Journal of Physics: Conference Series

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IOP Conf. Series: Journal of Physics: Conf. Series **830** (2017) 012145 doi:10.1088/1742-6596/830/1/012145

Luminescent centers in nanolayers of LiF crystals with embedded silver ions

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Abstract. The paper presents the results of studies of luminescent centers induced by irradiation of LiF crystals with flow of silver ions of a fluence varying in a range of 2×10^{13}–5×10^{17} ions/cm^2 and energy about of 150 keV. Two bands with maxima at 250 nm and 420 nm in the absorption spectra of the exposed crystals were observed. The former was due to the absorption of F colour centers and the latter consisted of F_2 (F_3^+) colour centers band and a plasmon resonance band arose due to the embedded silver ions. The peak of the latter remained stable after annealing the sample at 400 ^{0}C unlike the colour centers bands. The luminescence spectra of the crystals under excitation with a laser irradiation of 375 nm wavelength showed a band with a peak at 450 nm along with the bands with peaks at 530 and 680 nm corresponding to F_3^+ and F_2 colour centers, respectively. The peak of the former reached saturation, while the peaks of the colour centers bands increased with ion fluence increasing. These results show that sub-nanometre sized metal clusters Ag(n+) (n=3-6) are responsible for the observed luminescence, while the Ag particles of a nanometer scale are not luminescent.

1. Introduction

The luminescence of noble metal nanoparticles (NPs) has attracted a lot of attention in the last decades. Their unique optical properties can be applied in different fields such as luminescent labels [1], sensors [2], data storage [3] and fiber lasers [4]. The works in this field largely focus on the studies of optical properties of NPs in liquid media [1, 2] or in glasses, i.e. amorphous media, [3,4]. Along with this, it is of interest to study these properties of NPs produced in crystal media, in particular, in LiF crystals or thin polycrystalline LiF films. This material is remarkable due to an opportunity to produce the so-called colour centers therein. Interest in the study of colour centers in lithium fluoride crystals is supported by numerous practical applications of this material. In particular, the colour centers are used in thermoluminescent detectors of the X-radiation [5]. Also, it is known that the introduction of various impurities (Mg, Cu, etc.) into the LiF matrix increases the sensitivity of the luminescent detectors [6]. Recent studies have shown that such an effect also resulted from doping polycrystalline LiF film with Ag atoms [7]. The objective of this work is to establish changes in the optical properties of the LiF crystal irradiated by high energy silver ions embedded into the crystal matrix and produced both NCs and colour centers.

2. Experimental details

2.1. Experimental setup

The LiF samples were irradiated by a flow of silver ions produced with a compact pulsed implanter MEVVA.RU. An ion beam of 200 µs duration and a single pulse fluence of 2×10^{13} ions/cm^2 was extracted by a three-grid accelerating system from a vacuum arc plasma flame and accelerated by a voltage of 50 kV. Since the mean charge state of silver ions in these pulsed discharges is between +2 and +3, we guess that energy of the accelerated ions lies in a range of 100–150 keV. The research in spectral-kinetic characteristics of photoluminescence of lithium fluoride samples irradiated with silver ions was performed with a sensitive scanning confocal fluorescence microscope MicroTime 200 (by PicoQuant Gmbh company) with picosecond time resolution with a spatially-selective time-correlated count single photons. Photoluminescence spectra measured under excitation by picosecond laser with a wavelength of 375 nm were recorded by the spectrometer Ocean Optics 6500. To suppress scattered excitation radiation from the sample, the luminescence was recorded through a filter with a cutoff wavelength of 400 nm. The absorption spectra of the samples were recorded on a spectrophotometer SF-56.

2.2. Results and discussion

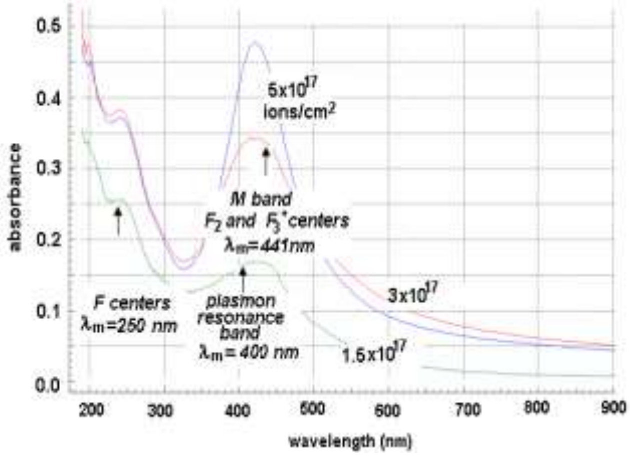

Figure 1. Absorption spectra of LiF crystals irradiated with Ag ions of various fluencies

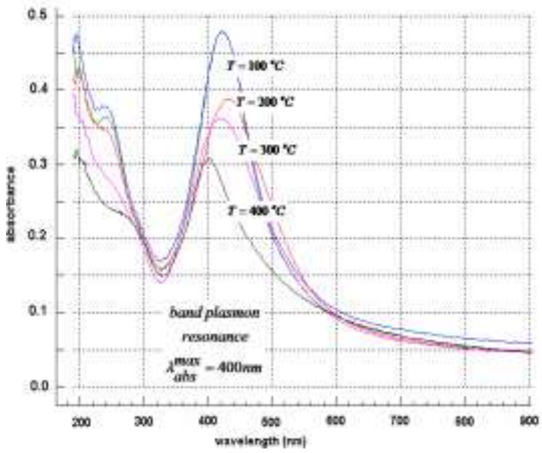

Figure 2. Changes in the absorption spectra of LiF crystals irradiated by Ag ions with fluencies of 3×10^{17} ion/cm^2 during thermal annealing

Figure 1 presents the absorption spectra of LiF crystals irradiated by Ag ions with a few high fluencies. Two bands with maxima at 250 nm and 430 nm wavelengths in the absorption spectra of the exposed crystals were observed. The former was due to the absorption of F colour centers and the latter consisted of F_2 (F_3^+) colour centers band and a plasmon resonance band that arose owing to embedding high energy silver ions into the matrix of the sample and following formation of silver NPs. One can see that increase in the fluencies results in corresponding increase in the absorption bands. Subsequent annealing of the exposed sample at temperature up to 400 ^{0}C results in decrease of the peaks and shift of the latter peak to 400 nm wavelength (see Figure 2). This result demonstrates that this band is thermally stable and, in fact, caused by the silver NPs, while bands due to color centers have disappeared because of the destruction of centers. Note that a marked absorption band can be observed only at sufficiently large fluencies. This means that the embedded ions merge into metallic particles of a nanometer scale only when the ion density in the host matrix is sufficiently large.

Now let us consider the results on studies of luminescent characteristics of the exposed samples. Figure 3 shows the luminescence spectra of LiF crystals irradiated by ion flow of various fluencies. It can be seen that the spectra of the exposed LiF crystals excited by laser radiation of 375 nm wavelength show that in addition to the luminescence bands with maxima at 550 and 680 nm, a luminescence band with a maximum at 460 nm was detected. The two former bands attributed to F_2 and F_3^+ colour centers, respectively, are formed in a thin surface layer by ion irradiation. The luminescence band with a maximum at 460 nm is due to the embedded silver ions. Figure 4 shows also that at low fluencies the peaks of the band due to silver ions are close to peak of the band due to F_2 and F_3^+ colour centers. Note that at high fluencies the latter exceeds significantly the former one.

The curve of the luminescence kinetic depicted in Figure 4a contains components with decay times 13.4 and 5.2 ns, that are close to the characteristic luminescence decay times of F_2 and F_3 centers in LiF crystal, which are of 15 and 8 ns, respectively [8]. In addition, two fast components with the decay times of 0.26 and 1.3 ns are observed. After annealing the sample at 400 ^{0}C for 30 min, the components due to the F_2 and F_3 centers, practically, diminished, while the fast components retained significant value. Taking into account the previous results, one can suppose that these fast luminescent components are due to silver ions.

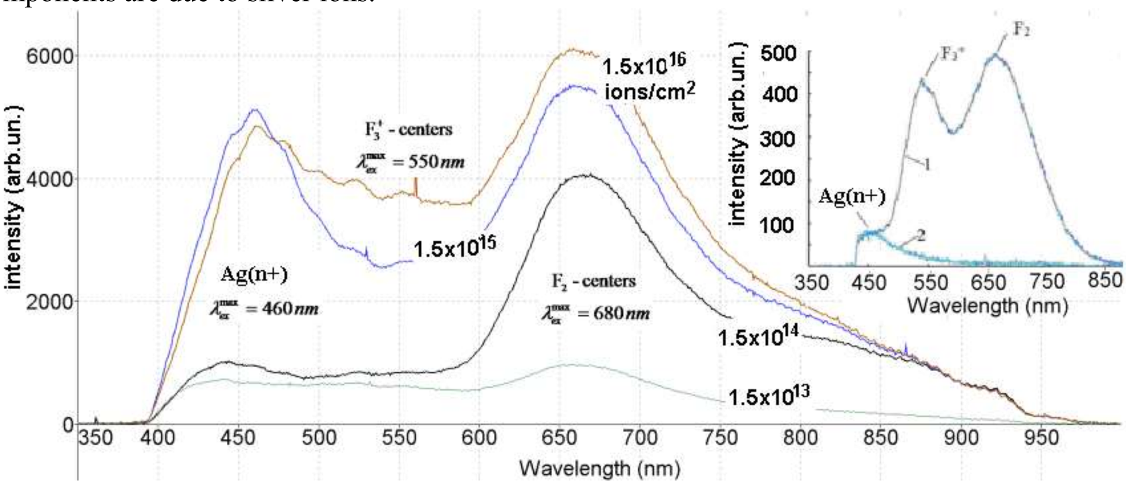

Figure 3. The luminescence spectra LiF crystals irradiated with Ag ions of various fluencies.

The results presented above permitted us to submit the following scenario of behaviour of silver ions imbedded into the host LiF matrix. At low ion fluencies, when the concentration of ions in the matrix is insignificant, these ions combine sub-nanoscale molecular charged clusters (MCs) consisting of *n* ions (atoms) Ag(n+), here *n* = 3–6. Under excitation, these clusters produce a luminescent band with peak at 460 nm wavelength and short decay times [9]. The intensity of this band is comparable with intensity of luminescence bands emitted by F_2 and F_3 colour centers resulting from the silver ion exposure of the matrix. When the ion fluencies increase, the concentration of ions embedded in the matrix increases as well. This results in merging these ions into metal particles of a nanometer size (NPs, 10–100 nm) which do not luminesce. These particles are resistant to annealing unlike the F_2 and F_3 colour centers.

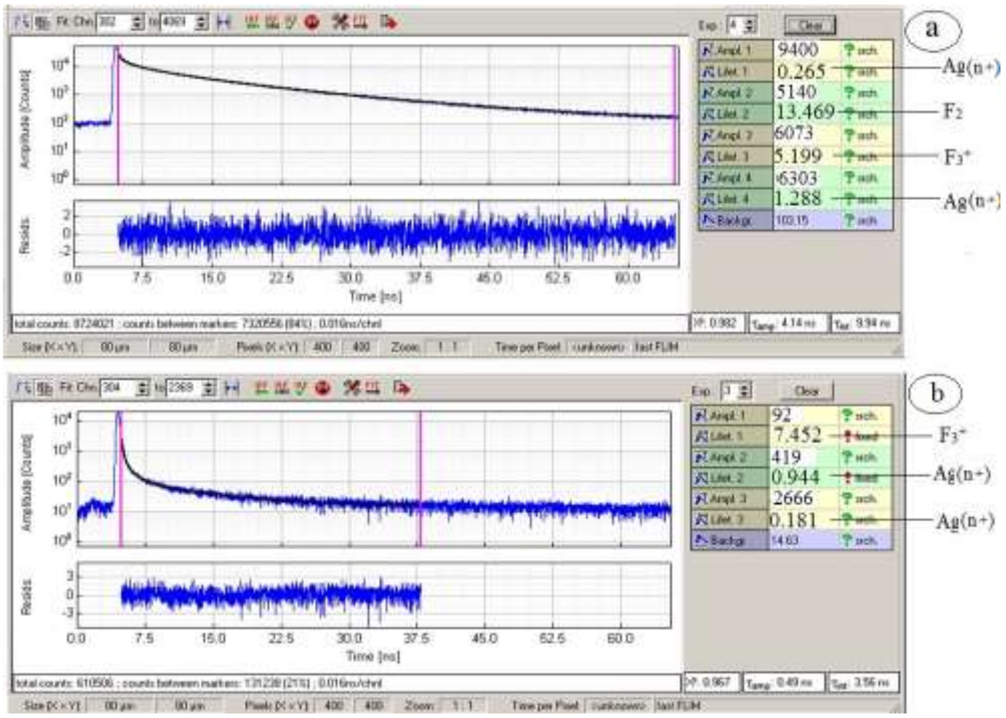

Figure 4. Luminescence decay curve of LiF fluorescence spectrum of the crystal irradiated of fluence of $5\cdot10^{17}$ion/cm^2 before (a) and after (b) annealing at 400 C^0 for 30 min

Conclusion

Thus, the presented results show that implantation of high energy silver ion is an effective method for production of a new type of luminescent medium. By varying the ion fluencies, we can produce silver particle from a sub-nanometer size scale up to several tens of nanometers. These particle types have significantly different luminescent characteristics, namely, while the former ones luminesce with the peak of the band at 460 nm, the latter ones do not luminesce.

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