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Submicron-Sized Gamma-HMX: 1. Preparation and Initial Characterization

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As part of our ongoing nanotechnology research effort, we have developed a novel method for the preparation of submicron-sized HMX (sm-HMX) by a simple fast-cooling technique. Surface structure analysis of the sm-HMX by field emission scanning electron microscopy reveals particles that are oblong in shape with average width of $\sim 300\,\text{nm}$ *and length of* ~ 1–$2\,\mu\text{m}$. *Raman spectroscopic features in the 200–2000* cm^{-1} *range and high-intensity powder neutron diffraction were used to determine the crystallographic polymorph of the sm-HMX. Comparison of the Raman spectrum and the neutron powder diffraction pattern of sm-HMX to literature data show that sm-HMX is the gamma polymorph. The Raman data also illustrate that the polymorphic purity of the gamma sm-HMX produced by our method is greater than 99%.*

Keywords: gamma-HMX, nanoenergetics, neutron powder diffraction, Raman spectrum, submicron energetic materials

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Introduction

In recent years, by virtue of their unusual physical, chemical, and mechanical properties, nanostructured materials and nanocomposites have attracted the interest of researchers globally in the areas of advanced materials, electronics, biotechnology, pharmaceutics, cosmetics, and sensors. Tremendous efforts have been made by the plastic industry for the synthesis and development of nanoparticle materials and polymer nanocomposites aiming for specific applications. However, little has been done in the preparation and development of nano-sized energetic materials. In an earlier study, we developed a novel method for the preparation of nano-sized NTO [1]. Data from the floret shock sensitivity test indicated that nano-NTO offers full detonation as measured on a copper witness plate. Pivkina et al. [2] reported an increase of burn rate for nano-sized RDX powder as compared to that for conventional RDX. In addition, they observed that the heat released during decomposition of nano-sized powdered ammonium nitrate (AN) is less than that released during decomposition of conventional powdered AN.

It is well known that HMX is a powerful energetic material with many uses. Aside from being used widely as the main ingredient in weapons systems and propellants, HMX has also been studied as a candidate for treatment of proliferative disorders (cancerous and benign) [3]. Unfortunately, due to the nature of its molecular structure, HMX is sensitive to impact stimuli and hence is restricted in its usage.

Our motivation in this work has been to investigate ways to prepare nano-sized energetic materials and characterize their physical, chemical, and explosive properties. In this article, the novel approach for the preparation of submicron-sized HMX (sm-HMX) will be described, together with the analysis techniques used to identify its crystallographic polymorph (using Raman spectroscopy and neutron powder diffraction). Data on sm-HMX from small-scale sensitivity tests, differential scanning calorimetry (DSC) analysis, and scanning electronic microscope surface structure measurement will also be reported.

Experimental

Preparation of Submicron-Sized HMX (sm-HMX)

The preparation of sm-HMX by fast cooling was carried out based on the procedures of Lee et al. [4]. Briefly, sm-HMX can be prepared by dissolving HMX in acetone or any other solvent, followed by mixing the solution in an anti-solvent at cold temperatures. Thus, to obtain the material used in this study, a solution of HMX in acetone (1.57 g/70 mL) was poured into cold hexane ($\sim$300 mL) while stirring at high speed. The resulting product was immediately collected by filtration and dried, either in a desiccator under house vacuum or in a vacuum oven at 50°C for about one hour.

Characterization and Polymorph Analysis

We characterized the sm-HMX thus produced using small-scale sensitivity tests, differential scanning calorimetry (DSC), and field emission scanning electron microscopy (FESEM). We also used Raman spectroscopy and neutron powder diffraction to identify the polymorph type of the sm-HMX material.

Small-Scale Sensitivity Tests. In addition to the Los Alamos standard impact sensitivity test, both friction and electrostatic discharge (ESD) sensitivity tests were also performed. Information obtained from the tests serve as a safety guideline for classifying and establishing precautions with new or unknown molecules. The drop-weight impact sensitivity tests were done with a Type 12 machine, used to determine the H_{50} (height at which 50% of the samples react) of sample materials. The friction tests were done using a BAM (*Bundesanstalt für Materialprüfungen*) friction sensitivity instrument. The electrostatic discharge sensitivity tests were performed using an Allegany Ballistics Laboratory Electrostatic Discharge (ABL-ESD) instrument and the data are used to determine the tendency of materials to ignite or explode as a result of energy input by electric shock [5].

DSC Analysis. A TA Instruments DSC (Model Q1000) with the modulation option was used to characterize the thermal behavior of sm-HMX. About 1 mg sm-HMX sample material crimped in an aluminum pan was heated from 0 to 300°C at 5°C min^{-1}.

FESEM Analysis. A Leo FESEM (Model 1525) was used to study the surface structure (geometric size and shape) of the sm-HMX samples.

Raman Spectroscopy Measurements. The crystallographic polymorph of the sm-HMX material was identified using Raman spectroscopy, particularly the Raman spectral features in the 200–2000 cm^{-1} range, and neutron diffraction. Raman spectra were obtained using an InPhotote™ portable Raman system with 785-nm excitation wavelength and an optical fiber–coupled probe with 5-mm focal length objective. Ten Raman measurements of 20 s each with 75-mW excitation power at the sample were accumulated and averaged. The system was controlled by a Pentium II–based laptop running the InPhotote™ acquisition software (Inphotonics) and the spectral data were manipulated using GRAMS/AI™ (Thermo Electron Corp.) and Igor Pro Carbon (Wavemetrics). The sample holder was a cylindrical hole 1.5 mm deep and 12.4 mm diameter drilled in an aluminum base plate, which attached to the bottom of a cylindrical holder that fit over the fiber probe and held the probe lens 5 mm from the sample surface. In several instances, spectra from different portions of the sm-HMX sample were obtained by rotation of the sample holder.

Powder Neutron Diffraction. We used the Los Alamos high-intensity powder diffractometer (HIPD) [6] to obtain powder neutron diffraction data on sm-HMX for the characterization of its polymorph type. Standard HIPD experimental protocols and setup were used. About 0.5 g of the sample powder (the sm-HMX or the standard beta-HMX) was sealed in a cylindrical vanadium tube and diffraction patterns were collected at $T = 300$ K for about 12 h.

Table 1
Comparison of sensitivities between standard HMX and sm-HMX

Samples	Impact sensitivity H_{50} (cm; type 12)	Friction sensitivity 50% load (in kg)	ABL-ESD (threshold of initiation, Joules)
sm-HMX	26.4	15.6	0.625
Standard HMX (HOL83L030–050)	24.9	11.6	0.25

Results and Discussion

Small-Scale Sensitivity Tests

A total of three small-scale sensitivity tests—impact, friction, and electrostatic discharge (ESD)—were performed on sm-HMX powder samples, and the results are tabulated in Table 1. It can be seen that sm-HMX is less sensitive to friction, impact, and ESD by ABL method, as compared to conventional (Holston impact standard) beta-HMX.

Thermal Analysis by DSC

Figure 1 presents the DSC thermal analysis data for the sm-HMX. The DSC waveform shows only a single exotherm and no other features. This particular DSC used a 1 K/min temperature ramp from ambient to 200°C, then 5 K/min through the exotherm, in order to accentuate any endothermic features. Figure 1 also presents the thermogravimetric data, showing negligible loss in mass until the single exotherm. These data indicate that sm-HMX is stable until reaching the exotherm temperature at 280°C and that no polymorphic or other phase changes with significant thermal signatures occur at temperatures between ambient and 280°C.

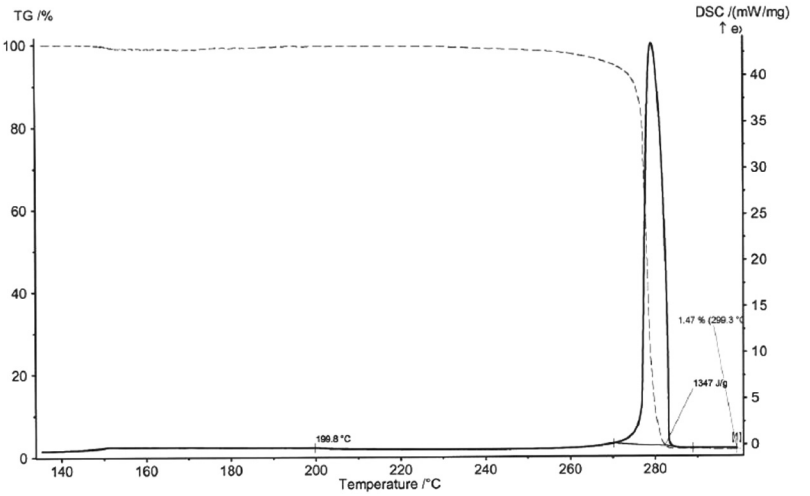

Figure 1. Differential scanning calorimetry and thermogravimetric analysis plot for sm-HMX. The temperature ramp was 1 K/min from ambient to 200°C, then 5 K/min. The DSC trace shows only a single exotherm at 281°C and no other features.

Surface Structure by Field Emission Scanning Electron Microscopy (FESEM)

As shown in Fig. 2 (left), the morphology of sm-HMX is quite interesting. The individual particles of sm-HMX powder appear to be oblong in shape with average width of $\sim$300 nm and length of $\sim$1–2 μm. For comparison, an SEM micrograph of Holston fine beta-HMX is displayed in Fig. 2 (right). Obviously, there are significant differences in morphology between sm-HMX and standard beta-HMX.

Raman Spectroscopy

The crystallographic polymorph of the sm-HMX was identified using Raman spectroscopy. Since we were unable to obtain a standard gamma HMX powder sample, Raman spectra of the other three standard HMX polymorphs (alpha, beta, and delta) were taken and the results compared to that from sm-HMX in

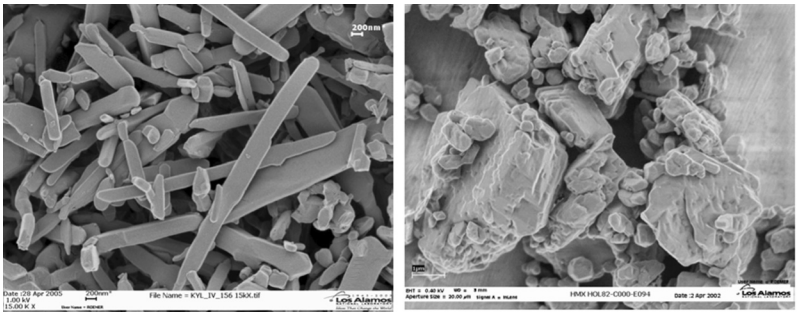

Figure 2. (Left) FESEM image of the sm-HMX showing flat oblong crystals of $\sim$300 nm average width and $\sim$1–2 μm average length (size bar in upper right is 200 nm); (right) FESEM of the beta-HMX starting material (Holston; size bar in lower left is 1 μm).

Fig. 3. It can be seen that the spectrum of sm-HMX does not match any one of the three. To confirm that the sm-HMX is the gamma polymorph, we compared the sm-HMX Raman

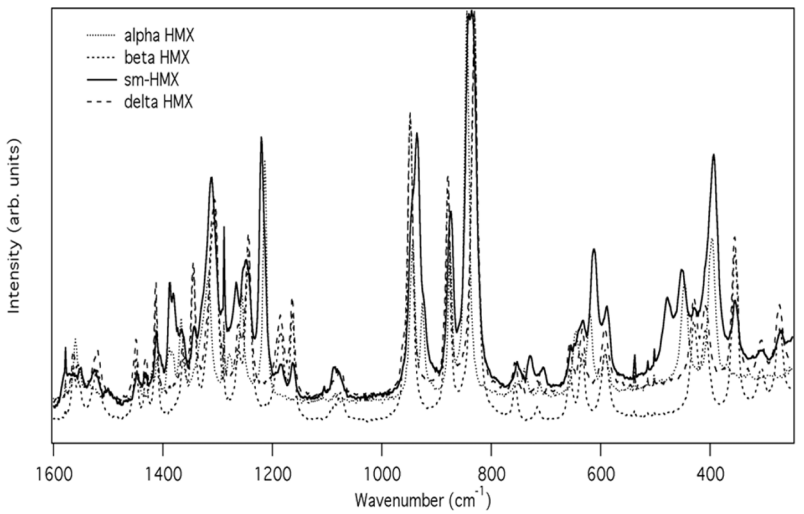

Figure 3. Raman spectra of sm-HMX and three other HMX polymorphs.

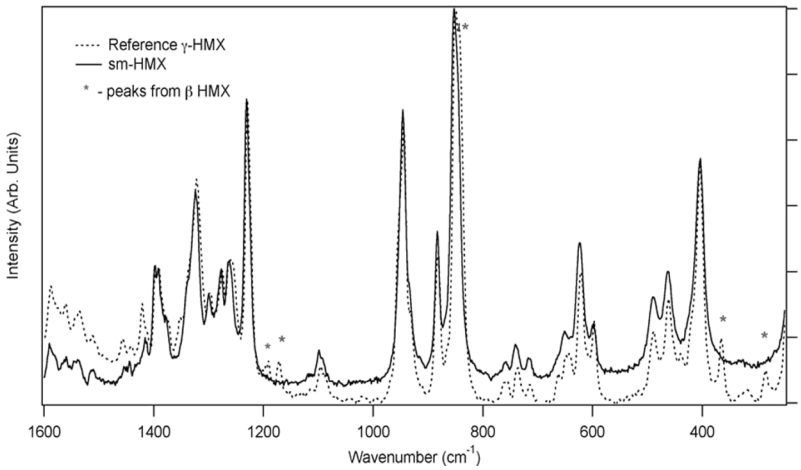

Figure 4. Raman spectra of sm-HMX and reference gamma HMX.

spectrum to an archive gamma-HMX Raman spectrum, Fig. 4, as well as to literature spectra [7]. Although there are apparent beta-HMX peaks (marked by asterisks) in the archive Raman spectrum[1] (indicating the archive gamma sample is actually $\sim$10% beta), it can be clearly seen that the sm-HMX is the gamma-HMX polymorph.

Yongxu et al. [8] have reported the preparation and characterization of the reticular nano-sized gamma-HMX by reprecipitation. However, they also reported that the reticularly structured HMX has both the gamma and beta phases of HMX. On the contrary, as illustrated by the Raman spectrum of Figs. 3 and 4, the purity of the gamma sm-HMX powder produced by our method is more than 99%. This polymorph purity estimate was made by measuring the Raman spectra of the beta-HMX starting material (Holston impact standard) and the sm-HMX product at high signal-to-noise ($>$100). The lack of any observable beta HMX Raman features in the sm-HMX,

[1]Raman spectrum of gamma-HMX from Alex Tappan of Sandia National Laboratory Albuquerque, NM.

along with the signal-to-noise ratio of the sm-HMX spectrum, was used to estimate the purity.

Neutron Powder Diffraction of sm-HMX

To further support the findings that sm-HMX is the gamma-HMX polymorph, we have analyzed the sample using neutron powder diffraction. The diffraction patterns are shown in Fig. 5. Visual inspection of the data collected for both samples showed a very large difference in the crystallographic structure of the two samples. As shown in Fig. 5, when the neutron powder diffraction pattern of sm-HMX was compared with that from Holston beta-HMX, several differences in absorption can be seen. For example, sm-HMX has peaks at larger *d*-spacings than standard beta-HMX, supporting the conclusion that sm-HMX is the gamma polymorph. Then we simulated the diffraction peak positions for beta-HMX and gamma-HMX phases from data reported in literature [9]. That is, using the gamma-HMX cell parameters a = 10.95, b = 7.93, c = 14.61, $\beta = 119.4$, and space group P 1 2/c 1 and the beta-HMX cell

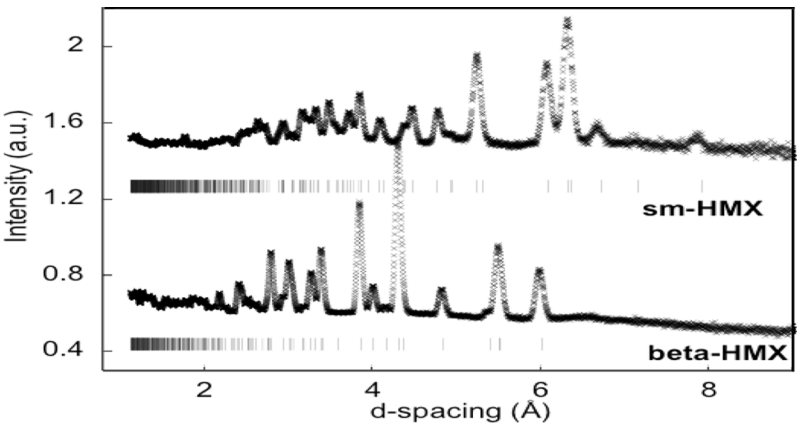

Figure 5. Neutron powder diffraction patterns for sm-HMX and beta-HMX. (Tick marks under each pattern correspond to the modeled diffraction peak positions for sm-HMX and beta-HMX, respectively).

parameters a = 6.54, b = 11.05, c = 8.70, $\beta = 124.3$, and space group P 21/c. The comparison of the simulated patterns with measured patterns showed that the sm-HMX sample diffraction pattern contained diffraction peaks at the positions expected for gamma-HMX.

Summary

We have successfully prepared submicron-sized HMX (sm-HMX) by a simple fast-cooling method. SEM measurement of the powder surface reveals that particles of sm-HMX are oblong in shape with average width of $\sim$300 nm and length of $\sim$1–2 μm. Results from thermal analysis by DSC showed that the sm-HMX sample is very pure and there is no phase conversion observed before it reaches a single exotherm at 280°C. Data from small-scale sensitivity tests indicate that sm-HMX is less sensitive than impact standard beta-HMX to friction, impact, and ABL-ESD. Analysis of data from both Raman spectroscopy and neutron powder diffraction indicate that sm-HMX is produced as the gamma polymorph of HMX. The Raman spectrum also illustrates that the purity of gamma sm-HMX powder produced by this method is greater than 99%.

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