The Influence of Europium Impurity on the Recombination Luminescence in Y_2O_3

S.S. Novosad, I.S. Novosad*, O.M. Bordun, L.V. Kostyk, I.O. Bordun

and O.Ya. Tuzyak

Ivan Franko National University of Lviv, 1 Universytetska Str., Lviv, 79000, Ukraine

In this work the researched results of the spectral characteristics of the luminescence and the thermostimulated luminescence curves of Y_2O_3 and Y_2O_3:Eu ceramic materials at the X-ray excitation in the 85–295 K range were generalized. Considering the features of Y_2O_3 crystal structure and the possibility of the formation of the short-lived and stable hole and electron centers of V- and F-type by the ionizing radiation X-ray luminescence spectrum of ceramics at 85 K is fitted into the elementary Gaussian shape bands with the maxima near 3.40, 3.06, 2.67, 2.33, 2.09, and 1.91 eV. The main 3.40 and 3.06 eV bands of the luminescence are caused by the self-trapped excitons of $(YO_6)^{9-}$ complex, when the cation is localized in the field of the trigonal (C_{3i}) and monoclinic (C_2) symmetries. The emission at 2.67 eV and the weak bands in the 1.65–2.61 eV region are considered as the radiation of excitons localized on the anion vacancies and the electron centers of F-type (F^+, F and F^-). The thermoluminescence of Y_2O_3 in the 186 and 204 K main peaks range is connected with the thermal destruction of the self-trapped states of O^- ions that located in the field of the trigonal and monoclinic symmetries. The activator bands caused by $^5D_0 \rightarrow {}^7F_j$ electronic transitions in Eu^{3+} are only observed in the X-ray and thermostimulated luminescence spectra of Y_2O_3:Eu ceramics. It was assumed that both at the X-rays irradiation and an optical excitation in the band of the charge transfer of Y_2O_3:Eu sample the energy goes to Eu^{3+} through $(Eu^{2+}O^-)$ complexes (states) of the charge transfer.

1. Introduction

Y_2O_3 crystals with the width of band gap ≈ 6 eV have a cubic syngony with the space group T_h^7 [1]. Such structure derives from the structure of fluorite (CaF_2) and some anions are not in this structure. In a cube only six anions are in surround of cation. The anion vacancies, which set in the opposite ends of the main diagonal of the cube (the type environment of cation $C_{3i}(S_6)$ symmetry) are characterized for eight cations. The remaining twenty four cations have the anion vacancies that set in the ends of the diagonal of the lateral face of the cube (the type environment C_2 symmetry). Y_2O_3 crystal lattice contains two types of the alternated cation layers, one of which contains only C_2 position, and the second ones have an equal number of C_2 and C_{3i} positions.

The interest for europium as the doping impurity for the X-ray and cathodoluminophors is driven by its spectral features of the luminescence and the ability to change its valence and capture electrons and holes easily. It was revealed in Refs. [2–4] that F-type centers appear in the monocrystals on the base of Y_2O_3 after the X-ray and ultraviolet light irradiations at liquid nitrogen temperature. The spectra of F-type centers are easily discolored by an optical light from 1 μm region and thermally. During last years the obtainment and investigation of micron dispersion of Y_2O_3 with an europium impurity and the

effect of co-activators on Eu^{3+} luminescence in Y_2O_3:Eu were given special attention [5–8].

The low-temperature luminescence of Y_2O_3 ceramics is non-elementary [9]. The doping of the material by Eu^{3+} ions leads to the appearance of the activator centers luminescence [10]. In this paper we have done the comparative study and have analyzed the spectra of X-ray luminescence (XRL) and the curves of thermostimulated luminescence (TSL) of Y_2O_3 and Y_2O_3:Eu^{3+} ceramics at the X-ray excitation in the 85–295 K range for the obtaining of additional information about the influence of Eu^{3+} ions on the features of the recombination processes in Y_2O_3.

2. Experiment

The polycrystalline ceramic samples were used to research in tablet form with a diameter of ≈ 8 mm and a height of 1.0–1.5 mm obtained by the standard technology by sintering at $\approx 1100\,^\circ C$ temperature pressed a powder Y_2O_3 mark "ItO-I" and a phosphor Y_2O_3:Eu mark "E" in a steel mold under pressure of 150 kg/cm². The optical-luminescent researches were carried out in a metallic cryostat in vacuum of $\approx 10^{-4}$ Torr. XRL spectra were measured using the monochromator of a SF-4A spectrophotometer and a FEU-51 photomultiplier. An increased signal was fed to a dc amplifier and visualized on a PDA-1 XY recorder. The ceramics were excited by X-rays using a URS-55A unit (a Cu-anode BSV-2 X-ray tube, $U = 45$ kV, $I = 12$ mA). The samples temperature was measured by a copper-constantan thermocouple mounted on the holder next to the sample. A constant heating rate was ≈ 0.15 K/s.

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*corresponding author; e-mail: iryna.novosad@lnu.edu.ua

3. Results

At 85 K XRL spectrum of Y_2O_3 ceramics is characterized by wide non-elementary 3.19 eV band (Fig. 1a). XRL spectrum of the undoped ceramics at 85 K is fitted into the elementary Gaussian shape bands with the maxima near 3.40, 3.06, 2.67, 2.33, 2.09, and 1.91 eV considering the features of Y_2O_3 crystal structure [1] and the possibility of the formation of the short-lived and stable hole and electron centers of V- and F-type [2–4] by the ionizing radiation in the oxide compounds [11–13].
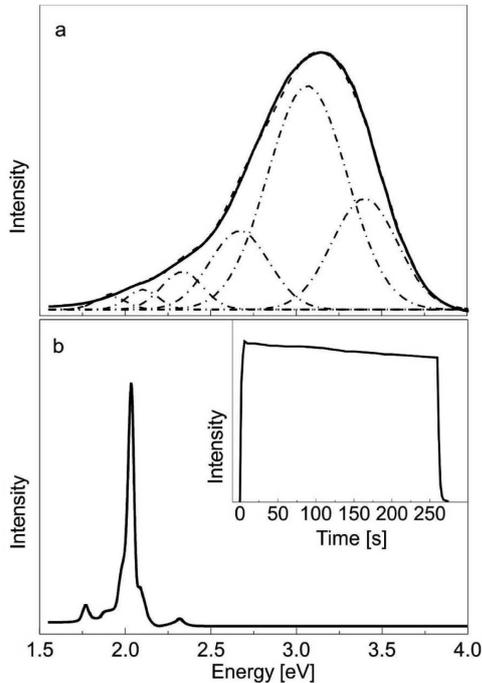

Fig. 1. (a) XRL spectra of Y_2O_3 ceramics at 85 K (solid line). The results of an approximation of the experimental band (dash line) and the fit into the elementary bands (dash dot lines) are shown; (b) XRL spectra of Y_2O_3:Eu ceramics at 85 K; inset — the kinetics of the steady-state XRL in 2.03 eV maximum of Y_2O_3:Eu at 85 K.

The doping of the material by europium ions leads to the appearance of Eu^{3+} centers luminescence with C_2 symmetry. The weak bands observed in XRL spectra are caused by $^5D_0 \rightarrow {}^7F_j$ electronic transitions in Eu^{3+} (Fig. 1b). The similar spectral characteristics are inherent to Y_2O_3:Eu luminescence at 295 K. At 85 K Y_2O_3:Eu material is characterized by a fast increase and a slight weakening of the steady-state XRL and a lagless decay of the emission after the excitation was turned off (Fig. 1b, inset).

After growing the temperature from 85 to 210 K of Y_2O_3 sample XRL intensity in the maximum spectrum is enhanced slightly and after growing the temperature up to 295 K it is sharply monotonously quenched to ≈ 0.15 value from the maximum intensity with the activation energy ≈ 0.33 eV (Fig. 2a, curve 1).

Fig. 2. (a) The temperature dependence of the XRL intensity (1) and TSL curve (2) of Y_2O_3 ceramics after the X-ray excitation at 85 K during 20 min. The results of an approximation of the experimental TSL curve (dash line) and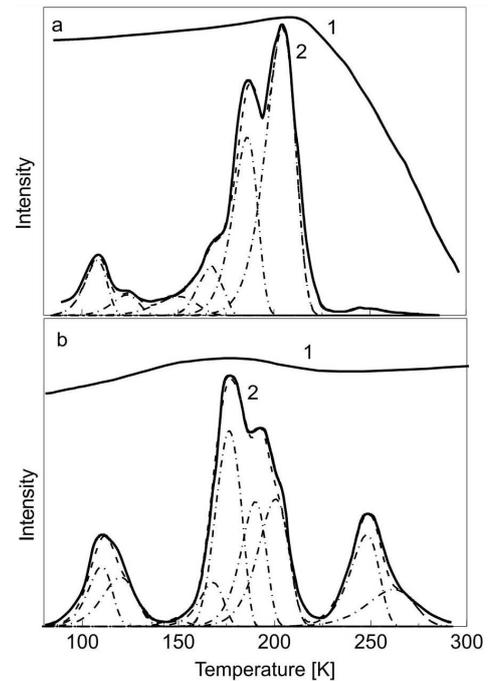 the fit into the elementary peaks (dash dot lines) are shown; (b) the temperature dependence of the XRL intensity (1) and TSL curve (2) of Y_2O_3:Eu ceramics after the X-ray excitation at 85 K during 20 min. The results of an approximation of the experimental TSL curve (dash line) and the fit into the elementary peaks (dash dot lines) are shown.

At 85 K three groups of peaks with the different intensity in the 85–140, 140–230, and 230–280 K ranges are observed in TSL curve after the X-ray excitation of Y_2O_3 with the dose power ≈ 550 R/min during 20 min (Fig. 2a, curve 2). The peak at 125 K with a lower intensity appears in a low-temperature range besides the peak at 108 K. In the intermediate temperature range TSL is the most effective and the glow curve is formed by a few peaks with the different intensity that is strongly overlapped. In the high-temperature range TSL curve is presented by a weak non-elementary peak in the 230–280 K range. With the increase of the X-ray quanta radiation duration of Y_2O_3 material the peak intensities in TSL curve are headed of saturation. It was found by the method of the heat clearing that the recombination processes that occur in materials researched by TSL, are described by the linear kinetics. The analysis of TSL curve of Y_2O_3 using the model of the first order kinetics [14] is allowed to separate elementary peaks at 108, 124, 151, 167, 186, and 204 K. According to the formula $E(eV) = T_{max}(K)/540$ proposed in [15] it was estimated that the location depth of the capture levels responsible for the found peaks are about 0.20, 0.23, 0.28, 0.31, 0.34, and 0.38 eV, respectively.

The temperature dependence of the luminescence intensity of Y_2O_3:Eu in the main 2.03 eV band in the low-temperature range of 85–210 K is similar to a similar dependence of Y_2O_3. However, in the high-temperature range after a slight weakening yield of XRL at temperature above 230 K the increase of Eu^{3+}-centres luminescence is observed (Fig. 2b, curve 1). The doping of Y_2O_3 by an europium impurity leads to the increase of TSL intensity about the order. In TSL of the material the radiation of Eu^{3+}-centres dominates. In TSL curve obtained after the irradiation of Y_2O_3:Eu during 20 min also there are three main groups of peaks (Fig. 2b, curve 2). The doping of Y_2O_3 by an europium impurity results in change of the ratio intensities of TSL peaks in the 140–230 K range in favor of the peak at 179 K and more efficient display of the peaks group in the 230–280 K range. An additional action of the infrared light of the incandescent lamp through an IKS-7 optical filter on the excited samples at 85 K by the X-rays quanta leads to the decrease of TSL peaks. The analysis of TSL curve of Y_2O_3:Eu material using the model of the first order kinetics [14] is allowed to separate the elementary peaks at 110, 120, 150, 168, 176, 190, 200, 248, and 262 K, due to the capture levels of the location depth about 0.20, 0.22, 0.28, 0.31, 0.33, 0.35, 0.37, 0.46, and 0.49 eV, respectively.
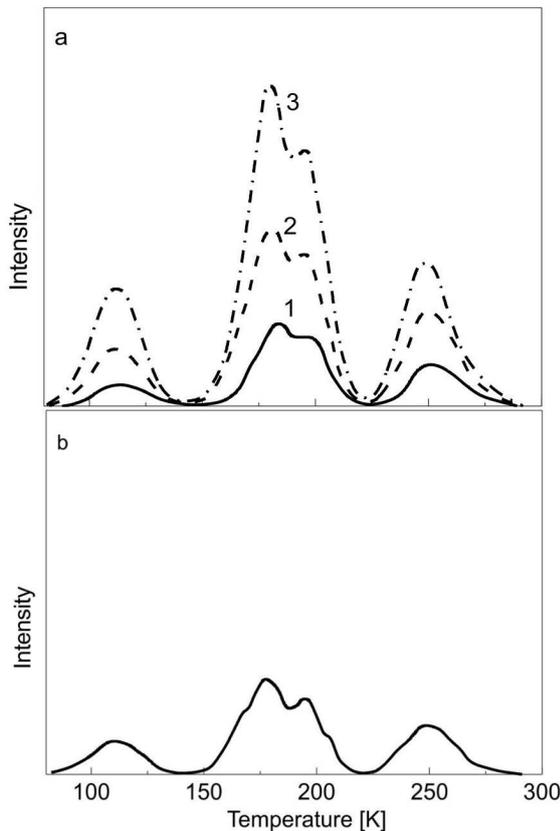
In Fig. 3a TSL curves of Y_2O_3:Eu material after the X-ray excitation at 85 K for 5, 10, and 15 min, respectively, are shown. In this figure it is seen that in case of the irradiation of Y_2O_3:Eu by the lowest radiation dose TSL curve in the intermediate temperature range is represented by non-elementary peaks at 113, 184, and 251 K (curve 1). The increase of the X-ray irradiation of the ceramics to 10 min leads to the growth of the stored light sum about twice and to the change the shape of TSL curve in the 140–230 K range due to the increase and the shift of the main peaks of 180 and 195 K (curve 2). After growing the radiation time up to 15 min the further increase of the light sum storage in the doped material is observed (curve 3). With the difference of 2 and 1 curves, as shown in Fig. 3a, it follows that the change of TSL curve shape in the intermediate temperature range is mainly caused by the localization of the light sum on an additional peak of 177 K (Fig. 3b).
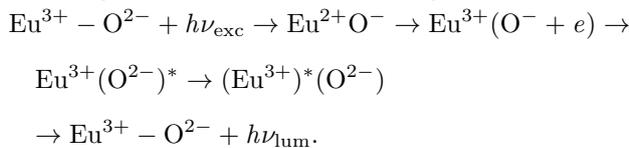
4. Discussion of the results

Aleksandrov et al. [16] in the case of the synchrotron excitation of Y_2O_3 powders found the ultraviolet emission of the self-trapped excitons (STEs) with a maximum at about 3.4 eV, which is the most efficiently excited by photons in the 5.7–7.0 eV area of the excitons formation and increases at the cooling of the samples from 300 to 80 K. From the obtained results it follows that the luminescence spectrum of Y_2O_3 ceramics at 85 K can be represented by a superposition of five elementary bands with Gaussian shape. The main 3.40 and 3.06 eV bands of XRL are caused by STEs of $(YO_6)^{9-}$ complex that is containing Y^{3+} ions surrounded by six O^{2-} ions and two stoichiometric anionic vacancies for the case, when the cation is localized in the field of the trigonal (C_{3i}) and monoclinic (C_2) symmetries. The emission at 2.67 eV and the weak bands in the 1.65–2.61 eV region are considered as the radiation of the excitons localized on the anion vacancies and the electron centers of F-type (F^+, F and F^-). The temperature quenching of Y_2O_3 luminescence can be due to the thermostimulated destruction of STEs and a nonradiated relaxation of the electronic excitations.

The nature of the capture centers responsible for the peaks in TSL curves at the X-ray irradiation of Y_2O_3 is mainly caused by its own defects and the uncontrolled impurities [17–19]. The thermoluminescence of Y_2O_3 in the main 186 and 204 K peaks range is associated with the thermal destruction of the self-trapped states of O^- ions, which are in the field of the trigonal and monoclinic symmetries. The recombination of the thermodelocalized holes with the electron centers leads to the emission of the localized excitons in the long-wavelength bands. Thus by the analogy with related Al_2O_3 system, whose thermoinduced migration holes delocalized from V-centers are proved [20], we can assume that the diffuse-controlled tunnel recombination caused by the thermal migration of the holes delocalized from V-centers with F-type centers are observed in Y_2O_3.

Fig. 3. (a) TSL curves of Y_2O_3:Eu ceramics at 85 K at different time of the X-ray excitation: 5 (1), 10 (2) and 15 (3) min; (b) the difference of curves 2 and 1 shown in Fig. 3a.

The radii of Y^{3+} and Eu^{3+} ions are close enough and equal to 0.90 and 0.94 Å, respectively [21]. If Y^{3+} is replaced by Eu^{3+} the cubic structure of the matrix is saved with little change in the lattice parameters [5]. In XRL spectrum of Y_2O_3:Eu ceramics only the activator band due to $^5D_0 \rightarrow {}^7F_j$ electronic transitions in Eu^{3+} is observed. The europium ions in the studied doped material mainly form the emission centers with C_2 symmetry. The intensity of 2.03 eV band is determined by the electric-dipole transition $^5D_0 \rightarrow {}^7F_2$ that is sensitive to the near surroundings of Eu^{3+} ion. The weak emission 2.08 eV band is determined by the magnetic-dipole transition $^5D_0 \rightarrow {}^7F_1$ that is not sensitive to the nearest surroundings [7].

Taking into account that Eu^{3+} ions tend to have a stable half-filled $4f$-shell and effectively capture electrons we can assume that at the time of Y_2O_3:Eu material excitation electron detaches from O^{2-} ion with the following conversion of the activator at the localization electron on the Eu^{3+} ion. With regard to the above mentioned the O^- hole center appears in the nearest surrounding of the activator (the hole localized on $2p$-orbitals of oxygen). In the result a short-lived $(Eu^{2+}O^-)$ quasimolecule is formed in an emitted system. The recombination of the electrons delocalized from Eu^{2+} centers with O^- ions leads to the recovery of the europium luminescence centers and the appearance of the localized excitons on the activator. The recombination energy of the exciton is nonradiatively transmitted to Eu^{3+} for the transition of ion into the excited state from which it spontaneously returns to the main state with the simultaneous emission of the light quantum. The luminescence of Eu^{3+} in Y_2O_3 is very effectively optical excited in a charge transfer band [22]. At similar excitation the energy stores in the phosphor at "dissociation" of the excited state of the charge transfer in yttrium oxysulfides, in the result of Eu^{2+} ions and "holes" — S^- ions form [23]. Based on the obtained results it can be assumed that both at the X-rays irradiation and an optical excitation in the band of the charge transfer of Y_2O_3:Eu sample [7, 8, 22] energy goes to Eu^{3+} through $(Eu^{2+}O^-)$ complexes (states) of the charge transfer with the following scheme:

$$Eu^{3+} - O^{2-} + h\nu_{exc} \rightarrow Eu^{2+}O^- \rightarrow Eu^{3+}(O^- + e) \rightarrow$$

$$Eu^{3+}(O^{2-})^* \rightarrow (Eu^{3+})^*(O^{2-})$$

$$\rightarrow Eu^{3+} - O^{2-} + h\nu_{lum}.$$

The lagless increase and the decrease of the steady-state low-temperature XRL of Y_2O_3:Eu material during the radiation indicate that the formation of such centers causes the reduction number of the main activator centers formed and excited during the charge transfer. A fast stage of the increase of the steady-state luminescence is also determined by the probability of the internal center transitions.

Based on the studied results of the recombination of the luminescent materials and reviewed literature data it was shown that the light sum is stored by Y_2O_3:Eu on both the electron and hole capture centers. The discovered flashing at an infrared irradiation of the light sum that was reserved in Y_2O_3:Eu during the X-ray irradiation indicates that the photothermal released electrons from the centers of F-type recombine with the holes localized in the traps. The luminescence occurs at previous binding of the electron and the hole in the exciton.

During the X-ray irradiation of Y_2O_3:Eu some part of electrons lost by O^{2-} ions during the ionization can be captured by the stoichiometric anion vacancies near Eu^{3+} ions forming both the short-lived and stable electronic F_A-type centers. It is probable that Eu^{3+} ions in Y_2O_3 are associated with F-type centers. The formation of such associates and the distortion of the crystal field of Y_2O_3 by the activator increase the probability of the holes localization on the O^{2-} ions near the defects responsible for TSL peak at 177 K. Perhaps this peak corresponds to the traps associated with O^- ions near Eu^{2+} ions.

The increase of the recombination TSL intensity of Y_2O_3 doped by Eu^{3+} ions is caused by the growing of the localization number of generated charge carriers by the excitation on the traps, characterized for the matrix, and the activator traps located near the structural inhomogeneities, and a high efficiency of the energy transfer to the activator recombination centers. The low-temperature activator recombination luminescence may be associated with some complex that consists of the approximately placed trap and the emission center. Whereas Eu^{3+} ions effectively capture the electrons it is assumed that TSL of Y_2O_3:Eu material is caused by the recombination of the holes delocalized from O^--centers with Eu^{2+}-centers. The recombination processes, which involves the thermodelocalized holes from the capture levels form the localized excitons. At that time Eu^{3+}-centers are created in an excited state and they relax with the quanta radiation of the intra-activator luminescence.

Perhaps Eu^{3+} ions in Y_2O_3 effectively form the associates with the short-lived and stable F-type centers [4]. The formation of such associates leads to the reduction of the concentration of the main activator centers. For this reason the decrease of the stationary luminescence intensity is associated with $^5D_0 \rightarrow {}^7F_2$ electronic transitions in Eu^{3+} during the X-ray irradiation of the sample. A slight decrease of the excitation intensity of Y_2O_3:Eu luminescence in the 85–150 K range is caused by the losses of the energy transfer efficiency to Eu^{3+}-centers, resulting in localization of the carriers part on the capture centers. XRL high yield by the heating of Y_2O_3:Eu^{3+} sample from 285 to 295 K can be explained by both the decrease of the localization carriers generated by the excitation on the defects and the high probability of the energy transfer to the activator centers. After growing the temperature up the number of donor–acceptor pairs $(O^-–Eu^{3+}F)$ increases and the average distance in such pairs is reduced thus the probability of the tunnel hole capture is increased. The recombination of the thermodelocalized

holes from O^--centers with such associated pairs in the doped materials is more effective than their recombination with F-centers that is characterised for the matrix. For this reason in the TSL of Y_2O_3:Eu^{3+} material the activator luminescence is mainly observed.

5. Conclusions

Considering the features of Y_2O_3 crystal structure and the possibility of the formation of the short-lived and stable hole and electron centers of V- and F-type by ionizing radiation XRL spectrum of Y_2O_3 ceramics at 85 K is fitted into the elementary Gaussian shape bands with the maxima near 3.40, 3.06, 2.67, 2.33, 2.09, and 1.91 eV. The main 3.40 and 3.06 eV bands of the luminescence are caused by the STEs of $(YO_6)^{9-}$ complex, when the cation is located in the field of the trigonal (C_{3i}) and monoclinic (C_2) symmetries. The emission at 2.67 eV is considered as the radiation of the excitons localized on the anion vacancies. TSL of Y_2O_3 in the 186 and 204 K main peaks range is connected with the thermal destruction of the self-trapped states of O^- ions that are located in the field of the trigonal and monoclinic symmetries. In XRL and TSL spectra of Y_2O_3:Eu ceramics the activator bands caused by $^5D_0 \rightarrow {}^7F_j$ electronic transitions in Eu^{3+} are only observed. The capture centers characterized for the matrix and the hole O^-- centers of V-type associated with Eu^{2+} are in the doped material. The thermostimulated diffusely-controlled tunnel recombination of the holes delocalized from V-type centers with Eu^{2+} leads to the formation of the exciton states with the following excitation of Eu^{3+}-centers, which relax with the emission quanta of the intra-activator luminescence.

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