ZnO nanorods alloyed with Mo/Er. The effect of post-deposition treatment on defect states and luminescence

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Abstract. Free-standing ZnO nanorods alloyed with Er/Mo were synthesized by the hydrothermal growth method. To characterize them, the number of experimental techniques was applied including X-ray diffraction (XRD), scanning emission microscopy (SEM), electron paramagnetic resonance (EPR), photo- and radioluminescence (PL, RL). EPR confirmed the existence of F⁺ centres common for ZnO-based structures in the ZnO:Er(30%) nanorods whereas in the ZnO:Mo(30%) this kind of defect was absent. Air annealing at elevated temperatures results in the reduction of F⁺ centres in all the materials studied. Moreover, Er³⁺ EPR signal also undergoes changes including broadening in the ZnO:Er. This allowed suggesting oxidation of Er ions on the ZnO nanorods surface. Red luminescence (~680 nm) appears in all studied samples regardless the dopant origin and doping level after the annealing in air. The exciton-related band at 380 nm never observed in the samples before the annealing appears upon the annealing at 350 ºC in ZnO:Mo(10%) and ZnO:Er(30%). No such band was observed in the ZnO:Mo(30%) sample under the same conditions. According to SEM there are nanorods no more but microrods upon the content of Mo/Er as compared to the as-grown untreated ZnO as reported in a recent work.

1. Introduction

Scintillators application in computer tomography (CT) and positron emission tomography (PET) is of the utmost importance. This requires the improved coincidence time resolution (CTR) of the scintillating system in the time-of-flight (TOF) PET extension [1]. Significant improvement of the TOF PET is expected at the value around 100 ps [1] what is nowadays the focus of the worldwide research community in a hot field of the ultrafast scintillators engineering. However, the expected limit of the CTR for a scintillating material is 10 ps.

Presently, excellent timing properties have been observed in zinc oxide (ZnO) nanostructures like nanopowders, free-standing (hedgehog) or deposited nanorods. ZnO shows strong room temperature defect related luminescence, high exciton binding energy (60 meV) and most interestingly the ultrafast excitonic luminescence [2]. In most cases it has the hexagonal (wurtzite) structure [3]. Very recently, the preparation of nanocomposite consisting of ultrafast ZnO:Ga scintillating powder incorporated into the scintillating polystyrene matrix was reported [4]. Following the requirements of different applications and band-gap engineering strategy, there were attempts of doping ZnO material (bulk,
thin films, quantum dots, and nanocrystalline/nanoparticles) also with other ions originally expected to be paramagnetic (e.g. rare earths or 3d ions like Co$^{2+}$, Mn$^{2+}$ etc.) [5-8]. Numerous works report data obtained in these systems by EPR and EPR-based techniques (e.g. [9,10]). However, to the best of our knowledge, no works were found reporting studies of the Mo incorporation and its influence on physical and optical properties. Rare earth ions doping of the ZnO matrix is widely known subject, especially from luminescence point of view [11,12]. However, their incorporation inside the host remains rather obscure. Only several works raise this problem by carrying out EPR measurements in ZnO:Er/Gd/Yb [13,14]. Nonetheless, these data are not systematic and can be judged as the preliminary ones gaining very poor insight into the underlying problem. Er$^{3+}$ ions are of great importance because of the luminescence and paramagnetic properties. In most cases EPR spectra measured in as-grown doped or undoped ZnO materials contain only the commonly known resonance line at g factor $g = 1.96$ [15-18] related to an electron captured by an oxygen vacancy, F$^-$ centre [19,20]. Post-deposition treatment, conditions of growth, additional doping or all this altogether can influence the amount of F$^-$ centres in the material. Moreover, this also affects the luminescence properties [4,21]. This requires deep understanding of the energy and charge transfer processes including trapping of charge and defects creation. Therefore, this work is aiming at comparison of undoped and doped zinc oxide nanorods alloyed with Er/Mo to find out the peculiarities of the energy and charge transfer and the possibilities of the ZnO-based structures improvement by the embedding of Er or Mo into the structure bulk or their deposition on surface.

2. Experimental conditions

2.1. Samples preparation

All reagents were obtained from commercial suppliers and used without further purification. Zinc nitrate hexahydrate ($\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_6$) were purchased from Slavus and erbium nitrate pentahydrate $\text{Er(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O}$ (Precursor Er) and ammonium heptamolybdate tetrahydrate $\text{(NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Precursor Mo) from Sigma-Aldrich. Deionised water was purified with a So~Safe Water Technologies, having a conductivity 0.20 µS cm$^{-1}$ at 25 ºC.

Undoped ZnO nanorods and ZnO nanorods alloyed with Er or Mo with expected nominal compositions $\text{Zn}_{1-x}\text{Mo}_x\text{O}$ ($x = 0, 0.1, 0.3$) and $\text{Zn}_{0.7}\text{Er}_{0.3}\text{O}$ were prepared by the hydrothermal growth method. First, the corresponding stoichiometric amounts of $\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Er(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O}$ or ($\text{NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in 200 ml and 50 ml of deionised water, respectively, with vigorous stirring by a magnetic stirrer. At the same time a 25 mM aqueous solution of HMTA was prepared. All the solutions were filtered through a Whatman 2 filter. Secondly, the solutions of the $\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Er(NO}_3\text{)}_3 \cdot 5\text{H}_2\text{O}$ or ($\text{NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were mixed under vigorous stirring for 15 min. The nominal concentration of each of the $\text{Zn}_{1-x}\text{Mo}_x\text{O}$ ($x = 0, 0.1, 0.3$) and $\text{Zn}_{0.7}\text{Er}_{0.3}\text{O}$ in the final suspensions was 25 mM. The solution of HMTA was added to the mixture. Thirdly, after stirring of the reaction mixture, the hydrothermal growth was performed at 90 ºC for 3 hours. Fourthly, the residuals of salts were removed from the grown samples by 5 times washing with deionised water followed by centrifugation at 18 000 rpm (RCF: 23542×g) for 15 minutes. Finally, the samples were dried by lyophilisation.

The MoO$_3$ nanorods were grown only for comparison with the $\text{Zn}_{1-x}\text{Mo}_x\text{O}$ ($x = 0, 0.1, 0.3$) samples. MoO$_3$ nanorods were prepared by hydrothermal method as reported in [22]. 1.2 g of ($\text{NH}_4\text{)}_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 20 ml of deionised water. Subsequently, 65% HNO$_3$ (80 ml) was added to the solution. Then it was stirred at 85 ºC for 30 minutes. After that, the stirring was turned off and the solution held at 85 ºC for 1 hour. The synthesized nanorods were isolated from the solution, washed 5 times with deionised water, and dried at room temperature.

2.2. Experimental techniques

XRD was performed using RigakuMiniFlex 600 (Ni-filtered Cu-Kα1,2 radiation) equipped with the NaI:Tl scintillation detector and XRD patterns were compared to the relevant records in the ICDD.
PDF-2 database (version 2013). The angular range was $10^\circ - 80^\circ$ with a step of 0.02° and a scanning speed of 2°/min.

The size and morphology of ZnO nanorods has been checked by scanning electron microscopy (SEM) using MAIA3, TESCAN electron microscope with the in-beam SE detector placed in objective lens and the electron beam energy 5 keV.

The Raman spectra of the undoped ZnO and ZnO:Mo:Er powders were measured at room temperature by a Renishaw In Via Reflex Raman spectrometer using a CCD camera and the 442 nm He-Cd laser excitation. Other parameters were ×100 Olympus objective, 65 µm slits, and a grating with 2400 grooves/mm.

The photoluminescence (PL) measurements were done on powder samples pressed in Suprasil glass tube featuring a low florescence background and converted from wavelength to energy scale taking into account the Jacobian correction [23].

The spectra of steady-state PL excited at the wavelength 340 nm by optically filtered pulsed 1 mW UV LED were recorded in the 355-800 nm spectral range with 2 nm spectral resolution using the spectrally calibrated E/4 double gratings SPEX 1672 monochromator, long-pass filters, a multi-dynode multi-alkali red sensitive cooled photomultiplier, and a lock-in amplifier referenced to the LED frequency 337 Hz [24]. All PL spectra were normalized at the wavelength 355 nm on the same value.

The steady-state PL spectra in the 1200-1650 nm spectral range were recorded with 4 nm spectral resolution under excitation by optically filtered pulsed 150 mW laser diode (LD) at the wavelength 980 nm using the spectrally calibrated Horiba H20IR monochromator, a long-pass filter, an InGaAs photodiode, and a lock-in amplifier referenced to the LD frequency 337 Hz [25].

The optical absorption spectra were measured in the 300-1650 nm spectral range using photothermal deflection spectroscopy (PDS) on pellets with the diameter of 3 mm made from powder pressed onto double sided copper tape glued on copper substrates. The samples were immersed into liquid and the relative temperature of the illuminated sample was measured independently for each wavelength as a deflection of probe laser beam parallel to the sample surface. The spectra were spectrally calibrated by measuring PDS of a black carbon sample and normalized on 1 in the region of full absorption [26].

Ultrafast decays under pulsing X-ray excitation were measured using picosecond (ps) X-ray tube N5084 (Hamamatsu, 40 kV). The X-ray tube is driven by the ps light pulser equipped with a laser diode with the repetition rate up to 1 MHz. The signal was detected by hybrid picosecond photon detector and Fluorohub unit (Horiba Scientific). The setup instrumental response function FWHM is about 76 ps. The spectrally unresolved luminescence decay curves were detected from the surface excited by X-rays.

The radioluminescence (RL) was measured using the Horiba Jobin-Yvon 5000 M spectrometer with Janis liquid nitrogen cryostat and TBX-04 (IBH) photomultiplier operating in the 200–800 nm spectral range. The spectral resolution of the monochromator was 8 nm. All the spectra were corrected for experimental distortions caused by the setup. The powder samples were deposited on a silver paste and pressed on the sample holder. The samples were irradiated by a Seifert X-ray tube operated at 40 kV with a tungsten target. The RL spectra were measured at 300 K and 77 K. PL decay curves were measured using similar setup equipped with ns excitation nanoLED light sources. The deconvolution procedure was applied to the decay curves to determine true decay times (SpectraSolve software package, Ames Photonics).

Electron paramagnetic resonance (EPR) measurements were performed with a commercial Bruker EMXplus spectrometer in the X-band (9.4 GHz) within the 4-296 K temperature range using Oxford Instruments ESR900 cryostat. The spectrometer sensitivity is about $10^{12}$ spins/mT.

The annealing in air was done in a quartz sample holder within the modular vertical tube furnace Tersid Carbolite with the possibility to elevate temperature up to the 1000 °C.
3. Results and discussion

3.1. Structural and phase purity analysis
In order to check whether the synthesized ZnO:Mo(10%), ZnO:Mo(30%), and ZnO:Er(30%) powders are indeed nanostructured, the samples were examined using SEM. The corresponding images are shown in figure 1. One can immediately see that the undoped ZnO powder (figure 1(a)) represents the commonly known nanorods structure studied in many previous works (see e.g. [17,21,27]) with the circumference of a single nanorod smaller in average than 200 nm having length of the order of 1-2 μm. However, as soon as the doping with 10 at% of Mo was applied, the nanorods size was drastically changed (figure 1(b)). Now it is inappropriate to consider nanorods but rather microrods as the averaged circumference of a single rod has become of the order of 0.5-1 μm with the length over 2 μm. Interestingly, the microrods preserve wurtzite-like [3] hexagonal shape being more massive at the base and getting narrower at the top (see figure 1(b)).

Figure 1. SEM images of the samples: (a) undoped ZnO, (b) ZnO:Mo(10%), (c) ZnO:Mo(30%), (d) ZnO:Er(30%).

The increased level of doping from 10% to 30% results in the degradation of the structures shown in figure 1(b) and so only the shape of flakes can be observed (figure 1(c)). Their shape is no more hexagonal but rather irregular. These flakes are smaller and larger with the size varying from approximately 100×200 nm to 1×2 μm. Doping of the hydrothermally grown ZnO powder with 30% Er results in the appearance of very small flakes approximately 100×200 nm and large hexagonal rods (figure 1(d)) approximately of the size of the microrods observed in the ZnO:Mo(10%) sample (figure 1(b)). Their circumference reaches 0.5-1 μm in average and the length surpasses 2 μm. These rods are also thicker at the base and narrower at the top as well as the ones in the ZnO:Mo(10%).

The XRD patterns of the undoped ZnO and ZnO:Mo/Er samples are shown in figure 2(a). From this follows that the undoped ZnO nanostructures are single phase, composed only of the wurtzite ZnO. As for the ZnO:Mo/Er samples, they exhibit the presence of both the wurtzite ZnO and some other phase(s)/structure(s) further, in general, referred as the not-ZnO$_{Mo}$ and not-ZnO$_{Er}$ in the ZnO:Mo and ZnO:Er, respectively. According to figure 2(a) the wurtzite ZnO phase in the ZnO:Mo(10%) and
ZnO:Er(30%) is dominating. Oppositely, the ZnO:Mo(30%) exhibits much weaker peaks originating from the wurtzite ZnO phase as compared to the not-ZnO:Mo phase. In case of the ZnO:Er(30%), the not-ZnO:Er phase is unlikely the Precursor Er in its original form as it is too hygroscopic [28]. Probably, the not-ZnO:Er phase in the ZnO:Er(30%) sample is the combination of Er-based oxides or hydroxides created out of the part of the Precursor Er decomposition during the hydrothermal reaction. Note, that the not-ZnO:Mo,Er reflections emerged in ZnO:Mo/Er samples could not be matched with any relevant record from the ICDD PDF-2 database (version 2013). The not-ZnO:Mo,Er reflections are getting stronger in the ZnO:Mo(30%) sample as compared to the ZnO:Mo(10%). Therefore, the not-ZnO:Mo,Er phase, most likely, originates from the mix of the residual of Precursor Mo and the products of the partial Precursor Mo decomposition in the ZnO:Mo(10%)/(30%). Note that the Precursor Mo is decomposing upon thermal treatment into MoO$_3$, oxides or hydroxides as reported in [29]. Therefore, it was impossible to find out precisely the exact origin of the not-ZnO:Mo,Er in the ZnO:Mo/Er samples.

To have better insight into the structural and phase properties of the samples, they were examined by Raman spectroscopy. The spectra are shown in figure 2(b). The identification of the peaks originating from the hexagonal wurtzite ZnO phase was done basing on a recent work dedicated to ZnO nanorods [30] whereas the groups of peaks belonging to the Precursor Mo were identified by comparing the obtained results (figure 2(b)) with the data reported in [31]. Remarkably, the obtained Raman data (figure 2(b)) are complementary to the XRD data (figure 2(a)) confirming the presence of the Precursor Mo in the ZnO:Mo samples. The undoped ZnO exhibits typical single phase of hexagonal wurtzite structure whereas the Mo doping results in the presence of Precursor Mo phase getting stronger upon the doping level (A and B group of peaks in figure 2(b)). Interestingly, the peaks originating from ZnO are lost in noise in case of ZnO:Mo(30%). On the contrary, it seems that the ZnO:Er(30%) with the same 30% doping level exhibits one relatively weak peak (considering large doping level) which might originate from Precursor Er or rather some hydrate-like modification of it according to [32] besides those originating from ZnO. This allows to conclude along with SEM and XRD data that doping with Er is less harmful to the rods shape and the material phase purity than the doping with Mo.

![Figure 2](image-url)  
**Figure 2.** (a) XRD patterns of ZnO:Mo/Er structures prepared by hydrothermal growth along with the precursors used as the source of the specific dopant. Vertical lines indicate the wurtzite ZnO phase according to PDF database record #01-080-0075. (b) Raman spectra of the as-prepared ZnO materials (doping levels are given in a legend). The 1-5 numbers correspond to the specific vibrational modes in the way [30]: 1 - ($E_2^{\text{high}}$ - $E_2^{\text{low}}$); 2 - $A_1$(TO); 3 - $E_2^{\text{high}}$, 4 - $A_1$(LO); 5, 6 - 2$A_1$(LO), 2$E_2$(LO). The group of peaks A and B originate from Precursor Mo [31]. Peak C might originate from Precursor Er or rather a modified Precursor Er-based hydrate.
3.2. Photothermal deflection spectroscopy measurements

By measuring PDS it was possible to determine the optical absorption properties of the ZnO:Mo(10\%)/Er(30\%) samples. The corresponding spectra are shown in figure 3. Their envelope function was typical for ZnO [17,33] in undoped ZnO, ZnO:Mo(10\%), and ZnO:Er(30\%). In ZnO:Mo(30\%), the absorption edge was distorted as compared to the rest of samples. Obviously, small content of the ZnO phase confirmed above by XRD and Raman spectroscopy and the presence of parasitic phases are responsible for this. The absorption is peculiar in ZnO:Er(30\%). Except the typical for undoped ZnO envelope it exhibits multi-peak structure. These peaks were very narrow. The presence of Er as a dopant allowed to conclude that they can originate from it. Er\(^{3+}\) is a rare earth ion with the 4f-4f transitions (shielded from the local crystal (ligand) field). Therefore, comparing with the [34] where the Er\(^{3+}\) absorption was measured in germanate glass the typical Er\(^{3+}\) absorption transitions were indicated in figure 3.

![Figure 3. Absorption spectra in undoped ZnO, ZnO:Mo(10\%)/Er(30\%), and ZnO:Er(30\%). The \(4_{15/2} \rightarrow 2_{5/2}\) transitions of Er\(^{3+}\) and corresponding wavelengths are indicated.](image)

This is also the reason why it was hard to determine whether the Er\(^{3+}\) ions were incorporated into the ZnO microrods, deposited onto the microrods surface or stay as the part of some parasitic phase discussed above in the sample. It is known that the absorption edge in ZnO is shifting to higher energy values upon the increased charge carrier concentration [33,35]. This is indeed observed in figure 3, i.e. the absorption edge in undoped ZnO is shifted to the higher energies as compared to the ZnO:Mo/Er samples. ZnO nanorods have large area and thus, even deposition of the Mo or Er on the rods surface can have the effect of the suppression of the charge carriers concentration. Therefore, one may expect at least deposition of Mo or Er on the wurtzite phase ZnO rods surface. Study of luminescence will complete the obtained results.

3.3. Peculiarities of photoluminescence

PL spectra have been measured in the as-grown ZnO:Mo(10\%)/Er(30\%) within the 290 – 4 K temperature range. They are demonstrated in figures 4(a)-(c). At least two bands E1 and E3 peaking at about 1.91 and 3.45 eV could be distinguished in ZnO:Mo(10\%). Moreover, the E3 band is further triply split upon decreasing temperature from 290 to 4 K into E3' (3.39 eV), E3'' (3.35 eV), and E3''' (3.18 eV). The PL intensity of the E1 and E3 emission bands is increasing upon the decreasing temperature. The E3', E3'', and E3''' peaks should originate from the bound excitons similar to the ones discussed in [36] for undoped ZnO. Remarkably, the E3' (3.39 eV) and E3'''
(3.18 eV) peaks were also detected in the ZnO:Mo(30%) sample at temperatures below 150 K. The behaviour of the PL intensity seems to be similar to the one observed in ZnO:Mo(10%). Therefore, one may expect influence of Mo ions on ZnO in both cases. However, the E1 band is totally absent at all temperatures in the ZnO:Mo(30%) as can be seen in figure 4(b). The E1 band is present in the PL spectra measured in ZnO:Er(30%), however, shifted to higher energies (1.96 eV). It demonstrates steeper dependence of the PL intensity upon the decreased temperature as compared to the ZnO:Mo(30%) (see figures 4(a),(c)). The E3 band is split triply as well at very low temperatures. The three new peaks 1, 2, and 3 can be observed having maxima at 3.39 eV, 3.33 eV, and 3.25 eV. Remarkably, the maxima of the peaks 1 and E3' and 2 and E3'' are (almost) the same pointing out the possibility that their origin is the same in all three samples with no effect of dopants. However, the PL intensity distribution over the peaks 1 and 2 in the ZnO:Er(30%) and E3' (3.39 eV) and E3'' (3.35 eV) in ZnO:Mo(10%) is different. The peak 2 seems to be unique and thus it was referred to the exciton bound at Er$^{3+}$. All this may allow to at least expect Mo or Er deposition onto the surface of ZnO microrods, if not the incorporation in the microrods bulk, to affect the energy transfer to excitons.

It is known that annealing in air caused drastic changes to luminescence properties of undoped ZnO nanorods [21]. Therefore, the samples in the present case were also thermally treated in air at elevated annealing temperatures. The corresponding PL spectra were measured at room temperature. They are

![Figure 4. Temperature dependence of PL spectra measured in (a) ZnO:Mo(10%), (b) ZnO:Mo(30%), and (c) ZnO:Er(30%). PL spectra measured in (d) ZnO:Mo(10%), (e) ZnO:Mo(30%), and (f) ZnO:Er(30%) at room temperature upon annealing in air for 15 minutes at temperatures given in legends. E1-E3, E3', E3'', E3''', E3v, and E3v indicate specific emission bands and peaks whereas numbers 1-3 indicate emission of bound excitons in E3 band in the panel (c). The ordinate scale was equalized for the (d)-(f) panels for comparison.](image-url)
shown in figures 4(d)-(e). The PL spectra of ZnO:Mo(10\%) (figures 4(a),(d)) demonstrate E1 and E3 emission after drying at 120 °C. However, as soon as the temperatures is elevated up to 250 °C and higher, the new emission E2 with the maximum at about 1.82 eV (680 nm) appears (to the best of our knowledge it has never been observed before in the ZnO-based structures doped with Mo or Er) while the E1 drops down. Moreover, the E2 is getting stronger upon the annealing up to 600 °C with the small decrease at 350 °C and it goes down again after the annealing at 700 °C.

This trend can be explained by the creation of the new defect state within the ZnO band-gap either on the rods surface or in bulk due to interaction with air. The E3 emission is getting a bit stronger upon the annealing especially at 250-350 °C and disappears completely after 400 °C. Similar effect was observed and discussed in detail in undoped ZnO recently [21].

The situation is even more drastic in ZnO:Mo(30\%) sample upon the annealing procedure (figure 4(e)) where the evolution of emission can clearly be observed. After the drying at 120 °C, the E3' band peaking at ~2.82 eV appears. Its low-energy tail is obviously composed of some other contribution as the annealing at elevated temperatures seemingly causes the band increase and red shift of the maximum to ~2.52 eV for 250 °C, ~2.28 eV for 350 °C, and finally ~2.07 eV for 400 °C (the E3' band in figure 4(e)). After the 400 °C (i.e. annealing at 500-700 °C) the E3' band intensity goes down. This image is very different from what was observed in the ZnO:Mo(10\%). Obviously the annealing activates/creates new emission centres, however, most probably, they have nothing in common with that very little of the pure ZnO phase presented in the ZnO:Mo(30\%) sample. The E3 band was never observed there.

The effects of much stronger amplitude were observed in the ZnO:Er(30\%) sample (figure 4(f)) as compared to the ZnO:Mo(10\%) one. The E2 emission band reached maximum at 500 °C and it was about three times of the E2 maximum intensity measured in the ZnO:Mo(10\%) after annealing at 400 °C (see figures 4(d),(f)). The E2 exhibited increase all the time within the 250-500 °C with the subsequent drop at 600 °C and increase again at 700 °C. This trend is a bit different than observed in the ZnO:Mo(10\%) (figure 4(d)). This may suggest the influence of the dopant on the created defect states. Moreover, since the E2 band was observed in the ZnO:Mo/Er samples, having in common only the ZnO host, one may expect the defect states responsible for the E2 band to be created within the ZnO band-gap, at least at the surface of the microrods. The exciton-related emission in the vicinity of 3.26 eV, the E3 band, is also much stronger in the ZnO:Er(30\%) sample. Its intensity reaches maximum after the annealing at 350 °C and then drops down until disappeared completely at 500 °C. It has never appeared again afterwards at higher annealing temperatures. This allows to conclude that the presence of large number of Mo ions results in the exciton emission quenching. Again, the Er doping seems more suitable for the scintillator use purpose. In order to find out the effect of the air annealing on the Er\textsuperscript{3+} emission, ZnO:Er(30\%) PL was measured in the infrared range. The corresponding spectra are demonstrated in figure 5.

The observed $^4\text{i}_{13/2} \rightarrow ^4\text{i}_{15/2}$ optical transition of the Er\textsuperscript{3+} ion is split into several peaks. This is because the $^4\text{i}_{13/2}$ and $^4\text{i}_{15/2}$ levels are degenerate, 7 and 8 times, respectively, in a free ion and become split by the local crystal (ligand) field in a host. Therefore, the peaks in figure 5 correspond to the transitions which occur between these new levels (for detail see e.g. [37,38]). The splitting of the $^4\text{i}_{13/2}$ and $^4\text{i}_{15/2}$ levels is governed by the local electric field strength and thus, the intensity and position of the single peaks in the $^4\text{i}_{13/2} \rightarrow ^4\text{i}_{15/2}$ band changes from host to host (from surrounding to surrounding). This trend is observed in figure 5 upon the annealing temperature as well. The $^4\text{i}_{13/2} \rightarrow ^4\text{i}_{15/2}$ band exhibits no peaks after the drying at 120 °C. Even the annealing at 250 °C has effect of the very small increase in intensity. The air annealing at 350 °C causes very strong raise of the band magnitude and the A1-A4 peaks become observed. At 400 °C, the intensity of the band reaches maximum. Annealing at 500 °C causes drop of the intensity down to the level of the 250 °C, however, some peak structure still can be detected. Further annealing at 600-700 °C results in monotonous increase in intensity of the new B1-B8 peaks. The B1-B8 peaks are narrower than the A1-A4 ones and their spectral position is different. Since the annealing was performed in air (oxidizing atmosphere), the Er\textsuperscript{3+} → Er\textsuperscript{2+} charge state transformation can hardly be expected. But Er\textsuperscript{2+} → Er\textsuperscript{3+} and Er\textsuperscript{3+} → Er\textsuperscript{4+} is, in principle, possible
Fig. 5. Er$^{3+}$ emission, the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition, measured at room temperature. It is split due to numerous transitions between the Stark levels [37,38]. Dashed vertical lines serve to indicate the shift of the peaks upon the annealing temperature $T_{\text{ann}}$. A1-A5 and B1-B8 indicate peaks for $T_{\text{ann}}$ within 350-400 °C and 500-700 °C, respectively.

as discussed e.g. for nanocrystalline CeO$_2$:Er [39]. Probably, the Er$^{3+}$ → Er$^{4+}$ transformation happens at the step of the Er$^{3+}$ emission decrease and two different Er$^{3+}$ → Er$^{3+}$ transformations occur at the steps of the Er$^{1+}$ emission increase. Altogether this may point out to the existence of one site for Er$^{3+}$ and two different sites for Er$^{2+}$ ions (two rising tendencies in figure 5 related to the change in the local surrounding of the Er$^{3+}$ ions).

3.4. PL and RL decay kinetics of the E2 and E3 bands
To study the kinetics of the E2 (1.82 eV) and E3 (3.25 eV) emission bands (see figure 4), the PL (excited with 310 nm laser light) and RL (excited with X-ray) decay curves were measured, respectively. The corresponding curves were obtained in the ZnO:Mo(10%) and ZnO:Er(30%) annealed at 350 °C, where the E2 and E3 bands were possible to measure, especially taking into account that the E3 band reaches maximum upon the annealing at this temperature. The curves were fitted and are demonstrated in figure 6. The decay of the E3 band was fitted with three exponentials in both ZnO:Mo(10%) and ZnO:Er(30%) (figures 6(a),(b)).

The decay curves in figure 6 have been fitted by using the following expression (convoluted with the instrumental response function)

$$I(t) = \sum_{i=1}^{n} A_i \exp\left(-t/\tau_i\right) + I_0,$$

where $I(t)$, $A_i$, and $\tau_i$ are the intensity varying in time (the number of photons detected in the given time interval), the amplitude of a single component and the corresponding decay time. $n$ is the number of components. In the case of the curves in figures 6(a),(b) is $n = 3$. The characteristic decay times were found as follows: (i) $\tau_1 = 49$ ps, $\tau_2 = 571$ ps, and $\tau_3 = 16.4$ ns in ZnO:Mo(10%) (figure 6(a)); (ii) $\tau_1 = 53$ ps, $\tau_2 = 615$ ps, and $\tau_3 = 18.9$ ns in ZnO:Er(30%) (figure 6(b)). Apart from the very fast ps components, the 16.4 ns and 18.9 ns components are, most probably, the contributions from some defect with emission overlapping with the E3 band in both materials. The 571 ps determined in the
Figure 6. Room temperature decay curves measured with the X-ray excitation in (a) ZnO:Mo(10%) and (b) ZnO:Er(30%) at the E3 band ($E_{\text{emission}} = 3.26$ eV, $\lambda_{\text{emission}} = 380$ nm). Room temperature decay curves measured with the 310 nm excitation at the E2 band ($E_{\text{emission}} = 1.82$ eV, $\lambda_{\text{emission}} = 680$ nm) in (c) ZnO:Mo(10%) and (d) ZnO:Er(30%).

ZnO:Mo(10%) and 615 ps determined in the ZnO:Er(30%) can be considered as the real decay constants of the E3 exciton-related bands. So, one may expect the influence of the dopants on the exciton decay kinetics rate. These values are of the same order of magnitude as reported in literature for the exciton-related emission in ZnO [36].

The decay of the E2 band is double exponential in the ZnO:Mo(10%) (figure 6(c)) whereas it is three exponential in the ZnO:Er(30%) (figure 6(d)). They were fitted by using equation (1) with $n = 2$ and $n = 3$, respectively. The characteristic decay times were determined as follows: (i) $\tau_1 = 15$ ns, $\tau_2 = 30.6$ μs in ZnO:Mo(10%) (figure 6(c)); (ii) $\tau_1 = 636$ ns, $\tau_2 = 7$ μs, and $\tau_3 = 82.2$ μs in ZnO:Er(30%) (figure 6(d)). These decay times are mostly of the submicrosecond or microsecond order. The largest decay time $\tau_2$ determined in the ZnO:Mo(10%) is about 2.7 times smaller than that ($\tau_3$) in the ZnO:Er(30%) whereas, the middle component of $\tau_2$ is approximately 4 times smaller in the ZnO:Er(30%) as compared to the $\tau_3$ in ZnO:Mo(10%). The smallest decay time $\tau_1$ determined in the ZnO:Mo(10%) is by more than one order of magnitude smaller than the smallest decay time $\tau_1$ in the ZnO:Er(30%). Due to the existence of two or three exponential components in the decay curves (see figures 6(c),(d)), which presumably originate from the similar emission mechanisms, the mean PL decay times were assessed by using the following expression...
\[ \tau_{\text{mean}} = \left( \sum_{i=1}^{n} A_i \tau_i^2 \right)^{-1} \sum_{i=1}^{n} A_i \tau_i^2 . \]  

They are almost the same in both samples: \( \tau_{\text{mean}}(\text{ZnO:Mo(10\%))} = 28.96 \ \mu\text{s} \) and \( \tau_{\text{mean}}(\text{ZnO:Er(30\%))} = 28.34 \ \mu\text{s}. \) All of this may benefit to the suggestion of strongly overlapping multicomponent structure of the E2 band where each component is differently sensitive to annealing and dopants. Note, that the E2 bands demonstrated different dependence on the annealing temperatures in the ZnO:Mo(10\%) and ZnO:Er(30\%) (figures 4(d),(f)).

### 3.5. Peculiarities of radioluminescence

RL can afford the general image of the processes occurring in the samples and therefore, the luminescence spectra in ZnO:Mo(10\%)/(30\%) and ZnO:Er(30\%) was also measured under the X-ray excitation. The spectra are shown in figure 7.

![Figure 7](image)

**Figure 7.** (a) RL spectra measured at different temperatures \( T_{\text{meas}} \) after annealing in air at chosen temperatures \( T_{\text{ann}} \) in ZnO:Mo(10\%). RL spectra of ZnO:Mo(30\%), MoO\(_3\), and Precursor Mo samples were measured at \( T_{\text{meas}} = 295 \ \text{K}. \) Dashed vertical line emphasizes the same emission in ZnO:Mo(30\%) and Precursor Mo. (b) RL spectra of ZnO:Er(30\%) sample, not annealed and after annealing in air at 350 °C. RL spectrum of Precursor Er is also plotted. The E2 and E3 bands are indicated. NA stands for “not annealed”.

RL spectrum was also measured in MoO\(_3\) nanorods (see SEM image in figure 8). It is shown in figure 7(a) for comparison as well. The RL signal from MoO\(_3\) nanorods is negligible as compared to the strength of the emission measured in the ZnO:Mo(10\%)/(30\%) samples and therefore, the creation of the MoO\(_3\) in the ZnO:Mo(10\%)/(30\%) was excluded. By comparing the RL observed in the as-grown ZnO:Mo(10\%)/(30\%) samples and Precursor Mo, one can see, that they have identical spectral position, shape, and width. Therefore, the observed emission in the as-grown ZnO:Mo(10\%)/(30\%) samples was attributed to the Precursor Mo remained in the materials. The RL intensity in the as-grown ZnO:Mo(10\%) is approximately three times lower than the RL intensity in the as-grown ZnO:Mo(30\%) indicating larger amount of the Precursor Mo remained in the latter. This correlates very well to the observations done analysing the corresponding XRD patterns (figure 2(a)) and Raman spectra (figure 2(b)). Annealing in air at 350 °C annihilates the Precursor Mo emission in the ZnO:Mo(10\%) sample and the E2 band observed also in PL can now be observed. This makes
Figure 8. SEM image of the MoO$_3$ sample.

evidence for the diminishing/decay of the Precursor Mo caused by the interaction with air. Further annealing at 700 °C improves the E2 band intensity approximately two times as expected from PL measurements (figure 4(d)). In order to study the behaviour of this band upon the temperature of observation, the sample was cooled down to 77 K stepwise and thus the temperature dependence of the E2 band was obtained by measuring RL spectrum at every step. The corresponding spectra are shown in figure 7(a) for chosen temperature points. They demonstrate monotonous increase in the intensity revealing negligible changes in the band position and shape. This allows to suggest that at least down to 77 K no extra charge or energy transfer appear to affect the source(s) of the band.

Since RL of the Precursor Mo (figure 7(a)) was very strong in the ZnO:Mo(30%) and the ZnO phase was hardly detected in this sample according to XRD and Raman spectroscopy (see figure 2), the annealing procedures were not carried out.

The RL spectrum of the as-grown ZnO:Er(30%) seems to consists of one band, E1, with the maximum at 1.91 eV that is split in two with a dip having minimum at 1.9 eV (see figure 7(b)). The RL spectrum measured in the Precursor Er is composed of two narrow bands and one broad band (2.2-4 eV) peaking at 1.74 eV, 2.05 eV, and 3.25 eV (figure 7(b)). By comparing the obtained RL spectra the observed dip at 1.9 eV was thus attributed to the mixing of the E1 band with the bands from Precursor Er. However, absence of the broad band (2.2-4 eV) with the maximum at 3.25 eV in the RL spectrum of the ZnO:Er(30%) may point out to the somehow modified Precursor Er remained in the material. Maybe it is an additional phase indicated by the XRD and Raman spectroscopy studies (figure 2) created from the Precursor Er, probably, by adsorbing/desorbing additional H$_2$O molecule to/from the original formulae (see subsection 2.1) in the solution during the hydrothermal growth.

3.6. Characterization of paramagnetic states by EPR

EPR technique was used in order to find out which paramagnetic particles are present in ZnO:Mo(10%), ZnO:Mo(30%), and ZnO:Er(30%) microrods and MoO$_3$ nanorods (for comparison) and possibly to determine correlations with optical measurements above. The EPR spectra measured in the ZnO:Mo(10%) are shown in figure 9. Prior to air annealing only EPR signal at g factor $g = 1.954$ was detected. It is typical resonance for ZnO reported in many other works [15-18,21]. Its $g$ factor value varies from 1.95 to 1.96 in different ZnO materials [36]. Its origin was deduced to be F$^-$ centre [19,20], an electron captured by an oxygen vacancy. The signal is getting a bit stronger after annealing in air at $T_{\text{ann}} = 250 \, ^{\circ}\text{C}$ with consequent intensity drop at $T_{\text{ann}} = 350-450 \, ^{\circ}\text{C}$. The rise of the spectrum intensity is observed after further annealing at $T_{\text{ann}} = 500-600 \, ^{\circ}\text{C}$. The increase of the signal at $T_{\text{ann}} = 250 \, ^{\circ}\text{C}$ can, in principle, be explained as follows. The material can have some number of empty
oxygen vacancies and imperfections which can change their charge state in the oxidizing atmosphere. Some part of the imperfections may supply the vacancies with electrons (one electron per one vacancy) during the annealing and thus the new F+ centres of the same sort are created contributing to the increase of the F+ EPR signal intensity. Annealing at higher temperatures ($T_{\text{ann}} = 350-450$ °C) causes partial refilling of the vacancies with oxygen from air thus annihilating the F+ centres and the F+ signal is getting significantly weaker (figure 9(a)). This tendency was observed and reported previously in the undoped ZnO nanorods [21]. However, some small number of F+ centres, most probably, from the microrods bulk, withstand the annealing at even higher $T_{\text{ann}} = 500-600$ °C as long as the F+ signal is slightly rising again indicating the creation of new F+ centres of the same sort. The material may contain some amount of F centres, two electrons trapped in one vacancy. They are not paramagnetic and thus cannot be detected by EPR. Probably, by annealing at $T_{\text{ann}} = 500-600$ °C, some part of these centres loses electrons (one from each centre) and thus the F+ centres are created contributing to the increase of the F+ centres signal intensity. No correlation can thus be found with PL (see subsection 3.5 and figure 4(d)).

Besides the described above transformations another change occurs in the ZnO:Mo(10%) EPR spectrum under annealing: a new signal appears at $T_{\text{ann}} = 350$ °C (figures 9(a),(b)). This signal is centred at $g$ factor $g = 1.905$ (3520 G). Remarkably, it has never been observed before in the undoped ZnO upon air annealing [21]. Therefore, it was related to the Mo ion. Since no other lines of this sort were observed in EPR spectra and the position of the $g = 1.905$ resonance line was unchanged upon

**Figure 9.** (a) EPR spectra measured at $T = 296$ K in ZnO:Mo(10%) before and after annealing in air (the annealing temperatures $T_{\text{ann}}$ are given in a legend). The spectrum measured in Precursor Mo is also plotted. Blue dashed region, zoomed in the panel (b), indicates the signal possibly originating from Mo5+ ion incorporated (deposited on surface) into ZnO microrods bulk (MoZnO5+). (c) EPR spectra measured at $T = 60$ K in ZnO:Mo(10%) before and after annealing in air at $T_{\text{ann}} = 350$ °C. The spectrum measured in an empty quartz holder is also plotted. P and QH indicate the signals coming from Precursor Mo and quartz holder, respectively.
the sample cooling down to 10 K, the Mo charge state is expected to be “5+”. Moreover, the $g$ factor has the value typical for Mo$^{5+}$ measured in different oxide materials [40-44]. The $g = 1.905$ signal is broad and obviously multicomponent having rather powder-like shape [45]. To increase the signal intensity the ZnO:Mo(10%) sample was measured also at $T = 60$ K (figure 9(c)). All this allowed to suppose the Mo$^{5+}$ to be embedded into some host. In order to find out whether the signal is coming from microrods or Precursor Mo, the latter underwent annealing in air at $T_{\text{ann}} = 350$ °C and then measured. Corresponding EPR spectrum is demonstrated in figures 9(a),(b) as well.

It contains also one signal at $g$ factor $g = 1.921$ (3491 G), indicated P in figures 9(a),(b), presumably originating from Mo$^{5+}$ as well. This $g$ factor is larger ($1.921 > 1.905$) and the signal shape is different than that of the $g = 1.905$ signal. Therefore, the $g = 1.905$ signal cannot originate from the Precursor Mo. However, it is known that Precursor Mo is unstable decomposing under heating on MoO$_{2.5}$(OH)$_{0.5}$ (annealing at ca. 325 °C to 475 °C), MoO$_{2.69}$(OH)$_{0.3}$ (annealing at ca. 575 °C) and MoO$_{3-x}$ (annealing at ca. 675 °C) [29]. Therefore, the MoO$_3$ nanorods were also measured. Corresponding EPR spectra are shown in figure 10 for different temperatures.

![EPR spectra measured at different temperatures (293 - 3.5 K) in MoO$_3$ nanorods. “QH” stands for “quartz holder”.

Figure 10. EPR spectra measured at different temperatures (293 - 3.5 K) in MoO$_3$ nanorods. “QH” stands for “quartz holder”.

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There the dominating resonance at $g = 2.21$ at 296 K, most probably, belongs to Mo$^{3+}$ [46] since it is too large for the Mo$^{5+}$ [40-44]. Moreover, it exhibits temperature dependence typical to some extent for magnetic ordering (the line is getting broader and shifted upon the cooling) [47]. Nothing similar was observed in the case of the ZnO:Mo(10%).

All this leads to conclusion that the $g = 1.905$ EPR signal belongs to the Mo$^{5+}$ from the microrods (Mo$_{ZnO}^{5+}$). Further annealing at $T_{\text{ann}} = 400-600$ °C results in the Mo$_{ZnO}^{5+}$ signal decrease and complete disappearance. This allows to suppose the starting charge state (before the treatment) of the Mo to be either “2+” (4d$^4$ outer shell) or “4+” (4d$^2$), both were not detected in the X-band EPR because of large spin-orbit coupling constant (SOC), 695 and 950 cm$^{-1}$, respectively. Annealing in air causes stepwise oxidation to the highest possible “6+” charge state, which is not paramagnetic and thus, the Mo$_{ZnO}^{5+}$ signal disappears. No traces of Mo$^{3+}$ were detected during the annealing procedure. This benefits to the starting Mo$^{4+}$ charge state in the ZnO before the treatment. Remarkably, the Mo$^{4+}$ ion has ionic radius 0.65 Å in the sixfold ligand coordination [48] and thus it is expected to be even smaller in the fourfold one (unfortunately, no data on this subject are available in literature) in ZnO. The Zn$^{2+}$ ionic radius is 0.6 Å in the fourfold coordination whereas it is 0.74 Å in the sixfold one. Thus, it seems possible for the Mo$^{4+}$ to be embedded into the ZnO host at Zn site.

EPR spectra measured in the ZnO:Mo(30%) sample before and after annealing in air at different temperatures are demonstrated in figure 11. The spectrum measured in the ZnO:Mo(30%) nanorods was marked as Mn$_{1}^{2+}$ in figure 11(a). Larger number of transitions (better resolved structure) becomes visible after cooling down to $T = 60$ K. They were most easily identified due to the forbidden transition (F.T.) in figure 11(a). It is situated at the half-field position (full-field position corresponds

![Figure 11](image_url)

**Figure 11.** (a) EPR spectra measured at $T = 60$ and 296 K in ZnO:Mo(30%) before annealing in air. P and F.T. indicate the signals coming from Precursor Mo and forbidden transition of Mn$^{2+}$. The sextet of lines due to $^{55}$Mn nucleus is indicated by the set of vertical lines. Mn$^{2+}$ EPR spectrum measured in Precursor Mo is designated as Mn$_{P}^{2+}$. (b) EPR spectra measured at $T = 296$ K in ZnO:Mo(30%) before and after annealing in air (the annealing temperatures are given in a legend).
to the $g$ factor about 2 typical for the Mn$^{2+}$, the $S$ ion with $^6S_{5/2}$ ground level, i.e., quenched orbital moment [44,45]). F.T. had the most pronounced structure, i.e, hyperfine structure (HFS) due to $^{55}$Mn nucleus with nuclear spin $I = 5/2$ and 100% abundance (figure 11(a)) as compared to the full-field position (1/2 $\leftrightarrow$ -1/2 electron spin transition) which is too intermixed with other transitions either allowed (in general there should be 5 of them [44,45]) or forbidden. The splitting between lines in the F.T. sextet was about 95 G, typical value for the Mn$^{2+}$ measured in other materials [44]. Annealing in air at elevated temperatures results in transformation of the Mn$^{1+}$ signal shown in figure 11(a) to different Mn$^{2+}$ spectrum (figure 11(b)). The new spectrum was identified due to the two pronounced sextets of lines (with about 95-100 G spacing) centred at approximately 1600 G magnetic field (figure 11(b)) using the same considerations as above for the Mn$^{1+}$ spectrum identification. Manganese is an uncontrolled impurity, most probably, originating from Precursor Mo since the typical Mn$^{2+}$ EPR spectrum [49] was measured there as well (for more details see figure 11(a) where it is designated as Mn$^{2+}_P$). The Mn$^{2+}$ EPR spectrum has never been detected in the rest of samples.

No sign of the typical signal of F$^+$ centre was detected before annealing. It becomes visible at $g$ factor $g = 1.956$, but negligibly weak, after the annealing at 500 °C with the intensity approximately doubled for 600 °C. Note, that the $g$ factor is a bit shifted in the ZnO:Mo(30%) as compared to the ZnO:Mo(10%) above. Above the annealing temperature of 600 °C this signal is vanished (see figure 11(b)). Moreover, the F spectrum from Precursor Mo appeared after annealing at 250 °C and disappeared completely at 550 °C. All this finds correlate with the low content of ZnO phase predicted by XRD and Raman analyses (see figure 2 in subsection 3.1).

Oppositely, EPR spectra measured in the ZnO:Er(30%) sample exhibit strong signal from the F$^+$ centre (see figure 12(a)) before annealing ($g$ factor $g = 1.953$). The subsequent annealing in air at

![Figure 12](image_url)
elevated temperatures causes drop of the intensity and almost total disappearance of the signal within the 250-600 °C range of annealing temperatures. Above 600 °C the signal starts to rise again.

To measure rare-earth Er$^{3+}$ EPR spectra, the sample should be cooled down to 10 K since shielded 4f shell in this case results in very short time of spin-lattice relaxation making the spectra very broad at room temperature [45]. The spectra measured at 10 K are shown in figure 12(b) for the same set of annealing temperatures as in figure 12(a). Prior to the annealing the spectrum is very broad (extends the magnetic field range allowed by the magnet of spectrometer) and strong. It was attributed to Er$^{3+}$ since the correlation between the doping level and EPR intensity was observed. Moreover, according to the absorption spectrum in figure 3 Er$^{3+}$ is present in the sample. It is also not excluded that the observed EPR spectra shown in figure 12(b) are the combination of contributions from Er$^{2+}$, Er$^{3+}$, and Er$^{4+}$. Annealing makes the signal even broader while the peak-to-peak intensity goes down after the annealing within the 250-400 °C.

Linewidth of the EPR signal is proportional to the paramagnetic particles’ concentration [49]. Therefore, the broader signal the larger number of paramagnetic particles. This behaviour correlates well to the observed tendencies in the Er$^{3+}$ emission (figure 5). Therefore, similarly one may expect the Er$^{3+}$ → Er$^{4+}$ transformation at the step of the Er EPR signal narrowing and two different Er$^{2+}$ → Er$^{3+}$ transformations at the steps of the Er EPR signal broadening. This supports the supposition of the existence of one site for Er$^{3+}$, probably Er$^{3+}$ (figure 12(b)), and two different sites for Er$^{2+}$ ions. Basing on the analysis done for the infrared Er$^{3+}$ emission (figure 5) and Er EPR spectra (figure 12(b)) it may be concluded that one of the Er$^{2+}$ ions could be implanted inside the ZnO host. Er$^{2+}$ and Zn$^{2+}$ both have the same charge state.

4. Conclusions

According to SEM, the ZnO nanorods when alloyed with Mo or Er become microrods. EPR confirmed the existence of F$^-$ centres common for ZnO-based structures in the ZnO:Er(30%) microrods whereas in the ZnO:Mo(30%) this kind of defect was almost absent and appeared only after annealing in air. Annealing in air at elevated temperatures results in the reduction of F$^-$ centres in the ZnO:Mo(10%) and ZnO:Er(30%). Moreover, Er$^{3+}$ EPR signal also undergoes changes under annealing getting broader at 250-400 °C and then narrower again at 500-800 °C. This allowed to suggest oxidation of Er ions in the ZnO:Er(30%) sample in correlation with similar behaviour of infrared emission of Er$^{3+}$. The existence of Er$^{2+}$ ions inside the ZnO host could be concluded. Annealing also results in the Mo$^{5+}$ appearance presumably in the ZnO:Mo(10%) microrods bulk. Red luminescence peaking near 680 nm appears under air annealing (to the best of our knowledge it has not been observed before) in all studied samples regardless the dopant origin and doping level. However, its origin remains unknown. The exciton-related band at 380 nm never observed in the samples before the annealing appears under the annealing in air reaching maxima at 350 °C in ZnO:Mo(10%) and ZnO:Er(30%). The decay time of this exciton-related emission measured in both samples was about 600 ps. No such band was observed in the ZnO:Mo(30%) sample at all.

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