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Title: Unifying Observations of Solid-Solid Polymorphic Phase Transitions in HMX

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Blaine Asay
Valery Levitas

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Unifying Observations of Solid-Solid Polymorphic Phase Transitions in HMX

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We have studied the kinetics of the solid-solid phase transition in the energetic organic crystal octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Different observables are compared for measuring the kinetics of the solid state phase transition. The heterogeneous nature of the material leads to difficulties intercomparing the various observables. A macroscopic view of the phase transition in the heterogeneous solid allows one to develop a model for the phase transition mechanism which accounts for all observables. This model incorporates a second order nucleation and growth mechanism for the high temperature phase with the growth kinetics dominated by the heat of fusion, despite the occurrence of the phase transition at a temperature approximately 100 K below the thermodynamically stable melt.

Unifying Observations of Solid-Solid Polymorphic Phase Transitions in HMX

Laura Smilowitz, Bryan Henson,

Blaine Asay, Valery Levitas*

Los Alamos National Laboratory

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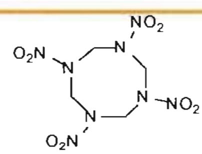
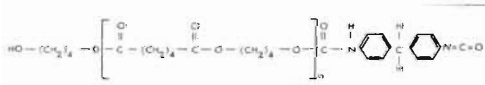
**Iowa State University,*

Ames Iowa

PBX 9501 - Plastic Bonded Explosive



HMX (95%)

+ 

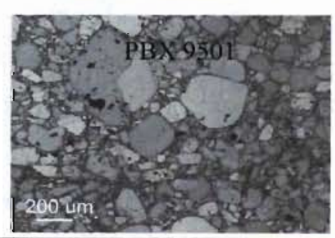
Estane (2.5%)

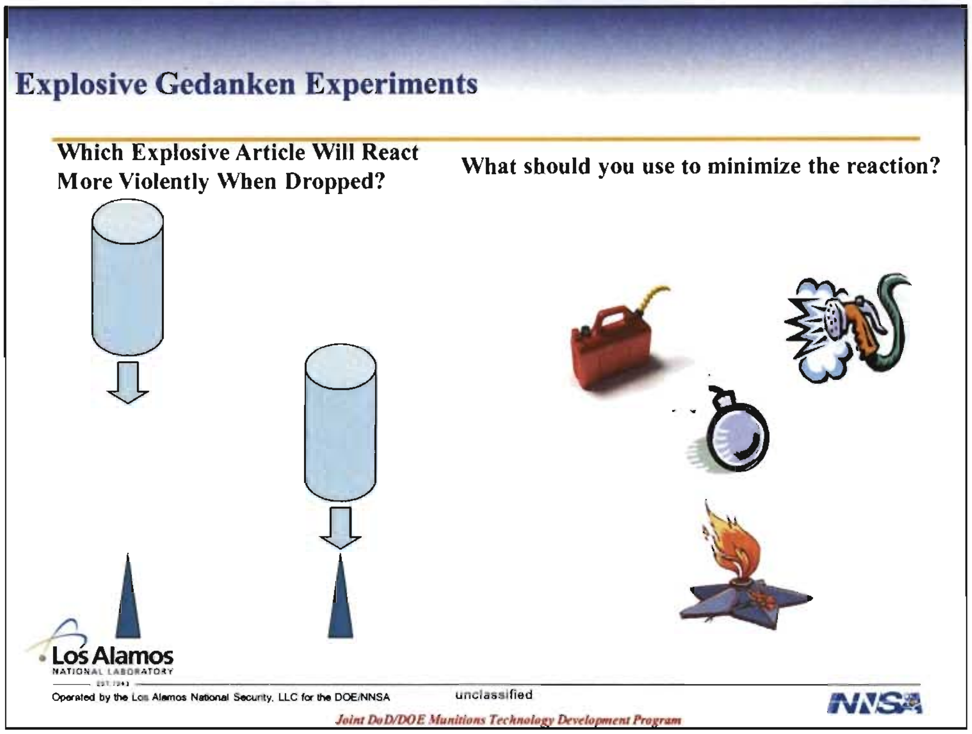
$$CH_3C(NO_2)_2CH_2\text{-}O\text{-}CH(CH_3)\text{-}O\text{-}CH_2C(NO_2)_2CH_3$$

+

$$CH_3C(NO_2)_2CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2C(NO_2)_2CH_3$$

BDNPA/F (2.5%)




Explosive Gedanken Experiments
Which Explosive Article Will React More Violently When Dropped?
What should you use to minimize the reaction?
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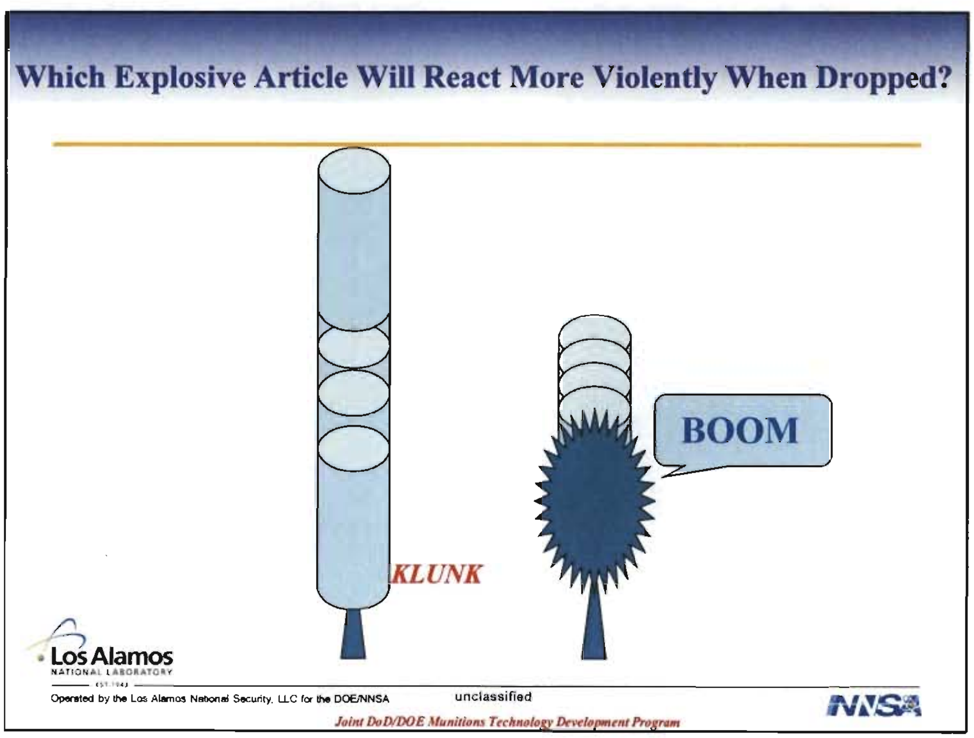
Which Explosive Article Will React More Violently When Dropped?
BOOM
KLUNK
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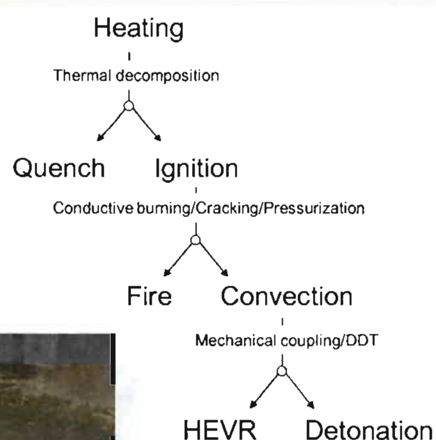
Which is the best way to respond to this scenario?

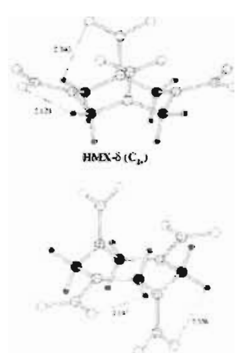
Motivation: Predicting Reaction Violence in an Abnormal Thermal Event



Outline

- Introduction to Thermal Explosion
  - Pre-ignition thermal decomposition
    - HMX Polymorphs
  - Transition to ignition
  - Ignition
  - Post-ignition burn propagation
- Experimental tools
  - SHG, Raman, DSC
  - comparison of observables
- Kinetics results
- Model of phase transition

HMX Polymorphs



HMX-β (C_i)

Optimized geometries of HMX in δ and β form

Chakraborty et al. (2001) *J. Phys. Chem.* A

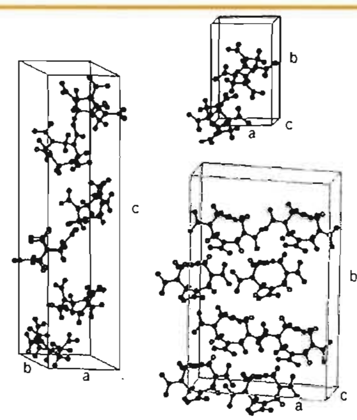


Figure 1. Unit cells for HMX polymorphs. Clockwise from top: β, α, and δ.

D. Bedrov et al. (2004) *Journal of Computer Aided Materials Design*, 8, 77-85.

HMX Polymorphs: β,α,δ

Thermodynamics- which phase is stable, not how to get there
Kinetics- how to get there- needs to return thermodynamic phase diagram

Phase	β	α	δ
Sensitivity (drop hammer)	35cm	12cm	7cm
Volume change	0	β +4%	β +7%
Temperature stability	<105	103-160	>160

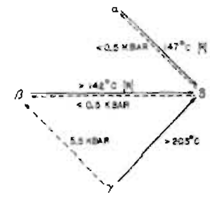


Figure 5. A summary of the temperature- and pressure-induced phase transitions of the α-, β-, γ-, and δ-polymorphs of HMX. The solid lines are transitions with slow heating (ref 1) and the dashed lines are transitions with pressure. (R) indicates reversibility with cooling.

Reference: LAMS-2652Studies on the polymorphs of HMX

***Author: Cady, H.H., Smith, Louis C., LANL**, Oct. 18, 1961.*

Reference: Brill, JCP 24 Aug 1978; vol.82, no.17, p.1912-1917

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Chemical Kinetic Model for Decomposition of HMX

β-HMX ⟷ δ-HMX

β-HMX + δ-HMX ⟷ δ-HMX

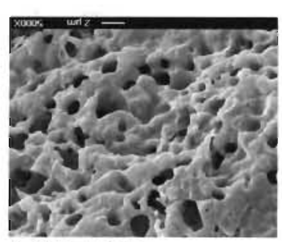
L. Smilowitz (Los Alamos)

δ-HMX → $4CH_2O + 4N_2O$
δ-HMX → $4HCN + 2NO_2 + 2NO + 2H_2O$

$CH_2O + NO_2 \rightleftarrows HCO + HONO$

$HCO + NO_2 \longrightarrow CO + HONO$

$HCO + NO_2 \longrightarrow H + CO_2 + NO$



R. Behrens (SNL)

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Focus on 1st step: solid-solid phase transition

- What we've done:
  - –Developed SHG probe as an instantaneous measure of the solid state fraction of beta and delta
  - –Used SHG in an imaging mode (SHG microscope) to make ansatz about mechanism of phase change: nucleation and growth
  - –Used integral SHG signal as measure of delta fraction
  - –Compare SHG observable to other observables: Raman, X-ray, DSC

- Results:

  A nucleation and growth model for the solid state phase transition with growth kinetics determined by thermodynamic properties of HMX and the nucleation kinetics empirically fit

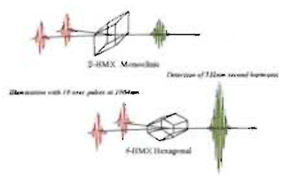
Experimental suite for solid-solid phase transition studies:

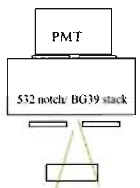
SHG microscope
Integrated SHG
Raman (in situ, post mortem)
FTIR (post mortem)
DSC (differential scanning calorimetry)
Temperature

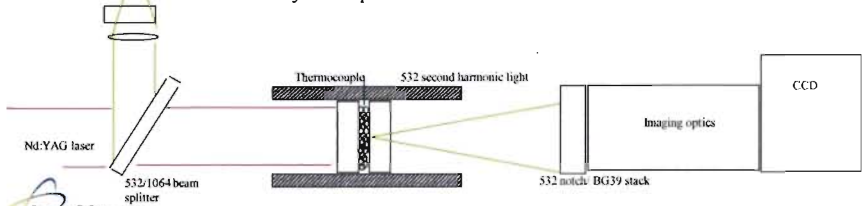
Detailed study of initial thermal decomposition steps via dynamic SHG microscopy of β–δ transition

SHG microscope developed in C-PCS images with contrast is generated by the SHG symmetry selection rules (only generated from noncentrosymmetric systems).

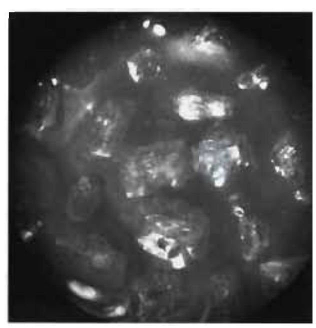
SHG in crystalline media has been a tool of chemical physics and optical spectroscopy for decades. We apply this technique as a dynamic probe of crystalline morphology by observing the dramatic change in harmonic efficiency from a polycrystalline material as a function of thermodynamic phase.







Crystal bed photos



Beta vs delta phase: white light images

Multi HMX crystal isothermal SHG microscopy

- go to AVI's

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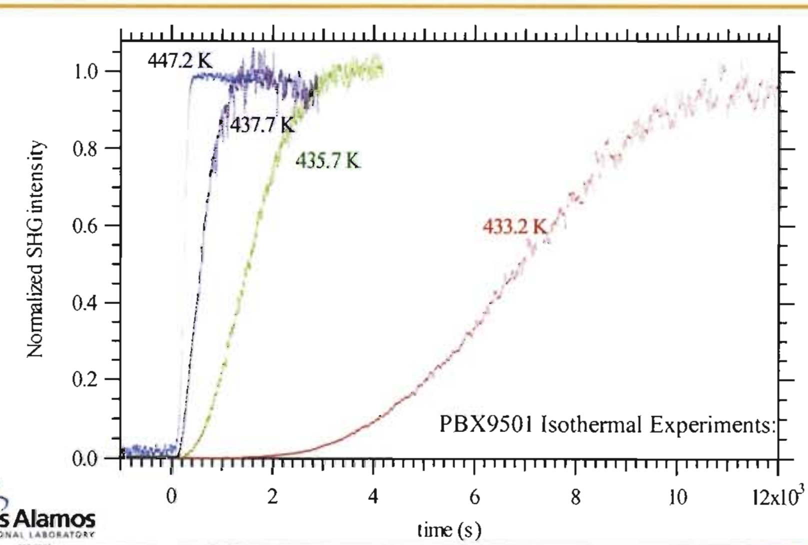
Integrated SHG Results



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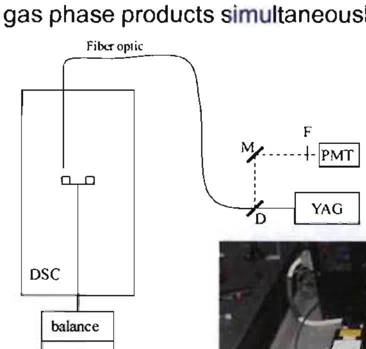
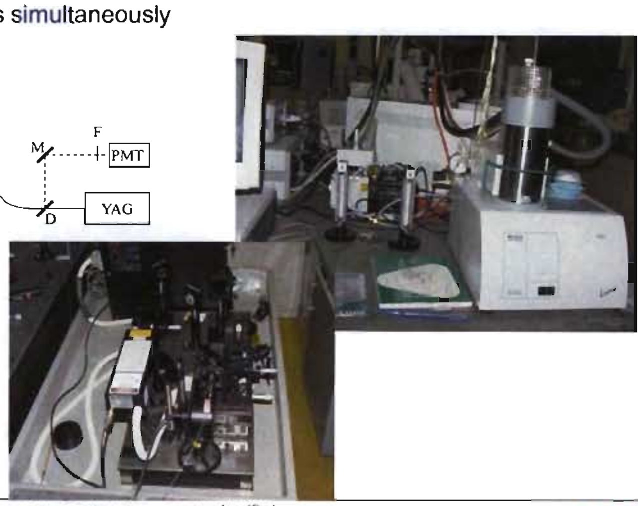
Comparison of observables

- There are inherent difficulties in observing solid to solid phase transitions- solids are heterogeneous and optically opaque, hindering observation.
- There have been confusing and contradictory reports with different kinetics reported depending on the observable- SHG vs Raman vs DSC vs X-ray vs dilatometry
- The goal of this study was to validate SHG as a probe of δ fraction, and understand the contradictions between observables

Experiment: DSC/TGA/MS: with SHG

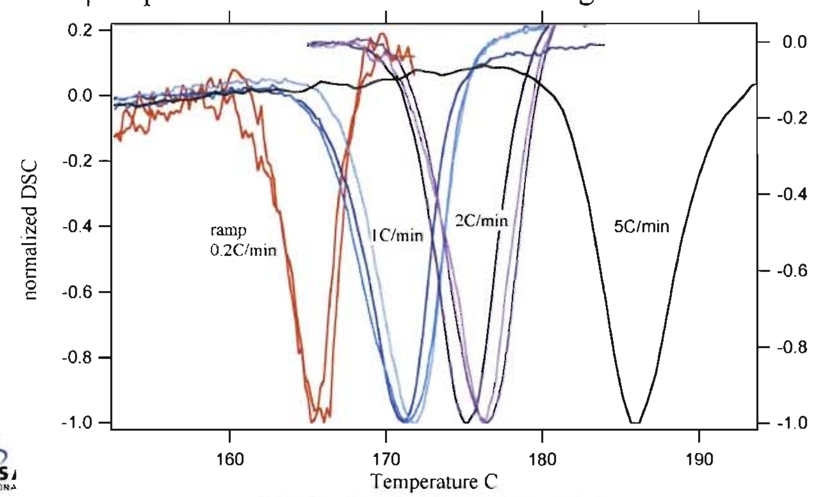
Goal- couple existing diagnostics to probe solid state lattice, solid to gas dynamics, and gas phase products simultaneously



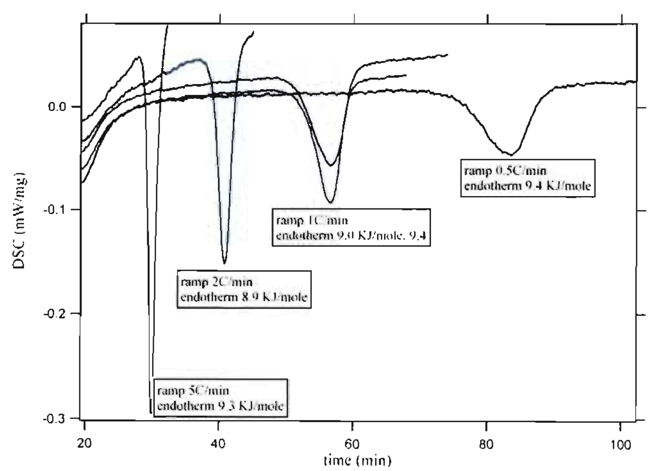


DSC results overview

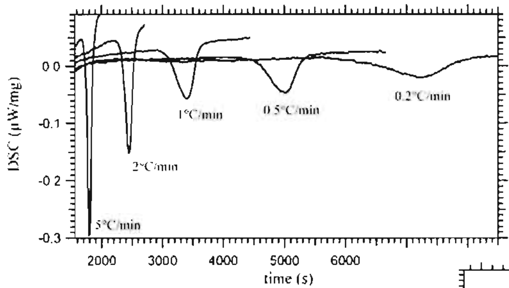
β–δ phase transition endotherm ~30 J/g ~9 kJ/mole

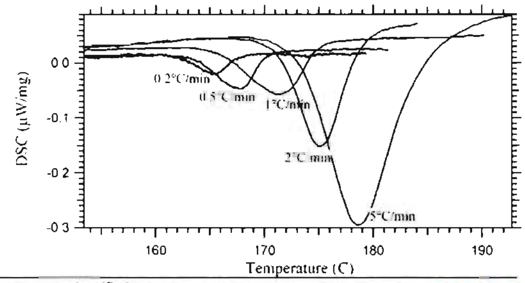


DSC



DSC vs time and temperature





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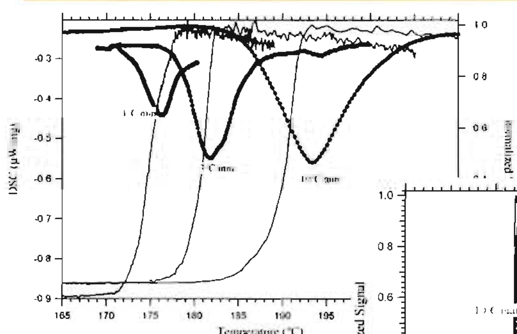
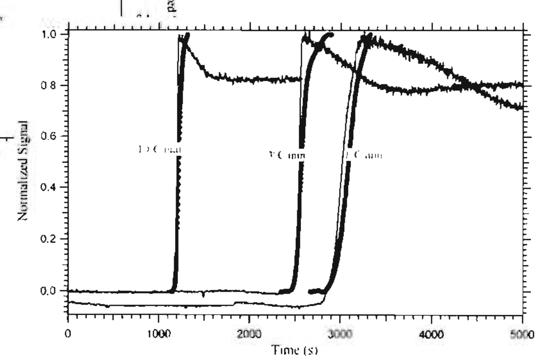
SHG vs DSC





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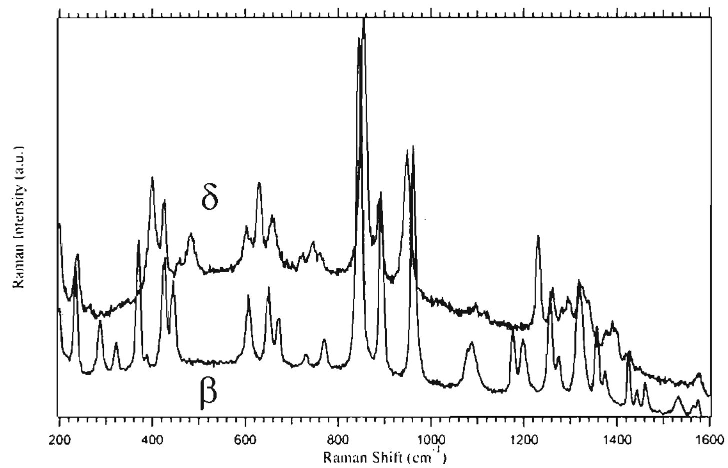
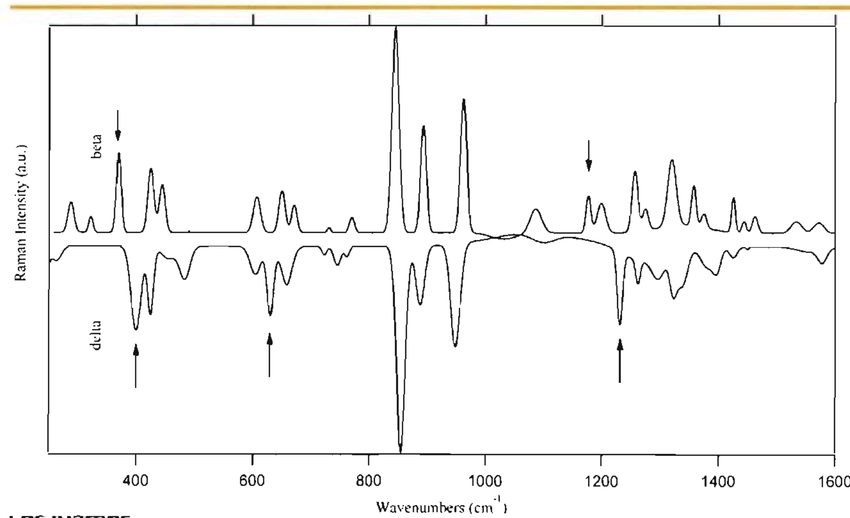
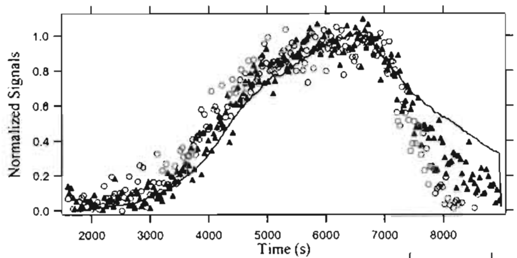
Raman

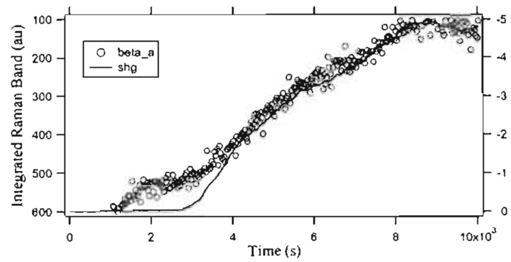


Raman baseline corrected



Raman vs SHG





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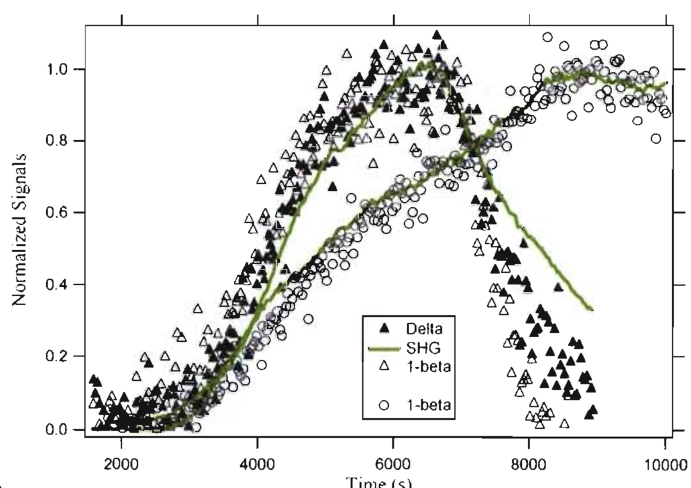
Raman/SHG



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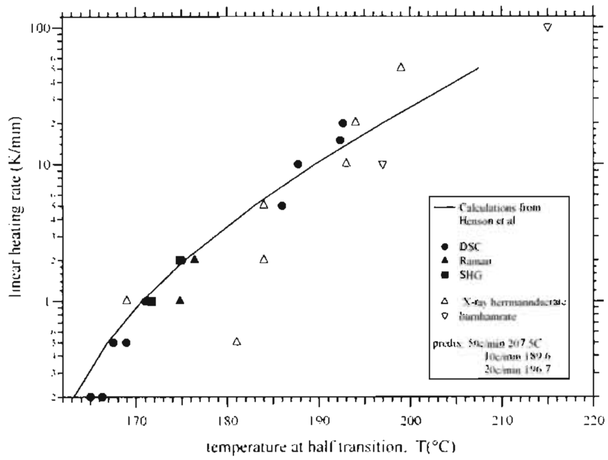
Raman/SHG/DSC vs model



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Conclusions on comparison of observables

- All are in agreement, *assuming* that the observable probes a representative volume element
- Relative advantages/disadvantages of each:
  - SHG- sensitivity, but it's a relative measure
  - Raman- lose sensitivity when do spatial integration, but can distinguish non-centrosymmetric phases. Hard to use as an absolute measure (baseline flourescence, change in optical properties)
  - DSC- not an integral measure, so less sensitive and rate dependent, but best for use as an absolute measure. There is a minimum conversion rate needed for observation (dependent on baseline thermal stability)

Smilowitz, L.; Henson, B. F.; Romero, J. J., Intercomparison of Calorimetry, Raman Spectroscopy, and Second Harmonic Generation Applied to Solid-Solid Phase Transitions. *JOURNAL OF PHYSICAL CHEMISTRY A* **2009**, 113, (35), 9650-9657.

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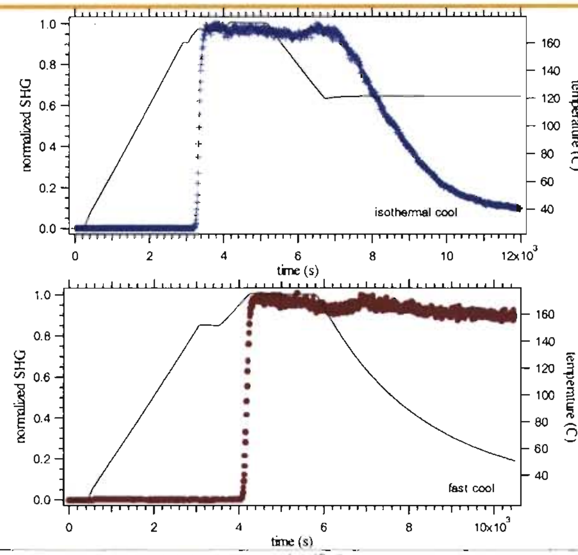
Controlling Reversion



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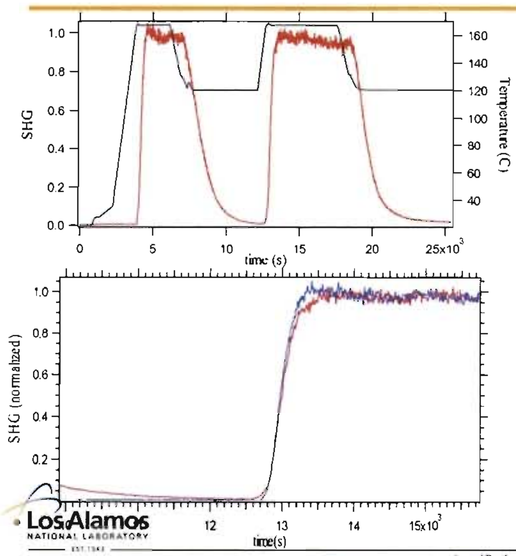
Reversibility of phase transition



Surface area does not change
SHG cycles with delta

Implies: not a SA effect
and, mechanical damage
does not significanly affect
kinetics

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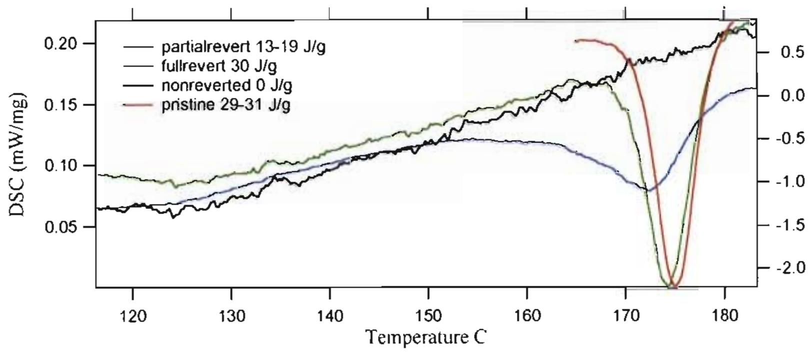
Reversion experiments



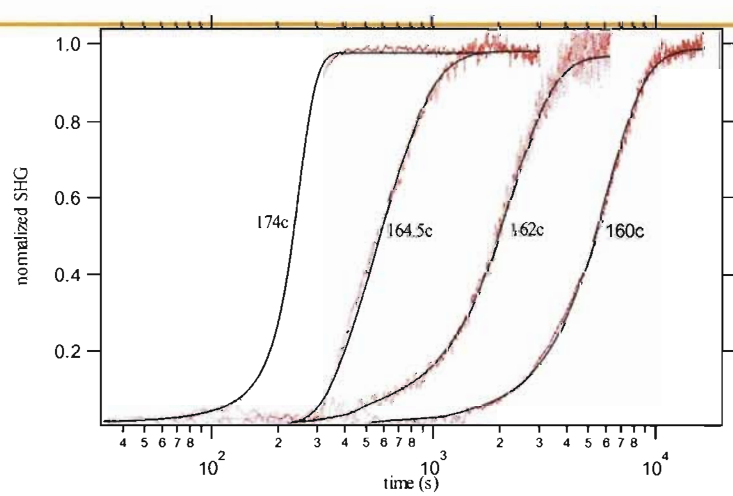
Seeded growth

Fully reverted β – same calorimetry as pristine β

Quenched δ – no endotherm

Therefore- we can separate polymorph phase from mechanical damage state

Kinetics



Kinetics of PBX9501

- Observe- reversible transition
- Sigmoidal kinetics
- Use reversible nucleation and growth model with Arrhenius rates and transition state for growth step= melt state
- determine thermodynamic parameters to fit forward reaction rates at different temperatures/ramp rates (feedback into larger scale experiments)

Model β-δ phase transition:

Coupled first order nucleation and second order growth

$$\beta\text{-HMX} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \delta\text{-HMX}$$

$$\beta\text{-HMX} + \delta\text{-HMX} \xrightarrow{k_2} \delta\text{-HMX}$$

$$\beta\text{-HMX} + \delta\text{-HMX} \xrightarrow{k_{-2}} \beta\text{-HMX}$$

Transition kinetics

$$\beta\text{-HMX} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \delta\text{-HMX}$$

$$\beta\text{-HMX} + \delta\text{-HMX} \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} \delta\text{-HMX}$$

Nucleation and growth rate law:

$$d\delta/dt = k_1\beta + k_2\,\beta{*}\delta - k_{-1}\,\delta - k_{-2}\,\beta{*}\delta$$

Where: $k_i(T) = kT/h \exp((T\Delta S^*-\Delta H^*)/RT)$

$= kT/h \exp(-\Delta G^*/RT)$

the rate is determined by the thermodynamic parameters of the transition state

Transition state= melt state

$\Delta G^* = \Delta G_{fusion}$

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β- δ phase transition: Parameters

Nucleation

Use temperature dependence to constrain first order component of mechanism due to lack of a known activation state

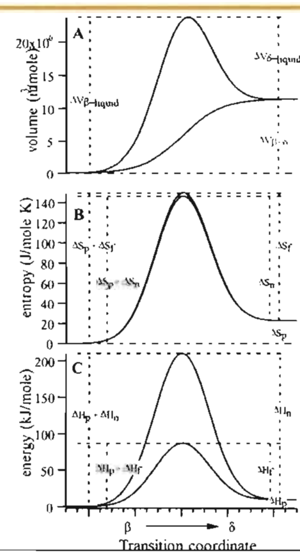
Data sets in agreement with literature values

(fit 2 parameters: E1, S1, V1)

Growth

Based on observations of Cady et al. and theoretical prediction: Assume that the growth mechanism is via melt and recrystallization. Therefore, energy of activation for growth step based on heat of fusion and β–δ energy difference

(thermodynamics determine E2, S2, V2, E-2, S-2, V-2, E-1, S-1)



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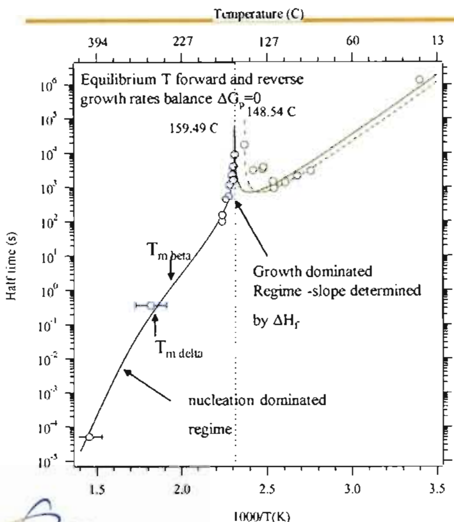
β-δ phase transition: Temperature extrapolation



Detailed study of phase transition kinetics involving SHG probe yielded "virtual melt" phase transition model

Ref- Levitas, Smilowitz, Henson, Asay, **PRL, JUN 11 2004**

$$t=\frac{2\left(Arctan\left(\frac{-(k_1+k_{-1})}{\sqrt{B}}\right)\pm Arctan\left(\frac{((k_1+k_{-1})+\beta_o(k_{-2}-k_2))}{\sqrt{B}}\right)\right)}{\sqrt{B}}$$

Plot of the transition 'half life' as a function of temperature

Kinetic data show slowing near the stability temperature of delta HMX and reflect regimes of temperature where the growth or nucleation process dominate the conversion rate.

Kinetic Model Summary

Rate controlled by an activation energy which is equivalent to the heat of fusion.

Balance of forward and reverse growth rates defines equilibrium temperature (cusp in half-time curve)

2nd order kinetics- acceleratory behavior due to dependence on interface between β–δ

2nd order kinetic component yields a 1st order thermodynamic transition

virtual melt state- activation energy = heat of fusion,

but phase transition is occurring at $T< T_m$

Theory by V. Levitas based on the lowering of the melt temperature for a region of local tension at the interface – solves many previously reported conundra

Levitas, V. I.; Henson, B. F.; Smilowitz, L. B.; Asay, B. W., Solid-solid phase transformation via virtual melting significantly below the melting temperature. *Physical Review Letters* **2004**, 11, (92), 235702-1

Levitas, V. I.; Smilowitz, L. B.; Henson, B. F.; Asay, B. W., Solid-solid phase transformation via internal stress-induced virtual melting: Additional confirmations. *Applied Physics Letters* **2005**, 87, (19), 1-3

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~~Smilowitz, L., B. F. Henson, et al. (2002). "The beta - delta phase transition in the energetic nitramine-octahydro-1,3,5,7-~~ tetranitro-1,3,5,7-tetrazocine: Kinetics." Journal of Chemical Physics **117**(8): 3789.

Levitas, V. I., B. F. Henson, et al. (2004). "Solid-solid phase transformation via virtual melting significantly below the melting temperature." Physical Review Letters **11**(92): 235702-235701.

Smilowitz, L., B. F. Henson, et al. (2004). "On the nucleation mechanism of the β-δ phase transition in the energetic nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine." Journal of Chemical Physics **121**(11): 5550-5552.

Levitas, V. I., L. B. Smilowitz, et al. (2005). "Solid-solid phase transformation via internal stress-induced virtual melting: Additional confirmations." Applied Physics Letters **87**(19): 1-3.

Levitas, V. I., L. B. Smilowitz, et al. (2006). "Interfacial and volumetric kinetics of the beta ->delta phase transition in the energetic nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine based on the virtual melting mechanism." Journal of Chemical Physics **124**(2): 025101.

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Levitas, V. I., B. F. Henson, et al. (2007). "Coupled phase transformation, chemical decomposition, and deformation in plastic-bonded explosive: Models." Journal of Applied Physics **102**(11): 113502.

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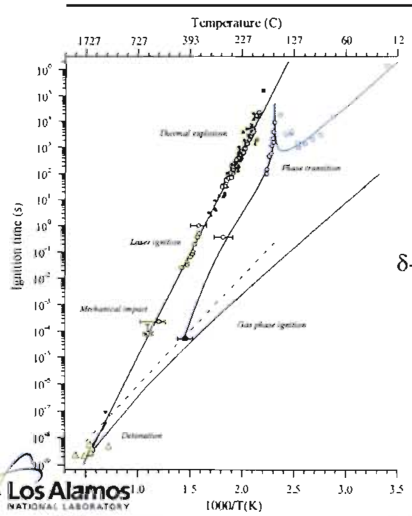
The phase transition and chemical decomposition



Solid state phase transformation

β-HMX $\longleftrightarrow$ δ-HMX

β-HMX + δ-HMX $\longleftrightarrow$ δ-HMX

Solid to gas decomposition

δ-HMX $\rightarrow$ $4CH_2O + 4N_2O$

δ-HMX $\rightarrow$ $4HCN + 2NO_2 + 2NO + 2H_2O$

Gas phase ignition reactions

$CH_2O + NO_2 \longleftrightarrow HCO + HONO$

$HCO + NO_2 \rightarrow CO + HONO$

$HCO + NO_2 \rightarrow H + CO_2 + NO$

Summary

- β–δ phase transition in HMX occurs via 2nd order nucleation and growth mechanism
- The rate of growth is controlled by the heat of fusion at a temperature 100C below the thermodynamically stable melt
- A virtual melt mechanism has been developed which explains this phenomenon
- SHG as a viable tool for studying solid state phase transitions has been validated against DSC
- Previously reported inconsistencies between various observables have been explained.
- Next: solid to gas step – radiography, TG/DSC under pressure?