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Generation of color centers in alkali halide single crystals using ultrafast laser pulses

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The evolution of color centers generated by 400-nm femtosecond laser radiation in three single-crystal alkali halides (sodium chloride, potassium chloride and potassium bromide) were probed by focusing appropriately chosen probe lasers through the femtosecond laser spot. The evolution of coloration after the termination of femtosecond laser radiation, and subsequently after the resumption of femtosecond radiation, was also probed. While all three materials color gradually during initial femtosecond laser radiation, rapid changes are often observed when femtosecond radiation is terminated or resumed.

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1. Introduction

The high power densities associated with femtosecond (fs) laser pulses allow for strong nonlinear interactions in nominally transparent materials. Femtosecond pulses color many alkali halides at modest pulse energies, and have long been exploited to study the kinetics of defect formation on subpicosecond time regimes [1]. The most prominent color center is typically the F center, which consists of an electron trapped at a halide vacancy. Thus the F center site has the same nominal charge as the same site without the defect. Two F centers on adjacent sites form an M center (or F_2 center). When an F center captures a free electron it becomes an F^- center (two electrons trapped at a halide vacancy — also called an F' center). Color center formation in the alkali halides has been extensively studied [2–6], providing a wealth of information for the interpretation of new results. In this work, we examine the fate of defects produced by fs laser radiation in single crystal sodium chloride, potassium chloride and potassium bromide on time scales ranging from milliseconds to several tens of seconds. The visible absorption due to these defects was monitored by measuring the intensity of CW probe lasers with appropriate wavelengths, focused through the center of a spot of material modified by a fs laser.

2. Experiment

Femtosecond laser pulses were produced by a Spectra Physics Hurricane laser system, with maximum energy 1 mJ/pulse at 800 nm and a pulse width of 120 fs at a repetition rate of 1 kHz [7]. Frequency doubled radiation was obtained by directing the 800 nm pulses through an appropriately phase matched potassium dihydrogen phosphate (KDP) crystal. The resulting 400 nm pulses were focused through a 1 m lens to form a 0.5 mm spot on the sample. At this wavelength, three-photon excitations are required to produce electron hole pairs in each of the three alkali halide materials in this study. Nevertheless, each material darkens rapidly during irradiation due to the production of color centers via electron hole recombination.

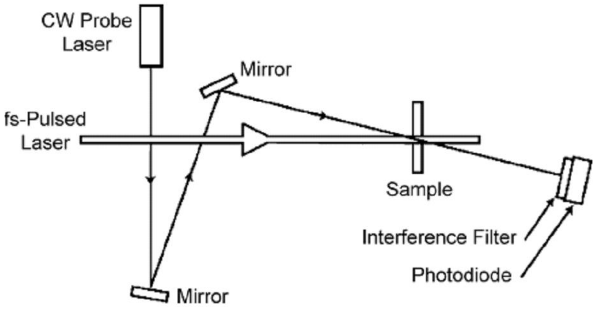

Fig. 1. Experiment set-up for transmission measurements during fs laser irradiation.

The geometry of the transient absorption measurements is indicated schematically in Fig. 1 [7]. The output beams of the CW probe lasers were directed obliquely to the fs laser and focused to a 0.1 mm diameter spot at the center of the fs laser spot. The intensity of the probe beams were reduced with neutral density filters to minimize the effect of the probe light on the sample. The probe intensities were monitored with ThorLabs Det 210 high speed photodiodes. Interference filters matched to the appropriate CW wavelength minimized signals due to scattered fs radiation. The diode output was digitized and recorded with a LeCroy LC584AXL 1 GHz digital oscilloscope.

3. Results and discussion

As discussed below, transient F^- centers play an important role in several of the measured signals. The expected contribution of the F^- center to the absorption at the F and M center probe wavelengths is illustrated for NaCl, KCl and KBr in Fig. 2 [8]. The energies of the peak F and M center absorptions are also indicated [7,9]. In NaCl, the F^- absorption maximum is near the peak F center absorption. Although the F^- center contributes little to absorption at the peak of the M band (720 nm), it absorbs significantly at our M center probe wavelength (633 nm). In KCl and KBr, F^- band absorption is especially strong at the M center probe wavelengths, and contributes significantly to absorption at the F center probe wavelengths.

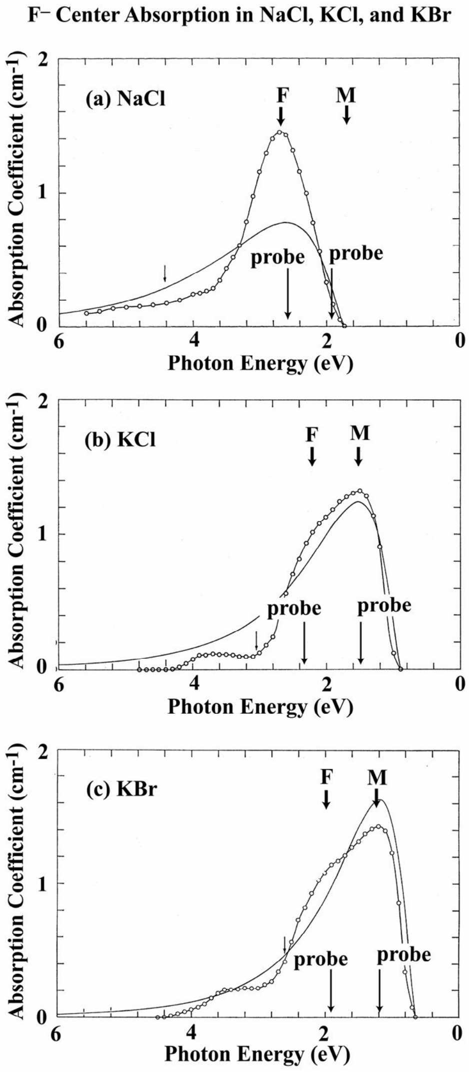

Fig. 2. Experimental (dots) and calculated (smooth lines) values for F^- center absorption in (a) NaCl, (b) KCl, and (c) KBr, adapted from ref. [8]. The short, dark arrows show the peak absorption energies for F and M centers. The light, long arrows show the probe laser energies used to monitor absorption by these defects.

Coloration in NaCl. Defect production by fs laser radiation is a strong function of pulse energy [10]. The transmission of the F center and M center probe beams through a transparent NaCl single crystal appears in Fig. 3. During fs laser radiation, both signals drop gradually—consistent with the production of F and M centers. F^- centers are produced when electrons are trapped at F centers. (This process also produces halide vacancies that lack trapped electrons. These vacancies do not contribute to probe absorption.) When the fs laser source is blocked, transmission at both probe wavelengths increases rapidly—with an especially large increase in the M center band. The transmission at 633 nm recovers about 60% of its original value in a few hundred milliseconds.

The F^- center in alkali halides is generally unstable at room temperature [11] and releases its electron on time-scales of one to a hundred milliseconds. The rapid increase in transmission in the M center band when the fs laser beam is blocked suggests that transient F^- centers are responsible for much of the absorption *during* fs exposure. When the fs beam is blocked, the F^- centers decay rapidly (by releasing electrons), and their contribution to the M center probe absorption falls rapidly. The effect of F^- centers on absorption in the F band is much smaller—in part due to the high initial F-center densities. Since both F and F^- centers absorb strongly at 473 nm, the loss of absorption due to F^- center decay is largely compensated by the gain of absorption due to F centers produced when the released electrons are trapped at empty halide vacancies. When fs laser radiation is resumed, the transmission at 633 nm drops rapidly: the first fs laser pulse is responsible for the majority of the total transmission drop. Conduction band electrons produced by F center ionization are trapped at F centers produce F^- centers—rapidly decreasing the 633 nm signal to the previous minimum level.

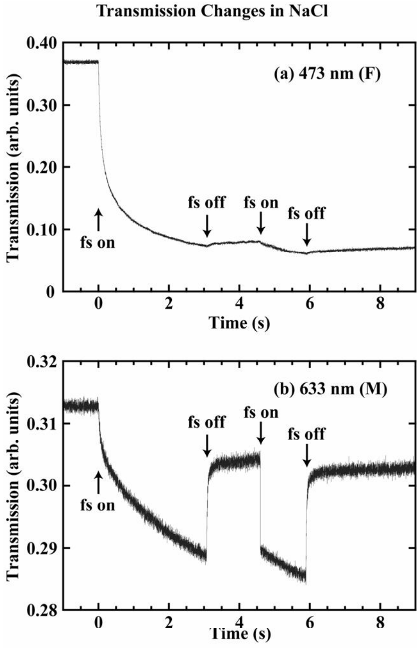

Fig. 3. Transmission through an NaCl crystal during exposure to 400 nm fs laser radiation at 90 μJ/pulse: (a) probed at 473 nm; (b) probed at 633 nm.

Coloration in KCl. The transmission of the F center probe through an initially clear KCl single crystal (20 μJ/pulse) appears in Fig. 4 (a). The gradual, initial drop in transmission is again consistent with the production of F and F^- centers. When the fs laser beam is blocked, the transmission drops rapidly over tens of milliseconds, and then slowly recovers over tens of seconds. The rapid transmission drop after the fs laser is blocked is *not* observed in the NaCl F center transmission of Fig. 2 (a). The rapid drop in KCl is consistent with electron transfer from F^- centers to empty halide vacancies (producing F centers) when the fs laser is blocked. Since F centers in KCl absorb more strongly at 532 nm than F^- centers, the conversion of F^- centers to F centers rapidly *decreases* transmission at 532 nm. When fs radiation is resumed, the reverse process rapidly increases transmission in the F center band.

The intensity of the M center probe at 808 nm during fs irradiation is displayed in fig. 4b. During the initial stage of fs radiation, M and F^- center production gradually decreases transmission. Since F^- center absorption peaks near 808 nm [9,11,12], it contributes strongly to probe absorption. When the fs laser is blocked, transmission at 808 nm rises to 90% of its initial value within tens of milliseconds. Subsequently, a *single* fs laser pulse reduces transmission to near its previous minimum value.

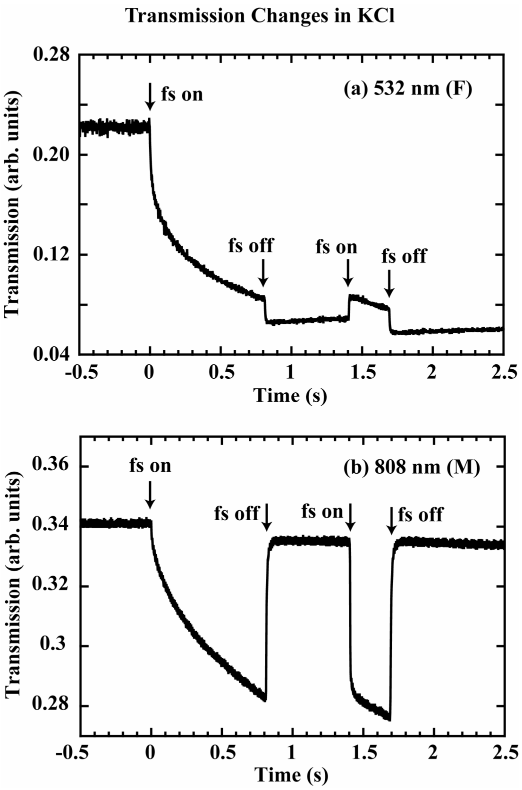

Fig. 4. Transmission through an initially transparent KCl crystal during exposure to 400 nm fs laser pulses (20 μJ/pulse): (a) probed at 532 nm; (b) probed at 808 nm.

Coloration in KBr. Transmission measurements at 633 nm during fs laser exposure at 200 μJ/pulse is shown in Fig. 5 (a), where the fs beam was blocked twice during the experiment. Transmission in the M center band (1064 nm—a separate experiment under similar conditions) is shown in Fig. 5 (b). The transmission at both wavelengths gradually drops during fs irradiation. Unlike NaCl and KCl, however, transmission in the M center band *continues* to drop when the fs laser is blocked. When fs radiation is resumed, transmission rises quickly to relatively high levels. We tentatively attribute this gradual increase in F band transmission and the decrease in M band transmission to the aggregation of F centers to form M centers. Unlike the M centers in NaCl and KCl, the M centers in KBr are relatively unstable. The thermal activation energy for M center dissociation in KBr is 0.08 eV (versus 0.19 eV in KCl) [13], suggesting that M centers are easily dissociated during fs laser exposure. When the fs beam is blocked, F centers gradually aggregate to reform M centers, thereby increasing transmission at 633 nm and decreasing transmission at 1064 nm.

If F^- centers contribute significantly to absorption in the M center band *during* fs irradiation, as they do in NaCl and KCl, this absorption may account for the small, positive-going spikes observed when the fs beam is blocked, and the small negative-going spikes observed when the fs laser beam is unblocked in Fig. 5 (b).

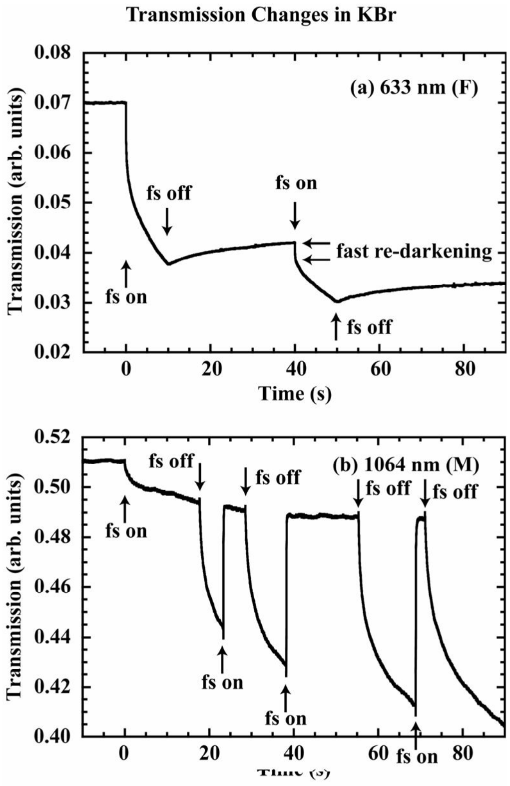

Fig. 5. Transmission through a KBr crystal during exposure to 400 nm fs laser (200 μJ/pulse): (a) probed at 633 nm; (b) probed at 1064 nm. The data in (a) and (b) were acquired in different experimental runs.

4. Conclusions

Significant changes in the transmission in the F and M bands of three alkali halide crystals are observed when pulsed fs laser radiation is turned on and off after initial coloring. On millisecond time-scales, these changes typically reflect charge transfer between defects. In NaCl and KCl, this transfer has especially strong effects on absorption at the M center probe wavelengths. F^- centers produced by a single fs laser pulse on previously darkened material can *decrease* transmission almost to its previous minimum level. In contrast, transmission at the KBr M center probe wavelength rapidly *increases* when fs laser radiation is resumed. We attribute this increase to the rapid dissociation of KBr M centers during fs laser exposure.

Rapid transmission changes during exposure to intense laser radiation can be exploited to protect users and equipment from intense radiation. Although alkali halides are not sufficiently robust for many applications, they are useful model materials for the study of these effects.

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