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Optical properties of lithium fluoride fibers grown by micro-pulling-down method

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Abstract

Fluoride single-crystalline fibers were grown by the micro-pulling-down (μ-PD) technique. The optical properties of the LiF fiber and the bulk crystal (grown by Czochralski technique) were compared. Both samples were irradiated with 40 Mrad of gamma rays at room temperature and color centers were successfully produced. The emission spectra of the fiber and the bulk crystal when excited at 447 nm show the typical broad emission bands related to the F_3^+ and F_2 centers, with peaks at 535 and 650 nm, respectively. Both spectra contain a very strong emission band centered at 1120 nm with the same half width of 1350 cm^{-1} when excited with a InGaAs diode laser at 968 nm. These results indicate a potential use of these new LiF fibers in miniaturized active optical devices.

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Keywords: Micro-pulling-down growth; Single-crystal growth; Fluorides; Optical fiber devices

1. Introduction

Nowadays there is an increasing interest in single-crystalline fibers. Their unique properties indicate a great potential for a variety of applications in optical and electronic devices [1]. Several materials in the fiber shape as eutectics, semiconductors and oxide single-crystals have already been grown by the Laser Heated Pedestal Growth (LHPG) [2,3] and the micro-pulling-down (μ-PD) methods [4,5]. Growth and hence applications of fluoride single-crystalline fibers have opened a new area of investigation. Recently, we have successfully grown high-quality lithium fluoride (LiF) single-crystalline fibers by the μ-PD technique [6]. We have observed that growth of LiF fibers under inert gas flow results always in single-crystals with spurious OH$^-$ contamination. Applying a pre-treatment to the growth chamber under vacuum is very efficient to minimize this moisture contamination generally observed in fluoride crystals.

Color centers are easily created in LiF crystals by irradiation with ionizing radiation [7,8] at room temperature. These centers in ionic crystals have some important optical characteristics such as a four level optical cycle with broad absorption and emission bands, and a fairly high transition oscillator strength, being easily detected by optical spectroscopy. Some of these centers are used nowadays for lasers in the near infrared [9,10] that are continuously tunable over a wide spectral range. The F_2^- color center is stable at room temperature [11] in LiF crystals containing a minimum amount of OH$^-$. The LiF : F_2^- color center laser holds an important position amongst lasers because it emits in a spectral range which is very important for optics communications

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[12]. Additionally, it is simple to operate and can be pumped by the fundamental emission of neodymium lasers or InGaAs laser diodes.

In this work, LiF single-crystalline fibers have been grown by the micro-pulling-down method (μ-PD) and LiF bulk crystals have been grown by Czochralski method (Cz). The samples were irradiated by gamma rays to produce color centers. The optical properties of both, $LiF : F_2^-$ fiber and bulk crystal, were compared.

2. Experimental

2.1. LiF crystals growth

Commercial LiF powder (99.99%) was first submitted to the zone refining process under reactive atmosphere to eliminate spurious contamination. Zone refining runs were carried out using vitreous-carbon crucibles placed in a platinum reactor under HF flow [13]. The obtained LiF crystals were used as starting material for the growth of both μ-PD fibers and Czochralski bulk crystals.

Transparent and homogeneous LiF single-crystalline fibers with diameter of 0.6 mm and length of 100 mm were pulled with a constant rate of 45 mm/h by the μ-PD technique using resistive crucible heating. The experiments were performed in a closed chamber under argon gas flow. As already known, under such conditions traces of humidity present in the growth chamber react strongly with the melt and hydrogen and hydroxide ions are produced corresponding to the ionic product of water dissociation [14,15]. Generally, OH^- ions are incorporated non-homogeneously along alkali halide crystals grown under inert gas flow by the Cz technique. This effect occurs due to the low value of the effective distribution coefficient of OH^- ions in alkali halide hosts [16]. Segregation effect is strongly reduced in single-crystalline fibers grown by μ-PD technique. OH^- incorporation along the fiber is favored by the high thermal gradient in the region close to the solid-liquid interface and higher pulling rates than those normally used for the Cz method. Studies on the effect of the segregation behavior in the fibers grown by the μ-PD method have demonstrated that the impurity distribution along the fibers trends to be uniform [17]. In order to produce color centers in similar conditions inside the single-crystalline fiber and the bulk crystal, the $LiF:OH^-$ bulk crystal was grown by Cz method. The starting material was placed in a platinum crucible with resistive heating. The LiF melt was doped with 1 mol% of LiOH before the growth. The crystal growth was carried out under argon flow and the crystal was pulled with a rotation rate of 15 rpm and a pulling rate of 1 mm/h. The furnace temperature was 860 °C. High quality, single-crystals with total absence of cracks were obtained.

2.2. Optical characterization

Infrared measurements were carried out using a Nexus-670, far-infrared spectrophotometer in transmission mode from 4000 cm^{-1} to 400 cm^{-1}. The powdered samples were dissolved in KBr solution and pressed into tablets of 12 mm in diameter and 1 mm in thickness.

Samples were sectioned along the LiF fiber and the bulk crystal for absorption and emission measurements. The sample surfaces were polished flat and parallel. Bulk and fiber crystal samples were irradiated simultaneously at room temperature with 40 Mrads of gamma rays during 60 h.

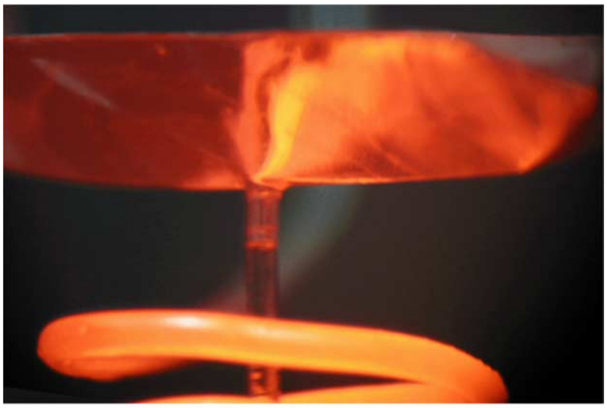
Absorption spectra in the range of 200–2500 nm were measured at room temperature using a Varian Spectrometer (Cary 17 D). The emission spectra were obtained by exciting the samples at 447 nm with a xenon lamp and at 968 nm with a GaAlAs laser diode (Optopower A020). This diode system contains a broad area semiconductor laser with a maximum of 20 W of continuous output power. The diode laser beam was treated with a beamshaper [18] and focused by a single $f = 5$ cm lens. Close to the focus, and for a focal depth of 2 mm, the beam has a square profile, with transverse dimensions of approximately 260 μm × 260 μm. During the emission measurements the sample was pumped with 7.5 W of diode laser radiation modulated at 40 Hz. The emissions of the samples were analyzed by a 0.5 m monochromator (Spex), a S-20 PMT, and a Germanium detector. The signal was amplified with a EG&G7220 lock-in and processed by a computer. The relative errors in the emission measurements are estimated to be less than 5%.

3. Results and discussion

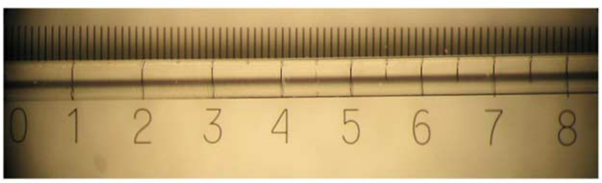
Fig. 1a shows a fiber during the steady-state pulling process by the μ-PD method and Fig. 1b shows a typical as-grown LiF fiber, completely transparent and free of cracks along its length.

The gamma irradiation of LiF fiber and bulk $LiF:OH^-$ crystal resulted in the formation of several color centers, which could be easily observed by the coloration change of the irradiated samples showed in Fig. 2. The presence of OH^- ions can be observed by the absorption bands close to 3400 cm^{-1} present in the IR absorption spectra of both samples obtained before gamma irradiation (Fig. 3).

The LiF crystal has a wide optical gap (~11.8 eV), therefore being a very good media to study the formation of color centers. The simplest color center, formed by an electron trapped in an anion vacancy, is the F center. When two, three and four F centers are aggregated, F_2, F_3 and F_4 centers are formed, respectively. When ionized or when an electron is additionally trapped by



(a)



(b)

Fig. 1. (a) Steady-state pulling process of a LiF fiber by the μ-PD technique. (b) As-grown LiF single-crystal fiber with diameter of 0.6 mm (scale in mm).

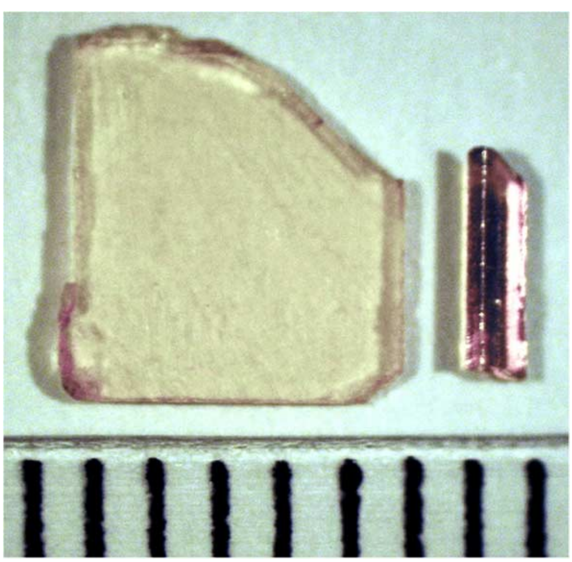


Fig. 2. Photo of the samples from the bulk and fiber LiF crystals after receiving the same dose of gamma radiation.

these centers, positively or negatively charged color centers are formed (F_2^+ or F_2^- centers in the case of the F_2 center). Table 1 resumes the known spectral characteristics of such color centers in LiF crystals [1].

The absorption spectra obtained from the fiber and bulk crystals are shown in Fig. 4. F_3^+ and F_2 centers are responsible for the absorption band, generally called M band, around 448 nm (F_3^+) and 444 nm (F_2). Along with the main M absorption band, other types of aggregate defects have been detected: the 315 and 375 nm bands due to the R_1 and R_2 transition of three associated F centers (F_3 center) and the 520 and 545 nm bands, attributed to N_1 and N_2 transitions of four associated F centers (N center).

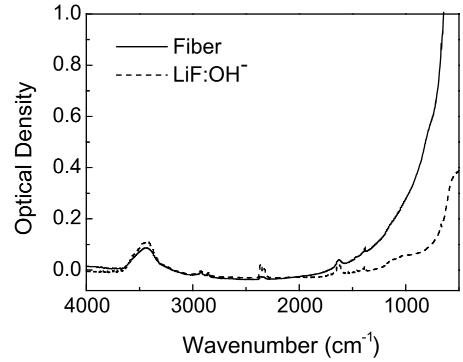


Fig. 3. IR absorption spectra of the fiber and the bulk LiF crystals after gamma irradiation.

Table 1
Spectral characteristics of color centers in LiF

Color center	Absorption wavelength (nm)	Emission wavelength (nm)
F	248	–
F_3	316, 374	–
F_2	444	678
F_3^+	448	541
F_2^+	645	910
F_2^-	960	1120

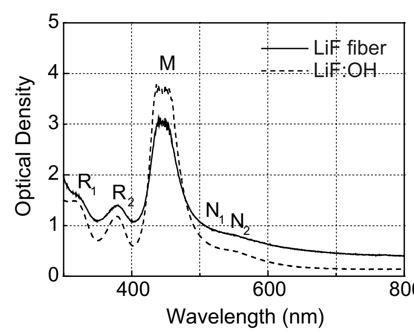


Fig. 4. Absorption spectra of the fiber and the bulk LiF crystals after gamma irradiation.

The emission spectra obtained from the fiber and bulk crystals with excitation at 447 nm are shown in Fig. 5. In these spectra we observe the typical broad emission bands related to transitions of the F_3^+ and F_2 centers at 535 and 650 nm, respectively.

Due to the small sample thickness (1 mm) and the low gamma rate dose, the F_2^- absorption coefficient in the range 900–1100 nm is very small or not measurable. Even so, we observe a very strong emission band of the bulk and the fiber LiF crystals when exciting at

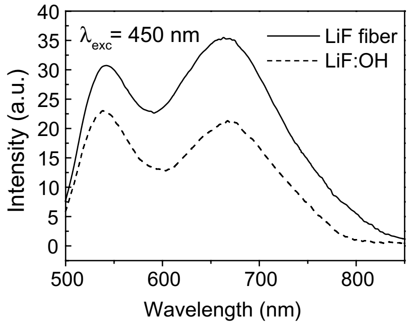


Fig. 5. Emission spectra of the fiber and the bulk LiF crystals obtained with excitation in 447 nm.

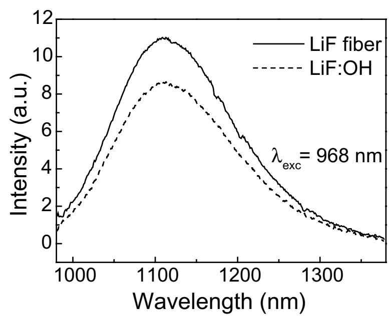


Fig. 6. Emission spectra of the fiber and the bulk LiF crystals obtained with excitation in 968 nm.

968 nm, centered at 1120 nm with a half width of 1350 cm^{-1}, as shown in Fig. 6. The spectrum is consistent with the previous results on the LiF : F_2^- luminescence spectrum [1,19].

4. Conclusion

Regular and transparent single-crystalline fibers of lithium fluoride with diameter of 0.6 mm and length of 100 mm can be easily grown by the micro-pulling-down technique under inert gas flow. Color centers were successfully produced with gamma irradiation of bulk and fiber LiF single-crystals. The ratio of the absorption bands attributed to each color center produced is the same in both materials. The results show that the LiF single-crystalline fibers present the same spectroscopic properties as the bulk crystal and therefore also show potential as a laser media candidate. The fibers grown by the μ-PD method show also faster growth rate and lower costs than the Czochralski technique, which is promising for research and production of optical devices.

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