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Excitation capture efficiency of $^5D_0$ europium emission level in $Gd_{0.94-x}Eu_xNb_yTa_{1-y}O_4$

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The article is devoted to the study of the excitation capture efficiency of Eu^{3+} emission levels in $Gd_{1-x}Eu_xNb_yTa_{1-y}O_4$ ($x = 0.01-0.4$, $y = 0-1$) solid solutions. On the basis of the luminescence spectra analysis, it was shown that the main phase modification of the studied materials was monoclinic (M-polytype, $I2/a$). The quantitative describe of the excitation capture efficiency for these materials has been obtained for the first time. It was found that for all solid solutions containing Nb the excitation capture efficiency of $^5D_0$ Eu^{3+} level was the same within the measurement error (about $\sim 2500\,\mu m^2 ms^{-1} nA^{-1}$). In gadolinium tantalates the capture efficiency was about 15% higher. This phenomenon was associated with different excitation channels of $^5D_0$ Eu^{3+} level in gadolinium tantalum niobates with various Nb/Ta ratio.

Keywords: Gadolinium tantalum niobates, Eu^{3+}, Cathodoluminescence, Excitation capture efficiency, Ceramic.

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Introduction

Scintillators and phosphors are widely used in various fields, such as science, mining and nuclear industries, and medicine [1,2]. Complex oxides, including those activated by rare-earth ions (REI) [3,4], enjoy great popularity as such materials. In this case, REI act as efficient luminescence centers.

In the development of new promising scintillators and phosphors, an important question is the study of mechanisms for converting high-energy excitation into optical emission. The efficiency of these mechanisms directly affects the key parameter of such materials — luminescence yield. Luminescence intensity depends on the probability of excitation capture by emission levels and the probability of excitation relaxation. It is quite difficult to experimentally separate these two processes. However, a method was previously proposed that allows quantitative assessment of the excitation capture efficiency by radiative levels of luminescence centers [5]. The method is based on determining the dependence of the rise rate of cathodoluminescence (CL) band intensities on excitation power density [6].

Studying the excitation capture efficiency of REI luminescence centers can contribute to the development of new cascade schemes for excitation energy transfer in scintillators or phosphors. For example, in YAG:Tm^{3+},Cr^{3+} and YAG:Eu^{3+} it was shown that sensitizers or defects (grain boundaries) can influence this parameter [5]. Additionally, it has been established that for different excited levels of the same rare-earth ion in YAG:Eu^{3+} the capture efficiency may differ [7].

An interesting question is how the gradual substitution of one element in the complex oxide matrix by another will affect the excitation capture efficiency by REI activators. In other words, how this parameter will change in solid solutions. Gadolinium tantalum niobate solid solutions are well suited for studying such substitution. They are interesting because Nb and Ta in their composition have nearly identical ionic radii [8]. Moreover, these materials exhibit intrinsic luminescence bands associated with NbO_4^{3-} or TaO_4^{3-} groups [9,10], and gadolinium ions can actively participate in excitation energy transfer to activators [11,12].

There are a limited number of studies on REI-activated gadolinium tantalum niobates. Solid solutions activated by Tb^{3+}, were investigated in [13]. However, materials activated by europium are of greater interest. Europium has a rich luminescence spectrum with well-resolved narrow bands, making it suitable as a luminescent probe for studying the local environment [14]. Luminescence spectra and CL decay kinetics in Eu^{3+}, activated gadolinium tantalum niobates were examined in detail in [15]. The influence of the Nb/Ta ratio on the fine structure of CL spectra was also considered [16]. However, the excitation capture efficiency of Eu^{3+} levels in these materials has not been studied previously, and no model of excitation energy transfer in them has been proposed.

The aim of this work was to investigate the efficiency of high-energy excitation capture by the emission levels of Eu^{3+} in gadolinium tantalum niobate solid solutions.

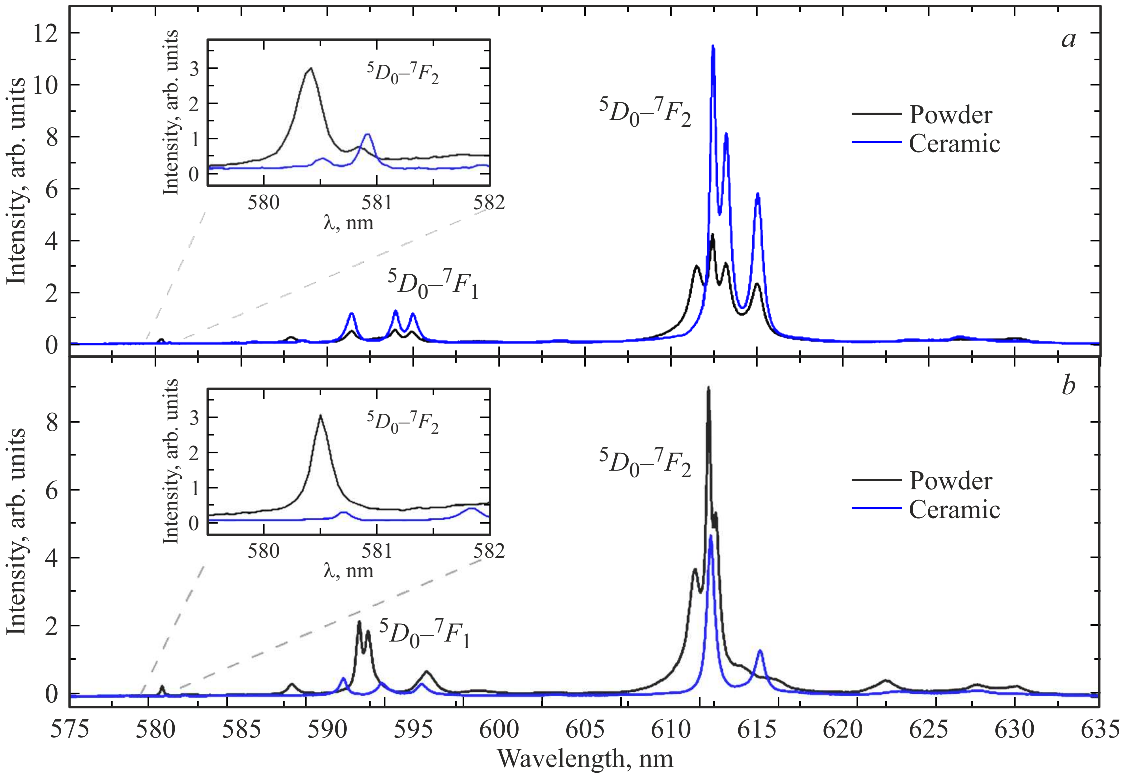

Figure 1. Photoluminescence spectra of powders and ceramics of compositions $(Gd_{0.94}Eu_{0.06})Nb_{0.9}Ta_{0.1}O_4$ (*a*) and $(Gd_{0.94}Eu_{0.06})TaO_4$ (*b*) .

Samples and methods of investigation

A detailed scheme of the coprecipitation method for obtaining europium-activated gadolinium tantalum niobate powders is presented in [17]. The methods for preparing ceramic samples, as well as studies of their elemental and phase compositions and structural parameters, are described in [15,16].

This work investigated the series $(Gd_{1-x}Eu_x)Nb_yTa_{1-y}O_4$ ($x = 0.01-0.4$; $y = 0-1$).

Photoluminescence (PL) spectra at an excitation wavelength of 260 nm, as well as PL excitation spectra, were obtained using a *Fluorolog-3 „Horiba“* spectrofluorimeter (spectral resolution about 0.25 nm).

Cathodoluminescent (CL) properties of the materials were studied on a *Camebax* setup (spectral resolution — 0.1–0.2 nm, temporal resolution — up to 0.3 μs). For measurements, an original-design optical-range spectrometer was used [18]. The accelerating voltage for obtaining CL spectra and kinetic dependencies was 20 kV, absorbed current — 10-50 nA, electron probe diameter — $\sim 2\,\mu$m. CL spectra were measured several times at random points on the sample and averaged.

Kinetic dependencies of Eu^{3+} CL were obtained in the electron beam deflection mode. Several local measurements were performed in random areas of each sample, followed by averaging.

All described studies were carried out at room temperature. The excitation capture efficiency by emission levels was determined based on measuring the dependence of the rise time of the emission band on the primary electron beam current density. The method is based on the assumption that the emitting center can be considered as a two-level system [5]. The main conditions for the applicability of this approximation are strong localization of the excited and ground states and the absence of interaction between excited levels. These requirements are approximately satisfied for Eu^{3+} emission levels in the matrix at low activator concentrations. Within this model, the luminescence intensity is proportional to the content of excited centers. The rate of change in the number of excited centers is determined by two processes: excitation capture and spontaneous deactivation. This process can be described by the following expression [5]:

$$\frac{dn_1}{dt} = LJn_0 - n_1P,$$

where n_0, n_1 — the numbers of excited and unexcited luminescence centers, L — a coefficient proportional to the excitation capture efficiency by the emission level ($m^2s^{-1}A^{-1}$) under electron beam irradiation, J — primary electron beam current density (A/m^2), P — spontaneous transition rate (s^{-1}). In solving the equation, it was taken into account that the sum of excited and unexcited centers equals the total content of luminescence centers

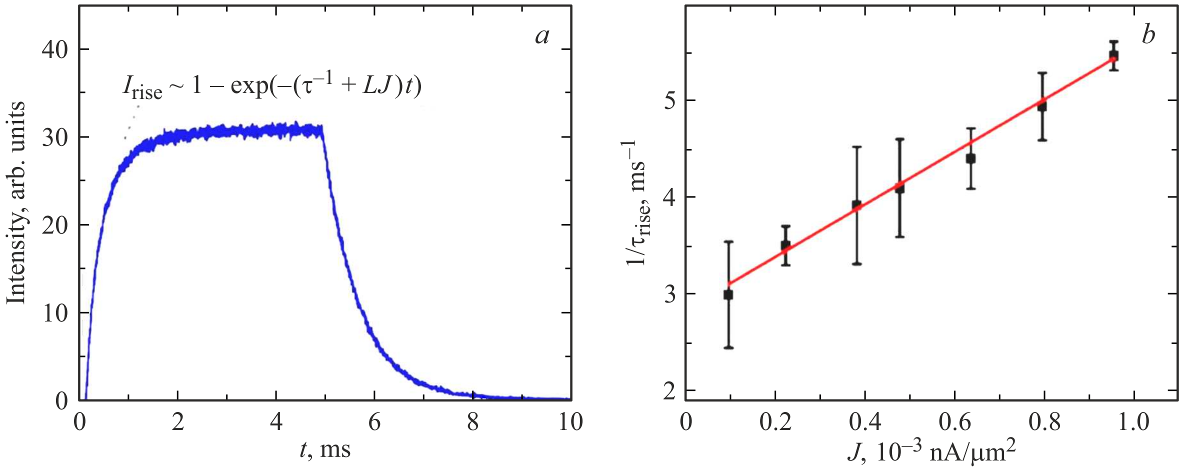

Figure 2. Examples of CL kinetics for the $(Gd_{0.94}Eu_{0.06})NbO_4$ sample (*a*) and the rise rate dependence of $1/\tau_{rise}$ on the primary beam current density J for $(Gd_{0.94}Eu_{0.06})Nb_{0.3}Ta_{0.7}O_4$ (*b*).

$N = n_0 + n_1$. The solution to this equation yields the following dependence of the number of excited centers (CL intensity) from the start of excitation:

$$I \sim n_1 = \frac{LJN\tau^{-1}}{LJ+\tau^{-1}}\big(1-\exp(-(LJ+\tau^{-1})t)\big),$$

where τ — the lifetime of the radiative transition. As seen from the equation, the rise rate $\tau_{\rm rise}^{-1} = LJ + \tau^{-1}$ depends not only on the lifetime of the excited level but also on the primary electron beam current density and the coefficient L. This coefficient indicates the number of excitation acts of luminescence centers per unit time (1 s) at a current density of 1 A/m^2. It allows assessment of the excitation efficiency of the luminescence center for different energy levels of the activator.

Rise times were determined by approximating the obtained kinetic curves with an exponent for the CL intensity rise sections. The excitation capture efficiency L for different REI emission levels in gadolinium tantalum niobates was estimated from the slope of the rise rate dependence $1/\tau_{\rm rise}$ on the primary beam current density J.

For CL measurements, the ceramics were fixed in cassettes using Rose alloy. After that, a thin carbon film was sputtered onto their surfaces using a JEE-4C vacuum universal post to ensure electrical conductivity.

Results and Discussion

Phase composition

For the correct determination of the coefficient L for REI levels in solid solutions, it is necessary to be confident that all samples have the same structural modification. Gadolinium tantalum niobates can have three main phase modifications: high-temperature tetragonal T and two different low-temperature monoclinic — $M\,(I2/a)$ and $M'\,(P2/a)$. It is known that trivalent europium ions can be used as a luminescent probe to study their local environment [14]. For this purpose, PL spectra in the range 575–635 nm were obtained, an example of which is shown in Fig. 1. Their interpretation was performed using literature data [19,20] and the Dieke diagram [21]. The spectra showed only low-energy transitions from the $^5D_0$ level to the $^7F_0$, $^7F_1$ and $^7F_2$ levels. Importantly, the $^5D_0{-}^7F_0$ transition line was also observed, which cannot be resolved in CL spectra due to its overlap with bands belonging to the $^5D_1$ energy level. This transition was of particular interest. The maximum number of Stark splittings for it is 1 [16]. Consequently, the presence of two $^5D_0{-}^7F_0$ transition lines in the PL spectrum should indicate the presence of two different luminescent phases in the material composition. In the spectra of some studied samples, such as the powder and ceramic of $(Gd_{0.94}Eu_{0.06})Nb_{0.9}Ta_{0.1}O_4$ (Fig. 1, *a*) or the ceramic of $(Gd_{0.94}Eu_{0.06})TaO_4$ (Fig. 1, *b*), two $^5D_0{-}^7F_0$ lines were observed. This indicated the presence of luminescent impurity phases in these samples. The observed differences in the $^5D_0{-}^7F_1$ and $^5D_0{-}^7F_2$ bands in the Eu^{3+} PL spectra matched existing literature data related to the M and M' polytypes [22]. They allowed determination of the main phase of europium-activated gadolinium tantalum niobate based on the spectrum shape. The shape of most spectra corresponded to the monoclinic M polytype. Powder samples of the tantalate series $(Gd_{1-x}Eu_x)TaO_4$ exhibited a spectrum shape different from the other samples, corresponding to the M polytype. At the same time, these samples showed only one $^5D_0{-}^7F_0$ transition, indicating the predominance of M' phase luminescence. Additionally, in some powder samples, an extra Eu^{3+} band was observed around 610 nm. It was most likely associated with gadolinium oxide impurity phase luminescence, since the rest of the PL spectrum shape remained unchanged, and two lines related to the $^5D_0{-}^7F_0$ transition were present around 612 nm.

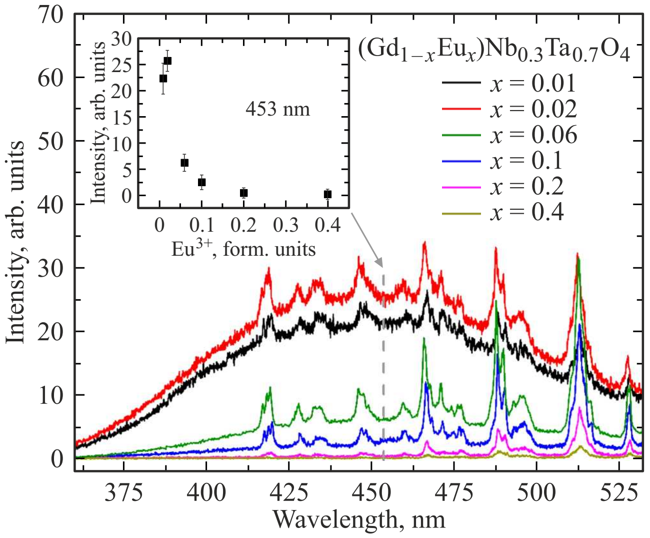

Figure 3. CL spectrum section of the $(Gd_{1-x}Eu_x)Nb_{0.3}Ta_{0.7}O_4$ series with a broad band associated with the NbO_4^{3-} group (inset — dependence of the maximum intensity of the broad band associated with the NbO_4^{3-} group on Eu^{3+} content).

Values of the coefficients L for $(Gd_{0.94}Eu_{0.06})Nb_yTa_{1-y}O_4$ samples with various Nb/Ta ratios

Ceramic sample	L, $\mu m^2 ms^{-1} nA^{-1}$
$(Gd_{0.94}Eu_{0.06})NbO_4$	2300−600
$(Gd_{0.94}Eu_{0.06})Nb_{0.9}Ta_{0.1}O_4$	2300−300
$(Gd_{0.94}Eu_{0.06})Nb_{0.3}Ta_{0.7}O_4$	2700−150
$(Gd_{0.94}Eu_{0.06})TaO_4$	3400±400

The PL data on phase composition obtained agree well with data from X-ray diffraction phase analysis (XRD) [15]. Thus, it was confirmed that the studied ceramic $(Gd_{1-x}Eu_x)Nb_yTa_{1-y}O_4$ samples have the same main phase modification — the M polytype with space group $I2/a$.

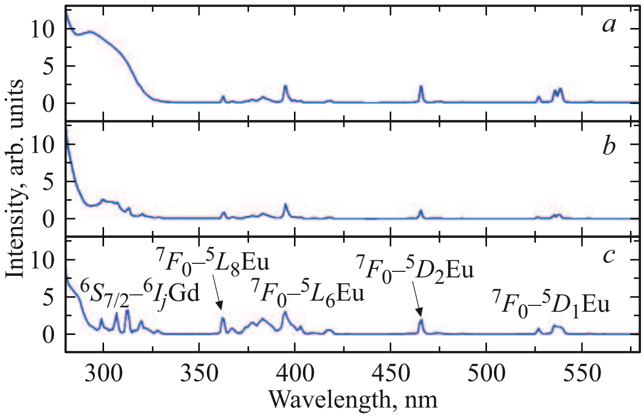

Figure 4. Excitation spectra (for the 612 nm band) $(Gd_{0.94}Eu_{0.06})NbO_4$ (a), $(Gd_{0.94}Eu_{0.06})Nb_{0.9}Ta_{0.1}O_4$ (b) and $(Gd_{0.94}Eu_{0.06})TaO_4$ (c).

Excitation capture efficiency

CL spectra of $(Gd_{1-x}Eu_x)Nb_yTa_{1-y}O_4$ were studied in detail in [15,16]. These spectra showed not only transitions from the $^5D_0$ level but also higher-energy transitions from the $^5D_1$, $^5D_2$ and $^5D_3$ levels. For the emission band corresponding to the most intense $^5D_0$–$^7F_2$ Eu^{3+} transition in the ceramic series $(Gd_{0.94}Eu_{0.06})Nb_yTa_{1-y}O_4$ the excitation capture efficiency was evaluated for ceramic samples with various Nb/Ta ratios. Importantly, the excitation capture efficiency by the activator's emission level does not depend on the activator concentration [7]. For each sample, kinetic dependencies of the $^5D_0$–$^7F_2$ Eu^{3+} CL band were obtained (Fig. 2, a). After processing, dependencies of the inverse CL intensity rise time from the start of excitation on the primary electron beam current density in the range 10^{-4}–10^{-3} nA/μm^2 were derived. The experimental inverse rise time dependencies on current density for all measured samples were linear (Fig. 2, b). The L coefficients — excitation capture efficiencies — were obtained from their slopes. Values for samples with various Nb/Ta ratios are presented in the table.

From the obtained results, it can be concluded that for all compositions containing Nb, the excitation capture efficiency of the $^5D_0$ Eu^{3+} level is the same ($L \sim 2500\,\mu m^2 ms^{-1} nA^{-1}$) within the measurement error. For gadolinium tantalate, the capture efficiency is higher by $\sim 15\%$.

The difference in the $^5D_0$ Eu^{3+} level excitation capture efficiencies in $(Gd_{0.94}Eu_{0.06})Nb_yTa_{1-y}O_4$ at $y = 0$ and all other solid solution compositions could be related to different excitation energy transfer channels to the activator. In [5], it was shown that the presence of a sensitizer for the emitting center can increase the capture efficiency of its emission levels. CL spectra in the range 350–530 nm were obtained to study the behavior of the broad intrinsic luminescence band in $(Gd_{1-x}Eu_x)Nb_yTa_{1-y}O_4$. For materials containing Nb and Eu^{3+} at concentrations up to 0.2 form. un., a broad intrinsic luminescence band in the 350–550 nm range with a maximum intensity around 450 nm was observed (example for the $(Gd_{1-x}Eu_x)Nb_{0.3}Ta_{0.7}O_4$ series — Fig. 3). NbO_4^{3-} groups responsible for this band can participate in excitation energy transfer to the REI activator [12]. This process was indirectly confirmed by the obtained dependencies of the broad band maximum intensity on Eu^{3+} content (inset in Fig. 3). As europium concentration increased, the broad band intensity decreased. It is also known that the higher the Ta content in the solid solution, the weaker the intrinsic luminescence of the NbO_4^{3-}group [8]. In the gadolinium tantalate series $(Gd_{1-x}Eu_x)TaO_4$, bands related to TaO_4^{3-} groups were not observed even at low activator ion concentrations. This could be due to more efficient excitation energy transfer from TaO_4^{3-} groups to Gd^{3+}

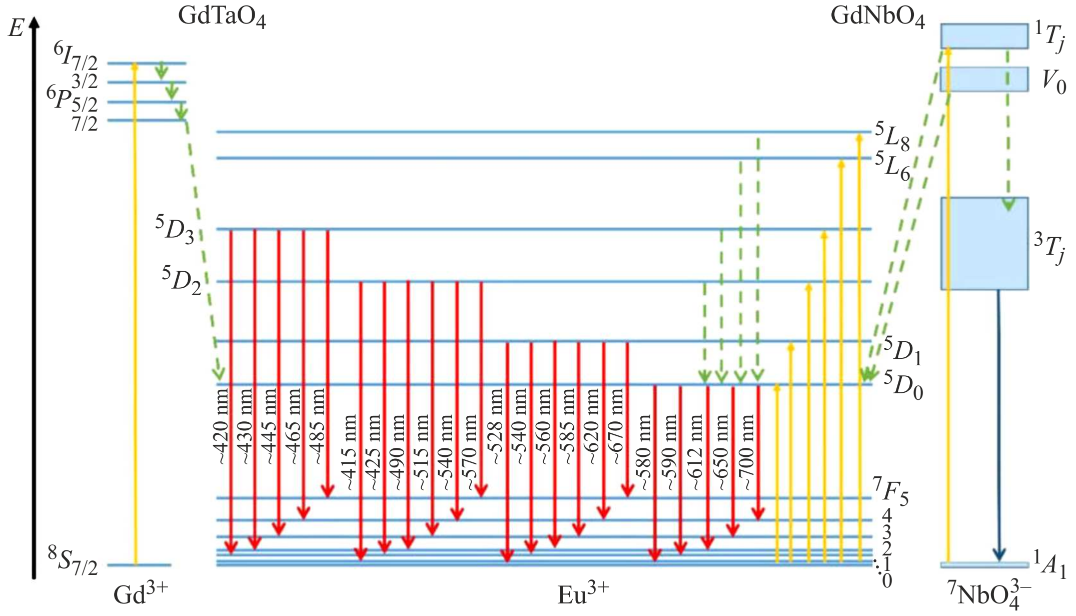

Figure 5. Scheme of excitation energy transfer between various energy levels for $(Gd_{1-x}Eu_x)Nb_yTa_{1-y}O_4$.

atoms in gadolinium tantalates [22] and thermal quenching. Apparently, these processes in gadolinium tantalate ensure more efficient excitation energy transfer to Eu^{3+}.

For a more detailed study of the ^{5}D$_0$ Eu^{3+} excitation channels, excitation spectra for the 612 nm band were obtained (Fig. 4). The lines corresponding to energy transitions in the excitation spectra were interpreted using literature data [20,23]. It is evident that for all studied samples, $^5D_0$ Eu^{3+} level excitation occurred from the $^5D_1$, $^5D_2$, $^5L_6$ and $^5L_8$ Eu^{3+} levels. However, in the 280−330 nm region, the spectra shapes differed significantly. For gadolinium tantalate, capture actively occurred from Gd^{3+} levels in this region. For gadolinium niobate, these levels were not observed, and a broad band associated with oxygen vacancies appeared in the 280−330 nm region [23]. The intensity of this broad band decreased significantly as soon as Ta was added to the composition. Intermediate solid solutions exhibited mixed excitation channels, but gadolinium-related bands were less pronounced than in $(Gd_{0.94}Eu_{0.06})TaO_4$.

It can be assumed that more active energy transfer from gadolinium to the activator in gadolinium tantalates accounts for the higher excitation capture efficiency of the $^5D_0$ Eu^{3+} level in this material.

Thus, although the $^5D_0$ level excitation channels for gadolinium niobates and tantalates are well studied, quantitative investigation of the excitation capture efficiency through these channels was conducted for the first time.

The excitation transfer model for $(Gd_{1-x}Eu_x)Nb_yTa_{1-y}O_4$ based on experimental data and incorporating CL data from [15], is presented in Fig. 5. The scheme shows that $^5D_0$ Eu^{3+} level excitation occurs via gadolinium ions (for GdTaO$_4$), oxygen vacancy levels, and NbO$_4^{3-}$ group luminescence levels (for GdNbO$_4$). The position of oxygen vacancy levels is highly uncertain. Determining their more precise position requires further studies.

Conclusions

Samples of $(Gd_{1-x}Eu_x)Nb_yTa_{1-y}O_4$ were investigated. ($x = 0.01, 0.02, 0.06, 0.1, 0.2, 0.4$; $y = 0, 0.3, 0.9, 1$).

Based on photoluminescence spectrum analysis, it was confirmed that the main structural modification of the ceramic samples is the monoclinic modification with space group $I2/a$ (M-polytype).

For materials containing Nb and Eu^{3+} at concentrations up to 0.2 form. units, a broad intrinsic luminescence band associated with NbO$_4^{3-}$ groups was observed. As europium concentration increased, the intensity of this band decreased. This indirectly confirmed excitation energy transfer from NbO$_4^{3-}$ groups to Eu^{3+}.

A quantitative description of the excitation capture efficiency for the ^{5}D$_0$ Eu^{3+} level in $(Gd_{1-x}Eu_x)Nb_yTa_{1-y}O_4$ was obtained for the first time. For all samples containing Nb, the $^5D_0$ Eu^{3+} level excitation capture efficiency was the same ($L \sim 2500\,\mu m^2 ms^{-1} nA^{-1}$) within the measurement error. For gadolinium tantalate, the capture efficiency was higher by $\sim 15\%$.

The difference in the $^5D_0$ Eu^{3+} level excitation capture efficiencies in $(Gd_{0.94}Eu_{0.06})Nb_yTa_{1-y}O_4$ at $y = 0$ and all other solid solution compositions could be related to different excitation energy transfer channels to the activator. This was demonstrated based on analysis of the excitation spectra of the same samples.

The results of this work can aid in understanding excitation energy transfer mechanisms in solid solutions. Such studies may be useful in developing new efficient phosphors and scintillators.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J. Li, X. Chen, M. Nikl, Scintillators, *Processing of Ceramics: Breakthroughs in Optical Materials*, ed. by A. Ikesue (The American Ceramic Society, 2021). DOI: 10.1002/9781119538806.ch3
[2] P. Lecoq, A. Gektin, M. Korzhik. *Inorganic Scintillators for Detector Systems: Physical Principles and Crystal Engineering*, second ed. (Springer, Switzerland, 2017). DOI: 10.1007/978-3-319-45522-8
[3] M. Nikl, V.V. Laguta, A. Vedda, Phys. Status Solidi B., **245**, 1701 (2008). DOI: 10.1002/pssb.200844039
[4] V. Kumar, Z. Luo, Photonics., **8**, 71 (2021). DOI: 10.3390/photonics8030071
[5] M.V. Zamoryanskaya, K.N. Orekhova, E.V. Dementeva, V.A. Kravets, G.A. Gusev, J. Lumin., **239**, 118350 (2021). DOI: 10.1016/j.jlumin.2021.118350
[6] A.N. Trofimov, M.V. Zamoryanskaya, J. Surf. Invest., **3**, 15 (2009). DOI: 10.1134/S1027451009010030.
[7] G.A. Gusev, K.N. Orekhova, V.A. Kravets, A.I. Isakov, A.N. Trofimov, M.V. Zamoryanskaya, J. Lumin., **222**, 117084 (2020). DOI: 10.1016/j.jlumin.2020.117084
[8] O.V. Voloshyna, I.A. Boiaryntseva, V.N. Baumer, A.I. Ivanov, M.V. Korjik, O.T. Sidletskiy. Nucl. Instrum. Methods Phys. Res., Sect. A., **764**, 227 (2014). DOI: 10.1016/j.nima.2014.07.044
[9] O. Voloshyna, S.V. Neicheva, N.G. Starzhinskiy, I.M. Zenya, S.S. Gridin, V.N. Baumer, O.T. Sidletskiy, Mater. Sci. Eng. B., **178**, 1491 (2013). DOI: 10.1016/j.mseb.2013.08.003
[10] H. Brunckova, H. Kolev, L.A. Rocha, E.J. Nassar, S.B. Moscardini, L. Medvecky, Appl. Surf. Sci., **504**, 144358 (2020). DOI: 10.1016/j.apsusc.2019.144358
[11] S.K. Lee, H. Chang, C.H. Han, H.J. Kim, H.G. Jang, H.D. Park, J. Solid State Chem., **156**, 267 (2001). DOI: 10.1006/jssc.2000.8941
[12] M.V. Nazarov, D.Y. Jeon, J.H. Kang, E.J. Popovici, L.E. Muresan, M.V. Zamoryanskaya, B.S. Tsukerblat, Solid State Commun., **131**, 307 (2004). DOI: 10.1016/j.ssc.2004.05.025
[13] G.A. Gusev, S.M. Masloboeva, M.A. Yagovkina, M.V. Zamoryanskaya, Opt. Spectrosc., **130**, 265 (2022). DOI: 10.21883/EOS.2022.02.53221.2759-21
[14] S.W. Wi, J.W. Seo, Y.S. Lee, J.-S. Chung, Ceram. Int., **49**, 19766 (2023). DOI: 10.1016/j.ceramint.2023.03.094
[15] G.A. Gusev, S.M. Masloboeva, M.A. Yagovkina, T.B. Popova, M.V. Zamoryanskaya, Ceram. Int., **49**, 30403 (2023). DOI: 10.1016/j.ceramint.2023.06.302
[16] G.A. Gusev, S.M. Masloboeva, T.B. Popova, M.A. Yagovkina, M.V. Zamoryanskaya, J. Lumin., **252**, 119281 (2022). DOI: 10.1016/j.jlumin.2022.119281
[17] G.A. Gusev, S.M. Masloboeva, V.A. Kravets, M.A. Yagovkina, Inorg. Mater., **57**, 383 (2021). DOI: 10.1134/S0020168521040063
[18] M.V. Zamoryanskaya, S.G. Konnikov, A.N. Zamoryanskii, Instrum. Exp. Tech., **47**, 477 (2004).
[19] B. Liu, M. Gu, X. Liu, K. Han, S. Huang, C. Ni, G. Zhang, Z. Qi, Appl. Phys. Lett., **94**, 061906 (2009). DOI: 10.1063/1.3079413
[20] K. Binnemans, Coord. Chem. Rev., **295**, 1 (2015). DOI: 10.1016/j.ccr.2015.02.015
[21] P.S. Peijzel, A. Meijerink, R.T. Wegh, M.F. Reid, G.W. Burdick, J. Solid State Chem., **178**, 448 (2005). DOI: 10.1016/j.jssc.2004.07.046
[22] B. Li, Z. Gu, J. Lin, M.-Z. Su, Mater. Res. Bull., **35**, 1921 (2000). DOI: 10.1016/S0025-5408(00)00404-9
[23] O. Voloshyna, O. Sidletskiy, D. Spassky, I. Gerasymov, I. Romet, A. Belsky, Opt. Mater., **76**, 382 (2018). DOI: 10.1016/j.optmat.2018.01.003

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