Characterization of the Lattice Vibrations of Ammonium Nitrate in an ANFO Mixture After Authentic Explosions Using Micro-Raman Spectroscopy and Single Crystal X-Ray Diffraction

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Background

- ANFO: Mixture of Ammonium nitrate and fuel oil
- Common commercial blasting agent
- Used in manufacture of IEDs in terrorist attacks
  - 1995 Oklahoma City Bombing
  - Bomb exploded in front of Alfred P. Murrah Federal Building

Ammonium Nitrate (AN) (NH_4NO_3) Polymorphism

Form	Phase	Stable Temperature (° C)	Crystal System
Form I	Phase V	Below - 16° C [3] |	Tetragonal [1 and 3] | Orthorhombic [2]
Form II	Phase IV	- 16° to 32° C [3]	Orthorhombic [1, 2 and 3]
Form III	Phase III	32° to 84° C [3]	Monoclinic or Orthorhombic [3] | Orthorhombic [1 and 2]
Form IV	Phase II	84° to 125° C [3]	Tetragonal [3]
Form V	Phase I	125° C to 169° C [2]	Cubic and isotropic [1, 2 and 3]
Phase VI		Above 169° C, at pressures higher than 9000 kg/cm^2 [	
Phase VII		Below – 170° C [1 and 2]	

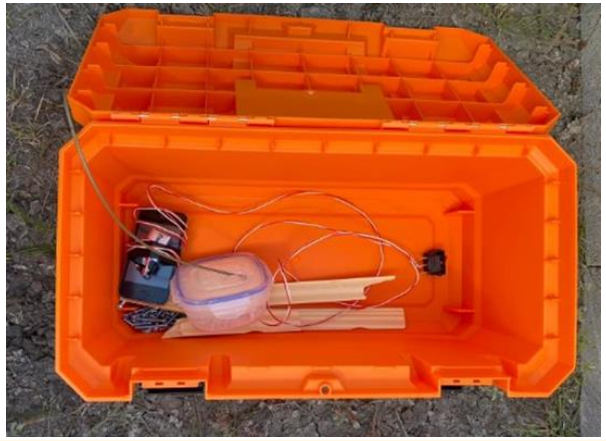
Théorêt and Sandorfy, 1964 [1], Dunuwille and Yoo, 2013 [2], McCrone, Andreen and Tsang – 1944 (Report on The Microscopic Examination of High Explosives and Boosters) [3]

Shift in Terminology from “Form" to “Phase“

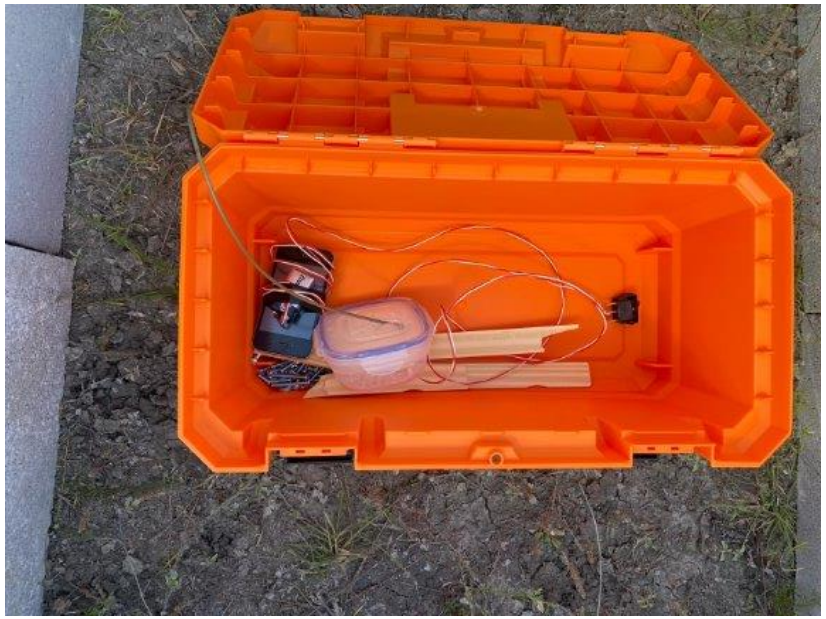
- Term "polymorph" (from the Greek "poly" meaning many and "morph" meaning form) - Initially focused on different visible crystal structures - Distinct "forms" that a substance could take
- Over the years, in areas like materials science and crystallography, focus shifted to broader term "phase“ – States of matter that a substance could exist in – Encompassing not just crystal structures but also liquids and vapors

Construction of Devices

- Two devices constructed
- Both were constructed using the same components
  - Commonly found in real IEDs

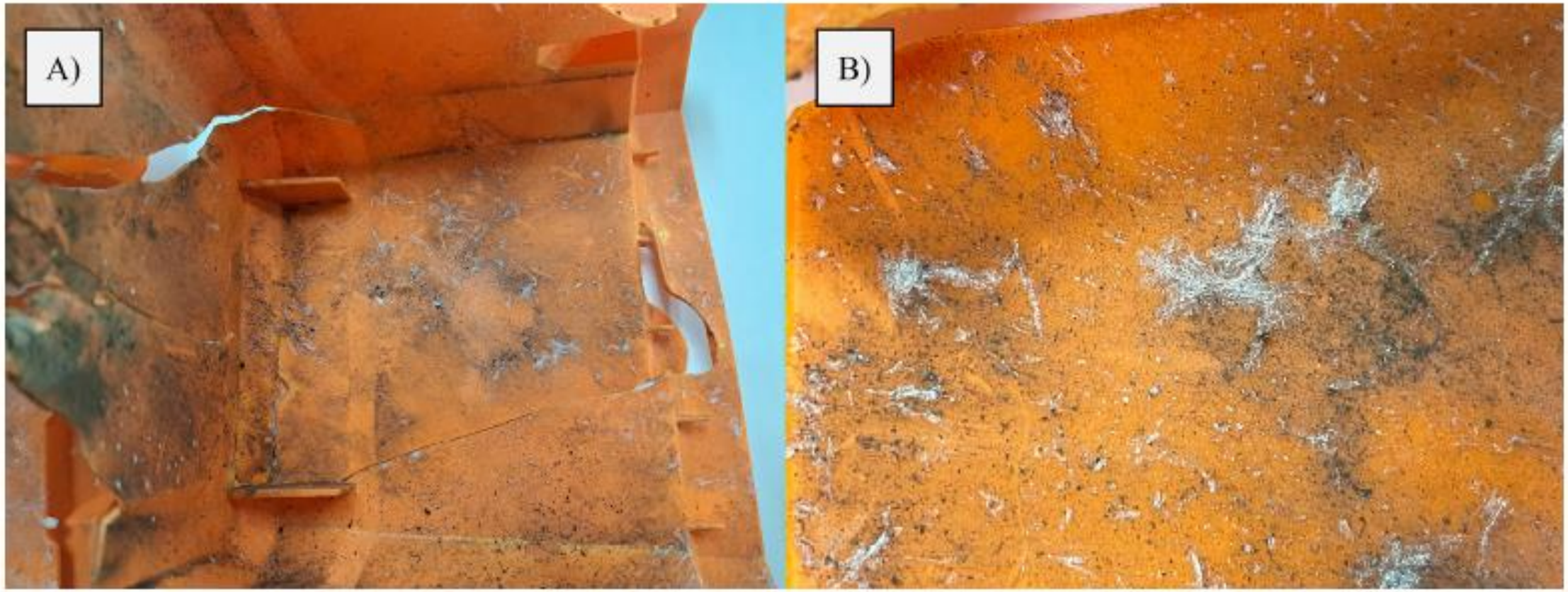


Set-up and post-blast debris collection

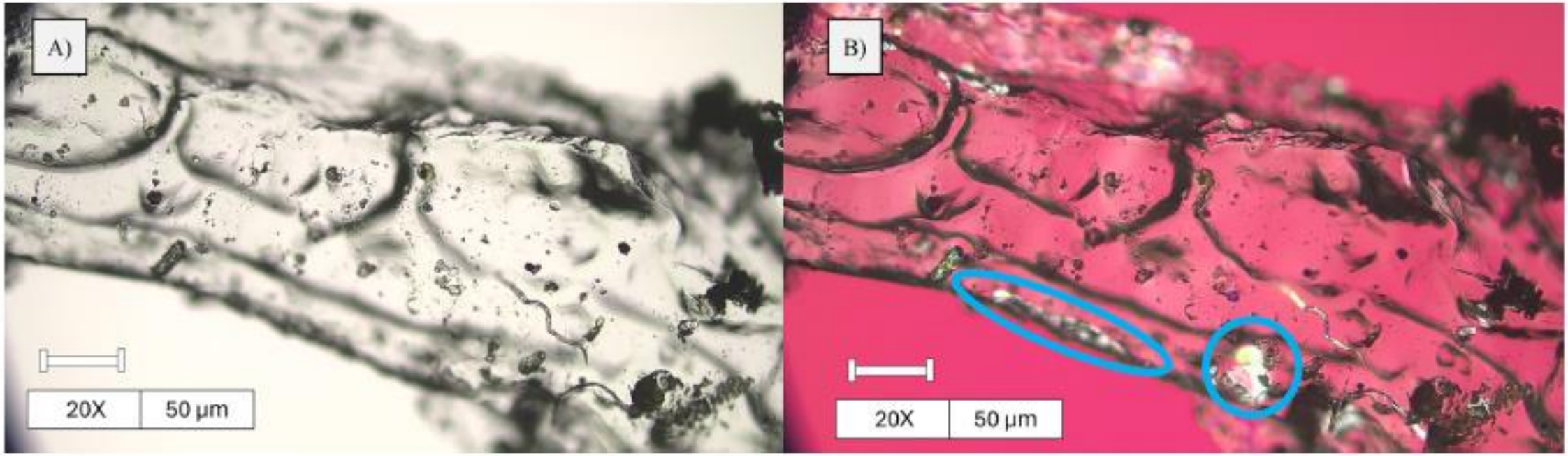


- 4 × 4 × 2-foot square made of cinderblocks to facilitate collection and limit spread of debris post-blast
- Collected into unlined paint cans

Macroscopical Examination

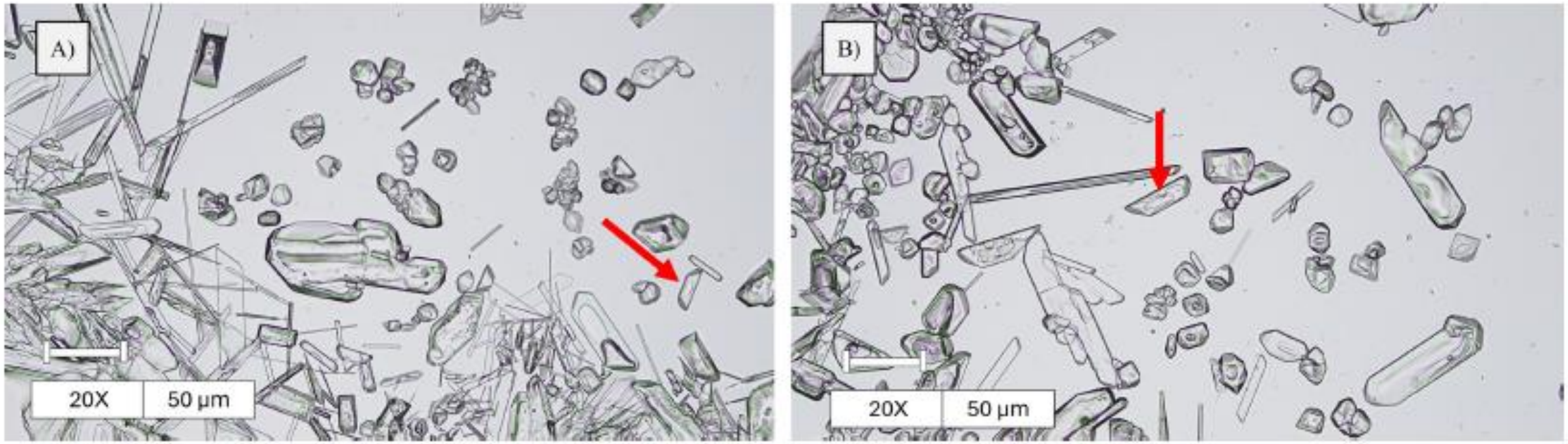


Initial Microscopical Examination



- OSAC 2022-S-0023 Standard Practice for the Forensic Analysis of Explosives by Polarized Light Microscopy
- BF: Lacked recognizable crystallographic morphology and instead looked irregular
- First-order red compensator: Presence of minor anisotropic properties

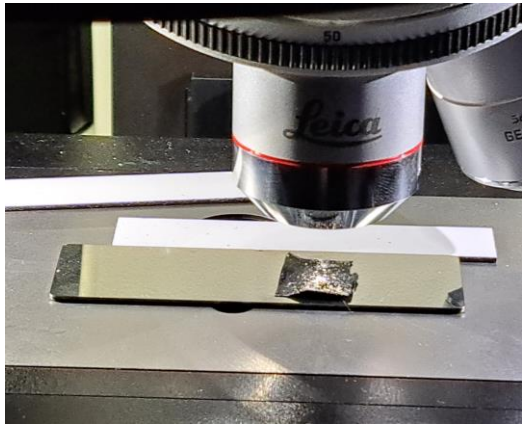
Recrystallization and Microscopy

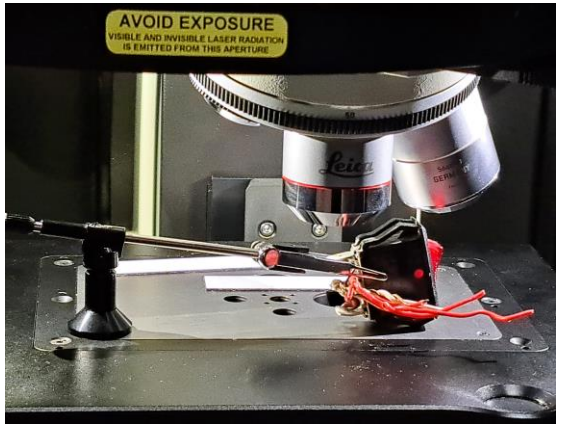


- Euhedral crystals observed growing with various crystal morphologies (blades, tablets, and prisms) – Prisms lying on a {101} prism face & displayed high order retardation colors
- Crystal morphologies consistent with AN standards and literature

Micro-Raman Spectroscopy Data Collection (1 of 2)

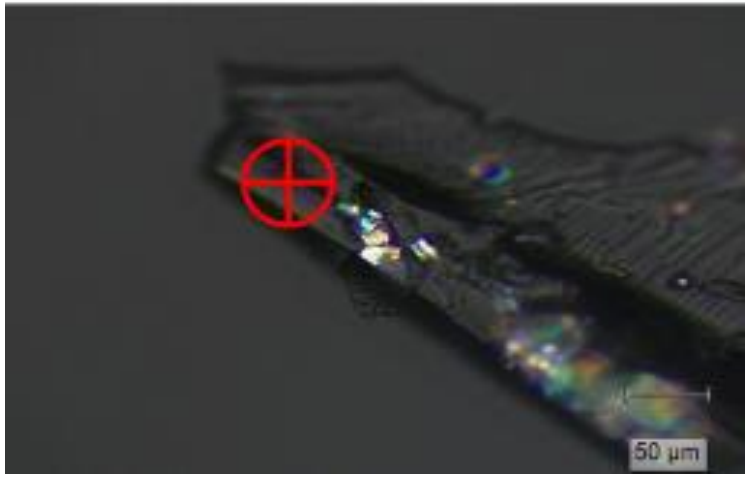
- Renishaw inVia™ InSpect confocal Raman microscope
- 785 nm wavelength laser
- Preliminary in-situ data collected with 5X objective and 3 accumulations at 1 mW
- Major background interference from many of the substrates observed





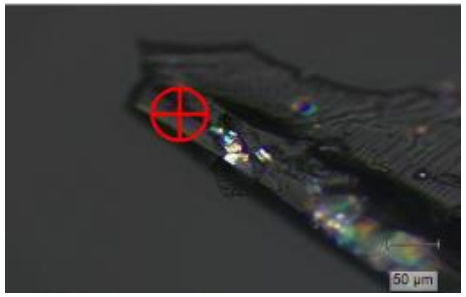
Micro-Raman Spectroscopy Data Collection (2 of 2)

- Fragments of grown crystalline materials were removed from substrate and placed onto glass slide
- Use of confocal Raman microscope enabled selection of isotropic areas of interest for measurement



- Ten isotropic fragments were each measured three times
- Three measurements were averaged for each fragment
- Ex-situ analysis conducted with 20X objective and 3 accumulations at 1 mW

Micro-Raman Analysis Results (1 of 2)



139.62 B_{3g} coupled translational and librational modes

170.69 B_{1g} libration mode

714.08 N-O in-plane deformation mode

109.5

173.18

173.48

107.08

141.36

221.21

172.33

ANFO reference
Isotropic Fragment 1
Isotropic Fragment 2
Isotropic Fragment 3

A
B
C
D

Raman intensity/Arbitr. units

Wavenumber/cm^{-1}

Micro-Raman Analysis Results (2 of 2)

- Raman lattice vibrations and isotropic nature of fragments suggests an altered crystal structure of AN is present in post blast debris
- General trend of peak shifting to higher wavenumbers also indicates history of stress, either in form of heat or pressure
- Suggest crystalline material recovered is stressed Form II (Phase IV) of AN

Single-crystal XRD needed to confirm crystallinity and crystalline Form (Phase) of post blast crystals

XRD Data Collection (1 of 2)

- All XRD data collected on an XtaLAB Mini™ diffractometer (Rigaku) using Mo-Kα radiation
- Six crystals taken from different locations on post blast toolbox fragment
- Crystals isolated from debris and immersed in immersion oil (Cargille type NVH) on glass slides
- Mounted on a glass capillary pin using Thomas Lubriseal stopcock grease
- Initial unit cell analysis performed at 293(2) K using three sets of frames (10 frames per set) with exposure times between 12 to 440 s per frame

XRD Data Collection (2 of 2)

- Full data collection: A large, irregular, colorless crystal was cut down to plate (0.50 mm × 0.40 mm × 0.10 mm)
- Mounted using Lubriseal grease
- Full data collection conducted using 30-s exposures per frame, with two sets of frames (194 and 190 frames per set, respectively)
- Data collection, reduction, and a multi scan absorption correction performed using CrysAlisPro 1.171.40.53 (Rigaku)
- Structures were solved with SHELXT program (Sheldrick, 2015) using Intrinsic Phasing and refined with SHELXL-2014 program

XRD Analysis Results (1 of 3)

Crystal	Distances of unit cell of crystal			Angles of unit cell of crystal			Dimension of crystal (in mm)
1	4.913(18)	5.470(2)	5.760(2)	89.7(3)	89.9(3)	89.4(3)	0.5×0.25×0.1
2	4.953(19)	5.410(2)	5.790(2)	89.9(3)	89.8(3)	89.8(3)	3.6×3.2×2.1
3	4.89(3)	5.51(3)	5.77(4)	89.6(5)	89.9(5)	89.9(5)	5.5×2.6×2.4
4	4.93(11)	5.46(15)	5.76(15)	90.6(2)	90.2(2)	90.7(2)	4.6×4.1×4.6
5	5.47(3)	5.77(3)	4.95(3)	89.4(4)	91.0(4)	89.9(4)	6.2×4.5×6.3

- Optically isotropic crystals gave clean diffraction patterns, without signs of twinning or polycrystallinity
- Only largest crystals gave sufficiently strong data for analysis
- Unit cell parameters consistent with Form II (Phase IV) of AN

XRD Analysis Results (2 of 3)

Unit cell metrics	Postblast (this work)	Methanol recrystallization [4]	Water recrystallization [5]
a/Å	5.748(2)	5.7497(3)	5.724(5)
b/Å	5.464(2)	5.4440(3)	5.455(4)
c/Å	4.936(1)	4.9232(2)	4.945(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	155.02 (9)	154.10 (1)	154.4

- Results generally consistent with prior studies
- Slight statistical differences in unit cell parameters, along with Raman and PLM observations, suggest thermal or pressure-induced stresses within crystal
- Also corroborated with change in anisotropy – change in structure due to stress

XRD Analysis Results (3 of 3)

Bond distances and angles	Postblast (this work)	Methanol recrystallization [4]	Water recrystallization [5]
N1–O1/Å	1.263(3)	1.265(1)	1.268(3)
N1–O2/Å	1.230(2)	1.2313(9)	1.230(3)
O1–N1–O2/°	120.1(1)	120.78(1)	119.9(1)
O2–N1–O2′/°	119.8(2)	119.61(6)	120.3(2)

- O–N distances and O–N–O angles in the nitrate ion also compared to previous studies
- Results generally consistent with prior studies; however, O–N–O angles are slightly outside range of statistical equivalence

Conclusions

- Combination of crystalline properties obtained, and spectral information indicates post blast crystals to be stressed Form II (phase IV) of AN
- Low frequency Raman spectroscopy (10–250 cm^{-1}) essential to support hypothesis of structural changes and correlate optical observations of crystalline material

Future Work

- Study of lattice vibrations using polarized Raman
- Correlating optical and chemical properties of AN post blast crystals with varying detonation conditions and fuel/oxidizer ratios
- Would provide forensic examiners with valuable insights into the bomb's construction

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Questions?

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Estevanes J, Jernigan N, Zall C, and Monjardez G. The Characterization of the Lattice Vibrations of Ammonium Nitrate in ANFO Mixture After Authentic Detonations using Confocal Raman Microscopy and Single Crystal X-ray Diffraction. *Journal of Raman Spectroscopy*. https://doi.org/10.1002/jrs.6752