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Author(s): Laura B. Smilowitz
Bryan F. Henson
Blaine W. Asay
Peter M. Dickson
Jeanne M. Robinson

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KINETICS OF THE β - δ PHASE TRANSITION IN PBX9501

L. B. Smilowitz, B. F. Henson, B. W. Asay, P. M. Dickson, J. M. Robinson

Los Alamos National Laboratory, Los Alamos, NM 87545

Abstract. The initial step in the thermal decomposition of HMX is the solid state phase transition from the centrosymmetric beta form to the noncentrosymmetric delta form. The symmetry change makes the phase transition amenable to the application of second harmonic generation (SHG) as a probe of transition kinetics. We have used SHG to study the temperature dependence of the kinetics for unconfined PBX9501 and HMX. Spatially resolved SHG measurements have shown a nucleation and growth mechanism for the solid state phase transition. We have measured the transition rate as a function of temperature in order to obtain the activation energy and entropy of transition, which determine the phase transition kinetics. Additionally, we have observed temperature dependent reversion of the delta phase to beta phase and have found that we can control the reversion rate by controlling the cooling.

INTRODUCTION

PBX9501 is based on the energetic material HMX, which is found to have four polymorphs, three of which are stable under various conditions of pressure and temperature[1]. The solid state phase of the material which is most stable at ambient temperatures and pressures is the relatively insensitive β phase [1]. The phase that becomes stable at higher temperatures and is the sensitive phase of the material is the δ phase [1]. Due to a change in the symmetry of the material during this phase transition, second harmonic generation (SHG) is a physical observable which is strongly correlated with the δ phase of the material and virtually nonexistent with the β phase[1, 2]. Thus, SHG provides a virtually instantaneous probe of the δ fraction with a nearly zero background generated by the β phase. This allows us to use SHG to measure the kinetics of the solid state phase transition as a function of temperature history of the material. Additionally, we have used spatially resolved SHG images to identify the transition mechanism as consistent with nucleation and growth of the new phase. By measuring the conversion rates as a function of temperature and using the rate equations for a nucleation and growth process, we are able to

model the full temperature dependent behavior of the transition kinetics. Using the transition state theory formulation for rates, we are able to fully define the kinetics of the transition based on independently measured thermodynamic parameters for the β - δ phase transition in HMX. The thermodynamic behavior shows how well we are able to predict the dependence on temperature for the transition time. The kinetics show how well the model predicts the details of the process. The qualitative dependencies of the reverse phase transition from δ back to β will be discussed.

EXPERIMENTAL

The experimental work presented here is based on an application of SHG as a probe for the phase fraction of δ -HMX. We have demonstrated the utility of SHG in this application in a previous letter[2]. We have shown the signal measured from HMX samples to have the narrow spectral distribution and square intensity dependence of an elastic χ^2 process[2]. We have not measured an absolute χ^2 efficiency. In these experiments, the SHG intensity is normalized to that from the fully converted sample and we use the progress from zero

to one as a measure of the transition from zero to 100% delta. The SHG is interpreted as being proportional to the square of the delta fraction present.

Materials and Methods

For this study, we have used PBX 9501 samples obtained by pressing molding powder made from 95% Holsten HMX with 2.5% estane and 2.5% nitroplasticizer by weight.

The experiments were conducted in a sample oven with optical access to allow uniform heating of the samples. Thermocouples are placed on the sample and oven to monitor and control the sample temperature. We have found that for heating rates of 5 K/minute or slower, radial gradients across the samples of less than ½ K can be maintained. The extreme sensitivity of the reaction kinetics on temperature makes this temperature uniformity essential. Heating profiles used are a 5 K/minute ramp to a temperature at which the phase transition can occur. The sample is held at that temperature to allow the transition to occur. Cooling is done at approximately 3 K/minute to 293C, or to a temperature below the delta phase stability temperature to allow phase reversion to occur.

The SHG microscope consists of a pulsed Nd:YAG pump laser with approximately 50 ps pulses at 1064 nm and approximately 10 mJ per pulse at 10 Hz repetition rate. The beam is very mildly focused onto the sample using a 1 m focal length lens. The sample is imaged by a microscope that is directly coupled to a low noise CCD. Filters are used between the sample and the microscope to insure that imaging shows only the 532 nm second harmonic light generated by the sample. Typically, SHG microscopy is performed in transmission through the sample. A magnification of 4.5x is used and the pixels are 24 micron squares yielding a pixel image size of ~5 microns on a side. Collection time per image varies from hundreds of milliseconds to tens of seconds depending on light level.

The total second harmonic light generated by the sample is monitored by a photomultiplier tube which measures the backscattered SHG from the sample. A small percentage of the laser intensity is split off and monitored to normalize out laser intensity fluctuations.

RESULTS AND DISCUSSION

An important result of this work comes from spatially resolved SHG imaging of the transition which indicates a nucleation and growth mechanism for the phase transition. The qualitative imaging observations are that the delta phase grows via nucleation and growth in HMX crystals. Initial nucleation occurs at one or two sites within a crystal and then growth of the delta phase propagates within the crystal from those sites. The spatially resolved nucleation and growth is not as clearly observable in PBX9501 due to its highly scattering nature, but the integrated SHG signal from PBX9501 has the recognizable sigmoid shape representative of a nucleation and growth process.

We have mapped out the kinetics of the phase transition as a function of the temperature history of the samples for a range of temperatures and heating rates. The rate equation for the reversible nucleation and growth of a new phase is:

$$\frac{\partial \delta}{\partial t} = k_1 \beta + k_2 \beta \delta - k_{-1} \delta - k_{-2} \beta \delta. \quad (1)$$

We have assumed a fully reversible nucleation and growth mechanism based on our observations of the reversion from δ to β phase upon controlled cooling of the samples. The rate constants from Eq. (1) are given by [2]

$$k_i(T) = e^{-\frac{k_B T}{h}} Q \exp\left(\frac{TS_i^* - (H_i^* + PV_i^*)}{RT}\right) \quad (2)$$

where $k_i(T)$ is a canonical rate constant in s^{-1} or $cm^3/mole \cdot s$, depending on reaction order, T the absolute temperature, k_B and h are Boltzman's and Plank's constants respectively, E_i^* , S_i^* and V_i^* are the activation energy, entropy and volume of the activated state, R is the gas constant and e is the base of the natural logarithm. Q is an equilibrium constant relating the concentrations of the activated complex to those of the stable reagent(s). The units of Q determine the concentration units in the problem, and vary according to the order of the reaction. By taking the transition state to be the melt state of HMX in accordance with experimental observations, we can base the rate constants for the growth step entirely on thermodynamic parameters for HMX that have been independently measured.

The nucleation rates have been determined by starting with values within the range cited in the literature for the thermodynamic parameters E_a and S and optimizing the best fit for the integrated rate law to a series of conversions at different temperatures [3].

The times for conversion as a function of conversion temperature are shown in Fig. 1. This figure compares the expected half time (time for 50% conversion) with the experimentally observed half times for approximately isothermally heated samples. The times are measured with time zero being the time at which the sample reaches 158C. At temperatures below 158C, the degree of conversion to delta phase would be negligible.

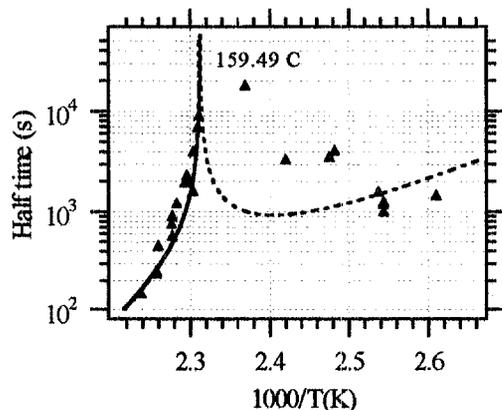


FIGURE 1. Compilation of measurements. All points are from measurements made by second harmonic generation. The data are plotted as the time to half conversion as a function of $1000/T(K)$, where $T(K)$ is the isothermal temperature. Both β - δ conversion and δ - β reversion data are shown (triangles).

As shown in Fig. 1, the model predicts the half time for conversion. What can be seen in Figure 2 is that it is also able to predict the detailed kinetics for the phase transitions quite well. We have made several simplifying assumptions in this model. Additional parameters which affect the kinetics but have not yet been included in our model include pressure effects and the third thermally accessible phase of HMX which is the noncentrosymmetric alpha phase. Other limitations of our model are that we have not identified the exact reversion mechanism and have made the simplifying assumption that the SHG is quadratically proportional to the delta fraction.

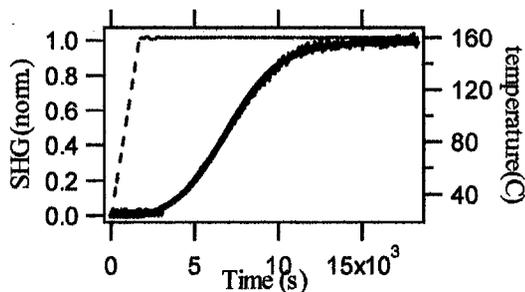


FIGURE 2: Fit of conversion data to model. The integrated SHG data are shown as points. The solid lines are optimized fits to the data using the integrated form of the rate law, and the dashed line is the temperature history.

We have also addressed the question of the stability of the delta phase. We have found that we can control the reversion to beta phase by controlling the cooling rate of the material. Figure 3 demonstrates the difference in phase behavior between a rapid cooling and a slowly stepped cooling process. FTIR spectra were taken to confirm the identifications of the final states as beta and delta. This demonstrates that the final phase of the material upon cooling back to room temperature is dependent on the cooling rate. From previous work on the phase diagram for HMX, we know that the thermodynamically stable phase at standard temperature and pressure is the beta phase [1, 4]. However, by rapidly cooling samples, we have kinetically trapped the material in its delta phase. This dependence on temperature history explains the wide range of previously reported stability times for the metastable delta phase upon cooling to room temperature.

The exact mechanism for the phase reversion is still not known nor is its dependence on physical parameters understood. However, the assumption of a reversible nucleation and growth mechanism allows us to predict forward going kinetics as well as to approximately predict the half times for reversion as a function of cooling. Understanding the reversion mechanism is important for addressing safety issues for explosives that have been heated to temperatures below ignition and then

quenched.

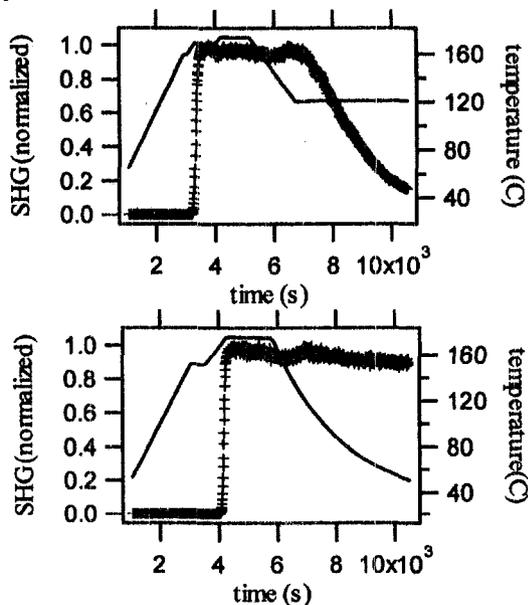


FIGURE 3. The dependence of reversion on cooling rate. SHG data (points, left axis) and temperature (solid curve, right axis) are plotted. In the top panel the temperature is raised to 174 C to generate conversion and then lowered to 121 C, leading to reversion. In the bottom panel the temperature is allowed to relax to room temperature..

By cycling a sample through the β - δ conversion, reversion back to β phase, and then a second conversion to δ phase, we can test the affects of irreversible work done during the initial conversion process on the phase transition kinetics. We found that we could fully revert the sample to β phase, confirming the source of the SHG as a volumetric phase transition and showing that the contribution to the SHG from the surface area generated by cracking the material does not have a significant contribution to the SHG signal. Also, the kinetics of the second conversion process closely match the original onset behavior implying that the nucleation and growth rates are insensitive to the degree of cracking of the sample as well.

CONCLUSIONS

We conclude that the beta to delta phase transition in PBX 9501 proceeds via nucleation and growth of the delta phase. It is a thermodynamically

first order phase transition whose kinetics are governed by a mixed second order reaction mechanism. Using the experimental observation of the transition state being the melt state, we are able to determine the governing rates based almost entirely on independently obtained entropies and energies [5]. These rate equations provide an excellent prediction for transition times as a function of temperature over a broad range of times and temperatures. The model additionally is able to predict the detailed kinetic behavior of the phase transition at each temperature. Observation of reverse delta to beta phase transitions upon cooling to temperatures below the delta phase stability point led us to use a fully reversible nucleation and growth model. While the thermodynamics predicted by this model approximately capture the reversion process, the details of the behavior are not captured. Further work is underway to understand the detailed mechanism for the reverse phase transitions. All work to date has been performed at atmospheric pressures. Future work will address the question of how pressure will impact the dynamics of the transition through the volume change between the phases.

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