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**Title:** Near-IR Luminescence of Rare-Earth Ions ( $\text{Er}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$ ) in Titanate-Germanate Glasses under Excitation of  $\text{Yb}^{3+}$

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## Article

# Near-IR Luminescence of Rare-Earth Ions ( $\text{Er}^{3+}$ , $\text{Pr}^{3+}$ , $\text{Ho}^{3+}$ , $\text{Tm}^{3+}$ ) in Titanate–Germanate Glasses under Excitation of $\text{Yb}^{3+}$

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**Abstract:** Inorganic glasses co-doped with rare-earth ions have a key potential application value in the field of optical communications. In this paper, we have fabricated and then characterized multicomponent  $\text{TiO}_2$ -modified germanate glasses co-doped with  $\text{Yb}^{3+}/\text{Ln}^{3+}$  ( $\text{Ln} = \text{Pr}, \text{Er}, \text{Tm}, \text{Ho}$ ) with excellent spectroscopic properties. Glass systems were directly excited at 980 nm (the  ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$  transition of  $\text{Yb}^{3+}$ ). We demonstrated that the introduction of  $\text{TiO}_2$  is a promising option to significantly enhance the main near-infrared luminescence bands located at the optical telecommunication window at 1.3  $\mu\text{m}$  ( $\text{Pr}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_5$ ), 1.5  $\mu\text{m}$  ( $\text{Er}^{3+}: {}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ ), 1.8  $\mu\text{m}$  ( $\text{Tm}^{3+}: {}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ ) and 2.0  $\mu\text{m}$  ( $\text{Ho}^{3+}: {}^5\text{I}_7 \rightarrow {}^7\text{I}_8$ ). Based on the lifetime values, the energy transfer efficiencies ( $\eta_{\text{ET}}$ ) were estimated. The values of  $\eta_{\text{ET}}$  are changed from 31% for  $\text{Yb}^{3+}/\text{Ho}^{3+}$  glass to nearly 53% for  $\text{Yb}^{3+}/\text{Pr}^{3+}$  glass. The investigations show that obtained titanate–germanate glass is an interesting type of special glasses integrating luminescence properties and spectroscopic parameters, which may be a promising candidate for application in laser sources emitting radiation and broadband tunable amplifiers operating in the near-infrared range.

**Keywords:** germanate glasses; ytterbium ions; energy transfer; luminescence property relationship



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## 1. Introduction

Numerous inorganic glass materials are fabricated and widely applied industrially. Novel glass host matrices are still developed and must fulfill the rising demand for good-quality optical components and devices such as active optical fibers, solid-state laser sources, broadband near-IR fiber amplifiers, photonic integrated devices, and so on [1–4]. Systematic studies clearly demonstrate that positions and spectral linewidths for characteristic luminescence bands of lanthanides ions can be tuned according to the chemical compositions of glass and glass-ceramic matrices and dopant ions [5–9]. One of the most perspective options to remedy the drawbacks and improve the photoluminescence properties of lanthanide ions is a modification of the glassy network with suitable additives. In this context,  $\text{TiO}_2$ -modified glasses [10,11] have gained much importance due to their interesting properties that make them promising candidates for luminescent sources and optical devices. The beneficial effect of these additives is the improvement of the thermal and chemical stability of glasses [12–14]. It is also assumed that presence of titanium dioxide in matrices with low phonon energy may significantly broaden and enhance the luminescence bands of lanthanides ions.

From the accumulated experience and literature data [15,16], it is known that the trivalent ytterbium ions have been extensively studied for use as efficient emitters of radiation in the infrared range. It should be noted that  $\text{Yb}^{3+}$  ions with a broad absorption band in the wavelength region of 860–1060 nm and a relatively long fluorescence lifetime (1–2 ms) can be excellent sensitizers to activate other lanthanide ions for luminescence [17,18]. For this reason, co-doping of materials with  $\text{Yb}^{3+}$  ions allows for the efficient pumping of around 980 nm using a commercially available diode [19,20]. From the experimental approach, it

can be concluded the near-IR radiative transitions of lanthanide ions are greatly dependent on the reduction of matrix phonons to achieve high luminescence efficiency. Indeed, in the past few years, subsequent research on germanate glass remains a perspective option as an oxide glass host matrix for lanthanide ions thanks to its favorable properties, such as smaller multiphonon relaxation probabilities due to relatively low phonon energy ( $\sim 800\text{ cm}^{-1}$ ), high transparency from the visible to the infrared region and presence of non-linear optical effects [21,22]. One should remember that the following lanthanides  $\text{Ln}^{3+}$  ions such as  $\text{Pr}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ , and  $\text{Ho}^{3+}$  are proposed as co-activators for photoluminescence in  $\text{Yb}^{3+}/\text{Ln}^{3+}$ -doubly doped glasses owing to their favorable location of energy levels and the possibility of radiative transitions at the infrared [23]. Among them,  $\text{Tm}^{3+}$  [24] has gained increasing attention because the near-IR emission associated with the  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  transition at 1800 nm is useful as a medical light source. The  $\text{Er}^{3+}$  ions [25] are widely used in materials for optical applications. Main  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  near-IR transition of  $\text{Er}^{3+}$  at 1500 nm corresponds to the C + L telecommunication window. Next,  $\text{Ho}^{3+}$  ions [26] are one of the interesting dopants appropriate for laser sources operated at 2000 nm owing to the  ${}^5\text{I}_7 \rightarrow {}^7\text{I}_8$  transition. Although such interesting observations, insufficient attention has been paid to the effects of  $\text{TiO}_2$  on near-IR emission properties of low-phonon germanate glasses co-doped with lanthanides. From this point of view, it is interesting to find out how emission bands of selected lanthanide ions located in the near-IR range are changed with different  $\text{GeO}_2:\text{TiO}_2$  molar ratios in chemical composition under  $\text{Yb}^{3+}$  ions excitation.

This paper concerns novel multicomponent titanate–germanate glasses belonging to the low-phonon oxide glass family. Glass samples were successfully synthesized using the conventional high-temperature melting technique. The optical properties of glass series containing two network-formers,  $\text{TiO}_2$  and  $\text{GeO}_2$ , were characterized using luminescence spectroscopy. In our studies,  $\text{Yb}^{3+}$  plays an important role, such as a sensitizer to activate selected lanthanide ions. Our attention has been paid to titanate–germanate glass systems co-doped with  $\text{Yb}^{3+}/\text{Er}^{3+}$ ,  $\text{Yb}^{3+}/\text{Ho}^{3+}$ ,  $\text{Yb}^{3+}/\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}/\text{Pr}^{3+}$ , and their energy transfer process. Near-infrared luminescence spectra and decay curves were examined for samples where  $\text{GeO}_2$  was substituted by  $\text{TiO}_2$ . In the studied glass systems, molar ratios are changed from  $\text{GeO}_2:\text{TiO}_2 = 5:1$  up to  $\text{GeO}_2:\text{TiO}_2 = 1:5$ . Based on the measured values of luminescence lifetimes, the energy transfer efficiencies  $\text{Yb}^{3+} \rightarrow \text{Ln}^{3+}$  ( $\text{Ln} = \text{Pr}, \text{Er}, \text{Tm},$  and  $\text{Ho}$ ) were determined for glass samples differing in  $\text{TiO}_2$  content. The influence of  $\text{TiO}_2$  on structural properties has already been carried out on the previous titanate–germanate glasses published recently [27].

## 2. Materials and Methods

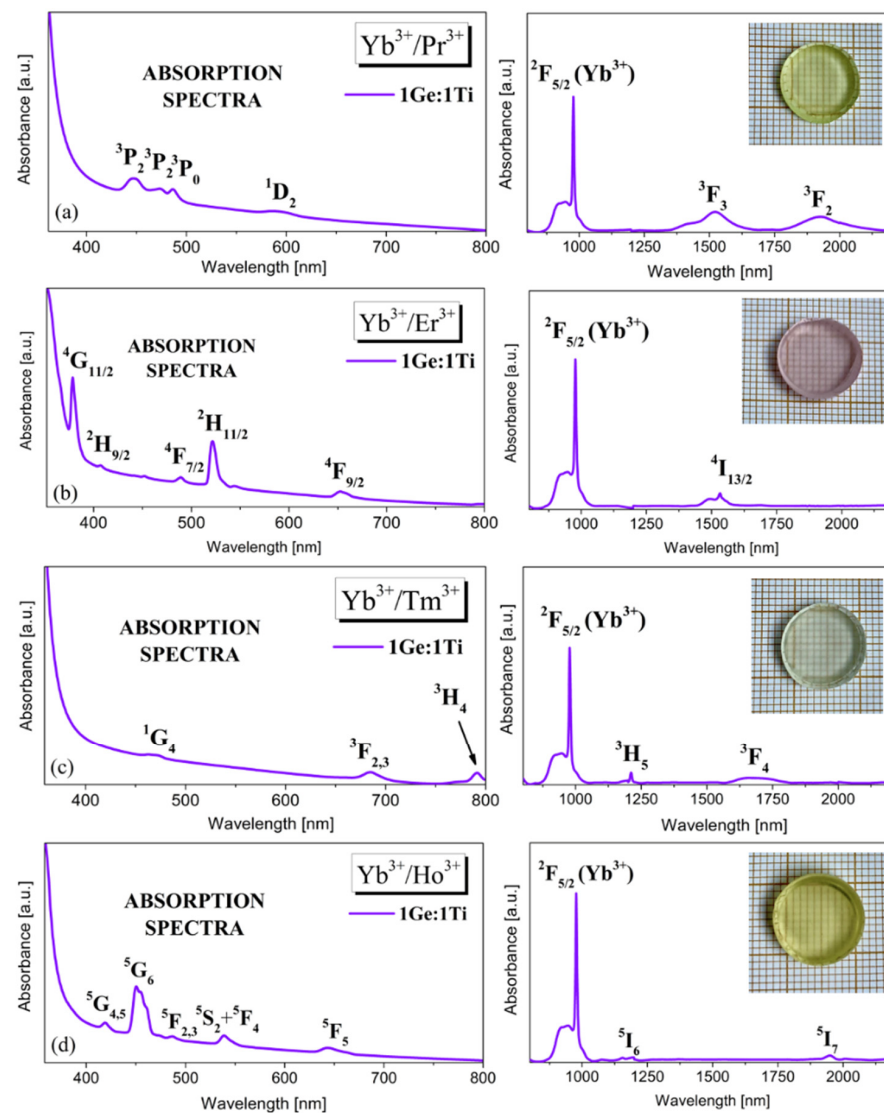
The investigated  $\text{TiO}_2$ -modified germanate glasses co-doped with lanthanides ions with chemical composition (given in mol%):  $x\text{TiO}_2-(60-x)\text{GeO}_2-30\text{BaO}-9.5\text{Ga}_2\text{O}_3-0.5\text{Yb}_2\text{O}_3$  and  $x\text{TiO}_2-(60-x)\text{GeO}_2-30\text{BaO}-9.4\text{Ga}_2\text{O}_3-0.5\text{Yb}_2\text{O}_3-0.1\text{Ln}_2\text{O}_3$ , (where  $\text{Ln} = \text{Er}, \text{Tm}, \text{Pr}, \text{Ho}$ , and  $x = 10, 20, 30, 40, 45, 50$ ) were obtained by traditional melt quenching technique. In present research, glasses containing various molar ratios  $\text{GeO}_2:\text{TiO}_2$  are equal to 5:1, 2:1, 1:1, 1:2, 1:3, and 1:5 and glass codes are as follows: 5Ge-1Ti, 2Ge-1Ti, 1Ge-1Ti, 1Ge-2Ti, 1Ge-3Ti, and 1Ge-5Ti. All of the glass components used during synthesis were of high purity (99.99%) from Aldrich Chemical Co. (St. Louis, MO, USA). Appropriate precursor metal oxides were mixed in an agate mortar. After homogenization of the components, 5 g glass bathes were placed in a platinum crucible (Łukasiewicz Research Network, Institute of Ceramics and Building Materials, Cracow, Poland). In the present procedure, the melting conditions were  $T = 1250\text{ }^\circ\text{C}$  for 60 min in an electric furnace. Finally, each glass sample was cooled to room temperature and polished to meet the requirements for optical measurements. A series of transparent glass samples with the dimensions  $12\text{ mm} \times 12\text{ mm}$  and thickness  $\pm 3\text{ mm}$  was successfully prepared to determine their optical properties. The luminescence measurements of glasses were performed on a Photon Technology International (PTI) Quanta-Master 40 (QM40) UV/VIS Steady State Spectrofluorometer (Photon Technology International, Birmingham, NJ, USA) supplied with a tunable pulsed optical parametric

oscillator (OPO) pumped by the third harmonic of an Nd:YAG laser (Opotek Opolette 355 LD, OPOTEK, Carlsbad, CA, USA). The laser system was coupled with a 75 W xenon lamp, a double 200 mm monochromator, and a Hamamatsu H10330B-75 detector (Hamamatsu, Bridgewater, NJ, USA). The emission spectra were recorded with a spectral resolution of 0.5 nm. Decay curves were recorded by a PTI ASOC-10 (USB-2500) oscilloscope with an accuracy of  $\pm 2 \mu\text{s}$  and have been measured under excitation wavelengths 980 nm and monitoring emission wavelength 1030 nm. In order to compare the emission intensity under the same experimental conditions, measurements of glass systems were carried out at the same slit settings. Measurements were performed at room temperature.

### 3. Results and Discussion

#### 3.1. Optical Absorption Properties

In this study, measurements of the absorption spectra of glass systems 1Ge:1Ti co-doped with  $\text{Yb}^{3+}/\text{Ln}^{3+}$  ( $\text{Ln} = \text{Er}, \text{Pr}, \text{Tm}, \text{Ho}$ ) were carried out and presented in Figure 1.



**Figure 1.** Typical absorption spectra of titanate–germanate glasses co-doped with  $\text{Yb}^{3+}/\text{Pr}^{3+}$  (a),  $\text{Yb}^{3+}/\text{Er}^{3+}$  (b),  $\text{Yb}^{3+}/\text{Tm}^{3+}$  (c) and  $\text{Yb}^{3+}/\text{Ho}^{3+}$  (d). Inset shows a photographic image of the glass sample.

Absorption spectra measured for representative titanate–germanate glasses consist of the characteristic bands corresponding to transitions originating from the ground state to

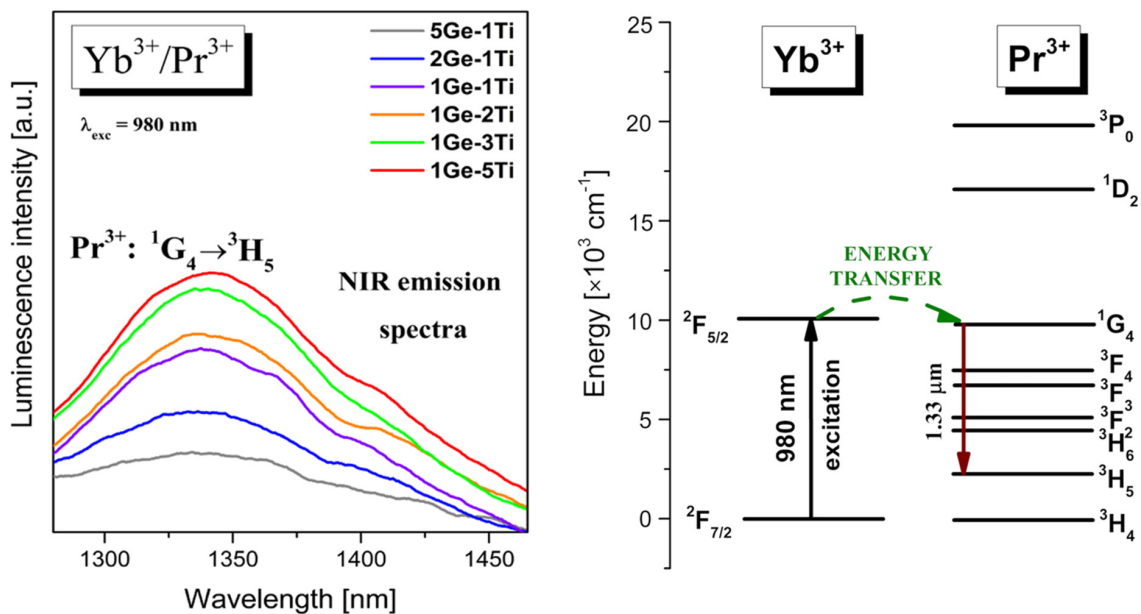
higher-lying excited states of selected lanthanide ions. The glass sample co-doped with  $\text{Yb}^{3+}/\text{Pr}^{3+}$  ions (Figure 1a) shows four weakly intense absorption bands in the 350–800 nm range. The two most intense absorption bands due to  ${}^3\text{H}_4 \rightarrow {}^3\text{F}_3$  and  ${}^3\text{H}_4 \rightarrow {}^3\text{F}_2$  transitions are well observed in the infrared spectral range. Interestingly, literature data indicate that on the band edge, due to  ${}^3\text{H}_4 \rightarrow {}^3\text{F}_3$ , a weakly separated absorption band at about 1400 nm associated with the  ${}^3\text{H}_4 \rightarrow {}^3\text{F}_4$  transition is detected [28]. Next, it is evidently seen for titanium germanium glass co-doped with  $\text{Yb}^{3+}/\text{Er}^{3+}$  that the absorption bands (Figure 1b) due to the transition from the  ${}^4\text{I}_{15/2}$  state of  $\text{Er}^{3+}$  are well observed at 380 nm ( ${}^4\text{G}_{11/2}$ ), 407 nm ( ${}^2\text{H}_{9/2}$ ), 489 nm ( ${}^4\text{F}_{7/2}$ ), 522 nm ( ${}^2\text{H}_{11/2}$ ), 652 nm ( ${}^4\text{F}_{9/2}$ ) and band centered in the near-infrared range at 1530 nm due to  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{13/2}$  transition [29]. Figure 1c shows the absorption spectrum of the  $\text{Yb}^{3+}/\text{Tm}^{3+}$  co-doped titanate–germanate sample. The five absorption bands at 471 nm, 685 nm, 790 nm, 1210 nm, and 1690 nm correspond to the transitions from the ground state  ${}^3\text{H}_6$  to excited states  ${}^1\text{G}_4$ ,  ${}^3\text{F}_2 + {}^3\text{F}_3$ ,  ${}^3\text{H}_4$ ,  ${}^3\text{H}_5$ , and  ${}^3\text{F}_4$ , respectively [30]. In turn, the absorption spectrum measured for  $\text{Yb}^{3+}/\text{Ho}^{3+}$  co-doped glass is shown in Figure 1d. The results show that the obtained glass characterizes seven absorption bands in the spectral region of 350–2200 nm. The spectrum exhibits the bands due to the following absorption transitions:  ${}^5\text{I}_8 \rightarrow {}^5\text{G}_{4,5}$ ,  ${}^5\text{I}_8 \rightarrow {}^5\text{G}_6$ ,  ${}^5\text{I}_8 \rightarrow {}^5\text{F}_{2,3}$ ,  ${}^5\text{I}_8 \rightarrow {}^2\text{S}_2 + {}^5\text{F}_4$ ,  ${}^5\text{I}_8 \rightarrow {}^5\text{F}_5$  in the visible range and  ${}^5\text{I}_8 \rightarrow {}^5\text{I}_6$ ,  ${}^5\text{I}_8 \rightarrow {}^5\text{I}_7$  in the NIR region [31]. For all glass samples, note that the main peak in the absorption spectra was concentrated at 980 nm, defining the lowest  $\text{Yb}^{3+}$ :  ${}^2\text{F}_{5/2}$  Stark splitting energy level is the most intense; therefore, in the following section, the excitation line at 980 nm had been selected to investigate the near-infrared luminescence properties of the fabricated glasses co-doped with  $\text{Yb}^{3+}/\text{Pr}^{3+}$ ,  $\text{Yb}^{3+}/\text{Er}^{3+}$ ,  $\text{Yb}^{3+}/\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}/\text{Ho}^{3+}$ , where  $\text{Yb}^{3+}$  plays an important role of emission sensitizer for lanthanides ions.

### 3.2. Near-Infrared Luminescence Properties

Trivalent ytterbium ( $\text{Yb}^{3+}$ ) has a simple energy-level structure, i.e., the  ${}^2\text{F}_{7/2}$  ground level and the  ${}^2\text{F}_{5/2}$  excited level, with an energy separation between them of about  $10,000 \text{ cm}^{-1}$  [32]. The  $\text{Yb}^{3+}$  ion has been demonstrated to be an excellent emission sensitizer for other lanthanides due to its effective absorption cross-section at 980 nm [33]. In the presented work, four titanate–germanate glass systems co-doped with  $\text{Yb}^{3+}/\text{Pr}^{3+}$ ,  $\text{Yb}^{3+}/\text{Er}^{3+}$ ,  $\text{Yb}^{3+}/\text{Tm}^{3+}$ , and  $\text{Yb}^{3+}/\text{Ho}^{3+}$  varying with  $\text{TiO}_2$  referred to as 5Ge-1Ti, 2Ge-1Ti, 1Ge-1Ti, 1Ge-2Ti, 1Ge-3Ti, and 1Ge-5Ti were selected and their near-IR emission properties under direct excitation of  $\text{Yb}^{3+}$  at wavelength 980 nm were compared. In addition, the interactions between  $\text{Yb}^{3+}$  and the second lanthanide ion and their mechanisms are discussed and presented schematically for each glass system on diagrams of the energy levels in order to understand the energy transfer processes. One of the interesting aspects of the ongoing research focusing on the properties of co-doped glasses is the observation of the sensitization of near-IR emission of  $\text{Pr}^{3+}$  at  $1.35 \mu\text{m}$  under excitation  $\text{Yb}^{3+}$ . Figure 2 presents near-IR luminescence spectra for  $\text{Yb}^{3+}/\text{Pr}^{3+}$  co-doped titanate–germanate glasses varying with  $\text{TiO}_2$ .

The observed near-IR emission bands at about  $1.35 \mu\text{m}$  correspond to  ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$  transition of  $\text{Pr}^{3+}$ . It should be particularly pointed out that the emission intensities of  $\text{Pr}^{3+}$  ions increased significantly with increasing  $\text{TiO}_2$  concentration from 5Ge-1Ti to 1Ge-5Ti. Hence, it could be suggested that the introduction of titanium dioxide to germanate glass favor near-infrared luminescence attributed to the  ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$  transition of  $\text{Pr}^{3+}$  under direct excitation of  $\text{Yb}^{3+}$ . The observed  ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$  transition of  $\text{Pr}^{3+}$  ions in titanate–germanate glass under excitation of  $\text{Yb}^{3+}$  is presented on the energy level diagram in Figure 2. It is clearly seen that both excited levels  ${}^2\text{F}_{5/2}$  ( $\text{Yb}^{3+}$ ) and  ${}^1\text{G}_4$  ( $\text{Pr}^{3+}$ ) lie close to each other and the energy gap between them is very small. Moreover, the absorption cross-section at around 980 nm is larger for  $\text{Yb}^{3+}$  than  $\text{Pr}^{3+}$  ions, which is crucial for the pumping efficiency of praseodymium-doped fiber amplifiers PDFAs [34,35]. Due to this fact, the energy transfer process  $\text{Yb}^{3+} \rightarrow \text{Pr}^{3+}$  is nearly resonant and supposed to be much more efficient in titanate–germanate glass. Thus, we observe near-IR emission at  $1.35 \mu\text{m}$  due

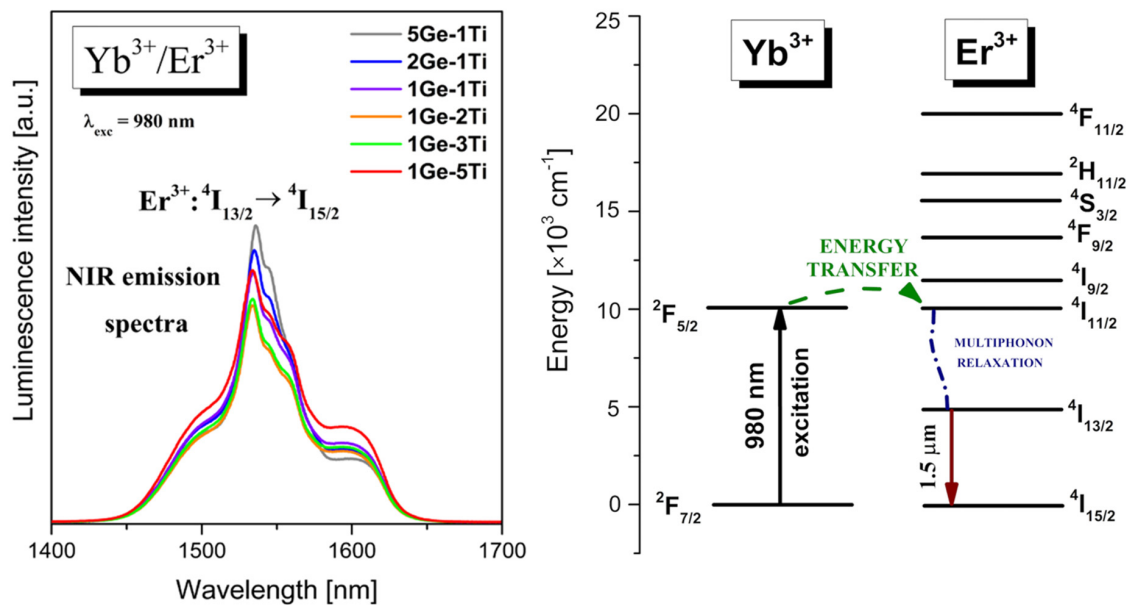
to  $^1G_4 \rightarrow ^3H_5$  transition of  $\text{Pr}^{3+}$ , which enhanced rapidly with increasing in  $\text{TiO}_2$  content. Based on the above experiment analysis, it can be concluded that  $\text{Yb}^{3+}/\text{Pr}^{3+}$  co-doped germanate glass in the presence of  $\text{TiO}_2$  is promising for near-IR emission and sample 1Ge-5Ti seems to be a potential precursor active glass material to realize a fiber laser operating at 1.35  $\mu\text{m}$  [36,37].



**Figure 2.** Near-infrared emission spectra and energy level diagram for titanate–germanate glasses co-doped with  $\text{Yb}^{3+}/\text{Pr}^{3+}$ .

From the literature [38–40], it is well known that broadband near-infrared emission bands of  $\text{Er}^{3+}$  ions in inorganic glasses depend strongly on their chemical compositions. The rapid development of optical telecommunications requires the broadening of the near-IR range for erbium-doped fiber amplifiers (EDFA), in which signal transmission occurs at about 1500 nm. In fact, the EDFA systems based on silicate glasses [41,42] exhibit relatively narrow bandwidth, which contributes to the limited near-infrared broadband transmission. For that reason, many precursor glass systems singly doped with  $\text{Er}^{3+}$  and co-doped with  $\text{Yb}^{3+}/\text{Er}^{3+}$  are still tested and selected in order to obtain enhanced near-IR luminescence in the so-called third telecommunication window. Figure 3 presents near-IR emission spectra measured in the wavelength range from 1400 nm to 1700 nm for  $\text{Yb}^{3+}/\text{Er}^{3+}$  co-doped titanate–germanate glasses under excitation by a 980 nm line. Near-IR emission bands centered at about 1.53  $\mu\text{m}$  correspond to the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition of  $\text{Er}^{3+}$ .

The intensity of the near-IR emission band at 1.5  $\mu\text{m}$  is reduced from 5Ge-1Ti to 1Ge-2Ti and then increased with further increasing  $\text{TiO}_2$  concentration up to glass sample 1Ge-5Ti. The emission linewidth for the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition of  $\text{Er}^{3+}$  ions, referred to as the full width at half maximum, is larger for sample 1Ge-5Ti (FWHM = 55 nm) than 5Ge-1Ti (FWHM = 38 nm). Schematic representation of energy levels, possible energy transfer between  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  ions and the main near-IR laser transition of  $\text{Er}^{3+}$  ions at 1.5  $\mu\text{m}$  are presented in Figure 3. Similar to the  $\text{Yb}^{3+}/\text{Pr}^{3+}$  system, the excitation energy transfers resonantly very fast from the  $^2F_{5/2}$  ( $\text{Yb}^{3+}$ ) to the  $^4I_{11/2}$  ( $\text{Er}^{3+}$ ) due to a small energy mismatch between the interacting excited levels [43]. The absorption cross-section of  $\text{Yb}^{3+}$  ions at around 980 nm is higher by a factor of ten roughly than that of  $\text{Er}^{3+}$  [44], favoring an efficient  $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$  energy transfer process. Next, the excitation energy relaxes nonradiatively to the  $^4I_{13/2}$  state by multiphonon process and consequently, we observe  $^4I_{13/2} \rightarrow ^4I_{15/2}$  near-IR transition of  $\text{Er}^{3+}$ .

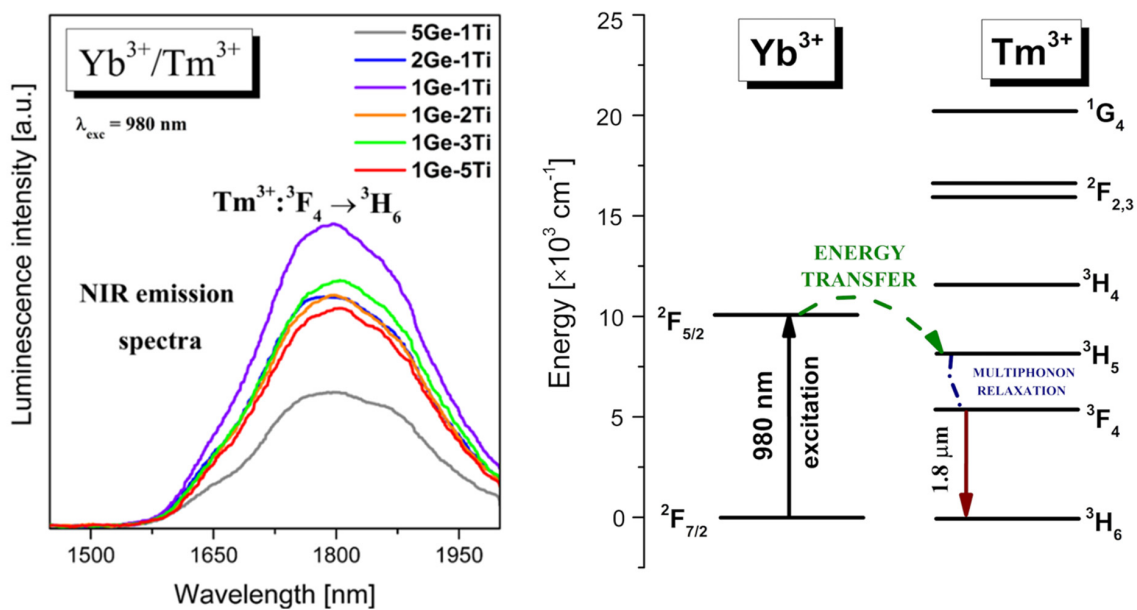


**Figure 3.** Near-infrared emission spectra and energy level diagram for titanate–germanate glasses co-doped with  $\text{Yb}^{3+}/\text{Er}^{3+}$ .

Our previous studies [27] indicate that the introduction of  $\text{TiO}_2$  to germanate glass resulted in higher asymmetry and better covalent bonds between rare earth and oxygens. In addition, these structural changes led to the site-to-site variation of the crystal field strength in the local environment of rare earths. It resulted in the inhomogeneous broadening of spectral lines corresponding to the presence of various sites for the optically active ions. As a consequence, the profiles of emission spectra and their values of FWHM are dependent on the symmetry, the ligand field strength, and the site-to-site variation of the  $\text{Ln}^{3+}$  local environment. This is the main reason that the spectral profiles of  $\text{Er}^{3+}$ , i.e., the emission peak position, emission linewidth (FWHM), and the relative intensities of shoulders existing at about 1600 nm, are changed during the modification of glass matrices. In some cases, the glass modifiers have a minor influence on absorption properties but a strong impact on the emission cross-sections attributed to the  ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$  near-infrared transition of  $\text{Er}^{3+}$  ions. Recently, it was well demonstrated for  $\text{Er}^{3+}$  ions in silicate glass with various  $\text{Al}_2\text{O}_3$  content [45] and  $\text{Er}^{3+}/\text{Yb}^{3+}$  co-doped phosphate glass modified by  $\text{Y}_2\text{O}_3$  [46].

Thulium is another well-known lanthanide dopant, which is introduced to various glass systems in order to generate near-IR luminescence at about 1.8  $\mu\text{m}$  [47]. In particular, co-doping with  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions is an excellent way to achieve enhanced near-infrared emission by using a 980 nm wavelength as an excitation source [48]. Figure 4 shows near-IR emission spectra of series titanate–germanate glass samples co-doped with  $\text{Yb}^{3+}/\text{Tm}^{3+}$ . Near-IR emission bands centered at 1.8  $\mu\text{m}$  are associated with  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  transition of  $\text{Tm}^{3+}$ . The intensities of near-IR emission bands increase and then decrease with increasing  $\text{TiO}_2$  concentration in the glass composition. The highest intensity of emission band related to the  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  transition of  $\text{Tm}^{3+}$  was observed for sample 1Ge-1Ti, where the molar ratio  $\text{GeO}_2$  to  $\text{TiO}_2$  is close 1:1. The energy level diagram for  $\text{Yb}^{3+}/\text{Tm}^{3+}$  co-doped titanate–germanate glasses is shown in Figure 4.

In contrast to the  $\text{Yb}^{3+}/\text{Er}^{3+}$  system, the energy mismatch between interacting  ${}^2\text{F}_{5/2}$  ( $\text{Yb}^{3+}$ ) and  ${}^3\text{H}_5$  ( $\text{Tm}^{3+}$ ) excited levels is much higher [49] and thus, non-resonant  $\text{Yb}^{3+} \rightarrow \text{Tm}^{3+}$  energy transfer process in titanate–germanate glasses occurs. The excitation energy is transferred nonradiatively by multiphonon relaxation from the  ${}^3\text{H}_5$  level to the lower-lying  ${}^3\text{H}_5$  level generating near-IR emission at 1.8  $\mu\text{m}$  due to  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$  transition of  $\text{Tm}^{3+}$ . Nearly the same mechanism was proposed for  $\text{Yb}^{3+}/\text{Ho}^{3+}$  co-doped glass systems, which are also interesting from the optical point of view [50].



**Figure 4.** Near-infrared emission spectra and energy level diagram for titanate–germanate glasses co-doped with  $\text{Yb}^{3+}/\text{Er}^{3+}$ .

These glass systems present near-IR emission at 2  $\mu\text{m}$  due to the  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  transition of  $\text{Ho}^{3+}$  [51,52]. The energy transfer mechanism has been mentioned in the literature by Wang et al. [53]. Upon excitation wavelength at 980 nm, the excited level of  $\text{Yb}^{3+}$  is well populated and then the excitation energy is transferred from the  $^2\text{F}_{5/2}$  state of  $\text{Yb}^{3+}$  to the  $^5\text{I}_6$  state of  $\text{Ho}^{3+}$ . The energy transfer process  $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$  is non-resonant. In the next step, very fast multiphoton relaxation to the lower-lying  $^5\text{I}_7$  level of  $\text{Ho}^{3+}$  is observed and consequently, we can observe near-IR emission at about 2000 nm associated with the  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  transition of  $\text{Ho}^{3+}$  [54,55]. Figure 5 presents near-IR luminescence spectra measured for titanate–germanate glasses co-doped with  $\text{Yb}^{3+}/\text{Ho}^{3+}$ . The emission bands are more intense for glass samples containing higher concentrations of  $\text{TiO}_2$ . All transitions are also indicated in the energy level diagram, which is shown in Figure 5.

In order to achieve intense IR emission of rare-earth ions, the heavy doping of the activators such as  $\text{Pr}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Tm}^{3+}$  is usually required. Remarkably interesting results were presented in work by Tu et al. [56], where they successfully developed heavily  $\text{Tm}^{3+}$ -doped germanate glasses, promising for glass fibers. On the other hand, the concentrations of activators should be optimal and relatively low in order to reduce luminescence quenching. In our case, luminescence quenching in the studied glass samples is negligibly small because of the low concentrations of acceptors ( $\text{Pr}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$ ) and the lack of energy transfer processes between pairs of  $\text{Pr}^{3+}$ - $\text{Pr}^{3+}$ ,  $\text{Er}^{3+}$ - $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ - $\text{Tm}^{3+}$ , and  $\text{Ho}^{3+}$ - $\text{Ho}^{3+}$  ions, respectively. The non-radiative transfer processes become dominant for glass samples with higher  $\text{Ln}^{3+}$  concentrations. These effects are especially stronger for glass systems with diagrams of excited states favoring the presence of cross-relaxation processes. Thus, the probabilities of these non-radiative relaxation processes increase and the luminescence is quenched due to the increasing interaction among the  $\text{Ln}^{3+}$  ions at higher concentrations. Our spectroscopic investigations indicate that the relative intensities of emission bands of rare-earth ions in germanate glasses are changed drastically with the presence of  $\text{TiO}_2$ . Figure 6 shows the integrated intensities of emission bands related to the main  $^1\text{G}_4 \rightarrow ^3\text{H}_5$  ( $\text{Pr}^{3+}$ ),  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  ( $\text{Er}^{3+}$ ),  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  ( $\text{Tm}^{3+}$ ) and  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  ( $\text{Ho}^{3+}$ ) near-IR transitions of rare-earth ions in the studied glass samples varying with  $\text{TiO}_2$  content. For pairs  $\text{Yb}^{3+}/\text{Pr}^{3+}$  and  $\text{Yb}^{3+}/\text{Ho}^{3+}$ , the integrated intensities of near-infrared emission bands located at 1.35 and 2  $\mu\text{m}$  increase with increasing  $\text{TiO}_2$  concentration. A completely different situation is observed for pairs of  $\text{Yb}^{3+}/\text{Er}^{3+}$  and  $\text{Yb}^{3+}/\text{Tm}^{3+}$  ions in titanate–germanate glasses. The integrated intensities of near-infrared emission bands



due to the  $^4I_{13/2} \rightarrow ^4I_{15/2}$  transition of  $Er^{3+}$  ions are reduced from 5Ge-1Ti to 1Ge-2Ti and then increase with further increasing  $TiO_2$  content. Contrary to  $Yb^{3+}/Er^{3+}$ , the emission intensities of near-infrared bands related to the  $^3F_4 \rightarrow ^3H_6$  transition of  $Tm^{3+}$  ions are enhanced to the 1Ge-1Ti system and then start to decrease with increasing  $TiO_2$  content in the glass composition; however, the changes in emission intensities with  $TiO_2$  content are non-linear for pair  $Yb^{3+}/Tm^{3+}$ .

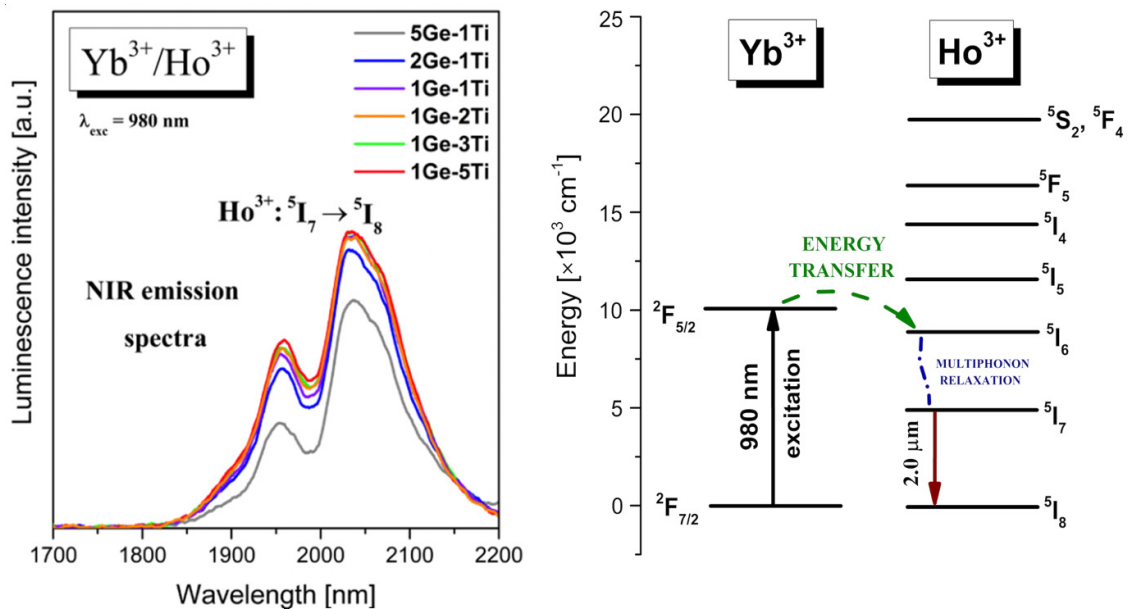


Figure 5. Near-infrared emission spectra and energy level diagram for titanate–germanate glasses co-doped with  $Yb^{3+}/Ho^{3+}$ .

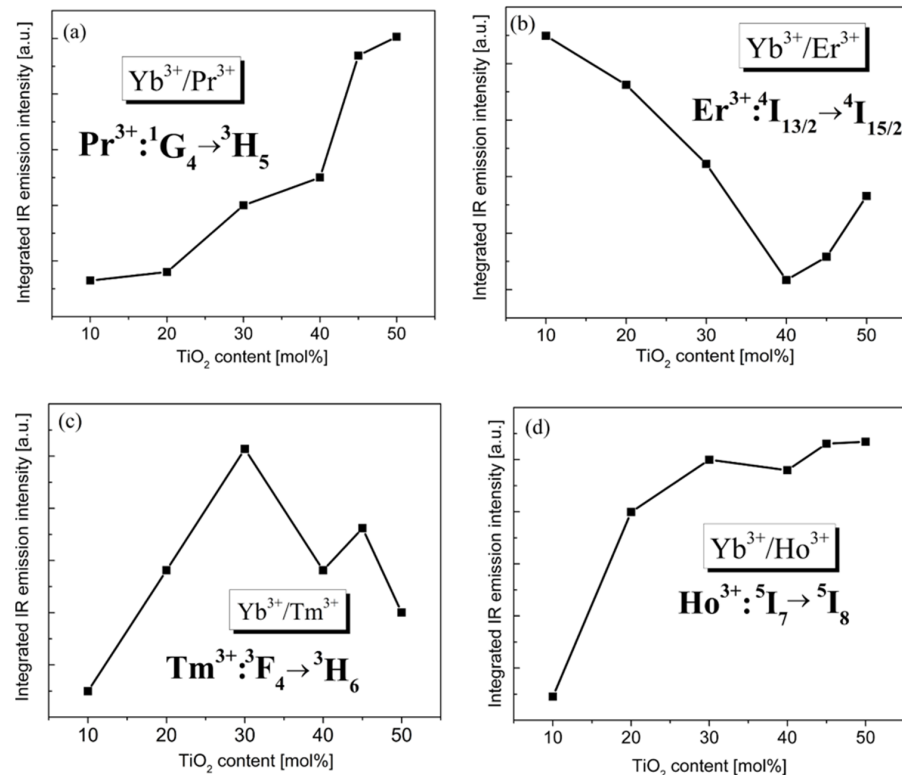
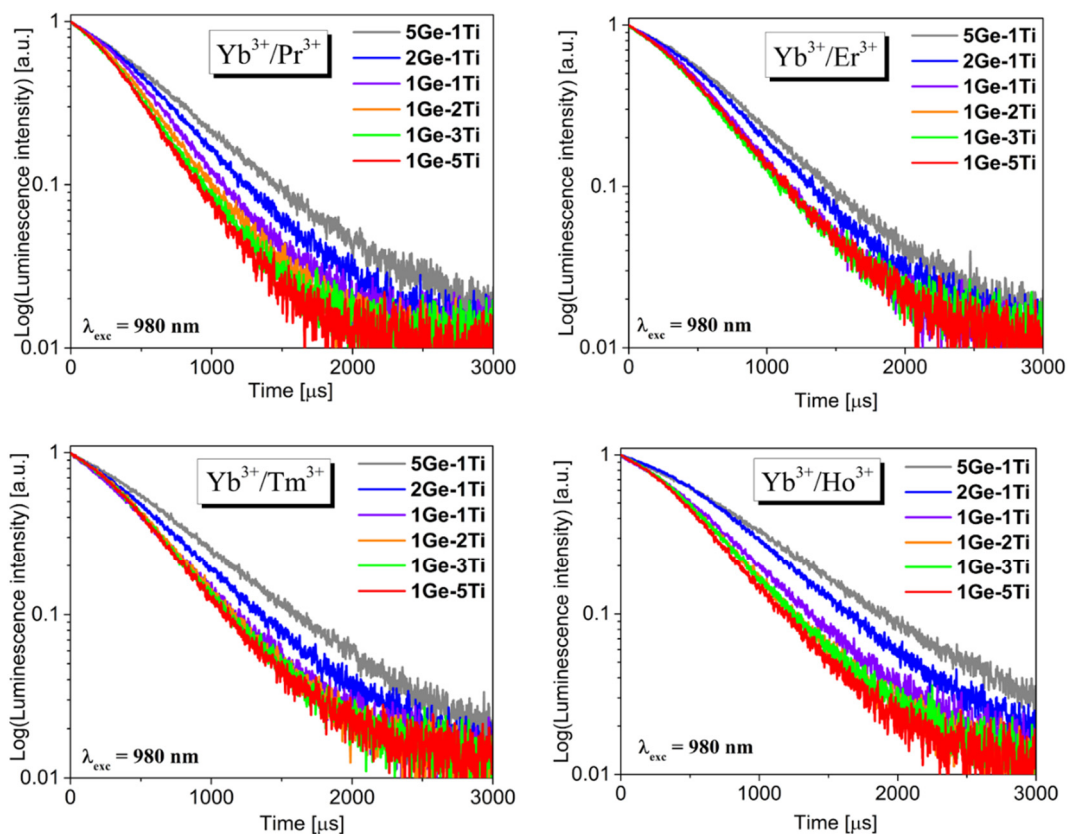


Figure 6. The integrated intensities of emission bands of rare-earth ions  $Yb^{3+}/Pr^{3+}$  (a),  $Yb^{3+}/Er^{3+}$  (b),  $Yb^{3+}/Tm^{3+}$  (c) and  $Yb^{3+}/Ho^{3+}$  (d) vary with  $TiO_2$ .

To summarize this part of the research, the authors declare that near-IR emission studies will be devoted in the future to further optimization of the  $\text{TiO}_2$  content of individual systems containing  $\text{Yb}^{3+}/\text{Ln}^{3+}$  ( $\text{Ln} = \text{Pr}, \text{Er}, \text{Tm}, \text{Ho}$ ). Obtained results for near-IR emission presented here will contribute to the fabrication of titanate–germanate optical fibers.

### 3.3. Luminescence Decays and Energy Transfer Efficiencies

The systematic studies indicate that luminescence lifetimes for excited states of  $\text{Yb}^{3+}$  in several low-phonon glass systems are completely different and depend significantly on the glass network-former and network-modifier added to the base composition [57,58]. To determine the efficiency of the energy transfer process between  $\text{Yb}^{3+}$  and  $\text{Ln}^{3+}$  ions ( $\text{Ln} = \text{Pr}, \text{Er}, \text{Tm}, \text{Ho}$ ), the luminescence decays for titanate–germanate glasses were measured and analyzed. Figure 7 shows decay curves measured for co-doped samples under 980 nm excitation. Based on decays, luminescence lifetimes were determined and compared to  $\text{Yb}^{3+}$  singly doped glass samples. The results are given in Table 1.



**Figure 7.** Luminescence decay curves for co-doped titanate–germanate glasses ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ).

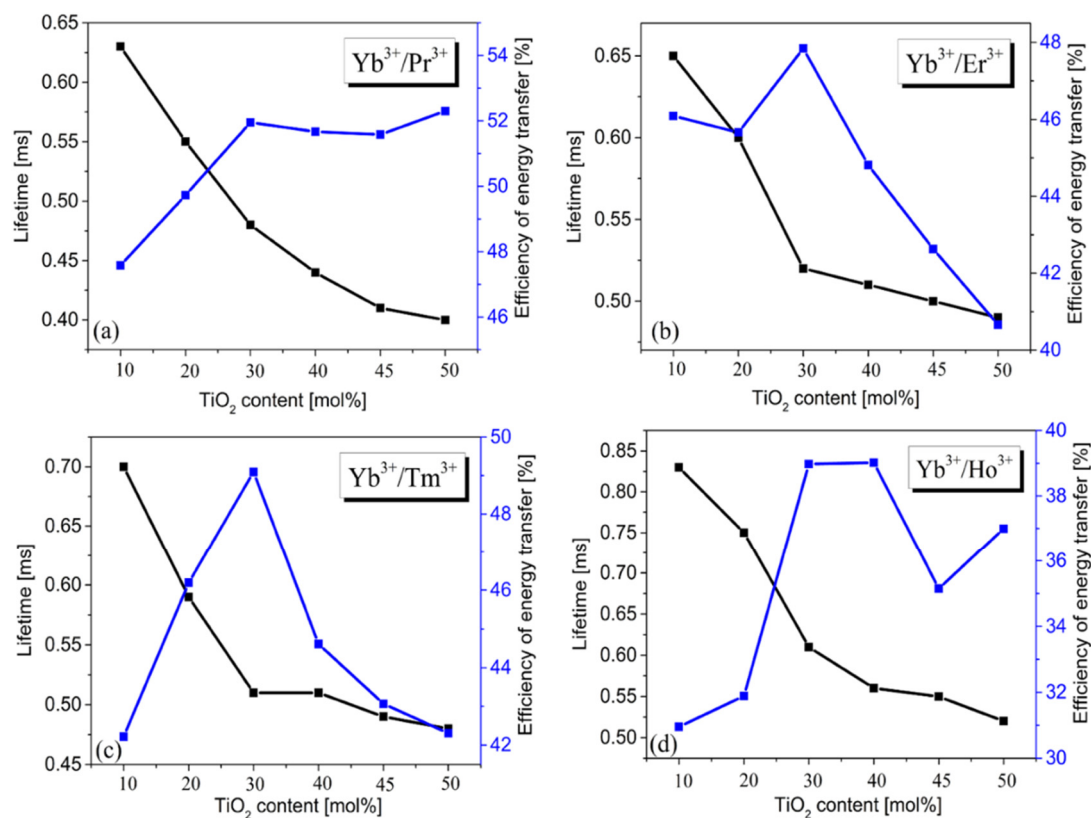
**Table 1.** Measured lifetimes for  $^5\text{F}_2$  state of  $\text{Yb}^{3+}$  in single and co-doped titanate–germanate glasses.

TiO <sub>2</sub> (mol%)	GeO <sub>2</sub> :TiO <sub>2</sub>	$\tau_m$ (ms)				
		Yb <sup>3+</sup>	Yb <sup>3+</sup> /Pr <sup>3+</sup>	Yb <sup>3+</sup> /Er <sup>3+</sup>	Yb <sup>3+</sup> /Tm <sup>3+</sup>	Yb <sup>3+</sup> /Ho <sup>3+</sup>
10	5:1	1.21	0.63	0.65	0.70	0.83
20	2:1	1.10	0.55	0.59	0.59	0.75
30	1:1	1.00	0.48	0.52	0.51	0.61
40	1:2	1.91	0.44	0.51	0.51	0.56
45	1:3	0.86	0.42	0.50	0.49	0.54
55	1:5	0.84	0.40	0.49	0.48	0.52

In general, measured lifetimes are reduced from 5Ge-1Ti to 1Ge-5Ti with increasing TiO<sub>2</sub> concentration in the glass composition. The experimental values of emission lifetimes decrease from 0.63 ms (5Ge-1Ti) to 0.40 ms (1Ge-5Ti) for Yb<sup>3+</sup>/Pr<sup>3+</sup> co-doped glass systems, 0.65 ms (5Ge-1Ti) to 0.49 ms (1Ge-5Ti) for Yb<sup>3+</sup>/Er<sup>3+</sup> systems, 0.70 ms (5Ge-1Ti) to 0.48 ms for Yb<sup>3+</sup>/Tm<sup>3+</sup> systems, and 0.83 ms (5Ge-1Ti) to 0.52 ms (1Ge-5Ti) for Yb<sup>3+</sup>/Ho<sup>3+</sup> systems, respectively. Luminescence lifetimes measured for Yb<sup>3+</sup> singly doped glasses and samples co-doped with Yb<sup>3+</sup>/Ln<sup>3+</sup> were applied to calculate the energy transfer efficiencies [59]. The energy transfer efficiency  $\eta_{ET}$  between Yb<sup>3+</sup> and lanthanides ions in fabricated glasses was evaluated by calculations with the formula given below:

$$\eta_{ET} = 1 - \frac{\tau_{Yb(Ln)}}{\tau_{Yb}}$$

where  $\tau_{Yb(Ln)}$  and  $\tau_{Yb}$  are the measured lifetimes for the <sup>2</sup>F<sub>5/2</sub> level of Yb<sup>3+</sup> ions in the presence and absence of acceptor Ln (where Ln = Pr, Er, Tm, Ho), respectively. The results are presented schematically in Figure 8.



**Figure 8.** The measured luminescence lifetime and the energy transfer efficiency Yb<sup>3+</sup> → Ln<sup>3+</sup> (where Ln = Pr (a), Er (b), Tm (c), Ho (d)) in the function of TiO<sub>2</sub> content.

Our studies indicate that measured lifetimes decrease with increasing TiO<sub>2</sub> content, while changes in the energy transfer efficiency seems to be completely different. For all pairs of Yb<sup>3+</sup>/Ln<sup>3+</sup> (Ln = Pr, Er, Tm, Ho), the energy transfer efficiency is the highest for the 1Ge-1Ti system, but the trend of  $\eta_{ET}$  values varying with TiO<sub>2</sub> content is not the same. For the pair of Yb<sup>3+</sup>/Pr<sup>3+</sup>, the values of  $\eta_{ET}$  increase to 1Ge-1Ti, whereas they are nearly independent for glasses with higher TiO<sub>2</sub> content. For pairs Yb<sup>3+</sup>/Er<sup>3+</sup> and Yb<sup>3+</sup>/Tm<sup>3+</sup>, the energy transfer efficiency increases from 5Ge-1Ti to 1Ge-1Ti and then decreases to 1Ge-5Ti with further increasing TiO<sub>2</sub> concentration. For the pair of Yb<sup>3+</sup>/Ho<sup>3+</sup>, the values of  $\eta_{ET}$  are the highest for 1Ge-1Ti to 1Ge-2Ti glass systems, respectively; however, the changes of  $\eta_{ET}$  with TiO<sub>2</sub> content are non-linear. Our calculations indicate that the energy transfer effi-

iciencies are changed from 31% for Yb<sup>3+</sup>/Ho<sup>3+</sup> glass (5Ge-1Ti) to nearly 53% for Yb<sup>3+</sup>/Pr<sup>3+</sup> glass (1Ge-5Ti). At this moment, it should also be mentioned that the up-conversion luminescence pathways [60] make an important contribution to the energy transfer processes and their efficiencies in Yb<sup>3+</sup>/Ln<sup>3+</sup> (Ln = Pr, Er, Ho, Tm) co-doped glasses.

#### 4. Conclusions

Multicomponent titanate–germanate glasses co-doped with Yb<sup>3+</sup>/Ln<sup>3+</sup> (Ln = Pr<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Ho<sup>3+</sup>) were synthesized and then studied their near-IR luminescence properties. The spectroscopic properties of glasses have been examined under the excitation of Yb<sup>3+</sup> ions by 980 nm. Obtained results were discussed based on the energy level diagrams for sensitizer (Yb<sup>3+</sup>) and acceptors (Pr<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Ho<sup>3+</sup>) and interactions between them. The near-IR luminescence bands corresponding to the <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>5</sub> (Pr<sup>3+</sup>), <sup>4</sup>I<sub>13/2</sub> → <sup>4</sup>I<sub>15/2</sub> (Er<sup>3+</sup>), <sup>3</sup>F<sub>4</sub> → <sup>3</sup>H<sub>6</sub> (Tm<sup>3+</sup>) and <sup>5</sup>I<sub>7</sub> → <sup>5</sup>I<sub>8</sub> transitions of lanthanide ions have been examined with TiO<sub>2</sub> concentration. Our investigations indicate that the intensities of emissions are dependent on titanium dioxide content. The resonant Yb<sup>3+</sup> → Pr<sup>3+</sup> and Yb<sup>3+</sup> → Er<sup>3+</sup> and non-resonant Yb<sup>3+</sup> → Tm<sup>3+</sup> and Yb<sup>3+</sup> → Ho<sup>3+</sup> energy transfer process in co-doped titanate–germanate is observed. The analysis of decay profiles allowed for the deeper optical characterization of the energy transfer processes between Yb<sup>3+</sup> and Ln<sup>3+</sup> ions (Ln = Pr, Er, Tm, Ho) and for establishing the relation between luminescence lifetimes and the role of titanium dioxide in germanate glasses. Based on decay measurements and values of luminescence lifetimes, the efficiencies of energy transfer were estimated. The values of η<sub>ET</sub> are changed from 31% for Yb<sup>3+</sup>/Ho<sup>3+</sup> to nearly 53% for Yb<sup>3+</sup>/Pr<sup>3+</sup>. For all studied pairs Yb<sup>3+</sup>/Ln<sup>3+</sup>, the maximal values of η<sub>ET</sub> are 53% (Yb<sup>3+</sup>/Pr<sup>3+</sup>), 48% (Yb<sup>3+</sup>/Er<sup>3+</sup>), 49%, (Yb<sup>3+</sup>/Tm<sup>3+</sup>), and 40% (Yb<sup>3+</sup>/Ho<sup>3+</sup>). Further studies revealed that the luminescence lifetimes are reduced with increasing TiO<sub>2</sub> content, whereas the energy transfer efficiencies are changed completely different, depending on pair Yb<sup>3+</sup>/Ln<sup>3+</sup> (Ln = Pr<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Ho<sup>3+</sup>) in titanate–germanate glass.

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