Optical and Photoluminescence Properties of Dy$^{3+}$ doped ZnO-Al$_2$O$_3$-B$_2$O$_3$ Glasses for UV Sensor Application

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Keywords: dysprosium, borate glass, optical properties, UV sensor

Abstract. The importance of product authenticity becomes more attention due to the increase of counterfeiting medicines, beverages, and foods. One of solutions of the problem is by inserting invisible bar code UV sensor in the product to keep the authentication. The bar code will show under UV light and emit visible light. The present UV sensor was developed by melt-quenching method with composition 10ZnO:10Al$_2$O$_3$:20BaO: (60-$x$)B$_2$O$_3$:xDy$_2$O$_3$ where x is 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, and 2.5 mol%. Glass medium doped rare earth is chosen as host material of UV sensor due to the strengthened of light emission and reliable detection. The characterization of physical and optical of the glass medium such as density, molar volume, absorption, excitation, and emission spectra were analysed. The highest peak of absorption intensity occurs at the wavelength of 1266 nm. From emission spectra, prepared glass medium emitted 482, 575, 664, and 752 nm wavelength when excited by 350 nm wavelength. The highest intensity of emission spectra was shown in 0.5 mol% of Dy$^{3+}$ ion concentration. The developed glass medium doped Dy$^{3+}$ is suitable candidate for application of UV sensor that is excited by 297, 325, 350, 364, 387, 426, 452, and 471 nm wavelength.

1. Introduction

The rise of counterfeiting medicines, food, and beauty products of the past few years have caused cares of consumers due to the negative effects such as food poisoning and skin cancer in consequence of consuming the faked products in long time period. Moreover, the production level decrease and the company incur losses. Various efforts have been tried to overcome the problem. One of them is to put on the security system like inserting the invisible bar code in the package of products. Furthermore, it can avoid the counterfeiting and ensure the authenticity of their products. The hidden picture or text of invisible bar code uses ultraviolet (UV) sensor which can only show under UV light. However, if the sensor is irradiated under visible, or infrared light the picture and text will be not shown. Nowadays, invisible bar code reading is the popular method for security system of medicines and automotive field [1].

Several methods have been developed to create UV sensor such as Silicon on Insulator (SOI) technology which has been investigated by [2]. This UV sensor is capable to detect UV A and UV B light. As for, the self-assembly method has been expended for synthesis of the ZnO hollow spheres to increase the UV sensor performance and the characterizations consist of SEM, TEM, and XRD pattern have been analysed [3]. However, these methods have limitations that are high cost, complicated
manufacturing process, and long sample preparation. Moreover, [4–6] have been developed UV sensor on semiconductor and thin film substrate. These methods are difficult to expand for security system in the products due to the UV light is converted to electric signal like voltage or current. Therefore, it needs to add electric circuit to detect the presence of UV light. There are many kinds of invisible ink that emit visible light when it is excited by ultraviolet including invisible ink based on dyes and pigment. Moreover, precipitation will occur after 3 months in invisible ink based on dyes [7]. Meanwhile, the particle size will be change after several hours, in invisible ink based on pigment. These will affect the color and properties of the invisible ink [8]. G.P. Darshan et al. have been developed Tm$^{3+}$ ion doped several hosts including glass, aluminum foil, metal, freshly cut leaf, and polyethylene sheet for fingerprint detection application in the crime scene. The results show when the sample was excited by 365 nm wavelength, Tm$^{3+}$ ion doped glass emits light more intense and reliable than other hosts in the blue region [9].

In this research, we proposed melt-quenching method, which is simple, low cost and easy manufacturing, to fabricate UV sensor. The detection can rapidly occur without inserting the electrical circuit because the UV sensor is converted to visible light which can be directly seen by human eye. The glass medium doped with trivalent rare earth ion is chosen as UV sensor material. The properties of glass oxide is transparent, malleability, and lower melting point [10, 11]. The transparent medium will keep off the sensor from corrosion and physical scratches [6]. The addition of heavy metal oxide on glass medium will increase the rare earth solubility and decrease the phonon energy [9]. From previous research, it is well known that Dy$^{3+}$ ion can emit visible light when it is excited by UV light at range 275-388 nm [13–15]. In this research, the prepared glass medium is characterized including the physical, and optical properties. The physical properties consist of density and molar volume of glass medium. Meanwhile, the optical properties are absorption, excitation, and emission spectrum. The effect of rare earth addition with glass structure and the relation of glass medium luminescence are analysed. In the future, it is expected that the glass medium can be inserted in packaging of medicines, food, beverages products, etc. Furthermore, the consumer can directly know the authenticity of products that they consume.

2. Experimental

We developed glass medium doped Dy$^{3+}$ ion by melt and quenching method [13,14]. The glass sample composition is 10ZnO:10Al$_2$O$_3$:20BaO: (60-x)B$_2$O$_3$:xDy$_2$O$_3$ where x is 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, and 2.5 mol%. The formula for glass medium was calculated by batch calculation. The glass sample was melted at 1100°C for 3h and annealed at 500°C for 3h. Subsequently, the glass medium was cut and polish to be characterized. The dimension of the glass medium is 2 x 1 x 0.031 cm$^3$. Figure 1 shows the prepared glass medium doped Dy$^{3+}$ from 0.1 until 2.5 mol%. The characterization consists of physical, and optical properties. The physical properties come under density, and optical properties. The physical properties consist of density and molar volume of glass medium. Meanwhile, the optical properties are absorption, excitation, and emission spectrum. The effect of rare earth addition with glass structure and the relation of glass medium luminescence are analysed. In the future, it is expected that the glass medium can be inserted in packaging of medicines, food, beverages products, etc. Furthermore, the consumer can directly know the authenticity of products that they consume.

\[ \rho = \left( \frac{W_s}{W_s - W_b} \right) \rho_c \]  
\[ V_m = \frac{M_w}{\rho} \]  

where \( M_w = x_1z_1 + x_2z_2 + x_3z_3 + \cdots + x_nz_n \). Mol fraction and molecular weighted of each compound are denoted by \( x_1, x_2, x_3, \ldots, x_n \) and \( z_1, z_2, z_3, \ldots, z_n \), respectively. The absorption spectra of glass medium was measured by UV-Vis-NIR Spectrometer (UV-3600 Shimadzu) under wavelength
of 300-2000 nm. The light source of the spectrometer is 50-watt halogen lamp and a deuterium lamp. The excitation and emission spectra were measured by Cary Eclipse Fluorescence Spectrophotometer (Agilent Technology Inc.). The detector of this instrument is a photomultiplier tube (PMT) and the light source is flash xenon lamp. All of the measurements were observed at room temperature.

3. Results and Discussion

3.1 Density and Molar volume

Table 1 shows the physical properties of glass medium including density and molar volume. The density of the glass medium has tendency to increase from 0.5 until 2.5 mol%. It is due to the molecular mass of Dy$_2$O$_3$ is higher than B$_2$O$_3$. More adding Dy$_2$O$_3$ more free interstices replaced by them. The molar volume also increases from 0.5-2.5 mol% of Dy$^{3+}$ concentration. The increasing can be affected by improving the glass structure due to non-bridging oxygen or conversion of B$_3$ to B$_4$ coordination [16,17]. Meanwhile, the molar volume of 0.3 to 0.5 mol% of Dy$^{3+}$ concentration decrease due to the rare earth ion has not act as modifier. It may be affected by the less concentration of rare earth ion.

<table>
<thead>
<tr>
<th>Properties</th>
<th>0.1Dy</th>
<th>0.3Dy</th>
<th>0.5Dy</th>
<th>1.0Dy</th>
<th>1.5Dy</th>
<th>2.0Dy</th>
<th>2.5Dy</th>
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<td>Density [g/cm$^3$]</td>
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<td>3.00334</td>
<td>3.05982</td>
<td>3.10817</td>
<td>3.13029</td>
<td>3.17582</td>
</tr>
</tbody>
</table>

3.2 Absorption Spectra

The absorption spectrum of glass medium doped Dy$^{3+}$ is presented in Fig. 2. The light source of UV-Vis-NIR spectrometer was varied from 300 to 2000 nm wavelength and showed 8 absorption bands. The level transition of the glass medium are $^4$M$_{21/2}$, $^4$I$_{15/2}$, $^6$F$^{3/2}$, $^6$F$^{5/2}$, $^6$F$^{7/2}$, $^6$F$^{9/2}$, $^6$F$_{11/2}$+$^4$H$_{9/2}$, and $^4$H$_{11/2}$ that are originated from $^6$H$_{15/2}$. 

Fig. 1. The prepared glass medium after cut and polished
All of the transitions is corresponded by wavelengths that are 385 nm, 451 nm, 753 nm, 801 nm, 896 nm, 1089 nm, 1266 nm, and 1674 nm respectively. The highest intensity of absorption spectra is the \(^{6}H_{15/2} \rightarrow ^{6}F_{11/2}\) transition centered at 1266 nm. The strongest absorption bands in the middle infrared region are due to molecular vibration \([18]\). The transition level has been compared to previously research and resulted in similar transition \([13, 14, 19, 20]\).

### 3.3 Photoluminescence Spectra

The excitation spectra of glass medium doped Dy\(^{3+}\) by \(\lambda_{em}=575\) nm is presented in Fig.3(a). It shows that the transition level of excitation occurs at the transition that originated from \(^{6}H_{15/2}\) to other level energy including \(^{14}H_{9/2}\), \(^{6}P_{3/2}, ^{6}P_{1/2}, ^{4}I_{11/2}+{^{4}I_{9/2}}, ^{4}G_{15/2}, ^{4}G_{11/2}, ^{4}F_{9/2}\). These transitions are related by several wavelengths that are 297 nm, 325 nm, 350 nm, 364 nm, 387 nm, 426 nm, 452 nm, and 471 nm respectively. Other literatures describe that the transition of excitation level has similar results \([13, 14, 21, 22]\). The diagram of the energy level of excitation transition is shown at Fig. 4(a). From these pictures, it is well known that developed glass medium can be excited by several UV light at range 297 to 387 nm wavelength. The sharpest peak among the excitation transition is the \(^{6}H_{15/2} \rightarrow ^{6}P_{7/2}\) transition centered at 350 nm.

![Absorption spectrum glass medium doped Dy\(^{3+}\)](image)

**Fig. 2. Absorption spectrum glass medium doped Dy\(^{3+}\)**

**Fig. 3. Photoluminescence graph:** (a) Excitation spectra of glass medium doped Dy\(^{3+}\) by \(\lambda_{em}=575\) nm, (b) Emission spectra of glass medium doped by Dy\(^{3+}\) under excitation of \(\lambda_{ex}=350\) nm
Fig. 3(b) presents the emission spectra of glass medium doped Dy$^{3+}$ ion excited by 350 nm wavelength. The excitation causes 4 emissions that are resulted from several transitions from $^4F_{9/2}$ to transitions are $^6H_{15/2}$, $^6H_{13/2}$, $^4H_{9/2}$, $^6H_{13/12}$, and $^6H_{9/2}$. These transition is similar with other literature [13, 14, 23, 24]. The emission intensity increase from 0.1 to 0.5 mol% of Dy$^{3+}$ ion concentration and the highest peak of emission spectra is about 575 nm in the $^4F_{9/2}$→$^6H_{13/12}$ transition. The quenching concentration occur at 0.5 mol% of Dy$^{3+}$ concentration. Therefore, the emission intensity decrease from 1.0 to 2.5 mol% of Dy$^{3+}$ ion concentration. It is predicted that NBOs occur in this concentration due to the decreasing emission intensity and increasing the molar volume (see Table 1). Moreover, the increasing molar volume, from 0.5 to 1.0 mol% of Dy$^{3+}$ ion concentration, shows that the glass medium acts as modifier. From Fig. 4(b), it is well known that the strong transition of $^6H_{15/2}$→$^6H_{13/12}$ at 350 nm is an effective pumping to excite the metastable state of $^4F_{9/2}$ [25]. The non-radiative decay takes place at $^4I_{3/2}$→$^4F_{7/2}$→$^4F_{9/2}$, so this transition does not produce the light emission.

4. Conclusion

Glass medium doped Dy$^{3+}$ ion based on melt quenching method has been successfully developed. The density of glass medium have the tendency toward increase due to heavier mass molecular of Dy$_2$O$_3$ than B$_2$O$_3$. Meanwhile, the increasing molar volume from 0.5 to 1.0 mol% of Dy$^{3+}$ ion concentration due to conversion of B$_3$ to B$_4$ coordination. The increasing molar volume of glass medium and decreasing emission intensity from 1.0 to 2.5 mol% is affected by the presence of non-bridging oxygen. The quenching concentration occurs in 0.5 mol% of Dy$_2$O$_3$. The glass medium absorbs the light and electron move up from $^6H_{15/2}$ to $^4M_{21/2}$, $^4I_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}$, and $^6H_{11/2}$. These transitions are correlated by wavelength of 385, 451, 753, 801, 896, 1089, 1266, and 1674 nm respectively. From emission spectra, it is well known that the glass medium is capable to emit visible light in the wavelength of 482, 575, 664, and 752 nm excited by $\lambda_{ex}$=350 nm. The highest emission intensity of glass medium occur due to the $^4F_{9/2}$→$^4H_{13/12}$ transition (575 nm). From the results, it can be summarized that glass medium doped Dy$^{3+}$ ion is potential material to develop for UV sensor application excited by 297, 325, 350, 364, 387, 426, 452, and 471 nm wavelength.
Acknowledgements

The author would like to thank Nakhon Pathom Rajabhat University, for instrumentation and facilities, all of the Center of Excellent Glass and Material Technology staffs helping this research, and Kemenristek Dikti for PMDSU scholarship.

References


