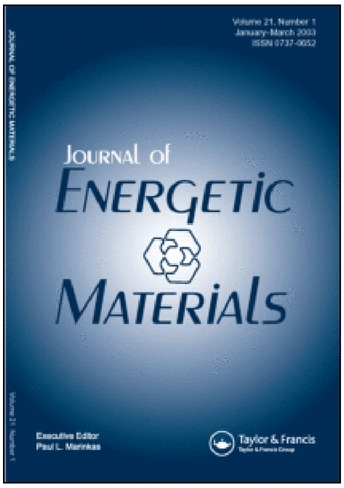

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Submicron-Sized Gamma-HMX: II. Effect of Pressing on Phase Transition

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In a previous article we described the preparation and initial characterization of a novel submicron-sized HMX (sm-HMX). Using Raman spectroscopy, the sm-HMX was found to be the gamma polymorph and to be stable with respect to conversion to beta-HMX under ambient conditions for at least a year. Pressing of sm-HMX powder in a small diameter pellet press at pressures from 10,000 to 31,000 psi and 1- to 5-min hold times was found to promote the gamma-to-beta polymorphic phase transition. The fraction converted and rate of conversion versus time after pellet removal from the press were found to fit a sigmoidal curve, indicating nucleation and growth as a possible polymorphic transition mechanism.

Keywords: gamma-HMX, polymorphic phase transition, Raman spectroscopy

Introduction

HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) is known to be a powerful high explosive that exists in four solid-state

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polymorphs labeled alpha, beta, gamma, and delta. Under certain conditions, polymorphic phase change does occur among the different polymorphs. For example, experiments have shown that the beta-HMX powder is converted to delta-HMX upon heating at 184°C overnight [1]. In an earlier study by Cady et al., it was found that the gamma polymorph is converted to beta on grinding [2]. However, not all HMX polymorphs are equivalent in respect to detonation properties, thermal properties, sensitivity, and stability. In addition, not all the polymorphs have been fully studied, in particular the explosive properties and performance of gamma-HMX. Due to the nature of its molecular structure, HMX is sensitive to impact stimuli and hence is restricted in its usage. A less sensitive form of HMX is sought for both commercial and military applications.

We are exploring the characteristics of nanostructured energetic materials for a wide variety of applications. Nanostructured materials have been found to exhibit unusual physical, chemical, and mechanical properties of use in many areas, including defense, communications, and pharmaceuticals. In a previous report we described the preparation and initial characterization of a novel submicron-sized HMX (sm-HMX) that has been shown to be $>99\%$ gamma polymorph using Raman spectroscopy and neutron diffraction [3]. The long-term stability of the gamma sm-HMX was studied by Raman spectroscopy and was found to be stable at ambient conditions for at least a year [4]. In order to study the detonation performance of sm-HMX we are attempting to press sm-HMX samples into pellets at a desired density. We found that the gamma polymorph becomes unstable toward conversion to the beta polymorph after the pellets are pressed. Depending on pressing conditions and hold time, the fraction converted from gamma to beta and the rate of conversion varies. We present here preliminary data on the dependence of this particular polymorphic conversion process on pressing conditions and its implications about the conversion mechanism.

Experimental

The sm-HMX was prepared as described in Lee et al. [3]. Briefly, a solution of HMX in acetone was poured into a cold anti-solvent with high agitation. The resulting product was collected by filtration and dried under house vacuum.

The pressing of sm-HMX was carried out as described in a Los Alamos National Laboratory (LANL) internal document [5]. The press is a LANL site-built 15-ton pneumatic press with gauge pressure up to 100 psig. The pellets (6 mm diameter) were all pressed with an open mold (no shims were used).

Basically, powder samples of sm-HMX ($\sim$0.13 g) were loaded into the pellet press die and pressing was accomplished by setting the desired pressure on the regulator, loading the pellet fixture, and applying the pressure for either 1 or 5 min (hold time). The pressure was then released and the pellet removed from the die fixture and a Raman spectrum was obtained immediately. Raman spectra were then taken on each pellet at fixed intervals after their release from the die. To investigate whether the phenomenon was limited to the pellet surface, small pieces were broken off a couple of the pellets and spectra were taken from both the pellet pressing surface as well as the interior.

Raman spectra were obtained using an InPhotote™ (InPhotonics, Inc., Norwood, MA) using 785 nm excitation and cooled CCD detection. The InPhotote™ system uses an optical fiber–coupled probe with either 5- or 7.5-mm focal length objective. The Raman shift abscissa calibration was performed on the InPhotote™ using Ar emission lines and a polystyrene Raman standard [3]. The InPhotote was controlled by a laptop running the InPhotote acquisition software. All spectra were converted to ASCII x,y pairs and further analyzed and plotted using Igor Pro (Version 5.02, Wavemetrics, Inc., Lake Oswego, OR). For each Raman spectrum, 10 Raman spectral acquisitions of 20 s each at 75-mW laser power were averaged.

To estimate polymorph conversion fraction, we carried out quantitative Raman measurements using kinematic sample and Raman (or optical fiber probe) placements. Mixtures of beta- and gamma-HMX powders at various gamma-HMX content were prepared and Raman spectra were taken on each.

In an attempt to understand the potential surface structure change as a result of pressing-induced polymorph transition, scanning electron microscopy (SEM) was also employed to characterize the HMX pellet samples. SEM images were also taken from small pieces broken off from a pellet at the same time the remainder of the pellet was used to obtain the Raman spectra.

Results and Discussion

The Raman spectra of both the gamma- and beta-HMX polymorph are shown in Figure 1. A freshly prepared sample of the submicron HMX was used to obtain the gamma spectrum. The beta spectrum was obtained from a Holston Impact Test standard starting material. The relevant fingerprint region for the Raman spectra of mixtures of the gamma and beta at various percentages of gamma-HMX content is shown in

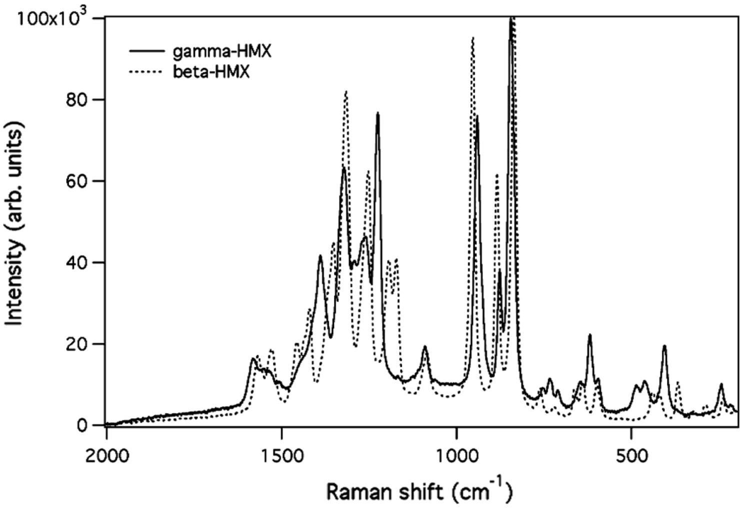

Figure 1. Comparison of the Raman spectra of the gamma and beta polymorphs of HMX.

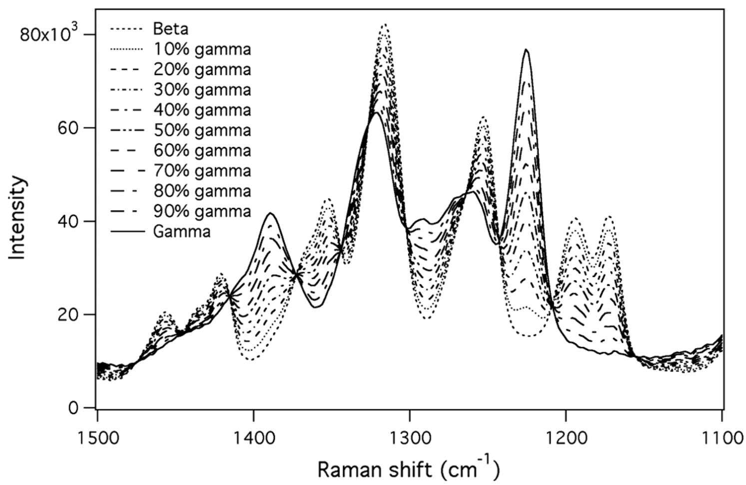

Figure 2. Raman spectra of mixtures of gamma- and beta-HMX at various percentages.

Figure 2. For example, the spectrum "10% gamma" is $0.9 \times$ the beta spectrum plus $0.1 \times$ the gamma spectrum. We also studied a set of peaks in the low-frequency region; see Figure 3.

From these plots, we selected two sets of Raman peaks to use in the quantitative study. First, we used the peak area ratio of the $1225\,cm^{-1}$ peak (gamma-HMX) to the 1168 and $1190\,cm^{-1}$ doublet (beta-HMX) to estimate the percentage of gamma polymorph. We assumed a constant baseline and used the value measured at $1152\,cm^{-1}$ in each spectrum. The second set used was the ratio of the $405\,cm^{-1}$ (gamma) to the $362\,cm^{-1}$ (beta). We found the second set was noisier (lower peak strengths) and so only report the ratios obtained from the first set of peaks. The peak area ratio versus percentage gamma in the mixture spectra is plotted in Figure 4. The ratio does not pass through zero at 0% gamma content, probably because of the decision to use a constant baseline.

We then used the calibration curve from Figure 4 to deduce the percentage gamma polymorph in each of the spectra obtained from the pressed pellets as a function of time after

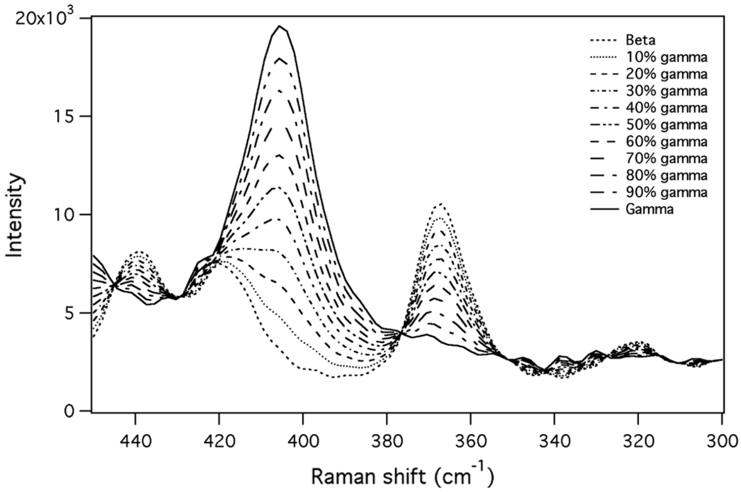

Figure 3. Raman spectra of mixtures of beta- and gamma-HMX, low-frequency region.

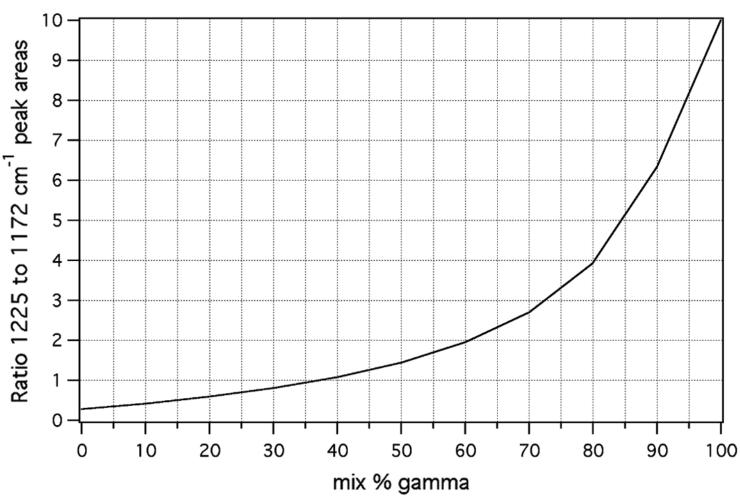

Figure 4. Ratio of gamma to beta peak areas of the $1225\,cm^{-1}$ peak (gamma) to the 1171 and $1196\,cm^{-1}$ doublet (beta-HMX) versus percentage gamma in the synthetic spectra.

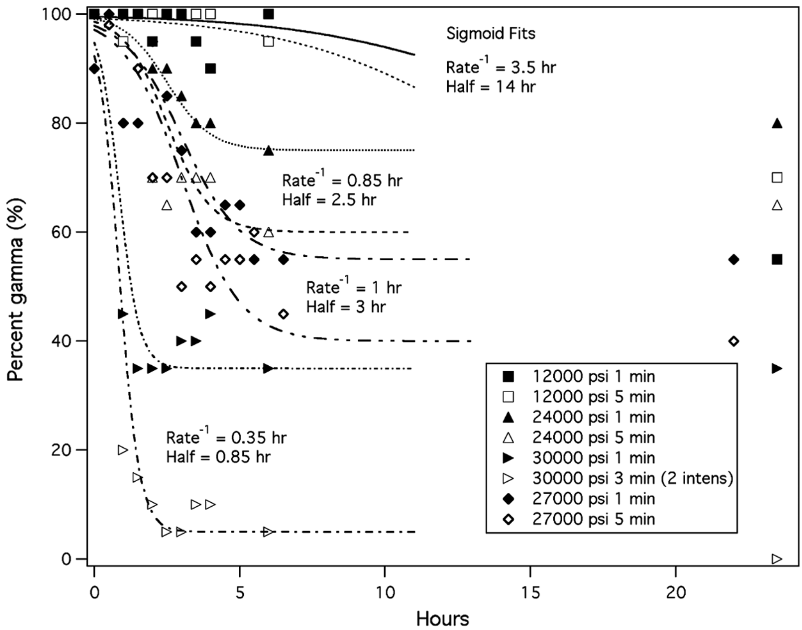

Figure 5. Plot of percentage gamma-HMX versus time after pellet pressing at several pressing conditions and times.

pressing. These values are plotted in Figure 5. It can be seen that the percentage gamma-to-beta conversion varies with the pressing pressure. The higher the pressure, the higher the conversion rate is. For example, 5 h after the pellets were pressed more than 70% of the gamma phase converted to beta at pressing pressure 30,000 psi (with 1 min hold time), whereas at pressing pressure 24,000 psi (same 1 min hold time), only 25% conversion is obtained. Similarly, at the same pressing pressure, the longer the hold time, the larger the fraction converted from gamma to beta. In addition, sample storage time also has an impact on the overall conversion rate. At long storage times, the higher the pressure and the longer the hold time, the larger the fraction converted from gamma to beta polymorph.

We fit the data to sigmoidal curves as shown in Figure 5 and extracted rates and half-times. The apparent sigmoidal

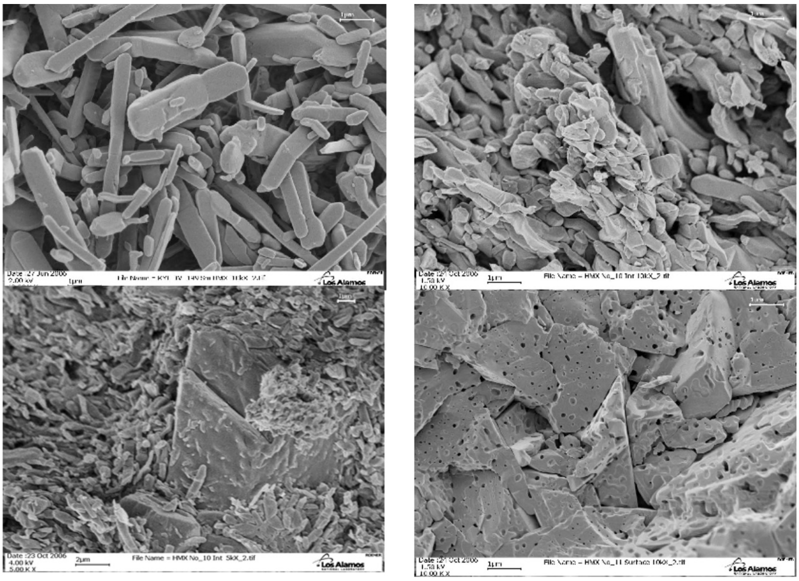

Figure 6. SEM images (bar scale = 1 μm) of the gamma-beta polymorphic phase transition at various stages after pressing. Top left: starting material sm-HMX; top right: 4 h after pressing; bottom left: intermediate time; bottom right: fully converted to beta.

form of the data indicates the pressing-induced polymorph conversion process follows nucleation and growth kinetics.

It is fascinating to observe the impact of pressing pressure on the surface structure of an sm-HMX pellet. As shown in Figure 6, 4 h after pressing, each of the surfboard-shaped nanoscale particles of the gamma polymorpoh sm-HMX (top left) appear to align with each other (top right) and then are somewhat fused after the pellet was pressed but before the complete conversion to beta occurs (intermediate time, bottom left). Even more amazing is that the beta-HMX thus converted from the gamma polymorph has a distinct surface morphology, with many small holes or voids (bottom right). This beta-HMX morphology is much different from that of conventional beta powder materials.

Conclusion

We have demonstrated that the novel submicron-sized gamma-HMX becomes unstable toward conversion to the beta polymorph after the powder materials are pressed to pellets. And the fraction converted to beta appears to be dependent on pressing pressure and hold time. Measured by Raman spectroscopy as a function of time after pressing, the fractional polymorph content data were fit to a sigmoidal function, which is characteristic of nucleation and growth kinetics. We plan to conduct more pressing experiments to further investigate the polymorph phase transition kinetics and their dependence on pressing conditions. For a better understanding of the conversion mechanism, we also plan to conduct hydrostatic compression experiments in a diamond anvil or other static high-pressure cell with submicron-sized gamma-HMX samples.

Acknowledgements

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