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# Impact of $Eu^{3+}$ on the luminescent, physical and optical properties of $BaSO_4 - B_2O_3 - P_2O_5$ glasses

Y.A. Yamusa [a,b,*], Rosli Hussin [a], W.N. Wan Shamsuri [a], Y.A. Tanko [a], Siti Aisha Jupri [a]

[a] Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia
[b] Centre For Energy Research and Training, Ahmadu Bello University, Zaria 1014, Kaduna State, Nigeria

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ABSTRACT

The investigations of the impact on the luminescent, physical and optical properties of Alkaline earth metal borophosphate glasses doped with rare earth (RE) ions became demanding owing to their several distinct features that are advantageous for applications in diverse photonic devices. A new series of $BaSO_4 - B_2O_3 - P_2O_5$ glasses doped $Eu^{3+}$ with different compositions of $25BaSO_4 - 30B_2O_3 - (45\text{-}x)\ P_2O_5 - xEu_2O_3$ (where x = 0.1, 0.3, 0.5, 0.7, 1.0, 2.0 and 2.1 mol%) were prepared by melt – quenching technique. X-ray diffraction and scanning electron microscope examined the amorphous state of the prepared glasses. Differential thermal analyser was used to determine the transition peaks. Some of their physical properties have been calculated. The direct band gap, indirect band gap and urbach energy were found to be within (4.654–4.199 eV), (3.902–3.656 eV) and (0.576–0.428 eV). The absorption spectra in the UV–vis and near infrared region revealed seven prominent peaks centred at 379, 393, 414, 463, 532, 2091 and 2206 nm corresponding to $^7F_0 \rightarrow {}^5G_2$, $^5L_6$, $^5D_3$, $^5D_2$, $^5D_1$, $^7F_0 \rightarrow {}^7F_6$ and $^7F_1 \rightarrow {}^7F_6$ transitions respectively. Photoluminescence spectra monitoring at the excitation of 391 nm exhibits four emissions band positioned at 591, 613, 655 and 701 nm corresponding to $^5D_0 \rightarrow {}^7F_1$, $^7F_2$, $^7F_3$ and $^7F_4$ transition of $Eu^{3+}$ ions. Judd-ofelt parameters have been calculated. The decay time of $^5D_0$ level decreases from 2.02 to 1.52 ms. The excellent features demonstrated by the current glasses affirm their suitability for solid state lasers and red LEDs applications.



## 1. Introduction

The developmental sustainability of the society depends on the environmental pollution and energy crises. To overwhelm the current problems, the new technological source and energy saving devices are needed. The light emitting diodes are model environmentally friendly and energy saving devices. The different rare earth activated with inorganic phosphor materials have gained many considerations owing to their potential and broad applications in the field of luminescent devices. The applications include solid state lasers, optical filters, cathode ray tubes, fluorescent lamps, plasma displays, field emission displays and white light emitting diodes [1,2]. Therefore, due to the increasing demands for the development of these new efficient optical devices doped with rare earth ions, a good network former of glass matrix is an essential factor that must be taken into consideration. Among numerous possible host materials, borophosphate glasses are the most suitable for rare

* Corresponding author at: Department of Physics, Faculty of Science, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.
*E-mail address:* ayyamusa2@live.utm.my (Y.A. Yamusa).

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**Table 1**
Composition of barium sulphate borophosphate glasses doped $Eu_2O_3$ in (mol%).

| Glass code | $BaSO_4$ | $B_2O_3$ | $P_2O_5$ | $Eu_2O_3$ |
|---|---|---|---|---|
| BPCS1 | 25 | 30 | 44.9 | 0.1 |
| BPCS2 | 25 | 30 | 44.7 | 0.3 |
| BPCS3 | 25 | 30 | 44.5 | 0.5 |
| BPCS4 | 25 | 30 | 44.3 | 0.7 |
| BPCS5 | 25 | 30 | 44.0 | 1.0 |
| BPCS6 | 25 | 30 | 43.0 | 2.0 |
| BPCS7 | 25 | 30 | 42.9 | 2.1 |

earth ions due to their low dispersion, low refractive indices excellent optical properties and excellent transparency from the ultraviolet to the near-infrared regions [3].

Borophosphate glassy system is prominently known because of their so called combined glass host. When phosphate substitutes the boron without changing the modifier content in the network, one can anticipate vital changes in the properties as well as structure of the borophosphate glasses [4–8]. Moreover, combining $P_2O_5$ and $B_2O_3$ with additional oxides in the same glass matrix leads to the enhancements of the material properties [3]. In this glassy system, the fundamental units of pure phosphate glasses are $PO_4$ tetrahedral linked through covalent bridging oxygens while those of pure borate glasses are trigonal $BO_3$ groups.

Phosphate and borate networks produce different optoelectronics effects when a modifier like BaO is added. The coordination of boron from $BO_3$ to $BO_4$ changes when a modifier like BaO is present in low concentrations in the $B_2O_3$ glass system, while an ultra-phosphate network involving of $Q^2$ and $Q^3$ tetrahedra could be formed for $O/P < 3.0$ [9].The $B_2O_3$ and $P_2O_5$ combined glasses exhibit distinguish properties from both pure phosphate and borate networks and such influences are anticipated to change the emission characteristics of the lasing ions existing in the glass host.

Among the rare earth ions, Europium ion is regarding exclusive from spectroscopic point of view due to the following reasons: (1) In order to estimate the local structure of rare earth ions in glasses, Europium ion is the most suitable choice because of its high sensitivity fluorescence on the environment and relatively simple energy level structure [10]. (2) Information concerning the local environment around the europium ion solemnly relies only on the splitting of the $^5D_o \rightarrow {}^7F_j$ (J = 0–6) transitions spectra, this is due to the facts that the fluorescent $^5D_o$ state and ground $^7F_0$ state of europium ions are non-degenerate under any symmetry [11]. (3) Repetitive burning of hole spectra may be accomplished for the $^7F_o \rightarrow {}^5D_o$ transition of europium ion at room temperature that can be used in high density optical data storage [12]. (4) Phonon side band measurement in association with the $^7F_o \rightarrow {}^5D_2$ transition discloses information on the local structure of europium ion sites which influence the non-radiative decay and (5) Phonon-electron coupling strength in a network former may calculate from the ratio of the integrated intensities of the phonon sideband to that of the electronic band [13].

Going by the consideration of their practical importance, it is aimed to synthesis borophosphate glasses doped $Eu^{3+}$ ions and examine their optical and physical properties by varying the rare earth ion content. This is to study the impact of adding europium ions into borophosphate glasses and how both physical and optical properties change as the glass composition changes. The Judd-ofelt parameters and decay time were studied. Also, the photo luminescence spectra that are beneficial for fabrication of new solid-state laser devices were analysed, discussed and compared with the existing reported work.

## 2. Materials and method

### *2.1. Sample preparation*

$BaSO_4 - B_2O_3 - P_2O_5$ sample doped $Eu^{3+}$ with different compositions of $25BaSO_4 - 30B_2O_3 - (45\text{-}x)P_2O_5 - xEu_2O_3$ (where x = 0.1, 0.3, 0.5, 0.7 1.0, 2.0 and 2.1 in mol%), were prepared by melt quenching technique. The imported pure chemicals high purity glass constituents (sigma Aldrich 99.99%) used for this work were barium sulphate ($BaSO_4$), Boric acid ($H_3BO_3$), Phosphoric acid ($H_3PO_4$), and europium oxide ($Eu_2O_3$) in consignments of about (30g) were accurately weighed using standard analytical balance (Table 1). The mixture of the sample was carried in an alumina crucible and then taken to an electric furnace, pre- heated at 200 °C for 30 min to eliminate the $H_2O$ and $H_2S$ content. Furthermore, the samples were heated at 1300 °C for 1 h. The melt prepared glass samples were air quenched by transferring it into a preheated stainless steel mold and kept for annealing at a rate of 300 °C for 3 h to eradicate thermal strains and then gradually allowed to cool to room temperature. After that, the glassy samples were polished to their flat surfaces for transparency and further characterization.

### *2.2. Parameters of the instrumentations*

The amorphous state of the prepared glass samples was assessed by x-ray diffraction studies using a Bruker D8 advance diffractometer employing Cu–Kα radiations (λ = 1.54 Å) functioned at a rate of 100 mA and 40 kV. The diffraction shapes of the prepared samples were used at the scanning rate of 0.05°/s and recorded in the range of 2θ = 0°–100°. While, SEM-FIB-zeiss Auriga was used for the scanning electron microscope analysis.