The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2019

Volume 6, Pages 122-125

ICRES 2019: International Conference on Research in Education and Science

Upconversion Emission Properties of Nb_2O_5 Modified Tellurite-Based Glasses Activated with Rare Earth Ions

Huseyin ERTAP
Kafkas University

Gokhan BILIR
Kafkas University

Lidong MA
Boston College

Baldassare DI BARTOLO
Boston College

Abstract: The upconversion emission properties of Nb_2O_5 modified tellurite-based glasses activated with Er^{3+}, Tm^{3+}, Ho^{3+}, and Yb^{3+} ions were studied. The glass samples wer obtained using melt-quenching method. The optical absorption spectra of the samples were collected in the 400-1100 nm wavelenth range at room temperature. The forbidden gap of the glasses were determined using the absorption spectra of the samples. The upconversion emission of samples were obtained under the 975 nm laser excitation and recorded in the 350-900 nm wavelength range. Three primary colors were simultaneously obtained from the samples under the 975 nm excitation. The CIE-1931 coordinates and the correlated color temperaatures of obtained upconversion emissions were also determined using the upconversion emission spectra.

Keywords: Tellurite glasses, Nb_2O_5, Rare earth ions, Upconversion

Introduction

Rare earth ions (RE) activated heavy metal oxide glasses, like tellurite and antimony-based glasses, have been subject to a special interest in last few decades due to their low phonon energies among other oxide glass systems which increases the quantum efficiency from excited states of RE ions via decreasing the non-radiative energy losses due to the phonon vibrations in these matrices and provides the possibility of developing more efficient photonic devices. On the other hand, the upconversion (UC) mechanisms of the RE ions activated glasses are also attract special attention because they are possessing some superior properties compared to bulk crystals like longer lifetime of REs in glasses and their ability to contain considerable amount of RE ions without inducing crystallization (Bilir, 2017).

Tellurite glasses emerge for the many excellent properties for photonics applications, like low melting temperature (~750^oC), chemical and thermal stability, high dielectric constant, wide transparency region (0.3 – 7 μm). They also exhibit phonon energies of about 780 cm^{-1} and high refractive index (2.1 to 2.3) which are excellent properties for UC purposes because of decreasing the non-radiative energy losses due to the phonon vibrations and increasing the local field correction at the dopant site, respectively (Bilir, et al., 2016; Bilir&Ozen, 2011; Bilir, 2015; Bilir, et al., 2011; Burtan-Gwizdala, et al., 2017; El-Mallawany, 2002).

Since TeO_2 is a conditional glass former and is the most stable oxide form of the tellurium, it cannot able to form glassy matrix easily by itself. Network modifiers should be added into the system to obtain tellurite glasses. In this context, we added Niobium Oxide (Nb_2O_5) into the system to obtain tellurite glasses. We also

- Selection and peer-review under responsibility of the Organizing Committee of the Conference

added Er^{3+}, Tm^{3+}, Ho^{3+} and Yb^{3+} ions into the system to investigate the UC emission properties of the glasses. To do so, we measured the optical absorption, and the UC emission spectra of samples.

Method

The glass samples with the compositions $0.1Nb_2O_5 + (0.9\text{-}x\text{-}y\text{-}z)TeO_2 + xEr_2O_3 + yTm_2O_3 + zYb_2O_3$ (x = 0.005, y = 0.003, and z = 0.03), and $0.1Nb_2O_5 + (0.9\text{-}x\text{-}y\text{-}z)TeO_2 + xTm_2O_3 + yHo_2O_3 + zYb_2O_3$ (x = 0.005, y = 0.007, and z = 0.03) were synthesized by melting the ultrapure (99.99%) TeO_2, Nb_2O_5, Er_2O_3, Tm_2O_3, and Yb_2O_3 powders which is followed by rapid quenching of the glass melts. 7g of batches were prepared using a high precision scale, mixed in an agate mortar, and transferred into a platinum crucible with a lid. The mixture put into an electric furnace and heated up to 850 ^oC for an hour. The obtained glass melts, then, were poured onto a preheated (250 ^oC) stainless steel mold. After that, the glass samples were thermally treated below their glass transition temperature (at about 250 ^oC) for an hour to reduce thermal stresses due to the high synthesis temperatures. The obtained as-cast glass samples were polished to form two parallel shiny surfaces for optical measurements.

The optical absorption characteristics of the samples were determined using a Perkin Elmer Lambda 25 UV-Vis spectrophotometer in the 300 – 1100 nm wavelength range. The UC luminescence spectra of the samples were collected using a Sheaumann model laser diode operated at 975 nm as an excitation source and an Ocean Optics USB4000-VIS-NIR spectrophotometer for the detection of the luminescence signal. A short pass filter with a 950 nm cut off wavelength was used to avoid the spurious modes of the laser and the harmonics of the emission. All optical measurements were conducted under ambient conditions.

Results and Discussion

Glass samples were successfully synthesized using the melt quenching technique. The optical absorption spectra of the samples, in the 300 – 1100 nm wavelength range are given in Figure 1 with the corresponding transitions of the doped Re ions. As seen from Figure, several characteristic group of ground state transitions were observed due to the $4f^n$ electronic configuration of the RE ions. The increase in the spectra below the 450 nm is due to the forbidden energy gap of glass samples. The calculated direct and indirect band gap values using the Davis – Mott theory (Davis&Mott, 1970) were found to be 2.856 eV and 2.504 eV for the Er^{3+}-Tm^{3+}-Yb^{3+} activated sample, and 2.866 eV and 2.582 eV for the Tm^{3+}-Ho^{3+}-Yb^{3+} activated sample, respectively.

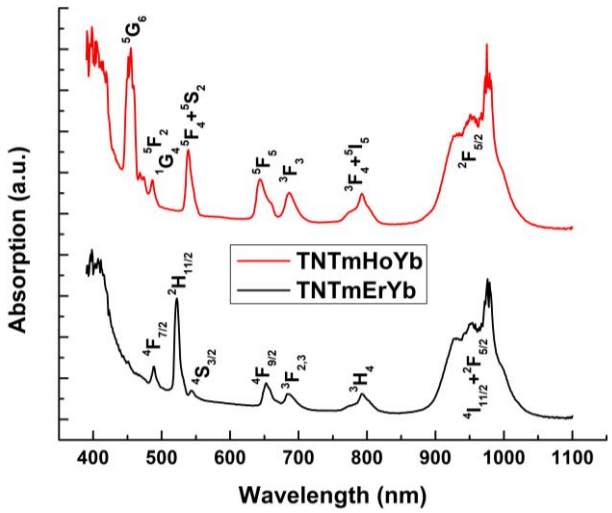

Figure 1. Absortion spectra of the glass samples

The upconversion emission spectra of samples which is collected under 975 nm excitation in the 350 – 900 nm wavelength range are given in Figure 2. The insets are the energy level diagrams of the RE ions which show the possible mechanisms responsible for the appearance of different UV-Visible emissions upon 975 nm laser diode excitation. As seen from Figure, five upconversion bands in the blue (476 nm), green (524 nm and 546 nm), red (655 nm), and near-infrared (808 nm) spectral regions for the Er^{3+}-Tm^{3+}-Yb^{3+} activated sample and three upconversion emission bands in the green (547 nm), red (660 nm), and near-infrared (804 nm) for the Tm^{3+}-

Ho^{3+}-Yb^{3+} activated sample have been observed. The observed upconversion emission bands can be easily assigned to the transitions from upper populated levels to the lower energy levels of the RE ions. In Er^{3+}-Tm^{3+}-Yb^{3+} activated case, the emission bands are due to the $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$ transitions of Tm^{3+}, the $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$ transitions of Tm^{3+}, $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}, $^4F_{9/2} \rightarrow {}^4I_{15/2}$, $^1G_4 \rightarrow {}^3F_4$ transitions of Er^{3+} and Tm^{3+}, and $^1G_4 \rightarrow {}^3H_5$, $^3H_4 \rightarrow {}^3H_6$ transitions of Tm^{3+}, respectively. The upconversion emission bands in the Tm^{3+}-Ho^{3+}-Yb^{3+} activated sample assigned to the $^5S_2 \rightarrow {}^5F_4$, $^5F_4 \rightarrow {}^5I_8$ transitions of Ho^{3+}, the $^1G_4 \rightarrow {}^3F_4$, $^5F_5 \rightarrow {}^5I_8$ transitions of Tm^{3+} and Ho^{3+}, and $^1G_4 \rightarrow {}^3H_5$, $^3H_4 \rightarrow {}^3H_6$ transitions of Tm^{3+}, respectively.

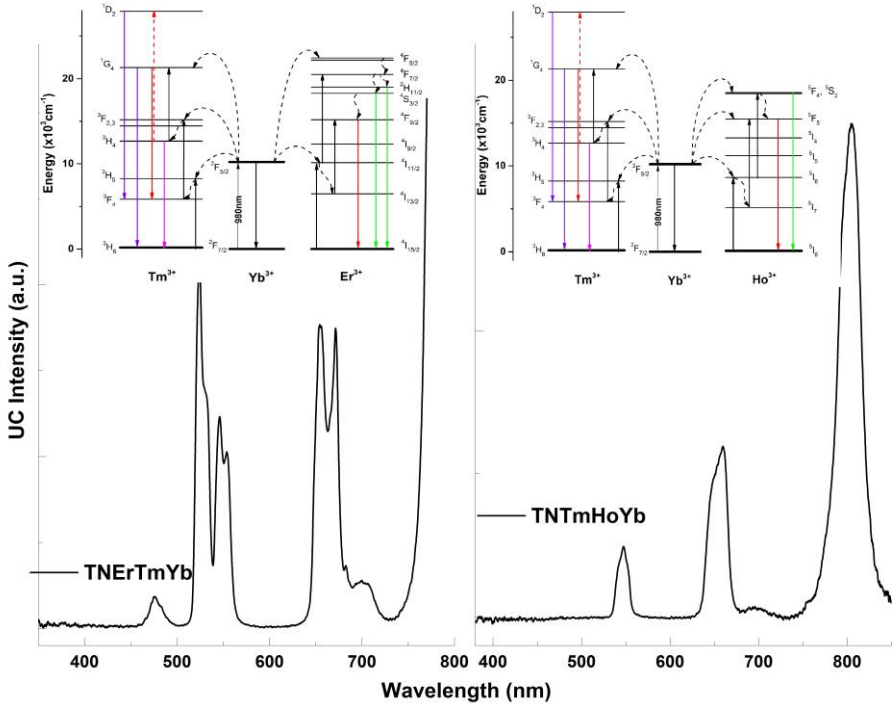

Figure 2. Upnconversion emission spectra of samples. Insets show the energy level diagrams

The responsible mechanism to obtain UC emissions is mostly Energy Transfer (ET) process from ytterbium ions to the other RE ions because of Yb^{3+} ions having the highest concentration and its high absorption cross-section in the wavelength of the excitation source. To better understand the mechanisms behind the upconversion emissions, the band intensities dependence on the pumping excitation power were measured (the power law; $I \propto P^n$, where n is the number of excitation photons involved in process) was employed to determine the how many excitation photons included in the upconversion mechanisms. The n values were found as 2.42, 2.14, 1.78, and 1.65 for blue, green, red and IR emission in the Er^{3+}-Tm^{3+}-Yb^{3+} activated sample and 1.87, 1.78, and 1.68 for green, red, and IR emissions in the Tm^{3+}-Ho^{3+}-Yb^{3+} activated sample, respectively.

The CIE 1031 color coordinates of the samples were also determined to estimate the color of the visible emissions and results are given Figure 3. It is clearly seen from figure that the visible upnconversion emissions from Er^{3+}-Tm^{3+}-Yb^{3+} activated sample lie in the reddish-orange region to greenish region of the CIE diagram, while those of the Tm^{3+}-Ho^{3+}-Yb^{3+} activated sample lie in the reddish-orange region of the CIE 1931 diagram.

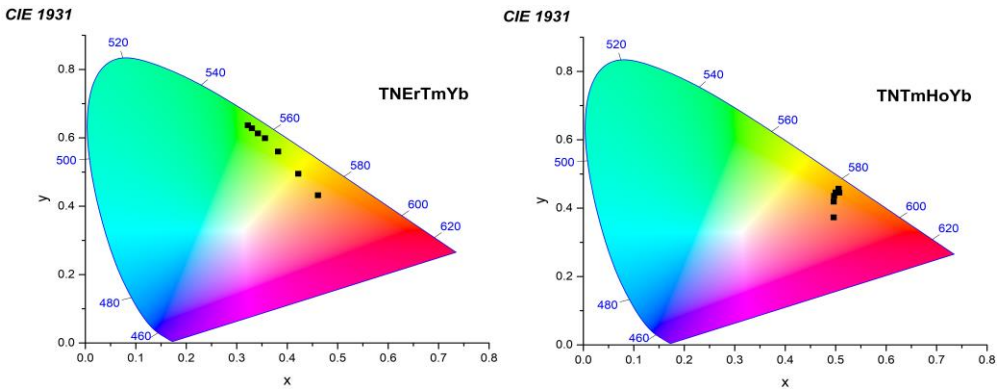

Figure 3. CIE 1931 coordinates of obtained upconversion visible emissions

Conclusion

Nb_2O_5 modified tellurite glasses triply doped with different type of RE ions were successfully synthesized using traditional melting and quenching method. The upconversion emission properties of samples were determined. The primary colors were simultaneously obtained from samples and the possible mechanisms responsible for the upconversion visible emissions were explained in the light of energy level diagrams and the power law, which gives number of excitation photons involved in the upconversion mechanisms.

Acknowledgements

This research has been supported by the Coordination Office of the Scientific Research Projects of Kafkas University under the project numbered 2017-FM-57.

References

Bilir, G. (2017). Intense upconverted white light emission fromTm^{3+}-Er^{3+}+Yb^{3+} doped zinc tungsten tellurite glasses. *SDU J. Nat. Appl. Sci., 21*, 768-790.

Bilir, G., Kaya, A., Cinkaya, H., Eryürek, G. (2016). Spectroscopic investigation of zinc tellurite glasses doped with Yb^{3+} and Er^{3+} ions. *Spectrochim. Acta A Mol. Biomol. Spectrosc., 165*, 183-190.

Bilir, G., Ozen, G. (2011). Optical absorption and emission properties of Nd^{3+} in TeO_2–WO_3 and TeO_2–WO_3–CdO glasses. *Physica B., 406*, 4007-4013.

Bilir, G. (2015). Synthesis and Spectroscopy of Nd^{3+} doped tellurite-based glasses. *Int. J. Appl. Glass Sci., 6*, 397-405.

Bilir, G., Mustafaoğlu, N., Ozen, G., Di Bartolo, B. (2011). Characterization of emission properties of Er^{3+} ions in TeO_2–CdF_2–WO_3 glasses. *Spectrochim. Acta A Mol. Biomol. Spectrosc., 83*, 314-321.

Burtan-Gwizdala, B et al. (2017). Spectroscopic properties of Er^{3+}-doped fluorotellurite glasses containing various modifiers. *Opt. Mater., 73*, 509-516.

Davis, F. A., Mott, N. F. (1970). Conduction in non-crystalline systems V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors. *Philos. Mag., 22*, 903-922.

El-Mallawany, R. A. H. (2002). Tellurite Glasses Handbook: Physical Properties and Data. (New York:CRC Press)

Author Information

Hüseyin Ertap
Kafkas University
36100 Kars / TURKEY
Contact E-mail: *huseyinertap@gmail.com*

Gökhan Bilir
Kafkas University
36100 Kars / TURKEY

Lidong MA
Boston College
MA 02467, USA

Baldassare Di Bartolo
Boston College
MA 02467, USA