



Article

Nonradiative Energy Transfer in Bi₂O₃/Tm₂O₃ Powders under IR Excitation at Liquid Nitrogen Temperature

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Abstract: The presented work shows the study of energy transitions in the NIR and visible regions in the system of Bi₂O₃ and Tm₂O₃ powders. Mechanisms of upconversion luminescence and NIR luminescence between two Bi³⁺ and Tm³⁺ ions at T = 80 K accompanied with nonradiative energy transfer through the vibrational levels were investigated under IR photoexcitation. The absorption bands of the samples on the reflection spectra were examined in the visible region. The values of the emission cross-section parameters were calculated for the Bi₂O₃/Tm₂O₃ complexes.

Keywords: energy transfer; upconversion luminescence; low temperatures; reflectance; level splitting



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1. Introduction

In recent years, there has been a great interest in the conversion of IR radiation to shorter wavelengths using materials doped with a rare-earth element (REE), such as Tm³⁺, Er³⁺, Ho³⁺ [1,2]. Solid-state compact matrices based on REEs have become the subject of intensive spectroscopic studies due to their potential application as laser media for the visible range with upconversion (UC) emission [3–5]. High quantum efficiency solves the problem of the limited efficiency of silicon solar cells due to dopanding the different combinations of rare earth ions such as Tb³⁺-Yb³⁺ and Tm³⁺-Yb³⁺. The activated ions convert the high-energy part of the solar spectrum to the NIR wavelength region [6,7]. The Tm³⁺ ion has rich spectral energy levels in the range from the UV to the IR region. In addition, Tm³⁺ ions play a key role as an active dopant in doping in various solid media to produce laser radiation via an upconversion activation mechanism [8–10].

At the same time, the presence of wide energy levels in the bismuth ion of different valency is well known, which cause the possibility of photoluminescence generation and inter-level energy transfer in the presence of other closely located ions [11–14]. NIR luminescence has been observed at 1210 nm, 1173 nm and 1300 nm in quartz glasses doped with bismuth ions when the glass was irradiated by wavelengths of 405 nm and 808 nm, respectively [15,16]. It should be noted that the structure of glass significantly influences the hardness, density, refractive index and optical properties of glass, affecting the position of emission maxima, intensity and half-width of the maximum emission of Bi ions [17–19]. The low-temperature conditions are extremely important to observe energy transitions with single-band and narrow emission peaks in systems consisting of two different RE ions [20–22]. Thus, in conditions of low temperatures of liquid nitrogen due to spectral splitting of energy levels, spectral shifts in photoluminescence spectra in the NIR region are also possible [23]. The present work is a continuation of our previous work on the study of photo processes involving REE ions [20,24,25].

Since changes in the luminescence spectra of REE can be observed at low temperatures and since energy-transfer processes through energy levels are possible, due to the overlap of the Bi³⁺ and Tm³⁺ spectral bands in the visible region, a mixture of Bi₂O₃/Tm₂O₃ oxides

is an interesting subject as an optical element for luminescence generation in the visible-IR ranges. Therefore, the purpose of this work was to establish the phase composition of the oxide mixture and to determine the necessary atomic ratios at which the generation of luminescent properties in the $\text{Bi}_2\text{O}_3/\text{Tm}_2\text{O}_3$ system is possible. In addition, the key photophysical task of this study was to establish the spectral features of the upconversion luminescence of the oxides system and the ways of photoexcitation energy degradation at low temperatures.

2. Materials and Methods

2.1. Preparation of Bi_2O_3 with Tm_2O_3 Powders

Bismuth oxide was prepared by dissolving metallic bismuth (purity of 99.999%) mass of $m = 2$ g in the nitric acid with following preparation of bismuth oxalate and sintering in a muffle oven at a temperature of $T = 750$ °C for 2 h. A detailed description of the synthesis technique was presented in [24,26]. The obtained powder was light-yellow color. Then the obtained Bi_2O_3 was mixed with Tm_2O_3 (purchased from Sigma-Aldrich, St. Louis, MO, USA, purity of 99.999%). The powders were grinded in a mortar for 60 min. Then powder mixture was pressed into a pellet and annealed at a temperature of 750 °C for 2 h. The atomic concentration of Tm^{3+} changed in the range of (2.3–28) at.%.

2.2. Experimental Measurements

Luminescence experiments were performed by means of a Fluorolog-3 optical system (Horiba and Jobin Yvon Technology, Horiba Scientific, Palaiseau, France) equipped with an FL-1073 detector operating in the UV-VIS radiation bands. The IR laser (model LSR-PS-II) (China Ningbo Fingco Optoelectronic Co., Ltd., Ningbo, China) with continuously adjustable energy (0.1–1.0 W) and a wavelength of 980 nm was used as an excitation source. A cooled solid-state IR detector (Horiba Scientific, Longjumeau Cedex, France) (model 1427C) with a PS/TC-1 controller was used to measure luminescence in the infrared region.

The XRD pattern of the powders was recorded with using Dron-3 diffractometer Radikon LLC X-ray (Burevestnik, Ufa, Russia).

The morphological features of the oxides were studied by scanning electron microscopy on the Zeiss Cross Beam-540 FIBSEM (Zeiss, Oberkochen, Germany). The SEM/EDX analysis of the powders was examined by means of JEOL JSM-6390LV scanning electron microscope (Akishima, Tokyo, Japan) equipped with an Oxford instrument Inca X-Act SSD energy dispersive X-ray spectrometer. Secondary electron images and EDX data of the powders were obtained at 20 kV accelerating voltage.

The reflection spectra were measured on a spectrophotometer (Shimadzu, Kyoto, Japan) with an integrating sphere application in the range of 200–800 nm.

3. Results and Discussion

In the first series of the experiment, X-ray diffraction analysis of the studied powders and their morphological features were carried out. Figure 1 shows the XRD pattern of the Tm_2O_3 , Bi_2O_3 , $\text{Bi}_2\text{O}_3/\text{Tm}_2\text{O}_3$ (22 at.%) oxides.

According to the X-ray analysis, the Tm_2O_3 has a cubic body centered lattice with the type of symmetry $\text{Ia}\bar{3}$ (card No.631) with the following parameters of the unit cell: The length of the cube edge— $a = 10.45$ Å, the number of formula units included in the unit cell— $Z = 16$ (32 atoms of Tm and 48 atoms of O). Bismuth oxide has a monoclinic lattice with the space group of a $\text{P} 21/c$ (card No. 2-498). The unit cell parameters are: $a = 5.83$ Å, $b = 8.14$ Å, $c = 7.48$ Å, $\alpha = 90^\circ$, $\beta = 67.7^\circ$, $\gamma = 90^\circ$. A comparison was made with the PDWin base library for the most intense XRD pattern peaks.

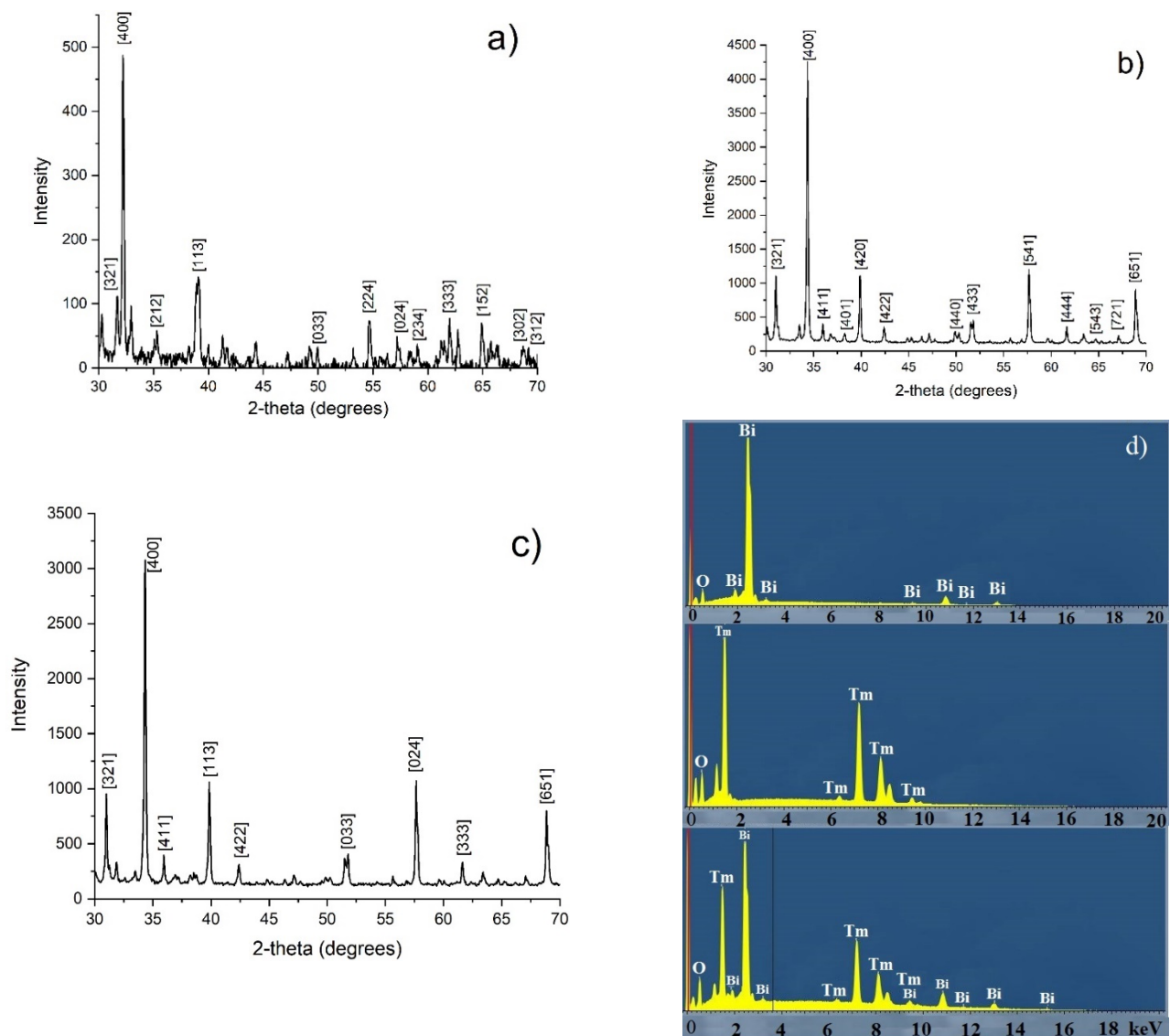


Figure 1. XRD patterns of the oxides Bi_2O_3 —(a); Tm_2O_3 —(b); $\text{Bi}_2\text{O}_3/\text{Tm}_2\text{O}_3$ (28 at.%)—(c); EDX analysis with atomic concentrations—(d).

The interplanar distances (d) corresponding to Bi_2O_3 and Tm_2O_3 in the mixture are presented in Table 1.

As can be seen from Figure 1c, on the diffraction pattern corresponding to the mixture of the oxides and Table 1 containing the peaks, in the structure of the powder, peaks corresponding to the two main phases were observed: cubic lattice (Tm_2O_3) and monoclinic lattice (Bi_2O_3). However, in the spectrum presented in Figure 1c, there were no intense reflexes [224] and [152] corresponding to the monoclinic Bi_2O_3 phase. In this regard, it can be concluded that as a result of sintering, the transformation of the crystal lattice of bismuth oxide occurs. Thus, during the annealing process at $T = 750\text{ }^\circ\text{C}$, as a result of surface diffusion in the mixture, a new phase is formed in the surface layer of the mixture ($\text{Bi}_2\text{O}_3/\text{Tm}_2\text{O}_3$), while in the depth of the composition of the mixture, the main phase composition remains.

Table 1. The most intense XRD pattern reflections characteristic of the Bi₂O₃ and Tm₂O₃ content in the Bi₂O₃/Tm₂O₃ (28 at.%).

Bi ₂ O ₃		Tm ₂ O ₃	
2θ (Degree)	d (Å)	2θ (Degree)	d (Å)
31.000	2.882	31.850	2.807
35.300	2.540	33.200	2.696
45.250	2.002	33.500	2.673
45.950	1.973	34.350	2.609
46.350	1.957	38.250	2.351
53.650	1.707	57.650	1.598
54.250	1.689	59.600	1.550
54.700	1.677	61.650	1.503
55.650	1.650	63.400	1.466
62.831	1.478	64.700	1.440
65.800	1.418	67.106	1.619

To determine the elemental composition of the synthesized samples, the studies were supplemented with the EDX spectral analysis. The spectral elemental composition of the mixture was performed in the 10 μm² area of the investigated powder with following averaging of the spectrum. Thus, the elemental composition for samples Bi₂O₃, Tm₂O₃ and Bi₂O₃/Tm₂O₃ in atomic percentages is shown in Figure 1d. Therefore, Figure 1d demonstrates that the synthesis method presented in this paper is a suitable method to obtain sufficiently homogeneous oxides without foreign impurities in the specified temperature range. The EDX-analysis for different atomic concentration of the thulium and bismuth ions presented in the supplementary materials.

The presence of an additional phase of thulium oxide in the microstructure of the mixture Bi₂O₃/Tm₂O₃ affects the X-ray diffraction analysis. Thus, on the diffraction pattern corresponding to the mixture of oxides (Figure 1c), the partial or complete quenching of individual peaks characteristic of the phase composition of a single component is observed.

Next, it was of interest to consider the morphological features of the studied oxides. Figure 2 shows the results of SEM microscopy of the powders.

Figure 2a shows that the surface structure of Tm₂O₃ is homogeneous without the periodic clusters formation. In the cross-section, a plate-like structure with a height of ≈0.1 μm is observed. The structure of the formations is dense with large layered formations. In Figure 2b, they are a solid, to the cells' similar structure.

Figure 2c shows that the surface of Bi₂O₃ consists of clusters with an average size of 1 μm. The surface of Bi₂O₃ is smooth without roughness. When looking at the surface on the scale of 200 nm, there are no cellular structures as it was observed for Tm₂O₃ (Figure 2b). Periodicity in the formation of the structure is also not observed. There are irregularities with the formation of internal tunnels with an average diameter of 3 μm.

Figure 2e,f shows that the Bi₂O₃/Tm₂O₃ complex has a granular surface structure.

Thus, the inset of Figure 2f shows a diagram of the quantitative distribution of granules by size. The diagram was constructed based on a detailed analysis of the SEM image from Figure 2f. Thus, the linear dimensions of crystal structures with a mathematical ratio of the image scale of Figure 2f (300 nm) were estimated on an area of 3.96 μm². Therefore, the size of granules in a mixture of Bi₂O₃/Tm₂O₃ with the atomic concentration of thulium ions of 28 at.% varies in the range of 50–320 nm. The average linear size was calculated by using quantitative-numerical analysis, considering the total number of granules (150). Thus, the average size was approximately 100 nm.

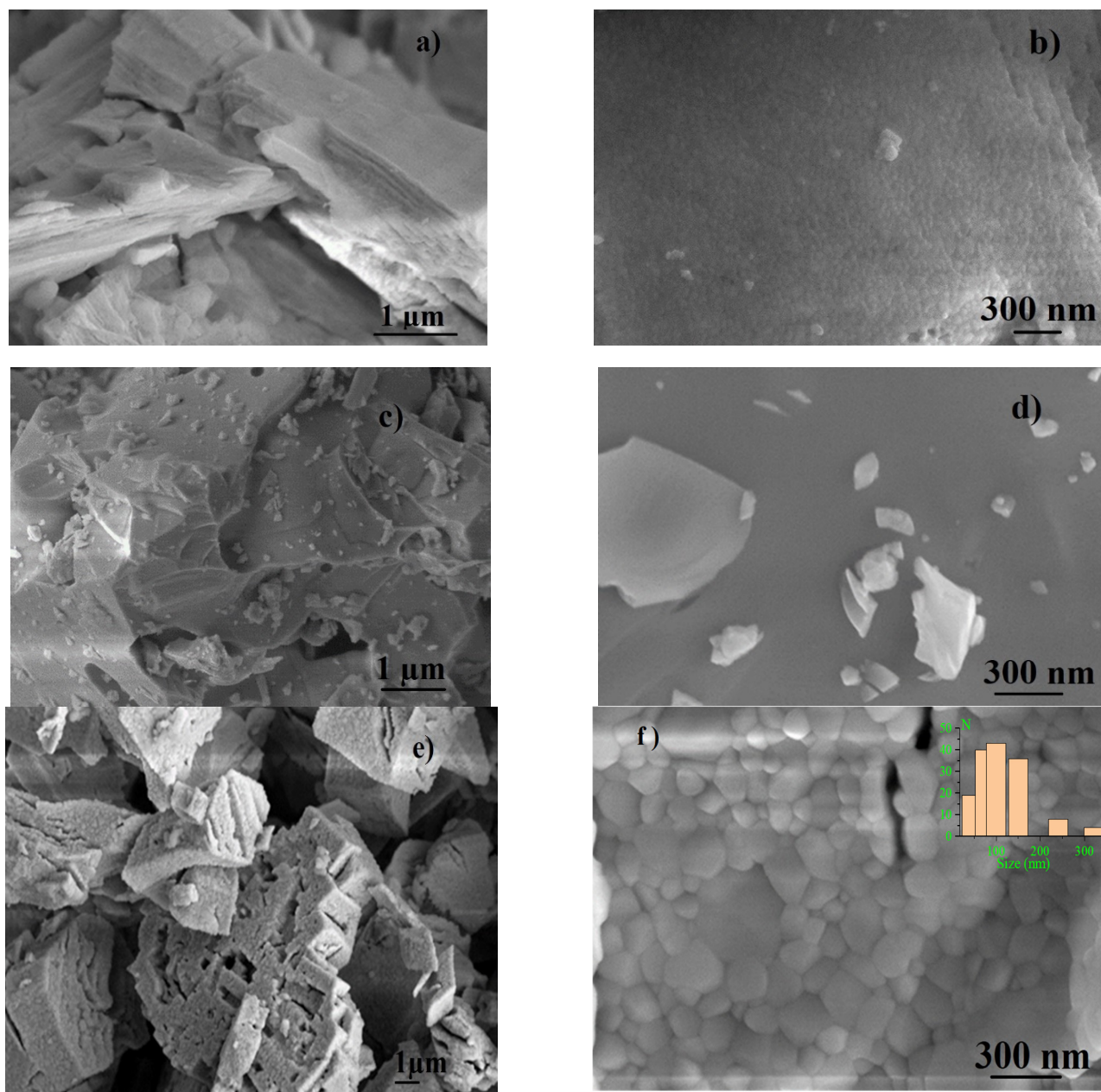


Figure 2. SEM images of the powders at different scales: (a,b)— Tm_2O_3 ; (c,d)— Bi_2O_3 ; (e,f)— $\text{Bi}_2\text{O}_3/\text{Tm}_2\text{O}_3$. Insert—size distribution of the crystallites.

The structure presents a columnar formation with a rough surface height of 12 μm . The shape of the grains is rounded; the density of the grains is high without appreciable porosity. The arrangement is chaotic over the entire surface of the sample. The formation of cellular structures due to the presence of bismuth oxide in the mixture is also characteristic here.

Then, the luminescence studies of the $\text{Bi}_2\text{O}_3/\text{Tm}_2\text{O}_3$ mixture in the visible and infrared regions at liquid nitrogen temperature were carried out under conditions of changing the atomic concentration of Tm^{3+} in the mixture.

Let us consider how the intensity of Bi^{3+} luminescence changes with a change in the concentration of Tm^{3+} in the NIR region. As a result of the Tm^{3+} presence, an increase in the IR luminescence of Bi^{3+} was observed. It is important to point out a linear type of the concentration dependence of intensity (inset Figure 3a). Therefore, at the lowest concentration of Tm^{3+} (2.3 at.%), the maximum value of the NIR luminescence intensity at the 1240 nm wavelength was observed and amounted up to $I = 2000 \mu\text{V}$. At the same

time, the formation of a new spectral maximum at a wavelength of 1280 nm was found. It is important to note that when a single thulium oxide powder was excited under photoexcitation with a wavelength of 980 nm at 80 K, no luminescence signal was observed in the Tm_2O_3 powder. Hence, the obtained spectral maxima in the NIR region are due to ${}^3\text{P}_1 \rightarrow {}^3\text{P}_0$ transitions for Bi^{3+} atoms. The appearance of the maximum at 1280 nm apparently could be due to the influence of the Tm_2O_3 crystal field surrounding the Bi^{3+} atoms. As a result of the influence of the additional field at low nitrogen temperatures, the excited ${}^3\text{P}_1$ level splits into Stark sublevels. The magnitude of the splitting of the main electron term (${}^3\text{P}_1$) can reach up to 1000 cm^{-1} [27], and since the emission wavelength lags behind the main maximum by 40 nm, consequently the value of the Stark splitting is $\Delta E \approx 200\text{ cm}^{-1}$. As a result of the activation of ultrafast processes ($>10^{-12}\text{ s}$) of absorbed energy degradation (wavelength 980 nm) between vibrational sublevels (internal conversion) at low temperatures, emission transitions of microsecond duration can be observed [28,29]. The mechanisms of energy transfer and ways of energy degradation in the complex by energy levels are discussed below.

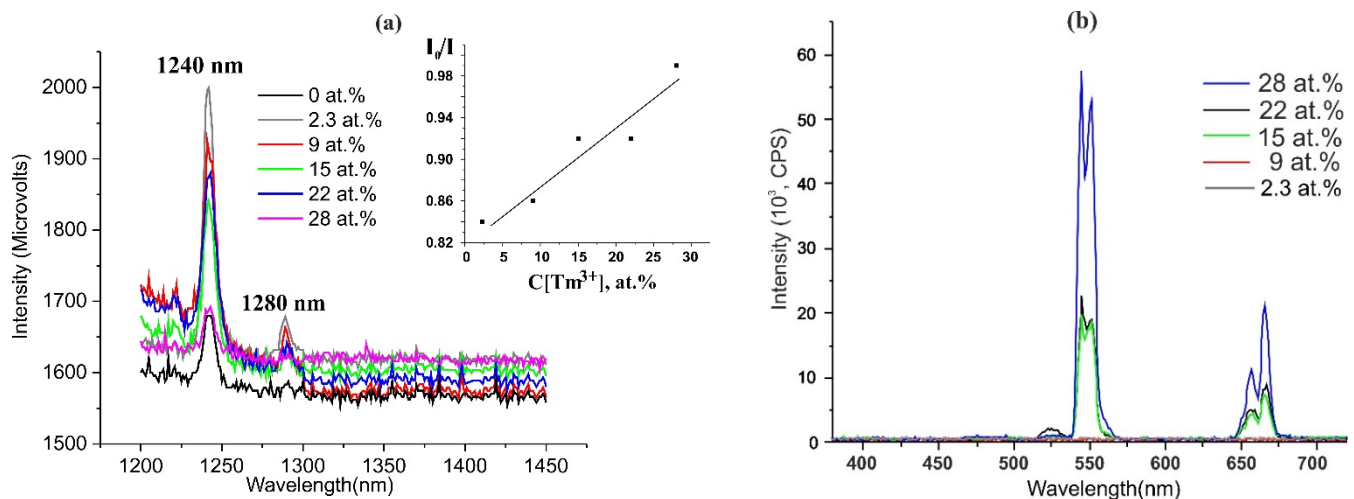


Figure 3. Luminescence spectra in the infrared region (a) and upconversion luminescence spectra in the visible region (b) of $\text{Bi}_2\text{O}_3/\text{Tm}_2\text{O}_3$ powders with different concentrations of Tm^{3+} atoms (2.3–28). The excitation wavelength $\lambda_{\text{ex}} = 980\text{ nm}$, $T = 80\text{ K}$.

Let us consider the processes of luminescence of powders in the visible region under photoexcitation with a wavelength of 980 nm. In the region of green wavelengths and red wavelengths, emission maxima due to the upconversion mechanism of luminescence were observed. The lifetimes of the upconversion luminescence are 172 ns and 670 ns at 545 nm and 665 nm, respectively. The kinetic curves are shown in Figure 4. With an increase in the atomic concentration of thulium ions, an increase in the intensity of upconversion luminescence at wavelengths in the region of 550 and 670 nm has occurred (Figure 3b). The highest UCL intensity corresponds to the maximum of Tm^{3+} concentration (28 at.%).

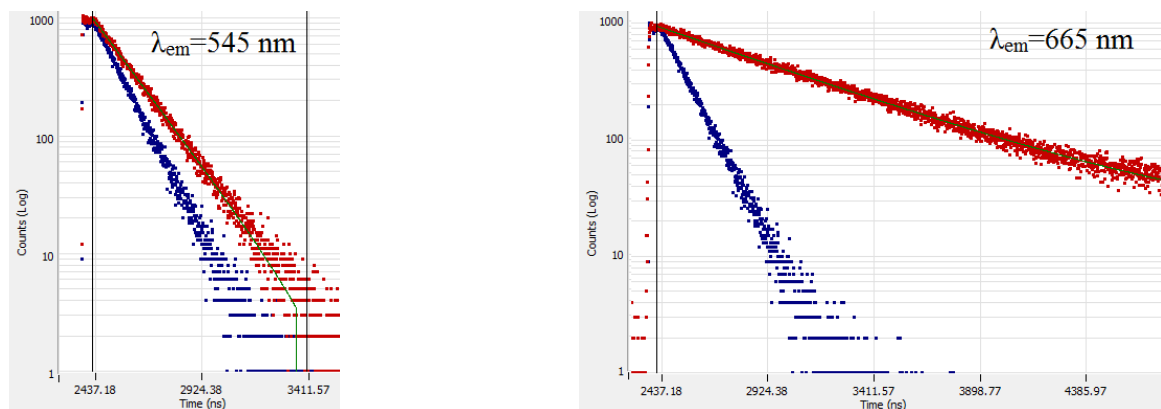


Figure 4. Kinetic decay curves (red curves) of UCL recorded at 545 nm and 665 nm under excitation with wavelengths of 980 nm (concentration of Tm^{3+} was of 28 at.%) at $T = 80$ K. Blue curves—excitation source pulse.

The energy diagram of Tm^{3+} and Bi^{3+} ions, taking into account the theoretical data [30,31] and experimentally observed transitions in the visible and infrared regions at nitrogen temperature, is shown in Figure 5.

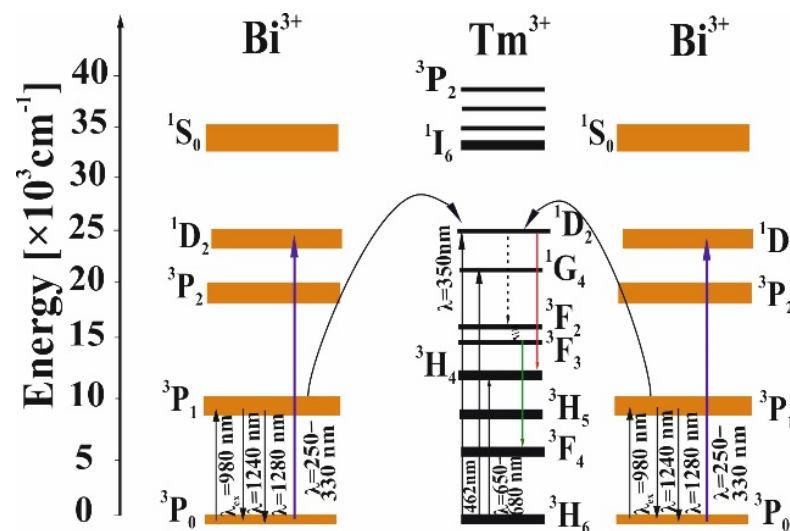


Figure 5. Energy diagram of Tm^{3+} and Bi^{3+} ions with experimentally observed transitions in the visible and infrared regions at $T = 80$ K.

Thus, the process of the appearance of UCL in the visible region is due to the simultaneous excitation of two Bi^{3+} ions with a wavelength of 980 nm, accompanied by a transition between levels ${}^3\text{P}_0 \rightarrow {}^3\text{P}_1$. The absorbed energy is deactivated in the form of luminescence at a wavelength of 1240 nm and 1280 nm from two vibrational sublevels of one electronic energy level (${}^3\text{P}_1$). At the same time, the total energy of two excited Bi^{3+} ions after absorption of a quantum with a wavelength of 980 nm accumulates at a higher level of ${}^1\text{D}_2$, corresponding to the mechanism of cooperative sensitization [16,27,32] accompanied by deactivation of UCL in the red region (${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$). Further, by ultrafast intercombination conversion ${}^1\text{D}_2 \rightarrow {}^3\text{F}_2$ and deactivation of ${}^3\text{F}_2 \rightarrow {}^3\text{F}_3$, a transition of ${}^3\text{F}_3 \rightarrow {}^3\text{F}_4$ is observed in the green area. Therefore, based on the presented data it can be concluded that in the system (Bi^{3+} - Bi^{3+})- Tm^{3+} it is possible to observe the nonradiative energy transfer with the UCL and NIR emission activation. This energy transfer could be considered just at low temperature to produce the mechanism of acceleration of energy degradation through the vibration levels.

Further, it was of interest to determine the cross-section of the UCL emission at the observed wavelengths using the following equation [29]:

$$\sigma_{em} = \frac{\lambda_0^2}{4\pi n^2 c \tau \Delta\lambda} \left(\frac{\ln 2}{\pi} \right)^{0.5} \quad (1)$$

where λ_0 is the emission wavelength, n is the refractive index, τ is the UCL lifetime, c is the speed of light and $\Delta\lambda$ is the half-width of the UCL spectrum.

Substituting the following values into the equation: $n = 2$; $\Delta\lambda \approx 10$ nm; $\tau = 172$ ns and $\tau = 664$ ns for $\lambda_0 = 550$ and $\lambda_0 = 665$ nm, respectively, it can be calculated:

$$\sigma_{em} = 29.3 \times 10^{-17} \text{ cm}^2 \text{ (for } \lambda_0 = 550 \text{ nm)} \text{ and } \sigma_{em} = 62.7 \times 10^{-17} \text{ cm}^2 \text{ (for } \lambda_0 = 660 \text{ nm)}.$$

The multiplication of σ_{em} and τ was also calculated: $\sigma_{em}\tau = 0.5 \times 10^{-22} \text{ cm}^2 \text{ s}$ (for $\lambda_0 = 550$ nm) and $4.1 \times 10^{-22} \text{ cm}^2 \text{ s}$ (for $\lambda_0 = 660$ nm).

These obtained values are well-correlated with the theoretical data [33] and indicate that the resulting powder of $\text{Bi}_2\text{O}_3/\text{Tm}_2\text{O}_3$ with a cell-like structure (Figure 2e,f) can generate an intense luminescence in the visible region under IR excitation with an acceptable value of the emission cross-section of the crystal structure.

Due to the presence of UCL luminescence in the visible region of the spectrum, it is important to consider the reflectance spectra of the powders in the UCL region. The reflection spectra at liquid nitrogen temperatures are presented in Figure 6.

In the reflection spectra, the absorption bands at wavelengths of 350,360 nm correspond to the transition ${}^3\text{H}_6 \rightarrow {}^1\text{D}_2$ in Tm^{3+} ; bands at 463, 475 nm correspond to ${}^3\text{H}_6 \rightarrow {}^1\text{G}_4$; and bands at wavelengths of 650–680 nm correspond to the ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$ transition. The wide absorption band for Bi^{3+} at 400 nm is associated with the ${}^1\text{S}_0 \rightarrow {}^3\text{P}_1$ transition.

A few brief notes can be made on the spectral features recorded at low temperatures. Thus, when considering a reflectance spectrum obtained for Bi_2O_3 powder without Tm_2O_3 at $T = 80$ K (Figure 6a), there are two minima in the ultraviolet region: at 254 nm and 306 nm (with a value of $R \approx 47\%$) and a peak at 400 nm. In all powders, the wide absorption peak at 400 nm corresponding to Bi_2O_3 is presented. For instance, at $T = 293$ K no peaks in ultraviolet were observed (Figure 6b). In addition, at $T = 80$ K, a minimum in the reflection function in the green region (566 nm) for Bi_2O_3 powder has occurred.

The reflection coefficient 22 at.% at 420 nm at $T = 80$ K increased 3.2 times.

When considering a sample of Tm_2O_3 in the absence of Bi_2O_3 , the reflection coefficient in the whole considered absorption range at $T = 80$ K increases 1.5–4 times in comparison with the reflection function recorded at $T = 293$ K. In addition, the appearance of clearly resolved minima in the UV region (on 286 and 225 nm) for Tm_2O_3 oxide (Figure 6a) should be noted.

Figure 6c shows that the reflection coefficient does not change linearly by increasing the Tm^{3+} concentration at $T = 80$ K. At the concentration of 15 at.%, the maximum value of the reflection coefficient at all considered wavelengths is observed. The highest value of the coefficient ($R = 55\%$) corresponds to the wavelength of 665 nm. At $T = 293$ K, the dynamics of the reflection coefficient changes linearly in all spectral ranges. The other optical constants (refractive index, dielectric permittivity functions and polarization) of the material and the reflection coefficients at room temperature depending on the Tm^{3+} concentration are presented in the supplementary materials.

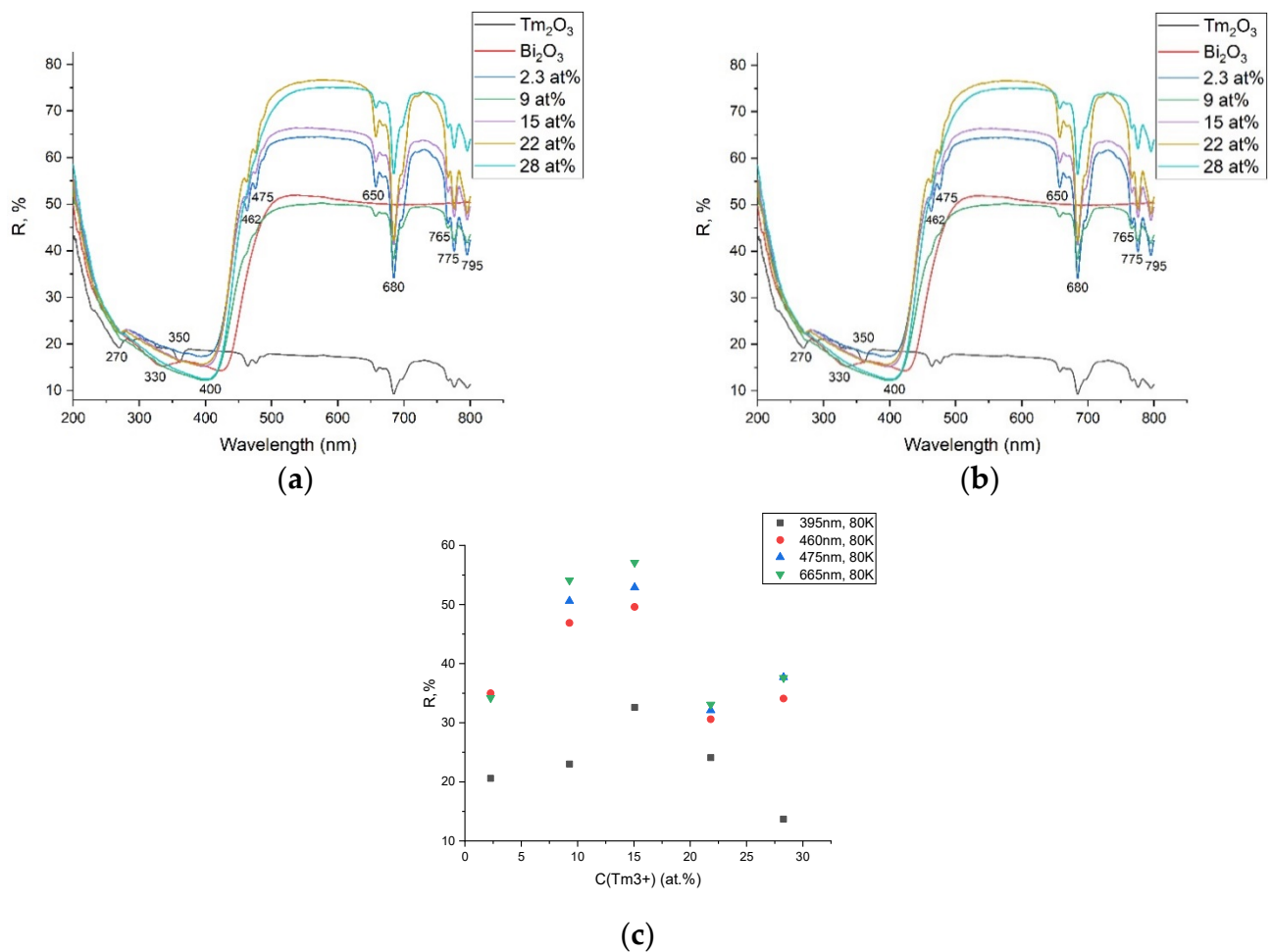


Figure 6. Reflection spectra of Bi₂O₃/Tm₂O₃ oxides with different atomic concentrations of Tm³⁺ in the mixture (2.3–28 at.%) at T = 80 K (a), at T = 293 K (b) and dynamic of R(%) depending on the Tm³⁺ concentration at T = 80 K (c).

4. Conclusions

A two-component material Bi₂O₃/Tm₂O₃ with granule sizes of about 100 nm was synthesized in this work. Based on the X-ray diffraction analysis data, the presence of a cubic phase for thulium oxide and a monoclinic phase for bismuth oxide was established. In addition, the presence of additional peaks on the diffraction pattern for the mixture was due to the transformation of the crystal lattice of bismuth oxide in the presence of thulium oxide in the process of temperature synthesis.

It was shown that the synthesized complex of Bi₂O₃/Tm₂O₃ with a specific surface granular structure is capable of emission in the NIR region and luminescence by the mechanism of upconversion in the red and green regions of the visible spectral range at low temperatures (T = 80 K). It was established that upconversion energy transfer is a result of nonradiative energy transfer in the (Bi³⁺-Bi³⁺)-Tm³⁺ system. The upconversion luminescence lifetimes in the visible region of the spectrum were $\tau = 172$ ns and $\tau = 664$ ns for $\lambda = 550$ and $\lambda = 665$ nm, respectively. The calculated values of the emission cross-section indicate a sufficiently efficient conversion of the IR absorbed energy with a nanosecond deactivation duration.

At the same time, the presence of two-band IR luminescence (1250 nm and 1280 nm) of the Bi₂O₃/Tm₂O₃ complex at liquid nitrogen temperature was established. It was shown that the intensity of IR luminescence from the concentration of thulium ions in the mixture was determined by a linear dependence. NIR luminescence in the region of 1240 and 1280 nm was due to the absorption by Bi³⁺ ions of a wavelength of 980 nm and energy

deactivation through the $^3P_1 \rightarrow ^3P_0$ levels. Studies of reflection spectra in the visible region at low temperatures have shown the presence of the spectrum splitting for thulium oxide in the UV region. The concentration dependences of the reflection coefficient at the absorption wavelengths were determined by a nonlinear dependence during spectral measurements at liquid nitrogen temperatures.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13030534/s1>, Figure S1: The EXD analysis of the samples with the different atomic concentrations of the thulium and bismuth ions; Figure S2: The dynamic of R(%) depending on the Tm^{3+} concentration at $T = 293$ K at absorption wavelength (395, 460, 474, 665 nm); Figure S3: Kinetic decay curves of UCL recorded at 665 nm under excitation with wavelengths of 980 nm (concentration of Tm^{3+} was of 15 at.% and 22 at.%) at $T = 80$ K; Figure S4: Refractive index spectrum in visible region for Bi_2O_3/Tm_3O_3 system. Figure S5: Complex dielectric function in visible region for Bi_2O_3/Tm_3O_3 system; Figure S6: Polarization in visible region for Bi_2O_3/Tm_3O_3 system.

Author Contributions: D.A.A.—sample preparation, measurements; A.V.T.—conceptualization, original draft preparation; V.A.S.—data analysis; A.S.K.—investigation; I.G.S.—project administration; I.I.L.—investigation, data analysis; V.V.B.—data curation. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: Authors declare no conflict of interests.

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