ABSTRACT
An approach is made to quantify micro strain in energetic materials with X-ray diffraction. Samples of HMX were crystallized under varying conditions yielding different defect concentrations, and the mechanical sensitivities of the samples were measured.

X-ray diffraction patterns were measured with varying diffraction geometry, and the widths of diffraction peaks were determined. The data were evaluated with Williamson Hall plots revealing the micro strain for each sample.

The investigation shows that X-ray diffraction is capable for detecting qualities of coarse crystals, when suited measuring systems are applied. Moreover, the correlation of micro strain and mechanical sensitivities gives an idea, how lattice imperfections influence macroscopic properties of energetic materials.

INTRODUCTION
The mechanical sensitivity is an important issue for energetic materials and explosives, which has been discussed as a function of lattice defects originated during crystallization. However, hitherto a conclusive correlation was not achieved, because the quantitative measurement of defects is difficult. An approach is made to quantify lattice defects in energetic materials with powder X-ray diffraction and to correlate the results with macroscopic properties.
This document was presented at the Denver X-ray Conference (DXC) on Applications of X-ray Analysis.

Sponsored by the International Centre for Diffraction Data (ICDD).

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SAMPLE PREPARATION

β-HMX from Dyno Industrier with a purity of 98.6% was solved in hot propylene carbonate. The solutions were cooled from 75 to 5 °C with different cooling rates and stirrer frequencies. The crystallization procedures delivered coarse crystals with a size not well suited for X-ray diffraction measurements. However, grinding the particles to smaller particle sizes had to be avoided, as the procedure can create defects by itself.

XRD SYSTEMS

The quantitative strain analysis is based on peak profile analysis, especially the measurement of the broadening of diffraction peaks. Therefore measuring systems are needed with a minimal geometrical peak broadening combined with reasonable count rates. Besides, difficulties are expected with the relatively large crystals obtained by crystallization procedures, considering poor orientation statistics or uneven sample surfaces as demonstrated in Fig. 1. Such effects are assumed causing split or shapeless profiles, which hinder peak profile analysis.

![Fig. 1. Uneven surface caused by relatively large crystals in polycrystalline samples](image)

Different diffraction geometries were tested with the following systems.

**System 1:** The system consists of a conventional Bragg-Brentano diffractometer D5000 or D8 of Bruker AXS equipped with copper tube, scintillation counter, vertical Soller slits, Kβ-filter and flat specimen holder of the low temperature chamber TTK of Paar Inc.

**System 2:** The system consists of the diffractometer described above equipped, however, with a Debye-Scherrer device with rotating capillary and a secondary monochromator.
System 3: The system consists of the diffractometer described in system 1, however, equipped with Göbel mirror, secondary monochromator and long horizontal Soller slit.

System 4: The system consists of a Guinier diffractometer with transmission geometry equipped with a Johannson monochromator of Huber in incident beam and a position sensitive proportional counter (PSPC) of Braun. The vertical divergence of incident and diffracted beam was reduced by Soller slits to 1°. The samples were prepared on a rotating sample holder of Huber.

System 5: The system consists of a diffractometer equipped with Göbel mirror and asymmetric channel-cut monochromator in incident beam and a V5-Cannel Cut monochromator in diffracted beam.

EVALUATION AND ADJUSTMENT OF XRD SYSTEMS

For the evaluation of the measuring systems standard materials of Quartz and Silicon were measured. The Full Widths at Half Maximum (FWHM) and intensities of measured diffraction peaks were determined with the program EVA of Bruker-AXS. The results are summarized in Tab. 1. With the broad geometrical peak widths above 0,15 and 0,12 °2Theta and the relatively low intensities of the systems 2 and 3, respectively, these systems do not meet the requirements for a significant detection of peak broadening by micro strain.

<table>
<thead>
<tr>
<th>System No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
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<td>FWHM [20]</td>
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<td>&gt; 0,15</td>
<td>&gt; 0,12</td>
<td>0,05</td>
<td>0,028</td>
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<tr>
<td>Int. [cps]</td>
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<td>&lt; 80</td>
<td>500</td>
<td>2800</td>
<td>125</td>
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</tbody>
</table>

XRD MEASUREMENTS OF THE HMX SAMPLES

Based on the results mentioned above the differently crystallized HMX samples were measured with the X-ray systems 1, 4 and 5. The X-ray reflections measured with system 1 were significantly shifted against each other, split or broadened, which is presumably caused by poor
orientation statistics and uneven sample surfaces. The measurements confirm the assumption, that large crystals hinder the evaluation of diffraction patterns.

The measurements with system 4 delivered well formed profiles and small peak shifts. The system is therefore well suited to overcome the problems raised by large crystals. With system 5 the peak shifts are also strongly reduced, indicating that difficulties with large crystals are overcome. However, especially annoying are noisy peak profiles and low count rates, as a profile analysis is difficult with such data.

EVALUATION OF HMX PATTERNS

Full widths at half maximum FWHM and integral widths of the diffraction peaks measured with HMX and Silicon were determined with the program EVA of Bruker-AXS. The pure peak widths of the HMX samples were calculated by subtracting geometrical peak widths determined and interpolated from the silicon measurements.

The resulting pure peak widths were evaluated by the Williamson Hall method [1], where the reciprocal peak widths $\beta^* = \beta \cos \theta \lambda$ are plotted versus the reciprocal lattice distances $d^* = 2 \sin \theta \lambda$, and the resulting curves were fitted using $y = mx + b$. The plots reveal the mean micro strains of the samples represented by the slopes $m$ of the fitted lines, as shown in Fig. 2 for selected HMX samples measured with system 4.

RESULTS AND CORRELATION

The Williamson Hall plots and their evaluation revealed significantly different values of micro strain of the differently crystallized HMX samples. Within the three tested measuring systems, the highest coincidence of the measured and fitted values in the plots was found with the Guinier data of system 4 (Fig. 2). The coincidence indicates, that the problem of measuring relatively large crystals with reasonable count rates was overcome with this system.
Fig. 2: Williamson Hall plot of various HMX samples.
The different slopes represent different mean micro strain.

Fig. 3: Pin load of sensitivity test against friction plotted versus micro strain.
Increasing micro strain effects decreasing friction sensitivity (= increasing pin load)
Plotting the mechanical sensitivities, measured with friction and impact tests according to BAM, versus the mean micro strain in Fig. 3 shows that micro strain decreases sensitivity against friction. The effect may be explained by the mobility of defects as dislocations or deformation twinning of HMX [2], which causes a better plasticity and therefore lower vulnerability.

The investigation shows that X-ray diffraction is capable for detecting micro strain of coarse particles, as obtained by common crystallization techniques, when suited measuring systems are applied. Moreover, the correlation of micro strain and mechanical sensitivities gives an idea, how lattice imperfections influence macroscopic properties of energetic materials. The results shall be verified by further investigations including a broader variety of HMX samples and a detailed characterization of strain fields.

ACKNOWLEDGEMENT

The research reported herein has been sponsored in part by the United States Army through its European Research Office.

REFERENCES
