National Academy of Science of Ukraine
Institute for Scintillation Materials

# Doped ion redistribution in $Y_2SiO_5:Pr^{3+}$ nanocrystals detected by spectroscopic techniques

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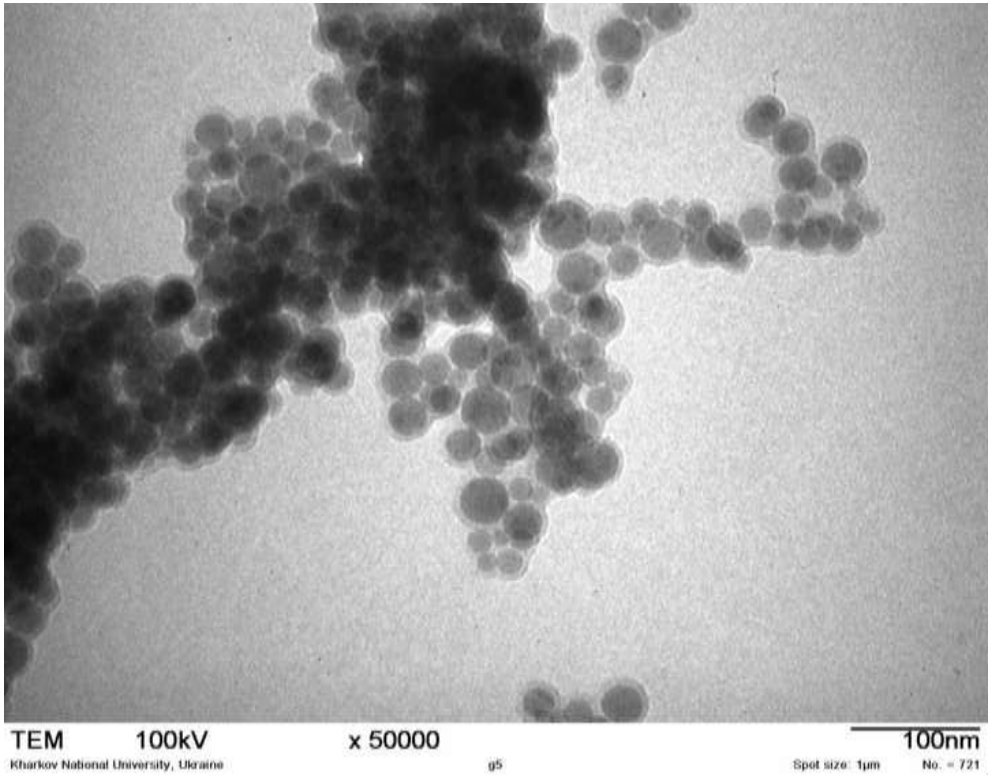
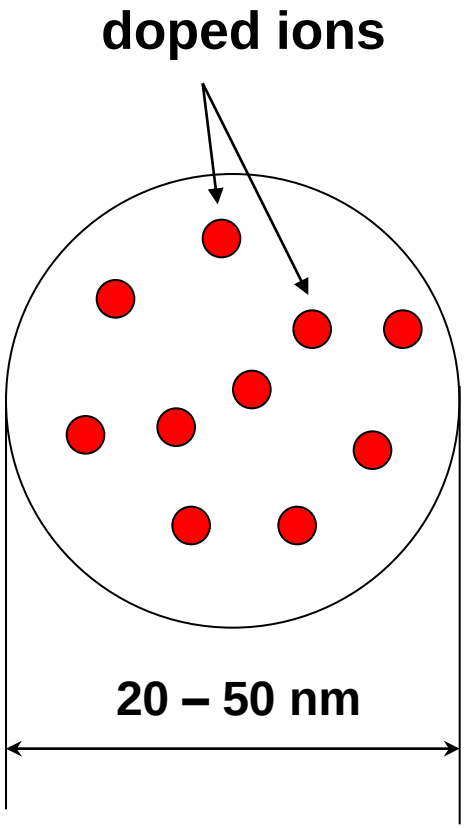
# Rare-earth doped nanocrystals for luminescent applications

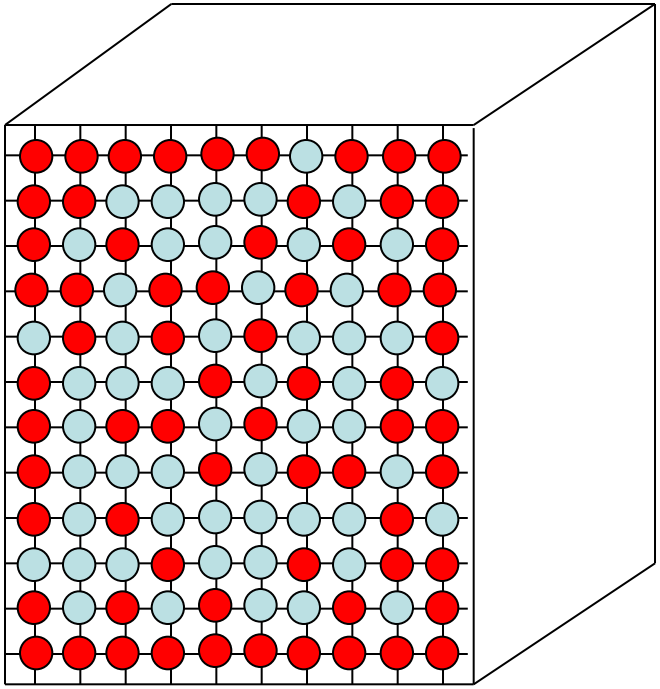



Typical TEM of our nanocrystals

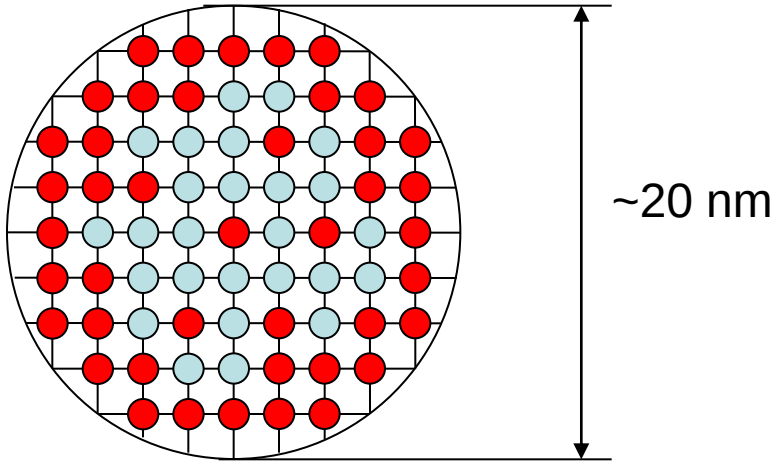



**Luminescent properties of RE-doped bulk and nanocrystals must be similar but there are some unexpected pitfalls...**

# Influence of doped ions segregation on the luminescence properties of nanocrystal



bulk crystal – the role of segregated doped ions in luminescence processes is negligible




nanocrystals – ?

# Simplified energy scheme of $Pr^{3+}$ in $Y_2SiO_5$ bulk and nanocrystals

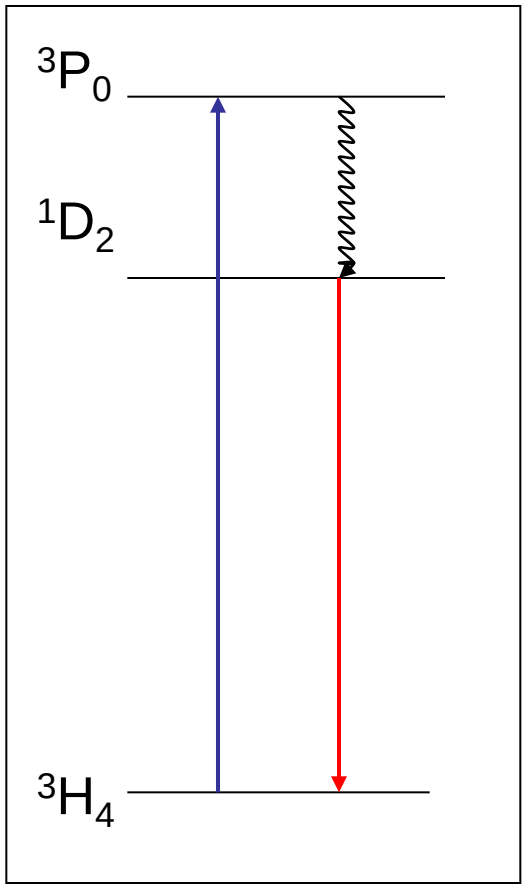



fig.1. Occurrence of $^1D_2 \rightarrow {}^3H_4$ $Pr^{3+}$ luminescence

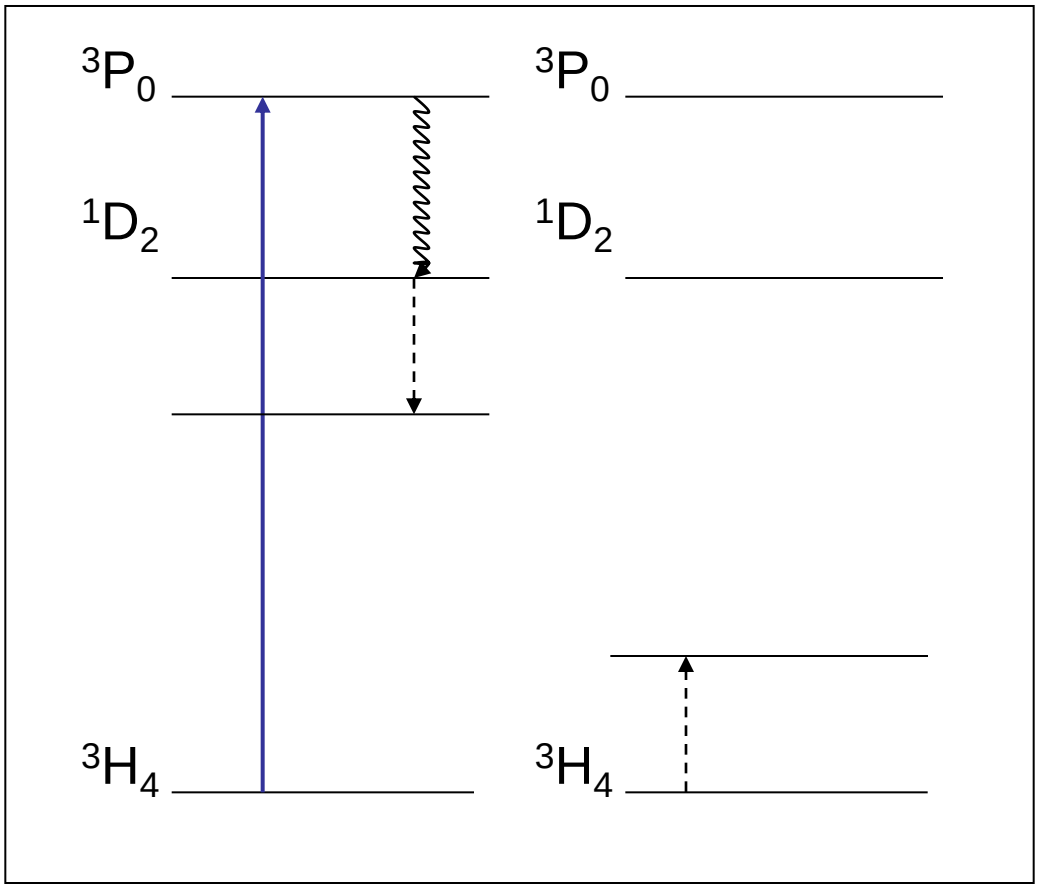



fig.2. Concentration quenching of $^1D_2 \rightarrow {}^3H_4$ $Pr^{3+}$ luminescence

# Abnormal strong $^1D_2 \rightarrow {}^3H_4$ concentration quenching in $Y_2SiO_5:Pr^{3+}$ nanocrystals

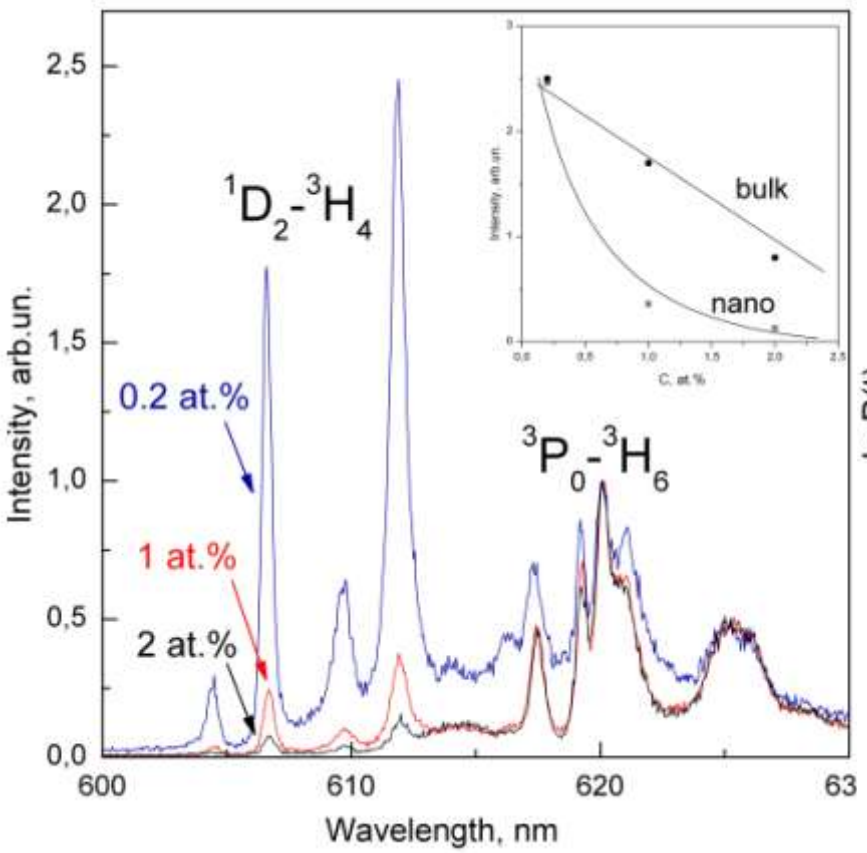



fig.3. Luminescence spectra of $Y_2SiO_5:Pr^{3+}$ nanocrystals

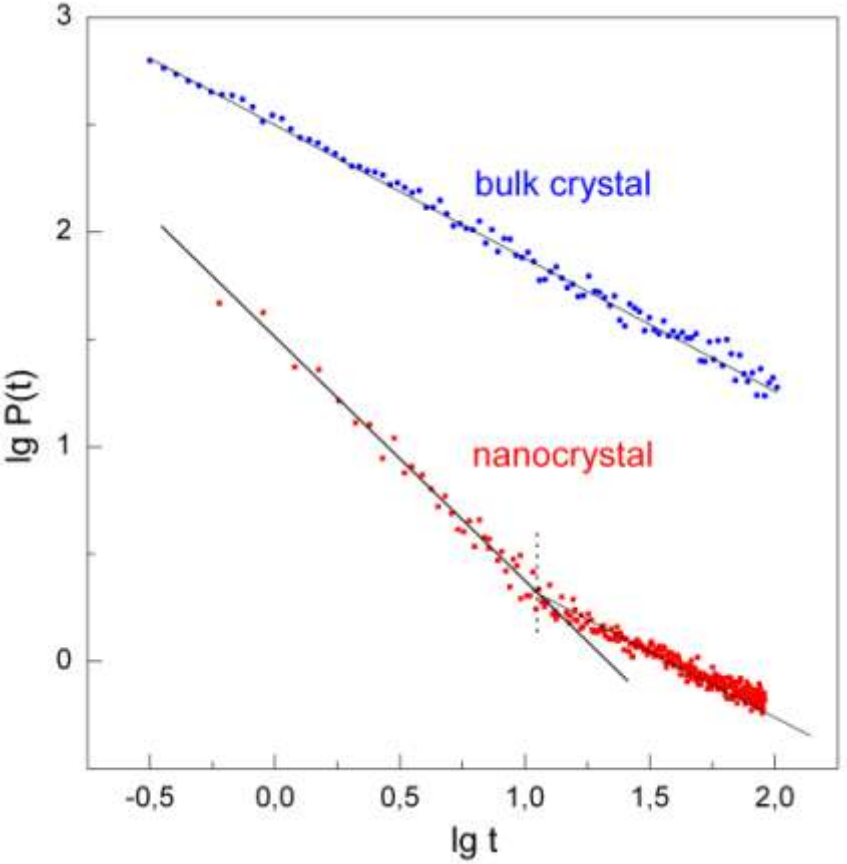
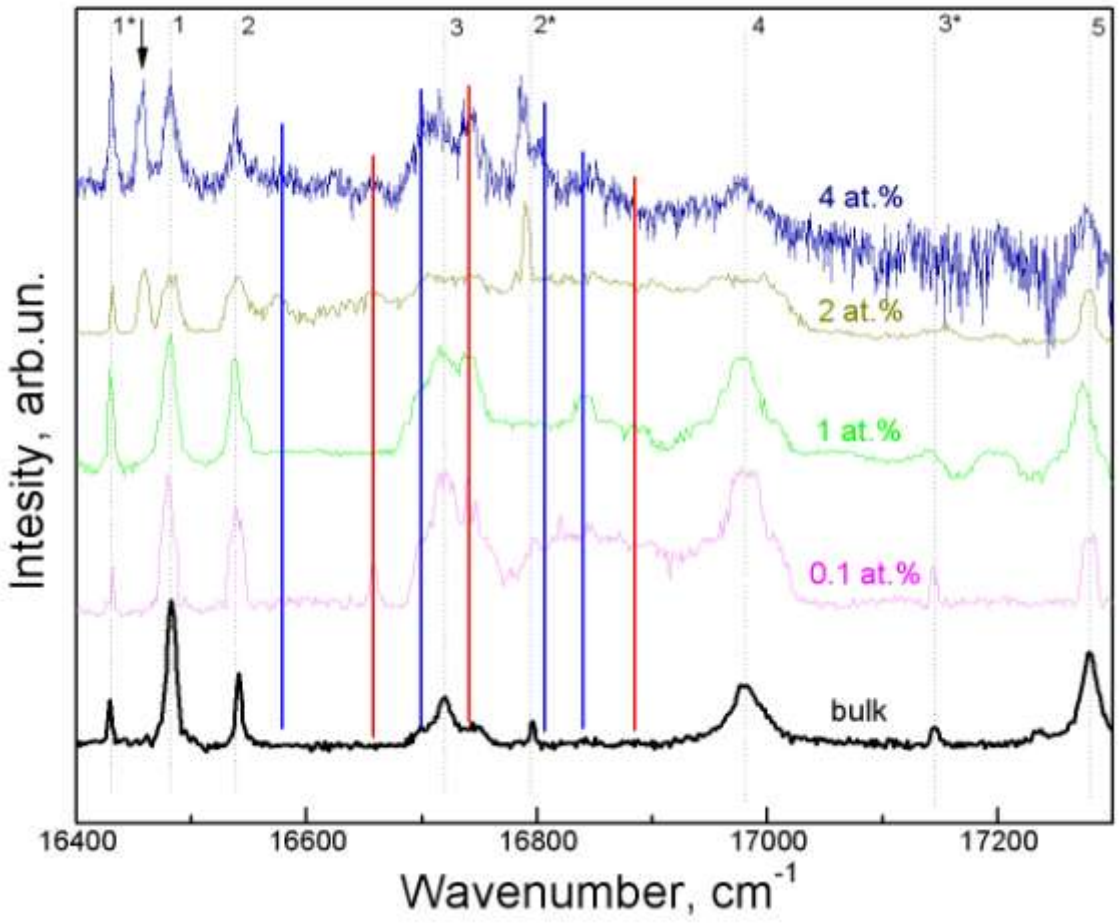



fig.4. $^1D_2 \rightarrow {}^3H_4$ luminescence decay curves of $Y_2SiO_5:Pr^{3+}$ nanocrystals

# Cooperative absorption as a sign of $Pr^{3+}$ pair formation in $Y_2SiO_5:Pr^{3+}$ nanocrystals



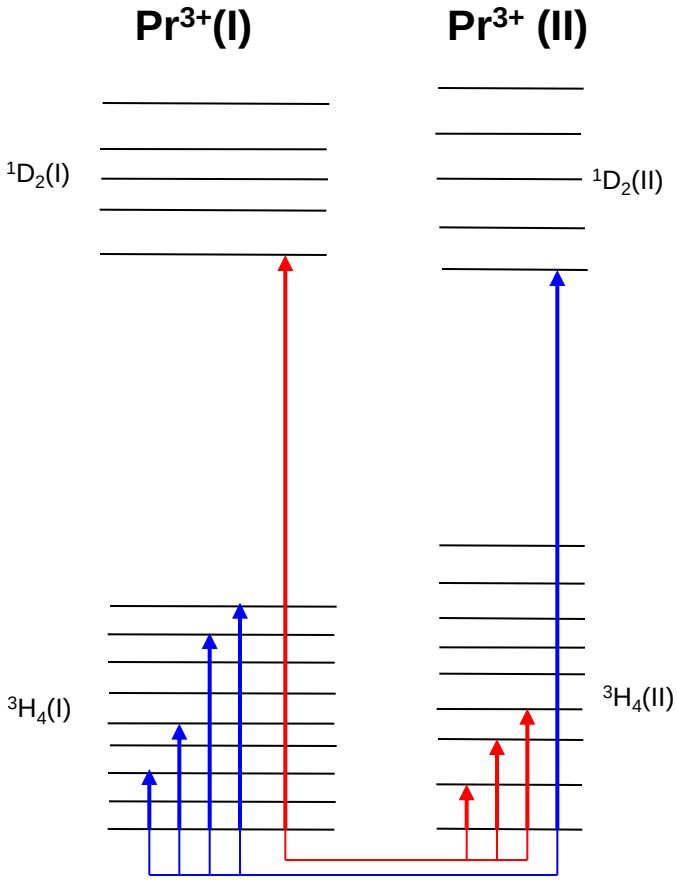
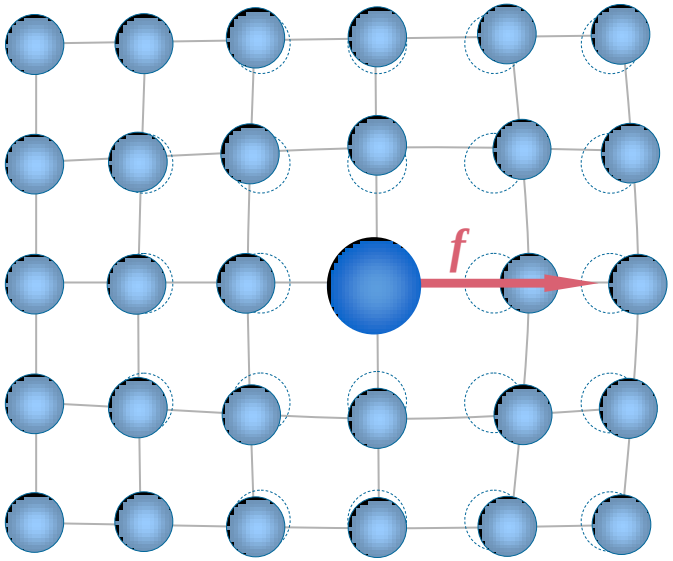




fig.5. $Y_2SiO_5:Pr^{3+}$ nanocrystals excitation spectra

# Segregation of doped ions in $Y_2SiO_5:Pr^{3+}$ nanocrystals?

$R_{Pr3+}$ = 1.01 Å, $R_{Y3+}$ = 0.89 Å




$$E_{def} = \frac{2G^2(\Delta\Omega)^2}{3\pi K R^3}$$

lattice distortion energy

$E_{def}(Y_2SiO_5:Pr^{3+})$ ~ 0.03 eV

K, G – bulk and shear modulus,
R – radius of doped ion,
ΔΩ – ionic volume difference

$$\sigma = \frac{G\Delta\Omega}{\pi r^3}$$ elastic stress created by the point defect

$$C_{surf} / C_{bulk} \approx e^{-E_{def}/kT} \approx 4$$

**So, the segregation concept predicts $Pr^{3+}$ concentration in the near-surface layer four times greater than in the bulk**

# Tracing the process of $Pr^{3+}$ segregation in $Y_2SiO_5:Pr^{3+}$ nanocrystals. Luminescence spectra.

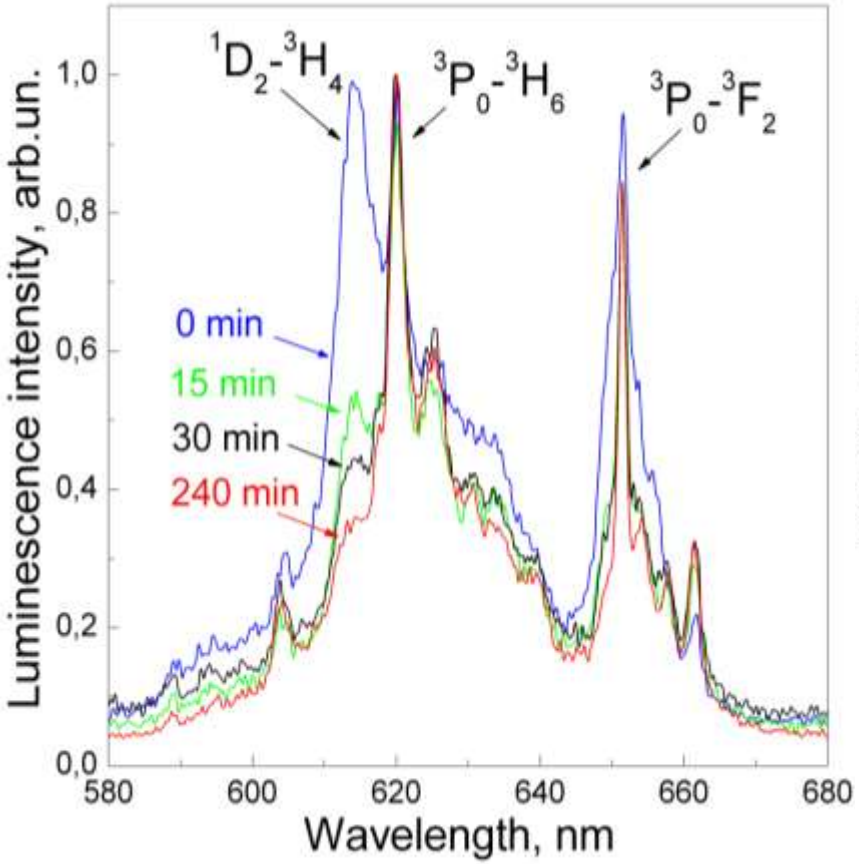



fig.6. $Y_2SiO_5:Pr^{3+}$ (2 at.%) nanocrystals luminescence spectra at different temperature treatment

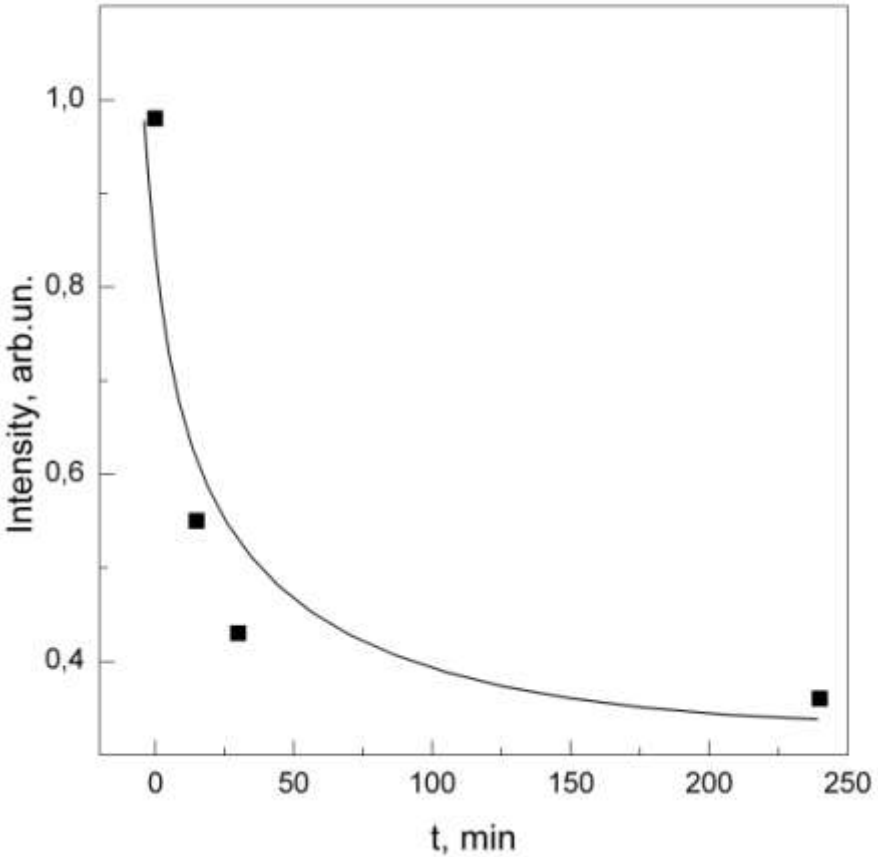



fig.7. $^1D_2 \rightarrow {}^3H_4$ intensity temperature treatment dependence

# Tracing the process of $Pr^{3+}$ segregation in $Y_2SiO_5:Pr^{3+}$ nanocrystals. Decay curves.

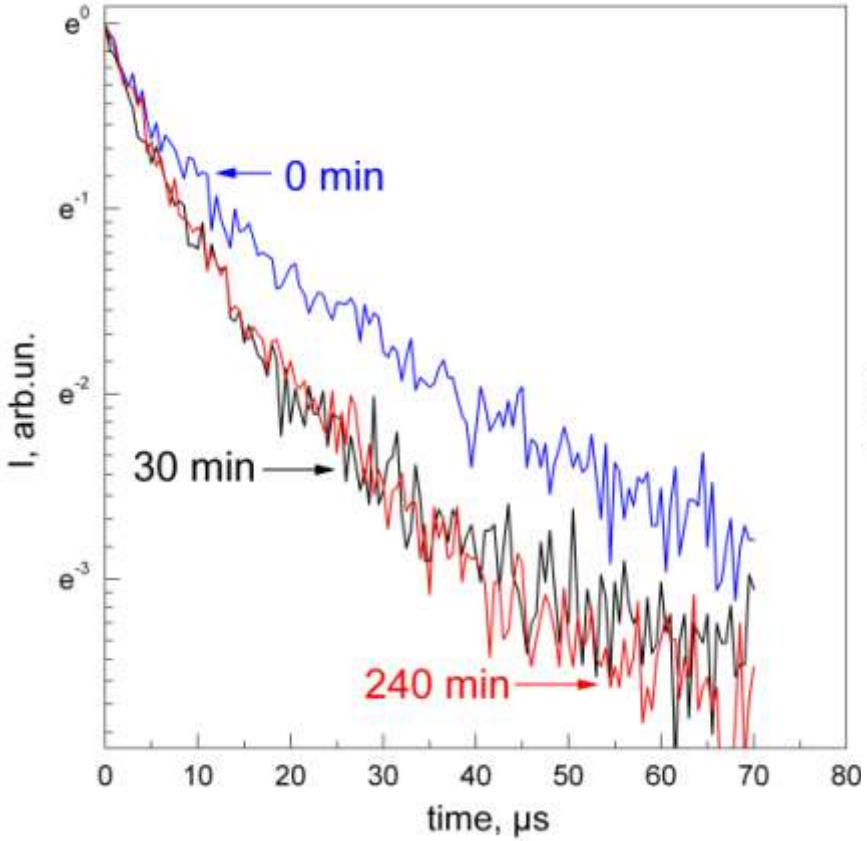



fig.8. $Y_2SiO_5:Pr^{3+}$ nanocrystals decay curves at different temperature treatment

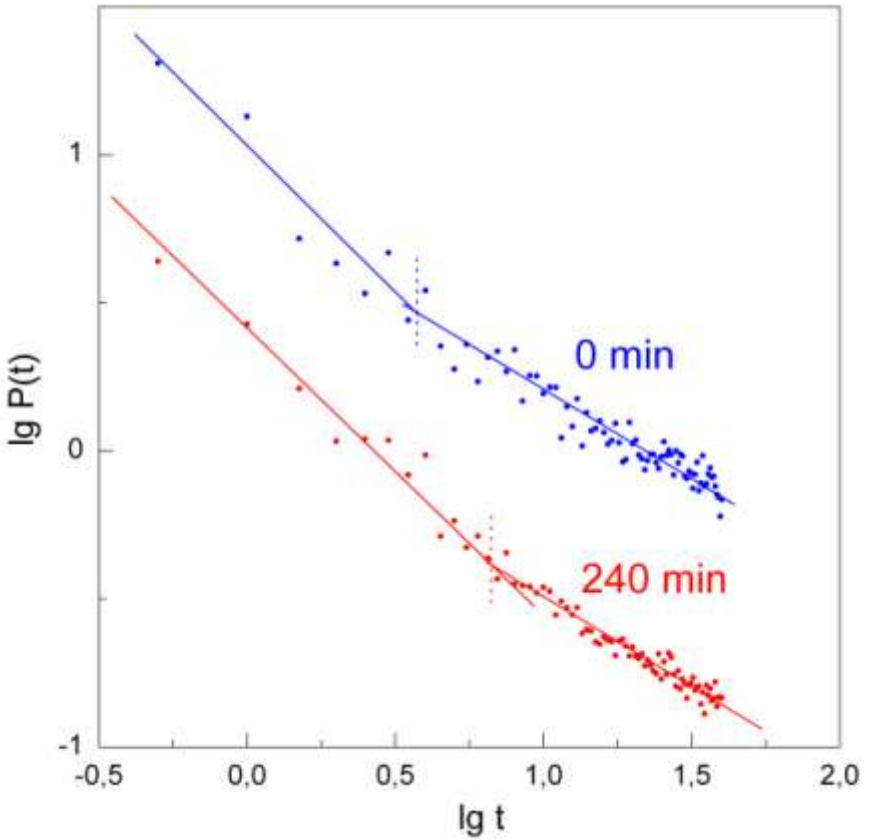



fig.9. $Y_2SiO_5:Pr^{3+}$ decay curves in {lg P(t), lg t} coordinates

# Verification of segregation concept. $Y_2O_3:Pr^{3+}$

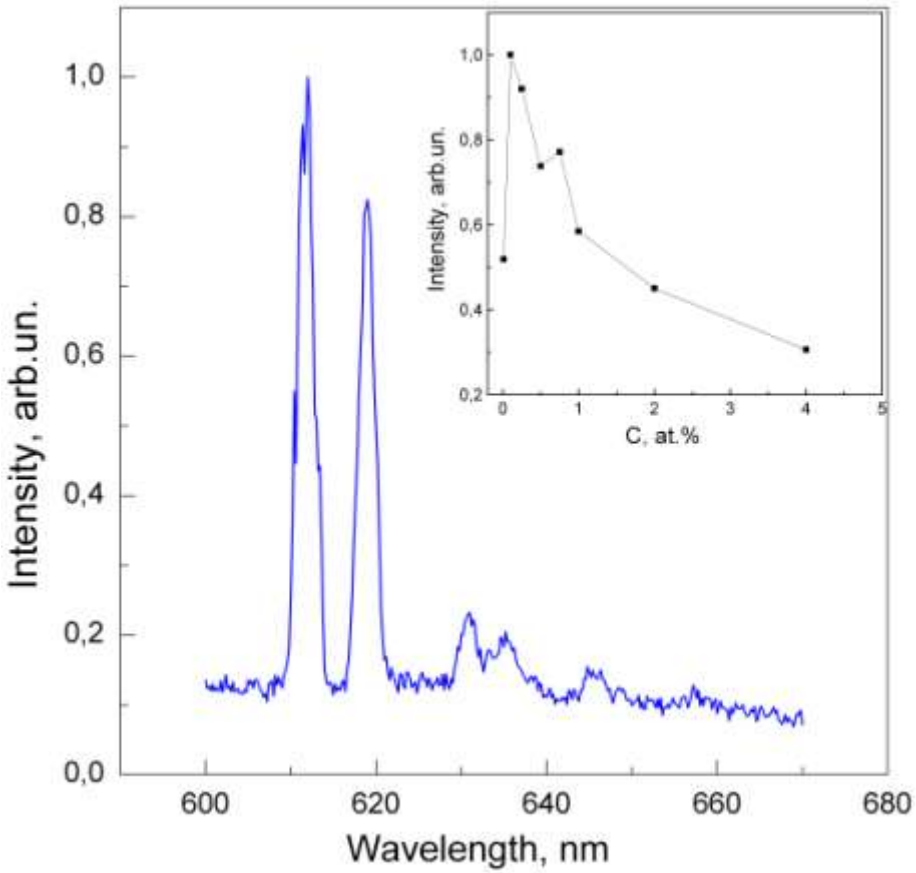



fig.10. Luminescence spectra of $Y_2O_3:Pr^{3+}$ nanocrystals

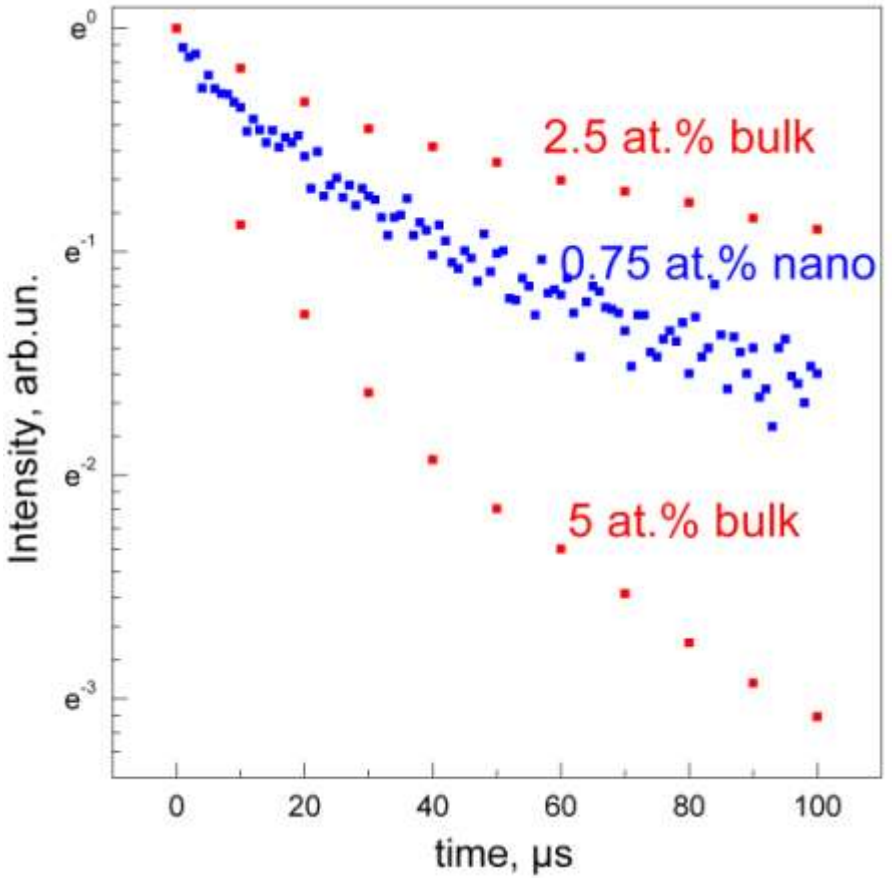
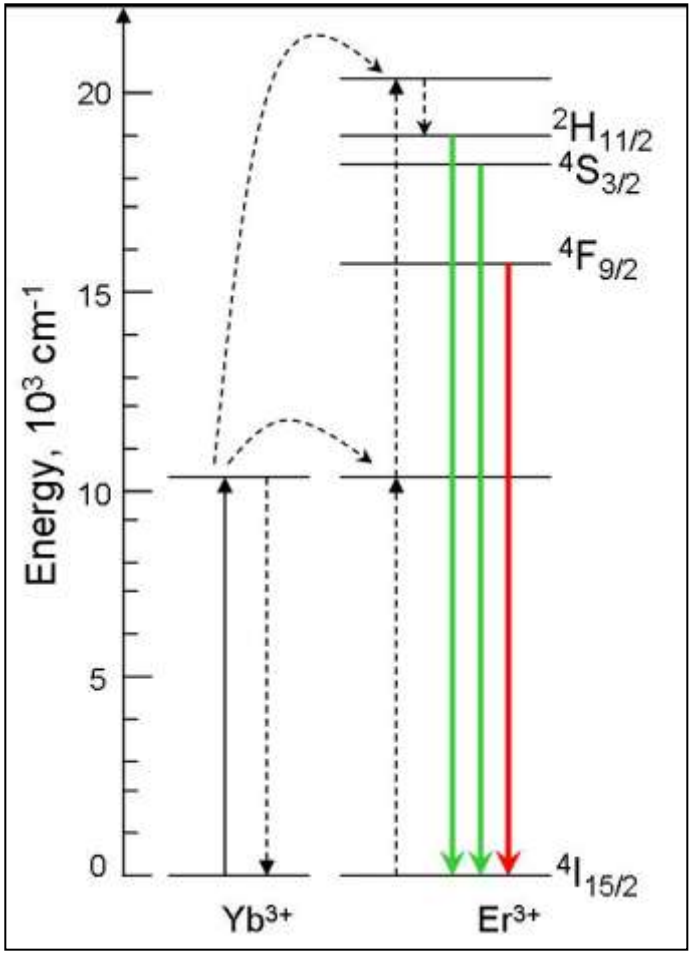



fig.11. Decay curves of $Y_2O_3:Pr^{3+}$ bulk crystals and nanocrystals

# Segregation as a key to luminescence properties modification




Up-conversion scheme for $Er^{3+}$-$Yb^{3+}$ pair

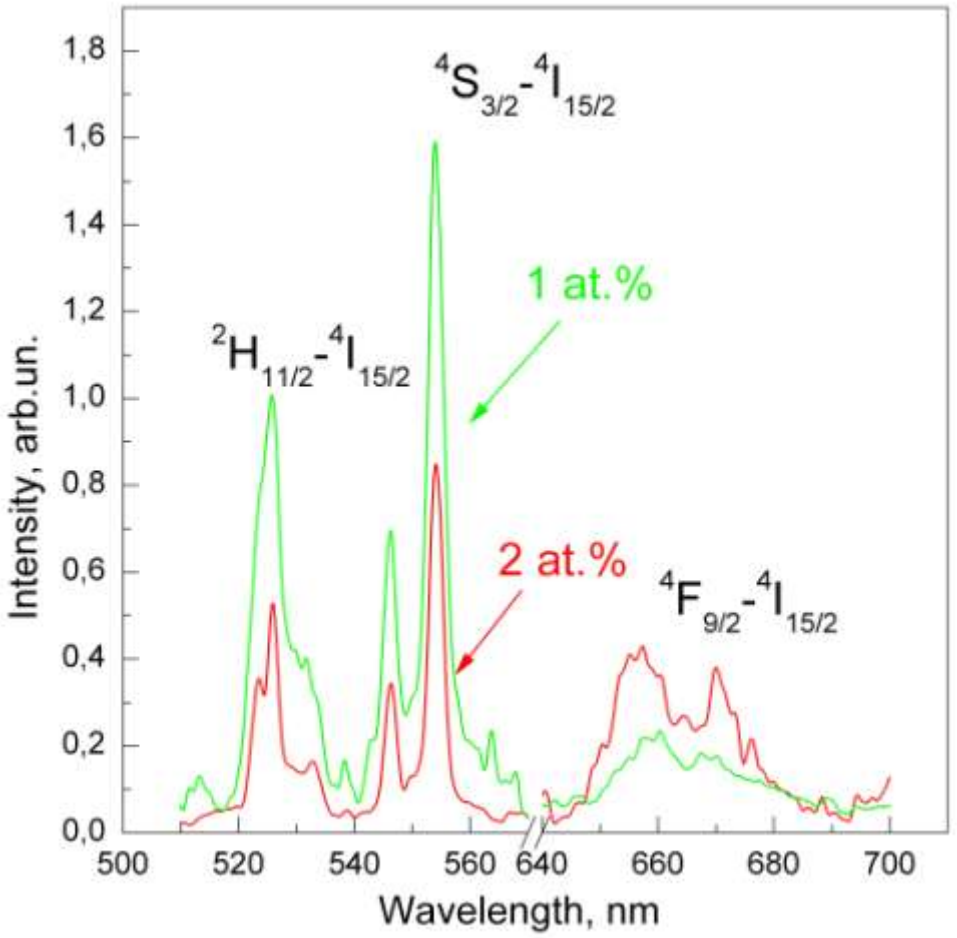



fig.12. Up-conversion luminescence spectra of $YVO_4$:$Er^{3+}$, $Yb^{3+}$ nanocrystals ($\lambda_{ex}$=980 nm)

# Segregation – determined redistribution of luminescence intensities in $YVO_4:Er^{3+}, Yb^{3+}$ nanocrystals

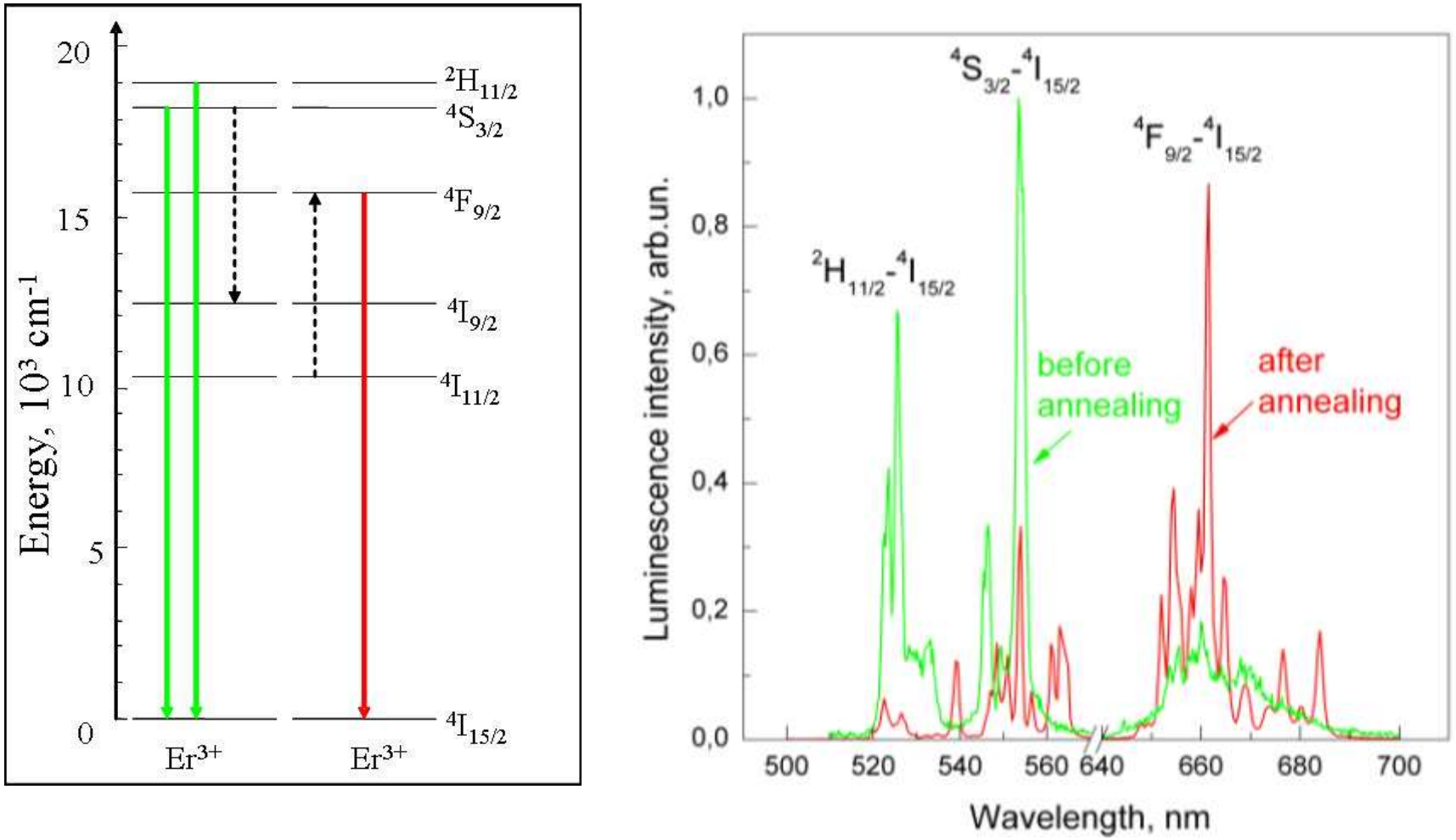



fig.13. Luminescence spectra of $YVO_4:Er^{3+}, Yb^{3+}$ nanocrystals ($\lambda_{ex}$=980 nm) before and after temperature treatment

# Conclusions:

**For the first time, strong temperature controlled segregation of dopant ions in $Y_2SiO_5:Pr^{3+}$, $Y_2O_3:Pr^{3+}$ and $YVO_4:Er^{3+},Yb^{3+}$ nanocrystals was detected by means of spectroscopic techniques. This effect can manifest itself as in more intensive concentration quenching of luminescence, so in modification of luminescence properties of doped nanocrystals.**

**Thank you for attention!**