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Enhancement of photoluminescence from rare-earth ions in fluoride crystals by ion-implanted silver nanoparticles

V.L. Paperny[1,], A.A. Chernykh[1], A.S. Ishchenko[2], S.V. Murzin[2], A.S. Myasnikova[3], R.Yu. Shendrik[3], E.F. Martynovich[2], and V.P. Dresvyansky[2]*

[1]*Irkutsk State University, Irkutsk, Russia*
[2]*Irkutsk Branch of Institute of Laser Physics, SB RAS, Irkutsk, Russia*
[3]*Vinogradov Institute of Geochemistry, SB RAS, Irkutsk, Russia*
[*]*paperny@math.isu.runnet.ru*

Abstract. The work shows that the photoluminescence in the visible spectral range of Er^{3+} ions in fluoride crystals $BaF_2:Er^{3+}$, which were pre-irradiated with a beam of high-energy (~100 keV) Ag ions, increases up to 10 times. This value is approximately two orders of magnitude greater than the earlier observed enhancement of the photoluminescence of erbium ions in the $Mg:Er:LiNbO_3$ crystal, pre-irradiated with the high-energy Au ions. Experimental evidences are obtained that the observed increase in the luminescence of Er^{3+} ions is due to non-radiative energy transfer to them from excited silver NPs, which form a layer about 400 nm thick in the irradiated crystal.
Keywords: ion implantation, erbium ions, luminescence enhancement, fluoride crystals

1. Introduction

Photonic materials, including those for optical amplifiers based on rare-earth ions such as Er^{3+}, are in wide use today. For instance, erbium-doped materials have attracted considerable interest in optical communication devices because of the emission of Er^{3+} ions at 1.54 μm, which coincides with the low-loss window of standard optical telecommunications fibers.

Earlier, it has been shown that the embedding of colloidal Ag nanoparticles into silica glasses significantly enhances Er^{3+} photoluminescence at a wavelength of 1.54 μm [1]. Up to now, most investigations on metallic NPs have only focused on glass substrates, there has been little scientific study of the synthesis and applications of metallic NPs in crystals. Let us note here the article [2], where only a slight (≤ 20%) increase in the photoluminescence intensity at a wavelength of 1.54 nm of the $Mg:Er:LiNbO_3$ crystal as a result of implantation of Au ions with an energy of 200 keV and a fluence of 1.0×10^{16} ion/cm^2 was recorded.

In the present work, ion implantation is used to embed the Ag dopant ions in the BaF_2 crystal. As a non-equilibrium technique, ion implantation can enable larger doping concentrations than the classical thermodynamic doping methods such as melt or diffusion [3]. In particular, by adjusting the implantation parameters, the concentration and depth of the dopant ions, in the implanted thin layer can be controlled and modified. Moreover, ion implantation is a flexible method for tuning the intrinsic characteristics of metal nanoparticles formed in a crystalline matrix from implanted ions, allowing wide variations in their optical properties

2. Experimental

BaF_2 crystals were grown by the Bridgman method in a six-barreled graphite crucible in vacuum [4]. A few percent of CdF_2 was added to the raw material to remove oxygen impurities. Crystals of alkaline earth fluorides activated by Er were grown (the introduced concentration was 1mol.%).

Irradiation of the BaF_2 samples 1 mm thick was carried out using a MEVVA ion implanter [5]. The samples were placed in a vacuum chamber at a residual gas pressure of ~ 10^{-2} Pa and irradiated with a pulsed beam of Ag ions with a duration of 200 μs with a current density of about 5 mA/cm^2 at an accelerating voltage of 50 kV, which is for Ag^{2+} ions that make up the main part of the ion beam, corresponds to an energy of 100 keV.

The spectral characteristics of the luminescence of the irradiated samples were studied using a MicroTime 200 confocal scanning fluorescence microscope (PicoQuant Gmbh Company). To excite photoluminescence, highly stable lasers with radiation at wavelengths of 405 nm was used, operating in a pulsed mode with a pulse repetition rate of 10 MHz and a pulse duration of about 50 ps. Photoluminescence spectra were recorded with an Ocean Optics 6500 spectrometer combined with a MicroTime 200 microscope through a filter with a cutoff wavelength of the transmission spectrum of 430, cutting off the exciting radiation scattered by the sample. Processing of photoluminescence decay curves was carried out using a specialized software product SymPho Time, which is included in the information support of the MicroTime 200 microscope. The processing algorithm is based on the analysis of histograms recorded when implementing the method of time-correlated counting of single photons and providing a time resolution of about 16 ps.

The absorption spectra of the samples are measured using a spectrophotometer based on the AvaSpec 2024 spectrometer in the wavelength range 250 - 750 nm with a resolution of about 1 nm.

3. Results and Discussion

Figure 1 shows the absorption spectra of BaF_2 crystals, irradiated by an Ag ion beam with a fluence of $5 \cdot 10^{16}$ ion/cm^2. It can be seen from the figure that the spectrum shows intense absorption band with a maximum at a wavelength near 400 nm. This band, repeatedly recorded as a result of implantation of Ag ions into various matrices, is due to the effect of surface plasmon resonance (SPR) associated with silver NPs formed in the irradiated matrix [6].

Experiment shows that the absorption spectra of similar crystals with an Er^{3+} content of 0.1 mol.%, irradiated by an Ag ion beam with the same fluence are very close to those above. This result means that the content of erbium ions does not affect the characteristics of the layer of formed metal NPs. Fig.1also shows that the positions of the absorption band for all samples are quite close, but the magnitude of the maximum is noticeably different.

To establish the possible mechanism of this relatively large amplitude of the absorption band of silver NPs in the BaF_2 crystal,, model calculations of the distribution of implanted ions with the above parameters in these matrices were carried out by the Monte Carlo method using the SRIM package [7]. As an example, the inset in Fig. 1 shows the calculated profile of implanted Ag ions with an energy of 100 keV in the BaF_2 matrix. This picture shows that the concentration gradient of implanted Ag ions, and therefore the ion diffusion flux, in the matrix BaF_2 is relatively low.

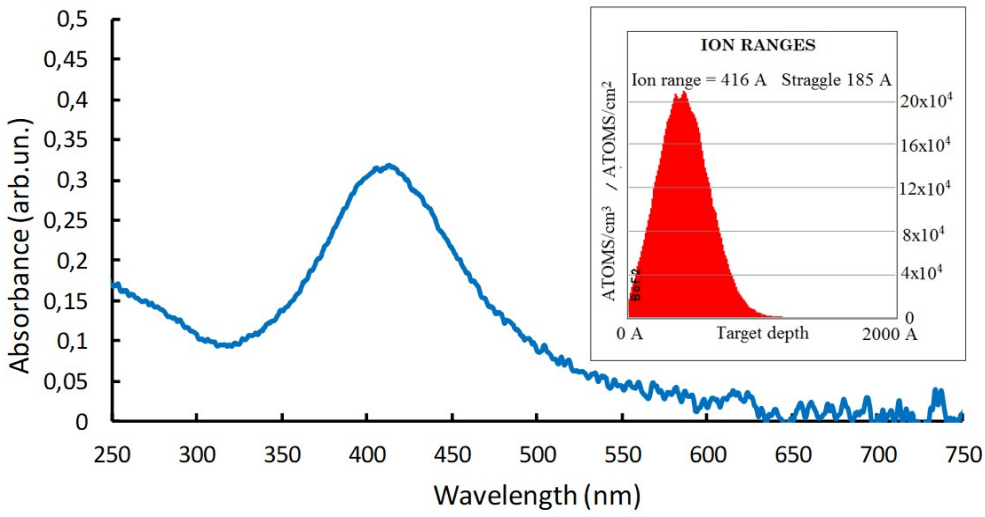

Fig. 1. Absorption spectra of BaF_2 crystal implanted with silver ions with a fluence of $5 \cdot 10^{16}$ ion/cm^2.

On the other hand, it is known from the literature that the ratio of the lattice constant of BaF_2 to the radius of the Ba+ cation is 4.62. This relatively small value means that this lattice is quite densely packed.

According to these two reasons, thermal diffusion, which leads to a spreading of the concentration profile of implanted Ar ions and, consequently, a decrease in their concentration, is difficult in this crystal. This fact promotes the fusion of silver ions/atoms into nanoparticles, which, in turn, provides a sufficiently large observed amplitude of the plasmon resonance band.

The luminescence spectra of the BaF_2 crystals depicted in Fig. 2 show the presence of three bands in the vicinity of 550, 660 and 990 nm, characteristic of the emission of Er_{3+} ions [8]. A comparison of panels (a) and (b) shows that reducing the content of the ions by ten times in the virgin crystals practically does not change the intensity of the bands at 550 nm, but significantly reduces the intensity of the bands at 660 and 990 nm below the detection threshold. After irradiation of crystals with silver ions with a low fluence of $2 \cdot 10^{14}$ ion/cm^2, the following characteristics are observed in the spectra:

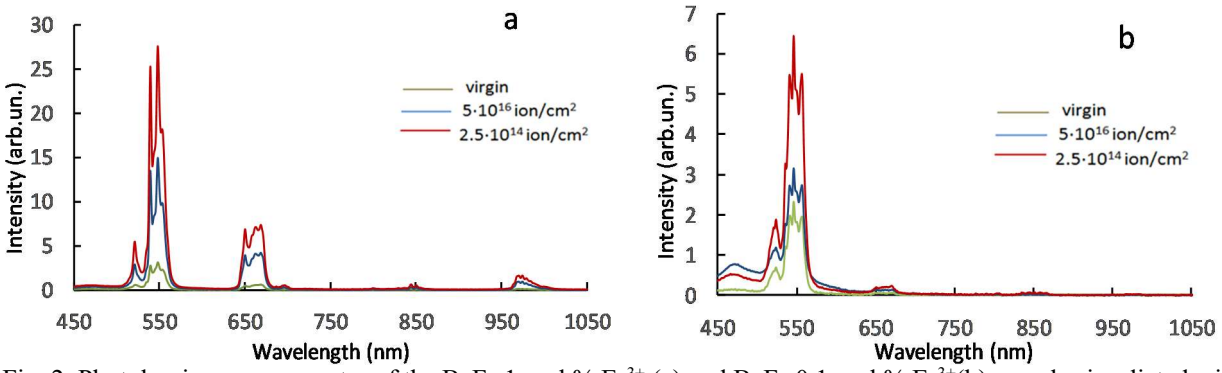

Fig. 2. Photoluminescence spectra of the BaF_2-1 mol.% Er^{3+} (a) and BaF_2-0.1 mol.% Er^{3+}(b) samples irradiated with the Ag ion beam of various fluencies, shown in legendю

1. There are no luminescence bands of silver NPs, which were previously recorded in the spectral range of 400–1000 nm in the virgin crystals of BaF_2 [9].

2. The amplitude of the band at 550 nm For an BaF_2-1 mol.% Er^{3+} crystal at a relatively low irradiation fluence of $2.5 \cdot 10^{14}$ ion/cm^2, increases by about 5 times, and the amplitude of the band at 660 nm increases by more than 10 times; the enhancement of photoluminescence as a result of irradiation with silver ions for a BaF*2*-0.1 mol.% Er^{3+} crystal is much weaker, i.e. about 3 times at fluence $2.5 \cdot 10^{14}$ ion/cm^2 and ~20% at fluence $5 \cdot 10^{16}$ ion/cm^2.

3. The intensity of the luminescence drops by ~ 2 times when the radiation fluence increases to $5 \cdot 10^{16}$ ion/cm^2 relative to the case of a low dose.

The above results show that under these experimental conditions, a significant increase in the intensity of photoluminescence of Er3+ ions is observed, reaching 5–10 times as a result of the implantation of silver ions into various fluoride matrices. This value is approximately two orders of magnitude higher than this one observed for a similar effect for PL at 1.54 nm with Au ions implanted in the matrix Mg:Er:LiNbO3 [2].

Now let's look at the possible reasons for the observed effects. First, note that it is well-known that the principal mechanism responsible for photoluminescence (PL) enhancement under similar experimental conditions is energy transfer from the sensitizer species to the Er^{3+} ions [1]. As mentioned above, metal NPs embedded in a dielectric are known to exhibit specific optical properties resulting from collective electronic excitations at the interface between the metal and the dielectric matrix, i.e., a local surface plasmon resonance. In this case, the PL enhancement is shown

to occur only when the excitation wavelength is absorbed by the Er^{3+} ions, whereas the energy transfer-based mechanisms for PL intensification occurs both under resonant and non-resonant excitation, with the excitation spectrum having a shape similar to the absorption spectrum of the NP doped materials.

Silver is one of the metals with highest efficiency of plasmon resonance in the visible range, which includes some of the typical absorption wavelengths of the Er^{3+} ions. The frequency and intensity of the SPR are known to depend on the concentration, shape and size of the NPs, the dielectric function of the surrounding medium, and the near field interactions between the NPs. Apparently, it is precisely these characteristics of silver NPs and the structural features of the matrix of our crystals that explain the observed anomalously large increase in the luminescence of Er^{3+} ions due to the Ag ion implantation.

We also emphasize that in these experiments, performed with fluoride crystals containing Er^{3+} ions and pre-irradiated with silver ions, intense luminescence bands in the spectral range 400–800 nm, earlier observed in similar samples without Er dopant and attributed to the radiation of silver NPs [8], are not detected. In accordance with the above mechanism, it is natural to assume that this is due to the non-radiative transfer of energy from excited silver NPs to erbium ions.

Earlier, a significant (a few times) increase in the PL of erbium ions in the presence of metal NPs was recorded only in amorphous matrices, where NPs were formed directly during the sample fabrication process and were distributed throughout the entire volume of the sample [10].

In our case, a similar effect is recorded as a result of irradiating a sample with high-energy silver ions and forming NPs in a thin layer with a thickness of only a few tens of nanometers. We believe that this is due to the high density of implanted silver ions ($>10^{20}$ ion/cm^3), which is unattainable in the fabrication of amorphous matrices using equilibrium thermal and chemical methods. The high density of ions embedded in the host matrix leads, correspondingly, to a high density of formed Ag NPs, which, in turn, significantly increase the efficiency of energy transfer from exited NPs to erbium ions.

4. Conclusions

Thus, the work shows that PL of the Er^{3+} ions in the visible range of the spectrum of BaF_2:Er^{3+} crystals irradiated with a beam of high-energy (~100 keV) silver ions increases up to 10 times. This enhancement is almost two orders of magnitude higher than the observed earlier enhancement of PL at a wavelength of 1.54 nm of the Mg:Er:$LiNbO_3$ crystal irradiated with high-energy Au ions. Moreover, the effect is comparable to that earlier observed in amorphous optical media containing Ag ions embedded into the matrix during their fabrication and distributed throughout the entire volume of the sample. Experimental evidence are obtained that the observed effect is due to the efficient non-radiative energy transfer to the Er^{3+} ion from excited silver NPs formed in a layer about 400 nm thick as a result of ion irradiation.

Considering that the studied crystals are widely used in the manufacture of detectors of various types of radiation, the discovered effect can be used to significantly enhance the efficiency of these detectors.

5. References

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