Journal of
Thai Interdisciplinary Research
Volume 14, Number 2, Pages 44 – 47

# Spectroscopy characteristics of $Eu^{3+}$ doped zinc barium tellurite oxyfluoride glasses for laser materials

**Yaowalak Yamsuk[1,2], Patarawegee Yasaka[1,2*], Jakrapong Keawkao[1,2], and Narong Sangwaranateec[3]**

[1]Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, 73000, Thailand
[2]Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand
[3]Applied Physics, Faculty of Science and Technology, Suan Sunandha Rajabhat University, Bangkok 10300, Thailand

## Abstract

$Eu^{3+}$ doped tellurite glasses samples (55-x)$TeO_2$-10$ZnF_2$-35BaO-x$Eu_2O_3$ (where x = 0, 0.05, 0.1, 0.5, 1.0 and 1.5 mol%) were prepared. Their physical and optical properties were studied through absorption, luminescence and decay time measurements. An intense red luminescence was observed due to $^5D_0 \rightarrow {}^7F_2$ transition of $Eu^{3+}$ ion in these glasses that were studied. The optical spectra of glasses showed two discrete absorption bands at 2074 nm and 2207 nm. These were thought to be due to the transitions of $^7F_0 \rightarrow {}^7F_6$ and $^7F_1 \rightarrow {}^7F_6$ respectively. The emission spectra were observed and assigned to 578, 591, 612, 652 and 700 nm by excitation at 465 nm. The emission intensity of $Eu^{3+}$ increased with increasing concentration of $Eu_2O_3$. The experimental lifetime of the $^5D_0$ level was found to be single exponential for all the glass samples that were studied. The results that were obtained are discussed and reported in this paper.

**Keywords:** Photoluminescence, $Eu^{3+}$ ion, tellurite glasses

**Article history:** Received 14 January 2019, Accepted 19 April 2019

## 1. Introduction

Rare earth ion doped glasses are materials that are drawing considerable interest because of the correlation structure and optical properties. They constitute important optical materials since they have applications in the development of lasers, sensors, optical fibers, optical data storage and display monitors [1-3]. Europium ($Eu^{3+}$) has the most intense emission of $Eu^{3+}$. On the optical spectrum it is placed at a wavelength of approximately 610 nm. This is the wavelength of red light [4, 5]. It is well known that the optical properties of the $Eu^{3+}$ ion are highly sensitive to the environment in which it is located. Although, there is significant information available about $Eu^{3+}$ doped tellurite glasses [6], it was thought that it would be of interest to find out the variation of optical properties of $Eu^{3+}$ ion in tellurite glasses in sample with varying concentrations of $Eu^{3+}$ ions. Tellurite glasses have similar stability to oxide based glasses. This is due to the low phonon energy of fluorine based glass systems [7]. Recently researchers have paid more attention to tellurite based glasses due to their excellent physical properties. These include low process temperature, high refractive index and chemical durability. [8] Pure $TeO_2$ does not form a glass on its own without adding other elements to it. However $TeO_2$ based ternary glasses possess good transparency and moisture resistant properties [9, 10]. This work presents a study of the physical and optical properties of tellurite glasses with varying concentrations of $Eu^{3+}$ions.

## 2. Experiment

The $Eu^{3+}$ doped tellurite glasses were prepared by the normal melt quenching technique. The chemical composition of the glasses that were prepared was as follows (55-x)$TeO_2$-10$ZnF_2$-35BaO-x$Eu_2O_3$ (where x = 0.00, 0.05, 0.10, 0.50, 1.00 and 1.50 mol%). The raw materials, which totaled 15 g per batch, were thoroughly mixed and crushed in an agate mortar to obtain homogeneous mixture. The homogeneous mixture was put into a porcelain crucible and kept in an electrical furnace at 950°C for 1 hour. The mixture

*Corresponding author; email: pyasaka@hotmail.com

DOI 10.14456/jtir.2019.17

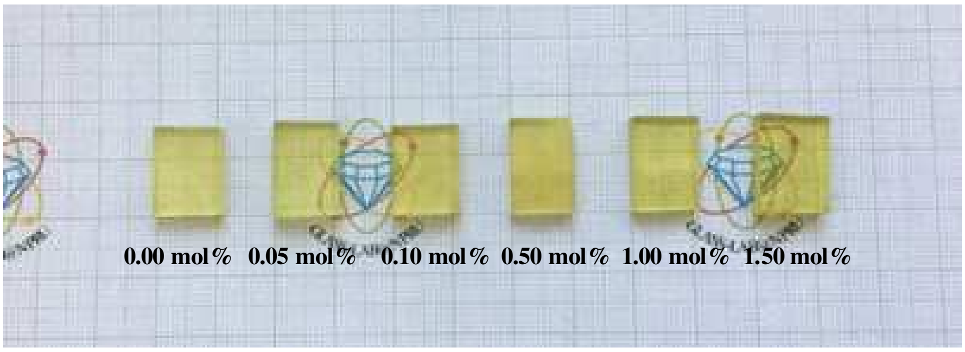


**Figure 1**: Glasses sample of the $Eu^{3+}$ doped tellurite glasses.

**Table 1**. Phycal properties of the Eu3+ dope tellurite glasses.

| MOL % $Eu_2O_3$ | Density($g/cm^3$) | Molar Volume ($cm^3$/mol) | Refractive index |
|---|---|---|---|
| 0.00 mol% | 5.2791±0.0029 | 28.7515 | 1.60 |
| 0.05 mol% | 5.2904±0.0099 | 30.2165 | 1.84 |
| 0.10 mol% | 5.2783±0.0067 | 30.3041 | 1.85 |
| 0.50 mol% | 5.2793±0.0072 | 30.4439 | 1.87 |
| 1.00 mol% | 5.2609±0.0057 | 30.7334 | 1.88 |
| 1.50 mol% | 5.2741±0.0011 | 30.8388 | 1.89 |

was poured to a preheated graphite plate then pressed by another graphite plate to obtain a uniform thickness. The glass samples were annealed for 3 hours at 350°C to remove strain and to improve their mechanical strength. The glass samples were allowed to reach room temperature slowly. The glass samples were cut and polished to a size of 1.0×1.5× 0.3 $cm^3$ before they were used for optical studies.

The density of the $Eu^{3+}$ doped tellurite glass samples was measured using the Archimedes method with a densitometer HR-200 weighing balance. The refractive index of the samples was measured at room temperature using a Reflectivity Meter (PRM). The physical properties of each sample such as density, molar volume, refractive index and concentration of $Eu^{3+}$ ion are summarized in Table 1. The optical absorption spectra of the glass samples was recorded. It was analyzed in the UV-Vis-NIR regions in the range of 200-2,500 nm using a UV-3600 Shimadzu UV-VIS-NIR spectrophotometer. The excitation and emission spectra of the glass samples was measured using a Cary Eclipse Fluorescence Spectrophotometer. The lifetimes of the $^5D_0$ excited level of $Eu^{3+}$ ion were measured under the excitation at 465 nm also by using a Cary Eclipse Fluorescence Spectrophotometer.

## 3. Results and Discussions

### 3.1. *Physical properties*

The densities of $Eu^{3+}$ doped tellurite glass samples are shown in Table 1. It was found that the fluctuating densities of the glass samples produced did not depended on $Eu_2O_3$ concentration. All of the densities were found to be in the range 5.2610 ± 0.0057 – 5.2904±0.0099 g/$cm^3$. On the other hand, it was found that the molar volumes and refractive index of the samples increased with increasing $Eu_2O_3$ concentration. This finding reflects that the glass structure was expanded more with higher concentrations of $Eu_2O_3$. It was thought that the increased value of the molar volume was on account of the higher ionic radius of the $Eu^{3+}$ ions [10, 11], reflecting that the amount of non-bridging oxygen had been increased. The molar volumes were found to be in the range 28.7515-30.8388 $cm^3$/mol.

### 3.2. *Optical properties*

Fig. 2. shows the absorption spectra of $Eu^{3+}$ doped tellurite glass at room temperature in the range of 500-2500 nm. It was observed that the absorption intensity was in the NIR region. The optical spectra of glass samples showed two absorption bands at 2074 nm and 2207 nm. These were thought to be due to the transitions of $^7F_0{\rightarrow}^7F_6$ and $^7F_1{\rightarrow}^7F_6$ respectively. The absorption was found to increase with increasing $Eu_2O_3$ concentrations.

### 3.3. *Excitation spectra*

The excitation spectra of $Eu^{3+}$ doped tellurite glass with monitoring emission 612 nm are shown in Fig. 3. The spectra show different excitation peaks from the ground state to various excited states of the $Eu^{3+}$ions. The excitation bands were observed as seven discrete bands of $Eu^{3+}$ ions. They were centered at $^7F_0 \rightarrow {}^5D_4$ (363 nm), $^7F_0{\rightarrow}^5L_7$ (382 nm), $^7F_0{\rightarrow}^5L_6$ (394 nm),

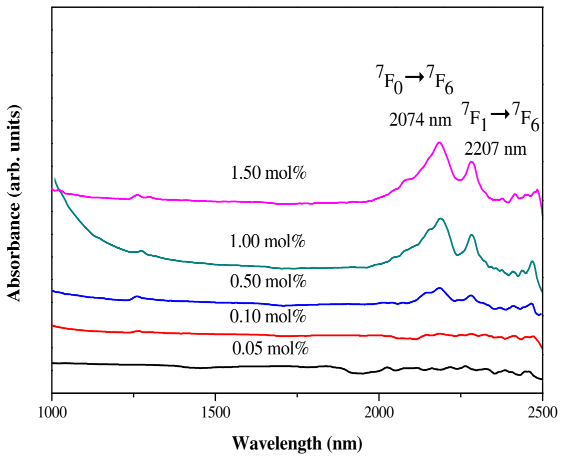


**Figure 2**: UV-VIS-NIR absorption spectra of the $Eu^{3+}$ doped tellurite glass samples.

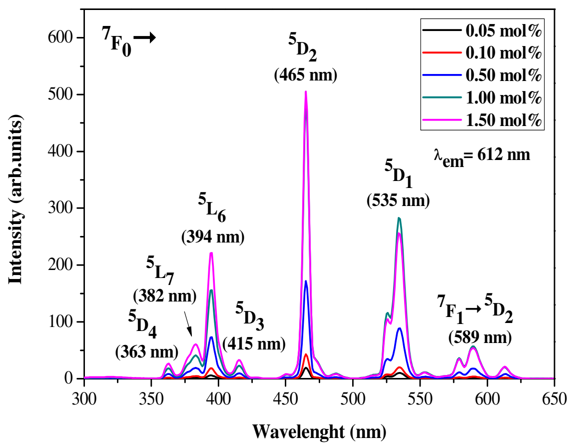


**Figure 3**: The excitation spectra of the $Eu^{3+}$ doped tellurite glass samples as obtained at an emission wavelength of 612 nm.

$^7F_0{\to}^5D_3$ (415 nm), $^7F_0{\to}^5D_2$ (465 nm), $^7F_0{\to}^5D_1$ (535 nm) and $^7F_1{\to}^5D_2$ (589 nm). The highest peak in the excitation spectra was observed at 465 nm.

### 3.4. Emission spectra

Fig. 4 presents the emission spectra of the glass samples with differing concentrations of $Eu^{3+}$ ions at an excitation wavelength of 465 nm. The spectra show five significant peaks along with a small peak at a longer wavelength. The emission peaks, that were observed, are centered at 578 nm, 591 nm, 612 nm, 652 nm, and 700 nm. These peaks are correspond to $^5D_0{\to}^7F_0$, $^5D_0{\to}^7F_1$, $^5D_0{\to}^7F_2$, $^5D_0{\to}^7F_3$ and $^5D_0{\to}^7F_5$. The highest peak of the emission spectra was observed at 612 nm.

### 3.5. Lifetime

The luminescence lifetime of $Eu^{3+}$ doped tellurite glass was measured by monitoring the emission of radiation at 612 nm under excitation from radiation at a wavelength of 465 nm. The results of this are shown in Fig. 3.and Fig. 4. The estimated average lifetimes of the samples were found to be 0.976, 0.975, 0.973, 0.972 and 0.971 ms for the 0.05, 0.10, 0.50, 1.0 and 1.5 mol% $Eu^{3+}$ doped glass samples respectively. A slight decrease in decay time with increasing Eu3+ ion concentration was noted. It was thought that this was as a result of the decrease in asymmetry around Eu3+ ion. The decay time values of the glass samples that were produced are comparable with that reported for other tellurium based glasses and glass ceramics doped with $Eu^{3+}$ ions. [12, 13]

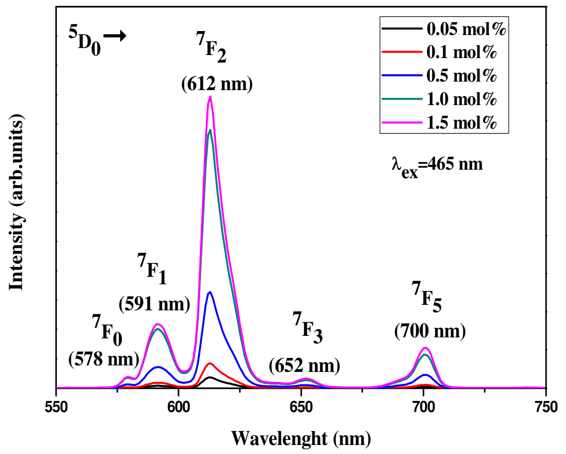


**Figure 4**: The emission spectra of the $Eu^{3+}$ doped tellurite glasses at an excitation wavelength of 465 nm.

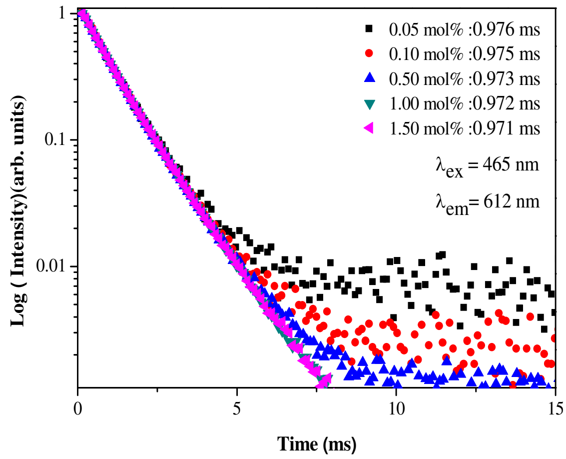


**Figure 5**: The decay time of $Eu^{3+}$ doped the tellurite glass samples.

## 4. Conclusions

The physical and optical properties of $Eu_2O_3$ doped glass samples of the composition (55-x) $TeO_2$-10$ZnF_2$-35BaO-x$Eu_2O_3$ were studied in this work. $Eu^{3+}$ doped multicomponent tellurite glasses with good optical quality and transparency were produced for analysis. It was found that the molar volumes and refractive index of the glass was increased with increasing Eu2O3 concentrations. The absorption band slightly increased with increasing $Eu_2O_3$concentrations. The excitation spectra of $Eu^{3+}$ doped tellurite glass samples were measured from 300-650 nm at 1.50 mol%. It was found that the highest peak was at 457 nm, this meant that the tellurite glass should be excited at this wavelength for the best luminescence application. The emission spectra of the glass samples showed peaks centered at 578 nm, 591 nm, 612 nm, 652 nm and 700 nm. The lifetime values corresponding to the $^5D_0$ excited state was found to decrease with the increase in $Eu^{3+}$ ion concentrations.

**Acknowledgements**

The authors would like to thank the Center of Excellence in Glass Technology and Materials Science (CEGM), Faculty of Science and Technology, Nakhon Pathom Rajabhat University for instrument and facilities. Thanks are also due to Research and Development Institute, NPRU for facilities.

**References**

[1] A. Mori, Y. Ohishi, T. Kanamori, S. Sudo, Optical amplification with neodymium-doped chalcogenide glass fiber, Applied Physics Letters 70 (10) (1997) 1230–1232.

[2] T. Schweizer, B. N. Samson, R. C. Moore, D. W. Hewak, D. N. Payne, Rare-earth doped chalcogenide glass fibre laser, Electronics Letters 33 (5) (1997) 414–416.

[3] S. Thomas, S. N. Rasool, M. Rathaiah, V. Venkatramu, C. Joseph, N. Unnikrishnan, Spectroscopic and dielectric studies of $Sm^{3+}$ ions in lithium zinc borate glasses, Journal of Non-Crystalline Solids 376 (2013) 106 – 116.

[4] L. P. Durante, L. A. Rocha, D. P. dos Santos, F. O. Coelho, M. A. Schiavon, S. J. L. Ribeiro, J. L. Ferrari, Synthesis, characterization and evaluation of scintillation properties of $Eu^{3+}$-doped $Gd_2o_3$ obtained using PEG as precursor, Journal of Alloys and Compounds 648 (2015) 467 – 473.

[5] N. Vijaya, C. Jayasankar, Structural and spectroscopic properties of $Eu^{3+}$-doped zinc fluorophosphate glasses, Journal of Molecular Structure 1036 (2013) 42 – 50.

[6] K. Maheshvaran, K. Marimuthu, Concentration dependent $Eu^{3+}$ doped boro-tellurite glasses – structural and optical investigations, Journal of Luminescence 132 (9) (2012) 2259 – 2267.

[7] J. Fu, J. Parker, P. Flower, R. Brown, $Eu^{2+}$ ions and $CaF_2$-containing transparent glass-ceramics, Materials Research Bulletin 37 (11) (2002) 1843 – 1849.

[8] K. Selvaraju, K. Marimuthu, T. Seshagiri, S. Godbole, Thermal, structural and spectroscopic investigations on $Eu^{3+}$ doped boro-tellurite glasses, Materials Chemistry and Physics 131 (1) (2011) 204 – 210.

[9] M. Wachtler, A. Sphegini, K. Gatterer, H. Fritzer, D. Azo, M. Bettinelli, Stability of aqueous $\alpha$-$Al_2o_3$ suspensions with poly(methacrylic acid) polyelectrolyte, Journal of the American Ceramic Society 81 (1988) 2045–2052.

[10] D. Ramteke, V. Kumar, H. Swart, Spectroscopic studies of $Sm^{3+}/Dy^{3+}$ co-doped lithium boro-silicate glasses, Journal of Non-Crystalline Solids 438 (2016) 49 – 58.

[11] D. Ramteke, H. Swart, R. Gedam, Spectroscopic properties of $Pr^{3+}$ ions embedded in lithium borate glasses, Physica B: Condensed Matter 480 (2016) 111.

[12] X. Joseph, R. George, S. Thomas, M. Gopinath, M. Sajna, N. Unnikrishnan, Spectroscopic investigations on $eu^{3+}$ ions in Li-K-Zn fluorotellurite glasses, Optical Materials 37 (2014) 552 – 560.

[13] S. Selvi, K. Marimuthu, N. S. Murthy, G. Muralidharan, Red light generation through the lead boro-telluro-phosphate glasses activated by $Eu^{3+}$ ions, Journal of Molecular Structure 1119 (2016) 276 – 285.