



ISSN 2231-346X

(Print)

JUSPS-A Vol. 34(1), 6-12 (2022). Periodicity-Monthly

Section A

(Online)



ISSN 2319-8044



Estd. 1989

JOURNAL OF ULTRA SCIENTIST OF PHYSICAL SCIENCES
An International Open Free Access Peer Reviewed Research Journal of Mathematics
website:- www.ultrascientist.org

Upconversion Luminescence Enhancement in Lanthanide Ions Doped Bismuth Tellurite Glasses

YOGESH K. JAYASWAL^a, GHIZAL F. ANSARI^{a*}, S. K. PATIDAR^a, SUNIL JAT^b^aPhysics department, Madhyanchal professional university Bhopal M.P. (India)^bPhysics department, Govt. College Umarban, Dist. Dhar M.P. (India)Corresponding Author E-mail : ansarigf@rediffmail.com<http://dx.doi.org/10.22147/jusps-A/340102>

Acceptance Date 29th December, 2021,

Online Publication Date 11th January, 2022

Abstract

Lanthanide ions doped glasses are studied by researchers for upconversion luminescence. Rare earth doped bismuth tellurite glasses codoped with and without silver nanoparticle were synthesized by melt and quench procedure for the study of enhanced upconversion luminescence. Physical parameters as molar mass, molar volume, and density were evaluated. Amorphous nature of samples was verified by x-ray diffraction. DSC is carried for information of thermal properties. UV-Visible absorption and fluorescence spectra is obtained to get detail information of upconversion luminescence. Upconversion mechanism of rare earth erbium and ytterbium ions discussed. Three prominent upconversion luminescence is observed two in green region and one is in red.

Key words : rare earth ions; upconversion; luminescence.

1. Introduction

The upconversion phenomenon has been observed in transition metals, actinides, but mainly in the rare earth (RE) elements, which contain the lanthanide (Ln) series, yttrium, scandium¹, ytterbium and erbium² and ytterbium and thulium ions³. Ln₃₊ ions have special 4fⁿ 5d⁰⁻¹ inner shell configurations that are well-shielded by outer shells and have abundant and unique energy level structures. These Ln₃₊ ions can exhibit sharp luminescence emissions via intra-4f or 4f-5d transitions. Their remarkable luminescence properties, such as narrow bandwidth, long-time emission, and anti-Stokes emission, have been widely applied in lasers, solar

cells, analytical sensors, optical imaging, photodynamic therapy, and so on. At present, the low luminescence efficiency is one of the main limiting factors. Therefore, to obtain the highest upconversion luminescence efficiency, it is critical to choose an appropriate host material with lower phonon energy (high phonon frequencies of the host lattice lead to nonradiative relaxation). To date, host materials, including fluoride, chloride and bromide, have been shown to enhance upconversion luminescence intensity. Most of chlorides and bromides are sensitive to moisture, and thus are not suitable for labeling biomolecules (used mostly in aqueous solutions)⁴. RE fluorides, mainly REF₃ and AREF₄ (A = alkali), have been considered as an excellent host material due to their high refractive index and high transparency arising from low-energy phonons. These two advantages further lead to low probability of nonradiative decay and increased luminescence quantum yield. Most fluorescent materials, including dye molecules, quantum dots, and dye-doped silica/gold nanomaterials, emit light by the downconversion process (emitting lower-energy photons under higher-energy irradiation). Although the uses of a conventional organic dye molecule or quantum dot (QD) based biomarker have achieved significant progress in real-time detection and bioimaging, they still have drawbacks. These fluorescent materials are generally excited by ultraviolet (UV) or visible light, which may induce autofluorescence and photodamage to biological samples, resulting in low signal-to-noise ratio and limited sensitivity. These limitations prompted the development of a new type of high-quality and well-shaped nanomaterials known as upconversion nanomaterials (UCNs). These UCNs usually consist of an inorganic host that is doped with Ln₃₊ ions. They show good biocompatibility and generally low cytotoxicity, and are in fact non-cytotoxic to a broad range of cell lines^{5,6}. Furthermore, surface modification by ligand engineering⁷⁻⁹, ligand attraction¹⁰, surface polymerization^{5,11-15}, self-assembly¹⁶⁻¹⁸ or layer-by-layer assembly technology¹⁷, broadens their application fields. Surface modification by a silica shell is by far the most popular, common, and practical approach^{5,13,20-22}. Proteins, DNA, biological macromolecules or other desirable targets can be easily linked to UCNs. In particular, the UCNs' unique property of emitting visible light under NIR irradiation makes them a suitable candidate both for in vivo and in vitro bioimaging²³⁻²⁵. Theoretically, most lanthanide ions can undergo the NIR-to-visible upconversion process; however, relatively efficient upconversion is only possible with a few trivalent lanthanide ions (e.g., Er₃₊ and Tm₃₊) under low pump densities (980 nm excitation). Up to now, the most often-used upconversion nanoparticles are Yb₃₊-Er₃₊ or Yb₃₊-Tm₃₊ co-doped NaYF₄ nanomaterials. In this review, we will briefly discuss the mechanisms of upconversion phenomenon, but mainly focus on the recent progress in UCNs' chemical syntheses and their applications in different areas, especially in the biological field.

The properties of the host lattice and its interaction with the dopant ions have a strong influence on the upconversion process, because the lattice of host materials determines the distance between the dopant ions, their relative spatial position, coordination numbers, and the type of anions surrounding the dopant. Therefore, selection of appropriate host materials is also essential in the design of UCNPs with favorable optical properties such as high efficiency and tunable emission color. Ideal host materials should have low lattice phonon energies, which have a great influence on the upconversion efficiency. In order to minimize non-radiative loss and maximize the radiative emission.

This article deals with upconversion properties of rare-earth doped bismuth tellurite glasses with and without co-doped silver nanoparticles (AgNPs).

2. Synthesis :

Without and with silver nano particle rare earth doped bismuth tellurite glasses with batch compositions 78%TeO₂-10%Bi₂O₃-10%Na₂CO₃-1%Er₂O₃-1%Yr₂O₃ (BTEY) and 77.9%TeO₂-10%Bi₂O₃-10%Na₂CO₃-1%Er₂O₃-1%Yb₂O₃-0.1%AgNO₃ (BTEYA) have been synthesized by melting and quenching technique. All the required compounds were taken in powder form mix well mechanically. Alumina crucible was used for melting,

first of 18-20 gram was put in furnace at 400 °C for 30 minutes then increases temperature upto 900 °C for one hour. In between molten liquid is mechanically stirred. Then melt poured in pellet shaped die. Different annealing treatment had been done with both the samples. BTEY is kept in oven at 350 °C for one hour whereas BTEYA was kept two and half an hour. Prepared samples are transparent and pinkish in color.

3. Physical Properties :

Physical parameters as heaviness, mol. Mass and Volume were evaluated (Table 1)

Table 1. The physical properties of synthesized bismuth tellurite glasses doped with erbium- ytterbium (BTEY) and erbium- ytterbium- silver (BTEYA)

Name of the Sample	BTEY	BTEYA
Molar Mass (M) gm/mol	188.96	184.63
Density ρ (g/cm ³)	5.12	5.11
V_m (cm ³ /mol)	36.90	36.13

4. Characterization

4.1 XRD

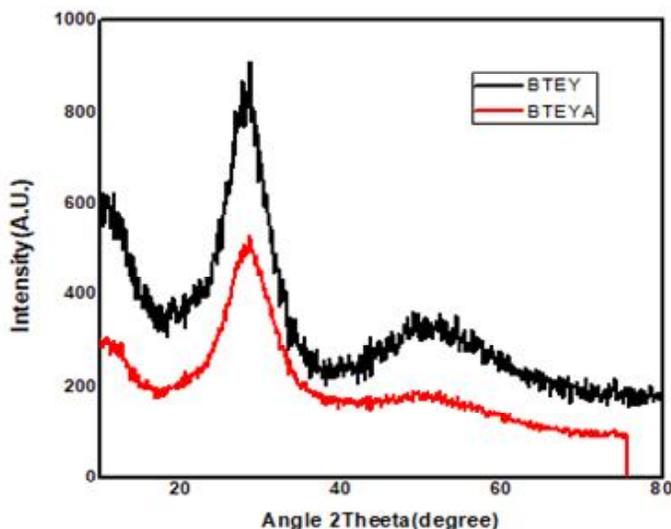


Fig.1. XRD of BTEY and BTEYA samples

X-ray diffraction of samples were carried by Rigaku Miniflex II in 20° to 90° two degree angle range. The pattern obtained does not have spikes, justified the amorphous nature only a wide hill like structure is seen near 30° region.

4.2. Differential Scanning Calorimetry :

Differential scanning calorimetry of base sample BTEYA is carried out by Perkin Elmer (Pyris 6 DSC) and TA Instruments in the United States instruments (figure 2). DSC of BTEYA is carried between 40 °C to 460 °C. Glass transition temperature is observed at 322 °C.

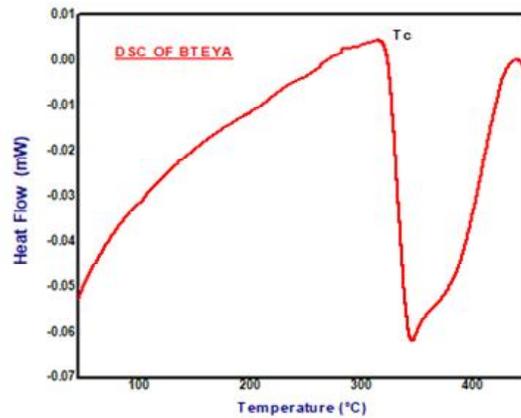


Figure 2. DSC of BTEYA glass sample.

5. Optical Properties :

The UV-VISIBLE-IR absorption spectra were carried out by using Research India Spectrophotometer in 300– 1000 nm spectral range . The fluorescence spectra were carried out by Horriba, Jobin Vyon (Fluorofog-3). All the studies carried out at room temperature.

The UV-VISIBLE-IR absorption of 78%TeO₂-10%Bi₂O₃-10% Na₂CO₃-1%Er₂O₃-1%Y₂O₃ (BTEY) and 77.9%TeO₂-10%Bi₂O₃- 10%Na₂O-1%Er₂O-1%Y₂O₃-0.1%AgNO₃ (BTEYA) sample were shown in Fig. 3.

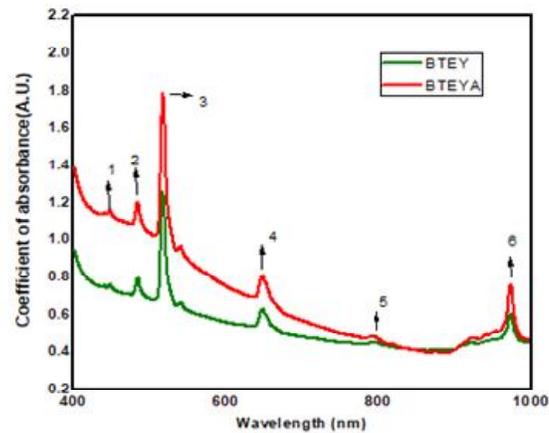


Fig. 3. UV-VISIBLE-absorption spectra of BTEY and BTEYA samples

Six clear absorption bands were observed in the spectra . both the samples having similar bands indicated by 1,2,3,4,5 and 6. The transition band are identified as-

1. At 485 nm $^4I_{15/2}$ to $^4F_{7/2}$ of Er³⁺ ions
2. At 520 nm $^4I_{15/2}$ to $^2H_{11/2}$ of Er³⁺ ions
3. At 540 nm $^4I_{15/2}$ to $^4S_{3/2}$ of Er³⁺ ions

4. At 652 nm $^4I_{15/2}$ to $^4F_{9/2}$ of Er^{3+} ions
5. At 795nm $^4I_{15/2}$ to $^4I_{9/2}$ of Er^{3+} ions
6. At 980nm $^2F_{7/2}$ to $^2F_{5/2}$ of Yb^{3+} ions

All the above transitions are very clear and prominent.

Upconversion spectra of BTEY and BTEYA samples were carried out at 980 nm excitation wavelength at room temperature shown in the figure 4. Prominent three colors were observed two in green regions and one in red region. In the observed upconversions of erbium and ytterbium are responsible. With Ytterbium ions concentration, the lifetime of Erbium ions excited state was increased significantly benefited from the energy sensitization effect of Ytterbium ions, indicating the important role of the ET process on the Upconversion amplification. Further it is clearly observed that AgNPS enhance the intensity of upconversion.

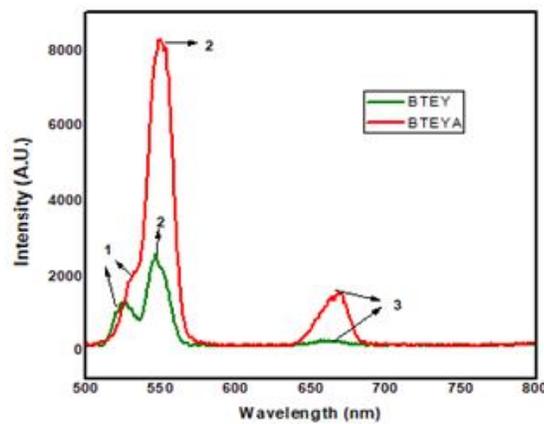


Figure 4. Upconversion of BTEY and BTEYA samples.

With the help of results, it is concluded that Ytterbium ions are acceptable sensitizer to increase upconversion emission in Erbium ions doped bismuth tellurite glasses. Ytterbium ions can enhance the absorption of input energy and hand over energy to Erbium ions. Hence Ytterbium ions increase the number of Erbium ions excited to the $^4I_{11/2}$ level. As a result, an increased upconversion emission was observed in Erbium/Ytterbium doped bismuth-tellurite glasses. The mechanism of Erbium-Ytterbium ions doped BT glasses shown in figure 5.

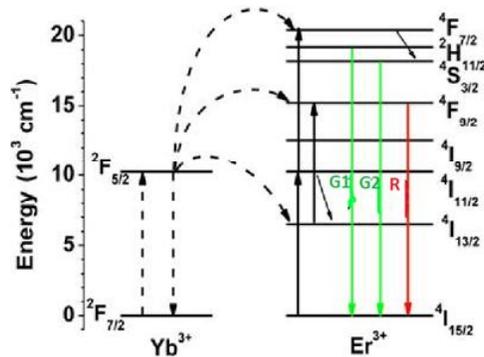


Fig.5 upconversion mechanism in Er-Yb doped BT glass

6. Upconversion Mechanism :

At 980 nm excitation radiation Erbium and Ytterbium ions get excited, the process were as

(i) Yb^{3+} get excited from $^2\text{F}_{7/2}$ to $^2\text{F}_{5/2}$

(ii) Er^{3+} get excited from $^2\text{I}_{15/2}$ to $^2\text{I}_{11/2}$

Further excited Yb^{3+} ion transfer its energy from $^2\text{F}_{5/2}$ to Er^{3+} excited ions in three levels as

(i) $^2\text{F}_{5/2}(\text{Yb}^{3+})$ to $^4\text{I}_{13/2}(\text{Er}^{3+})$

(ii) $^2\text{F}_{5/2}(\text{Yb}^{3+})$ to $^4\text{F}_{9/2}(\text{Er}^{3+})$

(iii) $^2\text{F}_{5/2}(\text{Yb}^{3+})$ to $^4\text{F}_{7/2}(\text{Er}^{3+})$

Finally, Erbium ions get come down in ground state and releases energy in following steps

(i) $^2\text{H}_{7/2}$ to $^4\text{I}_{15/2}$ green emission

(ii) $^4\text{S}_{3/2}$ to $^4\text{I}_{15/2}$ green emission

(iii) $^2\text{F}_{9/2}$ to $^4\text{I}_{15/2}$ red emission

With use of silver nano particles upconversion emission in BTEYA glasses were observed enhanced.

7. Conclusion

The Erbium Ytterbium ions doped bismuth tellurite glasses with and without silver nanoparticle synthesized via melting and quenching procedure. The hydrothermal method, and the upconversion emission of Erbium Ytterbium ions doped bismuth tellurite observed. Silver nano-particles enhance the upconversion. The upconversion emission of BTEYA was constructively increases due to coupling surface plasmons of silver particles with optical energy band gap. Clear and intense green and red upconversion were obtained. Synthesized glasses claimed their candidature as light emitting, and display devices.

Tellurite base glasses are excellent host for rare earth ions. Frequency upconversion luminescence phenomenon is used to convert IR electromagnetic radiation in visible region. In the present work green and red color is achieved by 980nm excitation. By doping of combination of three suitable rare earth ions, white light can be achieved. Future scope of research and applications of the upconversion luminescence nanoparticles is in bioimaging and making contrast against biomaterials.

8. Acknowledgment

Authors are acknowledging the M/s Research India and BIT Mesra for their support in characterization.

References

1. F. Auzel, *Chem. Rev.*, *104*, 139-174 (2004).
2. G. F. Ansari, J. Parashar, S. K. Mahajan. *Journal of Physics: Conference Series* 1913 012034 (2021).
3. S. Patidar, G. F. Ansari, S. K. Mahajan. *AIP Conference Proceedings* 2220, 080066 (2020)
4. P. Egger, P. Rogin, T. Riedener, H. U. Gudel, M. Wickleder, J. Hulliger. *Adv. Mater.*, *8*, 668-672 (1996).
5. J. Yang, Y. Deng, Q. Wu, J. Zhou, H. Bao, Q. Li, F. Zhang, F. Li, B. Tu, D. Zhao. *Langmuir*, *26*, 8850-8856 (2010).
6. J. Zhou, Y. Sun, X. Du, L. Xiong, H. Hu, F. Li. *Biomaterials*, *31*, 3287-3295 (2010).

7. T. Cao, Y. Yang, Y. Gao, J. Zhou, Z. Li, F. Li. *Biomaterials*, *32*, 2959-2968 (2011).
8. H. Hu, M. Yu, F. Li, Z. Chen, X. Gao, L. Xiong, C. Huang. *Chem. Mater.*, *20*, 7003-7009 (2008).
9. R. Naccache, F. Vetrone, V. Mahalingam, L.A. Cuccia, J.A. Capobianco. *Chem. Mater.*, *21*, 717-723 (2009).
10. G. Yi, G.M. Chow. *Chem. Mater.*, *19*, 341-343 (2007).
11. H. Hu, L. Xiong, J. Zhou, F. Li, T. Cao, C. Huang. *Chem. Eur. J.*, *15*, 3577-3584 (2009).
12. S. Jiang, Y. Zhang, K.M. Lim, E.K.W. Sim, Ye, L. *Nanotechnology.*, *20(15)*, 155101 (2009).
13. S. Jiang, Y. Zhang. *Langmuir*, *26*, 6689-6694 (2010).
14. F. Zhang, G.B. Braun, Y. Shi, Y. Zhang, X. Sun, N.O. Reich, D. Zhao, G. Stucky. *J. Am. Chem. Soc.*, *132*, 2850-2851 (2010).
15. Z. Li, Y. Zhang. *Angew. Chem. Int. Ed.*, *45*, 7732-7735 (2006).
16. Q. Liu, C. Li, T. Yang, T. Yi, F. Li. *Chem. Commun.*, *46*, 5551-5553 (2010).
17. Q. Liu, M. Chen, Y. Sun, G. Chen, T. Yang, Y. Gao, X. Zhang, F. Li. *Biomaterials*, *32*, 8243-8253 (2011).
18. Q. Liu, Y. Sun, C. Li, J. Zhou, C. Li, T. Yang, X. Zhang, T. Yi, D. Wu, F. Li. *ACS Nano*, *5*, 3146-3157 (2011).
19. X. Wang, J. Zhuang, Q. Peng, Y. Li, *Nature*, *437*, 121-124 (2005).
20. R.A. Jalil, Y. Zhang. *Biomaterials*, *29*, 4122-4128 (2008).
21. H. Guo, H. Qian, N. M. Idris, Y. Zhang. *Nanomedicine*, *6*, 484-495 (2010).
22. Z. Li, L. Wang, Z. Wang, X. Liu, Y. Xiong. *J. Phys. Chem. C*, *115*, 3291-3296 (2011).
23. Q. Liu, Y. Sun, T. Yang, W. Feng, C. Li, F. Li. *J. Am. Chem. Soc.*, *133*, 17122-17125 (2011).
24. S.F. Lim, R. Riehn, R.W.S. Ryu, N. Khanarian, C. Tung, D. Tank, R.H. Austin. *Nano Lett.*, *6*, 169-174 (2006).
25. L. Xiong, Z. Chen, Q. Tian, T. Cao, C. Xu, F. Li. *Anal. Chem.*, *81*, 8687-8694 (2009).