

# Low-phonon tellurite glass co-doped with $\text{Tm}^{3+}/\text{Ho}^{3+}$ ions for optical fiber technology

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**Abstract**—In this paper the material and optical properties of tellurite glasses co-doped with  $\text{Tm}^{3+}/\text{Ho}^{3+}$  ions were investigated. Near infrared luminescence at a wavelength of 2060 nm ( $^5\text{I}_7 \rightarrow ^5\text{I}_8$ ) in holmium ions was obtained as a result of energy transfer between  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  ions. The energy transfer (ET) between  $\text{Tm}^{3+} \rightarrow \text{Ho}^{3+}$  ions was investigated pumping at 795nm. As a result of optimization of rare earth concentration, the best efficiency of energy transfer in fabricated glasses was obtained for molar composition 0.2mol%  $\text{Tm}_2\text{O}_3$ : 0.2mol%  $\text{Ho}_2\text{O}_3$ .

Emission in the region of  $2\mu\text{m}$  is possible through using  $\text{Tm}^{3+}$  or  $\text{Ho}^{3+}$  ions as activators [1-3]. A direct excitation of  $\text{Tm}^{3+}$  ions from their ground state to the  $^3\text{H}_4$  level resulting from absorption of radiation, takes place at the maximum wavelength of 795 nm. As a consequence, emission at a wavelength of  $1.8\mu\text{m}$  can be observed corresponding to the quantum transition of  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  ( $\text{Tm}^{3+}$ ) in the structure of thulium ions. However, in the case of  $\text{Ho}^{3+}$  ions, a lack of high-power semiconductor diodes which would allow for effective excitation of this element is a significant problem. Therefore, it is necessary to apply sensibilisators in the form of  $\text{Tm}^{3+}$  or  $\text{Yb}^{3+}$  ions. They transit excitation energy, thus making it possible to produce emission at a wavelength of  $2\mu\text{m}$ , corresponding to the  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  ( $\text{Ho}^{3+}$ ) transition [4-5].

The selection of a suitable glass system is a key factor in obtaining efficient infrared emission. Tellurite glasses, which are characterised by low phonon energy ( $\sim 750\text{cm}^{-1}$ ) have important advantages over other common oxide glasses such as silicate ( $\sim 1100\text{cm}^{-1}$ ) and germanate ( $\sim 900\text{cm}^{-1}$ ). They possess good solubility of rare earth, high refractive index ( $\sim 2$ ) and good thermal stability [5]. In addition, their infrared transparency range is up to  $5\mu\text{m}$ . Hence tellurite glasses are attractive materials when considering the design of a tunable laser host in mid-IR.

The present letter discusses the properties of active tellurite glasses from the perspective of optical fiber production. Co-doping with  $\text{Tm}^{3+}/\text{Ho}^{3+}$  ions allowed to establish systems of active dopants, and in consequence to present the results concerning broadband emission in the near infrared emission produced in the course of energy transfer between the ions of thulium and holmium.

The glass with a system:  $\text{TeO}_2 - \text{GeO}_2 - \text{PbO} - \text{PbF}_2 - \text{BaO} - \text{Nb}_2\text{O}_5 - \text{LaF}_3$  (TGP) co-doped with  $\text{Tm}^{3+}/\text{Ho}^{3+}$  ions was melted from spectrally pure (99.99%) raw materials. The homogenized set was placed in a platinum crucible and melted in an electric furnace in a temperature of  $900^\circ\text{C}$  for 30 minutes in an argon atmosphere. The molten glass was poured out onto a brass plate and then exposed to the process of annealing in a temperature approximate to that of transformation for 12 hours. Homogenous and transparent glasses were obtained without any visible effect of crystallization. In order to determine their spectral properties, a series of samples with dimensions of  $10 \times 10 \times 2\text{mm}^3$  were prepared. The glass density  $\rho$  was calculated using the method of hydrostatic weighing. The refractive index (at  $633\text{nm}$ ) was determined with the aid of a Metricon 2010 refractometer. The characteristic temperatures of the obtained glasses were calculated based on the measurement taken with a SETARAM Labsys thermal analyzer using the DSC (Differential Scanning Calorimetry) method. Infrared absorption spectra (FTIR) were measured with a DigilabFTS60v Fourier transform spectrometer in the range of  $400-2000\text{cm}^{-1}$  with a resolution of  $2\text{cm}^{-1}$ . The samples were pulverized and shaped in the form of KBr plates. Absorption spectra of rare-earth ions doped samples were determined using an Acton SpectraPro 2300i monochromator in the spectral range of  $350-2200\text{nm}$ . As for the luminescence spectra in the range of  $1350-2300\text{nm}$ , they were measured in the lock-in technique with an Acton SpectraPro 2300i spectrometer, using a high power laser diode ( $\lambda_p=795\text{nm}$ ) as a pump source. All the measurements were made in room temperature.

Tellurite glasses are characterized by a high refraction index (2.07), which is the reason for the high value of the emission cross-section. In the course of the FT-IR analysis conducted in the range of  $400-2000\text{cm}^{-1}$  (Fig. 1), three absorption bands were detected in the tellurite glasses. The bands at  $665\text{cm}^{-1}$  and  $790\text{cm}^{-1}$  resulted from stretching vibrations of respectively  $\text{TeO}_4$  and  $\text{TeO}_3$  groups [6]. Additionally, the band at the  $472$

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$\text{cm}^{-1}$  region was related to symmetric vibrations of Te-O-Te bonds.

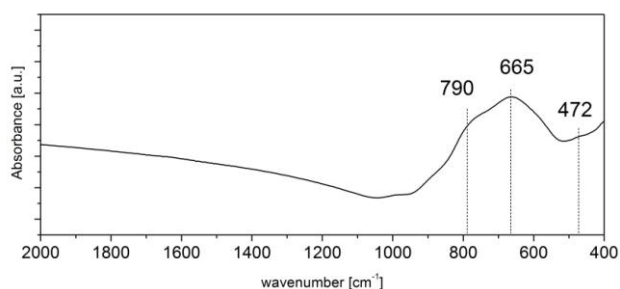


Fig. 1. FTIR spectrum of tellurite glass.

In order to evaluate the thermal stability of fabricated glass, measurements of DSC were performed. Figure 2 presents the DSC curve of TGP glasses. The DSC curve shows the glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_x$ ) in the glass sample.

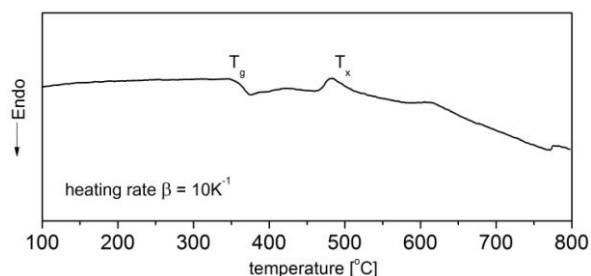


Fig. 2. DSC curve of fabricated glass.

The stability of glass against crystallization is evaluated by the parameter  $\Delta T = (T_g - T_x)$ . Glasses with higher  $\Delta T$  may be stable against crystallization while drawing an optical fiber. In fabricated TGP glass the value of  $\Delta T$  is  $139^\circ\text{C}$  and it is comparable to other tellurite glasses [7]. The results of thermal and physicochemical parameters are listed in Table 1.

Table 1. Physicochemical and thermal properties of tellurite glass

PARAMETER	VALUE
Refractive index $n$ (at 633nm)	2.07
Density $\rho$ [ $\text{g}/\text{cm}^3$ ]	3.3
Thermal expansion coefficient $\alpha_{100}^{400}$ [ $10^{-7}$ 1/K]	55.1
Dilatometric softening point $T_s$ [ $^\circ\text{C}$ ]	429
Transformation temperature $T_g$ [ $^\circ\text{C}$ ] (DSC)	341
Crystallisation temperature $T_x$ [ $^\circ\text{C}$ ] (DSC)	480
Maximum of phonon energy $\hbar\omega_{\text{max}}$ [ $\text{cm}^{-1}$ ]	790

Figure 3 shows the optical density spectrum of the glass co-doped with  $0.2\text{Ho}_2\text{O}_3/0.2\text{Tm}_2\text{O}_3$  ions. Introducing two different activators to the glassy matrix leads to complication of the energy structure and division of the pumping radiation quantum by means of energy transfer between the donor and the acceptor.

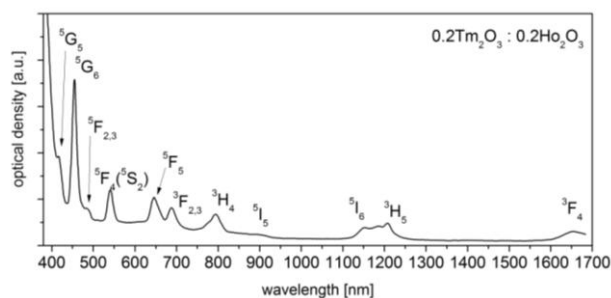


Fig. 3. Absorbance spectrum of tellurite glass co-doped with 0.2  $\text{Tm}_2\text{O}_3$ : 0.3  $\text{Ho}_2\text{O}_3$ .

In the spectral range from 350 to 1700 nm four absorption bands of  $\text{Tm}^{3+}$  were observed corresponding with the transitions from the ground state  $^3\text{H}_6$  to the excited states  $^3\text{F}_4$ ,  $^3\text{H}_5$ ,  $^3\text{H}_4$ ,  $^3\text{F}_{2,3}$ . Also the next seven bands corresponding to the transitions  $^5\text{I}_8 \rightarrow ^5\text{I}_6$ ,  $^5\text{I}_5$ ,  $^5\text{F}_5$ ,  $^5\text{F}_4(^5\text{S}_2)$ ,  $^5\text{F}_2(^5\text{F}_3)$ ,  $^5\text{G}_6$ ,  $^5\text{G}_5$  related to the presence of  $\text{Ho}^{3+}$  ions were noted.

The luminescence spectra of tellurite glass doped with  $\text{Tm}^{3+}$  ions and co-doped with  $\text{Tm}^{3+}/\text{Ho}^{3+}$  are shown in Fig. 4. The glass with thulium ions are characterized by strong luminescence bands at 1460nm and 1800nm corresponding to the transitions of  $^3\text{H}_4 \rightarrow ^3\text{F}_4$  and  $^3\text{F}_4 \rightarrow ^3\text{H}_6$ , respectively. Introducing holmium ions to glass results in a decrease in the emission of  $\text{Tm}^{3+}$  ions at 1800 nm. At the same time, a strong emission line appears at 2 $\mu\text{m}$  corresponding to the  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  transition in the holmium ions. As a result, a significant broadening of the luminescence spectrum, caused by overlapping of the  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  ( $\text{Tm}^{3+}$ ) and  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  ( $\text{Ho}^{3+}$ ) transitions was observed in the glass which was doped at a molar ratio of 0.2  $\text{Tm}_2\text{O}_3$ : 0.05 $\text{Ho}_2\text{O}_3$ . The full width at half maximum (FWHM) of the (Tm/Ho) emission spectra amounts to 450nm and to 290nm for the glass doped only with  $\text{Tm}^{3+}$  ions. Increasing the molar volume of holmium ions leads to decreasing the luminescence of the  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  ( $\text{Tm}^{3+}$ ) transition and to the appearance of a strong luminescence line in the region of 2 $\mu\text{m}$  (Fig. 4).

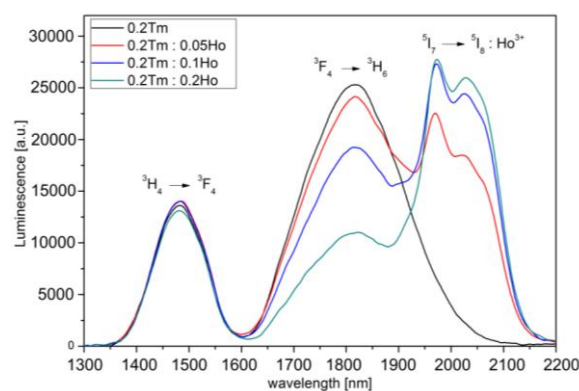


Fig. 4. The luminescence spectra of tellurite glasses doped with  $\text{Tm}^{3+}$  and  $\text{Tm}^{3+}/\text{Ho}^{3+}$  ions under 795nm LD excitation.

The simplified energy level diagram for  $\text{Tm}^{3+}/\text{Ho}^{3+}$  co-doped tellurite glass shown in Fig. 5 is helpful in understanding the mechanism of thulium sensitization of holmium ions in a lattice under 795nm excitation. In thulium ions, optical pumping (795nm) results in the population of the  $^3\text{H}_4$  level, which enables transfer to lower energetic levels:  $^3\text{H}_5$  and  $^3\text{F}_4$ . The  $^3\text{H}_5$  level in thulium is characterised by a short lifetime and its role in the relaxation process can be neglected, whereas the lifetime of the  $^3\text{F}_4$  level is long and, as a result, it allows for reaching a high population density at this level.

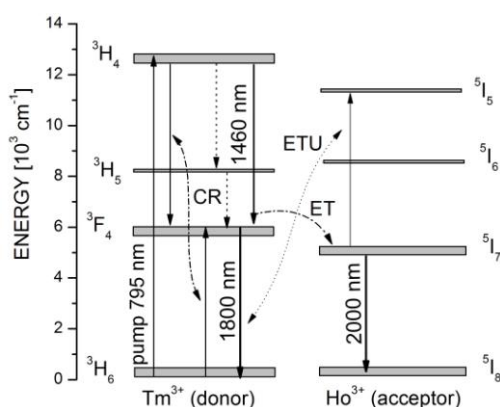


Fig. 5. Simplified energy level scheme with a mechanism of energy transfer (CR – cross-relaxation, ETU – energy transfer upconversion).

The energy transfer (ET) efficiency between the donor and the acceptor was calculated by analysing changes in the quantum leap of  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  in glasses doped with thulium as well as with thulium and holmium ions. The dependence developed on the basis of Förster's theory was applied for that purpose [8]:

$$\eta = 1 - \frac{I_{\text{TmHo}}}{I_{\text{Tm}}}, \quad (1)$$

where:  $I_{\text{TmHo}}$  – luminescence intensity in  $\text{Tm}^{3+}/\text{Ho}^{3+}$  glasses,  $I_{\text{Tm}}$  – luminescence intensity in  $\text{Tm}^{3+}$  glasses. The values of ET efficiency are listed in Table 2.

Table 2. Efficiency of energy transfer

$\text{Tm}^{3+}/\text{Ho}^{3+}$	0.2/0	0.2/0.05	0.2/0.1	0.2/0.2
$\eta$ [%]	---	5	24	55

It should be noted that increasing holmium ions up to 0.1 mol % leads to an increase in energy transfer efficiency and the appearance of an emission band at  $2\mu\text{m}$ . Despite the significant value of  $\eta$  for glass co-doped 0.2/0.2, the level of a luminescence band at  $2\mu\text{m}$  did not change. In this case it is likely that the concentration of RE was too high and some excitation energy was lost by phonon-induced processes (eg. ETU) which lead to luminescence quenching.

As presented in the letter, low-phonon tellurite glass co-doped with  $\text{Tm}^{3+}/\text{Ho}^{3+}$  was synthesized. The high thermal stability of fabricated glass  $\Delta T=136^\circ\text{C}$  was confirmed by DSC measurements. As a result of luminescence measurements, a significant broadening of the spectrum caused by superposition of the  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  ( $\text{Tm}^{3+}$ ) and  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  ( $\text{Ho}^{3+}$ ) transitions was observed in the glass co-doped with 0.2  $\text{Tm}_2\text{O}_3:0.05\text{Ho}_2\text{O}_3$ . The full width at half maximum of the (Tm/Ho) emission amounts to 450nm. According to Förster's theory the highest efficiency of energy transfer  $\eta=55\%$  was calculated. Despite the significant value of  $\eta$  for glass co-doped 0.2/0.2, the emission at  $2\mu\text{m}$  did not change, hence the concentration quenching effect was observed.

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