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Active glasses as the luminescent sources of radiation for sensor applications

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Abstract. The article presents physicochemical, thermal and spectroscopic properties of two different glass systems: TeO_2-GeO_2-PbO-PbF_2-BaO-Nb_2O_5-LaF_3 and SiO_2-Al_2O_3-Sb_2O_3, co-doped with Yb^{3+}/Tm^{3+} ions. Blue upconversion luminescence at a wavelength of 478 nm corresponding to the thulium $^1G_4 \rightarrow {}^3H_6$ transition was observed under 976 nm pump radiation in both of the co-doped glasses. This indicated the existence of efficient $Yb^{3+} \rightarrow Tm^{3+}$ energy transfer via three-photon absorption mechanism. Thermal and optical results substantiate the claim for practical applicability of the manufactured glasses in design of optical fiber sources.

Key words: tellurite glasses, antimony-silicate glasses, Yb^{3+}, Tm^{3+}, upconversion, blue luminescence, energy transfer, active glasses.

1. Introduction

The ongoing progress in the field of sensor technology necessitates search for new sources of radiation which would meet the requirements concerning not just specified spectral properties, but also stability and compactness. One of the widely known solutions allowing to obtain desired emission involves the use of lanthanide-doped materials. Such materials are particularly attractive because of their strictly defined energy levels which are marked by only small shifts, irrespective of the used cladding. For this reason, rare earth elements are frequently taken advantage of in laser systems. As well as that, allotting ions of several different lanthanides in a single matrix makes it possible to obtain luminescence by means of energy transfers which are difficult to achieve in the course of direct optical pumping. Moreover, in co-doped materials such processes may take place, among others, as energy transfers resulting in the appearance of emission bands with wavelengths shorter than the pumping wavelength (i.e. upconversion) [1–7]. Donor-acceptor energy transfer processes depend on many factors which must be optimized in order to achieve the assumed emission band. For instance, the efficiency of upconversion is largely dependent on the type of used matrix, and in particular on the energy of phonon vibrations. Specifically, the lower the maximum lattice vibrations frequency $h\omega_{\max}$, the higher the probability of excitation energy conversion [7–11]. Among the materials with low phonon energy are fluoride glasses [12] or HMO (Heavy Metal Oxide) glasses [13], whose phonon vibrations (300–600 cm^{-1}) preclude the occurrence of unwanted nonradiative decays. Unfortunately, low mechanical and thermal resistance make it difficult to use these kinds of glasses in optical fibers manufacturing. The problem can be possibly overcome by using tellurite glasses having relatively low phonon energy (750 cm^{-1}), and at the same time exhibiting higher thermal stability. Additionally, such glasses are characterized by a high capacity for dissolving rare earth elements. Moreover, the refractive index of ca. 2 allows to obtain large absorption and emission cross-section coefficients, as well as longer life times on laser levels. Other kind of materials which can be employed for the construction of fiber lasers include antimony-silicate glasses, comprising glass-forming elements with extremely varied phonon vibrations frequency.

The present article discusses properties of tellurite and antimony-silicate glasses from the perspective of optical fiber production. Co-doping with Yb^{3+}/Tm^{3+} allowed to establish systems of active dopants, and in consequence to present results concerning blue emission produced in the course of energy transfer between ions of thulium and ytterbium. The presented active structures can find application in sensor systems as the emitters of optical radiation.

2. Experiments

Glasses with molar configurations of $50SiO_2$-$10Al_2O_3$-$40Sb_2O_3$ (SAS) and $40TeO_2$-$20GeO_2$-25(PbO-PbF_2)-5BaO-$8Nb_2O_5$-$2LaF_3$ (TGP) were doped simultaneously with Yb^{3+} and Tm^{3+} ions. In both of the cases, the homogenized set was placed in a platinum crucible, and melted in an electric furnace in temperatures of 1550°C (antimony glass) and 900°C (tellurite glass) respectively. To ensure repeatability of sample dimensions, the molten glass was poured into brass moulds and subsequently underwent annealing for 12 hours. The process resulted in homogeneous and transparent glasses without crystallization effect (base on XRD measurement). Density of thus obtained glasses was measured by hydrostatic weighing. Refractive index at a wavelength of 633 nm was determined with the use of Metricon 2010 prism coupler. Characteristic temperatures were established by means of DSC method, using a SETARAM Labsys thermal analysis instrument. Infrared absorption spectra (FTIR) were measured with a DigilabFTS60v Fourier transform spectrometer

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in the range of 400–2000 cm^{-1} with the resolution of 2 cm^{-1}. The samples were pulverized and shaped in the form of KBr plates. Measurements of spectral transmission of the plates with 10 mm diameter and thickness of 2 mm were carried out with a Acton Spectra Pro 2300i monochromator with a silicon detector in the range of 0.3–1.6 μm. Luminescence spectrum in the 400–750 nm interval was measured in a laboratory stand equipped with a Hamamatsu TM-C10082CAH spectrometer and a laser diode ($\lambda_p = 976$ nm) with fiber output of maximum optical power $P = 30$ W.

3. Results and discussion

Table 1 presents material and thermal properties of the manufactured tellurite (TGP) and antimony-silicate (SAS) glasses doped with Yb^{3+} and Tm^{3+}.

Comparing the physicochemical characteristics of the glasses it was noted that in the case of antimony-silicate matrix the combination of two glass-forming element with extremely different bond energies yielded thermally stable and mechanically durable glasses with both high and wide spectral transmission. As for the TGP glasses, the dominance of Te^{4+} ions resulted in lower maximum phonon energy (790 cm^{-1}). Furthermore, both kinds of the glasses were capable of taking in significant amounts of rare earth elements (up to 25000 ppm) without the occurrence of precipitation or crystallization effects.

Table 1
Material and thermal parameters obtained in manufactured glasses

Parameter	Value	
	TGP	SAS
Refractive index n (633 nm)	2.07	1.71
Mass density ρ [g/cm^3]	6.2	3.3
Thermal expansion coefficient α_{100}^{400} [10^{-7} 1/K]	108.9	55.1
Dylatometric softennig point T_s [°C]	364	429
Transformation temperature T_g [°C] (DSC)	345	451
Maximum of phonon energy $h\omega_{\max}$ [cm^{-1}]	790	1186

In the course of FI-IR analysis conducted in the range of 400–2000 cm^{-1} (Fig. 1), three absorption bands were detected in the tellurite glasses. The bands at 665 cm^{-1} and 790 cm^{-1} resulted from stretching vibrations of respectively TeO_4 and TeO_3 groups [14]. Additionally, the band located at 472 cm^{-1} region was related to the bending mode of Te-O-Te linkages which may be overlapped with that assigned to the bending mode of the Pb-O-Pb stretch in the [PbO_4] structural units [18].

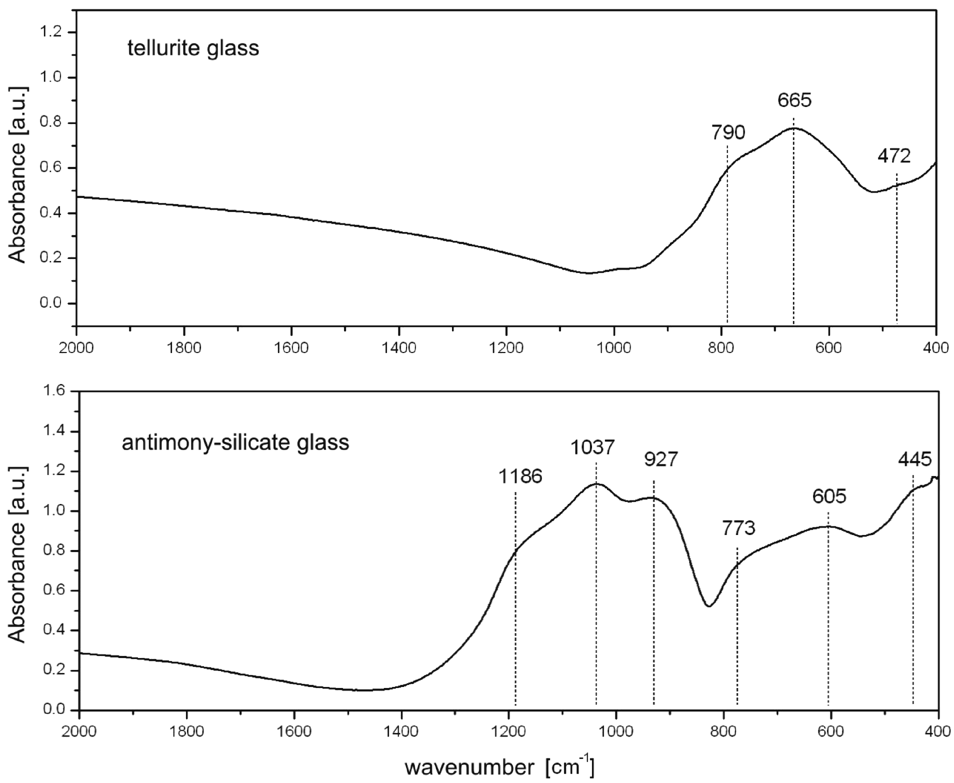

Fig. 1. FTIR absorption spectra of tellurite and antimony-silicate glasses

Antimony-silicate glass exhibited a much more extended infrared spectrum, composed of six different absorption bands. The band at 445 cm^{-1} originated from symmetric vibrations of SbO_3 pyramids, similarly as it had been observed in [15]. Another band, at 600 cm^{-1} region, was related to asymmetric vibrations of the Sb-O-Sb bond structure. Furthermore, the absorption band whose maximum corresponded to wavenumber equal 1037 cm^{-1} was typical of the Si-O-Si bond vibrations [16], whereas the band at 927 cm^{-1} stemmed from oxygen bridge vibrations. Finally, maximum phonon energy at 1186 cm^{-1} in the discussed glass was a consequence of symmetric SiO_4 groups vibrations [17], and a very weak band at 773 cm^{-1} was an effect of doubly degenerate vibrations of Sb-O bands. In comparison to the tellurite glass, the complexity of chemical bonds structure in the antimony-silicate glass led to a greater competitiveness in radiative transfers with multiphonon relaxation.

3.1. Absorption coefficient. Absorption coefficient spectrum for the tellurite glass doped simultaneously with 1 mol% Yb_2O_3: 0.2 mol% Tm_2O_3 is shown in Fig. 2. Higher concentration of Yb^{3+} ions ensures a strong absorption cross-section of the pump radiation at 976 nm and high efficiency of energy transfer between donor and acceptor. In the range from 400 to 1600 nm, four absorption bands of thulium were detected; they corresponded with transitions from the ground state $^3H_6$ to higher energy states $^3H_5$, $^3H_4$, $^3F_{2,3}$, $^1G_4$ respectively. As well as that, there was a characteristically marked and wide band at a wavelength of 978 nm related to the presence of the ytterbium ions. In practical applications, taking advantage of Yb^{3+} allows efficient excitation of the manufactured active glasses with widely available high-power semiconductor laser diodes.

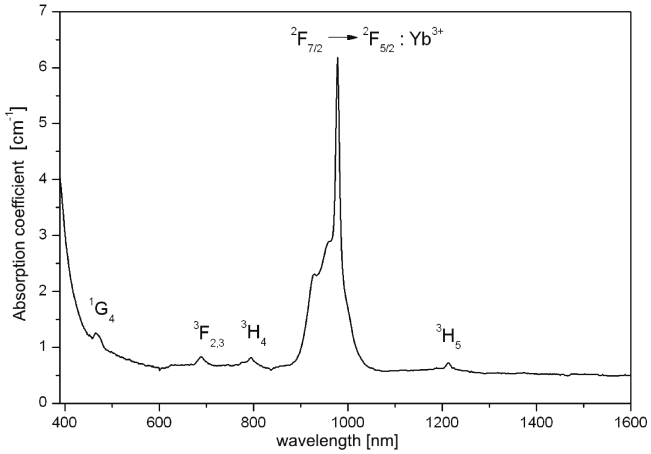

Fig. 2. Absorption coefficient of tellurite glass co-doped with 1%mol Yb_2O_3: 0.2%mol Tm_2O_3

3.2. Luminescence spectra. When exciting the produced glass samples with 976 nm wavelength radiation, blue emission corresponding with the $^1G_4 \rightarrow {}^3H_6$ transition in thulium was observed. Figure 3 shows luminescence spectra of the active glasses with maximum emission (upconversion) at a wavelength in the band of 478 nm.

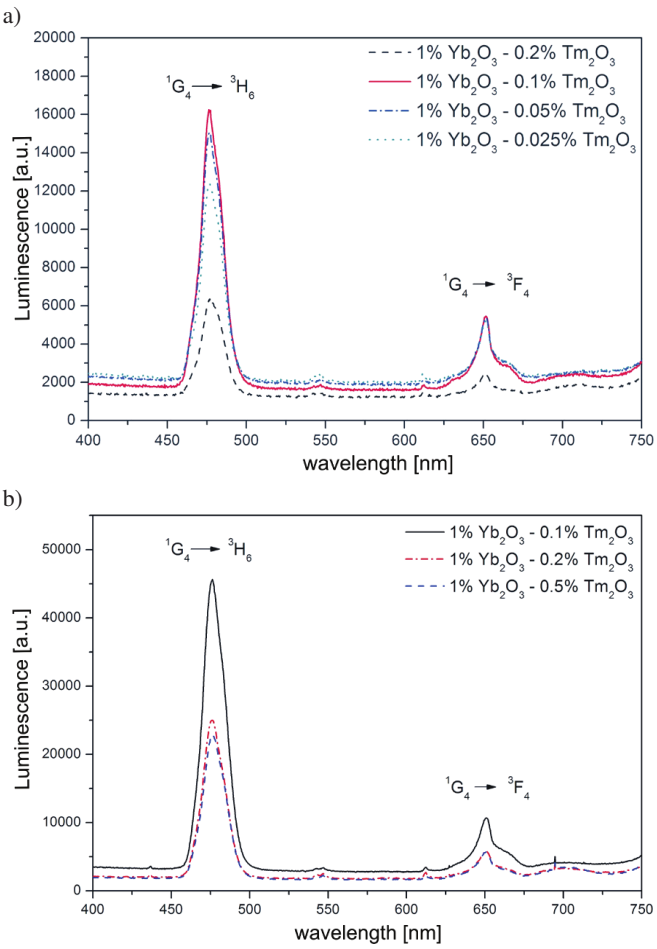

Fig. 3. Luminescence spectra of tellurite (a) and antimony-silicate (b) glasses with different Tm^{3+} concentration

Additionally, in the visible range at a wavelength of 651 nm a considerably weaker radiative transfer was observed which corresponded with the $^1G_4 \rightarrow {}^3F_4$ relaxation. The conversion of optical pump radiation ($\lambda_p = 976$ nm) manifested as spontaneous blue emission confirmed that in both of the manufactured glass matrices energy was exchanged between Yb^{3+} and Tm^{3+} ions. It is worth noticing that the maximum level of luminescence at a wavelength within the band of 478 nm in either kind of the glass was achieved at the same ratio (10:1) of ytterbium to thulium ions. This phenomenon is related to similarity of lattice vibrations in the 400 to 700 cm^{-1} interval which are responsible for the rate of photon transitions, and thus influencing the efficiency of energy transfer.

3.3. Energy transfer. Due to the lack of spatial adjustment between the emission field of ytterbium ions and the absorption field of thulium ions, energy transfer occurred with the participation of phonons. Relying on the results of spectroscopic measurements, Fig. 4 features an energy diagram of mutually coupled ytterbium and thulium ions, in which the

mechanisms of energy transfer between Yb^{3+} and Tm^{3+} ions are presented. Multiplet $^1G_4$ was populated in the upconversion process, in the course of a three-stage energy transfer between ytterbium and thulium ions. Strong absorption of the pumping radiation (976 nm) in the ground state $^2F_{7/2}$ (Yb^{3+}) caused the population of a higher multiplet $^2F_{5/2}$. Excited Yb^{3+} ion, in transition from the excited state, transferred a portion of its energy (ET1) to Tm^{3+} ions, which led to the population of $^3H_5$ level. Short life time and small energy difference effected in a prompt nonradiative relaxation to $^3F_4$ level. Concurrently, another Yb^{3+} ion discharging a quantum of energy (ET2) caused excitation of a Tm^{3+} ion to $^3F_{2,3}$ level. Subsequently, during a quick multiphonon relaxation (MPR), a lower excited level $^3H_4$ was populated. In the same vein, absorption from excited level $^3H_4$ occurred in the aftermath of energy transfer (ET3) from the next Yb^{3+} ion, leading to the population of $^1G_4$ level. Equations (1)–(3) below describe the mechanism of emission in the course of energy transfer with upconversion within the visible range.

$$\text{ET1: } {}^2F_{5/2}(Yb^{3+}) + {}^3H_6(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^3H_5(Tm^{3+}) \rightarrow \text{MPR} \rightarrow {}^3F_4(Tm^{3+}), \quad (1)$$

$$\text{ET2: } {}^2F_{5/2}(Yb^{3+}) + {}^3F_4(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^3F_2(Tm^{3+}) \rightarrow \text{MPR} \rightarrow {}^3H_4(Tm^{3+}), \quad (2)$$

$$\text{ET3: } {}^2F_{5/2}(Yb^{3+}) + {}^3H_4(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^1G_4(Tm^{3+}). \quad (3)$$

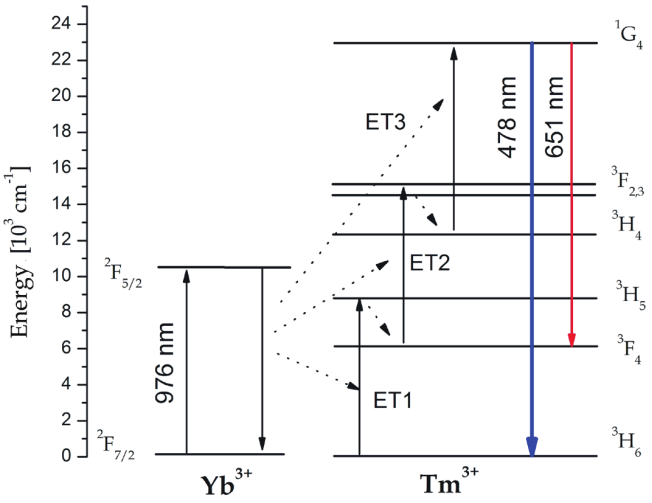

Fig. 4. Scheme of upconversion energy transfer between Yb^{3+}/Tm^{3+} ions

In effect of a three-photon excitation conversion, strong emission at a wavelength of 478 nm ($^1G_4 \rightarrow {}^3H_6$) is obtained. At the same time, a weaker luminescence band is exhibited at 651 nm which corresponds to $^1G_4 \rightarrow {}^3F_4$ transition.

4. Conclusions

Within the scope of the presented research, glasses from the systems of $50SiO_2$-$10Al_2O_3$-$40Sb_2O_3$ (SAS) and $40TeO_2$-$20GeO_2$-$25(PbO\text{-}PbF_2)$-$5BaO$-$8Nb_2O_5$-$2LaF_3$ (TGP) were manufactured and subsequently doped simultaneously with Yb^{3+} and Tm^{3+} ions. The conducted analysis of material properties of the glasses proved that both of the matrices possessed characteristics which made them eligible for optical fiber production. Moreover, due to the fact that the used glass-forming elements had different vibration energy, it was possible to achieve rare earth element concentration at the level of 25000 ppm. Excited with a wavelength of 976 nm, the glasses produced blue emission which corresponded to $^1G_4 \rightarrow {}^3H_6$ transition between quantum levels of thulium ions. Furthermore, during analysis of luminescence properties it was confirmed that the samples of co-doped glasses exhibited effective excitation energy transfer between Yb^{3+} and Tm^{3+} ions. Because of the energy difference between multiplets $^3H_5$ (Tm^{3+}) and $^2F_{5/2}$ (Yb^{3+}) amounting to ca. 1100 cm^{-1}, energy could be transferred in the course of a nonresonant process with the participation of phonons. Taking into consideration a three-photon absorption of excitation radiation, the mechanism of upconversion at a wavelength within the band of 478 nm corresponding to $^1G_4 \rightarrow {}^3H_6$ transition was demonstrated. The achieved research results substantiate the claim for practical applicability of the manufactured glasses co-doped with ytterbium and thulium ions in design of optical fiber sources.

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