Laser-induced photochromic damage in potassium titanyl phosphate

R. Blachman and P. F. Bordui
Crystal Technology Inc., 1040 E. Meadow Circle, Palo Alto, California 94303

M. M. Fejer
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305

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We report studies of photochromic damage induced in $KTiOPO_4$ single crystals by ultraviolet (UV) irradiation with peak intensities from 0.3 to 4.0 MW/cm^2. The photochromic damage progressed to asymptotic values which were not linear with respect to UV intensity. Following UV exposure, transparency of damaged crystals recovered completely over tens of hours at room temperature, faster at elevated temperature. UV irradiation at significantly lower peak but higher average power did not produce damage. We also studied photochromic damage occurring during 1.064-μm second-harmonic generation. Fundamental infrared intensities ranged from 1.3 to 5.5 times larger than those producing highest nonlinear frequency conversion efficiency. Damage sites produced by the two methods exhibited similar absorption spectra.

Photochromic damage induced in $KTiOPO_4$ (KTP) crystals used to frequency double infrared (IR) radiation significantly limits performance in certain applications (the greytrack problem). The mechanism responsible for photochromic damage in KTP is not understood. Although simultaneous exposure to IR and visible radiation as occurs, for example, in second-harmonic generation (SHG), can lead to greytracking, it has been observed that neither IR nor visible radiation alone lead to damage.[1] Damage has also been observed in 532-nm pumped optical parametric oscillators operated significantly off degeneracy, indicating that harmonically related IR and visible radiation is not necessary for greytracking to occur.[2] Although photochromic susceptibility in KTP has been reported to depend on aspects of the crystal growth processing, all crystals appear to be susceptible at some level to damage.[1,3]

In this work, we induced photochromic damage in KTP crystals both by 1.064-μm SHG and by direct UV irradiation. We report conditions that led to photochromic damage, kinetics of damage onset, and relaxation, and a comparison of the damage created by the two methods.

All crystals used in this work were commercial quality, single-domain KTP produced by slow cooling in platinum crucibles using immersion-seeded growth from a $K_6P_4O_{13}$ flux as described in Ref. 4. Crystal surfaces were prepared using customary fabrication methods and were left uncoated.

For the UV exposure tests we used crystals either 4 or 7 mm thick with polished faces normal to the crystallographic x direction. We irradiated the crystals with the 355-nm third harmonic of a Nd:YAG laser (Fig. 1). The YAG laser was Q switched at 10 Hz with ~10-ns pulses full width at half-maximum (FWHM) and operated in multiple longitudinal modes. Second and third harmonics were generated with KD*P mixing crystals. The transverse intensity distribution of the 355-nm light required homogenization to avert profound damage to the crystals at hot spots in the beam. A UV grade silica plate with ground faces was used to scatter the beam which was then focused onto the KTP crystal. An aperture was placed in front of the crystal to control stray light and to allow accurate measurement of pulse energy. Ultraviolet light across the 2.5-mm spot formed at the crystal face had a 2:1 intensity ratio from center-to-edge; intensity fell sharply at the edge. For pulse energies of 0.8–1.6 mJ, the peak intensities of the UV radiation were 2 to 4 MW/cm^2, respectively.

Photochromic damage was detected in the KTP specimen by measuring absorption of a probe beam from a 670-nm diode laser polarized along the crystallographic z axis. When each exposure to the 355-nm radiation began, the KTP darkened rapidly (Fig. 2). The photochromic damage was located at the entry face and extended approximately a millimeter in depth. Absorption of z-polarized light was about five times as great as for light polarized in the xy plane, consistent with qualitative, visual observation of the damage through a film polarizer. Damage susceptibility was observed to be independent of both UV propagation and polarization directions.

After several minutes of UV exposure, the absorption of the probe beam reached an asymptotic value. This asymptotic value increased nonlinearly with UV intensity. After UV exposure was stopped, KTP crystals at 20 °C recovered their

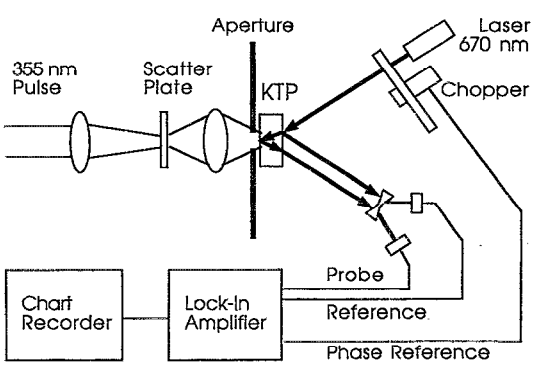

FIG. 1. Ultraviolet pulses of 10-ns duration are scattered and focused onto the $KTiOPO_4$ crystal. Absorption is measured by comparison of the power in 670-nm reference and probe beams reflecting off the first and second surfaces of the crystal, respectively; the second reflection intersects the UV-damaged region.

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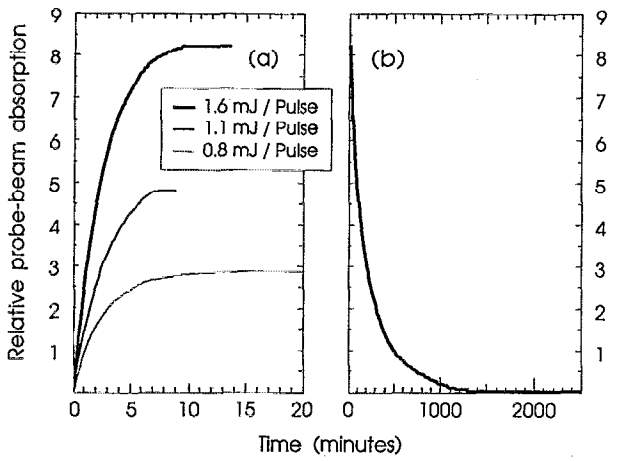

FIG. 2. (a) Absorption of z-polarized 670-nm light in $KTiOPO_4$ as photochromic damage is formed. As exposure continues, accumulated damage approaches a constant value. Degree of damage at asymptotic value is dependent on UV fluence. For pulse energies of 1.6, 1.1, and 0.8 mJ, corresponding intensities were 4.0, 2.8, and 2.0 MW/cm^2, respectively. (b) Characteristic recovery at 20 °C from damage of crystals damaged at the greatest energy in (a).

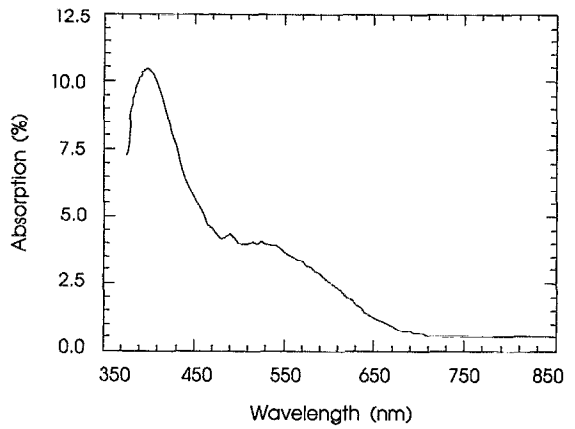

FIG. 3. Unpolarized absorption of an extensively SHG-damaged 1×1×1 cm^3 $KTiOPO_4$ crystal (normalized to an undamaged reference crystal).

original transparency over tens of hours, the time increasing with the degree of damage. Heating the crystals to 65 °C after UV exposure produced recovery within 1 h. Once recovered, previously damaged sites exhibited no change in photochromic susceptibility with repeated exposure to UV radiation. The recovered sites damaged at the same rates and to the same asymptotic values as with the first UV exposure.

In a second set of experiments the apparatus in Fig. 1 was reproduced except a continuous wave (cw) argon-ion ultraviolet laser was substituted for the pulsed 355-nm source, a 633-nm laser was substituted for the 670-nm probe laser and no scatter plate was needed. The ion laser provided 200±20 mW in a TEM_{00} mode at 351.1, 351.4, or 368.8 nm. Experiments were performed at each of these wavelengths. The diameter of the UV beam at the entry face was typically 150 μm($1/e^2$) with a peak internal UV intensity of 2 kW/cm^2.

For any duration of exposure up to 16 h, no change in a crystal's absorption was detected. The 2 kW/cm^2 cw intensity exceeded the 0.2 to 0.4 W/cm^2 average intensity of the pulsed laser by four orders of magnitude, while the 2- to 4-MW/cm^2 peak intensities used with the pulsed laser exceeded those of the cw laser by three orders of magnitude. These data indicate that the kinetics of UV induced darkening are nonlinear.

We also studied damage occurring during SHG of a Q switched 1.064-μm Nd:YAG laser in KTP crystals oriented for angle-critical phase matching (θ=90°; ϕ=23.3°). The laser was injection seeded for single longitudinal mode operation and 10-ns pulses of 120 to 200 mJ were Q switched at 10 Hz. We used a 4-mm-diam beam to darken 7- and 10-mm-thick crystals. The 1.064-μm beam was polarized at 45° to the crystallographic z axis.

Incident 1.064-μm peak intensities exceeded those for optimum second-harmonic conversion efficiency.[5] Here, we normalize peak intensities to experimentally determined optimum values of 130 and 70 MW/cm^2 for 7- and 10-mm-long crystals, respectively. SHG-induced damage occurred in less than 10 min with 200 MW/cm^2 (1.5 times the optimum) in 7-mm crystals. Damage was visibly darker after extended exposure at 250 MW/cm^2 (1.9 times the optimum). For both cases the crystal was operated for more than 1 h; the damage approached its asymptotic value in less than 20 min. As with UV-induced damage, the SHG-induced photochromic absorption was both polarized and reversible. Visible, diffuse, SHG-induced damage in the crystals was symmetric about the beam axis and the degree of darkening and diameter of the darkened region increased monotonically toward the exit face of the crystal. For 385 MW/cm^2 in 10-mm crystals (5.5 times the optimum) darkening occurred within 1 min and the crystals suffered catastrophic thermally induced fractures. In one such experiment, we arranged filters at the crystal's output face to block radiation of wavelengths above 400 nm. UV radiation collinear with the infrared and green outputs. Based on the sensitivity of our fluorescent sensor, we estimate typical UV intensities of >10 W/cm^2 during SHG (on the order of that expected for generation in one 4.15 μm coherence length). Significantly higher UV intensities (>100 W/cm^2) were seen transiently before catastrophic damagein one experiment.

In further experiments we created damage by 1.064-μm SHG in a 10-mm-long crystal with an 8-mm beam diameter and peak intensity of 90 MW/cm^2 (1.3 times the optimum). This allowed us to induce the asymptotic degree of damage over a 7-mm-diam region extending 5 to 6 mm along the propagation axis in the KTP without risk of catastrophic failure. The absorption spectrum for this extensive damage is shown in Fig. 3. Similar to what was observed for UV-induced damage, the KTP recovered completely from this damage in 36 h at 20 °C or in 1 h at 65 °C.

To compare the spectral dependence of absorption induced by SHG to that due to UV exposure, unpolarized measurements were carried out with a Perkin-Elmer Lambda-9 spectrophotometer. Spectra of damaged samples were normalized to those of undamaged reference samples. Absorption spectra were taken within 2 h after inducing damage; 1.064-μm SHG damage was produced in a 7-mm-thick crys-

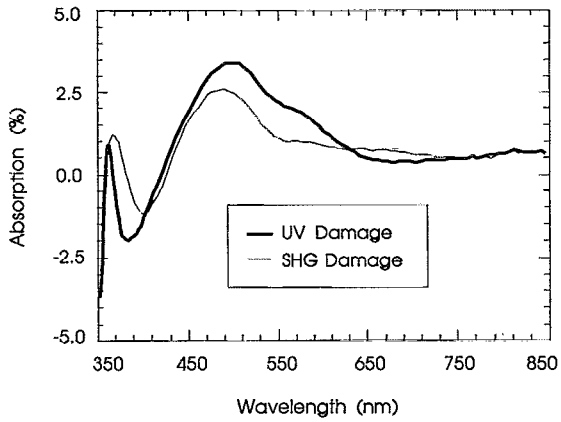

FIG. 4. Photochromic absorption spectra are compared for unpolarized light in crystals damaged by SHG and by ultraviolet irradiation. Absorption is normalized to that of undamaged crystals. For both samples the damage is not extensive. Negative absorption near 350 and 400 nm indicates bleaching has occurred.

tal with a 3-mm beam having 440-MW/cm^2 peak intensity (3.4 times the optimum). Exposure was stopped before the rapidly forming damage reached its asymptotic value. Four sites were damaged to cover a 6×8 mm^2 area for spectroscopy. To produce UV damage for comparison, we irradiated 4-mm-thick x-cut samples. Four sites, each 4 mm in diameter were exposed for 5 min each with 0.4-mJ pulses at 355 nm (0.3 MW/cm^2) to cover a 6×8 mm^2 area with damage. In Fig. 4, the spectra of this damage produced by UV irradiation and by SHG are compared. Although multiple-site UV- and SHG-induced absorption was inhomogeneously distributed in the crystals and hence, difficult to compare quantitatively, the photochromic absorption spectra are qualitatively similar. For subasymptotic induced damage the native absorption of the KTP near 400 nm was bleached while absorption at wavelengths longer than about 430 nm was enhanced. The absorption spectra show that the bleached absorption near 400 nm in lightly damaged crystals evolved into an absorption maximum near that wavelength in more extensively damaged KTP.

Photochromic damage to KTP commonly entails simultaneously large intensities of second-harmonic radiation and infrared radiation such as are present during 1.064-μm SHG.[6] One mechanism for greytracking consistent with our observations is that photochromic damage in KTP is created through nonlinear absorption of sum-frequency-generated UV radiation. The observed sum-frequency generation of UV radiation during greytracking greatly exceeded that predicted theoretically for generation in one coherence length under the most extreme conditions of 1.064-μm SHG in our experiments. It is highly improbable that resonant enhancement of the nonlinear susceptibility near KTP's UV band edge is large enough to account for the large amount of UV generation observed.

Several further experiments are indicated. Simultaneous, polarized and time-resolved spectroscopy of evolving photochromic damage are needed to elucidate the initial bleaching near 400 nm and the subsequent increased absorption. Quantitative characterization of the intensity dependence of darkening induced by nonlinear absorption of combinations of UV with green or IR radiation is necessary to elucidate the photochromic damage process which dominates during SHG. Characterization of the temporal evolution of UV generation during SHG may clarify the mechanism responsible for the anomalously large UV intensity we observed transiently before catastrophic damage.

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