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SUPPRESSION OF IMPURITY IONS OPTICAL TRANSITIONS DEPHASING IN NANOCRYSTALS

Key words: *narrow lines, electron-phonon interaction, nanocrystals*

Abnormally narrow spectral lines have been observed in the luminescence spectra of $Y_2SiO_5:Pr^{3+}$ and $YVO_4:Eu^{3+}$ nanocrystals at the room temperature. This fact was interpreted as the result of optical transitions dephasing processes suppression in the nanocrystals. The general cause of the observed effect is the weakening of phonon scattering on the impurity centre as a result of the quantum size effect in nanocrystal phonon subsystem. At first the dependence of spectral line width on the nanocrystal size has been shown. Unnecessary of the deep cooling for narrow optical resonances obtaining makes these nanocrystals a potential candidate for the wide set of applications in the optical memory and quantum computing devices.

Introduction

Electron-phonon interaction (EPI) [1] as the ubiquitous fundamental effect of condensed-matter physics nowadays has been transformed into potentially useful tool for modern materials with purposeful functional properties (such as photoswitches [2, 3], phase shifting materials GeSbTe [4, 5], high-temperature superconductors [6, 7]) creation. There are several manifestations of EPI for impurity centres result in solid matrices. At first, EPI provides the ultra-fast relaxation of excited electronic states for impurity centres [8]. For rare-earth (RE) ions, for instance, EPI provides the relaxation between the Stark components of split terms and the terms itself [9, 10]. In addition, EPI leads to temperature broadening and spectral shift of spectral lines corresponding to impurity centers optical transitions [11, 12]. In the low temperature range temperature broadening makes additive contribution $\gamma(T)$ to the homogeneous width of spectral line hidden inside the inhomogeneous broadened spectral profile [10]. And in the contrary, at the room temperature phonon scattering on the impurity centre makes dominating contribution into the homogeneous width of spectral line exceeding the inhomogeneous broadened profile [11–13]. Temperature broadening mechanisms for spectral lines of impurity centers optical transitions are well-known [10]. For impurity RE ions in solids in the range of helium temperatures Orbach mechanism of spectral lines broadening $\gamma(T) \sim e^{-\Delta/kT}$ (where Δ is the activation energy for corresponding Stark component, T is the temperature, k is the Boltzmann constant) are realizing with participation of nearest Stark component of the split term [14] or quasi-local oscillation [15] is common. At the higher temperatures spectral lines broadening is determined by the law $\gamma(T) \sim T^7$ [12, 16–17].

In the paper [18] have been shown that as the exception for impurity RE ion in the $Y_2SiO_5{:}Pr^{3+}$ bulk crystal the spectral lines temperature broadening mechanism characteristic for amorphous solid-state matrices (glasses, polymers) [19–21] is realized $(\gamma(T) \sim sh^{-1}(\Delta_{TLS}/kT)$, where Δ_{TLS} is the activation energy of two-level system).

The homogeneous linewidth of impurity centres optical transitions is closely concerned with so-called dephasing time (time of phase relaxation) $T_2 = (\pi\gamma_{hom})^{-1}$ [22]. For impurity RE ions at low temperatures the value of T_2 can vary in the range of 100 ns – 100 мs [23–24]. Dephasing time T_2 plays an important part in the wide set of impurity ions optical resonances applications. For instance, there is important for design of optical memory cells [25] and quantum computers [26, 27]. Practical application of optical resonances requires the impurity crystals with large T_2 [28]. Thus there is the strong request for materials providing minimal inhomogeneous broadening of optical transitions and (that is the most important) the minimal contribution to the homogeneous width determined by the phonon-stimulated processes [28]. At the same time for the real operation with optical resonances in the case of doped bulk crystals the deep cooling for phonon impurity centre scattering suppression is required.

In this paper the abnormally narrow spectral lines of impurity RE ions in $Y_2SiO_5{:}Pr^{3+}$ and $YVO_4{:}Eu^{3+}$ nanocrystals observed even at the room temperature are shown. The narrow optical resonances have been analyzed and found the preliminary explanation based on the manifestation of quantum size effect on the phonon subsystem of the nanocrystals. At first the dependence of spectral line width on the nanocrystal size has been shown.

Materials and Methods

$Y_2SiO_5{:}Pr^{3+}$ and $YVO_4{:}Eu^{3+}$ nanocrystals have been obtained by means of sol gel method [29]. Detailed description of nanocrystal synthesis is shown in [30]. Excitation and luminescence spectra of impurity Pr^{3+} and Eu^{3+} ions were measured by the specially created spectrofluorimeter equipped by the microobjective [31, 32].

Results and Discussions

In the fig.1 the absorption spectrum of $Y_2SiO_5{:}Pr^{3+}$ bulk crystal and excitation spectrum of the same nanocrystal (~20 nm) in the range of $^3H_4 \rightarrow {}^1D_2$ Pr^{3+} optical transitions are shown. For the bulk $Y_2SiO_5{:}Pr^{3+}$ (as it was expected) at the helium temperature (fig. 1a) spectral lines are well-resolved and their full width at half maximum (FWHM) is minimal and determined by the inhomogeneous broadening [33, 34].

At the same time at the room temperature spectral lines are subject to a homogeneous broadening [22, 28] due to phonon scattering and the decreasing of $T_2 = (\pi\gamma_{hom})^{-1}$ is observed.

At the same time in the case of $Y_2SiO_5{:}Pr^{3+}$ nanocrystal spectral lines in the excitation spectrum remain narrow even at the room temperature (fig. 1*b*). Narrowness of spectral lines remains also in the $Y_2SiO_5{:}Pr^{3+}$ nanocrystal luminescence spectra measured at the room temperature (fig. 2*a*). Contrary to nanocrystal, the bulk crystal luminescence spectrum is sufficiently blurred and its spectral structure appears weakly (fig. 2*b*).

So the luminescence spectrum of $Y_2SiO_5{:}Pr^{3+}$ nanocrystal (fig. 2*a*) looks like the spectrum of $Y_2SiO_5{:}Pr^{3+}$ bulk crystal under the deep cooling. This peculiarity has been shown at first in [31, 32]. For the confirmation of observed spectral peculiarities generality $YVO_4{:}Eu^{3+}$ nanocrystal has been investigated. Spectral lines of Eu^{3+} ion luminescence spectrum in $YVO_4{:}Eu^{3+}$ nanocrystals remain narrow at the room temperature making the spectrum well structured (fig. 3).

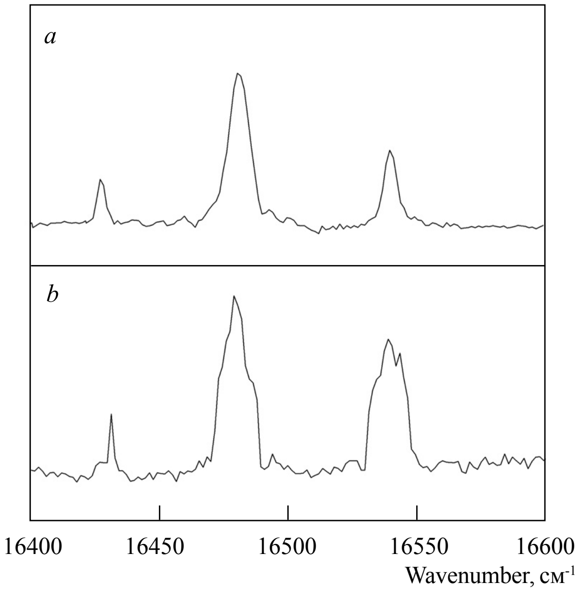

Fig. 1. Absorption spectrum of $Y_2SiO_5:Pr^{3+}$ crystal at T = 1.5 K in the range of $^3H_4 \rightarrow {}^1D_2$ transition (*a*); excitation spectrum of $Y_2SiO_5:Pr^{3+}$ nanocrystal at T = 300 K in the range of $^3H_4 \rightarrow {}^1D_2$ transition (*b*)

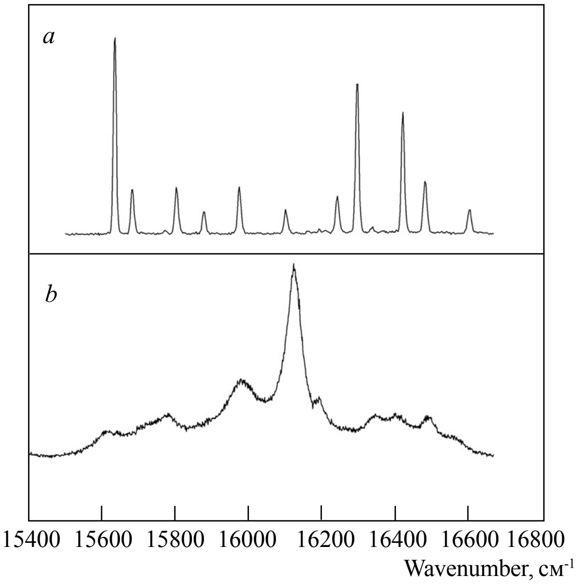

Fig. 2. Luminescence spectra at T = 300 K of the: *a*) $Y_2SiO_5:Pr^{3+}$ bulk crystal, *b*) $Y_2SiO_5:Pr^{3+}$ nanocrystal

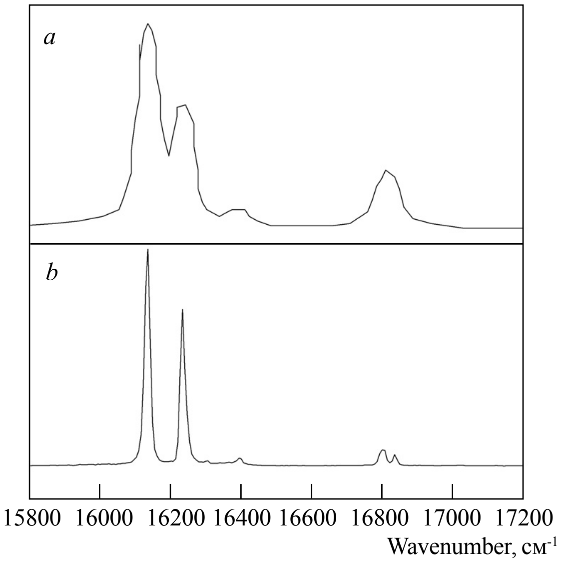

Fig. 3. Luminescence spectra at T = 300 K of the: *a*) $YVO_4:Eu^{3+}$ bulk crystal, *b*) $YVO_4:Eu^{3+}$ nanocrystal

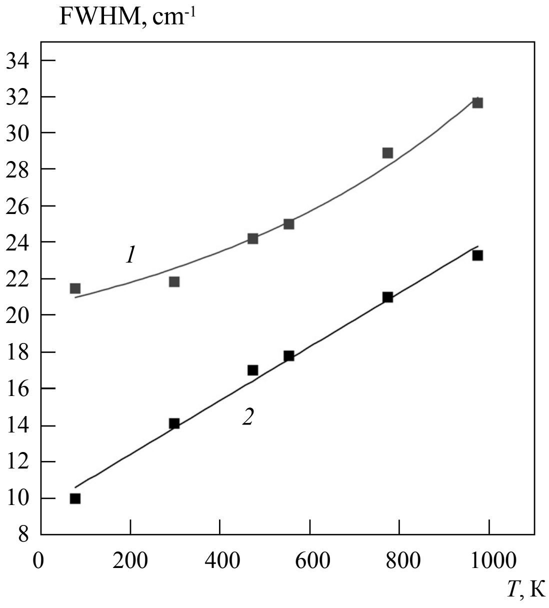

Fig. 4. Dependence of the $YVO_4:Eu^{3+}$ nanocrystal luminescence linewidths on the temperature: *1* – 30 nm, *2* – 5 nm

According to well-known patterns [22, 28] it can be mentioned that spectral lines in absorption and luminescence spectra of impurity RE ions in bulk crystals at the low temperature are inhomogeneously broadened. Temperature increasing leads to increasing of phonon scattering contribution to the homogeneous linewidth. At the room temperature phonon scattering contribution becomes determinative and spectral lines are homogeneously broadened. Optical transitions dephasing time at the room temperature becomes too short (10^{-12}–10^{-15} s) for using of these optical resonances for the optical memory devices and quantum computers creation.

In the general case the contribution of the phonon scattering processes to the homogeneous linewidth is determined by the expression [12]:

$$\gamma(T)=\int_0^\infty \frac{d\omega}{2\pi}\ln\left\{1+W^2\cdot\rho^2(\omega)\cdot sh^{-2}(\hbar\omega/kT)\right\} \quad (1)$$

where: W is the constant of electron-phonon coupling for the impurity centre; $\rho(\omega)$ is the phonon state density; k is the Boltzmann constant; T is the temperature.

Expression (1) remains correct independently on the crystal size. Constant of electron-phonon coupling is concerned with the impurity ion adiabatic potential change under the photoexcitation and determined by the ligand field structure only. It is clear that the ligand field of the impurity centre changes only within the first coordination sphere, so, it is independent on the crystal size up to few nanometers [35, 36]. Direct confirmation of this statement was obtained in the experiment [31, 32]. In [31, 32] it have been shown that the splitting peculiarities of impurity Pr^{3+} ion degenerate terms remained the same as for the bulk crystal after decreasing of nanocrystal size up to 20 nm [37, 38].

The main parameter in the expression (1) critically dependent on the crystal size in the range of nanometers is the phonon state density [39]. Depletion of nanocrystal phonon state density leads to the suppression of the fast nonradiative relaxation of impurity centre electron states [37–38, 40]. In addition, in [37, 38] has been shown that nanocrystal vibrational modes are high-Q with the low anharmonicity. The phonon mode quantity in a nanocrystal becomes explicitly discrete and these modes can be expressed as the set of functions $\rho(\omega) \sim 1/((\omega - \omega_i)^2+(2\tau_{ph})^{-2})$, where ω_i and τ_{ph} are the frequency and decay time of the phonon mode, respectively. Thus at $\tau_{ph} \to \infty$ the integration in (1) is performed with δ – functions leading to minimization of $\gamma(T)$. According to our interpretation increasing of nanocrystal size must lead unambiguously to the phonon density increasing manifesting itself in the increasing of phonon contribution to the impurity ion homogeneous linewidth. The experimental results (fig. 4) totally confirm our predictions. Spectral lines in the impurity luminescence spectrum of YVO_4:Eu^{3+} nanocrystal broaden with the nanocrystal size increasing.

Conclusion

Thus, rare-earth doped nanocrystals of wide-gap dielectrics exhibit narrow optical resonances of impurity ions at the room temperature. This effect is closely concerned with the optical transitions dephasing suppression due to weakening of phonon scattering on the impurity centre as a result of the quantum size effect in nanocrystal phonon subsystem. Due to the properties mentioned above doped nanocrystals can find their application in the optical memory and quantum computing devices due to unnecessary of the deep cooling.

На спектрах люмінесценції нанокристалів Y_2SiO_5:Pr^{3+} та YVO_4:Eu^{3+} за кімнатної температури спостерігалася наявність аномально вузьких спектральних ліній. Це було інтерпретовано як результат заглушення процесів дефазування оптичних переходів у нанокристалах. Причиною зазначеного ефекту є ослаблення розсіювання фононів на домішковому центрі внаслідок впливу квантово-розмірного ефекту на підсистему фононів у нанокристалі. Уперше отримано залежність ширини спектральних ліній від розміру нанокристала. Відсутність потреби глибокого заморожування для отримання вузьких оптичних резонансів відкриває можливості використання таких нанокристалів для створення пристроїв оптичної пам’яті та квантових комп’ютерів.

Ключові слова: *вузькі лінії, електрон-фононна взаємодія, нанокристали*

На спектрах люминесценции нанокристаллов Y_2SiO_5:Pr^{3+} и YVO_4:Eu^{3+} при комнатной температуре наблюдалось наличие аномально узких спектральных линий. Это было интерпретировано как результат подавления процессов дефазировки оптических переходов в нанокристаллах. Причиной наблюдаемого эффекта является ослабление рассеяния фононов на примесном центре в результате влияния квантово-размерного эффекта на подсистему фононов в нанокристалле. Впервые получена зависимость ширины спектральных линий от размера нанокристалла. Отсутствие необходимости глубокого замораживания для получения узких оптических резонансов открывает широкие возможности применения данных нанокристаллов для создания устройств оптической памяти и квантовых компьютеров.

Ключевые слова: *узкие линии, электрон-фононное взаимодействие, нанокристаллы*

1. *Лифшиц Е.М., Питаевский Л.П.* Теоретическая физика: Статистическая физика. Ч. 2, т. 9. – М.: Наука, 1978. – 568 с.
2. *Belser P., Bernhard S., Blum C.* Molecular architecture in the field of photonic devices // Coordination Chemistry Reviews. – 1999. – **190–192**. – P. 155–169.
3. *Yassar A., Rebiere-Galy N., Frigoli M.* Molecular switch devices realised by photochromic oligothiophenes // Synthetic Metals. – 2001. – **124,** N 1. – P. 23–27.
4. *Ovshinsky S.R.* Optically induced phase changes in amorphous materials // Journal of Non-Crystalline Solids. – 1992. – **141**. – P. 200–203.
5. *Shintani T., Nakamura K., Hosaka S.* Phase change writing in a GeSbTe film with scanning near-field optical microscope // Ultramicroscopy. – 1995. – **61**, N 1–4. – P. 285–289.
6. *Kulic M.L.* Interplay of electron–phonon interaction and strong correlations: the possible way to high-temperature superconductivity // Physics Reports. – 2000. – **338**, N 1–2. – P. 1264.
7. *Tang D., Li J., Gong C.* Role of the electron–phonon interaction in the d-wave superconductor // Physics Letters A. – 2004. – **327**, N 4. – P. 344–351.
8. *Terzi N., Dominoni M.* Ultrafast electron-lattice relaxation of optically excited centers in crystals. In: B. di Bartolo (ed.), Ultrafast Dynamics of Quantum Systems: Physical Processes and Spectroscopic Techniques. – New York: Plenum Press, p. 569–582.
9. *Каминский А.А.* Физика и спектроскопия кристаллов. – М.: Наука, 1986. – 272 с.
10. *Spectroscopy* of Solids Containing Rare Earth Ions, ed. by A.A. Kaplyanskii, R.M. Macfarlane. – Amsterdam: North-Holland, 1987. – 754 p.
11. *Лубченко А.Ф.* Квантовые переходы в примесных центрах твердых тел. – К.: Наукова думка, 1978. – 293 с.
12. *Osad'ko I.S.* Optical dephasing and homogeneous optical bands in crystals and amorphous solids: Dynamic and stochastic approaches // Phys. Reports. – 1991. – **206**, N 2. – P. 43–97.
13. *Stoneham A.M.* Theory of defects in solids. – Oxford: Clarendon Press, 1975. – 976 p.
14. *Takeuchi N.* Measurement of the relaxation time in LaF$_3$:Pr^{3+} by photon echo // Journal of Luminescence. – 1976. – **12–13**. – P. 743–747.
15. *Slepyan G.Ya., Maksimenko S.A., Magyarov A.V.* Excitonic Rabi oscillations in a quantum dot: local field impact // Superlattices and Microstructures. – 2004. – **36**, N 4–6. – P. 773–781.
16. *Kubo R., Toyozawa Y.* Application of the Method of Generating Function to Radiative and Non-Radiative Transitions of a Trapped Electron in a Crystal // Progr. Teor. Phys. – 1955. – **13**, N 2. – P. 160–182.
17. *Silsbee R.S.* Thermal Broadening of the Mцssbauer Line and of Narrow-Line Electronic Spectra in Solids // Phys. Rev. – 1962. – **128**. – P. 1726–1733.
18. *Погребняк Н.Л., Жмурін П.Н., Семиноженко В.П.* Фотонна луна в кристалах Y$_2$SiO$_5$:Pr^{3+} i Gd$_2$SiO$_5$:Pr^{3+} // УФЖ. – 1994. – **39**, № 7–8. – С. 791–793.
19. *Jacowiak R., Small G.J.* Hole-Burning Spectroscopy and Relaxation Dynamics of Amorphous Solids at Low Temperatures // Science. – 1987. – **237**. – P. 618–625.
20. *Meijers H.C., Wiersma D.A.* Low temperature dynamics in amorphous solids: A photon echo study // J. Chem. Phys. – 1994. – **101**, N 8. – P. 6927–6943.
21. *Осадько И.С.* Флуктуирующая флуоресценция одиночных молекул и полупроводниковых нанокристаллов // УФН. – 2006. – **176**, № 1. – С. 23–57.
22. *Osad'ko I.S., Zaitsev N.N.* Dephasing time in solids and homogeneous optical linewidth: are the mechanisms of the electron-phonon coupling the same? // Chemical Physics Letters. – 1985. – **121**, N 3. – P. 209–213.
23. *Broer M.M., Golding B.* Low temperature optical dephasing of rare earth ions by tunneling systems in glass // Journal of Luminescence. – 1984. – **31–32**. – P. 733–737.
24. *Meltzer R.S., Jang K.W., Hong K.S.* Optical dephasing of rare earth ions in mixed crystalline and size-restricted systems // Journal of Alloys and Compounds. – 1997. – **250**, N 1–2. – P. 279–286.
25. *Samartsev V.V., Kalachev A.A.* Optical memory based on the long-lived photon echo and optical superradiance in crystals doped by rare-earth ions // Journal of Luminescence. – 2002. – **98**, N 1–4. – P. 331–339.
26. *Dahm A.J., Heilman J.A., Karakurt I.* Quantum computing with electrons on helium // Physica E: Low-dimensional Systems and Nanostructures. – 2003. – **18**, N 1–3. – P. 169–172.
27. *Governale M., Grifoni M., Schцn G.* Decoherence and dephasing in coupled Josephson-junction qubits // Chemical Physics. – 2001. – **268**, N 1–3. – P. 273–283.
28. *Macfarlane R.M.* High-resolution laser spectroscopy of rare-earth doped insulators: a personal perspective // Journal of Luminescence. – 2002. – **100**, N 1–4. – P. 1–20.

29. *Zhang W., Xie P., Duan C.* Preparation and size effect on concentration quenching of nanocrystalline Y_2SiO_5:Eu // Chem. Phys. Letters. – 1998. – **292**, N 1–2. – P. 133–136.
30. *Energy* and resource saving technologies for manifacturing of high melting oxide crystals / Malyukin Yu.V., Zhmurin P.N., Borovoy I.A. et al. // Functional Materials. – 2003. – **10**, N 3. – P. 554–558.
31. *Malyukin Yu.V., Masalov A.A., Zhmurin P.N.* Single-ion fluorescence spectroscopy of a Y_2SiO_5:Pr^{3+} nanocluster // Physics Letters A. – 2003. – **316**. – P. 147–152.
32. *Malyukin Yu.V., Masalov A.A., Zhmurin P.N.* New fluorescence dynamics of a single Y_2SiO_5:Pr^{3+} nanocrystal // Opt. Commun. – 2004. – **239**. – P. 409–414.
33. *Погребняк Н.Л., Малюкин Ю.В., Семиноженко В.П.* Аномальная дефазировка оптических переходов иона Pr^{3+} в кристалле Y_2SiO_5 // ФНТ. – 1994. – **20**, № 6. – С. 610–616.
34. *Ю.В. Малюкин.* Новые каналы релаксации фотонного эха в кристаллах Y_2SiO_5: Pr^{3+} и LaF_3: Pr^{3+} // ФНТ. – 1997. – **23**, № 9. – С. 993–998.
35. *Wang X., Huang S.H., Reeves R.* Studies of the spectroscopic properties of Pr^{3+} doped LaF_3 nanocrystals/glass // Journal of Luminescence. – 2001. – **94–95**. – P. 229–233.
36. *Fu Z., Zhou S., Pan T.* Preparation and luminescent properties of cubic Eu^{3+}:Y_2O_3 nanocrystals and comparison to bulk Eu^{3+}:Y_2O_3 // Journal of Luminescence. – 2007. – **124**, N 2. – P. 213–216.
37. *Селективная* спектроскопия примесных ионов Pr^{3+} в кристаллах Y_2SiO_5 , Gd_2SiO_5 , Lu_2SiO_5 / Малюкин Ю.В., Борисов Р.С., Жмурин П.Н. и др. // ФНТ. – 2000. – **26**, № 12. – С. 1207–1213.
38. *Взаимодействие* оптических центров Pr^{3+} в кристалле Y_2SiO_5 // Малюкин Ю.В., Жмурин П.Н., Лебеденко А.Н. и др. // ФНТ. – 2002. – **28**, № 1. – С. 73–80.
39. *Chen X.Y., Zhuang H.Z., Liu G.K.* Confinement on energy transfer between luminescent centers in nanocrystals // Journal of Applied Physics. – 2003. – **94**, N 9. – P. 5559–5566.
40. *Meltzer R.S., Yen W.M., Zheng H.* Effect of the matrix on the radiative lifetimes of rare earth doped nanoparticles embedded in matrices // Journal of Luminescence. – 2001. – **94–95**. – P. 217–220.