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FABRICATION AND OPTICAL CHARACTERISATION OF RARE EARTH ACTIVE IONS DOPED TELLURITE GLASS SYSTEM

(Fabrikasi dan Pencirian Optik Sistem Kaca Telurit Didopkan Ion–Ion Aktif Nadir Bumi)

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Abstract

Five samples of tellurite glasses with the system of (78-x) TeO_2-10PbO- 10Li_2O-2Nd_2O_3-xEr_2O_3 where *x* = 0.0, 0.5, 1.0, 1.5, 2.0 mol % have been prepared by using the conventional melt-quenching method. In this work, the optical properties by mean of their up-conversion luminescence as well as the optical parameters related to Judd-Ofelt theory were measured. The result reveals that six distinctive up-converted 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 $^4G_{11/2} \rightarrow {}^4I_{11/2}$, $^4G_{11/2} \rightarrow {}^4I_{15/2}$, $^4G_{7/2} \rightarrow {}^4I_{13/2}$, $^4F_{3/2} \rightarrow {}^4I_{13/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions whereas, three upconverted bands contributed from Er^{3+} ions to be centered at 493 nm, 524 nm and 550 nm are found originating from $^4F_{7/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions under the excitation at 585 nm. Meanwhile, the optical parameters according to Judd-Ofelt theory such as the radiative lifetime, τ_R, stimulated emission cross-section σ_{eff}. and the non-radiative relaxation, W_{nr} of the glass were found ranging from 0.812ms to 1.248ms, 0.812 x 10^{20} cm^2 to 1.248 x 10^{20} cm^2 and from 0.144 ms^{-1} to 0.180 ms^{-1} respectively with respect to mol% of composition . Further analysis and discussion will be elaborated in brief.

Keywords: up-conversion, excitation, Judd-Ofelt, radiative, relaxation

Abstrak

Lima sampel kaca tellurite dengan sistem (78-x) TeO_2-10PbO- 10Li_2O-2Nd_2O_3-xEr_2O_3 dimana *x* = 0.0, 0.5, 1.0, 1.5, 2.0 mol % telah disedia menggunakan kaedah sepuh-lindap konvensional. Dalam kerja ini, sifat-sifat optikal seperti pendarkilau pertukaran atas serta parameter optikal yang berkaitan dengan teori Judd-Ofelt telah diukur. Keputusan menunjukkan bahawa enam jalur pertukaran atas tersendiri sumbangan dari ion-ion Nd^{3+} telah dicerap berpusat di 485 nm, 605 nm, 665 nm, 880 nm, 1062 nm dan 1340 nm ditentukan dari transisi $^4G_{11/2} \rightarrow {}^4I_{11/2}$, $^4G_{11/2} \rightarrow {}^4I_{15/2}$, $^4G_{7/2} \rightarrow {}^4I_{13/2}$, $^4F_{3/2} \rightarrow {}^4I_{13/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ manakala, tiga jalur pertukaran atas adalah sumbangan dari ion-ion Er^{3+} dijumpai berpusat di 493 nm, 524 nm and 550 nm hasil dari transisi $^4F_{7/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$ dan $^4S_{3/2} \rightarrow {}^4I_{15/2}$ di bawah pengujaan 585nm. Sementara itu, parameter optikal merujuk kepada teori Judd-Ofelt seperti jangkahayat radiasi, τ_R, keratan rentas penyinaran terangsang, σ_{eff}. dan relaksasi tak bersinar, W_{nr} bagi kaca didapati dalam julat masing-masing dari 0.812ms hingga 1.248ms, 0.812 x 10^{20} cm^2 hingga 1.248 x 10^{20} cm^2 dan dari 0.144 ms^{-1} hingga 0.180 ms^{-1} terhadap mol% komposisi. Analisa lanjut dan perbincangan akan dihurai dengan lebih lanjut.

Kata kunci: pertukaran-atas, pengujaan, Judd-Ofelt, penyinaran, relaksasi

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, 2]. A great deal of recent interest for lasing transition in the near infrared (NIR) region of Nd^{3+}(1.06μm) and Er^{3+}(1.53μm) doped glass are most suited for optical devices and laser technology [3, 4]. Therefore, the rare-earth doped borotellurite glasses have been the subject of several spectroscopic investigation due to their potential applications in various area like optical sensing, telecommunications, or biochemical studies [3, 4]. A study of upconversion in single as well as multi-ions doped glasses has been found increased vigoriously in recent years. To study the VIS-NIR lasing transition, tellurium has been identified to be appropriate glass host in a development of laser glasses for the laser application since the strong rare-earth ions-host interaction results in efficient upconversion emissions [5-7]. In addition, due to its reputation as they are good in chemical durability, good thermal stability, high refractive index, good transparency in mid-IR region and high solubility for rare earth ions borotellurite glass which, possess lower phonon energies has been proved to be the most stable hosts for obtaining efficient luminescence in rare earth compare to other oxide glasses [8, 9]. 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. Hence, the purpose of the present paper is to study systematically the lasing transition and the upconversion luminescence of Nd^{3+}/Er^{3+} co-doped borotellurite glass in the visible and near infrared region. Some analysis on the Judd-Ofelt theory is also been reported and discussed with respect to the composition.

Materials and Methods

The tellurite glass of $(78\text{-}x)TeO_2\text{-}10PbO\text{-}10Li_2O\text{-}2Nd_2O_3\text{-}xEr_2O_3$ system is prepared by melt-quenching technique. Batches of 20g are prepared from certified reagent grades of TeO_2 (99.95% purity), Li_2CO_3 (97%), PbO (98% purity), Nd_2O_3 (99.995%) and Er_2O_3 (99.995%). The chemicals are firstly mixed thoroughly in a platinum crucible before being heated at 1000 ^oC 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 ^oC 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).

Results and Discussion

Upconversion Luminescence

The upconversion fluorescence spectrum of Nd^{3+}/Er^{3+} 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^{3+} ions are observed to be centered at 485 nm, 605 nm, 665 nm, 880 nm, 1062 nm and 1340 nm attributed from $^4G_{11/2} \rightarrow {}^4I_{11/2}$, $^4G_{11/2} \rightarrow {}^4I_{15/2}$, $^4G_{7/2} \rightarrow {}^4I_{13/2}$, $^4F_{3/2} \rightarrow {}^4I_{13/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions whereas, three upconverted bands contributed from Er^{3+} ions to be centered at 493 nm, 524 nm and 550 nm are found originating from $^4F_{7/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions under the excitation at 585 nm. Similar upconversion spectra are found for all samples with different Er_2O_3 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.

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^{3+} ions are pumped with 585 nm excitation wavelength through the ground state absorption (GSA) they excites to the $^2G_{7/2}$ level. The Nd^{3+} 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^{3+} 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 [1,2]. As they populated the $^4G_{11/2}$ level, some of the Nd^{3+} 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^{3+} ions are found relax non-radiatively to lower level $^4G_{7/2}$ and $^4F_{3/2}$. The Nd^{3+} 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^{3+} 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.

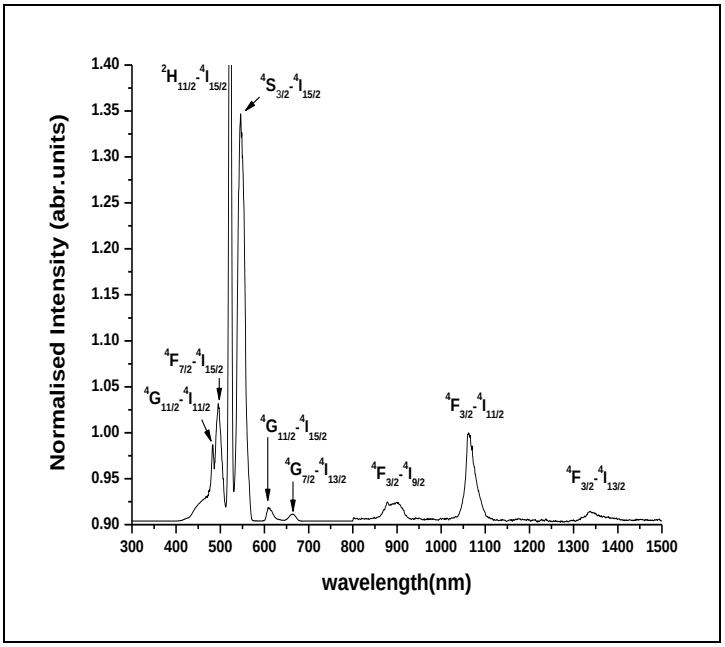

Figure 1. A typical upconversion luminescence spectrum of the (78-x)-10PbO-10Li_2O-2Nd_2O_3-xEr_2O_3 glass system.

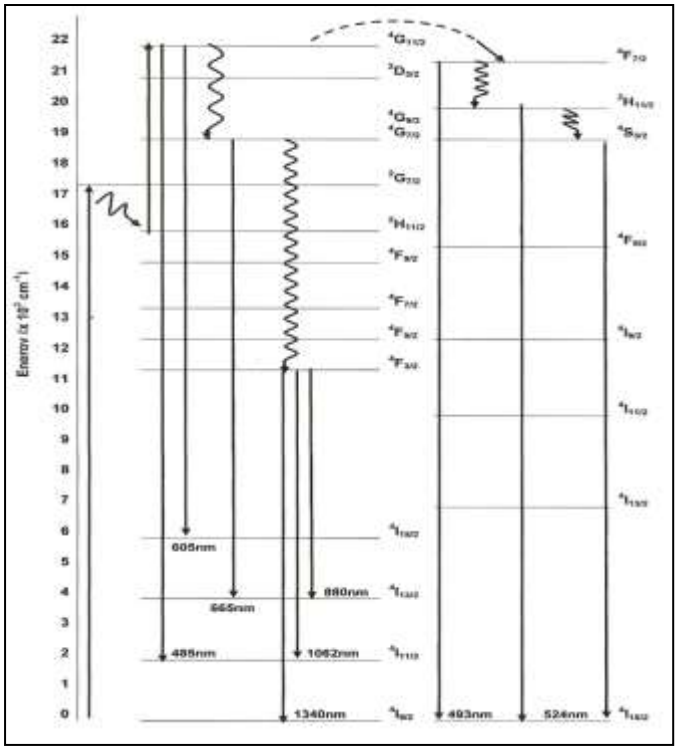

Figure 2. A schematic energy diagram of the (78-x)TeO_2-10PbO-10Li_2O-2Nd_2O_3-xEr_2O_3 glass system

As the Nd^{3+} ions relaxed from $^4G_{11/2}$ level their respective energy is transferred to Er^{3+} ions that populated the $^4F_{7/2}$ level. In this work, an efficient excitation energy transfer (ET) has been observed between Nd^{3+} as a donor and Er^{3+} as the acceptor. This has been confirmed by Nazabal *et.al* (2003), Kumar *et.al* (2008) and later by Lakshminarayan *et.al* (2009) in their works [10-12]. At this level, some Er^{3+} ions are relax directly to $^4I_{15/2}$ level radiatively by emitting near infrared emission spectra centered at 732 nm. However, some Er^{3+} ions are found to relax non-radiatively to $^2H_{11/2}$ and $^4S_{3/2}$ level. From the $^2H_{11/2}$ level the Er^{3+} ions relaxed to $^4I_{15/2}$ thus emitting weak green spectra centered at 524 nm. Meanwhile, for the Er^{3+} ions that populated $^4S_{3/2}$ level decay directly to the ground level $^4I_{15/2}$ by generates green spectra centered at 547 nm.

Judd-Ofelts Analysis

Table 1 shows results of radiative lifetime, τ_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_2O_3 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 1:

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

whereas 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 x 10^{20} cm^2 to 1.248 x 10^{20} cm^2 depending on the mol% of Er_2O_3 content. Similar trend has also been observed and discussed by other researcher [13-15]. The emission cross-section which is the laser gain per unit population inversion is the relevant spectroscopy parameter for laser application

[16]. The stimulated emission cross section, σ_{em} has been measured for different emission bands using the following expression as proposed by Fuchtbauer-Ladenburg (equation 2) [17]:

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

whereas A is the radiative transition probability and $\Delta\lambda$ is the fluorescence band width. Meanwhile, has 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 Nd^{3+}/Er^{3+} ions. Romanowski (1990) in his works notice that the non-radiative decay rate is dependent upon the strength of ion-lattice coupling, phonon spectrum, sample temperature as well as the energy separation to the next lower lying level [18]. Recently, works done by Meisong et.al confirmed that the non-radiative rate could also been affected from the multiphonon relaxation rate, self-quenching rate and relaxation rate induced by certain transition metal ions and other rare earth ions [19]. The fluorescence decay rate is governed by the probability of the radiative and non-radiative relaxation described by following expression in equation 3:

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

Table 1. A results of radiative lifetime, τ_R, stimulated emission cross-section, $\sigma_{eff.}$ and non-radiative relaxation, W_{nr} of (78-x)TeO_2 - 10PbO - 10Li_2O-2Nd_2O_3-xEr_2O_3 glass system under the 1062nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) emission band.

Sample No.	Nominal Composition (mol%)					$\tau_R(ms)$	$\sigma_{eff.}$ ($x10^{20}$ cm^2)	$W_{nr}(ms^{-1})$
	TeO_2	PbO	Li_2O	Nd_2O_3	Er_2O_3			
S41	78.0	10.0	10.0	2.0	-	2.234	0.812	0.144
S42	77.5	10.0	10.0	2.0	0.5	2.279	0.917	0.149
S43	77.0	10.0	10.0	2.0	1.0	2.341	0.893	0.154
S44	76.5	10.0	10.0	2.0	1.5	1.981	1.248	0.180
S45	76.0	10.0	10.0	2.0	2.0	2.196	0.942	0.149

Conclusion

Nd^{3+}/Er^{3+} co-doped tellurite glasses 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 $^4G_{11/2} \rightarrow {}^4I_{11/2}$, $^4G_{11/2} \rightarrow {}^4I_{15/2}$, $^4G_{7/2} \rightarrow {}^4I_{13/2}$, $^4F_{3/2} \rightarrow {}^4I_{13/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transitions whereas, three upconverted bands contributed from Er^{3+} ions to be centered at 493 nm, 524 nm and 550 nm are found originating from $^4F_{7/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ 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 $^4I_{9/2}$ ground state to the $^2G_{7/2}$ excited state level. The Nd^{3+} ions which are unstable relax non-radiatively to the $^2H_{11/2}$ level. Then a second pump photon resonantly re-excites the Nd^{3+} ions to the $^4G_{11/2}$ excited level through the excited state absorption (ESA). The ions that populated the $^4G_{11/2}$ 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 $^4G_{11/2}$ to $^4F_{3/2}$ 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+}.

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