

The Upconversion of co-doped Nd³⁺/Er³⁺ Tellurite Glass

Azman, K., Sahar, M.R., Rohani, M.S.

Abstract—Series of tellurite glass of the system 78TeO₂-10PbO-10Li₂O-(2-x)Nd₂O₃-xEr₂O₃, where x = 0.5, 1.0, 1.5 and 2.0 was successfully been made. A study of upconversion luminescence of the Nd³⁺/Er³⁺ co-doped tellurite glass has been carried out. From Judd-Ofelt analysis, the experimental lifetime, τ_{exp} of the glass serie are found higher in the visible region as they varies from 65.17ms to 114.63ms, whereas in the near infrared region (NIR) the lifetime are varies from 2.133ms to 2.270ms. Meanwhile, the emission cross section, σ results are found varies from 0.004 x 10²⁰ cm² to 1.007 x 10²⁰ cm² with respect to composition. The emission spectra of the glass are found been contributed from Nd³⁺ and Er³⁺ ions by which nine significant transition peaks are observed. The upconversion mechanism of the co-doped tellurite glass has been shown in the schematic energy diagrams. In this works, it is found that the excited state-absorption (ESA) is still dominant in the upconversion excitation process as the upconversion excitation mechanism of the Nd³⁺ excited-state levels is accomplished through a stepwise multiphonon process. An efficient excitation energy transfer (ET) has been observed between Nd³⁺ as a donor and Er³⁺ as the acceptor. As a result, respective emission spectra had been observed.

Keywords—Tellurite glass, co-dopant, upconversion luminescence spectra.

I. INTRODUCTION

INCORPORATION of rare earth into various glass oxides has been a key to the development of many optical devices such as infrared lasers, IR-visible upconverters, fibre and waveguide amplifiers for optical transmission network [1]. Therefore, the rare-earth doped tellurite glasses have been the subject of several spectroscopic investigation due to their potential applications in various area like optical sensing, telecommunications, biomedical, biochemical studies etc [2,3]. A study of upconversion in single as well as multi-ions doped glasses has been found increased vigorously in recent years. Tellurium has been identified to be appropriate glass host for the laser application since the strong rare-earth ions-host interaction results in efficient upconversion emissions [4]. In addition, tellurite glass which, possess lower phonon energies has been proved to be the most stable hosts for

Azman K is with the Universiti Teknologi MARA Malaysia, Shah Alam, 40450 Shah Alam, Selangor, Malaysia. (phone: +6094602699; e-mail: mann152615@yahoo.co.uk).

Sahar, M., R. is with Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia in Department of Physics, Fac.of Science, UTM.(e-mail: mrahim@dfiz2.utm.edu.my).

Rohani, M., S. is with Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia in Department of Physics, Fac.of Science, UTM.(e-mail: mdsupar@dfiz2.utm.edu.my).

obtaining efficient luminescence in rare earth compare to other oxide glasses [5]. The study of upconversion process is important in order to understand the mechanisms of interaction between rare earth with the glass hosts which leads to the discovery of the new lasers based on energy transfer in the neither single ions or multi-ions material. In this work, a systematic study on the optical transition and the upconversion of Nd-doped tellurite glass will be reported and discussed with respect to the composition.

II. EXPERIMENTAL PROCEDURE

The tellurite glass of (78-x)TeO₂-10PbO-10Li₂O-2Nd₂O₃-xEr₂O₃ system is prepared by melt-quenching technique. Batches of 20g are prepared from certified reagent grades of TeO₂ (99.95% purity), Li₂CO₃ (97%), PbO (98% purity), Nd₂O₃ (99.995%) and Er₂O₃ (99.995%). The chemicals are firstly mixed thoroughly in a platinum crucible before being heated at 1000 °C for half an hour. After the batch is completely melted, the melts was cast onto the preheated stainless steel plate followed by annealing at 300 °C for 5 hours before allowed to cool down to room temperature. The glass is then cut and polished at the thickness of about 2.0mm. Electronic absorption spectra are determined at room temperature by using a Perkin Elmer UV Spectroscopy in the range of 400 – 900 nm. The luminescence spectra are also obtained at room temperature by using *Nanosecond Luminescence Spectroscopy System, Model NT340/1 Ekspla* excited at 585nm using the tunable Nd: YAG laser system NT342. The signal is monitored by monochromator SP2300 equipped with photomultiplier in the photon counting mode and recorded under data acquisition unit (DAQ).

III. RESULTS AND DISCUSSION

A. Upconversion Luminescence

The upconversion fluorescence spectrum of Nd³⁺/Er³⁺ co-doped tellurite glass at room temperature is presented in Figure 1. From Figure 1, it can be seen that there are six distinctive upconverted bands contributed from Nd³⁺ ions are observed to be centered at 485 nm, 605 nm, 665 nm, 880 nm, 1062 nm and 1340 nm attributed from ⁴G_{11/2} → ⁴I_{11/2}, ⁴G_{11/2} → ⁴I_{15/2}, ⁴G_{7/2} → ⁴I_{13/2}, ⁴F_{3/2} → ⁴I_{13/2}, ⁴F_{3/2} → ⁴I_{11/2} and ⁴F_{3/2} → ⁴I_{9/2} transitions whereas, three upconverted bands contributed from Er³⁺ ions to be centered at 493 nm, 524 nm and 550 nm are found originating from ⁴F_{7/2} → ⁴I_{15/2}, ²H_{11/2} → ⁴I_{15/2} and ⁴S_{3/2} → ⁴I_{15/2} transitions under the excitation at 585 nm. Similar upconversion spectra are found for all samples with different Er₂O₃ content. From these emission bands, a possible of blue, green and red emission as well as the near infrared emission

spectra could be expected. It should be noted out that the blue emission band centered at 493 nm is correspond to ${}^4F_{7/2} \rightarrow {}^4I_{15/2}$ transition. The green emission bands observed at 524 nm and 550 nm peaks are correspond to ${}^2H_{11/2} \rightarrow {}^4I_{15/2}$ and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions respectively. The red emission bands observed at 605 nm and 665 nm peaks are attributed from the ${}^4G_{11/2} \rightarrow {}^4I_{15/2}$ and the ${}^4G_{7/2} \rightarrow {}^4I_{13/2}$ transitions respectively. Meanwhile, the near infrared upconversion spectra are observed to be centered at 880 nm, 1062 nm and 1340 nm respectively.

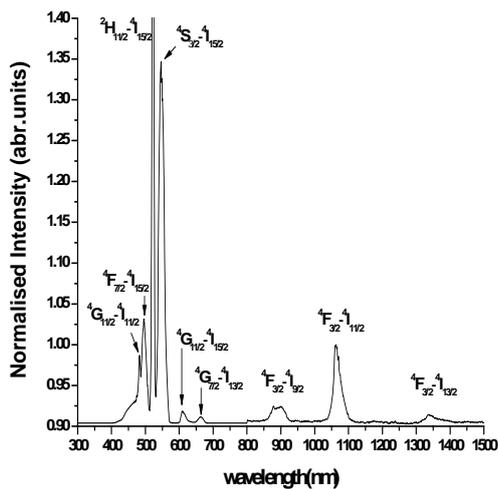


Fig. 1 A typical upconversion luminescence spectrum of the (78-x)TeO₂-10PbO-10Li₂O-2Nd₂O₃-xEr₂O₃ glass system.

Meanwhile, the possible upconversion mechanism for the glasses has been shown in Figure 2. From the schematic energy level it could be seen that as the Nd³⁺ ions are pumped with 585 nm excitation wavelength through the ground state absorption (GSA) they excites to the ${}^2G_{7/2}$ level. The Nd³⁺ ions are found to relax to metastable ${}^2H_{11/2}$ level before re-excited to the ${}^4G_{11/2}$ level through the excited state absorption (ESA) process. The Nd³⁺ ions are found to undergone stepwise upconversion process. This has been confirmed by Kumar et.al (2007) in their works revealed that the resulting fluorescence is due to step wise absorption of two photons [6]. As they populated the ${}^4G_{11/2}$ level, some of the Nd³⁺ ions relaxed radiatively to ${}^4I_{11/2}$ and ${}^4I_{15/2}$ level thus emitting the emission spectra centered at 485 nm and 605 nm. Meanwhile, some of the Nd³⁺ ions are found relax non-radiatively to lower level ${}^4G_{7/2}$ and ${}^4F_{3/2}$. The Nd³⁺ ions that populated the ${}^4G_{7/2}$ are then decay to ${}^4I_{13/2}$ by emitting the red emission spectra centered at 665 nm. Whereby, the Nd³⁺ ions at ${}^4F_{3/2}$ level emitting the near infrared emission as they decay to ${}^4I_{9/2}$ (880 nm), ${}^4I_{11/2}$ (1062 nm) and ${}^4I_{13/2}$ (1340 nm) level respectively.

As the Nd³⁺ ions relaxed from ${}^4G_{11/2}$ level their respective energy is transferred to Er³⁺ ions that populated the ${}^4F_{7/2}$ level. At this level, some Er³⁺ ions are relax directly to ${}^4I_{15/2}$ level radiatively by emitting near infrared emission spectra centered at 732 nm. However, some Er³⁺ ions are found to relax non-

radiatively to ${}^2H_{11/2}$ and ${}^4S_{3/2}$ level. From the ${}^2H_{11/2}$ level the Er³⁺ ions relaxed to ${}^4I_{15/2}$ thus emitting weak green spectra centered at 524 nm. Meanwhile, for the Er³⁺ ions that populated ${}^4S_{3/2}$ level decay directly to the ground level ${}^4I_{15/2}$ by generates green spectra centered at 547 nm.

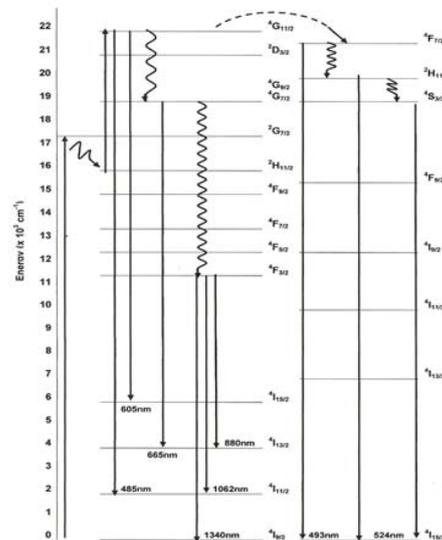


Fig. 2 A schematic energy diagram of the (78-x)TeO₂-10PbO-10Li₂O-2Nd₂O₃-xEr₂O₃ glass system

B. Judd-Ofelts Analysis

Table 1 shows a results of radiative lifetime, τ_R , stimulated emission cross-section, σ_{eff} and non-radiative relaxation, W_{nr} . From Table 1, it could be seen that the radiative lifetime of the glass is ranging from 0.812ms to 1.248ms with respect to mol% of Er₂O₃ content. According to Judd-Ofelt theory the fluorescent level relaxation generally involves the transitions from upper-levels to all probable low-lying levels therefore, the radiative lifetime of the transitions could be estimated from the equation:

$$\tau_R(\Psi J) = [A_T(\Psi J)^{-1}] \quad (1)$$

whereby, A_T is total radiative probability. As depicted from Table 1, it can be observed that results of stimulated emission cross-section are ranging from $0.812 \times 10^{20} \text{ cm}^2$ to $1.248 \times 10^{20} \text{ cm}^2$ depending on the mol% of Er₂O₃ content. Similar trend has also been observed and discussed by other researcher [7]. The emission cross-section which is the laser gain per unit population inversion is the relevant spectroscopy parameter for laser application [8]. The stimulated emission cross section, σ_{em} has been measured for different emission bands using the following expression as proposed by Fuchtbauer-Ladenburg [9] :

$$\sigma_{em} = \frac{\lambda^4 A}{8\pi n^2 c \Delta\lambda} \quad (2)$$

whereby, A is the radiative transition probability and $\Delta\lambda$ is the fluorescence band width. Meanwhile, as been observed in Table 1, it could be seen that the non-radiative relaxation, W_{nr} is found varies from 0.144 ms^{-1} to 0.180 ms^{-1} with respect to composition. From these results, it is obvious that the results for co-doped glasses (S42-S45) are slightly higher compare to the S41 glass which only has Nd^{3+} as single dopant. This is due to the fact that an existence of Nd^{3+} as a single dopant has less ion-ion interaction and ion-lattice coupling compare to co-doped glasses which has $\text{Nd}^{3+}/\text{Er}^{3+}$ ions. Romanowski (1990) in his works notice that the non-radiative decay rate is dependant upon the strength of ion-lattice coupling, phonon spectrum, sample temperature as well as the energy separation to the next lower lying level [10]. Recently, works done by Meisong et.al (2009) confirmed that the non-radiative rate could also be affected from the multiphonon relaxation rate, self-quenching rate and relaxation rate induced by certain transition metal ions and other rare earth ions [11]. The fluorescence decay rate is governed by the probability of the radiative and non-radiative relaxation described by following expression:

$$W_T = W_R + W_{NR} \quad (3)$$

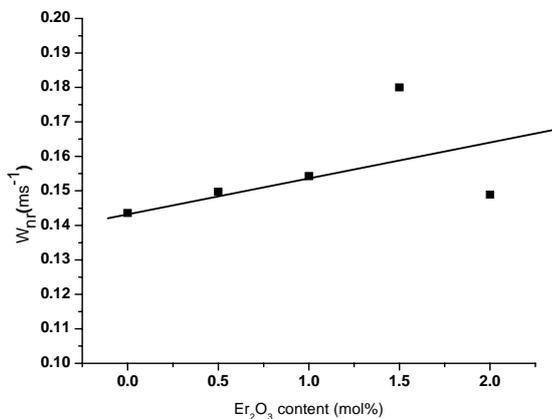


Fig. 3 The non radiative decay rate, W_{nr} of the S4 glass with respect to Er_2O_3 content. The line is drawn for the guide of the eye.

IV. CONCLUSION

$\text{Nd}^{3+}/\text{Er}^{3+}$ co-doped tellurite glasses of the system $\text{TeO}_2\text{-PbO-Li}_2\text{O}$ has successfully been synthesized by using melt-quenched techniques. From the emission spectra, it is found that there are six distinctive upconverted bands contributed from Nd^{3+} ions are observed to be centered at 485 nm, 605 nm, 665 nm, 880 nm, 1062 nm and 1340 nm attributed from ${}^4\text{G}_{11/2} \rightarrow {}^4\text{I}_{11/2}$, ${}^4\text{G}_{11/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^4\text{G}_{7/2} \rightarrow {}^4\text{I}_{13/2}$, ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{13/2}$, ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ and ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$ transitions whereas, three upconverted

TABLE I
RESULTS OF RADIATIVE LIFETIME, STIMULATED EMISSION CROSS-SECTION AND NONRADIATIVE RELAXATION

Sample No.	Er Content (mol%)	τ_R (ms)	$\sigma_{eff.}$ ($\times 10^{20} \text{ cm}^{-2}$)	W_{nr} (ms^{-1})
S41	0	2.234	0.812	0.144
S42	0.5	2.279	0.917	0.149
S43	1.0	2.341	0.893	0.154
S44	1.5	1.981	1.248	0.180
S45	2.0	2.196	0.942	0.149

bands contributed from Er^{3+} ions to be centered at 493 nm, 524 nm and 550 nm are found originating from ${}^4\text{F}_{7/2} \rightarrow {}^4\text{I}_{15/2}$, ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transitions under the excitation at 585 nm. The possible upconversion luminescence mechanism has shown that through the ground state absorption (GSA) a resonant pump photon promotes the Nd^{3+} ions from the ${}^4\text{I}_{9/2}$ ground state to the ${}^2\text{G}_{7/2}$ excited state level. The Nd^{3+} ions which are unstable relax nonradiatively to the ${}^2\text{H}_{11/2}$ level. Then a second pump photon resonantly re-excites the Nd^{3+} ions to the ${}^4\text{G}_{11/2}$ excited level through the excited state absorption (ESA). The ions that populated the ${}^4\text{G}_{11/2}$ are unstable since they are found to undergone relaxation process by which correspond to the emission peaks observed at 450nm, 485 nm, 560nm, 605nm. Some of the ions may also non-radiatively transit from ${}^4\text{G}_{11/2}$ to ${}^4\text{F}_{3/2}$ then emits a photon at 880nm, 1062nm and 1340nm. Meanwhile, the Judd-Ofelts analysis has been employed to obtain the radiative lifetime, τ_R , stimulated emission cross-section, σ and non-radiative relaxation, W_{nr} . It is found that most values are dependence of Nd^{3+}

ACKNOWLEDGMENT

The author would like to thanks Universiti Teknologi MARA Malaysia for the financial assistance and MOHE for the research grant.

REFERENCES

- [1] Upendra Kumar K., Prathyusha V.A., Babu P., Jayasankar C.K., Joshi A.S., Speghini A., Bettinelli M., (2006), J. Spectrochimica Acta Part A.
- [2] Kumar, K., Rai, S.B., Anita Rai, (2008), J. Spectrochimica Acta Part A 71:508-512.
- [3] Wade, S.A., Collins, S.F., Baxter, G.W., (2003), J. Appl. Phys. 94: 4743
- [4] Koepke, Cz., Wisniewski, K., Sikorski, L., Piatkowski, D., Kowalska, K., Naftaly, M., (2006) J. Optical Materials, 28: 129-136
- [5] Nazabal V., Todoroki S., Nukui A., Matsumoto T., Suehara S., Hondo T., Araki T., Inuo S., Rivero C., Cardinal T., (2003), J. Non-Cryst. Solids 325, 85-102.
- [6] Kumar K., Rai, S.B., Anita Rai, (2008), J. Spectrochimica Acta Part A, 71, 508-512.
- [7] Ajith Kumar, G., Biju, P.R., Venugopal, C., Unnikrishnan, N.V., (1997), J. Non-Cryst. Solids 221:47-58
- [8] Ramos, F., Jaque, D., Romero, J., Garcia, S.J., Caldino, U.G., (1999), J. Phys. Condens. Matter, (11), 3201-3207.

- [9] Sudesh, V., Goldys, E.M., (2000), J.Opt.Soc.America B, 17:1068.
- [10] Ryba-Romanowski, W., (1990), J.Luminescence 46:163-172.
- [11] Meisong, L., Tatsuya, Y., Lihui, H., Yusuke, A., Takenobu, S., Yasutake, O., (2009), J.Non-Cryst.Solids, Vol.355, No.2:96-100.

Azman K. was born in Johor State, Malaysia on September 18, 1971. He obtained Ph.D on the lasing materials from Universiti Teknologi Malaysia (UTM), Johor State, Malaysia in 2010. He obtained his MSc. in Physics Ultrasonic from Universiti Putra Malaysia (UPM) in 2000. He completed his first degree in Physics in 1995

Currently, he is a SENIOR LECTURE in Universiti Teknologi MARA Malaysia (UiTM) for 10 years. Previously, he worked as a lecturer in private collage. Collectively, he had published many research papers locally and internationally. His recent research is focus on the singly and doubly doped rare earth on the tellurite glass. Has completed several research which are related to the optical properties of glassy material.

Dr Azman K. enrolled as life member of Malaysia Association of Solid State, Malaysia. He also enrolled as a member of Glass Society UK in 2008.