

# Optical Upconversion Properties Of $Tm_2O_3 / Yb_2O_3$ Doped Lead Tellurite Glasses

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**Abstract:** The melt-quench process was used to create the lead-tellurite glasses codoped with lanthanides as thulium and ytterbium. Thermal characterization carried by differential scanning calorimetry. X-ray diffraction is studies to get the nature of sold sample. The UV-Visible-IR absorption spectra was carried in range of 300 nm to 1100 nm. There were four unique absorption peaks on the glass thulium –ytterbium doped glass. The frequency up-conversion (UC) fluorescence has been seen at room temperature by 975 nm excitation.

**Key Words:** Melt-Quench, Absorption Spectra, Frequency up-conversion

## 1. Introduction

The advancement of opto - electronic devices based on lanthanide (Ln) ions doped substances for their potential applications opto-electronics, fibres, optical amplifiers, wide range lasing materials, high density optical data storage, and three-D displays, is currently one of the most fascinating fields of research [1–3]. The focus of efforts has been on improving the spectral characteristics of the Ln ions implanted in various oxide and fluoride hosts. In this view, to decrease the

non-radiative de-excitations and improve the cross-sections of the Ln ions, good optical quality, high transparency, and low phonon energies are required. Because of their outstanding stability, mechanical durability, and ease of manipulation to generate diverse shapes such as rods, optical fibres, or planar waveguides, Ln-doped silica glasses have been employed frequently for these applications. However, the large phonon energies ( $>1000\text{ cm}^{-1}$ ) and high multiphonon non-radiative de-excitation probabilities as

well as the low cross-sections and low efficiencies of the Ln ions cause these glasses to fail. In light of their high transparency into mid-infrared (IR) frequencies, a range inaccessible to silica fibres, and on the other hand, their low-phonon energies ( $1000\text{ cm}^{-1}$ ) in comparison to silica hosts, oxide, fluoride, mixed-halides, chalcogenides, and sulphide glass hosts appear to be the best candidates [4]. But these substances also have a number of drawbacks, among them low chemical, thermo-chemical, and mechanical reliabilities, challenging processing and fabrication, and poor durability [1] in addition to a low laser damage threshold for glass fibres, making them unsuitable for single-mode fibres. The transparent glass-ceramic has been the subject of extensive research over the past ten years as a novel material type doped with Rare earth ions. Glass-ceramic materials have been interwoven into our everyday life and technology through a wide assortment of uses that span a variety of industries, including health, electronics, engineering, and telecommunications, since its unintentional discovery by S. D. Stookey in the 1950s. A glass-ceramic is made up of a minimum of one glass stage and a minimum of one crystal phase that has undergone

controlled formation and crystallisation in a predecessor glass through a thermal process. Since Beall and Duke [5] introduced oxide complex organization on developing spinel, magnetite, or  $\alpha$ -quartz crystallites in an aluminosilicate glass host in 1969, transparent oxide glass-ceramics have been known to exist. Auzel et al. [6] reported the first RE-doped oxyfluoride glass-ceramic mixing pure oxide elements with  $\text{PbF}_2$  and RE oxide a few years later, in 1975. Although they were not transparent because of the huge crystal sizes, the rare earth ions' optical characteristics in this substrate were better than those of oxides (around 10 microns). The groundbreaking work of Wang and Ohwaki [7] in 1993, in which a novel sort of appropriate glass-ceramic was described, brought these materials to the attention of photonic researchers, who began to pay close attention to them. These researchers discovered a clear oxyfluoride glass-ceramic doped with rare earth ions that is composed of a glassy aluminosilicate phase and a nanocrystalline fluoride phase. This matrix benefits from the combination of several exceptional qualities in one substance, including the material's simplicity in air-atmosphere manufacturing and manipulation, its high transparency, and its

capacity to contain Ln ions in fluoride materials. This substance is unusual in the realm of photonic material engineering since its macroscopic properties are typical of aluminosilicate glass, with the exception of the spectroscopic characteristics of the Ln ions, which are typical of moderate -phonon energy fluoride crystals [2, 3, 8].

## 2. Synthesis and Physical Properties of The Lanthanide doped Lead Tellurite Glasses

The Lanthanide doped lead Tellurite glasses with composition (in mol%) of

TPN0- (85)%[TeO<sub>2</sub>] – 5%[Pb<sub>3</sub>O<sub>4</sub>]-

10% [Na<sub>2</sub>O]-0% [Tm<sub>2</sub>O<sub>3</sub>]-0% [Yb<sub>2</sub>O<sub>3</sub>],

TPNTY1-(83.5)%[TeO<sub>2</sub>]-5%[Pb<sub>3</sub>O<sub>4</sub>]-

10% [Na<sub>2</sub>O]-0.5% [Tm<sub>2</sub>O<sub>3</sub>]-1% [Yb<sub>2</sub>O<sub>3</sub>] and

TPNTY2-(83)% [TeO<sub>2</sub>] – 5%[Pb<sub>3</sub>O<sub>4</sub>]-

10% [Na<sub>2</sub>O]-1% [Tm<sub>2</sub>O<sub>3</sub>]-1% [Yb<sub>2</sub>O<sub>3</sub>]

were made by completely mixing the composition, melting it in an alumina crucible at 950 °C for 60–90 minutes in the air, and then pouring the molten mixture onto a stainless-steel die. Although normal manipulation precautions and no controlled environment are required, there are several issues that must be considered during the fabrication of the glass, such as sudden crystallization, Ln clustering, or inhomogeneous dopant circulation [9, 10]. X-

ray diffraction can be used to monitor the structural phase that is anticipated following a heat treatment of the sample glass. As with one wide hump distinctive of structures without a long-range organization like glasses, as seen in Fig. 1. along with one broad bands, typical of structures lacking long-range arrange like glasses.

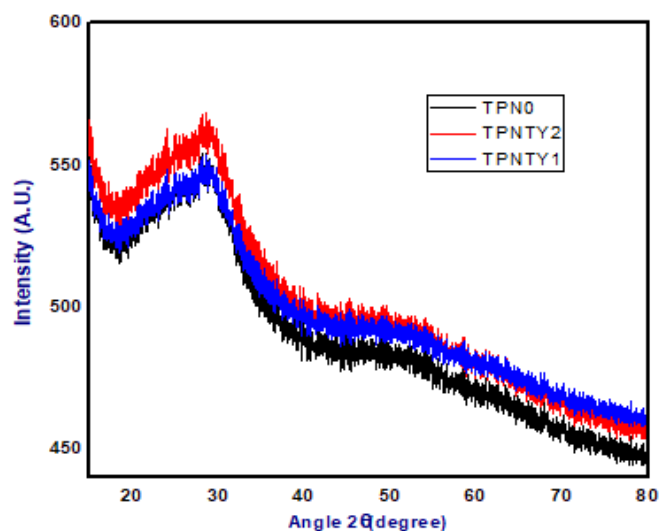


Figure 1. X-Ray diffractogram of TPN0, TPNTY1 and TPNEY2 glasses

The thermal properties of the predecessor glass sample TPNTY2 was performed by DSC using TA instruments, USA, Q10, in the temperature range of 45 °C to 480 °C at a heating rate of 10 °C/min, and the results were used to get the thermal study of lead tellurite glass TPNTY2. According to figure

5.2, the TPNTY2 sample's glass transition, melting, and critical temperatures are 305°C.

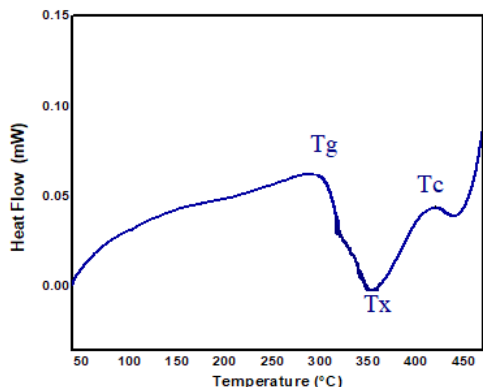


Figure 2. DSC plot of TPNTY2 glass

{792nm (Tm<sup>3+</sup>)}, and <sup>3</sup>F<sub>7/2</sub> → <sup>2</sup>F<sub>5/2</sub> {980nm (Yb<sup>3+</sup>)}.

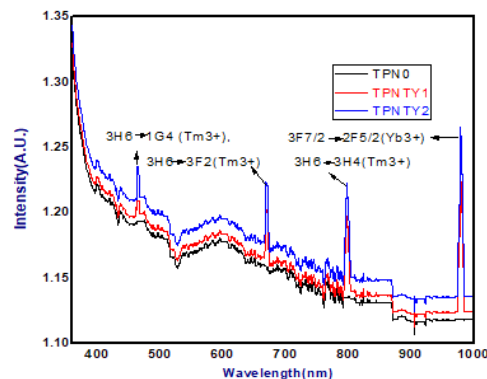


Figure 3. Absorption spectra of TPN0, TPNTY1 and TPNTY2 glasses

### 3. Absorption Properties of The Lanthanide doped Lead Tellurite Glasses

Thulium oxide/ytterbium oxide doped and withed lead tellurite glasses' UV-Visible-IR absorption spectra were recorded using a Research India UV-Visible-IR spectrometer in the 300 nm to 1100 nm range as shown in figure 5.3. The glass samples from TPNTY1 and TPNTY2 showed four distinct absorption peaks. There are four peaks, three of which correspond to thulium ions and one to ytterbium ions. Spikes are observed at 472nm(Tm<sup>3+</sup>), 681nm(Tm<sup>3+</sup>), 792nm(Tm<sup>3+</sup>) and 980nm(Yb<sup>3+</sup>) and the corresponding transitions are <sup>3</sup>H<sub>6</sub> → <sup>1</sup>G<sub>4</sub> {472nm (Tm<sup>3+</sup>)}, <sup>3</sup>H<sub>6</sub> → <sup>3</sup>F<sub>2,3</sub> {681nm (Tm<sup>3+</sup>)}, <sup>3</sup>H<sub>6</sub> → <sup>3</sup>H<sub>4</sub>

### 4. Frequency Upconversion Dynamics

Different mechanisms are involved in the frequency upconversion (UC) phenomena in rare earth doped composites, which results in the emission of greater energy photons after the absorbing of low-energy laser pumping photons. Since the multiphonon de-excitation rates are lower in oxide matrices, the rare earth ions have demonstrated a significant capacity to achieve upconverted luminescence. Main advantages for this effect include optical amplifiers and upconverted visible lasers. The population of the excited state may be caused through excited state absorption (ESA) and energy transfer, respectively (ET). In the earlier, a

single optically active ion is incrementally elevated to higher levels by the resonating absorption of two or more laser photons, whereas in the latter, a multiple optically active ions that are next to one another interact are involved. Although often one of them predominates the upconversion process, both pathways are not mutually exclusive and can cooperate to efficiently participate to the population of the high excited emission level [11]. Additionally, there is a special upconversion procedure that, under certain circumstances, is essentially and unavoidably dependent on the fusion of the aforementioned two systems. One of the most effective and intricate upconversion processes, this one is known as a photon avalanche [12, 13]. The mechanisms underlying the upconverted luminescence in  $\text{Tm}^{3+}$ - $\text{Yb}^{3+}$  codoped glasses are examined in this section. The implications to the rare earth ion upconversion activities in the glasses' glassy phase are investigated.

## 5. Upconversion in $\text{Tm}^{3+}$ - $\text{Yb}^{3+}$ doped Lead-Tellurite Glasses

Thulium ions in the codoped materials have produced up-conversion (UC) fluorescence, which has been seen at room temperature

following 975 nm excitation. The  $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ,  $^1\text{G}_4 \rightarrow ^3\text{F}_4$ ,  $^3\text{F}_{2,3} \rightarrow ^3\text{H}_6$ , and  $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transitions of Thulium ions, respectively, are represented by bands in the UC emission spectra at 478, 651, 700, and 800 nm, respectively.

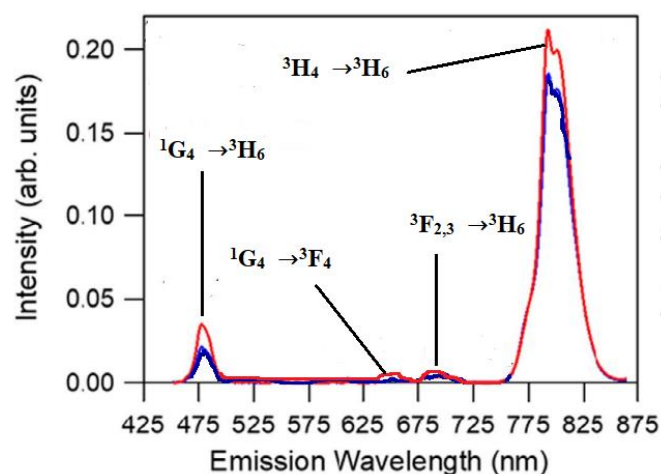


Figure. 4. PL spectra of TPNTY1 and TPNTY2 glasses

Figure 4 depicts a rise in UC intensity in TPNTY2 glass compared to TPNTY1 glass. This increase, though, is not as significant as anticipated. Therefore, the slight increase in UC emission intensity in TPNTY2 glass over untreated glass merits special attention. Additionally, raising the  $\text{Tm}^{3+}$  content by up to 1 mol% has no effect on the overall  $\text{Tm}^{3+}$  UC luminosity. Additionally, there is less intensity overall. The effect might be

attributed to energy transfer to quencher centres, energy reverse transfer from  $Tm^{3+}$  to  $Yb^{3+}$ , or energy mobility among  $Yb^{3+}$  ions as a result of the greater concentration [14]. Figure 5, shows the frequency up-conversion mechanisms involved in the population of the pertinent emission states of the  $Tm^{3+}$  ion. First, a 975 nm photon was used to excite the ground-state  $Yb^{3+}$  ion to the  $2F_{5/2}$  state, and the energy was then transmitted to the  $Tm^{3+}$  ions in the ground state using the mechanism  $2F_{5/2} \rightarrow 2F_{7/2}$  ( $Yb^{3+}$ ):  $3H_6 \rightarrow 3H_5$  ( $Tm^{3+}$ ) (ET1). The  $3F_4$  ( $Tm^{3+}$  state is mostly populated as the  $3H_5$  level decays non-radiatively. Then,  $Yb^{3+}$  and  $Tm^{3+}$  ions can participate in a second energy transfer process via the following mechanism:  $2F_{5/2} \rightarrow 2F_{7/2}$  ( $Yb^{3+}$ ):  $3F_4 \rightarrow 3F_{2,3}$  ( $Tm^{3+}$ ) (ET2).

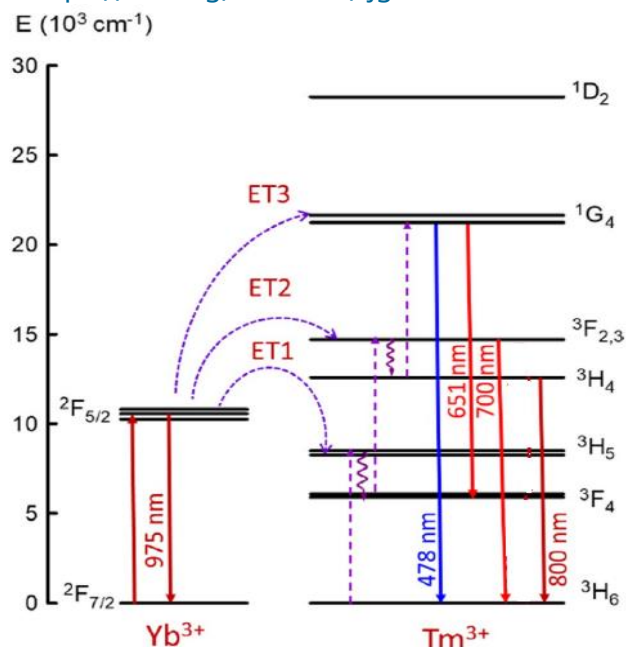


Figure. 5 upconversion Mechanism of TPNTY glass at 975 nm excitation

The  $3H_4$  state is populated by further multiphoton relaxation from level  $3F_{2,3}$ , and the  $1G_4$  state is populated by a third energy transfer upconversion process,  $2F_{5/2} \rightarrow 2F_{7/2}$  ( $Yb^{3+}$ ):  $3H_4 \rightarrow 1G_4$  ( $Tm^{3+}$ ) (ET3) [15].

## 6. CONCLUSIONS

By using the melting quenching technique, lead tellurite glasses that are combined with thulium and ytterbium have been produced successfully. Glass was present in the synthetic samples, as shown by XRD. Using DSC, thermal characteristics were investigated. After  $\text{Yb}^{3+}$  excitation at 975, the NIR and frequency upconversion emissions show that energy was transferred from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  ions. Only in  $\text{Tm}^{3+}$ - $\text{Yb}^{3+}$  codoped samples are visible frequency upconversion emissions seen, proving that  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions effectively transfer energy. By the specificity of the excitation, codoped materials having the application in the frequency upconversion emission from NIR to blue region.

## References

1. Dejneka, M. J. 1998, Mater. Res. Soc. Bull. 23, 57; and references therein.
2. Höland, W., and Beall, G. 2002, Glass-Ceramic Technology, The American Ceramic Society.
3. Clara Gonçalves, M., Santos, L. F., and Almeida, R. M. 2002, C. R. Chimie, 5, 845.
4. Adam, J.-L. 2001, J. Non-Cryst. Solids, 287, 401; Ibid. 2002, Chem. Rev., 102, 2461.
5. Beall, G.H., and Duke, D.A. 1983, "Glass-ceramic Technology" in "Glass Science and Technology", vol. 1, Academic Press, New York, p. 403.
6. Auzel, F., Pecile, D., and Morin, D. 1975, J. Electrochem. Soc., 122, 101.
7. Wang, Y., and Ohwaki, H. 1993, Appl. Phys. Lett., 63, 3268.
8. Tick, P. A., Borrelli, N. F., and Reaney, I. M. 2000, Opt. Mat., 15, 81.
9. Méndez-Ramos, J., Lavín, V., Martín, I. R., Rodríguez-Mendoza, U. R., Rodríguez, V. D., Lozano-Gorrín, A. D., and Núñez, P. 2001, J. Appl. Phys., 89, 5307; Ibid. 2003, J. Appl. Phys., 94, 2295.

10. Abril, M., Méndez-Ramos, M., Martín, I. R., Rodríguez-Mendoza, U. R., Lavín, V., Delgado-Torres, A., Rodríguez, V. D., Núñez, P., and LozanoGorrín, A. D. 2004, J. Appl. Phys., 95, 5271.
11. Fernández, J., Balda, R., Mendioroz, A., Sanz, M., Adam, J.-L. 2001, J. NonCryst. Solids, 287, 437.
12. Scheps, R. 1996, Prog. Quant. Electr., 20, 271.
13. Joubert, M.-F. 1999, Opt. Mat., 11, 181; and references therein.
14. QuintanillaM, NúñezNO, CantelarE, Ocaña M, Cussó F. J Appl Phys. 2013;113(17):174308.
15. Albalawi A, Varas S, Chiasera A, Gebavi H, Albalawi W, Blanc W,. Opt Mater Express. 2017;7(10):3760

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