**Abstract:** We report room-temperature two-photon induced fluorescence of the F_2^- color centers in LiF crystal in the $\sim 960 - 1300\ nm$ spectral range. The fluorescence spectra and kinetics were measured using the first (1.906 μm) and second harmonics (0.953 μm) of a H_2–Raman Shifted single frequency Nd:YAG laser. The fluorescence spectra and kinetics under two-photon (1.906 μm) and one-photon (0.953 μm) excitation were identical. A nonlinear dependence of the fluorescence intensity versus excitation energy of 1.906 μm radiation was demonstrated. The two-photon absorption cross section of F_2^- color center was measured to be $(0.9 \pm 0.4) \times 10^{-49}$ cm^4 sec at 1.906 μm.
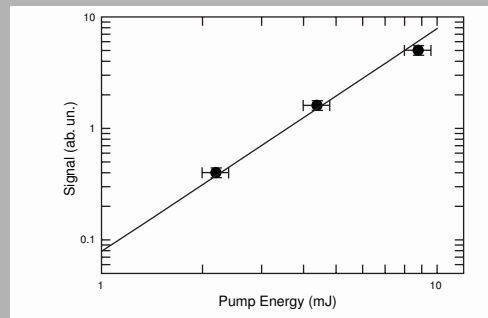
Intensities of the anti-Stokes fluorescence versus pulse energy of 1.906 μm radiation (solid line shows quadratic dependence)

Two-photon absorption of F$_2^-$ color centers in LiF crystal at 1906 nm

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1. Introduction

Two-photon absorption (TPA) transitions have recently attracted a lot of attention due to their potential applications for optical power limiting, optical data storage, photonic crystal fabrication, and up-conversion lasing (see [1–3] and references herein). The majority of studies are focused on he development of organic materials with a large TPA cross-section. However, for many TPA applications, solid-state materials are more desirable. Hence, color center (CC) crystals combining good spectroscopic characteristics typical for organic dyes with the thermo-optical properties of solids are very attractive for TPA studies. LiF crystals with CCs are the most outstanding among alkali-halides for their low hygroscopicity and a unique combination of operational (high photo-thermo stability), spectroscopic, and laser characteristics. Recent progress in the technology of LiF crystals with CCs resulted in the development of room temperature stable CC lasers tunable over

a broad near-IR spectral range (see [4–6] and references herein). Two photon excitation of F_2 and F_3^+ CC has been demonstrated in [7,8]. Here we present the first demonstration of two-photon induced fluorescence of F_2^- color centers in LiF crystal under 1.906 μm excitation.

2. Results and Discussion

F_2^- CC (LiF:F_2^-) are the most widely used CC crystals in quantum electronics, specifically as passive Q-switchers of resonators of neodymium lasers and as active elements of near IR tunable lasers [4]. The F_2^- CCs constitute pairs of adjacent anion vacancies with three captured electrons [4]. The LiF:F_2^- crystals are characterized by wide absorption and emission bands in the near IR spectral region, $0.9 - 1.1$ and $1.04 - 1.30$ μm, respectively, and a high quantum efficiency of luminescence at room temperature ($\eta \approx 0.5$). The LiF crystals were grown by the

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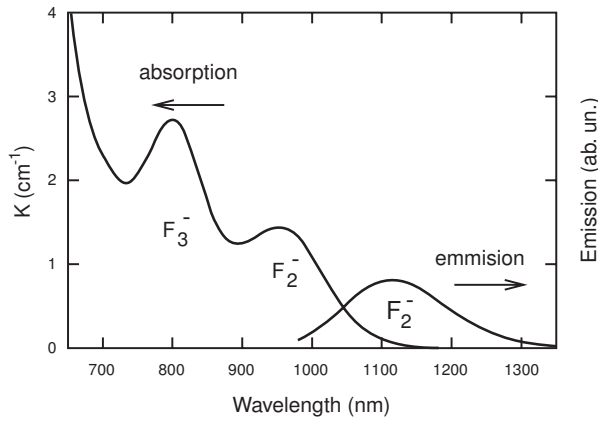
Figure 1 Absorption and fluorescence spectra of LiF:F_2^- color center crystal

Figure 2 Experimental set-up

Kyropulos method. To produce F_2^- CCs, the LiF crystals were γ-irradiated at 300K with a dose of 10^8 rad using a ^{60}Co source. The maximum absorption coefficients of the studied LiF:F_2^- crystals at room temperature were $k = 1\text{-}3 \text{ cm}^{-1}$ (at $\lambda = 960$ nm). The absorption spectra were obtained using a Shimadzu UV3101-PC spectrophotometer. The absorption and single photon calibrated emission spectra of the studied LiF:F_2^- CC crystal are shown in Fig.1. The absorption coefficient of the used crystal at room temperature was found to be $k = 1.5 \text{ cm}^{-1}$ at 960 nm.

The fluorescence measurements were performed using 0.75 m Acton Research "SpectraPro" spectrometer with an InGaAs detector (ID-441-C), which covers the spectral region from 800 to 1700 nm, and a photomultiplier tube (PD-439, Model R5108) sensitive over the $400 - 1200$ nm range. The entire detection system was calibrated using a tungsten halogen lamp (Oriel Instruments Model 9-205) with a known spectral output. Data acquisition for fluorescence experiments was performed with a boxcar-averager (SR250 Stanford Research System) – SpectraSense (Acton Research) controller combination. For single and two-photon excitations the second and first harmonics of the H_2 Raman Shifted Nd:YAG laser operating at 1.906 μm were utilized. The Raman Shifting was realized in the backscattering geometry using a H_2 Raman cell pumped by the 1.064 μm radiation of the single frequency Q-switched Nd:YAG laser with a repetition rate of 10 Hz. A schematic of the optical system is depicted in Fig. 2. An optical isolator was placed before the Raman cell to prevent possible damage of the Nd:YAG laser optics by amplified backscattered 1.06 μm radiation. Pump pulses from the Raman cell had pulse duration of 7 ns at FWHM and the output energy reached 100 mJ. In our study the pump beam was propagated along the [100] crystal axis and had liner polarization along [010] axis (k_p//[100], E//[010]). The fluorescence radiation was collected by the registration system at $90°$ with respect to pump radiation. The fluorescence
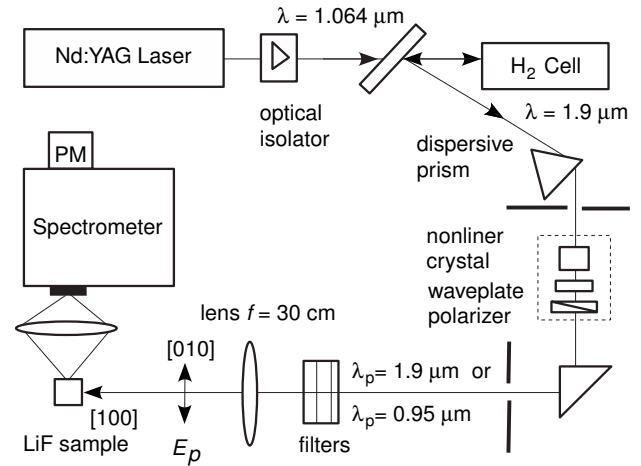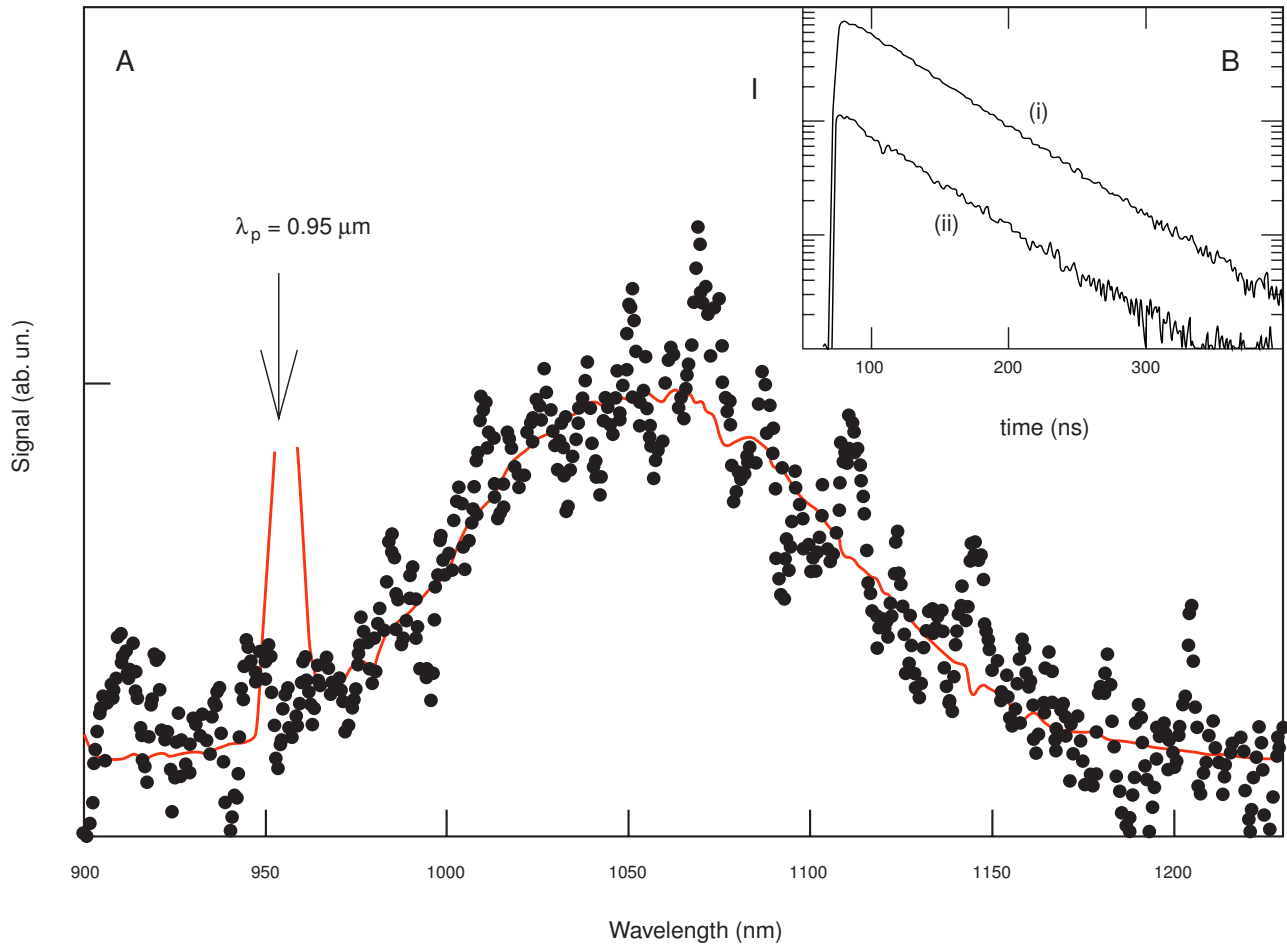
spectrum, measured under 0.95 μm excitation, is shown in Fig. 1. The emission band of the F_2^- CCs is well fitted by a Gaussian profile with a maximum at 113 nm and a half width of 1300 cm^{-1}. Fig. 3A demonstrates the non-calibrated fluorescence spectra measured under 0.95 μm (single photon) and 1.906 μm (two-photon) excitations. As one can see, the measured fluorescence spectra were identical. In both cases of single- and two-photon excitation the fluorescence of F_2^- CC's was unpolarized. The kinetics of fluorescence were exponential for single and two-photon excitations (see Fig. 3B) with a decay time consistent with a RT life time of LiF:F_2^- CC (50-65 ns) [4]. In the last experiments to verify the nature of excitation of the LiF:F_2^- CC crystals, we studied the dependence of the fluorescence intensity versus pump energy. The intensities of anti-Stokes fluorescence were measured to vary quadratically with respect to pump energy (see Fig. 4).

From the measured intensities of photoluminescence under one and two photon excitation one can estimate the TPA cross-section. One way to make numerical calculation of TPA cross-section from photoluminescence measurements is by means of absolute calibration of the registration system [9]. Another way is the utilization of a signal of luminescence intensity under single photon absorption as a reference signal. According to the basic principals the change of intensity of radiation (I) along the propagation direction (z) due to single and two photon absorption of F_2^- CC's can be written as follows [9]:

$$dI/dz = -\sigma N_g I - \beta N_g I^2 \qquad (1)$$

where σ, and β are single and two photon absorption cross-sections, respectively, N_g–concentration of the F_2^- CC's at the ground level. In our experiments for two-photon 1.906 μm excitation, we assume that: (1) changes in intensity and (2) changes of CC's concentration at the ground state due to TPA are very small. The first assumption has been checked out by measuring the intensity of radiation

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Figure 3 (online color at www.interscience.wiley.com) A – Non-calibrated fluorescence spectrum measured under 0.95 μm (single photon-solid line) and 1.906 μm (two-photon- dots) excitations; B – Kinetics of fluorescence for single (i) and two-photon (ii) excitations

before and after the sample. According to the second assumption concentration of the CC's at ground state practically equals to the total concentration of F_2^- CCs (N_0). For samples of thickness L the change of intensity due to TPA can be calculated as

$$\Delta I_{TPA} = -\beta N_0 I^2 L \qquad (2)$$

Number of exited CC's (M^*) can be obtained using Eq. (2) as follows:

$$M^* = 0.5 I_{1.9}^2 \tau \beta N_0 L S \qquad (3)$$

where, τ–laser pulse duration and S–beam cross-section area at the sample . The factor 0.5 derives from the fact that absorption of two photons results in excitation of a single center. Similarly, for single photon excitation the number of excited CC's can be estimated as

$$M^* = I_{0.9} \sigma \tau N_0 L S \qquad (4)$$

The intensity of photoluminescence is proportional to the number of excited centers (M^*), geometry factor (Γ), and quantum efficiency of luminescence (η) as follows:

$$I_{PL} = \eta M^* \Gamma \qquad (5)$$

As one can see from the luminescence experiments, the emissions under single and two photon absorptions are identical. Thus, for the same geometry of experimental setup for single and two photon excitations, the ratio of photoluminescence intensities will be equal to the ratio of the number of excited centers. Hence, TPA cross-section can be calculated as follows:

$$\beta = 2 \left(\frac{V_{1,9}}{V_{0,9}} \right) \left(\frac{I_{0.9}\sigma}{I_{1.9}^2} \right), \qquad (6)$$

where $V_{1.9(0.9)}$ – amplitude of the luminescence signal under two (single) photon excitations. From the data obtained in our experiments we estimate TPA cross-section of F_2^-
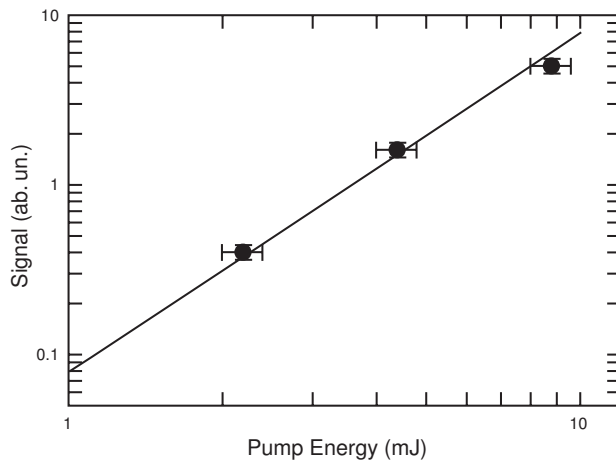
Figure 4 Intensities of the anti-Stokes fluorescence versus pulse energy of 1.906 μm radiation (solid line shows quadratic dependence)

CC to be $\beta = (0.9 \pm 0.5) \times 10^{-49}$cm^4 sec. The calculated value of β is smaller than values reported early for other CC's in alkali-halide crystals. In [9] the TPA cross-sections for F_3^+ and N_1 centers in NaF have been estimated for 1.064 μm two-photon excitation to be

$$\beta_{F_3^+} = 6.5 \times 10^{-49}\text{cm}^4\text{sec} \quad \text{and}$$

$$\beta_{N_1} = 5.5 \times 10^{-48}\text{cm}^4\text{sec}, \quad \text{respectively.}$$

The TPA cross-section value of $\beta_F = 2.7 \times 10^{-47}$ cm^4 sec for F centers in KCl was obtained in [10] on the basis of hydrogen atom model of F center. As one can see TPA cross-sections of different types of CCs in different alkali-halides differ by more than two orders of magnitude. Hence, it is of interest to clarify in future the influence of the crystal host on the TPA. In addition, TPA for the same types of CC's should be compared in different crystals.

In summary, the fluorescence spectra and kinetics were measured using first and second harmonics of the Raman Laser with 1.906 μm oscillation wavelength. The fluorescence spectra and kinetics under two- (1.906 μm) and single photon (0.953 μm) excitations were identical. A nonlinear dependence of the Anti-Stokes fluorescence intensity versus excitation energy of 1.906 μm was demonstrated. The 1.906 μm two-photon absorption cross section was measured to be $(0.9 \pm 0.4) \times 10^{-49}$ cm^4 sec.

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