

Crystallization and Characterization of RDX, HMX, and CL-20

Antoine E. D. M. van der Heijden* and Richard H. B. Bouma

TNO Prins Maurits Laboratory, Research Groups Pyrotechnics and Energetic Materials & Properties of Energetic Materials, P. O. Box 45, 2280 AA Rijswijk, The Netherlands

Received January 18, 2004; Revised Manuscript Received March 31, 2004

ABSTRACT: In this paper, a selection of the results obtained on the crystallization of the energetic materials RDX, HMX, and CL-20 will be briefly reported. Furthermore, the shock sensitivity of these explosives, when incorporated in a so-called plastic bonded explosive (PBX), will be discussed in more detail. One of the most important results is a direct correlation between the mean density of the energetic material and the shock sensitivity of the PBX containing this explosive. This implies that, similar to many other solid materials, the ability to control the product quality is also one of the major key factors playing a role during the crystallization of these energetic materials.

1. Introduction

At TNO Prins Maurits Laboratory, the crystallization and characterization of energetic materials were initiated at the end of the 80s. The research topics focused in the first instance on the crystallization and product characterization of the nitramine RDX¹⁻³ and later also of HMX⁴⁻⁶ and CL-20.^{7,8} Particular emphasis was given to the relation between product quality and sensitivity of plastic bonded explosives (PBXs) containing these energetic crystals. The results can be applied in the development of insensitive munitions (IM), with the objective to reach safer storage, transport, and handling of munition items and explosives while (at least) maintaining their performance.

Recently, a new grade called I-RDX, where the I refers to insensitive, was introduced.⁹ It was shown that this I-RDX is considerably less sensitive compared to the normal RDX grades, although a thorough understanding of what is causing this effect is still lacking.

In this paper, the crystallization and characterization of the nitramines RDX, HMX, and CL-20 are reported. Special attention is given to the relation between the product quality and the final sensitivity of the energetic material when incorporated in a PBX or density-matched liquid.

2. Crystallization

The crystallization of energetic materials in general involves standard techniques such as cooling, evaporative, or drowning-out crystallization.¹⁰ For the majority of energetic materials, comprising both explosives and oxidizers, melt crystallization is not an option because these materials generally decompose close to their melting point. Exceptions to this are, for example, trinitrotoluene (TNT), ammonium nitrate (AN), and ammonium dinitramide (ADN).

The equipment available at TNO comprises a 0.5- and 2.0-L jacketed crystallization vessel (see Figure 1). The jacket allows the vessel to be temperature controlled. The vessels are further equipped with a stirrer (marine type) and a thermocouple; the 2.0-L vessel has a draft



Figure 1. The 2.0-L crystallizer.

tube and four baffles. A reflux unit prevents evaporation of the solvent, especially during cooling crystallization experiments in which the initial temperatures generally are > 50 °C. The crystallization process is carried out batchwise.

Prior to the 0.5- or 2.0-L batches, generally laboratory scale experiments are carried out using a closed, reusable ampule containing ~ 20 mL of a solution that can be easily cooled and heated to crystallize or dissolve material. In this way, numerous experiments can be performed with the same solution. With this method also different solvents and the effect of the solvent on, for example, the shape of the crystal and the tendency to form inclusions, can be quickly screened.

Table 1 shows the crystallographic data of the energetic materials RDX, HMX, and CL-20.

2.1 RDX. The prediction of the RDX crystal shape by means of a periodic bond chain analysis has been performed by Ter Horst.¹⁴ The results of this analysis were used to perform molecular modeling calculations to predict or explain solvent effects on the RDX crystal morphology.¹⁴⁻²⁰ Figure 2 shows some typical examples of RDX crystals grown from different organic sol-

* Corresponding author. E-mail: heijdena@pml.tno.nl.

Table 1. Crystallographic Data^a

explosive	chemical name	crystal structure	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β	<i>Z</i>	ρ [g cm ⁻³]	space group
RDX ¹¹ C ₃ H ₆ N ₆ O ₆	cyclotrimethylene trinitramine	orthorhombic	13.182	11.574	10.709		8	1.806	<i>Pbca</i>
β -HMX ¹² C ₄ H ₈ N ₈ O ₈	cyclotetramethylene tetranitramine	monoclinic	6.54	11.05	8.70	124.3°	2	1.91	<i>P2₁/c</i>
ϵ -CL-20 ¹³ C ₆ H ₆ N ₁₂ O ₁₂	2,4,6,8,10,12-(hexanitro-hezaaza)-tetracyclododecane	monoclinic	13.696	12.554	8.833	111.18°	4	2.055	<i>P2₁/a</i>

^a *Z* = number of molecules per unit cell, ρ = density.

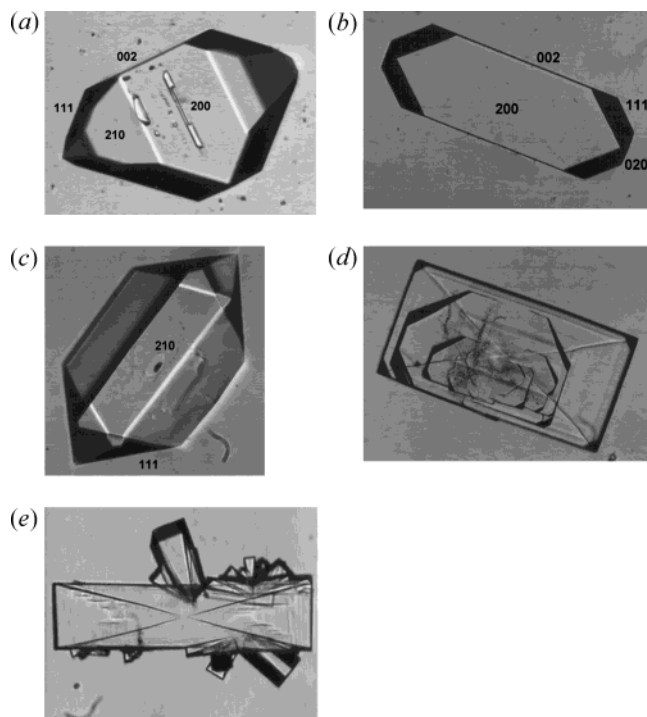


Figure 2. RDX crystals grown from the organic solvent (a) acetone, (b) cyclohexanone (with water), (c) γ -butyrolactone and, (d, e) cyclohexanone (without water).^{14–20}

vents.^{14,16–18} These experiments were carried out in the small scale setup using ampoules containing ~ 20 mL of an RDX solution. The changes in the shape of the crystals can arise from solvent/surface interactions, variations in supersaturation, and the presence of (unintentional) impurities in the system. In all cases, p.a. liquids have been used to minimize the presence of unintentional impurities. RDX procured from Dyno Nobel ASA (Norway) was used, containing 2.4 wt % HMX as a remainder of the RDX synthesis process as the most important impurity. The relative supersaturation in the case of the solvent acetone (see Figure 2a) is in the range of 15–20 to 30%.¹⁴ A so-called “dead zone” was reported for the (002) face up to a supersaturation of 15–20%, indicating the presence of an impurity in the solution blocking the growth of the crystals. For cyclohexanone containing ~ 3 wt % water (see Figure 2b), very clear and inclusion-free crystals could be grown up to supersaturations of 30%; up to a relative supersaturation of 4%, blocking of growth was observed for the (020) and (002) faces, again pointing to a “dead zone”, although much more narrow than in the case of acetone. For γ -butyrolactone (see Figure 2c), inclusion-free crystals could be grown up to supersaturations as high as 70%. The macrosteps found on the (200) faces of the RDX crystals grown from cyclohexanone without

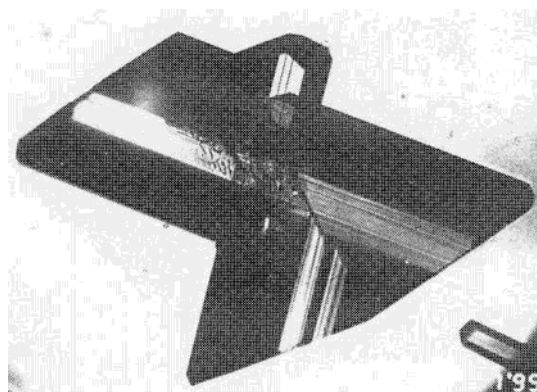


Figure 3. Twinned HMX crystal grown from cyclohexanone, as observed by means of optical microscopy. In the center of the crystal an area with many crystal defects can be discerned, like cracks and inclusions (courtesy of J. H. ter Horst).

water (Figure 2d) were formed above a supersaturation of 20%, leading to very high macrosteps and inclusions at a supersaturation of 40%. Close to and above 40% supersaturation, new crystals with a random orientation sprout from the crystals growing from the stagnant solution (see Figure 2e), in particular on the {200} forms.^{14,19}

The crystallization of RDX on 2.0-L scale verified that the shape of the crystals on this scale of production is very similar to the shapes found on small scale, as described above and illustrated in Figure 2.¹⁵ Similar results with acetone (Figure 2a) have been reported by, for example, Connick and May.²⁰

2.2 HMX. Four different polymorphs are known for HMX, α to δ . The β -polymorph is the most stable one and has the highest density, which is important for the energy content of the energetic material. Therefore, β -HMX is the desired polymorph to be crystallized and used as an explosive. See Table 1 for the crystallographic data of β -HMX. A prediction of the morphologically important crystal surfaces by means of a periodic bond chain analysis has been carried out for both β - and α -HMX.²¹

The β -HMX crystals, unlike RDX, show a tendency to form twins. The tendency for twinning depends on the solvent from which the HMX is grown. An example is shown in Figure 3. Cady²² studied twinning of HMX under the influence of an externally applied stress in more detail. Twinning occurs on the (101) plane of HMX.

Twinning is an effect that is often encountered for monoclinic crystal structures, like β -HMX. It was experimentally found that HMX when grown from acetone shows much less twinning, whereas in cyclohexanone practically every crystal consisted of twins. Growing from γ -butyrolactone leads, after filtration and drying of the product, to “spongy” looking crystals because a

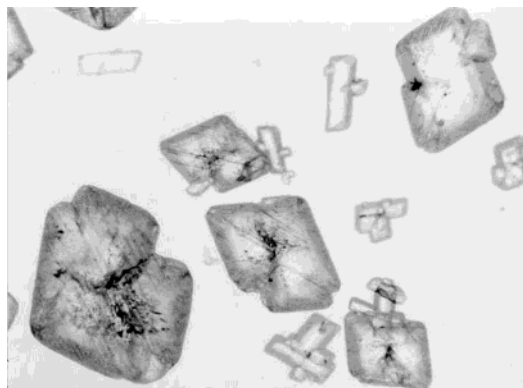


Figure 4. HMX crystals grown from 1:1 molar acetone/ γ -butyrolactone mixture on the 2.0-L scale.

1:1 complex is formed between the HMX and solvent molecules. Upon drying, the solvent molecules are removed from the lattice, and a porous HMX particle is left with an irregular shape and holes in the surface. It was found that the presence of acetone in γ -butyrolactone prevents the complex formation between HMX and γ -butyrolactone.

HMX cooling crystallization batches on a 2.0-L scale have been performed using a 1:1 molar mixture of acetone and γ -butyrolactone as a solvent. The process conditions such as stirrer rotation rate and cooling rate were varied, and the resulting product was characterized (see next section). An example of the resulting HMX

crystals is shown in Figure 4.⁴ The PBC analysis of β -HMX²¹ predicts that the morphologically important crystal forms on the vacuum morphology, so uninfluenced by the mother liquor, of β -HMX are $\{011\}$, $\{020\}$, $\{111\}$, $\{102\}$, and $\{100\}$; in case of the presence of the mother liquor, also the forms $\{11\bar{2}\}$ and $\{110\}$ might become more important if the interaction of the solution with these surfaces is larger compared to the other crystal faces.

2.3 CL-20. Five polymorphs, α to ϵ , are known for CL-20. The ϵ -polymorph is stable at room temperature and shows the highest density. The crystallographic data of this polymorph are summarized in Table 1. No morphology prediction is known for this or any of the other polymorphs of CL-20.

The commercially available ϵ -CL-20 grade consists of agglomerated particles, with a very irregular shape; see Figure 5a. Although the exact details of the production process have not been disclosed, it is known that this grade is crystallized by means of a so-called solvent/nonsolvent or drowning-out process. Reprocessing of this grade, as performed on a lab scale in-house, shows that much better defined crystals can be obtained, which appear to be free of macroscopic inclusions (see Figure 5b).

3. Characterization

3.1 Product Quality. Similar to the increasingly stringent demands required for chemicals in general,

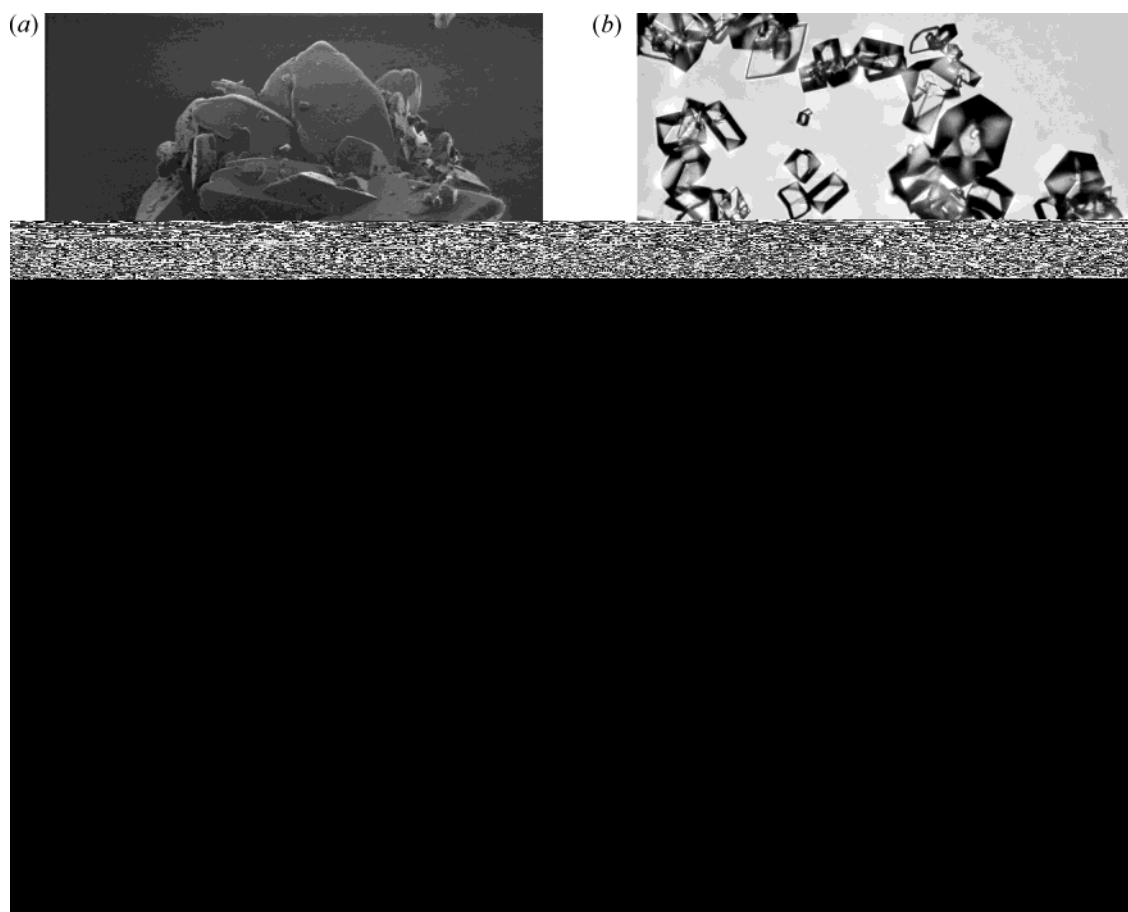


Figure 5. (a) Commercial and (b) reprocessed CL-20, as observed by means of SEM and optical microscopy, respectively. (c) SEM picture of reprocessed CL-20. (d) Magnification of a part of the image shown in (b), including crystallographic orientations.

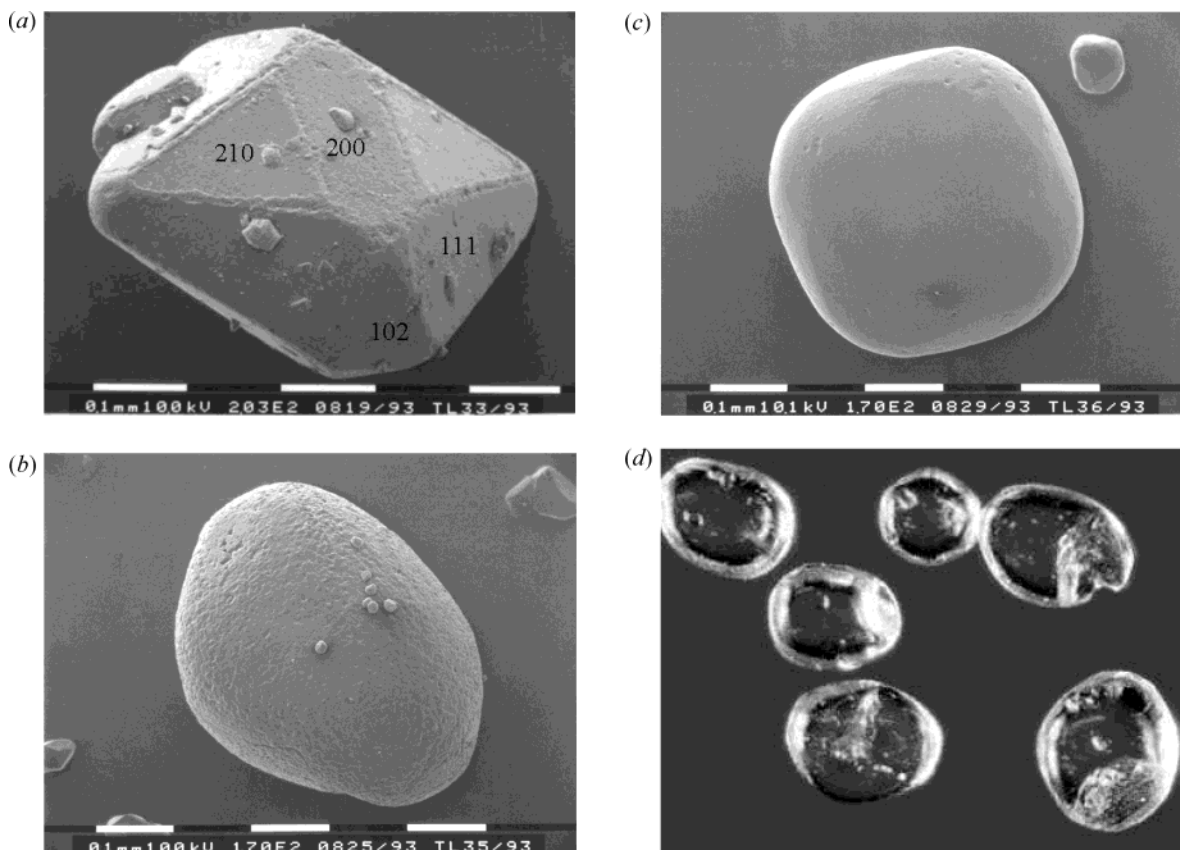


Figure 6. SEM pictures of (a) as-received RDX particle showing a faceted crystal (similar findings have been reported by Armstrong²⁴), (b) spheroidized, and (c) spheroidized + surface-smoothed RDX particle. (d) Optical microscopy picture of crystals similar to the one in (c).

this becomes more and more important for energetic materials as well. This need for improved product qualities is directly related to the shift in the application of “normal” or “standard” explosive materials to less sensitive explosives. Along with improvements of the production process to obtain better quality products, also the use of different and more sophisticated analytical techniques to characterize the energetic materials has developed over the years. As an example of one of these techniques, powder X-ray diffraction can be mentioned.²³

The energetic materials are generally characterized with regard to density, shape, mean size, purity, thermal and hazard properties, etc. In this paper, a selection of these results will be reported. As will be demonstrated later, the shock sensitivity is found to be strongly related to the product quality of the energetic crystals used in the final explosive composition (PBX).

3.1.1 RDX. Previous studies trying to relate the shock sensitivity of RDX to particulate properties in first instance focused on the mean size of the RDX particles and on the spheroidization and smoothing of the particle surface of the RDX crystals.^{1–3} The spheroidization process is a mechanical treatment of the original RDX crystals in an RDX-saturated solution of acetone.¹ These spheroidized particles can be further treated by means of slightly etching the particles in ethyl acetate, transforming the spheroidized particles, which are initially opaque due to the rough surfaces, into transparent particles with very smooth surfaces (see Figure 6, showing the sequence from as-received, spheroidized

to smoothed RDX crystals; for the as-received RDX (Figure 6a), similar observations have been made by Armstrong²⁴). Later it was recognized that the interior of the crystals, i.e., crystal defects such as inclusions, dislocations, grain boundaries, etc., affect the sensitivity of the explosive as well (see next section). A detailed study of the dislocation defect structure of RDX was performed by Halfpenny et al.^{25–28}

Of particular interest is the finding that a small amount of water present in an RDX/cyclohexanone solution, prevents or suppresses random 3D nucleation effects observed on the {200} crystal surfaces of RDX when grown from pure cyclohexanone (see Figure 2b,d,e). A possible explanation of this effect is provided by Ter Horst et al.¹⁹ and is related to the presence of byproducts such as cyclic nitramines with one or more of the N–NO₂-groups replaced by an N–(C=O)–CH₃ group in the RDX resulting from the synthesis process. In Figure 2d, the formation of macrosteps can be observed. In general, the formation of macrosteps could also promote the formation of inclusions, in this way deteriorating the purity and quality of the final product. On the basis of these results, it is recommended to use cyclohexanone saturated with water rather than pure cyclohexanone during the large scale production of RDX.

3.1.2 HMX. The characterization of the inclusion content in HMX crystals was carried out by means of confocal scanning laser microscopy (CSLM), in combination with scanning electron microscopy (SEM).

By using a CSLM in reflection mode, it is possible to make optical slices from a transparent object down to a

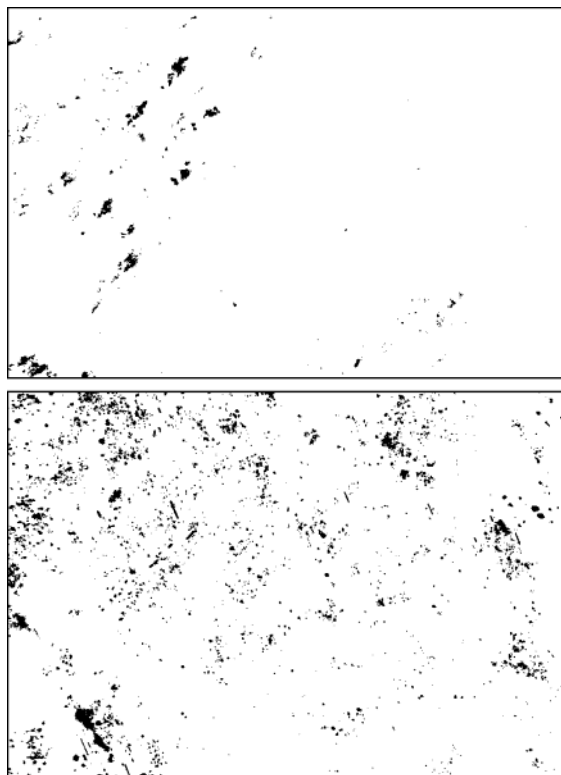


Figure 7. Two-dimensional projection of a stack of slices within two different HMX crystals taken from a commercial grade (lateral dimension: $\sim 140 \times 93 \mu\text{m}^2$).

thickness of about $0.5 \mu\text{m}$. In this way, local differences in the refractive index inside a crystal will be revealed as bright spots on a dark background. Hereto, the crystals were embedded in an epoxy resin, which was then cut and polished. The first slice is taken $15 \mu\text{m}$ below the surface of an HMX crystal to avoid surface artifacts due to the cutting and polishing steps when preparing the sample. Each step in the z -direction is $0.5 \mu\text{m}$ deeper into the crystal. At least 70 slices (so $15\text{--}50 \mu\text{m}$ below the surface) are recorded. Each image (768×512 pixels) covers an area of about $140 \times 93 \mu\text{m}^2$. The images are recorded with a BioRad MRC600, equipped with a $40\times$ objective, zoomfactor setting of 2. The deconvolution package Huygens2 is used to correct for the point spread function of the objective, resulting in a much better estimate of the size of the objects. The images of the separate slices of $0.5 \mu\text{m}$ thickness can be superimposed, leading to a two-dimensional mapping of the refractive index differences in a certain volume of a crystal.

Up to 10 different crystals per batch were investigated. Some of the results obtained with this technique when applied to a commercial and recrystallized HMX grade are shown in Figures 7 and 8. Image processing of the pictures resulted in a “negative” image, now showing the refractive index differences as black spots against a bright background. The images show that there is a considerable difference between the commercial and recrystallized HMX grades: when scanning through a commercial grade crystal, many localized areas with “clouds” of spots are observed, whereas only several distributed spots are found in a recrystallized particle. The size of the refractive index differences is estimated at $\sim 2 \mu\text{m}$. Furthermore, the bright spots are

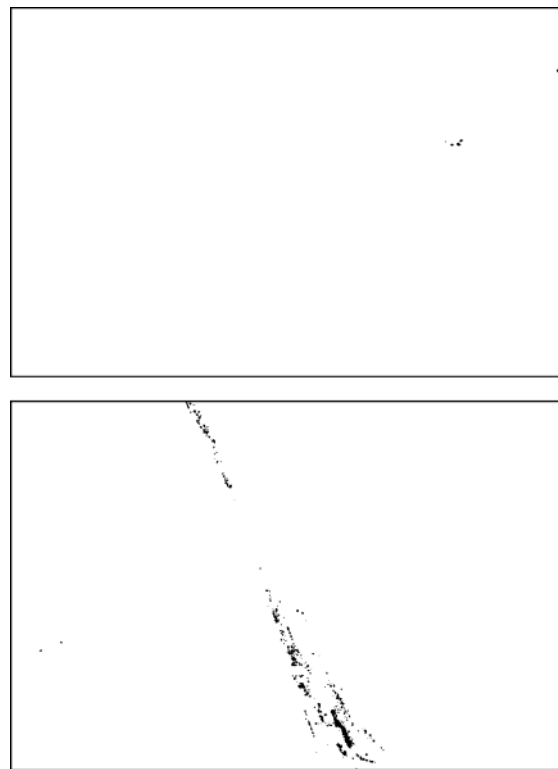


Figure 8. Two-dimensional projection of a stack of slices within two different HMX crystals taken from a recrystallized grade (lateral dimension: $\sim 140 \times 93 \mu\text{m}^2$).

found to be located along lines or in planes within the crystals, as was observed when viewing the CSLM images of each slice successively. It is likely to assume that these lines or planes correspond to the crystallographic directions of dislocations, grain boundaries, or possibly twin planes within the HMX crystals. However, since the sample preparation for the CSLM experiments did not allow a specific crystallographic orientation of the HMX crystals, their orientation is random. Moreover, (open) literature of the dislocation defect structure of HMX similar to that performed for RDX^{25–28} is lacking, so statements on possible dislocation directions would be speculative. Armstrong et al.^{24,29} have reported a type II twinning $\{101\}\langle 101 \rangle$ in HMX and also Cady²² reported twinning of HMX in the (101) plane; this plane might therefore correspond to (one of) the crystallographic orientation(s) in which the bright spots are preferentially located.

To find out to what kind of defects the refractive index differences are related to, another imaging technique was used (SEM). For the SEM investigation, the HMX crystals are fractured with a scalpel and mounted on conductive, adhesive carbon. Fractured surfaces are imaged with a field emission gun-SEM at a low acceleration voltage, so that the application of a conductive coating can be avoided. The absence of a coating ensures the visibility of minor details on the fractured crystal surfaces. The SEM results are depicted in Figures 9 and 10. Also in this case, a significant difference is found between the two grades: the commercial HMX contains many small inclusions in the range of ~ 0.5 to $\sim 2 \mu\text{m}$, whereas the recrystallized grade hardly contains any. The size of the inclusions agrees well with the estimated size based on the CSLM observations.

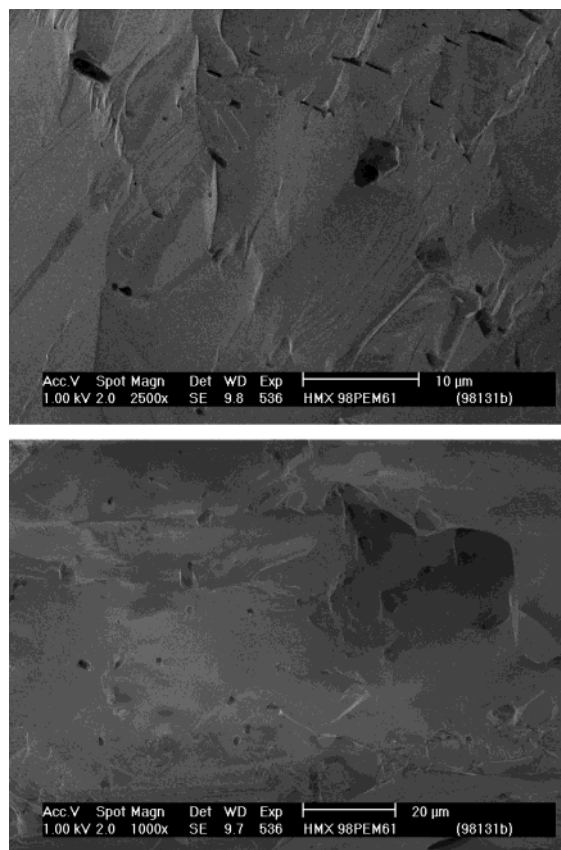


Figure 9. SEM pictures of fractured HMX surfaces (commercial grade), revealing many tiny holes, distributed over the surface.

The combined results of the CSLM and SEM observations show that the refractive index differences can be related to microinclusions. From the literature, it is known that crystalline defects such as microinclusions can be found preferentially on or near growth sector boundaries or along line dislocations (so-called “decorated dislocations”).³⁰ The observations indicate that this is also the case for HMX.

The distinct difference between the microinclusion content of the commercial and the recrystallized HMX grade might be related to the production method (evaporative and cooling crystallization, respectively) and/or the scale of production (~1000 vs 2.0 L, respectively), but this was not investigated further.

The density determination of the two HMX grades by means of liquid pycnometry further supports the fact that the commercial grade contains more inclusions than the recrystallized grade: 1.886 ± 0.002 vs 1.902 ± 0.002 g cm⁻³, respectively. Both values refer to the density of 250–425 μm sieve fractions of the original commercial and recrystallized batches.

The results of the sensitivity of these two as well as a third (recrystallized) HMX batch are described in section 3.2 of this paper.

3.1.3 CL-20. The characterization of CL-20 has only been limited up to now to optical microscopic and SEM observations (Figure 5), in combination with density (2.018 g cm⁻³), FTIR, X-ray powder diffraction, and thermal analysis (TG/DTA and DSC).⁷ All these measurements confirm the fact that the ϵ -polymorph of CL-20 is used.

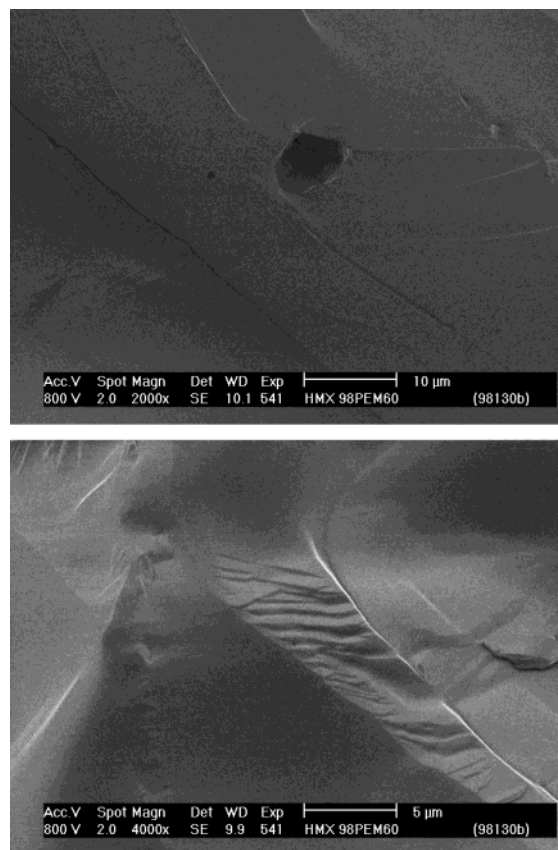


Figure 10. SEM pictures of fractured HMX surfaces (recrystallized grade), revealing smooth surfaces, with a much smaller amount of tiny holes compared to the commercial grade (see Figure 9).

The CL-20 has been applied as-received to determine the shock sensitivity (see section 3.2).

3.2 Shock Sensitivity. To determine the detonative properties of an energetic material, generally the explosive crystals are embedded in a polymer matrix, e.g., hydroxy-terminated polybutadiene (HTPB), resulting in a PBX.³¹ The prepolymer is a viscous liquid in which the solids are mixed to obtain a homogeneous mixture. During the last mixing step, a curing agent (an isocyanate containing NCO-groups) is added which, upon curing, reacts with the hydroxyl groups on the prepolymer, forming a polyurethane bond. This reaction leads to a cross-linking of the prepolymer with the curing agent and finally a rubber matrix is formed embedding the explosive crystals. See, for example, Wanninger³¹ for technical details on the production techniques of PBX charges.

Samples from this PBX are then tested regarding its shock sensitivity by means of standardized tests. For example, in the water gap test a cylindrical PBX sample (21-mm diameter and 40-mm height) is mounted in a hollow cylinder further filled with water, which in turn is mounted on top of a booster charge, of which the detonative properties are accurately known. The booster charge is detonated and depending on the length of the water gap, the PBX sample either detonates or not. The water gap acts as an attenuator, delivering a certain shock pressure to the PBX sample. In this way, the “go/no go” level of a certain PBX composition can be determined by repeating this test with 8–10 samples

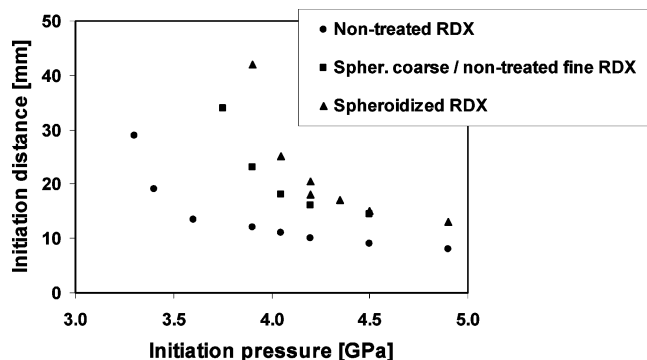


Figure 11. Initiation distance vs initiation pressure for the PBXs with nontreated RDX (●), spheroidized RDX (▲), and spheroidized coarse and nontreated fine RDX (■).²

at different shock pressure levels (different gap lengths). Instead of a water gap, also a PMMA gap can be used. This setup requires 50-mm diameter, cylindrical PBX samples.

An initiation test that requires much smaller samples than the test described above is the so-called flyer impact initiation test (see Prinse et al.³² for further details): by the discharge of a capacitor bank (10–40 kV) into an aluminum bridge, an aluminum plasma is created, which accelerates a 250 μm Kapton polyimide flyer having a diameter of 21.4 mm. At the end of a 5-mm long PVC barrel, the flyer impacts the sample having a diameter and height of 20 mm. A so-called fiber optic probe has been placed at the central axis to monitor the shock-to-detonation transition or decay of the input shock wave, as a function of the impact velocity. Similar tests to assess the shock sensitivity of PBXs containing RDX and HMX have been conducted by Borne and co-workers.^{33–35}

A recently developed method is the use of a liquid instead of a polymer to embed the explosive particles. This liquid should be selected to match the average crystal density of the explosive particles to suspend the particles without effects of sedimentation. Furthermore, the liquid should sufficiently wet the particles. The major advantage of such a density-matched liquid is that the shock wave experiences one single density when passing the sample. This prevents reflections within the sample and deterioration of the shock wave on its passage through the sample. In case of a proper wetting of the particles by the liquid, bubbles or voids at the solid/liquid interface can be avoided. Generally such voids are present at the polymer/particle interface due to bad bonding properties of the polymer and the particles and these voids may act as initiation spots leading to a detonation of the sample. The use of a density-matched liquid therefore focuses on the shock sensitivity of the explosive particles, and it avoids a potential influence of the sample preparation method on the shock sensitivity.

3.2.1 RDX. The effect on the pressure at which a PBX containing either spheroidized or smoothed RDX particles as compared to as-received RDX is initiated has been demonstrated using a 50-mm diameter PMMA gap test.^{2,3} The results showed that an increase in initiation pressure from 3.3 to 3.9 GPa can be achieved for a 85 wt % RDX/HTPB-based PBX containing untreated and spheroidized RDX particles, respectively (see Figure 11).

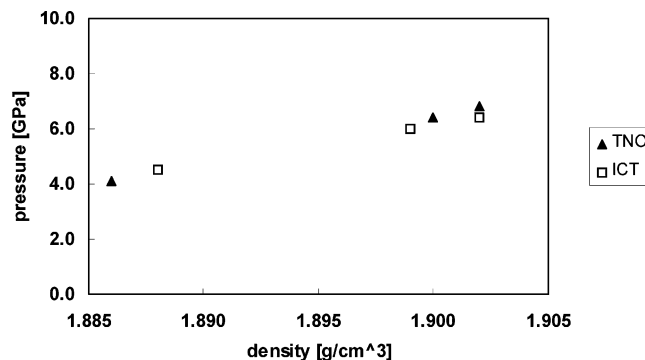


Figure 12. Initiation pressure as a function of the averaged HMX density of the particles embedded in a 70 wt % HMX/HTPB-based PBX. The data refer to independent measurements by both TNO and the Fraunhofer Institute for Chemical Technology (ICT) in Karlsruhe, Germany.⁵

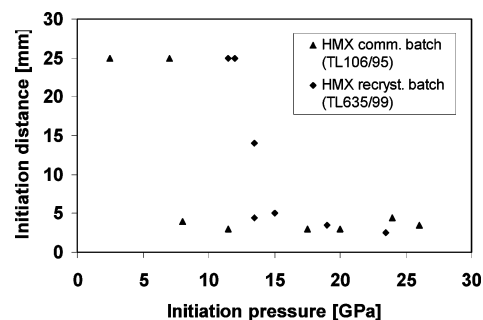


Figure 13. Initiation distance as a function of pressure for two grades of HMX suspended in a density-matched liquid and subjected to flyer impact tests.

These data indicated that a change in the shape of the explosive particles from faceted to more or less spherical leads to a significantly less sensitive explosive.

3.2.2 HMX. Two types of formulations, either using a polymer or a density-matched liquid, have been tested regarding its detonative properties. To avoid influences of size on the shock sensitiveness, sieve fractions were used (250–425 μm). An HTPB-based PBX containing 70 wt % HMX was tested by means of the water gap test. Three different grades of HMX were characterized: a commercial grade (as a reference) and two HMX grades recrystallized using the reference as starting material. The results are shown in Figure 12. In this graph, the initiation pressure is expressed as a function of the (averaged) crystal density of the HMX particles embedded in the PBX. A clear trend is found of a less sensitive PBX (i.e., higher initiation pressure, and therefore more difficult to initiate) at a higher averaged crystal density of the HMX particles. A significant increase in initiation pressure from 4 GPa for the commercial grade to >6 GPa for the recrystallized grades is found.

Samples using a density-matched liquid were characterized in the flyer impact initiation test. This time, two of the above-mentioned HMX batches were tested: the commercial grade, as a reference, and one of the recrystallized grades. These results confirm the previous data that a less sensitive explosive is found at a higher averaged crystal density of the HMX (see Figure 13). In this case, an initiation pressure of 7 vs 12 GPa was found for the commercial and recrystallized HMX grade

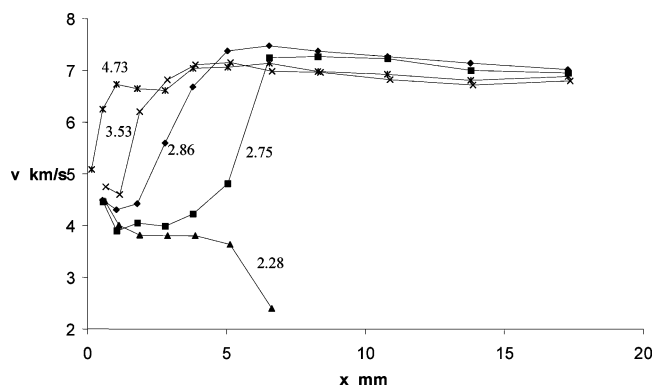


Figure 14. Shock wave velocity vs distance in an HTPB-based PBX with 62 wt % CL-20, after flyer impact at the velocities of the flyer impacting on the sample as indicated in the plot.

having averaged crystal densities of 1.885 and 1.895 g cm^{-3} (both $\pm 0.002 \text{ g cm}^{-3}$), respectively.

The absolute values of the initiation pressure at and above which the sample detonates as found by means of the water gap and the flyer impact test is different. This is related to the different shapes of the shock wave depending on how these are generated. For instance, with the flyer impact setup a sharp pressure peak with a short pulse duration is generated within the sample, whereas the pressure pulse is much broader showing a slow decay in the sample in case of the water gap test. Furthermore, the solid load of the samples is different.

These results clearly indicate that the (averaged) density of the crystalline product has a significant effect on the shock sensitiveness of these particles when incorporated in a PBX or in a density-matched liquid. A lower density of a crystalline material generally corresponds to a higher inclusion content and hence to a lesser product quality and purity, for example, in case the inclusions contain residual solvent. However, at this moment it is not yet clear whether the microinclusions which were found in the commercial HMX grade by means of CSLM and SEM should be held responsible for the higher shock sensitiveness of the samples containing the commercial HMX. More insight in the mechanisms of the interaction of such microinclusions with a shock wave will certainly contribute to a better understanding of the effect of the presence of such inclusions on the shock sensitiveness.

3.2.3 CL-20. For CL-20, both PBX and density-matched liquid samples were characterized by means of the flyer impact initiation test. As no liquid with a density similar to the density of CL-20 (slightly above 2.0 g cm^{-3}) was available, a liquid with a density of 1.95 g cm^{-3} was used. To be able to compare the results, the same volumetric solid load was used for the polymer and liquid based samples, namely, 42 vol %. This corresponds to a mass-based solid load of 62 wt % for the PBX samples and 43 wt % for the density-matched liquid suspensions.

As an example, the results of the flyer impact tests with the PBX samples is shown in Figure 14. This plot shows the detonation velocity built up in the sample in case it has been initiated at sufficiently high flyer impact velocities. Below a certain threshold flyer impact velocity (2.5–2.7 km s^{-1}), the sample will not be

initiated, the shock wave decays and no detonation will build up. Since only one CL-20 batch has been characterized (as-received), in this case no data are available on the effect of different densities on the shock sensitiveness.

Currently, research is ongoing with as-received as well as recrystallized CL-20 to establish to what extent this explosive behaves similar to HMX.

4. Conclusions

In this paper, it has been shown that different crystallization techniques, process conditions, and post-treatment may affect the product quality of the energetic material being crystallized. In this respect, the product quality refers to for example density, defect content, purity, crystal size distribution, shape, surface smoothness, etc. Apart from effects of particle shape and surface smoothness (for RDX), it has been demonstrated that specifically the (averaged) crystal density of the energetic material HMX determines the shock sensitivity of the compositions containing these explosive particles. Depending on the exact contents of the compositions and the initiation test setup used, improvements in the initiation pressure of the explosive composition of at least a factor of 1.5 can be achieved, whereas the corresponding crystal density increase is only marginal. This shows that in the case of HMX the crystal density of the explosive material is of major importance in determining whether the explosive composition is sensitive or not. The exact mechanisms determining which kind of internal crystal defects (e.g., the microinclusions found in HMX) are responsible for the observed sensitiveness is part of ongoing (international) research.

Acknowledgment. The authors acknowledge funding of parts of this work by the NL MoD.

Abbreviations

ADN	ammonium dinitramide
AN	ammonium nitrate
CSLM	confocal scanning laser microscopy
DSC	differential scanning calorimetry
HMX	cyclotetramethylene tetranitramine, $\text{C}_4\text{H}_8\text{N}_8\text{O}_8$
HTPB	hydroxy-terminated polybutadiene
p.a.	pro analysi
PBX	plastic bonded explosive
PMMA	polymethyl methacrylate
RDX	cyclotrimethylene trinitramine, $\text{C}_3\text{H}_6\text{N}_6\text{O}_6$
SEM	scanning electron microscopy
TG/DTA	thermogravimetry/differential thermal analysis
TNO	Netherlands organization for applied scientific research
TNT	trinitrotoluene

References

- (1) Van der Steen, A. C.; Skjold, E. *Proceedings of the Joint Government/Industry Symposium on Insensitive Munitions Technology*, White Oak, USA, March 13–14, 1990; p 235.
- (2) Van Ham, N. H. A.; Van der Steen, A. C.; Meulenbrugge, J. *J. AGARD Conference Proceeding 511*, October 21–23, 1991, Bonn, BRD, p 9-1.
- (3) Van der Steen, A. C.; Duvalois, W.; Hordijk, A. C. *Proceedings of the Insensitive Munitions Technology Symposium*, June 16–18, 1992, Williamsburg, VA, USA.

- (4) Van der Heijden, A. E. D. M.; Duvalois, W. *Proceedings of the 27th International Annual Conference of ICT*, June 25–28, 1996, Karlsruhe, BRD; p 32-1.
- (5) Van der Heijden, A. E. D. M.; Bouma, R. H. B. *Proceedings of the 29th International Annual Conference of ICT*, June 30–July 3, 1998, Karlsruhe, BRD; p 65-1.
- (6) Van der Heijden, A. E. D. M.; Duvalois, W.; Van der Wulp, C. J. M. *Proceedings of the 30th International Annual Conference of ICT*, Karlsruhe, BRD, June 1999; p 41-1.
- (7) Bouma, R. H. B.; Duvalois, W.; Van der Heijden, A. E. D. M.; Van der Steen, A. C. *Proceedings of the 31st International Annual Conference of ICT*, Karlsruhe, BRD, 2000; p 105-1.
- (8) Bouma, R. H. B.; Van der Heijden, A. E. D. M. *Proceedings of the 32nd International Annual Conference of ICT*, Karlsruhe, BRD, 2001; p 27-1.
- (9) Spycckerelle, C. *Proceedings of the 32nd International Annual Conference of ICT*, Karlsruhe, BRD, 2001; p 16-1.
- (10) Van der Heijden, A. E. D. M. In *Trends in Chemical Engineering Current Topics in Crystal Growth Research*, Research Trends, Poojopura, India, 1998; Vol. 4, pp 99–114.
- (11) Choi, C. S.; Prince, E. *Acta Crystallogr.* **1972**, B28, 2857.
- (12) Choi, C. S.; Boutin, H. P. *Acta Crystallogr.* **1970**, B26, 1235.
- (13) Zao, X.; Shi, N. *Chin. Sci. Bull.* April **1996**, 41 (7), 574–576.
- (14) Ter Horst, J. H. *Molecular Modelling and Crystallization: Morphology, Solvent Effect and Adsorption*, Ph.D. Thesis, Delft University of Technology, 2000.
- (15) Ter Horst, J. H.; Geertman, R. M.; Van der Heijden, A. E. D. M.; Van Rosmalen, G. M. *Proceedings of the 27th International Annual Conference of ICT*, Karlsruhe, BRD, 1996; p 126-1.
- (16) Ter Horst, J. H.; Geertman, R. M.; Van der Heijden, A. E. D. M.; Van Rosmalen, G. M. *Proceedings of the 4th Int. Workshop on Crystal Growth of Organic Materials*, Germany, 1997; p 94.
- (17) Ter Horst, J. H.; Geertman, R. M.; Van der Heijden, A. E. D. M.; Van Rosmalen, G. M. *J. Cryst. Growth* **1999**, 198/199, 773–779.
- (18) Ter Horst, J. H.; Geertman, R. M.; Van der Heijden, A. E. D. M.; Van Rosmalen, G. M. *Proceedings of the 14th International Symposium on Industrial Crystallization*, Cambridge, UK, 1999.
- (19) Ter Horst, J. H.; Geertman, R. M.; Van der Heijden, A. E. D. M.; Van Rosmalen, G. M. *Proceedings of the 30th International Annual Conference of ICT*, Karlsruhe, BRD, 1999; p 42-1.
- (20) Connick, W.; May, F. C. *J. Cryst. Growth* **1969**, 5, 65.
- (21) Ter Horst, J. H.; Kramer, H. J. M.; Van Rosmalen, G. M.; Jansens, P. J. *J. Cryst. Growth* **2002**, 237–239, 2215.
- (22) Cady, H. H. *Mater. Res. Soc. Proc.* **1993**, 296, 243.
- (23) Herrmann, M.; Engel, W. *Proceedings of the 31st International Annual Conference of ICT*, Karlsruhe, BRD, 2000; p 97-1.
- (24) Armstrong, R. W. *J. Phys. IV, Coll.* **1995**, 5, C4-89.
- (25) Halfpenny, P. J.; Roberts, K. J.; Sherwood, J. N. *J. Cryst. Growth* **1984**, 69, 73.
- (26) Halfpenny, P. J.; Roberts, K. J.; Sherwood, J. N. *J. Mater. Sci.* **1984**, 19, 1629.
- (27) Halfpenny, P. J.; Roberts, K. J.; Sherwood, J. N. *J. Cryst. Growth* **1983**, 65, 524.
- (28) Halfpenny, P. J.; Roberts, K. J.; Sherwood, J. N. *Philos. Mag.* **1986**, A53, 531.
- (29) Armstrong, R. W.; Ammon, H. L.; Du, Z. Y.; Elban, W. L.; Zhang, X. J. *Energetic Crystal-Lattice-Dependent Responses in Structure and Properties of Energetic Materials*; Liebenberg, D. H., Armstrong, R. W., Gilman, J. J., Eds.; Materials Research Society: Pittsburgh, PA, 1993; Vol 296; p 227.
- (30) Smet, F.; Van Enckevort, W. J. P. *J. Cryst. Growth* **1988**, 88, 169–179.
- (31) Wanninger, P. *Proceedings of the 27th Int. Annual Conference of ICT*, June 25–28, 1996, Karlsruhe, BRD; p 2-1.
- (32) Prinse, W. C.; Van Esveld, R. J.; Oostdam, R.; Van Rooijen, M. P.; Bouma, R. H. B. *Proceedings of the 23rd International Congress on High-Speed Photography and Photonics*, September 20–25, 1998, Moscow, Russia.
- (33) Borne, L. *Proceedings of the 5th Congrès International de Pyrotechnie*, EUROPYRO 93, June 6–11, 1993, Strasbourg, France; p 155.
- (34) Borne, L. *Proceedings of the 10th International Detonation Symposium*, July 12–16, 1993, Boston, USA; p 286.
- (35) Borne, L. *Proceedings of the 6th Congrès International de Pyrotechnie*, EUROPYRO 95, 1995, Tours, France; p 125.

CG049965A