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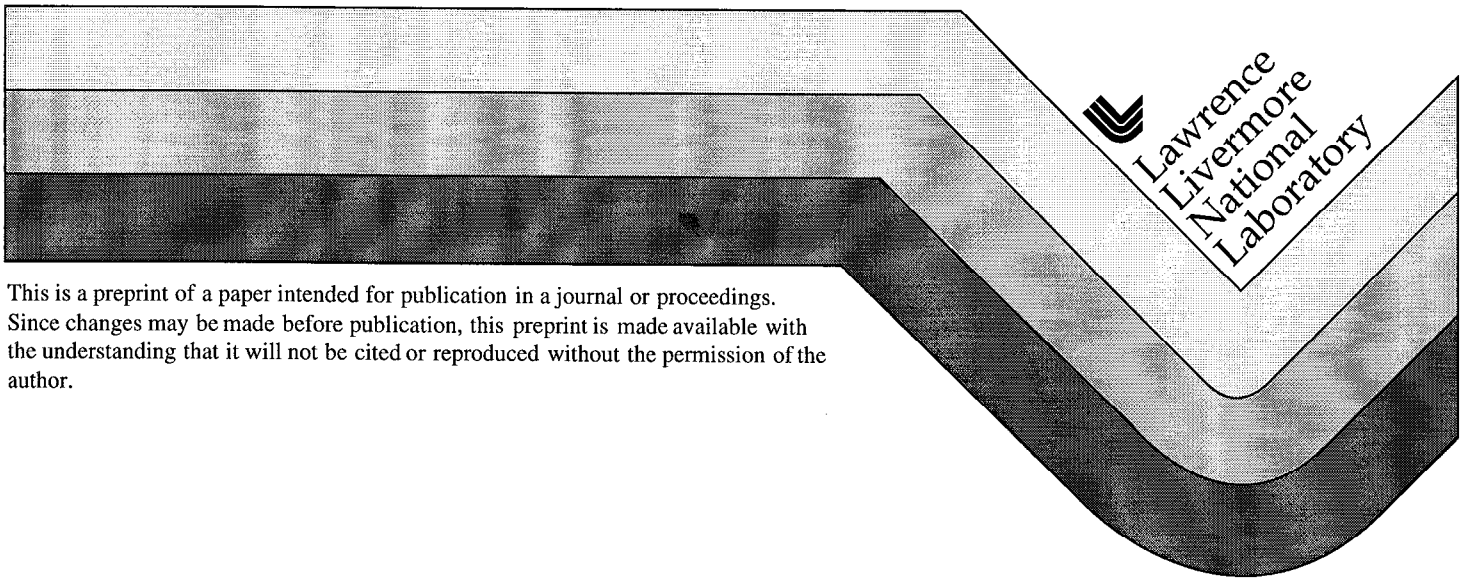

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QUASI-DYNAMIC PRESSURE AND TEMPERATURE INITIATED β <-> δ SOLID PHASE TRANSITIONS IN HMX

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Abstract. The phase transformation of β-HMX (< 0.5% RDX) to the δ phase has been studied for over twenty years and more recently with an optically sensitive second harmonic generation technique. Shock studies of the plastic binder composites of HMX have indicated that the transition is perhaps irreversible, a result that concurs with the static pressure results published by F. Goetz *et al.* [1] in 1978. However the stability field favors the β polymorph over δ as pressure is increased (up to 5.4 GPa) along any sensible isotherm. In this experiment strict control of pressure and temperature is maintained while x-ray and optical diagnostics are applied to monitor the conformational dynamics of HMX. Unlike the temperature induced β ->δ transition, the pressure induced is heterogeneous in nature. The room pressure and temperature δ ->β transition is not immediate although it seems to occur over tens of hours. Transition points and kinetics are path dependent and so this paper describes our work in progress.

INTRODUCTION

Performance and safety issues concerning HMX and TATB are of national interest. The magnitude of both parameters is, among others, a function of crystal symmetry. [2] Recently the frequency doubling or second harmonic generation (SHG) properties of HMX have been exploited to provide the very first real-time probe of the β ->δ solid phase transition as a function of temperature. [3] X-ray powder diffraction (XRD) is employed to verify symmetry changes, lattice constants, and consequently volume. The work presented here brings into play the aspect of pressure and how it alters the β -> δ transition temperature. If you take β-HMX up to 2-3 kbar and then heat the sample, the solid phase transition never occurs and indeed, β-HMX decomposes. [4] If one heats β-HMX to 150°C and then increases pressure the β ->δ transition occurs at approximately 5 kbar.

SHG & XRD MEASUREMENTS IN THE HDAC

Hydrothermal diamond anvil cells (HDAC's) [5] were built and modified to accept a hydraulically actuated piston cylinder. The HDAC has high dimensional stability throughout the temperature range (-200 to 1200°C) and a dual heater system that provides excellent temperature balance between the anvils. The 2θ optical access is 44°. This system allows for fast(>300 milliseconds), uniform, and controlled pressure jump conditions all while monitoring SHG intensity. The HDAC pressure range has been tested to 40 GPa and may extend to 70 GPa. [6] The modified HDAC gives us the opportunity to observe isothermal quasi-dynamic (low shock) initiated solid phase transitions using the real-time optical SHG diagnostic. The compact design of the HDAC makes it suitable for mounting onto an x-ray diffractometer. Prior to and after

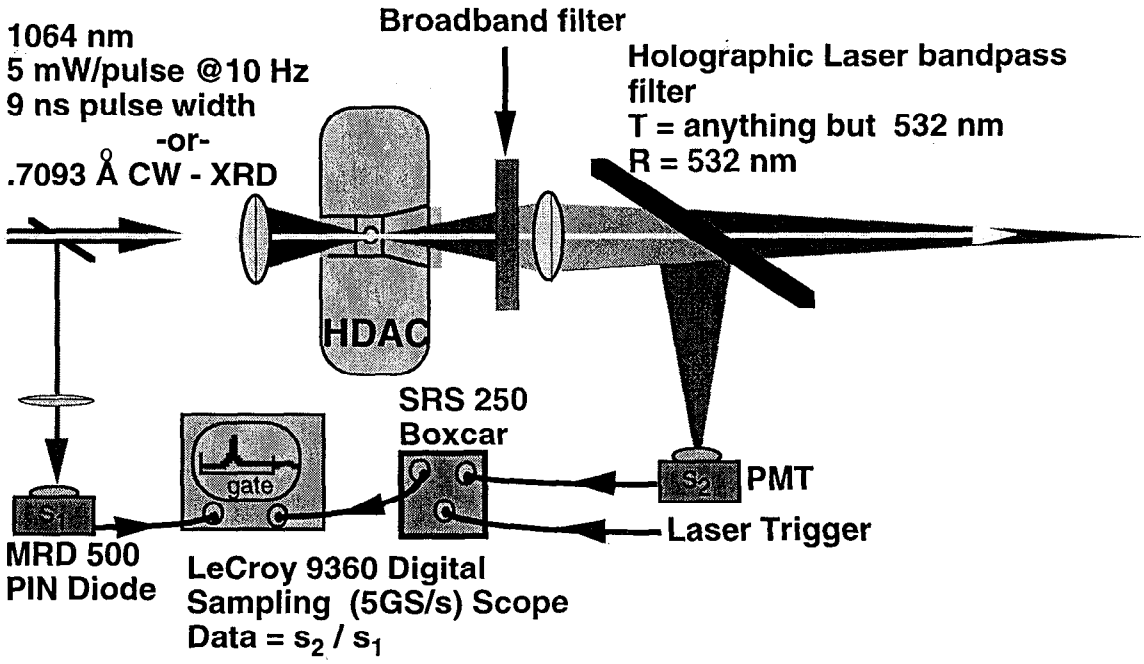

FIGURE 1. SHG / XRD diagnostic block diagram for phase stability and transition studies over pressure and temperature.

pressure jump experiments, XRD is used to to determine crystal symmetry and lattice constants. The diagram shown in Figure 1 shows the beam configuration for both SHG and XRD probes. The HMX (<400 μm sample diameter) frequency doubles a Nd:YAG fundamental pulse (~ 175 μm spot size) to 532 nm. A broadband filter blocks most of the 1064 nm light which is then completely removed by a holographic bandpass filter. The integrated area under each gated 532 nm signal pulse is normalized by a corresponding integrated pulse picked off directly from the laser. XRD measurements are made by simply sliding the SHG optics out of the beam path. If one so desires the system could be arranged to allow for simultaneous SHG and XRD monitoring.

PRELIMINARY RESULTS

The first challenge met in this study was to observe the β->δ phase change initiated by heating at 1 bar in the HDAC. Sample diameters were on the order of 300-400 microns with a thickness range of 60-70 microns at 1-bar. (Our β-HMX was produced by Holston using the Bachman process.) The onset of detectable SHG levels from the beta phase required a threshold power of 5 mW. Once achieved the sample was heated at about 9°C/min. A dramatic change in SHG intensity occurred yielding a delta transition temperature of about 165°C. The result corresponds well with previously published results. [7] The isobaric transition appeared to be spatially uniform in nature and as a result one can develop a model [3] to describe the kinetics of the transition.

The second challenge met in this study was to pressure initiate the β->δ transition. Several questions arose concerning recent heated shock studies of samples containing HMX. Therefore, the experimental parameters presented here were chosen to match the shock study. The sample was heated to 150 C and maintained at 1-bar for 20 minutes. The HDAC temperature gradient was <1.6°C. Bachman-produced HMX contains 0.5% RDX and has a 1°C/min delta transition temperature of about 159°C. [8] Figure 2 shows SHG intensity (after 20 minutes of 150°C thermal soaking) as we slowly increased the pressure from 1- bar to 5 kbar in 60 seconds. The β-HMX SHG intensity is described by the red baseline. The peak at region 1 shows a dramatic increase in SHG, due to the formation of δ-HMX, that occurs 3-5 seconds after ~5 kbar is achieved in the HDAC.

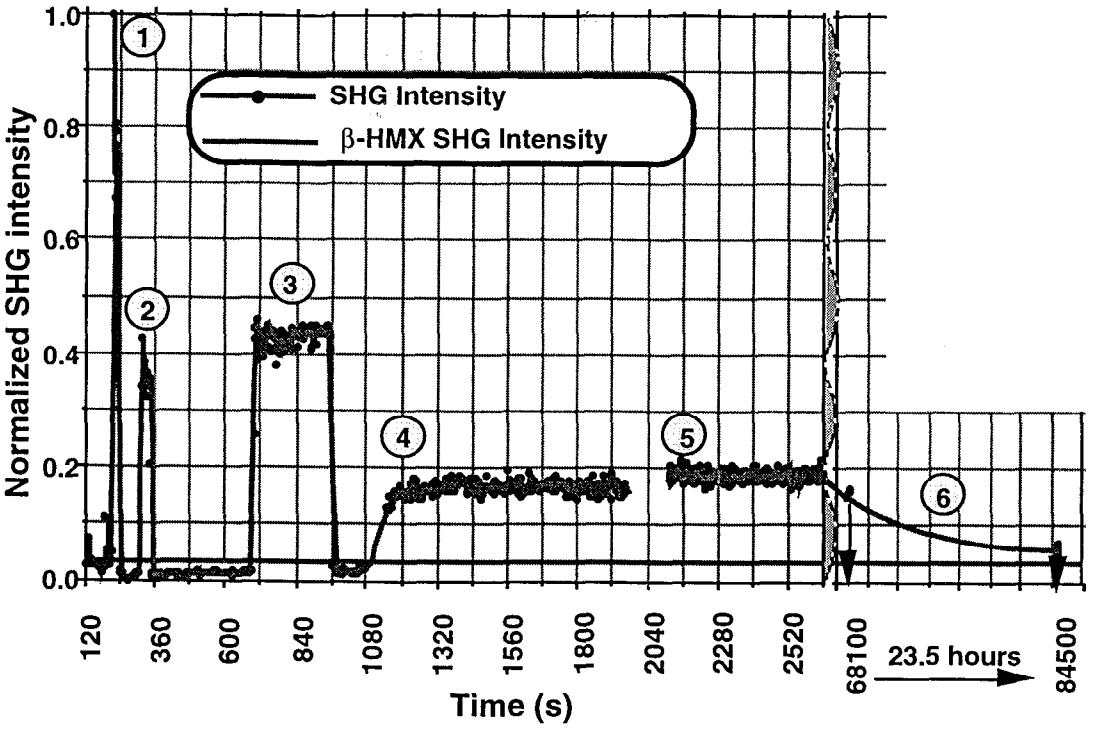

FIGURE 2. 150°C pressure induced β -> δ SHG intensity as a function of time.

Accompanying the change in SHG intensity was an audible popping sound due to the +7% volume expansion of the material and the consequential rupturing of the 625 stainless steel gasket used to constrain the lateral flow of HMX. So either during or immediately after the β->δ phase transition the pressure jumped back down to 1 bar. Immediately after the phase change occurred the PMT was shut off and the sample position was checked to ensure that the laser was not clipping the gasket. Regions 2 and 3, in Figure 2, show the SHG intensity resulting from repositioning the 175 micron laser spot within the sample. In both regions the PMT was borderline saturated. In region 4 the PMT voltage was dropped by 15% and the hydraulic pressure was released. The decay in SHG intensity observed in region 6 indicates that occurrence of the δ->β transition.

Unlike the 1 bar isobaric temperature induced transition the pressure-induced transition is heterogeneous in nature. A recovered sample of β/δ-HMX is shown in figures 3 & 4. The black and white photo is interesting in that it shows 4 distinct regions of material; voids, pure β-HMX, pure δ-HMX and aggregate regions of both β and δ HMX. Also interesting are the fingers or inclusions of δ–HMX protruding into the pure β-HMX region on the far right. The final sample state looks as if a geological process took place albeit on a slightly different time scale. Indeed there may be the impetus to augment solid state phase transitions to the already accepted slip friction mechanics that preclude the onset of large seismic events. When pressure and temperature increase along a fault is it possible that volume changes in relevant minerals help the line to slip? Figure 4 provides a different perspective of the sample and helps show regions of concentrated δ and β phase. Predominate δ regions look like lakes and β regions look more like mountains. Phase regions were confirmed visually by observing 532 nm intensity.

DISCUSSION

Some issues concerning heated shock experiments on PBX and LX materials have been resolved from the work described above. HMX will phase change

at 150°C when pressure is increased to 5 kbar. Under these conditions the transition is rather

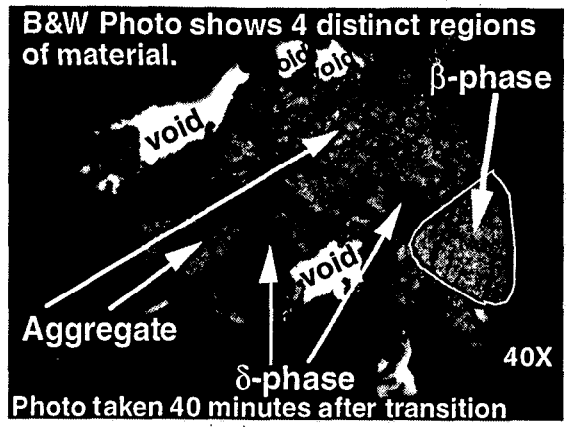

FIGURE 3. Recovered HMX sample after pressure-induced transition at 150° C.

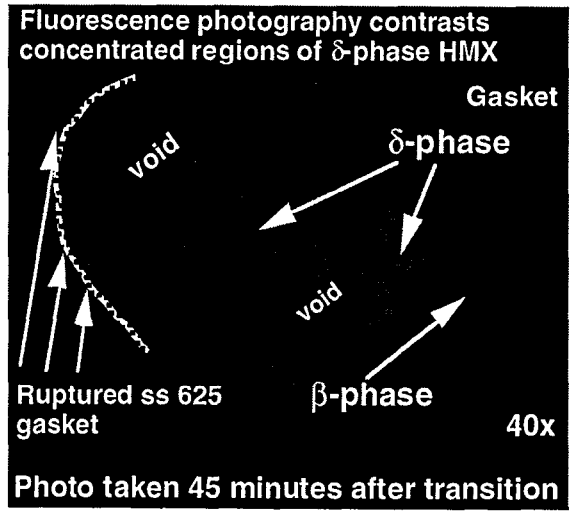

FIGURE 4. Fluorescence photograph of recovered HMX sample.

heterogeneous in nature. There is an indication that the reverse transition occurs on the time scale of tens of hours. We also observed that simply pressing HMX uniaxially to less than 1 kbar, followed by release to 1 bar all at room temperature dramatically changes the transition temperature. In fact precompressing the HMX, followed by release to 1 bar, resulted in the transition occurring during the 20 minute soak period prior to the addition of pressure! The initial motivation for precompressing HMX prior to the pressure jump experiment was to decrease the number of grain boundaries. We no longer precompress the sample. The fact that there is a ~1% volume compression [7] prior to the volume expansion may shed some light on why increasing pressure at temperature causes the β -> δ transition to occur in the first place. Normally the β phase is stabilized with pressure. Reference 8 indicates that RDX (<0.5%) plays a significant role in the temperature stability of beta phase HMX.

Our intent for the next year is to map out the transition over different temperature and pressure paths. We can also change the pressure jump time. Currently we are in the process of making fast films that will show, in real time, the spontaneous nature of the transition. Issues concerning the effect of nucleation in solid phase transitions or perhaps even geophysical phenomena may benefit from these efforts.

ACKNOWLEDGMENTS

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