



Changes of fluorescent spectral features after successive rare earth doping of gadolinium oxide powders

W. Kuznik^{a,b}, M.G. Brik^b, I. Cieřlik^c, A. Majchrowski^c, L. Jaroszewicz^c, N.S. AlZayed^d, A.M. El-Naggar^{d,f}, I. Sildos^b, S. Lange^b, V. Kiisk^b, I.V. Kityk^{e,d,*}

^a Chemical Department, Silesian University of Technology, Gliwice, Poland

^b Institute of Physics, University of Tartu, Riia 142, Tartu 51014, Estonia

^c Institute of Applied Physics, Military University of Technology, Kaliskiego 2,00-908 Warsaw, Poland

^d Physics & Astronomy Dept., College of Science, P.O. Box 2455, King Saud University, Riyadh 11451, Saudi Arabia

^e Electrical Engineering Department, Czestochowa University of Technology, Armii Krajowej 17, Czestochowa, Poland

^f Permanent address: Physics department, Faculty of Science, Ain Shams University, Abassia, Cairo 11566, Egypt

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ABSTRACT

We present a complex fluorescence study of a series of gadolinium oxide polycrystalline powders singly, doubly and triply doped with trivalent rare earth ions (Er^{3+} , Tb^{3+} , and Dy^{3+}), to explore a possibility of their use as materials for white light emitting diodes. The excitation and luminescence spectra along with the decay kinetics were measured in the temperature range from 6 to 300 K. The luminescence efficiency was studied within the visible spectral range, i.e. ~ 400 nm to 750 nm under excitation by 355 nm third harmonic Nd:YAG laser pulses. Singly doped Er^{3+} sample gave stronger luminescence signals, but others showed significantly larger decay lifetimes. The successive rare earths doping leads to substantial changes of the spectral positions due to the up-conversion processes. In the singly (Er^{3+}) doped sample, following the time resolved spectrum and decay curves, there are two different types of emissions: at 660 nm and at shorter wavelengths (below 640 nm) the red emission's lifetime is ten times longer than at shorter wavelengths. The singly doped sample shows unclear temperature-dependence of luminescence with lifetime at 550 nm (the longest at 100 K, similarly at 6 K and 300 K) and achieved luminous efficacy 73.5 lm/W.

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1. Introduction

The search of the white light emitting diodes requires additional intensive search of materials possessing the good efficient luminescent features [1–12]. Some efforts were done concerning the Ce:YAG ceramics [6].

As for the host materials, the gadolinium oxide Gd_2O_3 is a very promising candidate, since it can be easily doped with different rare earth ions occupying the Gd^{3+} local site positions without any charge compensation [13–15], on one hand, and due to the wide energy gap ($\sim 32,000$ cm^{-1}) between the ground and first excited states of Gd^{3+} , on the other hand. The former factor favors relatively easy sample preparation processes, whereas the latter one ensures spectral compatibility of the host and impurities, since a large number of emitting levels of trivalent lanthanides are located in the region of optical transparency of Gd_2O_3 .

Therefore, in the present work we explore the spectroscopic properties of Gd_2O_3 doped with different trivalent lanthanides. After careful consideration of different rare earth ions, we have chosen Er^{3+} , Tb^{3+} , and Dy^{3+} ions. Moreover, to study possible interactions between different impurities and their influence on the overall appearance of optical spectra and lifetimes of the excited levels, various combinations of dopants were considered, such as singly doped with Er, doubly (Tb^{3+} , Er^{3+}) doped, and, finally, triply doped (Tb^{3+} , Er^{3+} , and Dy^{3+}) matrices. Following such a route, it is possible to evaluate the role of additional doping in variations of fluorescent spectra and their effective emission.

2. Materials and methods

2.1. Synthesis of Gd_2O_3 doped with combinations of Tb^{3+} , Er^{3+} , and Dy^{3+} ions

The Gd_2O_3 samples doped with combinations of rare earth ($\text{RE} = \text{Tb}^{3+}$, Er^{3+} , and Dy^{3+}) ions were obtained by the Pechini method [16]. High purity (4N) gadolinium oxide, dysprosium oxide, erbium oxide and terbium oxide powders were used as sources of RE cations. Firstly, 1.38 mmol of gadolinium oxide and proper amounts of dopants were dissolved in nitric acid under stirring and heating in order to obtain clear solution. Citric acid was used to chelate the metal ions due to their interaction with carboxyl groups. Uniform distribution of RE ions was obtained in this way. The

* Corresponding author at: Physics & Astronomy Dept., College of Science, P.O. Box 2455, King Saud University, Riyadh, Saudi Arabia.

E-mail addresses: ikityk@el.pcz.czest.pl, iwank74@gmail.com (I.V. Kityk).

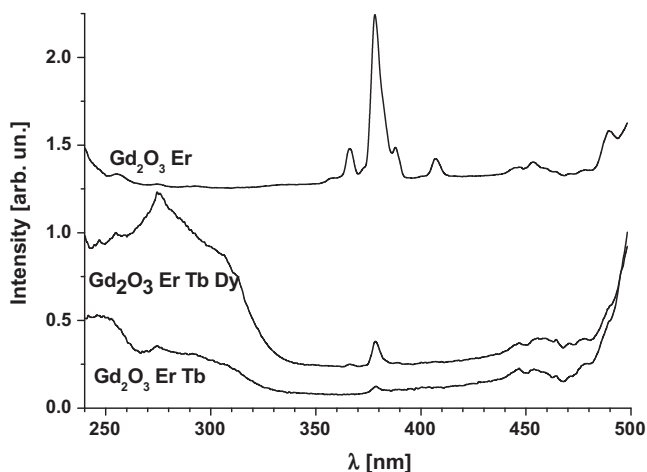


Fig. 1. Excitation spectra of rare earth doped Gd_2O_3 powders measured at 550 nm.

addition of mannitol was used to create rigid polymer containing homogeneously distributed RE^{3+} ions. Mannitol and citric acid solutions were obtained by dissolving in water. The molar ratio of the citric acid to mannitol was 1:1, 20 mmol of both compounds were used. The solutions of citric acid chelate and mannitol were mixed using a magnetic stirrer and heated at 60°C in air atmosphere for one and half hours. The mixture was dried at 80°C in furnace for 15 h and then kept at 300°C for 3 h. The last stage of the synthesis was the pyrolysis process of the obtained powder carried out at 900°C for 4 h.

Three samples were prepared: (1) Gd_2O_3 matrix with 2 at.% of Er_2O_3 , (2) Gd_2O_3 matrix with 2 at.% of Er_2O_3 and 1 at.% of Tb_4O_7 , and (3) Gd_2O_3 matrix with 2 at.% of Er_2O_3 , 1 at.% of Tb_4O_7 and 1 at.% of Dy_2O_3 .

2.2. Fluorescence spectral measurements

Photoluminescence (PL) emission and excitation spectra, as well as luminescence decay kinetics were examined. For measurement of PL emission spectra and decay kinetics, a pulsed (pulse duration 10 ns) third harmonic of $\text{Nd}^{3+}:\text{YAG}$ laser (355 nm) and 10 kHz was used as an excitation source. The pulse energy was equal to about $1\ \mu\text{J}$. The laser beam was focused in a backscattering geometry onto about $1\ \text{mm}^2$ spot on the surface of a sample. Spectra were recorded by a spectrograph (Andor SR-303i) equipped with an intensified charge coupled device (Andor DH-501) with spectral resolution up to 1 nm. This detector could be used to acquire time-resolved PL spectra with time-resolution down to 5 ns. Decay curves were recorded with a Hamamatsu H8259-01 photomultiplier operating in photon counting mode with time resolution 100 ns. For measurement of the PL excitation spectra, a 150 W Hamamatsu Xenon lamp was used together with a monochromator (MDR-23, spectral width 2 nm) as the tunable excitation source. The luminous efficacy was measured by quantum integrating sphere.

3. Results and discussion

Figs. 1 and 2 show the excitation and PL spectra of the studied compounds. Following the presented spectra one can see that for the single Er^{3+} dopant there exist sharp excitation peaks within 370–420 nm wavelength range. Addition of Tb^{3+} ions leads to significant decrease of emission efficiencies for the mentioned spectral lines and simultaneously to a drastic enhancement of the spectral line's intensities at wavelengths 250 nm and 280 nm. The triply doped samples give substantially higher ultraviolet excitation and some increase of the blue excitation.

The observed dependences unambiguously indicate an effective transfer of the excitation energy between the studied rare earth ions. An essential requirement for the efficient energy transfer is the close location of interacting energy levels. Fig. 3 shows the energy level diagrams of free Tb^{3+} , Dy^{3+} and Er^{3+} ions. Following this figure, the emitting $^5\text{D}_4$ levels of Tb^{3+} ions are very close to other emitting states: $^4\text{F}_{9/2}$, $^4\text{I}_{15/2}$ manifolds of Dy^{3+} ions and with $^4\text{F}_{7/2}$ level of Er^{3+} ions.

The spectral dependences of the fluorescence at ambient temperature are shown in Fig. 4. For the singly Er^{3+} -doped Gd_2O_3 powders there are three principal groups of the emission lines. The

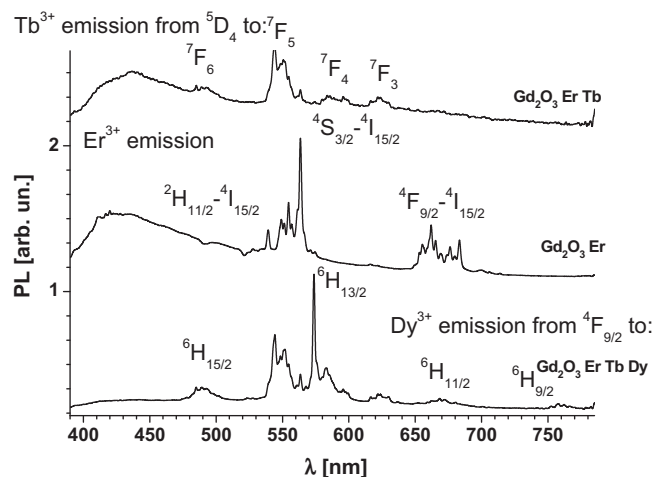


Fig. 2. PL emission spectra of the studied compounds at room temperature.

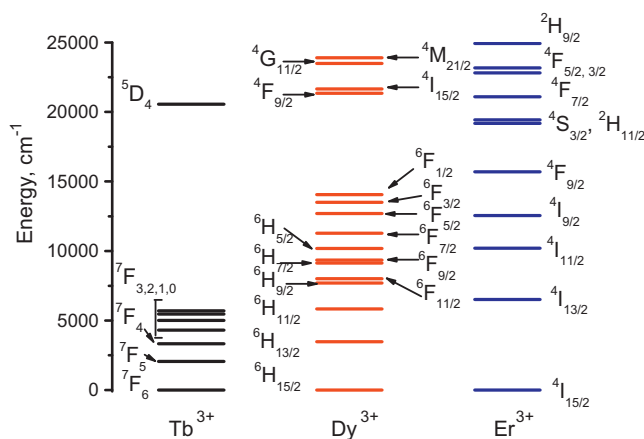


Fig. 3. Energy levels of Tb^{3+} , Dy^{3+} , and Er^{3+} ions.

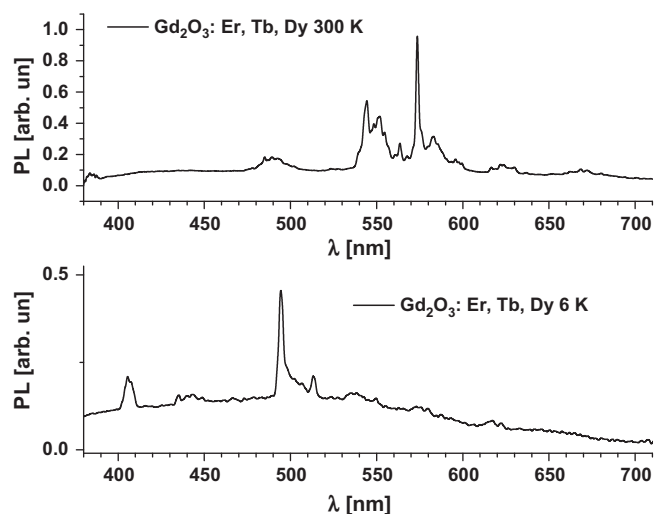


Fig. 4. Temperature dependence of PL emission spectra of $\text{Gd}_2\text{O}_3:\text{Er,Tb,Dy}$.

more prominent – (between 532 nm and 570 nm) corresponds to the $^4\text{S}_{3/2}-^4\text{I}_{15/2}$ emission. The second group of the spectral lines – (between 660 nm and 690 nm) corresponds to the transitions between the $^4\text{F}_{9/2}-^4\text{I}_{15/2}$ manifolds. The spectrally narrow emission lines indicate a long-range ordered environment for the particular rare earth's ions. The more delocalized are the short wavelength

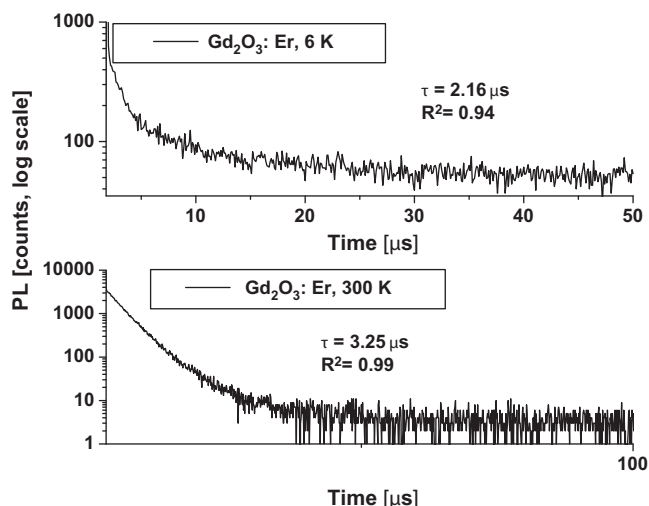


Fig. 5. Temperature dependence of PL decay of $\text{Gd}_2\text{O}_3:\text{Er}$ at 6 K (top, 563 nm) and 300 K (bottom, 550 nm).

spectral emission maxima at 420–500 nm originating from the $^2\text{H}_{11/2}-^4\text{I}_{15/2}$ emission lines.

The addition of Tb^{3+} ions leads to substantial changes of the spectral properties. The first group of emission peaks at 532–750 nm gets now blue shift and there is clear increase of the $^5\text{D}_4-^7\text{F}_5$ Tb^{3+} transition, which correlates well with decrease of the $^5\text{D}_4-^4\text{S}_{3/2}-^4\text{I}_{15/2}$ transition, which may be responsible for the observed energy transfer. Additionally there occur some spectral fluorescent maxima between 620 nm and 660 nm, which originated from the following transitions: $^5\text{D}_4$ to $^7\text{F}_5$ and $^5\text{D}_4$ to $^7\text{F}_4$. So we observe some extension of the spectral emission, however the previous sharp structure is partially lost. Only after addition of the third rare earth ions, i.e. Dy^{3+} we detected substantial increase of the total luminous efficiency, which was equal to 120 lm/W within 400–750 nm spectral range for the triply doped compounds with respect to 23 lm/W and 45 lm/W for one a two- and two-doped polycrystalline powders with sizes within 2–40 μm .

The temperature has a significant influence on behavior of the observed fluorescent spectra (see Fig. 4). One can see that the spectral maxima at 490–600 nm partially disappear and there appear some maxima at 420 nm. This fact may indicate on a principal role of the phonon subsystem and its interaction with the impurity ions' electronic states.

The corresponding decay spectra of fluorescence for the main fluorescence bands are given in Figs. 6–9. One can see that the longer wavelength emission seems to be temperature dependent for the triply doped samples (Figs. 10 and 11). The singly doped sample shows unclear temperature-dependence of luminescence lifetime at 550 nm (the longest at 100 K, similar at 6 and 300 K).

As it can be seen in Figs. 6–10, successive doping causes drastic changes in the luminescence lifetime. In the case of the singly doped sample, the emission can be interpreted as the first order decay, with the R^2 parameter higher than 0.9. As the time resolved spectrum clearly shows (Fig. 8), the emission at 670 nm lasts much longer than at other wavelengths, which is confirmed by decay curves obtained with a photomultiplier (Figs. 5 and 9). The values of τ are equal to 22.5 and 3.25 μs for 670 nm and other wavelengths, respectively.

Successive doping with terbium ions changes the decay kinetics significantly. It can no longer be approximated by the first order exponential decay equation, but it is evidently longer (Fig. 6). In the case of triply doped sample, the PL emission is two orders of magnitude longer than in singly doped sample and reaches 228 μs (Fig. 7). A similar result was obtained from a less accurate method

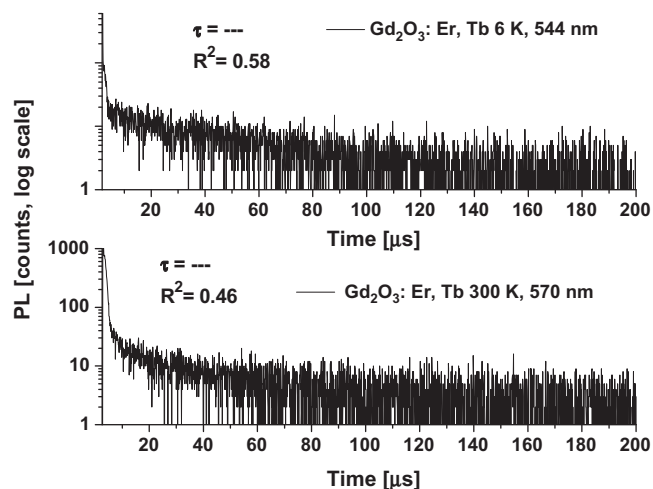


Fig. 6. Temperature dependence of PL decay of $\text{Gd}_2\text{O}_3:\text{Er},\text{Tb}$.

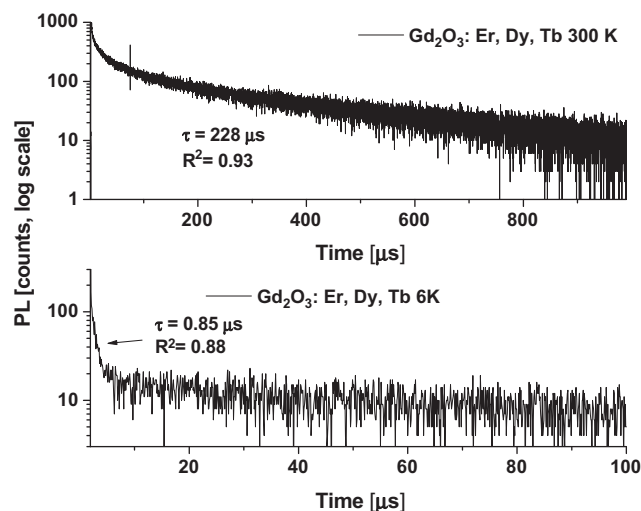


Fig. 7. Temperature dependence of PL decay of $\text{Gd}_2\text{O}_3:\text{Er},\text{Tb},\text{Dy}$ at 550 nm. In the top panel the vertical line is the beginning of the function fitting region. In the bottom panel only the first, quick emission was possible to be properly fitted with exponential function (depicted by arrow).

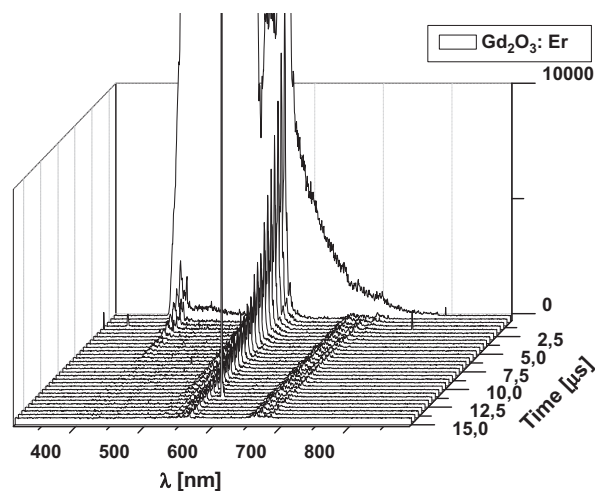


Fig. 8. Time resolved spectrum of $\text{Gd}_2\text{O}_3:\text{Er}$ at room temperature. It can be seen that the lifetime at 660 nm is much longer than that at 570 nm.

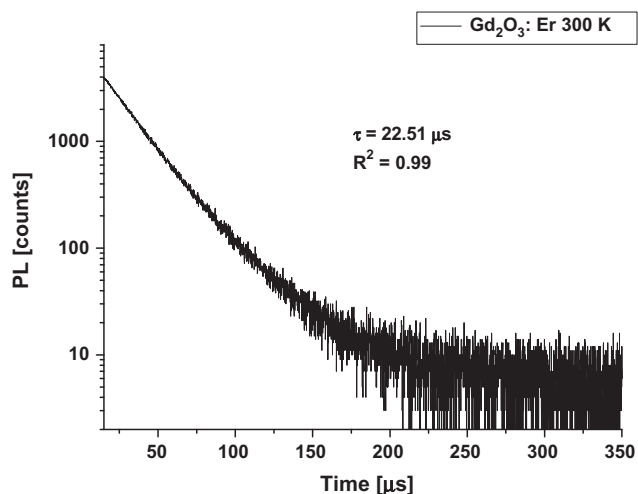


Fig. 9. Gd_2O_3 :Er room temperature PL decay at 660 nm. Time of decay is approximately seven times longer than at 550 nm (Fig. 4).

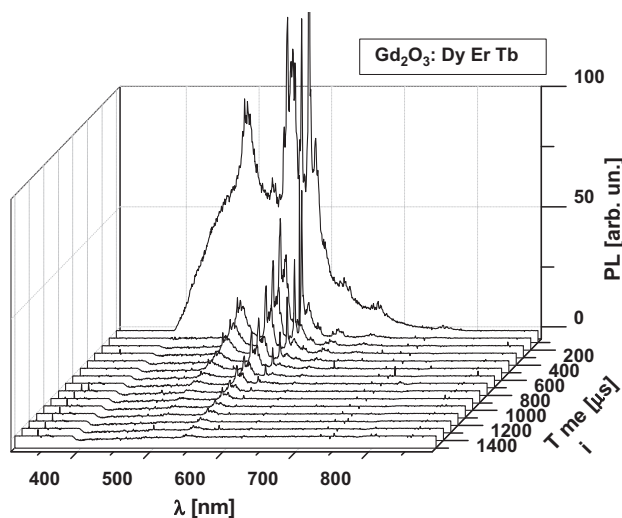


Fig. 10. Time resolved spectrum of Gd_2O_3 :Er, Tb, Dy at room temperature.

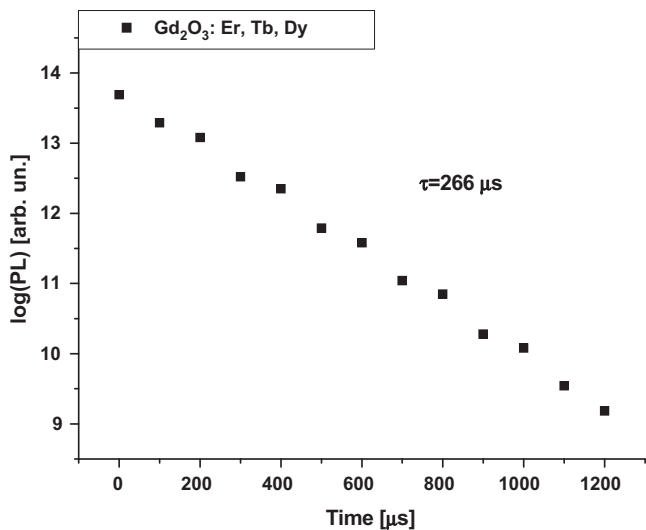


Fig. 11. Time of decay derived from integrations of time resolved spectrum of Gd_2O_3 :Er, Tb, Dy at room temperature, 540–560 nm. This lifetime estimation method is far less accurate than in Fig. 6, but the results are similar.

– time resolved spectra integration (266 μs , Fig. 11). This effect of drastically longer emission, however, is not present at low temperature (Fig. 7), where only a short-lived emission could be fitted with single exponential function, possibly coming from the background emission.

The substantial increase of the emission lifetime of triply doped samples is due to the energy transfer between emitting levels of all three impurities (see Fig. 3). It should be pointed out that in this case the role of the phonon subsystem is very important, since the interacting energy levels are not in the exact resonance, and participation of several host's phonons can effectively eliminate the existing gaps between the electronic levels. Since the number of phonons is decreasing with lowering temperature, it may be expected that such an energy transfer would become less efficient at low temperatures, and, as a direct consequence, the excited state lifetime would become shorter, as it was indeed confirmed by the measurements.

4. Conclusions

In the present work we prepared a series of Gd_2O_3 samples doped with different combinations of trivalent lanthanide ions: (i) Er^{3+} , (ii) Er^{3+} and Tb^{3+} , and (iii) Er^{3+} , Tb^{3+} , Dy^{3+} and performed their spectroscopic studies. The main aim of preparing such a series of samples was to follow the changes of the spectroscopic properties of the studies samples induced by adding another impurity ion. The choice of such a group of dopants was determined by the closeness of emitting levels of these ions, which eventually leads to the energy transfer between these ions and drastic re-distribution of intensities of different emission lines.

For the singly Er^{3+} doped polycrystalline powders there are three principal spectral groups of the emission lines: (i) sharp lines between 532 nm and 570 nm (the $^4\text{S}_{3/2}$ – $^4\text{I}_{15/2}$ transition); (ii) sharp lines between 660 nm and 690 nm (the $^4\text{F}_{9/2}$ – $^4\text{I}_{15/2}$ transition), and (iii) the short wavelength spectral emission maxima at 420–500 nm originating from the $^4\text{H}_{11/2}$ – $^4\text{I}_{15/2}$ transitions. An addition of Tb^{3+} leads to substantial changes in the spectrum. The first group of emission peaks at 532–750 nm shifts to the higher energies; besides, there is an obvious increase of intensity of the $^5\text{D}_4$ – $^7\text{F}_5$ Tb^{3+} transition, which occurs on account of decreasing intensity of the Er^{3+} $^4\text{S}_{3/2}$ – $^4\text{I}_{15/2}$ transition. Additional emission peaks arising from the Tb^{3+} transitions can be also seen in the spectra. After addition of the third rare earth ions, i.e. Dy^{3+} we have received substantial increase of the total luminous efficiency, which was equal to 120 lm/W. It was also shown that the lifetime of the red emission (at 660 nm) is about 10 times longer than that one of other emission transitions.

Successive doping with terbium and dysprosium drastically changes the luminescence decay kinetics. In the case of triply doped sample, the PL lifetime is two orders of magnitude longer than in singly doped sample and reaches 228 μs (Figs. 7 and 11). This effect is not present at lower temperatures (Fig. 7). Such an increase of the excited state life times can be attributed to the phonon-assisted energy transfer between the emitting states of different ions. This effect disappears at low temperatures since there are not enough phonons, which may help in bridging the gap between the electronic states of impurity ions.

The combination of three dopants and the multicolored luminescence obtained in this case may be used for mixing up all emissions to get white light.

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References

- [1] Xianghong He, Mingyun Guan, Chunyong Zhang, Tongming Shang, Ning Lian, Yao Yan, *Journal of Alloys and Compounds* 509 (2011) L341–L343.
- [2] K. Park, M.H. Heo, *Journal of Alloys and Compounds* 509 (2011) 91119115.
- [3] Huaiyong Li, Hyun Kyoung Yang, Byung Kee Moon, Byung Chun Choi, Jung Hyun Jeong, Kiwan Jang, Ho Sueb Lee, Yi Soung Soo, *Journal of Alloys and Compounds* 509 (2011).
- [4] Ch. Srinivasa Rao, I.V. Kityk, T. Srikumar, G. Naga Raju, V. Ravi Kumar, Y. Gandhi, N. Veeraiah, *Journal of Alloys and Compounds* 509 (2011) 9230.
- [5] G. Lakshminarayana, Rong Yang, Mengfei Mao, Jianrong Qiu, I.V. Kityk, *Journal of Non-Crystalline Solids* 355 (2009) 2668–2673.
- [6] S. Nishiura, S. Tanabe, K. Fujioka, Y. Fujimoto, *Optical Materials* 33 (2011) 688.
- [7] S. Nishiura, S. Tanabe, K. Fujioka, Y. Fujimoto, *Optical Materials* 33 (2011) 688–691.
- [8] CHENG. Guang, W.E.I. Xiaoyan, CHENG. Liqun, L.I.U. Quansheng, W.A.N.G. Xiaochun, S.U.N. Haiying, ZHANG. Xiyan, Q.I.U. Guanming, *Rare Metals* 30 (2011) 14.
- [9] G. Lakshminarayana, J. Qiu, M.G. Brik, I.V. Kityk, *Journal of Physics D: Applied Physics* 41 (2008) 175106.
- [10] A. Brenier, I.V. Kityk, *Journal of Applied Physics* 90 (1) (2001) 232–236.
- [11] A. Majchrowski, I.V. Kityk, E. Mandowska, A. Mandowski, J. Ebothe, T. Lukasiewicz, *Journal of Applied Physics* 100 (2006) 053101.
- [12] H. Ryu, B.K. Singh, K.S. Bartwal, M.G. Brik, I.V. Kityk, *Acta Materialia* 56 (2008).
- [13] Y. Dwivedi, Anita Rai, S.B. Rai, *Journal of Applied Physics* 104 (2008) 358–363.
- [14] Hai Guoa, Yunfeng Li, Dianyuan Wang, Weiping Zhang, *Journal of Alloys and Compounds* 376 (2004) 23–27.
- [15] V. Bedekar, D.P. Dutta, M. Mohapatra, S.V. Godbole, R. Ghildiyal, A.K. Tyagi, *Nanotechnology* 20 (12) (2009) 125707.
- [16] L. Macalik, P.E. Tomaszewski, R. Lisiecki, J. Hanuza, *Journal of Solid State Chemistry* 181 (2008) 2591.