Simultaneous fabrication of laser-active colour centres and permanent microgratings in lithium fluoride by a single femtosecond pulse

LETTER TO THE EDITOR

Simultaneous fabrication of laser-active colour centres and permanent microgratings in lithium fluoride by a single femtosecond pulse

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Abstract
We report, for the first time, simultaneous fabrication of laser-active F_2 and F_3^+ colour centres in lithium fluoride and permanent periodic gratings with fringe spacings as fine as sub-micron size by two interfering infrared femtosecond (fs) laser pulses. In particular, the optical properties (absorption and luminescence) of F_2 and F_3^+ colour centres produced by a single fs laser pulse are compared with those created by damage from radiation such as x-rays. The present technique of simultaneously fabricating laser-active colour centres and functional fine-periodic structures in photo-insensitive transparent materials may well be a useful method for making miniaturized optical devices.

Among the alkali halide crystals, lithium fluoride (LiF) is of particular interest because of the excellent thermal and optical stabilities of its laser-active colour centres even at room temperature (RT) as well as the good physical and chemical properties. Moreover, LiF doped with Ti and Mg impurities has been widely used as a radiation dosemeter of high sensitivity for a long time. In particular, the F_2 and F_3^+ colour centres (two electrons bound to two or three neighbouring anion vacancies, respectively) in LiF are very promising candidates for producing visible laser action from the green-to-red spectral range [1–3] at RT and the realization of miniaturized optical devices [4–6]. However, due to it having the strongest ionic

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binding and a larger energy band gap ($\sim$14 eV) [7] compared to those of NaCl (7.7 eV) and KCl (7.5 eV) [8], and the low vapour pressure of lithium metal, LiF, in the form of bulk or films, cannot be coloured with the usual techniques of additive coloration, and colour centres are produced with low-ionizing radiation such as electrons, γ-rays, and x-rays.

As a typical example of additional functionalities encoded in the alkali halides, a distributed feedback (DFB) colour centre laser action in the 2700 nm region achieved using the KCl:Li F_A (II) centres was first reported by Bjorklund *et al* [9]. We have also reported [10] DFB laser action in the 1300 nm region achieved using KCl F_4 ($=N_2$) centres. A periodic grating with fringe spacings as fine as 900 nm for the former and 440 nm for the latter was encoded by means of a two-photon coloration process using two interfering intense beams of the fourth harmonic (266 nm) of a Q-switched Nd:YAG laser. From a technical point of view, in these cases we need considerable time to write a DFB laser grating several millimetres long, and both coloration and photo-aggregation processes to obtain the laser-active colour centres inside a crystal.

In this letter, we report the first demonstration of simultaneous fabrication of laser-active colour centres such as F_2 and F_3^+ centres and fine-pitched micrograting structures in LiF by a single laser pulse. Also, the optical properties of these centres produced by femtosecond (fs) laser pulses are compared with those created by damage from radiation such as x-rays. As a typical example, the present technique is applied in the production of waveguides and gratings inside a LiF crystal.

The samples used in this study were commercially available polished LiF crystals with thickness of approximately 1.5 mm. They contained Ca (7 wt ppm), Fe (1 wt ppm) and Mg (1 wt ppm) as the main impurities. In order to encode both laser-active colour centres and fine-pitched gratings simultaneously inside LiF crystals, a regenerative amplified fs pulse from a mode-locked Ti:sapphire laser (wavelength: 800 nm; pulse duration: 100 fs; repetition: 10 Hz) was split into two beams; then these were crossed on the surface of LiF plates to give a spot size of approximately 50 μm diameter. The pulse energy was varied from 0.01 to 3 mJ/pulse. The colliding angle between the two beams was varied from 15° to 158°, corresponding to the recorded fringe spacings of 3–0.4 μm, respectively. The optical paths of the two beams were adjusted precisely, both spatially and temporally, to produce the interference. The sample stage had a capability for precisely positioning samples, including translational motion along three orthogonal directions. A single pulse is selected during the 10 Hz operation of the laser by a mechanical shutter. An outline sketch of this experimental set-up has already been given elsewhere [11–13].

In contrast, the colour centres produced by x-rays at RT were achieved with a Cu tube, operated at 30 kV and 30 mA for 30 min. Optical absorption spectra at RT were measured with a Hitachi U-3500 spectrophotometer in the spectral range from 190 to 800 nm, while the emission spectra were taken with a Hitachi F-3010 spectrofluorometer. Moreover, all the optical spectra were best fitted with a sum of single-Gaussian bands to obtain peak positions and spectral widths precisely. Irradiation-induced morphological changes on surface or near-surface regions of samples were observed with a differential interference optical microscope, a confocal laser scanning microscope (LSM 510, Carl-Zeiss), and an atomic force microscope.

Figure 1 shows the optical absorption spectra of a LiF crystal, kept in the dark for more than 24 h after the irradiation with fs laser pulses (solid curve) and x-rays (dotted curve) at RT. In the case of fs pulse irradiation, the single pulse was a Fourier-transform-limited one with 70 μJ/pulse energy and 100 fs duration. In this case, there was no interference with the beam and it was focused by a convex lens ($f = 60$ mm) onto the sample. The surface of a sample was periodically irradiated with a number of laser shots at a separation of 50 μm, large enough to allow the fluorescence detection of a single shot. As detailed in the literature [1], two main
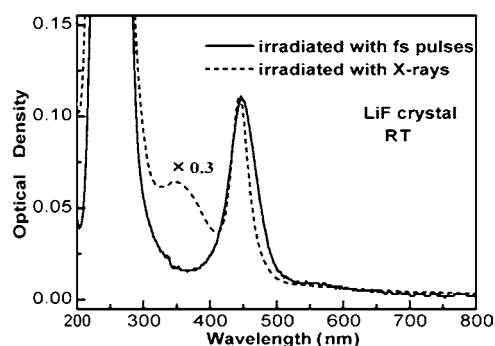
Figure 1. Absorption spectra at RT taken 24 h after the colouring of a LiF crystal irradiated with 100 fs laser pulses (solid curve) and x-rays (dotted curve).
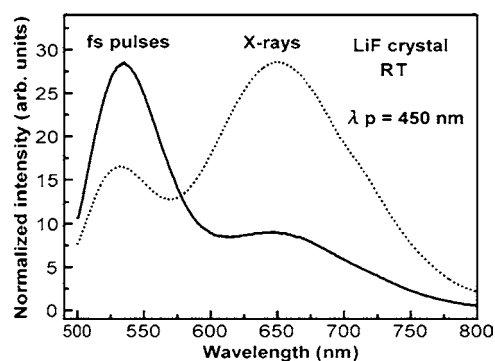

Figure 2. Normalized luminescence spectra, corresponding to the absorption spectra, as shown in figure 1, of LiF crystals irradiated with fs laser pulses (solid curve) and x-rays (dotted curve) by pumping with the M band at 450 nm.
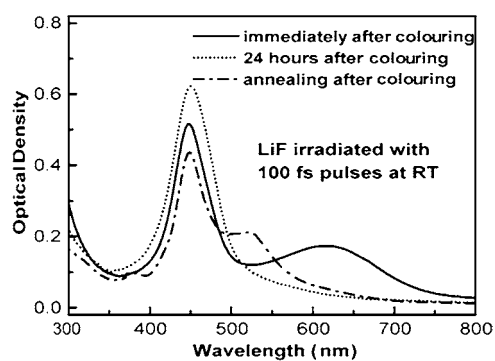

Figure 3. Absorption spectra at RT taken immediately after the irradiation (solid curve), 24 h after the colouring (dotted curve), and after the annealing (dashed–dotted curve) for LiF irradiated with fs laser pulses.

absorption bands can be observed—peaking at 250 nm, due to the F centres, i.e., an electron trapped in an anion vacancy, and at 450 nm, due to the unresolved F_2 and F_3^+ centres, whose band was previously called an M band. 'M band' means both the F_2 and the F_3^+ absorption bands hereafter.
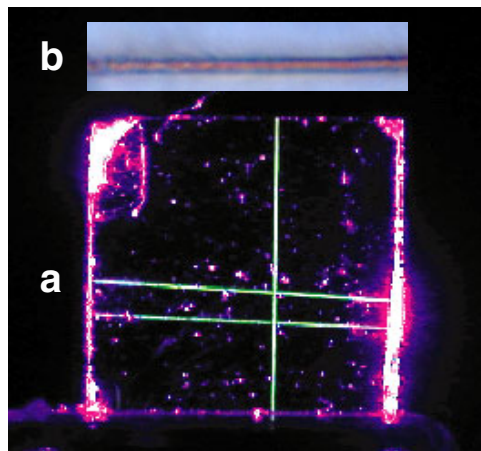
Figure 4. (a) A photograph of the fluorescence pattern of the waveguide excited by the M band light at 450 nm and (b) a microscope photograph of the waveguide produced by fs pulses at a larger magnification.
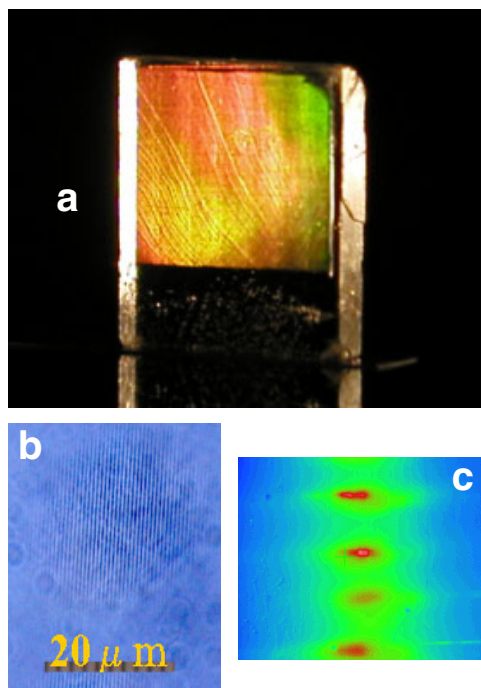

Figure 5. (a) A photograph of gratings encoded on LiF fabricated by fs laser pulses, (b) a confocal microscope image of microgratings, enlarged, and (c) a luminescence image of the side surface in the crystal excited by the M band light.

As clearly shown by the normalized M absorption band in figure 1, the major differences between the absorption spectra for samples coloured with fs laser pulses and x-rays were as regards their half-widths, i.e., full widths at half-maxima (FWHMs), and their peak positions for the M band around 450 nm. In the case of fs irradiation, a much wider absorption band and a peak slightly shifted towards longer wavelengths can be distinctly observed. The half-

widths at RT were 0.17 and 0.28 eV for the samples irradiated with x-rays and fs laser pulses, respectively; these values agree quite well with the data (i.e., the values of the half-width of the absorption band are 0.16–0.19 eV for F_2 centres and 0.29–0.35 eV for F_3^+ centres) from the previous measurements [14, 15] on samples coloured by ionizing radiations at RT. These results indicate a predominance of the F_3^+ centres in the case of fs irradiation. These differences can also be seen with the naked eye, because the former samples were yellow and the latter were green–yellow after coloration. However, a final check was made by means of emission measurements. The mechanisms which led to coloration of the wide-band-gap (∼14 eV) material LiF by means of near-infrared fs pulses of a 800 nm (1.55 eV) laser may be explained by the non-linear excitation of electrons to the conduction band via processes such as avalanche ionization, tunnelling ionization, and multiphoton absorption [16, 17].

Figure 2 represents the normalized luminescence spectra corresponding to the absorption spectra in figure 1 after the irradiation with fs laser pulses (solid curve) and x-rays (dotted curve) at RT, exciting the samples with the M band at 450 nm. Two separate broad emission bands due to F_2 and F_3^+ centres are observed at 650 nm (red component) and 530 nm (green component), respectively. It was found that the green component was dominant for the irradiation with fs laser pulses, while the red component was dominant for the irradiation with x-rays. In general, one can hardly get F_3^+ centres in LiF with sufficiently high density by ordinary coloration processes such as radiation damage at RT. In order to attain the selective production of the F_3^+ centres, the following procedure was reported to be used [18]: the sample was coloured by ionizing radiation at liquid nitrogen temperature (LNT) and then there was irradiation with the UV radiation at the same temperature, and finally the sample was kept in the dark at RT. It may be considered that with fs pulses, energy is deposited into the material before any energy transfer to the lattice can occur.

Moreover, the radiative lifetimes for the green (F_3^+ centres) and red (F_2 centres) components of the emission excited by the M band light at 450 nm were also measured by using a time-correlated photon-counting technique at RT. The sample was kept in the dark for more than 24 h to allow the complete stabilization of the colour centres. The lifetime values (8.08 ns for the former and 16.7 ns for the latter) coloured by fs laser pulses were identical to those previously reported [19] for LiF coloured by x-rays at RT.

Figure 3 shows the absorption spectra for LiF exposed to different procedures after the coloration by 100 fs pulses between 300 and 800 nm, namely in the spectral range where the F_2 and F_3^+, F_3 (=R), F_4 (=N), and F_2^+ absorption bands lie. In this case, the beam was focused to an area of 4 mm × 10 μm by a cylindrical lens ($f = 50$ mm) to allow the concentration of the M absorption band to be found exactly. The pulse energy was 1.0 mJ/pulse and the duration was 100 fs. There was irradiation with about 120 pulses at the same position on the sample and the total coloured area was 4 mm × 4 mm. The absorption curves were taken immediately following the irradiation (solid curve), 24 h after the colouring (dotted curve), and after the annealing procedure (dashed–dotted curve) for a LiF crystal at RT. Comparing these spectra, we see that the F_2^+ band located at 640 nm emerges immediately after the crystal coloration, and in 24 h the F_2^+ band is almost completely destroyed together with the M band production. After annealing in air for 30 min up to a temperature of 473 K, as the M band decreases, other aggregate bands such as F_3 (375 nm) and F_4 (520, 545 nm) bands were produced. In these cases, the half-widths at RT were 0.26 eV for just irradiation, 0.33 eV 24 h after the colouring, and 0.23 eV after the annealing procedure. As expected, because of the thermal treatment, the green component of the emission spectrum due to the F_3^+ centres was almost eliminated and the colour of the crystal changed to brown upon annealing.

The concentration of the F_3^+ centres produced by fs laser pulses has been calculated via the Smakula formula for Gaussian-shaped bands by assuming an oscillator strength of 0.5,

chosen arbitrarily because it is unknown, for the absorption band 24 h after the colouring. A maximum concentration of F_3^+ centres of $\sim 1 \times 10^{18}$ centres cm^{-3} is reached.

Figure 4 shows (a) a photograph of the fluorescence patterns of F_3^+ (more) and F_2 (fewer) colour centres written inside a LiF crystal with 100 fs laser pulses and (b) an optical microscope image of waveguides at a larger magnification. The waveguides were formed by focusing the laser pulses through a convex lens ($f = 50$ mm) and translating the LiF sample perpendicular to the axis of the laser beam at a rate of 50 μm s^{-1}. The pulse energy was 80 μJ/pulse. The observed emission in the green spectral region in figure 4(a) is similar to that obtained for excitation of the absorption band peaked at 450 nm as shown in figure 2. The width of the waveguide was about 10 μm. We also examined the refractive index variation of the waveguide by using a He–Ne laser (633 nm). As a result, it was found that the value of the refractive index of the coloured region was 1.406 at 633 nm; this value was compared to that for the virgin area of the crystal, i.e., 1.3912 [20] at 640 nm. The induced change in refractive index was assessed to be about $\sim$1%.

Figure 5 shows (a) a photograph of the gratings inside a LiF crystal fabricated by two-beam interference of a single fs pulse, (b) a confocal laser scanning microscopic photograph of the gratings encoded on LiF (enlarged), and (c) a luminescence image of the side surface in the crystal excited by the M band light. In this case, the pulse energy was 100 μJ/pulse and the duration was 100 fs. The gratings were encoded inside the sample at depths of 40–540 μm at intervals of 100 μm from the top surface. The periodic fringe spacing is 1.0 μm, which agrees with the calculated line spacing. Each grating spot of 30–40 μm diameter was encoded by a single shot.

In conclusion, the present technique is a fast method that is applicable not only for producing laser-active colour centres, but also for encoding non-erasable periodic structures in the refractive index inside the wide-gap material LiF. It has also been confirmed by absorption and luminescence measurements that the laser-active F_3^+ centres are mainly produced even at RT by fs laser irradiation. Moreover, we have succeeded in producing three-dimensional active waveguides several millimetres inside the crystal by moving the irradiation beam spot. The present technique of simultaneously fabricating laser-active colour centres and functional fine-periodic structures may well be a useful method in making miniaturized optical devices such as DFB lasers, distributed Bragg reflectors, three-dimensional active waveguides, and microcavities.

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