Investigation of the electronic and physical properties of defect structures responsible for laser-induced damage in DKDP crystals

Stavros G. Demos*, Paul DeMange, Raluca A. Negres, and Michael D. Feit

Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA
* demos1@llnl.gov

Abstract: Laser-induced damage at near operational laser excitation conditions can limit the performance of potassium dihydrogen phosphate (KH₂PO₄, or KDP) and its deuterated analog (DKDP) which are currently the only nonlinear optical materials suitable for use in large-aperture laser systems. This process has been attributed to pre-existing damage precursors that were incorporated or formed during growth that have not yet been identified. In this work, we present a novel experimental approach to probe the electronic structure of the damage precursors. The results are modeled assuming a multi-level electronic structure that includes a bottleneck for 532 nm excitation. This model reproduces our experimental observations as well as other well-documented behaviors of laser damage in KDP crystals. Comparison of the electronic structure of known defects in KDP with this model allows for identification of a specific class that we postulate may be the constituent defects in the damage precursors. The experimental results also provide evidence regarding the physical parameters affecting the ability of individual damage precursors to initiate damage, such as their size and defect density; these parameters were found to vary significantly between KDP materials that exhibit different damage performance characteristics.

©2010 Optical Society of America

OCIS codes: (160.4330) Nonlinear optical materials; (140.3330) Laser damage.

References and links


42. J. Bude, G. Guss, M. Matthews, and M. L. Spaeth, “The effect of lattice temperature on surface damage in fused


44. S. G. Demos, M. Stagg, and H. B. Radousky, “Investigation of bulk defect formations in KH2PO4 crystals using

45. J. Swain, S. Stokowski, D. Milam, and F. Rainer, “Improving the bulk laser damage resistance of potassium

Lane, R. L. Luthi, J. N. McElroy, A. M. Rubenchik, J. R. Stanley, W. D. Sell, J. L. Vickers, T. L. Weiland, and
D. A. Willard, “Wavelength and pulse length dependence of laser conditioning and bulk damage in doubler-cut

Meissner, S. Nakajima and T. Izumitani, Lawrence Livermore National Laboratory report UCRL-53932, (May
26, 1989).


49. R. A. Negres, N. P. Zaitseva, P. DeMange, and S. G. Demos, “Expedited laser damage profiling of KD2H16−xPO4

50. L. Liang, Z. Xian, S. Xun, and S. Xueqin, “Sulfate may play an important role in the wavelength dependence of


1. Introduction

The study of defects in various materials of technological importance has been driven mainly
by cost analysis and performance characteristic considerations. Typically, some type of
defect(s) is incorporated during the manufacturing process and the challenge becomes to first
identify and subsequently remove or passivate these defects in order to avoid the adverse
effects on the performance of the material. There are many such examples in the literature
demonstrating that the identification of the defects is not always a simple problem, and
finding a solution often requires extensive research and development.

The optical materials for UV and high power lasers are one typical example of a class of
materials that requires the identification of defects to enhance performance. As the operational
envelope of various laser systems continues to expand, it is anticipated that one of the major
near-future achievements of laser physics, enabled by a new generation of large aperture laser
systems, will be laser-driven net energy gain nuclear fusion in a laboratory environment [1].
Maybe most important, emerging research suggests that laser-based designs of both inertial
confinement fusion (ICF) and fusion-fission hybrid reactors may be used to satisfy future
global electricity demands in a safe, reliable, cost-effective and sustainable manner while
avoiding carbon emissions and drastically shrinking stockpiles of spent nuclear fuel [2,3].
These advancements highlight the importance of improving the laser damage performance of
optical materials suitable for such large aperture systems. These include the nonlinear
crystalline material KDP and its deuterated analog DKDP, currently the only materials
suitable for polarization beam control and frequency conversion that can be grown to
sufficiently large size [4,5].

Laser induced damage is observed in the bulk of the best current KDP material at laser
fluences estimated to be more than an order of magnitude lower that the intrinsic breakdown
threshold of the pure material. As the damage initiating defect structures (referred to as
precursors) remain “invisible” prior to damage, their interaction with laser pulses is
manifested by the formation of damage sites that bear the fingerprint of exposure to localized
high temperatures and pressures [6,7]. The size of the final damage site is far larger than the
size of the precursors and depends strongly on the laser pulse length [7,8]. This indicates that
the size of the final damage site depends on the time of exposure to the damaging pulse after
the material surrounding the precursor has transformed to an absorbing state. This multi-phase
process has arguably complicated efforts to understand the nature of the precursors since the
results of every experiment to probe the damage initiation mechanisms is affected by the
distinct steps that involve the interaction of the laser beam with a) the precursor, b) the modified host material and c) the breakdown plasma formed in the bulk. Efforts to directly identify the defects responsible for damage initiation in KDP have failed, possibly because the size and/or concentration of these clusters of defects are lower than the limit of detection of current chemical analysis tools [8]. However, the better understanding of the damage initiation process has helped design experiments that have provided a significant amount of information regarding the nature and properties of the damage precursors.

Recent work by our group in KDP has demonstrated that there are two distinct populations of damage precursors. The first population initiates damage at longer wavelengths (such as at the fundamental of an Nd:YAG laser at 1064 nm) while the second population (denoted as SW precursors) initiates at shorter wavelengths (second and third harmonics at 532 nm and 355 nm, respectively). The latter population of damage precursors represents the major problem in terms of the performance characteristics of the material as it leads to damage at lower fluences [9–11]. It was also shown that the SW precursors initiate damage in a specific order for exposure to 2ω or 3ω or combinations of these two wavelengths (the difference in damage threshold between two specific precursors does not change sign with varying excitation conditions) suggesting that there are one or more physical properties that determine the damage threshold of an individual precursor [9]. It has been postulated that the size of the precursor is a key property as it determines the heating of a precursor (i.e., maximum temperature reached) resulting from exposure to a given fluence at a given pulse length [12]. However, other parameters such as the absorptivity of the precursor or its geometrical shape may also be important in setting the threshold [13,14].

To obtain information regarding the electronic structure of the precursor, the only available method may be to perform wavelength dependent damage testing experiments. Such experiments yield information regarding the “effective” absorption efficiency at each wavelength averaged over all processes leading ultimately to plasma formation. There are two sets of measurements of this type reported in the literature. Carr et al. reported on the damage threshold of KDP as a function of wavelength [15]. Distinct steps in the fluence threshold as a function of wavelength occurring at frequencies of sub-multiples of the band gap of the pure material (i.e., E_g/n) were observed. These results provided the first direct evidence that a nonlinear absorption process plays an important role in the overall behavior, as previously suggested by Demos et al. following time-resolved Raman scattering measurements [16]. The latter study failed to indicate a localized linear sub-threshold temperature rise in the bulk of KDP, as anticipated for a linear absorption process.

More recently, DeMange et al. reported on damage testing experiments in DKDP under simultaneous exposure to 532 nm (2ω), 355 nm (3ω) pulses and combinations of 1064 nm (1ω), 2ω and 3ω pulses in order to simulate the operational conditions during frequency conversion [17,18]. The results demonstrated that the fluence at one wavelength could be related to an effective fluence at the other wavelength that provides an equivalent density of damage events in the material. In addition, the relative effective absorption efficiencies at the two wavelengths were found to depend on the laser fluence. On the other hand, the absorption efficiency at 1ω was shown to be very small compared to that at 2ω and 3ω, indicating a relatively inefficient coupling of the 1ω laser energy in the damage initiation process of the SW precursors [18].

The objective of the present work is to reveal the electronic and physical properties of the precursors that determine their ability to initiate damage and their individual damage thresholds. By estimating the relative effective absorption efficiencies at the two wavelengths for different PPDs, we hypothesized that we can extract information on how the physical and electronic properties of the precursors affect their damage threshold. The experimental results provide information on the electronic structure of the defects that make up the precursor. A rate equation model of the electronic structure is proposed to estimate the excitation processes leading to the deposition of sufficient energy to turn the host material into an absorber. Comparison of this information with the properties of known defect species in KDP allows for the identification of a class of defects with the appropriate electronic structure. The results
also provide insight into the physical properties (size and defect density) of the precursors and their distribution in a given material affecting the overall damage performance.

2. Experimental approach and results

The present experimental results were obtained using a system that has been described in detail elsewhere [19]. In brief, the material was exposed to spatially and temporally overlapping $2\omega$ and $3\omega$ pulses obtained from the same laser system at various fluence combinations and the resulting density of damage sites or “pin-point density” (PPD) was estimated. The $2\omega$ and $3\omega$ pulses, having full-width-at-half-maximum durations of 4 ns and 3.5 ns, respectively, were aligned to co-propagate and focused by a 200-mm focal length cylindrical lens at the same location within the bulk of the material. The damage-tested volume was illuminated by a counter propagating 632.8 nm He–Ne laser beam focused into the volume by a 250-mm focal length cylindrical lens and imaged through the side of the sample using a microscope system equipped with a long-working-distance objective lens. The PPD was estimated over the region exposed to peak laser fluence having a height of 340 µm and length of 5.8 mm. The samples were obtained from two conventionally grown crystal boules [4,5] having significantly different damage characteristics (boules LL16 and D10) and were cut to 1x5x5 cm$^3$ size plates, with uncoated, diamond-turned finished surfaces.

In contrast with the analysis performed in Ref. 17, where the PPD is plotted as a function of the $3\omega$ fluence for various $2\omega$ fluences, the objective here is to determine the fluence pairs that yield the same PPD. We postulate that creating the same PPD under different combinations of fluences is the net result of damage-equivalent precursor populations with similar physical properties. The experimental results were analyzed by maintaining the $2\omega$ fluence constant at various levels (0, 5, 8, 12, 16, 20, and 24 J/cm$^2$) while adjusting the fluence at $3\omega$ to generate specific damage testing PPD values. Hence, this set of experiments yielded seven pairs of $2\omega$ and $3\omega$ fluences that provided the same PPD values, chosen as follows: 50, 100, 300, 600, 1000, 1500, 2000, 3000, 4000, and 5000 damage sites per mm$^2$.

For the analysis of the experimental results, we will adapt the method presented by DeMange et al. [17,18] where an effective $3\omega$ fluence for each $2\omega$ fixed fluence in the series was estimated by subtracting the actual $3\omega$ fluence in each of these fluence pairs from the $3\omega$ fluence that yields the same PPD when the $2\omega$ fluence is zero, i.e.:

$$\phi_{\text{eff}}^{3\omega} (x, PPD = y) = \phi^{3\omega} (x, PPD = 0) - \phi^{2\omega} (x, PPD = y).$$

(1)

The ratio of the $3\omega$ effective fluence over the corresponding $2\omega$ fluence, $\gamma$, quantifies the relative contributions of the $2\omega$ and $3\omega$ laser light in the damage initiation process for different excitation conditions, i.e. resulting in different PPDs, and is defined as:

$$\gamma (x, PPD = y) = \frac{\phi_{\text{eff}}^{3\omega} (x, PPD = y)}{\phi^{3\omega} (x, PPD = y)}.$$

(2)

Values of $\gamma$ calculated as a function of the PPD from the experimental data are shown in Figs. 1(a) and 1(b) for DKDP samples obtained from the two different crystal boules. The first sample (LL16) exhibits a relatively high damage resistance (lower PPD for same laser fluence) while the second sample (D10) exhibits a relatively poor damage performance [see Figs. 1(a) and 1(b), respectively].

The data shown in Fig. 1 show that $\gamma$ exhibits a stronger dependence on the excitation conditions than on the resulting PPD. In particular, the $\gamma$ vs. PPD profiles obtained for different $2\omega$ laser fluences show distinct differences within the same material. In addition, both similarities and differences are observed when comparing the profiles obtained at the same $2\omega$ fluence but in different materials. Specifically, the $\gamma$ vs. PPD profiles obtained at constant $2\omega$ fluence of 5 and 8 J/cm$^2$ exhibit a decrease with increasing PPD (or $3\omega$ fluence) until the $3\omega$ fluence reaches a value of about 14 and 12.5 J/cm$^2$, as seen in Figs. 1(a) and 1(b), respectively. On the other hand, the profiles of $\gamma$ obtained at constant $2\omega$ fluences of 16 and 20 J/cm$^2$ exhibit an initial increase in Fig. 1(a) while in Fig. 1(b) the value of $\gamma$ is continuously decreasing with increasing PPD. The profile obtained at constant $2\omega$ fluences of 12 J/cm$^2$ in
Fig. 1. The experimentally determined dependence of the relative absorption efficiency ($\gamma$) as a function of the damage density (PPD) at fixed values of $2\omega$ fluence in DKDP material from (a) LL16 and (b) D10 crystal boules. The corresponding $3\omega$ fluence values are indicated at each data point.

Figure 1(b) can be considered similar to that shown in Fig. 1(a) if we take into account the trend discussed above for $2\omega$ fluences of 16 and 20 J/cm$^2$, i.e. exhibiting a negative slope at lower combined fluences in the lower damage performance material.

3. Theoretical approach

The complex behaviors revealed by the results shown in Fig. 1 may be the result of the different mechanisms involved in the interaction of the precursors with the laser light leading to damage initiation. In particular, there are a number of distinct physical properties of the precursors believed to play a key role in the interaction with the laser pulse and the subsequent heating of the surrounding lattice that triggers the damage initiation process:

i) The size of the precursor via heating and cooling efficiencies (as described in the absorbing particle model)

ii) The size of the precursor via absorption efficiency $Q$ (from Mie Theory)

iii) The electronic structure of the precursor governing its ground state and excited state absorption cross-sections and thus, the absorption mechanism leading to damage initiation

iv) The density of absorbing atomic defect centers within the precursor (defect cluster).

We will next discuss in more detail each one of these properties and their possible roles in damage initiation. It must be noted that, because isolated atomic defects cannot deposit enough energy to initiate macroscopic damage, the precursor here is considered to be a cluster of stoichiometric or non-stoichiometric defects as previously proposed.

For interpretation of the results shown in Fig. 1, it must be recognized that only a portion of the precursors that result in damage at a particular combination of fluences dominate the experimentally measured behaviors, namely those precursors that absorbed just enough energy to initiate damage. The other precursors have absorbed more energy than needed to initiate damage.

3.1 The role of the size of the precursor

A generalized model involving linear absorption at embedded nanoparticles (damage precursors) has been applied for over a decade to describe damage initiation for pulses longer than a few tens of picoseconds [12,20–24]. Damage is associated with a nanoparticle having reached a critical temperature which results in localized modification of the immediate...
surrounding material to make it absorbing [24]. In general terms, this model predicts that, for a fixed pulse-length $\tau$, particles of size comparable to $\sqrt{D\tau}$, where $D$ is the thermal diffusivity, require the lowest laser fluence to reach a given temperature due to i) greater difficulty to heat larger particles and ii) faster cooling of smaller particles owing to their higher surface to volume ratio. It was proposed that the transformation of the host material to an absorber takes place via the deposition of enough energy into the surrounding host material to reach a threshold temperature $T_{th}$ above which the host becomes absorbing. Although this model is still not well developed, it is clear that some sort of transformation takes place in the host material due to the energy deposition process. Independent of the exact mechanism for energy coupling between the laser pulse and the precursor (e.g. linear vs. nonlinear), smaller precursors should initiate damage at a higher fluence. Therefore, a KDP/DKDP material that contains only smaller precursors will exhibit better damage performance (higher damage threshold and lower PPD for a fixed laser fluence and pulse length). Since the basic mechanism associated with the role of the size of the precursors in the energy dissipation process has been discussed elsewhere, we will not discuss it further here. Within the context of the experimental results shown in Fig. 1, it must be recognized that the observed behavior of the value of $\gamma$ with increasing PPD is related to increasing numbers of smaller size precursors initiating damage within the population.

The importance of the size of the precursors is also evident within Mie theory. Specifically, the absorption efficiency depends on the particle size in terms of the wavelength of the absorbed light by way of the complex refractive index ($n = n_0 - ik$). The total energy $E$ absorbed by the particle due to exposure to $2\omega$ and $3\omega$ light within the Mie theory [12,25] solution of the scattering of light by spherical particles of radius $a$ can be written as:

$$E \propto \pi a^2 \cdot Q_{2\omega} \cdot \phi^{2\omega} + \pi a^2 \cdot Q_{3\omega} \cdot \phi^{3\omega}$$

where $\phi^{2\omega,3\omega}$ refer to fluences at $2\omega$ and $3\omega$, the $Q$’s refer to the absorption efficiencies at the respective wavelengths and $\pi a^2$ is the geometric cross-section of the particle. From this expression, a given fluence at $2\omega$ can be related to the effective fluence at $3\omega$ that provides equivalent absorption of energy at the nanoparticle as determined by the ratio of the absorption efficiencies at each wavelength. Since the absorbed energy is the determinant of the ultimate PPD, we have:

$$\phi_{eff}^{3\omega} = \frac{Q_{2\omega}}{Q_{3\omega}} \cdot \phi^{3\omega} \quad \text{or} \quad \gamma = \frac{Q_{2\omega}}{Q_{3\omega}}.$$  

Fig. 2. The predicted change in relative absorption efficiency ($\gamma$) with precursor size within the Mie theory formulation using exemplary values of the imaginary part of the index of refraction, $k$, and (a) the same and (b) different values at 532 and 355 nm.
It is therefore possible to compare the experimental observations with the predicted behavior of $\gamma$ using the Mie theory approach for various values of the complex index of refraction. Typical estimated profiles of $\gamma$ as a function of particle size are shown in Figs. 2(a) and 2(b). Our analysis indicates that, for imaginary index of refraction greater than 1, the Mie theory calculation results reproduce the same qualitative increase of the $\gamma$ ratio with increasing PPD (decreasing particle size) as that observed in Fig. 1 only for a size range of nanoparticles smaller than about 100 nm and within a range of values of the complex refractive index. However, in this range of parameters, the calculated $\gamma = Q_{2\omega}/Q_{3\omega}$ is greater than 1. This would imply that the absorption at 532 nm is higher than that at 355 nm and, therefore, the damage threshold fluence should be lower at 532 nm than at 355 nm. This prediction contradicts the experimentally observed damage behaviors, i.e., the damage threshold at 355 nm is always lower. Variation of this approach using different values of the real and imaginary parts of the index of refraction at each wavelength does not alter this general trend. Thus, the qualitative behaviors depicted in Figs. 2(a) and 2(b) do not agree with the experimental results shown in Fig. 1. Specifically, the Mie theory results predict that a decreasing value of $\gamma$ with decreasing particle size (and thus increasing PPD) should be observed when the particle size becomes small enough (on the order of 100 nm in diameter). This conclusion will be used later to address part of the experimental observations.

3.2 Modeling of defect electronic structure

The changing value of $\gamma$ for increasing PPD (corresponding to increased combined absorbed laser fluences) observed in Fig. 1 suggests that the effective absorptivity at each wavelength is a function of the excitation conditions at the onset of damage initiation. Furthermore, for the lower $2\omega$ fluence profiles ($2\omega$ fluence of 5 and 8 J/cm$^2$), a decrease in the value of $\gamma$ is initially observed with increasing $3\omega$ fluence while the minimum value occurs at approximately the same fluence combination in both materials, but at very different PPDs. This suggests that this behavior is dependent on the excitation conditions of the precursors.

In contrast to the linear absorption approach utilized previously, here we will consider that the excitation of the constituent defects of the precursor during damage initiation involves more complex processes. Excited state absorption is known to play a key role in the photo-excitation process of defects in dielectric materials such as in ion-doped solid-state laser materials. Such material systems may be the appropriate model to follow in our case where defect structures possibly occupy lattice sites thus creating defect states within the bandgap of the host material.

As per our discussion above regarding the role of the size of the precursor on the damage initiation process, for decreasing precursor size a larger power density is required at the precursor site to reach $T_{th}$ due to the more efficient cooling via heat conduction. This in turn leads to an increase in the relative number of ground state electrons that are excited to one of the defect states lying within the bandgap of the host material. The minimum observed in the value of $\gamma$ vs PPD may then indicate the presence of a bottleneck in the excited state absorption pathway for the $2\omega$ photons that is not present for the $3\omega$ photons. This scenario can take place if an excited state absorption coefficient for $2\omega$ is much lower than that for $3\omega$. It then follows that the separation between the excited states is smaller than the $3\omega$ photon energy but larger than the $2\omega$ photon energy (i.e., transition requires a 2-photon absorption process). This conclusion may be used to develop a preliminary understanding of the electronic structure of the defect states of the precursor. In addition, the fact that $\gamma$ starts from a value of about 0.5 and then it declines suggests that the bottleneck is not associated with the first excited state (which can efficiently be reached by both $2\omega$ and $3\omega$ photons), and thus its separation from the ground state is lower than about 2.3 eV. The presence of the $2\omega$ bottleneck discussed above indicates that the second excited state is at least 2.4 eV above the first excited state. Furthermore, the subsequent increase of the value of $\gamma$ after reaching the minimum may indicate that the energy separation between the second excited state and the
conduction band (at ≈7.8 eV) is smaller than the energy of the 2ω photons. These energy level assignments are summarized in the schematic of the electronic structure of the precursor defects provided in Fig. 3 in which states 1 and 2 in the bandgap assist promoting electrons from the ground state to the conduction band.

When such an electronic system is in a transient state, a significant portion of the electrons (responsible for absorption) occupy excited states and the transient absorption coefficient $\alpha^\lambda_{\text{trans}}$ can be described as follows assuming only the linear absorption components:

$$\alpha^\lambda_{\text{trans}} = \sigma_{0,1}^\lambda (n_0 - \sum n_i) + \sigma_{1,2}^\lambda n_1 + \sigma_{2,3}^\lambda n_2 + \Gamma^\lambda n_3$$

where $n_0$ represents the total density of defects, $n_i$ is the density of defects that have their $i$-th excited state populated ($i = 1, 2, \text{etc.}$) while $\sigma_{0,1}^\lambda$ and $\sigma_{ij}^\lambda$ represent the linear (ground state) and excited state absorption cross-sections, respectively. Absorption from the conduction band electrons is described by $\Gamma^\lambda$. The instantaneous value of $\gamma$ for this system can then be expressed as $\gamma = \alpha^\lambda_{\text{trans}} / \alpha^\lambda_{\text{bulk}}$.

The excitation dynamics of the system can be described by a simple set of rate equations:

$$\frac{dn}{dt} = \frac{n_1}{\tau_1} - \frac{\sigma_{0,1}^\lambda}{E_i - E_0} In_i,$$

$$\frac{dn_1}{dt} = - \frac{n_1}{\tau_{1}} + \frac{\sigma_{0,1}^\lambda}{E_i - E_0} In + \frac{n_2}{\tau_2} - \frac{\sigma_{1,2}^\lambda}{E_2 - E_1} In - \frac{\beta_{1,2}^\lambda}{E_2 - E_1} I^2 n_1,$$

$$\frac{dn_2}{dt} = - \frac{n_2}{\tau_2} + \frac{\sigma_{1,2}^\lambda}{E_2 - E_1} In_1 + \frac{\beta_{1,2}^\lambda}{E_2 - E_1} I^2 n_1 + \frac{n_3}{\tau_3} - \frac{\sigma_{2,3}^\lambda}{E_3 - E_2} In_2,$$

$$\frac{dn_3}{dt} = - \frac{n_3}{\tau_3} + \frac{\sigma_{2,3}^\lambda}{E_3 - E_2} In_2 - \frac{\Gamma^\lambda (n_1)}{\Delta E} I,$$

where $E_i$ are the energy levels, $I$ is the laser intensity, $\tau_i$ represents the relaxation time of the corresponding excited state and $\sigma_{i,j}^\lambda$ is the linear absorption cross section from one electronic state to the next. To account for the 2ω bottleneck in the excitation pathway from the first to the second excited state, a two photon absorption coefficient $\beta_{1,2}^\lambda$ is also included in the rate
equations and is intended to represent the dominant excitation mechanism bridging the 1st and 2nd excited states with 2ω photons. The last term in Eq. (9), $\Gamma^2(n_2)$, represents electrons lost from the conduction band giving up energy $\Delta E$. This term is negligible when $n_2$ is small (at relatively low excitation conditions associated with damage of the most vulnerable precursors at near operational laser fluences) and will be ignored below. We will briefly discuss the opposite case when $n_2$ is large.

Although the values of the parameters involved in Eqs. (6)–(9) are not directly known, there are some hints. For example, elegant experiments have shown the lifetime of conduction band electrons in fused silica to be ~1 ps and we have utilized this value here for $\tau_3$ [26]. In addition, pump-probe experiments in Ref. 18 suggested a lifetime of the first excited state $\tau_1$ on the order of 1 ns or shorter and that value is used. We have also assumed that $\sigma_{2\omega}^{3\omega} = \sigma_{2\omega}^{3\omega} = \sigma_{2\omega}^{3\omega}$, considering that these cross-sections should be of the same order of magnitude. The rest of the parameters were allowed to vary and the system of rate equations was explored to determine whether it can reproduce the behaviors observed in Fig. 1. Considering for simplicity flat in time pulses of 2ω and 3ω light, the rate equations above rapidly (on the order of $\tau_1$) lead to steady state values of the electron populations at each level. These populations determine the effective energy absorption rates for the two wavelengths. The relative effectiveness ($\gamma$) of 2ω compared to 3ω light can then be calculated as shown in Fig. 4(a). In order to compare the theoretical and experimental values of $\gamma$, we have to involve a relation between the laser fluence ($\phi$) and the resultant damage density (PPD). In agreement with previous experimental studies, we chose a power law dependence of the damage density on total absorbed energy fluence, PPD $\sim \phi^3$ [8]. Using Eqs. (6)–(9), we have computed the best semi-quantitative fit to the experimental results shown in Fig. 1, as illustrated in Fig. 4(b). The two figures are qualitatively similar. The fit parameters used to generate the model predictions shown in Fig. 4 are:

$$E_1 - E_0 = 2.3 \text{ eV}, \quad E_2 - E_1 = 3.2 \text{ eV}, \quad E_3 - E_2 = 2.2 \text{ eV}$$  \hspace{1cm} (10)

$$\tau_1 = 1 \text{ ns}, \quad \tau_2 = 50 \text{ ps}, \quad \tau_3 = 1 \text{ ps}$$  \hspace{1cm} (11)

$$\sigma_{0\omega}^{2\omega} = 1, \quad \sigma_{2\omega}^{2\omega} = 1, \quad \beta_{2\omega}^{2\omega} = 0, \quad \sigma_{3\omega}^{3\omega} = 7, \quad \Gamma^{2\omega} = 700$$  \hspace{1cm} (12)

$$\sigma_{0\omega}^{3\omega} = 1, \quad \sigma_{2\omega}^{3\omega} = 0, \quad \beta_{3\omega}^{2\omega} = 0.005, \quad \sigma_{3\omega}^{3\omega} = 14, \quad \Gamma^{3\omega} = 700$$  \hspace{1cm} (13)

where all the cross-sections are in arbitrary units.

The various fitting parameters affect the profiles shown in Fig. 4(b) differently and our choices were based on those best reproducing the experimental observations shown in Fig. 1. Specifically, the effect of decreasing the value of $\tau_2$ is minimal resulting mainly in an increase of the minimum value of $\gamma$ on the lower 2ω fluence profiles. Changing the value of $\sigma_{2\omega}^{3\omega}$ has an effect on the lower 2ω fluence profiles affecting mainly the value of $\gamma$ at low PPD. The value of $\beta_{2\omega}^{2\omega}$ has a major effect on the shape of the lower 2ω fluence profiles and the minimum value of $\gamma$ in each profile. The values of $\sigma_{2\omega}^{3\omega}$ and $\sigma_{2\omega}^{3\omega}$ affect the recovery of $\gamma$ (at higher PPD) of the lower 2ω fluence profiles from its minimum value, as well as the value of $\gamma$ for the higher 2ω fluence profiles. Finally, the value of $\Gamma^{2\omega}$ (which was assumed to be equal at both wavelengths) affects the value of $\gamma$ for the 2ω fluence profiles at the highest excitation conditions.

Comparison of the experimental results shown in Fig. 1 with the corresponding behaviors shown in Fig. 4(b) predicted by the model shows a generally good agreement but also some characteristic differences. Specifically, although the general shape of the profiles predicted by the model as a function of the PPD and for increasing 2ω fluence is similar to those observed by the experiment, there are two differences: i) The recovery of $\gamma$ as a function of the PPD for
the lower 2\(\omega\) fluence profiles is considerably slower than that observed by the experiment, and ii) the relative ratios of 2\(\omega\) fluences in the experiment (5/8/12/16/20/24 J/cm\(^2\) or \(\approx 1/2/3/4/5/6\)) are considerably different than those used to achieve best fit to the results (1/2/4/7/10/13). These differences may be attributed to that the cooling of the particle during the energy deposition phase is not accounted for in this model. As discussed earlier, as the PPD increases, the size of the corresponding precursors initiating damage decreases. Since smaller precursors lose energy faster via heat conduction, additional laser intensity is required to achieve the damage threshold temperature within the precursor. Within the boundaries of this model, this will lead to crossing from a predicted profile at specific \(2\omega\) fluence, as shown in Fig. 4(b), towards higher \(2\omega\) fluence profiles as the PPD increases (the precursor size decreases). In terms of the representation of \(\gamma\) as a function of the \(2\omega\) and \(3\omega\) fluence shown in Fig. 4(a), the actual experimentally measured profiles at constant \(2\omega\) fluences will require increasingly higher \(3\omega\) fluences from those predicted by the model as the size of the precursors decreases. This will lead to a faster recovery of \(\gamma\) as a function of the PPD for the lower \(2\omega\) fluence profiles. In addition, the profiles at higher excitation conditions (i.e., \(n_3\) is large) would correspond to a much higher \(3\omega\) fluence than that predicted by the model. Thus, for increasing PPD, a predicted profile at even higher \(2\omega\) excitation conditions would be suitable to describe the experimental behaviors. This qualitative explanation could be incorporated into the model by assuming a relationship between the PPD and the corresponding precursor size. However, as shown later, in addition to the size, the defect density of the precursor is an additional important parameter that differs between materials or maybe between precursors of the same material, thus further complicating a more detailed modeling effort at this stage.

We can test the order of magnitude of various quantities in the model for reasonableness. For example, as the melting point for KDP is 260 °C, for argument’s sake lets consider that threshold temperature \(T_0\) above which the host becomes absorbing is about 0.1 eV (about 1000 K). Using the specific heat of KDP at room temperature, 1000 K corresponds to an absorbed energy of about 880 J/cm\(^3\) [27]. In our model, electrons cascading down from level to level via non-radiative relaxation can transfer energy to the lattice at a rate per volume of

\[
\frac{n_i}{\tau_i}(E_i - E_0) + \frac{n_i}{\tau_i}(E_2 - E_1) + \frac{n_i}{\tau_i}(E_3 - E_2).
\]

As the values of \(n_i\) are a function of the laser intensities, the profiles describing the combination of incident fluences under \(2\omega\) and \(3\omega\) excitation that lead to an absorbed energy of about 880 J/cm\(^3\) can be calculated as a function of the initial defect density. At steady state conditions, the above expression for the rate of
energy absorption can be restated in terms of the population densities and products of intensity with cross-sections. Thus, once the populations are determined, this latter expression can be used to determine the cross-sections in physical units.

Fig. 5. Calculation of the required combination of incident fluences under 2ω and 3ω excitation for localized absorbed energy to heat the host material to ~1000 K and initiate damage with a 2 ns, flat in time pulse. To best approximate the experimentally observed damage thresholds at 2ω and 3ω, we have assumed an initial defect density of n₀ = 5x10¹⁹ cm⁻³.

To best approximate the experimentally observed damage thresholds at 2ω and 3ω, we have assumed an initial defect density of n₀ = 5x10¹⁹ cm⁻³ for the precursors that first initiate damage in the bulk of a material. The corresponding absorption cross section from the ground to the first excited state was estimated to be 1.4x10⁻¹⁹ cm² which is a reasonable magnitude for this quantity. All other absorption cross-sections used in Eqs. (6)–(9) can also be estimated as they have been normalized with respect to σ₂₀ [or σ₃₀, see Eqs. (12)–(13)]. Figure 5 illustrates the calculated 2ω and 3ω combination of incident fluences required to locally heat the host material to ~1000 K. We note that the estimated damage threshold fluences for the above defect density are about 8.5 and 11 J/cm² under 3ω or 2ω excitation alone, respectively, which is remarkably similar to those observed in high quality KDP materials. The exact value of the 2ω threshold for a given 3ω threshold is most sensitive to the magnitude of the nonlinear absorption coefficient, β. The precise parameter values used in Fig. 5 are not important, but again the reasonable orders of magnitude argue for the reasonableness of the model. It must also be noted the similarity in the estimated by the model profile shown in Fig. 5 to the experimentally measured damage density for combination of 1ω and 3ω incident fluences presented in Ref. 28 despite the wavelength difference. If we assume the onset of damage initiation at a lower threshold temperature T_{th}, the fitting parameters can be modified accordingly. In addition, precursors that damage at a higher fluence may have a smaller defect density (or size).

Let us turn now to the expected pulse-length dependence of the damage threshold. As discussed above, the transient absorption coefficient depends on the intensity. It has been previously shown how the absorbed energy is expected to change with size, absorptivity and laser fluence in a population of absorbers with differing sizes [29]. The fluence ϕ needed to heat the absorber up to temperature T_{th} was found to be:

\[
ϕ = \frac{4κT_{th}}{Qa} \left[ 1 - \exp \left( -\frac{4Dr}{a^2} \right) \right],
\]

where κ is the thermal conductivity, τ is the pulse-length, D is the thermal diffusivity, a is the absorber radius and Q is the absorptivity. The threshold is set by the absorbers that heat most efficiently (larger precursors). When the absorptivity Q itself depends on the laser intensity (or fluence), this equation becomes an implicit equation for the threshold fluence. Solving this
equation as a function of laser pulse-length $\tau$ reveals the pulse-length dependence of the damage threshold.

![Figure 6](image)

**Figure 6.** Solid squares represent the measured damage threshold values at $3\omega$ as a function of laser pulse-length (from Ref. 30) while the solid line fit was obtained using this model.

Figure 6 compares the best fit using our model to the damage threshold experimentally measured by Adams et al. as a function of pulse-length for the same DKDP material (LL16) used to obtain the data shown in Fig. 1(a) [30]. Similar results have also been presented by other groups [8,31] A good fit of the experimental data for pulse lengths longer than about 1 ns (which is relevant to the operational pulse-length of ICF class laser systems) is obtained. We did not calculate model predictions for pulse-lengths less than the relaxation time of the first excited state (1 ns) since steady state populations (utilized to generate the fit) are not reached in such short times. Moreover, at the higher intensities required for shorter pulse-lengths, additional nonlinear absorption processes not included in the rate equations can become important, further lowering the actual damage threshold compared to the prediction of this model. This effect is a key component of the recently developed ADM model which uses a phenomenological approach to understand and predict the damage and conditioning behaviors as a function of pulse-width and pulse-shape [30,32].

### 4. Discussion

The above results indicate that the model for bulk damage initiation in KDP presented in this work is consistent with well-documented empirical behaviors. However, there is a key element of the experimentally observed behaviors that is not predicted by this model and may be attributed to additional properties of the damage precursors that affect the damage process. Specifically, the results shown in Fig. 1 indicate that the value of $\gamma$ starts decreasing for higher irradiation levels (profiles with $2\omega$ fluence of 16, 20 and 24 J/cm$^2$). This behavior is not predicted by the rate equation model discussed earlier but it can be explained from the effect of the size of the precursor on the absorptivity based on Mie theory considerations discussed earlier and exemplified in Fig. 2. As the PPD is increased (via increase of the damage testing laser fluence), a precursor size is reached (on the order of 100 nm in diameter) below which the ratio $Q_{2\omega}/Q_{\omega}$ becomes size dependent thus affecting $\gamma$ with increasing PPD as shown in Fig. 2. In addition, the results shown in Fig. 1 indicate that the onset of decreasing $\gamma$ is observed at a different PPD and fluence combinations in the two materials used. Specifically, the lower damage performance material (D10) exhibits a decrease of $\gamma$ at lower fluences compared to the higher damage performance material (LL16). Since the onset of this effect is associated with the precursors having a particular size (at the onset of the decline of $\gamma$ shown in Fig. 2), these results suggest that the damage threshold of this specific set of precursors (having about the same size on the order of 100 nm in diameter) is different in the two materials. This is a direct indication that yet another physical parameter plays a role in the damage initiation process. This additional parameter can be the defect density in the
precursors. Specifically, a higher defect density in the lower damage performance material will result in a higher rate of energy deposition which will lead to a lower damage threshold for the same size of precursors. Thus, for the precursor sizes at the onset where Mie theory effects induce a decrease of $\gamma$ for increasing PPD, the precursors of the lower performance material (having higher defect density) will initiate damage at a lower fluence than for the higher performance material, in accordance with the experimental observation. In the context of ICF class laser systems operating at fluences on the order of 10 J/cm$^2$ for pulses of a few ns in duration, the results suggest that damage initiation is dominated by large precursors (on the order of 100 nm or larger) since the onset of the decline of $\gamma$ is observed at higher fluences for both materials.

Imperfections within the crystalline material (such as lattice dislocations) affect the formation and stability of stoichiometric atomic defects and, thus, their density can vary between different crystal boules or even within the same boule. As the damage precursors represent a volume of the host material that contains a high concentration of atomic defects (a defect cluster), we can also postulate that the density of defects in a precursor (and thus its absorptivity) differs between materials. Increasing the density of atomic defects in such defect clusters (precursor) of a given size will lead to an increased absorptivity and, in turn, a decrease in the precursor’s damage initiation threshold. On the other hand, for a fixed density of atomic defects, smaller clusters will generally initiate damage at a higher fluence due to a more efficient cooling. The damage behavior observed in the two materials used in this study, i.e. the results shown in Figs. 1(a) and 1(b), appear to reflect in part the different distributions in size and defect density of the precursors within each crystal.

The general description of the electronic structure of the damage initiating defects can be compared to the optical and electronic structure properties of bulk defects in KDP provided in the literature, in an effort to narrow down the search to identify the damage-initiating defects. Recent experimental work combining EPR and optical spectroscopies has revealed the absorption spectrum of defect species generated in bulk KDP following irradiation with X-rays [33]. Specifically, various bulk (atomic) defects were identified with EPR spectroscopy and their optical absorption spectra were subsequently characterized. These are:

1. [HPO$_4$]$^-$ center: A hole trapped next to a H vacancy
2. [H$_2$PO$_4$]$^0$ center: Self trapped hole shared by two adjacent O ions
3. (H$^0$) atoms: Electron traps that migrate to interstitial positions
4. [PO$_3$]$^{2-}$ center: Electron trapped next to an O vacancy.

Furthermore, density functional theory was utilized to carry out electronic structure calculations of H and O defect clusters, which helped identify species that provide states in the band-gap [34–37]. Although the model assumes clusters of defects while experimental data are believed to originate from atomically dispersed defects, there is overall a reasonable agreement between the modeling results and the experimental observation for the same defect species. Specifically, all hydrogen defects provide only one state in the band-gap and are unstable at room temperature. From the O defects, the [PO$_3$]$^{2-}$ defect does not create states in the band-gap but it is stable at room T due to its role for charge compensation in the presence of a hydrogen or potassium vacancy. On the other hand, the +1 O-vacancy (hole trapped to an O-vacancy) is predicted to provide two states in the band-gap. They have not been experimentally detected yet but may be considered to be similar to the [H$_2$PO$_4$]$^0$ center (self trapped hole shared by two adjacent O ions) whose optical absorption spectrum suggests the presence of two absorption bands between about 2 and 4 eV and the onset of another band above 5.5 eV. The last two examples may be representative of the electronic structure of similar systems of holes trapped near O sites. The formation and stability of such clusters can be promoted at locations of defective lattice. Therefore, based on the existing literature and the results of this work, it seems likely that clusters of holes trapped near oxygen sites are the
key ingredients in the structure of the damage precursors. These holes may be associated with localized charge compensation at locations of defective lattice (to justify stability at room T).

Returning to the experimental results on the damage threshold of KDP as a function of wavelength [15], it is clear that the presence of “steps” in the damage threshold profile at $E_g/n$ cannot be explained with the current model dealing with the electronic structure of the precursor. However, as discussed earlier, damage initiation is a multi-phase process involving first the absorption of light by the precursor and subsequently the absorption of light by the modified host. The “steps” in the laser-induced damage threshold in bulk KDP crystals as a function of laser wavelength using 3 ns laser pulses appear identical to the “step” observed in laser-induced damage in titania using 130 fs pulses [38]. In this case, multi-photon absorption is mainly responsible for damage initiation. If we consider that the “steps” observed in KDP arise from the contribution to the overall process of the surrounding, temperature-modified host material [39–42], i.e. damage initiation via defect-assisted multi-photon absorption [15], the remaining features in the damage threshold vs. laser wavelength profile could be assigned to the electronic structure of the precursor. Figure 7 shows the damage threshold vs. laser wavelength profile after the “steps” were removed by translating the profile along the y-axis at the location of each step and removing the data points within each step. The inset shows the original data that were presented in Ref. 15. The remaining profile after the removal of the “steps” exhibits a structure that can be interpreted as the inverse of the damage-related absorption spectrum of the precursor (lower damage threshold is associated with higher absorption). It can be appreciated that this spectrum exhibits a multi-level structure with states above and below 2.5 eV and is similar to the absorption spectrum of the \([\text{H}_2\text{PO}_4\text{O}]^0\) center (self trapped hole) reported in Ref. 33.

The hypothesis that the damage precursors may be clusters of intrinsic, thermodynamic defects (rather than non-stoichiometric particles that were incorporated during crystal growth) was introduced after fluorescence microscopy measurements indicated the presence of emissive structures under CW green to UV laser excitation. These fluorescent centers with diameters less than 1 µm (upper limit was determined by the resolution of the microscope) were detected in various concentrations in different parts of the same crystal as well as between different crystals [43,44]. As discussed earlier, in addition to these fluorescing defect structures, there are at least two other types of defect structures existing in bulk KDP that are
responsible for damage initiation, the first at 1\(\omega\) and the other at 2\(\omega\) and 3\(\omega\) (SW precursors). All three types of defect structures exhibit some kind of modification when exposed to relatively high power laser irradiation. For the case of 1\(\omega\) and SW precursors, this modification is often referred to as “conditioning”, a very important salient behavior of KDP material [11]. This laser conditioning effect enables an enhancement in the laser damage performance via pre-exposure to laser pulses at the same or shorter wavelengths [45,46]. Furthermore, it has been shown that there are two types of conditioning behaviors for the SW precursors [10]. The first is associated with pre-exposure to 2\(\omega\) or 3\(\omega\) light and is manifested as a gradual improvement in the damage threshold at the second harmonic (2\(\omega\)), with the degree of improvement depending on the pre-exposure laser fluence and the number of pulses, but it provides no improvement in the damage performance at the third harmonic (3\(\omega\)). The second type of conditioning behavior is associated with a significant improvement in the damage performance at the third harmonic, but is observed only with pre-exposure to fluences above a threshold that is very close to the damage threshold under 3\(\omega\) pre-exposure [10].

It was first assumed that laser conditioning might arise from a change in the size of the precursors (which in that model were assumed likely to be foreign particles incorporated during growth) via thermally-induced fragmentation following irradiation by the pre-exposure pulse [12], a type of behavior that was known to occur for metallic inclusions in laser glass [47]. It was later proposed that the defect cluster might be undergoing a “passivation” via a mechanism that alters the electronic structure of the defects [34,44]. DeMange et al. proposed that the first conditioning behavior of the SW precursors may be associated with a rate limiting mechanism (interaction of two types of defects or a pair of defects) while the second behavior may be due to a change in the size of the precursor [10,11]. These phenomenological descriptions of the experimental observations were most recently incorporated into a model by Duchateau [48]. The latter model assumes that i) the precursors are planar defects which may annihilate via thermal migration and ii) a rise in the temperature of the precursors results in a phase transition and a subsequent re-arrangement of the lattice. In the present work, although all experiments were performed in pristine (unconditioned) material, we were able to determine that the size and the defect density of the precursors are very important in determining their individual damage thresholds. Therefore, the conditioning process may be associated with changes in these two physical parameters as a result of pre-exposure to laser pulses. Experiments similar to those presented in this work using “conditioned” material could provide information on the electronic structure of the precursors after conditioning thus testing the hypothesis that a passivation process is involved in laser conditioning of KDP.

The formation of the precursors is still not well understood. It has been shown that the number of damage sites created under exposure to fixed laser fluence is directly related to the crystal growth conditions [49]. It has also been postulated that the impurities incorporated in the growth solution to control the aspect ratio or other parameters of the growth process may also play an important role [44,50]. The results discussed in this work suggest that the defect density in the precursors of the higher damage performance material is lower than that of the lower damage performance material. The size of the clusters (precursors) also seems to be related to the defect density as the material with higher defect density precursors also has more and overall larger precursors. The hypothesis that the pool of atomic defects available to form more and denser damage precursors plays an important role in the final damage characteristics of the material is also supported by recent studies on DKDP crystals following X-ray irradiation to create additional defects [51]. These results indicated that the damage behavior of the material was affected by exposure to X-rays. This behavior was attributed to a change in the physical properties of the precursors arising from the interaction with the X-ray generated defects. The combination of these two parameters (density and size) provides a possible explanation of why the damage threshold and the number of damage sites created under exposure to specific laser fluence differ between materials.

Identification of the class of defects responsible for damage initiation arguably can help guide the methods to eliminate or greatly reduce them during the growth process, possibly by providing impurity ions that can capture these defects and thus limit the number of defects.
available to create aggregation sites (precursors). In this manner, the defect density as well as the number and size of the precursors could be reduced, thereby allowing for a higher damage performance material.

5. Conclusion

As the size and/or concentration of the absorbing defect structures (precursors) responsible for damage initiation in bulk KDP and DKDP crystal remain below the detection limit of current instrumentation, we employed a novel method to obtain information regarding their electronic structure. This method involved measuring the relative absorption efficiency at 355 nm and 532 nm during damage initiation under a wide range of total laser fluence and fluence combinations. The results revealed a salient behavior suggesting that the relative absorption efficiency at these wavelengths is a function of the excitation conditions. We hypothesized that this behavior arises from the electronic structure of the precursors which is associated with a bottleneck for 532 nm excitation. Using a model that involves a set of rate equations to describe the excitation of electrons in a multi-level structure, we found that it closely reproduces the experimental observations. The model provided an estimate of the defect density for the most damage-susceptible precursors (on the order of $5 \times 10^{19} \text{ cm}^{-3}$) and the corresponding linear absorption cross section (on the order of $1.4 \times 10^{-19} \text{ cm}^2$). The experimentally established dependence of the damage threshold as a function of pulse-length was also well reproduced using this model. In addition, the experimental results presented evidence regarding the key physical parameters affecting the ability of individual damage precursors to initiate damage, namely their size and defect density. These parameters were found to vary significantly between KDP materials that exhibit different damage performance characteristics. The results support the hypothesis that there is a distribution of precursor sizes but also that the precursors that initiate at the lowest fluence (representing the damage threshold of a material) are larger than about 100 nm in diameter. Furthermore, the results suggest that the defect density in the precursors of the higher damage performance material is lower than that of lower damage performance material. Thus, the lower damage performance material is associated with a larger number of precursors that have a higher defect density. Based on the experimental observations and the modeling results, we propose that clusters of holes trapped near oxygen sites are the constituent defects of the damage precursors. We also propose that laser conditioning (increase of the damage threshold following pre-exposure to sub-threshold laser fluences) is associated with a decrease in the size of the precursor defect structures following transient heating by the pre-exposure pulses.

Acknowledgments

The authors wish to thank J. J. Adams for stimulating discussions and help in understanding the data presented in Ref. 31 and P. J. Wegner for helpful review of the manuscript. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.