

# Simultaneous upconversion luminescence and color centers generated by femtosecond laser irradiation of LiF crystals

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We report the upconversion luminescence of lithium fluoride single crystals excited by an infrared femtosecond laser at room temperature. The luminescence spectra demonstrate that upconversion luminescence originates from the color center of  $F_3^+$ . The dependence of fluorescence intensity on pump power reveals that a two-photon excitation process dominates the conversion of infrared radiation into visible emission. Simultaneous absorption of two infrared photons is suggested to produce the  $F_3^+$  center population, which leads to the characteristic visible emission. The results are on the reveal and evaluation of the simultaneous two-photon absorption on the green upconversion process.

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Multi-photon absorption spectroscopy has long been a subject of widespread concern in the field of spectral studies. However, studies on the applications of multi-photon absorption have been limited because the multi-photon absorption cross section of most materials is very small. Since the successful development of high nonlinear absorption interface materials has recently been achieved, the research on multi-photon absorption has also steadily increased<sup>[1,2]</sup>. In the field of biology, two- and three-photon absorptions are mainly employed in microscopic imaging systems<sup>[3,4]</sup>, where multi-photon absorption-excited fluorescence can provide three-dimensional (3D) imaging with sub-micron precision<sup>[5]</sup>. Besides, multi-photon absorption has been evaluated for application in ultra-high density optical storage and 3D high-precision micro-machining<sup>[6-8]</sup>. This type of absorption has two preconditions. First, the material must have a level corresponding to the plurality of the excitation photon energy. Photon transitions from the ground state to the levels may be forbidden, but multi-photon absorption can surpass these transition constraints. Second, the optical density requires a relatively high excitation source, which may be met by using an ultrashort-pulse laser. Current research on the conversion mechanism has determined successive energy transfer (SET), excited-state absorption (ESA), cooperative upconversion (CU), and photon avalanche (PA) as possible mechanisms<sup>[9-12]</sup>.

Research in recent decades has focused on rare-earth and transition-metal ion-doped materials<sup>[13]</sup>. Thus, ignoring those that are not doped intrinsic luminescent

materials, which rely on material defects luminescence. Quartz glass and lithium fluoride (LiF) crystals are the most common defect-related luminescent materials. As early as 1999, Qiu *et al.*<sup>[14]</sup> found that quartz glass shows bright blue-violet fluorescence at 800 nm femtosecond laser irradiation, whose analysis concluded that internal material defects induce luminescence. The entire upconversion process is based on simultaneous multi-photon absorption. Color centers (CCs) are lattice defects trapping electrons or holes, and are easily created in LiF crystals at room temperature by irradiation with ionizing radiation<sup>[15]</sup>. Up to now CCs were created mainly by ionizing radiation beams. High contrast photoluminescence patterns in LiF crystals were produced by soft x rays from laser-plasma sources<sup>[16]</sup>. While studies on LiF mainly focus on CCs, the use of femtosecond laser research to evaluate the upconversion process of LiF defect luminescence is relatively rare. For example, Courrol, Basiev, *et al.*<sup>[17-19]</sup> only investigate the threshold and possible mechanisms for CC generation, but did not reveal and evaluate the simultaneous two-photon absorption on the upconversion process.

In the present work, we used an 800 nm femtosecond laser to excite LiF single crystals to generate upconversion luminescence. The dependence of the fluorescence intensity on the pump power reveals that a two-photon excitation process dominates in the conversion of infrared radiation to the visible emission. LiF crystals occupy a landmark position in the history of laser development. Our experimental results are promising for the applications of LiF crystals

in integrated CC lasers, full color all-solid state display, high-density optical storages, etc.<sup>[20-24]</sup>.

The LiF sample was cut into dimensions of 10 mm × 10 mm × 2 mm. All six surfaces of the sample were optically polished to facilitate femtosecond laser irradiation and optical spectral measurements.

A regeneratively amplified 800 nm Ti: sapphire laser emitting 120 fs and 1 kHz mode-locked pulses was used as the irradiation source. To achieve a high power density, the laser beam was focused onto the samples by an objective or optical lens. The focal point beneath the sample surface can be monitored by a confocal microscope system linked to a charge coupled device. The spot size can be controlled to at least below several microns by choosing the appropriate objective or optical lens, which adjusts the power density of the laser beam. The fluorescence spectra obtained after excitation by a focused femtosecond laser were recorded by a ZOLIX SPB300 Spectrometer. The scanning rate of this spectrometer was 150 nm/min. The fluorescence spectra were measured at an angle of ~90° with respect to the pump beam. The fluorescence spectra obtained through excitation by a 448 nm monochromatic light from a Xe lamp were measured by a JASCO FP6500 Spectrometer. The excitation and emission spectra of the sample were measured by an FLSP920 Fluorescence Spectrometer.

To measure the absorption spectra, the focal point was positioned 1 mm beneath the LiF crystal sample surface. An internal grating structure comprising CCs with dimensions of 6 mm × 4.5 mm was fabricated by scanning the sample using a 3D XYZ stage during femtosecond laser irradiation. A laser beam with an average power of 40 mW was focused by a 20 times objective with a 0.45 numerical aperture; the focused laser spot size is 2.84 μm. The scanning rate of the laser beam and scanning interval were set at 1000 μm/s and 20 μm, respectively. The optical absorption spectra were measured at room temperature using a JASCO V570 spectrometer.

When the LiF crystal sample is irradiated by focused femtosecond laser pulses, strong visible green emission is observed on the focal spot area (inset of Fig. 1). Figure 1 shows the emission spectrum obtained through excitation

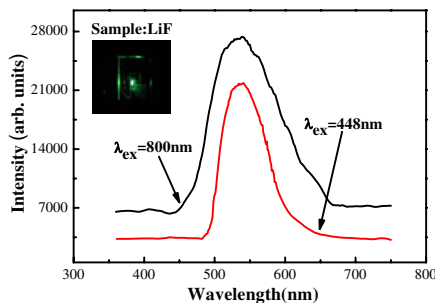


Fig. 1. Emission spectra of the LiF crystal sample under focused femtosecond laser irradiation and 448 nm monochromatic light excitation (using a 600 nm IR cut filter). Inset: The sample irradiated by a focused femtosecond laser in a darkroom.

by the femtosecond laser with a power of 60 mW. The laser beam is focused by an optical lens with a focal length of 160 mm; the focused laser spot size is 21.42 μm. In order to better compare with the femtosecond laser excitation, Fig. 1 also shows the luminescence spectrum of the femtosecond laser-processed LiF crystal excited by a 448 nm monochromatic light from a Xe lamp (using a 600 nm IR cut filter by a JASCO FP6500 spectrometer). The 600 nm IR cut filter can filter more than 600 nm of near-IR light; the broadband emission peaking of F<sub>2</sub> CCs at 680 nm is filtered<sup>[17]</sup>. The spectrum of the sample irradiated by the femtosecond laser exhibits a broadband emission peaking at 540 nm, similar to the sample excited by a 448 nm monochromatic light. This is probably a two-photon excitation process, which will be discussed in the next paragraph.

Several interesting characteristics on the formation of CCs are also observed, one of which is the formation and aggregation of F during irradiation, and can be confirmed by the green emission (broadband peaking at 540 nm) observed during laser irradiation; this emission is characteristic of F<sub>3</sub><sup>+</sup> CCs<sup>[17,19]</sup>. Furthermore, Fig. 2 shows the absorption spectra of a LiF sample before and after femtosecond laser irradiation. A peak ranging from 200 to 300 nm (peaked at 248 nm) is attributed to the F centers<sup>[19]</sup>. Another apparent increase in absorption occurs in the wavelength range from 400 to 500 nm (peaked at 448 nm) in the irradiated region, which is well known and commonly labelled as the M band<sup>[17]</sup>. In particular, the M absorption is known to be formed by the cooperative spectral bands produced by the F<sub>2</sub> centers (peaked at 445 nm) and F<sub>3</sub><sup>+</sup> centers (peaked at 448 nm)<sup>[17]</sup>, which corresponds to Fig. 1. This peak is a characteristic emission of LiF: F<sub>3</sub><sup>+</sup> CCs (Fig. 3)<sup>[17,19]</sup>. The appearance of the peak at 540 nm after irradiation demonstrates that F<sub>3</sub><sup>+</sup> centers are formed by the laser pulses<sup>[19]</sup>. This result indicates that the emission of LiF excited by a femtosecond laser can be attributed to the <sup>1</sup>E<sub>1</sub>(1) → <sup>1</sup>A<sub>1</sub>(1) transition of F<sub>3</sub><sup>+</sup> centers<sup>[18]</sup>. For F<sub>3</sub><sup>+</sup> CCs<sup>[18,25]</sup>, the electronic states are

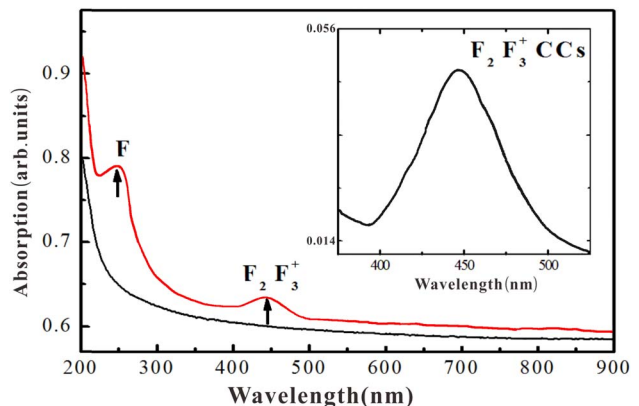


Fig. 2. Absorption spectra of the LiF crystal before (black curve) and after (red curve) femtosecond laser irradiation. Inset: Spectral differences after and before femtosecond laser irradiation.

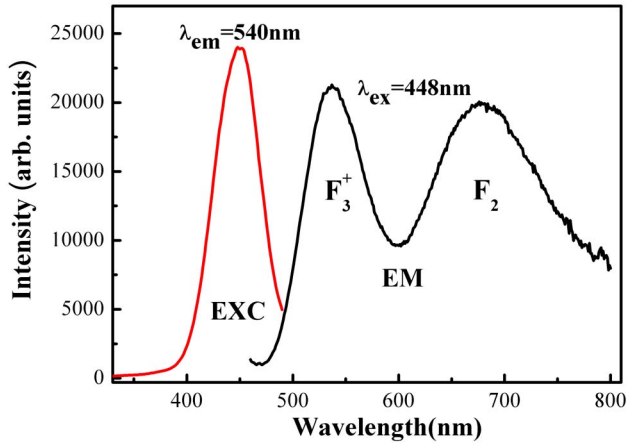


Fig. 3. Excitation and emission spectra for the femtosecond laser induced CCs in LiF crystals at room temperature. ( $\lambda_{\text{excitation}} = 448 \text{ nm}$ ,  $\lambda_{\text{emission}} = 540 \text{ nm}$ ).

spin-singlets and spin-triplets with symmetry  $A_1$ ,  $A_2$ , and E. Levels  $A_1$  and  $A_2$  are orbital singlets, and levels E are orbital doublets. The analysis based on the 1 s hydrogen-like wavefunctions give nine eigenfunctions: three of these functions are for triplets,  $^3E$  and  $^3A_2$ ; the other six for singlets, ground level  $^1A_1(1)$ , excited  $^1A_1(2)$ , and two excited levels  $^1E$ . Thus, the excitation of the pumping bands of  $^1E_1^*(1)$  can be observed by a 448 nm monochromatic light. After a relaxation time of the order of ps, the excitation reaches the relaxed excited state  $^1E_1(1)$ . At room temperature, the fluorescence emitting from  $^1E_1(1)$  appears as a bandwidth with a peak at 540 nm<sup>[18,26]</sup>.

Figure 3 presents the emission and excitation spectra for the femtosecond laser induced CCs in LiF by the FLSP920 Fluorescence Spectrometer at room temperature. The irradiated LiF shows two broadband optical emissions peaking at 540 and 680 nm, respectively, when excited by a 448 nm monochromatic light. The broadband optical emission peaking at approximately 680 nm should be ascribed to  $F_2$  centers. Therefore, the F,  $F_2$ , and  $F_3^+$  CCs were mainly induced by the femtosecond laser irradiation under the present irradiation conditions<sup>[18,19,27,28]</sup>.

We propose that multi-photon ionization is the starting mechanism for CC formation under femtosecond laser irradiation. Fluorine in the form of a negative ion in the LiF crystal would become neutral via femtosecond pulse multi-photon ionization. Once it loses its charge, the fluorine atom is not held in place due to the crystalline field, and can be “kicked off” from its original position by the quivering motion of the accelerated electrons, hence leaving a vacancy. After the laser pulses, an electron may be captured by this vacancy, thereby forming an F center. Other types of CCs are formed via aggregation of F centers<sup>[17,19]</sup>. We assume that coloring includes the formation of electrons (e) and holes (p) that then form excitons through recombination. Then the process develops according to the following scheme<sup>[27,29,30]</sup>:

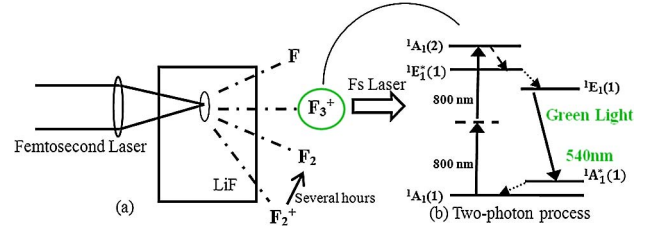
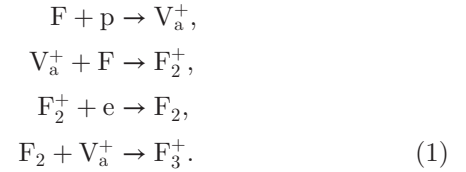


Fig. 4. (a) Illustration of upconversion luminescence of LiF by femtosecond laser irradiation. (b) Energy level diagram for  $F_3^+$  CCs in LiF and the radiative (—), nonradiative (---), and relaxation (···) transitions by femtosecond laser irradiation.



Here, the arrows indicate the kinetic particles providing the aggregation of centers; the  $F_2^+$  CCs are unstable at room temperature and disappear after a 12-24 h time period, as shown in Fig. 4(a)<sup>[19]</sup>.

In general, the conversion of infrared radiation into visible emissions can be ascribed to a multi-photon absorption process. The relationship between the pumping power and the fluorescence intensity can be described as<sup>[31]</sup>:

$$I \propto P^n, \quad (2)$$

where  $I$  is the integrated intensity of the upconversion luminescence,  $P$  is the average power of the pumping laser, and  $n$  is the photon number, respectively. The total energy of photons with the  $n$  photon number must exceed or equal the excitation energy for electrons excited from ground state to required excited state. The value of  $n$  can be experimentally determined from the slope coefficient of the linear fitted line of the logarithmic plot of fluorescence integrated intensity versus pump average power. The pump power density is controlled below  $12 \text{ TW/cm}^2$ . No appearance of the self-focusing or damage to the sample is observed. Figure 5 shows the Log-Log relationship between the pump average power of the femtosecond laser and fluorescence integrated intensity by a ZOLIX SPB300

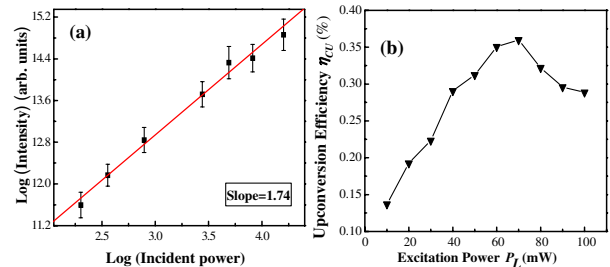


Fig. 5. (a) Luminescence intensity of the LiF crystals as a function of femtosecond pump power. (b) Dependence of the upconversion luminescence efficiency on excitation power.

spectrometer of the LiF crystals by varying the pumping power of the femtosecond laser at a fixed focused point (10–70 mW). The slope coefficient of the fitted line is 1.74. This result indicates that upconversion must be a two-photon absorption process (a two-photon process is sufficient to induce the green emission of the  $F_3^+$  CCs). We also measured the conversion efficiency of the upconversion luminescence as shown in Fig. 5(b). As can be seen, the maximum conversion efficiency is 0.36% when the excitation power is 70 mW, which is not too high for practical applications.

We agree that the mechanism of anti-Stokes luminescence excitation may play a role in the green fluorescence, but we think this mechanism (i.e., supercontinuum) only accounts for a small portion of green fluorescence, which has also been reported by substantial work verifying that two-photon emitting plays a dominant role in green fluorescence<sup>[17,18,26]</sup>. There are several mechanisms that account for the successive absorption process corresponding to upconversion fluorescence, e.g., ESA, SET, and cross relaxed, as well as CU, all of which require a middle metastable energy level between the ground state and the excited state for resonating with pump photon energy. Among others, the PA process without a middle metastable energy level could also be taken into account in the successive absorption process associated with upconversion fluorescence. In the above successive absorption mechanism with a middle metastable energy level, pump photons are absorbed successively instead of absorbed simultaneously, which means that there must be an absorption center corresponding to the pump energy. However, as shown in Fig. 2, there is no absorption peak around 800 nm, meaning no absorption center. Besides, the PA process does not account for the upconversion fluorescence, because there is no threshold value representing the PA process in the emission spectra, as shown in Fig. 3. Therefore, it could be concluded that there is no metastable energy level between the ground state and the excited state corresponding to upconversion fluorescence in a laser-processed LiF crystal, and all of the successive absorption mechanisms mentioned above should be ruled out<sup>[32]</sup>.

From the above analysis, we are convinced that the absorption process corresponding to upconversion fluorescence is a two-photon absorption process absorbing two photons simultaneously<sup>[33]</sup>. In the field of upconversion luminescence, luminescent materials doped with rare-earth ions and transition-metal ions have attracted considerable interest; however, there is seldom research about intrinsic luminescent pure materials or luminescent materials by virtue of the defect state. Among these pure materials, the quartz glasses and LiF crystals are commonly used luminescent materials by virtue of the defect state. Therefore, we choose the LiF crystal that is the most representative classic fluorescent material as a demonstration object. The LiF crystal sample was induced by a 800 nm femtosecond laser followed by the generation of the  $F$ ,  $F_2$ , and  $F_3^+$  centers of a stable number within the vast areas

around a laser-irradiated focal point, where a strong 400–500 nm M absorption band was composed. Besides, the visible green fluorescence was generated when the  $F_3^+$  center was excited by the femtosecond laser at the laser-irradiated area. However, when using a 448 nm monochromatic light to excite the original LiF crystal sample, there is no green fluorescence. In our experiment, the upconversion luminescence spectrum of the LiF:  $F_3^+$  CCs by a 800 nm femtosecond laser exhibits a broadband emission peaking at 540 nm, which corresponds to the simultaneously efficient absorption of two infrared pump photons. The pumping of the  $F_3^+$  CCs by using a focused 800 nm femtosecond laser produces a population of electrons in the excited state  $^1A_1(2)$ , then the excited electrons with subsequent rapid nonradiative relaxation move to  $^1E_1^*(1)$ . After a relaxation time of the order of ps, the excitation reaches the relaxed excited state  $^1E_1(1)$  from where it can decay radiatively to the unrelaxed ground state  $^1A_1^*(1)$ , leading to the characteristic optical emission of  $F_3^+$  CCs. From here the excitation eventually relaxes to the ground state  $^1A_1(1)$  in a time of the order of ps (Fig. 4(b))<sup>[34]</sup>.

The visible upconverted fluorescence of LiF crystals is proved experimentally via infrared femtosecond laser excitation. It is concluded from the relationship between the fluorescence intensity and pump power that the upconverted fluorescence is a process of simultaneous two-photon excitation. Analysis shows that the process of absorbing two photons is simultaneous rather than continuous. These results in our work about studying the upconversion fluorescence of LiF crystals using femtosecond laser pulses pave the way for research of visible laser crystal aiming for optical data storage, 3D display, upconversion fluorescence, etc.

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