

# The Upconversion of co-doped Nd<sup>3+</sup>/Er<sup>3+</sup> Tellurite Glass

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

**Abstract**—Series of tellurite glass of the system 78TeO<sub>2</sub>-10PbO-10Li<sub>2</sub>O-(2-x)Nd<sub>2</sub>O<sub>3</sub>-xEr<sub>2</sub>O<sub>3</sub>, where x = 0.5, 1.0, 1.5 and 2.0 was successfully been made. A study of upconversion luminescence of the Nd<sup>3+</sup>/Er<sup>3+</sup> co-doped tellurite glass has been carried out. From Judd-Ofelt analysis, the experimental lifetime,  $\tau_{\text{exp}}$  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,  $\sigma$  results are found varies from 0.004 x 10<sup>20</sup> cm<sup>2</sup> to 1.007 x 10<sup>20</sup> cm<sup>2</sup> with respect to composition. The emission spectra of the glass are found been contributed from Nd<sup>3+</sup> and Er<sup>3+</sup> 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 Nd<sup>3+</sup> excited-state levels is accomplished through a stepwise multiphonon process. An efficient excitation energy transfer (ET) has been observed between Nd<sup>3+</sup> as a donor and Er<sup>3+</sup> 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

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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)TeO<sub>2</sub>-10PbO-10Li<sub>2</sub>O-2Nd<sub>2</sub>O<sub>3</sub>-xEr<sub>2</sub>O<sub>3</sub> system is prepared by melt-quenching technique. Batches of 20g are prepared from certified reagent grades of TeO<sub>2</sub> (99.95% purity), Li<sub>2</sub>CO<sub>3</sub> (97%), PbO (98% purity), Nd<sub>2</sub>O<sub>3</sub> (99.995%) and Er<sub>2</sub>O<sub>3</sub> (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 Nd<sup>3+</sup>/Er<sup>3+</sup> 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 Nd<sup>3+</sup> ions are observed to be centered at 485 nm, 605 nm, 665 nm, 880 nm, 1062 nm and 1340 nm attributed from <sup>4</sup>G<sub>11/2</sub> → <sup>4</sup>I<sub>11/2</sub>, <sup>4</sup>G<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>G<sub>7/2</sub> → <sup>4</sup>I<sub>13/2</sub>, <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>13/2</sub>, <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>9/2</sub> transitions whereas, three upconverted bands contributed from Er<sup>3+</sup> ions to be centered at 493 nm, 524 nm and 550 nm are found originating from <sup>4</sup>F<sub>7/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions under the excitation at 585 nm. Similar upconversion spectra are found for all samples with different Er<sub>2</sub>O<sub>3</sub> 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.

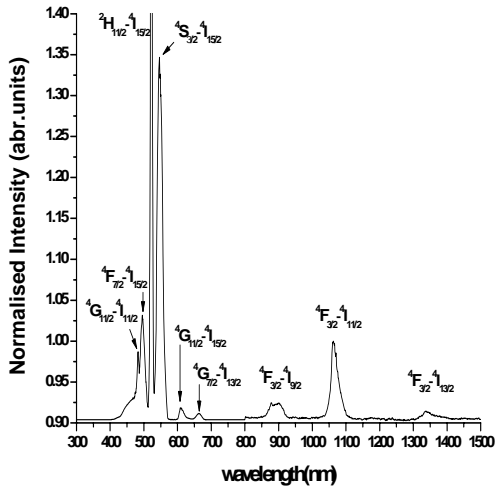


Fig. 1 A typical upconversion luminescence spectrum of the (78-x)TeO<sub>2</sub>-10PbO-10Li<sub>2</sub>O-2Nd<sub>2</sub>O<sub>3</sub>-xEr<sub>2</sub>O<sub>3</sub> glass system.

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 Nd<sup>3+</sup> ions are pumped with 585 nm excitation wavelength through the ground state absorption (GSA) they excites to the  ${}^2G_{7/2}$  level. The Nd<sup>3+</sup> 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 Nd<sup>3+</sup> 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 Nd<sup>3+</sup> 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 Nd<sup>3+</sup> ions are found relax non-radiatively to lower level  ${}^4G_{7/2}$  and  ${}^4F_{3/2}$ . The Nd<sup>3+</sup> 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 Nd<sup>3+</sup> 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 Nd<sup>3+</sup> ions relaxed from  ${}^4G_{11/2}$  level their respective energy is transferred to Er<sup>3+</sup> ions that populated the  ${}^4F_{7/2}$  level. At this level, some Er<sup>3+</sup> ions are relax directly to  ${}^4I_{15/2}$  level radiatively by emitting near infrared emission spectra centered at 732 nm. However, some Er<sup>3+</sup> ions are found to relax non-

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

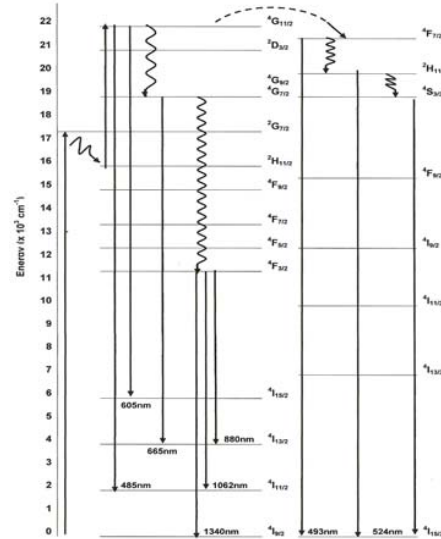


Fig. 2 A schematic energy diagram of the (78-x)TeO<sub>2</sub>-10PbO-10Li<sub>2</sub>O-2Nd<sub>2</sub>O<sub>3</sub>-xEr<sub>2</sub>O<sub>3</sub> glass system

### B. Judd-Ofelts Analysis

Table 1 shows a results of radiative lifetime,  $\tau_R$ , stimulated emission cross-section,  $\sigma_{eff}$  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 Er<sub>2</sub>O<sub>3</sub> 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 Er<sub>2</sub>O<sub>3</sub> 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,  $\sigma_{em}$  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  $0.144 \text{ ms}^{-1}$  to  $0.180 \text{ ms}^{-1}$  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  $\text{Nd}^{3+}$  as single dopant. This is due to the fact that an existence of  $\text{Nd}^{3+}$  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:

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

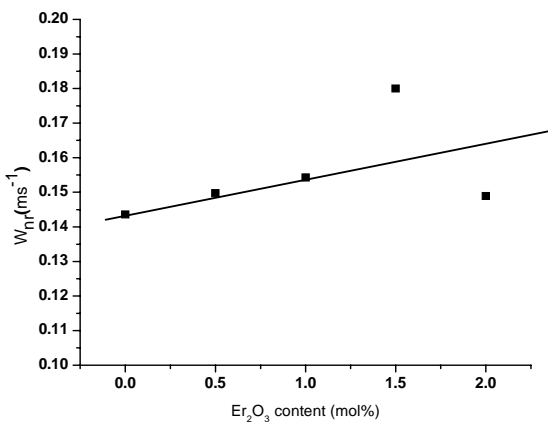


Fig. 3 The non radiative decay rate,  $W_{nr}$  of the S4 glass with respect to  $\text{Er}_2\text{O}_3$  content. The line is drawn for the guide of the eye.

#### 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  $\text{Nd}^{3+}$  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%)	$\tau_R$ (ms)	$\sigma_{eff.}$ ( $\times 10^{20} \text{ cm}^{-2}$ )	$W_{nr}$ ( $\text{ms}^{-1}$ )
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  $\text{Er}^{3+}$  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  $\text{Nd}^{3+}$  ions from the  ${}^4\text{I}_{9/2}$  ground state to the  ${}^2\text{G}_{7/2}$  excited state level. The  $\text{Nd}^{3+}$  ions which are unstable relax nonradiatively to the  ${}^2\text{H}_{11/2}$  level. Then a second pump photon resonantly re-excites the  $\text{Nd}^{3+}$  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,  $\tau_R$ , stimulated emission cross-section,  $\sigma$  and non-radiative relaxation,  $W_{nr}$ . It is found that most values are dependence of  $\text{Nd}^{3+}$

#### ACKNOWLEDGMENT

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

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