APPLIED PHYSICS LETTERS VOLUME 79, NUMBER 15 8 OCTOBER 2001

# Spectroscopic analysis and persistent photon-gated spectral hole burning in LiF:$F_2^-$ color center crystal

V. V. Fedorov,[a] S. B. Mirov, M. Ashenafi, and L. Xie
*Department of Physics, University of Alabama at Birmingham, Birmingham, Alabama 35294*

(Received 21 March 2001; accepted for publication 26 July 2001)

Luminescence and absorption spectra of LiF crystals with $F_2^-$ color centers (CCs) were studied in the 14–300 K temperature range. The Huang–Rhys factors measured from absorption and emission spectra were equal in magnitude and calculated to be 3.2 and 2.72 at 77 and 300 K, respectively. It was shown that below 40 K inhomogeneous broadening of the zero phonon line of the $F_2^-$ CC prevails over homogeneous broadening. Inhomogeneous broadening of the zero phonon line was observed to vary from 5 to 15 $cm^{-1}$ for different crystal preparations. Persistent spectral hole burning stable at room temperature was realized in LiF:$F_2^-$ crystals. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1406563]

Spectral hole (SH) burning has attracted significant attention as a powerful technique for high resolution spectroscopy and may also have potential use in optical memories.[1] We report results of spectroscopic characterization and persistent SH burning in the zero phonon line (ZPL) transition of $F_2^-$ color centers (CCs) in LiF (LiF:$F_2^-$) crystals. $F_2^-$ CCs are point defects produced by ionizing irradiation. $F_2^-$ CCs can be considered as three electrons trapped by two adjacent anion vacancies with axial symmetry along the (110) direction.[2] LiF:$F_2^-$ crystals are characterized by wide absorption and emission bands in the near-IR spectral region, 0.9–1.1 and 1.04–1.3 $\mu$m, respectively, and high quantum efficiency of the luminescence at room temperature. LiF:$F_2^-$ crystals are widely used as passive $Q$ switchs in resonators of neodymium lasers and as active elements of near-IR tunable lasers.[3–6] Numerous studies[2] have been devoted to spectroscopic characterization of LiF:$F_2^-$ crystals. However, a detailed investigation of absorption and emission bands broadening has been never performed. The current study is focused on analysis of spectral broadening of $F_2^-$ CC absorption and emission bands, and elucidation of the merit of LiF:$F_2^-$ crystals as a medium for SH burning experiments.

To produce $F_2^-$ CCs, LiF crystals were $\gamma$ irradiated at 300 K with a dose of $10^8$ rad using a $^{60}$Co source. The maximum absorption coefficients of the LiF:$F_2^-$ crystals studied at room temperature were $K = 1-3$ $cm^{-1}$ (at $\lambda = 960$ nm). The absorption and emission spectra were obtained using an Acton Research ARC-750 spectrometer with spectral resolution of 0.6 $cm^{-1}$. The data for absorption and emissions spectra were acquired with a lock-in amplifier (Model 7265, EG&G Instruments) and a SR250 boxcar integrator (Standard Research Systems), respectively. All spectra were corrected for sensitivity using an Oriel calibration lamp (model 9-2050). For the fluorescence and SH burning experiments we used a tunable LiF:$F_2^{+**}$ laser pumped by an alexandrite laser (Light Age, Inc.).[7] The LiF:$F_2^{+**}$ pulses had a duration of 60 ns and spectral width of 0.2 $cm^{-1}$.

To establish the type of transition broadening the absorption and emission spectra of LiF:$F_2^-$ CCs were studied in the 14–300 K temperature range (see Fig. 1). At temperature below $T = 120$ K the ZPL transition with a wavelength of 1040 nm can be resolved in the absorption and in the luminescence bands. The broadband transitions to the high vibration levels separated by energy gap $\Delta E = 267$ $cm^{-1}$ are seen in the absorption and luminescence spectra at $T = 14$ K. The temperature dependencies of the ZPL transition width [full width at half maximum (FWHM)] are shown in Fig. 2. As one can see, a fast decrease in the FWHM in the 100–40 K temperature range gives way to a temperature independent relationship for temperatures below $T = 40$ K. Generally, the FWHM is a convolution of inhomogeneous ($\Gamma_{inh}$) and homogeneous broadening ($\Gamma_{hom}$). In solids, inhomogeneous broadening results from local lattice distortion and does not depend on the temperature. The $\Gamma_{hom}$ is strongly temperature dependent in this temperature range.[1] In our experiments, FWHMs of the ZPL at $T = 14$ K were observed to vary from 5 to 15 $cm^{-1}$ for different crystal preparations depending on the overall concentration of the $F_2^-$ CCs and the crystal preparation technique. From the above it follows that inhomogeneous broadening ($\Gamma_{inh}$) of the ZPL in LiF:$F_2^-$ is dominant at temperatures below $T = 40$ K and is equal to 5–15 $cm^{-1}$ for the crystals studied.

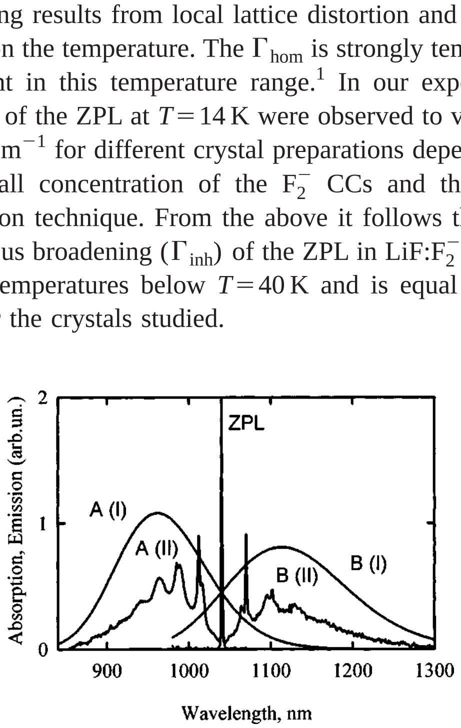

FIG. 1. Absorption (A) and emission (B) spectra of a LiF:$F_2^-$ crystal at 300 (I) and 14 K (II).

---

[a] Author to whom correspondence should be addressed; electronic mail: vfedorov@phy.uab.edu

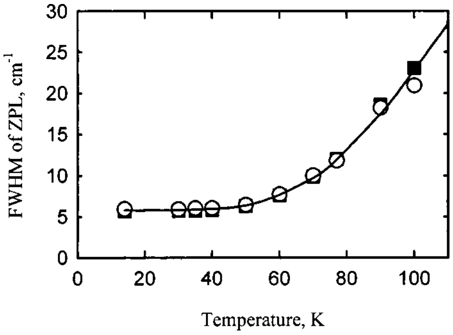

FIG. 2. Temperature dependence of the ZPL width of $F_2^-$ CCs in LiF for luminescence (■) and absorption (○) measurements.

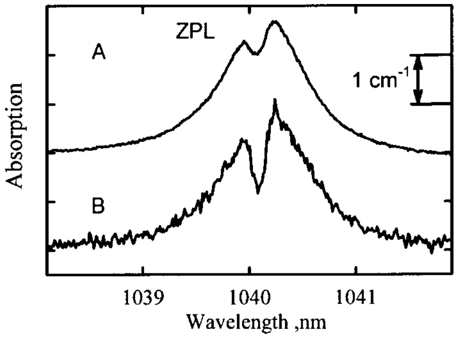

FIG. 4. Hole spectra for light polarization $E \perp E_{520\ \mathrm{nm}}$ (A) and $E \| E_{520\ \mathrm{nm}}$ (B) at 14 K.

In most cases, the temperature dependence of the absorption and emission bands of CCs can be calculated by the Huang–Rhys model.[8] According to this model, the optical center interacts only with one "effective" phonon ($v_0$). As a result, the temperature dependencies of optical transition bands can be established analytically as a function of the effective phonon frequency and Huang–Rhys factor ($S_0$) as

$$(I_{\mathrm{ZPL}}/I_{\mathrm{total}}) = \exp[-S_0 \,\mathrm{cth}(hv_0/2kT)], \tag{1}$$

$$(\Delta)^2 = 8\ln(2) S_0 (hv_0)^2 \,\mathrm{cth}(hv_0/2kT), \tag{2}$$

$$E_{\mathrm{abs}} - E_{\mathrm{em}} = 2S_0 hv_0, \tag{3}$$

where $E_{\mathrm{abs}} - E_{\mathrm{em}}$ is the Stokes shift, $\Delta$ is the FWHM of multiphonon bands at high temperature, $I_{\mathrm{ZPL}}$ is the area under the ZPL band and $I_{\mathrm{total}}$ is the total area under the absorption or luminescence spectrum. There is a common relationship between absorption and the emission band within the limit of the linear approximation of electron–phonon coupling. Based on Refs. 9 and 10 conjugate absorption and emission bands satisfy a mirror–image relationship with respect to the energy of the ZPL transition, i.e.,

$$I_{\mathrm{ab}}(v) = I_{\mathrm{em}}(2v_{\mathrm{ZPL}} - v), \tag{4}$$

where $I_{\mathrm{ab}}(v) = K(v)/v$, $I_{\mathrm{em}} = \mathrm{const}^* E(v)/v^3$, $v_{\mathrm{ZPL}}$ is the frequency of the ZPL transition, $K(v)$ is the absorption coefficient, and $E(v)$ is the spectral density of the luminescence. To verify the validity of the linear mechanism of electron–phonon coupling, we checked whether a mirror–image relationship between the emission and absorption bands takes place. The conjugate absorption $I_a(v)$ and emission $I_e(v)$ bands, measured at $T = 77$ K and calculated according to Eq. (4), are depicted in Fig. 3. As one can see from Fig. 3, the mirror–image relationship between the emission and absorption bands holds over a wide frequency range. Calculation of the Huang–Rhys factor according to Eq. (1) was made at $T = 77$ K, because at this temperature the absorption and emission bandwidths of ZPLs are much wider than the apparatus function of the spectrometer and inhomogeneous broadening. In addition to this, the value of $\mathrm{cth}(hv_0/2kT)$ only weakly depends on the phonon frequency, and the change of effective phonon ($v_0$), from 150 to 300 cm$^{-1}$, causes only a 12% change of $S_0$. The $S_0$ value calculated from this equation for absorption and luminescence bands was equal to 3.2.

On the other hand, the $v_0$ and $S_0$ values can be obtained from Eqs. (2) and (3) independently. For these experiments, we measured the temperature dependence of the absorption and emission bandwidths in the 200–350 K temperature range, since at these temperatures the band profile is described well by Gaussian curves. The parameters calculated from Eqs. (3) and (4) at room temperature were $S_0 = 2.72$ and $v_0 = 267\ \mathrm{cm}^{-1}$. It is rather close to their values calculated earlier[11,12] based on the temperature dependencies of the absorption and emission bandwidths. It is worth noting that calculations of the parameters ($S_0$ and $v_0$), based only on Eq. (2), are very sensitive to measurement accuracy.

The $F_2^-$ CCs are photostable when excited in the main absorption band, which is centered at 960 nm at room temperature (RT). However, $F_2^-$ CC photoionization occurs under simultaneous action of radiation of the first and second harmonics of the neodymium laser.[12] Persistent photon-gated SH burning at the ZPL transition was realized at 14 K by using first (1040 nm) and second (520 nm) harmonic oscillations of the pulsed LiF:$F_2^{+}$** CC laser.[7,13] Light polarization of first and second harmonics of the LiF:$F_2^{+}$** CC laser were along the (100) and (010) crystals axes, respectively. Simultaneous irradiation of LiF:$F_2^-$ crystals with 1040 and 520 nm radiation results in their two-step photoionization. At the first step $F_2^-$ CCs are resonantly excited by narrow (0.2 cm$^{-1}$) 1040 nm radiation lying within the inhomogeneously broadened $F_2^-$ CC ZPL. At the second step, excited $F_2^-$ CCs are photoionized to the conduction band of LiF by 520 nm radiation, forming neutral $F_2$ CCs and free electrons. The peak power densities in our experiments were 14 and 0.1 MW/cm$^2$ for the first and second harmonic oscillations of the LiF:$F_2^{+}$** CC laser, respectively. For SH burning experiments we used LiF:$F_2^-$ crystals with inhomogeneous broadening equal to $\Gamma_{\mathrm{inh}} = 9.2\ \mathrm{cm}^{-1}$.

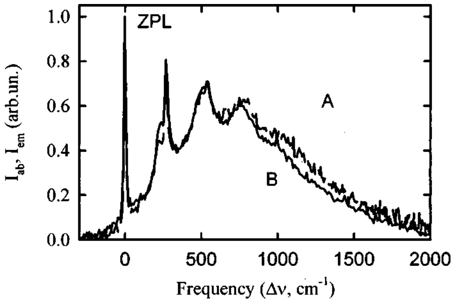

FIG. 3. Normalized absorption (A) and emission (B) spectra of $F_2^-$ CCs in LiF at 77 K.

The absorption spectra of the ZPL transition after 5 min of light exposure are presented in Fig. 4. As one can see from Fig. 4 a spectral hole with a FWHM of 1.7 cm$^{-1}$ was created in the LiF:$F_2^-$ CC crystal. The SH exhibits strong dichroic properties. The maximum amplitude of the SH was in the absorption spectra measured by the light with polarization along the (010) direction. For this polarization, the SH constitutes 50% of absorption maximum of the ZPL transition whereas the spectral hole amplitude was less than 10% for (100) light polarization. The SH amplitude was very stable and did not change after two weeks of storage at room temperature.

In conclusion, luminescence and absorption spectra of LiF crystals with $F_2^-$ color centers were studied in the 14–300 K temperature range. It was shown that below 40 K, inhomogeneous broadening of the ZPL of $F_2^-$ CC prevails over homogeneous broadening. Inhomogeneous broadening of the ZPL was observed to vary from 5 to 15 cm$^{-1}$ for different crystal preparations. The Huang–Rhys factors were calculated from absorption and emission spectra and were equal to 3.2 and 2.72 at $T=77$ and 300 K, respectively. A persistent photon-gated SH at the ZPL was realized in LiF:$F_2^-$ crystals. The SH was stable for more than 14 days when stored at room temperature.

The authors express their deep thanks to K. K. Pukhov and I. S. Osad'ko for valuable discussions. This work was partially supported by a Light Age, Inc. agreement and by DoD/BMDO/SBIR Project No. DASG60-97-M-0110.

[1] *Zero-Phonon Line and Spectral Hole Burning in Spectroscopy and Photochemistry*, edited by O. Sid and K. Haller (Springer, Berlin, 1988).

[2] T. T. Basiev and S. B. Mirov, *Room Temperature Tunable Color Center Lasers* (Harwood Academic, Chur, Switzerland, 1994).

[3] S. B. Mirov and T. T. Basiev, IEEE J. Sel. Top. Quantum Electron. **1**, 22 (1995).

[4] W. Gellermann, A. Muller, D. Wandt, S. Wilk, and F. Luty, J. Appl. Phys. **61**, 1297 (1987).

[5] T. T. Basiev, V. A. Konyushkin, S. B. Mirov, V. V. Ter-Mikirtychev, and V. V. Fedorov, Opt. Spectrosc. **74**, 721 (1993).

[6] T. T. Basiev, P. G. Zverev, A. G. Papashvili, and V. V. Fedorov, Quantum Electron. **27**, 574 (1997).

[7] A. Yu. Dergachev and S. B. Mirov, Opt. Commun. **147**, 107 (1998).

[8] A. M. Stonehan, *Theory of Defects in Solids* (Clarendon, Oxford, 1975).

[9] S. I. Pekar, Sov. Phys. Usp. **50**, 197 (1953).

[10] D. I. Blokhintsev, J. Phys. (Moscow) **1**, 117 (1939).

[11] P. Thevenard, A. Perer, J. Davenas, and C. H. S. Dupuy, Phys. Status Solidi A **9**, 517 (1972).

[12] T. T. Basiev, Yu. K. Voron'ko, E. O. Kirpichenkova, S. B. Mirov, and V. V. Osoko, Sov. Phys. Lebedev. Inst. Rep. **3**, 1 (1982).

[13] N. W. Jenkins, S. B. Mirov, and V. V. Fedorov, J. Lumin. **91**, 147 (2000).