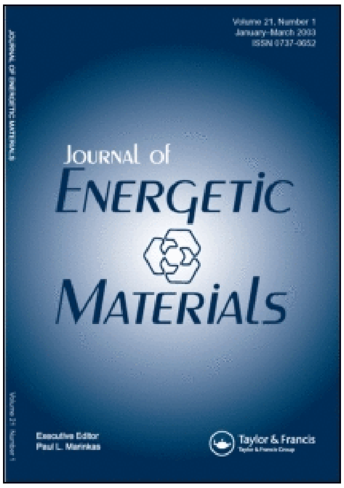

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Crystal State of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) Undergoing Thermal Cycling Process

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To cite this Article Sun, Jie , Kang, Bin , Xue, Chao , Liu, Yu , Xia, Yunxia , Liu, Xiaofeng and Zhang, Wei(2010) 'Crystal State of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) Undergoing Thermal Cycling Process', Journal of Energetic Materials, 28: 3, 189 — 201

To link to this Article: DOI: 10.1080/07370650903401254

URL: http://dx.doi.org/10.1080/07370650903401254

Journal of Energetic Materials, 28: 189–201, 2010
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ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370650903401254

Crystal State of 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) Undergoing Thermal Cycling Process

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The present report aims to discuss the crystal state variation of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) suffering from thermal cycling process. In this study, in situ X-ray powder diffraction (XRD) was employed to determine thermal expansion and crystal fragmentation, primarily attributed to its crystal state variation. The results showed that the change of crystal volume mainly stemmed from the thermal expansion at the c axis of crystal lattice, and TATB crystal had the same thermal expansion coefficients at a and b axes. It was also demonstrated that crystal fragmentation occurred during this process, and more auto-repair happened in the [002] plane

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of TATB than other planes. These results will have an implication on the process of TATB-based materials.

Keywords: crystal fragmentation, TATB, thermal expansion

Introduction

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) possesses excellent thermal stability and low sensitivity and thus is widely employed as an insensitive energetic explosive in its applications [1–3]. TATB is usually has a planar molecular structure and a triclinic crystal state. A strong hydrogen bonding (inter- and intramolecular) is formed within the a-b crystallographic plane (plane direction denoted as a and b axes) [3,4]. Consequently, it is prone to form crystal particles with a sheet structure. The thermal expansion coefficient at the direction perpendicular to its a-b plane (denoted as c direction) is higher than that at the a and b axes because of weaker van der Waals forces between the layers than hydrogen-bonding force within its a-b plane [5–8]. This difference from a-b and c axes endows TATB crystals with anisotropic expansion properties. Further, the a-b crystal plane tends to orient perpendicularly to the direction of applied pressure. In other word, the c axis aligns with the principal applied stress. The 16–19% difference of thermal expansion coefficients at the pressing direction (c axis) and at the tangential direction (a-b crystal plane) often occurs to the consolidated article (compact), resulting from cumulating the response of each particle [8]. Unfortunately, the huge difference frequently arrives at enough ability to distort the compact structure of explosives. Therefore, great care should be taken for the safety and reliability in its applications.

Equipment for use with explosives is often required to be available in the broad working temperature period, for example, from −50°C to +55°C. Thermal expansion of energetic materials has a major role in deciding the material's response to its environment [8–14]. It is necessary to fully understand the thermal expansion coefficient of TATB crystal in order to design its assembly conditions [4,7]. It is well known that significant thermal internal stress is dependent on anisotropy of single crystals. Moreover, internal crack happens in its crystal as the coherence strength is overloaded by the internal stresses. Therefore, the expansion properties of the crystal should be of great consideration. It has been demonstrated that TATB, as a lower symmetry triclinic system, possesses six independent coefficients of thermal expansion of the second rank tensor. In the temperature range from −59°C to +104°C, coefficients of thermal expansion (CTE) of TATB in the a, b, and c directions are 248 (4.0% expansion), 20.9 (0.3% expansion), and 8.3 μm/mK (0.1% expansion), respectively [6]. Gee and his coworkers studied the thermal expansion and irreversible expansion of polycrystalline TATB by theoretical simulation [5,7,9,15,16]. They recognized that the irreversible expansion of the polycrystalline resulted from crystal rupture during the thermal cycling process. Kolb and Rizzo also demonstrated that there was no permanent growth observed on single crystalline of TATB underwent by a varying temperature [6]. In the past 30 years, the accuracy of CTE of TATB crystals has not been reported even though the progress of XRD instrument made it possible to obtain more accurate values. Moreover, few studies focused on the crystal parameter and the crystal rupture of TATB when it undergoes the heat–cool cycling process. Therefore, this work employs in situ XRD to discuss CTE and crystal size of TATB with varying temperature.

Samples and Experiments

The TATB was synthesized by the Institute of Chemical Materials, China Academy Engineering Physics. The particle size is about 20 μm, and its purity is over 99%.

X-ray diffraction data were recorded on a Bruker D8 Advance X-ray diffractometer (Bruker Co., Germany) by using Cu Kα radiation without any monochromator. A temperature chamber (TTK450) was used to allow the temperature to be closely controlled during the experiments. The X-ray tube with Vantec-1 detector was operated under the condition of 40 kV and 40 mA.

The diffraction patterns were evaluated by Rietveld analysis using the TOPAS software. The fundamental parameters approach (FPA) profile function was adopted to fit the experiment data using a Chebychev polynomial of fourth order and the 1/X Bkg function. Tube tails information was used instead of receiving slit (RS) and fixed divergence slit (FDS) attributed to the use of Vantec-1 detector. The absorption correction was set to refine in order to correct the significant profile shape distortion caused by the low mass absorption of the sample. In addition, it was also necessary to refine zero error. Because the X-ray diffractometer was not equipped with a monochromator, the Lorentz polarization (LP) factor was zero for unpolarized radiation. Crystal structure data for Rietveld refinement were as follows: space group P1, with $Z = 2$, $a = 9.010$ Å, $b = 9.028$ Å, $c = 6.812$ Å, and $\alpha = 108.59°$, $\beta = 91.82°$, $\gamma = 119.97°$, and the density was $1.938\,g \cdot cm^{-3}$ [6,17,18].

Results and Discussion

In order to observe the crystal state of TATB suffering from thermal cycling process (from 30 to 240°C and subsequently from 240 to 30°C), XRD was employed to determine cell parameters of TATB crystals at various temperature points. The results (Table 1) show that 3.5% expansion (CTE) occurred at c axis direction, and the same CTEs occur between a and b directions, only 0.2%. The total volume change was 4.4% during the heating period. The phenomenon indicates that more thermal expansion occurred in the c axis direction than in the other two directions. It was not difficult to understand that the expansion in the c axis direction primarily resulted in the increased crystal volume of TATB. Moreover, the heating process promoted a small decrease of the cell angles α and β but kept the γ value constant during the whole temperature period. Crystal parameter variation of TATB always followed the changing temperature during this period. After the temperature returned to 30°C, crystal parameters returned to original values, which implies that a footprint was not observed on crystal parameters of TATB suffering from the cycling

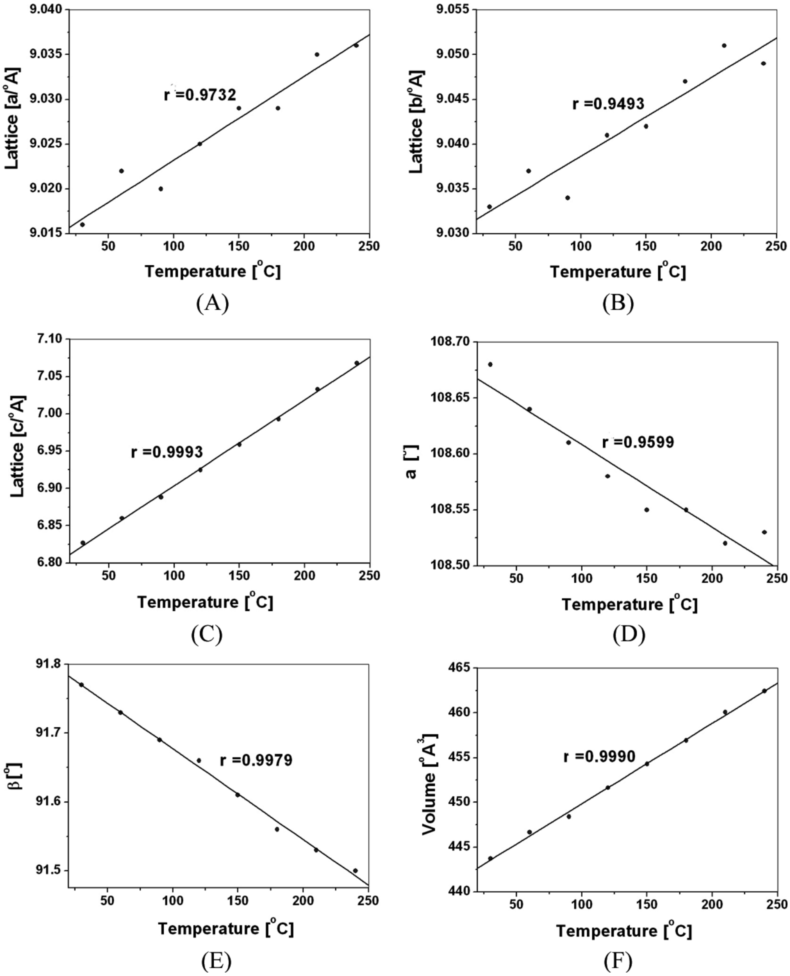
Table 1
Cell parameters of TATB undergoing the thermal cycling process

T (°C)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å^3)
30	9.016	9.033	6.827	108.68	91.77	119.97	443.70
60	9.022	9.037	6.860	108.64	91.73	119.97	446.66
90	9.020	9.034	6.888	108.61	91.69	119.98	448.40
120	9.025	9.041	6.925	108.58	91.66	119.97	451.63
150	9.029	9.042	6.959	108.55	91.61	119.98	454.29
180	9.029	9.047	6.993	108.55	91.56	119.98	456.91
210	9.035	9.051	7.033	108.52	91.53	119.99	460.08
240	9.036	9.049	7.068	108.53	91.50	119.97	462.43
240	9.036	9.052	7.067	108.54	91.49	120.01	462.36
210	9.037	9.051	7.031	108.52	91.54	119.99	460.12
180	9.034	9.049	6.995	108.56	91.56	119.98	457.35
150	9.028	9.044	6.962	108.57	91.59	119.98	454.49
120	9.023	9.039	6.922	108.60	91.63	119.97	451.22
90	9.019	9.035	6.890	108.60	91.67	119.99	448.52
60	9.021	9.038	6.861	108.65	91.71	119.98	446.63
30	9.015	9.032	6.827	108.68	91.76	119.97	443.67

process. This opinion can be proved by results of Kolb and Rizzo [6]. Further, it was easily speculated that the unit-cell state of TATB crystal arrived at equilibrium so quickly as to follow varying temperature.

In order to further understand the change of parameter with temperature, Fig. 1 illustrates the fit lines of a, b, c, α, β, and volume of crystal TATB with function of temperature according to data (Table 1) involving the heating process period. Moreover, similar fit lines of the reported data are also displayed to compare their accuracy and correlation coefficients, which are listed in Table 2.

Figure 1 shows that a, b, c values and volume of TATB had a similar tendency with the thermal cycling process. Moreover, the correlation coefficients from this work were much higher



(A) (B) (C) (D) (E) (F)

Figure 1. Crystal parameters of TATB with the function of temperatures: (A) a axis, (B) b axis, (C) c axis, (D) α, (E) β, (F) crystal volume.

than the results from Kolb and Rizzo, especially for the a and b axes [6]. The correlation coefficients of the fit line for the c axis and volume in this work were 0.9993 and 0.9990, respectively. High correlative coefficients may be explained by the large change with relatively high precision. The linear coefficients

Table 2
Comparing relative coefficients of each fit lines and CTE in this work and the previous report [6]

	r		CTE (10^{-6} K^{-1})	
Crystal parameters	This work	Ref.	This work	Ref.
a	0.9732	0.5288	10.4	8.3
b	0.9493	0.9421	9.8	20.9
c	0.9993	0.9913	169	248
α (°)	0.9599		−6.8	
β (°)	0.9979		−14.4	
Volume (Å^3)	0.9990	0.9896	201	302

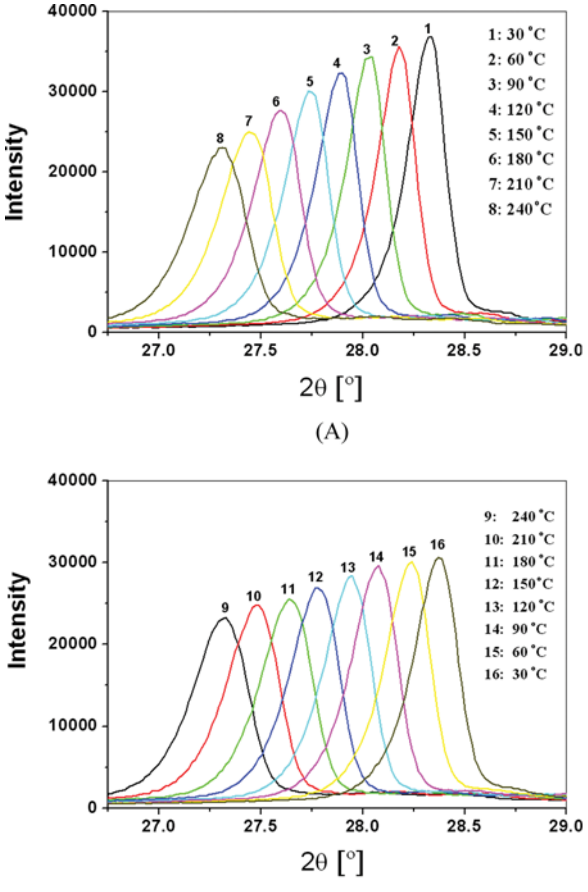
at the a, b, and c axes were 10.4×10^{-6}, 9.8×10^{-6}, and 1.69×10^{-6}, respectively. This meant that the relative expansion value at the c axis was approximately 16 and 17 times of those at the a and b axes, respectively. There were similar values at the a and b axes. However, Kolb and Rizzo reported that the linear coefficient at the a axis had 2.5 times of the value at the b axis. It was also found that the linear coefficients at the a, b, and c axes and volume were respectively 5/4, 1/2, 2/3, and 2/3 of the value reported by Kolb and Rizzo [6]. Except for the a axis, the linear coefficients of unit-cell expansion in this work were greatly lower than the data reported by Kolb and Rizzo [6]. This was because van der Waals forces between the layers (in the c direction) were weaker than hydrogen bonding forces in its a-b plane with high degree of network, thus the thermal expansion coefficient of TATB crystal in the c axis direction was significantly higher than those of the a and b axes [5–7]. This is consistent with the results of Roszak et al. that interactions between crystal sheets resulted in more anisotropy than those in the a and b directions [15]. Both a and b axes were in the a-b plane of TATB, so the thermal coefficients at the a and b axes might be similar to each other. Therefore, more accurate linear thermal expansion coefficients were obtained in our results.

Table 3
Peak shift of several crystal planes from 30 to 240°C

Crystal plane	30°C	240°C	Shift (°)
[010]	12.252	12.190	−0.062
[0–11]	14.638	14.387	−0.251
[011]	22.024	21.535	−0.489
[002]	28.346	27.328	−1.016

The peak position of plane [100] was very close to those of the plane [−101], and the peaks of selected crystal planes [010], [0–11], [011], [002] were separated; thus, they were employed to obtain exact peak position and full widths at half maximum (FWHM) of TATB. Table 3 shows the peak shift of several crystal planes at 30 and 240°C. It indicates that the peak position of all crystal planes had a little shift to the low value, but different kind of planes had different shifts after the temperature increased from 30 to 240°C. The peak position of the [002] plane took a little shift to a low value (−1.016°) but the [010] plane only had a shift of −0.062°, which implies that the expansion space between the [002] planes was much more than that between the [010] planes.

Figure 2 displays the magnified XRD photograph of TATB for the [002] crystal plane at various temperatures. It was very interesting to find that the peak height decreased with increasing temperature during the heating procedure. On the contrary, the peak height increased with decreasing temperature during the cooling procedure. Its peak height always had an inverse proportion with the temperature. However, the peak height in the cooling process was lower than that in the heating process. This suggested that it did not return to original height when the cycling process was completed. It was also observed that the FWHM had a positive tendency with increasing temperature. When other crystal planes were determined with the same methods, it found that their peak height and FWHM had little variation.



(A)

(B)

Figure 2. XRD photograph of TATB for [002] crystal planes at various temperatures: (A) heating process and (B) cooling process.

According to the Scherrer functions, crystal sizes were obtained from their FWHM. Figure 3 shows the changes of crystal size with the [010] and [002] planes and the sums of the plane are listed in Table 4. During the heating process, the crystal size decreased with increasing temperature and the distance between the planes increased with temperature; thus,

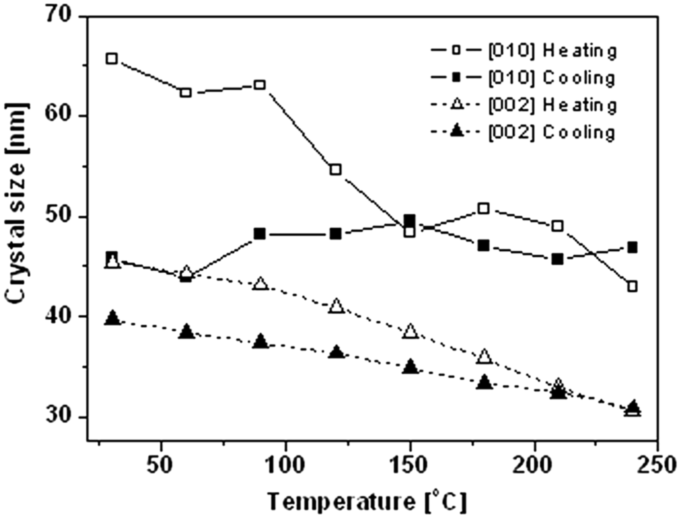


Figure 3. Crystal sizes of TATB for [010], [002] crystal planes at various temperatures.

the crystal fragmentation may occur in the heating process. Thereby, experimental results on the crystal fragmentation strongly proved theoretical simulation about crystal

Table 4
The sums of [010], [002] planes

	Sums of [010] plane		Sums of [002] plane	
T (°C)	Heating	Cooling	Heating	Cooling
30	9	6	14	13
60	9	6	14	12
90	9	7	14	12
120	8	7	13	12
150	8	7	12	11
180	8	7	11	11
210	7	6	10	10
240	6	6	10	10

fragmentation reported by Gee et al. [7]. During the cooling process, the crystal size of the [002] plane increased with decreasing temperature, but the crystal size of the [010] plane remained constant. There was a good linear relationship between the crystal size and temperature of the [002] plane. It was demonstrated that the [002] planes can be auto-repaired partly, but this repair action did not happen to the [010] planes in the cooling process.

As we all know, the only interplanar action of the [002] planes in TATB were weak van der Waals forces; thus, it had the primary attribution to thermal expansion than other planes. The crystal fragmentation easily occurred in this interplanar when the [002] plane expansion arrived at the maximum load. In the cooling process, the van der Waals force was generated again between them when the [002] plane was formed from two little crystals; consequently, the crystal size increased. However, the interplanar forces of the [010] plane mainly came from their hydrogen bonding. The hydrogen bonding can be formed only when the distance between relevant groups were very short. Therefore, the crystal size of the [010] plane was not increased in the cooling process.

Conclusion

This research has revealed the crystal state of TATB when it suffered from a thermal cycling process. It was found that the thermal expansion in the c axis direction had a major influence on crystal volume of TATB. TATB crystals had the same thermal expansion coefficients in the a and b axes directions. More accurate and reliable correlation coefficients were obtained in our research. On the other hand, crystal fragmentation was proved during this thermal cycling process, and auto-repair happened only in the [002] planes of TATB. This firstly proved the theoretical simulation of its crystal fragmentation reported by Gee [7]. Therefore, these results will provide guidance for the heat process of TATB-based materials.

Acknowledgments

This work is supported by the Science Foundation of China Academy of Engineering Physics, China (No. 2009A0203010). We thank Jun Luo and Fusheng Liu for their guidance in refinement of the structure parameters from diffraction data.

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