Using Simultaneous SHG and XRD Capabilities to Examine Phase Transitions of HMX and TATB

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Abstract: Simultaneous SHG (second harmonic generation) and XRD (x-ray diffraction) capabilities have been developed at SSRL (Stanford Synchrotron Radiation laboratory) to examine the phase behavior of energetic materials, for example, HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and TATB (1,3,5-triamino-2,4,6 trinitrobenzene). This unique capability provides information on the evolution at the molecular level (centro and non-centrosymmetric) on material stability, phase transformation or decomposition reactions, which are important to continue refinement of computational predictions of material properties. This paper reports x-ray diffraction experiments on both HMX and TATB with increasing temperature and on simultaneous SHG and XRD experiments at fixed temperature. Our results indicate that, for HMX, the β to δ transformation occurs over a range of temperature which do not correlate to the previously reported fast rise in SHG signal close to 170°C as a phase transformation. No phase transition is observed for TATB, even though, previous paper shows an increase in the SHG signal.

INTRODUCTION

Understanding of the phase transformations and kinetics of energetic materials are of importance to development of stable explosives. This is demonstrated by differences in burnt rates and drop height sensitivity of β and δ phases. Detailed understanding of the $\beta \rightarrow \delta$ transformation is still a point of discussion. Recently, a number of papers have been published which discuss the unusual observation of SHG during the transformation of $\beta \rightarrow \delta$ phase HMX [1] and TATB [2]. The appearance of SHG signifies the presence of non-centrosymmetric crystal structure from that of centrosymmetric. For HMX, several heating rates were used and it was reported that a fast rise in SHG signals have been observed as the temperature approaches that of the $\beta \rightarrow \delta$ transition at about 170°C. This observation of change in SHG is taken to be the transformation of $\beta \rightarrow \delta$ phase. In TATB, it was argued that a mixture of polymorphic forms existed at all times and the SHG is due to a non-centrosymmetric form. It was

also reported that an abrupt increase in SHG signal is caused by the transformation of $\beta \rightarrow \delta$ phase and on continuing heating, a reduction of SHG can be observed which is assigned decomposition.

In the thermal analysis study of HMX, Herrmann et. al. [3] reported on high temperature x-ray diffraction experiment of HMX utilizing chromium K_α radiation. For both β and δ phases, the volumes are observed to increase with increasing temperature and decrease with decreasing temperature. It is also interesting to note that the volume shrinkage is observed for β phase right before the conversion to the δ phase. Clearly, this result is important from the application point of view.

To further understand the behavior of these phases and phase kinetics of both the HMX and TATB, our group at the Lawrence Livermore National Laboratory focuses on performing simultaneous

SHG and XRD experiments at elevated temperatures and pressures. Hence, both the structural information and SHG signals can be correlated as a function of temperature, time and pressure, as noted by Brill et. Al [4] in their Raman experiment that these transitions occur quite differently with the application of pressure.

The present paper reports on some initial XRD results of HMX and TATB with increasing temperature and at fixed temperature of 165 °C, in order to understand the changes over time. Two types of XRD were performed, energy dispersive technique using beamline X17C at NSLS (National Synchrotron Light Source) and standard fixed energy diffraction technique at BL10-2 at SSRL (Stanford Synchrotron Research Laboratory) where the simultaneous experiments were performed.

MATERIALS ASPECT

The chemical composition HMX and TATB is given below. HMX is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine and TATB, 1,3,5-triamino-2,4,6 trinitrobenzene.

HMX
octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

TATB
1,3,5-triamino-2,4,6-trinitrobenzene

EXPERIMENTAL

The energy dispersive technique high temperature experiments are performed at X17C beamline at National Synchrotron Light Source, Brookhaven National Laboratory using the energy dispersive x-

ray diffraction technique. Briefly, a white synchrotron beam of about 20 μm in size is incident onto the sample, which is loaded in the Bassett diamond anvil cell. The DAC is fitted with high temperature capability. A solid state detector located at 13° (2θ), pointing to the sample, is used. During the experiment, no mechanical motion is needed. A few grains of HMX sample are loaded into the cell. The diamonds are 2 mm thick in transmission on each side of the sample. To avoid any large grainy material, the sample is first slightly pressed in the DAC until translucent and then the pressure is released for the experiment. Each data set is acquired for 20 minutes and temperature step change is immediate.

A set up has been designed and built to perform simultaneous XRD and SHG experiments. Schematically, the setup consists of an optical system to measure the SHG and the x-ray system for diffraction as shown in Figure 1. Both systems are aligned with their beams incident on the sample in the DAC. 1064 nm laser beam is used. Two beryllium mirrors of different sizes, polished on one side, were used, a smaller one before and the larger one after the sample. A small hole is drilled in the center of the mirrors to allow the main x-ray beam to pass, thus avoiding significant background scattering. These experiments are performed on the wiggler beam line BL 10-2 at the Stanford synchrotron source. 17 KeV x-ray energy is used. Both experiments are performed simultaneously and the only time the experiments are interrupted is during the change of the image plate for x-ray detection.

Figure 1: Schematic of the SHG and XRD setup.
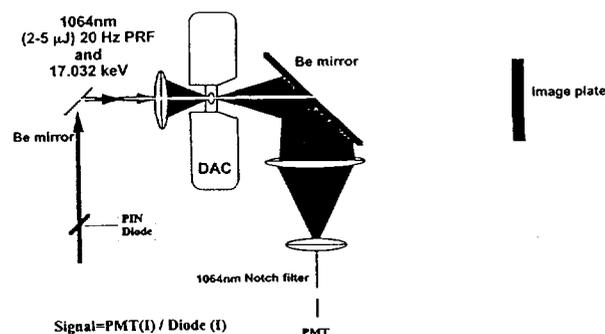
Two types of experiments are performed namely, to understand the structural changes during phase transformation by increasing and decreasing temperature and at fixed temperature to obtain information on structural changes as a function of time. The former is performed using the conventional diffraction technique at SSRL while the latter uses the energy dispersive technique on beamline X17C at NSLS.

RESULTS AND DISCUSSION

(a) Phase Transformation

Figure 2 shows the resulting diffraction pattern of HMX as a function of temperature. In the pressed sample (not shown) the x-ray peaks are broad, clearly affected by pressing, however, at 100 °C, a full sharp pattern emerges, indicating molecular reorganization and re-crystallization can still occur even at 100 °C . These patterns are compared to the calculated powder pattern from single crystal results [5,6] using LAZY-PULVERIC programs as well as the JCPDS listing for HMX (PDF42-1768) and TATB (PDF43-1768). A refinement of the lattice parameters indicates that the results are consistent with the published single crystal data. The results, as shown in Fig. 2, indicate a transition from $\beta \rightarrow \delta$ phase between 150 °C to 160 °C. What is interest is the development of small amount of δ even at 140 °C. At 165 °C, an amorphous region can be observed. A peak at about 25 KeV (d=3.55 Å) is observed as well, presently, not identified. By monitoring the position of the most pronounced 3 peaks, (-102), (-120) and (-132), no significant shifts are observed indicating

Figure 2: Energy dispersive XRD patterns for HMX along with the calculated powder diffraction pattern for β and δ phase.
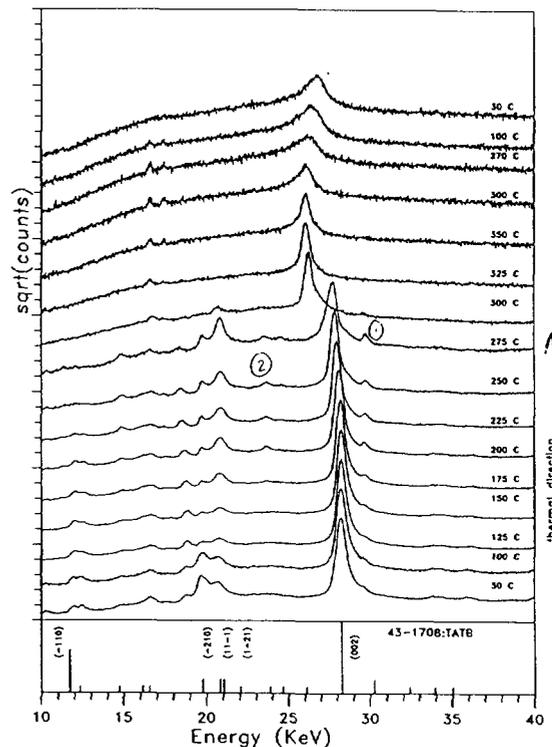
Figure 3: Energy dispersive XRD patterns for TATB along with the JCPDS listing for TATB

no change in the volume of the unit cell. However, there are some changes in peak intensities going from 100 °C to 150 °C, indicating cell re-organization or molecular rotation due to preferred orientation.

During cooling, there are indications of development of β and δ phase. Perhaps, there is insufficient time for HMX to fully convert to the δ phase. Fig. 3 shows the energy dispersive diffraction patterns of TATB as a function of increasing temperature. Data acquisition time is about 20 minutes per temperature. Also included in the plot are the peaks listing for TATB from JCPDS data base. The peaks are broader here than those observed in HMX. Our observations do not indicate the existence of solid-solid phase transition to a the high temperature phase. Asreported earlier [7], the material decomposed and sublimed above 300 °C.

Unlike HMX, several peaks in TATB, as labeled in the figure by (a), (b) and (c), are observed to shift in increasing d-spacings as demonstrated in Fig. 4 for the strongest (002) peak. At room temperature TATB is triclinic with a= 9.01 b=9.028 and c=6.812 (Å), α=108.59, β=91.82 and γ=119.97 (JCPDS 43-1708). Additional peaks marked by (1) and (2) can also be observed to increase in

intensity at elevated temperatures, suggesting that molecular reorganization continue to occur. This change cannot be taken as a phase transformation. It is interesting to note that at 300 °C, the (002) peak remains and shifts towards larger d-spacings. This result suggests at that temperature, a backbone structure of about 3.40 Å, probably due to the inter-molecular stacking remains. This peak continues to contract and broaden on continuing cooling, indicating the collapsing of the molecular stacks and destruction of the stacking order.

(b) Kinetics

Figure 5 shows the resulting diffraction for HMX held at 165°C as a function of time. This
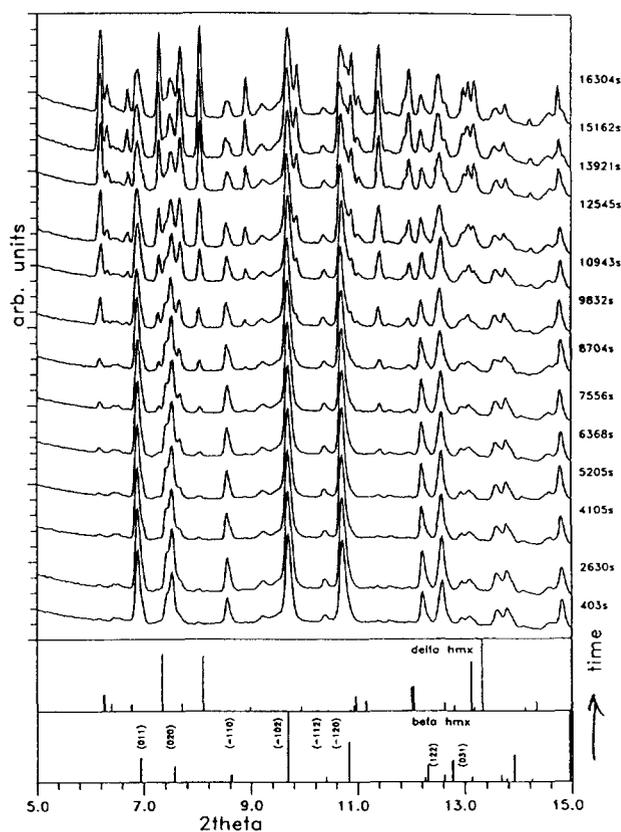
Figure 5: XRD patterns for HMX at 165°C versus time with the peak listing for the calculated powder patterns from published single crystal data.

Figure 4: Changes in d-spacing for the (002) reflection, most like due to the c- stacking

temperature is chosen to confine the conversion rate to within a few hours (observable experimental time). For simplicity, the number of spectra is reduced. The entire experiment runs for ~ 4 hours. The SHG experiment is interrupted only during the loading of the image plate for x-ray detection. Figure 6 shows the normalized SHG signal versus time over the 4 hours period. At the beginning, the SHG signal increases and appears to equilibrate at about 8000 seconds.
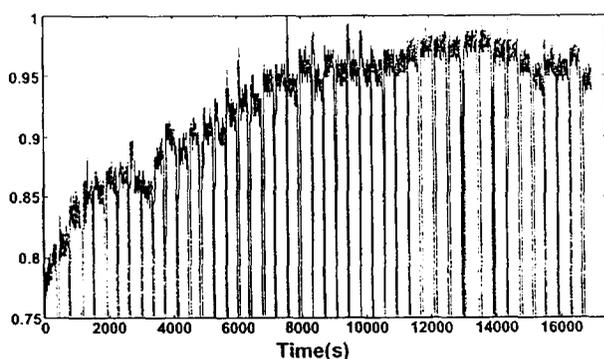
Figure 6: Normalized SHG intensity versus time for HMX held at 165 °C

The diffraction pattern for β and δ phases are calculated and listed in the plot for comparison in Fig. 5. The β phase is observed to convert to δ phase with time. Full conversion is not achieved. By monitoring the changes in the lattice parameters; a-, b-, c- and β for the monoclinic β HMX, and a- and c- for the hexagonal δ phase, our results indicated no significant changes in the unit cell volumes with time.

The peak intensity ratios for β and δ phases, which is directly related to the concentration of their phases are carefully monitored, and results are plotted in Fig. 7 with the SHG result which indicates that the main conversion from β to δ occurs at about 8000 seconds. However, the SHG signal continues to increase at 0 time to about 1000 seconds and then plateaus while β phase continues to transform to δ phase. Hence, the observed fast increase in SHG

does not appear to be correlated to the β to δ phase transition.
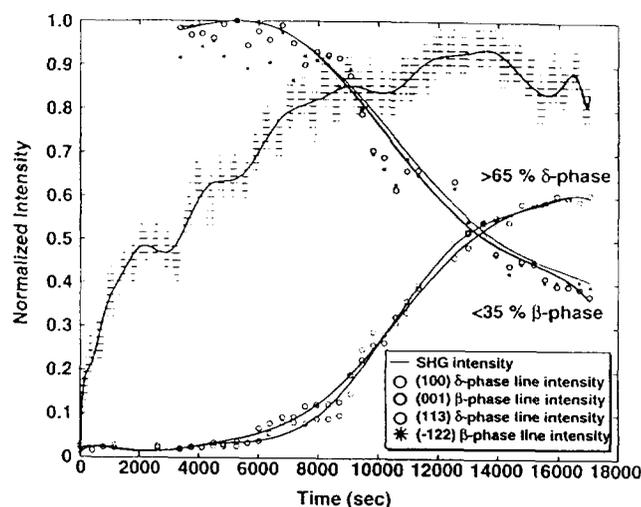
Figure 7: Normalized SHG intensity and peak intensity ratios versus time at 165°C.

CONCLUSIONS

High temperature experiments on HMX and TATB were performed using the energy dispersive x-ray diffraction technique and the conventional monochromatic diffraction technique. The results suggest that for HMX, phase transition occurs during heating as reported earlier, however, it is observed that there is a temperature region where both β and δ phases co-exist. There is no significant change in lattice parameters or unit cell volume during heating indicating that the conversion of β to δ is via a disorder structure at the local level. In fact, an amorphous component is observed for HMX at 165 °C.

For TATB, no phase transition is observed by going up in temperature. The growth of additional lines is probably due to molecular reorganization of the same triclinic cell. This change cannot be taken as a phase transformation. A backbone structure of about 3.40 Å, probably due to the inter-molecular stacking can be observed at 300 °C. Upon cooling,

the stacking collapses and reduces the stacking order.

The simultaneous SHG and XRD experiments for HMX show that at fixed temperature of 165°C, β phase can be transform to δ phases in time. Even though, full conversion is not achieved, our results do not reveal any lattice parameters changes or volume change for both β and δ phases. The maximum conversion from β to δ occurs at about 8000 seconds. This occurrence does not correlate with the increase in SHG signals even at zero time.

ACKNOWLEDGEMENTS

REFERENCES

[1] Henson, B.F., Asay, B.W., Sander, R.K., Son, S.F., Robinsoon, J.M. and Dickson ,P.M., Phys. Rev. Letts **82**, 1213-1216 (1999).

[2] Son, S.F., Asay, B.W., Henson, B.F., Sander, R.K., Ali, A.N., Zielinski, P.M., Philips, D.S., Schwarz, R.B. and Skidmore, C.B., J. Phys. Chem. B, **103** 5434-5440 (1999).

[3] Herrmann, M, Engel, W. and Eisenreich, N., Zeitschrift fur Kristollographie **204**, 121-128 (1993).

[4] Karpowicz, R.J. and Brill, T.B, AIAA Journal **20**, 1586-1591 (1982)

[5] Cobbledick, R.E. and Small, R.W.H., Acta Cryst. **B30**, 1918 (1974)

[6] Choi, C.S. and Boutin, H., Acta Cryst. **B26**, 1235 (1970).

[7] Sullenger, D.B., Cantrell, J.S. and Beiter, T.A., Powder Diffraction, **9**, 2 (1994).