UCRL-JC-145228

Kinetics of HMX and Phase Transitions: Effects of Grain Size at Elevated Temperature

C. K. Saw

June 13, 2002

12th International Detonation Symposium, San Diego, CA
August 11-16, 2002

KINETICS OF HMX AND PHASE TRANSITIONS: EFFECTS OF GRAIN SIZE AT ELEVATED TEMPERATURE

Cheng K. Saw
Lawrence Livermore National Laboratory
University of California
7000 East Ave, Livermore, CA 94550

To date a global kinetic rate law has not been written to accurately describe solid-solid phase transformations of HMX and TATB where contributions from grain size effects, binder contents, and impurity levels are explicitly defined. Our recent work presented at the 2001 SCCM topical APS meeting, Atlanta, GA, demonstrated one can not confidently use the second harmonic generation (SHG) diagnostic to study energetic material phase transitions where non-uniform grain size distributions are present. For example, in HMX, the early arrival of SHG before the XRD in the SHG/XRD simultaneous high temperature experiment clearly indicates the partial molecular conversion from centrosymmetric to non-centrosymmetric without any structural changes as exhibit by the XRD pattern. This conversion is attributed to the changes of the surface molecules due to the differences in potential between the surface and the bulk. The present paper reports on accurate XRD measurements following changes of β- HMX to δ-HMX at elevated temperature. The results are compared for sample with 2 different grain sizes for HMX. We report accurate temperature dependent lattice parameters and hence volume and linear thermal expansion coefficients along each crystallographic axis. We have also conducted kinetic studies of the behavior of 2 grain-sizes of HMX and concluded that their kinetics, are drastically different.

I. INTRODUCTION

HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine) is of interest because of its use in the area of explosive. It exists in many polymorphic forms, δ-, γ-, α- and β-, and has sensitivity order which goes as $\delta > \gamma > \alpha > \beta$. Hence, β- is the most stable and δ- is the least. Although there are many papers published on HMX, only a few have focused on monitoring experimentally the phase behavior of HMX[1-5]. The crystal structure has also been studied [6]. However, only one by Hermann et. al.[1], has detailed information on the phase behavior derived from XRD technique.

It was also reported that the sensitivity greatly depends on the particle size, the larger the particle size, the more sensitive it becomes and yet, there is no explanation given to the cause for this phenomenon. It is known that pores (or voids) play a major role in controlling the detonation process as some kind of energy concentrator, or rather, "hot spots"[7]. It is not clear what kind of character the pores (e.g. size and/or shape) possess in order to change the sensitivity of HE materials. It is also not clear if the ultimate pore character originated during the processing stage or during the initial stages of detonation. Pores can also be generated during phase transformation or temperature cycles,

---

This work was performed under the auspices of the U. S. Department of Energy by the University of is California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

by anisotropic changes in lattice parameters and thus, changes to the volume and density. Hence, phase transitions and anisotropy in thermal expansion can greatly influence the microstructure relating to the pore character as well as the crystallite size.

The cycling of phase transformation with temperature due to the changing weather has a direct implication on changing the microstructures, hence, the aging effect. It has been speculated that δ-HMX converts back to the more stable β-HMX over long period of time, however, at the moment, no data is available to support this phenomenon. There is also no detailed information on cycling of the phase transformation with pressure. A detailed description for this transformation, and its effects by grain size, binder interactions or impurities has not been presented.

This present effort undertakes to provide detailed examination on the thermal expansion and phase transition of HMX and to compare the kinetics of this transformation as a function of grain size.

II. SAMPLES

HMX was prepared by the method of Siele et. al.[8]. This involved the treatment of octahydro-1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocine (DADN) with 100% HNO_3 and P_2O_5 at 50°C for 50 minutes, followed by quenching in ice water. Slow re-crystallization from acetone yielded HMX as colorless microcrystals. The chemical formula for HMX is $C_4H_8N_8O_8$. The grain sizes are measured to have tri-model distribution centered roughly at 0.5, 8 and 100 μm. This sample is also grounded to about 3 μm size for comparison studies. The tri-model sample is referred to "**coarse**" and the 3μm size sample is "**fine**" in the following text.

From the literature, β- HMX has the monoclinic structure with 2 molecules per unit cell, a=6.537Å, b=11.054 Å and c=8.7018 Å, and β=124.443 (JCPDS 42-1768). The density is 1.91 gm/cc and volume of 259.3 $Å^3$. δ- HMX is hexagonal with a=7.711Å, c=32.553 Å density = 1.76 gm/cc and volume =279.4 $Å^3$ (JCPDS-44-1622). There is roughly 8% change in both density and volume going from one phase to another.

III. EXPERIMENTAL

The experimental setup uses the INEL curved position sensitive detector system mounted on an in-house sealed tube generator. The generator is set at 40KeV and 30 MA. Incident Ge monochromator is used to select only the $CuK_{\alpha 1}$ radiation. This unit enables the acquisition of the full 120 °(2θ) angular range simultaneously. For heating, the INEL capillary furnace, which has the capability of going to 400 °C, is used. The samples are loaded into capillary tubes of 0.7 mm diameter with about 2mm length of materials. The thermal couple is located right beneath the glass capillary. Hence, there is very little temperature lag. Only 1.4 mg of material is needed to fill up the capillary tube for each run.

In the 1st experiment, the temperature is raised from room temperature to 210°C and back to room temperature. Data acquisition is set for 10 minutes per temperature per scan. The 2nd experiment focuses on the changes of the hexagonal δ- phase over time. The temperature is maintained at 30 °C throughout the run. The total experimental time is approximately 3-4 hours. The 3rd experiment focuses on transformation of the δ- phase at elevated temperature by going up to 250 °C untill it decomposes.

Kinetics experiments and comparison of the structures at elevated temperature were also performed for both the coarse and fine samples. The initial temperature selected is165 °C and later 170 °C is selected because no transformation is observed for the fine sample at 165 °C. Data acquisition is performed for several hours to monitor the β to δ transformation.

The diffraction patterns acquired are analyzed using the Jade software (Version 6.0) and the lattice parameters are refined using well-defined and isolated peaks. A silicon powder standard is used for calibration at the start of the experiment. From the refined lattice parameters, the volume and density are also calculated and plotted according to temperature or time.

IV. RESUTLS AND DISCUSSION

A. HMX: PHASE TRANSFORMATION AT ELEVATED TEMPERATURE

Figure 1 shows the resulting diffraction patterns for HMX as a function of increasing and then decreasing temperature. The temperature profile direction is indicated by the arrow direction. The increasing temperature scans (1-7) (30°C to

150°C) can be indexed to the β-HMX and, the high and decreasing temperature scans (9-17) (190° to 30°C) to δ-HMX as indicated by the JCPDS listing in the figure for β- (42-1768) and δ- (44-1622) HMX. Scan (8) appears to have 2 phases. Clearly, a phase transformation has occurred.

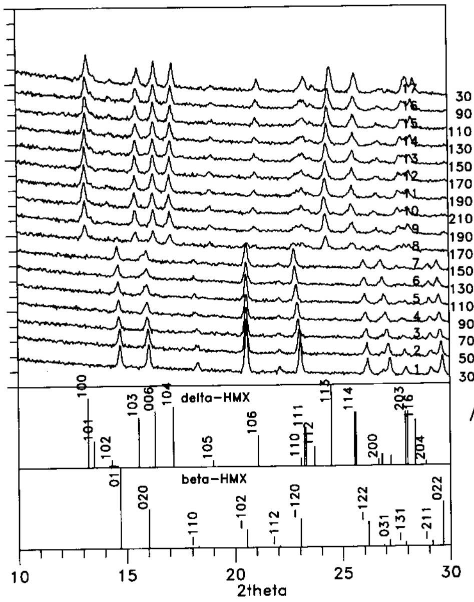


Figure 1: XRD of β- to δ- HMX phase transition

As shown in Figure 1, there is an abrupt change in the spectrum going from 150°C to 170°C. This result indicates that the generation of δ- phase does not require the complete destruction of β- phase. In fact, at some temperature range, the 2 phases can exist together. The kinetics of such behavior will be followed in the later experiment.

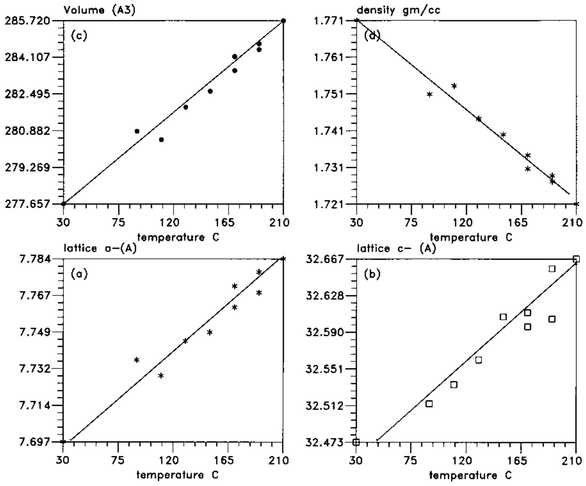
There is no continuous transition from the β- lattice to the δ- lattice. Hence, there are 2 independent processes occurring, destruction of the β- phase and the development of the δ- phase. This is also supported by the fact that the diffraction peaks close to the transformation temperature do not broaden to form a disorder structure in order to re-crystallize to the δ phase.

T °C	a-±Δa Å	b ±Δb Å	c ±Δc Å	β±Δβ	Vol Å^3	Den gm/cc
30	6.5339 (47)	11.0478 (49)	8.6956 (79)	124.404 (57)	259.0	1.899
50	6.5427 (49)	11.0705 (51)	8.7030 (92)	124.395 (69)	260.1	1.891
70	6.5395 (68)	11.0971 (54)	8.7104 (102)	124.295 (96)	261.1	1.883
90	6.5489 (88)	11.1407 (89)	8.7013 (174)	124.297 (139)	262.3	1.875
110	6.5517 (54)	11.1615 (67)	8.7036 (105)	124.273 (77)	263.0	1.870
130	6.5541 (121)	11.2122 (220)	8.6921 (366)	124.122 (248)	264.4	1.860
150	6.5532 (50)	11.235 (40)	8.6986 (70)	124.119 (68)	265.1	1.855

Table I: X-ray extracted unit cell parameters for β-HMX- monoclinic

T °C	a-±Δa Å	c ±Δc Å	Volume A^3	Density gm/cc
170	7.7880 (47)	32.6595 (196)	285.918	1.7199
190	7.7871 (39)	32.6654 (180)	285.907	1.7199
210	7.8007 (42)	32.7185 (155)	287.365	1.7112
190	7.8042 (39)	32.6717 (152)	287.220	1.7121
170	7.7878 (20)	32.6385 (50)	285.717	1.7211
150	7.7702 (32)	32.6401 (96)	284.442	1.7288
130	7.7583 (32)	32.6332 (107) ·	283.512	1.7345
110	7.7623 (32)	32.5994 (122)	283.510	1.7345
90	7.7588 (29)	32.5545 (014)	282.863	1.7385
30	7.7182 (41)	32.5160 (119)	279.583	1.7588

Table II: X-ray extracted parameters for δ-HMX during cooling



Figures 2a-d: Least linear square fit to (a) a-, (b) c-, (c)-volume and (d) density for the δ- HMX.

The refined lattice parameters results are listed in Tables I and II for β- and δ- HMX respectively. Further data set will not be presented due to length of the paper. The error bars for each lattice parameters are also listed in the tables. In β-HMX, the *b*-axis is highly correlated with the rise in temperature. A slight increase in *a*- axis and decrease of unit cell β angle with temperature can also be observed. It is difficult to conclude if there is significant change in *c*- with temperature. Figures 2a-2d show typical least square fit for the refined lattice parameters as a function of temperature. Clearly, the fits are quite good with reasonably small error bars. The cell information for both phases are listed in Table III, which indicates that our measurements are consistent with those published earlier. The coefficient of thermal expansion (contraction) (χ) for both phases are calculated and listed in Table IV. The errors are listed in parenthesis. There are

		Cell information	
Phase	Parameters	Published [1]	Present work
β-	a- Å	6.537	6.540 (.003)
	b- Å	11.054	11.034 (.004)
	c- Å	8.7018	8.700 (.006)
	β	124.443	124.46 (.04)
	Volume Å^3	259.3	258.8
	Density (gm/cc)	1.91	1.8991
δ-	a- Å	7.711	7.7182 (.004)
	c- Å	32.553	32.516 (.012)
	Volume Å^3	279.38	279.58
	Density (gm/cc)	1.76	1.759

Table III: Lattice parameters for β- and δ- HMX

small differences between our results and those published earlier[1] (shown in the 1st column). These differences may be due to experimental errors since the uncertainties were not included in previous paper.

Clearly, the volume increases and density decreases linearly with temperature. It was reported[1] from TMA measurement there is a 1% reduction in volume right before the transformation. The present data does not show any changes in the unit cell to account for this reduction. Therefore, the reduction may originate from changes in the microstructure.

	χ x 10^{-5}/° C^2	χ x 10^{-5} /°C	χ x 10^{-5} /°C	χ x 10^{-5} /°C	Fine χ x 10^{-5} /°C
β-phase		Heating		Cycling	Heating
a- Å	-.29	2.54 (.4)			3.85 (.6)
b- Å	11.6	14.77 (.7)			15.0 (.5)
c- Å	2.3	.41 (.7)			.92 (.4)
β	2.58	2.1 (.3)			1.60 (.6)
VCh.	13.1	20.1 (.3)			20.5 (.8)
% VCh		2.4%			2.85%
DCh		19.4 (.5)			19.7 (.8)
% DCh		2.34%			2.77%
β to δ T °C		150-170			180-190
δ-phase		cooling	Cycling	Heating	Fine heating
a- Å	6.18	7.19 (.6)	6.66 (.3)	6.50 (.2)	8.05 (.3)
c- Å	2.47	2.1 (.3)	2.81 (.3)	3.44 (.4)	2.10 (.3)
VCh	13.5	16.7 (.3)	16.3 (.6)	16.7(.6)	18.5 (.6)
% VCh		2.99 %	2.93%	3.66%	3.30%
DCh		16.0 (.5)	15.7 (.6)	15.9 (.5)	17.6 (.6)
% DCh		2.90%	2.84%	3.52%	3.2%

Table IV: Coefficient of thermal expansion (contraction).
Note: VCh- volume change, DCh- density change

There is roughly a 2.4% change in volume and density during the increase of temperature from 30 to 150°C. Our measured coefficients of thermal expansion for *b*- is about 15x10^{-5}/°C which is significantly higher that the published value. Hence, our coefficient of volume change, 20x10^{-5}/°C is also higher than the reported value of 13x10^{-5}/°C. The phase transition is observed to be between 150-170°C. There is about 7 % jump in volume going from β- to δ- phase. Upon cooling, δ-phase remains and the coefficient of thermal expansion is observed to be linear for both *a*- and *c*- of the hexagonal structure.

XRD examination is also carried out over a period of 4 hours time at room temperature. The resulting spectra are very similar and show no major change for the δ-phase. On continuing 2nd heating up to 210 °C and cooling down to room temperature, only changes in cell parameters can be observed. These parameters are then least square fitted and listed for the coefficient of expansion in Table IV. It can be concluded that the coefficients of thermal expansion (contraction) essentially obeys the linear fit indicating the linearity in thermal expansion (contraction) for both β- and δ- HMX phase. These values are consistent with those reported earlier [1]. On continue heating, at 290 °C the material lost its β-structure. Since the peaks do not broaden right before disappearing, the δ-phase HMX appears to have decomposed rather than transforming into the disordered/ amorphous/liquid structure.

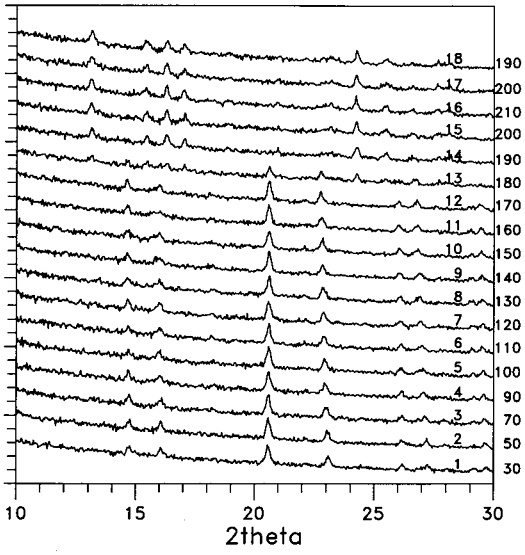


Figure 3: XRD patterns indicating β- to δ- HMX transformation.

Figure 3 shows the x-ray diffraction patterns for the fine sample at elevated temperature. β- HMX can be observed at the start of the experiment. During heating, δ-phase emerges at about 180°C. To ensure that all the β- phase is converted to δ-phase, the temperature is raised to 210°C before cooling. δ- HMX remains down to room temperature. The patterns are analyzed and least square fitted and the coefficients of expansion are listed in Table III. These values are essentially similar to those from the coarse sample, except for the transformation temperature, which is observed to be about 180°C for the fine and 160 °C for the coarse.

The estimated crystallite sizes, which are extracted from the peak widths for the coarse and fine samples are essentially similar, indicating the overall crystal sizes are not significantly change by grinding. Hence, the coefficients of thermal expansion calculated for each crystallographic axis, is not influence by the different grain size.

By taking the percent of change in lattice parameter over the room temperature value, it can be concluded that the major contribution to the expansion is in the *b*- direction for the β-phase and *a*-direction for δ-phase. It is interesting to note that the changes of *a*- and *c*- for β-phase and *c*- in the δ- phase are relatively small. It can then be concluded that the thermal expansion (contraction) is essential in one direction, which implies that it is possible to generate defects and voids during temperature cycle.

B. KINETIC STUDY

For kinetic study, the HMX samples are held at 165°C for several hours. Figure 4 shows the resulting diffraction patterns for the coarse sample indicate the conversion from β to δ at 165°C. It requires at least 4 hours for complete conversion. However for the fine sample, no change is observed when the temperature is set at 165 °C. The temperature is then raised to 170°C in order to enhance the conversion. A very slow conversion to δ-HMX can be observed. However, the conversion is not complete even for exposure up to 8 hours at 170 °C.

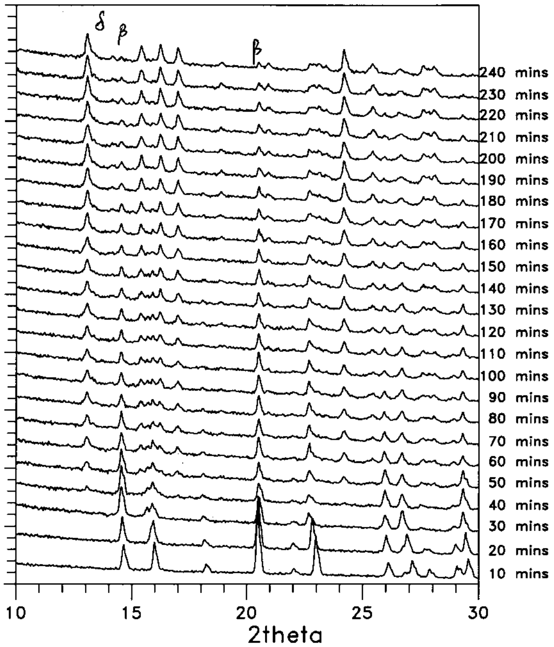


Figure 4: XRD patterns of kinetic study of coarse HMX

As pointed out by Karpowicz et. al.[3], the conversion of “chair” configuration (β-phase) to the “boat” configuration (δ-phase) can be accomplished by simply ring-puckering vibration which are generally low potential energy barriers. In the fine sample, these barriers are higher than those from the coarse sample. At the moment, there is insufficient data to provide an Arrhenius plot to determine the rate constant for either the coarse or fine sample.

V. RESULTS AND DISCUSSION

The present results establish that structure of HE materials can be accurately monitored at elevated temperature using the capillary furnace mounted on the INEL curved position sensitive detector system. The minimum sample required for each is about 1.4mg. On an in-house tube generator set at 40KeV and 30MA with incident germanium (220) monochromator, the acquisition time required per scan is 10 minutes. This time can be shortened if a rotating anode generator or synchrotron radiation is used.

For coarse HMX, a phase transition from β- to δ- can be clearly observed at about 160-170°C. However, for the fine HMX sample, the conversion occurred at 170-190°C. In both materials, anisotropic thermal expansion is observed and is independent of grain size.

The biggest thermal expansion change is in the *b*-axis for β-HMX and *a*- axis for δ-phase, which indicates anisotropy behavior with temperature. The lattice expansions (contractions) are observed to be linear with temperature for both phases. Our results also indicate that the coefficients of volume expansion for both β- and δ- phase are higher that those reported earlier.

The similarity in thermal expansions for the coarse and fine samples, suggest that grain size has no effect on the crystallographic unit cell. In fact, by comparing the peak widths for both the coarse and fine sample, the estimated crystallite size is essentially similar. The fine sample appears to have significantly higher resistant in the conversion from β- to δ-. This resistance, which originates in the size of the particle, may be related to molecular conformation changes due to different molecular surface and bulk potentials.

After conversion to δ-HMX and cooled to room temperature, there is essentially no structural change over a period of 4 hours indicating that the less stable δ- phase is stable when cooled to room temperature.

For kinetic study, the coarse sample shows phase conversion from β- to δ- phase, starting at the 1st 10 minutes at 165°C. It requires up to 4 hours for completion. This situation is quite different for the fine sample. At 165 °C, for the duration of the experiment, no conversion can be observed. Only at 170°C, the δ- phase emerges after 90 minutes and continues to develop with time. The above results indicate that the conversion kinetics greatly depend on the particle sizes. Hence, controlling particle sizes, which may be derived by temperature cycle, thermal history, internal stresses and fracturing, are important in managing the stability of HMX. Future experiments will focus on conversion rate to obtain rate constant using similar kinetic experiments.

VI. ACKNOWLEDGEMENTS

The author will like to acknowledge the support of J. Zaug and C. Tarver, and M. Hoffman for providing the samples.

VII. REFERENCES

1. Hermann, M, Engel, W. and Eisenreich, N. "Thermal Analysis of the Phases of HMX using X-ray Diffraction", Zeitschriff fur Kristallographie **204**, 1993, pp.121-128.

2. Hermann, M., Engel. W., and Eisenreich, E., "Thermal Expansion, Transitions, Sensitivities and Burning Rates of HMX", Propellants, Explosive, Pyrotechnics, **17**, 1992, pp.190-195.

3. Karpowicz, R.J., and Brill , T.B., “The β-δ Transformation of HMX: Its Thermal Analysis and Relationship to Propellants”, AIAA **20**, 1982 pp.1586-1591.

4. Henson, B.F., Asay, B.W., Sander, R.F., Sons, S.F., Robinson. J.M., and Dickson, P.M., "Dynamic Measurements of the HMX β-δ Phase Transition by Second Harmonic Generation", Phys. Rev. Letters, **82**, 1999, pp.1213-1216.

5. Saw, C.K., Zaug, J.M., Farber, D.L., Weeks, B.L. and Aracne, C.M., APS SCCM Topical Meeting on Shock, Atlanta, GA, 2001.

6. Choi, C.S., Boutin,P., "A Study of the Crystal structure of β-Cyclotetramethylene Tetranitramine by Neutron Diffraction", Acta Cryst. **B26**, 1970, pp.1235-1240.

7. Menikoff, R., and Sewell, T.S., "Constituent Properties of HMX Needed for Meso-Scale Simulations", LA-UR-00-3804-rev, March 26, 2001

8. Siele, V.I., Warman, M, Leccacorvi, J, Hutchinson, R.W., Motto, R, Gilbert, E.E, Benzinger, T.M., Corburn, M.D., Rohwer, R.K., Davey, R.K., Propell. and Explosiv., 6, 67-73 (1981).