanov E Yu and Boldyrev V V 1979 *Dokl. Akad. Nauk SSSR* **248** 862–5
[13] Gottfried C and Schusterius C Z 1932 *Z. Kristallogr., Mineral. Petrogr., Abt. A* **84** 65
[14] Stankevich A V, Kostitsyn O V, Smirnov E B, Taibinov N P and Tarasov A Yu 2014 Proc. 12th Zababakhin Sci. Readings (Snezhinsk: VNIITF)
[15] Young R A 1996 *The Rietveld Method* (Oxford: Univ. Press)
[16] Stankevich A V, Kostitsyn O V and Taibinov N P 2014 Method for determining the structure of molecular crystals Patent 2566399
[17] Belomestnykh V N and Tesleva E P 2005 *Izvestia of Tomsk Polytechnical University* **308** 23–8