

## Dynamic Observation of a Thermally Activated Structure Change in 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) by Second Harmonic Generation

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Using optical second harmonic generation (SHG) we observe, for the first time, a structural change in the energetic material (dry-aminated production grade) TATB (1,3,5-triamino-2,4,6-trinitrobenzene) upon heating. This structure change is verified by X-ray powder diffraction (XPD). The kinetics of this structure change are measured and are found to closely match commonly accepted thermal decomposition parameters for the first step, analogous to observations made for the  $\beta$  to  $\delta$  phase transition in HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). Consequently, these solid structure transitions appear to be coupled to the chemical decomposition mechanism or it may be the first physical process occurring. We apply this technique as a diagnostic to an ignition experiment. This experiment demonstrates that the structure change can be rapid (it is thermally activated) and that SHG can be used to indicate not only the solid structure change (large increase in SHG intensity) but also the onset to significant decomposition (subsequent drop in SHG intensity). The ability to selectively change the efficiency of the SHG, in a single piece of explosive, is also demonstrated and may have novel nonlinear optical applications. This application of SHG to TATB constitutes a fundamentally new probe in the dynamics of TATB decomposition, ignition, and combustion and may have application to optical integrated devices for frequency conversion and information encoding.

### 1. Introduction

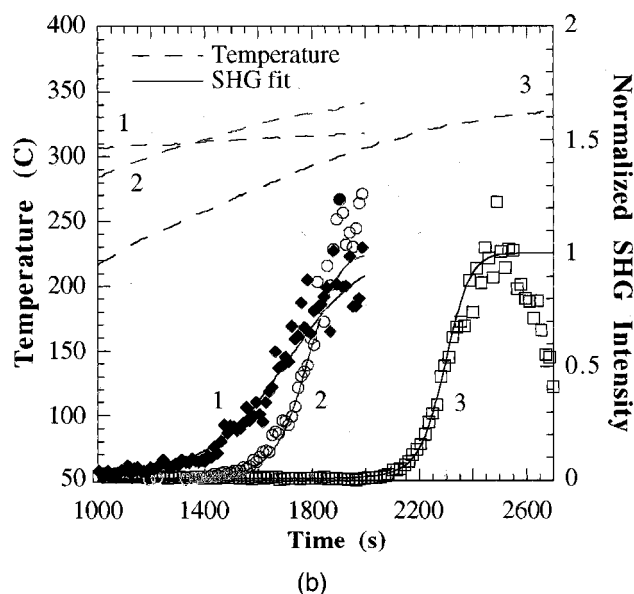
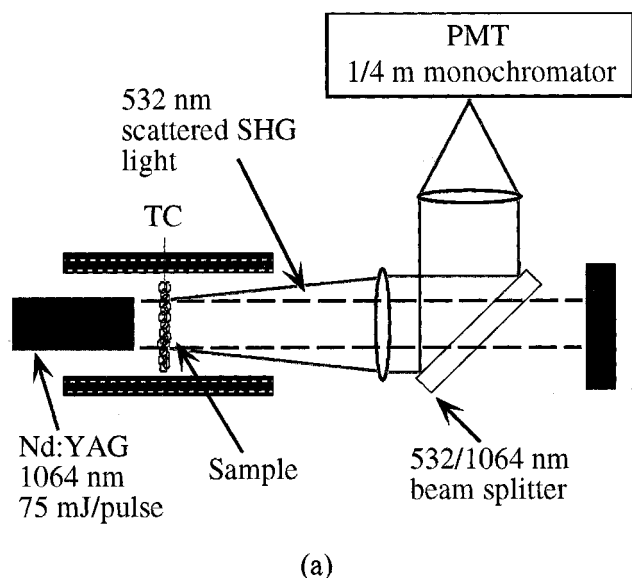
Recently there has been significant interest in the crystalline structure of TATB (1,3,5-triamino-2,4,6-trinitrobenzene).<sup>1–4</sup> This interest originated with the discovery of relatively strong second harmonic generation (SHG) efficiency<sup>4</sup> that is incompatible with the centrosymmetric crystal structure reported in the literature.<sup>5</sup> Our primary interest in TATB at Los Alamos National Laboratory (LANL) is in its use as an insensitive explosive.<sup>2</sup> Since a change in crystalline state can potentially affect the performance or safety of an explosive, it is critical that we understand its crystal morphology. For example, the sensitivity to impact of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) can increase significantly with the change from  $\beta$  to  $\delta$  polymorphs.<sup>6</sup> Consequently, the possibility that additional polymorphs or “structure changes” occur in TATB is of significant interest. The mechanism of “structure change” in TATB due to heating is explored here but is not fully understood. It is probably related to changes in mechanical and/or chemical structure. We are studying this material further to understand the structural change at an atomic level.

Given the observed SHG behavior, some have studied the optical properties of TATB, apparently with the ultimate aim of utilizing it in nonlinear optical applications.<sup>1–4</sup> It may seem odd to consider explosives for additional applications; however, this is common. Fortunately, TATB is extremely insensitive. It has a large failure diameter; therefore, in small quantities it cannot detonate. Transition to detonation from deflagration has not been observed with TATB. It has been shown that TATB

pellets will not sustain planar self-deflagration at pressures <10.3 MPa.<sup>7</sup> Commenting on its safety, Dobratz notes: “TATB is so insensitive to accidental ignition and initiation that it is now machined and drilled routinely without safety devices such as remote machining.”<sup>7</sup> Nevertheless, our main purpose in this paper is to explore the use of SHG as a diagnostic. SHG is a nonlinear elastic scattering phenomenon whereby the electronic structure of a material interacts with an incident laser field of frequency  $\omega$  through second-order components of the molecular polarizability tensor. This interaction results in the coherent generation of light at  $2\omega$ , the second harmonic. The generation of light by second-order processes is forbidden in a periodic medium possessing inversion symmetry and is accompanied by rigorous phase matching rules for momentum conservation in media without a center of symmetry.<sup>8</sup> Consequently, the presence of a relatively strong SHG in TATB<sup>4</sup> is unexpected given that the molecule is reported to be centrosymmetric.<sup>5</sup>

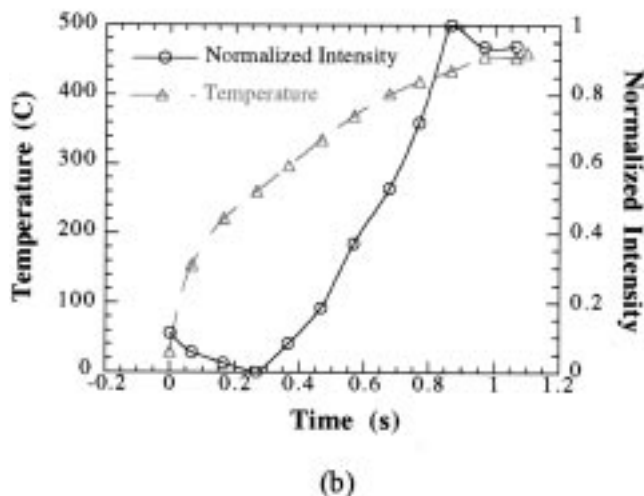
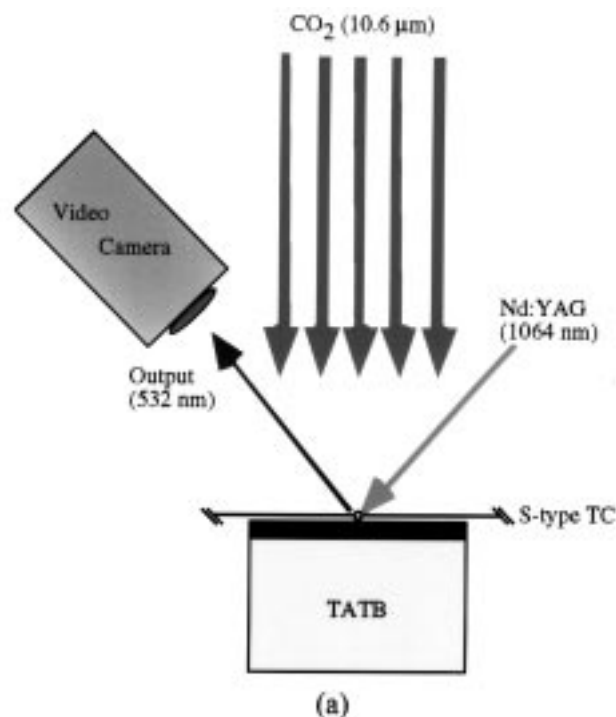
TATB has been studied for decades. Dobratz<sup>7</sup> extensively reviewed the development of TATB as an explosive. It was first synthesized as an intermediate over 100 years ago by Jackson and Wing;<sup>9</sup> however, extensive study did not begin until the 1960s. Modifications in the amination synthesis process significantly improved yield and particle characteristics.<sup>10</sup> Cady and Larson<sup>5</sup> first reported the crystal and molecular structures of TATB to be centrosymmetric, space group  $P\bar{1}$ ,  $Z = 2$ . In studies of the thermal expansion of TATB, Kolb and Rizzo<sup>11</sup> identified two other structures in TATB by X-ray crystallography that “are either actual polymorphs of TATB or impurities.” Interest in possible polymorphism in TATB appeared to wane until the relatively recent observation of highly efficient SHG in TATB,<sup>4</sup> which is incompatible with a centrosymmetric crystal structure. There is recent evidence that

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**Figure 1.** Slow heating experiment: (a) schematic showing the laser and detection apparatus used for slow heating and intensity calibration experiments, (b) data from slow heating of dry-aminated production grade TATB.

there may be polymorphism in TATB: one structure is centrosymmetric as originally identified and another type of crystal is noncentrosymmetric, which is responsible for second-harmonic generation.<sup>2</sup> In recent work at this laboratory, differences in the SHG efficiency between  $\beta$  and  $\delta$ -HMX were shown to provide excellent contrast for use as an in situ probe of the phase transition in dynamic experiments.<sup>12</sup> Values for the kinetic parameters, activation energy, and prefactor of the  $\beta$ - $\delta$  transition in HMX were shown to be very similar to those attributed to the first step(s) of chemical decomposition. There have been studies of TATB decomposition, but until this work, no suggestion has been made that the initial decomposition steps in TATB are coupled to, or preceded by, a structure change. Indeed, *no* structure change was anticipated to occur with heating. The primary focus of this study is an observed structure change with heating. This study was performed over a variety of heating rates, including the rapid combustion time scales of a laser ignition. Further work is suggested to fully address the crystallographic issues.

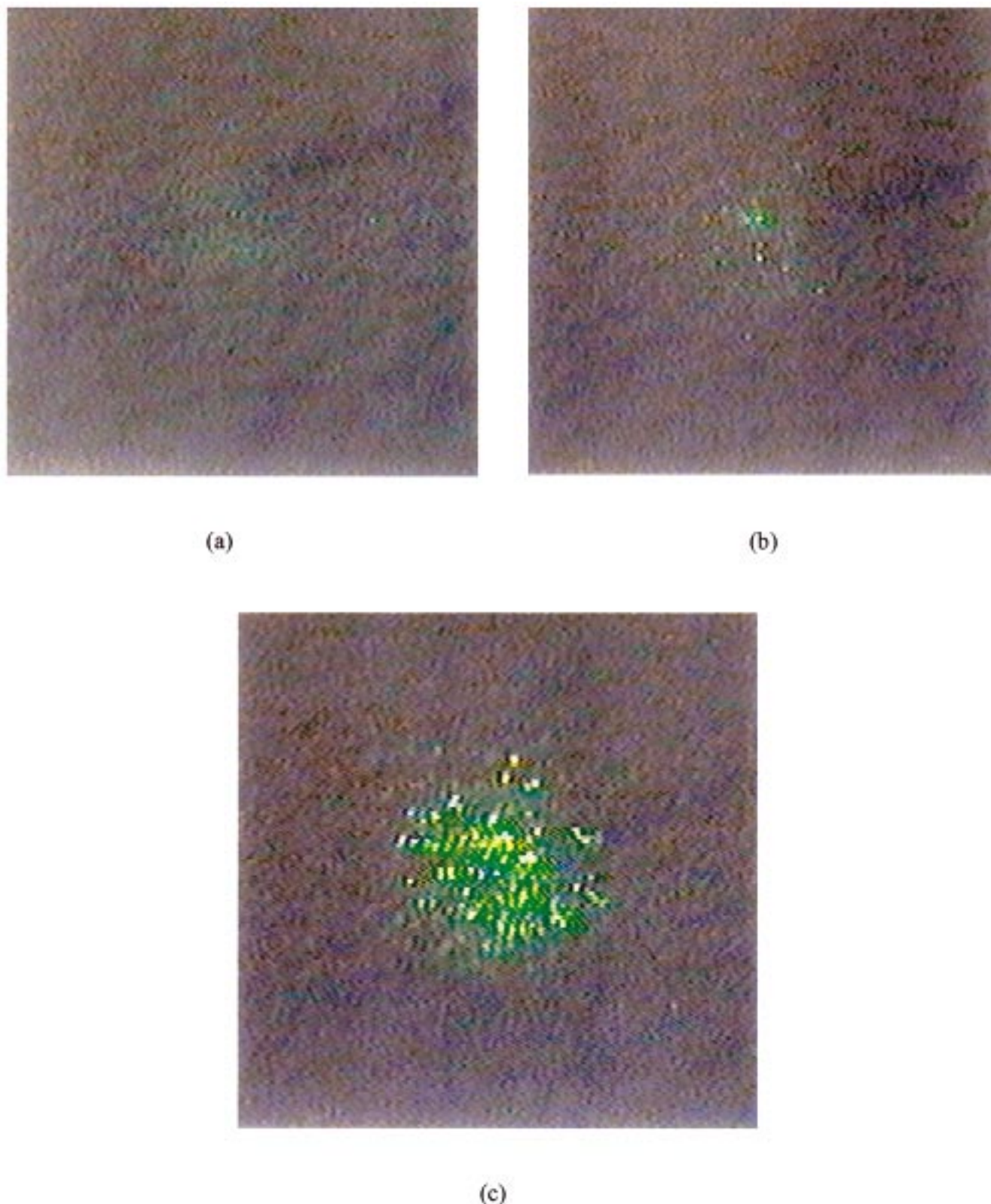


**Figure 2.** Laser ignition experiment: (a) schematic showing the CO<sub>2</sub> laser heating the entire pellet surface, with simultaneous 1064 nm illumination, (b) data showing the temperature rise and image intensity (averaged from video frames) evolution with time.

## 2. Experimental Methods

**2.1. Material Characterization.** The TATB studied was dry-aminated (production grade) TATB (lot 12-11-81-0921-264), unless otherwise stated. Other SHG studies have considered other grades of TATB, including recrystallized TATB. We have observed that recrystallized TATB grades tend to exhibit efficient SHG properties initially *without* heating and upon heating maintain significant SHG until significant decomposition occurs. X-ray powder diffraction (XPD) using an SCINTAG (Cupertino, CA) powder diffractometer with copper K $\alpha$  radiation was performed on TATB before and after heating. Microscopic analysis was also performed using a Leica DM RXA polarizing light microscope.

**2.2. Slow Heating Apparatus.** In the present work, SHG is observed both in transmission through a thin layer of powdered crystal and in reflection from the surface of a pressed poly-

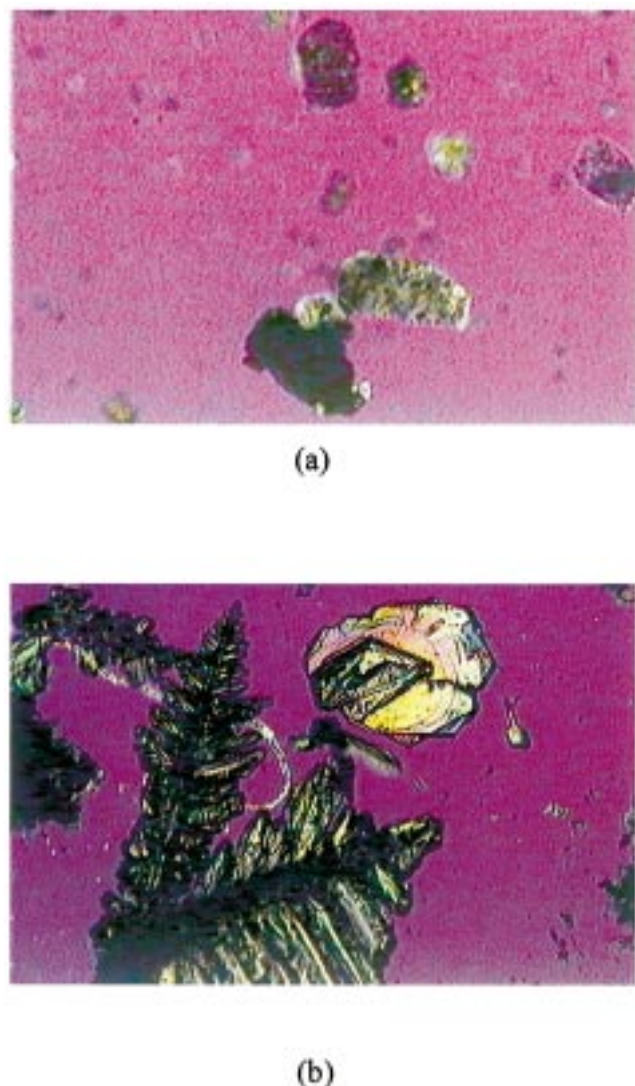


**Figure 3.** Observed SHG of powdered TATB on a hot plate: (a) initial SHG at room temperature, (b) SHG after 14 min of heating (320 °C plate temperature, ramping at about 20 °C/min), (c) SHG after 15 min of heating (340 °C plate temperature).

crystalline pellet or powdered sample. The experimental configuration for measuring the SHG cross section change in powdered TATB during slow heating is shown schematically in part a of Figure 1. Alternatively, a simple hot plate was used to heat the sample. Powdered crystalline samples of TATB were mounted as thin layers of powder between sapphire windows in a small cell. The particle sizes were in the range of 30  $\mu\text{m}$ ,

and the layer thickness was approximately 60  $\mu\text{m}$ . The cell was enclosed in an oven and placed in the optical path of a 10 Hz Nd:YAG laser delivering 10 ns pulses at 1064 nm. The delivered laser power varied from 10 to 100  $\text{MW}/\text{cm}^2$ . The SHG mechanism doubles the frequency of the fundamental to give a signal at 532 nm. Diffuse, forward scattering was collected over a solid angle of 5 steradian passed through a beam splitter that

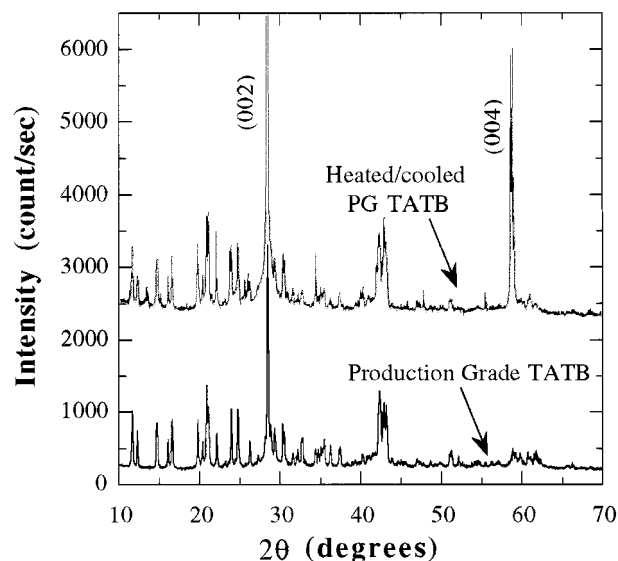




**Figure 4.** Morphologies of TATB crystals: (a) dry-aminated production grade TATB (mean particle size is about 30 microns), (b) TATB after heated near 310 °C (median particle sizes increase to hundreds of microns).

reflected only the 532 nm harmonic focused into a monochromator and detected with a phototube.

**2.3. Laser Ignition Apparatus.** The configuration used for the laser ignition experiments is shown in part a of Figure 2. In these experiments a pressed pellet of TATB is illuminated by the continuous output of a 10.6  $\mu\text{m}$   $\text{CO}_2$  laser directed normal to the surface. Again, 10 Hz Nd:YAG laser illumination was also directed to the surface; a color video camera was used to image the SHG at the surface. An indication of the intensity was obtained from the captured video frames. A 25  $\mu\text{m}$  diameter type S microthermocouple, centered on the pellet, was used to record the temperature during heating. Placing a thermocouple in the beam, without a sample present, quantified the interaction of the laser with the thermocouple. Heating of only a few degrees resulted for heating times and rates comparable to the laser ignition experiments considered. As the  $\text{CO}_2$  illumination commenced at  $t_0$ , the temperature rise was monitored until ignition in the gas phase approximately one second later. During heating, the SHG emission from the pellet surface was imaged at the video rate of 60 Hz.



**Figure 5.** X-ray powder diffraction of original dry-aminated production grade TATB and heated TATB.

### 3. Results

**3.1. Slow Heating Experiments.** Two types of slow heating experiments were performed. The first consisted of simply observing the change in SHG cross section of TATB powder on a hot plate (Figure 3). In this experiment, the hot plate was heated at approximately 20 °C/min to temperatures where a significant change in the SHG efficiency occurred. We have observed that certain grades of TATB are over 75 times more intense in SHG reflection (both materials pressed into pellets) than the common nonlinear optical material KDP ( $\text{KH}_2\text{PO}_4$ ). In contrast, production grade (PG) TATB initially exhibits relatively weak second harmonic generation. The material could be cooled at this point and the improved SHG efficiency was retained; otherwise, further heating yielded significant decomposition made evident by the darkening of the material. The temperature (measured using a thermocouple placed in an aluminum plate below the sample) and corresponding elapsed time are presented in the caption. Because of inevitable temperature gradients these results are not quantitative for the hot plate experiments.

Quantitative results were obtained with an experiment involving a thin layer of powder where the SHG is observed in transmission as previously described. The results of three quantitative slow heating experiments are shown in part b of Figure 1. The samples were standard production grade TATB, exhibiting a weak SHG signal detectable above background. The spectrum of SHG from the TATB was centered at 532 nm consistent with the elastic conversion of the 1064 nm input pulse to 532 nm. The data are plotted as the SHG intensity, normalized to maximum signal, on the right axis and the temperature (dashed lines) on the left, both as a function of time. The solid lines through the data are calculated (discussed later). The data points are the normalized SHG intensity values. The numbers denote the three different experiments performed, corresponding to different heating rates. A rapid jump in the SHG occurs at temperatures in the range of 320 °C. Upon further heating, the SHG signal decreases as significant decomposition occurs, as seen in experiment 3. Since decomposition is not included in the simple model considered here, the kinetic model discussed later does not replicate this decrease in SHG.

Figure 4 shows typical particle morphology from the initial and heated TATB. Initially, the TATB particles were spheroidal

with a median particle size near 30  $\mu\text{m}$ . Upon slow heating, the crystal size increased significantly and better ordered crystals were produced, including dendrite formation as shown in Figure 4, as well as well-formed hexagonal crystals that were transparent, and long transparent needles (only a few of the latter observed). This is consistent with observations by Catalano and Rolon<sup>13</sup> who also observed dendrites, hexagonal prisms, and a few long needles in TATB that had been heated to 324 °C. FTIR analyses of initial TATB and heated TATB (to about 310 °C and held for several minutes, then cooled to room temperature) were found to be essentially identical indicating little decomposition had occurred. The observed wavenumber range was 3800 to 800  $\text{cm}^{-1}$ . The heat-treated material did show a strong SHG in contrast to the original material that yielded relatively weak SHG. It does not appear that FTIR can be used to distinguish the structure change and that significant decomposition has not occurred upon heating to 310 °C.

X-ray powder diffraction (XPD) was conducted on both the initial and heated TATB samples. Figure 5 indicates subtle changes in the structure upon heating. At lower scattering angles the differences are relatively minor, but a significant difference occurs near 58° where a much higher peak is observed in the heat-treated material than is seen in the original material. One possibility is that this change in SHG efficiency is due to the formation of improved crystalline structure (e.g., the elimination of stacking faults) with heating. This would assume that the improved crystalline structure is not centrosymmetric. One might expect that grinding could disrupt such an ordering. However, significant mechanical grinding did not diminish the SHG, although it did pulverize the sample into a very fine powder. Another possibility is that perhaps the heating produces decomposition products dispersed throughout the TATB lattice causing small perturbations in the structure. This explanation would be consistent with the XPD results because a minor change is observed (e.g., no clear new lines appear). It should be noted, however, that efficient SHG has been obtained from recrystallized TATB and some other grades of TATB involving a sonicated amination process. Further, a recrystallized grade of TATB was heated and did not significantly change its SHG efficiency until significant decomposition occurred. It is not likely that recrystallization or the sonication process introduces decomposition products. With the current data it is not possible to say whether a new noncentrosymmetric polymorph is forming. An alternate possibility is that the second harmonic generation becomes allowed through a noncentrosymmetry produced by twinning. If heating produces decomposition gases which strain the crystal lattice, then the crystal might respond by producing a twin with graphitic layers rotated by 120°. The degree of twinning could be a sensitive function of the method of preparation of the TATB sample. In fact, Cady found that twinning was quite common in the recrystallized crystals he examined; his X-ray measurement results were reported for meticulously selected nontwinned crystals.<sup>14</sup> These issues are currently being pursued further.

In our opinion it is not likely that decomposition products directly could explain these results, without consideration of possible perturbations of the structure caused byproduct formation as discussed above. First, very little decomposition has occurred near 300 °C since it was not observed with FTIR. Catalano and Rolon<sup>13</sup> showed that virtually no decomposition takes place at temperatures as high as 357 °C; although there is some evidence for decomposition at lower temperatures near 300 °C. Second, SHG requires the interaction of the radiation field with an ordered crystalline structure, which is necessarily

destroyed with significant decomposition. Third, the monofurazan decomposition intermediate<sup>16</sup> 3,5-diamino-4,6-dinitrobenzofurazan shows very weak SHG. Also, the difurazan decomposition intermediate<sup>16</sup> 5-amino-6-nitrobenzodifurazan does yield some SHG but could not *directly* account for the strong SHG observed, especially in dilute concentration within the TATB powder. Another important question is whether surface SHG could explain the observations made. Grinding wet or dry-aminated TATB (specifically, "ultrafine" and "superfine" grades of TATB) appears to have very little affect on the SHG efficiency (factors of about 3, at most). In contrast, the change in SHG efficiency upon heating is about 2 orders of magnitude. Further, as noted elsewhere in this paper, grinding heat-treated TATB does not diminish the SHG efficiency significantly. Further, large (about 500  $\mu\text{m}$ ) well-formed crystals have been observed to exhibit efficient SHG. This evidence indicates that the observed changes in SHG with heating are not likely attributable to a surface area effect. Although further work may elucidate the detailed changes in the structure, this is beyond the scope of the present paper. However, the SHG and XPD results clearly indicate a structure change *is* occurring. Filippini and Gavezzotti<sup>3</sup> showed by potential energy calculations that two noncentrosymmetric (P1) crystal structures are energetically similar to the one with  $P1$ ,  $Z = 2$ , and that liberation or reorientation of the whole molecule in its plane within the crystal may be possible, *especially at high temperatures*.<sup>15</sup> In HMX it has been demonstrated that the phase change between  $\beta$  and  $\delta$  is thermally activated. It is of interest to analyze the kinetics of this structural change in TATB as well.

If one considers the normalized SHG intensity, scaled to vary from 0 to 1, as proportional to the mole fraction of the new state, which we will refer to as  $\beta$ , these data may be modeled using various simple kinetic rate laws. Growth of one crystalline state at the expense of another may occur at the interface between the two. This can be modeled by the following rate equation which is first order in the concentrations of each of the two states  $\alpha$  and  $\beta$ , where  $\alpha$  is the original state of the TATB and  $\beta$  is the state formed after heating.<sup>12</sup>

$$\frac{dc}{dt} = k(a_0 - c)(b_0 + c) \quad (1)$$

The subscript "0" indicates initial concentrations,  $t$  is the time and  $k$  is an Arrhenius rate expression,  $k = Ae^{-E_a/RT}$ . Scaling eq 1 by  $\alpha_0$  yields,

$$\frac{dx}{dt} = k(1 - x)(f + x) \quad (2)$$

where  $x$  is  $c/\alpha_0$ , and  $f$  is the initial ratio of  $\alpha$  to  $\beta$ ,  $\alpha_0/\beta_0$ . The normalized SHG intensity may be expressed as a function of  $x$  and a constant,  $\epsilon$ , which is the ratio of SHG intensity of the initial material to that of the heated material,  $I_{2\omega}/I_{2\omega}^{\text{max}} = (\epsilon(1 - x) + x)^2$ . The solid lines in part a of Figure 1 for each data set were calculated by numerically integrating eq 2, utilizing  $E_a$ ,  $A$ , and  $f$  as fitting parameters. The optimized parameters were  $E_a = 63(0.4)$  kcal/mol,  $A = 6.3(4.5) \times 10^{20}$   $\text{cm}^3/\text{g s}$  and  $\log(f) = -1.1(0.2)$ , where the standard deviation at 95% confidence is in parentheses. These parameters are very close to those measured or assumed for initial TATB decomposition, which is generally assumed to be first order. Rogers<sup>16</sup> measured an activation energy of 60 kcal/mol for the early endothermic step(s) in the Henkin test. Catalano and Crawford conclude that the activation energy for the first decomposition step is 50–60 kcal  $\text{mol}^{-1}$ .<sup>18</sup> Tarver et al.<sup>19</sup> assumed an activation



energy of 60 kcal/mol and a prefactor of  $7.02 \times 10^{20} \text{ s}^{-1}$  in the first decomposition step of their reaction model. The data in this paper represent the first observation of this structural change in TATB with slow heating, as indicated by both SHG and XPD. Laser ignition experiments were performed to determine if this change could occur with much faster heating rates (i.e., combustion time scales).

**3.2. Laser Ignition Experiments.** Part b of Figure 2 shows the temperature rise and average SHG image intensity (averaged from captured video frames) as a function of time during a typical ignition event. The applied laser flux was  $33 \pm 3 \text{ W/cm}^2$ . Ignition, as indicated by photodiode, occurred at 1.1 s. Images were captured by video and the average intensity obtained from image files. The data show a surface heating profile consistent with that observed in many laboratories.<sup>20</sup> A measurable SHG change first appears at approximately 500 ms. This change of SHG indicates the initial structural change of TATB near the surface that is induced by the temperature increase. The intensity likely depends on the depth of the structural changes in the spatially inhomogeneous temperature field and nonuniformities of the  $\text{CO}_2$  beam, as well as the extent of transformation. Consequently, the SHG intensity measurements, as used in these experiments, are viewed as qualitative or at best semiquantitative. However, from the averaged intensity of the video images, we can determine a time to transition (from start of experiment) of  $520 \pm 100 \text{ ms}$  at a surface temperature of  $355 \pm 30^\circ\text{C}$ . The transition time is roughly  $354 \pm 100 \text{ ms}$ . Using the kinetic parameters above and the measured surface temperature, 90% of the final intensity is calculated to occur at 870 ms. This compares well with the peak intensity observed (see Figure 2). In addition, after the solid structural change, we observe the onset of significant decomposition at the surface approximately 140 ms prior to ignition. The decomposition (darkened material) results in the loss of SHG (indicated by a drop in average intensity in part (b) of Figure 2).

These data represent the first observation of a structural change in TATB during a *dynamic* ignition experiment. Observation of the transition over such a wide range of temperature and time require consideration of this transformation as an important step in TATB decomposition, as has been suggested for HMX.<sup>12,21</sup> Indeed, the kinetics observed in this work implicate the transformation as a rate limiting process in decomposition. It is likely that this transformation is a function of pressure as well. For example, Foltz<sup>22</sup> observed breaks in measured reaction propagation rates measured in diamond anvil cells that were postulated to be attributable to high pressure phase transitions. Color changes were also observed as pressure was applied. The structure change proposed by Foltz appears to be more substantial than what appears to be occurring with heating based on XPD results; however, more work is needed to elucidate these issues further.

Other problems in energetic materials may now be amenable to investigation with this probe. In combination with standard analytical characterization techniques, SHG can be used to dynamically probe crystal transitions in situ. For example, this technique could be used to dynamically study the formation of localized heating ("hot spots") in energetic materials formed in impact experiments, which would verify this structural change under even shorter time scale dynamic conditions. These experiments are currently being performed. Also, nonintrusive post mortem determination of the surface spatial distribution of structural domains from a sample subjected to complex temperature and pressure environments are now possible with this technique.

**3.3. Selective Structural Change.** After heating induces the structural change, the material remains in that state upon cooling. Reversion to the initial condition has not yet been observed over a span of months. We have demonstrated selective crystal change in a pressed sample. Controlled localized heating (irradiated using a  $\text{CO}_2$  laser) of a pressed pellet of TATB was used to selectively change areas of a sample without visibly damaging the sample. Upon illumination with the Nd:YAG at 1064 nm, efficient SHG in the green at 532 nm appeared in the heat-treated areas. The difference in intensity between the heat-treated and unheated regions was observed to be very large. This ability to selectively change the efficiency of the SHG in TATB in a single pressed sample may possibly have novel nonlinear optical applications.

## 4. Summary and Conclusions

Using optical SHG we observe, for the first time, a structural change in dry-aminated production grade TATB upon heating. This change is verified by XPD, although the change appears to be subtle, such as possible reorientation of the molecule in a plane or twinning. Noncentrosymmetric crystal structures have been shown to be energetically similar to the standard centrosymmetric structure.<sup>1,3</sup> In fact, it has been argued that mixtures of polymorphs generally exist in TATB and that the noncentrosymmetric polymorph is responsible for the efficient SHG.<sup>2</sup> Consequently, it is possible that batch variations in the relative concentrations of these coexisting polymorphs occur. If the structural condition affects detonation performance of TATB, this has obvious importance to the consistent use of this explosive. Preliminary results indicate some correlation between SHG efficiency of some grades of TATB and detonation performance. This will be further explored and reported elsewhere. The kinetics of this change are measured and are found to closely match commonly accepted thermal decomposition parameters, analogous to observations made for the  $\beta$  to  $\delta$  phase transition in HMX.<sup>12,21</sup> Consequently, these solid transitions appear to be critically coupled to the chemical decomposition mechanism, and may be a first step in the mechanism. These unanticipated results, combined with the previous observations with HMX, require further investigation to understand the underlying mechanisms in detail.

We applied the SHG diagnostic to dynamically observe an ignition experiment. This experiment demonstrates that the structural change is thermally activated and that SHG can be used to indicate not only the rapid change (large increase in SHG intensity) but also the onset to decomposition (subsequent drop in SHG intensity). There are various applications of SHG in the study of ignition and combustion of TATB research that can now be pursued. Further, the rapid heating of thin (homogeneous) samples, similar to what is commonly done in the decomposition studies, would yield more quantitative results.

The ability to selectively change the efficiency of the SHG in a single piece of explosive was also demonstrated and could possibly have novel nonlinear optical applications. TATB is an explosive, but it is extremely insensitive and is virtually impossible to detonate unintentionally.<sup>7</sup> Consequently, it could possibly be considered in nonexplosive applications, such as optical integrated devices (e.g., frequency conversion and information encoding), since some grades of TATB exhibit efficient SHG properties (significantly better than KDP in reflected intensity).

This application of SHG to TATB constitutes a fundamentally new probe in the dynamics of TATB decomposition, ignition, and combustion. This discovery of thermally activated structural

change in TATB has also raised many issues, including the importance of improving our understanding of the possible crystalline states and the correlation of those states with detonation performance.

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