

## Energy transport in $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ nanocrystals with two-dimensional $\text{Eu}^{3+}$ sublattice

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Energy transport processes in  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  nanocrystals with two-dimensional arrangement of  $\text{Eu}^{3+}$  subsystem were investigated using the methods of stationary and time-resolved spectroscopy. Sufficient difference in  $\text{Eu}^{3+}$ – $\text{Eu}^{3+}$  distances inside and between (001) planes (4.58 Å vis 9.28 Å, respectively) leads to two-dimensional character of energy migration. Comparison of energy transport processes in aluminium borate nanocrystals with two-dimensional ( $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ ) and three-dimensional ( $\text{EuAl}_3(\text{BO}_3)_4$ ) arrangement of  $\text{Eu}^{3+}$  ions have shown that despite higher  $\text{Eu}^{3+}$ – $\text{Eu}^{3+}$  shortest distances (5.9 Å), energy migration in  $\text{EuAl}_3(\text{BO}_3)_4$  leads to stronger quenching of  $\text{Eu}^{3+}$  luminescence.

**Keywords:** Nanocrystals, energy transport processes.

Исследованы процессы переноса энергии в нанокристаллах  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  с двухмерным упорядочением ионов  $\text{Eu}^{3+}$  при помощи стационарной и разрешенной во времени спектроскопии. Существенное различие в расстояниях между ионами европия находящимися в одной плоскости (4.58 Å) и в разных плоскостях (9.28 Å) приводит к тому, что миграция энергии носит двухмерный характер. Сравнение процессов транспорта энергии в нанокристаллах с двухмерным ( $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ ) и трехмерным ( $\text{EuAl}_3(\text{BO}_3)_4$ ) упорядочением ионов  $\text{Eu}^{3+}$  показало, что, несмотря на большие расстояния между ближайшими ионами  $\text{Eu}^{3+}$  в  $\text{EuAl}_3(\text{BO}_3)_4$  (5,9 Å), чем в  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ , миграция энергии в трехмерной системе приводит к более сильному тушению люминесценции ионов  $\text{Eu}^{3+}$ .

**Транспорт енергії у нанокристаллах  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  з двовимірною підґраткою іонів  $\text{Eu}^{3+}$ .** *Н.В.Кононець, В.В.Семінько, П.О.Максимчук, І.І.Беспалова, Ю.В.Малюкін, Б.В.Гриньов.*

Досліджено процеси переносу енергії у нанокристаллах  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  із двовимірним упорядкуванням іонів  $\text{Eu}^{3+}$  з використанням стаціонарної та розподіленої за часом спектроскопії. Суттєва різниця у відстані між іонами европію, які знаходяться на одній площині (4.58 Å) та в різних площинах (9.28 Å) призводить до того, що міграція енергії носить двовимірний характер. Порівняння процесів транспорту енергії у нанокристаллах з двовимірним ( $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ ) та тривимірним ( $\text{EuAl}_3(\text{BO}_3)_4$ ) упорядкуванням іонів  $\text{Eu}^{3+}$  показало, що, не дивлячись на більшу відстань між найближчими іонами  $\text{Eu}$  у  $\text{Eu}^{3+}\text{Al}_3(\text{BO}_3)_4$  (5,9 Å), ніж у  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ , міграція енергії у тривимірній системі призводить до більш сильного гасіння люмінесценції іонів  $\text{Eu}^{3+}$ .

## 1. Introduction

Development of effective luminescent and scintillation materials for various applications including solid-state lasers, detectors of high-energy particles, lamp phosphors and fluorescent labels for biological uses requires materials with controllable transfer of excitation energy to the optical centers. From the vast number of rare-earth-doped crystals and nanocrystals, only the ones containing  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Gd}^{3+}$  as regular ions have shown the energy migration over sufficient distances (1 nm or more) [1–3], while for other RE ions luminescence is quenched effectively by cross-relaxation mechanism and any sufficient transport of energy cannot be expected.

As was shown recently, transport processes including excitation energy migration [4], spin [5], electron [6] and ion [7] transport in crystal lattices with anisotropic structure (with one- or two-dimensional arrangement of regular ions) are modified sufficiently as compared to energy transfer processes in lattices with three-dimensional arrangement of regular ions. Our previous investigations have shown that for rare-earth doped nanocrystals the processes of energy transport can depend both on the arrangement of rare-earth ions and on the restrictions provided by the size of nanocrystal [8].

Diffusion-limited energy migration was observed previously for  $\text{EuAl}_3(\text{BO}_3)_4$  aluminium borates with three-dimensional arrangement of  $\text{Eu}^{3+}$  ions [9]. The shortest  $\text{Eu}^{3+}$ – $\text{Eu}^{3+}$  distance in this structure is equal to 5.9 Å leading to energy transfer only via dipole-dipole (and not exchange) interactions. Strong temperature dependence of energy migration processes was caused by forbidden nature of  ${}^5D_0 \rightarrow {}^7F_0$  transition, so that thermal population of higher  ${}^7F_1$  energy level was crucial for realization of energy migration process.

In the last years a series of  $\text{REAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  (RE = La, Ce, Nd) aluminium borate crystals was grown [10].  $\text{REAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  structure is characterized as mica-like with  $\text{RE}^{3+}$  ions situated in (001) planes with  $\text{RE}^{3+}$ – $\text{RE}^{3+}$  distances equal to ~4.6 Å within the same plane and ~9.3 Å between the different planes. As was shown in our previous paper [11], relatively high distances between rare-earth cations and surrounding ligands (about 2.5 Å) made possible observation of so-called quantum splitting effect for  $\text{Pr}^{3+}$  doped  $\text{LaAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  bulk crystals at X-ray

excitation. In this research at first the peculiarities of energy transport in  $\text{REAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  are investigated. Characteristics of energy migration are compared for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  aluminium borates and the dependence of energy migration parameters on the arrangement of  $\text{RE}^{3+}$  ions is shown.

## 2. Experimental

$\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  aluminium borate nanocrystals were synthesized using solid-state method involving mixing and annealing of correspondent oxides ( $\text{Eu}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ ) taken in stoichiometric ratio.

The sizes of nanocrystals were determined using ZetaPALS analyzer (Brookhaven, NY). The purity of crystal phase was controlled by X-ray Diffraction (XRD).

Luminescence spectra were obtained using spectrofluorimeter based on the grating monochromator, luminescence was excited by the fourth harmonics of YAG:Nd laser ( $\lambda_{exc} = 266$  nm).

The luminescence decay was taken using the time-correlated single-photon counting (TCSPC) technique. Temperature was varied from 10 K to 300 K using ARS DE-204AE cryostat with LakeShore 335 temperature controller.

## 3. Results and discussion

Crystal structures of  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  aluminium borates are shown in the Fig. 1a and 1b, respectively. For  $\text{EuAl}_3(\text{BO}_3)_4$  crystals  $\text{Eu}^{3+}$  ions form three-dimensional substructure with the shortest  $\text{Eu}^{3+}$ – $\text{Eu}^{3+}$  distance equal to 5.9 Å. At the same time,  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  structure is characterized by quasi-two-dimensional arrangement of  $\text{Eu}^{3+}$  ions, which are situated in (001) planes with shortest  $\text{Eu}^{3+}$ – $\text{Eu}^{3+}$  distances equal to ~4.6 Å within the same plane and ~9.3 Å between the different planes. Sufficient differences in the structures of these two lattices allowed us to suppose the different mechanisms of energy migration. In order to reveal the features of energy transport in both cases, luminescence spectra and decay curves of  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  aluminium borate nanocrystals were taken at different temperatures.

The luminescence spectra of  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  aluminium borate nanocrystals ( $\lambda_{exc} = 266$  nm) are shown in the Fig. 2. Both spectra consist of characteristic  $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_J$  ( $J = 0, 1, 2, 3$ ) transitions. Temperature increase

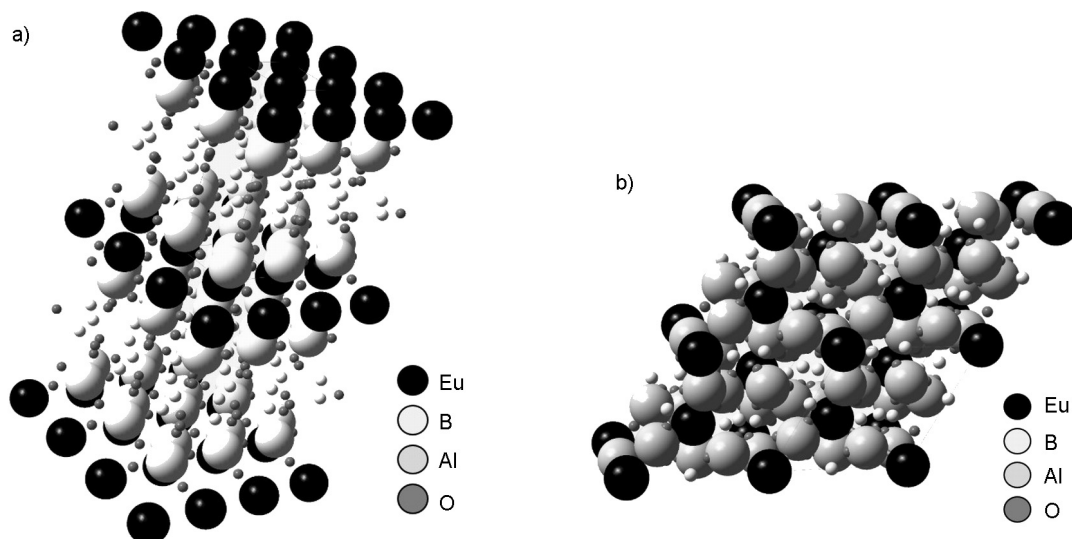


Fig. 1. Crystal structures of: a)  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ ; b)  $\text{EuAl}_3(\text{BO}_3)_4$ .

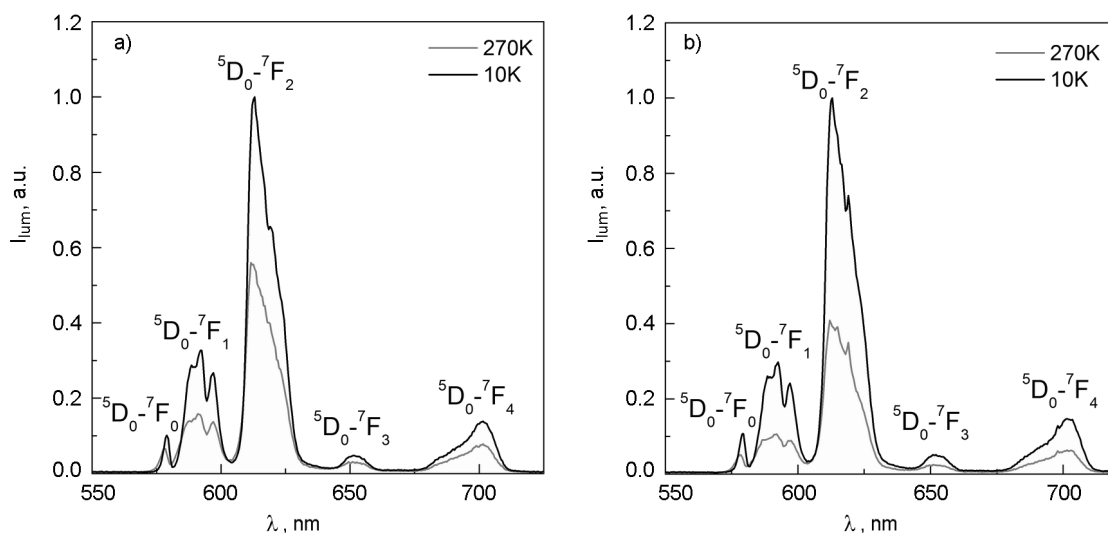


Fig. 2. Luminescence spectra of:  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  (a) and  $\text{EuAl}_3(\text{BO}_3)_4$  (b) nanocrystals ( $\lambda_{exc} = 266 \text{ nm}$ ) at different temperatures.

leads to  $\text{Eu}^{3+}$  luminescence quenching as for  $\text{EuAl}_3(\text{BO}_3)_4$ , so for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  nanocrystals. However, for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  the luminescence quenching is less pronounced than for  $\text{EuAl}_3(\text{BO}_3)_4$  — while for  $\text{EuAl}_3(\text{BO}_3)_4$  temperature increase from 10 K to 270 K leads to decrease of integral  $\text{Eu}^{3+}$  luminescence intensity in 1.97 times, for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  the same temperature increase leads to intensity decrease only in 1.63 times.

$\text{Eu}^{3+}$  luminescence intensity change with temperature variation can be caused by different factors, and, first of all, by energy transfer from initially excited  $\text{Eu}^{3+}$  ions to luminescence quenchers of different kinds,

for instance, to europium ( $\text{Eu}^{3+}$ ) ions with distorted coordination. This energy transfer can take the forms of single-step donor-acceptor energy transfer, or multi-step energy migration. In order to understand the mechanism leading to  $\text{Eu}^{3+}$  luminescence quenching for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  aluminium borate nanocrystals, decay curves of  ${}^5D_0 \rightarrow {}^7F_2$  luminescence were taken for different temperatures.

Decay curves of  $\text{Eu}^{3+}$  luminescence (taken for  ${}^5D_0 \rightarrow {}^7F_2$  transition) for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  nanocrystals are shown in the Fig. 3a and 3b, respectively. At 10 K decay curves as for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  so for  $\text{EuAl}_3(\text{BO}_3)_4$

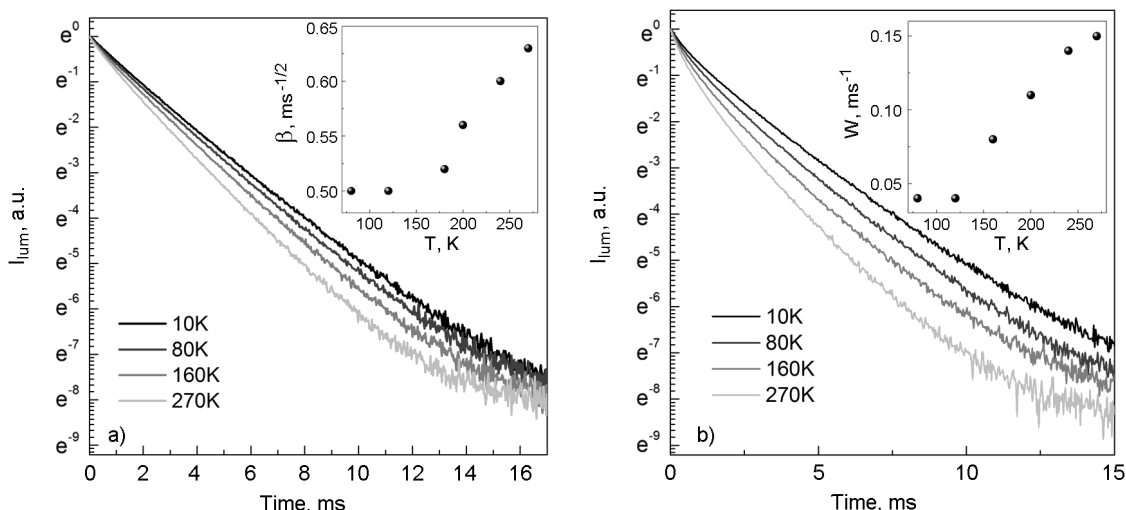


Fig. 3. Decay curves of  ${}^5D_0 \rightarrow {}^7F_2$   $\text{Eu}^{3+}$  luminescence for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  (a) and  $\text{EuAl}_3(\text{BO}_3)_4$  (b) nanocrystals at different temperatures. In the insets: temperature dependences of energy migration parameters  $\beta$  (for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ ) and  $W$  (for  $\text{EuAl}_3(\text{BO}_3)_4$ ).

are close to single exponential and can be fitted by well-known  $I = I_0 \exp(-t/\tau_0)$  dependence, where  $\tau_0$  is the decay time. Values of the decay time  $\tau_0$  are equal to 1.98 ms for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and 1.9 ms for  $\text{EuAl}_3(\text{BO}_3)_4$ . At higher temperatures the decay curves are not exponential anymore, but the average decay time can be estimated as

$$\tau_{avg} = \frac{\int I(t) t dt}{\int I(t) dt}.$$

Average decay times for  ${}^5D_0 \rightarrow {}^7F_2$  luminescence in  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  nanocrystals at temperature variation from 40 K to 270 K are listed in the Table. Temperature increase leads to quenching of  ${}^5D_0 \rightarrow {}^7F_2$  luminescence for both  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and  $\text{EuAl}_3(\text{BO}_3)_4$  with corresponding shortening of average decay time — from 1.94 ms at 40 K to 1.56 ms at 270 K for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and from 1.82 ms at 40 K to 1.2 ms at 270 K for  $\text{EuAl}_3(\text{BO}_3)_4$ . The relative changes in average decay time with temperature increase (1.27 times for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  and 1.52

times for  $\text{EuAl}_3(\text{BO}_3)_4$ ) show that the luminescence quenching is stronger for nanocrystals that for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  ones. This fact agrees well with the results obtained from luminescence spectra (Fig. 2). It worth noting that more effective energy transport (and, so lower values of average decay times) is usually observed for crystal structures with shorter  $\text{RE}^{3+}-\text{RE}^{3+}$  minimal distances. However, it is not the case for the structures compared in this paper, as the minimal distance between  $\text{Eu}^{3+}$  ions in  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  is equal to 4.6 Å, while in  $\text{EuAl}_3(\text{BO}_3)_4$  — 5.9 Å. So, there should be some factor hampering energy migration in  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  leading to lower luminescence quenching as compared to  $\text{EuAl}_3(\text{BO}_3)_4$  despite the shorter distances between rare-earth ions. This effect can be determined, for instance, by restriction of energy migration in  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  to (001) planes without energy transfer between  $\text{Eu}^{3+}$  ions in different planes. In this case, the migration of energy should be two-dimensional.

In the framework of the average-t-matrix approximation (ATA) decay curves in the presence of two-dimensional migration

Table 1.

	T, K	10	40	80	120	160	200	240	270
$\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$	$\tau_{avg}$ , ms	1.98	1.94	1.89	1.82	1.75	1.69	1.62	1.56
$\text{EuAl}_3(\text{BO}_3)_4$	$\tau_{avg}$ , ms	1.9	1.82	1.67	1.56	1.45	1.36	1.26	1.2

should be fitted by the following law:  $I = I_0 \exp(-t/\tau_0) \cdot (4\pi C_A D a^{-2} t)^{-1}$ , where  $C_A$  is the concentration of energy acceptors,  $D$  is the diffusion coefficient [12]. However, the fitting of experimentally obtained decay curves for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  by this law gave unsatisfactory results. Much better fitting was obtained using the approach of random walk (RW) over the donor sublattice to randomly distributed acceptors which trap the migrating excitation at first encounter [13, 14]. According to this approach the decay of excited  $\text{Eu}^{3+}$  ion should follow the law:  $I = I_0 \exp(-t/\tau_0 - \beta t^b/(b+2))$ , where  $b$  is the dimensionality of energy migration and  $\beta$  depends both on acceptor concentration and temperature. For two-dimensional transport  $b = 2$  and the decay law is  $I = I_0 \exp(-t/\tau_0 - \beta t^{0.5})$ , that is mathematically equivalent to well-known Forster decay law for one-step donor-acceptor energy transfer, but while for Forster decay  $\beta$  is temperature-independent, for two-dimensional energy migration this parameter should depend on the temperature. Fitting by this expression allowed to determine the values of  $\beta$  and to reveal the strong temperature dependence of this parameter (Fig. 3a, inset). So, in  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  nanocrystals two-dimensional energy migration over  $\text{Eu}^{3+}$  ions situated in (001) planes is really observed.

Long-time exponential parts of the decay curves for  $\text{EuAl}_3(\text{BO}_3)_4$  nanocrystals are well-fitted using the well-known expression for three-dimensional energy migration:  $\sim \exp(-t/\tau_0 - Wt)$  [15], where  $W = 11.404 C_A C_{DA}^{1/2} D^{3/4}$ ,  $C_{DA}$  is the interaction parameter for donor-acceptor energy transfer. Diffusion coefficient  $D$  depends on the temperature, so temperature increase leads to increase of  $W$  (Fig. 3b, inset). Temperature dependences of  $\beta$  (for  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$ ) and  $W$  (for  $\text{EuAl}_3(\text{BO}_3)_4$ ) have the same character — effective energy migration is observed only at temperatures higher than 100–120 K. It was shown previously [9] that energy transfer between  $\text{Eu}^{3+}$  ions at low temperatures is rather ineffective involving  ${}^5D_0 \rightarrow {}^7F_0$  transitions, which are considered as absolutely forbidden ones ( $0 \rightarrow 0$  transitions). The energy difference between  ${}^7F_0$  level and higher-lying  ${}^7F_1$  level is about  $200 \text{ cm}^{-1}$  [9], so, according to [9], energy transfer in concentrated  $\text{Eu}^{3+}$  compounds at low temperatures can be realized only as two-phonon assisted process.

Temperature increase leads to thermal population of higher-lying  ${}^7F_1$  levels, leading to possibility of energy migration via  ${}^5D_0 \rightarrow {}^7F_1$  transitions. So, the effective energy migration for both compounds can be observed only at the temperatures high enough for population of  ${}^7F_1$  levels of adjacent  $\text{Eu}^{3+}$  ions.

#### 4. Conclusions

Efficiency of excitation energy transport in europium aluminium borate nanocrystals strongly depends on the dimensionality of  $\text{Eu}^{3+}$  sublattice. Processes of energy migration in  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  nanocrystals with two-dimensional arrangement of  $\text{Eu}^{3+}$  ions despite relatively short  $\text{Eu}^{3+}$ – $\text{Eu}^{3+}$  distances ( $4.58 \text{ \AA}$ ) do not lead to such sufficient luminescence quenching and shortening of average decay time, as the ones observed for nanocrystals with three-dimensional  $\text{Eu}^{3+}$  sublattice (such as  $\text{EuAl}_3(\text{BO}_3)_4$ ). Analysis of decay kinetics for  $\text{Eu}^{3+}$  luminescence in  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  that luminescence decay can be described in the framework of random walk approach as two-dimensional migration within (001) planes of  $\text{EuAl}_{2.07}(\text{B}_4\text{O}_{10})\text{O}_{0.6}$  nanocrystal.

#### References

1. M.Buijs, A.Meyerink, G.Blasse, *J. Luminescence*, **37**, 9 (1987).
2. K.S.Sohn, Y.Y.Choi, H.D.Park et al., *J. Electrochem. Soc.*, **147**, 2375 (2000).
3. A.J.De Vries, H.S.Kiliaan, G.Blasse, *J. Solid State Chem.*, **65**, 190 (1986).
4. T.S.Ahn, N.Wright, C.J.Bardeen, *Chem. Phys. Lett.*, **446**, 43 (2007).
5. N.Tombros, C.Jozsa, M.Popinciuc et al., *Nature*, **448**, 571 (2007).
6. Z.Liu, D.Zhang, S.Han et al., *J. Adv. Mater.*, **15**, 1754 (2003).
7. B.Corry, *Energy Environ. Sci.*, **4**, 751 (2011).
8. N.V.Kononets, V.V.Seminko, P.O.Maksimchuk et al., *Spectrosc. Lett.*, **50**, 399 (2017).
9. F.Kellendonk, G.Blasse, *J. Chem. Phys.* **75**, 561 (1981).
10. F.Capitelli, G.Chita, N.I.Leonyuk et al., *Z. Kristallogr.*, **224**, 478 (2009).
11. N.V.Kononets, O.G.Viagin, V.V.Seminko et al., *Spectrosc. Lett.*, **50**, 359 (2017).
12. K.K.Ghosh, D.L.Huber, *J. Luminescence*, **21**, 225 (1980).
13. P.Grassberger, I.Procaccia, *J. Chem. Phys.*, **77**, 6281 (1982).
14. M.Buijs, G.Blasse, *J. Solid State Chem.*, **71**, 296 (1987).
15. M.Yokota, O.Tanimoto, *J. Phys. Soc. Jpn.*, **22**, 779 (1967).