Radiative properties of Tm$^{3+}$ doped TeO$_2$-ZnO-Na$_2$O-TiO$_2$ glasses studied using Judd-Ofelt Theory

A Marzuki*, Riyatun, M Larasati, G T Singgih

Department of Physics, Sebelas Maret University, Surakarta 57216 Indonesia

Email: amarzuki@mipa.uns.ac.id

Abstract. New Tm$^{3+}$-doped tellurite glasses were prepared by melt quenching technique. X-ray Diffraction (XRD) characterization were carried out to confirm the glassy state of the samples. Characterization using UV-VIS-NIR spectrophotometer and FTIR were performed in order to determine the width of the transparent window, optical band gap and bonding structure of the samples. Density and refractive index were measured at room temperature using pycnometer and Brewster’s angle technique. Utilizing these data, lasing performance of the samples was predicted. For this purpose, the Judd-Ofelt theory was applied to calculate Judd-Ofelt parameters ($\Omega_i$). From these results several radiative transitions were studied in terms of transition probabilities ($A_i$), branching ratios ($\beta_i$) and radiative lifetime ($\tau$). The predicted results were then compared to that obtained from fluorescence spectra measurement so that quantum efficiency of the samples can be calculated.

Keywords: Tellurite glasses, Judd-Ofelt analysis, Spectroscopic properties, Tm$^{3+}$ doped glasses, Optical absorption.

1. Introduction

Triggered by the need for optical amplifiers to compensate for the propagation loss in the second and third telecommunication windows, Nd$^{3+}$ and Er$^{3+}$ doped glasses have been attracted more attention and researched more than other rare earth ions doped glasses [1, 2, 3]. Among the less studied rare earth doped glasses, Tm$^{3+}$ doped glasses have been researched more than others especially due to their capability to provide mid-infrared laser source.

Many papers report emission characteristic at about 1.8 $\mu$m resulted from $^3F_4 \rightarrow ^3H_6$ transition for different glass hosts. Using the product of stimulated emission cross-section ($\sigma$) and lifetime ($\tau$) as an important parameter characterizing laser performance of a Tm$^{3+}$ doped glass, Tian et al., [4] who studied Tm$^{3+}$ doped 53.3BiO$_{1.5}$-33.3GeO$_2$-13.4NaO$_{0.5}$ glasses calculate $\sigma \times \tau$ and their results are compared to other glasses such as fluorophosphates glasses [5], tellurite glasses [6], germinate glasses [7] and ZBLAN glasses[8]. Glasses fabricated by Tian, et. al., [4] have $\sigma \times \tau$ which are higher than the first three glasses [5, 6, 7] but higher ZBLAN glasses [8] suggesting that Tm$^{3+}$ doped 53.3BiO$_{1.5}$-33.3GeO$_2$-13.4NaO$_{0.5}$ glasses are potentially used as materials for optical amplifiers.

Other laser transition encounters within the scheme of Tm$^{3+}$ ions energy level diagram is that resulted from $^3H_5 \rightarrow ^3H_6$ emitting light at about 1.22 $\mu$m. This emission is potentially used for optical amplifiers at 1.22 $\mu$m. This electronic transition, however, suffers from the narrow gap between $^3H_5$ and $^3F_4$ resulting in $^3H_5$ is easily depopulated [9]. For this purpose, low phonon energy glass host is required. In addition to the above transitions, glass host dependence are also apply for other transition schemes, e.g., $^3F_4 \rightarrow ^3H_5$, $^3H_4 \rightarrow ^3H_6$ and $^3H_5 \rightarrow ^3F_4$. In this study, we applied Judd-Ofelt theory to analyze different composition of Tm$_2$O$_5$:TeO$_2$:ZnO-Na$_2$CO$_3$:TiO$_2$ in order to predict the strength of an electronic transition relative to other
transitions originated from the same energy level expressed in oscillator strength \((f)\) and branching ratios \((\beta)\).

2. Experiment

Tm\(^{3+}\) doped tellurite glasses having compositions (in mol\%): 60TeO\(_2\)-25ZnO-(10-\(x\))Na\(_2\)CO\(_3\)-5TiO\(_2\)-\(x\)Tm\(_2\)O\(_3\) (with \(x = 1, 2, 3, 4, 5\)) were fabricated by melt quenching method. The starting materials in the form of powder were weighed in nitrogen controlled glove box so that a mixture of 10 gram was obtained. After thoroughly mixed, the mixture was transferred to platinum crucible. Melting was carried out in electric furnace at 900\(^\circ\)C for 60 minutes while periodically stirred to get a homogeneous melt. Casting was carried out by pouring the melt into a pre-heated parallel brass mold followed by annealing at 360\(^\circ\)C to remove any residual stressed formed during casting.

Density measurements were carried out at room temperature using pycnometer. Refractive indices were measured at wavelength of 625 nm at room temperature using Brewster angle method. Transmittance within UV-VIS-NIR region was measured using Spectrophotometer Perkin-Elmer UV-VIS-NIR Lambda-25. Based on the data of density, refractive index and absorption spectra; samples were analyzed their lasing performance by applying Judd-Ofelt theory.

3. Results and discussion

3.1. X-Ray diffraction

Six glasses fabricated in this experiment show good transparency (Figure 1). In order to confirm the amorphous nature of the samples, XRD analysis was performed. It can be seen from figure 2 that all the XRD patterns show no narrow sharp peak. Instead, broad peaks at 2\(\theta\) of about 29\(^\circ\) characterizing the amorphous nature of solids were observed.

3.2. Density and refractive index

Density of all the samples measured at room temperature are shown in figure 3. It shows that density increases with increasing Tm\(_2\)O\(_3\) concentration. Adding Tm\(_2\)O\(_3\) (MR = 388 smu) to replace Na\(_2\)O (MR = 62) leads to increasing average molecular mass of glass. From definition of density, which is mass \((m)\) divided by volume \((V)\), this Tm\(_2\)O\(_3\) addition contribute to the increasing \(m\). As can be seen from figure 3, however, this addition causes the molar volume is increased. This suggest that the change in average molecular mass is more dominant in determining the glass density than the change in molar volume.
Figure 4 shows compositional variation of refractive index obtained from both measurement and calculation based on Lorentz-Lorenz equation:

\[
n = \sqrt{\frac{2 N_A a_m \rho + 3 \sum x_i M_i}{3 \sum x_i M_i - N_A a_m \rho}}
\]

where \(n\) is refractive index, \(N_A\) is Avogadro number, \(a_m\) is molecular polarizability, \(M_i\) is molecular weight, \(x_i\) is molar fraction and \(\rho\) is density.

It is seen that refractive index increases as \(\text{Tm}_2\text{O}_3\) concentration is increased. From equation (1) it is clearly shown that the value of \(n\) is controlled by \(\rho\). In this regard, \(\rho\) can be related to electron density.

![Figure 3](image.png)  
**Figure 3.** The change in density and molar volume as different concentration of \(\text{Tm}_2\text{O}_3\) were added into the glass.

![Figure 4](image.png)  
**Figure 4.** Compositional variation of refractive resulted from experiment and calculation based on Lorentz-Lorenz equation.

### 3.3. Absorption spectra

Figure 5 shows linear absorption spectra of all samples. Four distinguishable peaks corresponding to \(f-f\) electronic transition of \(\text{Tm}^{3+}\) ions are observed. They are bands corresponding to electronic transitions: \(^3\text{H}_6 \rightarrow ^1\text{H}_4\) (793 nm), \(^3\text{H}_6 \rightarrow ^3\text{F}_3\) (687 nm), \(^3\text{H}_6 \rightarrow ^3\text{F}_2\) (660 nm) and \(^3\text{H}_6 \rightarrow ^1\text{G}_4\) (468 nm). Assignments were made referring to Carnall et al. [7]. From figure 5, it can also be seen that there is an increase in absorption band intensity with the addition of \(\text{Tm}_2\text{O}_3\). Adding \(\text{Tm}_2\text{O}_3\) means supplying more electrons at the ground energy level of \(\text{Tm}^{3+}\) resulting in more photons are absorbed.

![Figure 5](image.png)  
**Figure 5.** Absorption spectra of the present glasses at different concentration of \(\text{Tm}_2\text{O}_3\).
In order to evaluate the lasing performance from the data of absorption spectra, Judd-Ofelt theory was applied. All glass samples were evaluated in term of measured oscillator strength ($f_{\text{meas}}$), calculated oscillator strength ($f_{\text{calc}}$), radiative transition probabilities ($A$), lifetime ($\tau$) and branching ratios ($\beta$) expressed in the following equations:

$$f_{\text{meas}} = \frac{3hc}{8\pi^2e^2n^2} \frac{9}{(n^2+2)^2} \frac{2J+1}{\lambda} \int \sigma(\lambda) d\lambda$$  \hspace{1cm} (2)

$$f_{\text{calc}}(J \rightarrow J') = \sum_{\ell=2,4,6} \frac{4\pi^2\varepsilon_0^2}{3h^2} |\langle S, L | J \rangle| |\langle S', L' | J' \rangle|^2$$  \hspace{1cm} (3)

$$A[S, L];(S', L')j' = \frac{64\pi^2\varepsilon_0^2n^2}{3n(2J+1)\lambda^2} \sum_{\ell} \Omega_{\ell} |\langle S, L | J \rangle| |\langle S', L' | J' \rangle|^2$$  \hspace{1cm} (4)

$$\beta[S, L];(S', L')j' = \frac{A[S, L];(S', L')j'}{\sum_{S', L',j'} A[S, L];(S', L')j'}$$  \hspace{1cm} (5)

$$\tau_{\text{rad}} = \frac{1}{\sum_{S', L',j'} A[S, L];(S', L')j'}$$  \hspace{1cm} (6)

where $h$ is Plank’s constant, $c$ is velocity of light in vacuum, $n$ is refractive index, $N$ is number of Tm$^{3+}$ per mole, J and $J'$ are total angular momenta of ground state and excited states, respectively, $\Omega_{\ell=2,4,6}$ are Judd-Ofelt intensity parameters and $||U^2||^2$ are elements of doubly reduced matrix operator calculated from the intermediate-coupling approximation.

Since $||U^2||^2$ of a rare earth ion is insensitive to its environment, their values do not depend on the glass host. In most work, the value of $||U^2||^2$ are taken from Carnall table $[10]$. The measured oscillator strength ($f_{\text{meas}}$) was obtained from absorption spectra by firstly calculating area under absorption peaks $\int \sigma(\lambda) d\lambda$ as given in equation (2). In order to calculate $\Omega$, $A$, $\tau$ and $\beta$, firstly, we have to calculate $\int \sigma(\lambda) d\lambda$, area under the peak of an absorption band. Inserting $||U^2||^2$ corresponding to each absorption band into equation (3) and then using Root-mean-square deviation (rms), one can obtain $\Omega_{\ell=2,4,6}$ (Table 1).

**Table 1.** Judd-Ofelt intensity parameters ($\Omega_{\ell=2,4,6} \times 10^{-20}$ cm$^2$) of the present glasses and those taken from literatures.

| Samples       | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | $\Omega_d/\Omega_6$ | Reference   |
|---------------|------------|------------|------------|---------------------|-------------|
| T1            | 8.88       | 1.34       | 1.91       | 0.70                | Present work|
| T2            | 8.78       | 1.80       | 1.67       | 1.08                |             |
| T3            | 8.56       | 1.87       | 1.69       | 1.11                |             |
| T4            | 8.14       | 1.75       | 1.56       | 1.12                |             |
| T5            | 8.95       | 1.88       | 1.66       | 1.13                |             |
| TNZL: Tm      | 4.16       | 1.87       | 1.14       | 1.64                | [11]        |
| Fluorophosphate| 3.01       | 2.56       | 1.54       | 1.66                | [4]         |

It can be seen from table 1 that the magnitudes of $\Omega_{\ell=2,4,6}$ are similar to those reported values. Except for sample T1, their magnitude increase following the trend of $\Omega_2 > \Omega_6 > \Omega_4$. The high value of $\Omega_2$ indicates that the present glasses possess high covalence and asymmetry. The values of the spectroscopic factor defined by $\Omega_d/\Omega_6$ are also similar to those reported in other papers, which are in the range of 0.65 – 1.46. Once the values of $\Omega_{\ell=2,4,6}$ are obtained, one can then compute radiative transition rate ($A$), branching ratios ($\beta$) and radiative lifetime ($\tau$) using equation (4-6) and the results for transition originated from $^3H_4$ and $^3H_5$ are tabulated in Table 2. Radiative transition rate ($A$) in all samples for $^3H_5 \rightarrow ^3H_6$ are the higher than that for $^3H_5 \rightarrow ^3H_4$ and so are their branching ratios, which are more than 94% of the emitted light from $^3H_5$ goes to $^3H_6$ resulting in emission at about 1220 nm.
There are three possible electronic transition originated from $^3\text{H}_4$. They are $^3\text{H}_4 \rightarrow ^3\text{H}_5$, $^3\text{H}_4 \rightarrow ^3\text{F}_4$ and $^3\text{H}_4 \rightarrow ^3\text{H}_6$. Among them, emission resulted by transition $^3\text{H}_4 \rightarrow ^3\text{H}_6$ resulting in emission at about 800 nm is the strongest ($\beta > 91\%$). This value tends to decrease with increasing Tm$_2$O$_3$.

### Table 2. Transition probabilities ($A$), branching ratio ($\beta$), dan radiative lifetime ($\tau$) of the present glasses at different concentration of Tm$_2$O$_3$ for electronic transition originated from $^3\text{H}_4$ and $^3\text{H}_5$.

| Samples | Transitions | Energy (cm$^{-1}$) | $A$ (s$^{-1}$) | $\beta$ (%) | $\tau$ (ms) |
|---------|-------------|--------------------|---------------|-------------|-------------|
| T1      | $^3\text{H}_5 \rightarrow ^3\text{F}_4$ | 2167               | 51.08         | 5.96        | 1.17        |
|         | $\rightarrow ^3\text{H}_6$ | 8264               | 806.07        | 94.04       |             |
|         | $^3\text{H}_4 \rightarrow ^3\text{H}_5$ | 4362               | 51.74         | 1.19        | 0.23        |
|         | $\rightarrow ^3\text{F}_4$ | 6529               | 310.51        | 7.11        |             |
|         | $\rightarrow ^3\text{H}_6$ | 12626              | 4003.04       | 91.70       |             |
| T2      | $^3\text{H}_5 \rightarrow ^3\text{F}_4$ | 2167               | 50.65         | 5.93        | 1.17        |
|         | $\rightarrow ^3\text{H}_6$ | 8264               | 803.06        | 94.07       |             |
|         | $^3\text{H}_4 \rightarrow ^3\text{H}_5$ | 4362               | 63.70         | 1.48        | 0.23        |
|         | $\rightarrow ^3\text{F}_4$ | 6529               | 315.34        | 7.32        |             |
|         | $\rightarrow ^3\text{H}_6$ | 12626              | 3927.07       | 91.20       |             |
| T3      | $^3\text{H}_5 \rightarrow ^3\text{F}_4$ | 2167               | 50.15         | 5.83        | 1.16        |
|         | $\rightarrow ^3\text{H}_6$ | 8264               | 810.62        | 94.17       |             |
|         | $^3\text{H}_4 \rightarrow ^3\text{H}_5$ | 4362               | 65.73         | 1.53        | 0.23        |
|         | $\rightarrow ^3\text{F}_4$ | 6529               | 315.24        | 7.33        |             |
|         | $\rightarrow ^3\text{H}_6$ | 12626              | 3918.44       | 91.14       |             |
| T4      | $^3\text{H}_5 \rightarrow ^3\text{F}_4$ | 2167               | 48.12         | 5.84        | 1.21        |
|         | $\rightarrow ^3\text{H}_6$ | 8264               | 775.98        | 94.16       |             |
|         | $^3\text{H}_4 \rightarrow ^3\text{H}_5$ | 4362               | 63.18         | 1.54        | 0.24        |
|         | $\rightarrow ^3\text{F}_4$ | 6529               | 302.69        | 7.38        |             |
|         | $\rightarrow ^3\text{H}_6$ | 12626              | 3738.37       | 91.09       |             |
| T5      | $^3\text{H}_5 \rightarrow ^3\text{F}_4$ | 2167               | 54.35         | 5.97        | 1.10        |
|         | $\rightarrow ^3\text{H}_6$ | 8264               | 856.50        | 94.03       |             |
|         | $^3\text{H}_4 \rightarrow ^3\text{H}_5$ | 4362               | 69.21         | 1.50        | 0.22        |
|         | $\rightarrow ^3\text{F}_4$ | 6529               | 338.18        | 7.33        |             |
|         | $\rightarrow ^3\text{H}_6$ | 12626              | 4203.30       | 91.16       |             |

### 4. Conclusions

New tellurite glasses with compositions (in mol%): 60TeO$_2$-25ZnO-(10 -$x$)Na$_2$CO$_3$-5TiO$_2$-Tm$_2$O$_3$ (with $x$ = 1, 2, 3, 4, 5) have been fabricated, characterized and analyzed in order to predict their lasing performance especially light emitted from $^3\text{H}_5$ and $^3\text{H}_4$. For transition from $^3\text{H}_5$, more than 94 % of the emitted light is at about $\lambda$ = 1220 nm while for the transition from $^3\text{H}_4$, about 91 % of the emitted light is at about $\lambda$ = 800 nm. This domination tend to slightly decrease with the increase of Tm$_2$O$_3$ concentration.

### Acknowledgements

The authors acknowledge for the financial support from PNBP UNS Research Funding 2019.
References

[1] Dan H K, Qiu J, Zhou D and Wang R 2018 Broadband near-infrared emission and energy transfer in Nd-Bi co-doped transparent silicate glass-ceramics for optical amplifiers Optical Materials 85 pp 517-522

[2] Marzuki A, Yunianto M, Riyatun and Purwanto H 2018 Absorption spectra analysis of Er$^{3+}$-Doped TeO$_2$-ZnO-Bi$_2$O$_3$ Glasses Key Engineering Materials 772 pp 85-89

[3] Marzuki A and Fausta D A 2018 Physical and Optical Studies of Bi$^{3+}$-Modified Erbium Doped Tellurite Glasses IOP Conf. Series: Materials Science and Engineering 333 012015

[4] Tian Y, Xu R, Zhang L, Hu L and Zhang J 2010 1.8 μm emission of highly thulium doped fluorophosphate glasses J. Appl. Phys. 108 083504

[5] Wang M, et al 2009 Effect of Al(PO$_3$)$_3$ content on physical, chemical and optical properties of fluorophosphate glasses for 2 μm application Mater. Chem. Phys. 114(1) pp 295-299

[6] Fusari F, et al 2008 Spectroscopic and lasing performance of Tm$^{3+}$-doped bulk TZN and TZNG tellurite glasses operating around 1.9 μm, Opt. Express 16(23) pp 19146-51

[7] Balda R, Lacha L M, Fernández M J, Fernández-Navarro J M 2005 Optical spectroscopy of Tm$^{3+}$ ions in GeO$_2$-PbO-Nb$_2$O$_5$ glasses Optical Materials 27(11) 1771-75

[8] Özen G, et al 1995 Excited state absorption mechanisms of red to UV and blue conversion luminescence in Tm$^{3+}$ doped fluorophosphate glass Journal of Luminescence 63(1-2) pp 85-96

[9] Huihua X, Gao T, Lan L and Wei C 2011 50GeSe$_2$-25In$_2$Se$_3$-25CsI glass doped with Tm$^{3+}$, Tm$^{3+}$/Ho$^{3+}$ and Tm$^{3+}$/Er$^{3+}$ for amplifiers working at 1.22 μm J. Rare Earth 29(10) 920-3

[10] Carnall W T, Fields P R and Rajnak K 1968 Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr$^{3+}$, Nd$^{3+}$, Pm$^{3+}$, Sm$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$, and Tm$^{3+}$ J. Chem. Phys. 49 4424 https://doi.org/10.1063/1.1669893

[11] Lachheb R, et al 2015 Characterization of Tm$^{3+}$ doped TNZL glass laser material Journal of Luminescence 161 pp 281-287