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Effect of UV irradiation on photoluminescence of Er^{3+} ions in matrices of metal oxides and fluorides

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Abstract. A comprehensive study of UV-irradiation of Er-activated solid luminophores on f-f-luminescence of Er^{3+}ions in metal oxide (ZrO$_2$, La$_2$O$_3$) and fluoride (LaF$_3$, YF$_3$) matrices has been carried out. Both increasing (LaF$_3$, YF$_3$), and decreasing (ZrO$_2$, La$_2$O$_3$) of luminescent emission intensity under monochromatic excitation at 377 nm caused by UV irradiation of dispersed samples have been observed. A possible mechanism of the established effect is briefly discussed

1. Introduction

Trivalent erbium as well as other trivalent rare-earth (RE) lanthanide ions are well known to be the activators of photo- and up-conversion luminophores. The unique properties of such phosphors are due to the violation of Laport rule: the forbidden f-f transitions in RE^{3+} ions can be partly allowed either in crystals or in glasses. The intensity of optical f-f transitions depends both on the crystal structure of the matrix and on the presence of intrinsic and extrinsic defects in a given host crystal or glass [1-3]. The latter opens are the way to control the luminescence of RE phosphors by introducing various impurities into the matrices [4]. In our previous work [5] it was demonstrated by diffuse reflectance spectroscopy (DRS) that UV irradiation of zirconia doped with Er and Yb ions changes the intensity of corresponding f-f absorption bands. Correlations between the UV induced alteration in the absorption of RE^{3+} ions and the changes in the absorption of photoinduced defects in the matrix (UV induced coloration) were also established. In order to confirm the general nature of the observed effect, the studies of UV induced coloration effect on luminescence of Er-doped ZrO$_2$, La$_2$O$_3$, LaF$_3$ and YF$_3$ have been performed.

2. Synthesis and characterization of phosphors

Zirconium matrices were synthesized by sol-gel method from zirconium butoxide and Er chlorides, followed by annealing of the synthesis product at 900-1000C for 10 hours. Doped lanthanum oxide was obtained by decomposition of lanthanum and corresponding RE metal hydroxides, followed by

annealing at 800 C for 10 hours. Matrices YF$_3$ and LaF$_3$ were synthesized by co-precipitation using a 40% aqueous solution of HF, dopants were introduced in the form of nitrate salts.

The phase compositions of the samples were determined by X-ray diffraction (diffractometer Bruker D2 Phaser). The concentration of introduced RE ions was monitored by energy dispersive X-ray spectroscopy (Oxford X-Max 20 spectrometer as part of a HITACHI S-3400N electron microscope). The particle morphology of the samples was determined by scanning electron microscopy (SEM) (table 1).

Table 1. Sample characterization data.

Sample	Me^{3+} concentration (at.%)	Lattice system	Particle size (μm)	Band gap energy. E$_g$ (eV)
ZrO$_2$ / Y	[Y] — 8.3	Cubic	500 – 700	5.9-6,0
ZrO$_2$ / Er	[Er] — 13.4	Cubic	5 – 25, 100 – 500	
La$_2$O$_3$	Pure	Trigonal	5 – 10	5.2
La$_2$O$_3$ / Er	[Er] — 0.58	Trigonal	500 – 1100	
LaF$_3$	Pure	Hexagonal	3 – 5, 10 – 20	7.7
LaF$_3$ / Er	[Er] — 8.3	Hexagonal	3 – 5, 10 – 20	
LaF$_3$ / Yb / Er	[Yb] — 16.3 [Er] — 1.9	Hexagonal	3 – 5, 10 – 20	
YF$_3$	Pure	Orthorhombic	3 – 5, 10 – 20	7.9
YF$_3$ / Er	-	Orthorhombic		

3. Experimental

Diffuse reflectance spectra of powdered samples in spectral range 200-800 nm were measured by spectrophotometer (Perkin-Elmer). Luminesce spectra of samples were recorded using FluoroMax Plus spectrofluorimeter (Jobin-Yvon).

In a series of pilot experiments to study the effect of UV irradiation on the absorption and photoluminescence of the samples, the following procedure was applied:

1) Registration of diffuse reflection spectra (DR spectra) and luminescence spectra (excitation at wavelength of 377 nm of samples in the initial state; 2) Irradiation of samples with a deuterium lamp Hamamatsu L2D2 Deuterium lamp L7296 (short-wavelength limit is about 185 nm) for 30 minutes; 3) Registration of DR spectra and luminescence spectra of the samples after UV irradiation.

The absorptance $A = 1 – R$, where R is the dimensionless diffuse reflection coefficient of a given sample, was taken as a measure of the sample absorption. The difference spectra $\Delta A = A – A_0$, where A_0 and A are the absorptance of sample before and after UV irradiation respectively, was a measure of the photoinduced coloration. The relative alteration in the intensity of the luminescence $\Delta I/I = (I – I_0)/I_0$, where I_0 and I are the RE luminescence intensity of the sample before and after UV irradiation respectively, was taken as a characteristic of the effect of UV irradiation on luminescence.

4. Results and discussion

UV irradiation of the powdered samples was carried out with a deuterium-hydrogen lamp (5 mW/cm^2) in the spectral region $185 <\lambda< 300$ nm (photon energy range $4.1< E_{hv} < 6.7$ eV) corresponding to the extrinsic absorption region of LaF$_3$ and YF$_3$ matrices ($E_g >7$ eV) and both extrinsic and intrinsic absorption of La$_2$O$_3$ and ZrO$_2$ ($E_g \leq 6$ eV). The UV irradiation of the samples results in two consequences. The first one is a redistribution of the extrinsic absorption bands of the matrix. The second consequence is an alteration of the intensity of Er^{3+} f-f absorption and emission bands. The first effect was observed earlier for absorption of Er^{3+} and Yb^{3+} ions in the c-ZrO$_2$ matrix [3]. As examples of the results obtained for the series of luminophores studied in this work, the absorption and luminesce spectra of Er^{3+} doped La$_2$O$_3$ and LaF$_3$ are presented below.

Er^{3+} doped La$_2$O$_3$ phosphor. UV irradiation of La$_2$O$_3$ matrix leads to a decrease in the intensity of f-f emission bands of Er^{3+} ions (520-570 nm, transitions: $^2P_{3/2} \to {}^4I_{9/2}$, $^2H_{1/2} \to {}^4I_{15/2}$, $^4S_{3/2} \to {}^4I_{15/2}$) and

(650 – 680 nm, transitions: $^4F_{9/2}$ $^4I_{15/2}$) in green and red spectral regions respectively (figure 1a). The relative alterations of luminescent emission, $\Delta I/I_0$, are negative and nearly equal in absolute value for "green" (0.40 – 0,43) and "red" (0,37- 0.39) emissions.
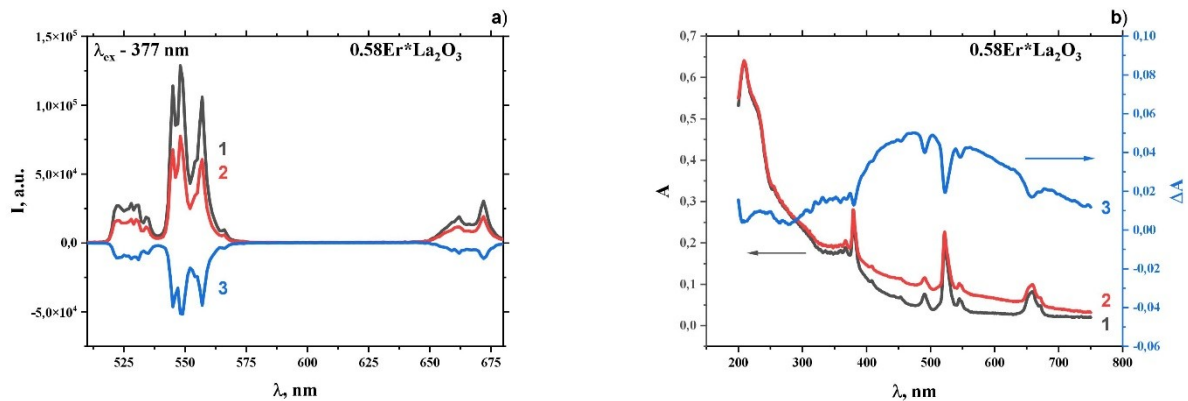
Figure 1. Luminescence spectra (a) and diffuse reflectance spectra (b) of La_2O_3 / Er, where (1) is initial spectrum before irradiation, (2) is spectrum after irradiation and (3) is difference spectrum.

Corresponding negative changes in A appear as narrow "dips" in the difference spectra against the background of the wide absorption band ($\Delta A > 0$) in the spectral range 350–750 nm with a maximum at 400–450 nm (figure 1 b, curve 3). The latter band can be assigned to UV-induced intrinsic color centers of La_2O_3 enhanced by europium doping since similar week band appears in ΔA spectrum of undoped La_2O_3 (figure 2a, curve 3).
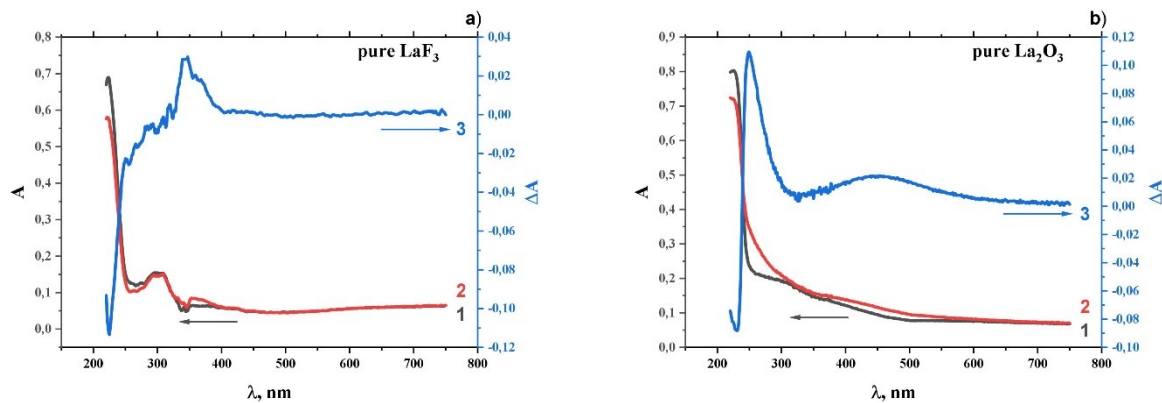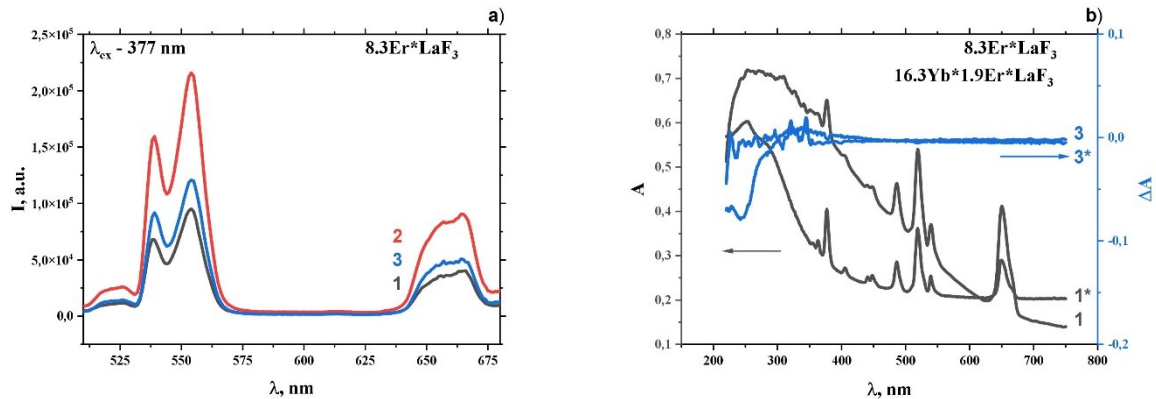

Figure 2. Diffuse reflectance spectra of a pure LaF_3 (a) and pure La_2O_3,(b) where (1) is initial spectrum before irradiation, (2) is spectrum after irradiation and (3) is difference spectrum.

Similar features are also characteristic of zirconium dioxide (table 1). The same features but more pronounced, were observed for heavy erbium doped (20%) c-ZrO_2 [3].

Er^{3+} doped LaF_3 phosphor. In contrast with Er^{3+} doped La_2O_3 phosphor UV irradiation of Er^{3+} doped LaF_3 sample leads to pronounced increasing of f-f emission bands (figure 3 a). The compared metal oxide and metal fluoride matrices differ in the nature of the anion and accordingly in crystal structure and band gap energy. They also differ in erbium content. The difference in particle sizes due to the synthesis conditions reaches two orders of magnitude. Any of these differences or a combination of them can be responsible for the sign alteration of $\Delta I/I_0$ in transition from La_2O_3 to LaF_3 matrices. Differences between the photo-induced response of doped La_2O_3 and LaF_3 matrices to UV irradiation are also observed in the DR spectra (Spectra 3, figures 1a and 2b respectively). As evident from the

SD spectra, UV irradiation of LaF_3 matrices does not change the intensity of the absorption f-f bands, which contradicts the results of the luminescent test (figure 3a).

Figure 3. Luminescence spectra (a) and diffuse reflectance spectra of LaF_3 / Er and LaF_3 / Yb / Er (b), where (1) is initial spectrum before irradiation, (2) is spectrum after irradiation and (3) is difference spectrum (Numbers with an asterisk refer to spectra of LaF_3 / Yb / Er).

In contrast to lanthanum oxide, the SD spectra of UV-induced absorption in doped LaF_3 matrices demonstrate no bands of color centers in the wavelength range above 300 nm. There is also a decrease in absorption at the short wavelength spectral region ($\lambda < 300$ nm). The same behavior with only a weak absorption band around 350 nm corresponding to intrinsic color centers, is also characteristic of pure lanthanum fluoride (figure 2b).

The observation described above can be related to the peculiarities of signal formation during measurements of SD spectra and luminescence emission spectra at a given effective penetration depth of actinic UV light, d_{hv}. In dispersed samples the effective penetration depth of light of a given wavelength is determined by the absorption, scattering, and reflection of light. Tthe luminescence signal is formed in a layer of powder with a thickness d_{ex}, i.e., in a layer penetrated by the exciting light ($\lambda = 377$ nm). At the same time, the signal of the SD spectrum is formed in a layer of thickness d_{DR} for a given sample in visible spectral range. The size of LaF_3 particles is relatively small. In addition, the absorption coefficients of powder substance are also rather small ($E_{hv} < E_g$). Thus, conditions for luminescence registration can be described by a ratio $d_{hv}/d_{ex} = \eta_{LE} < 1$. A numerical η_{LE} value depends on both the variation of intensity of luminescence, which originates only from a layer of depth d_{hv}, and the luminescence intensity measurement error. The effect becomes undetectable at a certain lower limit value η_{LE}

The similar condition for absorptance can be described as following: $d_{hv}/d_{DR} = \eta_{SD} < 1$. Note, that the condition $\eta_{SD} \ll \eta_{LE}$ may be valid for lanthanum fluoride matrix in contrast with that for La_2O_3 matrices. For finely dispersed powders that weakly absorb light, the depth of light penetration is determined mainly by scattering and sharply decreases with an increase in the scattering coefficient. Therefore, the fulfillment of the condition $d_{DR} \gg d_{ex}$ is more likely for finely dispersed samples due to a more pronounced increase in scattering with a decrease in the wavelength of light penetrating into the sample compared to coarse powders.

In this way, the luminescence method seems to be more effective in observation of the effect of UV irradiation on rare earth ions introduced into powdered solid particles. At the same time, this method also gives underestimated limit of the alteration of the absorption of RE ions in powdered matrices.

The summary results of the study of the effect of UV irradiation on the luminescence of Er^{3+} ions in different matrices are shown in figure 4. is seen that the established effect manifests itself under UV irradiation of matrices in the spectral regions of both intrinsic (La_2O_3, ZrO_2) and extrinsic (LaF_3)

absorption. The sign of $\Delta I/I_0$, which characterizes the effect, can be also as positive (LaF$_3$), as negative (La$_2$O$_3$, ZrO$_2$). As follows from the analysis of the criteria for the observability of the effect (see above), the values of $\Delta I/I_0$, shown in figure 4, estimates the minimum limit of the criteria. In the samples of phosphors, for which the condition $d_{hv} \approx d_{ex}$ is satisfied. the effect can be more pronounced.
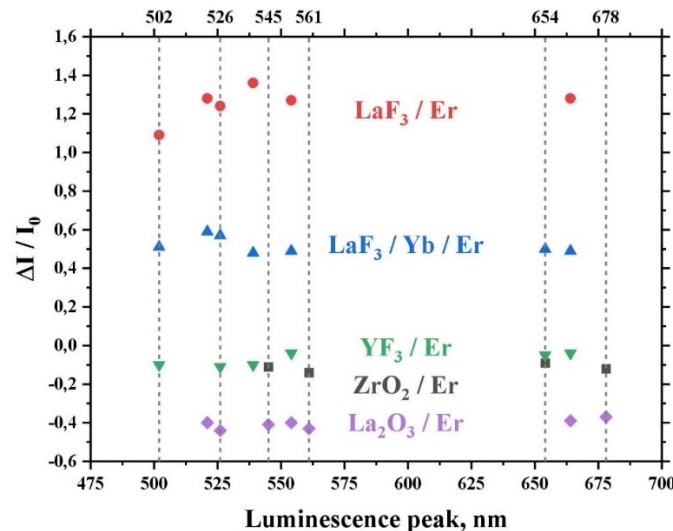
Figure 4. The relative changes in the intensity of Er^{3+} ions luminescence for the sample studied.

A possible mechanism of the effect related to photostimulated defect formation in wide-gap matrices containing RE ions is presented in our previous article [5].

5. Conclusion

The obtained results indicate the general nature of the effect of UV irradiation on the luminescence of erbium ions embedded in the matrices of metal oxides and fluorides. This opens a new opportunity to control the luminescence of phosphors containing ions of rare-earth metals.

Acknowledgments

References

[1]   Feofilov P and Ovsyankin V 1967 Cooperative Luminescence of Solids *Applied Optics Materials* **6(11)** 1828-33

[2]   Ausel F 2004 Upconversion and Anti-Stokes Processes with f and d Ions in Solids *Chem Rev* **104(1)** 139–74

[3]   Dragic P, Cavillon M and Ballato J 2018 Materials for optical fiber lasers: A review *Appl. Phys. Rev*. **5** 041302 DOI: 10.1063/1.5048410

[4]   Okazaki T, Sekiya E and Saito K 2008 Concentration dependence of local structure around Yb^{3+}ions and optical properties in Yb–P-doped silica glasses *Jpn. J. Appl. Phys*. **58** 062001 DOI:10.7567/1347-4065/ab17e4

[5]   Khabibrakhmanov R, Shurukhina A, Rudakova A, Barinov D, Ryabchuk V, Emeline A, Kataeva G and Serpone N 2020 UV-induced defect formation in cubic ZrO_2 center dot Optical demonstration of Y, Yb and Er dopants interacting with photocarriers *Chem. Phys. Letters* **742** 137136 DOI: 10.1016/j.cplett.2020.137136