Spectroscopic Characterization of Subsurface Thermal Degradation of Eu:Y(acac)3(DPEPO) in an Opaque Medium Using Wavefront-shaping Assisted Bidirectional Focusing

Benjamin R. Anderson (branderson@wsu.edu)  
Washington State University

Natalie Gese  
Washington State University

Hergen Eilers  
Washington State University

Research Article

Keywords:

Posted Date: June 7th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1720456/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.  
Read Full License
Spectroscopic Characterization of Subsurface Thermal Degradation of Eu:Y(acac)$_3$(DPEPO) in an Opaque Medium Using Wavefront-shaping Assisted Bidirectional Focusing

Benjamin R. Anderson$^1$, Natalie Gese$^1$, Hergen Eilers$^1$

Applied Sciences Laboratory, Institute for Shock Physics, Washington State University, Spokane, WA 99210-1495

Received: date / Revised version: date

Abstract We characterize the subsurface thermal degradation of an inert analogue of energetic molecular crystals (Eu:Y(acac)$_3$(DPEPO)) using a wavefront-shaping assisted bidirectional focusing microscope. This microscope provides the capability to focus inside of a heterogeneous material and measure both Raman and fluorescence spectra during thermal degradation. From these measurements we find that embedding the molecular crystal in the polymer results in improved thermal stability as the polymer acts to constrict the effects of melting, which is the primary mechanism for spectroscopic changes for this material in the temperature range explored. Additionally, we identify a significant challenge in the microscope with regards to signal arising from out of focus guidestar particles and scattering particles. To address this issue we propose the use of spatial filtering of the output signal to remove unwanted signal while keeping the in-focus signal.

1 Introduction

Plastic bonded explosives (PBXs) and some novel propellants consist of energetic molecular crystals mixed into polymer hosts along with additional additives (e.g., grit, antioxidants, taggants, plasticizers). This heterogeneity results in these materials being optically opaque, which limits traditional spectroscopic characterization techniques to probe only the surface of these materials. However, many chemical
reactions of interest are believed to occur in the bulk of the material [1], which means there is a need for an optical technique that can perform subsurface spectroscopy in these materials.

To address this need we have developed a novel microscope that uses wavefront-shaping to focus light through both the top and bottom surfaces of a heterogeneous material onto a fluorescent guidestar particle, which we call the Bidirectional Focusing Microscope (BFM) [2,3]. The BFM focuses inside of heterogeneous materials using the feedback-assisted wavefront-shaping (FAWS) technique, which involves using a spatial light modulator (SLM) and an optimization algorithm to modulate the phase of light incident on a heterogeneous material such that an optical feedback signal (fluorescence imaging of a buried guidestar for the BFM) is optimized [4]. This technique was first demonstrated in 2007 to optimize transmission through an opaque sample [5] and since then has been applied to numerous other feedback signals such as reflection [6], Raman scattering [7,8], fluorescence imaging [9–11], photocurrent [12], and non-linear optical signals[13–18].

To demonstrate the BFM’s sub-surface spectroscopy capabilities we have developed an organic molecular crystal (Eu:Y(acac)$_3$(DPEPO)) (EYAD) [19], which acts as an inert analogue to the energetic crystals in PBXs so that we could test the BFM’s capabilities safely. To accomplish this we first characterized EYAD’s photo- and thermal-degradation in air [19], with the next step being to measure both degradations when EYAD is embedded inside of a polymer. We have already done this for photodegradation in our initial report on the technique [2], but have now completed these measurements for thermal degradation, which is a significantly faster reaction than photodegradation (minutes versus hours). In this study we report on the results of these subsurface thermal degradation measurements.

2 Methods

The construction and operation of the BFM is described in detail in Ref’s [2] and [3], but described briefly it consists of a laser (Coherent Verdi V10), two spatial light modulators (Meadowlark 512 x 512), two long working distance objectives (Mitutoyo M Plan Apo HR 50x, 0.75 NA, 5.2 mm WD), a camera (PI-Max 4 ICCD 1024i, SB Phosphor), a fiber coupled spectrometer, and various mechanics and optics for positioning and beam control. See Figure 1 for a schematic of the setup.

The laser beam is split into two arms which are spatially filtered and expanded before being reflected off of an SLM and focused through two counter-propagating confocal objectives onto the sample. Sub-
surface focusing is performed by first optimizing the sample’s spatial alignment such that a fluorescence image obtains the brightest and most “in-focus” spot for a target subsurface guidestar particle. Once this initial spatial optimization is complete we next performed wavefront optimization using a genetic algorithm [20,21] with intensity feedback from fluorescence imaging.

To make our samples we first prepared a slurry of EYAD in THF using sonication, which was when applied to 50 mm long 36 gauge (0.19 mm) copper wires. Once dried, we placed several of these wires across a 3” × 1” glass slide and drop cast Epo-Tek 305 polymer with dispersed sugar at a concentration of 50 wt%. The resulting films were ≈ 350 μm thick with a scattering mean free path of 65 μm. As the EYAD crystals are on the surface of the wire and the wire is placed at the bottom of the sample, the resulting target depth is ≈ 160 μm. For further information on synthesis of EYAD and preparation of the sugar/polymer solution see References [19] and [2], respectively.

3 Results

The first step in our experiment is to focus onto a guidestar particle located on the wire to be our spectrally-monitored target during heating. To accomplish this we perform subsurface focusing using the BFM with only the reflective arm active. Note that we do not use the transmissive-arm as we find that its pump light is effectively blocked by the wire and does not contribute to the guidestar particle’s fluorescence image. Figure 2 shows example fluorescence images for flat field and optimized illumination.
Fig. 2: Fluorescence images of EYAD particles on wire embedded in heterogeneous sample for flat (a) and optimized (b) wavefront.

with the peak optimization found to be $\approx 4 \times$. Note that while there are multiple guidestar particles visible, our target region is the brightest flat-field spot located near (140, 70).

Having optimized the target’s fluorescence image, we next measure its’ fluorescence spectrum for both the flat field and optimized field, which are shown in Figure 3. From Figure 3 we find that the fluorescence spectrum displays significantly less enhancement than the images in Figure 2 ($\approx 1.333 \times$ vs $\approx 4 \times$). This reduced enhancement can be attributed to spectral measurements averaging over both the target particle and nearby “unoptimized” particles, which results in a smaller enhancement. Note that this was not a significant issue in our previous subsurface spectroscopy measurements where the guidestars were dispersed throughout the heterogeneous sample [2], which lead to the guidestars being spaced farther apart than in the current case of EYAD placed on a wire.

For the purposes of this study this effect is not much of an issue as all of the fluorescence is originating from buried particles on the heating wire such that all of our signal is coming from particles undergoing subsurface heating. However, in future work it may be desirable to optimize signal from a single particle, while minimizing unwanted signal from nearby particles in order to understand spatially varying chemical reactions. A possible modification to the BFM to accomplish this is the addition of a spatial filter in the signal path, such that the target signal passes through, but the out of focus signal is blocked [22, 23].
Fig. 3: Comparison of measured fluorescence spectrum for flat field and optimized field illumination. Note that the enhancement is less in the spectral response due to the presence of adjacent EYAD particles.

Fig. 4: Background subtracted subsurface PL spectra (a) and normalized spectra (b) during heating run.

Once we have used the BFM to focus inside of the heterogeneous material we next performed heating experiments. Note that we performed four heating experiments and found consistent results between all four. The heating experiments were performed as follows: first we started the optimization program, which ran throughout the heating run to maintain focus on the target guidestar the entire time. Next we slowly ramped the DC voltage up such that the resulting heating profile consisted of a linear ramp from 293 K to 612 K with a heating rate of 3.5 K/s followed by the power being cut off. During this time we measure both the fluorescence and Raman spectrum, with Figure 4 showing the fluorescence spectra and Figure 6 showing the Raman spectrum.
From Figure 4a we find that the overall fluorescence intensity decreases as the temperature is increased with the rate of change increasing above 400 K. We attribute this initial slow decrease to thermal quenching and the faster decrease to the EYAD melting as its melting point is near 400 K [19]. Additionally, to better show the shape of the spectrum during heating, we plot normalized spectra in Figure 4b, from which we find that as the temperature increases the spectra broaden.

Both the decreasing intensity and spectral broadening were observed in the bare wire case [19], but to a greater extent than observed for the embedded wire. To compare the two cases we plot both the peak intensity and effective “peak” width of the $^5D_0 \rightarrow ^7F_2$ transition in Figures 5a and 5b, where the effective peak width is defined as

$$w = \frac{1}{I_{\text{max}}} \int_a^b d\lambda I(\lambda),$$

(1)

with $I_{\text{max}}$ being the maximum intensity and the integration range is 600 nm to 625 nm.

Comparing Figures 5a and 5b, we find that below 400 K the embedded wire’s fluorescence intensity decays more quickly than the bare wire, but above 400 K the situation flips with the bare wire’s peak intensity decreasing more rapidly than in the embedded case. Additionally, for the effective peak widths, we find that below 400 K both cases display slow spectral broadening (due to thermal effects), while above 400 K the widths begin changing more rapidly due to the EYAD melting, with this effect far more pronounced in the bare wire case.

Based on these observations we hypothesize that embedding the wire in heterogenous material makes thermal quenching worse (i.e., faster intensity decay below 400 K) due to phonon coupling between the polymer and EYAD, but above the melting point the polymer host becomes beneficial in reducing the effects of melting on the fluorescence (i.e., reduction in intensity and increasing peak width). To understand how the polymer host provides this benefit during melting, we first note that the fluorescence changes in the bare wire case are due to EYAD being free to expand and move during melting. These two effects of translation and expansion affect both the alignment of the probe beam spot and allows for significant changes to the distribution of Eu$^{3+}$ sites within the crystal lattice as the lattice changes during melting. In the polymer case this freedom does not exist as the surrounding polymer constricts the EYAD particles’ volume and movement during melting. Thus the polymer mitigates the two main effects of melting on the fluorescence.
Fig. 5: Peak intensity and effective peak width as a function of wire temperature for bare wire (a) and wire embedded in a heterogeneous material (b)

Fig. 6: Raw (a) and background subtracted (b) Raman data at different temperatures during heating run.

Next, we turn to considering the Raman spectra shown in Figure 6, which are shown in both their raw (a) and background subtracted (b) form. From Figure 6a we find that the background changes significantly with temperature, with it first decreasing gradually from 293 K to 541 K after which it quickly increases. We note that this inflection point is near the degradation temperature of Epotek 305 (543 K) and therefore this change in background is most likely due to the wire causing the polymer to start melting. Also, from Figure 6a we find that the Raman peaks observed primarily correspond to
sugar [24] and the polymer, with EYAD’s Raman peaks drowned out by the sugar/polymer signal. See Figure 7 for reference Raman measurements of the polymer and sugar dispersed in polymer.

The lack discernible signal from the EYAD is due to the laser light scattering over multiple sugar particles and through a significant amount of polymer to reach the EYAD. This leads to a significant Raman signal from both the sugar and polymer. One possible solution to this unwanted signal is to use spatial filtering of the backward collected light such that light from the guidestar makes it to the spectrometer, but light from the background is blocked [22,23].

4 Conclusions

In this study we used Feedback Assisted Wavefront Shaping and a Bidirectional Focusing Microscope (BFM) to spectroscopically probe subsurface thermal degradation of EYAD molecular crystals under electrically driven heating. Using the BFM we focused on a target particle inside of the sample and obtained a fluorescence image enhancement of $\approx 4 \times$. However, when considering the fluorescence spectra we only found an enhancement of approximately $1.33 \times$ due to the majority of the fluorescence spectrum coming from of “out-of-focus” EYAD particles, rather than the target particle alone. We also found that a similar effect made Raman measurements ineffective as the signal from the polymer and dispersed sugar crystals overwhelmed the signal from the less plentiful EYAD. To address these setbacks and improve the performance of the BFM, we are planning on implementing a spatial filtering system for signal collection, which has previously been shown to improve depth-dependent spectroscopy [22].
Despite these setbacks we were still able to successfully perform subsurface fluorescence measurements during thermal degradation. From our these measurements we observed several similarities between the EYAD’s thermal degradation in air and embedded in a heterogeneous material, including: slow thermal quenching and broadening below 400 K, after which the quenching and broadening occur more rapidly due to the EYAD molecular crystals’ melting point being $\approx 400$ K. However, while the qualitative behavior is found to be the same both in air and when embedded, the quantitative behavior is different. Namely we find that embedding the EYAD in polymer results in faster thermal quenching due to phonon coupling between the polymer and the molecular crystal, but also that the polymer helps mitigate the effects of melting on EYAD’s spectroscopic properties making its signal survive to higher temperatures than in the air measurements.

Acknowledgements

This work was supported by the Army Research Office, Award # W911NF-18-1-0094 to Washington State University.

References

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SubsurfaceHeat.tex
- SubsurfaceHeat.tex