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Investigation of the Mechanisms Responsible for the Formation of Intrinsic and Impurity-Related Electron and Hole Trapping Centers by Measuring the Reflectance, Emission, and Excitation Spectra of YPO_4:Bi

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Abstract

In YPO_4:Bi irradiated with photons in the energy range of 5.5–6.2 eV and with X-rays, sensitization-related luminescent states are formed in the 4.43–3.35 eV energy range, appearing as a broad emission band. The excitation spectrum of this broad band lies in the photon-energy range of 5.9–6.2 eV. As in many phosphor materials, these sensitization-related luminescent states are formed as a result of charge transfer from an excited host anion to neighboring ions and impurity centers introduced into the lattice, leading to the formation of electron-trapping centers. Upon excitation of irradiated YPO_4:Bi with photons in the energy range of 4.43–3.35 eV, two groups of emission bands are observed: at 3.1–2.9 eV and at 2.8–2.25 eV. These emissions are excited within two spectral regions, from 4.43 to 3.8 eV and from 3.7 to 3.25 eV, and appear as several recombination-related bands. Reflectance spectrum measurements show that, within the transparency region of the host matrix, additional energy levels appear in the 4.43–3.35 eV spectral range. Excitation through these levels gives rise to the observed recombination luminescence, and their energy positions correspond to the excitation spectra of the respective recombination emission bands.

Keywords: electron-hole; trapping center; orthophosphate; reflectance spectrum; emission; recombination luminescence

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1. Introduction

The afterglow resulting from the accumulation of excitation energy under external irradiation is associated with recombination luminescence involving electron- and hole-trapping centers.

As a result of the recombination of electrons and holes released from trapping centers, the excitation energy accumulated at luminescence centers is converted into visible and short-wavelength infrared radiation with photon energies ranging from 1.37 to 0.73 eV, thereby exhibiting unique spectral properties. To generate visible and infrared emission efficiently, it is necessary to determine the positions of the energy levels of divalent and trivalent lanthanide ions within the band gap of inorganic crystals [1].

Most known persistent phosphors exhibit luminescence in the visible and near-infrared spectral regions and are used in displays, sensors, night-vision devices, and bioimaging systems [2–5].

In the study by the authors [6], the influence of size effects on the parameters and mechanisms of persistent afterglow in YPO_4:Bi was investigated. For this purpose, phosphors were synthesized using solid-state reaction and hydrothermal methods. The nature of the emission centers was determined, and analysis of the TSL glow curves using the general-order kinetic model made it possible to estimate the activation energies of the traps and to establish the mechanisms responsible for the formation of UV-C (5.1 eV) and UV-A (3.6 eV) emissions. These emissions were attributed, respectively, to hole recombination at Bi^{2+} centers and electron recombination at Bi^{3+}-Bi^{4+} pairs. The resulting afterglow duration of the phosphor powders ranged from 10 to 40 min, depending on the emission band.

The optical properties of YPO_4:Bi were investigated by the authors of [7]. They showed that, at 300 K, the excitation spectrum of the 5.16 eV emission exhibits a band centered at 5.46 eV, which was assigned to the A-band emission of Bi^{3+} ions. In addition to the impurity-related emission at 5.12 eV, the authors of Ref. [8] observed a weak emission band at 3.8 eV, which was attributed to paired Bi^{3+} centers. That study also examined the dependence of the 3.8 eV emission intensity on the Bi^{3+} dopant concentration.

The aim of the work [8] was to determine the origin of the low-energy and high-energy emission bands located at 3.81 and 5.12 eV, respectively, in the room-temperature emission spectra. The high-energy band was attributed to the $^3P_0 \rightarrow {}^1S_0$ radiative transition of isolated Bi^{3+} ions incorporated into the host lattice. The low-energy band, whose intensity depends strongly on the Bi^{3+} concentration, was convincingly assigned by the authors to emission from paired or clustered Bi^{3+} centers in the crystal lattice.

The X-ray-excited luminescence spectrum of YPO_4:Bi extends over a broad spectral range from 6.2 to 1.55 eV. The emission band at 5.12 eV is attributed to Bi^{3+} ions and corresponds to the A-band emission. Additional emission bands are observed in the 4.13–2.25 eV range and at 1.85 eV. The authors of [8] assigned the 1.85 eV emission band to the $^2P_3/_2 \rightarrow {}^2P_1/_2$ transition of Bi^{2+} ions. These ions are formed through electron capture by Bi^{3+} ions according to the reaction $Bi^{3+} + e^- \rightarrow Bi^{2+}$. The emission bands in the 4.13–2.25 eV range were attributed to defect-associated excitonic recombination processes.

In the work of the authors [9], experimentally identified energy levels corresponding to the ground and excited states of the Bi^{3+} ion in YPO_4:Bi phosphor were reported:

The ransitions from the ground $^1S_0$ state to the excited $^3P_1$ state ($^1S_0 \rightarrow {}^3P_1$) were assigned to Bi^{3+} ions.

Under X-ray excitation (a band at 5.46 eV), Bi^{2+} emission associated with the $^2P_3/_2 \rightarrow {}^2P_1/_2$ transition at 1.85 eV was observed. The authors suggested that free electrons generated under X-ray irradiation are captured by Bi^{3+} ions according to the reaction $e^- + Bi^{3+} \rightarrow Bi^{2+}$, resulting in the formation of Bi^{2+} centers.

In the study by the authors [10], excitation with photons of 5.51 eV resulted in emission bands at approximately 5.0 and 3.8 eV. The emission band at 5.0 eV was attributed to an intracenter transition of Bi^{3+} ions, whereas the 3.8 eV band was assigned to paired Bi^{3+} centers. In the same work, it was shown that, in YPO_4:Bi^{3+}, Bi^{3+} ions can act as deep electron-trapping centers, forming Bi^{2+} states. At the same time, Bi^{4+} hole-trapping centers are formed through a parallel process. At lower energies, the trapped holes become delocalized and recombine with Bi^{2+} electron centers, resulting in Bi^{3+} luminescence associated with the $^3P_1 \rightarrow {}^1S_0$ transition.

In the work of the authors [11], it was shown for the $BaSO_4$:Bi phosphor that the long-wavelength recombination emission bands at 2.34, 2.4, and 3.1 eV are associated with the recombination of electrons released upon ionization of $SO_4{}^{3-}$ electron-trapping centers

with nonequivalently localized SO_4^- hole centers oriented along different crystallographic directions in the host lattice.

In the work of the authors [12], a ten-trap model was developed to describe thermally stimulated recombination processes in the YPO_4:Bi system. The model was parameterized using previously obtained experimental thermoluminescence data recorded by monitoring emission at 3.6 and 5.1 eV. For each trap, the activation energy, frequency factor, trapping coefficient, and recombination coefficient were determined. Thus, the proposed model provides an explanation of the mechanisms of charge-carrier release and recombination and allows the main types of traps involved in the persistent afterglow phenomenon to be identified.

In the work of other authors [13], the control of persistent afterglow duration in YPO_4:Bi ceramics was investigated. Depending on the sintering conditions and the particle size of the precursor powder, the luminescence centers responsible for UV-C (5.1 eV) and UV-A (3.6 eV) emissions under X-ray excitation were identified as isolated Bi^{3+} ions and Bi^{3+}–Bi^{4+} pairs, respectively. LTHP (low-temperature high-pressure) ceramics prepared from coarse precursor powder exhibited the longest afterglow in the UV-C spectral range, whereas SPS (spark plasma sintering) ceramics synthesized from fine precursor powder showed the best afterglow characteristics in the UV-A range. Thus, controlling the trap parameters by adjusting the sintering conditions and the particle size of the precursor powder represents an effective strategy for the targeted control of the persistent afterglow duration in YPO_4:Bi ceramics.

Based on analyses of the temperature dependences and luminescence decay times, as well as estimates of the relevant parameters of the relaxed excited state (RES), the authors of [14–16] concluded that the ultraviolet emission band of $Lu_3Al_5O_{12}$:Bi at 3.9 eV originates from the $^3P_{1,0} \rightarrow {}^1S_0$ electronic transition of free Bi^{3+} ions. In contrast, the visible emission band at 2.5 eV has an exciton-like origin and results from the radiative decay of a triplet exciton state localized near a Bi^{3+} ion.

Visible recombination emission at 2.7 eV is also observed in other phosphors activated with impurity ions. The authors attribute the appearance of visible emission to the recombination of electrons released from ionized electron-trapping centers with complex hole-trapping centers formed as a result of the interaction of holes localized near impurity ions with holes in the valence band. As a result, exciton-like states are formed, which either emit radiation directly or transfer the energy released during the recombination process to impurity centers.

In [17–19], the formation of two types of emissions, namely ultraviolet and visible luminescence with similar characteristic features, was discussed for the $Y_3Ca_5O_{12}$:Bi and $Cd_3Ca_5O_{12}$:Bi phosphors.

In accordance with the objectives of the present study, the following aspects will be investigated systematically: the mechanisms responsible for the formation of intrinsic and impurity-related electron- and hole-trapping centers involved in the creation of sensitized electron-radiative states; the intrinsic and recombination emissions generated under irradiation; and the excitation processes and corresponding energy states responsible for these emissions within the spectral transparency region of the host matrix.

2. Materials and Methods

YPO_4 samples, both undoped and Bi-activated, were synthesized via the solid-state reaction method. Yttrium (III) nitrate hexahydrate, $Y(NO_3)_3 \cdot 6H_2O$ (99.8%, Sigma-Aldrich, St. Louis, MO, USA), bismuth (III) nitrate pentahydrate, $Bi(NO_3)_3 \cdot 5H_2O$ (98%, Alfa Aesar, Ward Hill, MA, USA), and diammonium hydrogen phosphate, $(NH_4)_2HPO_4$ ($\geq$98%, Carl Roth, Karlsruhe-Mühlburg, Germany), were used as starting materials. For the synthesis,

stoichiometric amounts of appropriate metal nitrates and $(NH_4)_2HPO_4$ were mixed in an agate mortar. The obtained mixture was transferred to a porcelain crucible and heated in a muffle furnace at 500 °C for 6 h in air. The obtained intermediate product was ground in a mortar and annealed at 1100 °C for 5 h in air. After annealing, the furnace was allowed to cool down naturally. The phase composition of the powder samples was determined using a Rigaku MiniFlex II X-ray diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a Ni-filtered Cu Kα radiation source working in Bragg-Brentano (θ/2θ) geometry.

Emission spectra in the energy range of 1.5–6.2 eV were recorded using a Solar SM 2203 spectrofluorometer (Solar LS, Minsk, Republic of Belarus). Low-temperature measurements at 77 K were performed in a vacuum cryostat (10^{-4} Pa) cooled with liquid nitrogen. Thermally stimulated luminescence (TSL) glow curves were obtained after X-ray irradiation of the samples using a BSV-23 X-ray tube equipped with a copper anode and operated at 40 kV and 10 mA, producing X-ray photons with energies of 10–15 keV. The rate of temperature heating during low-temperature measurements was 0.1–0.2 K per minute. Additional optical excitation was provided by a 150 W xenon XBO lamp (OSRAM GmbH, Garching, Germany), which generated photons in the 1.5–6.2 eV (200–830 nm) spectral range.

The luminescence decay kinetics were investigated using an FLS-1000 spectrometer (Edinburgh Instruments, Livingston, UK). Excitation was provided by a μF2 microsecond flash lamp, while the emitted light was detected with a PMT-900 photomultiplier tube. A 450 W xenon lamp served as the excitation source.

3. Results

The X-ray diffraction pattern of the $YPO_4:Bi^{3+}$ (3%) sample is in good agreement with the reference data (PDF card No. 95-153-0428). The diffraction pattern of the $YPO_4:Bi^{3+}$ is shown in Figure 1. All observed diffraction reflections can be assigned to the crystalline YPO_4 phase, while no additional peaks related to impurity phases are detected. The sharp and intense diffraction peaks indicate a high degree of crystallinity of the synthesized material. The incorporation of Bi^{3+} ions at a concentration of 3% does not cause any noticeable changes in the crystal structure of the YPO_4 host lattice.

In irradiated undoped YPO_4 orthophosphate, luminescent states with emission energies of 3.75, 3.35, 3.10, 2.95, 2.75–2.63, 2.40, 2.25, and 2.06–2.03 eV are formed at 77 K under excitation in the photon-energy range of 4.42–6.20 eV. The maximum intensity of the luminescent sensitization states is observed upon excitation at a photon energy of 5.40 eV. At this excitation energy, charge transfer from the excited anion to these trapping centers occurs with the highest efficiency (Figure 2, curves 1–3).

Figure 3 (curves 1–3) presents the emission spectra of the YPO_4:Bi phosphor containing 0.5 mol% Bi, excited by photons in the corresponding spectral range of 5.4–6.2 eV at 77 K. As can be seen from curve 1 in Figure 3, the emission spectrum measured at 77 K contains a band at 4.87–5.1 eV, broad emission bands in the ranges of 3.81–3.26 and 3.10–2.95 eV, bands at 2.65, 2.41, and 2.25 eV, and intense peaks at 1.73, 1.69, 1.62, and 1.58 eV.

The emission band at 4.87–5.1 eV corresponds, in terms of its spectral position, to the intracenter emission of Bi^{3+} ions (the A band) (Figure 3). The main broad emission band extending from 3.70 to 3.26 eV can be attributed to a sensitization-related emissive state. These emissive states are excited over a broad spectral range from 5.9 to 5.3 eV, in which electron-trapping centers are formed as a result of charge transfer from the excited anions of the host lattice to individual trapping centers (Figure 4).

The emission bands observed in undoped and Bi-doped YPO_4 can be classified into several groups.

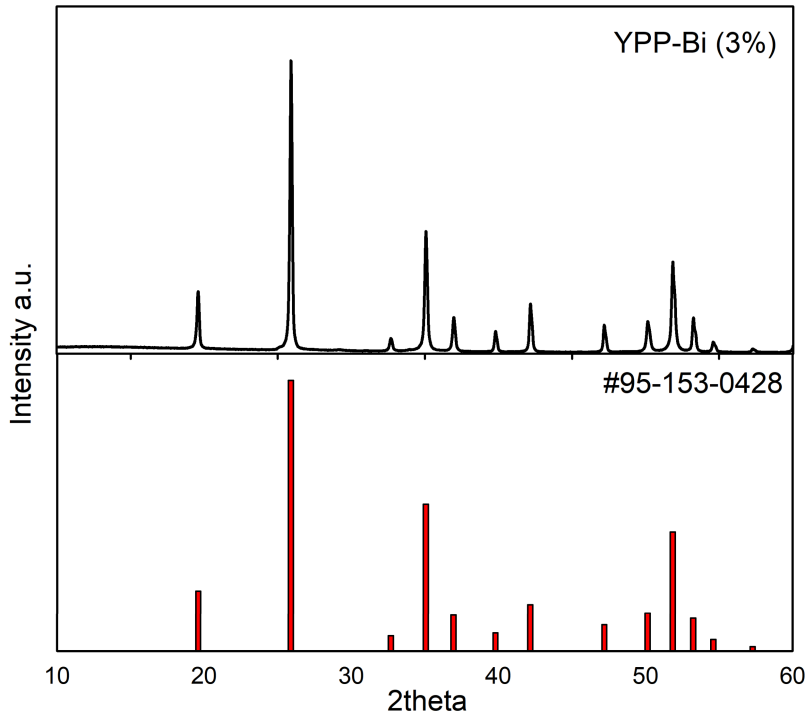

Figure 1. XRD pattern of YPO_4-Bi.

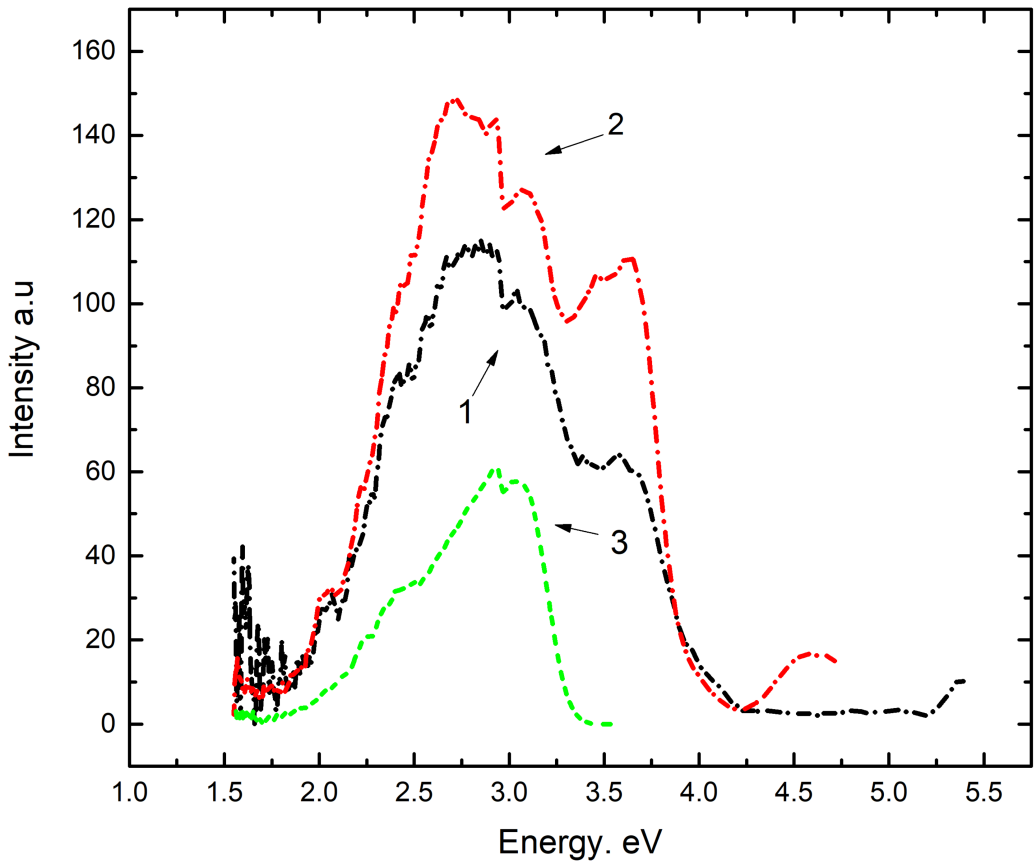

Figure 2. Emission spectra of YPO_4 measured at 77 K under excitation with photon energies of 5.9, 5.4, and 4.42 eV (curves 1, 2, and 3, respectively).

The first group comprises the emission bands detected in YPO_4:Bi and attributed to the intracenter luminescence of Bi^{3+} impurity ions in the YPO_4 host lattice. As shown in Figure 3

(curve 3), the emission band at 4.87–5.1 eV corresponds, in terms of its spectral position, to the intracenter emission of Bi^{3+} ions, commonly referred to as the A emission band.

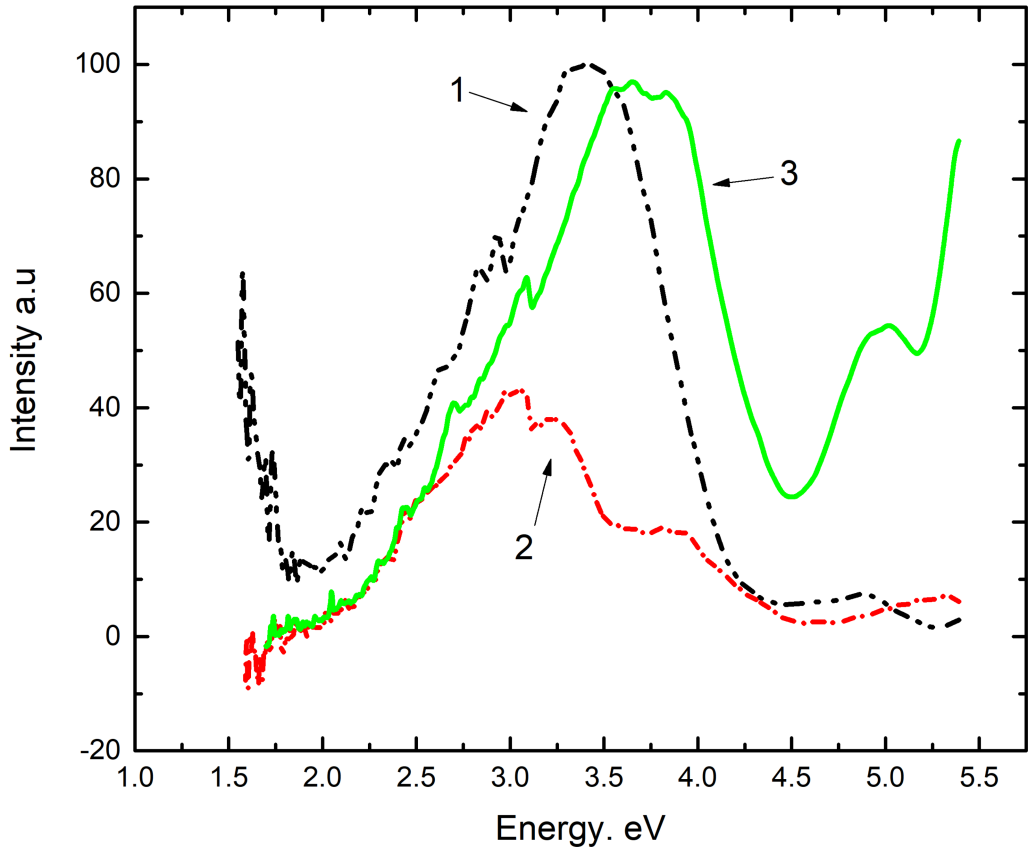

Figure 3. Emission spectra of YPO_4:Bi under excitation with photon energies of 6.2 and 5.4 eV at 77 K (curves 1 and 2, respectively) and 5.39 eV at 300 K (curve 3).

The second group of emissions occurs both in the pure YPO_4 host matrix and in Bi-doped YPO_4:Bi. These emissions are associated with the formation of a radiatively excited sensitization state in the energy range from 4.43 to 3.26 eV. This state is excited over a broad spectral range from 5.9 to 5.3 eV and is formed as electron–hole-trapping centers as a result of charge transfer from the excited $(PO_4)^{3-}$ anion of the host matrix to neighboring ions (Figure 4, curves 3, 4, 5, and 6).

In the following sections, the origin of the individual recombination emission bands arising from the decay of the combined electron-radiative state within the specified energy range from 4.43 to 3.26 eV will be discussed.

As shown in Figure 3, recombination emission bands at 3.1 and 2.9 eV appear in YPO_4:Bi at 77 K under excitation, with photon energies of 6.2 eV (curve 1) and 5.4 eV (curve 2). To clarify the origin of these newly observed recombination emission bands, their excitation spectra were measured at 77 K.

Figure 5 (curves 1 and 2) shows the excitation spectra of the 3.1 and 2.9 eV emission bands measured at 77 K. These emission bands are excited at photon energies of 4.8, 4.5–4.4, 3.9–3.8, 3.6, and 3.35 eV. They are also generated under excitation at 5.4, 5.3, and 5.1 eV in the transparency region of the host lattice. To verify whether these photon energies correspond to the excitation or absorption bands associated with the 3.1 and 2.9 eV emissions, additional measurements were carried out. As shown in Figure 5 excitation with photons of 4.4 and 3.9 eV results in the appearance of the corresponding primary emission bands at 3.1 and 2.9 eV.

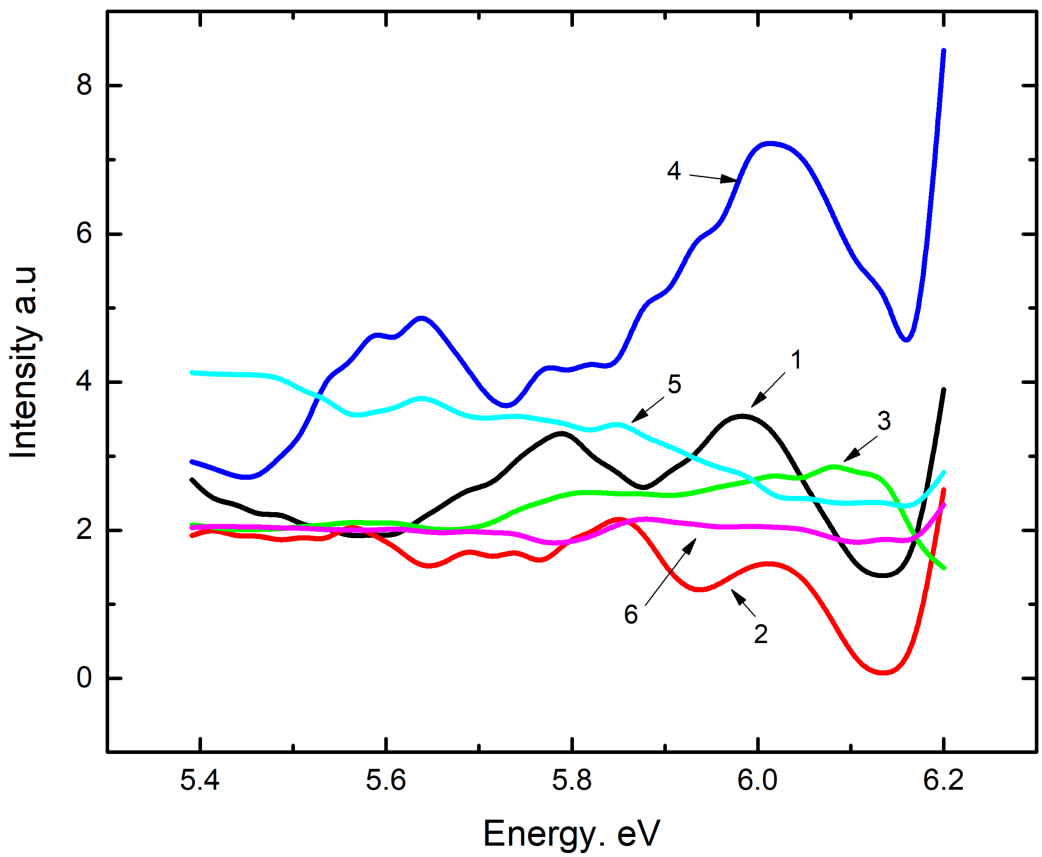

Figure 4. Excitation spectra of YPO_4:Bi monitored at the emission energies of 4.90, 4.38, and 3.64 eV at 300 K (curves 1, 3, and 6, respectively), and at the emission energies of 4.70, 3.81, and 3.35 eV at 77 K (curves 2, 4, and 5, respectively).

Thus, the excitation spectra of these emission bands in the transparency region of the host lattice can be attributed to localized states.

As shown in Figure 3, an emission band at 2.7 eV is also observed in irradiated YPO_4:Bi under excitation with photon energies of 6.2 eV and 5.4 eV at 77 and 300 K (curves 2 and 3). To clarify the origin of this emission, its excitation and formation spectra were measured.

Figure 6 (curves 1 and 2) presents the excitation and formation spectra of the 2.7 eV emission band. As can be seen, this emission is excited or generated at photon energies of 3.35, 3.64, 4.27, and 4.76 eV, as well as in the high-energy tail of the fundamental absorption region extending from 5.4 to 6.1 eV.

As shown in Figure 3, recombination emission bands appear in the long-wavelength region of the main emission spectrum after excitation with photons of 6.2 and 5.4 eV. Bands at 2.4 and 2.2 eV are observed at 77 K (curve 1), and a band at 2.06 eV is observed at 300 K (curve 2). To clarify the origin of these emissions, their excitation spectra were measured.

Figure 7 shows the excitation spectra of YPO_4:Bi monitored at the emission energies of 2.4 and 2.2 eV at 77 K (curves 1 and 2, respectively) and at 2.06 eV at 300 K (curve 3).

It can be seen from Figure 7 that the long-wavelength recombination emission bands at 2.4, 2.25, and 2.06–2.03 eV are excited by photons with energies from 3.7 to 3.5 eV, as well as in the tail of the fundamental spectral region from 6.04 to 5.4 eV at 77 K (Figure 7, curves 2 and 3).

One of the final stages of the relaxation processes in Bi-activated phosphate phosphors is the formation of Bi^{2+} ions after excitation in the tail of the fundamental absorption region by photons with an energy of 3.35 eV.

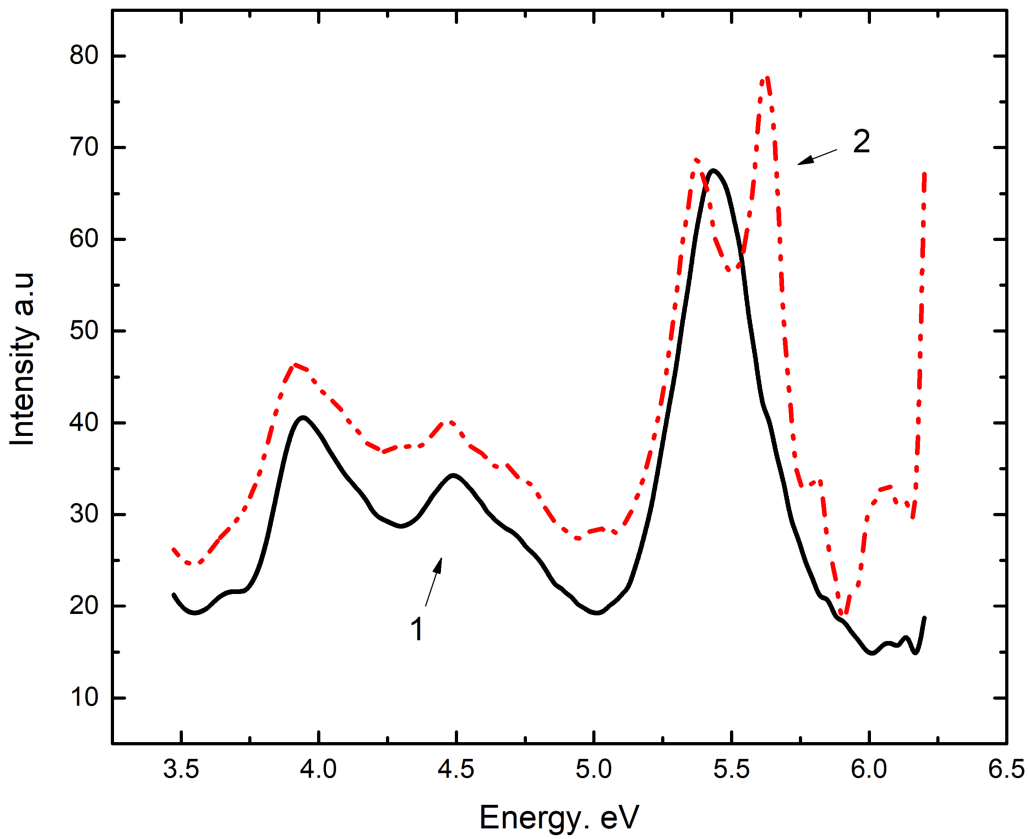

Figure 5. Excitation spectra of YPO_4:Bi monitored at the emission energies of 3.1 and 2.9 eV at 77 K (curves 1 and 2, respectively).

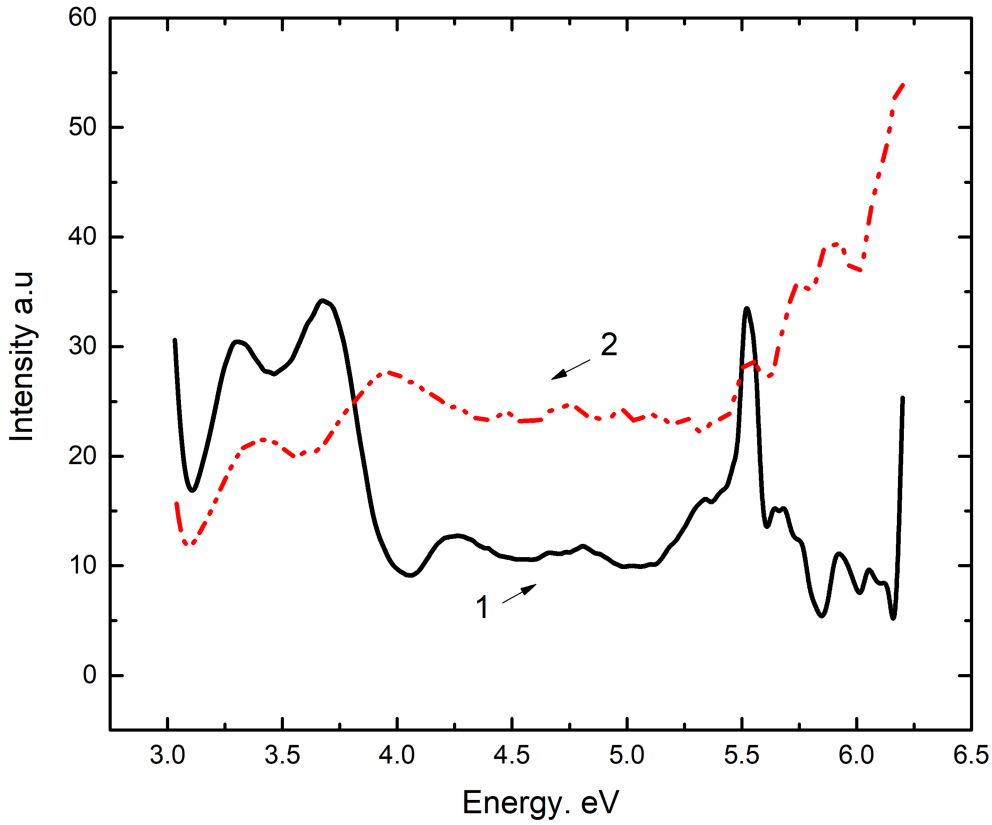

Figure 6. Excitation spectra of YPO_4:Bi monitored at the emission energy of 2.7 eV at 77 and 300 K (curves 1 and 2, respectively).

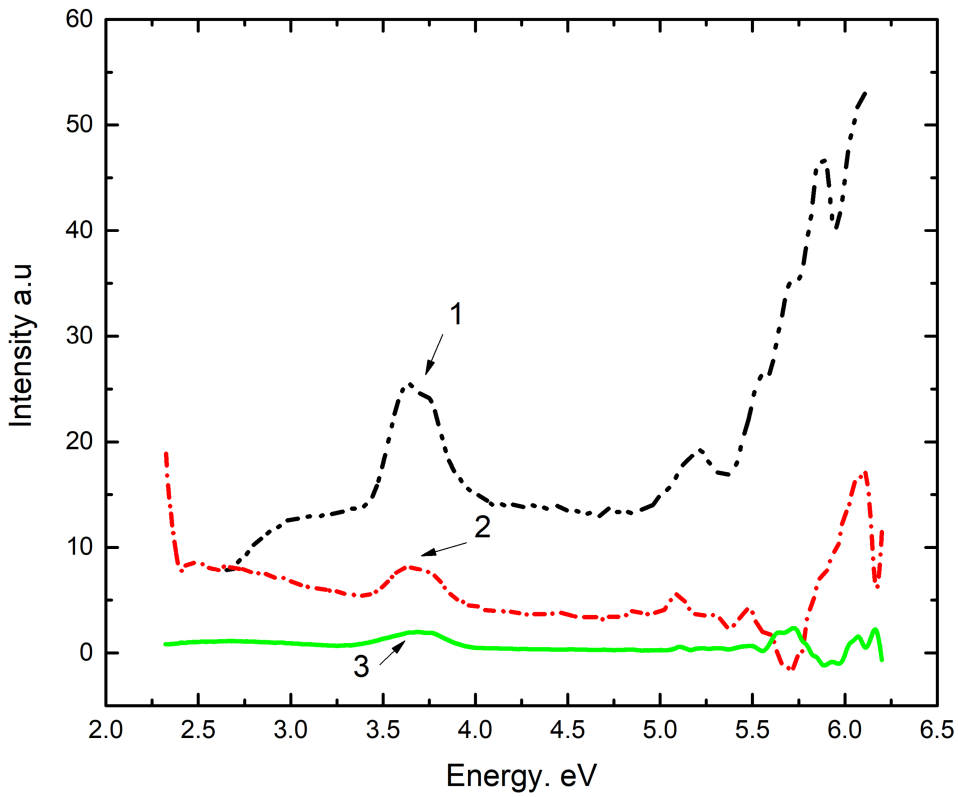

Figure 7. Excitation spectra of YPO_4:Bi monitored at the emission energies of 2.4 and 2.2 eV at 77 K (curves 1 and 2, respectively), and at 2.06 eV at 300 K (curve 3).

Figure 8 presents the excitation and formation spectra of Bi^{2+} ions in YPO_4:Bi. As can be seen from Figure 8 (curve 1), excitation with photons of 3.35 eV gives rise to recombination emission bands at 3.1–2.95 eV and 2.21 eV, as well as to the Bi^{2+} ion emission band at 1.7 eV (curve 5).

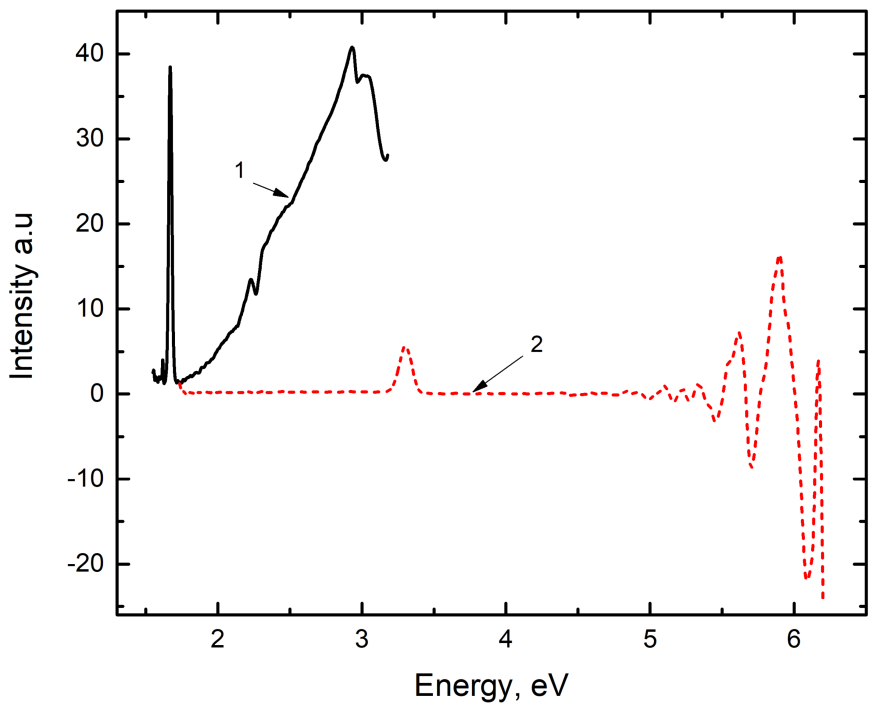

Figure 8. Formation and excitation spectra of Bi^{2+} ions in YPO_4:Bi (curve 1—excitation spectrum; curve 2—creation spectrum).

Figure 9 shows the temperature dependence of the intensities of the recombination emission bands at 3.08 and 2.95 eV, as well as the Bi^{2+}-related emission bands at 1.72 and 1.58 eV, measured after 10 min of X-ray irradiation under excitation with photons of 5.63 eV.

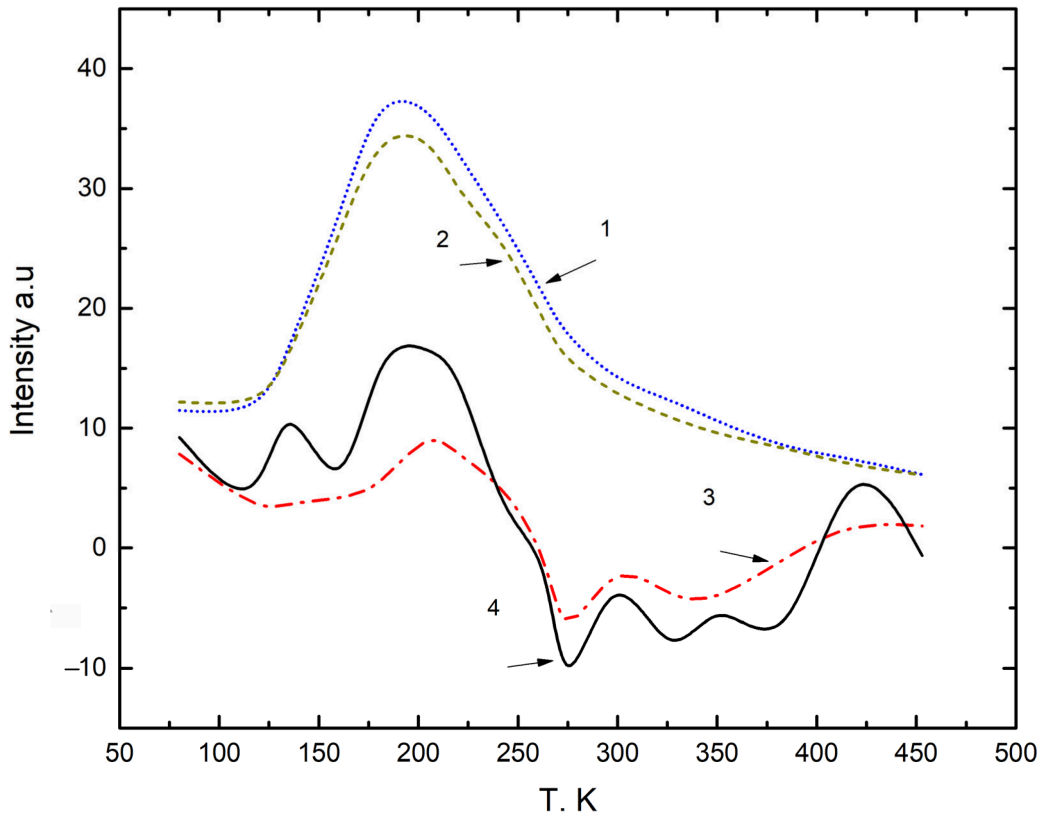

Figure 9. Temperature dependence of the emission intensity for the bands at 3.08 eV (curve 1), 2.95 eV (curve 2), 1.72 eV (curve 3), and 1.59 eV (curve 4).

As can be seen from Figure 9 (curves 1 and 2), the intensities of the 3.08 and 2.95 eV emission bands increase in the temperature range of 150–200 K. This enhancement is associated with the thermal delocalization of electrons from intrinsic PO_4^{4-} trapping centers. At higher temperatures, the emission intensity gradually decreases.

The enhancement of the Bi^{2+}-related emission and the formation of Bi^{2+} trapping centers in the temperature range of 150–230 K may be associated with the interaction of these centers with Bi^{4+}-type hole centers located above the valence band of the host lattice. These hole centers are partially delocalized within this temperature interval. Complete ionization of the Bi^{2+} centers is expected to occur at considerably higher temperatures, near 430–450 K.

Figure 10 presents the thermally stimulated luminescence (TSL) curve with a maximum at approximately 190 K, corresponding to the most efficient ionization of intrinsic electron-trapping centers. The TSL maximum lies within the same temperature range in which the enhancement of the 3.08 and 2.95 eV recombination emission bands is observed. The quantitative trap depth calculation via the peak shape method and the initial rise method has shown an energy of 0.093 eV.

Thus, the sensitization-related emissive states in the energy range of 4.42–3.35 eV can be attributed to intrinsic and impurity-related electron-trapping centers, including PO_4^{4-} and Bi^{2+} centers. These states may be described as combined electron-radiative states composed of intrinsic and impurity-related electron- and hole-trapping centers.

The decay of these combined states gives rise to recombination emission bands at 3.10, 2.95, 2.75, 2.40, 2.25, and 2.06 eV, together with the characteristic impurity-related emission of Bi^{2+} centers.

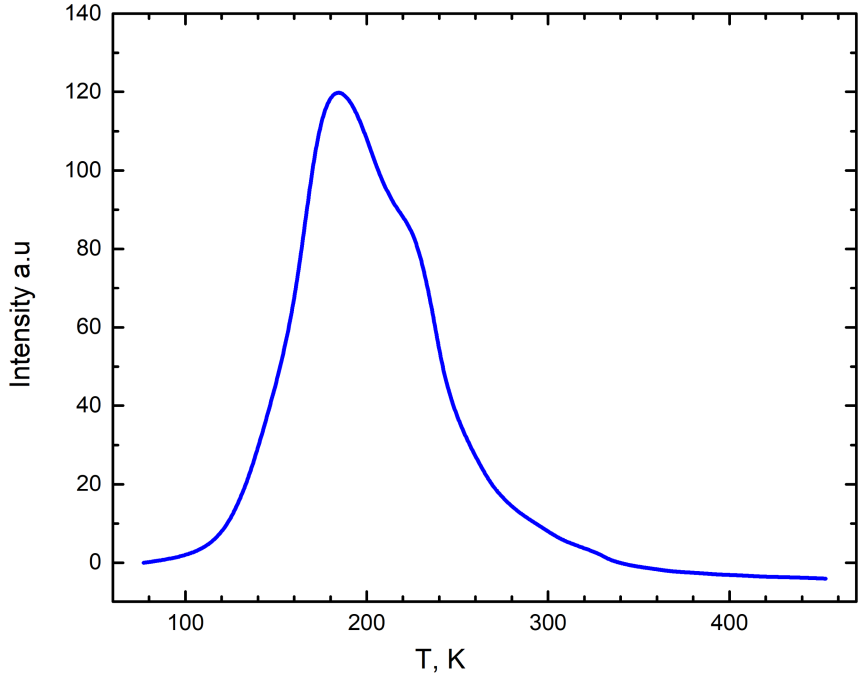

Figure 10. Thermally stimulated luminescence (TSL) glow curve of the YPO_4:Bi^{2+} phosphor after 5 min of X-ray irradiation.

Figures 11 and 12 show the reflection spectra of the YPO_4:Bi and YPO_4 phosphors after irradiation with X-rays for 5 and 10 min.

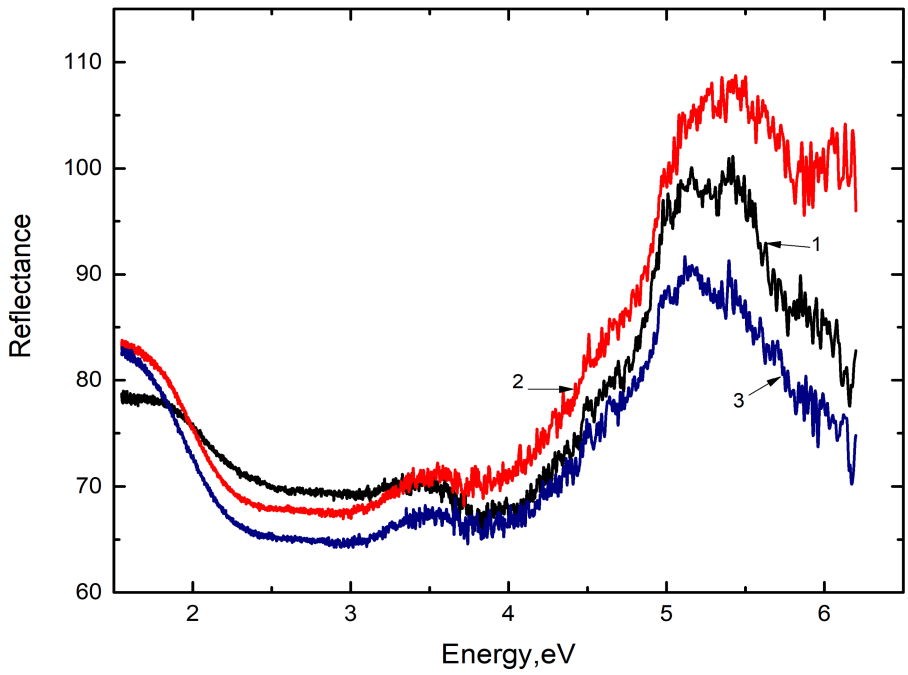

Figure 11. Reflection spectra of undoped YPO_4 before X-ray irradiation at 300 K (curve 1), and after 5 min of X-ray irradiation at 300 K (curve 2), and after subsequent annealing to 300 K (curve 3).

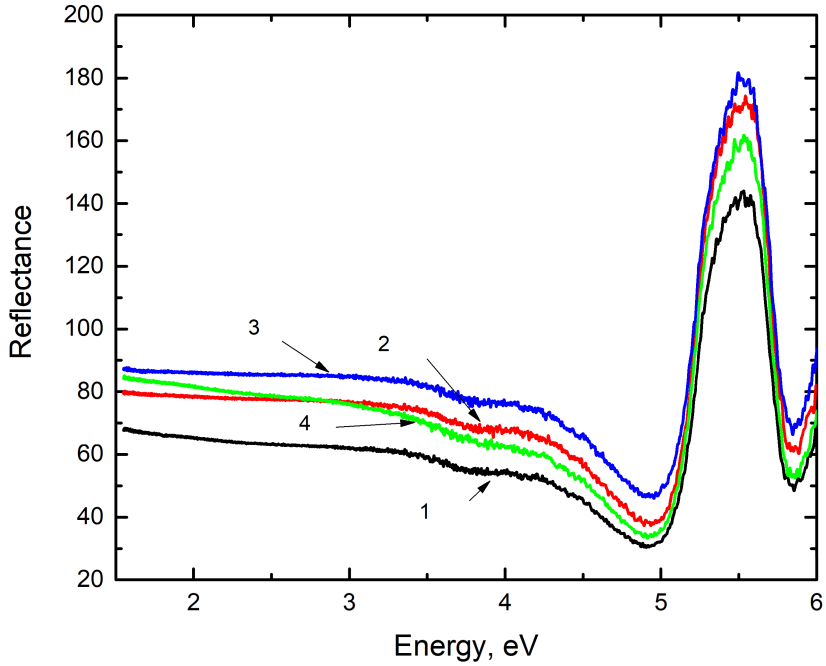

Figure 12. Reflection spectra of YPO_4:Bi measured at 77 K before X-ray irradiation (curve 1), after 5 min of X-ray irradiation (curve 2), after 10 min of X-ray irradiation (curve 3), and after subsequent annealing to 300 K (curve 4).

It can be seen from the figures that reflection bands appear in the spectral region of 4.42–3.8 eV, corresponding to absorption or reflection by induced trapping centers in the transparency region of the host lattice.

We assume that the induced reflection spectra correspond to the excitation or absorption spectra of the trapping centers created in the irradiated material, $(PO_4)^{3-} + e^- \rightarrow (PO_4)^{4-}$ and $Bi^{3+} + e^- \rightarrow Bi^{2+}$, created by charge transfer from the excited anion to neighboring $(PO_4)^{3-}$ anions or Bi^{3+} impurities. As shown in the work of the authors [10], the short-wavelength emission bands at 5 eV and 3.8 eV in YPO_4:Bi can be formed as a result of charge transfer from an excited ion to neighboring ions and impurity centers. In this case, electron-trapping centers are created in the energy range of 4.42–3.35 eV in the form of an absorption energy band in the transparency region of the YPO_4:Bi host lattice. In the spectral range of 5.27–5.51 eV, the reflection spectrum of the excited ion at the moment of trapping-center formation is shown.

4. Discussion

In accordance with the aim of the work, the mechanisms of formation and the structure of electron–hole-trapping centers arising upon excitation in the spectral region where their formation is possible as a result of charge transfer from the excited state of an anion to neighboring anions and impurities were investigated.

In YPO_4:Bi orthophosphate irradiated with photons of 6.2 and 4.42 eV and X-rays, radiative sensitization states arise in the energy range of 4.42–3.35 eV (Figure 13).

It was experimentally shown that these sensitization-related radiative states are created upon excitation near the fundamental region of the host lattice at energies from 6.04 to 5.51 eV as electron-trapping centers resulting from charge transfer from the excited $PO_4{}^{3-}$ anion to neighboring anions, impurities, and other pre-radiation defects of the host lattice (Figure 13). Thus, we showed that excitation with photons having energies of 6.04–5.51 eV or with X-rays creates a broad sensitization-related radiative energy state in the range of 4.42–3.35 eV. These states are created in irradiated undoped YPO_4 and Bi-doped YPO_4

(Figure 13). In this photon-energy range, almost all recombination emissions are created (Figure 14). Upon excitation with photons having energies of 4.43–3.35 eV, two groups of emissions are created: 3.1 and 2.9 eV, and from 2.8 to 2.25 eV (Figure 14).

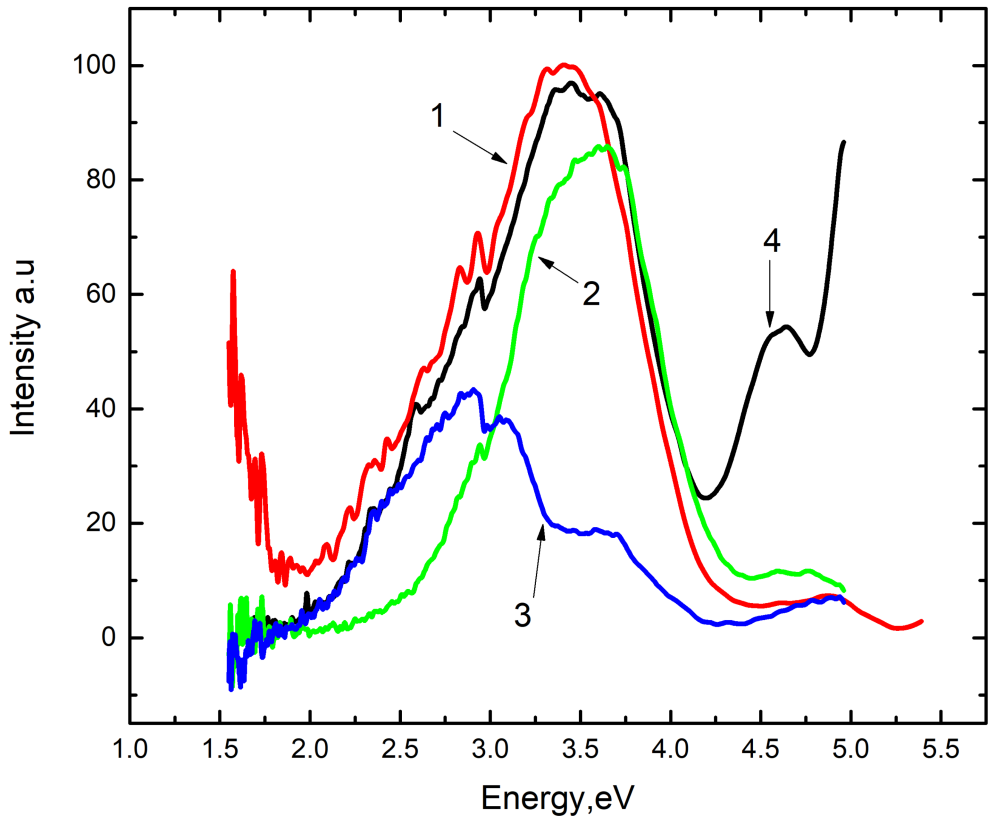

Figure 13. Emission spectra of YPO_4:Bi under excitation with photons of 6.2 and 5.4 eV at 77 K (curves 1 and 3, respectively), and 5.6 and 5.4 eV at 300 K (curves 2 and 4, respectively).

The recombination emission bands at 3.1 and 2.9 eV, which arise upon the recombination of electrons from the $(PO_4)^{4-}$ electron-trapping center with PO_4^{2-} holes localized above the valence band, are located in the spectral region of 3.1–2.95 eV, corresponding to the blue emission of semiconductor light-emitting diodes used for the excitation of phosphors.

The second group of recombination emissions at 2.8, 2.4, 2.25, and 2.06–2.03 eV arises upon the recombination of electrons from electron-trapping centers with hole-trapping centers localized above the valence band and located at nonequivalent crystallographic positions in the host lattice [11]. In practice, these recombination emissions are mainly used for lighting residential premises, in lamps for various vehicles, and for other applications.

Thus, in irradiated YPO_4-Bi, three types of emission are formed, characteristic, as in other phosphors, sulfates, garnets, and phosphates activated with bismuth ions: ultraviolet emission corresponding to intracenter transitions of the Bi^{3+} ion and visible recombination emission at the 2.7 eV–orange–red recombination emission.

We have not revealed the nature of the visible emission at 2.7 eV arising in irradiated YPO_4-Bi under excitation at 6.2 eV and 5.4 eV at 77 K. The authors [14–16], in studies of aluminum and gallium garnets, associated the appearance of visible emission with an exciton localized around the Bi^{3+} ion.

We assume that the 2.7 eV emission in YPO_4-Bi is efficiently excited in the spectral region of 5.5–6.2 eV, where electrons are created as a result of charge transfer from the excited $(PO_4)^{3-}$ ion, which relaxes and recombines with the hole (O^-–Bi^{3+}) localized above the valence band of the matrix near the Bi^{3+} impurity and forms exciton-like states. This

system $e^- + (O^- – Bi^{3+}) \rightarrow e^0$ can decay radiatively with the formation of emissions at 2.7 eV, or the energy in the recombination process is transferred to Bi^{3+} impurities.

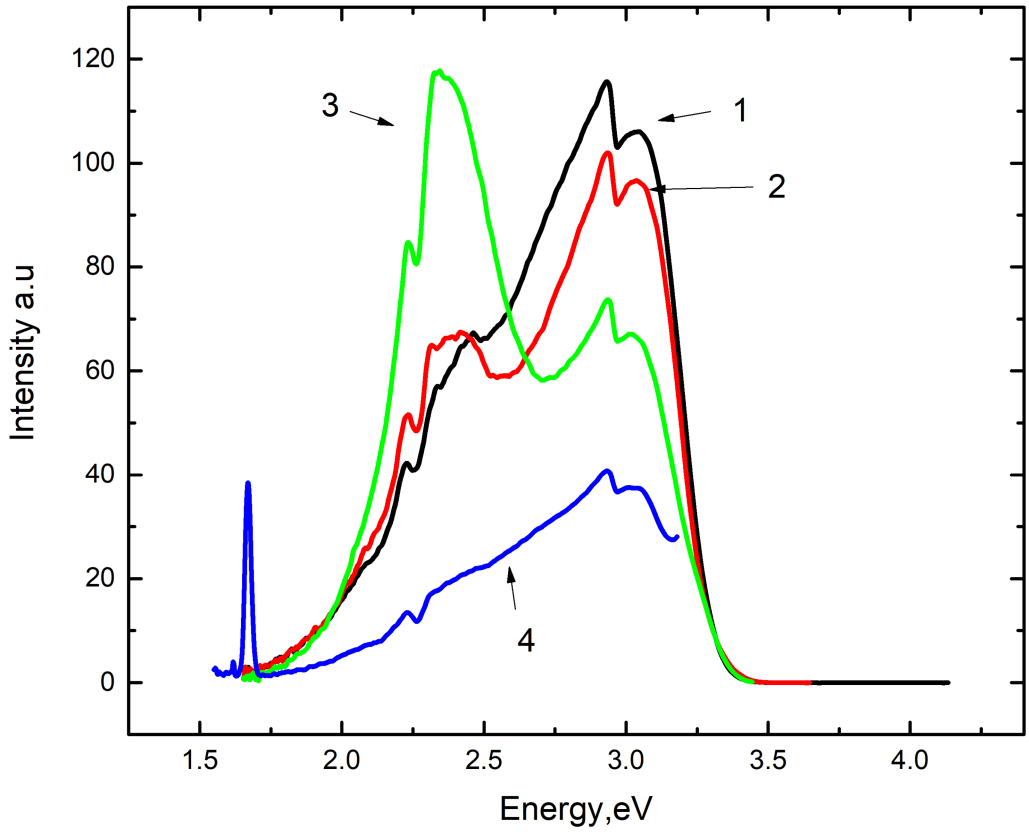

Figure 14. Emission spectra of YPO_4:Bi under excitation with photons of 4.42, 3.9, 3.6, and 3.35 eV at 77 K (curves 1, 2, 3, and 4, respectively).

The indicated recombination emissions, covering a broad spectral range from 3.1–2.9 eV and from 2.8 to 2.03 eV, are excited in two spectral intervals: from 4.43 to 3.8 eV and from 3.7 to 3.25 eV (Figure 15). These two spectral intervals in the transparency region of the host lattice correspond to local energy levels with a certain width (Figures 11 and 12).

For the first time, by measuring the reflection, emission, and excitation spectra of irradiated YPO_4:Bi phosphor at 77 and 300 K, we experimentally showed that, as a result of charge transfer at photon energies of 5.51–5.27 eV from the excited PO_4^{3-} ion to neighboring ions and Bi^{3+} impurities located at disturbed lattice sites, energy bands corresponding to the combined electron-radiative state of the host lattice appear in the transparency region of YPO_4:Bi within the spectral range of 4.42–3.35 eV (Figures 11 and 12).

Thus, upon excitation in the ultraviolet spectral region with photons having energies from 6.04 to 5.51 eV, combined electron-radiative states are created in YPO_4:Bi at 4.42–3.8 eV and 3.6–3.35 eV. These states represent the excitation, absorption, or reflection spectra of two recombination emission groups at 3.1–2.95 eV and 2.8–2.06 eV, which are used as radiation sources together with semiconductors and light-emitting diodes for the excitation of phosphors and in general-purpose lighting lamps.

The measured decay lifetimes (Figure 16) of the recombination emissions at 3.64 eV and 3.1 eV were 1.36 μs and 1.45 μs, respectively. The lifetime of the radiative state at 3.64 eV turned out to be shorter than the lifetime of the recombination emission at 3.1 eV.

The decay kinetics of 3.64 eV were satisfactorily described by a biexponential function, yielding lifetime components of $\tau_1 = 1.034 \pm 0.015$ μs and $\tau_2 = 5.173 \pm 0.434$ μs. The

fast component dominates the decay, accounting for 92.08% of the integrated intensity, whereas the slow component contributes 7.92%. The amplitude- and intensity-weighted mean lifetimes were 1.104 ± 0.020 µs and 1.362 ± 0.081 µs, respectively. The goodness parameter is $\chi^2 = 0.8291$. The luminescence decay kinetics of 3.1 eV were well-described by a biexponential function, indicating the presence of two relaxation pathways. The dominant fast component exhibited a lifetime of τ_1 = 1.13 µs with a relative contribution of 91.97%, while the slower component showed τ_2 = 5.15 µs and contributed 8.03%. The average lifetimes were 1.21 and 1.45 µs for the amplitude- and intensity-weighted approaches, respectively. The goodness parameter is $\chi^2 = 0.9296$.

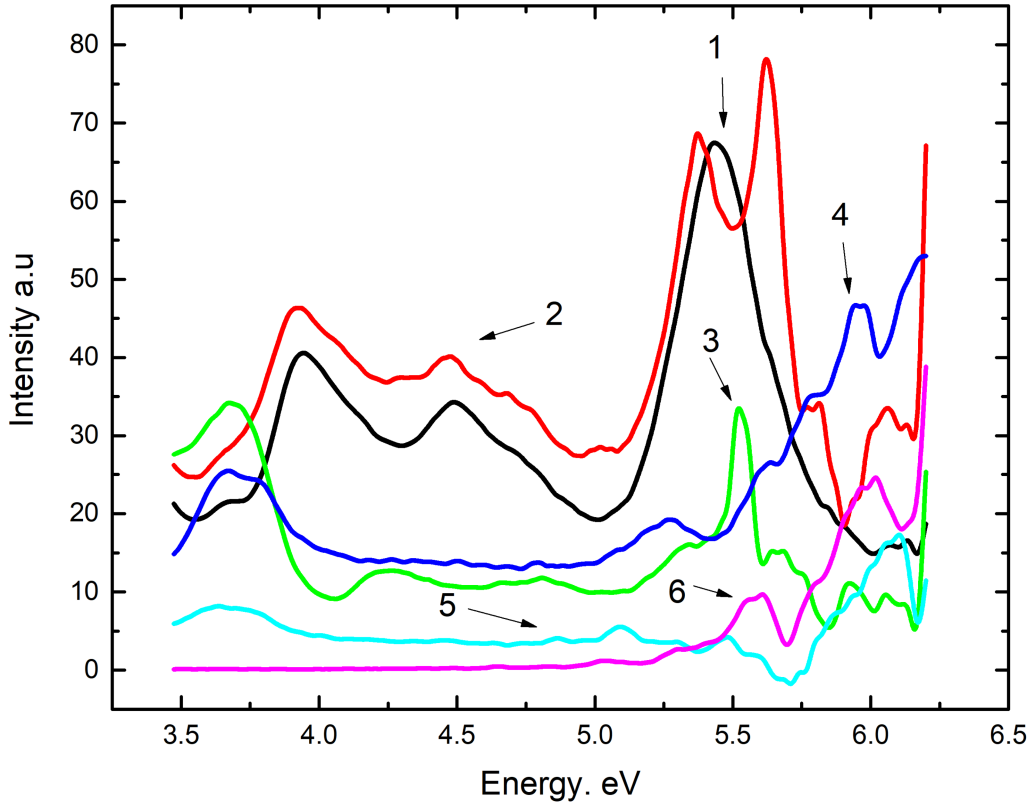

Figure 15. Excitation spectra of YPO_4:Bi monitored at the emission energies of 3.1, 2.9, 2.4, 2.25, and 1.67 eV at 77 K (curves 1, 2, and 4, 5, 6, respectively), and at 2.8 eV at 300 K (curve 3).

Now the third group of trapping centers remains, which are excited in the combined electron-radiative states at a photon energy equal to 3.35 eV. Upon excitation with photons at 3.35 eV or with photons having energies of 6.2–6.04 eV, where a free electron should be created, the Bi^{2+} ion is formed according to the reaction $Bi^{3+} + e^- \rightarrow Bi^{2+}$.

The Bi^{2+} trapping centers have ground and excited states $^2P_{3/2}$-$^2P_{1/2}$, which are revealed by emissions at 1.69 eV, 1.67 eV, 1.65 eV, and 1.58 eV. The kinetics of the appearance of such a Bi^{2+} trapping center is as follows. Upon excitation with high-energy photons of 6.2–6.04 eV, an electron-radiative local state at 3.35 eV (i.e., an electron-trapping center) should appear in the phosphor. Upon excitation with photons having an energy of 3.35 eV, an electron is ionized from the local state and is captured by a Bi^{3+} ion, and a Bi^{2+} trapping center is formed according to the reaction $Bi^{3+} + e^- \rightarrow Bi^{2+}$.

Figure 9 shows the temperature dependence of the Bi^{2+} emission intensity. It can be seen that, in the high-temperature region, an enhancement of the Bi^{2+} ion emission occurs.

It is assumed that the enhancement of the emission is associated not with the ionization of the Bi^{2+} ion but with its destruction during interaction with a delocalized Bi^{4+} hole center located above the valence band. During the recombination interaction of the Bi^{2+} electron

trapping center with the Bi^{4+} hole center, thermoluminescence arises, which can excite Nd^{3+} and Yb^{3+} ions, and infrared emission should arise during this energy transfer.

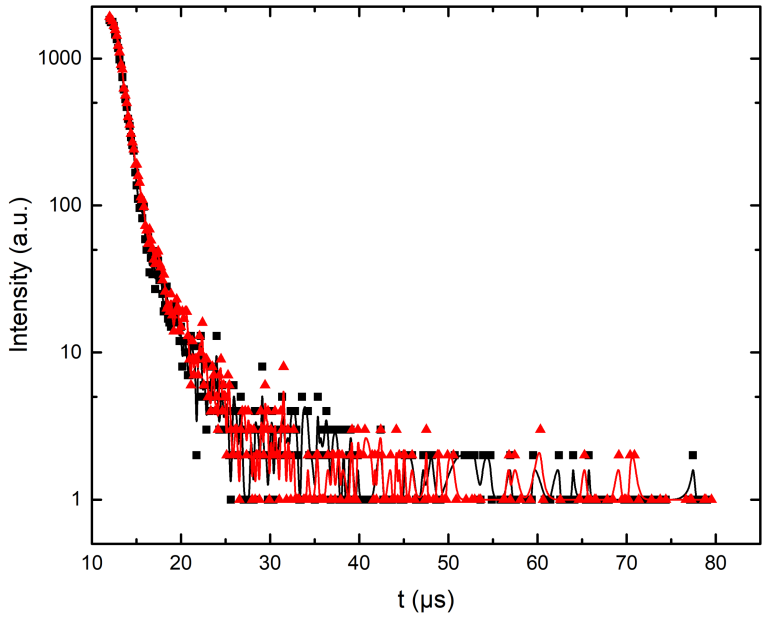

Figure 16. Emission decay kinetics in the YPO_4:Bi phosphor excited by 5.4 eV: for band 3.1 eV (red); for band of 3.64 eV (black).

The band diagram illustrates (Figure 17) the formation of electron–hole-trapping centers following excitation in the long-wavelength region of the fundamental absorption band. The right-hand side of the figure presents the relaxation processes associated with the formation of electron–hole-trapping centers under excitation with photons of 5.9 eV energy. At the initial stage after excitation, the 5.1 eV intracenter emission of Bi^{3+} ions in YPO_4:Bi appears. This emission was previously reported by the authors in Refs. [7–9,12,13]. At the next stage, under excitation with 5.9 eV photons, charge transfer occurs at energies of approximately 5.5 eV from the PO_4^{3-} anion to neighboring ions and Bi^{3+} impurity centers. As a result, electron–hole-trapping centers are formed according to the reactions $e^- + PO_4^{3-} \rightarrow PO_4^{4-}$ and $Bi^{3+} + e^- \rightarrow Bi^{2+}$. Simultaneously, PO_4^{2-} hole-trapping centers localized near Bi^{3+} impurity ions are formed above the valence band. After relaxation, emission bands at 3.0–3.1 eV and 2.90–2.95 eV appear. These emissions are excited by photons with energies of 4.4–4.5 eV and 3.9–4.0 eV, respectively. The appearance of analogous emission and excitation bands in the same spectral region was convincingly demonstrated in our previous studies of irradiated $CaSO_4$, $CaSO_4$:Dy, $BaSO_4$:Dy, $BaSO_4$:Bi sulfates and $Ca_2P_2O_7$:Mn, $Ca_2P_2O_7$:Tb, and $Ca_3(PO_4)_2$:Mn phosphates [11,20–23]. It was shown that the 3.0–3.1 eV and 2.90–2.95 eV emissions, excited at 4.45–4.5 eV and 3.9–4.0 eV, respectively, are formed in all these phosphors as a result of charge transfer from excited anionic complexes to neighboring anions at energies of approximately 5.5 eV. It was also demonstrated that the same recombination emission at 3.0–3.1 eV appears in $Ca_2P_2O_7$:Mn, $BaSO_4$:Dy, and $CaSO_4$:Dy as a result of the capture of free electrons with energies of approximately 8–9 eV by matrix anions. These measurements were carried out using a vacuum monochromator. It was shown that the efficiency of the 3.0–3.1 eV emission increases by a factor of 3–4 when the excitation photon energy is increased from 6 to 10 eV. The energy levels corresponding to intrinsic SO_4^{3-} electron-trapping centers and impurity-related Dy^{2+} and Mn^+ electron-trapping centers should be located below the conduction band. The ionization energies of these electron-trapping centers, estimated from the thermal release of the recombination emission, are approximately 0.4–0.6 eV. Thus, the formation of electron-trapping centers in

YPO_4 should proceed through analogous reactions: $e^- + PO_4^{3-} \rightarrow PO_4^{4-}$ and $e^- + Bi^{3+} \rightarrow Bi^{2+}$. As a result, intrinsic PO_4^{4-}–PO_4^{2-} electron–hole pairs, impurity-related Bi^{2+}–PO_4^{2-} pairs, and other impurity trapping centers are formed.

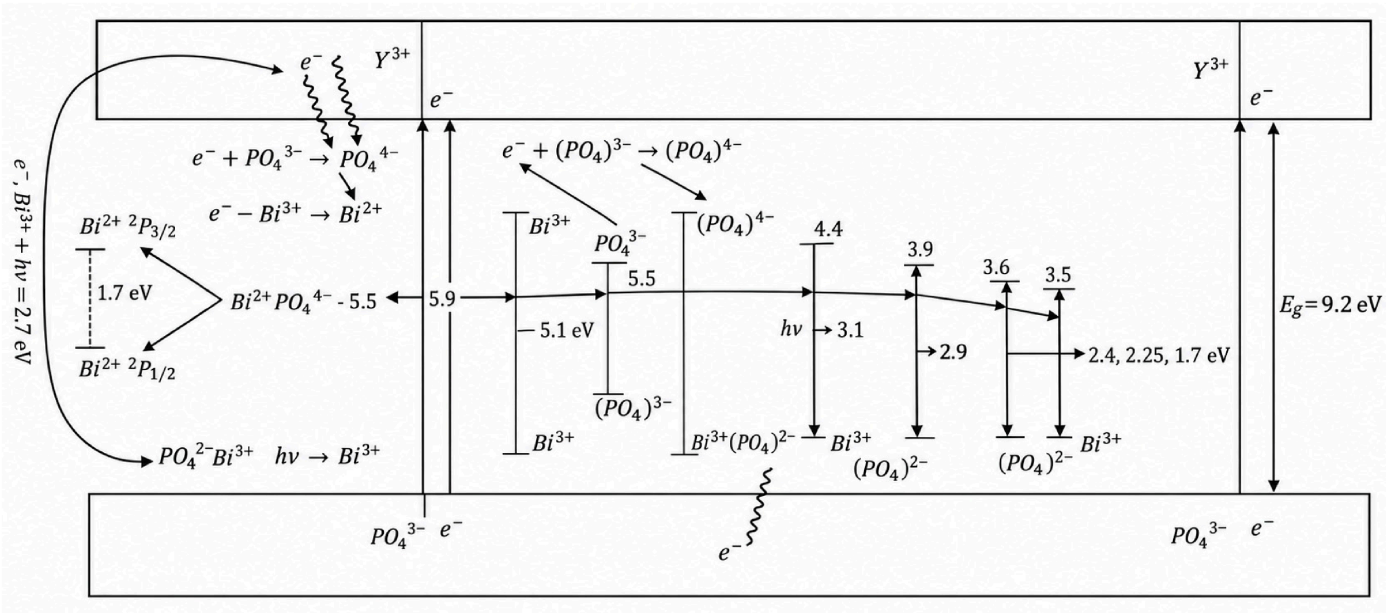

Figure 17. Energy band diagram illustrating the relaxation processes, accumulation, and decay of electron–hole-trapping centers.

Previous experimental studies have shown that the recombination emissions at 3.0–3.1 eV and 2.90–2.95 eV are excited at photon energies of 4.45–4.5 eV and 3.9–4.0 eV, as well as at an excitation energy of 3.6 eV. At the next stage, as a result of charge transfer induced by photons with an energy of 5.5 eV, localized electron-trapping centers are formed, giving rise to excitation bands at 3.6 and 3.5 eV. The emissions at 3.6 and 3.5 eV were previously associated with the formation of Bi^{3+}–Bi^{3+} pair centers [8]. Excitation in this spectral region gives rise to recombination emissions at 2.4, 2.25, 2.06, and 2.21 eV, as well as to the 1.7 eV emission of Bi^{2+} ions. All of these recombination emissions are excited by photons with energies of 3.5 and 3.6 eV, as well as within the long-wavelength tail of the fundamental absorption region (Figures 7 and 8). The left-hand side of the diagram also shows the formation of Bi^{2+} and PO_4^{4-} electron-trapping centers as a result of charge-transfer processes. In the crystal field, the energy levels of the Bi^{2+} ion are split into the $^2P_{3/2}$ and $^2P_{1/2}$ states. Radiative transitions between these levels give rise to emission at 1.7 eV.

As a result of the ionization of the PO_4^{4-} and Bi^{2+} electron-trapping centers, free electrons are generated. Recombination of these electrons with the corresponding holes leads to the formation of an excitonic state. As proposed by the authors [14–16], decay of the exciton in the vicinity of Bi^{3+} impurity ions may give rise to exciton-like visible emission at 2.7 eV.

Our previous results showed that, at the final stage of the relaxation processes, impurity-related emissions of Dy^{3+}, Mn^{2+}, and other impurity ions appear. In our previous studies, we assumed that part of the energy accumulated at the trapping centers is released through recombination emission of the host matrix, whereas the remaining part is transferred to impurity ions. In the present case, the recombination energy produced when an electron released from a trapping center recombines with its corresponding hole located above the valence band is transferred to Bi^{3+} impurity ions. An unresolved issue in these studies is the sensitized excitation of the main recombination emissions at 3.0–3.1 eV

and 2.90–2.95 eV within three spectral regions: 4.45–4.5 eV, 3.9–4.0 eV, and 3.5–3.6 eV. Measurements of the reflection spectrum in the energy range from 4.42 to 3.8 eV clearly indicate the presence of energy levels associated with electron-trapping centers within this spectral region.

5. Conclusions

1. In the irradiated YPO_4:Bi phosphor, a combined sensitized electron-radiative state is created in the spectral range from 4.42 to 3.35 eV, consisting of intrinsic and impurity electron–hole-trapping centers (Figures 3 and 15, curves 1, 2, and 3; Figure 5, curves 1 and 2) located below the conduction band of the host lattice;
2. It was experimentally shown that the main recombination emissions arising during the decay of the combined state at 3.1, 2.95, 2.75, 2.4, 2.25, and 2.06 eV, as well as the Bi^{2+} emission bands, are excited from the energy levels at 4.42–3.35 eV created as a result of charge transfer from the excited ion to neighboring ions and Bi^{3+} impurities located at disturbed sites in the band gap of the host lattice in the form of a combined electron-radiative state;
3. By measuring the reflection spectra of the irradiated YPO_4:Bi phosphor at 77 and 300 K, it was experimentally shown for the first time that, as a result of charge transfer at energies of 5.51–5.27 eV from the excited PO_4^{3-} ion to neighboring ions and Bi^{3+} impurities located at disturbed lattice sites, energy bands corresponding to the combined electron-radiative state of the host lattice appear in the transparency region of the YPO_4:Bi host lattice within the spectral range of 4.42–3.35 eV.

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