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Stoichiometric changes in KH_2PO_4 crystals during laser-induced breakdown

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The structure of KH_2PO_4 single crystals (so-called KDP) irradiated with ~ 3 -ns, 355-nm laser pulses with fluences above the laser-induced breakdown threshold is studied by a combination of Raman scattering, photoluminescence, and soft x-ray absorption spectroscopies. We compare spectra from the as-grown material, surface and bulk laser-induced damage sites, as well as from KPO_3 references. Results show that irradiation with fluences above the laser-induced breakdown threshold leads to stoichiometric changes at surface damage sites but not at bulk damage sites. New spectroscopic features are attributed to dehydration products. For the laser irradiation conditions used in this study, the decomposed near-surface layer absorbs photons at ~ 3.4 eV (364 nm). These results may explain the recently reported fact that surface laser damage sites in KDP crystals tend to grow with subsequent exposure to high-power laser pulses, while bulk damage sites do not.

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Potassium dihydrogen phosphate, KDP (KH_2PO_4), is an optical material widely used for frequency conversion and optoelectronic switching in laser systems.¹ What makes this material unique is that single-crystal KDP can be conveniently grown with linear dimensions in the range of 50 – 100 cm, as required for large-aperture high-power lasers.^{1,2} However, light intensities in lasers can be limited by the formation of laser-induced damage (LID) in KDP crystals, both at the surface and in the bulk.²

The formation of LID in KDP proceeds via localized nonlinear light absorption at some intrinsic lattice defects and/or impurities, which results in ultrafast melting, plastic deformation, and material fracture.^{3–8} Hence, both bulk and surface LID sites consist of a relatively small laser damage core (with an average size of 1 – 100 μm , strongly dependent on the laser pulse length)⁹ which has experienced ultrafast material melting and resolidification, surrounded by an extended volume of plastically deformed and fractured material.^{7,9,10} Although numerous previous studies have focused on the mechanisms of LID initiation in as-grown KDP crystals,^{2–9} the properties of the material modified during laser-induced breakdown have received little attention. It is, however, crucial to understand the properties of laser-modified KDP since they determine “reignition” and growth of LID sites with subsequent exposure to laser pulses.

In this letter, we investigate laser-induced structural and stoichiometric changes in KDP crystals by a combination of Raman scattering, photoluminescence (PL), and soft x-ray absorption near-edge structure (XANES) spectroscopies. These spectroscopic tools are sensitive to the local structure and bonding in the solid.¹¹ Our results reveal that irradiation leads to changes in mate-

rial stoichiometry at surface LID sites but not at bulk damage sites. This can explain recent observations that surface LID sites in KDP tend to grow with subsequent laser pulses,¹² whereas bulk LID sites do not.¹³

The z -cut [i.e., (001)-oriented] tetragonal KH_2PO_4 single crystals used in this study were grown by a rapid growth method at Lawrence Livermore National Laboratory, as described in detail elsewhere.² As-received KDP samples were polished with H_2O . The reference KPO_3 salt was prepared by annealing KDP crystals at 350 °C for 3 hours in air. The dehydrated salt prepared in this way was composed of a mixture of cyclophosphates and long-chain polyphosphates.¹⁴

Laser-induced damage sites were created on the front surface and in the bulk of KDP crystals by irradiation (at room temperature and ambient conditions) with ~ 3 -ns, 355-nm pulses from a Q -switched Nd:YAG laser. The laser beam profile at the sample plane was near-Gaussian with a FWHM of ~ 20 μm and a peak fluence of ~ 20 J/cm^2 . In order to minimize nonuniformities in the damaged volume, both surface and bulk damage regions, $\gtrsim 1 \times 1$ mm^2 in size, were created by slowly scanning the sample through the focused damaging beam so that each LID site has been exposed to multiple (~ 20) pulses.

These LID sites were studied at room temperature by a combination of Raman, PL, and XANES spectroscopies. Emission lines of a cw Ar laser, at 363.8 and 514.5 nm, were used as excitation sources for PL and Raman measurements, respectively. Both Ar laser lines were passed through narrow band pass filters. The Raman experiment was performed in a back-scattering geometry using a $\times 100$ microscope objective for both focusing the laser beam and collecting the Raman signal, which was then spectrally analyzed using a triple-grating spectrograph and recorded with a liquid-nitrogen-cooled CCD. The numerical aperture of the objective was 0.7 and provided ~ 1 μm and ~ 5 μm lateral and depth resolution, respectively. Raman spectra of KDP were normalized to the peak intensity of the H_2PO_4 mode at 911 cm^{-1} .

The XANES experiments were performed at undulator

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beamline 8.0 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Details of the beamline have been published elsewhere.¹⁵ In brief, XANES spectra were obtained by recording (i) the total fluorescence yield (TFY), measured with a negatively biased channeltron and (ii) the total electron yield (TEY), measured by monitoring the total sample photocurrent. The spot size of the x-ray beam was $\lesssim 0.1 \times 0.5 \text{ mm}^2$, well below the size of surface damage regions ($\gtrsim 1 \times 1 \text{ mm}^2$). After a linear background subtraction, all XANES spectra were normalized to the post-edge step heights.

Figure 1 (top graph) compares Raman spectra obtained from pristine bulk (labelled PB) KDP, bulk and surface LID sites (labelled BD and SD, respectively) in KDP, as well as from a KPO_3 reference. The most prominent bands between 300 and 1200 cm^{-1} in the PB spectrum (which is essentially identical to Raman spectra from the surface of pristine KDP) are due to internal vibrations of H_2PO_4 units.¹⁶ It is seen from Fig. 1 that the Raman spectrum from a bulk damage site does not exhibit any new peaks as compared to the spectrum from pristine KDP. The relative peak intensities are, however, significantly different in PB and BD spectra, indicating some structural changes and/or the presence of residual lattice stress produced during laser-induced breakdown.

Figure 1 also shows that spectra from surface LID sites exhibit four new bands centered on 296 , 688 , 1046 , and 1147 cm^{-1} in addition to changes in relative intensities of the KDP-related peaks, as discussed above. These new Raman features are evidence of laser-induced changes in material *stoichiometry*. Indeed, a comparison of the SD spectrum with that from KPO_3 in Fig. 1 reveals that three out of four new bands observed in SD spectra (at 296 , 688 , and 1147 cm^{-1}) correlate to peaks present in the KPO_3 spectrum. The band centered at 1147 cm^{-1} exhibits a single dominant peak. The other peak at 1046 cm^{-1} , observed in SD but not in the KPO_3 spectrum, has previously been reported in Raman studies of the $\text{K}_2\text{O-P}_2\text{O}_5$ glass system and assigned to polyphosphates with longer PO_4 chains.¹⁷ The formation of these latter products requires processing temperatures higher than $350 \text{ }^\circ\text{C}$, the annealing temperature used in this study to prepare KPO_3 reference samples.

The bottom graph in Fig. 1 shows Raman bands around 296 and 688 cm^{-1} in more detail. The Raman signal slightly varied at different sites within the surface damage region, as demonstrated in the two representative spectra shown in the bottom graph of Fig. 1. It is seen from this graph that the bands around 296 and 688 cm^{-1} exhibit additional splitting into individual peaks located at 296 , 308 , 326 cm^{-1} and 636 , 668 , 688 , 714 cm^{-1} , respectively (as indicated by asterisks). These results clearly demonstrate that changes to KDP during laser-induced breakdown are more complex than relatively simple material decomposition into water and KPO_3 salt.

Figure 2 shows O K -edge TEY [Fig. 2(a)] and TFY [Fig. 2(b)] XANES spectra from pristine KDP, surface

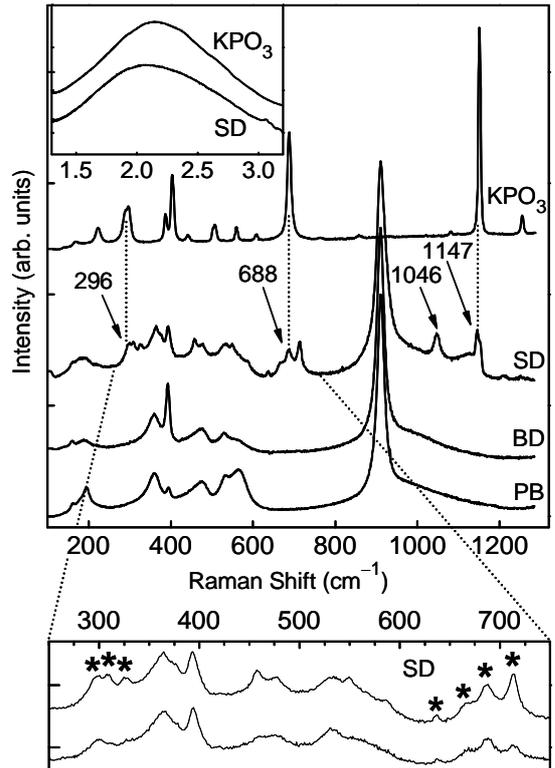


FIG. 1: Typical Stokes Raman spectra (top graph) from KDP at various locations: pristine bulk (PB) (i.e., undamaged) and bulk and surface damage sites (BD and SD, respectively). A spectrum from KPO_3 is also shown for comparison. The top inset shows normalized PL spectra [light intensity (in arbitrary units) versus photon energy (in eV)]. The bottom graph shows Raman spectra from two representative surface damage sites, expanded in the $250 - 750 \text{ cm}^{-1}$ region. All spectra are unpolarized and offset for clarity.

LID sites in KDP as well as from a KPO_3 reference sample. Such O K -edge XANES spectra reflect the transitions of O $1s$ core electrons into the O $2p$ -derived unoccupied states and essentially map the O $2p$ -projected density of states in the conduction band of KDP. It is seen from Fig. 2 that relative intensities of peaks labelled A and B in both TEY and TFY spectra are significantly increased in KPO_3 as compared to the case of pristine KDP. Figure 2(b) also shows that only a minor increase in the intensities of these peaks is observed in TFY spectra of laser-damaged KDP. In contrast, TEY spectra shown in Fig. 2(a) reveal a larger increase in the intensity of peaks A and B in spectra from surface LID sites. It should be noted, however, that peak intensities in such TEY spectra varied for different areas within the surface damage region. Such a lateral nonuniformity of laser-induced decomposition is consistent with the results of Raman studies discussed above. Since measurements in TEY and TFY modes probe the material properties averaged over the first $\sim 10 - 20 \text{ nm}$ and several hundred nanometers from the sample surface, respectively,¹⁸ such

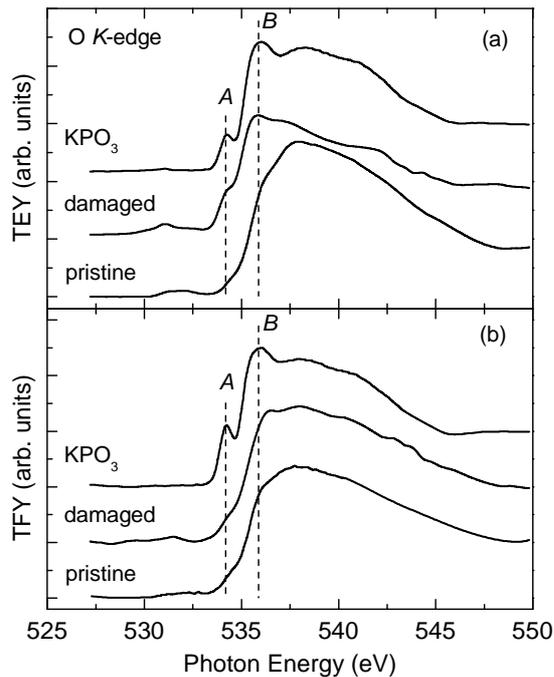


FIG. 2: Typical O K -edge total-electron-yield (a) and total-fluorescence-yield (b) XANES spectra from surface damage sites in KDP crystals. Spectra from KPO_3 and pristine (i.e., undamaged) KDP are also shown for comparison.

changes in TEY spectra and minor changes in TFY spectra from surface LID sites suggest that, in the samples processed as described above, laser-induced stoichiometric changes are laterally nonuniform and occur in a thin (sub-micron) near-surface layer.

Finally, the inset in Fig. 1 shows normalized PL spectra revealing a broad PL band centered on $\sim 2.1 - 2.2$ eV in KPO_3 and surface LID sites in KDP.¹⁹ Such broad emission originates from radiative recombination through deep defect levels in KDP and KPO_3 rather than from band-to-band radiative recombination. It should also be noted that the PL signal from bulk LID sites (as well as from pristine KDP) was much weaker, at least $\times 100$.

Hence, these PL results not only support the presence of decomposition products at surface LID sites (as revealed by Raman and XANES spectroscopies) but also provide evidence that such decomposition products absorb UV light (i.e., the 363.8 nm light used for PL excitation).

The presence of dehydration products — condensed phosphates with a reduced relative composition of oxygen and hydrogen — at surface LID sites, as revealed in this study, can be attributed to thermally-induced decomposition of KDP during laser-induced breakdown. Indeed, it is known that thermal processing of KDP at temperatures above ~ 175 °C results in material decomposition into water and KPO_3 salt, and the decomposition rate increases with increasing sample temperature.^{14,20} A recent experimental study²¹ has suggested temperatures of ~ 7000 K at 10 ns after the laser pulse in a deuterated KDP crystal exposed to an ~ 3 -ns, 355-nm laser pulse. At such temperatures (well above the melting point of KDP at ~ 260 °C),²² thermally-induced decomposition is not unexpected, particularly at the sample surface. In contrast, decomposition at bulk LID sites appears to be hindered due to the encapsulation by the surrounding material.²³

In conclusion, we have shown that irradiation of KDP with ~ 3 -ns, 355-nm laser pulses with fluences above the laser-induced breakdown threshold leads to stoichiometric changes (attributed to laser-induced material decomposition) at surface damage sites but not at bulk damage sites. The decomposed near-surface layer absorbs 364-nm UV light. Hence, this work may explain why surface damage sites in KDP tend to reignite and grow with subsequent exposure to high-power laser pulses, while bulk damage sites do not.

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