

# Recombination emission and the formation of combined electron-emitting states in garnets $Y_3Al_5O_{12}$ and $Y_3Al_5O_{12}:Dy$

T.N. Nurakhmetov<sup>1</sup>, T.T. Alibay<sup>\*,1</sup>, A.S. Nurpeissov<sup>1</sup>, S. Pazylbek<sup>2</sup>,  
A. Zarkov<sup>3</sup>, A. Kareiva<sup>3</sup>, A. Shakhantayeva<sup>1</sup>,  
B. Shaizada<sup>1</sup>, A. Idanova<sup>1</sup>, O. Shalkhar<sup>3</sup>

<sup>1</sup>Institute of Physical and Technical Sciences, L.N. Gumilyov Eurasian National University, Astana, Kazakhstan

<sup>2</sup>Faculty of IT and Natural Sciences, Tashenev University, Shymkent, Kazakhstan

<sup>3</sup>Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Vilnius, Lithuania

E-mail: alibai\_tt\_3@enu.kz

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In Dy-doped  $Y_3Al_5O_{12}$  garnets exposed to UV photons near the fundamental absorption region, the formation of composite electron–radiative states arising from both intrinsic and impurity-related electron–hole trapping centers has been studied. Under exposure with photons of 6.2 eV and 5.64 eV at 77 K, a new recombination emission in  $Y_3Al_5O_{12}-Dy$  has been observed for the first time at 3.05 eV and 2.92 eV, which is excited by photon energies of 3.85 eV and 4.45 eV at 77 K. On the basis of the obtained experimental data, it is assumed that during UV irradiation near the fundamental spectral region of the matrix, transfer of charge from oxygen in the  $Al_5O_{12}$  anionic complex of the valence band to a neighboring anion leads to the formation of intrinsic electron trapping centers  $(Al_5O_{12})^{3-} + e^- \rightarrow (Al_5O_{12})^{4-}$ ; in a similar way, impurity electron trapping centers are formed:  $Dy^{3+} + e^- \rightarrow Dy^{2+}$ . The intrinsic and impurity electron trapping centers form combined electron–radiative local states below the conduction band. As the combined electron–radiative state decays, ionization of both intrinsic and impurity-related electron traps occurs. The released electrons then recombine with hole trapping centers  $(Al_2O_7)^{2-}$  located near the ground state of  $Dy^{3+}$  ions. This process can lead to exciton formation, and the energy released during recombination is either transferred to the  $Dy^{3+}$  impurities or emitted as recombination radiation with energies of 3.05 eV and 2.92 eV.

**Keywords:** electron-hole; luminescent materials; emission; phosphate; combined electron state; radiation.

## Introduction

In pure and rare-earth-doped yttrium aluminum garnets  $Y_3Al_5O_{12}$ , the nature of recombination luminescence and electron–hole trapping centers has been investigated, which underlies their use in various applications such as lasers, scintillators, cathode-ray tubes, field-emission displays, plasma panels, and optical windows owing to their attractive optical properties.

The authors of [1] showed that in undoped single-crystalline  $Y_3Al_5O_{12}$  (YAG) and  $Lu_3Al_5O_{12}$  (LuAG) films, the emission is predominantly due to self-trapped excitons (STE) in the undisturbed garnet lattice, whereas in YAG and LuAG single crystals the radiative decay of exciton-like systems occurs in the vicinity of antisite defects in the form of localized excitons and via electron–hole recombination directly at antisite defect centers in  $Y_3Al_5O_{12}$  and  $Lu_3Al_5O_{12}$ .

Based on the obtained results of studies on  $Y_3Al_5O_{12}$  and  $Lu_3Al_5O_{12}$  garnets doped with  $Bi^{3+}$  ions, the authors of [2–5] proposed that under UV excitation the following processes occur in these oxides: electronic transitions from the ground state of the  $Bi^{3+}$  ion to its triplet excited state in the matrix lead to the formation of a  $Bi^{4+}$  hole center and an electron. During relaxation, the hole may delocalize from the  $Bi^{4+}$  ion onto a neighboring oxygen ion  $O^{2-}$ . As a result, two types of short-lived hole centers associated with  $Bi^{3+}$  may arise:  $Bi^{4+}$  and  $(O^- - Bi^{3+})$ . Recombination of an electron from the excited state of  $Bi^{3+}$  with these hole centers gives rise to UV or visible recombination luminescence. Recombination of electrons and holes in the vicinity of the  $Bi^{3+}$  ion leads to exciton-like visible emission.

Similar results concerning the nature of the intra-center  $Bi^{3+}$  emission and the visible exciton-like emission in the vicinity of the  $Bi^{3+}$  ion were obtained in [6–10] for the phosphors  $CdAlO_3 - Bi$ ,  $Y_3Al_5O_{12} - Bi$ ,  $Cd_3Ca_5O_{12} - Bi$ ,  $Lu_3Ca_5O_{12} - Bi$ .

In [11–14], it was shown that, in irradiated  $Lu_3NbO_4 - Bi, Eu$  phosphors, the emission of  $Bi^{3+}$  ions overlaps with the absorption bands of  $Eu^{3+}$  ions, which in turn indicates the possibility of energy transfer from the corresponding  $ex^0Bi^{3+} \rightarrow$  luminescence centers to the  ${}^5D_{0,1,2}$  and  ${}^5D_4$  levels of  $Eu^{3+}$  ions.

A long-persistent phosphor based on  $Y_3Al_5O_{12}Cr^{3+}$  garnet was proposed by the authors of [15] as a promising material for imaging. It was shown that the afterglow (TSL) can be efficiently stimulated by near-infrared light.

In [16], the properties of  $Y_3Al_5O_{12}$  and  $Y_3Cr_5O_{12}$  doped with  $Eu^{3+}$  were investigated. In the excitation spectra, after complete substitution of  $Al^{3+}$  by  $Cr^{3+}$ , a red shift of the charge-transfer band is observed. The optimal  $Eu^{3+}$  concentrations at which the highest intensity of red emission is achieved were found to be 3% and 11%, respectively. It is assumed that YAG-based phosphors may be more suitable for use with UV chips to obtain pure red light.

In [17–18], the transfer of electronic excitation energy from the host lattice to impurity ions in sulfates and phosphors doped with rare-earth and transition metals was examined under irradiation in the fundamental absorption region. This process was interpreted in terms of the formation of combined electron–radiative states involving both intrinsic and impurity-related trapping centers

situated below the conduction band of the matrix.

Previous studies have shown that electron–hole trapping centers play a crucial role in mediating energy transfer from the phosphor host to activator ions.

The present work focuses on studying energy transfer from the  $Y_3Al_5O_{12}$  garnet matrix to rare-earth ions through the formation of electron–hole trapping centers under UV excitation in the fundamental spectral region.

## Materials and methods

### Synthesis procedure

$Y_3Al_5O_{12}$ :Dy samples with a specified concentration of rare-earth ions were prepared using an aqueous sol–gel method described in [18]. Stoichiometric amounts of analytical-grade  $Y_2O_3$  and  $Al(NO_3)_3 \cdot 9H_2O$  were used as precursors. During the synthesis, yttrium oxide was initially dissolved in 0.2 M  $CH_3COOH$  at 65–70 °C. The mixture was then stirred for 12 hours in a beaker covered with a watch glass until a transparent solution was formed.

For the synthesis of Dy-doped  $Y_3Al_5O_{12}$ , an aqueous Dy solution was introduced into the prepared mixture. Subsequently, 1,2-ethanediol (2 mL) was added as a complexing agent. As the solution was gradually concentrated by slow evaporation at 80 °C under continuous stirring, the acetate–nitrate–glycolate Y(Dy)–Al–O sol evolved into a clear, transparent gel.

The gels were dried at 120 °C, after which the resulting powders were finely ground in an agate mortar and preheated in air at 800 °C for 3 hours. Following intermediate regrinding and granulation, the samples were further sintered in air at 1000 °C for 5 hours.

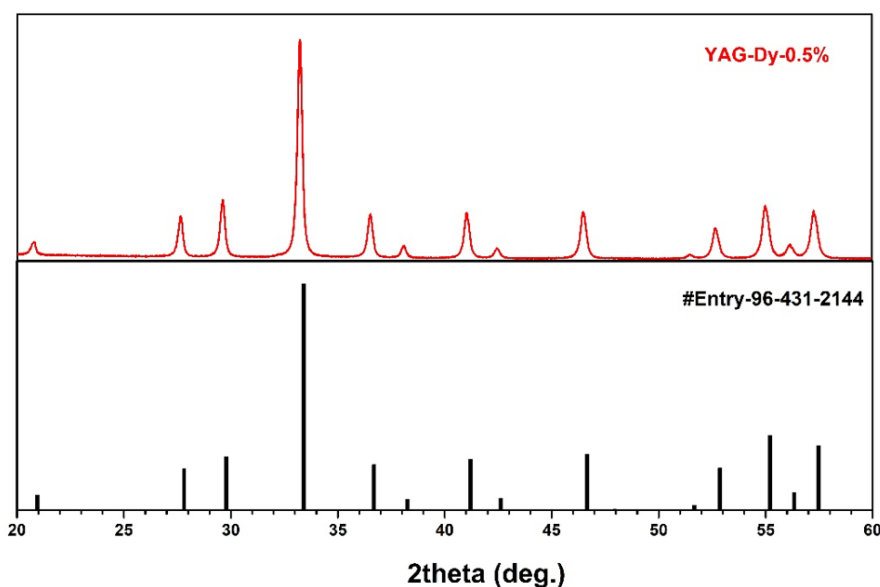


Figure 1. Powder XRD pattern of YAG:Dy compared with the reference pattern of  $Y_3Al_5O_{12}$  (bottom, PDF #96-431-2144). The complete agreement of the peaks confirms single-phase cubic YAG.

Powder X-ray diffraction was carried out on a diffractometer in  $\theta$ – $2\theta$  geometry with  $CuK\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), with a scanning step of  $0.02^\circ$  and

a counting time of 1–2 s per point, in the  $2\theta$  range of  $20\text{--}60^\circ$ . The diffraction pattern obtained for the YAG:Dy sample (Figure 1) fully corresponds, in terms of peak positions and relative intensities, to the reference pattern of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (PDF #96-431-2144). The absence of additional peaks (within the noise level) indicates phase purity, and the observed narrow reflections point to a high degree of crystallinity. Consequently,  $\text{Dy}^{3+}$  ion substitution does not alter the cubic garnet structure.

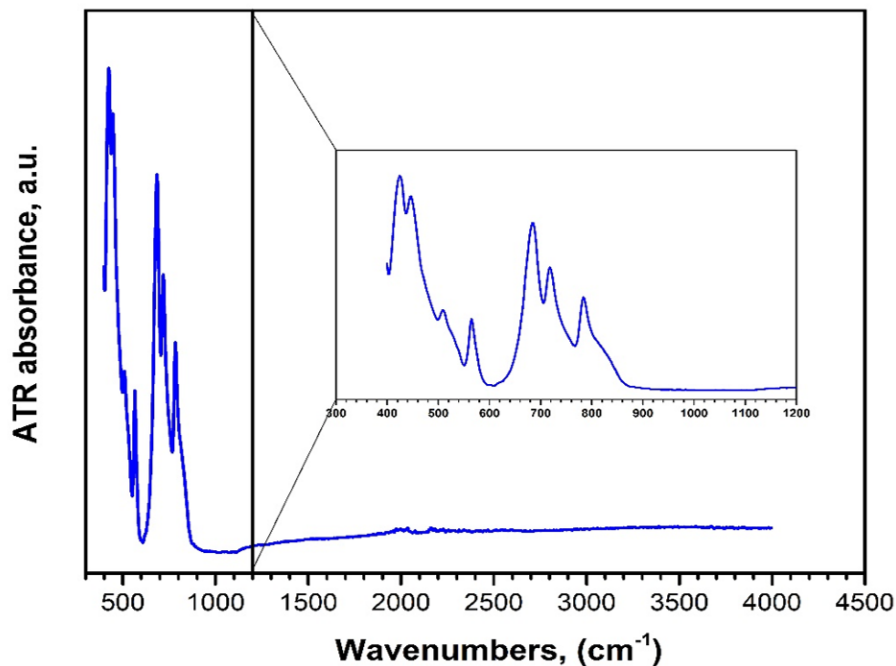


Figure 2. ATR-FTIR spectrum of  $\text{Y}_3\text{Al}_5\text{O}_{12}$ .

The ATR-FTIR spectrum of  $\text{Y}_3\text{Al}_5\text{O}_{12}$  in the range  $300\text{--}4500\text{ cm}^{-1}$  shows only weak intensity above  $1500\text{ cm}^{-1}$  and does not contain characteristic bands of organic impurities ( $\text{O-H}$   $3200\text{--}3600\text{ cm}^{-1}$ ,  $\text{C-H}$   $2850\text{--}2960\text{ cm}^{-1}$ ,  $\text{C=O}$   $\sim 1700\text{ cm}^{-1}$ ). The spectrum is governed by lattice vibrations in the  $350\text{--}900\text{ cm}^{-1}$  region: the bands at  $\sim 380\text{--}450\text{ cm}^{-1}$  are assigned to  $\text{Y-O}$  vibrations (dodecahedral sites), the intense bands at  $\sim 520\text{--}650\text{ cm}^{-1}$  to  $\text{Al-O}$  modes of  $\text{AlO}_6$  octahedra, and the high-frequency bands at  $\sim 680\text{--}820\text{ cm}^{-1}$  to  $\text{Al-O}$  stretching vibrations of  $\text{AlO}_4$  tetrahedra. Substitution of  $\text{Y}^{3+}$  by  $\text{Dy}^{3+}$  ions does not lead to the appearance of new vibrational modes and causes only small shifts in the band positions ( $< 5\text{--}10\text{ cm}^{-1}$ ), which is consistent with the preservation of the YAG structure and a low content of residual organic components.

Summary of band assignments:

$\sim 380\text{--}450\text{ cm}^{-1}$  —  $\text{Y-O}$  (dodecahedral sites).

$\sim 520\text{--}650\text{ cm}^{-1}$  —  $\text{Al-O}$ :  $\text{AlO}_6$  octahedra, bending/stretching modes.

$\sim 680\text{--}820\text{ cm}^{-1}$  —  $\text{Al-O}$ :  $\text{AlO}_4$  tetrahedra, stretching modes.

Absent bands:  $\sim 1630$  and  $3200\text{--}3600\text{ cm}^{-1}$  ( $\text{H-O-H}$ ,  $\text{O-H}$ ),  $1400\text{--}1500$  and  $\sim 870\text{ cm}^{-1}$  ( $\text{CO}_3^{2-}$ ),  $2850\text{--}2960\text{ cm}^{-1}$  ( $\text{C-H}$ ).

## Results

First, the mechanism of formation of electron–hole trapping centers was investigated in undoped  $Y_3Al_5O_{12}$  garnet. Figure 3 presents the emission spectra of  $Y_3Al_5O_{12}$  under irradiation with 5.9 eV photons at 300 K (curve 1) and 77 K (curve 2). As shown in the figure, additional recombination emission bands emerge at 3.05 eV and 2.92 eV.

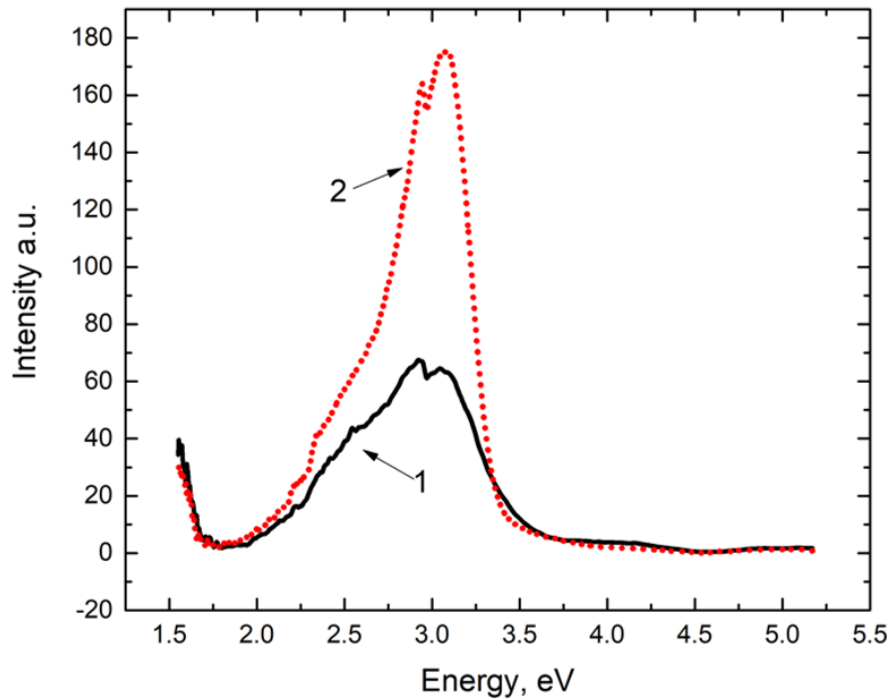


Figure 3. Emission spectrum of undoped  $Y_3Al_5O_{12}$  garnet at temperature: curve 1 – 300 K; curve 2 – 77 K.

At the next stage, the excitation spectra of the newly observed emission bands were recorded: for the 3.05 eV band (curve 1 at 300 K and curve 2 at 77 K) and for the 2.92 eV band (curve 3 at 300 K and curve 4 at 77 K), as presented in Figure 4. The results show that these recombination emission bands are excited by photons with energies of 3.9 eV and 4.45 eV, which lie within the transparency region of the host matrix.

To confirm that these bands are associated with the absorption and excitation of recombination emission in the garnet with induced trapping centers, the samples were additionally irradiated with photons of 3.9 eV and 4.45 eV. As shown in Figure 5, the recombination emission bands at 3.05 eV and 2.92 eV reappear under such excitation.

In line with the objectives of this work, we investigated  $Y_3Al_5O_{12}$  garnets activated with  $Dy^{3+}$  ions for the formation of combined electron–radiative states consisting of electronic trapping centers of the host matrix and impurity ions.

The  $Y_3Al_5O_{12} - Dy^{3+}$  phosphor was exposed to radiation of 6.2 eV and 5.64 eV at 300 K and 77 K (Figure 6: curves 1 and 3; 2 and 4, respectively). As can be seen from Figure 6, intra-center emissions of the  $Dy^{3+}$  impurity appear at 2.16 eV and 2.56 eV, associated with 4f–4f electronic transitions of the rare-earth  $Dy^{3+}$  ion in the matrix. In addition to the intra-center emission, new recombination emission

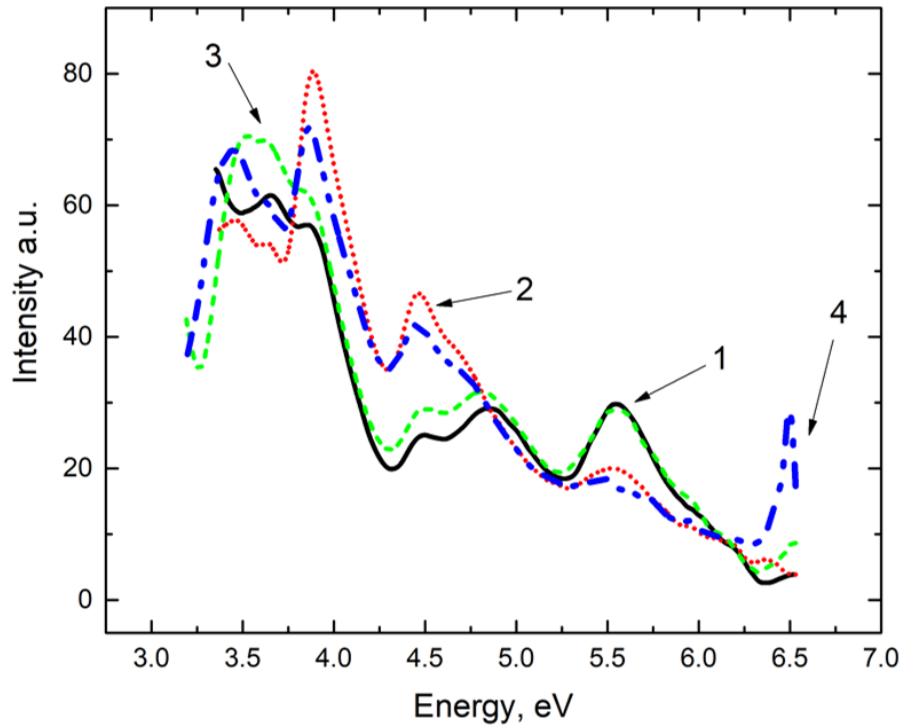


Figure 4. Excitation spectrum of undoped  $Y_3Al_5O_{12}$  garnet: curve 1 – for the 3.05 eV emission band at 300 K; curve 2 – for the 3.05 eV emission band at 77 K; curve 3 – for the 2.92 eV emission band at 300 K; curve 4 – for the 2.92 eV emission band at 77 K.

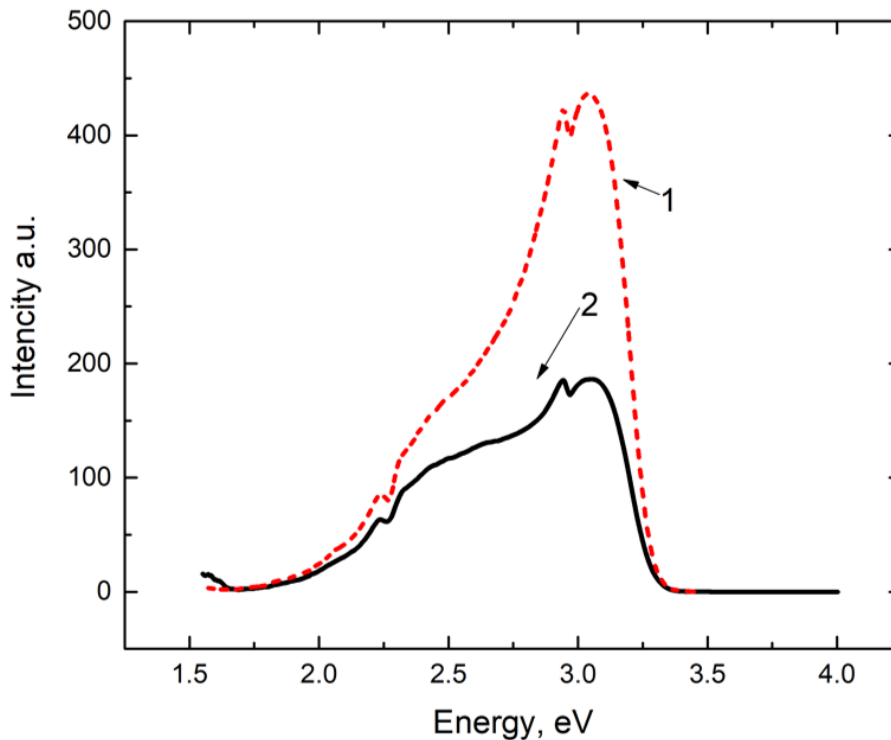


Figure 5. Emission spectrum of undoped  $Y_3Al_5O_{12}$  garnet at temperature: curve 1 – 77 K; curve 2 – 300 K.

bands arise at 3.05 eV and 2.92 eV (Figure 6, curves 1–4). The intensity of these new recombination bands at 77 K is twice as high as at 300 K.

Measurements of the excitation spectra of the newly observed recombination emissions at 3.05 eV and 2.92 eV indicate that these bands are excited within the

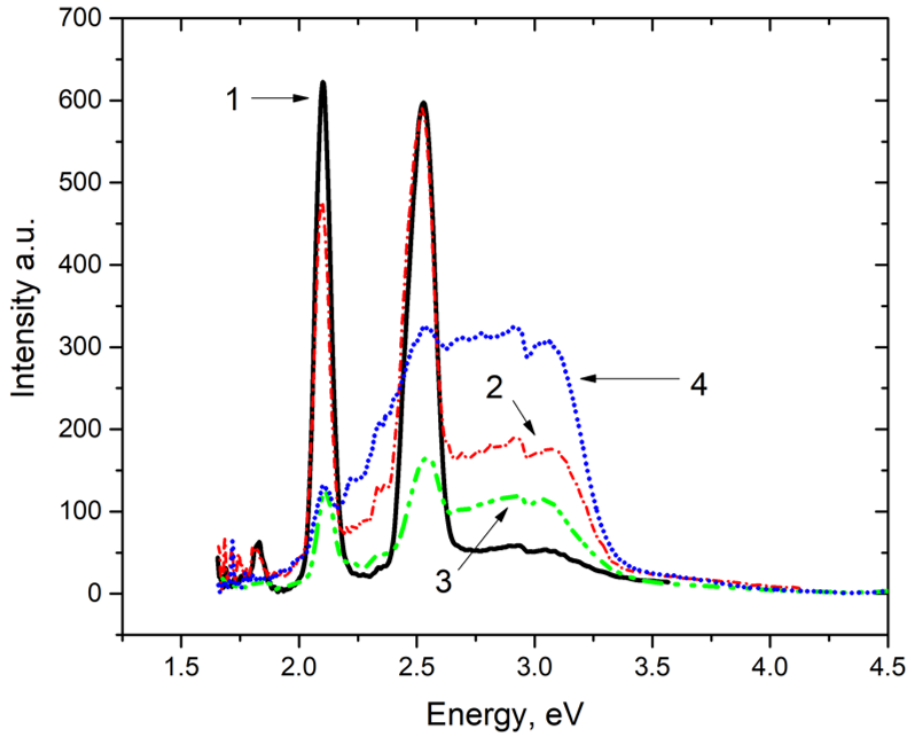


Figure 6. Emission spectrum of the  $Y_3Al_5O_{12}-Dy^{3+}$  phosphor under excitation with photons of energies 6.2 eV (curve 1 – 300 K, curve 2 – 77 K) and 5.64 eV (curve 3 – 300 K, curve 4 – 77 K).

transparency region of the  $Y_3Al_5O_{12}-Dy^{3+}$  matrix by photons with energies of 3.9–4.0 eV and 4.45–4.5 eV (Figure 7; curves 1–4). In addition, excitation is observed at 6.0, 5.8, and 5.5 eV in the long-wavelength region of the fundamental absorption band of the garnet (Figure 7: curves 1 and 3 at 300 K, and 2 and 4 at 77 K). According to [1], excitation of self-trapped excitons in  $Y_3Al_5O_{12}$  garnet occurs in the spectral range 7.0–7.7 eV, whereas electron–hole pairs should be created at still higher energies. The formation of local levels at 3.9 and 4.45 eV is apparently associated with charge transfer from the excited 2p-states of oxygen in the valence band of  $Al_5O_{12}$  to the excited states of neighboring anionic complexes or  $Dy^{3+}$  impurities, or to the energy states of so-called antisite trapping centers [1]. The creation of trapping centers with excitation energies of 3.9 and 4.45 eV is likely related to these processes.

In order to clarify whether the bands at 3.9 and 4.45 eV are absorption bands or excitation bands of the recombination luminescence at 3.05 and 2.92 eV, we performed a test experiment. Additional irradiation at 6.2 and 5.64 eV of the  $Y_3Al_5O_{12}-Dy$  garnet at 77 K was used to create electron–hole trapping centers, which should give rise to new recombination luminescence at 3.05 and 2.92 eV. After that, at 77 K and 300 K, the samples were excited with photons of 3.85 and 4.45 eV (Figure 8, curves 1 and 2; 3 and 4), and the emission spectrum was measured in the 1.6–4.0 eV range.

Figure 8 (curves 1, 2 and 3, 4) shows the emission spectrum of  $Y_3Al_5O_{12}-Dy$  garnet with induced defects, recorded under excitation by photons of 3.9 and 4.45 eV; curves 2 and 4 correspond to 77 K. From the figure, the appearance of intense recombination emissions at 3.05 and 2.92 eV is evident, which means that photons with energies of 4.45 and 3.9 eV excite the recombination emission at 3.05

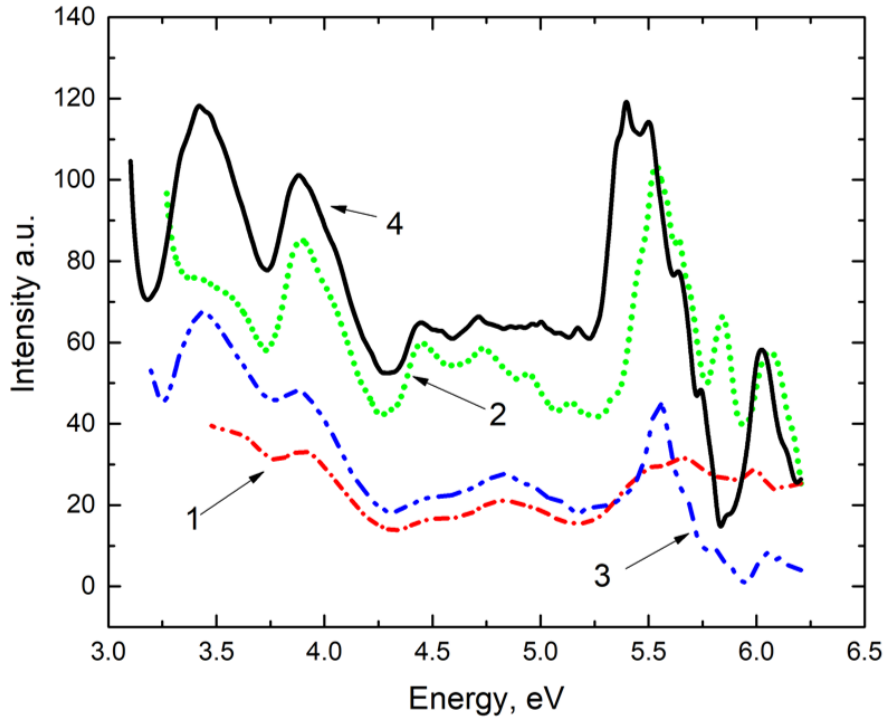


Figure 7. Excitation spectrum of the  $Y_3Al_5O_{12} - Dy^{3+}$  phosphor for emission bands at 3.05 eV (curve 1 – at 300 K and curve 2 at 77 K) and 2.92 eV (curve 3 – at 300 K and curve 4 at 77 K).

and 2.92 eV. It is also seen that, upon excitation with photons of 3.9 and 4.45 eV, in addition to the recombination emission,  $Dy^{3+}$  ion emission is observed.

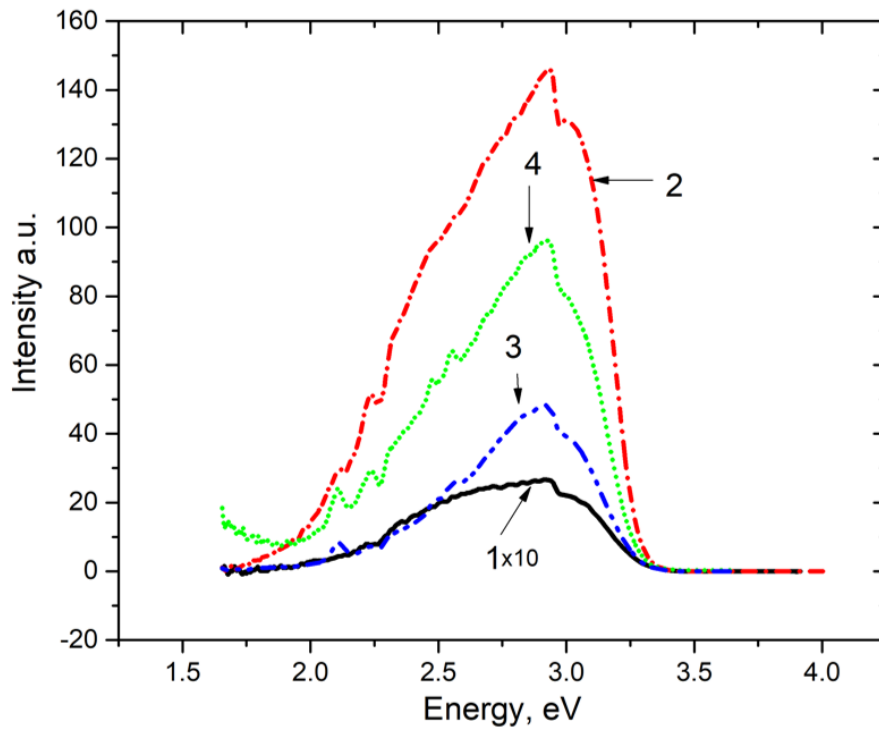


Figure 8. Emission spectrum of the  $Y_3Al_5O_{12} - Dy^{3+}$  phosphor with induced defects under excitation with photons of 3.85 eV (curve 3 at 300 K and curve 4 at 77 K) and 4.45 eV (curve 1 at 300 K and curve 2 at 77 K).

Figure 9 presents the excitation spectra of impurity emission bands at 2.16 eV and 2.56 eV in  $Y_3Al_5O_{12}:Dy^{3+}$  garnet pre-irradiated with 6.2 eV ultraviolet

photons at 77 K. In Figure 9 (curves 1 and 2), the excitation spectra of the intracenter emission at 2.16 eV are shown for 300 K and 77 K. It is observed that the 2.16 eV impurity emission is excited at 3.52 eV and within the range of 3.2–3.4 eV, corresponding to intracenter excitation of  $\text{Dy}^{3+}$  ions. In addition, excitation occurs at 3.85 eV and 4.45 eV, which are associated with the formation of long-wavelength recombination emissions at 3.05 eV and 2.92 eV. These emissions are also excited near the fundamental absorption region of the garnet, specifically at 5.0 eV and within the range of 5.5–6.2 eV (Figure 7). In this region, electron trapping centers are formed due to charge transfer from the excited 2p state of oxygen anions to  $\text{Dy}^{3+}$  impurities or antisite defects. Importantly, the impurity emission is also excited in the spectral regions around 3.85 eV and 4.45 eV, which coincide with the excitation regions of the recombination emissions at 3.05 eV and 2.92 eV.

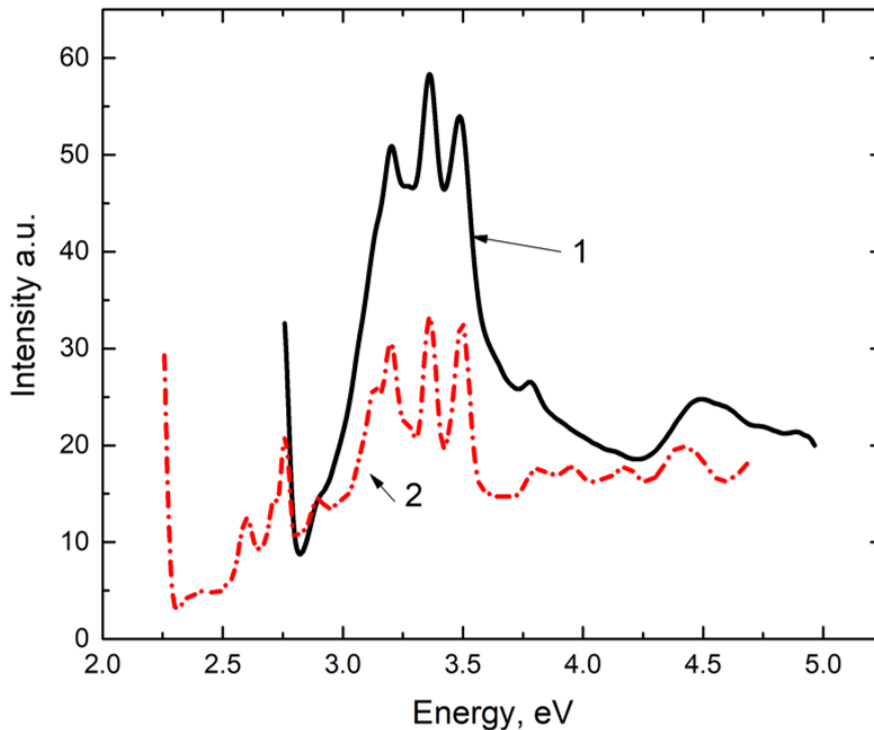


Figure 9. Emission spectrum of the  $\text{Y}_3\text{Al}_5\text{O}_{12} - \text{Dy}^{3+}$  phosphor (impurity emission at 2.16 eV) at 300 K (curve 1) and 77 K (curve 2).

At the next stage, the temperature dependences of the intensity of the recombination emission at 3.05 eV and 2.92 eV, as well as of the recovered intra-center impurity emission at 2.16 eV, were measured in the temperature range from 77 K to 400 K (Figure 10, curves 1, 2, and 3). From Figure 10 it can be seen that the intensities of the recombination emissions at 3.05 eV and 2.92 eV (curves 1 and 2) decrease in the temperature interval 150–270 K, then exhibit an increase in the range 300–370 K, followed by a decrease down to a minimum value. The intensity of the recovered intra-center emission at 2.16 eV decreases slightly in the 150–300 K range and then gradually increases in the range 300–450 K.

Figure 11 shows the TSL glow curve of  $\text{Y}_3\text{Al}_5\text{O}_{12} - \text{Dy}^{3+}$  garnet irradiated with X-rays for 5 minutes. It is seen that, in the temperature region where the recombination emission decreases and electron ionization occurs, a TSL peak

appears corresponding to recombination of an electron with a hole in the vicinity of a  $Dy^{3+}$  ion. The subsequent increase of the TSL peak up to 450–500 K corresponds to the dosimetric peak.

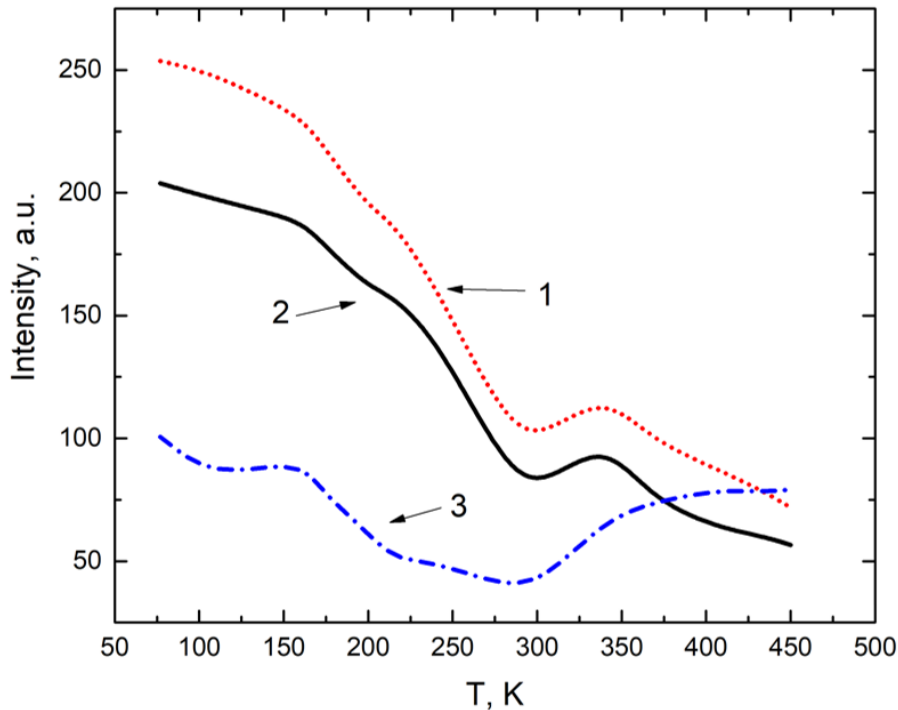


Figure 10. Temperature dependence of the emission intensity of  $Y_3Al_5O_{12} : Dy^{3+}$  at 3.05 eV (curve 1), 2.92 eV (curve 2), and 2.16 eV (curve 3).

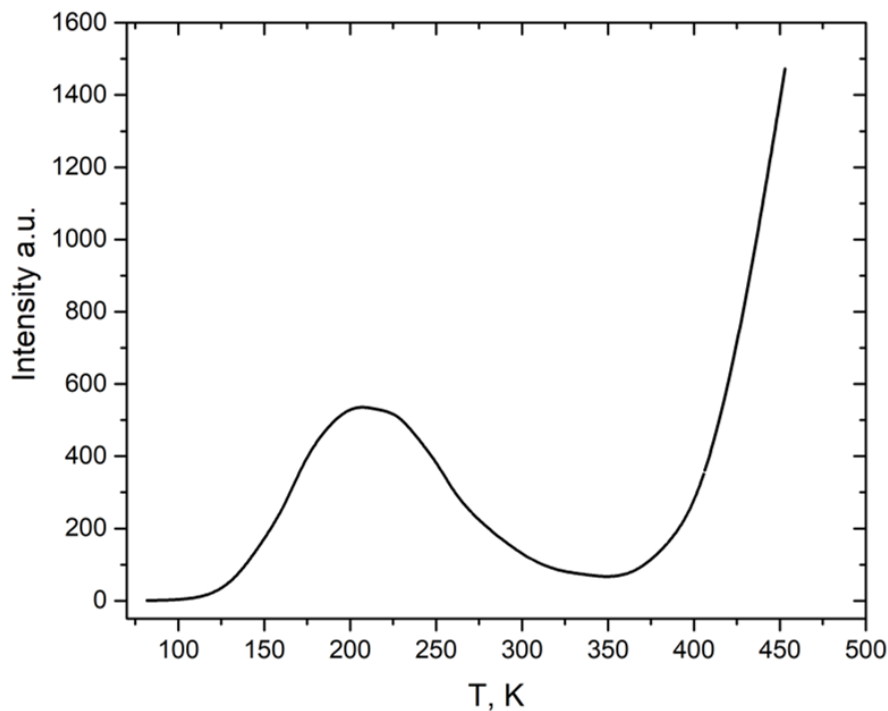


Figure 11. Thermally stimulated luminescence of  $Y_3Al_5O_{12} : Dy^{3+}$  under X-ray irradiation for 5 min at 77 K.

The formation of electron–hole trapping centers in the garnet under irradiation is illustrated in the band diagram in Figure 12. It is assumed that, during irradiation,

tion, charge transfer from an excited anion complex to a neighboring anion complex or to impurity ions leads, via the reactions  $(\text{Al}_5\text{O}_{12})^{3-} + e^- \rightarrow (\text{Al}_5\text{O}_{12})^{4-}$ ,  $(\text{Al}_5\text{O}_{12})^{3-} - e^- \rightarrow (\text{Al}_5\text{O}_{12})^{2-}$ , and  $\text{Y}^{3+} + e^- \rightarrow \text{Y}^{2+}$ , to the creation of intrinsic electron-hole trapping centers  $(\text{Al}_5\text{O}_{12})^{5-} - (\text{Al}_5\text{O}_{12})^{2-}$  and impurity-related electron-hole trapping centers  $\text{Y}^{2+} - (\text{Al}_5\text{O}_{12})^{3-}$ .

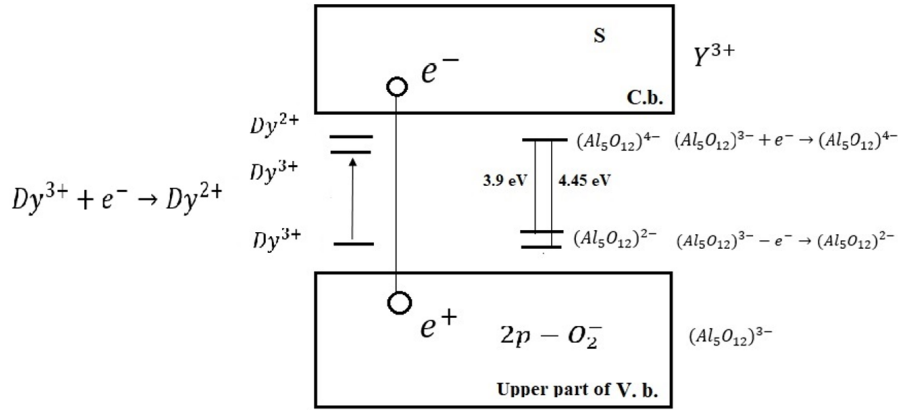


Figure 12. Energy-band diagram of the formation of electron-hole trapping centers in  $\text{Y}_3\text{Al}_5\text{O}_{12} - \text{Dy}^{3+}$ .

## Discussion

Thus, in irradiated  $\text{Y}_3\text{Al}_5\text{O}_{12}$  and  $\text{Y}_3\text{Al}_5\text{O}_{12} - \text{Dy}^{3+}$ , new recombination emissions at 3.05 eV and 2.92 eV are formed. These emissions, both in the undoped garnet and in the  $\text{Dy}^{3+}$ -doped garnets, are excited by photons with energies of 3.85 and 4.45 eV. In addition, they are efficiently excited near the fundamental absorption region of the host matrix at 6.0, 5.8, 5.5, 5.0, and 4.77 eV, where electron trapping centers are created as a result of charge transfer from the excited states of the oxygen anion complexes to  $\text{Dy}^{3+}$  impurities and to neighboring  $\text{Al}_5\text{O}_{12}$  anion complexes or to antisite defects of the matrix. Excitation of the impurity ions is also observed in the 3.2–3.5 eV spectral interval, where the intra-center impurity emissions of the dopants are excited.

To confirm that photons with energies of 3.85 eV and 4.45 eV indeed excite the recombination emissions at 3.05 eV and 2.92 eV, a control experiment was performed. The phosphor and the undoped garnet with induced trapping centers, after UV irradiation, were selectively excited with photons of 3.85 eV and 4.45 eV. As a result, the recombination emissions at 3.05 eV and 2.92 eV were reproduced.

The experimental result shows that, under irradiation with photons near the fundamental absorption region, charge transfer from excited oxygen in the anion complex to neighboring anions and  $\text{Dy}^{3+}$  impurities leads to the formation of electron-hole trapping centers, namely electron trapping centers  $(\text{Al}_5\text{O}_{12})^{4-}$  and hole trapping centers  $(\text{Al}_5\text{O}_{12})^{2-}$ . The hole trapping center  $(\text{Al}_5\text{O}_{12})^{2-}$  should be localized above the valence band, resulting in the formation of an electron-hole trapping center  $(\text{Al}_5\text{O}_{12})^{4-} - (\text{Al}_5\text{O}_{12})^{2-}$ . In parallel, upon excitation of the phosphor, charge transfer from the  $(\text{Al}_5\text{O}_{12})$  anion complex to  $\text{Dy}^{3+}$

impurities produces electron trapping centers  $(\text{Al}_5\text{O}_{12})^{4-} - (\text{Al}_5\text{O}_{12})^{2-}$ , which are complementary to the hole trapping center  $(\text{Al}_5\text{O}_{12})^{2-}$  above the valence band.

The experimental results showed that both intrinsic and impurity-related electron-hole trapping centers are excited at photon energies of 3.9–4.0 and 4.45–4.5 eV. Under excitation with photons of 3.9–4.0 and 4.45–4.5 eV in the  $\text{Y}_3\text{Al}_5\text{O}_{12}-\text{Dy}^{3+}$  phosphor, recombination emissions at 3.05 and 2.92 eV, as well as intra-center emissions of the  $\text{Dy}^{3+}$  impurity, arise simultaneously.

The main result is that, in the pre-irradiated  $\text{Y}_3\text{Al}_5\text{O}_{12}-\text{Dy}^{3+}$  phosphor with induced trapping centers, the impurity emission at 2.16 eV is simultaneously excited both via intra-center absorption and excitation of the  $\text{Dy}^{3+}$  ion (at 3.2, 3.40, and 3.52 eV) and under excitation at 3.9–4.0 and 4.45–4.5 eV, where the recombination emissions at 3.05 and 2.92 eV appear at 77 K. On the basis of these experimental data, it is assumed that, upon excitation of the  $\text{Al}_5\text{O}_{12}$  anion complex near the fundamental spectral region 4.77–6.0 eV, where, as a result of charge transfer from the excited p state of oxygen in the anion complex to intrinsic neighboring anions and  $\text{Dy}^{3+}$  impurities, combined electron-radiative states are formed, consisting of intrinsic and impurity electron trapping centers  $\text{Al}_5\text{O}_{12}^{4-}$  and  $\text{Dy}^{2+}$  below the conduction band. The hole components of the trapping centers  $\text{Al}_5\text{O}_{12}^{2-}$  form a local state above the valence band in the vicinity of the ground state of the  $\text{Dy}^{3+}$  impurity. Measurement of the temperature dependence of the intensity of the recombination emission at 3.05 and 2.92 eV, as well as of the impurity intra-center emission, showed that:

- In the temperature range 150–270 K, the intensity of the recombination emission at 3.05 and 2.92 eV gradually decreases; then, in the range 300–370 K, it increases and, up to 440 K, again gradually decreases.
- The impurity emission at 2.16 eV gradually decreases in the lower temperature range; starting from 300 K, it steadily increases up to 440 K.

The temperature dependence of the intensity of the two radiative processes shows how the combined electron-radiative states decay as a function of temperature. When the phosphor with induced defects is heated, starting from 150 K, ionization of the electron trapping centers occurs:  $(\text{Al}_5\text{O}_{12})^{5-} \rightarrow (\text{Al}_5\text{O}_{12})^{4-} - e^-$ ,  $\text{Dy}^{2+} \rightarrow \text{Dy}^{3+} - e^-$ .

The free electrons recombine with a hole located near the ground state of the  $\text{Dy}^{3+}$  impurity. In the course of recombination, part of the electron-hole pairs may form an exciton, which decays radiatively. Another part of the energy of the electron-hole recombination process can be transferred to  $\text{Dy}^{3+}$  impurities, leading to an increase in the impurity emission. The rise (glow) of the emission reflects the progress of the recombination process.

## Conclusion

1. In pure  $\text{Y}_3\text{Al}_5\text{O}_{12}$  garnets and  $\text{Y}_3\text{Al}_5\text{O}_{12}-\text{Dy}$  garnets doped with  $\text{Dy}^{3+}$ , irradiated in the vicinity of the fundamental spectral region, a new recomb-

nation emission band at 3.05 eV and 2.92 eV associated with the formation of electron–hole trapping centers has been observed for the first time.

2. By measuring the excitation spectra of the new recombination emission at 3.05 eV and 2.92 eV, it was shown that these emissions are excited by photon energies of 3.9 eV and 4.45 eV, also in the vicinity of the fundamental spectral region, where electron trapping centers are created as a result of charge transfer from excited matrix anions to neighboring anions or impurities.
3. By measuring the excitation spectra of the 3.05 eV and 2.92 eV recombination emissions and the Dy<sup>3+</sup> impurity emission at 2.16 eV, it was shown that they are generated simultaneously upon excitation with photons of 3.9 eV and 4.45 eV with the same energy.
4. Based on the experimental data, it is assumed that during irradiation in the vicinity of the fundamental spectral region, electron trapping centers  $(\text{Al}_2\text{O}_7)^{3-} + e^- \rightarrow (\text{Al}_2\text{O}_7)^{4-}$ , which are intrinsic electron trapping centers, are created as a result of charge transfer from oxygen in the Al<sub>5</sub>O<sub>12</sub> anionic complex of the valence band. In a similar way, impurity electron trapping centers  $\text{Dy}^{3+} + e^- \rightarrow \text{Dy}^{2+}$  are formed. The intrinsic and impurity trapping centers form a combined electron–radiative local state below the conduction band.
5. Upon the decay of the combined electron–radiative state, as a result of ionization of the intrinsic and impurity electron trapping centers, the excited electrons recombine with hole trapping centers Al<sub>2</sub>O<sub>7</sub><sup>2-</sup> in the vicinity of the ground state of the Dy<sup>3+</sup> impurity; excitons may then be formed, and the energy released in the recombination process is transferred to the Dy<sup>3+</sup> impurities or emitted as recombination radiation at 3.05 eV and 2.92 eV.

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